UC DAVIS CHEM 110B PHYSICAL CHEMISTRY II



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UC Davis Chem 110B Physical Chemistry II

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Licensing

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CHAPTER OVERVIEW

10: Bonding in Polyatomic Molecules

Valence bond (VB) theory is one of two basic bonding theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

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10.1: Hybrid Orbitals Account for Molecular Shape

Learning Objectives

- Introduce hybrid orbital to explain non-linear molecular structure

Valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory, which will be discussed elsewhere, predict wavefunctions that cover the entire molecule.

Review of Diatomics

Let us consider H_2. Recall that the Lewis structure for a single H atom is $H\cdot$ and for H_2, it is $H:H$. Thus, each hydrogen brings one unpaired electron to the bond. Let the two protons be denoted A and B and the two electrons 1 and 2. Now, consider the potential energy

$$V = V_{ee} + V_{en} + V_{nn} \tag{10.1.1}$$

$$= \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}}\right] \tag{10.1.2}$$

But as $R_{AB} \to \infty$, the $1/r_{12}$, $1/r_{1B}$, $1/r_{2A}$, and $1/R_{AB}$ terms vanish and the potential energy becomes simply that of two noninteracting hydrogen atoms

$$V \to -\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_{1A}} + \frac{1}{r_{2B}}\right]$$

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wavefunction should simply be a product $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$. But as we let $R_{AB} \to R_e$, where R_e is the equilibrium bond length, the electrons mix, and we can no longer tell if electron 1 belongs to atom A or atom B and the same for electron 2. Thus, we need to construct a combination of products that is consistent with the Pauli exclusion principle. If we just consider the coordinates r_1 and r_2 of the electrons, then the only wavefunction we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

where the u designator indicates that this is an odd function. The constant C_u is the overall noramlization constant. Unfortunately, like in the LCAO method, such a wavefunction is antibonding and is not a good representation of the ground state. If, however, we construct the wavefunction

$$\psi_g(r_1, r_2) = C_g[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)]$$

(where g designates that this is an even function), we violate the Pauli exclusion principle, even though such a wavefunction leads to a stable chemical bond.

What is missing here is the fact that we have not considered the spins of the electrons. Since the electrons are identical, if we exchange coordinates *and* spins, then the wavefunction should change sign. Thus, we can make both wavefunctions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wavefunction. We obtain

$$\psi_u(r_1, r_2, s_1, s_2) = \psi_u(x_1, x_2) = C_u[\psi^A_{1s}(r_1)\psi^B_{1s}(r_2) - \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.3}$$

$$\psi_g(r_1, r_2, s_1, s_2) = \psi_g(x_1, x_2) = C_g[\psi^A_{1s}(r_1)\psi_{1s}B(r_2) + \psi^A_{1s}(r_2)\psi^B_{1s}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.4}$$

where s_1 and s_2 are the z-components of spin for electrons 1 and 2, respectively. We can now use ψ_g as an approximate 2-electron wavefunction that leads to a stable chemical bond in H_2.

The fact that ψ_u is antibonding can be easily determined by looking for a nodal plane between the two atoms, in this case, in the plane that exactly bisects the line joining the two atoms, midway between them. That this is, indeed, a nodal plane can be seen by considering two points r_1 and r_2 for the two electrons that are taken to lie in this plane. By symmetry, the functions $\psi^A_{1s}(r_1)$ and $\psi^B_{1s}(r_1)$ have the same value for r_1 in this plane, and the same for $\psi^B_{1s}(r_2)$ and $\psi^A_{1s}(r_2)$. Let us assign the following values:

$$\psi_{1s}^{A}(r_1) = \psi_{1s}^{B}(r_1) = A \tag{10.1.5}$$

$$\psi_{1s}^{B}(r_2) = \psi_{1s}^{A}(r_2) = A' \tag{10.1.6}$$

Substituting these into $\psi_u(x_1, x_2)$, we obtain

$$\psi_u(x_1, x_2) = C_u[AA' - A'A][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] = 0$$

Since the wavefunction has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy* than the corresponding bonding wavefunction ψ_g.

A similar argument can be used for the molecule F_2. Each F has an electronic configuration

$$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$$

and the Lewis structure of F_2 is



Figure 10.1.1 : Lewis structure of F_2.

Most of the electrons are in lone pairs, but the $2p_z$ electrons, which are unpaired in each F come together to form the bond. Thus, the bonding wavefunction should be a 2-electron wavefunction constructed from $2p_z$ orbitals. The bonding wavefunction takes the "gerade" form as in H_2:

$$\psi_g(r_1, r_2, s_1, s_2) = C_g[\psi_{2p_z}^{A}(r_1)\psi_{2p_z}^{B}(r_2) + \psi_{2p_z}^{A}(r_2)\psi_{2p_z}^{B}(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]$$

For HF, the $2p_z$ orbital on F and $1s$ orbital on H come together to form the bonding wavefunction. To be consistent with the Pauli principle, we need a wavefunction of the form

$$\psi(r_1, r_2, s_1, s_2) = [\psi_{1s}^{H}(1)\psi_{2p_z}^{F}(2) + \psi_{1s}^{H}(2)\psi_{2p_z}^{F}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]) \tag{10.1.7}$$

Looking at the HF example, it becomes clear how much valence bond theory attempts to appear as a "quantum version" of the Lewis dot structure model. Valence bond theory attempts to construct very approximate wavefunctions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wavefunctions for the lone pair electrons. In the case of HF, we use the $2p_z$ orbitals of F, which leaves the $2s$, $2p_x$ and $2p_y$ orbitals unused. Since there are three lone pairs, these three orbitals are sufficient to hold each of the lone pairs as spin-up/spin-down couples.

Hybridization

For polyatomic molecules, the valence bond theory becomes a very poor approximation because the directionalities of the $2s$ and $2p$ orbitals is too restrictive to describe molecules with steric numbers ranging between 2 and 4. The example considered above of H_2O illustrates this rather dramatically! Let us consider an even simpler molecule, BeH_2, which has a steric number of 2 and is linear. Let the atoms lie entirely along the z-axis in the arrangement $H - Be - H$.

Although Be has a ground-state electronic configuration of $1s^2 2s^2$, but if we "promote" one of the $2s$ electrons to a state with higher energy and allow its electronic structure to be $1s^2 2s 2p_z$, then the unpaired electrons in the $2s$ and $2p_z$ orbitals can combine with the unpaired electrons in each of the hydrogen atoms to form bonds. The energy needed to excite the electron in Be would be ``repaid" by the energy gained in the formation of stable bonds. The two valence-bond wavefunctions we would construct would be

$$\psi_1(1,2) = C_1\left[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.8}$$

$$\psi_2(1,2) = C_2\left[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)\right][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.9}$$

Unfortunately, even this simple scheme does not work entirely because the two $Be - H$ bonds would be different due to their construction from different combinations of orbitals. By symmetry, however, we can see that the two BeH bonds should be equivalent. A solution to this problem was proposed by Linus Pauling in the 30s in the form of *orbital hybridization*, a scheme that we still use today.

Pauling used the fact that in the first and second periods, the $2s$ and $2p$ orbitals have similar energies. Indeed, for H, the energies are exactly the same. Given that these energies are not that different, we can combine s and p orbitals and still have a valid solution

of the Schrödinger equation. That is, a general orbital

$$\chi(r) = C_1\psi_{2s}(r) + C_2\psi_{2p_x}(r) + C_3\psi_{2p_y}(r) + C_4\psi_{2p_z}(r)$$

is also a solution of the Schrödinger equation with the same energy as a $2s$ or $2p$ orbitals individually (this is exactly true for H). In the case of BeH_2, the external potential on the electrons in Be by the two hydrogens changes the energy levels and creates a near degeneracy between the $2s$ and $2p_z$ orbitals, hence, we are now free to combine the into linear combinations that are more suitable to the construction both of valence bond wavefunctions *and* MOs via the LCAO procedure.

sp Hybrid Orbitals

For Be, we now allow the s and p orbitals to mix and create two *hybrid* orbitals known as *sp* orbitals. The two new hybrid wavefunctions as linear combination of the functions for 2s and $2p_z$ (using Dirac Notation):

$$|\chi_i\rangle = a_1|2s\rangle + b_1|2p_z\rangle \tag{10.1.10}$$

$$|\chi_j\rangle = a_2|2s\rangle + b_2|2p_z\rangle \tag{10.1.11}$$

These two wavefunctions must be orthogonal.

$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

Which can be separated into the following relationships:

$$\langle\chi_i|\chi_i\rangle = 1 \tag{10.1.12}$$

and

$$\langle\chi_j|\chi_j\rangle = 1 \tag{10.1.13}$$

and

$$\langle\chi_i|\chi_j\rangle = \langle\chi_j|\chi_i\rangle = 0 \tag{10.1.14}$$

Equations 10.1.12 and 10.1.13 are the normality requirement and Equation 10.1.14 is the orthogonality requirement for the new hybrid wavefunctions. Substituting 10.1.10 into 10.1.12 results in

$$\langle\chi_i|\chi_i\rangle = a_1^2\ \cancel{\langle 2s|2s\rangle}^{\,1} + a_1b_1\ \cancel{\langle 2s|2p_z\rangle}^{\,0} + a_1b_1\ \cancel{\langle 2p_z|2s\rangle}^{\,0} + b_1^2\ \cancel{\langle 2p_z|2p_z\rangle}^{\,1} = 1$$

and similarly for $\langle\chi_j|\chi_j\rangle$

$$\langle\chi_j|\chi_j\rangle = a_2^2\ \cancel{\langle 2s|2s\rangle}^{\,1} + a_2b_2\ \cancel{\langle 2s|2p_z\rangle}^{\,0} + a_2b_2\ \cancel{\langle 2p_z|2s\rangle}^{\,0} + b_2^2\ \cancel{\langle 2p_z|2p_z\rangle}^{\,1} = 1$$

results in the following relationships

$$\langle\chi_i|\chi_i\rangle = a_1^2 + b_1^2 = 1 \tag{10.1.15}$$

$$\langle\chi_j|\chi_j\rangle = a_2^2 + b_2^2 = 1 \tag{10.1.16}$$

and

$$\langle\chi_i|\chi_j\rangle = a_1a_2 + b_1b_2 = 0 \tag{10.1.17}$$

These are four unknowns and three equations. The fourth "constraint" is that we assume contribution of $|s\rangle$ is the same for both hybrid orbitals.

$$a_1 = a_2$$

Equations 10.1.15 to 10.1.17 revert to

$$a_1^2 + b_1^2 = 1 \tag{10.1.18}$$

$$a_1^2 + b_2^2 = 1 \tag{10.1.19}$$

$$b_1^2 = b_2^2 \tag{10.1.20}$$

Therefore

$$b_1 = -b_2$$

and

$$a_1 = b_1 \tag{10.1.21}$$

Insert Equation 10.1.21into 10.1.20to get

$$a_1 = \frac{1}{\sqrt{2}}$$

and the two hybrid orbitals are

$$\chi_1(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \tag{10.1.22}$$

$$\chi_2(r) = \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)] \tag{10.1.23}$$

Note that these orbitals are both normalized and orthogonal:

$$\int |\chi_1(r)|^2 dV = 1\ ;\ \int |\chi_2(r)|^2 dV = 1\ ;\ \int \chi_1^*(r)\chi_2(r) dV = 0$$

These orbitals appear as shown in Figure 10.1.3

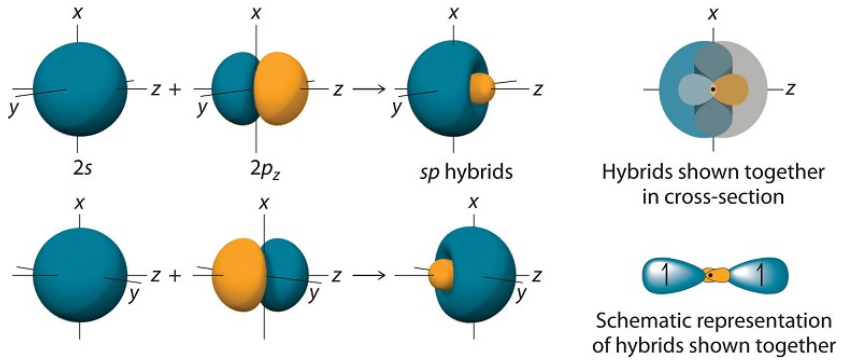


Figure 10.1.3 : The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

Given that the two *sp* hybrid orbitals are mirror images of each other, they can overlap with the $1s$ orbital of H (shown in the figure) and create two equal bonds, as needed for BeH_2. Using the valence bond formulation, now, one of the BeH bonds will be described by a wavefunction of the form:

$$\psi_1(1,2) = C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.24}$$

$$\psi_2(1,2) = C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \tag{10.1.25}$$

In the above wavefunctions, it is clear that H_1 is on the right and H_2 is on the left, based on the directionalities of χ_1 and χ_2.

sp^2 Hybrid Orbitals

For trigonal planar molecules such as BH_3, we start with the electronic configuration of B, which is $1s^2 2s^2 2p_x$, and we promote one of the $2s$ electrons to a $2p_y$ orbital, so that we have $1s^2 2s 2p_x 2p_y$. Suppose the geometry of BH_3 is such that one of the hydrogens lies along the positive x axis. The remaining hydrogens would be in the 3rd and 4th quadrants, respectively, as shown in Figure 10.1.4 .

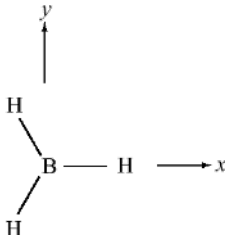


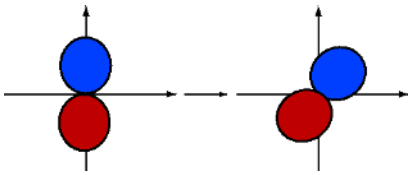
Figure 10.1.4 : Geometry of BH_3.

If we simply combine the $2s$ with the $2p_x$ and $2p_y$ orbitals of boron, the resulting hybrid orbitals will not point in the correct direction. For this reason, we will create rotated versions of the p_x and p_y orbitals, which, as we will see are tantamount to taking new combinations of $2p_x$ and $2p_y$ orbitals to combine with the $2s$. Since the rotation occurs in the xy plane, the coordinate that controls this is the azimuthal angle ϕ. For the p_x and p_y orbitals, the ϕ dependence is

$$\psi_{2p_x} \sim \cos\phi \; ; \; \psi_{2p_y} \sim \sin\phi$$

If we rotate $2p_y$ by -30 degrees (Figure 10.1.5 ; blue is positive and red is negative), the ϕ dependence becomes

$$\psi_{2p_y}^{(rot)} \sim \sin(\phi + 30)$$


Figure 10.1.5 : Rotation of a $2p_y$ orbital by -30 degrees.

Using the fact that

$$\sin(\alpha \pm \beta) = \sin\alpha\cos\beta \pm cos\alpha sin\beta$$

this rotation gives

$$\psi_{2p_y}^{(rot,1)} \sim \sin\phi\cos 30 + \cos\phi\sin 30 \tag{10.1.26}$$

$$\sim \left[\frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi\right] \tag{10.1.27}$$

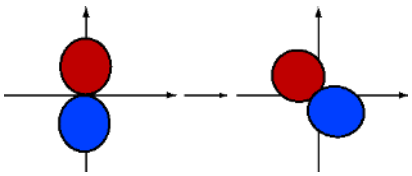
$$\sim \left[\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x}\right] \tag{10.1.28}$$

Similarly, consider rotating $-\psi_{2p_y}$ by $+30$ degrees (Figure 10.1.6). This gives

$$-\psi_{2p_y}^{(rot,2)} \sim -\sin(\phi - 30) \tag{10.1.29}$$

$$\sim -\left[\frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi\right] \tag{10.1.30}$$

$$\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x} \tag{10.1.31}$$


Figure 10.1.6 : Rotation of a $-2p_y$ orbital by 30 degrees.

So, we now take the hybrid orbitals to be of the form

$$\chi_1(r) = a\psi_{2s}(r) - b\psi_{2p_x} \tag{10.1.32}$$

$$\chi_2(r) = c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \tag{10.1.33}$$

$$\chi_3(r) = c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r) \tag{10.1.34}$$

The coefficients a, b, and c are determined by requiring that the orbitals are normalized and mutually orthogonal:

$$\int |\chi_1(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_2(r)dV = 0 \tag{10.1.35}$$

$$\int |\chi_2(r)|^2 dV = 1 \; ; \; \int \chi_1^*(r)\chi_3(r)dV = 0 \tag{10.1.36}$$

$$\int |\chi_3(r)|^2 dV = 1 \; ; \; \int \chi_2^*(r)\chi_3(r)dV = 0 \tag{10.1.37}$$

Carrying out the algebra, we obtain the following sp^2 hybrid orbitals:

$$\chi_1(r) = \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \tag{10.1.38}$$

$$\chi_2(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.39}$$

$$\chi_3(r) = \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)] \tag{10.1.40}$$

The sp^2 hybrids allow bonding at 120° degrees, and these orbitals appear as shown in Figure 10.1.7 :

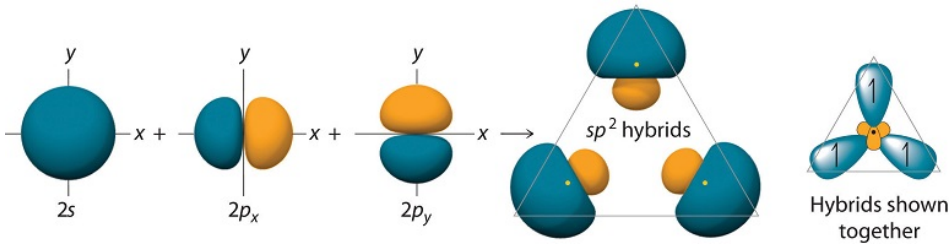


Figure 10.1.7 : Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

The figure also shows the overlaps of these orbitals with the $1s$ orbitals of H.

sp^3 Hybrid Orbitals

Finally, we consider the case of methane CH_4. The electronic configuration of C is $1s^2 2s^2 2p_x 2p_y$. We now promote one of the $2s$ orbitals to the $2p_z$ orbital and write C as $1s^2 2s 2p_x 2p_y 2p_z$. We can now hybridize the $2s$ orbital with each of the $2p$ orbitals to create four hybrids:

$$\chi_1(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.41}$$

$$\chi_2(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \tag{10.1.42}$$

$$\chi_3(r) = \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.43}$$

$$\chi_4(r) = \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \tag{10.1.44}$$

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 10.1.8). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

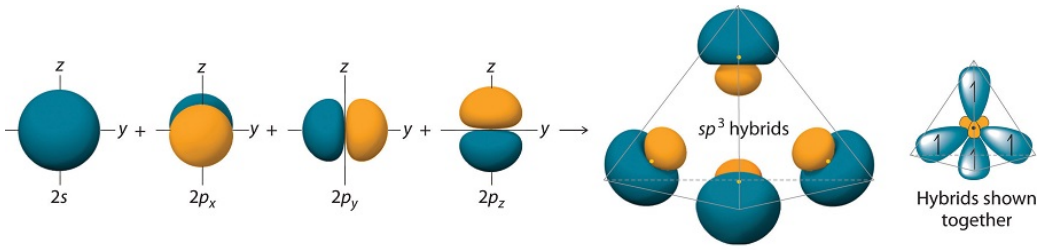


Figure 10.1.8 : Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Are hybrid orbitals Real?

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will not be formed because a molecule is hybridized in a certain way, it is the other way around, i.e. a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic *s*- and *p*-orbitals on the central atoms are not. By combining these into new orbitals of *sp*, sp^2 and sp^3 types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "sp^2" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the *electron density distribution*, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ-function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals (or colors) are actually present in the final product. So one could well argue that hybrid orbitals are not "real"; they simply turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

Summary

The shape and bonding valecies of polyatomic molecules can be accounted for by hybrid orbitals. Molecular orbitals are formed from linear combinations of atomic orbitals which are similar in energy. These atomic orbitals could come from different atoms, or from the same atom. For example, the 2 sand 2patomic orbitals are very close energetically. When a linear combo of more than one atomic orbital from the **same atom** is formed, we have a hybrid orbital.

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10.2: Different Hybrid Orbitals Used for Bonding in Water

The goal of applying Valence Bond Theory to water is to describe the bonding in H_2O and account for its structure (i.e., appropriate bond angle and two lone pairs predicted from VSEPR theory).

The ground state electronic configuration of atomic oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ and of course the ground state electronic configuration of atomic hydrogen atom is $1s^1$, i.e., a spherical atomic orbital with no preferential orientation. If only the unfilled $2p_y$ and $2p_z$ atomic orbitals of the oxygen were used as bonding orbitals, then two bonds would be predicted. These bonding wavefunctions would be mixture of only $|2p_y\rangle$ and $|2p_z\rangle$ orbitals on oxygen and the $|1s\rangle$ orbitals on the hydrogens (H_1 and H_2):

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + b_1|2p_y\rangle_O \tag{10.2.1}$$

$$|\chi_2\rangle = a_2|1s\rangle_{H_2} + b_2|2p_z\rangle_O \tag{10.2.2}$$

However, with a H-O-H bond angle for these bonds would be expected to be 90° since $2p_y$ and $2p_z$ are oriented 90° with respect to each other. Note that $|\chi_1\rangle$ and $|\chi_2\rangle$ are two-center bonding orbitals common to Valence Bond theory.

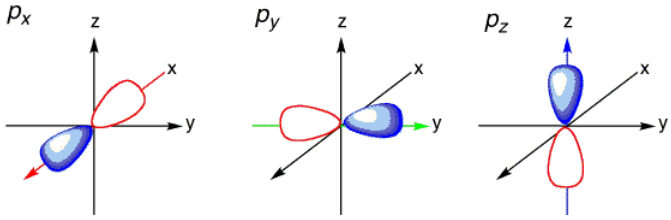


Figure 10.2.1 : The three p-orbitals are aligned along perpendicular axis (CC-SA-BY-NC; Nick Greeves ChemTube3D);

Using the oxygen atomic orbitals directly is obviously not a good model for describing bonding in water, since we know from experiment that the bond angle for water is 104.45° (Figure 10.2.2), which is also in agreement with VSEPR theory. Since the $2s$ orbital is spherical, mixing some $2s$ character into the $2p_z$ orbitals can adjust the bond angle as discussed previously by creating new hybrid orbitals.

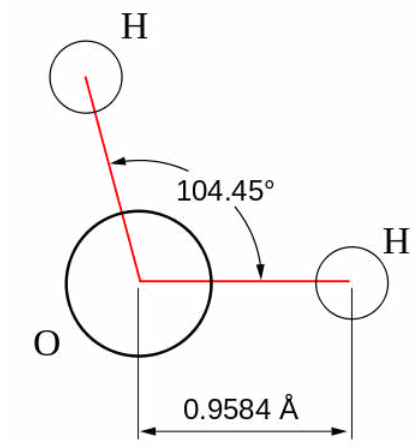


Figure 10.2.2 : Experimentally determined geometry of the water molecule (CC BY-SA 3.0 Booyabazooka).

Historically, Valence Bond theory was used to explain bend angles in small molecules. Of course, it was only qualitatively correct in doing this, as the following example shows. Let us construct the Valence Bond wavefunctions for the two bonding pairs in H_2O by mixing the $|2s\rangle$, $|2p_x\rangle$, $|2p_y\rangle$, and $|2p_z\rangle$ into four new sp^3 hybrid orbitals:

$$\begin{aligned}
\chi_1(r) &= \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) + \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \\
\chi_2(r) &= \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) - \psi_{2p_y}(r) + \psi_{2p_z}(r)\right] \\
\chi_3(r) &= \frac{1}{2}\left[\psi_{2s}(r) + \psi_{2p_x}(r) - \psi_{2p_y}(r) - \psi_{2p_z}(r)\right] \\
\chi_4(r) &= \frac{1}{2}\left[\psi_{2s}(r) - \psi_{2p_x}(r) + \psi_{2p_y}(r) - \psi_{2p_z}(r)\right]
\end{aligned}$$

Hence, the three $2p$ orbitals of the oxygen atom combined with the $2s$ orbitals of the oxygen to form four sp^3 hybrid orbitals (Figure 10.2.3).



Figure 10.2.4: This would leave the $2s$ and $2p_z$ orbitals of oxygen left over for the two lone pairs on the oxygen.

The bond angle for four groups of electrons around a central atom is 109.5 degrees. However, for water the experimental bond angle is 104.45°. The VSPER picture (general chemistry) for this is that the smaller angle can be explained by the presence of the two lone-pairs of electrons on the oxygen atom. Since they take up more volume of space compared to a bonding pair of electrons the repulsions between lone pairs and bonding pairs is expected to be greater causing the H-O-H bond angle to be smaller than the ideal 109.5°.

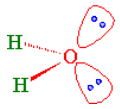


Figure 10.2.4 : Among the four hybrid orbitals, two are half filled and the remaining two are completely filled.

We can rationalize this by thinking about the s and p characters of the hybrids. In a perfectly sp^3 hybridized set of hybrid orbitals, each sp^3 orbital should have: 25% s character and and 75% p character. Since the bond angle is not 109.5° in water, the hybrid orbitals cannot have exactly this ratio of s and p character. So there there is uneven distribution of s and p character between the 4 hybrid orbitals. First we will write down the wavefunction and see what this means and then we will rationalize it.

Note: A few cautionary words about hybridization.

Hybridization is an often misconceived concept. It only is a mathematical interpretation, which explains a certain bonding situation (in an intuitive fashion). In a molecule the equilibrium geometry will result from various factors, such as steric and electronic interactions, and further more interactions with the surroundings like a solvent or external field. The geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around, i.e., a result of the geometry or more precise and interpretation of the wavefunction for the given molecular arrangement.

Estimating Character of Hybrid Orbitals

The terminology we use for hybridization actually is just an abbreviation:

$$\mathrm{sp}^x = \mathrm{s}^{\frac{1}{x+1}}\,\mathrm{p}^{\frac{x}{x+1}}$$

In theory x can have any value, hence any of the following combinations constitute valid hybridization schemes for 1 s orbital and 3 p orbitals:

$$\begin{aligned} 1\times\mathrm{s}, 3\times\mathrm{p} &\rightsquigarrow 4\times\mathrm{sp}^3 \\ &\rightsquigarrow 3\times\mathrm{sp}^2, 1\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}, 2\times\mathrm{p} \\ &\rightsquigarrow 2\times\mathrm{sp}^3, 1\times\mathrm{sp}, 1\times\mathrm{p} \\ &\rightsquigarrow \text{etc. pp.} \\ &\rightsquigarrow 2\times\mathrm{sp}^4, 1\times\mathrm{p}, 1\times\mathrm{sp}^{(2/3)} \end{aligned}$$

There are virtually infinite possibilities of combinations. Which one is "valid" is only determined by experiment (e.g., structure or spectroscopy). The generic sp^x hybrid orbitals wavefunction can be roughly written in terms of atomic orbital character:

$$|\chi_i\rangle = N(p + \gamma s) \tag{10.2.3}$$

where N is a normalization constant and γ is the relative contribution of s character to the hybrid orbital. For a pure sp^3 hybrid, γ would be 0.25 and for a pure sp hybrid, γ would be 1. The question is how to determine γ to get a better picture of the hybridization of water. Starting with the normalization criteria for wavefunctions:

$$\langle \chi_i | \chi_i \rangle = 1$$

and substituting Equation 10.2.3 into to get

$$\langle N(p+\gamma s) | N(p+\gamma s) \rangle = 1$$

which in integral notation is

$$\int N^2 (p+\gamma s)^2 d\tau = 1$$

where $d\tau$ represents all space. This is then expanded to

$$N^2 \int p^2 \, d\tau + N^2 2\gamma \int sp \, d\tau + N^2 \gamma^2 \int s^2 \, d\tau = 1 \tag{10.2.4}$$

These terms simplify either due to orthogonality or normality of the constitute atomic orbitals. Equation 10.2.4 simplifies to

$$N^2 + N^2 \gamma^2 = 1$$

and thus the normalization factor can be expressed in terms of γ

$$N = \frac{1}{\sqrt{1+\gamma^2}}$$

and the generic normalized sp^x hybrid orbital (Equation 10.2.3) is

$$|\chi_i\rangle = \frac{1}{\sqrt{1+\gamma^2}} (p+\gamma s) \tag{10.2.5}$$

The s and p characters to a hybrid orbital are now easy to obtain by squaring $|\chi_i\rangle$

- The magnitude of p-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}} \right)^2 = \frac{1}{1+\gamma^2} \tag{10.2.6}$$

  as $\gamma \rightarrow 0$, then the p character of the hybrid goes to 100%
- The magnitude of s-character is

$$\left(\frac{1}{\sqrt{1+\gamma^2}} \gamma^2 \right)^2 = \frac{\gamma^2}{1+\gamma^2} \tag{10.2.7}$$

  as $\gamma \rightarrow 1$, then the s character of the hybrid goes to 50%

As mentioned above, the geometric arrangement will **not** be formed because a molecule is hybridized in a certain way, it is the other way around. How do we choose the correct value of γ for the hybrid orbitals? The mixing coefficient γ is clearly related to the bond angle θ. Using some simple trigonometric relationships, it can be proven that:

$$\cos\theta = -\gamma^2 \tag{10.2.8}$$

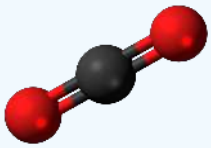
Equation 10.2.8 is an important equation as it related experimentally determined structure to the nature of the bonding and specifically, the composition of the atomic orbitals that create the hybrid orbitals used in the bonding.

Example 10.2.1 : Carbon Dioxide

What is the s-character in the hybrid orbitals for CO_2.

Solution

We know from simple VSEPR theory that the geometry of CO_2 is a linear triatomic molecule.



Thus $\theta = 180^\circ$ and via Equation 10.2.8, $\gamma = 1$ since $\cos 180^\circ = -1$. Hence, Equation 10.2.7 argues that the hybrid orbitals used in the bonding of CO_2 have 50% character; i.e., they are sp hybrid orbitals

$$|\chi_1\rangle = \frac{1}{\sqrt{2}}(s+p)$$

and

$$|\chi_2\rangle = \frac{1}{\sqrt{2}}(s-p)$$

Now, let's apply Equation 10.2.7 to water to find the character of the hybrid orbitals in water. The bond angle in water is 104.45° (Figure 10.2.2) hence

$$\cos 104.5^\circ = -0.25$$

and

$$\gamma = \sqrt{0.25} = 0.5$$

From Equation 10.2.6, then the amount of p character in the hybrid orbitals are

$$\frac{1}{1+\gamma^2} = \frac{1}{1+0.5^2} = 0.80\%$$

which leave 20% for s character (Equation 10.2.7).

$$\frac{\gamma^2}{1+\gamma^2} = \frac{0.5^2}{1+0.5^2} = 0.20$$

The two hybridized atomic orbitals of oxygen involved in bonding are each 80% p and 20% s character. This are not perfect sp^3 hybrid orbitals, as expected. Actually, the orbitals involved in the bonds would be better described as sp^4 hybridized. It does not mean that there are 4 p-orbitals in the hybrid orbital, but that each hybrid consists of 20% of s and 80% of p atomic orbitals.

Lone Pairs

Water has two sets of non-bonding electron pairs (Figure 10.2.4). Without a bond angle to start from, we cannot derive γ that describes the nonbonding hybrid orbitals that they occupy. However, we do know that the O atom has three p orbitals. So the TOTAL absolute p-character in all hybrid orbitals must be 3.

Let x be the p-character in the lone pairs hybrid orbitals:

$$0.8 + 0.8 + x + x = 3$$

This is assuming the lone pairs are **identical**. Solving for this, x = 0.7 (i.e. 70% p and 30% s). From this we can estimate the angle between the lone pair using Equations 10.2.6 and 10.2.8

- p-character:

$$\frac{1}{1+\gamma^2} = 0.7$$

so

$$-\gamma^2 = \frac{1}{0.7-1} = -0.42$$

and $\theta = 115^\circ$.

The angle between the lone pairs is greater (115°) than the bond angle (104.5°). The sp^3 hybrid atomic orbitals of the lone pairs have > 25% s-character. These hybrid orbitals are less directional and held more tightly to the O atom. The sp^3 hybrid atomic orbitals of the bonding pairs have < 25% s-character. They are more directional (i.e., more p-character) and electron density found in the bonding region between O and H.

Warning

It should be noted that the valence bond theory application described above predicts that the two lone electron pairs are in the same hybrid orbitals and hence have the same energies. As discussed in the next sections, that is not experimentally observed in photoelectron spectroscopy, which is a shortcoming of valence bond theory's application to water.

Contributors and Attributions

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10.3: Why is BeH_2 Linear and H_2O Bent?

In this section, we will construct approximate molecular orbitals for a water molecule by considering a simple linear triatomic of the general form HXH, where X is a second row element. We will take a multi-centered molecular orbital approach instead of the two-centered valence bond/hybrid approach discussed previously. As with previous discussions of Molecular Orbitals, we approximate them as a linear combinations of atomic orbitals (LCAO). In molecular orbital theory linear combinations of **all** available (atomic) orbitals will form molecular orbitals. These are spread over the whole molecule, or delocalized, and in a quantum chemical interpretation they are called canonical orbitals. Since it is absolutely wrong to assume that there are only three types of sp^x hybrid orbitals, it is possible, that there are multiple different types of orbitals involved in bonding for a certain atom.

AH_2 Molecules

We want to construct a reasonable argument for the energetic ordering and structure of the molecular orbitals. We first note that each H will donate a $1s$ orbital in the LCAO scheme, and A will likely donate at least $2s$ and possible $2p$ orbitals, depending on its chemical identity. In general, if we consider only the first row A elements, the molecule orbitals (via the LCAO) can be expressed as combination of $1s$ orbitals on the two Hydrogens (H_1 and H_2) and the four n=2 orbitals ($2s$ $2p_x$ $2p_y$; $2p_z$) on the A atom:

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_2|1s\rangle_{H_2} + a_3|2s\rangle_A + a_4|2p_x\rangle_A + a_5|2p_y\rangle_A + a_6|2p_z\rangle_A \tag{10.3.1}$$

These molecular orbitals were created with six atomic orbitals and hence six different $|\chi\rangle$ molecular orbitals can be created. As with previous molecular orbitals problems, the coefficients of this expansion ($\{a_i\}$) are determined by solving the secular determinant.

If we consider only linear AH_2 molecules, then Equation 10.3.1 can be simplified by ignoring $2p_x$ and $2p_y$ atomic orbitals since they are perpendicular to the bonds and are hence non-bonding (only for linear AH_2 molecules). Moreover, the molecule is symmetric about the center (the position of A), hence the orbitals have to have the same symmetry.

Only the $2p$ orbital of A that will overlap with $1s$ of H is the $2p_z$. Hence, Equation 10.3.1 can be simplified to consider the combination

$$|\chi\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A + a_6|2p_z\rangle_A \tag{10.3.2}$$

Note that the two coefficients in front of the $1s$ orbitals of hydrogen are the same by symmetry. This since no hydrogen is "special" and they must have the same contribution to the molecular orbital.

Mixing Amplitudes

How big should the $2s$ orbital contributors of A be compared to the $1s$ orbital of H?

This depends on several things. First, is the nuclear charge on A and the second is the **electronegativity** difference between H and A. The first determines how quickly the $2s$ orbitals, remembering that the exponential part is $exp(-Zr/a_0)$, and the electronegativity difference determines the relative magnitude of H_1 compared to H_2.

The six $|\chi\rangle$ molecular orbitals from Equation 10.3.1 are shown in Figure 10.3.1 .

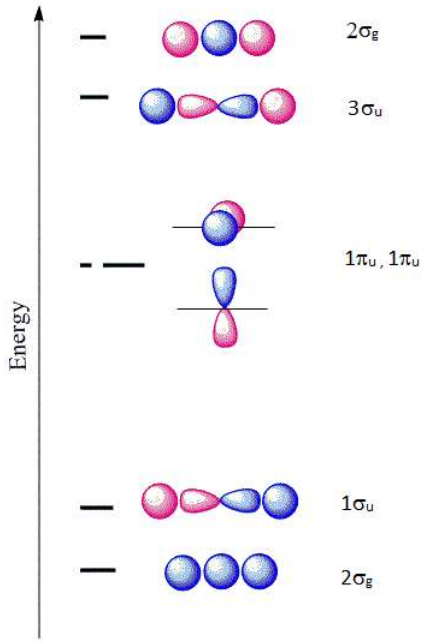


Figure 10.3.1 : The six molecular orbitals for the AH_2 molecule constrained to a linear geometry. The symmetry labels for each molecular orbital are indicated.

The first molecular orbital $|\chi_1\rangle$ constructed from Equation 10.3.1 is purely bonding because the $2s$ orbital is positive near the A nucleus, but becomes negative as we go away from the nucleus. This orbital is also even (*garade symmetry*), so we can denote it as a $2\sigma_g$ orbital signifying that it is constructed from a $2s$ orbital of A combined with the two $1s$ orbitals of H. The only other MO that can be constructed that has the right symmetry is $|\chi_6\rangle$ which is denoted as $2\sigma_u$. This is an antibonding molecular orbital and is also even (*garade symmetry*). The corresponding wavefunctions are:

$$|\chi_1\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_3|2s\rangle_A$$

$$|\chi_6\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} - a_3|2s\rangle_A$$

Next, if we combine a $2p_z$ orbital of A with the $1s$ of H, there are two possibilities that have the right symmetry. The first is

$$|\chi_2\rangle = a_1|1s\rangle_{H_1} + a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

which is a bonding orbital and denoted as $1\sigma_u$. This is purely antibonding and has an odd symmetry (*ungarede*). The other combination is

$$|\chi_5\rangle = a_1|1s\rangle_{H_1} - a_1|1s\rangle_{H_2} + a_6|2p_z\rangle_A$$

Hence, we denote this as $2\sigma_g$. The orbitals $2p_x$ and $2p_y$ from X are nonbonding and become π_{2p_x} and π_{2p_y} nonbonding orbitals and designated as $1\pi_u$ orbitals:

$$|\chi_3\rangle = |2p_x\rangle_A$$

$$|\chi_4\rangle = |2p_y\rangle_A$$

Beryllium Hydride (BeH_2) is Linear

Consider the BeF_2 molecule: Be has a $1s^2\ 2s^2$ electron configuration with is no unpaired electrons available for bonding. From a perspective of using only atomic orbitals to generate the bonding orbitals, we would conclude that the molecule could not exist since no free orientals exist on Be to bond. Clearly, atomic orbitals are not adequate to describe orbitals in molecules, but this can be solved by allowing the 2s and one 2p orbital on Be to mix to form *sp* hybrid orbitals. The experimental H-Be-H bond angle is 180°. Presumably, one electron from Be is shared with each unpaired electrons from H. We could promote and electron from the 2s orbital on Be to the 2p orbital to get two unpaired electrons for bonding (predicting 90° bond angles, not 180°). Thus the geometry is still not explained with atomic orbitals alone.

Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are 2 H atoms on the outside. We initially make combinations of the H atomic orbitals that we previously used to make diatomic hydrogen, except there is no overlap (i.e., $S = 0$). These combinations will mix with the 2s and $2p_z$ on Be, as shown in Figure 10.3.2 .

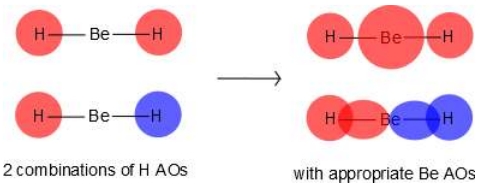


Figure 10.3.2 : Forming molecular orbitals for BeH_2.

Then we can put the Molecular Orbital diagram together, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons (Figure 10.3.3). The bond order is 2.

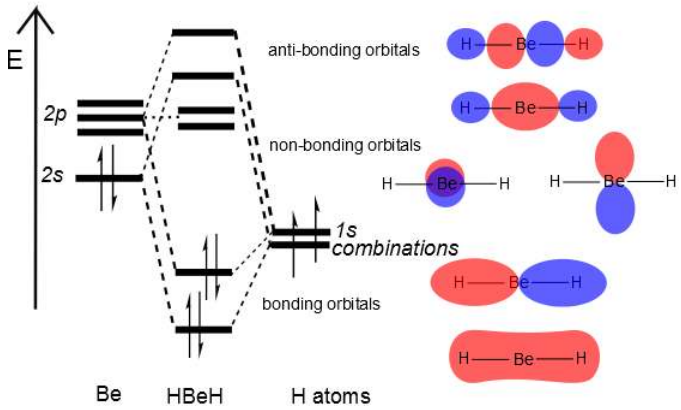


Figure 10.3.3 : Molecular orbitals diagram for BeH_2.

Walsh Correlation Diagrams

Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making quick predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations (i.e. why water adopts a bent conformation).

A major application of Walsh diagrams is to explain the regularity in structure observed for related molecules having identical numbers of valence electrons (i.e. why H_2O and H_2S look similar), and to account for how molecules alter their geometries as their number of electrons or spin state changes. Additionally, Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation. Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

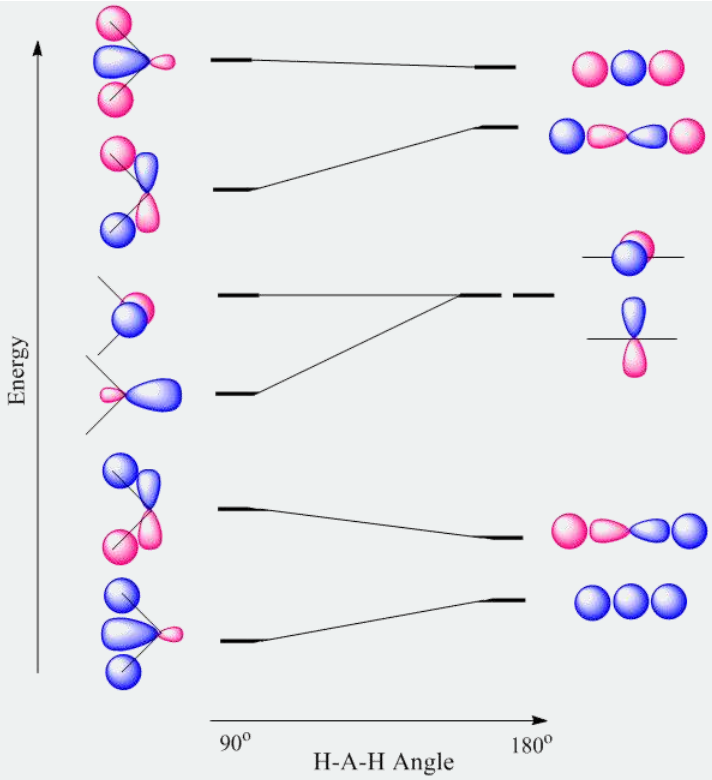


Figure 10.3.4 : A Walsh diagram for an AH_2 molecule. (public domain).

For the AH_2 molecular system, Walsh produced the first angular correlation diagram by plotting the orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180° (Figure 10.3.4). As the bond angle is distorted, the energy for each of the orbitals can be followed along the lines, allowing a quick approximation of molecular energy as a function of conformation.

A typical prediction result for water is an bond angle of 90°, which is not even close to the experimental value of 104°. At best, the method is able to differentiate between a bent and linear molecule.

> *Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.*

Figure 10.3.4 illustrates the difference between the actual linear case we just analyzed and the truly bent molecule, e.g. H_2O. The geometry changes the ordering somewhat, but the qualitative picture we obtain from the linear case makes it a useful construction. The oxygen atomic orbitals are labeled according to their symmetry (Figure 10.3.5) as a_1 for the 2s orbital and b_1 $(2p_x)$, b_2 $(2p_y)$ and a_1 $(2p_z)$ for the three 2p orbitals. The two hydrogen 1s orbitals are premixed to form a_1 and b_2 molecular orbitals.

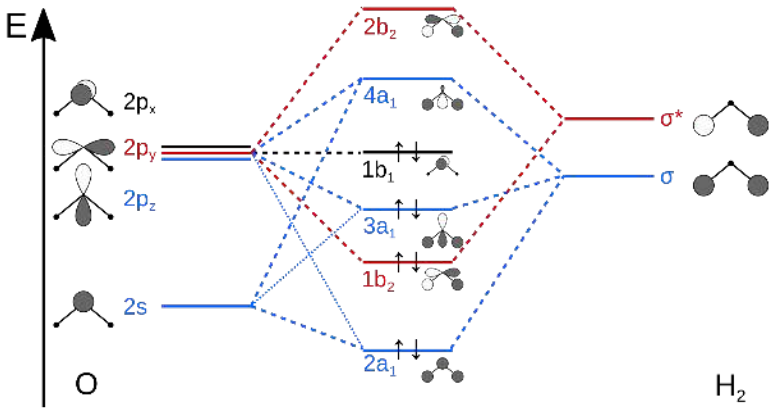


Figure 10.3.5 : MO diagram for water. (CC-SA-BY-3.0; Officer781).

Mixing takes place between same-symmetry orbitals of comparable energy resulting a new set of MO's for water:

- $2a_1$ MO from mixing of the oxygen 2s atomic orbital and the hydrogen σ MO. Small oxygen $2p_z$ atomic orbital admixture strengthens bonding and lowers the orbital energy.
- $1b_2$ MO from mixing of the oxygen $2p_y$ atomic orbital and the hydrogen σ* MO.
- $3a_1$ MO from mixing of the oxygen $2p_z$ atomic orbital and the hydrogen σ MO. Small oxygen 2s atomic orbital admixture weakens bonding and raises the orbital energy.
- $1b_1$ nonbonding MO from the oxygen $2p_x$ atomic orbital (the p-orbital perpendicular to the molecular plane).

In the water molecule the highest occupied orbital, $(1b_1)$ is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital $(2a_1)$ can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density. The electronic configuration of water in the ground state (Figure 10.3.5) is therefore

$$(a_1)^2(b_2)^2(a_1)^2(b_1)^2$$

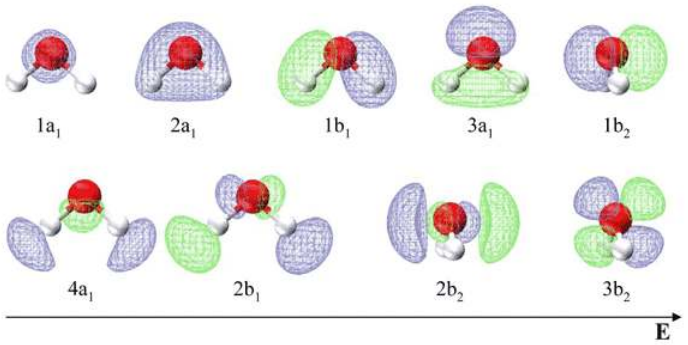


Figure 10.3.5 . Image from Anna Krylov (USC)

Table 10.3.1 list the respective LCAO coefficients for the six atomic orbitals. Table 10.3.1 combines the energy values with the description derived from the character table for molecules of point group C_{2v}

Table 10.3.1 : LCAO Coefficients of first six molecular orbitals of water

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
6.728	$2b_2$	0.525	0	0	-0.669	0	-0.525
5.440	$3a_1$	-0.553	0.306	0	0	-0.544	0.553
-12.191	$1b_1$	0	0	-1.000	0	0	0
-14.467	$2a_1$	-0.309	0.354	0	0	0.827	-0.309
-19.113	$1b_2$	-0.473	0	0	-0.743	0	0.473

Energy	Symbol	s(H)	s(O)	p_x(O)	p_y(O)	p_z(O)	s(H)
-40.032	$1a_1$	0.315	0.884	0	0	-0.143	0.315

Note in contrast to the valence bond theory discussed previous for water, the two lone electron pairs are **not in identical orbitals**. The $1b_1$ MO is a lone pair, while the $3a_1$, $1b_2$ and $2a_1$ MO's can be localized to give two O−H bonds and an in-plane lone pair. This is in agreement with the experimentally measured photoelectron spectrum discussed in the next section.

Summary

Walsh correlation diagram is a plot of molecular orbital energy as a function of some systematic change in molecular geometry. For example, the correlation between orbital energies and bond angle for an AH_2 molecule. The geometry of a molecule is determined by which possible structure is lowest in energy. We can use the Walsh diagram to determine the energy trends based on which orbitals are occupied.

Contributors and Attributions

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10.4: Photoelectron Spectroscopy

Learning Objectives

- Demonstrate how photoelectron spectroscopy can be used to resolve the absolute energies of molecular orbitals.

Photoelectron spectroscopy (PES) utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.

- **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels.
- **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation:

$$E = h\nu \tag{10.4.1}$$

where h is Planck constant and ν is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the topic of this page.

Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy). In UPS the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

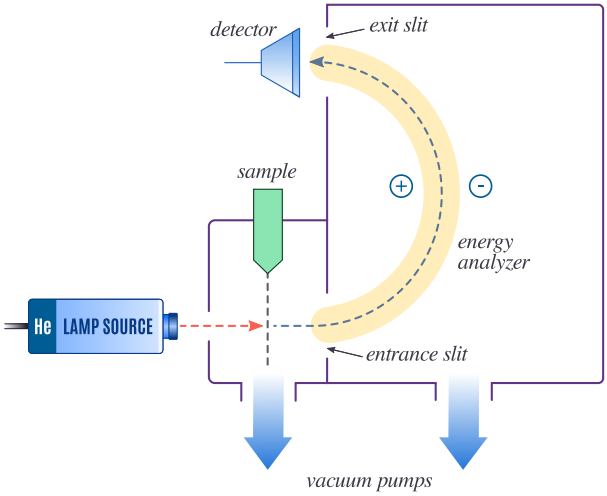


Figure 10.4.1 : Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit. (CC BY-NC; Ümit Kaya via LibreTexts)

The process of photoionization can be considered in several ways. One way is to look at the overall process for a species A:

$$A + \text{photon} \rightarrow A^+ + e^- \tag{10.4.2}$$

Conservation of energy then requires that (after using Equation 10.4.1):

$$E(A) + h\nu = E(A^+) + E(e^-) \tag{10.4.3}$$

Since the free electron's energy is present solely as kinetic energy (KE) (i.e., there is no internal energy in a free electron)

$$E(e^-) = KE$$

Equation 10.4.3 can then be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - \left[E(A^+) - E(A)\right] \tag{10.4.4}$$

The final term in brackets represents the difference in energy between the ionized and neutral species and is generally called the **vertical ionization energy** (IE) of the ejected electron; this then leads to the following commonly quoted equations:

$$KE = h\nu - IE \tag{10.4.5}$$

or

$$IE = h\nu - KE \tag{10.4.6}$$

The vertical ionization energy is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (i.e., a free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

Note

Equation 10.4.5 may look familiar to you as it the same equation Einstein used to describe the photoelectric effect except the vertical ionization energy (IE) is substituted for workfunction Φ. Both vertical ionization energy and workfunctions are metrics for the binding energy of an electron in the sample.

At a fundamental level, ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the molecular orbitals detailed and specific quantitative information regarding the electronic structure and bonding in molecules.

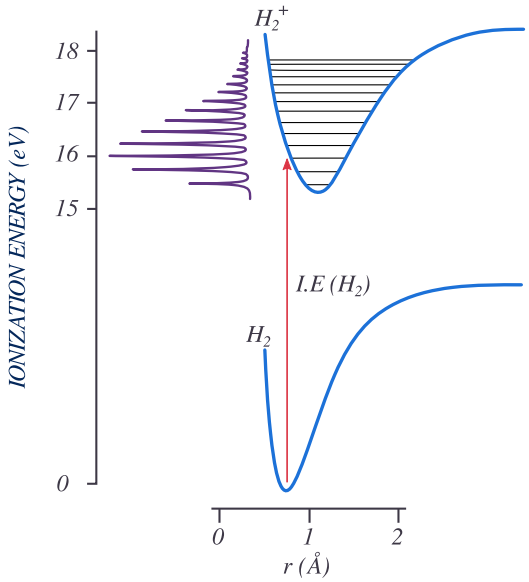


Figure 10.4.2 : Vertical ionization process for molecular hydrogen. (CC BY-NC; Ümit Kaya via LibreTexts)

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states as shown in Equation 10.4.6 and as illustrated in the Figure 10.4.2 . Nonetheless, the information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the *vertical ionization energy* to the ion state formed by removal of an electron from that orbital (Figure 10.4.3), provided the distributions of the remaining electrons do not change (i.e., frozen).

$$I_j = -\epsilon_j \tag{10.4.7}$$

There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

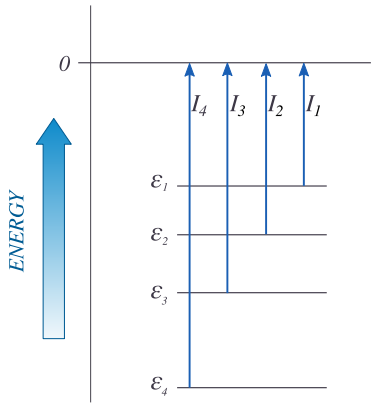


Figure 10.4.3 : Within Koopmans' Theorem, the energies of the orbitals (\epsilon\) have an attractively simple physical interpretation: they give the amount of energy necessary to remove (ionize) the electron out of the molecular orbital, which corresponds to the negative of the experimentally observable ionization potential (I). (CC BY-NC; Ümit Kaya via LibreTexts)

Koopmans' Theorem

Koopmans' theorem argues that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital.

Several different ionization energies can be defined, depending on the degree of vibrational excitation of the cations. In general, the following two types of ionization energies are considered (Figure 10.4.4):

- Adiabatic ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v" = 0) + h\nu \rightarrow M^+(x, v' = 0) + e^-$$

  Adiabatic ionization energy that is, the minimum energy required to eject an electron from a molecule in its ground vibrational state and transform it into a cation in the lowest vibrational level of an electronic state x of the cation.
- Vertical ionization energy corresponds to the ionization energy associated with this transition

  $$M(X, v" = 0) + h\nu \rightarrow M^+(x, v' = n) + e^-$$

  where, the value n of the vibrational quantum number v' corresponds to the vibrational level whose wavefunction gives the largest overlap with the v" = 0 wavefunction. This is the most probable transition and usually corresponds to the vertical transition where the internuclear separations of the ionic state are similar to those of the ground state.

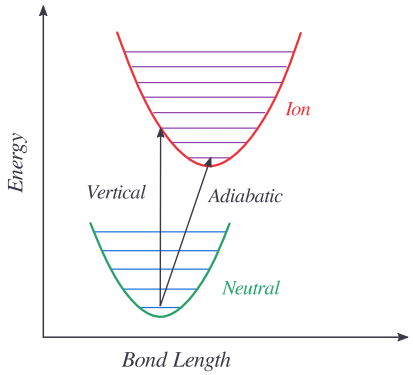


Figure 10.4.4 : Difference between vertical and adiabatic ionization energies for a simple harmonic oscillator system. (CC BY-NC; Ümit Kaya via LibreTexts)

The geometry of an ion may be different from the neutral molecule. The measured ionzation energy in a PES experiment can refer to the vertical ionization energy, in which case the ion is in the same geometry as the neutral, or to the adiabatic ionzaiton energy, in which case the ion is in its lowest energy, relaxed geometry (mostly the former though). This is illustrated in the Figure 10.4.4 . For a diatomic the only geometry change possible is the bond length. The figure shows an ion with a slightly longer bond length than the neutral. The harmonic potential energy surfaces are shown in green (neutral) and red (ion) with vibrational energy levels. The vertical ionzation energy is **always greater** than the adiabatic ionzation energy.

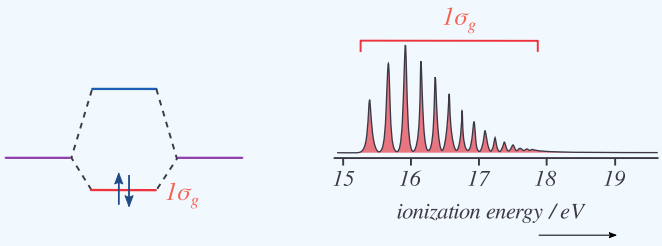
Differing Ionization Energies

You have been exposed to three metrics of ionization energies already, which are similar, but with distinct differences:

- The *ionization energy* (also called *adiabatic ionization energy*) is the lowest energy required to effect the removal of an electron from a molecule or atom, and corresponds to the transition from the lowest electronic, vibrational and rotational level of the isolated molecule to the lowest electronic, vibrational and rotational level of the isolated ion.
- The *binding energy* (also called *vertical ionization energy*) is the energy change corresponding to an ionization reaction leading to formation of the ion in a configuration which is the same as that of the equilibrium geometry of the ground state neutral molecule.
- The *workfunction* is the minimum energy needed to remove an electron from a (bulk) solid to a point in the vacuum.

Example 10.4.1 : Molecular Hydrogen

As you remember, the molecular orbital description of hydrogen involves two $|1s\rangle$ atomic orbitals generating a bonding $1\sigma_g$ and antibonding $2\sigma_u^*$ molecular orbitals. The two electrons that are responsible for the H_2 bond are occupied in the $1\sigma_g$.

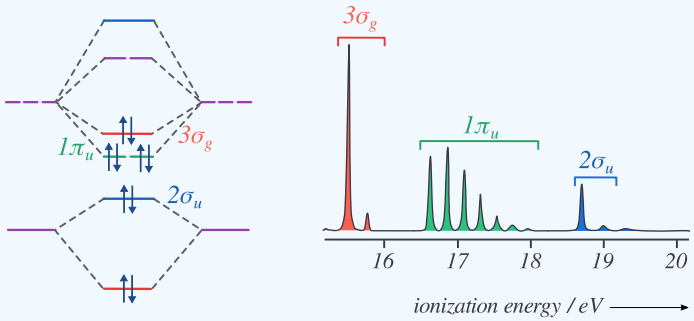


MO diagram and PES spectrum of H_2. (CC BY-NC; Ümit Kaya via LibreTexts)

The PES spectrum has a single band that corresponds to the ionization of a $1\sigma_g$ electron. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length since the bond order has been reduced).

Example 10.4.2 : Molecular Nitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Four molecular orbitals are occupied (the two $1\pi_u$ orbitals are both occupied). The UV photoelectron spectrum of N_2, has three bands corresponding to $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ occupied molecular orbitals. Both $3\sigma_g$ and $2\sigma_u$ are weakly bonding and antibonding. The $1\sigma_g$ orbital is not resolved in this spectrum since the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital.



MO diagram and PES spectrum of N_2. (CC BY-NC; Ümit Kaya via LibreTexts)

Note that extensive vibrational structure for the $1\pi_u$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

Hydrogen Chloride

The molecular energy level diagram for HCl is reproduced in Figure 10.4.5

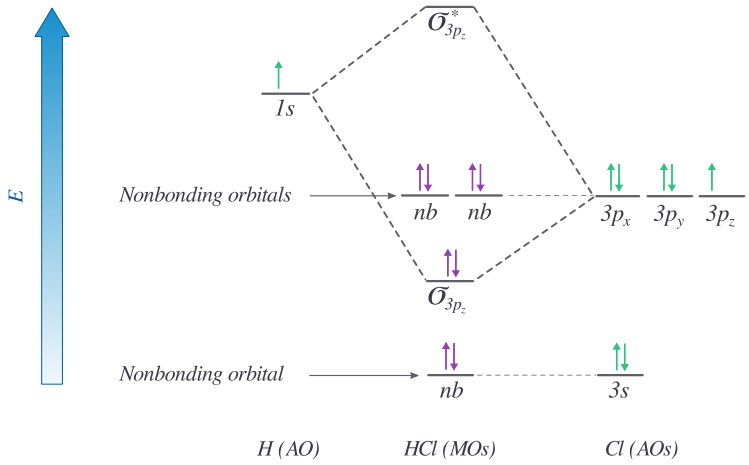


Figure 10.4.5 : Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts molecular orbitals strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1. (CC BY-NC; Ümit Kaya via LibreTexts)

Important aspects of molecular orbital diagram in Figure 10.4.5 :

- The H 1*s* energy lies well above the Cl 2*s* and 2*p* atomic orbitals;
- The valence electron configuration can be written $3\sigma^2 1\pi^4$;
- The H 1*s* orbital contributes only to the σ molecular orbitals, as does one of the Cl 2*p* orbitals (hence the lines in Figure 10.4.5 connecting these atomic orbitals and the 3σ and 4σ molecular orbitals);

- The remaining Cl 2*p* orbitals (ie those perpendicular to the bond axis) are unaffected by bonding, and these form the 1π molecular orbitals;
- The 1π orbitals are nonbonding - they are not affected energetically by the interaction between the atoms, and are hence neither bonding nor antibonding;
- The 3σ orbital is weakly bonding, and largely Cl 2*p*;
- The 3σ* orbital is antibonding, and primarily of H 1*s* character;

Figure 10.4.6 shows the analogous MO diagram and photoelectron spectrum for HCl. The spectrum has two bands corresponding to non-bonding 1*p* (or 1π) molecular orbitals (with negligible vibrational structure) and the 3*s* bonding molecular orbital (vibrational structure).

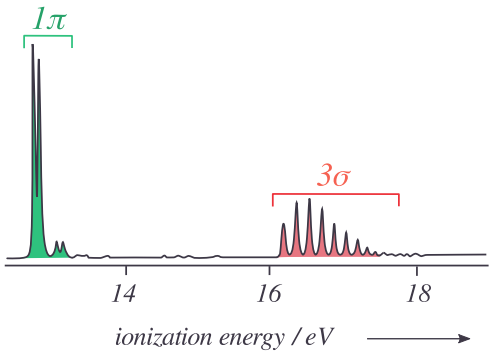


Figure 10.4.6 : Photoelectron spectrum HCl. (CC BY-NC; Ümit Kaya via LibreTexts)

The higher energy (more stabilized) core molecular orbitals are not observed since the incident photon energy $h\nu$ is below their ionization energies.

Water

In the simplified valence bond theory perspective of the water molecule, the oxygen atom form four sp^3 hybrid orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. Within the molecular orbital picture, the electronic configuration of the H_2O^+ molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry that will be discussed later (Figure 10.4.7). Within Koopmans' theorem:

- The energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$.
- The energy of the second-highest molecular orbitals $3a_1$ refers to the ion in the excited state $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$.

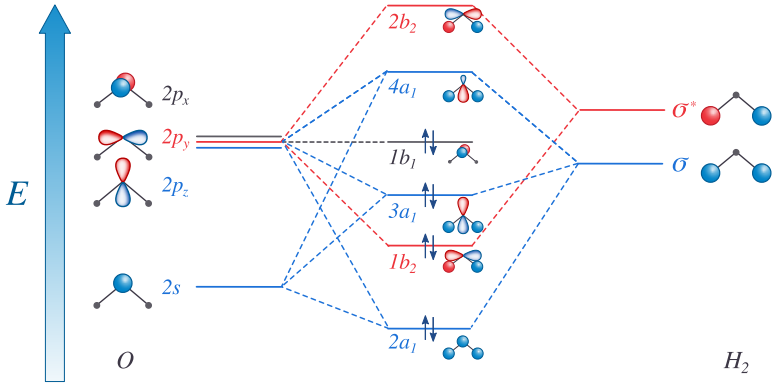


Figure 10.4.7 : MO diagram for water. (CC BY-NC; Ümit Kaya via LibreTexts)

The Hartree–Fock orbital energies (with sign changed) of these orbitals are tabulated below and compared to the experimental ionization energies.

Molecular orbital	Hartree–Fock orbital Energies (eV)	Experimental Ionization Energies (eV)
$2a_1$	36.7	32.2
$1b_2$	19.5	18.5
$3a_1$	15.9	14.7
$1b_1$	13.8	12.6

As explained above, the deviations between orbital energy and ionization energy is small and due to the effects of orbital relaxation as well as differences in electron correlation energy between the molecular and the various ionized states.

The molecular orbital perspective has the lone pair in different orbitals (one in a non-bonding orbital ($1b_1$ and one in the bonding orbitals). We tern to the photoelectron spectroscopy to help identify which theory is more accurate (i.e., describes reality better). The photoelectron spectrum of water in Figure 10.4.6 can be interpreted as having three major peaks with some fine structure arises from vibrational energy changes. The light source used in this experiment is not sufficiently energetic to ionize electrons from the lowest lying molecular orbitals.

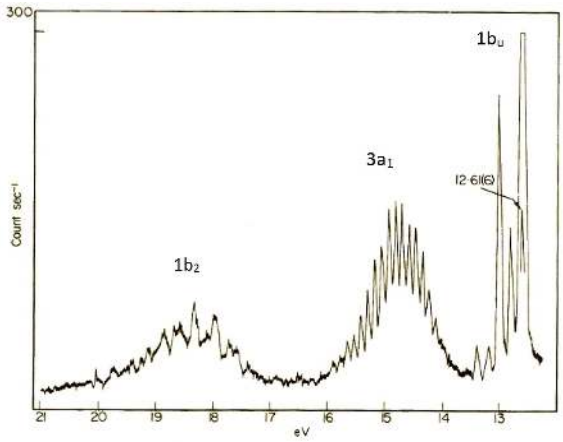


Figure 10.4.8 : Photoelectron spectrum of water. Note the energy axes is flipped compared to other spectra on this page.his spectrum does not go to high enough energy to show the deep $2a_1$ molecular orbital.

If water was formed two identical O-H bonds and two lone pairs on the oxygen atom line valence bond theory predicts, then the PES in Figure 10.4.8 would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs. The photoelectron spectrum clearly shows three peaks in the positions expected for the molecular orbitals in Figure 10.4.8 .

If the molecular orbitals in Figure 10.4.7 represent the real electronic structure, how do we view the bonding? These molecular orbitals are delocalized and bare little relationship to the familiar 2-center bonds used in valence bond theory. For example, the $2a_1$ $1b_1$ and $3a_1$ molecular orbitals all have contributions from all three atoms, they are really 3-centered molecular orbitals. The bonds however can be thought of as representing a build up of the total electron density which loosely put is a total of all the orbital contributions. Despite this, we keep the ideas of hybridization and 2-center bonds because they are useful NOT because they represent reality

Summary

A photoelecton spectrum can show the relative energies of occupied molecular orbitals by ionization. (i.e. ejection of an electron). A photoelectron spectrum can also be used to determine energy spacing between vibrational levels of a given electronic state. Each orbital energy band has a structure showing ionization to different vibrational levels.

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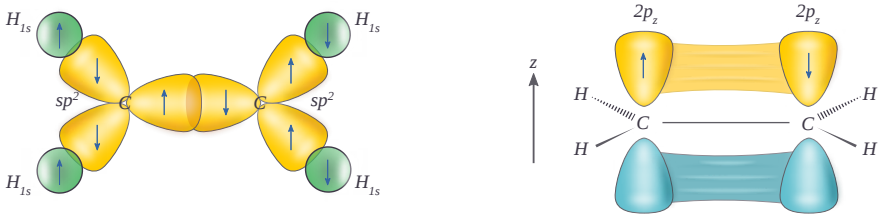
10.5: The π π -Electron Approximation of Conjugation

Learning Objectives

- Demonstrate how Hückel's theory approximates the full molecular orbital picture of molecules by treating the σ-bonding and π-bonding networks independently.

Molecular orbital theory has been very successfully applied to large conjugated systems, especially those containing chains of carbon atoms with alternating single and double bonds. An approximation introduced by Hückel in 1931 considers only the delocalized *p* electrons moving in a framework of π-bonds. This is, in fact, a more sophisticated version of a free-electron model.

The simplest hydrocarbon to consider that exhibits π bonding is ethylene (ethene), which is made up of four hydrogen atoms and two carbon atoms. Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part (a) of Figure 10.5.1).



(a) C_2H_4 σ - bonded framework *(b) C_2H_4 π bonding*

Figure 10.5.1 : (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.) (CC BY-NC; Ümit Kaya via LibreTexts)

The Hückel approximation is used to determine the energies and shapes of the π molecular orbitals in conjugated systems. Within the Hückel approximation, the covalent bonding in these hydrocarbones can be separated into two independent "frameworks": the σ-bonding framework and the the σ-bonding framework. The wavefunctions used to describe the bonding orbitals in each framework results from different combinations of atomic orbitals. The method limits itself to addressing conjugated hydrocarbons and specifically only π electron molecular orbitals are included because these determine the general properties of these molecules; the sigma electrons are ignored. This is referred to as *sigma-pi separability* and is justified by the orthogonality of σ and π orbitals in planar molecules. For this reason, the Hückel method is limited to planar systems. Hückel approximation assumes that the electrons in the π bonds “feel” an electrostatic potential due to the entire σ-bonding framework in the molecule (i.e. it focuses only on the formation of π bonds, given that the σ bonding framework has already been formed).

Conjugated Systems

A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds, that allow a *delocalization* of π electrons across all the adjacent aligned p-orbitals. These π electrons do not belong to a single bond or atom, but rather to a group of atoms.

Ethylene

Before considering the Hückel treatment for ethylene, it is beneficial to review the general bonding picture of the molecule. Bonding in ethylene involves the sp^2 hybridization of the $2s$, $2p_x$, and $2p_y$ atomic orbitals on each carbon atom; leaving the $2p_z$ orbitals untouched (Figure 10.5.2).

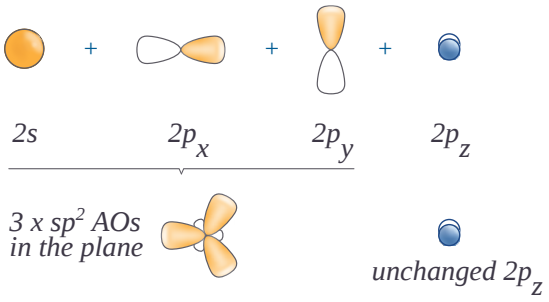


Figure 10.5.2 : Hybridizing of the carbon atomic orbitals to give sp^2 hybrid orbitals for bonding to hydrogen atoms in ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

The use of hybrid orbitals in the molecular orbital approach describe here is merely a convenience and not invoking valence bond theory (directly). An identical description can be extracted using exclusively atomic orbitals on carbon, but the interpretation of the resulting wavefunctions is less intuitive. For example, the i[th] molecular orbital can be described via hybrid orbitals

$$|\psi_1\rangle = c_1|sp_1^2\rangle + c_2|1s_a\rangle$$

or via atomic orbitals.

$$|\psi_1\rangle = a_1|2s\rangle + a_1|2p_x\rangle + a_1|2p_y\rangle + a_4|1s_a\rangle$$

where $\{a_i\}$ and $\{c_i\}$ are coefficients of the expansion. Either describe will work and both are identical approaches since

$$|sp_1^2\rangle = b_1|2s\rangle + b_1|2p_x\rangle + b_1|2p_y\rangle$$

where $\{c_i\}$ are coefficients describing the hybridized orbital.

The bonding occurs via the mixing of the electrons in the sp^2 hybrid orbitals on carbon and the electrons in the $1s$ atomic orbitals of the four hydrogen atoms (Figure 10.5.1 ; left) resulting in the σ-bonding framework. The π-bonding framework results from the unhybridized $2p_z$ orbitals (Figure 10.5.2 ; right). The independence of these two frameworks is demonstrated in the resulting molecular orbital diagram in Figure 10.5.3 ; Hückel theory is concerned only with describing the molecular orbitals and energies of the π bonding framework.

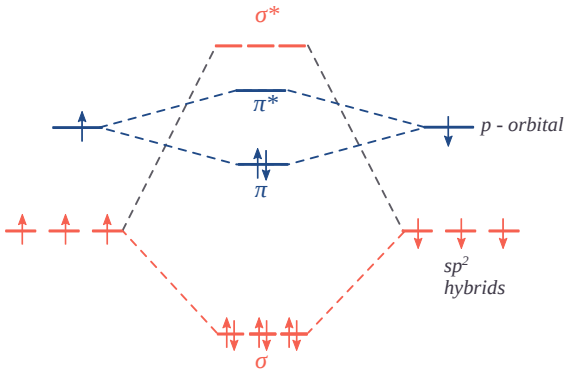


Figure 10.5.3 : Molecular orbitals demonstrating the sigma-pi separability of the π-bonding framework (blue) and the σ-bonding frameworks (red) of ethylene. (CC BY-NC; Ümit Kaya via LibreTexts)

> *Hückel treatment is concerned only with describing the molecular orbitals and energies of the π bonding framework.*

Since Hückel theory is a special consideration of molecular orbital theory, the molecular orbitals $|\psi_i\rangle$ can be described as a linear combination of the $2p_z$ atomic orbitals ϕ at carbon with their corresponding $\{c_i\}$ coefficients:

$$|\psi_i\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{10.5.1}$$

This equation is substituted in the Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

with $\hat{H}$ the Hamiltonian and E_i the energy corresponding to the molecular orbital to give:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle \tag{10.5.2}$$

If Equation 10.5.2 is multiplied by $\langle\phi_1|$ (and integrated), then

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \tag{10.5.3}$$

where H_{ij} are the Hamiltonian matrix elements (see note below)

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

If Equation 10.5.2 is multiplied by $\langle\phi_2|$ (and integrated), then

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \tag{10.5.4}$$

Both Equations 10.5.3 and 10.5.4 can better represented in matrix notation,

$$\begin{bmatrix} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) \\ c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) \end{bmatrix} = 0$$

or more simply as a product of matrices.

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.5}$$

All diagonal Hamiltonian integrals H_{ii} are called **Coulomb integrals** and those of type H_{ij} are called **resonance integrals**. Both integrals are negative and the resonance integrals determines the strength of the bonding interactions. The equations described by Equation 10.5.5 are called the ***secular equations*** and will also have the trivial solution of

$$c_1 = c_2 = 0$$

Within linear algebra, the secular equations in Equation 10.5.5 will also have a non-trivial solution, if and only if, the secular determinant is zero

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{10.5.6}$$

or in shorthand notation

$$\det(H - ES) = 0$$

Everything in Equation 10.5.6 is a known number except E. Since the secular determinant for ethylene is a 2×2 matrix, finding E, requires solving a quadratic equation (after expanding the determinant)

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0$$

There will be two values of E which satisfy this equation and they are the molecular orbital energies. For ethylene, one will be the bonding energy and the other the antibonding energy for the π-orbitals formed by the combination of the two carbon $2p_z$ orbitals (Equation 10.5.1). However, if more than two $|\phi\rangle$ atomic orbitals were used, e.g., in a bigger molecule, then more energies would be estimated by solving the secular determinant.

Solving the secular determinant is simplified within Hückel method via the following four assumptions:

1. All overlap integrals S_{ij} are set equal to zero. This is quite reasonable since the $\pi-$ orbitals are directed perpendicular to the direction of their bonds (Figure 10.5.1). This assumption is often call neglect of differential overlap (NDO).
2. All resonance integrals H_{ij} between non-neighboring atoms are set equal to zero.

3. All resonance integrals H_{ij} between neighboring atoms are equal and set to β.
4. All coulomb integrals H_{ii} are set equal to α.

These assumptions are mathematically expressed as

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

Assumptions 1 means that the overlap integral between the two atomic orbitals is 0

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = 0$$

Matrix Representation of the Hamiltonian

The Coulomb integrals

$$H_{ii} = \langle \phi_i | H | \phi_i \rangle$$

and resonance integrals.

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \;\; (i \neq i)$$

are often described within the matrix representation of the Hamiltonian (specifically within the $|\phi\rangle$ basis):

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

or within the Hückel assumptions

$$\hat{H} = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}$$

The Hückel assumptions reduces Equation 10.5.5 in two homogeneous equations:

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.7}$$

if Equation 10.5.7 is divided by β:

$$\begin{bmatrix} \dfrac{\alpha - E}{\beta} & 1 \\ 1 & \dfrac{\alpha - E}{\beta} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

and then a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.5.8}$$

then Equation 10.5.7 simplifies to

$$\begin{bmatrix} x & 1 \\ 1 & x \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \tag{10.5.9}$$

The trivial solution gives both wavefunction coefficients equal to zero and the other (non-trivial) solution is determined by solving the secular determinant

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which when expanded is $x^2 - 1 = 0$ so $x = \pm 1$.

Knowing that $E = \alpha - x\beta$ from Equation 10.5.8, the energy levels can be found to be

$$E = \alpha - \pm 1 \times \beta$$

or

$$E = \alpha \mp \beta$$

Since β is negative, the two energies are ordered (Figure 10.5.4)

- For π_1: $E_1 = \alpha + \beta$
- For π_2: $E_2 = \alpha - \beta$

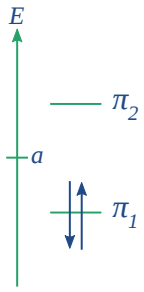


Figure 10.5.4 : π energies of ethylene with occupation. (CC BY-NC; Ümit Kaya via LibreTexts)

To extract the coefficients attributed to these energies, the corresponding x values can be substituted back into the Secular Equations (Equation 10.5.9). For the lower energy state ($x = -1$)

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$|\psi_1\rangle = N_1(|\phi_1\rangle + |\phi_2\rangle) \tag{10.5.10}$$

where N_1 is the normalization constant for this molecular orbital; this is the **bonding** molecular orbital.

For the higher energy molecular orbital ($x = -1$) and then

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

This gives $c_1 = -c_2$ and the molecular orbitals attributed to this energy is then (based off of Equation 10.5.1):

$$\psi_2\rangle = N_2(|\phi_1\rangle - |\phi_2\rangle) \tag{10.5.11}$$

where N_2 is the normalization constant for this molecular orbital; this is the **anti-bonding** molecular orbital.

The normalization constants for both molecular orbitals can obtained via the standard normalization approach (i.e., $\langle\psi_i|\psi_i\rangle = 1$) to obtain

$$N_1 = N_2 = \frac{1}{\sqrt{2}}$$

These molecular orbitals form the π-bonding framework and since each carbon contributes one electron to this framework, only the lowest molecular orbital ($|\psi_1\rangle$) is occupied (Figure 10.5.5) in the ground state. The corresponding electron configuration is then π_1^2.

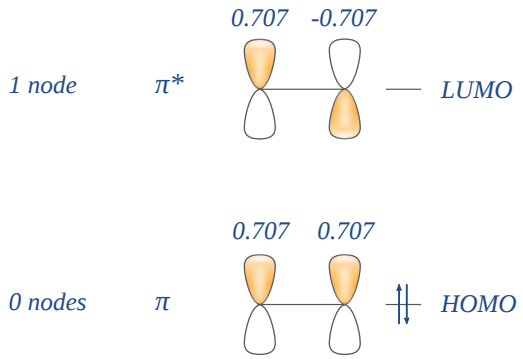


Figure 10.5.5 : Schemetic representation of the π molecular orbitals framework for ethylene . Notice that the antibonding molecular orbital has one more node than the bonding molecular orbital as expected since it is higher in energy. (CC BY-NC; Ümit Kaya via LibreTexts)

> *HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively and are often referred to as frontier orbitals. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap.*

The 3-D calculated π molecular orbitals are shown in Figure 10.5.6 .

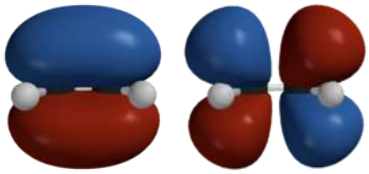


Figure 10.5.6 : Calculated π molecular orbitals for ethylene . (left) the bonding orbital (|\psi_1 \rangle\) and (right) the antibonding $(|\psi_2\rangle$ orbital.

Limitations of Hückel Theory

Hückel theory was developed in the 1930's when computers were unavailable and a simple mathematical approaches were very important for understanding experiment. Although the assumptions in Hückel theory are drastic they enabled the early calculations of molecular orbitals to be performed with mechanical calculators or by hand. Hückel Theory can be extended to address other types of atoms in conjugated molecules (e.g., nitrogen and oxygen). Moreover, it can be extended to also treat σ orbitals and this "Extended Hückel Theory" is still used today. Despite the utility of Hückel Theory, it is highly qualitative and we should remember the limitations of Hückel Theory:

- Hückel Theory is very approximate
- Hückel Theory cannot calculate energies accurately (electron-electron repulsion is not calculated)
- Hückel Theory typically overestimates predicted dipole moments

Hückel Theory is best used to provide simplified models for understanding chemistry and for a detailed understanding modern *ab initio* molecular methods discussed in Chapter 11 are needed.

Contributors

- Seymour Blinder (Professor Emeritus of Chemistry and Physics at the University of Michigan, Ann Arbor)
- Wikipedia
- StackExchange (Philipp)

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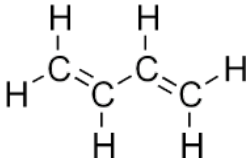
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10.6: Butadiene is Stabilized by a Delocalization Energy

Learning Objectives

- Apply Hückel theory to an extended π-bonding network
- Identify the origin of delocalization energy from Hückel theory and relate it to resonances structures in valence bond theory

1,3-Butadiene is a simple conjugated diene with the formula C_4H_6 and can be viewed structurally as two vinyl groups ($CH_2{=}CH_2$) joined together with a single bond. Butadiene can occupy either a cis or trans conformers and at room temperature, 96% of butadiene exists as the trans conformer, which is 2.3 kcal/mole more stable than the cis structure.



trans-1,3-Butadiene

For the simple application of applying Hückel theory for understanding the electronic structure of butadiene, we will ignore the energetic differences between the two conformers. As discussed previously, the molecular orbitals are linear combination of the four $|p\rangle$ atomic orbitals on the carbon atoms that are not participating in the σ bonding network:

$$|\psi_i\rangle = \sum_j^4 c_{ij}|p_i\rangle$$

or explicitly

$$|\psi_i\rangle = c_{i1}|p_1\rangle + c_{i2}|p_2\rangle + c_{i3}|p_3\rangle + c_{i4}|p_4\rangle \tag{10.6.1}$$

for the i[th] molecular orbital $|\psi_i\rangle$. The secular equations that need to be solved are

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.2}$$

If the standard Hückel theory approximations were used

$$H_{ii} - ES_{ii} = \alpha$$

and

$$H_{ij} - ES_{ij} = \beta$$

when $i = j \pm 1$, otherwise

$$H_{ij} - ES_{ij} = 0$$

then the secular equations for butadiene in Equation 10.6.2 become

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0 \tag{10.6.3}$$

Solving Equation 10.6.3 for $\{c_i\}$ coefficients and energy secular equation requires extracting the roots of the secular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{10.6.4}$$

If both sides of Equation 10.6.4 were divided by β^4 and a new variable x is defined

$$x = \frac{\alpha - E}{\beta} \tag{10.6.5}$$

then Equation 10.6.4 simplifies further to

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{10.6.6}$$

This is essentially the connection matrix for the butadiene molecule. Each pair of connected atoms is represented by 1, each non-connected pair by 0 and each diagonal element by x. Expansion of the determinant in Equation 10.6.6 gives the 4th order polynomial equation

$$x^4 - 3x^2 + 1 = 0 \tag{10.6.7}$$

While solving 4th order equations typically require numerical estimation, Equation 10.6.7 can be further simplified by recognizing that it is a quadratic equation in terms of x^2. Therefore, the roots are

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

or $x = \pm\, 0.618$ and $x = \pm\, 1.618$. Since α and β are negative, these molecular orbital energies can ordered in terms of energy (from lowest to highest):

$$E_1 = \alpha + 1.618\beta \tag{10.6.8}$$

$$E_2 = \alpha + 0.618\beta \tag{10.6.9}$$

$$E_3 = \alpha - 0.618\beta \tag{10.6.10}$$

$$E_4 = \alpha - 1.618\beta \tag{10.6.11}$$

This sequence of energies is displayed in the energy diagram of Figure 10.6.1 .

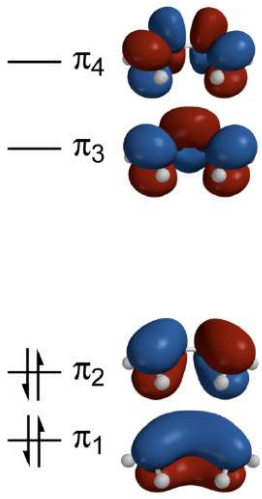


Figure 10.6.1 : The π molecular orbital energies from Hückel theory for butadiene with ground-state configuration. Structures calculated and images produced using HF/6-31G* (Public Domain; Ben Mills).

Each p atomic orbital of carbon contributes a single electron to the π manifold, so the ground-state occupation of the resulting four π electrons have a $\pi_1^2\pi_2^2$ configuration (Figure 10.6.1). The the total π-electron energy is then determined by adding up the energies in Equations 10.6.8-10.6.11 and scaling by their occupations to get

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_1 + 2\times E_2 + 0\times E_3 + 0\times E_4 \\ &= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) \\ &= 4\alpha + 4.472\beta \end{aligned} \tag{10.6.12}$$

If the bonding of butadiene were described only as two localized double bond as in its dominant valence-bond structure (Figure 10.6.1), then its π-electron energy would be given by twice the E_π predicted for the ethlyene molecule:

$$\begin{aligned} E_\pi(\text{butadiene}) &= 2\times E_\pi(\text{ethylene}) \\ &= 2\times 2(\alpha+\beta) \\ &= 4\alpha + 4\beta \end{aligned} \tag{10.6.13}$$

Comparing Equation 10.6.12 with Equation 10.6.12, the total π energy of butadiene lies lower than the total π energy of two double bonds by 0.48β(the σ bond does not contribute). This difference is known as the **delocalization energy**; a typical estimate of β is around -75 kJ/mol, which results in a *delocalization energy* for butadiene of -35 kJ/mol.

> *The delocalization energy is the extra stabilization resulting from the electrons extending over the whole molecule.*

Delocalization Energy in Valence Bond Theory

Delocalization energy is intrinsic to molecular orbital theory, since it results from breaking the two-center bond concept with the molecular orbitals that spread over more that just one pair of atoms. However, within the two-center theory of valence bond theory, the delocalization energy results from a stabilization energy attributed to resonance. Several conventional valence bond resonance structures that can be written for 1,3-butadiene, four of which are shown in Figure 10.6.2 . However, while structure $2a$ dominates, the other resonance structures also contribute to describing the total molecule and hence predict a corresponding stabilization energy akin to the delocalization energy in molecular orbital theory.

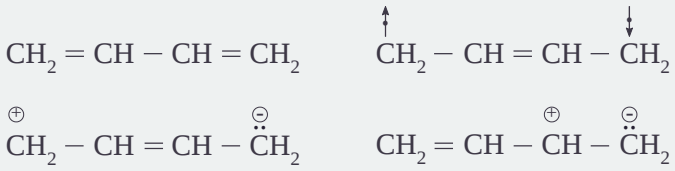


Figure 10.6.2 : Several resonance structures that can be written for 1,3-butadiene. The resonance structure in the upper left dominates, but does not exclusively describe the system since a delocalization energy is experimentally observed compared to two ethylene molecules. (CC BY-NC; Ümit Kaya via LibreTexts)

In general, the true description of the bonding within the valence bond theory is a superposition of resonance structures with amplitudes that are determined via a variational optimization to find the lowest possible energy for the valence bond wavefunctions.

The solving the secular equations (Equation 10.6.2) gives the $\{c_{ij}\}$ coefficients for the molecular orbitals in Equation 10.6.1 (not demonstrated):

$$|\psi_1\rangle = 0.37|p_1\rangle + 0.60|p_2\rangle + 0.60|p_3\rangle + 0.37|p_4\rangle \tag{10.6.14}$$

$$|\psi_3\rangle = 0.60|p_1\rangle + 0.37|p_2\rangle - 0.37|p_3\rangle - 0.60|p_4\rangle \tag{10.6.15}$$

$$|\psi_3\rangle = 0.60|p_1\rangle - 0.37|p_2\rangle - 0.37|p_3\rangle + 0.60|p_4\rangle \tag{10.6.16}$$

$$|\psi_4\rangle = 0.37|p_1\rangle - 0.60|p_2\rangle + 0.60|p_3\rangle - 0.37|p_4\rangle \tag{10.6.17}$$

These are depicted in Figure 10.6.3 .

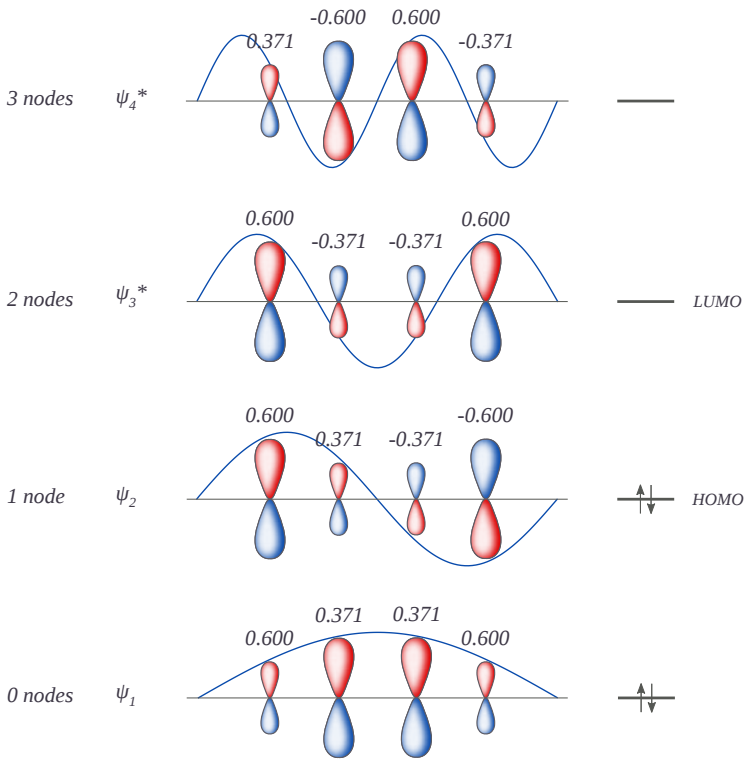


Figure 10.6.3 : Energy level diagram and decomposition of the π molecular orbitals of butadiene. This is view three-dimensionally in Figure 10.6.1 . (CC BY-NC; Ümit Kaya via LibreTexts)

Note the correlation of the energy of the π molecular orbitals of butadiene to the number of nodes in the wavefunction; this is the general trend observed in previous systems like the particle in the box and atomic orbitals. The four 3-D calculated molecular orbitals are contrasted in Figure 10.6.1 .

Exercise 10.6.1

What would Hückel theory predict for the energy levels and π molecular orbitals of cis-butadiene? Do you believe this approach adequately describes the energy levels of the cis-trans isomerization reaction of butadiene?

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CHAPTER OVERVIEW

11: Computational Quantum Chemistry

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. Its necessity arises from the fact that — apart from relatively recent results concerning the hydrogen molecular ion (see references therein for more details) — the quantum many-body problem cannot be solved analytically, much less in closed form. While computational results normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena. It is widely used in the design of new drugs and materials.

11.0: Overview of Quantum Calculations
11.1: Gaussian Basis Sets
11.2: Extended Basis Sets
11.3: Orbital Polarization Terms
11.4: The Ground-State Energy of H_2
11.5: Quantum Calculations

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11.0: Overview of Quantum Calculations

Multielectron Electronic Wavefunctions

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_l) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_1, r_2)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.0.1}$$

Equation 11.0.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_1, r_2)$$

so that

$$\left(e^{-i\varphi} \psi(r_1, r_2)^*\right) \left(e^{i\varphi} \psi(r_1, r_2)^*\right) = \psi(r_1, r_2)^* \psi(r_1, r_2) \tag{11.0.2}$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi} e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi} e^{i\varphi} = e^{i2\varphi} = 1$$

which is true only if $\varphi = 0$ or an integer multiple of π. The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature, but the behavior of elections is that the wavefunction be antisymmetric with respect to permutation $(e^{i\varphi} = -1)$. A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below.

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2)$$

Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom **must** be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component, but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) \tag{11.0.3}$$

After permutation of the electrons, this becomes

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1) \tag{11.0.4}$$

which is different from the starting function since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are different spin-orbital functions. However, an antisymmetric function must produce the same function multiplied by (–1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 11.0.4 from the right-hand side of Equation 11.0.3 has the desired antisymmetric behavior. The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(\mathbf{r}_1) \varphi_{1s\beta}(\mathbf{r}_2) - \varphi_{1s\alpha}(\mathbf{r}_2) \varphi_{1s\beta}(\mathbf{r}_1)]$$

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a Slater determinant.

The Slater determinant for the two-electron wavefunction for the ground state H_2 system (with the two electrons occupying the σ_{1s} molecular orbital)

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1) \\ \sigma_{1s}(2)\alpha(2) & \sigma_{1s}(2)\beta(2) \end{vmatrix}$$

We can introduce a shorthand notation for the arbitrary **spin-orbital**

$$\chi_{i\alpha}(\mathbf{r}) = \varphi_i\alpha$$

or

$$\chi_{i\beta}(\mathbf{r}) = \varphi_i\beta$$

as determined by the m_s quantum number. A shorthand notation for the determinant in Equation 8.6.4 is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 2^{-\frac{1}{2}}\, Det|\chi_{1s\alpha}(\mathbf{r}_1)\alpha\chi_{1s\beta}(\mathbf{r}_2)\beta|$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is

$$(N!)^{-\frac{1}{2}}$$

for a system of N electrons.

The generalized Slater determinant for a multe-electrom atom with N electrons is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{r}_1)\alpha & \chi_1(\mathbf{r}_1)\beta & \cdots & \chi_{N/2}(\mathbf{r}_1)\beta \\ \chi_1(\mathbf{r}_2)\alpha & \chi_2(\mathbf{r}_2)\beta & \cdots & \chi_{N/2}(\mathbf{r}_2)\beta \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_N)\alpha & \chi_2(\mathbf{r}_N)\beta & \cdots & \chi_{N/2}(\mathbf{r}_N)\beta \end{vmatrix} \tag{11.0.5}$$

In a modern *ab initio* electronic structure calculation on a closed shell molecule, the electronic Hamiltonian is used with a single determinant wavefunction. This wavefunction, Ψ, is constructed from molecular orbitals, ψ that are written as linear combinations of contracted Gaussian basis functions, φ

$$\varphi_j = \sum_k c_{jk}\psi_k \tag{11.0.6}$$

The contracted Gaussian functions are composed from primitive Gaussian functions to match Slater-type orbitals. The exponential parameters in the STOs are optimized by calculations on small molecules using the nonlinear variational method and then those values are used with other molecules. The problem is to calculate the electronic energy from

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \tag{11.0.7}$$

or in bra-ket notation

$$E = \frac{\left\langle \Psi | \hat{H} | \Psi \right\rangle}{\langle \psi | \psi \rangle}$$

The the optimum coefficients c_{jk} for each molecular orbital in Equation 11.0.6 by using the Self Consistent Field Method and the Linear Variational Method to minimize the energy as was described previously for atoms.

The variational principle says an approximate energy is an upper bound to the exact energy, so the lowest energy that we calculate is the most accurate. At some point, the improvements in the energy will be very slight. This limiting energy is the lowest that can be obtained with a single determinant wavefunction (e.g., Equation 11.0.5). This limit is called the *Hartree-Fock limit*, the energy

is the *Hartree-Fock energy*, the molecular orbitals producing this limit are called *Hartree-Fock orbitals*, and the determinant is the *Hartree-Fock wavefunction*.

Hartree-Fock Calculations

You may encounter the terms *restricted* and *unrestricted* Hartree-Fock. The above discussion pertains to a restricted HF calculation. In a restricted HF calculation, electrons with α spin are restricted or constrained to occupy the same spatial orbitals as electrons with β spin. This constraint is removed in an unrestricted calculation. For example, the spin orbital for electron 1 could be $\psi_A(r_1)\alpha(1)$, and the spin orbital for electron 2 in a molecule could be $\psi_B(r_2)\beta(2)$, where both the spatial molecular orbital and the spin function differ for the two electrons. Such spin orbitals are called *unrestricted*. If both electrons are constrained to have the same spatial orbital, e.g. $\psi_A(r_1)\alpha(1)$ and $\psi_A(r_2)\beta(2)$, then the spin orbital is said to be *restricted*. While unrestricted spin orbitals can provide a better description of the electrons, twice as many spatial orbitals are needed, so the demands of the calculation are much higher. Using unrestricted orbitals is particular beneficial when a molecule contains an odd number of electrons because there are more electrons in one spin state than in the other.

Example 11.1.1 : Carbon Monoxide

It is well known that carbon monoxide is a poison that acts by binding to the iron in hemoglobin and preventing oxygen from binding. As a result, oxygen is not transported by the blood to cells. Which end of carbon monoxide, carbon or oxygen, do you think binds to iron by donating electrons? We all know that oxygen is more electron-rich than carbon (8 vs 6 electrons) and more electronegative. A reasonable answer to this question therefore is *oxygen*, but experimentally it is carbon that binds to iron.

A quantum mechanical calculation done by Winifred M. Huo, published in J. Chem. Phys. 43, 624 (1965), provides an explanation for this counter-intuitive result. The basis set used in the calculation consisted of 10 functions: the ls, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of C and O. Ten molecular orbitals (mo's) were defined as linear combinations of the ten atomic orbitals (Equation 11.0.6. The ground state wavefunction Ψ is written as the Slater Determinant of the five lowest energy molecular orbitals ψ_k. Equation 11.0.7 gives the energy of the ground state, where the denominator accounts for the normalization requirement. The coefficients C_{kj} in the linear combination are determined by the variational method to minimize the energy. The solution of this problem gives the following equations for the molecular orbitals. Only the largest terms have been retained here. These functions are listed and discussed in order of increasing energy.

- $1s \approx 0.941 s_o$. The 1 says this is the first σ orbital. The σ says it is symmetric with respect to reflection in the plane of the molecule. The large coefficient, 0.94, means this is essentially the 1s atomic orbital of oxygen. The oxygen 1s orbital should have a lower energy than that of carbon because the positive charge on the oxygen nucleus is greater.
- $2s \approx 0.921 s_c$. This orbital is essentially the 1s atomic orbital of carbon. Both the 1σ and 2σ are "nonbonding" orbitals since they are localized on a particular atom and do not directly determine the charge density between atoms.
- $3s \approx (0.722 s_o + 0.182 p_{zo}) + (0.282 s_c + 0.162 p_{zc})$. This orbital is a "bonding" molecular orbital because the electrons are delocalized over C and O in a way that enhances the charge density between the atoms. The 3 means this is the third σ orbital. This orbital also illustrates the concept of hybridization. One can say the 2s and 2p orbitals on each atom are hybridized and the molecular orbital is formed from these hybrids although the calculation just obtains the linear combination of the four orbitals directly without the *à priori* introduction of hybridization. In other words, hybridization just falls out of the calculation. The hybridization in this bonding LCAO increases the amplitude of the function in the region of space between the two atoms and decreases it in the region of space outside of the bonding region of the atoms.
- $4s \approx (0.372 s_c + 0.12 p_{zc}) + (0.542 p_{zo} - 0.432 s_0)$. This molecular orbital also can be thought of as being a hybrid formed from atomic orbitals. The hybridization of oxygen atomic orbitals, because of the negative coefficient with $2s_O$, decreases the electron density between the nuclei and enhances electron density on the side of oxygen facing away from the carbon atom. If we follow how this function varies along the internuclear axis, we see that near carbon the function is positive whereas near oxygen it is negative or possibly small and positive. This change means there must be a node between the two nuclei or at the oxygen nucleus. Because of the node, the electron density between the two nuclei is low so the electrons in this orbital do not serve to shield the two positive nuclei from each other. This orbital therefore is called an "antibonding" molecular orbital and the electrons assigned to it are called antibonding electrons. This orbital is the antibonding partner to the 3σ orbital.

- $1\pi \approx 0.322p_{xc} + 0.442p_{xo} \text{and} 2\pi \approx 0.322p_{yc} + 0.442p_{yo}$ These two orbitals are degenerate and correspond to bonding orbitals made up from the p_x and p_y atomic orbitals from each atom. These orbitals are degenerate because the x and y directions are equivalent in this molecule. π tells us that these orbitals are antisymmetric with respect to reflection in a plane containing the nuclei.
- $5\sigma \approx 0.382_{sC} - 0.382_{pC} - 0.292p_{zO}$. This orbital is the sp hybrid of the carbon atomic orbitals. The negative coefficient for $2p_C$ puts the largest amplitude on the side of carbon away from oxygen. There is no node between the atoms. We conclude this is a nonbonding orbital with the nonbonding electrons on carbon. This is not a "bonding" orbital because the electron density between the nuclei is lowered by hybridization. It also is not an antibonding orbital because there is no node between the nuclei. When carbon monoxide binds to Fe in hemoglobin, the bond is made between the C and the Fe. This bond involves the donation of the 5σ nonbonding electrons on C to empty d orbitals on Fe. Thus molecular orbital theory allows us to understand why the C end of the molecule is involved in this electron donation when we might naively expect O to be more electron-rich and capable of donating electrons to iron.

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11.1: Gaussian Basis Sets

A basis set in theoretical and computational chemistry is a set of functions (called **basis functions**) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function; plane waves are frequently used in materials calculations.

The Variational Method and Basis Sets

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, ψ_i, as a linear combination of other functions, φ_j, which are called basis functions because they provide the basis for representing the molecular orbital.

$$\psi_i = \sum_j c_{ij}\varphi_j \tag{11.1.1}$$

The linear variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: σ is a general spin function (can be either α or β), φ is the basis function (this usually represents an atomic orbital), ψ is a molecular orbital, and Ψ is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

> *Selecting the ab initio model for a chemical system is almost always involves a trade-off between accuracy and computational cost. More accurate methods and larger basis sets make jobs run longer.*

In modern computational chemistry, quantum chemical calculations are typically performed using a finite set of basis functions. In these cases, the wavefunctions of the system in question are represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used.

The molecular spin-orbitals that are used in the Slater determinant usually are expressed as a linear combination of some chosen functions, which are called *basis functions*. This set of functions is called the *basis set*. The fact that one function can be represented by a linear combination of other functions is a general property. All that is necessary is that the basis functions *span-the-space*, which means that the functions must form a complete set and must be describing the same thing. For example, spherical harmonics cannot be used to describe a hydrogen atom radial function because they do not involve the distance r, but they can be used to describe the angular properties of anything in three-dimensional space.

This span-the-space property of functions is just like the corresponding property of vectors. The unit vectors ($\vec{x}$, $\vec{y}$, $\vec{z}$) describe points in space and form a complete set since any position in space can be specified by a linear combination of these three unit vectors. These unit vectors also could be called basis vectors.

? Exercise 11.2.1 : "Spanning the Space"

Explain why the unit vectors ($\vec{x}$, $\vec{y}$) do not form a complete set to describe your (three-dimensional) classroom.

Just as we discussed for atoms, parameters in the basis functions and the coefficients in the linear combination can be optimized in accord with the Variational Principle to produce a self-consistent field (SCF) for the electrons. This optimization means that the ground state energy calculated with the wavefunction is minimized with respect to variation of the parameters and coefficients

defining the function. As a result, that ground state energy is larger than the exact energy, but is the best value that can be obtained with that wavefunction.

Slater Type Orbitals (STOs)

Intuitively one might select hydrogenic atomic orbitals as the basis set for molecular orbitals. After all, molecules are composed of atoms, and hydrogenic orbitals describe atoms exactly if the electron-electron interactions are neglected. At a better level of approximation, the nuclear charge that appears in these functions can be used as a variational parameter to account for the shielding effects due to the electron-electron interactions. Also, the use of atomic orbitals allows us to interpret molecular properties and charge distributions in terms of atomic properties and charges, which is very appealing since we picture molecules as composed of atoms. As described in the previous chapter, calculations with hydrogenic functions were not very efficient so other basis functions, **Slater-type atomic orbitals (STOs)**, were invented.

A minimal basis set of STOs for a molecule includes only those STOs that would be occupied by electrons in the atoms forming the molecule. As with most variational method calculations, a larger basis set improves the accuracy of the calculations by providing more variable parameters to produce a better approximate wavefunction. However, this is at the expense of increased computational time (i.e., calculation "cost" or "expense"). STOs have the following radial part (the spherical harmonic functions are used to describe the angular part)

$$R(r) = Nr^{n-1}e^{-\zeta r}$$

where

- n is a natural number that plays the role of principal quantum number, $n = 1,\ 2,\ \ldots,$
- N is a normalizing constant,
- r is the distance of the electron from the atomic nucleus, and ζ is a constant related to the effective charge of the nucleus, the nuclear charge being partly shielded by electrons. Historically, the effective nuclear charge was estimated by Slater's rules.

Double-zeta basis Sets

One can use more than one STO to represent one atomic orbital, as shown in Equation 11.1.2, and rather than doing a nonlinear variational calculation to optimize each ζ value, use two STOs with different ζ variables. The linear variation calculation then will produce the coefficients (C_1 and C_2) for these two functions in the linear combination that **best** describes the charge distribution in the molecule (for the ground state). The function with the large zeta accounts for charge near the nucleus, while the function with the smaller zeta accounts for the charge distribution at larger values of the distance from the nucleus. This expanded basis set is called a **double-zeta basis set**.

$$R_{2s}(r) = C_1 re^{-\zeta_1 r} + C_2 re^{-\zeta_2 r} \tag{11.1.2}$$

The use of double zeta functions in basis sets is especially important because without them orbitals of the same type are constrained to be identical even though in the molecule they may be chemically inequivalent. For example, in acetylene the p_z orbital along the internuclear axis is in a quite different chemical environment and is being used to account for quite different bonding than the p_x and p_y orbitals. With a double zeta basis set the p_z orbital is not constrained to be the same size as the p_x and p_y orbitals.

Example 11.2.1

Explain why the p_x, p_y, and p_z orbitals in a molecule might be constrained to be the same in a single-zeta basis set calculation, and how the use of a double-zeta basis set would allow the p_x, p_y, and p_z orbitals to differ.

Gaussian Orbitals

Although any basis set that sufficiently spans the space of electron distribution could be used, the concept of Molecular Orbitals as **Linear Combinations of Atomic Orbitals** **(LCAO)** suggests a very natural set of basis functions: AO-type functions centered on each nuclei. One obvious choice are the exact hydrogen AO's, known as **Slater-type orbitals (STO)** -describing the radial component of the functions. However, the computation of the integrals is greatly simplified by using **Gaussian-type orbitals (GTO)** for basis functions.

While the STO basis set was an improvement over hydrogenic orbitals in terms of computational efficiency, representing the STOs with Gaussian functions produced further improvements that were needed to accurately describe molecules. A Gaussian basis

function has the form shown in Equation 11.1.3. Note that in all the basis sets, only the radial part of the orbital changes, and the spherical harmonic functions are used in all of them to describe the angular part of the orbital.

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}} \tag{11.1.3}$$

Unfortunately Gaussian functions do not match the shape of an atomic orbital very well. In particular, they are flat rather than steep near the atomic nucleus at $r = 0$, and they fall off more rapidly at large values of r (Figure 11.2.1).

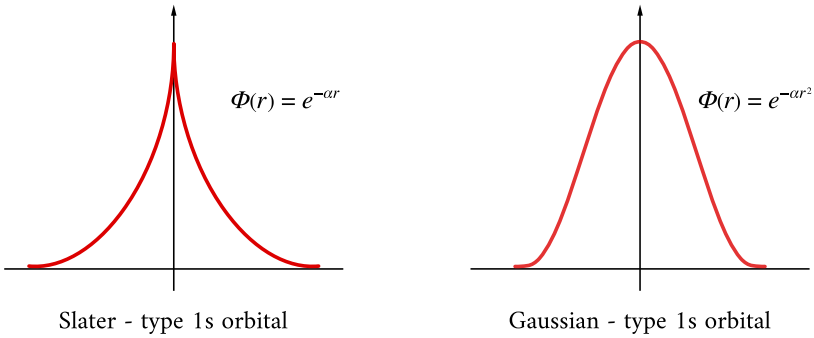


Figure 11.2.1 : Radial Dependence of Slater and Gaussian Basis Functions. (CC BY 4.0; Ümit Kaya via LibreTexts)

To compensate for this problem, each STO is replaced with a number of Gaussian functions with different values for the exponential parameter. These Gaussian functions form a *primitive Gaussian basis set*. Linear combinations of the primitive Gaussians are formed to approximate the radial part of an STO. This linear combination is not optimized further in the energy variational calculation, but rather is frozen and treated as a single function. The linear combination of **primitive Gaussian functions** is called a **contracted Gaussian function**. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials, so there is a net gain in the efficiency of the calculation.

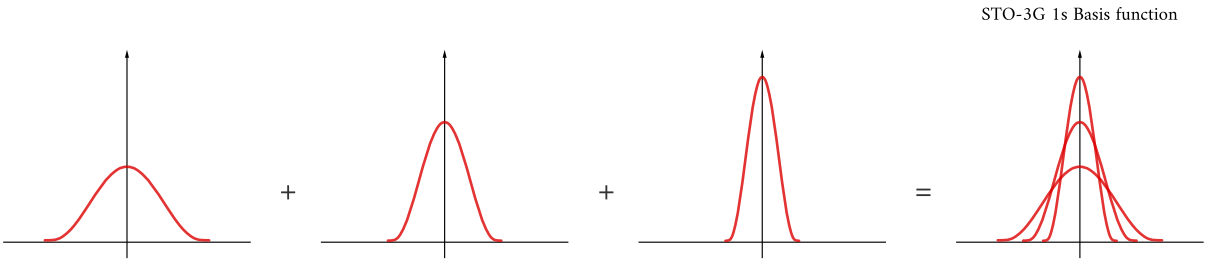


Figure 11.2.2 : To better represent the cusp in the electron density at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTOs (CGTO). The earliest CGTO basis sets, where constructed from N GTOs that best fit the desired STO. These are called STO-NG basis sets. (CC BY 4.0; Ümit Kaya via LibreTexts)

Gaussian basis sets are identified by abbreviations such as N-MPG*. N is the number of Gaussian primitives used for each inner-shell orbital. The hyphen indicates a split-basis set where the valence orbitals are double zeta. The M indicates the number of primitives that form the large zeta function (for the inner valence region), and P indicates the number that form the small zeta function (for the outer valence region). G identifies the set a being Gaussian. The addition of an asterisk to this notation means that a single set of Gaussian 3d polarization functions (discussed elsewhere) is included. A double asterisk means that a single set of Gaussian 2p functions is included for each hydrogen atom.

For example, 3G means each STO is represented by a linear combination of three primitive Gaussian functions. 6-31G means each inner shell (1s orbital) STO is a linear combination of 6 primitives and each valence shell STO is split into an inner and outer part (double zeta) using 3 and 1 primitive Gaussians, respectively (see Table 11.2.1 for other examples).

Table 11.2.1 : Different Gaussian Basis sets

Basis set	# functions	Basis set	# functions	Basis set	# functions

Basis set	# functions		Basis set	# functions		Basis set	# functions
STO-3G	5		6-31G	9		6-311G	13
3-21G	9		6-31G*	15		6-311G*	18*
4-31G	9		6-31+G*	19		6-311+G*	22*

Example 11.2.2

The 1s Slater-type orbital $S_1(r) = \sqrt{4\zeta_1 e^{-\zeta_1 r}}$ with $\zeta_1 = 1.24$ is represented as a sum of three primitive Gaussian functions,

$$S_G(r) = \sum_{j=1}^{3} C_j e^{-\alpha_j r^2}$$

This sum is the contracted Gaussian function for the STO.

a. Make plots of the STO and the contracted Gaussian function on the same graph so they can be compared easily. All distances should be in units of the Bohr radius. Use the following values for the coefficients, C, and the exponential parameters, α.

index j	α_j	C_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

b. Change the values of the coefficients and exponential parameters to see if a better fit can be obtained.
c. Comment on the ability of a linear combination of Gaussian functions to accurately describe a STO.

Summary

When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals (Equation 11.1.1), centered at each atomic nucleus within the molecule (linear combination of atomic orbitals ansatz). These atomic orbitals are well described with Slater-type orbitals (STOs), as STOs decay exponentially with distance from the nuclei, accurately describing the long-range overlap between atoms, and reach a maximum at zero, well describing the charge and spin at the nucleus. STOs are computationally difficult and it was later realized by Frank Boys that these Slater-type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. Because it is easier to calculate overlap and other integrals with Gaussian basis functions, this led to huge computational savings

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11.2: Extended Basis Sets

Today, there are hundreds of basis sets composed of Gaussian Type Orbitals (GTOs). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom.

Minimum Basis sets

A minimum basis set is one in which a **single** basis function is used for each orbital in a Hartree-Fock calculation on the atom. However, for atoms such as lithium, basis functions of p type are added to the basis functions corresponding to the 1s and 2s orbitals of each atom. For example, each atom in the first row of the periodic system (Li - Ne) would have a basis set of five functions (two s functions and three p functions).

> *In a minimum basis set, a single basis function is used for each atomic orbital on each constituent atom in the system.*

The most common minimal basis set is STO-nG, where n is an integer. This n value represents the number GTOs used to approximate the Slater Type orbital (STO) for both core and valence orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper (less calculations requires) than the larger basis sets discussed below. Commonly used minimal basis sets of this type are: STO-3G, STO-4G, and STO-6G.

Two is Often Better than One

Minimal basis sets are not flexible enough for accurate representation of, which requires the use multiple functions to represent each atomic orbital. The distribution of the electron density of valence electrons is better represented by the sum of two orbitals with different "effective charges". This is a double-ζ basis sets and includes split-valence set (inner and valence) and linear combination of two orbitals of same type, but with different effective charges (i.e., ζ). This flexibility can be used to generate atomic orbital of adjustable sizes.

For example, the double-zeta basis set allows us to treat each orbital separately when we conduct the Hartree-Fock calculation.

$$\phi_i = a_1 \phi_{2s}^{STO}(r, \zeta_1) + a_2 \phi_{2s}^{STO}(r, \zeta_2) \tag{11.2.1}$$

The 2s atomic orbital approximated as a sum of two STOs. The two equations are the same except for the value of ζ which accounts for how large the orbital is. The constants a_1 and a_2 determines how much each STO contributes to the final atomic orbital, which will vary depending on the type of atom that the atomic orbit (i.e., hydrogen and lithium orbitals will have different a_1, a_2, ζ_1, and ζ_2 values).

Extended Basis Sets

The triple and quadruple-zeta basis sets work the same way, except use three and four STOs instead of two like in 11.2.1. The typical trade-off applies here as well, better accuracy, however with more expensive calculations. There are several different types of **extended basis sets** including: n split-valence, n polarized sets, n diffuse sets, and n correlation consistent sets. The notation of this sort of basis set (with a Gaussian basis) is

$$N - MPG$$

for describing split-valence basis set. N is the number of Gaussian functions describing inner-shell orbitals, while the hyphen denotes a split-valence set. M and P designate the number of Gaussian functions used to fit the two orbitals of the valence shell:

- M corresponds to number of Gaussian functions used to describe the smaller orbital
- P corresponds to number of Gaussian functions used to describe the larger orbital (e.g., 6-31G and 3-21G).

A minimal basis set is when one basis function for each atomic orbital in the atom, while a double-ζ, has two two basis functions for each atomic orbital. Correspondingly, a triple and quadruple-ζ set had three and four basis functions for each atomic orbital, respectively. Higher order basis set have been constructed too, e.g., 5Z, 6Z,)..

There are hundreds of basis sets composed of Gaussian-type orbitals (Figure Figure 11.3.1). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain dozens to hundreds of basis functions on each atom.

Figure 11.3.1 : Commonly used split-valence basis sets

3-21G	3-21G	3-21G	3-21G* - Polarized	3-21+G - Diffuse functions	3-21+G* - With polarization and diffuse functions
4-21G	4-31G	4-31G	4-31G	4-31G	
6-21G	6-31G	6-31G*	6-31+G*	6-31G(3df, 3pd)	6-311G
6-311G	6-311G*	6-311+G*			

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11.3: Orbital Polarization Terms

Polarization functions denoted in Pople's sets by an asterisk. Two asterisks, indicate that polarization functions are also added to light atoms (hydrogen and helium). n Polarization functions have one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1 s atomic orbital. When polarization is added to this basis set, a p -function is also added to the basis set. The 6-31G** is synonymous to 6-31 G(d,p).

The use of a minimal basis set with fixed zeta parameters severely limits how much the electronic charge can be changed from the atomic charge distribution to describe molecules and chemical bonds. This limitation is removed if STOs with larger n values and different spherical harmonic functions, the $Y_l^m(\theta, \varphi)$ in the definition of STO's are included. Adding such functions is another way to expand the basis set and obtain more accurate results. Such functions are called polarization functions because they allow for charge polarization away form the atomic distribution to occur.

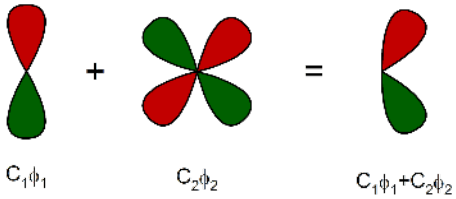


Figure 11.4.1 : A d-polarization function added to a p orbital. (CC-BY-SA-3.0; Rifleman 82)

The most common addition to minimal basis sets is probably the addition of polarization functions, denoted (in the names of basis sets developed by Pople) by an asterisk, *. Two asterisks, **, indicate that polarization functions are also added to light atoms (hydrogen and helium). These are auxiliary functions with one additional node. For example, the only basis function located on a hydrogen atom in a minimal basis set would be a function approximating the 1s atomic orbital. When polarization is added to this basis set, a p-function is also added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen nucleus.

This is an important result when considering accurate representations of bonding between atoms, because the very presence of the bonded atom makes the energetic environment of the electrons spherically asymmetric. Similarly, d-type functions can be added to a basis set with valence p orbitals, and f-functions to a basis set with d-type orbitals, and so on. Another, more precise notation indicates exactly which and how many functions are added to the basis set, such as (d, p).

Diffuse Functions

Another common addition to basis sets is the addition of **diffuse functions**, denoted in Pople-type sets by a plus sign, +, and in Dunning-type sets by "aug" (from "augmented"). Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These are very shallow Gaussian basis functions, which more accurately represent the "tail" portion of the atomic orbitals, which are distant from the atomic nuclei. These additional basis functions can be important when considering anions and other large, "soft" molecular systems.

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11.4: The Ground-State Energy of H_2

11.05: The Ground-State Energy of H

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11.5: Quantum Calculations

11.06: Quantum Calculations

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CHAPTER OVERVIEW

12: Group Theory - Exploiting Symmetry

12.1: Using Symmetry to Simplify Calculations
12.2: The Symmetry of Molecules
12.3: Symmetry Operations Define Groups
12.4: Symmetry Operations can be Represented by Matrices
12.5: The \(C_3V\) Point Group Has a 2-D Irreducible Representation
12.6: Character Tables
12.7: Relations involving Characters
12.8: Using Symmetry to Predict Zero in a Secular Determinant
12.9: Generating Operators for Irreducible Representations

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12.1: Using Symmetry to Simplify Calculations

To a fully understand the math behind group theory one needs to take a look at the theory portion of the Group Theory topic or refer to one of the reference text listed at the bottom of the page. Never the less as Chemist the object in question we are examining is usually a molecule. Though we live in the 21st century and much is known about the physical aspects that give rise to molecular and atomic properties. The number of high level calculations that need to be performed can be both time consuming and tedious. To most experimentalist this task is takes away time and is usually not the integral part of their work. When one thinks of group theory applications one doesn't necessarily associated it with everyday life or a simple toy like a Rubik's cube. A Rubik's cube is an a cube that has a 3×3 array of different colored tiles on each of its six surfaces, for a total of 54 tiles. Since the cube exist in 3D space, the three axis are x, y, z. Since the rubik's cube only allows rotation which are called operations, there are three such operations around each of the x, y, z axis.

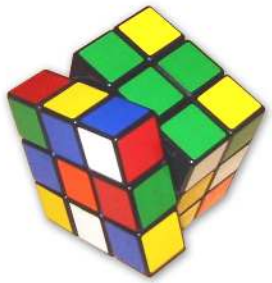


Figure: Reubik's cube. Use with permission from Wikipedia

Of course the ultimate challenge of a Rubik's cube is to place all six colors on each of the six faces. By performing a series of such operations on the Rubik's cube one can arrive at a solution (A link of a person solving a Rubik's cube[1] in 10.4s with operations performed noted, the operations performed will not translate to chemistry applications but it is a good example of how symmetry operations arrive at a solution). The operations shown in the Rubik's cube case are inherent to the make up of the cube, i.e., the only operations allowed are the rotations along the x, y, z axis. Therefore the Rubik's cube only has x,y,z rotation operations. Similarly the operations that are specific to a molecule are dependent on its symmetry.

Using group theory, we can exploit the symmetry of molecules to give us a rich amount of information on the molecular orbitals, rotations, and vibrations of bonds, to name a few. Making symmetry arguments, we can skip complicated quantum calculations to gain qualitatively accurate information.

In section 10.7, we used Hückel theory to explore the π bonding network of benzene by constructing linear combinations of $2p_x$ atomic orbitals on the carbon atoms. In doing so, the roots of the secular equations were found via solving the 6×6 secular determinant.

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{12.1.1}$$

Since the secular determinant is a 6×6 matrix, there are six solutions or values of x that can be determined after expanding the determinant into the resulting (6th-order) polynomial.

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{12.1.2}$$

Secular determinants are formulated in terms of a specific basis set; i.e., a set of functions that describe the wavefunctions. For the determinnat in Equation 12.1.1, that basis set is the the $\{|2p_z\rangle\}$ orbitals on the carbons. However, any basis set can be used to represent the determinant (long as it span the same space). For example, the following linear combination of $\{|2p_z\rangle\}$ orbitals could also be used:

$$|\phi_1\rangle = \frac{1}{\sqrt{6}}[|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle]$$

$$|\phi_2\rangle = \frac{1}{\sqrt{4}}[|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle]$$

$$|\phi_3\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle\right]$$

$$|\phi_4\rangle = \frac{1}{\sqrt{4}}[|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle]$$

$$|\phi_5\rangle = \frac{1}{\sqrt{3}}\left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle\right]$$

$$|\phi_6\rangle = \frac{1}{\sqrt{6}}[|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle]$$

In this new basis set $\{\phi\rangle\}$, the secular determinant Equation 12.1.1 is represented as

$$\begin{vmatrix} x+2 & 0 & 0 & 0 & 0 & 0 \\ 0 & x-2 & 0 & 0 & 0 & 0 \\ 0 & 0 & x+1 & \frac{x+1}{2} & 0 & 0 \\ 0 & 0 & \frac{x+1}{2} & x+1 & 0 & 0 \\ 0 & 0 & 0 & 0 & x-1 & \frac{x-1}{2} \\ 0 & 0 & 0 & 0 & \frac{x-1}{2} & x-1 \end{vmatrix} = 0 \tag{12.1.3}$$

This is the determinant into a bock diagonal form; which can be expanded into a product of smaller determinants to give the polynomial

$$\frac{9}{16}(x+2)(x-2)(x+1)^2(x-1)^2 = 0$$

The roots to this equation are ± 2, ± 1 and ± 1. This is not surprising since these are the same roots obtained from expanding the determinant in the original basis set (Equation 12.1.2). You may remember that the selection of a specific basis set to represent a function does not change the fundamental nature of the function (e.g., a parabola in 2D space is the same curve if represented in terms of Cartesian coordinates (x and y) or polar coordinates (θ and r), which both span 2-D space).

As you recall, Hückel theory (irrespective of the basis set) was used to simplify the general secular determinant (e.g., for benzene)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\ H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\ H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{6} \end{vmatrix} = 0 \tag{12.1.4}$$

where H_{ij} are the Hamiltonian matrix elements

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int \phi_i H \phi_j \mathrm{d}v$$

and S_{ij} are the overlap integrals.

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int \phi_i \phi_j \mathrm{d}v$$

In general, this involves solving 36 Hamiltonian matrix elements (H_{ij}) and 36 overlap integrals (S_{ij}), which can be a daunting task to do by hand without the assumptions of Hückel theory to help out. As with the application of Hückel theory, which was used to set most of these integrals to zero, solving for the energies from Equation 12.1.4 can be simplified by using the intrinsic symmetry

of the benzene system to demonstrate (rigorously) that many of these integrals are zero. This is the subject of group theory. Group theory is used to exploit the symmetry of molecules to quickly gain insights into their properties, such as vibrations and molecular orbitals.

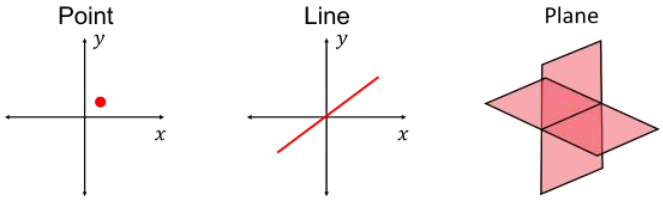
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12.2: The Symmetry of Molecules

Symmetry Elements

A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. Each symmetry operation has a corresponding *symmetry element*, which is the axis, plane (2-dimensional), line (1-dimensional) or point (0-dimensional) with respect to which the symmetry operation is carried out:



The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a *symmetry axis*; in a reflection the points that remain unchanged make up a *plane of symmetry*. The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

Symmetry Operations

The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses. There are five types of operations:

1. Identity, E
2. Rotation, C_n
3. Reflection, σ
4. Inversion, i
5. Improper Rotation, S_n

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

Identity Symmetry, E

The identity operator, E, consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule possesses at least this operation. For example, the $\mathrm{CHFClBr}$ molecule in Figure 12.2.1 . The identify symmetry operation is not indicated since all molecule exhibit this symmetry.

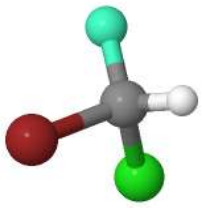


Figure 12.2.1 : Example of Identify Symmetry: The $\mathrm{CHFClBr}$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

n-fold Axis of Rotation, C_n

The rotation operation (sometimes called proper rotation), C_n, rotates an object about an axis by $2\pi/n$ radians or $360^\circ/n$. Rotation by C_n leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 12.2.2). Molecules can have more than one C_n axis, in which case the one with the highest value of n is called the *principal axis*. In some high symmetry systems, there may be

more than one principal axis. Note that by convention, rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

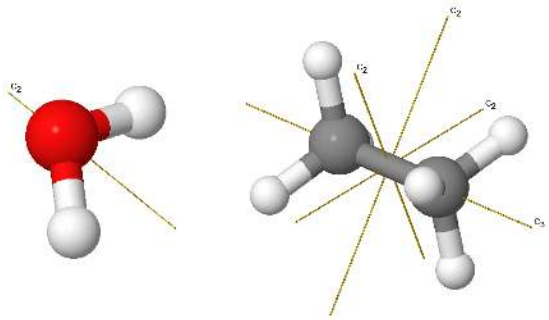


Figure 12.2.2 : Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

We always want to express rotations in their simplest equivalent fractions of m/n:

$$C_4^2 = C_2$$

$$C_6^4 = C_3^2$$

$$C_8^6 = C_4^3$$

Rotating an object n times brings the object back to the original object and is equivalent to the identity operation, E:

$$C_n^n = E$$

Linear molecules have a very high rotational symmetry: C_∞. Examples include diatomics such as CO, NO, and $\mathrm{CO_2}$.

Reflection, σ

Reflection, σ, defines the bilateral symmetry about a plane (mirror plane / reflection plane). Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labeled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labeled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d. If no principal axis exist, σ_h is defined as the plane of the molecule. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

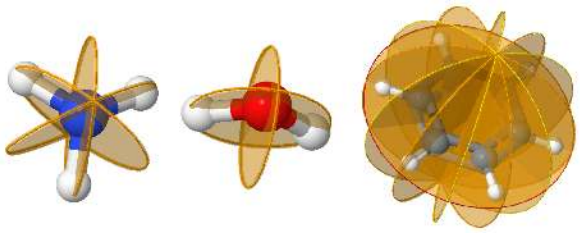


Figure 12.2.3 : Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) benzene contains a total of seven reflection planes, one horizontal plane (σ_h) and six vertical planes (σ_v and σ_d). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

For any mirror plane, performing two successive reflections about the same plane brings objects back to their original configuration:

$$\sigma\sigma = \sigma^2 = E$$

Inversion, i

Inversion, i, through the center of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the center of inversion and out to the same distance on the other side of the molecule. If inversion symmetry exists, a line drawn from any atom through the center will connect with an equivalent atom at an equivalent distance from the center. Examples of molecules with centers of inversion is shown in Figure 12.2.4 . Centers of inversion are indicated via a point, which may or may not overlap

with an atoms. The inversion center is always located at the central point of the molecule and there can only be one inversion center in any system. The centers of inversion in the examples below do not overlap with atoms.

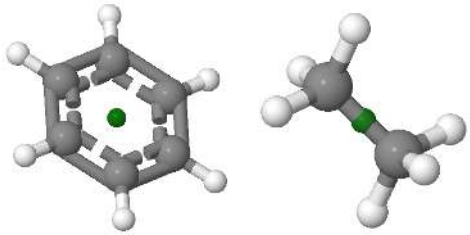


Figure 12.2.4 : Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Performing inversion twice in succession brings every point back to its original position:

$$ii = i^2 = E$$

Molecules with no inversion symmetry are said to be centrosymmetric.

n-fold Axis of Improper Rotation, S_n

Improper rotations, S_n, are also called rotation-reflections. The rotation-reflection operation consists of rotating by C_n about an axis, followed by reflecting in a plane perpendicular to the same axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 12.2.5 .

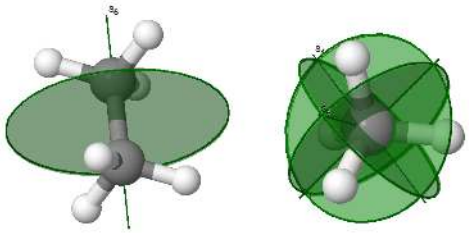


Figure 12.2.5 : Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Note

S_1 is the same as reflection and S_2 is the same as inversion.

The lowest-order improper rotation that is not a simpler operation is S_3. The pattern of successive operations depends on if n is even or odd. The general relationships for S_n operations are:

- If n is even, $S_n^n = E$
  - Molecule returns to original orientation configuration after each full rotation
  - There are an even number of rotation operators and reflection operators
- If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
  - First full rotation:
    - Molecular does not return to original configuration after first rotation
    - There are an odd number of rotation operators and reflection operators
  - Second full rotation:
    - Molecule returns to original orientation configuration
    - There are an even number of rotation operators and reflection operators
- When m is even, there is always a corresponding proper rotation (C_n):
  - $S_n^m = C_n^m$ when $m < n$
  - $S_n^m = C_n^{m-n}$ when $m > n$ (2nd rotation)
- If S_n with even n exists, $C_{n/2}$ exists

- If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist

Summary of Symmetry Operations

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called *proper symmetry operations*. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed *improper symmetry operations*. These five symmetry operations are tabulated in Table 12.2.1 .

Table 12.2.1 : The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360^\circ/n$ leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360^\circ/n$ about the axis, followed by reflecting in a plane perpendicular to the axis.

Defining the Coordinate System

Axis Definitions

Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

Generally, the following conventions are observed to define the coordinate system:

1. The origin of the coordinate system is located at the central atom or the center of the molecule.
2. The z-axis is collinear with the highest-order rotational axis (principal axis).
3. For planar molecules, if the z-axis is perpendicular to the molecular plane:
   - The x-axis lies in the plane of the molecule and passes through the greatest number of atoms.

   If the z-axis lies in the plane of the molecule:
   - The x-axis stands perpendicular to the plane
4. For non-planar molecules, once the z-axis has been defined, the x-axis is the usually chosen so that the xz plane contains as many atoms as possible.

Molecular Point Groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labeling symmetry groups, called the Schönflies and Hermann-Mauguin (or International) systems. Schönflies notation is used by chemists and spectroscopists, while Crystallographers prefer Hermann-Mauguin notation.The symmetry of individual molecules is usually described using the **Schönflies** notation, which is used below. The common point groups can be categorized into the following:

- Nonrotational groups
- Single-axis rotationa groups
- Dihedral groups
- Cubic groups

Shared Names

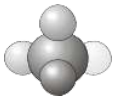
Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

Nonrotational groups

Nonrotational groups represent the lowest symmetry groups. They include:

C_1 - Contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation, E). Molecules that belongs to the C_1 group have no symmetry and are therefore asymmetric.

- Example: CHDFCl



C_i - Contains the identity E and a center of inversion i.

- Example: $C_2H_2F_2Cl_2$



C_S - Contains the identity E and a plane of reflection σ.



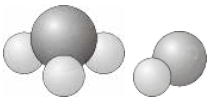
Single-axis rotation groups

Single-axis rotation groups are examples of cyclic groups. In cyclic groups, all of the operators commute (Abelian). In their multiplication tables, elements appear along right-to-left diagonals. Knowing this pattern makes it easy to construct multiplication tables! Single-axis rotational groups include:

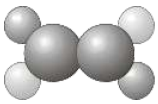
C_n - Contains the identity and an n-fold axis of rotation.



C_{nv} - Contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



C_{nh} - Contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



S_n - Contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been

classified).

Dihedral groups

The dihedral groups have n two-fold axes perpendicular to the principal n-fold axis. These C_2 axis are called dihedral axes. Dihedral groups groups include:

D_n - Contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

D_{nd} - Contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



D_{nh} - Contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

- There are n-fold vertical mirror places (σ_v)
- Includes n-fold improper axis when $n > 2$
- They are centrosymmetric when n is even

$D_{\infty h}$ - Same as D_{nh}, except the principal rotational axis is an infinite-fold C_∞.

- This is the point group for all linear centrosymmetric linear molecules (e.g. H_2, CO_2)

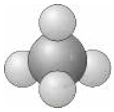


Cubic groups

The following groups are the cubic groups, which contain more than one principal axis. The cubic groups are associated with polyhedra that are geometrically related to the cube. All are characterized by the presence of multiple, intersecting, high-order rotational axes. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h).

T_d - Contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. CH_4.

- Example: Methane, C_4

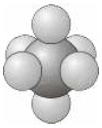


T - Same as for T_d but no planes of reflection.

T_h - Same as for T but contains a center of inversion.

O_h - The group of the regular octahedron.

- Example: Sulfur hexafluoride, SF_6



O - Same as for O_h, but with no planes of reflection.

I_h - Icoshedral, a geometric shape with 20 faces.

- Example: Buckminsterfullerene, (C_{60})

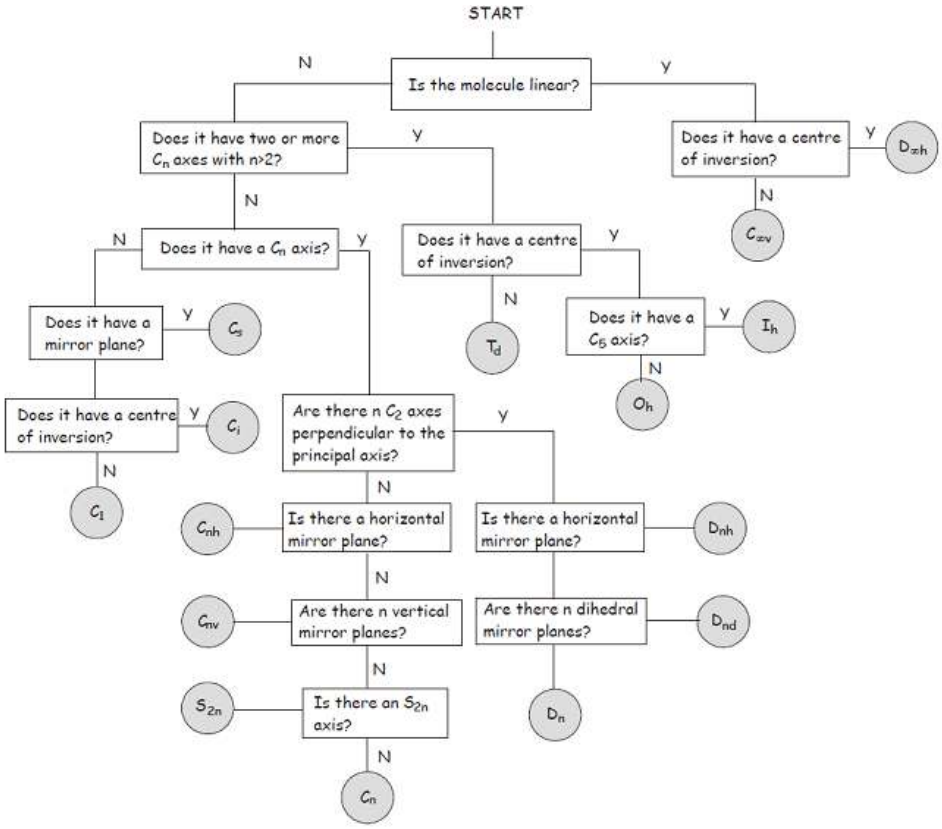
Summary of groups

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Table 12.2.2 : Common Point Groups for Molecules

Nonaxial groups	C_1	C_s	C_i	-	-	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8	-	-
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8	-	-
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	-	-
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	-	-
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	-	-
S_n groups	S_2	-	S_4	-	S_6		S_8	S_{10}	S_{12}
Cubic groups	T	T_h	T_d	O	O_h	I	I_h	-	-
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important.

Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.

Symmetry and Physical Properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point. If a molecule has a C_n axis with $n > 1$, it **cannot** have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis. The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

One example of symmetry in chemistry that you will already have come across is found in the isomeric pairs of molecules called enantiomers. Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical relationship is that they rotate the plane of polarized light passing through them in opposite directions. Such molecules are said to be chiral,[2] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group.

For example, a point group that has C_n and σ_h as elements will also have S_n. Similarly, a center of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot have be chiral if it has a center of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

Chirality

The word chiral has its origins in the Greek word for hand ($\chi\epsilon\rho\iota$, pronounced ‘cheri’ with a soft ch as in ‘loch’). A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as ‘handedness’ for this reason.

Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Identity, rotation, reflection, and inversion are symmetry operations (movement of the molecules such that after the movement, all the atoms of the molecules is coincidental with equivalent atom of the molecule in original).

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- **12.2: Symmetry Elements and Operations Define the Point Groups** by Claire Vallance, Delmar Larsen, Jerry LaRue is licensed CC BY 4.0.

12.3: Symmetry Operations Define Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group.

A mathematical group is defined as a set of elements (g_1, g_2, g_3...) together with a rule for forming combinations $g_i g_j$. The number of elements h is called the **order** of the group. For our purposes, the elements are the symmetry operations of a molecule and the rule for combining them is the sequential application of symmetry operations investigated in the previous section. The elements of the group and the rule for combining them must satisfy the following criteria.

1. The group must include the identity E, for which

$$Eg_i = g_i \tag{12.3.1}$$

   for all the elements of the group.
2. The elements must satisfy the **group property** that the combination of any pair of elements is also an element of the group.
3. Each element g_i must have an inverse g_i^{-1}, which is also an element of the group, such that

$$g_i g_i^{-1} = g_i^{-1} g_i = E \tag{12.3.2}$$

   (e.g. in C_{3v} the inverse of C_3^+ is C_3^-, the inverse of (σ_v is σ_v', the inverse g_i^{-1} effectively 'undoes' the effect of the symmetry operation g_i).
4. The rule of combination must be associative i.e.

$$(g_i g_j)(g_k) = g_i(g_j g_k) \tag{12.3.3}$$

The above definition **does not** require the elements to commute, which would require

$$g_i g_k = g_k g_i \tag{12.3.4}$$

As we discovered in the C_{3v} example above, in many groups the outcome of consecutive application of two symmetry operations depends on the order in which the operations are applied.

Note: Commuting is not a Requirement of Group Elements

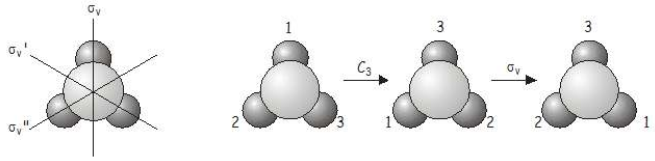
Groups for which the elements do not commute are called *non-Abelian* groups; those for which they elements do commute are *Abelian*.

Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

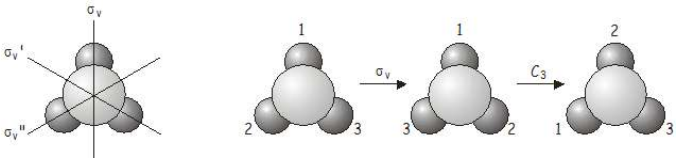
Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

Group Multiplication

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3rotation followed by a σ_v reflection. We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.



The combined operation $\sigma_v C_3$ is equivalent to σ_v'', which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order i.e. $C_3\sigma_v$ (σ_v followed by C_3).



Again, the combined operation $C_3\sigma_v$ is equivalent to another operation of the point group, this time σ_v'.

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general commute. In some groups the symmetry elements do commute; such groups are said to be *Abelian*.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same *class*. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane

The effects of applying two symmetry operations in sequence within a given point group are summarized in *group multiplication tables*. As an example, the complete group multiplication table for C_{3v} using the symmetry operations as defined in the figures above is shown below. The operations written along the first row of the table are carried out first, followed by those written in the first column (note that the table would change if we chose to name σ_v, σ_v' and σ_v'' in some different order).

C_{3v}	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

(12.3.5)

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12.4: Symmetry Operations can be Represented by Matrices

Matrices can be used to map one set of coordinates or functions onto another set. Matrices used for this purpose are called *transformation matrices*. In group theory, we can use transformation matrices to carry out the various symmetry operations discussed previously. As a simple example, we will investigate the matrices we would use to carry out some of these symmetry operations on a vector in 2D space (x, y).

The Identity Operation

The identity operation leaves the vector unchanged, and as you may already suspect, the appropriate matrix is the identity matrix.

$$(x, y)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = (x, y) \tag{12.4.1}$$

Reflection in a plane

The simplest example of a reflection matrix corresponds to reflecting the vector (x, y) in either the x or y axes. Reflection in the x axis maps y to $-y$, while reflection in the y axis maps x to $-x$. The appropriate matrix is very like the identity matrix but with a change in sign for the appropriate element. Reflection in the x axis transforms the vector (x, y) to $(x, -y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = (x, -y) \tag{12.4.2}$$

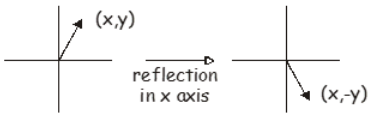


Figure 12.4.1: Reflection across the x-axis in 2D space.

Reflection in the y axis transforms the vector (x, y) to $(-x, y)$, and the appropriate matrix is

$$(x, y)\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = (-x, y) \tag{12.4.3}$$

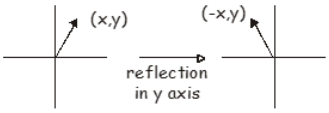


Figure 12.4.2: Reflection across the y-axis *in 2D space.*

More generally, matrices can be used to represent reflections in any plane (or line in 2D). For example, reflection in the 45° axis shown below maps (x, y) onto $(-y, -x)$.

$$(x, y)\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} = (-y, -x) \tag{12.4.4}$$

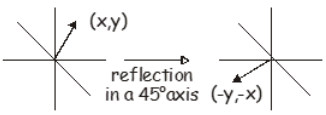


Figure 12.4.3: Reflection across the axis that is rotated 45° with with respect to x-axis *in 2D space.*

Rotation about an Axis

In two dimensions, the appropriate matrix to represent rotation by an angle θ about the origin is

$$R(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \tag{12.4.5}$$

In three dimensions, rotations about the x, y and z axes acting on a vector (x, y, z) are represented by the following matrices.

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{12.4.6}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \tag{12.4.7}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{12.4.8}$$

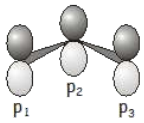
Matrix Representation

The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a *representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen *basis set* of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x, y). The basis was therefore a pair of unit vectors pointing in the x and y directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations. Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group.

1. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C_{3v} point group, we showed that the combined symmetry operation $C_3\sigma_v$ is equivalent to σ_v''. In a matrix representation of the group, if the matrix representatives of C_3 and σ_v are multiplied together, the result will be the representative of σ_v''.
3. The third rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.
4. The final rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.

Example: a matrix representation of the C_{2v} point group (the allyl radical)

In this example, we'll take as our basis a p orbital on each carbon atom (p_1, p_2, p_3).



Note that the p orbitals are *perpendicular* to the plane of the carbon atoms (this may seem obvious, but if you're visualizing the basis incorrectly it will shortly cause you a not inconsiderable amount of confusion). The symmetry operations in the C_{2v} point group, and their effect on the three p orbitals, are as follows:

$$\begin{aligned} E \quad & (p_1, p_2, p_3) \rightarrow (p_1, p_2, p_3) \\ C_2 \quad & (p_1, p_2, p_3) \rightarrow (-p_3, -p_2, -p_1) \\ \sigma_v \quad & (p_1, p_2, p_3) \rightarrow (-p_1, -p_2, -p_3) \\ \sigma_v' \quad & (p_1, p_2, p_3) \rightarrow (p_3, p_2, p_1) \end{aligned} \tag{12.4.9}$$

The matrices that carry out the transformation are

$$\begin{aligned} \Gamma(E) \quad & (p_1, p_2, p_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_1, p_2, p_3) \\ \Gamma(C_2) \quad & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} = (-p_3, -p_2, -p_1) \\ \Gamma(\sigma_v) \quad & (p_1, p_2, p_3) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = (-p_1, -p_2, -p_3) \\ \Gamma(\sigma_v') \quad & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (p_3, p_2, p_1) \end{aligned} \tag{12.4.10}$$

Note

We have written the vectors representing our basis as *row vectors*. This is important. If we had written them as column vectors, the corresponding transformation matrices would be the transposes of the matrices above, and would not reproduce the group multiplication table (try it as an exercise if you need to convince yourself).

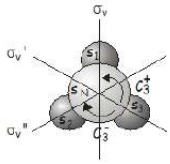
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12.5: The C 3 V C3V Point Group Has a 2-D Irreducible Representation

The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH_3, we will select a basis (s_N, s_1, s_2, s_3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{12.5.1}$$

By inspection, the matrices that carry out the same transformations are:

$$\begin{aligned} \Gamma(E) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_1, s_2, s_3) \\ \Gamma(C_3^+) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_2, s_3, s_1) \\ \Gamma(C_3^-) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_1, s_2) \\ \Gamma(\sigma_v) \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_1, s_3, s_2) \\ \Gamma(\sigma_v') \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (s_N, s_2, s_1, s_3) \\ \Gamma(\sigma_v'') \quad & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_3, s_2, s_1) \end{aligned} \tag{12.5.2}$$

These six matrices therefore form a representation for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis. They multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

Reduced Representations

If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$\begin{array}{cccccc} \Gamma(E) & \Gamma(C_3^+) & \Gamma(C_3^-) & \Gamma(\sigma_v) & \Gamma(\sigma_v') & \Gamma(\sigma_v'') \\ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \\ \chi(E)=4 & \chi(C_3^+)=1 & \chi(C_3^-)=1 & \chi(\sigma_v)=2 & \chi(\sigma_v')=2 & \chi(\sigma_v'')=2 \end{array} \tag{12.5.3}$$

A block diagonal matrix can be written as the *direct sum* of the matrices that lie along the diagonal. In the case of the C_{3v} matrix representation, each of the matrix representatives may be written as the direct sum of a 1×1 matrix and a 3×3 matrix.

$$\Gamma^{(4)}(g) = \Gamma^{(1)}(g) \otimes \Gamma^{(3)}(g) \tag{12.5.4}$$

in which the bracketed superscripts denote the dimensionality of the matrices. Note that a direct sum is very different from ordinary matrix addition since it produces a matrix of higher dimensionality. A direct sum of two matrices of orders n and m is performed by placing the matrices to be summed along the diagonal of a matrix of order $n+m$ and filling in the remaining elements with zeroes.

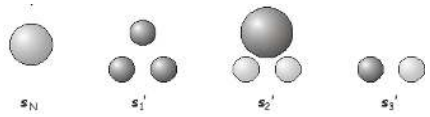
The reason why this result is useful in group theory is that the two sets of matrices $\Gamma^{(1)}(g)$ and $\Gamma^{(3)}(g)$ also satisfy all of the requirements for a matrix representation. Each set contains the identity and an inverse for each member, and the members multiply together associatively according to the group multiplication table[3]. Recall that the basis for the original four-dimensional representation had the s orbitals (s_N, s_1, s_2, s_3) of ammonia as its basis. The first set of reduced matrices, $\Gamma^{(1)}(g)$, forms a one-dimensional representation with (s_N) as its basis. The second set, $\Gamma^{(3)}(g)$ forms a three-dimensional representation with the basis (s_1, s_2, s_3). Separation of the original representation into representations of lower dimensionality is called *reduction* of the representation. The two *reduced representations* are shown below.

g	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''	
$\Gamma^{(1)}(g)$	(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_N)
$\Gamma^{(3)}(g)$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	3D representation spanned by (s_1, s_2, s_3)

(12.5.5)

The logical next step is to investigate whether or not the three dimensional representation $\Gamma^{(3)}(g)$ can be reduced any further. As it stands, the matrices making up this representation are not in block diagonal form (some of you may have noted that the matrices representing E and σ_v are block diagonal, but in order for a representation to be reducible *all* of the matrix representatives must be in the *same* block diagonal form) so the representation is not reducible. However, we can carry out a similarity transformation (see 10.1) to a new representation spanned by a new set of basis functions (made up of linear combinations of (s_1, s_2, s_3)), which *is* reducible. In this case, the appropriate (normalized) linear combinations to use as our new basis functions are

$$\begin{aligned} s_1' &= \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3) \\ s_2' &= \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) \\ s_3' &= \frac{1}{\sqrt{2}}(s_2 - s_3) \end{aligned} \tag{12.5.6}$$



or in matrix form

$$\begin{array}{ccccc} (s_1', s_2', s_3') & = & (s_1, s_2, s_3) & \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \\ \mathbf{x'} & = & \mathbf{x} & C \end{array} \tag{12.5.7}$$

The matrices in the new representation are found from $\Gamma'(g) = C^{-1}\Gamma(g)C$ to be

$$\begin{array}{cccccc} & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\ \Gamma^{(3),}(g) & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \end{array} \quad (12.5.8)$$

We see that each matrix is now in block diagonal form, and the representation may be reduced into the direct sum of a 1 x 1 representation spanned by (s_1') and a 2x2 representation spanned by (s_2', s_3'). The complete set of reduced representations obtained from the original 4D representation is:

E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''	
(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_N)
(1)	(1)	(1)	(1)	(1)	(1)	1D representation spanned by (s_1')
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	2D representation spanned by (s_2', s_3')

(12.5.9)

This is as far as we can go in reducing this representation. None of the three representations above can be reduced any further, and they are therefore called *irreducible representations*, of the point group. Formally, a representation is an irreducible representation if there is no similarity transform that can simultaneously convert all of the representatives into block diagonal form. The linear combination of basis functions that converts a matrix representation into block diagonal form, allowing reduction of the representation, is called a *symmetry adapted linear combination (SALC)*.

Irreducible Representations

The two one-dimensional irreducible representations spanned by s_N and s_1' are seen to be identical. This means that s_N and s_1' have the 'same symmetry', transforming in the same way under all of the symmetry operations of the point group and forming bases for the same matrix representation. As such, they are said to belong to the same *symmetry species*. There are a limited number of ways in which an arbitrary function can transform under the symmetry operations of a group, giving rise to a limited number of symmetry species. Any function that forms a basis for a matrix representation of a group must transform as one of the symmetry species of the group. The irreducible representations of a point group are labeled according to their symmetry species as follows:

i. 1D representations are labeled A or B, depending on whether they are symmetric (character $+1$) or antisymmetric (character -1) under rotation about the principal axis.
ii. 2D representations are labeled E, 3D representations are labeled T.
iii. In groups containing a center of inversion, g and u labels (from the German *gerade* and *ungerade*, meaning symmetric and antisymmetric) denote the character of the irreducible representation under inversion ($+1$ for g, -1 for u)
iv. In groups with a horizontal mirror plane but no center of inversion, the irreducible representations are given prime and double prime labels to denote whether they are symmetric (character $+1$ or antisymmetric (character -1) under reflection in the plane.
v. If further distinction between irreducible representations is required, subscripts 1 and 2 are used to denote the character with respect to a C_2 rotation perpendicular to the principal axis, or with respect to a vertical reflection if there are no C_2 rotations.

The 1D irreducible representation in the C_{3v} point group is symmetric (has character $+1$) under all the symmetry operations of the group. It therefore belongs to the irreducible representation A_1. The 2D irreducible representation has character 2 under the identity operation, -1 under rotation, and 0 under reflection, and belongs to the irreducible representation E.

Note

Sometimes there is confusion over the relationship between a function f and its irreducible representation, but it is quite important that you understand the connection. There are several different ways of stating the relationship. For example, the following statements all mean the same thing:

- "f has A_2 symmetry"
- "f transforms as A_2"
- "f has the same symmetry

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12.6: Character Tables

Now that we've learnt how to create a matrix representation of a point group within a given basis, we will move on to look at some of the properties that make these representations so powerful in the treatment of molecular symmetry. The trace of a matrix representative $\Gamma(g)$ is usually referred to as the *character* of the representation under the symmetry operation g. We will soon come to see that the characters of a matrix representation are often more useful than the matrix representatives themselves. Characters have several important properties.

1. The character of a symmetry operation is invariant under a similarity transform
2. Symmetry operations belonging to the same class have the same character in a given representation. Note that the character for a given class may be different in different representations, and that more than one class may have the same character.

Proofs of the above two statements are given in the Appendix.

Character Tables

A character table summarizes the behavior of all of the possible irreducible representations of a group under each of the symmetry operations of the group. The character table for C_{3v} is shown below.

$C_{3v}, 3m$	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	z, z^2, x^2+y^2
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y), (xy, x^2+y^2), (xz, yz), (R_x, R_y)$

(12.6.1)

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in both Schoenflies (C_{3v}) and Hermann-Mauguin ($3m$) notation.
ii. Along the first row are the symmetry operations of the group, E, $2C_3$ and $3\sigma_v$, followed by the order of the group. Because operations in the same class have the same character, symmetry operations are grouped into classes in the character table and not listed separately.
iii. In the first column are the irreducible representations of the group. In C_{3v} the irreducible representations are A_1, A_2 and E (the representation we considered above spans $2A_1$ + E).
iv. The characters of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products (z^2, x^2+y^2, xy, yz), and the rotations (R_x, R_y, R_z).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. As we shall see later, the transformation properties of x, y, and z can also be used to determine whether or not a molecule can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A simple way to determine the characters of a representation

In many applications of group theory, we only need to know the characters of the representative matrices, rather than the matrices themselves. Luckily, when each basis function transforms as a 1D irreducible representation (which is true in many cases of interest) there is a simple shortcut to determining the characters without having to construct the entire matrix representation. All we have to do is to look at the way the individual basis functions transform under each symmetry operation. For a given operation, step through the basis functions as follows:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation (i.e. the basis function is mapped onto itself);
ii. Add -1 to the character if the basis function changes sign under the symmetry operation (i.e the basis function is mapped onto minus itself);

iii. Add 0 to the character if the basis function moves when the symmetry operation is applied (i.e the basis function is mapped onto something different from itself).

Try this for the s orbital basis we have been using for the C_{3v} group. You should find you get the same characters as we obtained from the traces of the matrix representatives.

We can also work out the characters fairly easily when two basis functions transform together as a 2D irreducible representation. For example, in the C_{3v} point group x and y axes transform together as E. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. However, the new axes can each be written as a linear combination of our original x and y axes. Using the rotation matrices introduced in Section 9, we see that:

$$\begin{aligned} x' &= \cos\theta\, x + \sin\theta\, y \\ y' &= -\sin\theta\, x + \cos\theta\, y \end{aligned} \tag{12.6.2}$$

For one-dimensional irreducible representations we asked if a basis function/axis was mapped onto itself, minus itself, or something different. For two-dimensional irreducible representations we need to ask how much of the 'old' axis is contained in the new one. From the above we see that the x' axis contains a contribution $\cos\theta$ from the x axis, and the y' axis contains a contribution $\cos\theta$ from the y axis. The characters of the x and y axes under a rotation through θ are therefore $\cos\theta$, and the overall character of the E irreducible representation is therefore $\cos\theta + \cos\theta = 2\cos\theta$. For a C_3 rotation through 120 degrees, the character of the E irreducible representation is therefore $2\cos 120° = -1$.

In general, *when an axis is rotated by an angle θ by a symmetry operation, its contribution to the character for that operation is* $\cos\theta$.

In many cases, the characters for rotations C_n and improper rotations S_n are complex numbers, usually expressed in terms of the quantity $\epsilon = \exp(2\pi i/n)$. It is fairly straightforward to reconcile this with the fact that in chemistry we are generally using group theory to investigate physical problems in which all quantities are real. It turns out that whenever our basis spans an irreducible representation whose characters are complex, it will also span a second irreducible representation whose characters are the complex conjugates of the first irreducible representation i.e. complex irreducible representations occur in pairs. According to the strict mathematics of group theory, each irreducible representation in the pair should be considered as a separate representation. However, when applying such irreducible representations in physical problems, we add the characters for the two irreducible representations together to get a single irreducible representation whose characters are real.

As an example, the 'correct' character table for the group C_3 takes the form:

C_3	E	C_3	C_3^2
A	1	1	1
E	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{matrix} \epsilon \\ \epsilon* \end{matrix}$	$\begin{Bmatrix} \epsilon* \\ \epsilon \end{Bmatrix}$

(12.6.3)

Where $\epsilon = \exp(2\pi i/3)$. However, as chemists we would usually combine the two parts of the E irreducible representation to give:

C_3	E	C_3	C_3^2
A	1	1	1
E	2	−1	1

(12.6.4)

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12.8: Using Symmetry to Predict Zero in a Secular Determinant

As we continue with this course, we will discover that there are many times when we would like to know whether a particular integral is necessarily zero, or whether there is a chance that it may be non-zero. We can often use group theory to differentiate these two cases.

You will have already used symmetry properties of functions to determine whether or not a one-dimensional integral is zero. For example, cos(x) is an 'even' function (symmetric with respect to reflection through the origin), and it follows from this that

$$\int_{-\infty}^{\infty} \cos(x)dx = 0$$

In general integral between these limits for any other even function will be also be zero.

In the general case we may have an integral of more than one dimension. The key to determining whether a general integral is necessarily zero lies in the fact that because an integral is just a number, it must be invariant to any symmetry operation. For example, bonding in a diatomic (see next section) depends on the presence of a non-zero overlap between atomic orbitals on adjacent atoms, which may be quantified by an *overlap integral*. You would not expect the bonding in a molecule to change if you rotated the molecule through some angle θ, so the integral must be invariant to rotation, and indeed to any other symmetry operation.

In group theoretical terms, for an integral to be non-zero, *the integrand must transform as the totally symmetric irreducible representation in the appropriate point group*. In practice, the integrand may not transform as a single irreducible representation, but it **must include** the totally symmetric irreducible representation. These ideas should become more clear in the next section.

> It should be noted that even when the irreducible representations spanned by the integrand do include the totally symmetric irreducible representation, it is still possible for the integral to be zero. All group theory allows us to do is identify integrals that are *necessarily* zero based on the symmetry (or lack thereof) of the integrand.

Secular Equations

As we have seen already, any set of linear equations may be rewritten as a matrix equation $A\mathbf{x} = \mathbf{b}$. Linear equations are classified as *simultaneous linear equations* or *homogeneous linear equations*, depending on whether the vector $\mathbf{b}$ is non-zero or zero. For a set of simultaneous linear equations (non-zero $\mathbf{b}$) it is fairly apparent that if a unique solution exists, it can be found by multiplying both sides by the inverse matrix A^{-1} (since $A^{-1}A$ on the left hand side is equal to the identity matrix, which has no effect on the vector $\mathbf{x}$)

$$\begin{aligned} A\mathbf{x} &= \mathbf{b} \\ A^{-1}A\mathbf{x} &= A^{-1}\mathbf{b} \\ \mathbf{x} &= A^{-1}\mathbf{b} \end{aligned} \tag{12.8.1}$$

In practice, there are easier matrix methods for solving simultaneous equations than finding the inverse matrix, but these need not concern us here. We previously argued that in order for a matrix to have an inverse, **it must have a non-zero determinant**. Since A^{-1} must exist in order for a set of simultaneous linear equations to have a solution, this means that the determinant of the matrix A must be non-zero for the equations to be solvable.

> *For a matrix to have an inverse, it must have a non-zero determinant.*

The reverse is true for homogeneous linear equations. In this case the set of equations only has a solution if the determinant of A *is* equal to zero. The secular equations we want to solve are homogeneous equations, and we will use this property of the determinant to determine the molecular orbital energies. An important property of homogeneous equations is that if a vector $\mathbf{x}$ is a solution, so is any multiple of $\mathbf{x}$, meaning that the solutions (the molecular orbitals) can be normalized without causing any problems.

Solving for the orbital energies and expansion coefficients

Recall the secular equations for the A_1 orbitals of NH_3 derived in the previous section

$$\begin{aligned} c_1(H_{11}-ES_{11})+c_2(H_{12}-ES_{12}) &= 0 \\ c_1(H_{12}-ES_{12})+c_2(H_{22}-ES_{22}) &= 0 \end{aligned} \tag{12.8.2}$$

where c_1 and c_2 are the coefficients in the linear combination of the SALCs $\phi_1 = s_N$ and $\phi_2 = \frac{1}{\sqrt{3}}(s_1+s_2+s_3)$ used to construct the molecular orbital. Writing this set of homogeneous linear equations in matrix form gives

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{12}-ES_{12} & H_{22}-ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{12.8.3}$$

In order for the equations to have a solution, the determinant of the matrix must be equal to zero. Writing out the determinant will give us a polynomial equation in E that we can solve to obtain the orbital energies in terms of the Hamiltonian matrix elements H_{ij} and overlap integrals S_{ij}. The number of energies obtained by 'solving the secular determinant' in this way is equal to the order of the matrix, in this case two.

The secular determinant for Equation (21.3) is (noting that $S_{11} = S_{22} = 1$ since the SALCs are normalized)

$$(H_{11}-E)(H_{22}-E)-(H_{12}-ES_{12})^2 = 0 \tag{12.8.4}$$

Expanding and collecting terms in E gives

$$E^2(1-S_{12}^2)+E(2H_{12}S_{12}-H_{11}-H_{22})+(H_{11}H_{22}-H_{12}^2) = 0 \tag{12.8.5}$$

which can be solved using the quadratic formula to give the energies of the two molecular orbitals.

$$E_{\pm} = \frac{-(2H_{12}S_{12}-H_{11}-H_{22}) \pm \sqrt{(2H_{12}S_{12}-H_{11}-H_{22})^2-4(1-S_{12}^2)(H_{11}H_{22}-H_{12}^2)}}{2(1-S_{12}^2)} \tag{12.8.6}$$

To obtain numerical values for the energies, we need to evaluate the integrals H_{11}, H_{22}, H_{12}, and S_{12}. This would be quite a challenge to do analytically, but luckily there are a number of computer programs that can be used to calculate the integrals. One such program gives the following values.

$$\begin{aligned} H_{11} &= -26.0000\ eV \\ H_{22} &= -22.2216\ eV \\ H_{12} &= -29.7670\ eV \\ S_{12} &= 0.8167\ eV \end{aligned} \tag{12.8.7}$$

When we substitute these into our equation for the energy levels, we get:

$$\begin{aligned} E_+ &= 29.8336\ eV \\ E_- &= -31.0063\ eV \end{aligned} \tag{12.8.8}$$

We now have the orbital energies and the next step is to find the orbital coefficients. The coefficients for an orbital of energy E are found by substituting the energy into the secular equations and solving for the coefficients c_i. Since the two secular equations are not linearly independent (i.e. they are effectively only one equation), when we solve them to find the coefficients what we will end up with is the *relative* values of the coefficients. This is true in general: in a system with N coefficients, solving the secular equations will allow all N of the coefficients c_i to be obtained in terms of, say, c_1. The absolute values of the coefficients are found by normalizing the wavefunction.

Since the secular equations for the orbitals of energy E_+ and E_- are not linearly independent, we can choose to solve either one of them to find the orbital coefficients. We will choose the first.

$$(H_{11}-E_{\pm})c_1+(H_{12}-E_{\pm}S_{12})c_2 = 0 \tag{12.8.9}$$

For the orbital with energy E_- = -31.0063 eV, substituting numerical values into this equation gives

$$\begin{aligned} 5.0063c_1-4.4442c_2 &= 0 \\ c_2 &= 1.1265c_1 \end{aligned} \tag{12.8.10}$$

The molecular orbital is therefore

$$\Psi = c_1(\phi_1+1.1265\phi_2) \tag{12.8.11}$$

Normalizing to find the constant c_1 (by requiring $<\Psi|\Psi>$ = 1) gives

$$\begin{aligned} \Psi_1 &= 0.4933\phi_1 + 0.5557\phi_2 \\ &= 0.4933 s_N + 0.3208(s_1 + s_2 + s_3) \quad \text{(substituting the SALCs for } \phi_1 \text{ and } \phi_2) \end{aligned} \tag{12.8.12}$$

For the second orbital, with energy E_+ = 29.8336 eV, the secular equation is

$$\begin{aligned} -55.8336c_1 - 54.1321c_2 &= 0 \\ c_2 &= -1.0314c_1 \end{aligned} \tag{12.8.13}$$

giving

$$\begin{aligned} \Psi_2 &= c_1(\phi_1 - 1.0314\phi_2) \\ &= 1.6242\phi_1 - 1.6752\phi_2 \qquad \text{(after normalization)} \\ &= 1.6242 s_N - 0.9672(s_1 + s_2 + s_3) \end{aligned} \tag{12.8.14}$$

These two A_1 molecular orbitals Ψ_1 and Ψ_2, one bonding and one antibonding, are shown below.



The remaining two SALCs arising from the s orbitals of NH_3 ($\phi_3 = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)$ and $\phi_4 = \frac{1}{\sqrt{2}}(s_2 - s_3)$), form an orthogonal pair of molecular orbitals of E symmetry. We can show this by solving the secular determinant to find the orbital energies. The secular equations in this case are:

$$\begin{aligned} c_1(H_{33} - ES_{33}) + c_2(H_{34} - ES_{34}) &= 0 \\ c_1(H_{34} - ES_{34}) + c_2(H_{44} - ES_{44}) &= 0 \end{aligned} \tag{12.8.15}$$

Solving the secular determinant gives

$$E_\pm = \frac{-(2H_{34}S_{34} - H_{33} - H_{44}) \pm \sqrt{(2H_{34}S_{34} - H_{33} - H_{44})^2 - 4(1 - S_{34}^2)(H_{33}H_{44} - H_{34}^2)}}{2(1 - S_{34}^2)} \tag{12.8.16}$$

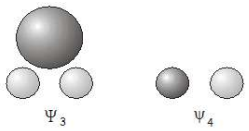
The integrals required are

$$\begin{aligned} H_{33} &= -9.2892\ eV \\ H_{44} &= -9.2892\ eV \\ H_{34} &= 0 \\ S_{34} &= 0 \end{aligned} \tag{12.8.17}$$

Using the fact that H_{34} = $S_{34} = 0$, the expression for the energies reduces to

$$E_\pm = \frac{(H_{33} + H_{44}) \pm (H_{33} - H_{44})}{2} \tag{12.8.18}$$

giving E_+ = H_{33} = -9.2892 eV and E_- = H_{44} = -9.2892 eV. Each SALC therefore forms a molecular orbital by itself, and the two orbitals have the same energy; the two SALCs form an orthogonal pair of degenerate orbitals. These two molecular orbitals of E symmetry are shown below.



Summary of the steps involved in constructing molecular orbitals

1. Choose a basis set of functions f_i consisting of the valence atomic orbitals on each atom in the system, or some chosen subset of these orbitals.
2. With the help of the appropriate character table, determine which irreducible representations are spanned by the basis set using Equation (15.20) to determine the number of times a_k that the k^{th} irreducible representation appears in the representation.

$$a_k = \frac{1}{h}\sum_C n_C \chi(g)\chi_k(g) \tag{12.8.19}$$

3. Construct the SALCs ϕ_i that transform as each irreducible representation using Equation 16.1

$$\phi_i = \sum_g \chi_k(g) g f_i \tag{12.8.20}$$

4. Write down expressions for the molecular orbitals by taking linear combinations of all the irreducible representations of the same symmetry species.
5. Write down the secular equations for the system.
6. Solve the secular determinant to obtain the energies of the molecular orbitals.
7. Substitute each energy in turn back into the secular equations and solve to obtain the coefficients appearing in your molecular orbital expressions in step 4.
8. Normalize the orbitals.

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12.9: Generating Operators for Irreducible Representations

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CHAPTER OVERVIEW

13: Molecular Spectroscopy

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Summer 2016: Delmar Larsen

Sorry, but all current instructors at UCD use the commercial textbook for this course.

Molecular spectroscopy is the study of absorption of light by molecules. In the gas phase at low pressures, molecules exhibit absorption in narrow lines which are very characteristic of the molecule as well as the temperature and pressure of its environment.

13.1: The Electromagnetic Spectrum
13.2: Rotational Transitions Accompany Vibrational Transitions
13.3: The Vibration-Rotation Spectrum
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13.10: Irreducible Representation of Point Groups
13.11: Time-Dependent Perturbation Theory
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13.13: The Harmonic Oscillator Selection Rule
13.14: Group Theory Determines Infrared Activity
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13.1: The Electromagnetic Spectrum

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century.[1] Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is $2.997\ 92 \times 10^8$ m/s. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, 3.00×10^8 m/s, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 13.1.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

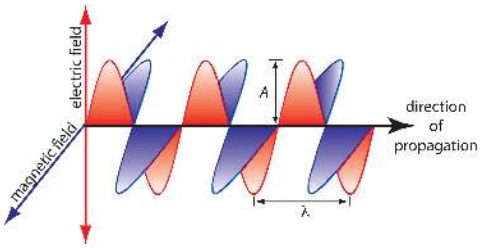


Figure 13.1.1: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{13.1.1}$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{13.1.2}$$

where A_m is the magnetic field's maximum amplitude.

Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure 13.1.1). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu} \tag{13.1.3}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda} \tag{13.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 13.1.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{589 \times 10^{-9}\ \text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1} \tag{13.1.5}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9}\ \text{m}} \times \frac{1\ \text{m}}{100\ \text{cm}} = 1.70 \times 10^{4}\ \text{cm}^{-1} \tag{13.1.6}$$

Exercise 13.1.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Click here to review your answer to this exercise.

Regions of the Spectrum

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 13.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

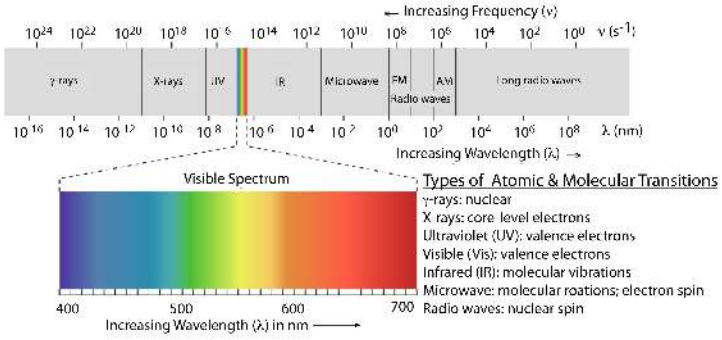


Figure 13.1.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 13.1.1 provides a list of several representative examples.

Table 13.1.1: Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea
	UV/Vis	*UV/Vis spectroscopy* *atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy* *phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

When given the energy level of the molecules along with wavelength, we can easily figure the frequency of the molecules where they fall in the electromagnetic spectrum regions. The given equation:

$$\Delta E = E_u - E_l = h$$

The above equation describes the energy change between upper state and lower state of energy.

- Frequency falls between 10^9 - 10^{11} which is in the microwave range correlates to the rotation of polyatomic molecules.
- Frequency falls between 10^{11} - 10^{13} which is in the far infared range correlates to the rotation of small molecules.
- Frequency falls between 10^{13} - 10^{14} which is in the infared range correlates to the vibrations of flexible bonds.
- Frequency falls between 10^{14} - 10^{16} which is in the visible and ultraviolet range correlates to the electronic transitions.

The powerful technique of figuring out the the frequency of the molecules can help us determine the bond length, temperature, probability distribution as you will learn later on from the degree of freedoms and how the process is undergo in specific a reaction.

Absorption and Emission

In absorption spectroscopy a photon is absorbed by an atom or molecule, which undergoes a transition from a lower-energy state to a higher-energy, or excited state (Figure 13.1.3). The type of transition depends on the photon's energy. The electromagnetic spectrum in Figure 13.1.2, for example, shows that absorbing a photon of visible light promotes one of the atom's or molecule's valence electrons to a higher-energy level. When an molecule absorbs infrared radiation, on the other hand, one of its chemical bonds experiences a change in vibrational energy.

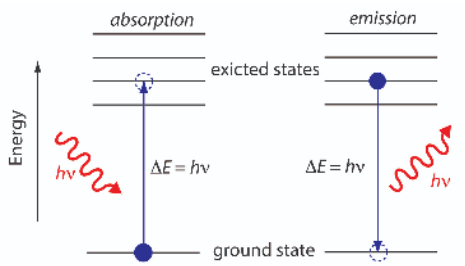


Figure 13.1.3: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hν strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hν, equals the difference in energy, ΔE, between the two states.

When it absorbs electromagnetic radiation the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call **absorbance**, is a useful analytical signal. Note that the each of the energy levels in Figure

13.1.3 has a well-defined value because they are quantized. Absorption occurs only when the photon's energy, *h*ν, matches the difference in energy, Δ*E*, between two energy levels. A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. Figure 13.1.4, for example, shows the absorbance spectrum of cranberry juice.

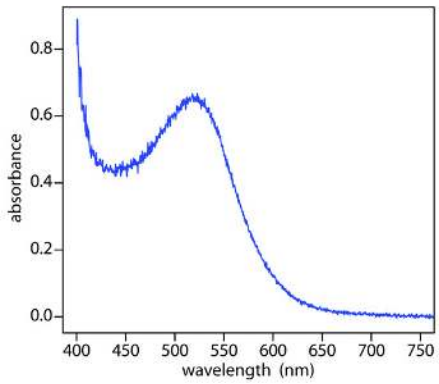


Figure 13.1.3). As a result, the juice appears red.

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call **emission** (Figure 13.1.4). There are several ways in which an atom or molecule may end up in an excited state, including thermal energy, absorption of a photon, or by a chemical reaction. Emission following the absorption of a photon is also called **photoluminescence**, and that following a chemical reaction is called **chemiluminescence**. A typical emission spectrum is shown in Figure 13.1.5.

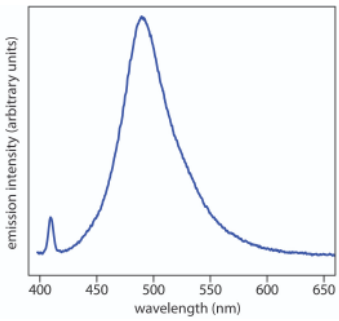


Figure 13.1.5: Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad band centered at approximately 500 nm is the dye's emission band. Because the dye absorbs blue light, a solution of coumarin 343 appears yellow in the absence of photoluminescence. Its photoluminescent emission is blue-green. Source: data from Bridget Gourley, Department of Chemistry & Biochemistry, DePauw University).

Contributors and Attributions

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13.2: Rotational Transitions Accompany Vibrational Transitions

Each of the modes of vibration of diatomic molecules in the gas phase also contains closely-spaced (1-10 cm^{-1} difference) energy states attributable to rotational transitions that accompany the vibrational transitions. A molecule's rotation can be affected by its vibrational transition because there is a change in bond length, so these rotational transitions are expected to occur. Since vibrational energy states are on the order of 1000 cm^{-1}, the rotational energy states can be superimposed upon the vibrational energy states.

Selection Rules

Rotational and Vibration transitions (also known as rigid rotor and harmonic oscillator) of molecules help us identify how molecules interact with each other, their bond length as mentioned in previous section. In order to know each transitions, we have to consider other terms like wavenumber, force constant, quantum number, etc. There are rotational energy levels associated with all vibrational levels. From this, vibrational transitions can couple with rotational transitions to give **rovibrational spectra**. Rovibrational spectra can be analyzed to determine average bond length.

We treat the molecule's **vibrations** as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)\frac{1}{2}$$

where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{13.2.1}$$

We treat the molecule's **rotations** as those of a rigid rotor (ignoring centrifugal distortion from non-rigid rotor aspects). The energy of a rotation is also quantized in discrete levels given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

In which I is the moment of inertia, given by

$$I = \mu r^2$$

where μ is the reduced mass (Equation 13.2.1) and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, $F(J)$ using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers

$$\tilde{F}(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = \tilde{B}J(J+1)$$

> It is important to note in which units one is working since the rotational constant is always represented as B, whether in frequency or wavenumbers.

- **Vibrational Transition Selection Rules**: At room temperature, typically only the lowest energy vibrational state v= 0 is populated, so typically v_0 = 0 and Δv = +1. The full selection rule is technically that Δv = ±1, however here we assume energy

can only go upwards because of the lack of population in the upper vibrational states.

- **Rotational Transition Selection Rules**: At room temperature, states with J≠0 can be populated since they represent the fine structure of vibrational states and have smaller energy differences than successive vibrational levels. Additionally, ΔJ = ±1 since a photon contains one quantum **of angular momentum** and we abide by the principle of **conservation of energy**. This is also the selection rule for rotational transitions.

These two selection rules mean that the transition ΔJ = 0 (i.e. J" = 0 and J' = 0, but $\nu_0 \neq 0$ is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an R-branch (when ΔJ = +1) and a P-branch (when ΔJ = -1). Each line of the branch is labeled R(J) or P(J), where J represents the value of the lower state Figure 13.2.1).

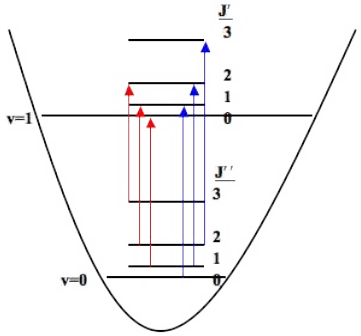


Figure 13.2.1 : Rotation-Vibration Transitions. Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.

R-branch

When ΔJ = +1, i.e. the rotational quantum number in the ground state is one more than the rotational quantum number in the excited state – R branch (in French, *riche* or rich). To find the energy of a line of the R-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \quad (13.2.2)$$

$$= h\nu_0 + hB[(J+1)(J+2) - J(J+1)] \quad (13.2.3)$$

$$= h\nu_0 + 2hB(J+1) \quad (13.2.4)$$

P-branch

When ΔJ = -1, i.e. the rotational quantum number in the ground state is one less than the rotational quantum number in the excited state – P branch (in French, *pauvre* or poor). To find the energy of a line of the P-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \quad (13.2.5)$$

$$= h\nu_0 + hB[J(J-1) - J(J+1)] \quad (13.2.6)$$

$$= h\nu_0 - 2hBJ \quad (13.2.7)$$

Q-branch

When ΔJ = 0, i.e. the rotational quantum number in the ground state is the same as the rotational quantum number in the excited state – Q branch (simple, the letter between P and R). To find the energy of a line of the Q-branch:

$$\Delta E = h\nu_0 + hB[J(J+1) - J'(J'+1)] \quad (13.2.8)$$

$$= h\nu_0 \quad (13.2.9)$$

The Q-branch can be observed in polyatomic molecules and diatomic molecules with electronic angular momentum in the ground electronic state, e.g. nitric oxide, NO. Most diatomics, such as O_2, have a small moment of inertia and thus very small angular momentum and yield no Q-branch.

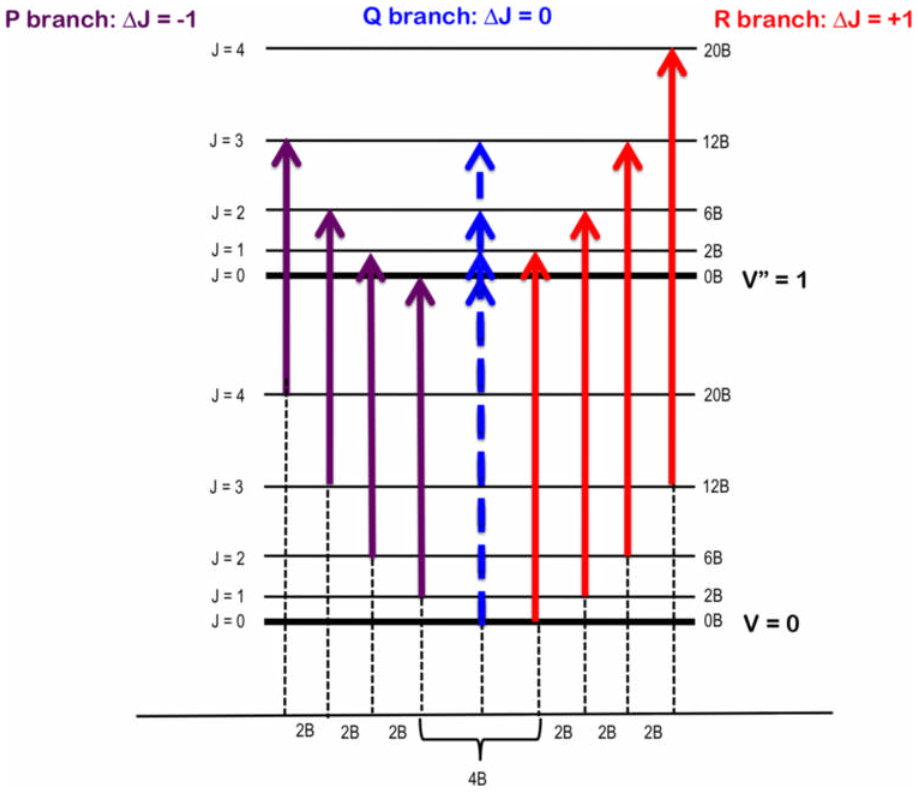


Figure 13.2.3 : Cartoon depiction of rotational energy levels, J, imposed on vibrational energy levels, v. The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

As seen in Figure 13.2.2 , the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of B (i.e, $2B$), thus the bond length can be deduced without the need for pure rotational spectroscopy.

The total nuclear energy of the combined rotation-vibration terms, $S(v, J)$, can be written as the sum of the vibrational energy and the rotational energy

$$S(v, J) = G(v) + F(J)$$

where $G(v)$ represents the energy of the harmonic oscillator, ignoring anharmonic components and $S(J)$ represents the energy of a rigid rotor, ignoring centrifugal distortion.

From this, we can derive

$$S(v, J) = \nu_0 \left(v + \frac{1}{2} \right) + BJ(J+1)$$

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of $2B$. The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

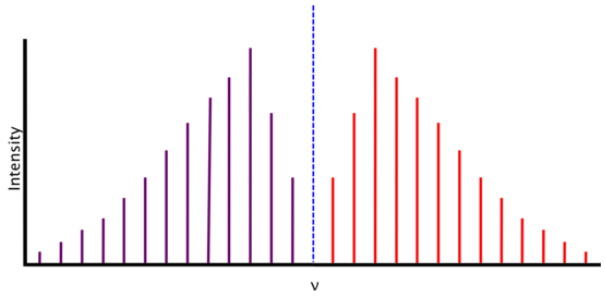


Figure 13.2.3 : A cartoon depiction of an ideal rovibrational spectrum.

In Figure 13.2.2 , between $P(1)$ and $R(0)$ lies the zero gap, where the the first lines of both the P- and R-branch are separated by $4B$, assuming that the rotational constant B is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

Advanced Concept: Occupations (Peak Intensities)

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the Jth upper level as N_J and the population of the lower state as N_0, we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{\left(-\frac{E_r}{kT}\right)}$$

(2J+1) gives the degeneracy of the Jth upper level arising from the allowed values of M_J (+J to –J). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J, the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max}. Thus, when

$$\frac{d}{dJ}\left(\frac{N_J}{N_0}\right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB}\right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase, as seen in Figure 13.2.2 .

From this relationship, we can also deduce that in heavier molecules, B will decrease because the moment of inertia will increase, and the decrease in the exponential factor is less pronounced. This results in the population distribution shifting to higher values of J. Similarly, as temperature increases, the population distribution will shift towards higher values of J.

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13.3: The Vibration-Rotation Spectrum

Vibration-rotation interaction describes the inversely proportional relationship of the rotational constant and the vibrational state. The rotational constants decrease as the vibrational states increase, and their interaction influences the frequencies at where the lines of R and P branches occurred. This effect can be observed well on a rotational-vibrational spectrum, and the vibration-rotation relationship also has its own mathematical form.

Introduction

When a rotational transition occurs with a vibrational transition, the vibrational-rotational spectrum of R branch and P branch is observed. Experimental data shows that the P branch has closer spaces between the lines as the frequencies decrease while R branch has further spaces between the lines as the frequencies increase. On the spectrum, R region is on the left and P region is on the right separated by a large gap in between. There are other graphs show differently, but the regions can be labeled using their spacing characteristic discussed below.

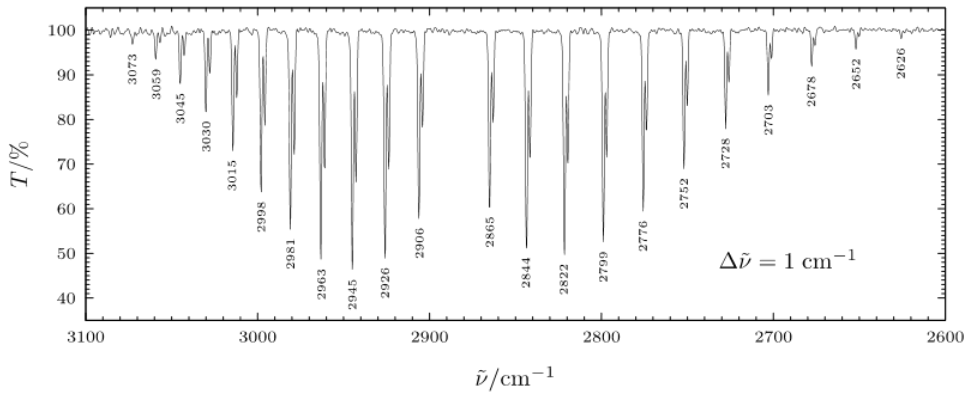


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Vibration-Rotation Interaction

Consider the rotational constant for a rigid rotator $\tilde{B} = h/8\pi^2 c\mu R_e^2$ where $\tilde{B}$ is the rotational constant, and R_e^2 is the bond length. It is clear from the equation that $\tilde{B}$ depends on R_e^2 in a inverse manner, so $\tilde{B}$ will decrease as R_e^2 increase, and vice versa.

Vibrational state and the bond length also possess a relationship, and that is bond length, R_e^2, will increase as the vibrational state, v increases. High vibrational states have large vibrational amplitudes (the amplitude can be visualized as the distance from one side to the other on the harmonic-oscillator parabola, and higher states has greater distance). On a potential graph, imagine a diatomic molecule with one of the atom fixed at the origin, the bond is along the x-axis, and the molecule vibrate toward and away from the origin along x-axis. The range at how much the bond can stretch or squeeze depend on the vibrational amplitude. So, at high vibrational state (thus high amplitude), the bond can squeeze in and stretch out more (just a little more) on the regular harmonic-oscillator potential, but it can stretch out greatly on an anharmonic oscillator. That's why bond length increase with vibrational state.

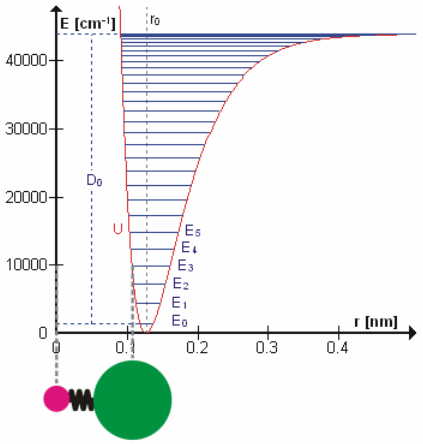


Figure used with permission from Wikipedia.

So far, there are two relationship established above

$$\tilde{B} \propto R_e^2 \tag{13.3.1}$$

(inversely proportional)

and

$$R_e^2 \propto v \tag{13.3.2}$$

(i.e., directly proportional). Therefore,

$$\tilde{B} \propto v \tag{13.3.3}$$

(i.e., inversely proportional). The rotational constant dependent on the vibrational state is denoted as $\tilde{B}_v$, and the dependence of $\tilde{B}$ on v is the vibrational-rotational interaction.

Frequencies of R and P Branches

The energies of the rigid rotator-harmonic oscillator is

$$\tilde{E}_{v,J} = G(v) + F(J) = \tilde{\nu}(v+\frac{1}{2}) + \tilde{B}J(J+1) \tag{13.3.4}$$

or in term of $\tilde{B}_v$

$$\tilde{E}_{v,J} = \tilde{\nu}(v+\frac{1}{2}) + \tilde{B}_v J(J+1) \tag{13.3.5}$$

Frequencies of vibrational transition from $v = 0 \rightarrow 1$ can be calculated from the equation above as the following:

For R branch, allowed $J = 0, 1, 2, \ldots$

$$\tilde{\nu}_R(\Delta J = +1) = \tilde{E}_{1,J+1} - \tilde{E}_{0,J} \tag{13.3.6}$$

$$= \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1) \tag{13.3.7}$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.8}$$

For P branch, allowed $J = 1, 2, 3, \ldots$

$$\tilde{\nu}_P(\Delta J = -1) = \tilde{E}_{1,J-1} - \tilde{E}_{0,J} \tag{13.3.9}$$

$$= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.10}$$

According to the vibration-rotation interaction, $\tilde{B}_1 < \tilde{B}_0$ because $R_e^2(v=1) > R_e^2(v=0)$.

Decrease in Spacing of Lines in the R Branch with Increasing J

A closer look at

$$\tilde{\nu}_R = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.11}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value for increasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}+$(smaller and smaller value) as J increase. Because the rotational frequencies keep getting smaller, the spacing between lines in R branch decreases as J increases.

Increasing in Spacing of Lines in the P Branch with Decreasing J

Using the same analysis as above,

$$\tilde{\nu}_P = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2 \tag{13.3.12}$$

shows that the last term in the parentheses $(\tilde{B}_1 - \tilde{B}_0)$ will be always negative because $\tilde{B}_1 < \tilde{B}_0$, and it also multiplies with J^2, so the square term $(\tilde{B}_1 - \tilde{B}_0)J^2$ will give a larger negative value even for decreasing J. As a result, $\tilde{\nu}_R = \tilde{\nu}-$(smaller and smaller value) as J decreases. Because the rotational frequencies keep getting larger, the spacing between lines in P branch increase as J decreases.

References

1. McQuarrie, Donald A. Quantum Chemistry. New York: University Science Books, 2007.

Problems

1. Why does the bond length increase as the vibrational state increases? Answer
2. Explain the decrease in line spacing for the R region as J increase. Answer
3. Explain the increase in line spacing for the P region as J decrease. Answer
4. Despite being parts of the same spectrum, why do P region and R region have different line spacing characteristics as discussed above. (Hint: Are their spacing characteristics really different?)
5. Given the relationship

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}(v = \frac{1}{2}) \tag{13.3.13}$$

What type of graph is expected for the graph of $\tilde{B}_v$ vs. v"?

Answers

1. Above
2. Above
3. Above
4. The spacing characteristics of R and P are exactly the same because the spacing always decreases as J increase regardless of the region. Spacing in P increases only because we look at it backwardly as J decreases.
5. The equation should give a linear relationship, so the graph is a straight line with a negative slope.

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- Dayton Dang

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13.4: The Pure Rotational Spectrum has Unequal Spacings

Vibrational energy which is a consequence of the oscillations/ vibrations of the nuclei along inter nuclear axis, is possible only when the distance between the nuclei is not fixed/ rigid; that means the separation between the two nuclei is flexible/ elastic (non-rigid rotator). Consequently, centrifugal force, when the molecule is rotating, tends to fly the reduced mass μ away from the axis of rotation. To keep the mass rotating about the axis, there must be some restoring force to counter balance the centrifugal force. The work done to supply this force is stored as potential energy. Therefore, unlike the case of rigid rotator, total energy of rotation in a molecule comprises of kinetic and the potential energy corresponding to centrifugal force of rotation.

Let r_e is the distance between the nuclei when the separation is taken to be rigid and r_c under the action of the centrifugal force. According to Hook's law, restoring force is proportional to change in internuclear distance $(r_c - r_e)$, or $= k(r_c - r_e)$ which in turn, will be equal to the centrifugal force.

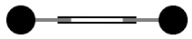


Figure 13.4.1: This animation can serve as an illustration of one of the aspects of the conservation of angular momentum. The animation is a schematic representation of two weights that are connected to each other. The two weights are circling around their common center of mass, the center of mass is stationary. The connection between the weight consists of pistons. When the connecting pistons contract, the rotation rate goes up. When the inward force exerted by the pistons relaxes the weight slide outwards, and the rotation rate goes down. (Public domain; Cleonis).

Centrifugal force,

$$F_c = \mu r_c \omega^2 = L^2/\mu {r_c}^3 \tag{13.4.1}$$

Equating the restoring force to the centrifugal force, one gets

$$k(r_c - r_e) = \frac{L^2}{\mu {r_c}^3} \tag{13.4.2}$$

$$r_c - r_e = \frac{L^2}{k\mu {r_c}^3} \cong \frac{L^2}{k\mu {r_e}^3} \tag{13.4.3}$$

Total energy, on adding kinetic energy, as expressed in Equation 13.4.3 to the potential energy,

$$\frac{1}{2}k(r_c - r_e)^2 \tag{13.4.4}$$

is given by

$$E_r = \frac{L^2}{2\mu {r_c}^2} + \frac{1}{2}k\,(r_c - r_e)^2 \tag{13.4.5}$$

Using $(r_c - r_e) = \Delta r$ and eliminating r_c from equation 13.4.5, one gets

$$E_r = \frac{L^2}{2\mu\ {r_e}^2(1 + \Delta r/r_e)^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.6}$$

$$= \frac{L^2(1 - 2\Delta r/r_e)}{2\mu\ {r_e}^2} + \frac{1}{2}k\Delta r^2 \tag{13.4.7}$$

using

$$(1 + \Delta r/r_e)^{-2} \approx (1 - 2\Delta r/r_e) \tag{13.4.8}$$

$$E_r = \frac{L^2}{2\mu {r_e}^2} - \frac{L^4}{k\mu^2 {r_e}^6} + \frac{1}{2}k\frac{L^4}{k^{2\mu 2}{r_e}^6} \tag{13.4.9}$$

$$= \frac{L^2}{2\mu {r_e}^2} - \frac{1}{2}\frac{L^4}{k\mu^2 {r_e}^6} \tag{13.4.10}$$

$$= \frac{\hbar^2\ J(J+1)}{2\mu {r_e}^2} - \frac{\hbar^4\ J^2(J+1)^2}{2k\mu^2 {r_e}^6} \tag{13.4.11}$$

Use of Equation 13.4.3 and of the relation regarding angular momentum of a rotor

$$L = \hbar\sqrt{J(J+1)} \tag{13.4.12}$$

has been made to obtain relation in Equation 13.4.11, which may be expressed in cm^{-1} as

$$F(J) = \underbrace{\tilde{B}J(J+1)}_{\text{rigid rotator term}} - \underbrace{\tilde{D}J^2(J+1)^2 cm^{-1}}_{\text{centrifugal stretching}} \tag{13.4.13}$$

where

$$\tilde{B} = \frac{\hbar}{4\pi\ \mu {r_e}^2 c}\ (\text{in cm}^{-1}) \tag{13.4.14}$$

and

$$\tilde{D} = \frac{\hbar^3}{4\pi k\ \mu^2 {r_e}^6\ c}\ (\text{in cm}^{-1}) \tag{13.4.15}$$

First term in the Equation 13.4.13 is same as for the rigid rotator; second term is the consequence of the centrifugal stretching. Recall Equation 13.4.3 wherein k is the spring constant that, as we will see in the following section, plays the same role as in the vibrational motion. In other words, centrifugal stretching constant $\tilde{D}$ is not only measures the influence of centrifugal force, but also hints upon the interaction between the rotational and vibrational motions.

Since $\tilde{D}$ is positive, it is clear from Equation 13.4.13 that the energy levels for the non-rigid rotator are slightly lower on energy scale than those of rigid rotator for the corresponding J values; the magnitude of decrease in energy of the non-rigid rotator states increases with J as shown in the Figure 13.4.2

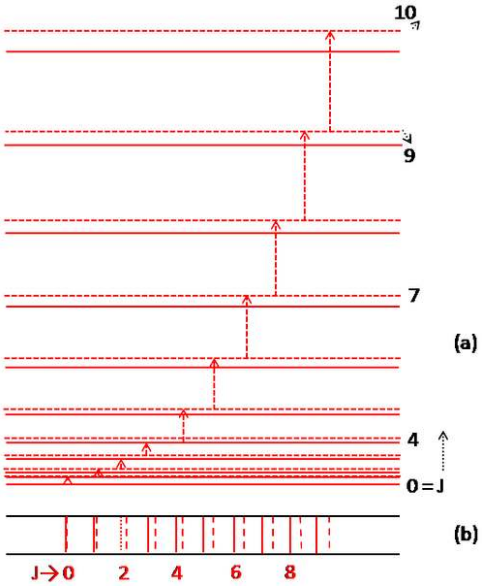


Figure 13.4.2: Energy levels and the transitions of rigid rotator (broken red lines) & of non-rigid rotator (solid red lines). (b) resulting spectra from both the models

Consequently, on applying the selection rule $\Delta J = \pm 1$, rotational spectrum of a non-rigid rotator consists of a series of lines (red lines) wherein separation, unlike the case of spectral series (broken red lines) of a rigid rotator, between the consecutive rotational

lines decreases with increase in J , as shown in the Figure $13.4.2$ It may be noted that value of D is very small compared to B with the result that the influence of D is significant only for very large J values.

For example, for HCl the values are $B \sim 10.4\ \ cm^{-1}$ and $D \sim 0.0004\, cm^{-1}$. Usually, D is ignored in the calculations. Figure $13.4.2$ exaggerates the decrease in energy to visualize its effect. Nevertheless, non-rigid rotator is the model that describes the rotational motion more accurately and hence explains the spectral experimental observations not only in the microwave region but also the rotation-vibration spectra and the rotational structure of the electronic bands discussed in the later sections.

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13.5: Vibrational Overtones

Although the harmonic oscillator proves useful at lower energy levels, like $v = 1$, it fails at higher numbers of v, failing not only to properly model atomic bonds and dissociations, but also unable to match spectra showing additional lines than is accounted for in the harmonic oscillator model.

Anharmonicity

Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to transition from $\Delta v = \pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation (Figure 13.5.1). For exaple, unlike the parabola given in the Harmonic Oscillator approximation, atoms that are too far apart will dissociate.

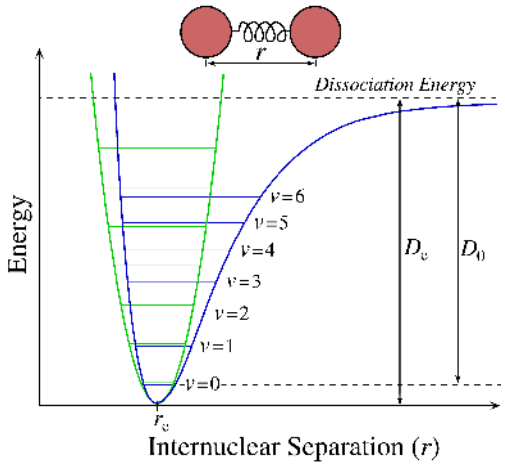


Figure 13.5.1 : Pictured above is the Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and R is the radius between the centers of the two atoms. Towards the left is compression of the bond, towards the right is extension. (CC BY-SA 3.0; Created by Mark Somoza March 26 2006).

As you can see in Figure 13.5.1 , the harmonic oscillator potential (in green) well only roughly fits over the more accurate anharmonic oscillator well (in blue). The solid line accounts for dissociation at large R values, which the dotted lines does not even remotely cover. However, this is just one important difference between the harmonic and anharmonic (real) oscillators.

The real potential energy can be expanded in the Taylor series.

$$V(R) = V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dR^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}(R-R_e)^4 + \ldots \quad (13.5.1)$$

This expansion was discussed in detail previously. The first term in the expansion is ignored since the derivative of the potential at R_e is zero (i.e., at the bottom of the well). The Harmonic Oscillator approximation only uses the next term, the quadratic term, in the series

$$V_{HO}(R) \approx V(R_e) + \frac{1}{2!}\left(\frac{d^2V}{dR^2}\right)_{R=R_e}(R-R_e)^2$$

or in terms of a spring constant (and ignore the absolute energy term) and defining r to equal the displacement from equilibrium ($r = R - R_e$), then we get the "standard" harmonic oscillator potential:

$$V_{HO}(R) = \frac{1}{2}kr^2$$

Alternatively, the expansion in Equation 13.5.1 can be shortened to the cubic term

$$V(x) = \frac{1}{2}kr^2 + \frac{1}{6}\gamma r^3 \quad (13.5.2)$$

where

- $V(x_0) = 0$, and $r = R - R_0$.
- k is the harmonic force constant, and

- γ is the first (i.e., cubic) *anharmonic* term

It is important to note that this approximation is only good for R near R_0.

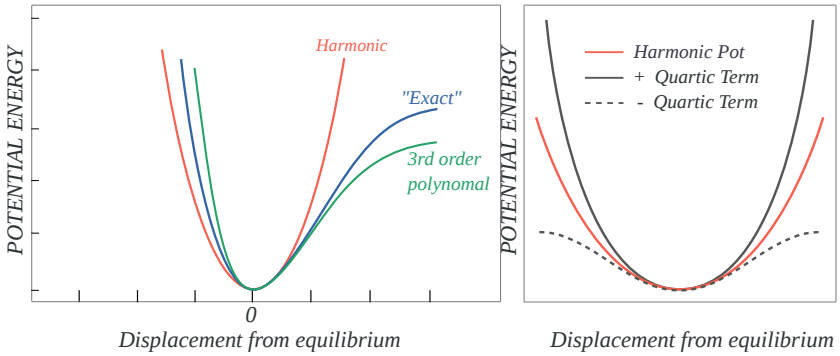


Figure 13.5.2 : (left) Deviation from simple harmonic potential approximation (red curve) of true/exact potential (blue curve) with cubic term (green). (right) Expansion with positive or negative quartic terms. (CC BY-NC; Ümit Kaya via LibreTexts)

The harmonic oscillator approximation and gives by the following energies:

$$E_v = \tilde{\nu}\left(v+\frac{1}{2}\right)$$

When cubic terms in the expansion (Equation 13.5.2) is included, then Schrödinger equation solved, using perturbation theory, gives:

$$E_v = \tilde{\nu}\left(v+\frac{1}{2}\right) - \tilde{\chi_e}\tilde{\nu}\left(v+\frac{1}{2}\right)^2$$

where $\tilde{\chi_e}$ is the **anharmonicity constant**. It is much smaller than 1, which makes sense because the terms in the Taylor series approach zero. This is why, although $G(n)$ technically includes all of the Taylor series, we only concern ourselves with the first and second terms. The rest are so small and barely add to the total and thus can be ignored. To get a more accurate approximation, more terms can be included, but otherwise, can be ignored. Almost all diatomics have experimentally determined $\frac{d^2V}{dx^2}$ for their lowest energy states. H_2, Li_2, O_2, N_2, and F_2 have had terms up to $n < 10$ determined of Equation 13.5.1.

Overtones

The Harmonic Oscillator approximation predicts that there will be only one line the spectrum of a diatomic molecule, and while experimental data shows there is in fact one dominant line--**the fundamental**--there are also other, weaker lines. How can we account for these extra lines?

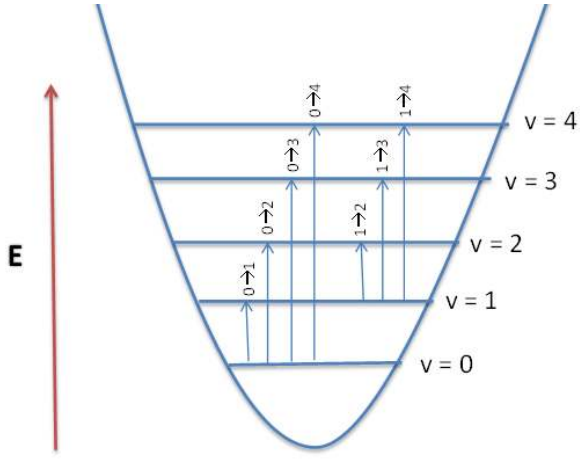


Figure 13.5.3 : A diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic (quadratic) oscillator. The transition $0 \rightarrow 1$ is the fundamental, transitions $0 \rightarrow n$ (n>1) are called overtones, and transitions $1 \rightarrow n$ (n<1) are called hot transitions (hot bands).

Any resonant frequency above the fundamental frequency is referred to as an *overtone*. In the IR spectrum, overtone bands are multiples of the fundamental absorption frequency. As you can recall, the energy levels in the Harmonic Oscillator approximation are evenly

spaced apart. Energy is proportional to the frequency absorbed, which in turn is proportional to the wavenumber, the first overtone that appears in the spectrum will be twice the wavenumber of the fundamental. That is, first overtone $v = 1 \rightarrow 2$ is (approximately) twice the energy of the fundamental, $v = 0 \rightarrow 1$.

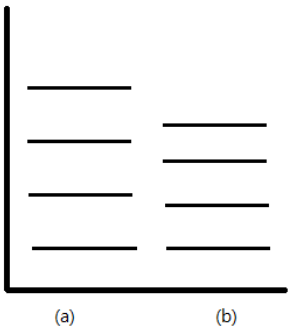


Figure 13.5.4 : An exaggerated view of the energy levels. (a) would be the harmonic oscillator, with the evenly spaced out energy levels. (b) would be the anharmonic, with the energy levels compressing until they converge.

The levels are not equally spaced, like in the harmonic oscillator, but decrease as v increases, until it ultimately converges, is implied by Figure 13.5.4 . Also as a result of anharmonicity, the $\Delta v = \pm 1$ selection rule is no longer valid and v can be any number. This leads to the observation of higher order transitions, or **overtones**, which result from the transition of the ground state to higher energy levels.

Anharmonic Oscillator Selection Rules

For the anharmonic oscillator, the selection rule is $\Delta V = \text{any number}$. That is, there are no selection rules (for state to state transitions)

Overtones occur when a vibrational mode is excited from $v = 0$ to $v = 2$ (the first overtone) or $v = 0$ to $v = 3$ (the second overtone). The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapid decreases as $\Delta v > \pm 1$ gets bigger. Based on the harmonic oscillator approximation, the energy of the overtone transition will be approximately v times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table 13.5.1 : HCl vibrational spectrum.

Transition	$\tilde{\nu}_{obs}$ [cm^{-1}]	$\tilde{\nu}_{obs}$ Harmonic [cm^{-1}]	$\tilde{\nu}_{obs}$ Anharmonic [cm^{-1}]
$0 \rightarrow 1$ (fundamental)	2885.9	2885.9	2,885.3
$0 \rightarrow 2$ (first overtone)	5668.0	5771.8	5,665.0
$0 \rightarrow 3$ (second overtone)	8347.0	8657.7	8,339.0
$0 \rightarrow 4$ (third overtone)	10 923.1	11 543.6	10,907.4
$0 \rightarrow 5$ (fourth overtone)	13 396.5	14 429.5	13,370

We can see from Table 13.5.1 that the anharmonic frequencies correspond much better with the observed frequencies, especially as the vibrational levels increase. Because the energy levels and overtones are closer together in the anharmonic model, they are also more easily reached. This means that there is a higher chance of that level possibly being occupied, meaning it can show up as additional, albeit weaker intensity lines (the weaker intensity indicates a smaller probability of the transition occuring).

Exercise 13.5.1

HCl has a fundamental band at 2885.9 cm^{-1} and an overtone at 5668.1 cm^{-1} Calculate $\tilde{\nu}$ and $\tilde{\chi_e}$.

Exercise 13.5.2

Write out the Taylor series, and comment on the trend in the increasing terms. Using a test number x, please add terms 3, 4, and 5, then compare this to term 2. How do they compare? We have seen that the anharmonic terms increase the accuracy of our oscillator approximation. Why don't we care so much about terms past the second?

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13.6: Electronic Spectra Contain Electronic, Vibrational, and Rotational Information

Molecules can also undergo changes in electronic transitions during microwave and infrared absorptions. The energy level differences are usually high enough that it falls into the visible to UV range; in fact, most emissions in this range can be attributed to electronic transitions.

Electron Transitions are not Purely Electronic

We have thus far studied *rovibrational transitions*--that is, transitions involving both the vibrational and rotational states. Similarly, electronic transitions tend to accompany both rotational and vibrational transitions. These are often portrayed as an electronic potential energy cure with the vibrational level drawn on each curve. Additionally, each vibrational level has a set of rotational levels associated with it.

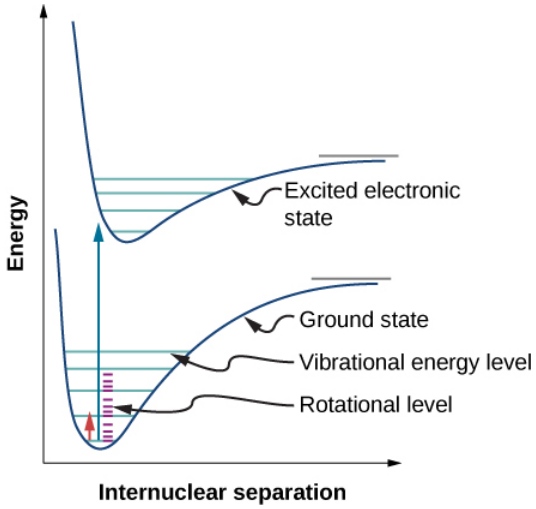


Figure 13.6.1 : Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. (CC BY 3.0; OpenStax).

Recall that in the Born-Oppenheimer approximation, nuclear kinetic energies can be ignored (e.g., fixed) to solve for electronic wavefunctions and energies, which are much faster than rotation or vibration. As such, it is important to note that unlike rovibrational transitions, electronic transitions aren't dependent on rotational or transitional terms and are assumed to be separate. Therefore, when using an anharmonic oscillator-nonrigid rotator approximation (and excluding translation energy), the total energy of a diatomic is:

$$\tilde{E}_{total} = \tilde{\nu}_{el} + G(v) + F(J) \tag{13.6.1}$$

where $\tilde{\nu}_{el}$ is the electronic transition energy change in wavenumbers, $G(n)$ is the vibrational energy with energy level v (assuming anharmonic oscillator), and $F(J)$ is the rotational energy, assuming a nonrigid rotor. Equation 13.6.1 can be expanded accordingly:

$$\tilde{E}_{total} = \underbrace{\tilde{\nu}_{el}}_{\text{electronic}} + \underbrace{\tilde{\nu}_e\left(v+\frac{1}{2}\right) - \tilde{\chi}_e\tilde{\nu}_e\left(v+\frac{1}{2}\right)^2}_{\text{vibrational}} + \underbrace{\tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}_{\text{rotational}} \tag{13.6.2}$$

Notice that both the vibration constant ($\tilde{\nu}_e$) and anharmonic constant ($\tilde{\chi}_e$) are electronic state dependent (and hence the rotational constants would be too, but are ignored here). Since rotational energies tend to be so small compared to electronic, their effects are minimal and are typically ignored when we do calculations and are referred to as *vibronic* transitions.

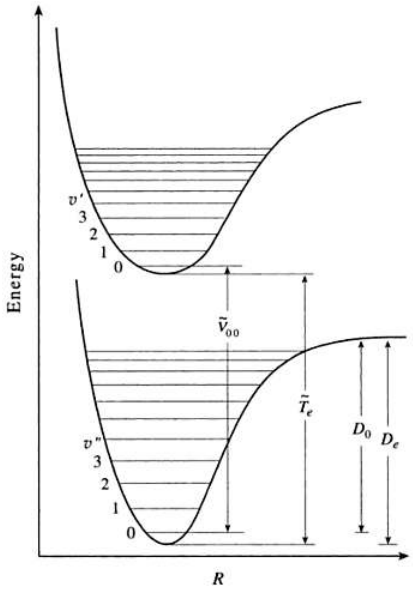


Figure 13.6.2 : As you can see, electronic transitions involve two energy potential wells! The vibrational levels are included, but rotational levels are excluded.

The eigenstate-to-eigenstate transitions (e.g., $1 \rightarrow 2$) possible are numerous and have absorption lines at

$$\tilde{\nu}_{obs} = \tilde{E}_2 - \tilde{E}_1 \tag{13.6.3}$$

and for simplification, we refer to constants associated with these states as $|'\rangle$ and $|''\rangle$, respectively. So Equation 13.6.3 is

$$\tilde{\nu}_{obs} = \tilde{E''(v'')} - \tilde{E'(v')}$$

Also important to note that typically vibronic transitions are usually the result of the vibrational $v' = 0$ vibratonal state. Within this assumption and excluding the rotational contributions (due to their low energies), Equation 13.6.2 can be used with Equation 13.6.3 to get

$$\tilde{\nu}_{obs} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right) + \tilde{\nu}'_e v'' - \tilde{\chi}'_e\tilde{\nu}'_e v''(v''+1) \tag{13.6.4}$$

A common transition of importance is the $\tilde{\nu}_{00}$, which is the $0 \rightarrow 0$ transition and include no vibrational change. For this case, equation 13.6.4 is then

$$\tilde{\nu}_{00} = \tilde{T}_{el} + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\chi}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\chi}''_e\tilde{\nu}''_e\right)$$

This is the lowest energy possible to observe in an electronic transition although it may be of low intensity as discussed in the following section.

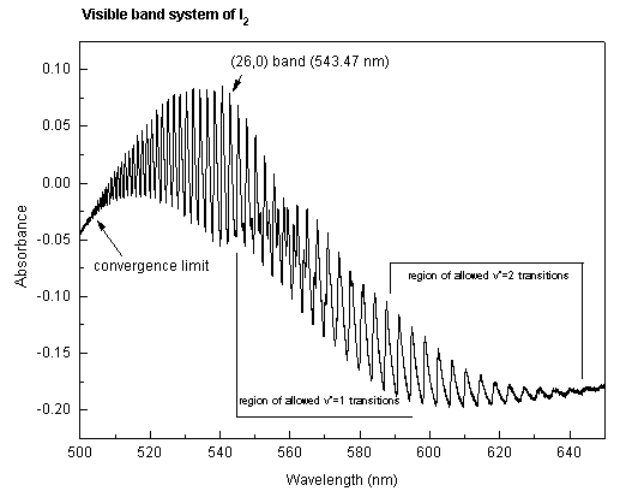
Iodine

The absorption spectrum of iodine yields information about the excited state well rather than the ground state well (notice that equation 13.6.4 depends primarily on excited state parameters). In this experiment you will characterize the excited state well by extracting values for the following excited state parameters.

Recall that as v' increases, the vibrational energy spacing decreases. At the upper edge of the well, the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit that **bond dissociation occurs**. The energy required to dissociate the bond is actually D'_o rather than D'_e because the molecule cannot have less than **the zero point energy**.

The vibrational-electronic spectrum of I_2 in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to v'<-- 0 transitions connecting the v" = 0 vibrational level of the ground electronic state (denoted as $X^1\Sigma^+$) to many different vibrational levels v' of the excited $B^3\Pi$ electronic state. Under the conditions of this

experiment (i.e., low resolution), the rotational lines within each band are not resolved. However, the peaks may be identified as R-branch band heads (1). For a molecule as heavy as I_2, the position of each band head is within a few tenths of one cm^{-1} of the band origin (2), and for the purposes of this experiment, the distinction between the two may be ignored. The general features of the absorption spectrum are shown below:



Each small bump, or peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a *band*. Each band is comprised of several hundred *lines*, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the *band head*. The set of all of these bands is referred to as the *visible band system* of I_2.

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light. The *hot bands* arising from absorption from v''=1 and v''=2 are shown very approximately on the absorption spectrum above.

At a point called the *convergence limit*, the spacing between bands decreases to zero. Beyond this convergence limit, the spectrum is continuous because the excited state of the I_2 molecule is not bound. One of the purposes of this experiment is to identify this convergence limit accurately.

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13.7: The Franck-Condon Principle

Learning Objectives

- To explain the vibrational fine structure in electronic spectroscopy for bound excited states in terms of the Franck-Condon approximation
- To calculate the vibrational progressions (Franck-Condon factors) in a single displaced harmonic oscillator vibronic system.

The **Franck-Condon Principle** describes the intensities of vibronic transitions, or the absorption or emission of a photon. It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.

If we picture the vertical transition from ground to excited electronic state as occurring from a vibrational wavefunction that gives a probability distribution of finding the nuclei in a give region of space we can determine the probability of a given vibrational level from the overlap integral $S_{v',v}$ which gives the overlap of the vibrational wavefunction in the ground and excited state. The v' quantum numbers refer to the ground state and the v quantum numbers refer to the excited state. The transition probability can be separated into electronic and nuclear parts using the Condon approximation.

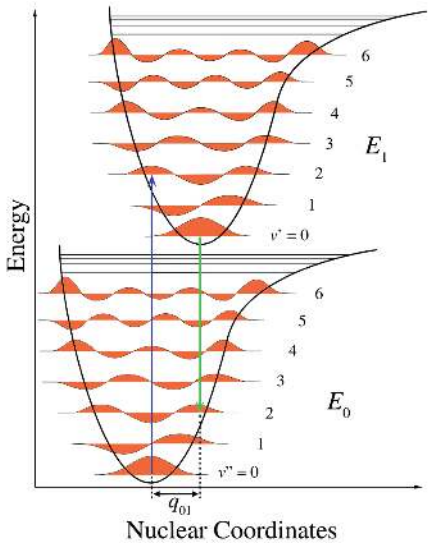


Figure 13.7.1 : Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $v = 0$ and $v' = 2$. (CC-SA-BY-3.0; Samoza).

In Figure 13.7.1 , the nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

The Classical Condon approximation

Condon approximation is the assumption that the electronic transition occurs on a time scale short compared to nuclear motion so that the transition probability can be calculated at a fixed nuclear position.

This change in vibration is maintained during a state termed the **rapid electronic excitation**. The resulting Coulombic forces produce an equilibrium as shown in the figure for the nuclei termed a turning point. The turning point can be mapped by drawing a

vertical line from the minimum of the lower curve to the intersection of the higher electronic state. This procedure is termed a **vertical transition** and was discussed before in the context of photoelectron spectroscopy (another electronic spectroscoy).

The Franck-Condon Principle explains the relative intensities of vibronic transitions by relating the probability of a vibrational transition to the overlap of the vibrational wavefunctions. It states that the probability of a vibrational transition occurring is weighted by the Franck-Condon overlap integral:

$$\begin{aligned} {}_{i\rightarrow f} &= |\langle \psi^*_{final}|\boldsymbol{\mu}|\psi_{initial}\rangle|^2 \\ &= \left|\int \psi^*_{final}\boldsymbol{\mu}\psi_{initial}\, d\tau\right|^2 \end{aligned}$$

Within the Franck-Condon approximation, the nuclei are considered "fixed" during electronic transitions. Thus, electronic transitions can be considered vertical transitions on electronic potential energy curves (vierical transitions in Figure 13.7.1).

The Quantum Franck-Condon Principle

The Franck-Condon Principle has both a Classical and Quantum application. Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

The Franck-Condon principle is based on the Born-Oppenheimer approximation, which allows separation of the electronic q and nuclear Q wavefunctions given the total wavefunction.

$$|\psi_{total}(Q,q) = |\psi_{nuc}(Q)\rangle\psi_{el}(Q;q)\rangle$$

Since the transition operator, $\hat{\mu}(q)$, is dependent only on the electronic component, the nuclear components can be separated from the transition moment integral that dictates the probability of the transition occurring:

$$\langle \psi^*_{total,f}|\hat{\mu}|\psi_{total,i}\rangle = \langle \psi^*_{nuc,f}|\langle \psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle|\psi_{nuc,i}\rangle \tag{13.7.1}$$

$$= \underbrace{\langle \psi^*_{nuc,f}|\psi_{nuc,i}\rangle}_{\text{nuclear overlap}}\langle \psi^*_{el,f}|\boldsymbol{\mu}|\psi_{el,i}\rangle \tag{13.7.2}$$

If the nuclear overlap integral is zero for this transition, then the transition will not be observed, irrespective of the magnitude of the electronic factor.

S_{00} Transition Evaluated within Harmonic Oscillator Model

The nuclear overlap for the zero-zero transition S_{00} can be calculated quite simply using the definition of the Gaussian form of the harmonic oscillator wavefunctions.

The zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2}\right\rangle$$

The zero-point wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left|\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-Q_e)^2/2}\right\rangle$$

where

- $\alpha = \dfrac{\sqrt{mk}}{\hbar}$
- R_e is the equilibrium bond length in the ground electronic state
- Q_e is the equilibrium bond length in the excited electronic state

The nuclear overlap integral is

$$S_{00} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \tag{13.7.3}$$

The exponent in Equation 13.7.3 can be expanded as

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} \int_{\infty}^{\infty} e^{-\alpha(2R^2 - RR_e - 2RQ_e + R_e^2 + Q_e^2)/2} dR \tag{13.7.4}$$

and we use

$$(R_e + Q_e)^2 = R_e^2 + Q_e^2 + 2R_eQ_e$$

and

$$(R_e - Q_e)^2 = R_e^2 + Q_e^2 - 2R_eQ_e$$

to substitute and complete the square inside the integral. We can express

$$R_e^2 + Q_e^2 = \frac{1}{2}[(R_e + Q_e)^2 + (R_e - Q_e)^2].$$

Thus, the integral in Equation 13.7.4 is

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} e^{-\alpha\{R - 1/2(R_e + Q_e)\}^2} dR$$

The integral is a **Gaussian integral**. You can show that if we let $z = \sqrt{\alpha}\{R - 1/2(R_e + Q_e)\}$ then $dz = \sqrt{\alpha} dR$ and the integral becomes

$$S_{00} = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} e^{z^2} dz \tag{13.7.5}$$

this integral has been solved already, from a table of integrals, Equation 13.7.5 becomes

$$S_{00} = e^{-\alpha(R_e - Q_e)^2/4}$$

We would follow the same procedure to calculate that overlap of the zeroth level vibration in the ground to the first excited vibrational level of the excited state: S_{01}.

S_{01} Transition Evaluated within Harmonic Oscillator Model

To calculate the overlap of zeroth ground state level ($v = 0$) with the first excited state level ($v' = 1$) we use the Hermite polynomial $H_1(x) = 2x$ for describing the excited state wavefunction (see here for a review on harmonic oscillator wavefunctions). Here $x = \sqrt{\alpha}(R - Q_e)$.

$$S_{01} = \langle \psi^*_{nuc,f} | \psi_{nuc,i} \rangle \tag{13.7.6}$$

with the zero-point wavefunction in the ground electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-R_e)^2/2} \right\rangle$$

The first excited-state wavefunction in the excited electronic state is

$$|\psi(R)\rangle = \left| \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R-Q_e)^2/2} \right\rangle$$

The overlap of zeroth ground state level with the first excited state level (Equation 13.7.6) is then

$$S_{01} = \frac{1}{\sqrt{2}} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} e^{-\alpha(R-R_e)^2/2} \sqrt{\alpha} 2(R - Q_e) e^{-\alpha(R-Q_e)^2/2}$$

and

$$S_{01} = \sqrt{\frac{2\alpha^2}{\pi}} e^{-\alpha(R_e - Q_e)^2/4} \int_{-\infty}^{\infty} (R - Q_e) e^{-\alpha\{R - 1/2(R_e + Q_e)^2\}}$$

The same substitutions can be made as above so that the integral can be written as (not shown and to be demonstrated in a homework exercises) and the final result is

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e - Q_e)^2/4}$$

We could continue and calculate that overlap of the zeroth level in the ground state with all the higher light vibrational levels: S_{02}, S_{03}, etc. Each term corresponds to a transition with a different energy since the vibrational levels have different energies. The absorption band then has the appearance of a progression (a Franck-Condon progression) of transitions between different levels each with its own probability.

Franck-Condon Progressions

To understand the significance of the above formula for the FC factor, let us examine a ground and excited state potential energy surface at $T = 0$ Kelvin. Shown below are two states separated by 8,000 cm^{-1} in energy. This is energy separation between the bottoms of their potential wells, but also between the respective zero-point energy levels. Let us assume that the wavenumber of the vibrational mode is 1,000 cm^{-1} and that the bond length is increased due to the fact that an electron is removed from a bonding orbital and placed in an anti-bonding orbital upon electronic excitation.

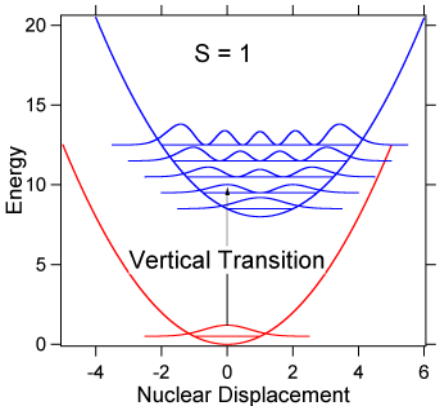


Figure 13.7.2 : Wavefunctions transitions for a harmonic oscillator model system with moderate displacement (S=1).

According to the above model for the Franck-Condon factor we would generate a "stick" spectrum (Figure 13.7.3) where each vibrational transition is infinitely narrow and transition can only occur when $E = h\nu$ exactly. For example, the potential energy surfaces were given for S = 1 and the transition probability at each level is given by the sticks (black) in the figure below.

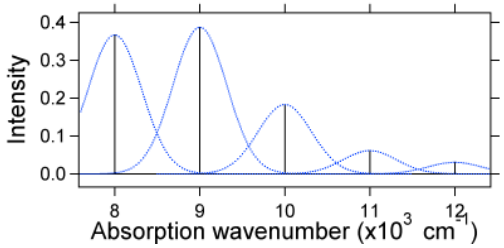


Figure 13.7.3 : Stick spectrum, dressed with Gaussians, for the moderate displacement (S=1) harmonic oscillator system from Figure 13.7.2 .

The dotted Gaussians that surround each stick give a more realistic picture of what the absorption spectrum should look like. In this first place each energy level (stick) will be given some width by the fact that the state has a finite lifetime. Such broadening is called homogeneous broadening since it affects all of the molecules in the ensemble in a similar fashion. There is also broadening due to small differences in the environment of each molecule. This type of broadening is called inhomogeneous broadening. Regardless of origin the model above was created using a Gaussian broadening

The nuclear displacement between the ground and excited state determines the shape of the absorption spectrum. Let us examine both a smaller and a large excited state displacement. If $S = ½$ and the potential energy surfaces in this case are:

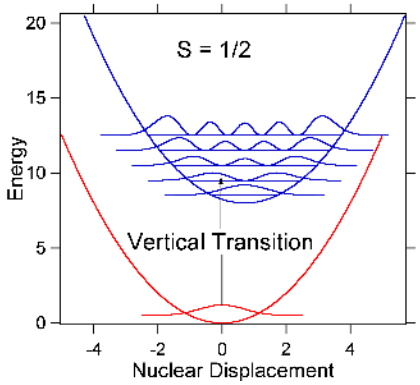


Figure 13.7.4 : Wavefunctions transitions for a harmonic oscillator model system with small displacement (S=1/2).

For this case the "stick" spectrum has the appearance in Figure 13.7.5

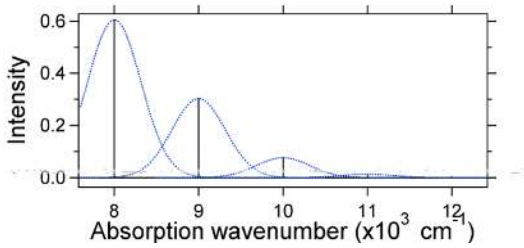


Figure 13.7.5 : Stick spectrum, dressed with Gaussians, for the small displacement (S=1/2) harmonic oscillator system from Figure 13.7.4 .

Note that the zero-zero or $S_{0,0}$ vibrational transition is much large in the case where the displacement is small.

> As a general rule of thumb the S constant gives the ratio of the intensity of the $v = 2$ transition to the $v = 1$ transition. In this case since $S = 0.5$, the $v = 2$ transition is 0.5 the intensity of $v = 1$ transition.

As an example of a larger displacement the disposition of the potential energy surfaces for S = 2 is shown below.

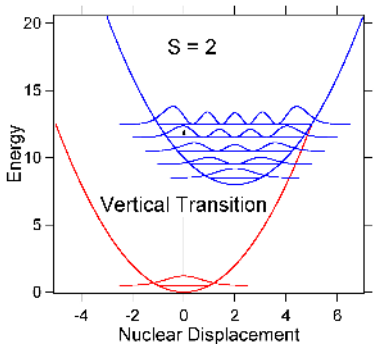


Figure 13.7.6 : Wavefunctions transitions for a harmonic oscillator model system with strong displacement (S=2).

The larger displacement results in decreased overlap of the ground state level with the v = 0 level of the excited state. The maximum intensity will be achieved in higher vibrational levels as shown in the stick spectrum.

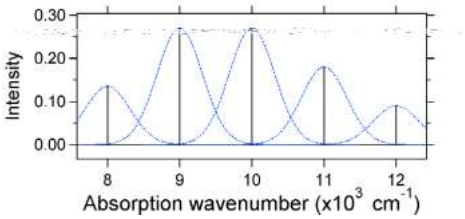


Figure 13.7.7 : Stick spectrum, dressed with Gaussians, for the large displacement (S=2) harmonic oscillator system from Figure 13.7.6 .

The absorption spectra plotted below all have the same integrated intensity, however their shapes are altered because of the differing extent of displacement of the excited state potential energy surface.

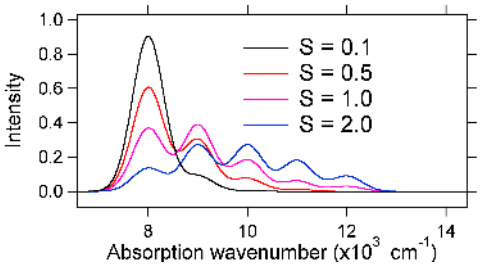


Figure 13.7.8 : Stick spectra, dressed with Gaussians, for the small to large displacements in harmonic oscillator system described above.

So the nature of the relative vibronic band intensities can tell us whether there is a displacement of the equilibrium nuclear coordinate that accompanied a transition. When will there be an increase in bond length (i.e., $Q_e > R_e$)? This occurs when an electron is promoted from a bonding molecular orbital to a non-bonding or anti-bonding molecular orbitals (i.e., when the bond order is less in the excited state than the ground state).

- Non-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ bonding molecular orbital
- Anti-bonding molecular orbital $\rightarrow$ non-bonding molecular orbital

In short, when the bond order is lower in the excited state than in the ground state, then $Q_e > R_e$; an increase in bond length will occur when this happens.

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13.8: Rotational Spectra of Polyatomic Molecules

Quick Review of Diatomic Rotation

As discussed previously, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]|\psi\rangle = E|\psi\rangle$$

or

$$\frac{L^2}{2\mu R^2}|\psi\rangle = E|\psi\rangle$$

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". The angles θ and φ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

$$E_J = \frac{\hbar^2 J(J+1)}{2\mu R^2} = BJ(J+1) \tag{13.8.1}$$

and are independent of M. B is the rotational constant. Thus each energy level is labeled by J and is $2J+1$-fold degenerate (because M ranges from $-J$ to J). The rotational energy in Equation 13.8.1 can be expressed in terms of the moment of inertia I

$$I = \sum_i m_i R_i^2 \tag{13.8.2}$$

where m_i is the mass of the i^{th} atom and R is its distance from the center of mass of the molecule. This moment of inertia replaces μR^2 in the denominator of Equation 13.8.1:

$$E_J = \frac{\hbar^2 J(J+1)}{2I} = BJ(J+1) \tag{13.8.3}$$

Rotation of Polyatomic Molecules

In contrast to diatomic molecules (Equation 13.8.2), the rotational motions of polyatomic molecules in three dimensions are characterized by multiple moments of inertia. typically reflected in an 3×3 inertia tensor. It is common in rigid body mechanics to express in these moments of inertia in *lab-based Cartesian coordinates* via a notation that explicitly identifies the x, y, and z axes such as I_{xx} and I_{xy}, for the components of the inertia tensor.

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \tag{13.8.4}$$

The components of this tensor can be assembled into a matrix given by

$$I_{xx} = \sum_{k=1}^{N} m_k\ (y_k^2 + z_k^2)$$

$$I_{yy} = \sum_{k=1}^{N} m_k (x_k^2 + z_k^2)$$

$$I_{zz} = \sum_{k=1}^{N} m_k (x_k^2 + y_k^2)$$

$$I_{yx} = I_{xy} = -\sum_{k=1}^{N} m_k x_k y_k$$

$$I_{zx} = I_{xz} = -\sum_{k=1}^{N} m_k x_k z_k$$

$$I_{zy} = I_{yz} = -\sum_{k=1}^{N} m_k y_k z_k.$$

The rotational motions of polyatomic molecules are characterized by moments of inertia that are defined in a *molecule based coordinates* with axes that are labeled a, b, and c. Measured in the body frame the inertia matrix (Equation 13.8.4) is a constant real symmetric matrix, which can be decomposed into a diagonal matrix, given by

$$I = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

These labels are assigned so that I_c is the **largest** principal moment of inertia with an order of the three moments set as

$$I_a < I_b < I_c$$

The rotational kinetic energy operator for a rigid non-linear polyatomic molecule is then expressed as

$$H_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \tag{13.8.5}$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \sin\chi \frac{\partial}{\partial\theta} \tag{13.8.6}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - (\sin\theta)^{-1} \frac{\partial}{\partial\varphi} \right] - -i\hbar \cos\chi \frac{\partial}{\partial\theta} \tag{13.8.7}$$

$$J_c = -\frac{ih\partial}{\partial\chi} \tag{13.8.8}$$

The angles θ, φ, and χ are the **Euler angles** needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2 \tag{13.8.9}$$

$$= -\frac{\partial^2}{\partial\theta^2} - \cot\theta \frac{\partial}{\partial\theta} - \left(\frac{1}{\sin\theta} \right) \left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\chi^2} - 2\cos\theta \frac{\partial^2}{\partial\varphi\partial\chi} \right) \tag{13.8.10}$$

and the component along the lab-fixed Z axis is

$$J_Z = -ih \frac{\partial}{\partial\varphi}.$$

Spherical Tops

When the three principal moment of inertia values are identical, the molecule is termed a spherical top. In this case, the total rotational energy Equation 13.8.5 can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J_2 and with one another; J_Z is the component of J along the lab-fixed Z-axis and commutes with J_a because

$$J_Z = -ih\frac{\partial}{\partial\varphi}$$

and

$$J_a = -ih\frac{\partial}{\partial\chi}$$

act on different angles. The energies associated with such eigenfunctions are

$$E(J,K,M) = \frac{\hbar^2 J(J+1)}{2I^2}$$

for all K (i.e., J a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenarate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J. The eigenfunctions of J^2, J_Z and J_a, $|J,M,K>$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J,M,K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^*_{J,M,K}(\theta,\varphi,\chi)$$

which obey

$$J^2|J,M,K\rangle = \hbar^2 J(J+1)|J,M,K\rangle$$

$$J_a|J,M,K\rangle = \hbar K|J,M,K\rangle$$

$$J_Z|J,M,K\rangle = \hbar M|J,M,K\rangle$$

Symmetric Tops

Symmetrical tops are molecules with two rotational axes that have the same inertia and one unique rotational axis with a different inertia. Symmetrical tops can be divided into two categories based on the relationship between the inertia of the unique axis and the inertia of the two axes with equivalent inertia. If the unique rotational axis has a greater inertia than the degenerate axes the molecule is called an **oblate symmetrical top** (Figure 13.8.1). If the unique rotational axis has a lower inertia than the degenerate axes the molecule is called a **prolate symmetrical top**. For simplification think of these two categories as either frisbees for oblate tops or footballs for prolate tops.

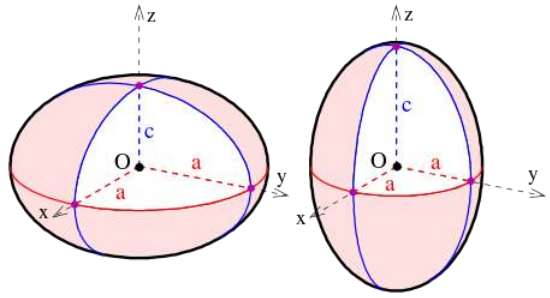


Figure 13.8.1 : The assignment of semi-axes on a spheroid. It is oblate if $c < a$ (left) and prolate if $c > a$ (right). (CC BY-SA 4.0; Ag2gaeh)

Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia.

For prolate tops, Equation 13.8.5becomes

$$H_{rot} = \frac{J^2}{2I} + J_a^2\left(\frac{1}{2I_a} - \frac{1}{2I}\right)$$

For oblate tops, Equation 13.8.5 becomes

$$H_{rot} = \frac{J^2}{2I} + J_c^2 \left(\frac{1}{2I_c} - \frac{1}{2I} \right)$$

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels.

The energies for prolate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I^2} + h^2 K^2 \left(\frac{1}{2I_a} - \frac{1}{2I} \right)$$

and the energies for oblate tops are

$$E(J,K,M) = \frac{h^2 J(J+1)}{2I2} + h^2 K^2 \left(\frac{1}{2I_c} - \frac{1}{2I} \right)$$

again for K and M (i.e., J_a or J_c and J_Z quantum numbers, respectively) ranging from $-J$ to J in unit steps. Since the energy now depends on K, these levels are only $2J+1$ degenerate due to the $2J+1$ different M values that arise for each J value. The eigenfunctions $|J,M,K>$ are the same rotation matrix functions as arise for the spherical-top case.

Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a **asymmetric top**) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. However, given the three principal moments of inertia I_a, I_b, and I_c, a matrix representation of each of the three contributions to the general rotational Hamiltonian in Equation 13.8.5 can be formed within a basis set of the $\{|J,M,K\rangle\}$ rotation matrix functions. This matrix will **not** be diagonal because the $|J,M,K\rangle$ functions are not eigenfunctions of the asymmetric top H_{rot}. However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors {C n, J,M,K } and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\psi_n(\theta,\varphi,\chi) = \sum_{J,M,K} C_{n,J,M,K} |J,M,K\rangle$$

Because the total angular momentum J^2 still commutes with H_{rot}, each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\psi_{n,J}(\theta,\varphi,\chi) = \sum_{M,K} C_{n,J,M,K} |J,M,K\rangle$$

To form the only non-zero matrix elements of H_{rot} within the $|J,M,K\rangle$ basis, one can use the following properties of the rotation-matrix functions:

$$\langle j,\rangle = \langle j,\rangle = 1/2 < j,\rangle = h2[J(J+1) - K2],$$

$$\langle j,\rangle = h^2 K^2$$

$$\langle j\rangle = -\langle j\rangle = h^2[J(J+1) - K(K\pm1)]1/2[J(J+1) - (K\pm1)(K\pm2)]1/2\langle j\rangle = 0$$

Each of the elements of J_c^2, J_a^2, and J_b^2 must, of course, be multiplied, respectively, by $1/2I_c$, $1/2I_a$, and $1/2I_b$ and summed together to form the matrix representation of H_{rot}. The diagonalization of this matrix then provides the asymmetric top energies and wavefunctions.

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13.9: Normal Modes in Polyatomic Molecules

Normal modes are used to describe the different vibrational motions in molecules. Each mode can be characterized by a different type of motion and each mode has a certain symmetry associated with it. Group theory is a useful tool in order to determine what symmetries the normal modes contain and predict if these modes are IR and/or Raman active. Consequently, IR and Raman spectroscopy is often used for vibrational spectra.

Degrees of Freedom

In general, a normal mode is an independent motion of atoms in a molecule that occurs without causing movement to any of the other modes. Normal modes, as implied by their name, are orthogonal to each other. In order to discuss the quantum-mechanical equations that govern molecular vibrations it is convenient to convert Cartesian coordinates into so called normal coordinates. Vibrations in polyatomic molecules are represented by these normal coordinates.

A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule. These degrees of freedom can be broken down into three categories.

- **Translational**: These are the simplest of the degrees of freedom. These entail the movement of the entire molecule's center of mass. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational**: These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom. However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational**: These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule. These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule. These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Table 13.9.1 : Overview of degrees of freedom

	Total Degrees of Freedom	Translational degrees of freedom	Rotational degrees of freedom	Vibrational degrees of freedom
Nonlinear Molecules	3N	3	3	3N -**6**
Linear Molecules	3N	3	2	3N - 5

Each of these degrees of freedom is able to store energy. However, In the case of rotational and vibrational degrees of freedom, energy can only be stored in discrete amounts. This is due to the quantized break down of energy levels in a molecule described by quantum mechanics. In the case of rotations the energy stored is dependent on the rotational inertia of the gas along with the corresponding quantum number describing the energy level.

Example 13.9.1 : Ethane vs. Carbon Dioxide

Ethane, C_2H_6 has eight atoms ($N = 8$) and is a nonlinear molecule so of the $3N = 24$ degrees of freedom, three are translational and three are rotational. The remaining 18 degrees of freedom are internal (vibrational). This is consistent with:

$$3N - 6 = 3(8) - 6 = 18$$

Carbon Dioxide, CO_2 has three atoms ($N = 3$ and is a linear molecule so of the $3N = 9$ degrees of freedom, three are translational and two are rotational. The remaining 4 degrees of freedom are vibrational. This is consistent with:

$$3N - 5 = 3(3) - 5 = 4$$

The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

Symmetricical Stretching	**Asymmetrical Stretching**	**Wagging**

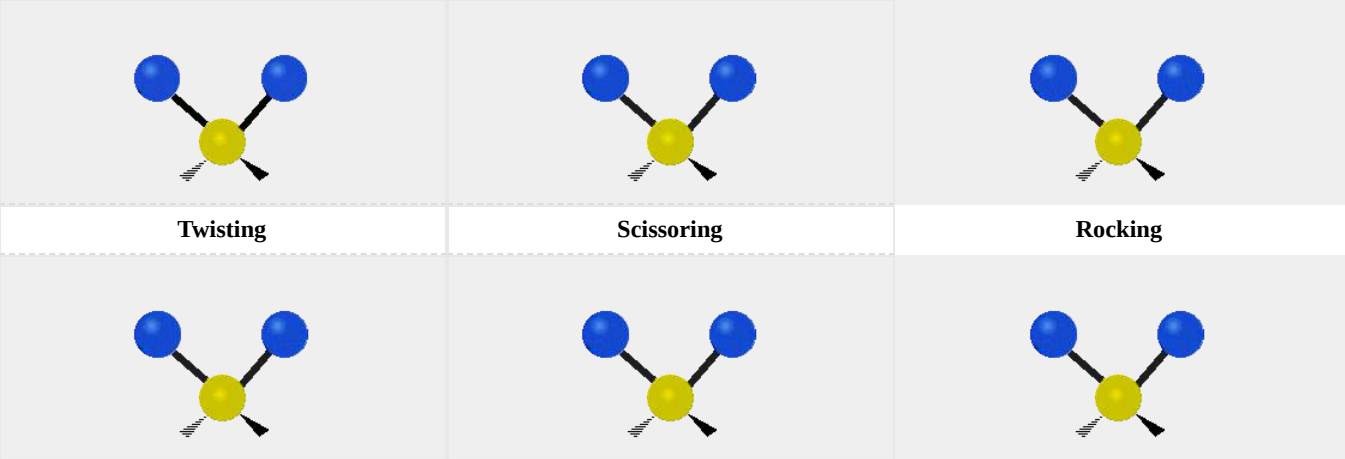


Figure 13.9.1 : *Six types of Vibrational Modes. Taken from publisher en.Wikipedia.org/wiki/Infrared_spectroscopy with permission from copyright holder.*

Normal Modes

If there is no external field present, the energy of a molecule does not depend on its orientation in space (its translational degrees of freedom) nor its center of mass (its rotational degrees of freedom). The potential energy of the molecule is therefore made up of its vibrational degrees of freedom only of $3N-6$ (or $3N-5$ for linear molecules). The difference in potential energy is given by:

$$\Delta V = V(q_1, q_2, q_3, \ldots, q_n) - V(0, 0, 0, \ldots, 0) \tag{13.9.1}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j \tag{13.9.2}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{vib}} \sum_{j=1}^{N_{vib}} f_{ij} q_i q_j \tag{13.9.3}$$

where q represents the equilibrium displacement and N_{vib} the number of vibrational degrees of freedom.

For simplicity, the *anharmonic* terms are neglected in this equation (i.e., higher order terms are ignore). A theorem of classical mechanics states that the cross terms can be eliminated from the above equation (the details of the theorem are very complex and will not be discussed in detail). By using matrix algebra a new set of coordinates $\{Q_j\}$ can be found such that

$$\Delta V = \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.4}$$

Note that there are no cross terms in this new expression. These new coordinates are called **normal coordinates** or **normal modes**. With these new normal coordinates in hand, the Hamiltonian operator for vibrations can be written as follows:

$$\hat{H}_{vib} = -\sum_{j=1}^{N_{vib}} \frac{\hbar^2}{2\mu_i} \frac{d^2}{dQ_j^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \tag{13.9.5}$$

The total wavefunction is a product of the individual wavefunctions and the energy is the sum of independent energies. This leads to:

$$\hat{H}_{vib} = \sum_{j=1}^{N_{vib}} \hat{H}_{vib,j} = \sum_{j=1}^{N_{vib}} \left(\frac{-\hbar^2}{2\mu_j} \frac{d^2}{dQ_i^2} + \frac{1}{2} \sum_{j=1}^{N_{vib}} F_j Q_j^2 \right) \tag{13.9.6}$$

and the wavefunction is then

$$\begin{aligned} \psi_{vib} &= Q_1, Q_2, Q_3 \ldots, Q_{vib} \\ &= \psi_{vib,1}(Q_1) \psi_{vib,2}(Q_2) \psi_{vib,3}(Q_3), \ldots, \psi_{vib,N_{vib}}(Q_{N_{vib}}) \end{aligned}$$

and the total vibrational energy of the molecule is

$$E_{vib} = \sum_{j=1}^{N_{vib}} h\nu_j \left(v_j + \frac{1}{2} \right) \tag{13.9.7}$$

where $v_j = 0, 1, 2, 3 \ldots$

The consequence of the result stated in the above equations is that each vibrational mode can be treated as a harmonic oscillator approximation. There are N_{vib} harmonic oscillators corresponding to the total number of vibrational modes present in the molecule.

Pictorial description of normal coordinates using CO

The normal coordinate q is used to follow the path of a normal mode of vibration. As shown in Figure 13.9.2 the displacement of the C atom, denoted by $\Delta r_o(\mathrm{C})$, and the displacement of the O atom, denoted by $\Delta r_o(\mathrm{O})$, occur at the same frequency. The displacement of atoms is measured from the equilibrium distance in ground vibrational state, r_o.

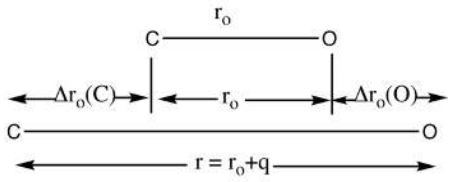


Figure 13.9.2 : The Normal coordinate for CO is equation to $\Delta r(C) + \Delta r(O)$

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13.10: Irreducible Representation of Point Groups

There exists an important fact about normal coordinates. Each of these coordinates belongs to an irreducible representation of the point the molecule under investigation. Vibrational wavefunctions associated with vibrational energy levels share this property as well. The normal coordinates and the vibration wavefunction can be categorized further according to the point group they belong to. From the character table predictions can be made for which symmetries can exist. The irreducible representation offers insight into the IR and/or Raman activity of the molecule in question.

Symmetry of normal modes

It is important to realize that every normal mode has a certain type of symmetry associated with it. Identifying the point group of the molecule is therefore an important step. With this in mind it is not surprising that every normal mode forms a basis set for an irreducible representation of the point group the molecule belongs to. For a molecule such as water, having a structure of XY_2, three normal coordinates can be determined. The two stretching modes are equivalent in symmetry and energy. The figure below shows the three normal modes for the water molecule:

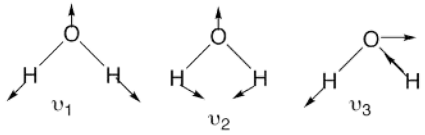


Figure 13.10.1 : Three normal modes of water

By convention, with nonlinear molecules, the symmetric stretch is denoted v_1 whereas the asymmetric stretch is denoted v_2. Bending motions are v_3. With linear molecules, the bending motion is ν_2 whereas asymmetric stretch is v_3.

The water molecule has C_{2v} symmetry and its symmetry elements are E, C_2, σ(xz) and σ(yz). To determine the symmetries of the three vibrations and how they each transform, symmetry operations will be performed. As an example, performing C_2 operations using the two normal mode v_2 and v_3 gives the following transformation:

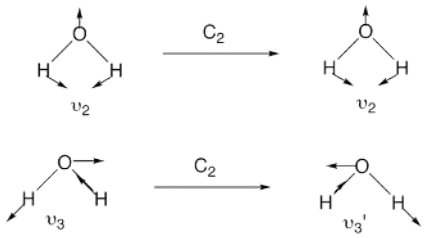


Figure 13.10.2 : Symmetry operations on the symmetric and asymmetric stretches of water

Once all the symmetry operations have been performed in a systematic manner for each modes the symmetry can be assigned to the normal mode using the character table for C_{2v}:

Table 13.10.2 : Character table for the C_{2v} point group

C_{2v}	E	C2	σ (xz)	σ (yz)	
v_1	1	1	1	1	= a_1
v_2	1	1	1	1	= a_1
v_3	1	-1	-1	1	= b_2

Water has three normal modes that can be grouped together as the reducible representation

$$\Gamma_{vib} = 2a_1 + b_2.$$

Determination of normal modes becomes quite complex as the number of atoms in the molecule increases. Nowadays, computer programs that simulate molecular vibrations can be used to perform these calculations. The example of $[PtCl_4]^{2-}$ shows the increasing complexity (Figure 13.10.2). The molecule has five atoms and therefore 15 degrees of freedom, 9 of these are vibrational degrees of freedom. The nine normal modes are exemplified below along with the irreducible representation the normal mode belongs to (D_{4h} point group).

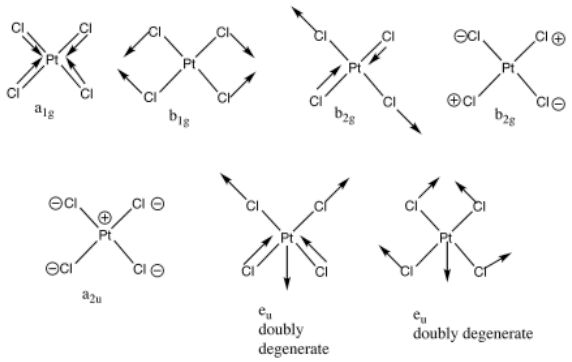


Figure 13.10.3 : A_{1g}, b_{1g} and e_u are stretching vibrations whereas b_{2g}, a_{2u}, b_{2u} and e_u are bending vibrations.

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13.11: Time-Dependent Perturbation Theory

In time-independent perturbation theory the perturbation Hamiltonian is static (i.e., possesses no time dependence). Time-independent perturbation theory was presented by Erwin Schrödinger in a 1926 paper,shortly after he produced his theories in wave mechanics. Time-dependent perturbation theory, developed by Paul Dirac, studies the effect of a time-dependent perturbation *V*(*t*) applied to a time-independent Hamiltonian H_0. Since the perturbed Hamiltonian is time-dependent, so are its energy levels and eigenstates. Thus, the goals of time-dependent perturbation theory are slightly different from time-independent perturbation theory, where one may be interested in the following quantities:

- The time-dependent expectation value of some observable *A*, for a given initial state.
- The time-dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

The first quantity is important because it gives rise to the classical result of a measurement performed on a macroscopic number of copies of the perturbed system. The second quantity looks at the time-dependent probability of occupation for each eigenstate. This is particularly useful in laser physics, where one is interested in the populations of different atomic states in a gas when a time-dependent electric field is applied. We will briefly examine the method behind Dirac's formulation of time-dependent perturbation theory. Choose an energy basis $|n\rangle$ for the unperturbed system. (We drop the (0) superscripts for the eigenstates, because it is not useful to speak of energy levels and eigenstates for the perturbed system.)

If the unperturbed system is in eigenstate $|j\rangle$ at time $t = 0$, its state at subsequent times varies only by a phase (this is the Schrödinger picture, where state vectors evolve in time and operators are constant)

$$|j(t)\rangle = e^{-iE_j t/\hbar}|j\rangle$$

Now, introduce a time-dependent perturbing Hamiltonian $H_1(t)$. The Hamiltonian of the perturbed system is

$$H = H_0 + H_1(t)$$

Let $|\psi(t)\rangle$ denote the quantum state of the perturbed system at time t and obeys the time-dependent Schrödinger equation,

$$H|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

The quantum state at each instant can be expressed as a linear combination of the complete eigenbasis of $|n\rangle$:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

where the $c_n(t)$ coefficients are to be determined complex functions of *t* which we will refer to as **amplitudes**

We have explicitly extracted the exponential phase factors $\exp(-iE_n t/\hbar)$ on the right hand side. This is only a matter of convention, and may be done without loss of generality. The reason we go to this trouble is that when the system starts in the state $|j\rangle$ and no perturbation is present, the amplitudes have the convenient property that, for all t, $c_j(t) = 1$ and $c_n(t) = 0$ if $n \neq j$.

The square of the absolute amplitude $c_n(t)$ is the probability that the system is in state n at time t, since

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-iE_n t/\hbar}|n\rangle$$

Plugging into the Schrödinger equation and using the fact that $\partial/\partial t$ acts by a chain rule, one obtains

$$\sum_n \left(i\hbar\frac{\partial c_n}{\partial t} - c_n(t)V(t)\right)e^{-iE_n t/\hbar}|n\rangle = 0\,.$$

By resolving the identity in front of *V*, this can be reduced to a set of partial differential equations for the amplitudes,

$$\frac{\partial c_n}{\partial t} = \frac{-i}{\hbar}\sum_k \langle n|H_1(t)|k\rangle\, c_k(t)\, e^{-i(E_k - E_n)t/\hbar}\,.$$

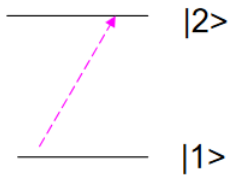
The matrix elements of H_1 play a similar role as in time-independent perturbation theory, being proportional to the rate at which amplitudes are shifted between states. Note, however, that the direction of the shift is modified by the exponential phase factor. Over times much longer than the energy difference $E_k - E_n$, the phase winds around 0 several times. If the time-dependence of

H_1 is sufficiently slow, this may cause the state amplitudes to oscillate (e.g., such oscillations are useful for managing radiative transitions in a laser).

Two-Level System

Consider the two level system (i.e. $n = 1, 2$)

$$|\psi\rangle = \sum_{n=1,2} c_n(t)|n\rangle_o$$



Solution of time-dependent perturbation for two level system:

$$i\hbar\frac{\partial c_1(t)}{\partial t} = c_1(t)H_{11}(t) + c_2 e^{-i\omega_o t}H_{12}(t)$$

$$i\hbar\frac{\partial c_2(t)}{\partial t} = c_2(t)H_{22}(t) + c_1 e^{+i\omega_o t}H_{21}(t)$$

where the matrix elements of the permutation (in terms of the eigenstates of $H(0)$) are

$$\langle m|H_1(t)|n\rangle = H_{mn}(t)$$

Assume initial state is $n = 1$, and $H_{11} = H_{22} = 0$

$$|\psi(t = 0)\rangle = |1\rangle$$

Probability of particle at $n = 2$ at time t after the perturbation is turned on (i.e., incident light):

$$c_2(t) = \frac{-i}{\hbar}\int_o^t e^{i\omega_o t}dt' H_{21}(t') \tag{13.11.1}$$

where

$$H_1(t) = \cos(\omega t)V(r)$$

$V(r)$ is an amplitude of polarization vector, which we can ignore for now.

If we assume incident frequency of incident light ω is comparable to the natural frequency of oscillation from ω_o

$$\omega \approx \omega_o$$

then Equation 13.11.1 can be simplified to

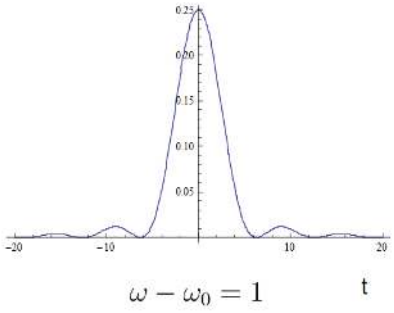
$$c_2(t) = -\frac{2i}{\hbar}\frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t}e^{i(\omega_0 - \omega)t/2}\ H_{21}$$

Transition Probability

Assume initial state is $n = 1$, and probability of transition from $n = 1$ state to $n = 2$ state is:

$$P_{12}(t) = |c_2(t)|^2 = \frac{4}{\hbar^2}|\frac{\sin(\omega - \omega_o)t/2}{(\omega - \omega_o)t}|^2|H_{21}|^2$$

What does this mean? Strangely, it means that the probability of making a transition is actually oscillating sinusoidally (squared)! If you want to cause a transition, should turn off perturbation after time $\pi/|\omega - \omega_o|$ or some odd multiple, when the system is in upper state with maximum probability.



$P_{12}(t)$ is peaked at $\omega - \omega_o = 0$. The height of $|H_{12}t/2\hbar|^2$ and width of $4\pi/t$ gets higher and narrower as time goes on. Recall this is perturbative treatment, however, and $P_{12}(t)$ cannot get bigger than 1, so perturbation theory breaks down eventually.

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13.12: The Selection Rule for the Rigid Rotator

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0 \cos(\omega t)$ that interacts with a transition dipole. The dipole operator is $\mu = e \cdot r$ where r is a vector pointing in a direction of space.

A dipole moment of a given state is

$$\mu_z = \int \Psi_1{}^* \mu_z \Psi_1 \, d\tau$$

A transition dipole moment is a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule

$$(\mu_z)_{12} = \int \Psi_1{}^* \mu_z \Psi_2 \, d\tau$$

In an experiment we present an electric field along the z axis (in the laboratory frame) and we may consider specifically the interaction between the transition dipole along the x, y, or z axis of the molecule with this radiation. If μ_z is zero then a transition is forbidden. The selection rule is a statement of when μ_z is non-zero.

> *The selection rule is a statement of when μ_z is non-zero.*

Rotational transitions

We can use the definition of the transition moment and the spherical harmonics to derive selection rules for a rigid rotator. Once again we assume that radiation is along the z axis.

$$(\mu_z)_{J,M,J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta,\phi) \mu_z Y_J^M(\theta,\phi) \sin\theta \, d\phi, d\theta$$

Notice that m must be non-zero in order for the transition moment to be non-zero. This proves that a molecule must have a permanent dipole moment in order to have a rotational spectrum. The spherical harmonics can be written as

$$Y_J^M(\theta,\phi) = N_{JM} P_J^{|M|}(\cos\theta) e^{iM\phi}$$

where N_{JM} is a normalization constant. Using the standard substitution of $x = \cos q$ we can express the rotational transition moment as

$$(\mu_z)_{J,M,J',M'} = \mu \, N_{JM} N_{J'M'} \int_0^{2\pi} e^{I(M-M')\phi} \, d\phi \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

The integral over f is zero unless M = M' so $\Delta M = 0$ is part of the rigid rotator selection rule. Integration over ϕ for $M = M'$ gives 2π so we have

$$(\mu_z)_{J,M,J',M'} = 2\pi\mu \, N_{JM} N_{J'M'} \int_{-1}^{1} P_{J'}^{|M'|}(x) P_J^{|M|}(x) dx$$

We can evaluate this integral using the identity

$$(2J+1)x \, P_J^{|M|}(x) = (J-|M|+1) P_{J+1}^{|M|}(x) + (J-|M|) P_{J-1}^{|M|}(x)$$

Substituting into the integral one obtains an integral which will vanish unless $J' = J+1$ or $J' = J-1$.

$$\int_{-1}^{1} P_{J'}^{|M'|}(x) \left(\frac{(J-|M|+1)}{(2J+1)} P_{J+1}^{|M|}(x) + \frac{(J-|M|)}{(2J+1)} P_{J-1}^{|M|}(x) \right) dx$$

This leads to the selection rule $\Delta J = \pm 1$ for absorptive rotational transitions. Keep in mind the physical interpretation of the quantum numbers J and M as the total angular momentum and z-component of angular momentum, respectively. As stated above in the section on electronic transitions, these selection rules also apply to the orbital angular momentum ($\Delta l = \pm 1$, $\Delta m = 0$).

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13.13: The Harmonic Oscillator Selection Rule

Selection rules are a very important concept in spectroscopy and physical chemistry, as they directly complement the concept that systems on the atomic level are quantized. Quantization tells us how electrons, neutrons, and protons are set up, and selection rules tell us how, energetically speaking, they may move about. For example, the principal quantum number, n, determines the energy state of particles in the Particle in a Box model. With respect to real systems, the quantum number n describes electronic transitions, such as the excitation of an electron. There are other transitions, such as the rotational transition, which applies to the rigid rotator model and occurs where there are spherical harmonics. Vibrational transitions occur where there is a system that can be visualized as two masses connected by a spring, such as a diatomic molecule.

Selection rules can be very useful in spectroscopy for obtaining information about an unknown substance; any given substance has properties and behaviors that operate within the selection rules and determine the wavelengths of electromagnetic radiation (light) that cause transitions. By tracking these properties, chemists can use techniques like IR spectroscopy to determine the chemical structure of a molecule. For example, a selection rule might govern how a quantum number changes during a transition. That quantum number appears in equations that determine the energy transition based on the mass and other structural properties of a molecule. Thus, if one knows the selection rules and the energy transition, he or she can determine other properties about the molecule, such as its mass or its bond strength.

✔ Example: Evaluating vibrational transitions using a transition moment integral.

Vibrational systems are described by the harmonic oscillator wavefunctions, which look like

$$\Psi_v(x) = N_v H_v(\alpha^{1/2}x)e^{-\alpha x^2/2}$$

A transition dipole moment can be written to describe a transition along the z-axis.

$$\mu_z = \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}\mu_z(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

μ is the dipole moment, so we pull it out of the integral.

$$\mu_z = \mu_z \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

Using the idea that the transition moment μ_z changes on x, we express it as a derivative.

$$\mu_z = \frac{d\mu}{dx} \int_{-\infty}^{\infty} N_v N_{v+1} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2} H_{v+1}(\alpha^{1/2}x)e^{-\alpha x^2/2}dx$$

To evaluate the integral, we take advantage of a special Hermite relationship: $\sqrt{\alpha}x H_v(\sqrt{\alpha}x) = vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)$

$$\mu_z = \frac{N_v N_{v+1}}{\sqrt{\alpha}}\left(\frac{d\mu}{dx}\right) \int_{-\infty}^{\infty} H_{v+1}(\sqrt{\alpha}x)e^{(}-\alpha x^2/2)[vH_{v-1}(\sqrt{\alpha}x) + \frac{1}{2}H_{v+1}(\sqrt{\alpha}x)]dx$$

By inspection, it is clear that the integral only allows transitions of $\Delta v = \pm 1$, because for any other value, the integral will be zero.

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13.14: Group Theory Determines Infrared Activity

Determining if a Normal Modes is IR or Raman Active

A transition from $v \rightarrow v'$ is IR active if the **transition moment integral** contains the totally symmetric irreducible representation of the point group the molecule belongs to. The transition moment integral is derived from the one-dimensional harmonic oscillator. Using the definition of electric dipole moment μ, the integral is:

$$M(v \rightarrow v') = \langle \text{final wavefunction} | \vec{\mu} | \text{initial wavefunction} \rangle$$

or in terms of vibrational wavefunctions for a specific normal mode $|\phi(v)\rangle$

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \vec{\mu} | \phi(v = 0) \rangle \tag{13.14.1}$$

assuming the transition from the $v = 0$ wavefunction to the $v' \neq 0$ wavefunction.

Now, consider the case that $\vec{\mu}$, is a constant and therefore independent of the vibration (i.e., the electric dipole moment does not change during the vibration). This it could be taken outside the integral in Equation 13.14.1becomes

$$M(v \rightarrow v') = \vec{\mu} \langle \phi(v' \neq 0) | \phi(v = 0) \rangle \tag{13.14.2}$$

Since $|\phi(v = 0)\rangle$ and $|\phi(v = \neq 0)\rangle$ are mutually orthogonal to each other, the integral in Equation 13.14.1will equal zero and the transition will **not** be allowed (i.e., it is forbidden). For the M to be nonzero, $\vec{\mu}$ must change during a vibration. This selection rule explains why homonuclear diatomic molecules do not produce an IR spectrum. There is no change in dipole moment resulting in a transition moment integral of zero and a transition that is forbidden.

For a transition to be Raman active, the same rules apply. The transition moment integral must contain the totally symmetric irreducible representation of the point group. The integral contains the polarizability tensor α (usually represented by a square matrix):

$$M(v \rightarrow v') = \langle \phi(v' \neq 0) | \alpha | \phi(v = 0) \rangle \tag{13.14.3}$$

Following a similar argument as above, α must be nonzero for the transition to be allowed and exhibits Raman scattering.

Character Table

For a molecule to be IR active the dipole moment has to change during the vibration. For a molecule to be Raman active the polarizability of the molecule has to change during the vibration. The reducible representation $\mathbf{\Gamma_{vib}}$ can also be found by determining the reducible representation of the 3N degrees of freedom of H_2O, $\mathbf{\Gamma}_{tot}$. By applying Group Theory it is straightforward to find $\mathbf{\Gamma_{x,y,z}}$ as well as UMA (number of unmoved atoms). Again, using water as an example with C_{2v} symmetry where 3N = 9, $\mathbf{\Gamma_{tot}}$ can be determined:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{T_{x,y,z}}$	3	-1	1	1	
UMA	3	1	1	3	
$\mathbf{\Gamma_{tot}}$	**9**	**-1**	**1**	**3**	**=3a_1 + a_2 + 2b_1 + 3b_2**
Note that $\mathbf{\Gamma}_{tot}$ contains nine degrees of freedom consistent with 3N = 9.					

$\mathbf{\Gamma}_{tot}$ contains $\mathbf{\Gamma}_{translational}$, $\mathbf{\Gamma}_{rotational}$ as well as $\mathbf{\Gamma}_{vibrational}$. $\mathbf{\Gamma}_{trans}$ can be obtained by finding the irreducible representations corresponding to x,y and z in the right side of the character table, $\mathbf{\Gamma}_{rot}$ by finding the ones corresponding to R_x, R_y and R_z. $\mathbf{\Gamma}_{vib}$ can be obtained by $\mathbf{\Gamma}_{tot}$ - $\mathbf{\Gamma}_{trans}$ - $\mathbf{\Gamma}_{rot}$.

$$\Gamma_{vib}(H_2O) = (3a_1 + a_2 + 2b_1 + 3b_2) - (a_1 + b_1 + b_2) - (a_2 + b_1 + b_2) = 2a_1 + b_2$$

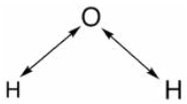
In order to determine which modes are IR active, a simple check of the irreducible representation that corresponds to x,y and z and a cross check with the reducible representation $\mathbf{\Gamma}_{vib}$ is necessary. If they contain the same irreducible representation, the mode is IR active.

For H_2O, z transforms as a_1, x as b_1 and y as b_2. The modes a1 and b2 are IR active since Γvib contains $2a_1 + b_2$.

In order to determine which modes are Raman active, the irreducible representation that corresponds to z^2, x^2-y^2, xy, xz and yz is used and again cross checked with Γvib. For H_2O, z^2 and x^2-y^2 transform as a_1, xy as a_2, xz as b_1 and yz as b_2.The modes a_1 and b_2 are also Raman active since Γ_{vib} contains both these modes.

The IR spectrum of H2O does indeed have three bands as predicted by Group Theory. The two symmetric stretches v1 and v2 occur at 3756 and 3657 cm-1 whereas the bending v3 motion occurs at 1595 cm-1.

In order to determine which normal modes are stretching vibrations and which one are bending vibrations, a stretching analysis can be performed. Then the stretching vibrations can be deducted from the total vibrations in order to obtain the bending vibrations. A double-headed arrow is drawn between the atom as depicted below:



Then a determination of how the arrows transform under each symmetry operation in C2v symmetry will yield the following results:

C_{2v}	E	C_2	σ (xz)	σ (yz)	
$\mathbf{\Gamma_{stretch}}$	2	0	0	2	**= $a_1 + b_2$**

$$\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch} = 2a_1 + b_2 - a_1 - b_2 = a_1$$

H_2O has two stretching vibrations as well as one bending vibration. This concept can be expanded to complex molecules such as $PtCl4^-$. Four double headed arrows can be drawn between the atoms of the molecule and determine how these transform in D_{4h} symmetry. Once the irreducible representation for $\mathbf{\Gamma}_{stretch}$ has been worked out, $\mathbf{\Gamma}_{bend}$ can be determined by $\mathbf{\Gamma}_{bend} = \mathbf{\Gamma}_{vib} - \mathbf{\Gamma}_{stretch}$.

Most molecules are in their zero point energy at room temperature. Therefore, most transitions do originate from the v=0 state. Some molecules do have a significant population of the v=1 state at room temperature and transitions from this thermally excited state are called **hot** bands.

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13.E: Molecular Spectroscopy (Exercises)

These are homework exercises to accompany Chapter 13 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q13.1

1. Calculate the energy difference for radiation wavenumber of, $\nu = 1.00 cm^{-1}$ including the type of molecular process that absorbs of this radiation corresponding to.
2. Given the wavelength of 3.4 x 10^{-4}, which molecular process does it fall into?
3. What are other advantages of knowing the spectroscopy of molecules?
4. Do you think the spectroscopy and molecular processes of the molecules have relationship to temperature? Explain.
5. What is other form that you can express in above equation?

Q13.20

The vibrational term of a diatomic molecule is

$$G(v) = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \chi_e \nu_e \tag{13.E.1}$$

Show that the spacing between adjacent levels is given by

$$\Delta G = G(v+1) - G(v) = \nu_e - 2\chi_e \nu_e (v+1)$$

Show that the maximum vibrational quantum number, v_{max} is given by

$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.2}$$

Use this result to show that the dissociation energy of the diatomic molecule can be written as

$$D_e = \frac{\nu_e - \nu_e \chi_e^2}{4\chi_e} \approx \frac{\nu_e}{4\chi_e} \tag{13.E.3}$$

Explain how the constants ν_e and χ_e can be evaluated from a plot of ΔG versus $v+1$, called a Birge-Sponer plot. After finding these constants, determine the dissociation energy of the molecule. Use the following experimental data of H_2 to determine the dissociation energy of the molecule.

v	G(v) / cm^{-1}
0	4161.12
1	8087.11
2	11782.35
3	15250.36
4	18497.92
5	21505.65
6	24287.83
7	26830.97
8	29123.93
9	31150.19
10	32886.65
11	34301.83
12	35351.01

v	G(v) / cm^{-1}
13	35972.97

Explain why your plot is not linear for high values of v. How does this dissocation energy differ with the experimental value of $38269.48 cm^{-1}$.

S13.20

$$\Delta G = G(v+1) - G(v) = \left(v+\frac{3}{2}\right)\nu_e - \left(v+\frac{3}{2}\right)^2 \chi_e\nu_e - \left(v+\frac{1}{2}\right)\nu_e + \left(v+\frac{1}{2}\right)^2 \chi_e\nu_e = \nu_e - \chi_e\nu_e(2v+2)$$
$$= \nu_e - 2\chi_e\nu_e(v+1)$$

In the limit that $\Delta G \to 0, v \to v_{max}$, solving for v_{max} gives

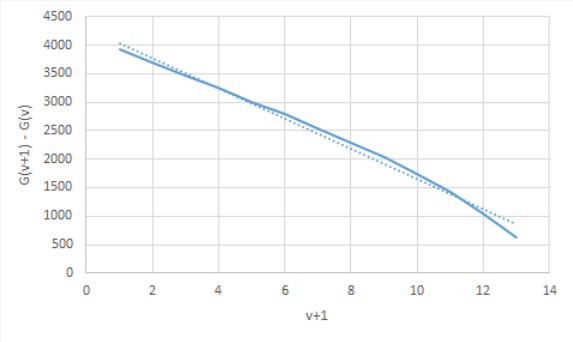
$$0 = \nu_e - 2\chi_e\nu_e(v_{max}+1) \tag{13.E.4}$$
$$2\chi_e(v_{max}+1) = 1 \tag{13.E.5}$$
$$v_{max} = \frac{1}{2\chi_e} - 1 \tag{13.E.6}$$

The molecule dissociates in the limit $\Delta G \to 0$, so the dissociation energy is given by

$$D_e = G(v_{max}) = (\frac{1}{2\chi_e} - \frac{1}{2})\nu_e - (\frac{1}{2\chi_e} - \frac{1}{2})^2\chi_e\nu_e = \frac{\nu_e}{2\chi_e}(1-\chi_e) - \frac{\nu_e}{4\chi_e}(1-\chi_e)^2 \tag{13.E.7}$$
$$= \frac{\nu_e}{4\chi_e}(2 - 2\chi_e - 1 + 2\chi_e - \chi_e^2) = \frac{\nu_e}{4\chi_e}(1-\chi_e^2) \approx \frac{\nu_e}{4\chi_e}$$

The final step can be made if we assume χ_e to be very small.

Looking at the equation for ΔG, we conclude that a plot of ΔG versus $v+1$ will have an intercept of ν_e and a slope of $-2\chi_e\nu_e$. The experimental data points for H_2 can be plotted as such:



If we use a best linear fit, we determine that the intercept is $\nu_e = 4164.4 cm^{-1}$ and the slope is $-2\chi_e\nu_e = -232.01 cm^{-1}$. Thus, $\chi_e = 0.0279$. Then, the dissociation energy is

$$D_e = \frac{\nu_e}{4\chi_e} = 37400 cm^{-1} \tag{13.E.8}$$

The plot is not linear for large values of v because the potential curve is not well described by the anharmonic potential energy function.

Q13.21

An analysis of the vibrational spectrum of the ground-state homonuclear diatomic molecule Na_2 gives $\tilde{\nu}_e = 159.125\ cm^{-1}$ and $\tilde{\nu}_e\tilde{x}_e = 0.7255\ cm^{-1}$. Suggest an experimental method that can be used to determine there spectroscopic parameters. Use $\nu_{max} = \frac{1}{2\tilde{x}_e} - 1$ to determine the number of bound vibrational levels for ground state of Na_2.

S13.21

First solve for $\tilde{x}$:

$$\tilde{x} = \frac{0.7255\ cm^{-1}}{159.125\ cm^{-1}} = 4.5593 \times 10^{-3}\ cm^{-1} \tag{13.E.9}$$

Then plug it in to the equation:

$$\nu_{max} = \frac{1}{2 \times 4.5593 \times 10^{-3}\ cm^{-1}} - 1 = 109.67\ cm^{-1} \tag{13.E.10}$$

There are 109 bound vibrational levels for the ground state of Ne_2.

Q13.22

A Morse potential is a decent representation of internuclear potential and is modeled by

$$U(q) = D_e(1 - e^{-/betaq})^2 \tag{13.E.11}$$

where $q = R - R_e$. Prove the force constant for the Morse Potential is evaluated

$$k = 2D_e\beta^2 \tag{13.E.12}$$

If $D_e = 6.23 \times 10^{-19} J \cdot Molecule^{-1}$ and $\beta = 1.37 \times 10^{10} m^{-1}$ for a given compound, calculate the force constant for that compound.

S13.22

Using a Maclaurin series expansion of the Morse potential, the formula can be rewritten

$$U(q) = D_e(1 - e^{-\beta q})^2 = D_e(1 - (1 - \beta q + \frac{\beta^2 q^2}{2} O(q)^3))^2 = D_e(\beta^2 q^2 + O(q)^3) \tag{13.E.13}$$

We know that

$$U(q) = \frac{kq^2}{2} \tag{13.E.14}$$

assuming that $O(q)^3$ approaches zero, we get

$$\frac{kq^2}{2} = D_e(\beta^2 q^2 + O(q)^3) \implies k = 2D_e\beta^2 \tag{13.E.15}$$

Plugging in our given values, we get

$$l = 2(6.23 \times 10^{-19} J \cdot Molecule^{-1})(1.37 \times 10^{10})^2 = 234 N \cdot m^{-1} \tag{13.E.16}$$

Q13.23

Given that $D_e = 7.33 \times 10^{-19} J \cdot molecule^{-1}, \tilde{v}_e = 1580.0 cm^{-1}, and R_e = 121 pm$, find k and β for $^{16}O_2$.

S13.23

Assuming a a harmonic oscillator model, we can use the equation:

$$\tilde{v}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{13.E.17}$$

We can find k from the parameters given in the problem. Solving for k gives

$$k = (2\pi c \tilde{v}_e)^2 \mu \tag{13.E.18}$$

$$= [2\pi(3 \times 10^{10} cm \cdot s^{-1})(1580.0 cm^{-1})]^2 (7.9975 amu)(1.661 x 10^{-27} kg \cdot amu^{-1}) \tag{13.E.19}$$

$$= 1176.3 N \cdot m^{-1} \tag{13.E.20}$$

Using the equation:

$$\beta = \left(\frac{k}{2D_e}\right)^{1/2} \tag{13.E.21}$$

We can solve for β using the information above

$$\beta = \left[\frac{1176.3N \cdot m^{-1}}{2(7.33 \times 10^{-19} J)}\right]^{1/2} \tag{13.E.22}$$

$$= 2.84 \times 10^{10} m^{-1} \tag{13.E.23}$$

Q13.24

The fundamental line in the IR spectrum of $^{12}C^{16}O$ cm^{-1}, and the first overtone occurs at 4260.0 cm^{-1}. Find $\tilde{v}_e$ and $\tilde{x}_e\tilde{v}_e$ for $^{12}C^{16}O$.

S13.24

The equations for the fundamental frequency and the overtone are

$$\tilde{v} = \tilde{v}_e - 2\tilde{x}_e\tilde{v}_e \tag{13.E.24}$$

and

$$\tilde{v} = 2\tilde{v}_e - 6\tilde{x}_e\tilde{v}_e, \tag{13.E.25}$$

respectively.

We can set the fundamental frequency equal to $2143.0 cm^{-1}$ and the first overtone equal to $4260.0 cm^{-1}$ which is given from the problem statement. Then, we want to solve for $\tilde{x}_e\tilde{v}_e$.

Multiply the fundamental frequency by 3 and subtract the overtone.

$$\tilde{v}_e = [3(2143.0) - 4260.0] cm^{-1} = 2169.0 cm^{-1} \tag{13.E.26}$$

Then multiply the fundamental frequency by 2 and subtract from the overtone.

$$\tilde{x}_e\tilde{v}_e = 13.0 cm^{-1} \tag{13.E.27}$$

Q13.24

Which of the following molecules exhibit a microwave rotational absorption spectrum: BF_2,SO_2,C_2F_2,NO_3^-

S13.24

SO_2

notes: microwave rotational absorption correlates to the rotation of polyatomic molecules. Would BF_2 and NO_3^- also fall in this range?

Q13-25 Slightly Incorrect

Calculate the fundamental and the first two overtones of

$$H^{35}Cl \tag{13.E.28}$$

given

$$\tilde{v_e} = 2990.946 cm^{-1} \tag{13.E.29}$$

$$\tilde{x_e}\tilde{v_e} = 52.819 cm^{-1} \tag{13.E.30}$$

S13-25

Use equation,

$$\tilde{v_{obs}} = \tilde{v_e}\nu - \tilde{x_e}\tilde{v_e}\nu(\nu+1) \tag{13.E.31}$$

with v =1,2...

The fundamental frequency is given by v=1 and the first two overtones are given by v=2 and v=3.

Fundamental:

$$\tilde{v_{obs}} = \tilde{v_e} - 2\tilde{x_e}\tilde{v_e} = 2990.946cm^{-1} - 2(52.819cm^{-1}) = 2885.308cm^{-1} \tag{13.E.32}$$

First overtone:

$$\tilde{v_{obs}} = 2\tilde{v_e} - 6\tilde{x_e}\tilde{v_e} = 2990.946cm^{-1} - 6(52.819cm^{-1}) = 5664.978cm^{-1} \tag{13.E.33}$$

Second overtone:

$$\tilde{v_{obs}} = 3\tilde{v_e} - 12\tilde{x_e}\tilde{v_e} = 3(2990.946cm^{-1}) - 12(52.819cm^{-1}) = 8339.01cm^{-1} \tag{13.E.34}$$

Q13.26

Plot the

$$\frac{\nu_{obs}}{\nu} \tag{13.E.35}$$

versus

$$(\nu + 1) \tag{13.E.36}$$

for the anharmonic oscillator approximation and use it to determine the values of

$$\nu_e \tag{13.E.37}$$

and

$$x_e\nu_e \tag{13.E.38}$$

for

$$H^35Cl \tag{13.E.39}$$

. Use the information in Table13.4.

S13.26

$$\nu_{obs} = \nu_{obs}\nu - x_e\nu_e\nu(\nu + 1) \tag{13.E.40}$$

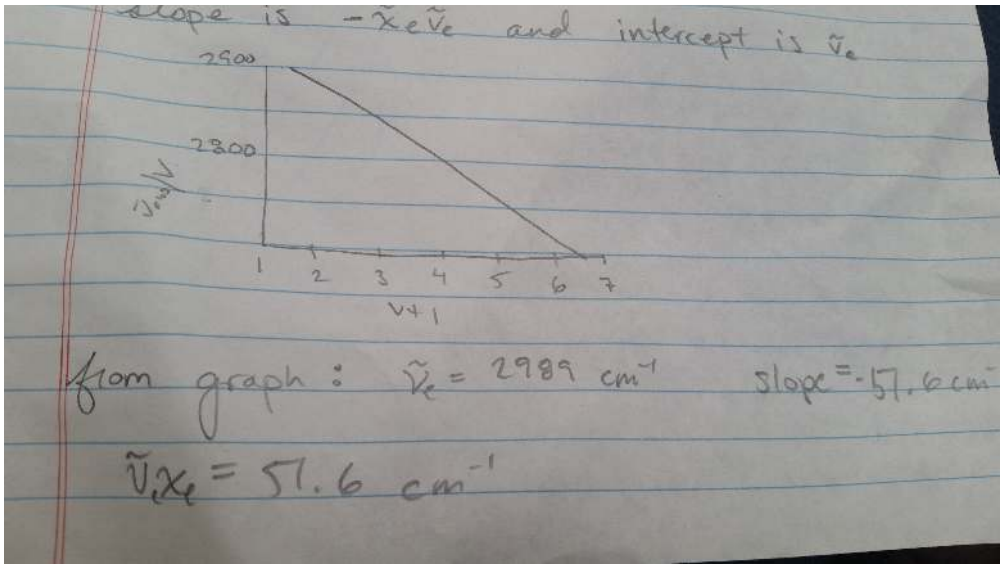
$$\frac{\nu_{obs}}{\nu} = \nu_e - x_e\nu_e(\nu + 1) \tag{13.E.41}$$

The slope is

$$-x_e\nu_e \tag{13.E.42}$$

and the intercept is

$$\nu_e \tag{13.E.43}$$



The problem is nice and straight forward. It would be great for an explanation of why the slope is negative for an insight of the graph

Q13.31

Phosphorus nitride (PN) is a heteronuclear diatomic molecule that is a similar to N_2 with a triple bond, although is substantially weaker because P is a larger atomic radius than N. Using the following data, calculate $\tilde{\nu_e}'$ and $\tilde{\chi_e}'\ \tilde{\nu_e}'$ for PN.

IR Transition	$\tilde{\nu_{abs}}$ [cm^{-1}]
$0 \rightarrow 0$	39,699.10
$0 \rightarrow 1$	40,786.80
$0 \rightarrow 2$	41,858.90

S13.31

We will use the following equation:

$$\tilde{\nu_{abs}} = \tilde{\nu_{0,0}}' + \tilde{\nu_e}'\tilde{\nu}' - \tilde{\chi_e}'\tilde{\nu_e}'\tilde{\nu}'(\nu' + 1) \tag{13.E.44}$$

Plugging in the appropriate values of ν', we get:

According to your table $\tilde{\nu_{0,0}}'$ should be 39,699.10 not 29,699.10.

- $\nu' = 0$:

$$\tilde{\nu_{0,0}}' = 29,699.10\ cm^{-1} \tag{1}$$

- $\nu' = 1$:

$$\tilde{\nu_{0,0}}' + \tilde{\nu_e}' - 2\tilde{\chi_e}'\tilde{\nu_e}' = 40,786.80\ cm^{-1} \tag{2}$$

- $\nu' = 2$:

$$\tilde{\nu_{0,0}}' + 2\tilde{\nu_e}' - 6\tilde{\chi_e}'\tilde{\nu_e}' = 41,858.90\ cm^{-1} \tag{3}$$

Solving as a system of equations, we subtract:

(2) - (1) = (4), (3) - (1) = (5), and finally (5) - 2x(4) = (6)

Equation (6) can be solved for $\tilde{\chi_e}'\tilde{\nu_e}'$, and then plugged back in to equation (4) or equation (5) to solve for $\tilde{\nu_e}'$. The answer is:

$$\tilde{\chi_e}'\tilde{\nu_e}' = 1103.3\ cm^{-1} \tag{13.E.45}$$

and

$$\tilde{\nu_e}' = 7.80\ cm^{-1} \tag{13.E.46}$$

from my calculations $\tilde{\nu_e}' = 1103.3$ and $\tilde{\chi_e}'\tilde{\nu_e}' = 7.80$ it looks like you had them switched

Q13.32

The frequencies of the first few vibronic transitions to an excited state of NaCl* are as follows:

Vibronic Transitions	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$
$\tilde{v}_{obs}/cm^{-}1$	12376	89706	15219

*not accurate values for NaCl

Use these data to calculate the values of $\tilde{v}_e$ and $\tilde{v}_e\tilde{x}_e$ for the excited state of NaCl

S13.32

$A = \tilde{v}'_e, B = \tilde{v}'_e\tilde{x}'_e$

$12376 = \tilde{v}_0, 0$

$89706 = \tilde{v}_0, 0 + \tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{v}_0, 0 = 77330 = +\tilde{v}'_e - 2\tilde{v}'_e\tilde{x}'_e$ (1)

$15219 = \tilde{v}_0, 0 + 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e - 12376 = \tilde{v}_0, 0 = 2843 = 2\tilde{v}'_e - 6\tilde{v}'_e\tilde{x}'_e$ (2)

77330 + 2B = A (1a)

2843 = 2A - 6B (2a)

77330+2B = A

2843 - 154660 = -2B

B = 75908.5 cm^{-1} = $\tilde{v}'_e$

A = 229147 cm^{-1} = $\tilde{v}'_e\tilde{x}'_e$

Q13.33

Determine the number of translational, rotational, and vibrational degrees of freedom in

a. Xe
b. HCl
c. CS_2
d. hemoglobin containing 9272 molecules

The total number of degrees of freedom is 3N, where N is the number of atoms in the molecule. All molecules have three translational degrees of freedom. A nonlinear molecule has three rotational degrees of freedom and a linear molecule has two rotational degrees of freedom. A linear molecule has $3N - 5$ vibrational degrees of freedom and a nonlinear molecule has 3N — 6 vibrational degrees of freedom.

S13.33

The number of translational degrees of freedom is 3, the number of rotational degrees of freedom is 2 for linear molecules and 3 for non-linear molecules. Therefore, the remaining degrees of freedom, which is equal to 3N-5 for linear molecules or 3N-6 for non-linear molecules, is equal to the number of vibrational degrees of freedom.

	Translation	Rotation	Vibration	Total
Xe	3	0	0	3
HCl	3	2	1	6
CS_2	3	2	4	9

	Translation	Rotation	Vibration	Total
hemoglobin	3	3	27810	27816

Q13.36

Classify each of the following molecules as either a prolate or an oblate symmetric top: XeF_4, $ClCH_3$, NH_3, and C_6H_6.

S13.36

- XeF_4 :oblate
- $ClCH_3$:prolate
- NH_3:prolate
- C_6H_6:oblate

Q13.37

Solve for the components of the moment of inertia of a trigonal planar molecule if all the masses are m, the bond lengths are unit length, and all bond angles are 120°.

S13.37

$$I_{xx} = \sum m_j y_j^2 = m(1)^2 + 2m(sin^2 30^\circ) = \frac{3}{2}m \tag{13.E.47}$$

$$I_{yy} = \sum m_j x_j^2 = m(0)^2 + 2m(cos^2 30^\circ) = \frac{3}{2}m \tag{13.E.48}$$

$$I_{zz} = \sum m_j x_j^2 + \sum m_j y_j^2 = 3m \tag{13.E.49}$$

Q13.38

This problem illustrates how the principal moments of inertia can be obtained as an eigenvalue problem. Consider a molecule where all the masses are unit masses and the long and short bond lengths are 2 and 1, respectively.

Show that

$$I_{xx} = 2\cos^2\theta + 8\sin^2\theta \tag{13.E.50}$$

$$I_{yy} = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.51}$$

$$I_{xy} = -6\cos\theta\sin\theta \tag{13.E.52}$$

Solve the secular determinant equation for λ

$$\begin{vmatrix} I_{xx} - \lambda & I_{xy} \\ I_{xy} & I_{yy} - \lambda \end{vmatrix} = 0 \tag{13.E.53}$$

and compare the result with the values of I_{xx} and I_{yy} that you would obtain if you align the "molecule" and coordinate system such that $\theta = 180^\circ$. What does this comparison tell you? What are the values of I_{xx} and I_{yy} if $\theta = 90$?

S13.38

We use trigonometric functions to find the x and y components

$$I_{xx} = \sum m_i y_i^2 = 2(1)(2\sin\theta)^2 + 2(1)\left[\sin\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\sin^2\theta + 2\cos^2\theta \tag{13.E.54}$$

$$I_{yy} = \sum m_i x_i^2 = 2(1)(2\cos\theta)^2 + 2(1)\left[\cos\left(\frac{\pi}{2}\right) - \theta\right]^2 = 8\cos^2\theta + 2\sin^2\theta \tag{13.E.55}$$

$$I_{xy} = -\sum m_i x_i y_i = -(2\cos\theta)(2\sin\theta) - 2\left[\cos(\pi) + \theta\right]\left[\sin(\pi) + \theta\right] - \left[\sin\left(\frac{\pi}{2}\right) - \theta\right]\left[\cos\left(\frac{\pi}{2}\right) - \theta\right] - \left[\cos\left(\frac{\pi}{2}\right) + \theta\right]\left[\sin\left(\frac{\pi}{2}\right) + \theta\right] \tag{13.E.56}$$

$$= -6\cos\theta\sin\theta$$

The secular determinantal equation becomes

$$\begin{vmatrix} 8\sin^2\theta + 2\cos^2\theta - \lambda & -6\cos\theta\sin\theta \\ -6\cos\theta\sin\theta & 8\cos^2\theta + 2\sin^2\theta - \lambda \end{vmatrix} = 0 \tag{13.E.57}$$

Expanding the determinant gives

$$0 = \lambda^2 - \lambda(10)(\sin\theta^2 + \cos\theta^2) + 16(\sin\theta^2 + \cos\theta^2)^2 \tag{13.E.58}$$

$$0 = \lambda^2 - 10\lambda + 16 \tag{13.E.59}$$

$$\lambda = 5 \pm 3 \tag{13.E.60}$$

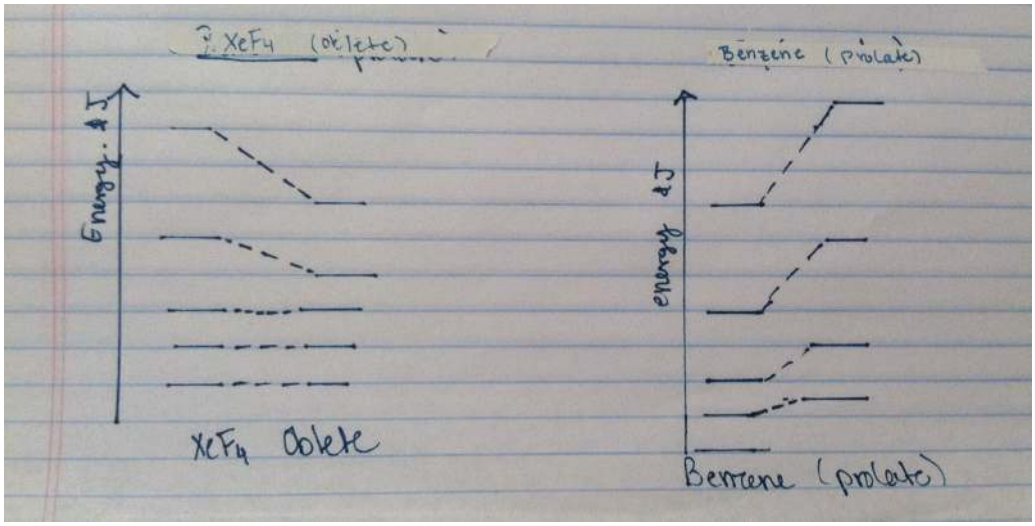
If $\theta = 180^\circ$ then $I_{xx} = 2, I_{yy} = 8, and I_{xy} = 0$. If $\theta = 90^\circ$ then $I_{xx} = 8, I_{yy} = 2, and I_{xy} = 0$. This tells us that the coordinate system does not affect the values of the principal momentum of inertia.

Q13.39

Sketch the energy level diagram of NH_3 (a prolate symmetric top molecule) and XeF_4 (an oblate symmetric top). How do they differ?

S13.39

The energies increase as the J levels increases for the prolate symmetry and the energies decrease as J increases for the oblate symmetry



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CHAPTER OVERVIEW

14: Nuclear Magnetic Resonance Spectroscopy

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Summer 2016: Delmar Larsen

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Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials through nuclear magnetic resonance spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

Topic hierarchy

14.1: Nuclei Have Intrinsic Spin Angular Momenta
14.2: Magnetic Moments Interact with Magnetic Fields
14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz
14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded
14.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus
14.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra
14.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed
14.8: The n+1 Rule Applies Only to First-Order Spectra
14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

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14.1: Nuclei Have Intrinsic Spin Angular Momenta

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.1.1}$$

You can see from Equation 14.1.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 14.1.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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14.2: Magnetic Moments Interact with Magnetic Fields

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? Exercise 14.2.1

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14.3: Proton NMR Spectrometers Operate at Frequencies Between 60 MHz and 750 MHz

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$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.3.1}$$

You can see from Equation 14.3.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

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? Exercise 14.3.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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14.4: The Magnetic Field Acting upon Nuclei in Molecules Is Shielded

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$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.4.1}$$

You can see from Equation 14.4.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

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? Exercise 14.4.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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14.5: Chemical Shifts is Sensitive to Chemical Environment of the Nucleus

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$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.5.1}$$

You can see from Equation 14.5.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

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14.6: Spin-Spin Coupling Results in Multiplets in NMR Spectra

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$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.6.1}$$

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? Exercise 14.6.1

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14.7: Spin-Spin Coupling Between Chemically Equivalent Protons Is Not Observed

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$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{14.7.1}$$

You can see from Equation 14.7.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

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? Exercise 14.7.1

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14.8: The n+1 Rule Applies Only to First-Order Spectra

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14.9: Second-Order Spectra Can Be Calculated Exactly Using the Variational Method

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CHAPTER OVERVIEW

15: Lasers, Laser Spectroscopy, and Photochemistry

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Summer 2016: Delmar Larsen

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Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400 – 750 nm) or infrared radiation (750 – 2500 nm). Photochemical reactions are valuable in organic and inorganic chemistry because they proceed differently than thermal reactions. Many thermal reactions have a photochemical counterpart. Photochemical paths offer an advantage over thermal methods of forming thermodynamically disfavored products, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes. Everyday examples include photosynthesis, the degradation of plastics or the formation of vitamin D with sunlight.

15.1: Electronically Excited Molecules
15.2: Transitions Modeled as Kinetics
15.3: Two-Level Systems Cannot Form Population Inversions
15.4: Population Inversion via Three-Level Systems
15.5: Laser Fundamentals
15.6: The Helium-Neon Laser
15.7: High-Resolution Laser Spectroscopy
15.8: Photochemical Dynamics

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15.1: Electronically Excited Molecules

To understand how lasers work we must first describe how a molecule in an excited state can relax back to the ground state because the light emitted by a laser is influenced by these relaxation processes. The two radiative decay pathways for an excited molecule are fluorescence and phosphorescence. Fluorescence differs from phosphorescence in that the energy transition that is responsible for fluorescence does not involve a change in electron spin multiplicity. Thus fluorescence lifetimes are short (10^{-9} - 10^{-6} s). In phosphorescence, there is a change in electron spin multiplicity, resulting in a longer lifetime of the excited state (second to minutes). A description of electron spin and the differences between singlet and triplet states will clarify the difference between fluorescence and phosphorescence.

Spin Multiplicity - Singlet and Triplet Excited States

The Pauli Exclusion principle states that two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s). Therefore, because two electrons can occupy each orbital, these two electrons must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules are diamagnetic, and are not attracted or repelled by an external magnetic or electric field. Molecules that contain unpaired electrons (free radicals) do have magnetic moments that are attracted to an external magnetic or electric field.

A molecule is said to be in a singlet state when all the electron spins are paired in the molecular electronic state, and the electronic energy levels do not split when the molecule is exposed to a magnetic field. A doublet state occurs when there is an unpaired electron that gives two possible orientations when exposed to a magnetic field and imparts different energies to the system. A singlet or a triplet state can form when one electron is excited to a higher energy level. In an excited singlet state, the promoted electron retains the spin orientation it had in the ground state (i.e., paired). In a triplet excited state, the promoted electron undergoes a change in spin, and so has the same spin orientation (parallel) to the unpaired electron that remains in the ground state orbital. The difference between the spins of ground singlet, excited singlet, and excited triplet is shown in Figure 15.1.1 . The terms singlet, doublet and triplet are derived using the equation for multiplicity, 2S+1, where S is the total spin angular momentum (sum of all the electron spins). Individual spins are denoted as spin up (s = +1/2) or spin down (s = -1/2). If we were to calculate the multiplicity for the singlet ground state or the singlet excited state, the equation would be

$$2(+1/2+-1/2)+1=2(0)+1=1$$

In a similar fashion, the spin multiplicity for the triplet excited state can be calculated as

$$2(+1/2++1/2)+1=2(1)+1=3$$

which gives a triplet state as expected.

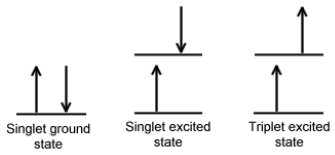


Figure 15.1.1 : Spin in the ground and excited states (Tyler Matthews - Paint Shop Pro, Public Domain, https://commons.wikimedia.org/w/inde...curid=64926546)

The difference between a molecule in the ground and the triplet excited state is that the molecule is diamagnetic in the ground state and paramagnetic in the triplet excited state. This difference in spin state makes the transition from singlet to triplet (or triplet to singlet) less likely than the singlet-to-singlet transitions. For this reason, the lifetime of the triplet state is longer than the lifetime of the singlet state by a factor of roughly 10^4 seconds. The transition from ground to excited triplet state has a low probability of occurring, thus these absorption bands are less intense than singlet-singlet state absorption bands. However, an excited triplet state can be populated from an excited singlet state of certain molecules. Jablonski diagrams can be used to explain transitions such as this that occur in photoluminescence molecules.

Jablonski Diagrams

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a graphic representation that shows the possible consequences of applying photons from the visible spectrum of light to a particular molecule. These schematics are referred to as Jablonski diagrams.

A Jablonski diagram is an energy diagram, arranged with energy on a vertical axis. The energy levels can be quantitatively denoted, but most of these diagrams use energy levels schematically. The rest of the diagram is arranged into columns. Every column usually represents a specific spin multiplicity for a particular species. However, some diagrams divide energy levels within the same spin multiplicity into different columns. Within each column, horizontal lines represent eigenstates for that particular molecule. Bold horizontal lines are representations of the limits of electronic energy states. Within each electronic energy state are multiple vibrational energy states that may be coupled with the electronic state. Usually only a portion of these vibrational eigenstates are represented due to the massive number of possible vibrations in a molecule. Each of these vibrational energy states can be subdivided even further into rotational energy levels; however, typical Jablonski diagrams omit such intense levels of detail.

Through the use of straight and wavy lines, these figures show transitions between eigenstates that occur from the exposure of a molecule to a particular wavelength of light. Straight lines show the conversion between a photon of light and the energy of an electron. Wavy lines show nonradiative transitions of electrons. Within a Jablonski diagram several different pathways show how an electron may accept and then dissipate the energy from a photon. Thus, most diagrams start with arrows originating from the ground electronic state and finish with arrows returning to the ground electronic state.

The Jablonski diagram that drawn below is a partial energy diagram that represents the energy of a photoluminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule which is the singlet state labeled as S_o. At room temperature, a majority of the molecules are in this state. The thicker lines on the left labeled S_1, S_2 , and S_3 represent the excited electronic states for the molecule in the singlet state. The thicker lines on the right labeled T_1, T_2, and T_3 represent excited triplet states.

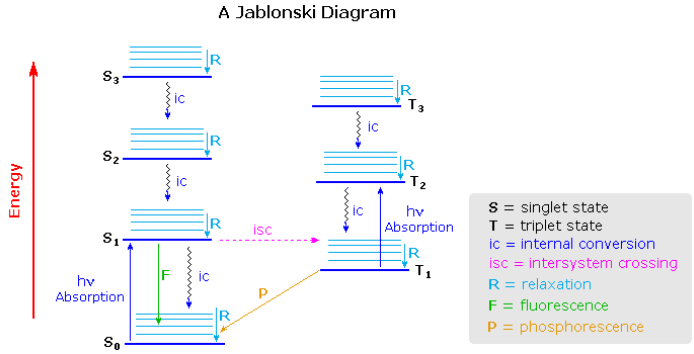


Figure 15.1.2 : Partial Jablonski Diagram for Absorption, Fluorescence, and Phosphorescence. (Bill Reusch, Michigan State University).

Deactivation Processes

A molecule that is excited can return to the ground state by several combinations of mechanical steps that will be described below and shown in Figure 15.1.2 .The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown by the straight arrow in Figure 15.1.2 . The wiggly arrows in Figure 15.1.2 are deactivation processes without the use of radiation. The favored deactivation process is the route that is most rapid and spends the least time in the excited state. If the rate constant for relaxation is more favorable in the radiationless path, the fluorescence will be less intense or absent.

Relaxation and Fluorescence

Often, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence" (Figure 15.1.3).

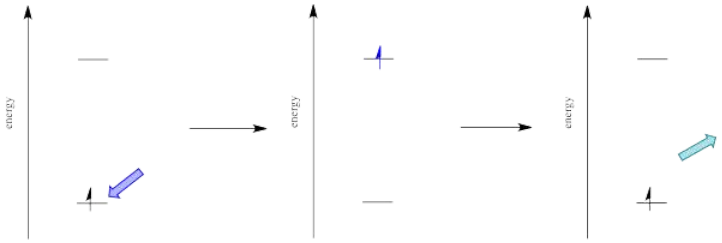


Figure 15.1.3: The absorption of purple light by a ground state particle, leading to the creation of an excited state particle. This excited state particle then emits blue light as it returns to the ground state.

How can that be? Isn't energy quantized? How is the molecule suddenly losing some of the energy that the original photon brought with it? This energy discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well (Figure 15.1.4). Vibrational energy, however, is not exchanged exclusively by means of photons. It can be gained or lost through molecular collisions and heat transfer.

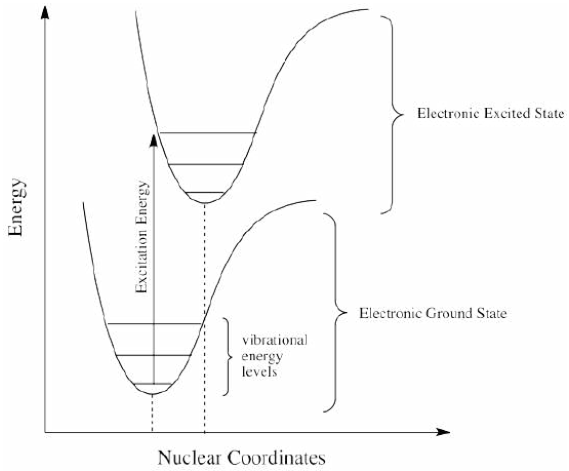


Figure 15.1.4: Transition from the ground state to an excited vibrational state within the excited electronic state.

Thus, an excited state molecule with an electron in a high-energy vibrational level within an excited electronic state might simply re-emit a photon of exactly the same wavelength as the one that was absorbed. But the excited electron is much more likely to relax into the lowest vibrational state within the excited electronic state, losing some of that initial excitation energy as heat. When the electron relaxes to this lower vibrational state, the energy gap between this excited state and the ground state is a little smaller. The photon that is emitted upon fluorescence will have lower energy and longer wavelength than a photon emitted from the original, higher vibrational level, excited state. See Figure 15.1.5.

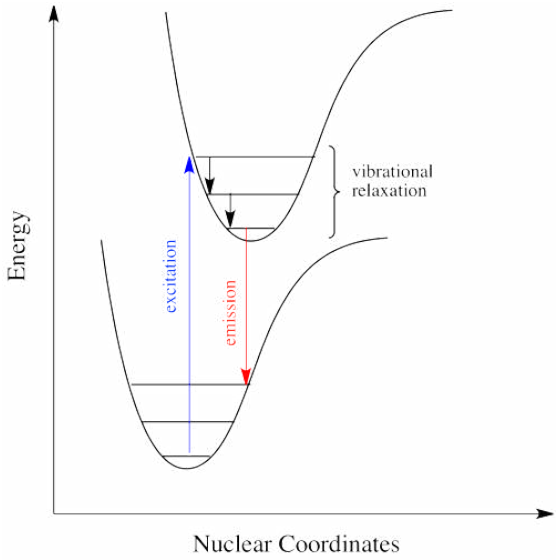


Figure 15.1.5: Excitation, followed by vibrational relaxation, and then emission.

Figure 15.1.6 shows the fluorescence transitions of a hypothetical diatomic molecule in which the equilibrium bond length of the ground state and the first singlet excited state are identical. In this molecule all absorptions involve transitions from the lowest vibrational level of the electronic ground state ($v'' = 0$) to various vibrational levels in the excited electronic state. Because vibrational relaxation occurs more rapidly than fluorescence, the fluorescence spectrum is composed of lines showing transitions from the lowest vibrational level of the excited state ($v' = 0$) to various vibrational levels in the electronic ground state.

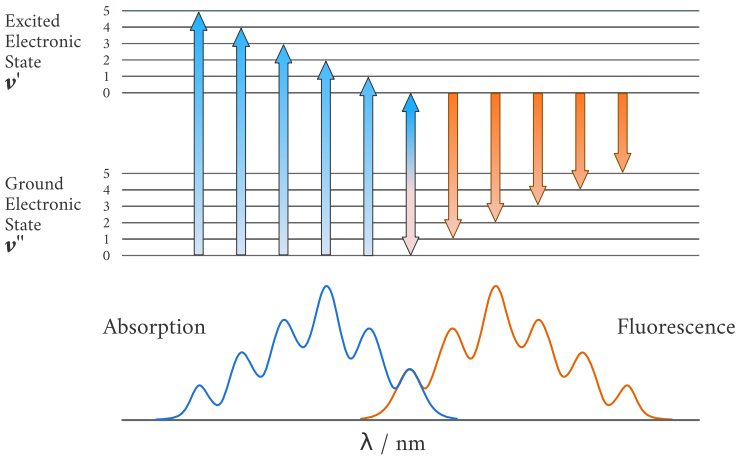


Figure 15.1.6: Absorption and fluorescence transitions in a hypothetical diatomic molecule in which the equilibrium bond length of the ground state is equal to the equilibrium bond length of the excited state. (CC BY-NC; Ümit Kaya, via LibreTexts)

Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a big enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its energy in collisions with other molecules. In molecules, as one molecule drops to a lower vibrational state, the other will hop up to a higher vibrational state with the energy it gains. In Figure 15.1.7 below, the red molecule is in an electronic excited and vibrational state. In a collision, it transfers some of its vibrational energy to the blue molecule.

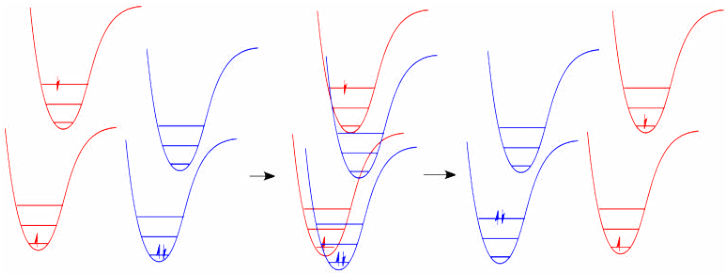


Figure 15.1.7: The transfer of vibrational energy (heat) through a collision.

Note

There are many examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister.

? Exercise 15.1.1

How does the energy of an electronic absorption compare to other processes? To find out, you might consider the excitation of an entire mole of molecules, rather than a single molecule absorbing a single photon. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 180 nm (ultraviolet)
b. absorbance at 476 nm (blue)
c. absorbance at 645 nm (red)

Answer

One method to carry out this calculation:

$$\frac{1}{x\text{nm}} \times \frac{1\,\text{nm}}{1x10^{-9}\,\text{m}} \times 6.626x10^{-34}\text{Js} \times \frac{3.000x10^{8}\text{m}}{\text{s}} \times \frac{6.022x10^{23}\text{photons}}{1.000\text{mole}} \times \frac{1\text{kJ}}{1000\text{J}}$$

a. 665.0 kJ/mol
b. 251.5 kJ/mol
c. 185.6 kJ/mol

Exercise 15.1.2

How does the energy of an excitation between vibrational states compare to that of an electronic excitation? Typically, infrared absorptions are reported in cm^{-1}, which is simply what it looks like: the reciprocal of the wavelength in cm. Because wavelength and frequency are inversely related, wavenumbers are considered a frequency unit. Calculate the energy in kJ/mol for the following transitions.

a. absorbance at 3105 cm^{-1}
b. absorbance at 1695 cm^{-1}
c. absorbance at 963 cm^{-1}

Answer

One method to carry out this calculation:

$$x\text{cm}^{-1} \times \frac{100\,\text{cm}}{1\,\text{m}} \times 6.626x10^{-34}\text{Js} \times \frac{3.000x10^{8}\text{m}}{\text{s}} \times \frac{6.022x10^{23}\text{photons}}{1.000\text{mole}} \times \frac{1\text{kJ}}{1000\text{J}}$$

a. 37.14 kJ/mol
b. 20.27 kJ/mol
c. 11.52 kJ/mol

By comparing these answers with those from Exercise 15.1.1, we can see that the energy difference between vibrational states is an order of magnitude less than the energy difference between electronic states.

Internal Conversion

If electrons can get to a lower energy state, and give off a little energy at a time, relaxing to lower and lower vibrational levels, do they need to give off a photon at all? Maybe they can relax all the way down to the ground state via vibrational relaxation. That is certainly the case. Given many vibrational energy levels, and an excited state that is low enough in energy so that some of its lower vibrational levels overlap with some of the higher vibrational levels of the ground state, an electron can relax from an excited electronic state back to the ground state without releasing a photon (Figure \(\PageIndex{8}\).

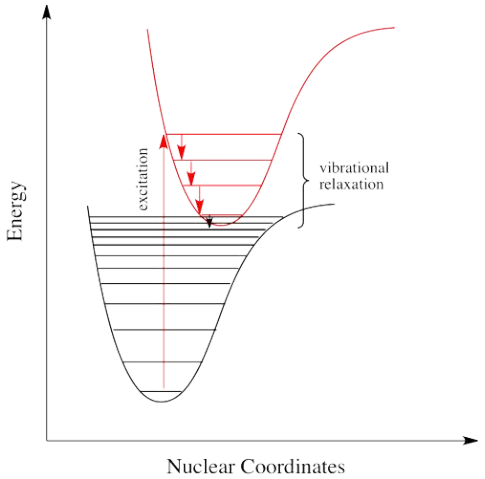


Figure 15.1.8: Relaxation of an excited state particle to the ground state through the nonradiative process of internal conversion.

This event is called a "radiationless transition", because it occurs without release of a photon. The electron simply slides over from a low vibrational state of the excited electronic state to a high vibrational state of the electronic ground state. If the electron simply keeps dropping a vibrational level at a time back to the ground state, the process is called **"internal conversion"**.

Internal conversion has an important consequence. Because the absorption of UV and visible light can result in energy transfer into vibrational states, much of the energy that is absorbed from these sources is converted into heat. That can be a good thing if you happen to be a marine iguana trying to warm up in the sun after a plunge in the icy Pacific. It can also be a tricky thing if you are a process chemist trying to scale up a photochemical reaction for commercial production of a pharmaceutical, because you have to make sure the system has adequate cooling available.

Intersystem Crossing

Intersystem crossing is a process that leads to the electron getting caught between the excited state and the ground state. Just as, little by little, vibrational relaxation can lead the electron back onto the ground state energy surface, it can also lead the electron into states that are intermediate in energy in which the spin multiplicity has changed.

For example, suppose an organic molecule undergoes electronic excitation. Generally, organic molecules have no unpaired electrons. Their ground states are singlet states. According to one of the selection rules for electronic excitation, the excited state must also have no unpaired electrons. In other words, the spin on the electron that gets excited is the same after excitation as it was before excitation.

However, that's not the lowest possible energy state for that electron. When we think about atomic orbital filling, there is a rule that governs the spin on the electrons in degenerate orbitals: in the lowest energy state, **spin is maximized** (Hund's rule). In other words, when we draw a picture of the valence electron configuration of nitrogen, we show nitrogen's three p electrons each in its own orbital, with their spins parallel.



Figure 15.1.9: The diagram on the left shows the energetically stable quartet spin state. The diagram on the right shows the less stable doublet spin state.

In Figure 15.1.9, the diagram on the left, with three unpaired electrons, all with parallel spins, shows a nitrogen in the quartet spin state. This is the most stable state. Having one of those spins point the other way would result in a different, higher energy spin state. The diagram on the right shows a different a different spin state, in which one pair of electrons in the p level is spin-paired, one up and one down, even though they are in different p orbitals. That would leave one electron without an opposite partner, so the nitrogen would be in a doublet spin state. The spin state on the left is **lower** in energy than the state on the right. That's just one of the rules of quantum mechanics (**Hund's rule**): maximize spin when degenerate orbitals are singly occupied.

A similar argument can be made for a molecule with the triplet state lower in energy than the singlet state, as shown in Figure 15.1.10 Why didn't the electron get excited to the triplet state in the first place? That is a forbidden (unlikely) electronic transition. But sliding down vibrationally onto the triplet state from the singlet excited state is not, because it doesn't involve absorption or emission of a photon.

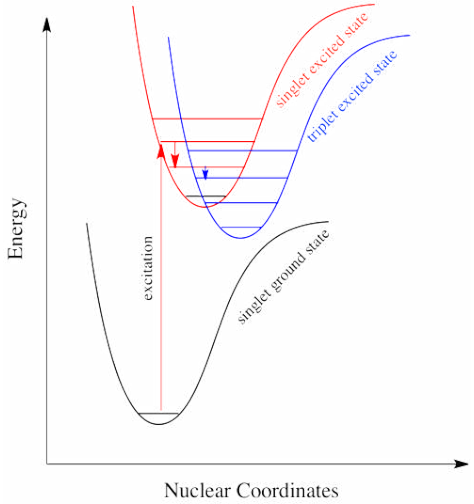


Figure 15.1.10: Intersystem crossing from a singlet excited state to a triplet excited state.

Intersystem crossing can have important consequences in reaction chemistry because it allows access to triplet states that are not normally available in many molecules. Because triplet states feature unpaired electrons, their reactivity is often typified by radical processes. That means an added suite of reactions can be accessed via this process.

Phosphorescence: A Radiationless Transition Followed by Emission

Intersystem crossing is one way a system can end up in a triplet excited state. Even though this state is lower in energy than a singlet excited state, it cannot be accessed directly via electronic excitation because that would violate the spin selection rule (\Delta S=0\). Once intersystem crossing has occurred, the process of reattaining the ground state slows down dramatically. The quick way back to ground state is to emit a photon. But because that would involve a change in spin state, it is not allowed. Realistically speaking, that means it takes a long time. By "a long time", we might mean a few seconds, several minutes, or possibly even hours. Eventually, the electron can drop back down, accompanied by the emission of a photon. This situation is called "phosphorescence" (Figure \(\PageIndex{11}).

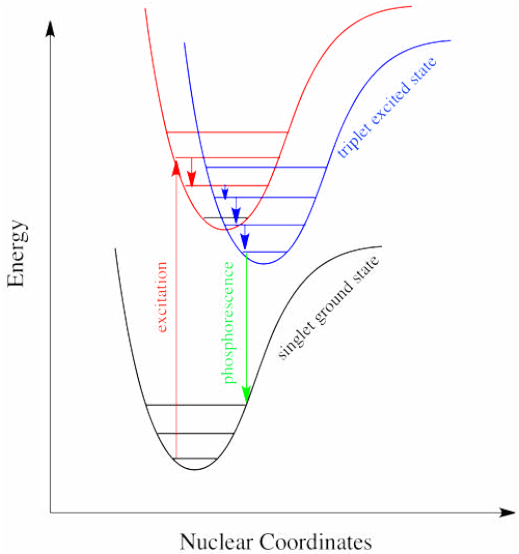


Figure 15.1.11: The process of phosphorescence - excitation, followed by vibrational relaxation, intersystem crossing, and phosphorescence.

Many plants and animals use phosphorescence as a means of signaling. Molecules that display phosphorescence are also often incorporated into toys and shirts so that they will glow in the dark.

External Conversion

Deactivation of the excited electronic state may also involve the interaction and energy transfer between the excited state and the solvent or solute in a process called **external conversion.** Low temperature and high viscosity lead to enhanced fluorescence

because they reduce the number of collision between molecules, thus slowing down this type of deactivation process.

Absorption and Emission Rates

The table below compares the absorption and emission rates of fluorescence and phosphorescence. The rate of photon absorption is very rapid. Fluorescence emission occurs at a slower rate. Since the triplet to singlet (or reverse) is a forbidden transition, meaning it is less likely to occur than the singlet-to-singlet transition, the rate of triplet to singlet is typically slower. Therefore, phosphorescence emission requires more time than fluorescence.

Table 15.1.1 : Rates of Absorption and Emission comparison.

Process	Radiative Process?	Transition	Timescale (sec)
Light Absorption (Excitation)	yes	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	no	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	no	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	no	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	yes	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	yes	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay to Ground State (Internal Conversion)	no	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

References

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2. D. C. Harris and M.D. Bertolucci "Symmetry and Spectroscopy, An Introduction to Vibrational and Electronic Spectroscopy" Dover Publications, Inc., New York. 1989.

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15.2: Transitions Modeled as Kinetics

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.2.1}$$

You can see from Equation 15.2.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 15.2.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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15.3: Two-Level Systems Cannot Form Population Inversions

Energy State Populations

For reasons that we cannot explain, it appears that all things in nature prefer to go to the lowest energy state available to them. This seems to be how nature behaves. Apples fall all the way to the ground, once they are let go by the tree branches they grew on. Of course unless they fall into a hole, in which case they go even lower than the ground level - to the bottom of the hole. To raise the energy of the fallen apple someone, or something, has to intervene. A child must pick it up off the ground, for example. Otherwise, the apple will remain at its lowest point. Similarly, atoms tend to prefer to always stay in their ground state, unless some intervening force causes them to reach an excited state. In the language used in the study of lasers, any process that feeds energy into a collection of atoms or molecules and causes them to vacate their ground state is referred to as an energy pump, or simply as a pump.

In most lamps electricity is used, by one mechanism or other, to pump atoms out of their ground-state into some excited state. We have already seen that incandescent bulbs produce light from Radiative transitions after excitation via collisions of the electrons in an electric current with the filament atoms. As we've also seen, other light sources, like the fluorescent lamps or neon tubes, use gas or vapor for their medium of excitation instead of a solid filament. In most lamps, the pumping mechanism is electricity. This is also the case for most lasers, but in some lasers optical pumping is the mechanism that is used to cause excitation. In optical pumping a light source generates photons with enough energy that they are able to get absorbed by the atoms in the lasing medium and cause them to go into an excited state.

Evidently, all excitations occur "instantaneously", but de-excitations can lag by a measurable time interval that depends on the properties of the excited state. That is to say, an atom in an excited state does not instantaneously de-excite. The time that it spends, on average, in that excited level is called the lifetime of that state. Lifetimes can vary in duration depending on the atom and on the energy level. Excited state lifetimes are typically a few nanoseconds (10-9 s, or a billionth of a second), but they could be as short as a picosecond (10-12 s, or a thousand times shorter still) or as long as a few milliseconds (10-3 s). The ground state, of course, has an infinitely long lifetime since an atom in its ground state can no longer decrease its energy. So, the most stable of states is the ground state. Long-lived states are referred to as meta-stable states.

In the case of Radiative emission, atoms happen to take two very distinctly different approaches: spontaneous emission, or stimulated emission. Spontaneous emission refers to the case when the excited atom de-excites, rather randomly whenever it "feels like it", and emits a photon. This photon has an energy equal to the difference between the two energy levels of the transition, but its direction of travel and its other properties, such as polarization are random. Stimulated emission was first theorized by Albert Einstein in 1917. For stimulated emission to occur a second, non-participating yet stimulating, photon must be present. The energy of this second photon must exactly match the allowed energy of the transition. Then the emitted photon will not only have the same energy as the stimulating one, but it will also travel in the same direction, and will be essentially identical to it.

So, independent of what type of medium is used in a laser, in the absence of a pump the atoms or molecules are almost all in their ground state. Let us imagine that we could count the number of atoms in our laser medium that are in each energy state and denote the ones which are in their ground state by Ngs , those in the first excite state by N1, those in the second excited state by N2 , and so on. Then in the absence of a pump we are mostly certain that N1= N2 = ... = 0, and Ngs = total number of all the atoms in the medium. Once the pump is turned on it will deplete the number of atoms that were originally in the ground state and increases the number of atoms in the excited states that it is pumping to. Because excited atoms de-excite quickly and return to their ground states by spontaneous emission, in almost all lasers even when the pump is feeding energy into the medium the number of atoms in their ground state remains many times more than atoms in any other energy state. That is to say, almost always we could safely state that:

$$N_{\text{ground state}} \text{ much bigger than } N_{\text{any other state}} .$$

To make a laser we need to not only excite the atoms in the laser medium, but somehow encourage them to undergo a decay through stimulated emission. In stimulated emission a passer-by photon which has an energy exactly equal to the transition energy stimulates the atom to emit a photon, identical to the passer-by photon, instantly. The problem with this is that the same passer-by photon could instead get absorbed by a de-excited atom. So, aside from pumping the atoms to excited states, we need to use clever procedures to insure that there are more excited atoms that could use the passer-by photon for stimulated emission than there are de-excited atoms which could absorb it; i.e. we need to generate a population inversion. Although Einstein predicted stimulation

emission in 1917, it was not found experimentally for over 10 years and took over another 30 years just to predict the possibility of a laser. This is basically because it was not considered possible to produce a population inversion because of the above inequality.

Lasing in Two-Level Systems

For the sake of our studies, let's first consider a laser medium whose atoms have only two energy states: a ground state and one excited state. In such an idealized atom the only possible transitions are excitation from the ground state to the excited state, and de-excitation from the excited state back into ground state. Could such an atom be used to make a laser?

There are several important conditions that our laser must satisfy. First of all, the light that it produces must be coherent. That is to say, it must emit photons that are in-phase with one another. Secondly, it should emit monochromaticlight, i.e. photons of the same frequency (or wavelength).Thirdly, it would be desirable if our laser's output were collimated, producing a sharply defined "pencil-like" beam of light (this is not crucial, but clearly a desirable condition). Lastly, it would also be desirable for our laser to be efficient, i.e. the higher the ratio of output energy - to - input energy, the better.

Let us begin by examining the requirements for our first condition for lasing, coherence. This condition is satisfied only when the lasing transition occurs through stimulated emission. As we have already seen, stimulated emission produces identical photons that are of equal energy and phase and travel in the same direction. But for stimulated emission to take place a "passer-by" photon whose energy is just equal to the de-excitation energy must approach the excited atom before it de-excites via spontaneous emission. Typically, a photon emitted by the spontaneous emission serves as the seed to trigger a collection of stimulated emissions. Still, if the lifetime of the excited state is too short, then there will not be enough excited atoms around to undergo stimulated emission. So, the first criteria that we need to satisfy is that the upper lasing state must have a relatively long lifetime, otherwise known as a meta-stablestate, with typical lifetimes in the milliseconds range. In addition to the requirement of a long lifetime, we need to ensure that the likelihood of absorption of the "passer-by" photons is minimized. This likelihood is directly related to the ratio of the atoms in their ground state versus those in the excited state. The smaller this ratio, the more likely that the "passer-by" photon will cause a stimulated emission rather than get absorbed. So, to satisfy this requirement, we need to produce a population inversion: create more atoms in the excited state than those in the ground state.

Achieving population inversion in a two-level atom is not very practical. Such a task would require a very strong pumping transition that would send any decaying atom back into its excited state. This would be similar to reversing the flow of water in a water fall. It can be done, but is very energy costly and inefficient. In a sense, the pumping transition would have to work against the lasing transition.

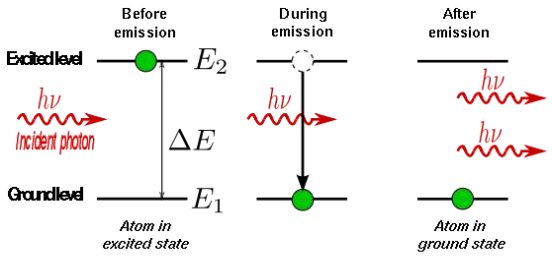
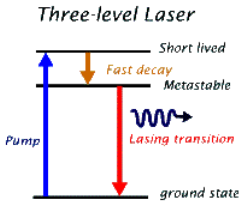


Figure 1: Stimulated emission in a two-level transition. (CC BY-SA 4.0; V1adis1av)

It is clear, from the above diagram, that in the two-level atom the pump is, in a way, the laser itself! Such a two-level laser would work only in jolts. That is to say, once the population inversion is achieved the laser would lase. But immediately it would end up with more atoms in the lower level. Such two-level lasers involve a more complicated process. We will see, in later material, examples of these in the context of excimer lasers, which are pulsed lasers. For a continuous laser action we need to consider other possibilities, such as a three-level atom.

Lasing in Three-Level Systems

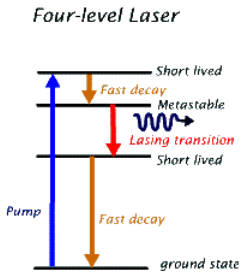
In fact, the first laser that was demonstrated to operate was a three-level laser, Maiman's ruby laser.



In the above diagram of a three level laser the pump causes an excitation from the ground state to the second excited state. This state is a rather short-lived state, so that the atom quickly decays into the first excited level. [Decays back to the ground state also occur, but these atoms can be pumped back to the second excited state again.] The first excited state is a long-lived (i.e. metastable) state which allows the atom to "wait" for the "passer-by" photon while building up a large population of atoms in this state. The lasing transition, in this laser, is due to the decay of the atom from this first excited metastable state to the ground state. If the number of atoms in the ground state exceeds the number of atoms that are pumped into the excited state, then there is a high likelihood that the "lasing photon" will be absorbed and we will not get sustained laser light. The fact that the lower lasing transition is the ground state makes it rather difficult to achieve efficient population inversion. In a ruby laser this task is accomplished by providing the ruby crystal with a very strong pulsating light source, called a flash lamp. The flash lamp produces a very strong pulse of light that is designed to excite the atoms from their ground state into any short-lived upper level.t In this way the ground state is depopulated and population inversion is achieved until a pulse of laser light is emitted. In the ruby laser the flash lamp light lasts for about 1/1000 of a second (1 ms) and can be repeated about every second. The duration of the laser pulse is shorter than this, typically 0.1 ms. In some pulsed lasers the pulse duration can be tailored using special methods to be much shorter than this, down to about 10 fs (where 1 fs = 10-15 s or one thousandth of a millionth of a millionth of a second). So, the output of a three-level laser is not continuous, but consists of pulses of laser light.

Lasing in Four-Level Systems

To achieve a continuous beam of laser light a four-level laser is required.



Here, the lower laser level is not the ground state. As a result, even a pump that may not be very efficient could produce population inversion, so long as the upper level of the laser transition is longer lived than the lower level. Of course, all attempts are made to design a pump that maximizes the number of excited atoms. A typical four-level laser is the helium-neon (He-Ne) gas laser. In these lasers electric pumping excites helium atoms to an excited state whose energy is roughly the same as the upper short-lived state in the neon atom. The sole purpose of the helium atoms is to exchange energy with neon atoms via collisional excitation. As it turns out, this is a very efficient way of getting neon atoms to lase.

Laser components

All lasers have three primary components:

- Medium
- Pump
- Resonant Cavity

The laser medium can be gaseous, liquid, or a solid. These could include atoms, molecules, or collections of atoms that would be involved in a laser transition. Typically, a laser is distinguished by its medium, even though two lasers using different media may have more in common than two which have similar media.

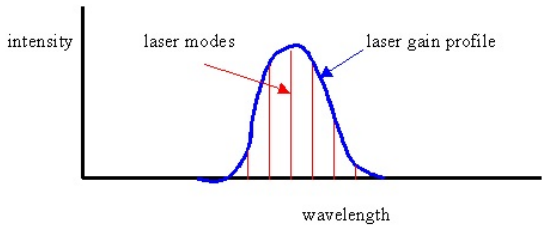
There are three different laser pumps: electromagnetic, optical, and chemical. Most lasers are pumped electro-magnetically, meaning via collisions with either electrons or ions. Dye lasers and many solid state lasers are pumped optically; however, solid state lasers are typically pumped with a broad band (range of wavelengths) flash-lamp type light source, or with a narrow band semiconductor laser. Chemically pumped lasers, using chemical reactions as an energy source, are not very efficient. So far, these lasers have been made to work not so much for their usefulness as for their curious operation.

Up to now in our discussion of laser theory we have not really seen how the beam is generated. We know that photons emitted by stimulated emission travel coherently in the same direction, but what is it that defines the beam direction and what allows the intensity of the laser light to get large? The answer to these two questions is coupled together in the resonant cavity. Laser resonant cavities usually have two flat or concave mirrors, one on either end, that reflect lasing photons back and forth so that stimulated emission continues to build up more and more laser light. The "back" mirror is made as close to 100% reflective as possible, while the "front" mirror typically is made only 95 - 99% reflective so that the rest of the light is transmitted by this mirror and leaks out to make up the actual laser beam outside the laser device.

The resonant cavity thus accounts for the directionality of the beam since only those photons that bounce back and forth between the mirrors lead to amplification of the stimulated emission. Once the beam escapes through the front mirror it continues as a well-directed laser beam. However, as the beam exits the laser it undergoes diffraction and does have some degree of spreading. Typically this beam divergence is as small as 0.05o but even this small amount will be apparent if the beam travels long distances.

Even more, the resonant cavity also accounts for the amplification of the light since the path through the laser medium is elongated by repeated passes back and forth. Typically this amplification grows exponentially, similar to the way compound interest works in a bank. The more money in your bank account, with compound interest, the faster you earn more interest dollars. Similarly, the more photons there are to produce stimulated emission, the larger the rate at which new coherent photons are produced. The term used for laser light is gain, or the number of additional photons produced per unit path length.

The last question to address in this section is: why is the resonant cavity called by that name? What does resonance have to do with having mirrors on either end of a region containing the laser medium? Recall that when we discussed resonance on a string, we spoke about the wave traveling one way along the string (say to the right) interfering with the wave reflected at the end traveling back to the left. At a resonant frequency, there are points at which the two waves exactly add or cancel all the time, leading to a standing wave. At other frequencies the waves will randomly add or cancel and the wave will not have a large amplitude. The case of a light wave traveling back and forth in the resonant cavity is exactly analogous in that only at certain resonant frequencies will the light wave be amplified. The required condition is easy to see. The mirror separation distance, L, must be equal to a multiple of half a wavelength of light, just as we saw in the case of a string. In symbols, we have that L = nl/2, where l is the wavelength of the light and n is some integer. In the case of light, because of the small wavelength n is a very large number, implying that there are a huge number of resonant frequencies. On the other hand, only those resonant frequencies that are amplified by the laser medium will have large amplitudes and so usually there are only a few so-called laser modes or laser resonant frequencies present in the light from a laser, as shown in the figure.



Questions on Laser Components

- What are the three primary components of a laser?
- What different types of laser medium are used?
- What is a pump? Describe the different types of pumps.
- What is a resonant cavity?
- Describe how the resonant cavity produces a collimated laser beam.
- What is the beam divergence of a laser caused by? What is a typical value for it?
- What does the term gain mean? Is it related to pain?
- Describe why a typical laser has only a few modes, while the resonant cavity produces a huge number of them.

Contributors

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15.4: Population Inversion via Three-Level Systems

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.4.1}$$

You can see from Equation 15.4.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 15.4.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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15.5: Laser Fundamentals

LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. Laser is a type of light source which has the unique characteristics of directionality, brightness, and monochromaticity. The goal of this module is to explain how a laser operates (stimulated or spontaneous emission), describe important components, and give some examples of types of lasers and their applications.

Introduction

The word LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. In 1916, Albert Einstein discovered the physical principle responsible for this amplification, and the foundation principle is called stimulated emission. It was widely accepted at that time that laser would represent a big leap in science and technology, even before Theodore H. Maiman built the first one in 1960. The 1951 Nobel Prize in physics was shared by Charles H. Townes, Nokolay Basov, and Aleksandr Prokhorov, in citation, “For Fundamental work in the field of quantum electronics, which has led to the construction of oscillator and amplifiers based on the maser-laser principle”.

The early lasers developed in the 1950s by Charles H. Townes and Arthur Shawlow were gas and solid-state lasers for use in spectroscopy. The principles of lasers were adapted from masers. MASER is an acronym that stands for Microwave Amplification by Stimulated Emission of Radiation. It uses the idea of stimulated emission and population inversion to produce a coherent amplified radiation of light in the microwave region. Stimulated emission is when an electron in an excited state falls back to ground state after absorbing energy from an incident photon. Amplified radiation or light is produced with the same direction and energy as the incident light. Population inversion is when you have a greater population of electrons in the excited state than in ground state. Population inversion is achieved through various pumping mechanisms. The laser uses these same ideas except that the electromagnetic wave created is in the visible light region. When emission begins the light oscillates within the resonant cavity and gains magnitude. Once enough light has been acquired, the laser beam is produced. This allows lasers to be used as a powerful light source. Three unique characteristics of a laser are its properties of monochromaticity, directionality, and brightness.

The monochromaticity of lasers is due to the fact that lasers are highly selective in the wavelength of light produced, which in itself is due to the resonant frequency inside the active material. Resonant frequency means that the light is oscillating in a single mode creating a monochromatic beam of light. The property of directionality depends on the angle of which the light propagates out of the source. Since lasers have large spatial and temporal coherence directionality is maximized. Temporal coherence is when there are small fluctuations in the phase. Spatial coherence has small changes in the amplitude of the emitted light. Like monochromaticity, directionality is dependent on the resonant cavity of the active material. The property of brightness is a result of the directionality and the coherence of the light. Due to these properties, lasers today are used in simple laser pointers, cutting devices, the development of military technologies, spectroscopy, and medical treatments. Their direct application to spectroscopy has allowed scientists to measure lifetimes of excited state molecules, structural analysis, probing far regions of the atmosphere, photochemistry and their use as ionization sources.

History

One of the most important characteristics of light is that it has wave-like properties and that it is an electromagnetic wave. Experiments on the blackbody radiation demonstrated a comprehensive idea of emission and absorption of electromagnetic waves. In 1900, Max Plank developed the theory that electromagnetic waves can only exist in distinct quantities of energy, which are directly proportional to a given frequency (ν). In 1905, Albert Einstein proposed the dual nature of light, having both wave-like and particle-like properties. He used the photoelectric effect to show that light acts as a particle, with energy inversely proportional to the wavelength of light. This is important, because the number of particles is directly related to how intense a light beam will be. In 1915, Einstein introduced the idea of stimulated emission- a key concept to lasers.

In 1957, Townes and Shawlow proposed the concept of lasers in the infrared and optical region by adapting the concept of masers to produce monochromatic and coherent radiation. In 1953, Townes was the first to build a maser with an ammonia gas source. Masers use stimulated emission to generate microwaves. Townes and other scientists wanted to develop the optical maser to generate light. Optical masers would soon adopt the name LASER: Light Amplification by Stimulated Emission of Radiation. An optical maser would need more energy than what can be provided by microwave frequencies and a resonant cavity of the order of 1μm or less. Townes and Shawlow proposed the use of a Fabry-Pérot interferometer equipped with parallel mirrors, where Interference of radiation which is traveling back and forth between parallel mirrors in the cavity allowed for selection of certain wavelengths. Townes built an optical maser with potassium gas. That failed because the mirrors degraded over time. In 1957,

Gordon Gould improved upon Townes' and Shawlow's laser concept. It was Gould who renamed the optical maser to laser. In April 1959, Gould filed a patent for the laser and later in March 1960, Townes and Shawlow had also made a request for a patent. Since Gould's notebook was officially dated the idea was his first, but he did not receive the patent until 1977.

Components

A laser consists of three main components: a lasing medium, a resonant or optical cavity, and an output coupler. The lasing medium consists of a group of atoms, molecules , or ions in solid, liquid or gaseous form, which acts as an amplifier for light waves. For amplification, the medium has to achieve population inversion, which means in a state in which the number of atoms in the upper energy level is greater than the number of atoms in the lower energy level. The output coupler serves as energy source which provides for obtaining such a state of population inversion between a pair of energy levels of the atomic system. When the active medium is placed inside an optical resonator, the system acts as an oscillator.

Figure 1. Diagram of a typical laser, showing the three major parts.

Lasing Medium

The lasing medium is the component used to achieve lasing, such as chromium in the aluminum oxide crystal-found in a ruby laser. Helium and neon gas are two materials most commonly used in gas lasers. These are only a few examples of lasing mediums or materials that have been used in the past and present states of the laser. For further information about different types of lasing mediums please refer to the section where *Types of Lasers* is discussed.

Optical Cavity and Output Coupler

Rays of light moving along an optical path tend to diverge over time, because the energy of radiation has very high frequency. Therefore an optical cavity is needed to refocus the light. **Figure 1**, represents the basics of an optical cavity where the light inside moves back and forth between two mirrors. These redirect and focus the light each time it hits the surface of the mirrors. There are two types of cavities: stable cavities and unstable cavities. A stable cavity is when the ray of light does not diverge far from the optical axis. An unstable cavity is when the ray of light bounces off and away from a mirrors surface. The importance of the cavities is that it allows for the laser to have properties of directionality, monochromaticity and brightness.

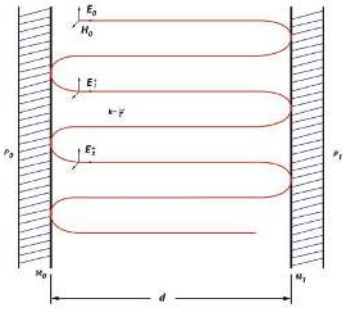


Figure 2. an optical cavity where the light inside moves back and forth between two mirrors

Light oscillating between the first mirror (M_o) and the second mirror (M_1) separated by distance, d, will have a round-trip phase shift (RTPS) of $2\theta=2kd=q2\pi-\phi$. In **Figure 1**, a round-trip can be described as the beam traveling from M_o to M_1back to M_o. Resonance occurs in the cavity because the light propagating between the two mirrors is uniform. The ABCD law describes that an optical cavity has a field distribution, because it reproduces itself as it is making these round-trips between the two parallel mirrors. The ABCD law was first applied to a Gaussian beam with a beam parameter, q, which is described as

$$q_2 = \frac{(Aq_1 + B)}{(Cq_1 + D)}$$

This law states that the beam, which is oscillating through an optical system, will experience some changing as it moves in the cavity. Fields that are created in an optical cavity have analogous shape and phase as they make each trip back and forth. However, the one thing that changes is the size of the field because the electromagnetic wave is unrestricted, unlike a wave in a short-circuited coaxial cable used to build a resonator or a microwave cavity mode. Since there is a field distribution of $E_o$at the surface of M_o, it can be said that there is a field distribution at the surface of M_1. Since there will be a change in size of the field this means that the electromagnetic wave will have change in amplitude by $\rho_0*\rho_1$ and a phase factor of $e^{-}jk2d$, creating additional fields.

This is an example of a phasorial addition of all fields between M_o and $M_{1,}$ creating a total field E_T (**Figure 2**). Phasorial addition is described by RTPS, where each additional E_n will have a delay of angle ϕ which is related to kd.

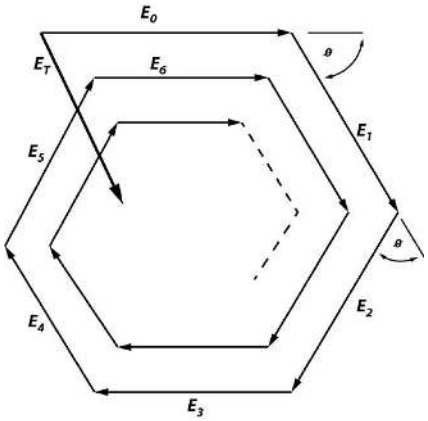


Figure 3. Totle field E_T

E_T will always be greater than $E_o$only if ρ_0 and $\rho_1$are not greater than 1 and ϕ=0. In this case, when ϕ=0 resonance is enhanced because all factors such as E_T travelling between M_o and M_1, the intensity of the electromagnetic waves, number of photons traveling between $M_o$and $M_{1,}$ and the amount of energy that is stored are maximized. The resonant wavelength can also be determined by using the relationship between RTPS, and because

$$k = \frac{\omega n}{c} = \frac{2\pi}{\lambda}$$

Using $2\theta = 2kd = q2\pi$

$$\frac{2\pi 2d}{\lambda} = q2\pi$$

$$d = \frac{q\lambda}{2}$$

Where the wavelength of interest is given by $\lambda = \lambda_0/n$, where n is the index of refraction and λ_0 is the free-space wavelength .

Since we are dealing with light as a wave, the light in the resonant cavity can be described in terms of frequency, ν. Where

$$k2d = \omega\frac{2nd}{c} = 2\pi\nu\frac{2nd}{c} = q(2\pi)$$

$$\nu = q\frac{c}{2nd}$$

A Fabry-Pérot interferometer is a prime example of an optical cavity used in a laser. The Fabry-Pérot is equipped with two parallel mirrors, one that is completely reflective and the other that is partially reflective. As light is accumulating in the cavity after taking several round trips between the two mirrors, some light is transmitted through the partially reflective mirror and a laser beam is produced. The beam can be in pulsed mode or continuous-wave (CW) mode. To increase the performance of the resonant cavity, the length of the cavity (d) must be considered as a way to avoid a decrease in the laser beam intensity due to any diffraction losses. The size of the aperture of the cavity is also important because it determines the strength or the intensity of the laser beam. In fact, determining the best length of a resonant cavity will enhance the coupling conditions of the output coupler by producing a frequency that is stable, which ultimately generates a laser beam that is coherent and has high power.

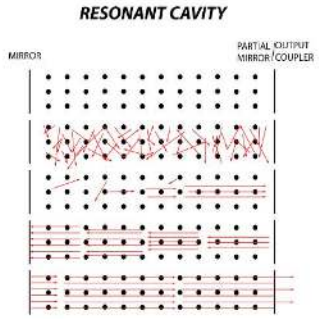


Figure 4. The first stage shows that all molecules present are in the ground state since there is no excitation energy present in the cavity. In the second stage, molecules become excited causing spontaneous emission of photons. In the third stage, photons collide with excited molecules causing an amplification of the light. This results in stimulated emission where the photon that is released has the same energy and direction of the photon that created it. Last is the fourth stage, where stimulated emission causes amplification of the light, and those photons that are traveling parallel to the cavities axis will hit one of the parallel mirrors and will be reflected back along the same axis. As the light is building up from the back and forth movement from one mirror to another, some of the light will pass through the partial mirror or the output coupler as a beam of rays. The remaining light in the cavity will continue producing more photons as long as there is a population inversion.

There are essentially six stages in the lasing process. First is the ground state where there is no excitation of the lasing medium. Second is pumping, which is applied to the medium where spontaneous emission occurs. Then the third stage is when emitted photons collide with an excited molecule where stimulated emission occurs. In the fourth stage the photons are produced in multiples, however those moving parallel in the cavity will hit a mirror and then hit the second mirror. During the fifth stage this process continues until there is an accumulation of light that is coherent and of a specific frequency. Finally, the sixth stage is when the light or laser beam exits the partially reflective mirror which is also known as the output coupler. An output coupler is the last important component of a laser because it must be efficient to produce an output of light with maximum intensity. If the output coupler is too transparent than there is much more loss of electromagnetic waves and this will decrease lasing significantly because population inversion will no longer be maintained. If the output coupler or partially reflective mirror is too reflective, then all the accumulated light that is built up in the resonant cavity will be trapped in the cavity. The beam will not pass through the output coupler, producing little to no light making the laser ineffective.

Emission

Lasers create a high energy beam of light by stimulated emission or spontaneous emission. Within in a molecule there are discrete energy levels. A simple molecular description has a low energy ground state (E_1) and a high energy excited state (E_2). When an electromagnetic wave, referred to as the incident light, irradiates a molecule there are two processes that can occur: absorption and stimulated emission.

Absorption occurs when the energy of the incident light matches the energy difference between the ground and excited state, causing the population in the ground state to be promoted to the excited state. The rate of absorption is given by the equation:

$$\frac{dN_1}{dt} = -W_{12}N_1$$

Where N_1 is the population in E_1, and W_{12} is the probability of this transition. The probability of the transition can also be related to the photon flux (intensity of incident light):

$$W_{12} = \sigma_{12}F$$

Where F is the photon flux and σ_{12} is the cross section of the transition with units of area. When absorption occurs photons are removed from the incident light and the intensity of the light is decreased.

Stimulated emission is the reverse of absorption. Stimulated emission has two main requirements: there must be population in the excited state and the energy of the incident light must match the difference between the excited and ground state. When these two requirements are met, population from the excited state will move to the ground energy level. During this process a photon is emitted with the same energy and direction as the incident light. Unlike absorption, stimulated emission adds to the intensity of the incident light. The rate for stimulated emission is similar to the rate of absorption, except that it uses the population of the higher energy level:

$$W_{21} = \sigma_{21}F$$

Like absorption the probability of the transition is related to the photon flux of the incident light through the equation:

$$\frac{dN_2}{dt} = -W_{21}N_2$$

When absorption and stimulated emission occur simultaneously in a system the photon flux of the incident light can increase or decrease. The change in the photon flux is a combination of the rate equations for absorption and stimulated emission. This is given by the equation:

$$dF = \sigma F(N_2 - N_1)d\tau$$

Spontaneous emission has the same characteristics as stimulated emission except that no incident light is required to cause the transition from the excited to ground state. Population in the excited state is unstable and will decay to the ground state through several processes. Most decays involve non-radiative vibrational relaxation, but some molecules will decay while emitting a photon matching the energy of the energy difference between the two states. The rate of spontaneous emission is given by:

$$\frac{dN_2}{dt} = -AN_2$$

Where A is the spontaneous emission probability which depends on the transition involved. The coefficient A is an Einstein coefficient obtained from the spontaneous emission lifetime. Since spontaneous emission is not competing with absorption, the photon flux is based solely on the rate of spontaneous emission.

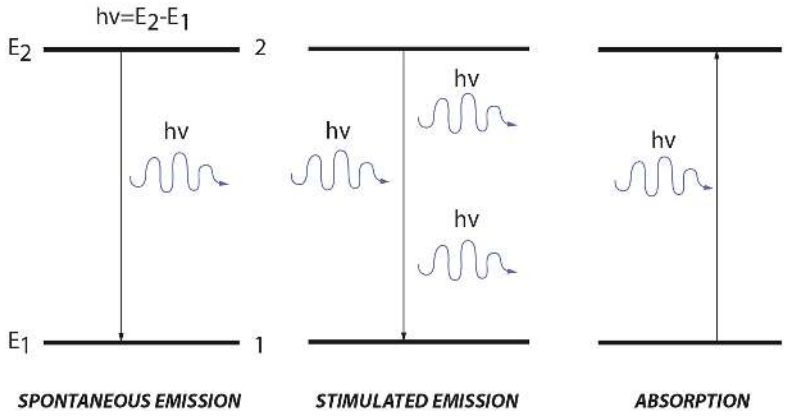


Figure 5. Diagram of spontaneous emission, stimulated emission and absorption in a two energy level system

The population ratio of a molecule or atom is found using the Boltzmann distribution and the energy of the ground state (E_1) and the excited state (E_2):

$$\frac{N_2}{N_1} = e^{\frac{-(E_2 - E_1)}{kT}}$$

Under normal conditions, the majority, if not all, of the population is in the lower energy level (E_1). This is because the energy of the excited is greater than the ground state. Normal thermal energy available (kT) is not enough to overcome the difference, and the ratio of population favors the ground state. For example, if the difference in energy between two states absorbes light at 500nm, the ratio of N_1 to N_2 is 5.1×10^{41}:1. The photon flux of the incident light is directly proportional to the difference in populations. Since the ground state has more populations, the photon flux decreases: there is more absorption occurring than stimulated emission. In order to increase the photon flux there must be more population in the excited state than in the ground state, generally known as a population inversion.

In a two level energy system it is impossible to create the population inversion needed for a laser. Instead three or four level energy systems are generally used (**Figure 5**).

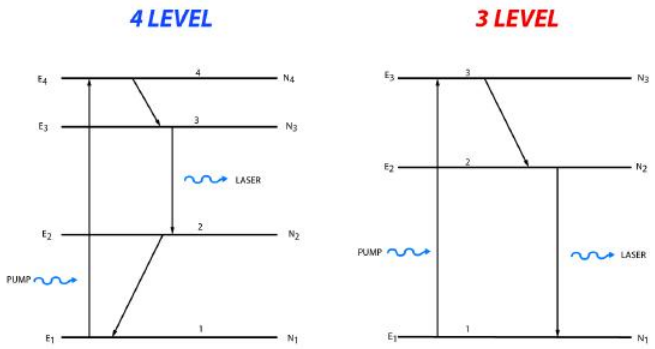


Figure 6. Three and four level energy system

Three level processes involve pumping of population from the lowest energy level to the highest, third energy state. The population can then decay down to the second energy level or back down to the first energy level. The population that makes it to the second energy level is available for stimulated emission. Light matching the energy difference between the second and first energy level will cause a stimulated emission. Four level systems follow roughly the same process except that population is moved from the lowest state to the highest fourth level. Then it decays to the third level and lasing happens when the incident light matches the energy between the third and second level. After lasing there is decay to the first level.

Pumping Process

Pumping is the movement of population from the ground state to a higher excited state. The general rate at which this is done is given by:

$$(\frac{dN_g}{dt})_p = W_p N_g$$

Where N_g is the population in the ground level and W_p is the pump rate. Pumping can be done optically, electronically, chemically (see chemical laser), using gases at high flow rates, and nuclear fission. Only optical and electrical pumping will be discussed in detail.

Optical Pumping

Optical pumping uses light to create the necessary population inversion for a laser. Usually high pressure xenon or krypton lamps are used to excite solid or liquid laser systems. The active material in the laser absorbs the light from the pump lamp, promoting the population from the ground state to the higher energy state. The material used in the laser can be continuously exposed to the pumping light which creates a continuous wave laser (CW). A pulsed laser can be created by using flashes of pumping light.

In optical pumping there are three types of efficiency: transfer, lamp radiative, and pump quantum efficiency. Transfer efficiency is the ratio of the energy created by the lamp and the power of the light emitted by the laser. The lamp radiative efficiency is the measure of how much electrical power is converted into light in the optical lamp. Pump quantum efficiency accounts for the ratio of population that decays to the correct energy level and population that decays either back to the ground state or another incorrect energy level. For example, the overall pumping rate of the first ruby laser was around 1.1%.

The average pump rate for optical pumping depends on the total efficiency of the pump (η_p), volume of the laser material (V), ground state population (N_g), power input (P), and frequency of the lasing transition (ν_0):

$$\langle W_p \rangle = \eta_p (P/(V N_g \hbar \nu_0))$$

Electrical Pumping

Electrical pumping is a much more complicated process than optical pumping. Usually used for gas and semiconducting lasers, electrical pumping uses electrical current to excite and promote the ground state population. In a simple gas laser that contains only

one species (A), current passes through the gas medium and creates electrons that collide with the gas molecules to produce excited state molecules (A^*):

$$A + e \longrightarrow A^* + e$$

During electron impact either an ion or an excited state can be created. The ability to make the excited state depends mostly on the material used in the laser and not the electrical pumping source making it difficult to describe the efficiency of the pumping. Total efficiencies have been calculated and tabulated for most active materials used in electrical pumping. Where eficiencies range from a < 0.1% N_2 gas laser to 70% for some CO_2 gas lasers.

Like the pumping rate of optical pumps, the rate of electrical pumping is found using the overall efficiency of the pump, power applied, and population of the ground state. However instead of using the frequency of the ground to upper state transition, electrical pumping uses the energy of the upper state ($\hbar\omega_p$) and the volume of the electron discharge (V):

$$\langle W_p \rangle = \eta_p (P/(V N_g \hbar \omega_p))$$

Pulsed operation

Q-Switching

The technique of Q switching allows the generation of laser pulses of short duration from a few nanoseconds to a few tens of nanoseconds and high peak power from a few megawatts to a few tens of megawatts.

Suggest we put a shutter into the laser cavity. If the shutter is closed, laser action cannot occur and the population inversion can be very high. If the shutter is opened suddenly, the stored energy will be released in a short and intense light pulse. This technique is known as Q-switching. Q here denotes the ratio of the energy stored to the energy dissipated in the cavity. This technique is used in many types of solid-stat lasers and CO_2 lasers to get a high-power pulsed output.

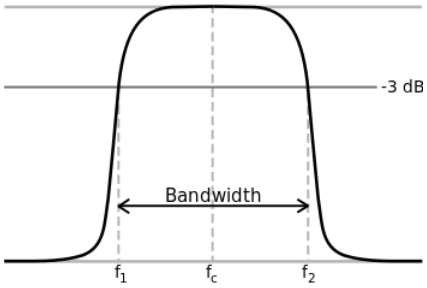


Figure 7. The bandwidth, Δf , or f1 to f2, of a damped oscillator is shown on a graph of energy versus frequency. The Q factor of the damped oscillator, or filter, is $f_c/\Delta f$. The higher the Q, the narrower and 'sharper' the peak is.

To produce high inversion required for Q-switching, four requirements must be satisfied.

1. The lifetime of the upper level must be longer than cavity buildup time.
2. The pumping flux duration must be longer than the cavity build up time.
3. The initial cavity losses must be high enough during the pumping duration to prevent oscillation occurring.
4. The cavity losses must be reduced instantaneously.

Mode-Locking

The technique of mode locking allows the generation of laser pulses of ultrashort duration from less than a picosecond to femtoseconds and very high peak, a few gigawatts.

Mode-locking is achieved by inducing the different longitudinal modes of a laser to a locked mode. When combining the electromagnetic waves modes with different frequencies and random phases, they produce a random and average output. When the modes are added in phase, they combine to produce a total amplitude and intensity output with a repeated pulse.

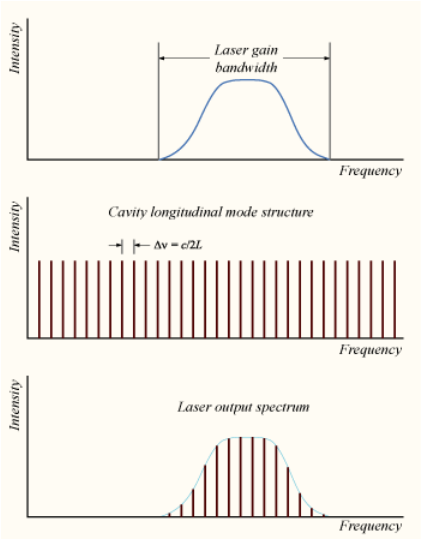


FIgure 8:Laser mode structure

Types of Lasers

There are many different types of lasers with a wide range applications, and below is a brief description of some of the main types.

Solid State Lasers

A solid-state laser is one that uses a solid active medium generally in a rod shape. Inside the active material is a dopant that acts as the light emitting source. Optical pumping is used to create population inversion of the active material. Solid-state lasers generally use stimulated emission as the mechanism for creating the high energy beam.

Ruby Laser

The ruby laser was the first operating laser and was built in 1960. It has a three-level (**Figure 6**) energy system that uses aluminum oxide with some of the aluminum atom replaced with chromium as its active material. The chromium in the aluminum oxide crystal is the active part of the laser. Electrons in the ground state of chromium absorb the incident light and become promoted to higher energy states. The short lived excited state relaxes down to a metastable state with a longer lifetime. Laser emission happens when there is relaxation from the metastable state back to the ground state.

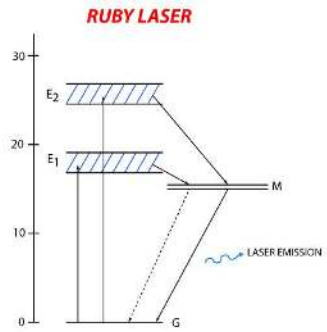


Figure 9. Schematic of Ruby laser

A xenon flash lamp emitting light at wavelengths of 6600Å and 4000Å (matching the energy needed to excite the chromium atoms). In order to create resonance of the incident light in the active material silver platting was put at both ends of the ruby rod. One end was completely covered while the other end was partially covered so lasing light could exit the system.

Nd: YAG Laser

Nd: YAG laser are the most popular type of solid state laser. The laser medium is a crystal of $Y_3Al_5O_{12}$ which are commonly called YAG, an acronym for yttrium aluminum garnet. A simplified energy-level scheme for Nd:YAG is shown in Fig. 9. The λ=1.06 μm laser transition is the strongest of the $4F_{3/2} \rightarrow 4I_{11/2}$ transitions.

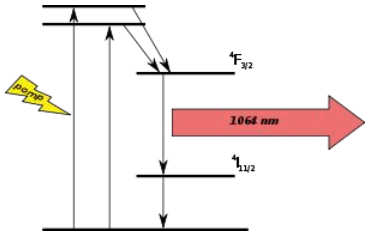


Figure 10. Simplified energy level diagram of the $^4F_{3/2}$---$4I_{11/2}$ laser transition in Nd:YAG showing the four- level nature of the system

The major application of the Nd laser is in various form of material processing: drilling, spot welding, and laser marking. Because they can be focused to a very small spot, the laser are also used in resistor trimming and in circuit mask , memory repair and also in cutting out specialized circuits. Medical applications include many types of surgeries. Many medical applications take advantage of low-loss optical fiber delivery systems that can be inserted into the body to wherever is needed. Nd lasers are also used in military applications such as range finding and target designation. High power pilsed versions are also used for X-ray spectral regions. In addition, Nd lasers are used in scientific lab as good sources for pumping dye laser and other types of lasers.

Semiconductor Laser

The semiconductor laser is another type of solid state laser that uses a semiconducting material like germanium or silicon. When the temperature of the semiconducting material is increased, electrons move from the valence band to the conducting band creating holes in the valence band (**Figure 7**). In between the conducting band and valence band is a region where there are no energy levels, called the band gap. Applying a voltage to the semiconductor causes electrons to move to the conduction band creating a population inversion. Irradiating a semiconductor with incident light matching the energy of the forbidden area causes a large transition from the conduction band to the valence band, increasing and amplifying the incident light.

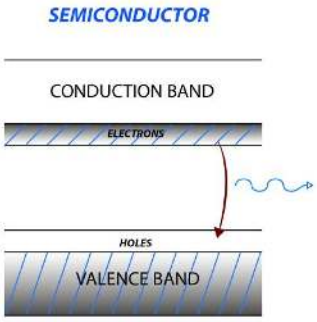


Figure 11. Schematic of semicondecor laser

Gas Lasers

A gas laser contains active material composed of a mixture of gases with similar energy states inside a small gas chamber. Electrical pumping is used to create the population inversion where one gas is excited through collisions with electrons and in turn excites the other gas through collisions.

Helium-Neon Laser

The helium-neon laser was the first gas laser. It consists of a long narrow tube that contains He and Ne gas. Mirrors are placed at both ends of the gas tube to form the resonant cavity with one of the mirrors partially reflecting the incident light. Stimulated emission of the gas mixture is carried out by first exciting the He gas to a higher energy state through electron collision with electrons from the electronic pumping source (electrical pumping). Then the excited He atoms collide with the Ne atoms transferring their energy and exciting them to a higher energy level. The Ne atoms in the higher energy level will then relax to a lower metastable energy state. Lasing occurs when there is relaxation from the metastable state to a lower energy state causing spontaneous emission. The Ne gas then returns to the ground state when it collides with the outer walls of the gas tube (**Figure 8**).

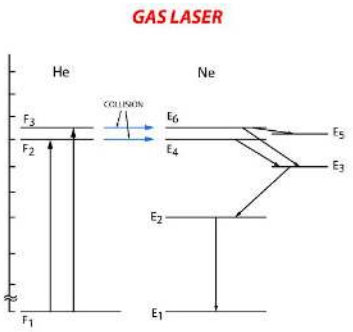


Figure 12. Schematic of gas laser

Carbon Dioxide Laser

The carbon dioxide laser is a gas laser that uses the energy difference between rotational-vibrational energy levels. Within the vibrational levels of CO_2 there are rotational sub-energy levels. A mixture of N_2 and CO_2 gas are placed inside a chamber. The N_2 atoms are excited through an electrical pumping mechanism. The excited atoms then collide with the CO_2 atoms transfer energy. This transfer of energy causes the CO_2 to go into a higher vibrational level. The excited CO_2 molecules then go through spontaneous emission when they are relaxed to lower rotational-vibrational levels increasing the signal of the incident light (**Figure 9**). Carbon dioxide lasers are extremely efficient, around 70%, and powerful compared to other gas lasers making them useful for welding and cutting.

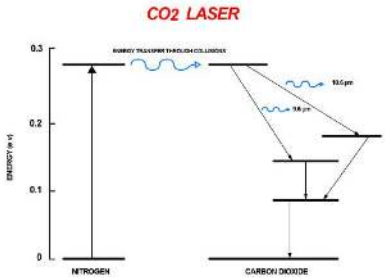


Figure 13. Schematic of carbondioxide laser

Liquid Lasers

Liquid lasers consist of a liquid active material usually composed of an organic dye compound. The most common type of liquid laser uses rhodamine 6G (**Figure 10**) dye mixed with alcohol and is excited by different types of lasers, such as an argon-ion laser or a nitrogen laser. Organic dyes are large compounds that have absorption bands in the UV or visible region with a strong intense fluorescence spectrum. The free π electrons of the dye are excited using an optical pumping source and the transition from the S_1 to the S_0 state creates the lasing light (see Jablonski diagrams). Liquids are generally used because they can easily be tuned to emit a certain wavelength by changing the resonant frequency within the cavity. Wavelengths from the visible to the infrared can be covered. There are many benefits of liquid lasers, some include that they can be cooled in a relative amount of time, they cannot be damaged unlike a solid-laser, and their production is cost-effective. The efficiency of liquid lasers is low because the lifetime of the excited state is relatively short; there are many non-radiative decay processes, and the material degrades over time. Liquid lasers tend to be used only as a pulse laser when tunability is required. Liquid lasers can be used for high-resolution spectroscopy since they are easily tuned over a wide range of wavelengths. They can also be used because they have concentrations which are manageable when dissolved in solids or other liquids.

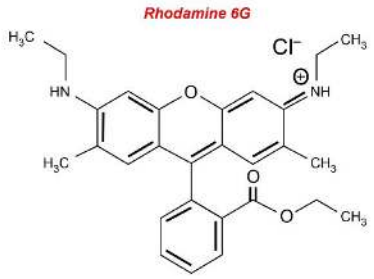


Figure 14. Rhodamine 6G molecule

Chemical Lasers

Chemical lasers are different from other lasers because the population inversion is the direct product of a chemical reaction when energy is released as a result of an exothermic reaction. Usually reactions involve gases where the energy created is used to make vibrationally excited molecules. Light used for lasing is then created from vibrational-rotational relaxation like in the CO_2 gas laser. An example of a chemical laser is the HF gas laser. Inside the gas chamber fluorine and hydrogen react to form an excited HF molecule:

$F + H_2 \rightarrow HF + H$

The excess energy from the reaction allows HF to stay in its excited state. As it relaxes, light is emitted through spontaneous emission. Deuterium can also be used in place of hydrogen. Deterium fluoride is useds for applications that require high-power. For example, MIRACL was built for military research and was known to produce 2.2 megawatts of power. The uniqueness of a chemical laser is that the power required for lasing is produced in the reaction itself.

Laser Applications

The applications of lasers are numerous and cover scientific and technological fields. In general, these applications are a direct consequence of the special characteristics of lasers. Below are a few examples of the laser applications, for a complete list please go to en.Wikipedia.org/wiki/List_of...ons_for_lasers

Lidar

Lidar is short for light detection and ranging which is an optical remote sensing technology can be used for monitoring the environment. A typical lidar system involves a transmitter of laser radiation and a receiver for the detection and analysis of backscattered light. A beam expander is usually used at transmitter to reduce divergence of the laser beam before it propagates into the atmosphere. The receiver includes a wavelength filter, a photo detector, and computers and electronics for data acquisition and analysis.

Lidar system dates back to the 1930, because of the laser, it has become one of the primary tools in atmospheric and environmental research. Other than that, Lidar has been put into various uses. In agriculture, lidar can be used to create topographic map to help farmer to decide appropriate amount of fertilizing to achieve a better crop yield. In Archaeology, lidar can be used to create a geographic information system to help archaeologists to find sites. In transportation, lidar has been used in autonomous cruise control system to prevent road accident and policemen are also using lidar speed gun to enforce the speed limit regulation.

Laser in Material Processing

The beam of a laser is usually a few millimeters in diagram. For most material processing applications, lenses are used to increase the intensity of the beam. The beam from a laser is either plane or spherical. After passing through a lens, the beam should get focused to a point. But in actual practice, diffraction effects have to be taken into consideration, the incoming will focus into a region of radius. If λ is the wavelength of the laser light, a is the radius of the beam, and f is the focal length of the lens, then the radius of the region is

$$b = \frac{\lambda f}{a}$$

If P represents the power of the laser beam, the intensity I, obtained at the focused region would be given by,

$$I = \frac{P}{\pi b^2} = \frac{Pa^2}{\pi\pi\lambda^2 f^2}$$

The high-power (P>100w) laser are widely used in material processing such as welding, drilling, cutting, surface treatment, and alloying. The main advantage of the laser beam can be summarized as follow: (1) The heating produced by the laser is less than that in conventional process. Material distortion is considerably reduced. (2) Possibility of working in inaccessible region. Any region which can be seen can be processed by a laser. (3) The process can be better controlled and easily automatized. However, against all these advantages, the disadvantages are: (1) high cost of the laser system. (2) Reliability and reproducibility problems of the laser system. (3) Safety problems.

Laser in Medicine

In field of medicine, the major use of lasers is for surgery such as laser eye surgery commonly known as LASIK. Besides that, there are also a few diagnosetic applications such as clinical use of flow microfluormeters, Doppler velocimetry to measure the blood velocity, laser fluorescence bronchoscope to detect tumors in their early phase.

For surgery, the laser beams are used instead of a conventional scalpel. The infrared beam from the CO^2 laser is strongly absorbed by water molecules in the tissue. It produces a rapid evaporation of these molecules, consequently cutting the tissue. The main advantage of laser beam surgery can be summarized as follows: (1) High precision. The incision can be made with a high precision particularly when the beam is directed by means of a microscope. (2) Possibility of operating in inaccessible region. Laser surgery can be operated in any region of the body which can be observed by means of an optical system. (4) Limited damage to blood vessel and adjacent tissue. However, the disadvantages are: (1) considerable cost. (2) Smaller velocity of the laser scalpel. (3) Reliability and safety problems associated with the laser procedure.

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Outside Links

- http://en.Wikipedia.org/wiki/Laser
- en.Wikipedia.org/wiki/List_of_laser_types
- en.Wikipedia.org/wiki/Q_factor
- en.Wikipedia.org/wiki/Mode-locking

Problems

1. Determine the free-space wavelength (λ_0) in Å, and frequency of the resonant cavity for a beam parameter q_1 that is 632,110 and q_2 that is 632,111 in a helium-neon gas laser at 1 atm. The index of refraction n is 1.00, the length of the resonant cavity is 20 cm and the wavelength region of interest is 6328Å.
2. What wavelength of light will be released by the spontaneous emission of Ne gas, where the the energy difference between the excited and ground state is 9.9 x 10^{-19} J.
3. What is the population ratio of the above question at 300K.

Answers

1. For q_1 $\lambda_0 = 6328.0125 \angstrom$Å, q_2 $\lambda_0 = 6328.0025 \angstrom$Å, and v=474 THz for both q values
2. 200 nm
3. N_2/N_1=1.9 x 10^{-105}

Contributors and Attributions

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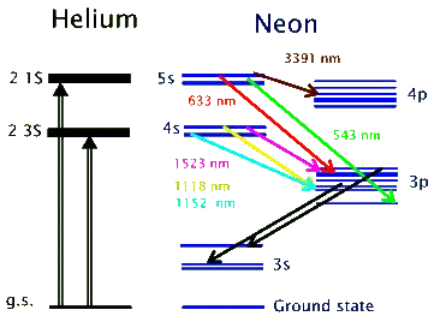
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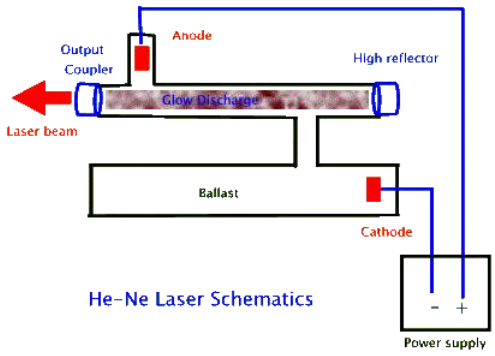
15.6: The Helium-Neon Laser

The He-Ne laser was the first continuous wave (cw) laser invented. A few months after Maiman announced his invention of the pulsed ruby laser, Ali Javan and his associates W. R. Bennet and D. R. Herriott announced their creation of a cw He-Ne laser. This gas laser is a four-level laser that use helium atoms to excite neon atoms. It is the atomic transitions in the neon that produces the laser light. The most commonly used neon transition in these lasers produces red light at 632.8 nm. But these lasers can also produce green and yellow light in the visible as well as UV and IR (Javan's first He-Ne operated in the IR at 1152.3 nm). By using highly reflective mirrors designed for one of these many possible lasing transitions, a given He-Ne's output is made to operate at a single wavelength.

He-Ne lasers typically produce a few to tens of mW (milli-Watt, or 10^{-3} W) of power. They are not sources of high power laser light. Probably one of the most important features of these lasers is that they are highly stable, both in terms of their wavelength (mode stability) and intensity of their output light (low jitter in power level). For these reasons, He-Ne lasers are often used to stabilize other lasers. They are also used in applications, such as holography, where mode stability is important. Until the mid 1990's, He-Ne lasers were the dominant type of lasers produced for low power applications - from range finding to scanning to optical transmission, to laser pointers, etc. Recently, however, other types of lasers, most notably the semiconductor lasers, seem to have won the competition because of reduced costs.

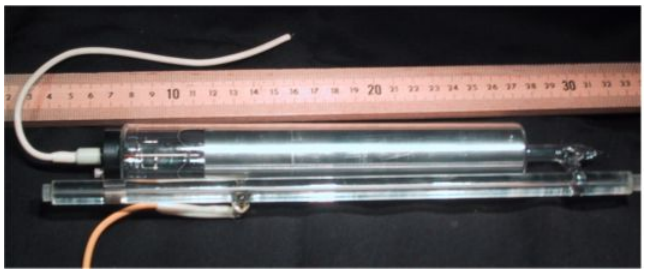


The above energy level diagram shows the two excited states of helium atom, the 2 3S and 2 1S, that get populated as a result of the electromagnetic pumping in the discharge. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way the 4s and 5s levels in neon get populated. These are the two upper lasing levels, each for a separate set of lasing transitions. Radiative decay from the 5s to the 4s levels are forbidden. So, the 4p and 3p levels serve as the lower lasing levels and rapidly decay into the metastable 3s level. In this way population inversion is easily achieved in the He-Ne. The 632.8 nm laser transition, for example, involves the 5s and 3p levels, as shown above.



In most He-Ne lasers the gas, a mixture of 5 parts helium to 1 part neon, is contained in a sealed glass tube with a narrow (2 to 3 mm diameter) bore that is connected to a larger size tube called a ballast, as shown above. Typically the laser's optical cavity mirrors, the high reflector and the output coupler, form the two sealing caps for the narrow bore tube. High voltage electrodes create a narrow electric discharge along the length of this tube, which then leads to the narrow beam of laser light. The function of

the ballast is to maintain the desired gas mixture. Since some of the atoms may get imbedded in the glass and/or the electrodes as they accelerate within the discharge, in the absence of a ballast the tube would not last very long. To further prolong tube lifetime some of these lasers also use "getters", often metals such as titanium, that absorb impurities in the gas.



Above photograph shows a commercial He-Ne tube. The thicker cylinder closest to the meter-stick (shown for scale) is the ballast. The thinner tube houses the resonant cavity where the lasing occurs. Notice the two mirrors that seal the two ends of the bore. For mode stability reasons, these mirrors are concave; they serve as the output coupler and the high reflector.

A typical commercially available He-Ne produces about a few mW of 632.8 nm light with a beam width of a few millimeters at an overall efficiency of near 0.1%. This means that for every 1 Watt of input power from the power supply, 1 mW of laser light is produced. Still, because of their long operating lifetime of 20,000 hours or more and their relatively low manufacturing cost, He-Ne lasers are among the most popular gas lasers.

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15.7: High-Resolution Laser Spectroscopy

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{15.7.1}$$

You can see from Equation 15.7.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 15.7.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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15.8: Photochemical Dynamics

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CHAPTER OVERVIEW

16: The Properties of Gases

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

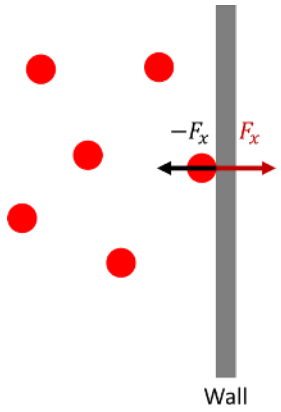
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16.1: All Dilute Gases Behave Ideally
16.2: van der Waals and Redlich-Kwong Equations
16.3: A Cubic Equation of State
16.4: The Law of Corresponding States
16.5: The Second Virial Coefficient
16.6: The Repulsive Term in the Lennard-Jones Potential
16.7: Van der Waals Constants in Terms of Molecular Parameters
16.E: The Properties of Gases (Exercises)

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16.1: All Dilute Gases Behave Ideally

Ideal gases have no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of length a and that two of the walls are located at $x = 0$ and at $x = a$. Thus, a particle moving along the x direction will eventually collide with one of these walls and will exert a force on the wall when it strikes it, which we will denote as F_x. Since every action has an equal and opposite reaction, the wall exerts a force $-F_x$ on the particle.



According to Newton's second law, the force $-F_x$ on the particle in this direction gives rise to an acceleration via

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{16.1.1}$$

Here, t represents the time interval between collisions with the same wall of the box. In an elastic collision, all that happens to the velocity is that it changes sign. Thus, if v_x is the velocity in the x direction before the collision, then $-v_x$ is the velocity after, and $\Delta v_x = -v_x - v_x = -2v_x$, so that

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{16.1.2}$$

Since the particles have no forces acting upon them, except for when they collide iwht the wall container, the particles move at constant speed. Thus, a collision between a particle and, say, the wall at $x = 0$ will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at $x = a$ first, bounce off that wall, and then return to the wall at $x = 0$. The total distance in the x direction traversed is $2a$, and since the speed in the x direction is always v_x, the interval $\Delta t = \frac{2a}{v_x}$. Consequently, the force is:

$$-F_x = -\frac{mv_x^2}{a} \tag{16.1.3}$$

Thus, the force that the particle exerts on the wall is:

$$F_x = \frac{mv_x^2}{a} \tag{16.1.4}$$

The mechanical definition of pressure is the average force over area:

$$P = \frac{\langle F \rangle}{A} \tag{16.1.5}$$

where $\langle F \rangle$ is the average force exerted by all N particles on a wall of the box of area A. Here $A = a^2$. If we use the wall at $x = 0$ we have been considering, then

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{16.1.6}$$

because we have N particles hitting the wall. Hence:

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{16.1.7}$$

from our study of the Maxwell-Boltzmann distribution, we found that:

$$\langle v_x^2 \rangle = \frac{k_B T}{m} \tag{16.1.8}$$

Hence, since $a^3 = V$:

$$\begin{aligned} P &= \frac{Nk_B T}{V} \\ &= \frac{nRT}{V} \end{aligned}$$

which is the ideal gas law. It relates the pressure, volume, and temperature of an ideal gas and is referred to as an equation of state. An equation of state is a relation between variables and describes the state of matter under a set of given physical conditions. One way to visualize any equation of state is to plot *isotherms*, which are graphs of P vs. V at fixed values of T . For the ideal-gas equation of state, some of the isotherms are shown in the figure below (left panel): If we plot P vs. T at fixed volume (called the *isochores*), we obtain the plot in the right panel. What is important to note, here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of "ideal liquid". In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

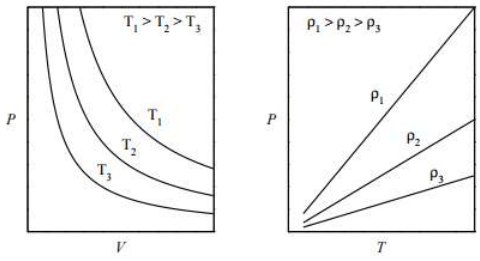


Figure 16.1.1 : (Left) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (Right) Pressure vs. temperature for different densities $\rho = N/V$.

We can rearrange the ideal gas equation of state to put all the constants and variables on one side:

$$\frac{PV}{nRT} = 1 = Z \tag{16.1.9}$$

Z is called the *compressibility* of the gas. In an ideal gas, if we compress the gas by increasing P , the volume decreases as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.

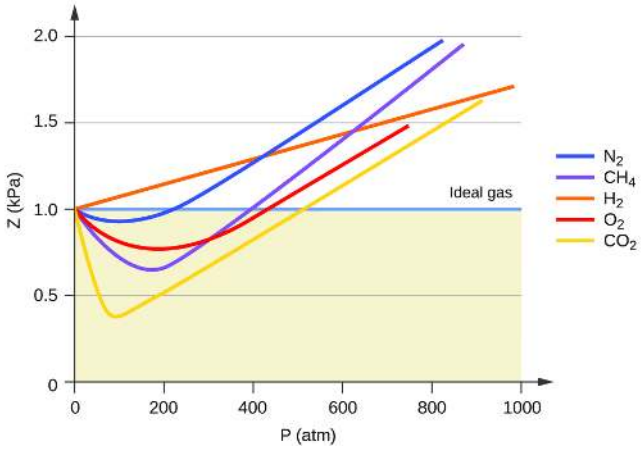


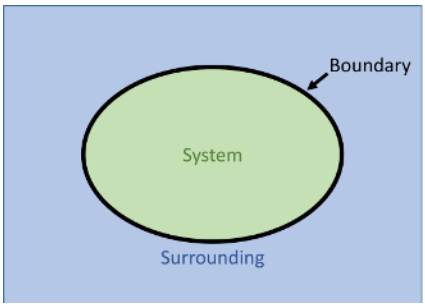
Figure 16.1.2 : A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. from Openstax (CC-BY)

Figure 16.1.2 shows a plot of Z vs. P for several real gases and for an ideal gas. The plot shows that for sufficiently low pressures (hence, low densities), each gas approaches ideal-gas behavior, as expected.

Extensive and Intensive Properties in Thermodynamics

Before we discuss ensembles and how we construct them, we need to introduce an important distinction between different types of thermodynamic properties that are used to characterize the ensemble. This distinction is *extensive* and *intensive* properties.

Thermodynamics always divides the universe into a *system* and its *surroundings* with a *boundary* between them. The unity of all three of these is the thermodynamic *universe*.



Now suppose we allow the system to grow in such a way that both the number of particles and the volume grow with the ratio N/V remaining constant. Any property that increases as we grow the system in this way is called an *extensive* property. Any property that remains the same as we grow the system in this way is called *intensive*.

The ideal gas equation of state can be written in an extensive form:

$$\begin{aligned} PV &= nRT \\ P\bar{V} &= RT \\ P &= \rho RT \end{aligned}$$

where $\bar{V} = V/n$ is called the molar volume and $\rho = N/V$ is called density. Unlike V , which increases as the number of moles increases (an *extensive* quantity, $\bar{V}$ and ρ do not exhibit this dependence and, therefore, are called *intensive*. Compressibility can also be written in an intensive form:

$$\begin{aligned} Z &= \frac{PV}{nRT} \\ &= \frac{P\bar{V}}{RT} \\ &= \frac{P}{\rho RT} \end{aligned}$$

Some examples of intensive and extensive properties include:

- Extensive: number of particles (N), moles (n), volume (V), mass (m), energy, free energy
- Intensive: pressure (P), density (ρ), molar heat capacity (C), temperature (T)

Contributors and Attributions

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16.2: van der Waals and Redlich-Kwong Equations

The ideal gas law is valid for low pressures, where the finite volume of particles and intermolecular attractions do not have a large impact. At higher pressures, we must account for these factors. The van der Waals and Redlich-Kwong equations of states are equations of state that attempt to account for real gas behavior by modifying the ideal gas law with two additional parameters.

The Van der Waals Equation of State

The van der Waals Equation of State is an equation relating the density of gases and liquids to the pressure, volume, and temperature conditions (i.e., it is a thermodynamic equation of state). It can be viewed as an adjustment to the ideal gas law that takes into account the non-zero volume of gas molecules and inter-particle attraction using correction terms a and b. It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for this work. The van der Waals equation of state is:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{16.2.1}$$

Equation 16.2.1 can also be rewritten as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

If the correction terms a and b go to zero, the equation reduces to the ideal gas equation of state:

$$PV = nRT$$

Let's first look first at the correction term b, which represents the volumes of the particles and assumes a hard-wall potential, $u_o(r)$. This potential energy term describes a system of hard sphere “billiard balls” of diameter σ. Figure 16.2.1 shows two of these billiard ball type particles at the point of contact (i.e, the distance of closest approach). At this point, they undergo a collision and separate, so they cannot be closer than that distance.

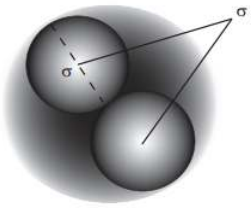


Figure 16.2.1 : Two hard spheres of diameter σ at closest contact. The distance between their centers is also σ. A sphere of radius σ just containing the two particles is shown in cross-section.

The distance between their centers is also σ. Because of this distance of closest approach, the total volume available to the particles is not the volume of the container, V, but some volume less than V. This reduction in volume can be calculated. Figure 16.2.1 shows a shaded sphere that just contains the pair of billiard ball particles. The volume of this sphere is the volume excluded from any two particles. The radius of the sphere is σ and the excluded volume for the two particles is $4\pi\sigma^3/3$, which is the volume of the shaded sphere. From this, we see that the excluded volume for any *one* particle is just half of this or $\frac{2}{3}\pi\sigma^3$. The excluded volume for a mole of such particles is the parameter b:

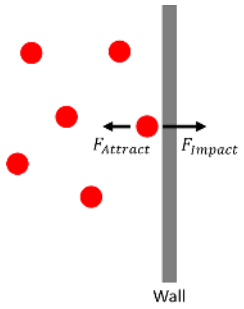
$$b = \frac{2}{3}\pi\sigma^3 N_0$$

Given n moles of gas, the total excluded volume is then nb, so that the total *available* volume is $V - nb$.

Let's turn our attention the a, which represents the intermolecular attractions of the particles. Molecular attractions tend to make the P exerted by the gas less than that predicted by the ideal gas law at low pressures. P is force over area:

$$P = \frac{F}{A}$$

Pressure is proportion to the net force on the wall of the container:



The net force is the force of the molecules impacting the container wall minus the intermolecular attraction of the molecules:

$$\bar{F}_{Net} = \bar{F}_{Impact} - \bar{F}_{Attract}$$

Therefore, the pressure will be less for the real gas than the ideal gas. We can add a correction term to pressure to account for intermolecular attractions:

$$P_{VDW} = P_{Real} + a\,(?)$$

V does influence the amount of intermolecular attraction because P is reduced as V is increased:

$$P \propto \frac{1}{V}$$

And pressure is proportional to the number of attractive interactions:

# of molecular interactions $\propto P^2$

# of molecular interactions $\propto \frac{1}{V^2}$

We now have an expression for the van der Waals P:

$$P = P_{Real} + \frac{an^2}{V^2}$$

The constants a and b depend on the substance. Some typical values are:[1]

Molecule	a $\left(\frac{L^2 \cdot bar}{mol^2}\right)$	b $\left(\frac{L}{mole}\right)$
H_2O	5.536	0.03049
N_2	1.43	0.03913
CH_4	2.283	0.04278
C_2H_6	5.562	0.0638

1. *R. C. Weast (1972). Handbook of Chemistry and Physics 53rd Edition. Chemical Rubber Pub.*

Redlich-Kwong Equation of State

The van der Waals Equation of State had to wait almost 100 years before a real, successful improvement was introduced to it. This progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter a proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter b for co-volume. It makes a lot of sense that b would not be modified by temperature, because it represents the *volume* of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature). The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949.

The Redlich–Kwong equation of state is an empirical, algebraic equation that relates temperature, pressure, and volume of gases. It is generally more accurate than the van der Waals and the ideal gas equations of state at temperatures above the critical temperature. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949, who showed that a simple two-parameter

equation of state could well reflect reality in many situations. Redlich and Kwong revised the van der Waals Equation of State (Equation 16.2.1) and proposed the following expressions:

$$\left(P+\frac{a}{\sqrt{T}\bar{V}(\bar{V}+b)}\right)(\bar{V}-b)=RT \tag{16.2.2}$$

The fundamental change they introduced was to the functional form of $\partial P_{\text{attraction}}$. Additionally, they introduced the co-volume b into the denominator of this functional form. The important concept here is that the attraction parameter a of van der Waals needed to be made a function of temperature to do a better job of quantitatively matching experimental data. This was a realization that van der Waals had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong equation.

We know what follows at this point. To come up with an expression for a and b of Equation 16.2.2, we apply the criticality conditions to this equation of state. As we recall, imposing the criticality conditions allows us to relate the coefficients a and b to the critical properties (P_c, T_c) of the substance. Once we have done that, we obtain the definition of a and b for the Redlich-Kwong equation of state:

$$a=0.42780\frac{R^2T_c^{2.5}}{P_c} \tag{16.2.3}$$

$$b=0.086640\frac{RT_c}{P_c} \tag{16.2.4}$$

The Redlich-Kwong equation of state radically improved, in a quantitative sense, the predictions of the van der Waals equation of state. We now recall that van der Waals-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation 16.2.2 into:

$$\bar{v}^3-\left(\frac{RT}{P}\right)\bar{v}^2+\frac{1}{P}\left(\frac{1}{T^{0.5}}-bRT-Pb^2\right)\bar{v}-\frac{ab}{PT^{0.5}}=0 \tag{16.2.5}$$

and, by defining the following parameters:

$$A=\frac{aP}{R^2T^{2.5}} \tag{16.2.6}$$

$$B=\frac{bP}{RT} \tag{16.2.7}$$

and introducing the compressibility factor definition:

$$Z=\frac{P\bar{v}}{RT}$$

we get:

$$Z^3-Z^2+(A-B-B^2)Z-AB=0 \tag{16.2.8}$$

We may also verify the two-parameter corresponding state theory by introducing Equations 16.2.3, 16.2.4, and 16.2.5 into Equation 16.2.8:

$$Z^3-Z^2+\frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}}-0.08664-0.007506\frac{P_r}{T_r}\right)Z-0.03704\frac{P_r^2}{T_r^{3.5}}=0 \tag{16.2.9}$$

Where:

$$P_r=\frac{P}{P_c}$$

$$T_r=\frac{T}{T_c}$$

P_r and T_r are the pressure and temperature at the reduced state. See Section 16.4 for more information on reduced states. In Equation 16.2.9, we can observe the same thing that we saw with the van der Waals equation of state: gases at corresponding states

have the same properties. Equation 16.2.9 is particularly clear about it: any two different gases at the same P_r, T_r condition have the same compressibility factor.

Just as any other cubic equation of state, Equations 16.2.2 through 16.2.9, as they stand, are to be applied to pure substances. For mixtures, however, we apply *the same equation*, but we impose certain mixing rules to obtain a and b, which are functions of the properties of the pure components. Strictly speaking, we create a new "pseudo" pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that van der Waals proposed for his eqution of state:

$$a_m = \sum_i \sum_j y_i y_j a_{ij}$$

with

$$a_{ij} = \sqrt{a_i a_j}$$

and

$$b_m = \sum_i y_i b_i$$

Naturally, Redlich and Kwong did not have the last word on possible improvements to the van der Waals equation of state. The Redlich-Kwong equation of state, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the Redlich-Kwong equation of state. After more than two decades, a modified Redlich-Kwong equation of state with very good potential was developed.

Contributors and Attributions

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16.3: A Cubic Equation of State

Isotherms

Isotherms are plots of the pressure of a gas as a function of volume at a fixed constant temperature. The isotherms for an ideal gas are hypberbolas:

$$P = \frac{RT}{\bar{V}}$$

where $\bar{V}$ is the molar volume V/n. We know that at sufficiently low temperatures, any real gas, when compressed, must undergo a transition from gas to liquid. The signature of such a transition is a discontinuous change in the volume, signifying the condensation of the gas into a liquid that occupies a significantly lower volume.

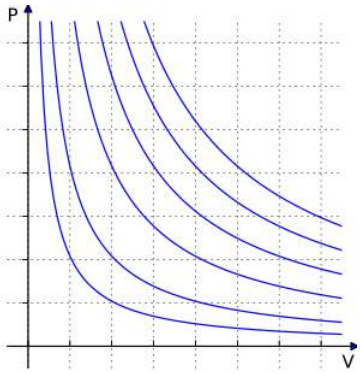


Figure 16.3.1 : Ideal gas isotherms for one mole of the gas and at select temperatures. (public domain).

CO_2 isotherms for the van der Waals Equation of state are shown in Figure 16.3.2 . At sufficiently high temperatures, the isotherms approach those of an ideal gas. At lower temperatures, the fluid obeys approximately the ideal gas law $PV = nRT$ at large volumes when the pressures are low. If we decrease the volume (go to the left in the figure along an isotherm), the pressure rises. Consider the (blue) isotherm of 10 °C, which is below the critical temperature. Decrease the volume until we reach the point B, where condensation (formation of liquid CO_2) starts. At this point the van der Waals curve is no longer physical (excluding the possibility of the occurrence of an oversaturated, metastable gas) because P and V increase together. It should be clear that many approximations and assumptions go into the derivation of the van der Waals equation so that some of the important physics is missing from the model. Hence, we should not be surprised if the van der Waals equation has some unphysical behavior buried in it. In reality, the pressure stays constant between the region A and B and the real physical behavior is given by the dashed blue line, called the *tie line*. This lines represents the gas-liquid coexistence and the pressure is equal to the vapor pressure of the liquid.

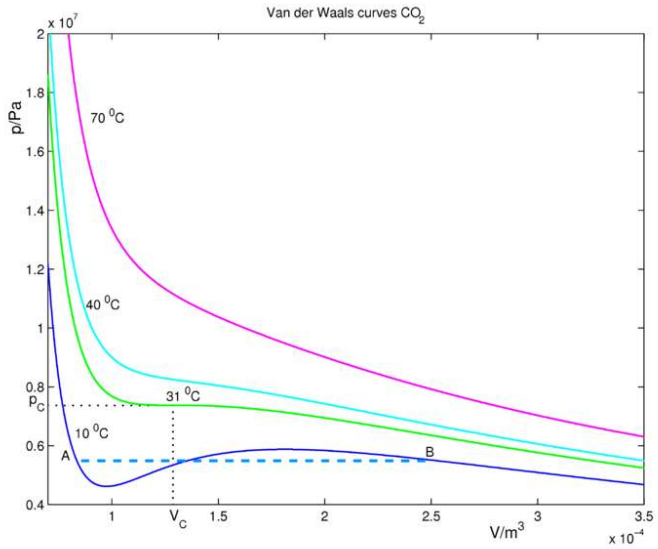


Figure 16.3.2 : Different isotherms (curves of constant temperature) of the van der Waals equation of state using parameters a and b computed for carbon dioxide. The dashed line from A to B is drawn in accordance with Maxwell's equal area rule. The carbon dioxide molecule (CO_2) has p_C = 7.37 MPa and T_C = 304.1 K = 31 ˚C , which gives a = 0.366 m^6 Pa and b = 42.9 10^{-6} m^3. The critical pressure is at 73.7 bar = 7370 kPa.

The tie line must be added in *ad hoc* by drawing a horizontal line through the isotherm (Figure 16.3.2). The vertical position of the line is chosen so that the area above the line (between the line and the isotherm) and below the line (again between the line and the isotherm) is exactly the same. This is known as *Maxwell's construction*. In this way, we entirely remove the artifact of the unphysical increase of P with V when we compute the compressional work on the gas from $\int P(V)\,dV$, to be discussed in our section on thermodynamics. Although the van der Waals curves have regions where they are not physical, the equation for these curves, derived by van der Waals in 1873, was a great scientific achievement.

Note

Even today it is not possible to give a *single* equation that describes correctly the gas-liquid phase transition.

Critical Point

Looking to the left of point A on the 10 °C isotherm (blue curve), the system is in the liquid state. Increasing the volume to point A leads to a rapid drop in the pressure of the system because the compressibility of a liquid is considerable smaller than that of a gas. The system is still in the liquid state at point A, but as we increase the volume further, we enter the gas-liquid coexistence line and the liquid begins to transition to gas. As we move along this line to the right, there is less liquid and more gas in the system until we reach point B, at which point the system will be completely in the gas phase. The areas, bounded by the 10 °C isotherm (blue curve) below and above the coexistence line are equal. Any further increase in the volume will lead to an expansion of the gas.There is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. If one follows the 31 °C isotherm (green curve in Figure 16.3.2) of critical temperature, the volume discontinuity captured by the tie line is shrunken down to a single point (so that there is no possibility of an increase of P with V!). This point is called the critical point and it exists at only one temperature, called the **critical temperature**, denoted T_c. The critical isotherm at the critical temperature corresponds to the highest possible temperature at which a gas-liquid transition can occur. Isotherms at higher temperatures have no liquid-gas phase transitions. Along those isotherms, the higher pressure fluid, called a supercritical fluid, resembles a liquid, while at lower pressures the fluid is more gas-like.

The critical point exists at an inflection where the first and second derivatives of P with respect to V are zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Substituting the van der Waals equation into these two conditions, we find the following:

$$-\frac{nRT_c}{(V_c-nb)^2}+\frac{2an^2}{V_c^3}=0$$
$$\frac{2nRT_c}{(V_c-nb)^3}-\frac{6an^2}{V_c^4}=0$$

Hence, we have two equations in two unknowns V_c and T_c for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure, P_c. To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

$$\begin{aligned}\frac{V_c-nb}{2}&=\frac{V_c}{3}\\ 3V_c-3nb&=2V_c\\ V_c&=3nb\end{aligned}$$

This is the **critical volume**. Now use either of the two conditions to obtain the critical temperature, T_c. If we use the first one, we find:

$$\begin{aligned}\frac{nRT_c}{(V_c-nb)^2}&=\frac{2an^2}{V_c^3}\\ \frac{nRT_c}{(3nb-nb)^2}&=\frac{2an^2}{(3nb)^3}\\ \frac{nRT_c}{4n^2b^2}&=\frac{2an^2}{27n^3b^3}\\ RT_c&=\frac{8a}{27b}\end{aligned}$$

Finally, plugging the critical temperature and volume into the van der Waals equation, we obtain the critical pressure:

$$\begin{aligned}P_c&=\frac{nRT_c}{V_c-nb}-\frac{an^2}{V_c^2}\\ &=\frac{8an/27b}{3nb-nb}-\frac{an^2}{(3nb)^2}\\ &=\frac{a}{27b^2}\end{aligned}$$

It comes as no surprise that cubic equations of state like the van der Waals (and Redlich-Kwong) equations of state yield three different roots for volume and compressibility factor. This is simply because they are algebraic equations, and any nth order algebraic equation will always yield “n” roots. However, those “n” roots are not required to be distinct, and that is not all: they are not required be real numbers, either. A quadratic expression (n = 2) may have zero real roots (e.g., $x^2+1=0$); this is because those roots are complex numbers. In the case of cubic expressions (n = 3), we will either have one or three real roots; this is because complex roots always show up in pairs (i.e., once you have a complex root, its conjugate must also be a solution). In our case, and because we are dealing with physical quantities (densities, volumes, compressibility factors), only real roots are of interest. More specifically, we look for real, positive roots such that $\bar{V}>b$ in the case of molar volume and $Z>\frac{Pb}{RT}$ in the case of compressibility factor.

In a cubic equation of state, the possibility of three real roots is restricted to the case of sub-critical conditions ($T<T_c$), because the S-shaped behavior, which represents the vapor-liquid transition, takes place only at temperatures below critical. This restriction is mathematically imposed by the criticality conditions. Anywhere else, beyond the S-shaped curve, we will only get one real root of the type $\bar{V}>b$. Figure 16.3.3 illustrates this point.

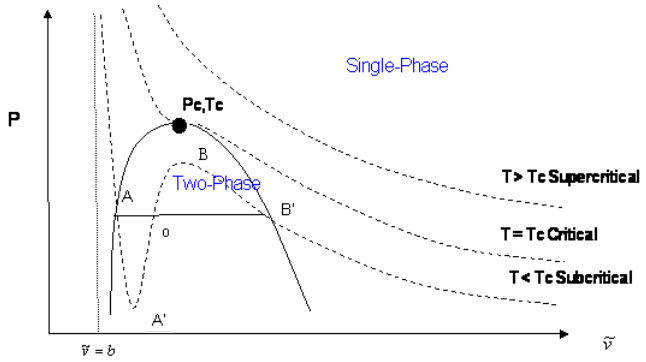


Figure 16.3.3 : Multiple Roots in Cubic EOS

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transitions from gas to liquid will occur. If we draw a curve through the isotherms joining all points of these isotherms at which the tie lines begin, continue the curve up to the critical isotherm, and down the other side where the tie lines end, this curve reaches a maximum at the critical point. The region inside this curve is when the gas and liquid phases coexist.

Let us summarize the three cases presented in Figure 16.3.3 :

1. Supercritical isotherms ($T > T_c$): At temperatures beyond critical, the cubic equation will have only one real root (the other two are imaginary complex conjugates). In this case, there is no ambiguity in the assignment of the volume root since we have single-phase conditions. The occurrence of a unique real root remains valid at any pressure: any horizontal (isobaric) line cuts the supercritical isotherm just once in Figure 16.3.3 .
2. Critical isotherm ($T = T_c$): At the critical point ($P = P_c$), vapor and liquid properties are the same. Consequently, the cubic equation predicts three real and equal roots at this special and particular point. However, for any other pressure along the critical isotherm ($P < P_c$ or $P > P_c$,) the cubic equation gives a unique real root with two complex conjugates.
3. Subcritical isotherm ($T < T_c$): Predictions for pressures within the pressure range for metastability ($P'_A < P < P'_B$) or for the saturation condition ($P = P^{sat}$) will always yield three real, different roots. In fact, this is the only region where an isobar cuts the same isotherm more than once. The smallest root is taken as the specific volume of the liquid phase; the largest is the specific volume of the vapor phase; the intermediate root is not computed as it is physically meaningless. However, do not get carried away. Subcritical conditions will not always yield three real roots of the type $\bar{\nu} > b$. If the pressure is higher than the maximum of the S-shaped curve, P_B, we will only have one (liquid) real root that satisfies $\bar{\nu} > b$. By the same token, pressures between $0 < P < P'_A$ yield only one (vapor) root. In the case of P'_A being a negative number, three real roots are to be found even for very low pressures when the ideal gas law applies. The largest root is always the correct choice for the gas phase molar volume of pure components.

Most of these considerations apply to the cubic equation of state in Z (compressibility factor). The most common graphical representation of compressibility factor is the well-known chart of Standing and Katz, where compressibility, Z, is plotted against pressure (Figure 16.3.4). Standing and Katz presented their chart for the compressibility factor of sweet natural gases in 1942. This chart was based on experimental data. Graphical determination of properties was widespread until the advent of computers, and thus the Standing and Katz Z-chart became very popular in the natural gas industry. Typical Standing and Katz charts are given for high temperature conditions ($T > T_c$ or $T_r > 1$).

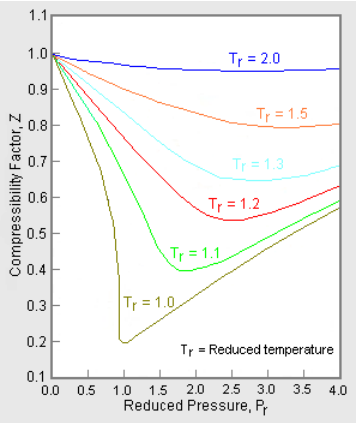


Figure 16.3.4 : Compressibility Factor versus Pressure

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16.4: The Law of Corresponding States

van der Waals assumed that all real gases at corresponding states should behave similarly. The corresponding state that van der Waals chose to use is called the reduced state, which is based on the deviation of the conditions of a substance from its own critical conditions. We can define reduced quantities:

$$P_r = \frac{P}{P_c}$$

$$V_r = \frac{V}{V_c}$$

$$T_r = \frac{T}{T_c}$$

By substitution into the van der Waals equation we find:

$$\left(P_r + \frac{3}{\bar{V}_r^2}\right)\left(\bar{V}_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{16.4.1}$$

Which means the critical parameters for a gas can be expressed in terms of a and b parameters:

$$V_c = 3b$$

$$P_c = \frac{a}{27b^2}$$

and:

$$T_c = \frac{8a}{27bR}$$

The formation of the van de Waal's equation of state in terms of the critical parameters in Equation 16.4.1 is a universal equation for all gases. Although the actual pressures and volumes may differ, two gases are said to be in corresponding states if their reduced pressure, volume, and temperature are the same. What it says is that the behavior of all gases (and liquids!!) is pretty much the same, except for a scaling factor that is related to the critical point of the substance. The compressibility value (Z) of 3/8 at the critical point for the van der Waals equation is actually not in such good agreement with measurement. This is why the more complicated Redlich-Kwong and Peng-Robertson expressions are better, although the idea is the same. Hence, all one needs to know to describe any fluid's behavior is its critical point. For example, argon behaves much the same at 300 K as ethane does at 600 K because these temperatures correspond to twice their respective critical temperatures (150.72 K and 305.4 K, respectively) so $T_r = 2.0$.

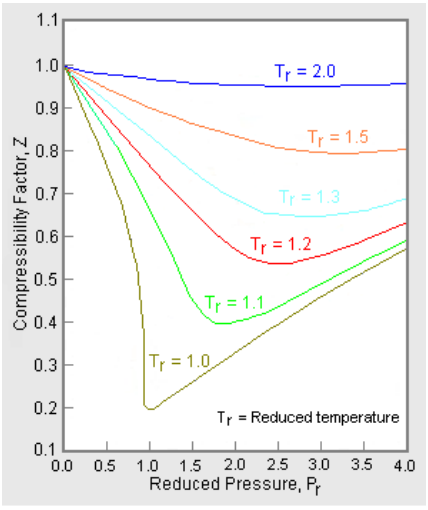


Figure 16.4.1 : Example of a generalized compressibility factor graph (Public domain; Milton Beychok)

We can rewrite the universal expression for compressibility Z using reduced variables and plot measured values of Z versus the reduced pressure, P_r (see Figure 16.4.1). As you can see, very different gases/liquids like nitrogen and water can be made to coincide if their properties are plotted relative to there critical points rather than in absolute terms. The compressibility factor Z can also be cast into the form of corresponding states showing that Z also can be expressed as a universal function of V_r and T_r or any other two reduced quantities:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

Van der Waals did not stop here. He went on to describe the root cause of condensation of gases into liquids at lower temperatures: the attractive interactions between the molecules.

Contributors and Attributions

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16.5: The Second Virial Coefficient

The second virial coefficient describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules, and so on and so forth.

Introduction

As the density is increased the interactions between gas molecules become non-negligible. Deviations from the ideal gas law have been described in a large number of equations of state. The *virial equation of state* expresses the deviation from ideality in terms of a power series in the density:

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \ldots$$

- $B_2(T)$ is the second virial coefficient,
- $B_3(T)$ is called the third virial coefficient, etc.

The j[th] virial coefficient can be calculated in terms of the interaction of j molecules in a volume V. The second and third virial coefficients give most of the deviation from ideal (P/rkT) up to 100 atm.

The **second virial coefficient** is usually written as B or as B_2. The second virial coefficient represents the initial departure from ideal-gas behavior. The second virial coefficient, in three dimensions, is given by:

$$B_2(T) = -\frac{1}{2}\int \left(\exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T} \right) - 1 \right) 4\pi r^2 dr$$

where $\Phi_{12}(\mathbf{r})$ is the intermolecular pair potential, T is the temperature, and k_B is the Boltzmann constant. Notice that the expression within the parenthesis of the integral is the *Mayer f-function*. In practice, the integral is often *very hard* to integrate analytically for anything other than, say, the hard sphere model, thus one numerically evaluates:

$$B_2(T) = -\frac{1}{2}\int \left(\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T} \right) \right\rangle - 1 \right) 4\pi r^2 dr$$

calculating:

$$\left\langle \exp\left(-\frac{\Phi_{12}(\mathbf{r})}{k_B T} \right) \right\rangle$$

for each r using the numerical integration scheme proposed by Harold Conroy [1][2].

Calculation of virial coefficients

The configuration integrals for Z_1, Z_2, and Z_3 are:

- $Z_1 = \int dr_1 = V$
- $Z_2 = \int e^{-U_2/kT} dr_1\ dr_2$
- $Z_3 = \int e^{-U_3/kT} dr_1\ dr_2\ dr_3$

The series method allows the calculation of a number of virial coefficients. Recall that the second and third virial coefficient can account for the properties of gases up to hundreds of atmospheres. We will discuss the calculation of the second virial coefficient for a monatomic gas to illustrate the procedure. To calculate $B_2(T)$ we need U_2. For monatomic particles it is reasonable to assume that the potential depends only on the separation of the two particles so $U_2 = u(r_{12})$, where $r_{12} = |r_2 - r_1|$. Using a change of variables we can write this integral $r_{12} = r_2 - r_1$ and after integration over r_1 we can transform variables from dr_{12} to $4\pi r^2 dr$. The result is:

$$B_2(T) = -2\pi \int [e^{-\beta u(r)} - 1] r^2\ dr$$

This expression can be used to obtain parameters from experiment. The second virial coefficient is tabulated for a number of gases. For a hard-sphere potential there is an infinite repulsive wall at a particle radius σ. There is no attractive part.

$$B_2(T) = -2\pi \int_0^\sigma [-1] r^2 \, dr$$

$$= \frac{2\pi\sigma^3}{3}$$

The Lennard-Jones potential cannot be calculated analytically, but the integral can be computed numerically. The second virial coefficient was a useful starting point for obtaining Lennard-Jones parameters that were used in simulations.

Isihara-Hadwiger Formula

The Isihara-Hadwiger formula was discovered simultaneously and independently by Isihara and the Swiss mathematician Hadwiger in 1950. The second virial coefficient for any hard convex body is given by the exact relation:

$$B_2 = RS + V$$

or:

$$\frac{B_2}{V} = 1 + 3\alpha$$

where:

$$\alpha = \frac{RS}{3V}$$

where V is the volume, S, the surface area, and R the mean radius of curvature.

Hard spheres

For the hard sphere model one has:[9]

$$B_2(T) = -\frac{1}{2} \int_0^\sigma \left(\langle 0 \rangle - 1 \right) 4\pi r^2 dr$$

leading to

$$B_2 = \frac{2\pi\sigma^3}{3}$$

Note that B_2 for the hard sphere is independent of temperature.

Van der Waals equation of state

For the Van der Waals equation of state one has:

$$B_2(T) = b - \frac{a}{RT}$$

Excluded volume

The second virial coefficient can be computed from the expression:

$$B_2 = \frac{1}{2} \iint v_{\text{excluded}}(\Omega, \Omega') f(\Omega) f(\Omega') \, \mathrm{d}\Omega \mathrm{d}\Omega'$$

where v_{excluded} is the excluded volume.

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Related reading

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- G. A. Vliegenthart and H. N. W. Lekkerkerker "Predicting the gas–liquid critical point from the second virial coefficient", Journal of Chemical Physics **112** pp. 5364-5369 (2000)

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16.6: The Repulsive Term in the Lennard-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

Introduction

Imagine two rubber balls separated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. To bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

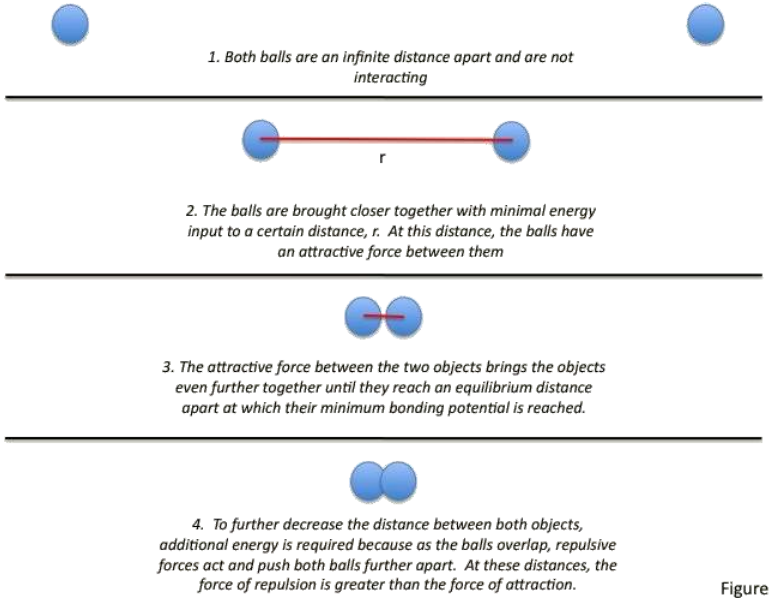


Figure A

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by the **Lennard-Jones potential**.

The Lennard-Jones Potential

The Lennard-Jones model consists of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{16.6.1}$$

or is sometimes expressed as:

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} \tag{16.6.2}$$

where

- V is the intermolecular potential between the two atoms or molecules.
- ϵ is the well depth and a measure of how strongly the two particles attract each other.
- σ is the distance at which the intermolecular potential between the two particles is zero (Figure $16.6.1$). σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the *van der Waals radius*. It is equal to one-half of the

internuclear distance between nonbonding particles.

- r is the distance of separation between both particles (measured from the center of one particle to the center of the other particle).
- $A = 4\epsilon\sigma^{12}$, $B = 4\epsilon\sigma^{6}$
- Minimum value of $\Phi_{12}(r)$ at $r = r_{min}$.

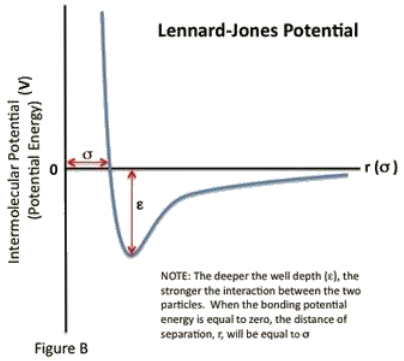


Figure 16.6.1: The Lennard-Jones potential describes both the attraction and repulsion between nonionic particles. The first part of the equation, the short-ranged $\sigma/r)^{12}$ term describes the repulsive forces between particles while the latter part of the equation and the longer-ranged σ/r^{6} term denotes the attraction.

Example 16.6.1: The van der Waals Radius

The ϵ and σ values for Xenon (Xe) are found to be 1.77 kJ/mol and 4.10 Angstroms, respectively. Determine the van der Waals radius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the internuclear distance between nonbonding particles. Because σ gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by:

r = σ/2 = 4.10 Angstroms/2 = 2.05 Angstroms

Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of separation decreases, the probability of interaction increases. The particles come closer together until they reach a region of separation where the two particles become bound; their bonding potential energy decreases from zero to a negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the separation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur: the particles are so close together that their electrons are forced to occupy each other's orbitals. Repulsion occurs as each particle attempts to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of separation decreases.

Example 16.6.2

Calculate the intermolecular potential between two Argon (Ar) atoms separated by a distance of 4.0 Angstroms (use ϵ=0.997 kJ/mol and σ=3.40 Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation 2.1 where V is the intermolecular potential between two non-bonding particles.

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are:

- $\epsilon = 0.997\ \text{kJ/mol}$,
- $\sigma = 3.40$ Angstroms, and
- the distance of separation, $r = 4.0$ Angstroms.

We plug these values into Equation 16.6.1 and solve as follows:

$$\begin{aligned} V &= 4(0.997\ \text{kJ/mol})\left[\left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{12} - \left(\frac{3.40\ \text{Angstroms}}{4.0\ \text{Angstroms}}\right)^{6}\right] \\ &= 3.988(0.14 - 0.38) \\ &= 3.988(-0.24) \\ &= -0.96 kJ/mol \end{aligned}$$

Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones separation distance. As the separation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavorable, as it indicates an overlapping of atomic orbitals. However, at long separation distances, the potential energy is negative and approaches zero as the separation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the separation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.

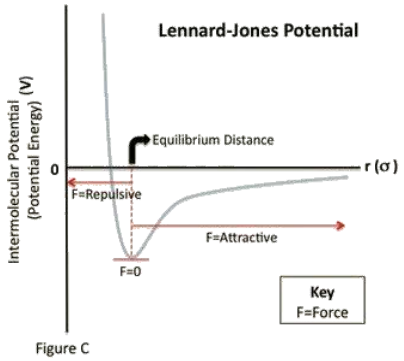


Figure C

Example 16.6.3

Two molecules, separated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the separation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles is zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones potential, any value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the separation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting separation (3.0 angstroms) is already less than σ (4.0 angstroms), decreasing the separation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

Exercise 16.6.1

The second part of the Lennard-Jones equation is $(\sigma/r)^6$ and denotes attraction. Name at least three types of intermolecular interactions that represent attraction.

Answer

From section 2.1, dipole-dipole, dipole-induced dipole, and London interactions are all attractive forces.

Exercise 16.6.2

At what separation distance in the Lennard-Jones potential does a species have a repulsive force acting on it? An attractive force? No force?

Answer

See Figure C. A species will have a repulsive force acting on it when r is less than the equilibrium distance between the particles. A species will have an attractive force acting on it when r is greater than the equilibrium distance between the particles. Lastly, when r is equal to t↑he equilibrium distance between both particles, the species will have no force acting upon it.

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16.7: Van der Waals Constants in Terms of Molecular Parameters

The van der Waals equation can be written as:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Using the binomial expansion:

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots$$

We can write the van der Waals equation of state as:

$$\begin{aligned} P &= \frac{RT}{\bar{V}}\left[1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots\right] - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} + (RTb - a)\frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \cdot \end{aligned}$$

Rearranging in terms of compressibility, Z:

$$Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots$$

Comparing to the Viral equation of state, we can see that the second Viral coefficient is related to the van der Waals coefficients:

$$B_{2V}(T) = b - \frac{a}{RT}$$

Using a combination of the hard sphere model and the Lennard-Jones potential, we obtain:

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\dfrac{C_6}{r^6} & r > \sigma \end{cases} \tag{16.7.1}$$

We can write the second Virial coefficient as

$$B_2(T) = \frac{2}{3}\pi N_0 \sigma^3 \left[1 - \frac{C_6}{3k_B T \sigma^6}\right] \tag{16.7.2}$$

Let us introduce to simplifying variables

$$b = \frac{2}{3}\pi N_0 \sigma^3 \tag{16.7.3}$$

$$a = \frac{2\pi N_0^2 C_6}{9\sigma^3} \tag{16.7.4}$$

In which the second Virial coefficient becomes:

$$B_2(T) = b - \frac{a}{RT} \tag{16.7.5}$$

From these equations, we can see that a is directly proportional to c_6, the intermolecular attraction between particles with a force proportional to r^{-6}. Likewise, b is equivalent to four times the volume of the particle. In other words, the van der Waals equations assumes the hard sphere model at small distances and weak interactions (attractive forces) at larger distances.

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16.E: The Properties of Gases (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

Template:HideTOC

These are homework exercises to accompany Chapter 16 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q16.10

One liter of N_2 (g) at 2.1 bar and two liters of Ar(g) at 3.4 bar are mixed in a 4.0-L flask to form an ideal-gas mixture. Calculate the value of the final pressure of the mixture if the initial and final temperature of the gases are the same. Then, repeat this calculation if the initial temperatures of the N_2 (g) and Ar(g) are 304 K and 402 K, respectively, and the final temperature of the mixture is 377 K. (Assume ideal-gas behavior.)

S16.10

Using the ideal gas law, we can find the number of moles of each gas.

$$n_{N_2} = \frac{P_{N_2}V_{N_2}}{RT} = \frac{(2.1x10^5 Pa) * (1x10^{-3} m^3)}{RT} = \frac{210 Pa * m^3}{RT}$$

$$n_{Ar} = \frac{P_{Ar}V_{Ar}}{RT} = \frac{(3.4x10^5 Pa) * (2x10^{-3} m^3)}{RT} = \frac{680 Pa * m^3}{RT}$$

The total moles of gas in the final mixture is the sum of the moles of each gas in the mixture, which is

$$\frac{210 Pa * m^3}{RT} + \frac{680 Pa * m^3}{RT} = \frac{890 Pa * m^3}{RT}$$

Therefore,

$$P = \frac{nRT}{V} = \frac{890 Pa * m^3}{0.0040 m^3} = 2.2x10^5 Pa = 2.2 bar$$

Now, considering the initial temperatures of the gases are different from each other and from the final temperature of the mixture, we calculate the total number of moles to be

$$n_{total} = n_{N_2} + n_{Ar} = \frac{210 Pa * m^3}{R * (304 K)} + \frac{680 Pa * m^3}{R * (402 K)}$$

Substituting this into the ideal gas law, we get the final pressure to be

$$P = [\frac{210 Pa * m^3}{R * (304 K)} + \frac{680 Pa * m^3}{R * (402 K)}] * \frac{R * (377 K)}{0.0040 m^3} = 2.2x10^5 Pa = 2.2 bar$$

Q16.12

What is the molar Gas Constant in units of cm^3 torr K^{-1} mol^{-1}.

S16.12

We know $R = 0.082058 L \cdot atm \cdot mol^{-1} K^{-1}$

using dimensional analysis:

$$R = 0.082058 L \cdot atm \cdot mol^{-1} K^{-1} \times \frac{760 torr}{1 atm} \times \frac{1 dm^3}{1 L} \times \frac{1 dm^3}{1000 cm^3} \quad (16.E.1)$$

$$R = 0.0623639 cm^3 \cdot atm \cdot mol^{-1} K^{-1} \quad (16.E.2)$$

Q16.13

Use the van der Waals equation to plot the compressibility factor, Z, against P for methane for T = 180 K, 189 K, 190 K, 200 K, and 250 K.

S16.13

First, calculate Z as a function of $\bar{V}$ and P as a function of $\bar{V}$ and plot Z versus P

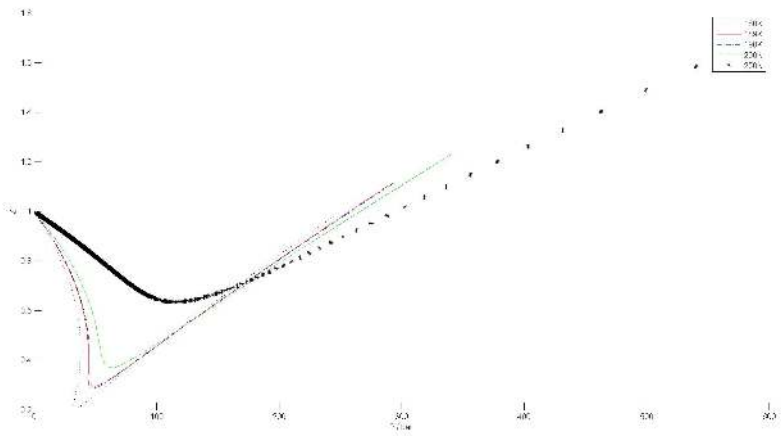
For methane, a = 2.3026 $dm^6 \cdot bar \cdot mol^{-2}$ and b = 0.043067 $dm^3 \cdot mol^{-1}$

$$Z = \frac{P\bar{V}}{RT} \tag{16.E.3}$$

and the van der Waals equation of state is:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{16.E.4}$$

Then create a parametric plot of Z versus P for the suggested temperatures as shown below.



Q16-15

Define the equation that could be solved by using the Netwon-Raphson method to find the molar volume of O2 at 300K and 200atm. Use the van der Waals anf Redlich-Kwong equations.

Constants:

- van der Waals:

$$a = 1.3820 dm^6 * bar * mol, b = 0.031860 dm^3 * mol^{-1} \tag{16.E.5}$$

- Redlich-Kwong:

$$A = 17.411 dm^6 * bar * mol^{-2} * K^{1/2}, B = 0.022082 dm^3 * mol^{-1} \tag{16.E.6}$$

S16.15

Solving van der Waals equation for volume produces:

$$\bar{V}^{3} - (b + \dfrac{RT}{P})\bar{V}^{2} + \dfrac{a}{P}\bar{V} - \dfrac{ab}{P}=0$$

Plugging in constants gives:

$$\bar{V}^{3} - 0.15486\bar{V}^{2} + 0.00691\bar{V} - 0.00022015=0$$

which can be solved numerically to find molar volume.

The Redlich-Kwong equation can be written as a cubic in volume:

$$\bar{V}^{3} - \dfrac{RT}{P}\bar{V}^{2} - \left(B^{2} + \dfrac{BRT}{P} - \dfrac{A}{T^{1/2}P}\right)\bar{V} - \dfrac{AB}{T^{1/2}P} = 0\]

Plugging in constants gives:

$$\bar{V}^{3} - 0.123\bar{V}^{2} + 0.001822\bar{V} - 0.00011099 = 0\]

which can be solved numerically to find molar volume.

Q16.16

Compare the Redlich-Kwong and the van der Waals equations for ethane. Take the molar volume to be 0.09416 .

S16.16

van der Waals:

$$P = \dfrac{RT}{\bar{V}-b}-\dfrac{a}{(\bar{V})^2}\]

Reference Table 16.3 for a, b

$$P = \dfrac{0.083145*400}{.09416-0.065144}-\dfrac{5.5818}{(0.09416)^2}\]

Redlich-Kwong equation of state improved the accuracy of the van der Waals equation by adding a temperature dependence for the attractive term:

$$P = \dfrac{RT}{\bar{V}-B} - \dfrac{A}{T^(\dfrac{1}{2})\bar{V}(\bar{V}+B)}\]

Reference Table 16.4 for A, B

$$P = \dfrac{0.083145*400}{0.09416-0.045153} - \dfrac{98.831}{400^(\dfrac{1}{2})0.09416*(0.09416+0.62723)}\]

Q16.17

$$p = \frac{RT}{\frac{V}{n} - b} - \frac{a}{\sqrt{T}\frac{V}{n}\left(\frac{V}{n} + b\right)} \tag{16.E.7}$$

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{16.E.8}$$

Use the equations above to calculate the temperature of a system with $1.5\ mol$ of methane at $300\ K$ confined to a volume of $100\ cm^3$. Compare the two calculated pressures.

S16.17

$R = 82.057338 \dfrac{cm^2\ atm}{K\ mol}$

Redlich-Kwong constants: $a = 31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\dfrac{cm^3}{mol}\right)^2$ and $b = 29.6\ \dfrac{cm^3}{mol}$

Van der Waals constants: $a = 2.25 \times 10^6\ (atm)\left(\dfrac{cm^3}{mol}\right)^2$ and $b = 42.8\ \dfrac{cm^3}{mol}$

Redlich-Kwong equation: $p = \dfrac{82.057338\dfrac{cm^2\ atm}{K\ mol}\ 300\ K}{\dfrac{100\ cm^3}{1.5\ mol} - 29.6\ \dfrac{cm^3}{mol}} - \dfrac{31.59 \times 10^6\ (atm)(K^{\frac{1}{2}})\left(\dfrac{cm^3}{mol}\right)^2}{\sqrt{300\ K}\dfrac{100\ cm^3}{1.5\ mol}\left(\dfrac{100\ cm^3}{1.5\ mol} + 29.6\ \dfrac{cm^3}{mol}\right)} = 379.95\ atm$

Van der Waals equation: $p = \dfrac{(1.5\ mol)(82.057338\dfrac{cm^2\ atm}{K\ mol})(300\ K)}{(100\ cm^3) - (1.5\ mol)(42.8\ \dfrac{cm^3}{mol})} - \dfrac{(1.5\ mol)^2(2.25 \times 10^6\ (atm)\left(\dfrac{cm^3}{mol}\right)^2)}{(100\ cm^3)^2} = 525.2\ atm$

There is a $145.25\ atm$ difference in the calculated pressures.

Q16.20

The following equation can be used to relate the pressure of propane to its density at temperatures below 400 K:

$$P = 33.258\rho - 7.5884\rho^2 + 1.0306\rho^3 - 0.058757\rho^4 - 0.0033566\rho^5 + 0.00060696\rho^6 \tag{16.E.9}$$

where the pressure (P) is in bar and the density (ρ) is in $\frac{mol}{L}$ and ranges from $0\frac{mol}{L} \leq \rho \leq 12.3\frac{mol}{L}$.

Calculate and plot the pressure for the given density range using:

a. the equation given above
b. the Van der Waals equation of state
c. the Redlich-Kwong equation of state

Compare your results from the above parts.

S16.20

a.) Straight forward to calculate.

Even though straight forward, should still put solution for students.



graph plotted using matlab.

b.) The following constants were used in the equation below:

$$a = 9.3919\frac{L^2 bar}{mol^2} \text{ and } b = 0.09049\frac{L}{mol}$$

$$P_{VDW} = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{16.E.10}$$

c.) The following constants were used in the equation below:

$$a = 183.01\frac{L^2 bar}{mol^2} \text{ and } b = 0.06272\frac{L}{mol}$$

$$P_{RK} = \frac{RT}{\bar{V} - b} - \frac{a}{\sqrt{T}\bar{V}(\bar{V} + b)} \tag{16.E.11}$$



As can be seen by the plot, the Van der Waals equation of state deviates greatly from the empirical fit at higher densities. The Redlich-Kwong equation provides a reasonable approximation to the empirical data. (All calculations were done in MATLAB, and the above plot was produced by me)

Q16.21

Use the data below to evaluate the van der waals and Redlich Kwong constants for benzene.

Species	T_c/K	P_c/bar	P_c/atm	V_{nc}/L mol^{-1}*	P_cV_{nc}/RT_c
Benzene	561.75	48.758	48.120	0.256	0.26724

*n to indicate molar volume

Van Der Waals

$$a = \frac{27(RT_c)^2}{64P_c} \; and \; b = \frac{RT_c}{8P_c}$$

Redlich-Kwong

$$A = 0.42748\frac{R^2T_c^{\frac{5}{2}}}{P_c} \; and \; B = 0.08664\frac{RT_c}{P_c}$$

S16.21

Van Der Waals

$$\text{a} = \frac{27 * (0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{64 * 48.758 bar} = \mathbf{18.8754\ dm^6 \cdot atm \cdot mol^{-2}}$$

$$\text{b} = \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{8 * 48.758 bar} = \mathbf{5.5927\ dm^3 \cdot mol^{-1}}$$

Redlich-Kwong

$$A = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^{\frac{5}{2}}}{48.758 bar} = \mathbf{453.315\ dm^6 \cdot atm \cdot mol^{-2} \cdot K^{\frac{1}{2}}}$$

$$B = 0.42748 * \frac{(0.083145 dm^3 \cdot bar \cdot mol^{-1}K^{-1})^2 * (561.75K)^2}{48.758 bar} = \mathbf{19.126\ dm^3 \cdot mol^{-1}}$$

Q16.22

Show that the van der Waals equation for argon at T = 142.69 K and P = 35.00 atm can be written as

$$\overline{V}^3 - 0.3664\overline{V}^2 + 0.001210 = 0 \qquad (16.E.12)$$

where, for convenience, we have suppressed the units in the coefficients. Use the Newton-Raphson method (MathChapter G) to find the three roots to this equation, and calculate the values of the density of liquid and vapor in equilibrium with each other under these conditions.

S16.22

Using Table 16.3, we can get the values of a and b for argon to use in Van der Waals equation of state.

By doing this, you can isolate $\bar{\bar{V}}$ in van der Waals equation of state. Next, by applying the Newton-Raphson method to the function given by van der Waals equation (which is only dependent on $\bar{\bar{V}}$), and the derivative of the function, we find the roots to the equation. On the case here, the smallest root represents the molar volume of liquid argon, and the largest root represents the molar volume of vapor argon.

Q16.23

Calculate the Volume occupied by $50\ kg$ of propane at $50^{\circ}C$ and $35\ bar$, using the Redlich-Kwong equation of state and the Peng-Robinson equation of state.

S16.23

Redlich-Kwong equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{16.E.13}$$

v is volume of gas per mole.

we have $T = 50^{\circ}C = 323\ K$, $P = 35\ bar = 35 \times (10^5) Pa$

For propane, we have $P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

so we have $a = \frac{0.42748 R^2 T_c^{2.5}}{P_c T^{0.5}}$;

$b = \frac{0.08664 * R * T_c}{P_c}$

so, $a = \frac{0.42748(8.314^2)369.522^{2.5}}{42.4924 \times 10^5 (323^{0.5})} = 1.015603$

$b = \frac{(0.08664)(8.314)(369.522)}{42.4924 \times 10^5} = 6.2640829 \times 10^{-5}$

so, $P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$

$(35 * (10^5)) = \frac{(8.314)(323)}{v-(6.2640829 \times 10^{-5})} - \frac{1.015603}{v(v+6.2640829 \times 10^{-5})}$

The only real solution is

$v = 0.00010933 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{50 * 1000}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.00010933) = 0.1239569 m^3 = 123.9569$ Liters is the answer.

Peng - Robinson's equation of state:

$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$

$a = 0.45724 R^2 * T_c^2 * \frac{\alpha}{P_c}$

$b = 0.0778 R \frac{T_c}{P_c}$

$\alpha = 1 + S(1 - \sqrt{T_r})$

$S = 0.37464 + 1.54226w - 0.26992w^2$

$T_r = \frac{T}{T_c}$

we have $P = 35 \times 10^5 Pa$ and $T = 323\ K$

$P_c = 42.4924\ bar = 42.4924 \times 10^5 Pa$ and $T_c = 369.522\ K$

we have accentric factor = $w = 0.152$.

$T_r = \frac{T}{T_c} = \frac{323}{369.522} = 0.87410$

$S = 0.37464 + (1.54226)(0.152) - (0.26992)(0.152^2) = 0.602827$

$\alpha = 1 + 0.602827 * (1 - \sqrt{0.87410}) = 1.0392240523$

$a = (0.45724)(8.314^2)(369.522^2)\frac{1.0392240523}{42.4924 \times 10^5} = 1.055462444$

$b = (0.0778)(8.314)\frac{369.522}{42.4924 \times 10^5} = 0.0000562494$

so, by the equation of state:

$(35 \times 10^5) = \frac{(8.314)(323)}{v - 0.0000562494} - \frac{1.055462444}{v(v + 0.0000562494 + 0.0000562494(v - 0.0000562494)}$

$v = 0.0000988504 \frac{m^3}{mol}$

so In $50\ Kg$ propane, number of moles = $\frac{(50)(1000)}{44.10} = 1133.78684$

total volume occupied by $50\ Kg$ propane at the specified conditions = $(1133.78684)(0.0000988504) = 0.1120752 m^3 = 112.0752$ liters is the answer.

Q16.25

A way to obtain the expressions for the van der Waals constants is to make $(\frac{\partial P}{\partial \bar{V}})_T$ and $(\frac{\partial^2 P}{\partial \bar{V}^2})_T$ zero at the critical point, but why do they equal to zero at critical point? Obtain the equation $\bar{V}_c = 3b$ from this procedure.

S16.25

$$(\frac{\partial P}{\partial \bar{V}})_T = 0$$

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$$

$$(\frac{\partial P}{\partial \bar{V}})_T = \frac{\partial}{\partial \bar{V}}\ (\frac{RT}{\bar{V} - b} - \frac{a}{\bar{T}^2})_T$$

$$= RT\ (-\frac{1}{(\bar{V} - b)^2})\ -\ a\ (\frac{-2}{\bar{V}^3})$$

$$= -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3}$$

At critical point,

$$\frac{RT_c}{(\bar{V}_c - b)^2} = \frac{2a}{\bar{V}_c^{\ 3}}$$ by equating $(\frac{\partial P}{\partial \bar{V}})_T = 0$.

By differentiating the equation $RT\ (-\frac{1}{(\bar{V} - b)^2})\ -\ a\ (\frac{-2}{\bar{V}^3})$ with respect to $\bar{V}$,

$$(\frac{\partial^2 P}{\partial \bar{V}^2})_T = \frac{\partial}{\partial \bar{V}}\ (-\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3})_T$$

$$= RT\ (-\frac{2}{(\bar{V} - b)^3}) + 2a\ (\frac{-3}{\bar{V}^4})$$

$$= \frac{2RT}{(\bar{V} - b)^3}\ -\ \frac{6a}{\bar{V}^4}$$

At critical point,

$$\frac{2RT_c}{(\bar{V}_c - b)^3} = \frac{6a}{\bar{V}_c^{\ 4}}$$ by equating $(\frac{\partial^2 P}{\partial \bar{V}^2})_T = 0$.

Now,

$$\frac{\frac{2a}{\bar{V}_c^{\ 3}}}{\frac{6a}{\bar{V}_c^{\ 4}}} = \frac{\frac{RT_c}{(\bar{V}_c - b)^2}}{\frac{2RT_c}{(\bar{V}_c - b)^3}}$$

$$\frac{\bar{V}_c}{3} = \frac{(\bar{V}_c - b)}{2}$$

$$\bar{V}_c = 3b$$

Q16.26

Show that the Redlich-Kwong equation can be rewritten in the following form:

$$\bar{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \tag{16.E.14}$$

S16.26

Starting with the Redlich-Kwong equation and manipulating it we get the following:

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \tag{16.E.15}$$

$$P(\bar{V} - B)T^{1/2}\bar{V}(\bar{V} + B) = RT^{3/2}\bar{V}(\bar{V} + B) - A(\bar{V} - B) \tag{16.E.16}$$

$$PT^{1/2}\bar{V}(\bar{V}^2 - B^2) = RT^{3/2}\bar{V}^2 + RT^{3/2}\bar{V}B - A\bar{V} + AB \tag{16.E.17}$$

$$\bar{(V)}^3 - \frac{RT}{P}\bar{V}^2 - (B^2 + \frac{BRT}{P} - \frac{A}{PT^{1/2}})\bar{V} - \frac{AB}{PT^{1/2}} = 0 \tag{16.E.18}$$

Q16.27

Use the results of the previous question, Q16.26, to derive Equations 16.14.

$(a)\bar{V}_c = 3.8473B$, $(b)P_c = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}}$, and $(c)T_c = .34504\left(\frac{A}{BR}\right)^{2/3}$

The following are solved from Q16.26 and are necessary to solve for Equation 16.14:

$$1)B = .25992\bar{V}_c \tag{16.E.19}$$

$$2)A = 0.42748\frac{R^2T_c^{5/2}}{P_c} \tag{16.E.20}$$

$$3)\frac{P_c\bar{V}_C}{RT_c} = \frac{1}{3} \tag{16.E.21}$$

S16.27

From equation (1) we see that solving for $\bar{V}_c$ yields the first equation

$$\bar{V}_c = 3.8473B \tag{16.E.22}$$

.

From equation (2) we can rewrite the expression with some manipulation as

$$A = .42748RT_c^{3/2}\left(\frac{RT_c}{P_c\bar{V}_c}\right)\bar{V}_c \tag{16.E.23}$$

Substituting equation (3) and 16.14a into the previous equation gives the expression

$$A = 3(.42748)RT_c^{3/2}(3.8473B) \tag{16.E.24}$$

Lastly, solving for T_c gives the equation for 16.14c

$$T_c = .34504\left(\frac{A}{BR}\right)^{2/3} \tag{16.E.25}$$

Finally, solving for equation 16.14b we must substitute the previously solved 16.14c into equation (2),solving for P_c

$$P_c = 0.42748\frac{R^2T_c^{5/2}}{A} = \left(\frac{.42748}{A}\right)R^2\left[.34504\left(\frac{A}{BR}\right)^{2/3}\right]^{5/2} = .029894\frac{A^{2/3}R^{1/3}}{B^{5/3}} \tag{16.E.26}$$

which is equation 16.14b.

Q16.28

Derive the Van der Waals cubic equation of state from

$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT \tag{16.E.27}$$

S16.28

The Van der Waal equation can be rewritten in terms of Z:

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}} \tag{16.E.28}$$

solving for $\bar{V}$

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0 \tag{16.E.29}$$

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CHAPTER OVERVIEW

17: Boltzmann Factor and Partition Functions

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Summer 2016: Delmar Larsen

Sorry, but all current instructors at UCD use the commercial textbook for this course.

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences
17.2: The Thermal Boltzman Distribution
17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System
17.4: The Heat Capacity at Constant Volume
17.5: Express the Pressure in Terms of a Partition Function
17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions
17.7: Partition Function of Indistinguishable Components
17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom
17.E: Exercises

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17.1: The Boltzmann Factor Is One of the Most Important Quantities in the Physical Sciences

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

The Microscopic Laws of Motion

Consider a system of N classical particles. The particles are confined to a particular region of space by a container of volume V. In classical mechanics, the state of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $r_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $\left(v_{x_i}, v_{y_i}, v_{z_i}\right)$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation:

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{17.1.1}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, \ldots, \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{17.1.2}$$

which is known as a force field (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where $\mathbf{F}_1, \ldots, \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles is $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we content ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ gigabytes which is also 10^2 yottabytes! The largest computers we have today have perhaps 10^6 gigabytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}NkT = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \tag{17.1.3}$$

which can be solved to give:

$$T = \frac{2}{3k}\left(\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m_i\mathbf{v}_i^2\right) \tag{17.1.4}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How do we determine which thermodynamic properties characterize an ensemble?
4. How many different types of ensembles can we construct, and what distinguishes them?

These questions will be addresses in the sections ahead.

Thermal energy

A confined monatomic gas can be seen as a box with a whole bunch of atoms in it. Each of these particles can be in one of the states given by the last formula. If all of them have large n values there is obviously a lot of kinetic energy in the system. The lowest energy is when all atoms have 1,1,1 as quantum numbers. Boltzmann realized that this should relate to temperature. When we add energy to the system (by heating it up without changing the volume of the box), the temperature goes up. At higher temperatures we would expect higher quantum numbers, and at lower T, lower ones. But how exactly are the atoms distributed over the various states?

This is a good example of a problem involving a discrete probability distribution. The probability that a certain level (e.g., $n = (n_1, n_2, n_3)$ with energy E_i) is occupied should be a function of temperature: $P_i(T)$. Boltzmann postulated that you could look at temperature as a form of energy. The thermal energy of a system is directly proportional to an absolute temperature.

$$E_{thermal} = kT$$

The proportionality constant k (or k_B) is named after him: the Boltzmann constant. It plays a central role in all statistical thermodynamics. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is given by:

$$e^{-\beta E_i} \tag{17.1.5}$$

where:

- E_i is the energy in the state i,
- T is the kelvin temperature, and
- k is Boltzmann constant.

As the following section demonstrates, the term β in Equation 17.1.5 is expressed as:

$$\beta = \frac{1}{kT}$$

The rates of many physical processes are also determined by the Boltzmann factor. For a random particle, its thermal energy of a particle is a small multiple of the energy kT. An increase in temperature results in more particles crossing the energy barrier characteristic of activation processes. If this is to occur, particles need to carry sufficient energy. This energy is needed for the particles to successfully cross the energy barrier and is usually called activation energy. The fraction of molecules that have sufficient energy to escape the original material surface is approximately proportional to the Boltzmann factor.

References

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2. Claudio Fazio, Onofrio R Battaglia, Ivan Guastella. (2012).Two experiments to approach the Boltzmann factor: chemical reaction and viscous flow. *European Journal of Physics*, *33*, *2*, *359*.doi:10.1088/0143-0807/33/2/359.

Problems

1. How are temperature and the average energy per particle for a system related?
2. What does the Boltzmann factor tell you? Why is it important?
3. When is it possible for particles to get extra energy?
4. Give three examples of activation processes.
5. What do "separate arrangements" mean? What are the differences between these arrangements?

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- **17.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System** by Mark Tuckerman is licensed CC BY 4.0.

17.2: The Thermal Boltzman Distribution

Consider a N-particle ensemble. The particles are not necessarily indistinguishable and possibly have mutual potential energy. Since this is a large system, there are many different ways to arrange its particles and yet yield the same thermodynamic state. Only one arrangement can occur at a time. The sum of the probabilities of each separate arrangement equals the total number of separate arrangements. Then the probability of a system is:

$$p_N = W_N p_i$$

where p_N is the probability of the system, W_N is the total number of different possible arrangements of the N particles in the system, and p_i is the probability of each separate arrangement. Heisenberg's uncertainty principle states that it is impossible to simultaneously know the momentum and the position of an object with complete precision. In agreement with the uncertainty principle, the total possible number of combinations can be defined as the total number of distinguishable rearrangements of the N particles.

The most practical ensemble is the canonical ensemble with N, V, and T fixed. We can imagine a collection of boxes with equal volumes and number of particles with the entire collection kept in thermal equilibrium. Based on the Boltzmann factor, we know that for a system that has states with energies e_1, e_2, e_3..., the probability p_j that the system will be in the state j with energy E_j is exponentially proportional to the energy of state j. The partition functions of the state places a very important role in calculating the properties of a system, for example, it can be used to calculate the probability, as well as the energy, heat capacity, and pressure.

The Boltzmann Distribution

We are ultimately interested in the probability that a given distribution will occur. The reason for this is that we must have this information in order to obtain useful thermodynamic averages. Let's consider an ensemble of A systems. We will define a_j as the number of systems in the ensemble that are in the quantum state j. For example, a_1 represents the number of systems in the quantum state 1. The total number of possible microstates is:

$$W(a_1, a_2, \dots) = \frac{A!}{a_1! a_2! \dots}$$

The overall probability that P_j that a system is in the jth quantum state is obtained by averaging a_j/A over all the allowed distributions. Thus, P_j is given by:

$$\begin{aligned} P_j &= \frac{\langle a_j \rangle}{A} \\ &= \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} \end{aligned}$$

where the angle brackets indicate an ensemble average. Using this definition we can calculate any average property (i.e. any thermodynamic property):

$$\langle M \rangle = \sum_j M_j P_j \tag{17.2.1}$$

The method of the most probable distribution is based on the idea that the average over P_j is **identical** to the most probable distribution. Physically, this results from the fact that we have so many particles in a typical system that the fluctuations from the mean are extremely (immeasurably) small. The equivalence of the average probability of an occupation number and the most probable distribution is expressed as follows:

$$P_j = \frac{\langle a_j \rangle}{A} = \frac{a_j}{A}$$

The probability function is subject to the following constraints:

- Constraint 1: Conservation of energy requires:

$$E_{total} = \sum_j a_j e_j \tag{17.2.2}$$

where e_j is the energy of the jth quantum state.

- Constraint 2: Conservation of mass requires:

$$A = \sum_j a_j \tag{17.2.3}$$

which says only that the total number of all of the systems in the ensemble is A.

As we will learn in later chapters, the system will tend towards the distribution of a_j that maximizes the total number of microstates. This can be expressed as:

$$\sum_j \left(\frac{\partial \ln W}{\partial a_j} \right) = 0$$

Our constraints becomes:

$$\sum_j e_j da_j = 0$$

$$\sum_j da_j = 0$$

The method of Lagrange multipliers (named after Joseph Louis Lagrange is a strategy for finding the local maxima and minima of a function subject to equality constraints. Using the method of LaGrange undetermined multipliers we have:

$$\sum_j \left[\left(\frac{\partial \ln W}{\partial a_j} \right) da_j + \alpha da_j - \beta e_j da_j \right] = 0$$

We can use Stirling's approximation:

$$\ln x! \approx x \ln x - x$$

to evaluate:

$$\left(\frac{\partial \ln W}{\partial a_j} \right)$$

to get:

$$\left(\frac{\partial A!}{\partial a_j} \right) - \sum_i \left(\frac{\partial \ln a_i}{\partial a_j} \right) = 0$$

as outlined below.

Application of Stirling's Approximation

First step is to note that:

$$\ln W = \ln A! - \sum_j \ln a_j! a \approx A \ln A - A - \sum_j a_j \ln a_j - \sum_j a_j$$

Since (from Equation 17.2.3):

$$A = \sum_j a_j$$

these two cancel to give:

$$\ln W = A \ln A - \sum_j a_j \ln a_j$$

The derivative is:

$$\left(\frac{\partial \ln W}{\partial a_j}\right) = \frac{\partial A \ln A}{\partial a_j} - \sum_i \frac{\partial a_i \ln a_i}{\partial a_j}$$

Therefore we have:

$$\left(\frac{\partial A \ln A}{\partial a_j}\right) = \frac{\partial A}{\partial a_j}\ln A - \frac{\partial A}{\partial a_j} = \ln A - 1$$

$$\left(\frac{\partial a_i \ln a_i}{\partial a_j}\right) = \frac{\partial a_i}{\partial a_j}\ln a_i - \frac{\partial a_i}{\partial a_j} = \ln a_j + 1$$

These latter derivatives result from the fact that:

$$\left(\frac{\partial a_i}{\partial a_i}\right) = 1$$

$$\left(\frac{\partial a_j}{\partial a_i}\right) = 0$$

The simple expression that results from these manipulations is:

$$-\ln\left(\frac{a_j}{A}\right) + \alpha - \beta e_j = 0$$

The most probable distribution is:

$$\frac{a_j}{A} = e^a \sum_j e^{-\beta e_j} \tag{17.2.4}$$

Now we need to find the undetermined multipliers α and β.

The left hand side of Equation 17.2.4 is 1. Thus, we have:

$$P_j = \frac{a_j}{A} = \frac{e^{-\beta e_j}}{\sum_j e^{-\beta e_j}}$$

This determines a and defines the Boltzmann distribution. We will show that β from the optimization procedure of method of Lagrange multipliers is:

$$\beta = \frac{1}{kT}$$

This identification will show the importance of temperature in the Boltzmann distribution. The distribution represents a thermally equilibrated most probable distribution over all energy levels (Figure 17.2.1).

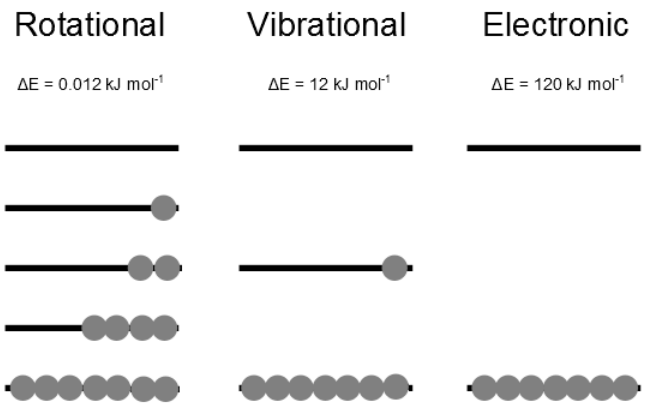


Figure 17.2.1 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. k_BT 2.5 $kJ\ mol^{-1}$ at 300 K. (CC SA-BY 3.0; Mysterioso via Wikiversity).

Boltzmann Distribution

The Boltzmann distribution represents a thermally equilibrated **most probable** distribution over all energy levels. There is always a **higher** population in a state of lower energy than in one of higher energy.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities (Equation 17.2.1). To calculate P_j, we need the energy levels of a system (i.e., $\{e_i\}$). The energy ("levels") of a system can be built up from the quantum energy levels

> *It must always be remembered that no matter how large the energy spacing is, there is always a non-zero probability of the upper level being populated. The only exception is a system that is at absolute zero. This situation is however hypothetical as absolute zero can be approached but not reached.*

Partition Function

The sum over all factors $e^{-\beta e_j}$ is given a name. It is called the molecular partition function, q:

$$q = \sum_j e^{-\beta e_j}$$

The molecular partition function q gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q, larger the number of states which are available for the molecular system to occupy (Figure 17.2.2).

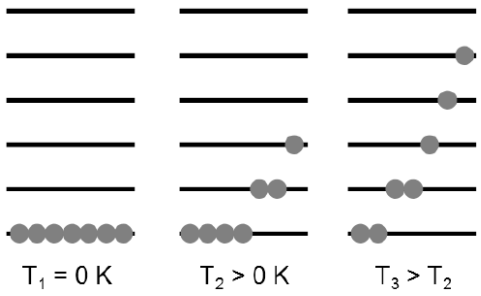


Figure 17.2.2 : At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less. (CC SA-BY 3.0; Mysterioso via Wikiversity).

We distinguish here between the partition function of the ensemble, Q and that of an individual molecule, q. Since Q represents a sum over all states accessible to the system it can written as:

$$Q(N,V,T) = \sum_{i,j,k\ldots} e^{-\beta(e_i+e_j+e_k\ldots)}$$

where the indices i, j, k represent energy levels of **different** particles.

Regardless of the type of particle the molecular partition function, q represents the energy levels of one individual molecule. We can rewrite the above sum as:

$$Q = q_i q_j q_k \ldots$$

or:

$$Q = q^N$$

for N particles. Note that q_i means a sum over states or energy levels accessible to molecule i and q_j means the same for molecule j. The molecular partition function, q counts the energy levels accessible to molecule i only. Q counts not only the states of all of the molecules, but all of the possible combinations of occupations of those states. However, if the particles are not distinguishable then we will have counted $N!$ states too many. The factor of $N!$ is exactly how many times we can swap the indices in $Q(N,V,T)$ and get the same value (again provided that the particles are not distinguishable). See this video for more information.

References

1. Hakala, R.W. (1967). Simple justification of the form of Boltzmann's distribution law. *Journal of Chemical Education. 44(11), 657.* **doi:** 10.1021/ed044p657
2. Grigorenko, I, Garcia, M.E. (2002). Calculation of the partition function using quantum genetic algorithms. Physica A: Satistical Mechanics and its Applications. 313. 463-470. Retrieved from http://www.sciencedirect.com/science...78437102009883

Problems

1. Complete the justification of Boltzmann's distribution law by computing the proportionality constant a.
2. A system contains two energy levels E_1, E_2. Using Boltzmann statistics, express the average energy of the system in terms of E_1, E_2.
3. Consider a system contains N energy levels. Redo problem #2.
4. Use the property of exponential function, derive equation (17.9).
5. What are the uses of partition functions?

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17.3: We Postulate That the Average Ensemble Energy Is Equal to the Observed Energy of a System

We will be restricting ourselves to the canonical ensemble (constant temperature and constant pressure). Consider a collection of N molecules. The probability of finding a molecule with energy E_i is equal to the fraction of the molecules with energy E_i. That is, in a collection of N molecules, the probability of the molecules having energy E_i:

$$P_i = \frac{n_i}{N}$$

This is the directly obtained from the Boltzmann distribution, where the fraction of molecules n_i/N having energy E_i is:

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q} \tag{17.3.1}$$

The average energy is obtained by multiplying E_i with its probability and summing over all i:

$$\langle E \rangle = \sum_i E_i P_i \tag{17.3.2}$$

> Equation 17.3.2 is the standard average over a distribution commonly found in quantum mechanics as expectation values. The quantum mechanical version of this Equation is
>
> $$\langle \psi | \hat{H} | \psi \rangle$$
>
> where Ψ^2 is the distribution function that the Hamiltonian operator (e.g., energy) is averaged over; this equation is also the starting point in the Variational method approximation.

Equation 17.3.2 can be solved by plugging in the Boltzmann distribution (Equation 17.3.1):

$$\langle E \rangle = \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{17.3.3}$$

Where Q is the partition function:

$$Q = \sum_i e^{-\frac{E_i}{kT}}$$

We can take the derivative of $\ln Q$ with respect to temperature, T:

$$\left(\frac{\partial \ln Q}{\partial T} \right) = \frac{1}{kT^2} \sum_i \frac{E_i e^{-E_i/kT}}{Q} \tag{17.3.4}$$

Comparing Equation 17.3.3 with 17.3.4, we obtain:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

It is common to write these equations in terms of β, where:

$$\beta = \frac{1}{kT}$$

The partition function becomes:

$$Q = \sum_i e^{-\beta E_i}$$

We can take the derivative of $\ln Q$ with respect to β:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\sum_i \frac{E_i e^{-\beta E_i}}{Q}$$

And obtain:

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

Replacing $1/kT$ with β often simplifies the math and is easier to use.

> It is not uncommon to find the notation changes: Z instead of Q and $\bar{E}$ instead of $\langle E \rangle$.

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17.4: The Heat Capacity at Constant Volume

The heat capacity at constant volume (C_V) is defined to be the change in internal energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} \tag{17.4.1}$$

Since:

$$E = -\frac{\partial \ln Q(N,V,\beta)}{\partial \beta} \tag{17.4.2}$$

We see that:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \\ &= \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} \\ &= \frac{1}{kT^2}\frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \\ &= k\beta^2 \frac{\partial^2}{\partial \beta^2}\ln Q(N,V,\beta) \end{aligned} \tag{17.4.3}$$

where k is the Boltzmann constant. Energy can be stored in materials/gases via populating the specific degrees of freedom that exist in the sample. Understanding how this occurs requires the usage of Quantum Mechanics.

Dulong-Petit Law on the Heat Capacities of Solids

Pierre Louis Dulong and Alexis Thèrèse Petit conducted experiments in 1819 on three dimensional solid crystals to determine the heat capacities of a variety of these solids (Heat capacity is the solids ability to absorb and retain heat). Dulong and Petit discovered that all investigated solids had a heat capacity of approximately 2.49 x 10^4 J kilomole^{-1} K^{-1} at around 298 K or room temperature. The result from their experiment was explained by considering every atom inside the solid as an oscillator with six degrees of freedom (an oscillator can be thought of as a spring connecting all the atoms in the solid lattice). These springs extend into three dimensional space. The more energy that is added to the solid the more these springs vibrate. Each atom has an energy of $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature. Thus,

$$C_V = \frac{6R}{2} = 3R \qquad \text{(Dulong-Petit Law)}$$

The number 6 in this equation is the number of degrees of freedom for the molecule. Petit and Dulong suggested that these results supported their foundation for the heat capacity of solids. The explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased as temperature approached absolute zero. The degrees of freedom do not slow down or cease to move when the solid reaches a sufficiently cold temperature. An additional model was proposed to explain this deviance. Two main theories were developed to explain this puzzling deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

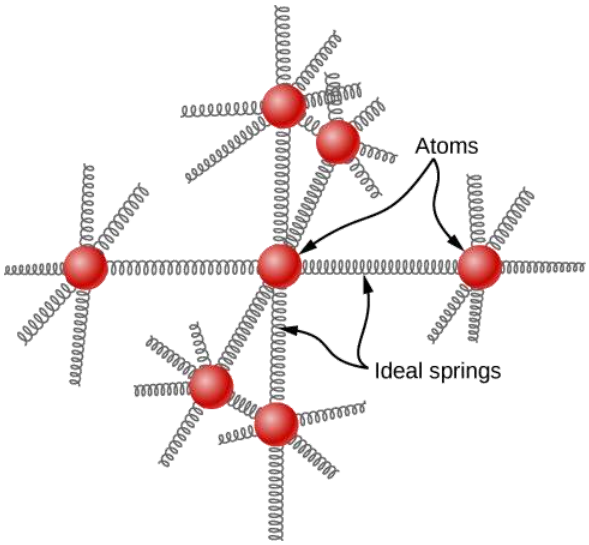


Figure 17.4.1 : In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Einstein's Theory on the Heat Capacities of Solids

Einstein assumed three things when he investigated the heat capacity of solids. First, he assumed that each solid was composed of a lattice structure consisting of N atoms. Each atom was treated as moving independently in three dimensions within the lattice (3 degrees of freedom). This meant that the entire lattice's vibrational motion could be described by a total of $3N$ motions, or degrees of freedom. Secondly, he assumed that the atoms inside the solid lattice did not interact with each other and thirdly, all of the atoms inside the solid vibrated at the same frequency. The third point highlights the main difference in Einstein's and Debye's two models.

Einstein's first point is accurate because the experimental data supported his hypothesis, however his second point is not because if atoms inside a solid could not interact, sound could not propagate through it. For example, a tuning fork's atoms, when struck, interact with one another to create sound which travels through air to the listener's ear. Atoms also interact in a solid when they are heated. Take for example a frying pan. If the pan is heated on one side, the heat transfers throughout the metal effectively warming the entire pan. Molecules that make up the frying pan interact to transfer heat. Much in the same way the oscillators in a solid interact when energy is added to the system. The extent of these interactions lead to the physically observed heat capacity.

The heat capacity of a solid at a constant volume is

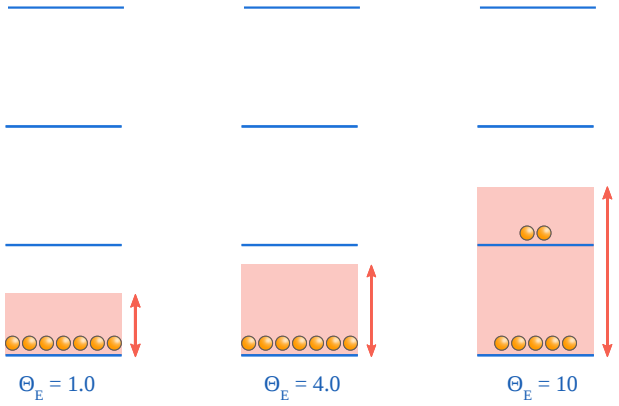
$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \\ &= \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\frac{\theta_E}{T}-1\right)^2} \end{aligned}$$

where

- $\theta_E = \dfrac{hv}{k}$ is the **Einstein temperature**,
- h is Planck's constant,
- k is Boltzmann's constant, and
- ν is the oscillator frequency of the atoms inside the solid.

The Einstein temperature's accessibility of the vibrational energy inside of a solid molecule determines the heat capacity of that solid. The greater the accessibility the greater the heat capacity. If the vibrational energy is easily accessible the collisions in the

molecule have a greater probability of exciting the atom into an upper vibrational level. This is displayed below.



Vibrational States of Excitement

Figure 17.4.2 : This Figure illustrates the effect of the Einstein temperature on the likelihood of an oscillator absorbing energy from a collision and transferring that energy into stored heat or heat capacity. As the Einstein temperature increases, the greater the probability of an oscillator being excited to the next vibrational state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

So the Einstein temperature specifically indicates the probability that a molecule has in its degrees of freedom to store energy in its atomic oscillators (or bonds). Comparing the Einstein temperature to the traditional classical values of Heat capacity will illustrate the differences the specific strengths (high temperature) and weaknesses (low temperature) of the Einstein model.

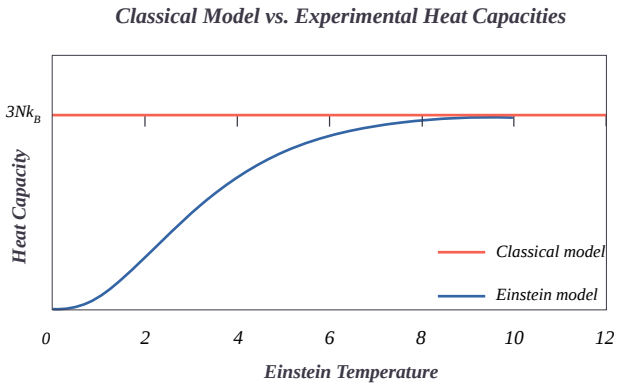


Figure 17.4.3 :This graph shows the accuracy of the of the Einstein temperature at low temperatures. The classical model is effective at temperatures above 10 Einstein Temperatures. (Cc BY-NC; Ümit Kaya via LibreTexts)

Thus, in the high temperature limit ($\frac{\theta_E}{T} \ll 1$) (i.e., the temperature is very large compared to the Einstein temperature) then

$$C_V \approx 3Nk = 3nR. \tag{17.4.4}$$

Einstein's model reveals the accuracy of the Petit and Dulong model and models high temperatures accurately. However, just as Petit and Dulong's model decreased in accuracy as the temperature decreased, so followed Einstein's.

When examining the extremely low temperature limit: $\frac{\theta_E}{T} \gg 1$, it can be seen:

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{\frac{-\theta_E}{T}} \tag{17.4.5}$$

As temperature (T) goes to zero, the exponential portion of the above equation goes to zero and therefore C_V also approaches zero. This supports the experimental values as temperature approaches zero the heat capacity of the solid likewise decreases to zero.

Einstein's theory also explains solids that exhibit a low heat capacity even at relatively high temperatures. An example of such a solid is diamond. The heat capacity of diamond approaches $3Nk$ as temperature greatly increases. Einstein's model supports this

through the definition of an Einstein temperature. As the Einstein temperature increases, ν must increase likewise. This is the equivalent of each atom possessing more energy and therefore vibrating more rapidly within the solid itself. The oscillator frequency, ν, can be written as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{17.4.6}$$

where κ is the force constant and μ is the reduced mass. This formula better predicts solids with high force constants or low reduced masses. This corrects deviations from the Petit and Dulong model.

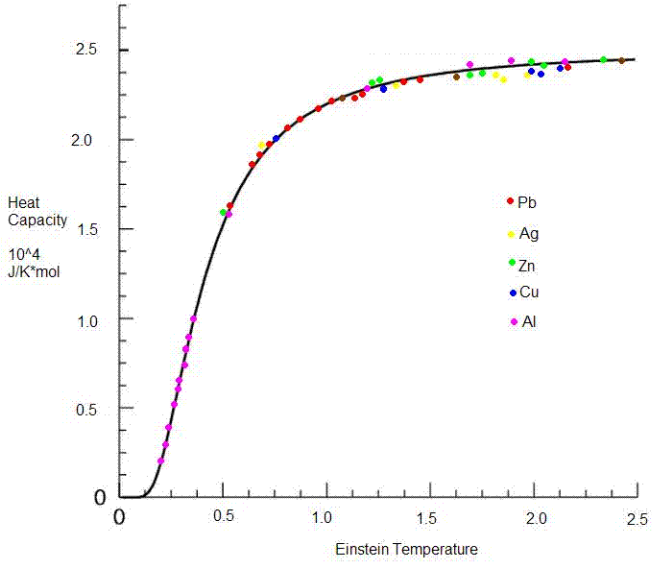


Figure 17.4.4 . This graph indicates the heat capacity of several solid metals as a function of the Einstein temperature: $\theta_E = \frac{hv}{k_B}$.

Essentially the Einstein temperature allows for the heat capacity equation and the vibrational frequencies in the solid to change as the temperature changes. This effectively adjusts for the deviations seen in the Petit/Dulong model. As the temperature increases or decreases, the Einstein temperature increases or decreases likewise to mirror the actual physical activity within the solid.

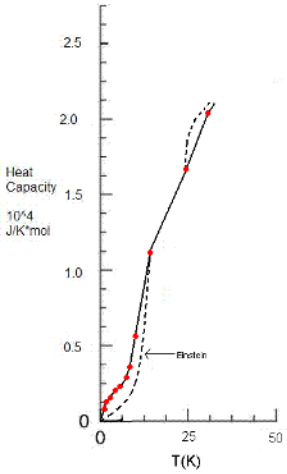


Figure 17.4.5 . This plot shows the heat capacity of lead compared to the expected values calculated from Einstein's model.

Einstein's model predicts relatively low temperatures well. However, when decreasing from approximately 15 K, Einstein's model deviates from experimental values. Also, this can be observed, although not as dramatically, for temperatures from 25 K to 30 K. Clearly a term or correction is still missing from Einstein's model to increase its accuracy.

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17.5: Express the Pressure in Terms of a Partition Function

Pressure can also be derived from the canonical partition function. The average pressure is the sum of the probability times the pressure:

$$\langle P \rangle = \sum_i P_i(N,V,T) P_i(N,V)$$

The pressure of a macroscopic system is:

$$P(N,V) = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

So we can write the average pressure as:

$$\begin{aligned}\langle P \rangle &= \sum_i P_i(N,V,\beta)\left(-\frac{\partial E_i}{\partial V}\right)_N \\ &= \sum_i \left(-\frac{\partial E_i}{\partial V}\right)_N \frac{e^{-E_i(N,V)/kT}}{Q(N,V,T)}\end{aligned}$$

In a few steps we can show that the temperature can be expressed in terms of the partition function:

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/kT}$$

Writing in terms of β instead of temperature:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_i(N,V)}$$

The derivative of the partition function with respect to volume is:

$$\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta \sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i(N,V)}$$

The average pressure can then be written as:

$$\langle P \rangle = \frac{kT}{Q(N,V,\beta)}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta}$$

Which shows that the pressure can be expressed solely terms of the partition function:

$$\langle P \rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

We can use this result to derive the ideal gas law. For N particles of an ideal gas:

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!}$$

where:

$$q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

is the translational partition function. The utility of expressing the pressure as a logarithm is clear from the fact that we can write:

$$\begin{aligned}\ln Q &= N \ln q - \ln N! \\ &= -\frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln V - \ln N!\end{aligned}$$

We have used the property of logarithms that $\ln(AB) = \ln(A) + \ln(B)$ and $\ln(X^Y) = Y\ln(X)$. Only one term in the ln Q depends on V. Taking the derivative of $N \ln V$ with respect to V gives:

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V}$$

Substituting this into the above equation for the pressure gives:

$$P = \frac{NkT}{V}$$

which is the ideal gas law. Recall that $Nk = nR$ where N is the number of molecules and n is the number of moles. R is the universal gas constant (8.314 J/mol-K) which is nothing more than k multiplied by Avagadro's number. $N_A k = R$ converts the constant from a "per molecule" to a "per mole" basis.

Gas Compressed by a Piston

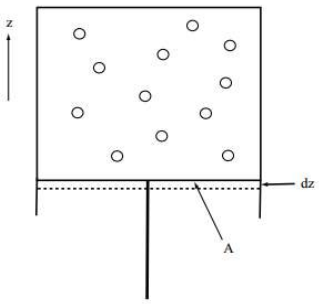


Figure 17.5.1 : Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive z axis.

Let us consider a simple thought experiment, which is illustrated in the figure above: A system of N particles is compressed by a piston pushing in the positive z direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude F on the system. The direction of the force is purely in the positive z direction, so that we can write the force vector $\mathbf{F}$ as $\mathbf{F} = (0, 0, F)$. At equilibrium (the piston is not moving), the system exerts an equal and opposite force on the piston of the form $(0, 0, -F)$. If the energy of the system is E, then the force exerted by the system on the piston will be given by the negative change in E with respect to z:

$$-F = -\frac{dE}{dz} \tag{17.5.1}$$

or:

$$F = \frac{dE}{dz} \tag{17.5.2}$$

The force exerted by the system on the piston is manifest as an observable pressure P equal to the force F divided by the area A of the piston, $P = F/A$. Given this, the observed pressure is just:

$$P = \frac{dE}{Adz} \tag{17.5.3}$$

Since the volume decreases when the system is compressed, we see that $Adz = -dV$. Hence, we can write the pressure as $P = -dE/dV$.

Of course, the relation $P = -dE/dV$ is a thermodynamic one, but we need a function of x that we can average over the ensemble. The most natural choice is:

$$p(x) = -\frac{d\mathcal{E}(x)}{dV} \tag{17.5.4}$$

so that $P = \langle p(x) \rangle$. Setting up the average, we obtain:

$$P = -\frac{C_N}{Q(N,V,T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{17.5.5}$$

$$= \frac{C_N}{Q(N,V,T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} \tag{17.5.6}$$

$$= \frac{kT}{Q(N,V,T} \frac{\partial}{\partial V} C_N \int e^{-\beta \mathcal{E}(x)} \tag{17.5.7}$$

$$= kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right) \tag{17.5.8}$$

Ideal Gas in the Canonical Ensemble

Recall that the mechanical energy for an ideal gas is:

$$\mathcal{E}(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{17.5.9}$$

where all particles are identical and have mass m. Thus, the expression for the canonical partition function $Q(N,V,T)$ is:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int dx \; e^{-\beta \sum_{i=1}^{N} \mathbf{p}_i^2 / 2m}$$

Note that this can be expressed as:

$$Q(N,V,T) = \frac{1}{N! h^{3N}} V^N \left[\int dp \; e^{-\beta p^2 / 2m} \right]^{3N}$$

Evaluating the Gaussian integral gives us the final result immediately:

$$Q(N,V,T) = \frac{1}{N!} \left[\frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]^N$$

The expressions for the energy:

$$E = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$$

which gives:

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT \tag{17.5.10}$$

and pressure:

$$P = kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V} \right)$$

giving:

$$P = \frac{NkT}{V} = \frac{nRT}{V} \tag{17.5.11}$$

which is the ideal gas law.

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17.6: Partition Functions of Systems of Distinguishable Molecules are Products of Molecular Partition Functions

A system, such as a container of gas, can consist of a large number of subsystems. How is the partition function of the system built up from those of the subsystems? This depends on whether the subsystems are distinguishable or indistinguishable. Let's start with energy. Energy is additive so that:

$$E_{\text{tot}}(N,V) = \epsilon_1(V) + \epsilon_2(V) + \epsilon_3(V) + \cdots$$

Each of the molecules can have their energy distributed over their respective energy states (e.g., vibrations, rotations, etc.). This means that each ϵ_i is already a summation over the states of the molecule. Let us assume that we can somehow distinguish all the molecules as: a, b, c, d… and denote the energy state they are in by i, j, k:

$$E_l(N,V) = \epsilon_i^a(V) + \epsilon_j^b(V) + \epsilon_k^c(V) + \cdots$$

A good example would be the molecules in a molecular crystal. They only move around a fixed site and so we can distinguish by how far molecule 'a' is from a given corner of the crystal. The systems partition function becomes:

$$Q(N,V,\beta) = \sum_i e^{-\beta E_l} = \sum_{i,j,k,\ldots} e^{-\beta(\epsilon_i^a + \epsilon_j^b + \epsilon_k^c)}$$

So far, we have done little effort to distinguish between the partition function of a molecular system q and the whole ensemble Q (e.g. the gas). If the entities that we called systems are **distinguishable** and independent, the whole ensemble partition function is the product of the molecular system partition functions. We get:

$$Q(N,V,\beta) = \prod_i q_i$$

for N distinguishable systems. We can split up the summation into a product of molecular partition functions:

$$Q(N,V,\beta) = \prod_i^N q_i(V,\beta) = q_a(V,\beta) q_b(V,\beta) q_c(V,\beta) \cdots$$

This results in each molecular system partition function being summed over independently:

$$Q(N,V,\beta) = \sum_i e^{-\beta\epsilon_i^a} \sum_j e^{-\beta\epsilon_i^b} \sum_k e^{-\beta\epsilon_i^c} \cdots$$

If the energy states of all the particles are the same, then the equation simplifies to:

$$Q(N,V,\beta) = [q(V,\beta)]^N$$

We can do this if, for example, the particles are embedded in a crystal where we can distinguish them by their location. We will see in the next chapter that for indistinguishable particles, such as those in a gas, we get a different result.

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17.7: Partition Function of Indistinguishable Components

In the previous section, the definition of the the partition function involves a sum of state formulism:

$$Q = \sum_i e^{-\beta E_i}. \tag{17.7.1}$$

However, under most conditions, full knowledge of each member of an ensemble is missing and hence we have to operate with a more reduced knowledge. This is demonstrated via a simple model of two particles in a two-energy level system in Figure 17.7.1. Each particle (red or blue) can occupy either the $E_1 = 0$ energy level or the $E_2 = \epsilon$ energy level resulting in four possible states that describe the system. The corresponding partition function for this system is then (via Equation 17.7.1):

$$Q_{\text{distinguishable}} = e^0 + e^{-\beta\epsilon} + e^{-\beta\epsilon} + e^{-2\beta\epsilon} = q^2 \tag{17.7.2}$$

and is just the molecular partition function (q) squared.

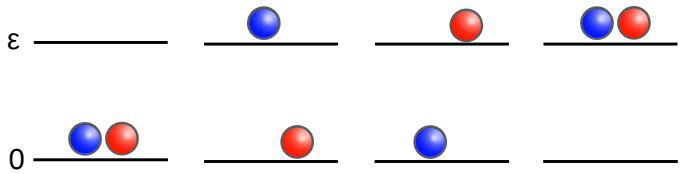


Figure 17.7.1: Four different states can exist for a two-level system with two distinguishable particles (red and blue balls). (CC BY 4.0; Delmar Larsen via LibreTexts)

However, if the two particles are indistinguishable (e.g., both the same color as in Figure 17.7.2) then while four different combinations can be generated like in Figure 17.7.1, there is no discernible way to separate the two middle states. Hence, there are effectively only three states observable for this system.

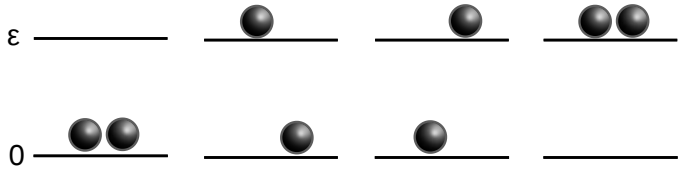


Figure 17.7.2: Three different states can exist for a two-level system with two indistinguishable particles (black balls). The two middle states are indescernable and represent a single state with one particle exited and the other in the ground state. (CC BY 4.0; Delmar Larsen via LibreTexts)

The corresponding partition function for this system (again using Equation 17.7.1) can be constructed:

$$Q(N, V, \beta) = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \neq q^2 \tag{17.7.3}$$

and this is not equal to the square of the molecular partition function. If Equation 17.7.2 were used to describe the indistinguishable particle case, then it would overestimate the number of observable states. From combinatorics, using q^N for a large N-particle system of indistinguishable particles will overestimate the number of states by a factor of $N!$. Therefore Equation 17.7.1 requires a slight modification to account for this over counting.

$$Q(N, V, \beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{17.7.4}$$

If we have N molecules, we can perform $N!$ permutations that should not affect the outcome. To avoid over counting (making sure we do not count each state more than once), the partition function becomes:

$$Q(N, V, \beta) = \frac{q(V, \beta)^N}{N!}$$

Note

As you may have noticed, using Equation 17.7.4 to estimate of Q for the two-indistinguishable particle discussed case above with $N = 2$ is incorrect (i.e., Equation 17.7.4 is not equal to Equation 17.7.3). That is because the $N!$ factor is only applicable for large N.

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17.8: A Molecular Partition Function Can Be Decomposed into Partition Functions for Each Degree of Freedom

From the previous sections, the partition function for a system of N indistinguishable and independent molecules is:

$$Q(N,V,\beta) = \frac{\sum_i e^{-\beta E_i}}{N!} \tag{17.8.1}$$

And the average energy of the system is:

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \tag{17.8.2}$$

We can combine these two equations to obtain:

$$\begin{aligned} \langle E \rangle &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \\ &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= N \sum_i \epsilon_i \frac{e^{-\epsilon_i / kT}}{q(V,T)} \end{aligned}$$

The average energy is equal to:

$$\langle E \rangle = N \langle \epsilon \rangle \tag{17.8.3}$$

where $\langle \epsilon \rangle$ is the average energy of a single particle. If we compare Equation 17.8.2 with Equation 17.8.2, we can see:

$$\langle \epsilon \rangle = \sum_i \epsilon_i \frac{e^{-\epsilon_i / kT}}{q(V,T)}$$

The probability that a particle is in state i, π_i, is given by:

$$\langle \epsilon \rangle = \frac{e^{-\epsilon_i / kT}}{q(V,T)} = \frac{e^{-\epsilon_i / kT}}{\sum_i e^{-\epsilon_i / kT}}$$

The energy of a particle is a sum of the energy of each degree of freedom for that particle. In the case of a molecule, the energy is:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}$$

The molecular partition function is the product of the degree of freedom partition functions:

$$q(V,T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

The partition function for each degree of freedom follows the same is related to the Boltzmann distribution. For example, the vibrational partition function is:

$$q_{\text{vib}} = \sum_i e^{-\epsilon_i / kT}$$

The average energy of each degree of freedom follows the same pattern as before. For example, the average vibrational energy is:

$$\langle \epsilon_{\text{vib}} \rangle = kT^2 \frac{\partial \ln q_{\text{vib}}}{\partial t} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta}$$

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17.E: Exercises

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{17.E.1}$$

You can see from Equation 17.E.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise 17.E.1

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

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CHAPTER OVERVIEW

18: Partition Functions and Ideal Gases

UC Davis Chemistry Chemistry 110B

Physical Chemistry II: Properties of Atoms and Molecules

Summer 2016: Delmar Larsen

Sorry, but all current instructors at UCD use the commercial textbook for this course.

In chemistry, we are typically concerned with a collection of molecules. However, if the molecules are reasonably far apart as in the case of a dilute gas, we can approximately treat the system as an ideal gas system and ignore the intermolecular forces. The present chapter deals with systems in which intermolecular interactions are ignored. In ensemble theory, we are concerned with the ensemble probability density, i.e., the fraction of members of the ensemble possessing certain characteristics such as a total energy E, volume V, number of particles N or a given chemical potential μ and so on. The molecular partition function enables us to calculate the probability of finding a collection of molecules with a given energy in a system. The equivalence of the ensemble approach and a molecular approach may be easily realized if we treat part of the molecular system to be in equilibrium with the rest of it and consider the probability distribution of molecules in this subsystem (which is actually quite large compared to systems containing a small number of molecules of the order of tens or hundreds).

18.1: The Translational Partition Function of a Monatomic Ideal Gas
18.2: Most Atoms Are in the Ground Electronic State at Room Temperature
18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms
18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature
18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures
18.6: Rotational Partition Functions Contain a Symmetry Number
18.7: The Vibrational Partition Function
18.8: The Rotational Partition Function Depends on the Shape of the Molecule
18.9: Molar Heat Capacities
18.E: Partition Functions and Ideal Gases (Exercises)

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18.1: The Translational Partition Function of a Monatomic Ideal Gas

Let us consider the translational partition function of a monatomic gas particle confined to a cubic box of length L. The particle inside the box has translational energy levels given by:

$$E_{\text{trans}} = \frac{h^2\left(n_x^2+n_y^2+n_z^2\right)}{8mL^2}$$

where n_x, n_y and n_z are the quantum numbers in the three directions. The translational partition function is given by:

$$q_{\text{trans}} = \sum_i e^{-\epsilon_i/kT}$$

which is the product of translational partition functions in the three dimensions. We can write the translation partition function as the product of the translation partition function for each direction:

$$q_{\text{trans}} = q_x q_y q_z \tag{18.1.1}$$

$$= \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \sum_{n_y=1}^{\infty} e^{-\epsilon_y/kT} \sum_{n_z=1}^{\infty} e^{-\epsilon_z/kT} \tag{18.1.2}$$

Since the levels are very closely spaced (continuous), we can replace each sum in Equation 18.1.2with an integral. For example:

$$q_x = \sum_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{18.1.3}$$

$$\approx \int_{n_x=1}^{\infty} e^{-\epsilon_x/kT} \tag{18.1.4}$$

and after substituting the energy for the relevant dimension:

$$\epsilon_x = \frac{h^2 n_x^2}{8mL^2}$$

we can extend the lower limit of integration in the approximation of Equation 18.1.4:

$$q_x = \int_1^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}} \approx \int_0^{\infty} e^{-\frac{h^2 n_x^2}{8mL^2kT}}$$

We then use the following solved Gaussian integral:

$$\int_o^{\infty} e^{-an^2}\,dn = \sqrt{\frac{\pi}{4a}}$$

with the following substitution:

$$a = \frac{h^2}{8mL^2kT}$$

we get:

$$q_x = \frac{1}{2}\sqrt{\frac{\pi}{a}} = \frac{1}{2}\sqrt{\frac{\pi 8mkT}{h^2}}L$$

or more commonly presented as:

$$q_x = \frac{L}{\Lambda}$$

where Λ is the **de Broglie wavelength** and is given by

$$\Lambda = \frac{h}{\sqrt{2\pi 8mkT}}$$

Multiplying the expressions for q_x, q_y and q_z (Equation 18.1.1) and using V as the volume of the box L^3, we arrive at:

$$q_{\text{trans}} = \left(\frac{\sqrt{2\pi 8mkT}}{h}\right)^{3/2} V = \frac{V}{\Lambda^3} \tag{18.1.5}$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 for small molecular masses. This means that such a large number of translational states are accessible and available for occupation by the molecules of a gas. This result is very similar to the result of the classical kinetic gas theory that said that the observed energy of an ideal gas is:

$$U = \frac{3}{2}nRT$$

We postulate therefore that the observed energy of a macroscopic system should equal the statistical average over the partition function as shown above. In other words: if you know the particles your system is composed of and their energy states you can use statistics to calculate what you should observe on the whole ensemble.

Example

Calculate the translational partition function of an I_2 molecule at 300K. Assume V to be 1 liter.

Solution

Mass of I_2 is $2 \times 127 \times 1.6606 \times 10^{-27} kg$

$$\begin{aligned} 2\pi mkT &= 2 \times 3.1415 \times (2 \times 127 \times 1.6606 \times 10^{-27}\ kg) \times 1.3807 \times 10^{-23}\ J/K \times 300K \\ &= 1.0969 \times 10^{-44}\ J\,kg \end{aligned}$$

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi mkT}} \\ &= \frac{6.6262 \times 10^{-34}\ J\,s}{\sqrt{1.0969 \times 10^{-44}\ J\,kg}} = 6.326 \times 10^{-12}\ m \end{aligned}$$

The via Equation 18.1.5

$$q_{\text{trans}} = \frac{V}{\Lambda^3} = \frac{1000 \times 10^{-6} m^3}{(6.326 \times 10^{-12}\ m)^3} = 3.95 \times 10^{30}$$

This means that 3.95×10^{30} quantum states are thermally accessible to the molecular system

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18.2: Most Atoms Are in the Ground Electronic State at Room Temperature

Writing the electronic energies as $E_1, E_2, E_3, \ldots$ with corresponding degeneracies $g_1, g_2, g_3, \ldots$. The electronic partition function is then given by the following summation:

$$q_{el}(T) = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + \ldots \tag{18.2.1}$$

Usually, the differences in electronic energies are significantly greater than thermal energy kT:

$$kT \ll E_1 < E_2 < E_3$$

If we treat the lowest energy electronic state E_1 as the reference value of zero of energy, the electronic partition function (Equation 18.2.1) can be approximated as:

$$q_{elec}(T) = g_1 + g_2 e^{-E_2/kT} + g_3 e^{-E_3/kT} + \ldots \tag{18.2.2}$$

Typically electronic states are tens of thousands of wave numbers above the ground state. For example, the first excited electronic state of nitric oxide (NO) is ~40,000 cm^{-1}. Using this value:

$$\frac{E_2}{kT} = \frac{40000\ \text{cm}^{-1}}{kT} = \frac{10^4\ \text{K}}{T}$$

That means, that even at 1,000 K, the value of the second term in {\reference{3.24}} is:

$$g_2 e^{-10} = g_2 4.5 \times 10^{-5}$$

The result is that the higher electronic states are not accessible under ordinary temperatures. There are some cases, however, where the first excited state lies much closer to the ground state, but these are the exception rather than the rule.

Example 18.2.1

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near $-32\ eV$ and the next level is about $5\ eV$ higher. Taking -32 eV as the zero (or reference value of energy), then

$$q_{el} = e_0 + e^{-5eV/kT} + \ldots$$

At 300 K, T = 0.02\; eV and

$$q_{el} = 1 + e^{-200} + \ldots$$
$$\approx 1.0$$

Where all terms other than the first are essentially 0. This implies that $q_{el} = 1$.

The physical meaning of the result from Example 18.2.1 is that only the ground electronic state is generally thermally accessible at room temperature.

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18.3: The Energy of a Diatomic Molecule Can Be Approximated as a Sum of Separate Terms

A monatomic gas has three degrees of freedom per molecule, all of them translational:

1. movement in x-direction
2. movement in y-direction
3. movement in z-direction

A polyatomic gas, including diatomic molecules, has other levels that you can 'stuff' energy into. Polyatomic molecules can rotate and vibrate, and if enough energy is available you could also excite the electrons involved in the σ and π bonds. A reasonable approximation of the partition function of the molecule would become:

$$q_{\text{tot}}(V,T) = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$

The partition function of a molecular idea gas is then:

$$Q(N,V,T) = \frac{(q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}})^N}{N!}$$

The total energy of the molecule is then the sum of the translation, vibrational, rotational, and electronic energies:

$$E_{tot} = E_{\text{trans}} E_{\text{vib}} E_{\text{rot}} E_{\text{elec}}$$

We will only scratch the surface of the additional degrees of freedom and their partition functions.

Electronic

At room temperature the system is usually in its ground electronic state. This means that the **electronic partition function** $q_{\text{elec}} = 1$. Usually we do not have to worry about these degrees of freedom. If we do, there are usually just a few levels to worry about. This includes their **degeneracy g**. If there is a single state at a certain energy ($g = 1$), two states ($g = 2$), or more states, we must multiply the Boltzmann factor by this degeneracy number.

If there are more than one state to worry about, we could follow the same procedure as we did for the translational states:

1. Define the energy states and their degeneracies
2. Compose the partition function q for the molecule and Q for the gas
3. Use the (β or T) derivative of $\ln Q$ to determine $\langle E \rangle$
4. Use the T derivative of $U \approx \langle E \rangle$ to find the contribution to the heat capacity

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18.4: Most Molecules Are in the Ground Vibrational State at Room Temperature

The vibrational energy levels of a diatomic are given by:

$$E_v = (v+1/2)h\nu$$

where is ν the vibrational frequency and v is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below:

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-(v+1/2)h\nu/kT} \\ &= e^{-h\nu/2kT}\left(1+e^{-h\nu/2kT}+e^{-2h\nu/2kT}+\ldots\right) \end{aligned}$$

or rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(1+x+x^2+x^3+\ldots\right) \tag{18.4.1}$$

where $x = e^{-h\nu/kT}$. Given the following power series expansion:

$$\frac{1}{1-x} = 1+x+x^2+x^3+x^4+\ldots.$$

Equation 18.4.1 can be rewritten as:

$$q_{\text{vib}} = e^{-h\nu/2kT}\left(\frac{1}{1-x}\right)$$

or:

$$q_{\text{vib}} = \frac{e^{-h\nu/2kT}}{1-e^{-h\nu/kT}} \tag{18.4.2}$$

If the zero of energy scale is at $h\nu/2kT$, then Equation 18.4.2 can be rewritten as:

$$q_{\text{vib}} \approx \frac{1}{1-e^{-h\nu/kT}} \tag{18.4.3}$$

A vibrational temperature Θ_{vib} may be defined as:

$$\Theta_{\text{vib}} = \frac{hc\tilde{\nu}}{k}$$

where $\tilde{\nu}$ is the vibrational frequency in cm^{-1}. Θ_{vib} is a good way to express the *stiffness* of the vibrating bond in units of the Boltzmann constant. Because the stiffness obviously depends on what bond your are talking about, this is a good way to do the same thing we did for the critical temperature of the non-ideal gases.

Table 18.4.1 : Representative molecular data for a few diatomics

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/mol)
$\boldsymbol{H_2}$	1	0.7474	4400	6332	60.9	87.6	5.749	103.2
$\boldsymbol{D_2}$	1	0.7415	3118	4487	30.45	43.8	5.77	104.6
$\boldsymbol{N_2}$	1	1.097	2358	3393	2.001	2.99	22.94	225.1
O_2	3	1.207	1580	2274	1.446	2.08	11.76	118.0
Cl_2	1	1.987	560	805	0.244	0.351	3.2	57.0
CO	1	1.128	2170	3122	1.931	2.78	19.03	255.8

Molecule	g	Bond Length (pm)	ω (cm^{-1})	Θ_{vib} (K)	$\tilde{B}$ (cm^{-1})	Θ_{rot} (K)	Force constant k (dynes/cm)	D_0 (kcal/mol)
NO	2	1.15	190	2719	1.695	2.45	15.7	150.0
HCl	1	1.275	2938	4227	10.44	15.02	4.9	102.2
HI	1	1.609	2270	3266	6.46	9.06	3.0	70.5
Na_2	1	3.096	159	229	0.154	0.221	0.17	17.3
K_2	1	3.979	92.3	133	0.0561	0.081	0.10	11.8

Example 18.4.1

The vibrational frequency of of I_2 is $214.57\ cm^{-1}$. Calculate the vibrational partition function of I_2 at 300 K.

Solution:

$$\frac{h\nu}{kT} = \frac{214.57}{209.7} = 1.0232$$

so

$$e^{-h\nu/kT} = 0.3595$$

and

$$q_{vib} = \frac{1}{1-0.3595} = 1.561$$

This implies, as before, that very few vibrational states are accessible and much less than rotation states and many orders less than translation states.

Vibrational Heat Capacity

The vibrational energy is given by the above expression and the molar heat capacity at constant volume, $\bar{C}_V$ is given by:

$$\bar{C}_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We have:

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} \tag{18.4.4}$$

$$= \frac{-1}{kT^2}\frac{\partial}{\partial \beta} \tag{18.4.5}$$

$$= \left(-k\beta^2\right)\left(\frac{\partial}{\partial \beta}\right) \tag{18.4.6}$$

Therefore:

$$\bar{C}_V = \left(-k\beta^2\right)\left(\frac{\partial \varepsilon_{vib}}{\partial \beta}\right)$$

and when the vibrational partition function (Equation 18.4.3) is introduced:

$$q_{\text{vib}} = -k\beta^2 \frac{\left[(1-e^{-hc\nu/kT})(-hc\tilde{\nu}) - e^{-hc\nu/kT}(+hc\tilde{\nu})\right] e^{-hc\nu/kT}}{(1-e^{-hc\nu/kT})^2} h\nu\tilde{\nu} \tag{18.4.7}$$

$$= k\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1-e^{-\Theta_{\text{vib}}/T}\right)^2} \tag{18.4.8}$$

For large T, the $\bar{C}_V$ becomes:

$$N_A k = R$$

and for small T, $\bar{C}_V$ goes to zero as demonstrated in Figure 18.4.1 .

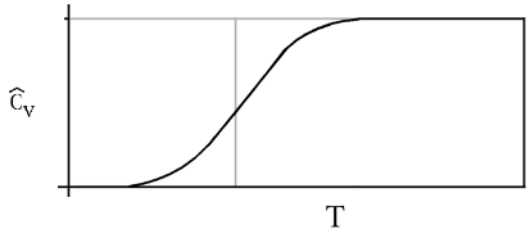


Figure 18.4.1 : Vibrational heat capacity of a diatomic

The vibrational heat capacity is shown as function of the reduced temperature T/Θ to get a general picture valid for all diatomic gases. Compare the parameters on Table 18.4.1 to see on what different absolute scales we have to think for different gases. Clearly the vibrational contribution to the heat capacity *depends on temperature*. For many molecules (especially light ones), the vibrational contribution only kicks in at quite high temperatures.

The value of Θ_{vib} is determined mostly by

1. the strength of a bond (the stronger the higher Θ_{vib})
2. the (effective) mass of the molecule (the lighter the higher Θ_{vib})

Molecules with low Θ_{vib} often dissociate at lower temperatures, although the *harmonic* oscillator model is not sufficient to describe that phenomenon.

Vibrational Populations

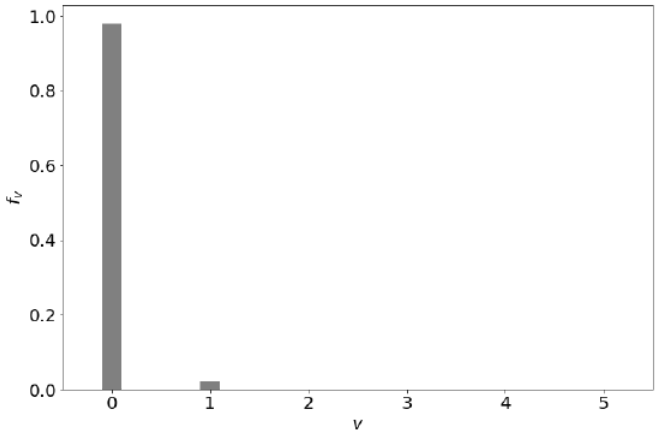
We can calculate the fraction of molecules in each vibrational state. The fraction of molecules in the vth vibrational state is given by:

$$f_v = \frac{e^{-h\nu(v+\frac{1}{2})/kT}}{q_{\text{vib}}}$$

Substituting in Equation 18.4.2, we get:

$$f_v = \left(1-e^{-h\nu/kT}\right) e^{-h\nu v/kT}$$
$$= \left(1-e^{-\Theta_{\text{vib}}/T}\right) e^{-\Theta_{\text{vib}} v/T}$$

We can plot the fraction molecules in each vibrational state.



The vibrational population of Cl_2 at 300 K. Most of the molecules are in the ground vibrational state, $v = 0$.

From the figure, we can see that most of the Cl_2 molecules are in the ground vibrational state at room temperature (300 K). This is true for most molecules. Only molecules with very weak bonds and low vibrational temperatures will populate a significant fraction of molecules in excited vibrational states.

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18.5: Most Molecules Are in Excited Rotational States at Ordinary Temperatures

The rotational quantum number is J and the energy of the rotations is:

$$E(J) = \tilde{B}J(J+1)$$

Where $\tilde{B}$ is in units of cm^{-1} and is equivalent to:

$$\frac{h}{8\pi^2 Ic}$$

Where c is the speed of light in units of cm^{-1}. However, with the exception of the ground state (i.e., $J = 0$), multiple eigenstates exist for a given value of J. This is a form of **degeneracy**, (g), and the number of levels per energy goes as 1, 3, 5, 7, 9 etc or:

$$g(J) = 2J+1$$

Therefore, the summation to find the partition function $q_{\text{rot}}(T)$ contains an extra factor $g = 2J+1$. This factor is mathematically very handy, because it is the derivative of:

$$g(J) = J(J+1)$$

This makes it possible to change variables to $X = J(J+1)$ and the integration becomes very easy. Notice that just like in the translation partition function, we approximate the summation with an integral. However, because we are dealing with far fewer levels, this is less justified in the rotational case. How justified it is depends on the gas and the temperature we consider. Roughly speaking we should be at a temperature $T >> \Theta_{\text{rot}}$.

? Exercise 18.5.1

Look at table 18.2. When do we need to actually work out the (discrete) summation instead of making a (continuous) integration out of it?

Answer

Only for the lightest gases like He and H_2 do we need to worry and then only at pretty low cryogenic circumstances. At room temperature, we can take the rotational levels as a continuous set and use an integral. Notice that the vibrational Θ values are much larger! At $T = 300\,\text{K}$, usually only a single level is occupied and we are in the discrete limit. On the surface of the sun that would be a different matter of course.

The rotational constant B is directly linked to the moment of inertia:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and r is the bond length. Again we can scale the behavior of different systems to one and the same picture by introducing a characteristic temperature:

$$\Theta_{rot} = \frac{hb}{k} = \frac{\hbar^2}{2Ik_b}$$

As we did for the translations, we can calculate the moment $\langle\epsilon\rangle$. For vibrations we get a relatively complicated function of temperature. However, for rotations, the moment is simply equal to NkT and this means that the rotational contribution to the molar C_v of a diatomic is simply R. As the vibrational and electronic contributions to the heat capacity are typically negligible at room temperature, we get:

- monatomic gas

$$C_v = C_v^{trans} = \frac{3}{2}nR$$

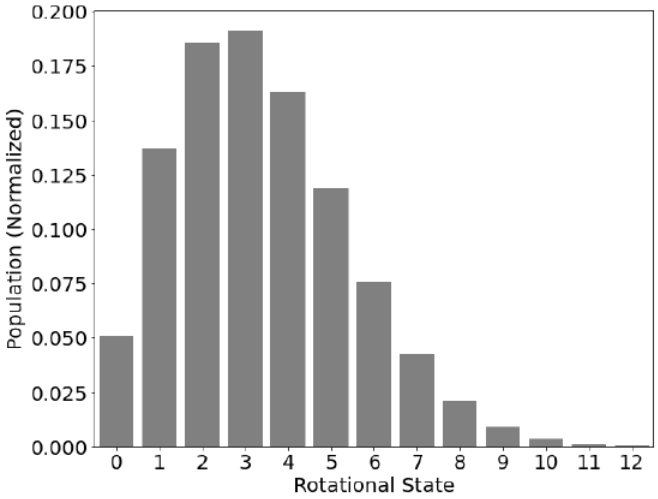
- diatomic

$$C_v = C_v^{trans} + C_v^{rot} \tag{18.5.1}$$

$$= \frac{3}{2}nR + nR \tag{18.5.2}$$

$$= \frac{5}{2}nR \tag{18.5.3}$$

Rotational energies are less than vibrational and electronic energies and, at room temperature, many rotational states will be populated.



The normalized rotational population of HCl at room temperature.

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18.6: Rotational Partition Functions Contain a Symmetry Number

The rotational energy levels of a **diatomic molecule** are given by:

$$E_{\text{rot}}(J) = \tilde{B}J(J+1) \tag{18.6.1}$$

where:

$$\tilde{B} = \frac{h}{8\pi^2 Ic}$$

Here, $\tilde{B}$ is the rotational constant expressed in cm^{-1}. The rotational energy levels are given by:

$$E_j = \frac{J(J+1)h^2}{8\pi I}$$

where I is the moment of inertia of the molecule given by μr^2 for a diatomic, and μ is the reduced mass, and r the bond length (assuming rigid rotor approximation). The energies can be also expressed in terms of the rotational temperature, Θ_{rot}, defined as:

$$\Theta_{\text{rot}} = \frac{r^2}{8\pi^2 Ik} \tag{18.6.2}$$

The interpretation of θ_{rot} is as an estimate of the temperature at which thermal energy ($\approx kT$) is comparable to the spacing between rotational energy levels. At about this temperature the population of excited rotational levels becomes important. See Table 1.

Table 1: Select Rotational Temperatures. In each case the value refers to the most common isotopic species.

Molecule	H_2	N_2	O_2	F_2	HF	HCl	CO_2	HBr	CO
Θ_{rot}	87.6	2.88	2.08	1.27	30.2	15.2	0.561	12.2	2.78

In the summation for the expression for rotational partition function (q_{rot}), Equation 18.6.3, we can do an explicit summation:

$$q_{\text{rot}} = \sum_{j=0} (2J+1)e^{-E_J/kT} \tag{18.6.3}$$

if only a finite number of terms contribute. The factor $(2J+1)$ for each term in the expansion accounts for the degeneracy of a rotational state J. For each allowed energy E_J from Equation 18.6.1there are $(2J+1)$ eigenstates. The Boltzmann factor must be multiplied by $(2J+1)$ to properly account for the degeneracy these states:

$$(2J+1)e^{-E_J/kT}$$

If the rotational energy levels are lying very close to one another, we can integrate similar to what we did for q_{trans} previously to get:

$$q_{\text{rot}} = \int_0^\infty (2J+1)R^{-\tilde{B}J(J+1)/kT}dJ$$

This integration can easily be done by substituting $x = J(J+1)$ and $dx = (2J+1)dJ$:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}} \tag{18.6.4}$$

For a homonuclear diatomic molecule, rotating the molecule by 180° brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states. To correct for this, we divide the partition function by σ, which is called the **symmetry number** and is equal to the distinct number of ways by which a molecule can be brought into identical configurations by rotations. The rotational partition function becomes:

$$q_{\text{rot}} = \frac{kT}{\tilde{B}\sigma} \tag{18.6.5}$$

or commonly expressed in terms of Θ_{rot}:

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}\sigma} \tag{18.6.6}$$

Example 18.6.1

What is the rotational partition function of H_2 at 300 K?

Solution

The value of $\tilde{B}$ for H_2 is 60.864 cm^{-1}. The value of kT in cm^{-1} can be obtained by dividing it by hc, i.e., which is $kT/hc = 209.7\ cm^{-1}$ at 300 K. $\sigma = 2$ for a homonuclear molecule. Therefore from Equation 18.6.5,

$$\begin{aligned} q_{\text{rot}} &= \frac{kT}{\tilde{B}\sigma} \\ &= \frac{209.7\ cm^{-1}}{(2)(60.864\ cm^{-1})} \\ &= 1.723 \end{aligned}$$

Since the rotational frequency of H_2 is quite large, only the first few rotational states are accessible at 300 K

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18.7: The Vibrational Partition Function

As with diatomic molecules, the energies of polyatomic molecules can be approximated by the sum of its individual degrees of freedom. Therefore, we can write the partition function as:

$$Q(N,V,T) = \frac{[q(V,T)]^2}{N!}$$

We can write the polyatomic analog to diatomic molecules:

$$Q(N,V,T) = \frac{(q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}})^N}{N!}$$

When derived for diatomic molecules, we assumed the rigid rotor model for rotations and the harmonic oscillator for vibrations. This allowed us to separate the rotational motion from the vibrational motion of the molecule. Polyatomic molecules are a bit more complicated, but we will still make use of these approximations.

The number of translational states available to any given molecule is far greater than the number of molecules in the system. q_{trans} is given by:

$$q_{\text{trans}} = \left[\frac{2\pi MkT}{h^2}\right]^{3/2} V$$

where M is the mass of the particle. Moving to the electronic partition function:

$$q_{\text{elec}} = \sum_i g_i e^{-E_i/kT}$$

where E_i is the energy of the electronic state i and {g_i} is its degeneracy. Electronic states are typically spaced far apart from each other. The probability of the system being in any state but the ground state is extremely small. We can therefore simplify the electronic partition function to include only the ground electronic state:

$$q_{\text{elec}} = g_{e1}e^{D_e/kT}$$

where $-D_e$ is the energy of the ground electronic state. To complete the polyatomic partition function, we still need q_{vib} and q_{rot}. We will finish this section with q_{vib} and talk about q_{rot} in the next.

The vibrational motion of diatomic molecules can be expressed as a set of independent harmonic oscillators. For polyatomic molecules, the independent vibrational motions are referred to as normal modes of vibration. The vibrational energy is then the sum of the energies for each normal mode:

$$E_{\text{vib}} = \sum_i^{\alpha}\left(v_i + \frac{1}{2}\right)h\nu$$

where ν_i is the vibrational frequency for the ith normal mode and α is the number of vibration degrees of freedom. A linear molecule has $3n-5$ vibrational degrees of freedom and a nonlinear molecule has $3n-6$ vibrational degrees of freedom. Because the normal modes are independent of each other, we can take out results from previous sections:

$$q_{\text{vib}} = \prod_i^{\alpha}\frac{e^{-\theta_{\text{vib},i}/2T}}{1-e^{-\theta_{\text{vib},i}/T}}$$

$$E_{\text{vib}} = Nk\sum_i^{\alpha}\left(\frac{\theta_{\text{vib},i}}{2} + \theta_{\text{vib},i}\frac{e^{-\theta_{\text{vib},i}/T}}{1-e^{-\theta_{\text{vib},i}/T}}\right)$$

$$C_{V,\text{vib}} = Nk\sum_i^{\alpha}\left(\left(\frac{\theta_{\text{vib},i}}{2}\right)^2 + \frac{e^{-\theta_{\text{vib},i}/T}}{(1-e^{-\theta_{\text{vib},i}/T})^2}\right)$$

where $\theta_{\text{vib},i}$ is the characteristic vibrational temperature defined by:

$$\theta_{\text{vib},i} = \frac{h\nu_i}{k}$$

Vibrational Entropy

There is a great deal of utility for thermodynamic functions calculated from the vibrational normal modes of a molecule. The vibrational energy and entropy depend on the shape a multidimensional potential energy surface. If one performs a conformational search of macromolecule it is one obtains energies and structures but little direct information concerning the shape of the potential energy surface for each conformation. The vibrational entropy gives a means determining whether there are significant entropic differences in the structures and therefore whether certain conformations will be favored based on the entropy.

However, it is possible to take appropriate linear combinations of the coordinates so that the cross terms are eliminated and the classical Hamiltonian as well as the operator corresponding to it contains no cross terms and in terms of the new coordinates, the Hamiltonian can be written as,

$$H = \sum_{i=1}^{f} \frac{h^2}{2\mu_i} \frac{\partial}{\partial q_i^2} + \sum_{i=1}^{f} \frac{k_i}{2} q_i^2 \tag{18.7.1}$$

Here, the degrees of freedom f is $3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule. Here, k_i is the force constant and μ_i is the reduced mass for that particular vibrational mode which is referred to as a **normal mode**.

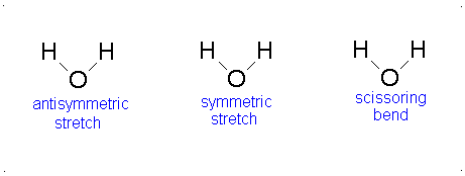


Figure 18.7.1 : The three vibrational modes of water, the symmetric stretch (3656.7 cm^{-1}, 5160 K), the asymmetric stretch (3755.8 cm^{-1} , 5360 K) and the bending mode (1594.8 cm^{-1} ,2290 K) are shown. The vibrational frequencies and the characteristic temperature for each mode are shown in parenthesis. Although not shown in the animation, the oxygen atom also moves with each of these normal modes.

The Equation 18.7.1 represents f linearly independent harmonic oscillators and the total energy for such a system is

$$\epsilon_{vib} = \sum_{i=1}^{f} \left(v_i + \frac{1}{2} \right) h\nu_i$$

The vibrational frequencies are given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

The vibrational partition function is given by the product of f vibrational functions for each frequency.

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}} \tag{18.7.2}$$

with

$$\Theta_{vib,i} = \frac{h\nu_i}{k_B}$$

As with the previous discussion regarding simple diatomics, $\Theta_{vib,i}$ is called the **characteristic vibrational temperature**. The molar energies and the heat capacities are given by

$$\langle E_{vib} \rangle = Nk \sum_{i=1}^{f} \left[\frac{\Theta_{vib,i}}{2} + \frac{\Theta_{vib,i} e^{-\Theta_{vib,i}/T}}{1 - e^{-\Theta_{vib,i}/T}} \right]$$

and

$$\bar{C}_V = Nk_B \sum_{i=1}^{f} \left(\frac{\Theta_{vib,i}}{T} \right)^2 \frac{e^{-\Theta_{vib,i}/T}}{\left(1 - e^{-\Theta_{vib,i}/T}\right)^2}$$

Example

The three characteristic vibrational temperatures for NO_2 are 1900 K, 1980 K and 2330 K. Calculate the vibrational partition function at 300 K.

Solution

The vibrational partition is (Equation 18.7.2)

$$q_{vib} = \prod_{i=1}^{f} \frac{e^{-\Theta_{vib,i}/2T}}{1 - e^{-\Theta_{vib,i}/T}}$$

If we calculate q_{vib} by taking the zero point energies as the reference points with respect to which the other energies are measured

$$q_{vib} = \prod_{i=1}^{f} \frac{1}{1 - e^{-\Theta_{vib,i}/T}} = \left(\frac{1}{1 - e^{-1900/300}}\right)\left(\frac{1}{1 - e^{-1980/300}}\right)\left(\frac{1}{1 - e^{-2330/300}}\right)$$

$$= (1.0018)(1.0014)(1.0004) = 1.0035$$

The implication is that very few vibrational states of NO_2 (other than the ground vibrational state) are accessible at 300 K. This is standard of the vibrations of most molecules.

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18.8: The Rotational Partition Function Depends on the Shape of the Molecule

For a polyatomic molecule containing N atoms, the total number of degrees of freedom is $3N$. Out of these, three degrees of freedom are taken up for the translational motion of the molecule as a whole. For nonlinear molecules, there are three rotational degrees of freedom and the $3N-6$ vibrational degrees. For linear molecules, the rotational motion along the molecular axis is quantum mechanically not meaningful as the rotated configuration is indistinguishable from the original configuration. Therefore, linear molecules have two rotational degrees of freedom and $3N-5$ vibrational degrees of freedom.

To investigate the rotational motion, we need to fix the center of mass of the molecule and calculate the three principal moments of inertia I_A, I_B, and I_C of the ellipsoid of inertia. The center of mass is defined as the point for which the following identities hold:

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i$$

The inertia products are defined by:

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right)$$

$$I_{xy} = \sum_i m_i \left(x_i y_i\right)$$

The other components I_{yy}, I_{xz},.. are defined analogously. To find the direction cosines $\alpha_i, \beta_o, \gamma_i$ of the three principle moments of inertia, we need to solve the following matrix equations:

$$\alpha(I_{xx} - \eta) - \beta I_{xy} - \gamma I_{xz} = 0$$

$$\alpha I_{xy} - \beta(I_{yy} - \eta) - \gamma I_{yz} = 0$$

$$-\alpha I_{xz} - \beta I_{yz} + \gamma(I_{zz} - \eta) = 0$$

If the off diagonal terms I_{xy} are zero in the above equations, then the x, y, z axis will be the principal axis. The energy of a rotor with the three moments of inertia I_A, I_B. and I_C is given by:

$$\begin{aligned} \epsilon &= \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \\ &= \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C} \end{aligned}$$

Each of the rotational degrees of freedom will have a characteristic rotational temperature in terms of the moment of inertia:

$$\Theta_{rot,i} = \frac{hbar^2}{2I_i k} \qquad i = A, B, C$$

There are many different shapes of molecules and these shapes affect the rotational behavior of the molecules. Molecules are therefore classified according to symmetry into different groups called tops. The three different tops are:

$$\begin{aligned} &\text{Spherical top} && \Theta_{rot,A} = \Theta_{rot,B} = \Theta_{rot,C} \\ &\text{Symmetric top} && \Theta_{rot,A} = \Theta_{rot,B} \neq \Theta_{rot,C} \\ &\text{Asymmetric top} && \Theta_{rot,A} \neq \Theta_{rot,B} \neq \Theta_{rot,C} \end{aligned}$$

Spherical Tops

The spherical top can be solved exactly to give:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

$$g_J = (2J+1^2) \qquad J = 0, 1, 2, \ldots$$

The rotational partition function is:

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{\hbar^2 J(J+1)/2IkT}$$
$$= \sum_{J=0}^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

For almost all spherical top molecules:

$$\Theta_{\text{rot}} \gg T$$

Therefore, we can convert the sum to an integral:

$$q_{\text{rot}} = \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{\Theta_{\text{rot}} J(J+1)/T}$$

where we have now included the symmetry term, σ. Solving for this integral, we get:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{q_{\text{rot}}} \right)^{3/2}$$

Symmetric Tops

Here, ω_A, ω_B, and ω_C are the three angular speeds and L_A, L_B, and L_C are the three angular momenta. For a symmetric top molecule such as ammonia, or chloromethane, two components of the moments of inertia are equal, i.e., $I_B = I_C$. The rotational energy levels of such a molecule are specified by two quantum numbers J and K. The total angular momentum is determined by J and the component of this angular momentum along the unique molecular axis is determined by K. The energy levels are given by:

$$\epsilon_{J,K} = \tilde{B} J(J+1) + (\tilde{A} - \tilde{B}) K^2$$

with rotational constants in units of wavenumbers:

$$\tilde{B} = \frac{h}{8\pi^2 c I_B}$$

and:

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}$$

where

- J takes on values $0, 1, 2, \ldots . \infty$and
- $K = -J, -J+1, -J+2, \ldots 0, 1, 2, \ldots J$.

The rotational partition function is given by:

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\tilde{B} J(J+1)/kT} \sum_{K=-J}^{J} (2J+1) e^{\tilde{A}-\tilde{B}) K^2/kT}$$

This can be converted to an integral and the result is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi I_B kT}{h^2} \right) \left(\frac{8\pi I_A kT}{h^2} \right)^{1/2}$$

Asymmetric Tops

For asymmetric tops, the expressions for rotational energies are more complex and the conversions to integrations are not easy. One can actually calculate the sum of terms using a computer. An intuitive answer can be obtained by integrating over the angular momenta L_A, L_B and L_C as:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{H(p,q)/kT} \, dL_A \, dL_B \, dL_C = \sqrt{2\pi I_A kT} \sqrt{2\pi I_B kT} \sqrt{2\pi I_C kT}$$

And then multiplying by a factor of $8\pi^2/\sigma h^3$, we get the rotational partition function. The factor of $8\pi^2$ accounts for the angular integration. For any axis chosen in a molecule, a complete rotation contributes a factor of 2π. Integration over all possible orientations of this axis contribute another factor of 4π. The factor of h^3 is for the conversion from the classical phase space to the quantum mechanical phase space.

Symmetry Number

As discussed previously, the **symmetry number** σ corrects for overcounting of rotational configurations. If the molecule has no center of symmetry (e.g. HCN) $\sigma = 1$ whereas if the molecule has a center of symmetry (e.g. CO_2) then $\sigma = 2$.

The final result is:

$$q_{rot} = \frac{\pi^2}{\sigma}\sqrt{\frac{8\pi I_A kT}{h^2}}\sqrt{\frac{8\pi I_B kT}{h^2}}\sqrt{\frac{8\pi I_C kT}{h^2}} \tag{18.8.1}$$

Classical Derivation (Optional)

We can explicitly obtain the classical rotational partition function of an asymmetric top by writing the classical expression for the rotational energy in terms of the Euler angles. The orientation of a rigid rotor can be specified by there Euler angles θ, φ, and ψ with the ranges of angles 0 to π, 0 to 2π and 0 to 2π respectively. The rotational Hamiltonian for the kinetic energy can be written in terms of the angles and their conjugate momenta (p_θ, p_ϕ, p_ψ)

$$H = \frac{\sin^2\psi}{2I_A}\left(p_\theta - \frac{\cos\psi}{\sin\theta\sin\psi}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{\cos^2\psi}{2I_B}\left(p_\theta - \frac{\sin\psi}{\cos\theta\cos\psi}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2I_C}p_\psi^2$$

The classical rotational partition function is given by

$$q_{rot} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{1}{h^3}e^{-H(p,q)/kT}dp_\theta\, dp_\phi\, dp_\psi\, d\theta\, d\phi\, d\psi$$

The integrations can be simplified by rewriting $H(p,q)/kT$ as

$$\frac{H}{kT} = \frac{1}{2I_A kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)\left(p_\theta + \left(\frac{1}{I_B} - \frac{1}{I_A}\right)\frac{\sin\psi\cos\psi}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2$$

$$+\frac{1}{2kTI_A I_B\sin^2\theta}\left(\frac{1}{\sin\theta\left(\frac{\sin^\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)}(p_\phi - \cos\theta p_\psi)\right)^2 + \frac{1}{2KTI_c}p_\psi^2$$

Using the following integral,

$$\int_{-\infty}^{\infty}e^{-a(x+b)^2}dx = \int_{-\infty}^{\infty}e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

Integration over p_θ gives using the above expression

$$\sqrt{2\pi kT}\left(\frac{\sin^2\psi}{I_A} + \frac{\cos^2\psi}{I_B}\right)^{-1/2} \tag{18.8.2}$$

Integration over p_φ gives the factor,

$$\sqrt{2\pi kTI_AI_B}\sin\theta\left(\frac{\sin^2\psi}{I_A}+\frac{\cos^2\psi}{I_B}\right)^{1/2}$$

This cancels partly the second square root in Equation 18.8.2. Integration over p_ψ gives the factor

$$\sqrt{2\pi kTI_c}$$

Integration over θ, φ and ψ gives a factor of $8\pi^2$.

$$\int_0^\pi \sin\theta\, d\theta = 2$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{2\pi} d\psi = 2\pi$$

Combining all the integrals, we finally get Equation 18.8.1 after reintroduced the symmetry number σ as before with diatomic molecular rotation.

We can simplify calculations by defining **characteristic rotational temperatures** for each axis of rotational:

$$\Theta_A = \frac{h^2}{8\pi^2 I_A k}$$

$$\Theta_B = \frac{h^2}{8\pi^2 I_B k}$$

$$\Theta_C = \frac{h^2}{8\pi^2 I_C k}$$

The polyatomic rotational partition function expressed in Equation 18.8.1 can then be re-expressed as:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{18.8.3}$$

or alternatively:

$$\ln q_{rot} = \frac{1}{2}\ln\frac{\pi T}{\Theta_A\Theta_B\Theta_C\sigma^2}$$

Example: Nitrogen Dioxide

The three characteristic rotational temperatures for NO_2 are $111.5\ K$, $0.624\ K$ and $0.590\ K$. Calculate the rotational partition function at 300 K.

Solution

The rotational temperature is given by Equation 18.8.3:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}$$

The rotational partition function becomes,

$$q_{rot} = \frac{1.772}{2}\sqrt{\frac{300\ K}{(11.5\ K)(0.624\ K)(22.55\ K)}} = 2242.4$$

Thermodynamics Properties

The molar thermodynamic functions can be readily calculated including average rotation energy and molar heat capacity:

$$E_{rot} = \frac{3}{2}RT$$

and:

$$\bar{C_V} = \frac{3}{2}R$$

Improvements over the classical approximation for the rotational partition function derived above have been obtained. One of the improved versions (with no derivation) is:

$$q_{rot} = q^0_{rot}\left[1 + \frac{h^2}{96\pi^2 kT}\left(\frac{2}{I_A} + \frac{2}{I_C} + \frac{2}{I_C} + \frac{I_C}{I_B I_B} - \frac{I_A}{I_B I_C} - \frac{I_B}{I_A I_C}\right)\right]$$

where q^0_{rot} is the classical approximation in Equation 18.8.1.

Comparing this result with the vibrational partition function calculation before ($q_{vib} = 1.0035$), give the implication that while multiple rotational states are accessible at room temperature, very few vibrational states (other than the ground vibrational state) are accessible.

Contributors and Attributions

- www.chem.iitb.ac.in/~bltembe/pdfs/ch_3.pdf

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18.9: Molar Heat Capacities

Learning Objectives

- **Goal**: Specific heat capacity data for a wide range of elements are used to assess the accuracy and limitations of the Dulong-Petit Law.
- **Prerequisites**: An introductory knowledge of statistical thermodynamics including the derivation of the vibrational (harmonic oscillator) contributions to the heat capacity are recommended.
- **Resources you will need**: This exercise should be carried out within a data analysis software environment which is capable of graphing and generating a best-fit line for an x-y data set.

The heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of that substance by one degree Kelvin. For a simple molecular gas, the molecules can simultaneously store kinetic energy in the translational, vibrational, and rotational motions associated with the individual molecules. In this case, the heat capacity of the substance can be broken down into translational, vibrational, and rotational contributions;

$$C = C_{trans} + C_{vib} + C_{rot} \tag{18.9.1}$$

Monoatomic crystalline solids represent a much simpler case. Einstein proposed a simple model for such substances whereby the atoms only have vibrational energy (each atom can vibrate in three perpendicular directions around its lattice position). Specifically, the 'Einstein Solid Model' assumes that the atoms act like three-dimensional harmonic oscillators (with the vibrational motion of each atom in each perpendicular dimension entirely independent). Statistical mechanics provides a relatively simple expression for the constant volume molar heat capacity ($C_{V,m}$) of a one-dimensional harmonic oscillator

$$C_{V,m}^{1-D} = R\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{18.9.2}$$

where R is the universal gas constant, T is absolute temperature, and Θ_v is called the 'characteristic vibrational temperature' of the oscillator and depends on the vibrational frequency (ν) according to

$$\Theta_v = \frac{hv}{k} \tag{18.9.3}$$

with h representing Plank's constant and k representing Boltzmann's constant.

Since the vibrations in each dimension are assumed to be independent, the expression for the constant volume molar heat capacity of a 'three-dimensional' Einstein Solid is obtained by simply multiplying Equation 18.9.2 by three;

$$C_{V,m}^{3-D} = 3R\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2 \tag{18.9.4}$$

The temperature variation of the heat capacity of most metallic solids is well described by Equation 18.9.4. Furthermore, plots of Equation 18.9.4 as a function of temperature for metals with widely varying vibrational frequencies reveal that the heat capacity always approaches the same asymptotic limit of $3R$ at high temperatures. Stated another way, at high temperatures

$$\lim_{T\to\infty}\left[\left(\frac{\Theta_v}{T}\right)^2\left(\frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}}\right)^2\right] = 1 \tag{18.9.5}$$

and Equation 18.9.4 reduces to

$$\lim_{T\to\infty}\left[C_{V,m}^{3D}\right] = 3R \tag{18.9.6}$$

(You will be asked to verify this result in the exercise below). According to Equation 18.9.6, the molar heat capacities of metallic solids should approach 24.9 J/(K mol) at high temperatures, regardless of the identity of the metal.

The vibrational frequencies of most metallic solids are usually small enough so that Θ_v lies considerably below room temperature ($\Theta_v \ll 298\ K$). For these substances, the limits implied by Equations 18.9.5 and 18.9.6 are well approximated even at room temperature, leading to the result that $C_{v,m} = 24.9\ J/(K\cdot mol)$ for most metals at room temperature.

In the early 1800s, two French scientists by the names of Pierre Louis Dulong and Alexis Therese Petit empirically discovered the same remarkable result. The Dulong-Petit Law is normally expressed in terms of the specific heat capacity (C_s) and the molar mass (M) of the metal

$$C_s M = C_{V,m} \approx 25 (J\,K^{-1}\,mol^{-1}) \tag{18.9.7}$$

where C_s represents how much heat is required to raise the temperature of 'one gram' of that substance by one degree Kelvin. Dulong and Petit, as well as other scientists of their time, used this famous relationship as a means of establishing more accurate values for the atomic weight of metallic elements (by instead measuring the specific heat capacity of the element and using the Dulong-Petit relationship, which is a relatively simple method of establishing weights in comparison to the more disputable gravimetric methods that were being used at the time to establish the equivalent weights of elements).

In the exercise below, you will look up the specific heat capacities of a number of elements that exist as simple monoatomic solids at room temperature and assess the accuracy of the Dulong-Petit law.

Experimental Data

Consult the CRC Handbook of Chemistry and Physics (CRC Press: Boca Raton, FL) and compile a table of specific heat capacities for a large number of elements that are known to exist as monoatomic solids at room temperature. Also look up and record the molar mass of these elements. The elements that you consider should be restricted to those appearing in groups 1-14 of the periodic table. Make sure you generate a fairly large list which includes a number of elements that are normally considered as metallic in character (such as copper, iron, sodium, lithium, gold, platinum, barium, and aluminum), but also some non-metallic elements that are nonetheless monoatomic isotropic solids (such as carbon-diamond, beryllium, boron, and silicon). Heat capacities that are usually reported in the literature are not actual constant volume heat capacities (C_v), but are instead constant pressure heat capacities (C_p). Fortunately, C_p and C_v are essentially equal for simple solids (within the level of precision that we consider in this exercise), and you can assume that the values from the CRC Handbook represent C_s.

Exercises

1. Enter the element name, the specific heat capacity, and the molar mass of each element in a spreadsheet. Calculate the product of specific heat and molar mass for each element and calculate how much this product differs from the Dulong-Petit prediction (express your result as a percent difference relative to $3R$).
2. Assess the generality of the Dulong-Petit law in an alternate way by generating a plot of specific heat as a function of reciprocal Molar Mass (C_s versus $1/M$), which should be linear with a slope equal to 3R if the data behave according to Equation 18.9.7.
3. Inspect your results from 1 and 2 above and identify any elements that significantly deviate from the Dulong-Petit law. When they occur, do deviations tend to be smaller or larger than 3R? Does the degree of deviation from the Dulong-Petit law seem to correlate with periodic trends in metallic (or covalent) bonding for these elements? Do deviations tend to occur more readily for elements of smaller or higher atomic weight? Explain how the type of bonding and the magnitude of the atomic weight can lead to deviations from the arguments made in Equations 18.9.5-18.9.7 above.
4. Use the plotting method that you employed in step 2 above as a means of determining a value for the universal gas constant (R) - but make sure you throw-out any specific heat data for elements that you suspect do not fall within the limit $\Theta_v \ll 298\ K$. Calculate the percent error in the value of R that you determine.
5. Verify that the limit expressed in Equation 18.9.5 above is true (HINT: expand each of the exponential terms in a power series and note that higher-order terms are negligible in the limit $T \gg \Theta_v$).

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