

# CHEM-UA 127: ADVANCED GENERAL CHEMISTRY I



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# Licensing

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## MODULES

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# 1: Mathematical preliminaries

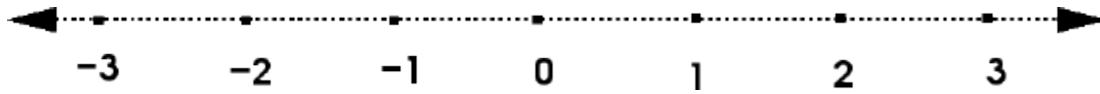


Figure 3:

The numbers 2 and -2 corresponding to the two points we have considered are the coordinates of these points. The statement  $2 + 1 = 3$  can be expressed as a *vector addition*. The figure below shows the two vectors corresponding to the points at 2 and 1, respectively:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig4.ps} {\small} \end{center}\end{figure}`

Figure 4:

The sum can be expressed by placing the vectors together such that the head of one touches the tail of the other. The net length and direction is the answer as shown below:

Figure 5:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig5.ps} {\small} \end{center}\end{figure}`

The result is vector "3 to the right." Rather than continuing to specify vectors in this clumsy way, we introduce a notation for them. Generally, vectors are designated by a boldface symbol, e.g.,  $\mathbf{v}$ . A standard notation is to specify a vector simply by the coordinates of the point it locates. Thus, if the vector  $\mathbf{v}$  is "2 to the right", then we write  $\mathbf{v} = 2$ , and if it is "2 to the left" it becomes  $\mathbf{v} = -2$ . Here, the minus sign allows the direction to be determined unambiguously.

In one dimension, directions are easy, as there are only two choices, "to the right" or "to the left". By contrast, in two dimensions, there is an infinite number of directions. Now two points are required to specify the location of a point in a plane; its  $x$  and  $y$  coordinates. The coordinates are written as an ordered pair  $(x, y)$ . Thus, the point shown below:

Figure 6:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig6.ps} {\small} \end{center}\end{figure}`

has coordinates  $(2, 1)$ . The vector locating this point appears as:

Figure 7:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig7.ps} {\small} \end{center}\end{figure}`

and is given simply by the coordinates  $\mathbf{v} = (2, 1)$ . Another way to express a vector is to introduce unit vectors  $\hat{i}$  and  $\hat{j}$  along the  $x$  and  $y$  axes and write :

$$\mathbf{v} = x\hat{i} + y\hat{j}$$

where  $\hat{i}$  is the vector  $(1, 0)$  and  $\hat{j}$  is the vector  $(0, 1)$ . Although we will not use this notation in the course, you should be aware of it as many other sources employ it.

The magnitude of the vector, written as  $|\mathbf{v}|$ , is its length, given by the length of the hypotenuse of the right triangle:  $|\mathbf{v}| = \sqrt{5}$ . Its direction is, by convention, given by the angle that the vector makes with the  $x$  axis:  $\theta = \tan^{-1}(1/2) = 26.57$  degrees. In general, if a vector is given by  $\mathbf{v} = (a, b)$ , then its length is

$$|v| = \sqrt{a^2 + b^2}$$

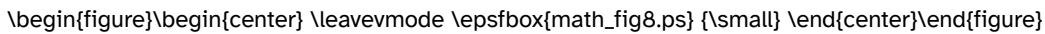
and its direction is

$$\theta = \tan^{-1} \frac{b}{a}$$

Note that the length and direction of a vector are the same as the polar coordinate representation of the point  $(a, b)$ . The numbers  $a$  and  $b$  are called the *components* of  $v$ .

The sum of two vectors, say  $v_1 = (2, 1)$  and  $v_2 = (1, 2)$  is obtained by adding the components separately:  $v_1 + v_2 = (2 + 1, 1 + 2) = (3, 3)$ . This is the same as placing the vectors end-to-end as in the one-dimensional case:

Figure 8:



In general, if  $v_1 = (a_1, b_1)$  and  $v_2 = (a_2, b_2)$ , then the sum  $v_3 = v_1 + v_2$  is given by

$$v_3 = (a_1 + a_2, b_1 + b_2)$$

or if  $v_3 = v_1 - v_2$ , then

$$v_3 = (a_1 - a_2, b_1 - b_2)$$

In general, if  $V$  is the sum of  $N$  vectors  $v_i, i = 1, \dots, N$ , then  $V$  will be given by

$$V = \sum_{i=1}^N v_i = \left( \sum_{i=1}^N a_i, \sum_{i=1}^N b_i \right)$$

Also, the product of a vector  $v$  and a constant  $c$  is obtained simply by multiplying the components of  $v$  by  $c$ :

$$cv = (ca, cb)$$

One other important operation involves finding the angle between two vectors:

Figure 9:



The angle  $\theta$  between the two vectors  $v_1$  and  $v_2$  is given by

$$\theta = \cos^{-1} \left[ \frac{v_1 \cdot v_2}{|v_1||v_2|} \right]$$

where the product  $v_1 \cdot v_2$  is called the *dot product* between the vectors  $v_1$  and  $v_2$ . If  $v_1 = (a_1, b_1)$  and  $v_2 = (a_2, b_2)$ , then

$$v_1 \cdot v_2 = a_1 a_2 + b_1 b_2$$

Note that the dot product is a number, not a vector!

Everything said here, generalizes to three dimensions, except that the vectors now have a third component, e.g.,  $v = (a, b, c)$ . Thus, for example, the dot product between two vectors becomes

$$v_1 \cdot v_2 = a_1 a_2 + b_1 b_2 + c_1 c_2$$

and the length of a vector is given by

$$|v| = \sqrt{a^2 + b^2 + c^2}$$

## Trigonometric identities

Trigonometry and the identities obeyed by trigonometric functions arise in many of the calculations we will be doing this semester. Hence, it is important for you to be familiar with these. Let us begin by recalling the definitions of the basic functions  $\cos(x)$  and  $\sin(x)$ . Here, we will assume  $x \in [0, 2\pi]$ , although since the functions are periodic, it does not matter if we extend the domain of  $x$ . However, by restricting  $x$  in this way, we can make the convenient connection of  $x$  to one of the angles in a right triangle (see figure).

Figure 10:

$\begin{figure} \begin{center} \leavevmode \epsfbox{triangle_trig.eps} \small \end{center} \end{figure}$

Let  $c$  be the length of the hypotenuse of the triangle, and let  $a$  and  $b$  be the sides adjacent and opposite to the angle  $x$ . Then, we have the definitions

Note that the definitions of  $\cos(x)$  and  $\sin(x)$  imply that for certain values of  $x$ ,  $x = 0$ ,  $x = \pi/2$ ,  $x = \pi$ ,  $x = 3\pi/2$  and  $x = 2\pi$ ,

$$\cos(0) = 1, \sin(0) = 0$$

$$\cos(\pi/2) = 0, \sin(\pi/2) = 1$$

$$\cos(\pi) = -1, \sin(\pi) = 0$$

$$\cos(3\pi/2) = 0, \sin(3\pi/2) = -1$$

$$\cos(2\pi) = \cos(0) = 1, \sin(2\pi) = \sin(0) = 0$$

A number of other identities concern trigonometric functions whose arguments are sums or differences of angles  $x \pm y$ :

$$\cos(x + y) = \cos(x)\cos(y) - \sin(x)\sin(y), \cos(x - y) = \cos(x)\cos(y) + \sin(x)\sin(y)$$

$$\sin(x + y) = \sin(x)\cos(y) + \cos(x)\sin(y), \sin(x - y) = \sin(x)\cos(y) - \cos(x)\sin(y)$$

In fact, the difference formulas can be derived from the sum formulas using the simple symmetry relations  $\cos(-x) = \cos(x)$  and  $\sin(-x) = -\sin(x)$ . In the next section, we will introduce a very simple technique for proving these relations.

Now, if we set  $x = y$ , we can derive a useful identity for  $\cos^2(x)$ . Setting  $x = y$  in the  $\cos(x + y)$  and  $\cos(x - y)$  identities, and adding the two identities together, we obtain

$$\cos(2x) = \cos^2(x) - \sin^2(x)$$

$$\cos(0) = 1 = \cos^2(x) + \sin^2(x)$$

$$1 + \cos(2x) = 2\cos^2(x)$$

$$\cos^2(x) = \frac{1}{2}[1 + \cos(2x)]$$

If we subtract the identities instead of adding them, we can derive a similar identity for  $\sin^2(x)$ :

$$\sin^2(x) = \frac{1}{2}[1 - \cos(2x)]$$

Finally, we note that  $\cos(x)$  and  $\sin(x)$  are expressible as infinite power series (also known as Taylor series) as

$$\cos(x) = 1 - \frac{1}{2!}x^2 + \frac{1}{4!}x^4 - \frac{1}{6!}x^6 + \dots = \sum_{k=0}^{\infty} (-1)^k \frac{1}{(2k)!} x^{2k}$$

$$\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 + \dots = \sum_{k=0}^{\infty} (-1)^k \frac{1}{(2k+1)!} x^{2k+1}$$

These power series expressions are actually used in calculators and computer programs to evaluate  $\cos(x)$  and  $\sin(x)$ .

## Complex numbers

Complex numbers play a key role in quantum mechanics, even though anything that can be measured experimentally must ultimately be expressed as a real number. Without quantum theory, it is not possible to understand the nature of the chemical bond, and since quantum theory is expressed in terms of complex numbers, it is important to review some of the basic facts about complex quantities. Complex numbers are so named because they are composed of two types of more fundamental numbers: real numbers and imaginary numbers. Real numbers are very familiar and are the numbers we deal with on a daily basis. However, when one embarks on the study of nonlinear algebraic equations, it rapidly becomes clear that some equations do not have solutions within the set of real numbers. Take the example of the equation

$$x^2 + 1 = 0$$

There are no real numbers  $x$  that satisfy this equation. The reason is clear if we just naively solve for  $x$  to find  $x = \pm\sqrt{-1}$ . The quantity  $\sqrt{-1}$  is not defined within the real numbers. But mathematicians are never satisfied with the idea that something cannot be defined. In this case, the conundrum can be solved by simply extending the concept of a "number" to allow  $\sqrt{-1}$  to be defined. This involves inventing a new set of numbers, called "imaginary numbers" (for no better reason than "imaginary" is one of the opposites to "real"), in which  $\sqrt{-1}$  has a definite value, denoted  $i$ . Then, the solution to the above equation is simply  $x = \pm i$ . The number  $i$  is the fundamental "integer" unit in the set of imaginary numbers just as 1 is the fundamental integer unit in the real numbers. So, just as any real number  $a$  can always be expressed as  $a \cdot 1$ , any imaginary number can be expressed as a multiple of  $i$ . If  $\beta$  is an imaginary number, then we can write  $\beta$  as  $b \cdot i$ , where  $b$  is a real number. The number  $i$ , itself, is really  $1 \cdot i$ , and clearly, 1 is real.

Given imaginary numbers, the most general kind of number we can now imagine has both real and imaginary parts, and such a number is known as a *complex number*. A complex number  $z$  is expressed as the sum of its real and imaginary parts. If the real part of  $z$  is  $a$  and the imaginary part of  $z$  is  $bi$ , then we would write

$$z = a + bi$$

Note that this is similar to expressing a two-dimensional vector  $v = x\hat{i} + y\hat{j}$ . Indeed, we can exploit this analogy and use the ordered-pair notation to write a complex number as  $z = (a, bi)$  as an alternate notation. As we will see, there are many such analogies between complex numbers and two-dimensional vectors. For instance, we can think of a complex number as a point in a plane in which the horizontal axis corresponds to the real parts of all complex numbers and the vertical axis corresponds to the imaginary parts. The complex number  $z = a + bi$  would be the point  $(a, b)$  in this plane. In order to extract the real and imaginary parts of  $z$ , we introduce the functions  $Re$  and  $Im$  such that  $Re(z) = a$  and  $Im(z) = b$ .

We noted above that experimental measurements ultimately yield real numbers, so we need a way of going from a complex number to a real one. For this, we exploit the analogy with two-dimensional vectors even more and define the "measure" or *magnitude* of a complex number  $z = a + ib$ , which we denote as  $|z|$ , as

$$|z| = \sqrt{a^2 + b^2}$$

which is the same as the magnitude of a two-dimensional vector  $v = (a, b) = a\hat{i} + b\hat{j}$ . Another important definition is the so-called *complex conjugate* of  $z$ , denoted  $z^*$ , which is defined as follows: If  $z = a + ib$ , then  $z^* = a - ib$ . In general, all we have to do to obtain the complex conjugate of a number is replace  $i$  by  $-i$ . Note that the magnitude of  $z$  is

$$|z| = \sqrt{z^*z} = \sqrt{(a - ib)(a + ib)} = \sqrt{a^2 + iab - iab + b^2} = \sqrt{a^2 + b^2}$$

where we have used the fact that  $i(-i) = -i^2 = 1$ . Thus, a complex number times its complex conjugate is a real number.

What happens if we are given a complex number, but it is not expressed in the simple form  $z = a + ib$ ? Can we manipulate it so that it finally does have this form? The answer is 'yes' with a little mathematical creativity. Consider, first, a simple product  $z = (u + iv)(x + iy)$ . This can be expressed in the canonical form by simply multiplying it out algebraically:

$$z = ux + ivx + iuy - vy = (ux - vy) + i(vx + uy)$$

Next, consider a ratio  $z = (u + iv)/(x + iy)$ . In order to simplify this, we use the fact that  $(x + iy)(x - iy)$  is real. Thus, we multiply  $z$  by 1 in the form of  $(x - iy)/(x - iy)$ :

$$z = \frac{u + iv}{x + iy} = \frac{(u + iv)(x - iy)}{(x + iy)(x - iy)} = \frac{ux + yv + i(vx - uy)}{x^2 + y^2} = \frac{ux + yv}{x^2 + y^2} + i \frac{vx - uy}{x^2 + y^2}$$

One of the most frequently occurring complex number forms is

$$z = e^{i\theta}$$

where  $\theta$  is a real number. The complex conjugate of  $z$  is obtained simply by replacing  $i$  by  $-i$ :

$$z^* = e^{-i\theta}$$

and so that magnitude of  $z$  is

$$|z|^2 = z^* z = e^{-i\theta} e^{i\theta} = 1$$

So,  $z$  is a complex number whose square magnitude is 1. On the other hand, if we seek to represent  $z$  in canonical form as  $z = a + ib$ , then it follows that

$$|z|^2 = a^2 + b^2 = 1$$

Since  $a$  and  $b$  are actually functions of  $\theta$ , we can ask what two functions of  $\theta$  are related by  $a^2 + b^2 = 1$ . We have already seen what these are - they are  $\cos(\theta)$  and  $\sin(\theta)$  since  $\cos^2(\theta) + \sin^2(\theta) = 1$ . Thus, in canonical form, we can let  $a = \cos(\theta)$  and  $b = \sin(\theta)$  and write

$$z = e^{i\theta} = \cos(\theta) + i \sin(\theta)$$

which is known as *Euler's formula*. The above argument is not a very rigorous one, as there are many other functions  $a$  and  $b$  of  $\theta$  we could have chosen that satisfy  $a^2 + b^2 = 1$ . However, we can actually prove rigorously that  $a$  and  $b$  must be, respectively,  $\cos(\theta)$  and  $\sin(\theta)$  using the fact that the function  $\exp(x)$  has the following Taylor series expression:

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \frac{x^5}{5!} + \frac{x^6}{6!} + \dots = \sum_{k=0}^{\infty} \frac{x^k}{k!}$$

Applying this to  $\exp(i\theta)$ , we obtain

$$e^{i\theta} = 1 + i\theta + \frac{(i\theta)^2}{2!} + \frac{(i\theta)^3}{3!} + \frac{(i\theta)^4}{4!} + \frac{(i\theta)^5}{5!} + \dots = \sum_{k=0}^{\infty} \frac{(i\theta)^k}{k!}$$

Now the even power terms are purely real, and the odd powers are purely imaginary, so if we wish to put the above power series into the canonical form, we obtain

$$e^{i\theta} = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \frac{\theta^6}{6!} + \dots + i \left( \theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \dots \right) = \cos(\theta) + i \sin(\theta)$$

which proves Euler's formula.

Euler's formula can be used to simplify proofs of trigonometric identities. For example, we know that  $z^* z = 1$ . But from Euler's formula,  $z^* z = \cos^2(\theta) + \sin^2(\theta)$ , so  $\cos^2(\theta) + \sin^2(\theta) = 1$ . If we use the fact that

$$z^* = e^{-i\theta} = \cos(\theta) - i \sin(\theta)$$

Thus, adding  $z$  to  $z^*$ , we obtain

$$\cos(\theta) = \frac{1}{2} (e^{i\theta} + e^{-i\theta})$$

Subtracting  $z$  from  $z^*$  yields

$$\sin(\theta) = \frac{1}{2i} (e^{i\theta} - e^{-i\theta})$$

Now consider  $\cos^2(\theta)$ . From the above formula, we have

$$\begin{aligned}\cos^2(\theta) &= \frac{1}{4}(e^{i\theta} + e^{-i\theta})^2 = \frac{1}{4}(e^{2i\theta} + 2e^{i\theta}e^{-i\theta} + e^{-2i\theta}) \\ &= \frac{1}{4}(2 + e^{2i\theta} + e^{-2i\theta}) = \frac{1}{2} + \frac{1}{4}(e^{2i\theta} + e^{-2i\theta}) = \frac{1}{2}[1 + \cos(2\theta)]\end{aligned}$$

Finally, note that if we multiply Euler's formula by a real number  $A$ , we have a complex number of the form

$$z = Ae^{i\theta}$$

In canonical form

$$z = A \cos(\theta) + iA \sin(\theta)$$

and  $|z|^2 = A \exp(-i\theta) * A \exp(i\theta) = A^2$ , so  $|z| = A$ . When we write  $z = A \exp(i\theta)$ , The angle  $\theta$  is called the *phase* of  $z$ .

## Derivative of a function

A line, described by the equation

$$y = mx + b$$

has a constant slope  $m$  defined by

$$m = \frac{\Delta y}{\Delta x}$$

where the above equations means compute the change,  $\Delta y$  in  $y$  for a given change,  $\Delta x$  in  $x$  as shown in the figure:

Figure 11:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig10.ps} {\small} \end{center}\end{figure}`

For a general function, such as that shown below:

Figure 12:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig11.ps} {\small} \end{center}\end{figure}`

the slope is not a constant. However, it is possible to define the slope of the curve at each point by taking the slope of the line tangent to the curve at each point. The slope will also be a function of  $x$  and is called the derivative of the function  $f(x)$ . To see how the slope is computed, consider a line connecting two points of the function corresponding to two points  $x$  and  $x + \Delta x$ , where  $\Delta x$  is a small number:

Figure 13:

`\begin{figure}\begin{center} \leavevmode \epsfbox{math_fig12.ps} {\small} \end{center}\end{figure}`

The slope of this line is

$$m = \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

To find the slope at the single point  $P$ , we need to let  $\Delta x$  go to 0, so that the line intersects the curve at the point  $P$ , where it will be tangent to the curve. Thus, by taking the *limit* as  $\Delta x \rightarrow 0$ , we obtain the derivative of  $f(x)$  at the point  $P$ . But since the point  $P$  is arbitrary, we may perform this operation at any point and, thus, obtain the derivative of  $f(x)$  at any point. The general

expression is

$$f'(x) = \frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

where  $f'(x)$  and  $df/dx$  are standard notations for the derivative.

As an example, consider the function  $f(x) = x^2$ . According to the formula:

$$f(x) = \ln x, f'(x) = \frac{1}{x}$$

$$f(x) = \sin x, f'(x) = \cos x$$

$$f(x) = \cos x, f'(x) = -\sin x$$

Other important rules of differentiation are the *product rule*:

$$\text{if } h(x) = f(x)g(x) \text{ then } h'(x) = f'(x)g(x) + f(x)g'(x)$$

and the *chain rule*:

$$\text{if } h(x) = f(g(x)), \text{ then } h'(x) = f'(g(x))g'(x)$$

## Integral of a function

It is often necessary to calculate the area under a function,  $f(x)$  between two points  $x_1$  and  $x_2$ . Such an operation is necessary, for example, in mechanics to compute the work performed by an agent exerting a force on an object. An analogous situation arises in thermodynamics in computing the work done by an agent exerting an external pressure on a system.

Consider the area under the curve designated below:

Figure 14:

$\begin{figure} \begin{center} \leavevmode \epsfbox{math_fig13.ps} {\small} \end{center} \end{figure}$

One way to calculate the area approximately would be to cover the area with narrow rectangles or width  $\Delta x$ :

Figure 15:

$\begin{figure} \begin{center} \leavevmode \epsfbox{math_fig14.ps} {\small} \end{center} \end{figure}$

\$a\$

. Thus, we have

From the transformation equations, it can be shown that an integral of a function  $f(x, y, z)$

$$I = \int \int \int f(x, y, z) \, dx \, dy \, dz$$

in spherical coordinates becomes

$$I = \int \int \int \tilde{f}(r, \phi, \theta) \, r^2 \, dr \, \sin \theta \, d\theta \, d\phi$$

Here  $\tilde{f}(r, \phi, \theta)$  is the transformed form of the function expressed in spherical polar coordinates. If the integral is over all space, then the limits in Cartesian coordinates are

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z) \, dx \, dy \, dz$$

and in spherical polar coordinates, this becomes

$$I = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \tilde{f}(r, \phi, \theta) \, r^2 \, dr \, \sin \theta \, d\theta \, d\phi$$

Note that

is integrated from

to

only, which covers only the positive

-axis, but

is integrated from

to

. Many of the functions

we will have to deal with are simple products of functions of one variable, i.e.

$$\tilde{f}(r, \phi, \theta) = g(r)h(\phi)v(\theta)$$

for this type of function, the three-dimensional integral in polar coordinates becomes a product of ordinary one-dimensional integrals:

$$I = \left[ \int_0^{2\pi} d\phi h(\phi) \right] \left[ \int_0^{\pi} d\theta \sin \theta v(\theta) \right] \left[ \int_0^{\infty} dr r^2 g(r) \right]$$

## Contributors and Attributions

Mark Tuckerman (New York University)

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## 2: Introduction and origins of atoms and molecules

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Let us begin our study of chemistry with a simple question:

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### 3: Physical principles underlying chemistry

Research in chemistry proceeds along two directions: Experimental and theoretical. Experimental chemistry is the science of observation. We pose a question to nature, carry out the corresponding experiment, and observe the outcome. What happens if we mix two substances? If we blast a molecule with a laser, what will it do? If we introduce a biomimetic into a living organism, how will it respond? Experiments produce data that relate to each individual observation. Theory, on the other hand, is concerned with building general frameworks for placing large numbers of individual observations into a rational order. It does so by building mathematical models, deducing general laws, and using these to predict the outcomes of future experiments. The tools of theory are usually mathematics and physics applied to chemical problems. Without theory, experimental science is just a vast catalog of unrationalized observations. Without experiment, theory is simply a long list of conjectures with no verification or falsification.

Keeping this juxtaposition in mind, we briefly review the basic laws of chemical transformations, keeping in mind their historical origins and the observations out of which they grew.

#### Fundamental laws of chemical reactions and chemical equations

1. The law of conservation of mass (Lavoisier, 18th century): Lavoisier was one of the first to carry out quantitatively accurate chemical measurements. He demonstrated that combustion required oxygen, and he demonstrated oxygen's role in the rusting of metals. His observations led him to deduce the following general law known as the law of conservation of mass:

2. law of definite proportions (Joseph Proust, shortly after Lavoisier): Proust studied metal compounds, including metal oxides, carbonates and sulfides. From the work of Robert Boyle in the 17th century, it was understood that substances that could be broken down into more fundamental components were mixtures or compounds. Substances that could not be further broken down were referred to as elements. Thus, Proust deduced the so-called law of definite proportions:

3. The law of multiple proportions: (John Dalton, shortly after Proust): Studied gases and gaseous mixtures under different external conditions. Building on Proust's work, he noted that mathematically discrete manner in which elements combined to form different compounds. For example, in carbon monoxide ( $CO$ ), the mass ratio of oxygen to carbon  $m_O/m_C = 1.33$  and in carbon dioxide ( $CO_2$ )  $m_O/m_C = 2.66$ . Thus, since the amount of carbon is fixed in each compound, we can look at how the amount of oxygen varies, and we find that  $m_O(\text{in } CO_2)/m_O(\text{in } CO) = 2$ . The generalization of this idea is the law of multiple proportions:

##### law of multiple proportions

In every chemical transformation, an equal quantity of matter exists before and after the reaction.

(Because he was a tax collector and nobleman, Lavoisier was branded a traitor during the French Revolution and beheaded in 1794.)

In a given chemical compound, the proportion by mass of the elements that compose it are fixed, independent of the origin of the compound or its mode of preparation. This is basically saying that sodium chloride, for example, is always  $NaCl$ , no matter how it is obtained, made, or prepared. There are no "intermediate" compounds.

When two elements form a series of compounds, the masses of one that combine with a fixed mass of the other are in the ratio of (small) integers to each other. This law is obeyed by all gaseous compounds, which is what Dalton studied. Certain solids are exceptions to both this rule and the law of definite proportions. An example is the solid wüstite, which can range from  $Fe_{0.95}O$  to  $Fe_{0.85}O$ , depending on the mode of preparation. These formulae express the incommensurate compositions possible in this solid. But, since atoms are essentially indestructible (we have to work hard to get them to fission!), this explains why we do not find compounds such as  $C_{13/7}H_{5/3}$  in nature. Dalton's observations led him to propose the notion of the atom as the fundamental and indestructible building blocks of matter.

4. The law of combining volumes (Joseph Gay-Lussac, Amedeo Avagadro, Stanislao Cannizzaro, early 19th century following Dalton): Again, based on studies of gases and how they combine, the law of combining volumes has been attributed to these three. The generalization of the observations is stated as follows:

When two gases are allowed to react, such that the gases are at the same temperature and pressure, the volumes of each gas consumed will be in the ratio of small integers. Moreover, the ratio of the volume of each product gas to the volume of either reacting gas will be a ratio of simple integers.

Example: 3 volumes of hydrogen + 1 volume of nitrogen  $\rightarrow$  2 volumes of ammonia. Although this is a statement about gases, its implications can be deduced: the coefficients in chemical equations express how much of different reactants combine to give products will be integers.

### 5. Avogadro's hypothesis (1811):

**Equal volumes of different gases (at the same temperature and pressure) contain equal numbers of particles.**

#### Example 3.1

How many particles are in 1 L of  $O_2$  gas, and how many particles are in 1 L of  $H_2$  gas? The density of  $O_2$  is 1.429 g/L, and the density of  $H_2$  gas is 0.0899 g/L.

#### Solution

$$\text{mass of } O_2 = (1 \text{ L})(1.429 \text{ g/L}) = 1.429 \text{ g/L}$$

$$\text{moles of } O_2 = \frac{1.429 \text{ g}}{31.998 \text{ g/mol}} = 0.04466 \text{ mol}$$

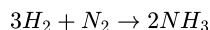
$$\text{molecules of } O_2 = (0.04466 \text{ mol})(6.022 \times 10^{23} \text{ molecules/mol}) = 2.69 \times 10^{22} \text{ molecules}$$

$$\text{mass of } H_2 = (1 \text{ L})(0.0899 \text{ g/L}) = 0.0899 \text{ g}$$

$$\text{moles of } H_2 = \frac{0.0899 \text{ g}}{2.0158 \text{ g/mol}} = 0.04466 \text{ mol}$$

$$\text{molecules of } H_2 = (0.04466 \text{ mol})(6.022 \times 10^{23} \text{ molecules/mol}) = 2.69 \times 10^{22} \text{ molecules}$$

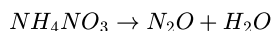
Combining Avogadro's hypothesis with the law of combining volumes allows the statement written above about volumes of hydrogen and nitrogen combining to give ammonia as a statement about definite numbers of molecules rather than volumes. This number could be expressed as moles, or even as individual molecules. The statement then reads:



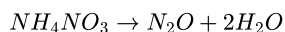
This is an example of a balanced chemical equation. What does it mean to be balanced? It means that the law of conservation of mass is obeyed - equal quantities of hydrogen and nitrogen exist on both sides of the reaction. Furthermore, the coefficients, i.e., the numbers multiplying  $H_2$ ,  $N_2$  and  $NH_3$  in the above equation, are expressible as simple integers. When balancing chemical equations, this serves as an important check.

## Methods of balancing chemical equations

### 1. Balancing by inspection: Consider the example:



We notice that there are 2 nitrogens on both the left and right sides, so nitrogen is already balanced. There are 3 oxygens on the left but only 2 on the right, so oxygen is not balanced. Similarly, there are 4 hydrogens on the left and only 2 on the right, so hydrogen is not balanced. The balancing of oxygen and hydrogen can be handled together by making the coefficient of  $H_2O$  equal to 2. Then, the balanced equation reads

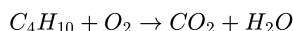


Now there are equal quantities of all elements on both sides of the reaction, and mass conservation is satisfied. Balancing by

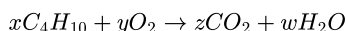
inspection in this way is quick and useful when you can see the solution easily.

## 2. Algebraic method:

Consider the reaction:



***This equation could be balanced by inspection. However, we will use it to illustrate another approach - the algebraic approach. To balance a reaction algebraically, we start by putting unknown coefficients in front of each molecular species in the equation:***



Then we write down the balance conditions for each element in terms of the unknowns. In this case, there are four unknowns,  $x$ ,  $y$ ,  $z$  and  $w$ . From carbon balance, we have the condition:

$$4x = z$$

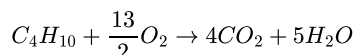
The hydrogen balance condition is:

$$10x = 2w$$

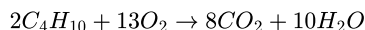
and the oxygen balance condition gives:

$$2y = 2z + w$$

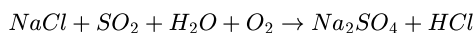
This constitutes a set of only three equations for the four unknowns. The fourth condition comes from recognizing that chemical equations specify relative amounts of reactants and products. Thus, one of the coefficients is arbitrary, and all the others can be expressed relative to it. Thus, we may take one of the coefficients to be 1, arbitrarily, which then leaves only three unknowns and three conditions to determine them. The choice of which coefficient to set to 1 is completely arbitrary and may be taken to be the one that is most convenient for solving the problem. In this case, the choice  $x = 1$  allows us to arrive at a solution almost immediately, for then it follows that  $z = 4$  and  $w = 5$ . From the oxygen balance condition,  $y$  can be determined to be  $2y = 8 + 5 = 13$  so  $y = 13/2$ . Thus, the balanced equation could be written as



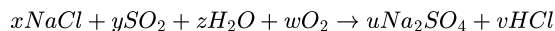
This is a perfectly fine way of writing the equation, however, customarily, it is preferable to express all the coefficients as integers, in accordance with the law of combining volumes and Avogadro's hypothesis. Thus, we can multiply through the equation by 2 on both sides (it can be treated as an algebraic equation in this way) and obtain the final result:



As a second example, consider the reaction:



Again, we put unknown coefficients in front of each molecular species:



Writing down the balance conditions on each element gives: Sodium balance:

$$x = 2u$$

Chlorine balance:

$$x = v$$

Sulfur balance:

$$y = u$$

Oxygen balance:

$$2y + z + 2w = 4u$$

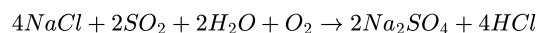
Hydrogen balance:

$$2z = v$$

Setting  $u = 1$  arbitrarily, gives the immediate solution:

$$x = 2 \quad v = 2 \quad y = 1 \quad z = 1$$

and  $2 + 1 + 2w = 4$  or  $w = 1/2$ . In order to clear the fraction, we multiply all the coefficients by 2 and write down the balanced equation:



## Law of Conservation of Energy

The law of conservation of energy is one of the basic laws of physics and therefore governs the microscopic motion of individual atoms in a chemical reaction. The Law of Conservation Energy states:

### Law of Conservation Energy

*In a closed system, i.e., a system that isolated from its surroundings, the total energy of the system is conserved.*

In SI units, energy has units of *Joules*.  $1 \text{ Joule} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$ .

### Some forms of energy:

1. Kinetic energy - energy of motion.
2. Potential energy - energy of "location" with respect to some reference point.
3. Chemical energy - energy stored in chemical bonds, which can be released in reactions.
4. Electrical energy - energy created by separating charges; energy stored in a battery, for example.
5. Thermal energy - energy given off as heat, such as friction.

Since everything has a microscopic origin, the last three are really special cases of potential and kinetic energies, however, the classification is useful.

The *kinetic energy* of an object of mass  $m$ , moving with a velocity  $v$  is given by

$$KE = \frac{1}{2} m |v|^2$$

Recall that  $|v|$  is the speed  $v$  of the particle, so that the kinetic energy can be written as  $1/2 \, mv^2$ .

*Potential energy* is a little less straightforward. Since it is an energy of location with respect to some reference point, the potential energy of an object depends on the specific situation. An example is gravity. An object of mass  $m$  at a height  $h$  above the Earth's surface has a gravitational potential energy

$$PE = mgh$$

where  $g$  is the acceleration due to the Earth's gravity. In this example, the potential energy has a simple form, namely that it depends linearly on the height  $h$ , which describes the object's location and may even be varying in time if, for example, the object is actually falling toward the Earth.

In general, the potential energy may not be such a simple function of location. In this case, one needs a *potential energy curve* to describe the potential energy as a function of some coordinate describing the object's location. Consider the example of a mass attached to a spring moving in one spatial dimension. Let  $x$  represent the mass's position along the x-axis, and let  $x_0$  represent its equilibrium position. As the mass stretches the spring ( $x > x_0$ ), its potential energy increases, and as it compresses the spring

compresses  $\backslash(x$

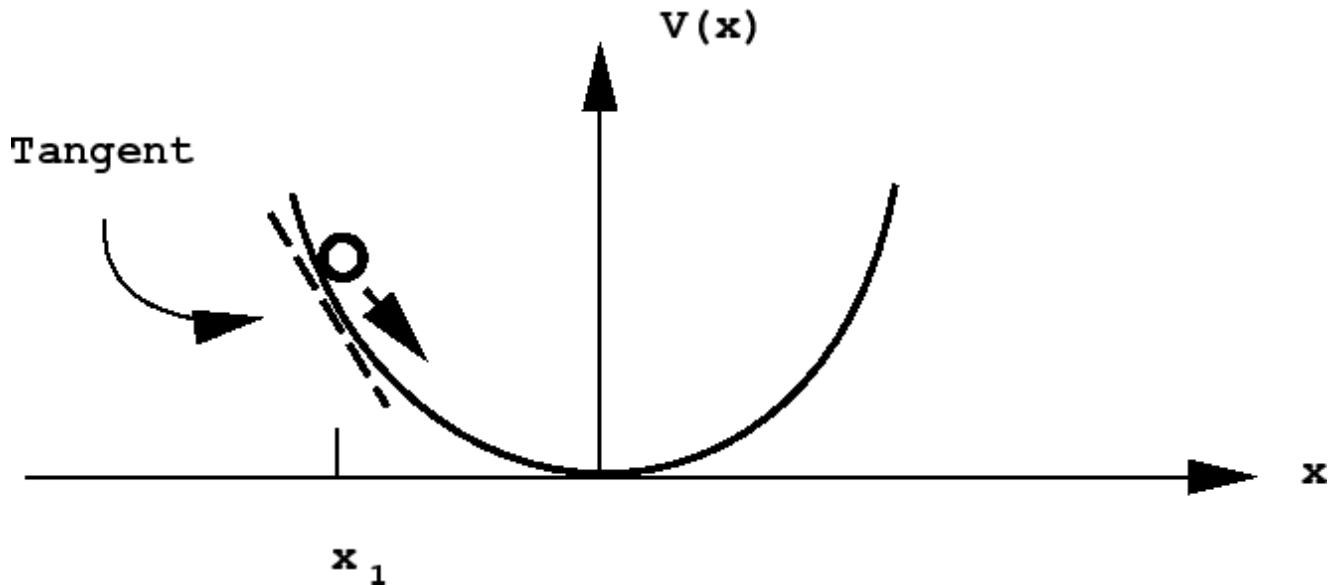


Figure 1:

Notice, also, that the mass actually moves under the action of a force, which also changes as a function of  $x$ . In fact, the force exerted by the spring on the mass can be determined from the potential energy curve via

$$\text{Force at } x = -\text{slope of the potential energy curve at } x$$

That is, the force is the slope of the line tangent to the curve at the point  $x$ , as shown in the figure above for the point  $x_1$ . In terms of a derivative, the force is given by

$$F = -\frac{dV}{dx}$$

Note that, at the bottom of the gully, where the curve is flat, the force is 0. The SI units of force are *Newtons*.  $1 \text{ N} = 1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-2}$ .

Consider the case of a diatomic molecule:

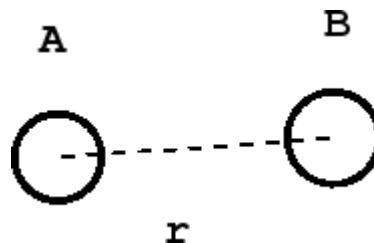


Figure 2:

The distance between the atoms A and B is  $r$ . The chemical forces that hold the molecule together come from a potential energy curve  $V(r)$  that depends only on the distance between them. Such a curve might look like:

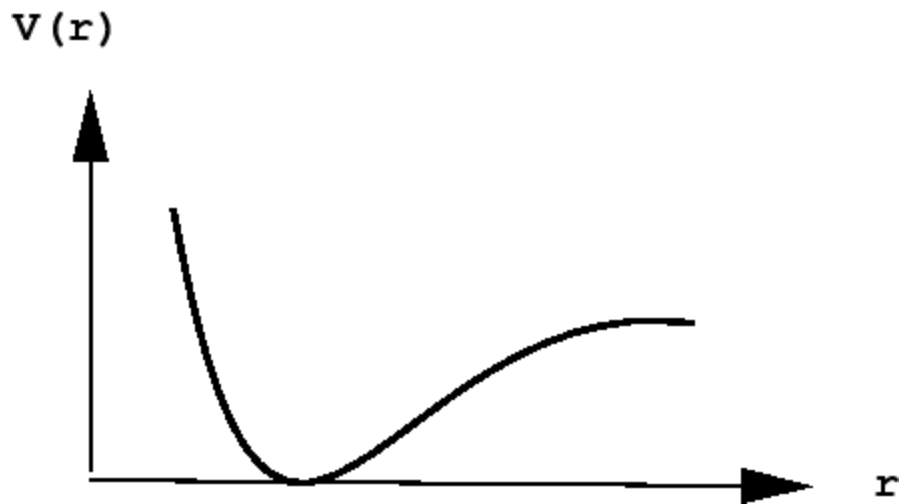


Figure 3: Potential Energy Curve

The presence of a deep "well" indicates a particular distance of lowest potential energy. This corresponds to the bond length of the molecule and is, therefore, the most likely value of the separation of the two atoms (think of a ball placed in a gully of this shape - if placed at the bottom of the well, the force on it would be 0, hence it would not move, but would remain there forever unless disturbed).

According to Newton's second law of motion, force is the action that causes a change in the motion of a particle or sets it in motion from rest. Consider a particle of mass  $m$  moving in one dimension so that its position is  $x$ . If a force  $F$  acts on the particle, it will be set in motion, so that  $x$  is no longer a fixed number but a function  $x(t)$  of time  $t$ . At any instant in time, the particle will have a velocity  $v$  defined to be the rate of change of  $x$  with respect to time

$$v(t) = \frac{dx}{dt}$$

In general  $v$  is not fixed but is also a function  $v(t)$  of time  $t$ . If  $v(t)$  is not constant, in fact, then the particle also has an acceleration  $a$  defined as the rate of change of  $v$  with respect to time

$$a(t) = \frac{dv}{dt}$$

Since  $v = dx/dt$ , it follows that

$$a(t) = \frac{d^2x}{dt^2}$$

Newton's second law of motion states that the force  $F$  acting on the particle is directly proportion to this acceleration, with the mass  $m$  as the constant of proportionality

$$F = ma = m \frac{dv}{dt} = m \frac{d^2x}{dt^2}$$

Since motion generally occurs in three rather than one dimension, position, velocity, acceleration, and force are all vector quantities. The position is usually denoted  $r$ , and  $r$  has three components  $r = (x, y, z)$ . Similarly velocity  $v$  has components  $v = (v_x, v_y, v_z)$ , acceleration  $a = (a_x, a_y, a_z)$ , and  $F = (F_x, F_y, F_z)$ . In vector notation, Newton's second law reads

$$F = ma = m \frac{dv}{dt} = m \frac{d^2r}{dt^2}$$

Hence, if  $r$  is not a fixed vector but a function  $r(t)$  of time, this means that each component of  $r$  is a function of time  $r(t) = (x(t), y(t), z(t))$ .

## Work

Consider again a particle of mass  $m$  moving in one spatial dimension. If a force  $F$  is needed to move the particle from position  $x_1$  to position  $x_2$ , then *mechanical work*  $W$  has been done on the particle. Since, as we have seen,  $F$  can be a function  $F(x)$  of  $x$ , the general definition of work is the area under the force function  $F(x)$  between  $x_1$  and  $x_2$ , i.e. the integral

$$W = \int_{x_1}^{x_2} F(x) dx$$

However, since  $F(x) = -dV/dx$ , this becomes

$$W = - \int_{x_1}^{x_2} \frac{dV}{dx} dx = -[V(x_2) - V(x_1)] = V(x_1) - V(x_2)$$

Now if the velocity of the particle at  $x_1$  is  $v_1$  and at  $x_2$ , it is  $v_2$ , then by energy conservation

$$\frac{1}{2}mv_1^2 + V(x_1) = \frac{1}{2}mv_2^2 + V(x_2)$$

Rearranging this gives

$$V(x_1) - V(x_2) = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2$$

Hence, the work  $W$  is also equal to the change in kinetic energy

$$W = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2$$

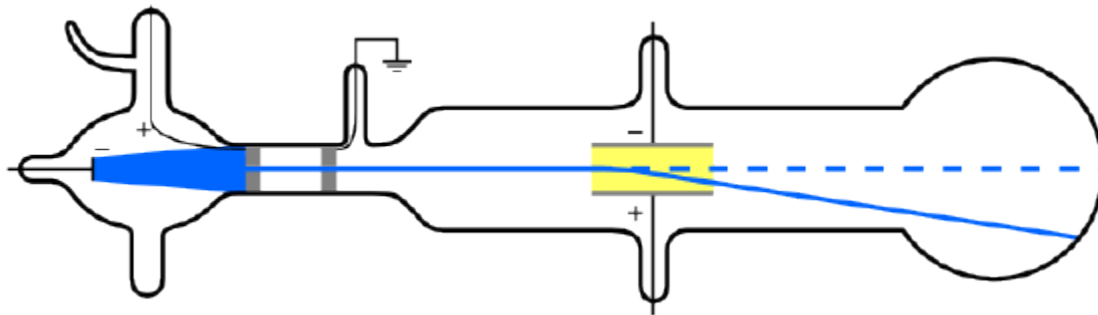
a result known as the *work-kinetic energy theorem*.

## 4: Analysis of key experiments revealing the structure of the atoms

### J.J. Thomson's experiment and the charge-to-mass ratio of the electron

The first is the experiment of Joseph John Thomson, who first demonstrated that atoms are actually composed of aggregates of charged particles. Prior to his work, it was believed that atoms were the fundamental building blocks of matter. The first evidence contrary to this notion came when people began studying the properties of atoms in large electric fields.

If a gas sample is introduced into the region between two charged plates, a current flow can be observed, suggesting that the atoms have been broken down into charged constituents. The source of these charged particles is a heated cathode that, in fact, causes the atoms of the sample to ionize. These were known as *cathode rays*. In 1897, Thomson set out to prove that the cathode rays produced from the cathode were actually a stream of negatively charged particles called electrons. From Maxwell's theory, he knew that charged particles could be deflected in a magnetic field. A schematic of the experimental setup is shown below:



1: Schematic of J.J. Thomson's experiment.

We now zero in on the field region and set up a coordinate system as shown in the figure below:

**Figure 2:**

\includegraphics[scale=0.6]{lec3\_fig1.eps}

In this coordinate system, electrons enter the region between the plates with an (unknown) velocity  $v$  in the  $x$ -direction. In order to determine this velocity, electric and magnetic fields are both applied, and each gives rise to a force on the electron. These forces are in the  $y$ -direction. The electric force  $F_E = eE$ , where  $E$  is the magnitude of the electric field, and the magnetic force is  $F_H = -evH$ , where  $H$  is the magnitude of the magnetic field, and is opposed to the force on the electric field.

If these forces balance, then there will be no deflection of the electron in the  $y$ -direction, i.e. all of the electrons' motion will be along the  $x$ -direction, which was the initial direction when they entered the field region. If the forces balance, then the total force on the electrons will be zero, that is  $F_E + F_H = 0$  or

$$eE - evH = 0$$

from which the unknown velocity can be determined as

$$v = \frac{E}{H}$$

Next, the magnetic field is switched off, so that the total force is due entirely to the electric field. Since the force is non-zero, if the charge carriers can be deflected by the force, this provides evidence for their being fundamental particles. If they are fundamental charged particles, then they should have a well defined mass and charge. In this second part of the experiment, the

specific trajectory followed by the particle will be used to determine the ratio of the charge to the mass of the particle.

When there is only an electric field, then there is a nonzero force  $F_E = eE$  in the  $y$ -direction but no force in the  $x$ -direction. Thus, this problem is exactly the same as that of a projectile in a gravitational field. As can be done in the projectile problem, the  $x$  and  $y$  motion of the electrons can be analyzed separately and independently.

In the  $x$ -direction, the motion is very simple because there is no force in this direction. The electrons simply move with a constant velocity  $v$ , which we already determined has the value  $E/H$ . Note that this value is correct even though there is no magnetic in this part of the experiment! It is just the velocity we determined from the previous part of the experiment, and this value has not changed. Thus, as a function of time  $t$ , the  $x$ -position of the electrons is

$$x(t) = vt = \frac{E}{H}t$$

The force in the  $y$ -direction is a constant, hence motion in the  $y$ -direction is analogous the gravitational force. The constant force  $F_E$  gives rise to an acceleration  $a = F_E/m$ , and the  $y$ -position at time  $t$  is then

$$y(t) = \frac{1}{2}at^2 = \frac{1}{2} \frac{F_E}{m} t^2 = \frac{eE}{2m} t^2$$

The electric field is tuned such that the particle traverses the entire plate region in the time required for it to strike the positive plate. Let the total  $y$  distance travelled be  $l$ , as shown in the figure. The time  $T$  required to traverse the plate region ( $x(T) = l$ ) is

$$l = \frac{E}{H}T$$

$$T = \frac{lH}{E}$$

This is also the time required to move a distance  $s$  in the  $y$  direction:

$$s = \frac{eE}{2m} \left( \frac{lH}{E} \right)^2$$

Solving the above for the ration  $e/m$  gives

$$\frac{e}{m} = \frac{2sE}{l^2H^2}$$

Thus, using his experimental apparatus, Thomson was able to determine the charge-to-mass ratio of the electron. Today, the accepted value of  $e/m$  is  $1.7588196 \times 10^{11} C/kg$ .

In 1906, Robert Millikan was able to determine the value of the charge on the electron in his "oil drop" experiment. A schematic of his experiment is shown below:

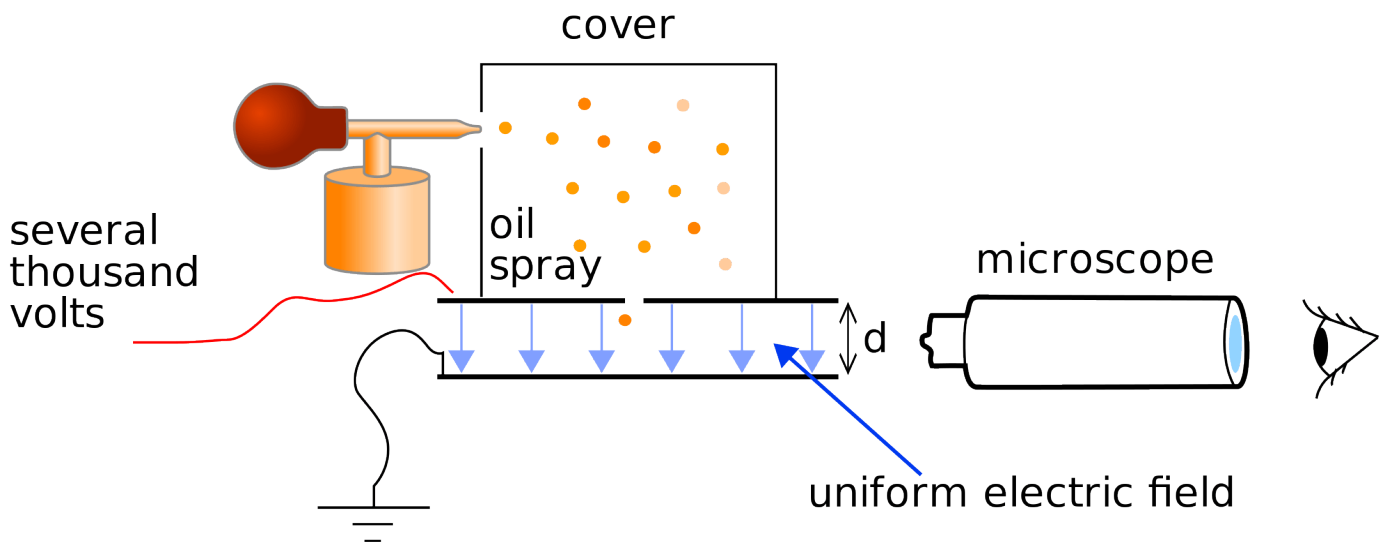


Figure 3: Schematic of Millikan's experiment.

Then using Thomson's value of  $e/m$ , he calculated the value of  $m$ . In his experiment, Millikan used a fine spray of ionized oil droplets, which he allowed to be acted on by gravity but to which he also applied an electric field in the direction opposite gravity, i.e. up. By tuning the electric field, he balanced the force due to the pull of gravity and the electric field force so that the drops remained suspended in space. Thus, if a drop has a positive charge  $q$  and a mass  $M$ , the force balance condition becomes

$$Mg = qE$$

where  $E$  is the magnitude of the electric field. Solving for the charge-to-mass ratio, we have  $q/M = g/E$ . In order to determine the mass, the drops are allowed to fall in the gravitational field without the influence of the electric field. In this case, there are still two forces acting on the drops. One is the gravitational force and the other is the frictional force due to air resistance. Since this force is proportional to the velocity, it vanishes when the drop is stationary, which is why it does not need to be taken into account when the electric field is on. However, when the drops are allowed to fall, the total force is  $F = Mg - \gamma v$ , since friction opposes gravitational force. Here,  $\gamma$  is the coefficient of air resistance. Thus, according to Newton's law of motion

$$Ma = F$$

$$M \frac{dv}{dt} = Mg - \gamma v$$

Assuming the drop starts initially at rest, the equation can be solved for  $v(t)$ , yielding

$$v(t) = \frac{Mg}{\gamma} (1 - e^{-\gamma t/M})$$

Since  $M$  is very small and  $\gamma$  is relatively large, the exponential factor quickly decays to 0, leaving simply a constant velocity  $v = Mg/\gamma$  known as the *terminal velocity*. This velocity can be measured and used to solve for the mass  $M$ . Once the mass is known, the charge-to-mass ratio determined above can be used to determine the charge  $q$ . The last remaining technical problem is that it is not known how many electrons are stripped off each drop before the experiment is performed. Thus, each drop will have a different charge  $q$  that is a multiple of the fundamental charge unit  $e$ . By subtracting successive values of  $q$  obtained for different drops, however, it is possible to find a "smallest" value, which can be assumed to be a prediction of  $e$ , although the possibility that the result is still a multiple of  $e$  cannot be ruled out.

The currently accepted values of  $e$  and  $m$  are:

$$e = 1.6021773 \times 10^{-19} \text{ C}$$

$$m = 9.109390 \times 10^{-31} \text{ kg}$$

## Rutherford's experiment and the nature of the atomic nucleus

The nature of the atomic nucleus was first elucidated experimentally by Ernest Rutherford in 1911. He observed the scattering of  $\alpha$ -particles (helium nuclei) from a thin gold foil (see schematic below):

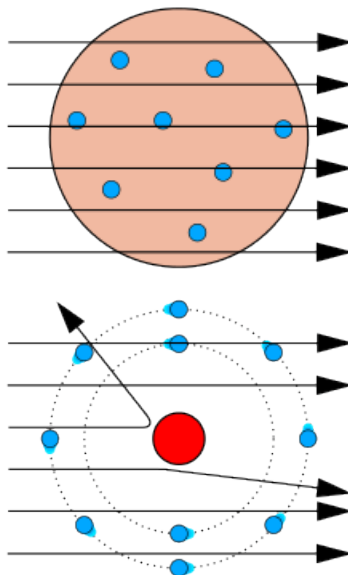


Figure 4: Schematic of Rutherford's **gold foil experiment**. Top: Expected results: alpha particles passing through the plum pudding model of the atom with negligible deflection. Bottom: Observed results: a small portion of the particles were deflected by the concentrated positive charge of the nucleus.

As he had assumed a relatively uniform mass distribution throughout the gold foil, he was surprised to observe that most of the  $\alpha$ -particles passed through the foil essentially undeflected, as if through empty space. Occasionally, an  $\alpha$ -particle would be scattered strongly, as if it had collided with a dense concentration of mass. He, thus, concluded that most of the mass of the gold atoms was concentrated in a tiny, dense kernel that he called the *nucleus*.

Rutherford estimated the "diameter" of an atom to be approximately  $10^{-8} \text{ cm}$  and that of the nucleus to be approximately  $10^{-13} \text{ cm}$ . He proposed a model of the atom as consisting of a small, dense nucleus surrounded by enough electrons to yield an overall charge-neutral aggregate. That is, if the nuclear charge is  $+Ze$ , then the atom must possess  $Z$  electrons. The model later introduced by Bohr, and even the current quantum mechanical picture of the atom (which you will see next semester), were built upon Rutherford's original model.

As mentioned in the first lecture, we know today that the atomic nucleus is composed of protons and neutrons. If a nucleus has  $Z$  protons and  $N$  neutrons, it is said to have a mass number  $A$  equal to  $Z + N$ . Thus, if  $X$  represents the chemical symbol of some element, then its nucleus is represented by

$${}^A_Z X$$

Nuclei of the same chemical species having different mass numbers, hence different numbers of neutrons, are called *isotopes* of that species. Thus,

$${}^A_Z X \text{ and } {}^{A'}_Z X$$

are isotopes of the element  $X$ . For example,

$${}^1_1 H, {}^2_1 H, \text{ and } {}^3_1 H$$

are isotopes in the hydrogen family, called "hydrogen," "deuterium," and "tritium," respectively.

## Expressing the mass of an atom

The mass of a hydrogen atom is  $1.6727 \times 10^{-27} \text{ kg}$ . To avoid having to work with such small numbers all the time, the tradition of

using a relative atomic mass scale was started. Although such a relative scale has undergone several incarnations, in 1961, by international agreement, a scale was settled upon.

A relative scale can be devised by assuming that one of the elements has exactly one mass unit for each of its nucleons. In 1961, it was decided that  $^{12}\text{C}$  would be the element that defined the scale. Thus, the scale of relative atomic mass of  $^{12}\text{C}$  is taken to be exactly 12 (and no units are assigned to this number). Then, the masses of *all* other elements are defined with respect to this scale. Thus, knowing the actual mass of a  $^{12}\text{C}$  atom ( $1.9927 \times 10^{-26} \text{ kg}$ ), and the actual mass of a hydrogen atom, we can determine the relative mass of hydrogen on this scale from

$$\frac{\text{mass of an atom of H}}{\text{mass of an atom of C}} = \frac{\text{relative mass of an atom of H}}{\text{relative mass of an atom of } ^{12}\text{C}}$$

$$\frac{1.6727 \times 10^{-27} \text{ kg}}{1.9927 \times 10^{-26} \text{ kg}} = \frac{\text{relative mass of H}}{12}$$

$$\text{relative mass of H} = 1.0073$$

A complete list of relative mass of atoms is given in the table in the inside back cover of the book.

Notice, however, that the number we computed above does not correspond to what is in the table under hydrogen. Since many elements have isotopes, it is customary to express the relative mass of an atom as an average over the different isotopes. Thus, if an element has isotopes  $^{A_1}\text{X}$ ,  $^{A_2}\text{X}$ ,  $^{A_3}\text{X}$ , ... with relative masses  $A_1$ ,  $A_2$ ,  $A_3$ , ... then the relative mass  $A$  associated with an atom of X is given by

$$A = A_1p_1 + A_2p_2 + A_3p_3 + \dots = \sum_{i=1}^n A_i p_i$$

where  $p_i$  is the *fractional abundances* of the  $i$ th isotope.

### Example 4.1

$^{12}\text{C}$  and  $^{13}\text{C}$  are stable isotopes of carbon with fractional abundances of 98.934% and 1.0664%, respectively. The relative mass of  $^{13}\text{C}$  is 13.003354. What is the average relative mass of carbon?

#### Solution

$$A = 12.00000 \times 0.98934 + 13.003354 \times 0.010664 = 12.00107$$

In order to establish a link between the mass of macroscopic amounts of matter that we ordinarily deal with and the masses of individual atoms, a connection exists through a number known as Avogadro's number ( $N_0$ ), which is defined to be the number of atoms in *exactly* 12 g of carbon. The currently accepted value of  $N_0$  is  $6.0221420 \times 10^{23}$ . Then, the mass of any atom can be determined by dividing its relative mass  $A$  by  $N_0$ :

$$m_X = \frac{A}{N_0}$$

For example, the mass of one atom of  $^{12}\text{C}$  is

$$m_{^{12}\text{C}} = \frac{12.000 \text{ g}}{6.022142 \times 10^{23}} = 1.9926465 \times 10^{-23} \text{ g}$$

## The mole concept

In everyday work, we deal with macroscopic amounts of substances. It is, therefore, useful to have a standard definition of macroscopic quantity of something. Avogadro's number is used to provide such a definition. We define 1 *mole* of something to be the amount of that something which contains  $N_0$  individual entities of that thing. Thus, 1 *mole of sodium atoms* =  $N_0$  sodium atoms. Now, if  $m_X$  is the mass of one atom of the element X, then the mass of one mole of X is given by

$$m_X(\text{g/atom}) \times N_0(\text{atoms/mol}) = m_X N_0(\text{g/mol})$$

But  $m_X = A/N_0$ . Thus, we see that the relative mass  $A$  also measures the mass of 1 mole of  $X$  (in g/mol, for example). For this reason, the relative mass  $A$  is also called the molar mass of  $X$ , however to distinguish relative mass  $A$  from molar mass, we will use the symbol  $M$  for molar mass. Note, therefore, that 12 g of  $^{12}\text{C}$  is exactly 1 mole of  $^{12}\text{C}$ , which explains why Avogadro's number is defined the way it is.

## Stoichiometry

### Chemical Formulae

Molecules are aggregates of individual atoms held together by *chemical bonds* (to be discussed in the next chapter). Thus, a symbolic representation of a molecule should be composed of the chemical symbols for the individual atoms that comprise the molecule. There are two types of chemical formulae that are commonly used to represent a molecule:

#### 1. Molecular Formula:

**The molecular formula for a molecule expresses the precise number of each type of atom in that molecule.**

**Examples:**  $\text{CO}_2$  is the formula for a molecule of carbon dioxide.  $\text{H}_2\text{O}$  is the formula for a molecule of water.  $\text{C}_6\text{H}_{12}\text{O}_6$  is the formula for molecule of glucose.

**Note that the molecular formula is also the formula for the (bulk) substance, itself. That is, we say  $\text{H}_2\text{O}$  is the molecular formula for water or ice, indicating bulk water or ice. This is true as long as the bulk substance has well defined molecular subunits.**

#### 2. Empirical Formula:

**The empirical formula is the simplest formula for a molecule that still expresses the correct relative numbers or ratios of numbers of atoms in the molecule.**

**Example:** The numbers of carbon, hydrogen and oxygen atoms in glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) are in the ratio:

$$6 : 12 : 6$$

$$1 : 2 : 1$$

**Hence, the empirical formula for glucose is**



*Which contains more information?*

Consider the empirical formula



This is a correct empirical formula for the following molecules:

- a. ethylene:  $\text{C}_2\text{H}_4$
- b. cyclopropane:  $\text{C}_3\text{H}_6$
- c. cyclobutane:  $\text{C}_4\text{H}_8$
- d. cyclohexane:  $\text{C}_6\text{H}_{12}$

or any other molecule for which the number of carbon atoms and the number of hydrogen atoms are in the ratio of 1 : 2. From this example, it is clear that the *molecular formula* carries more information and is clearly preferable to an empirical formula.

Put another way, an empirical formula specifies a class of molecules, in which the numbers of atoms are in certain basic ratios, while the molecular formula precisely identifies a particular molecule.

Although preferable, a molecular formula is not always possible. For example, in liquids and solids, it may not always be possible to define precise molecular units, in which case an empirical formula is the only possible choice.

Sometimes, enough information about a substance is given to determine the empirical formula only. Consider the following example:

### Example 1

A 10.0 g sample of a sand-like substance is known to contain 46.01% iron (*Fe*) and 53.99% silicon (*Si*) by mass. What is the formula for the substance?

#### Solution

The mass of *Fe* and *Si* in the sample can be determined from the given percentages:

$$\text{mass of Fe} = 10.0 \text{ g} * 0.4601 = 4.601 \text{ g}$$

$$\text{mass of Si} = 10.0 \text{ g} * 0.5399 = 5.399 \text{ g}$$

We convert masses to moles, since we want to know how many of each type of atom there is in the substance (expressed in moles), and hence how many of each type of atom in a molecule. This is done using the molar masses of each atom type.

$$\text{moles of Fe} = \frac{4.601 \text{ g}}{55.847 \text{ g/mol}} = 0.08237 \text{ mol}$$

$$\text{moles of Si} = \frac{5.399 \text{ g}}{28.086 \text{ g/mol}} = 0.19223 \text{ mol}$$

The ratio is:

$$0.08237 : 0.192234$$

$$1 : \frac{7}{3}$$

$$3 : 7$$

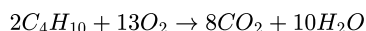
So the formula, which is an empirical formula, is



The reason it is only an empirical formula is that if the true formula were  $\text{Fe}_6\text{Si}_{14}$ , the same percentages by mass would still hold.

## Conservation of mass

Consider the balanced reaction from the previous lecture:



In this example, suppose 2 mol of  $\text{C}_4\text{H}_{10}$  are combined with 13 mol of  $\text{O}_2$ . What are the masses of the reactants and products?

Quantities in moles are converted to masses via the molar mass of each molecular species. The molar mass of a molecule is obtained by simply adding the molar masses of each of its atomic constituents. Thus, letting *M* be the symbol for molar mass,

$$M_{\text{C}_4\text{H}_{10}} = 4M_{\text{C}} + 10M_{\text{H}} = 4 * 12.011 + 10 * 1.0079 = 58.123 \text{ g/mol}$$

$$M_{\text{O}_2} = 2M_{\text{O}} = 2.0 * 15.998 = 31.996 \text{ g/mol}$$

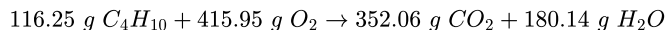
$$M_{\text{CO}_2} = M_{\text{C}} + 2M_{\text{O}} = 12.011 + 2.0 * 15.998 = 44.007 \text{ g/mol}$$

$$M_{H_2O} = 2M_H + M_O = 2.0 * 1.0079 + 15.998 = 18.014 \text{ g/mol}$$

Then, 2 mol of  $C_4H_{10}$  is equivalent to

$$2 \text{ mol } C_4H_{10} = (2 \text{ mol } C_4H_{10}) * 58.123 \text{ g/mol} = 116.25 \text{ g } C_4H_{10}$$

etc. Thus, the chemical equation can be written as a statement about masses of reactants and products:



The total mass on the left side is  $116.25 \text{ g} + 415.95 \text{ g} = 532.2 \text{ g}$ , and the total mass on the right is  $352.0 \text{ g} + 180.14 \text{ g} = 532.2 \text{ g}$ . Thus, mass conservation is satisfied. The study of such mass relations in chemical reactions is called *stoichiometry*.

## Limiting reagent

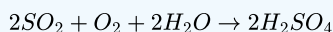
Chemical equations specify precise amounts of reactants that will combine to give products. In a real chemical reaction, arbitrary amounts of reactants are mixed together and allowed to form products, which means generally that one of the reactants will be used up completely, while excess amounts of other reactants will remain after the reaction has run to completion. The species that is fully consumed is called the *limiting reagent*. The limiting reagent will then determine what the yield of product will be.

When the quantities of reactants that are allowed to combine are specified, identifying the limiting reagent amounts to determining which of the reacting species yields the *smallest amount of product*.

Consider the following example.

### Example 2

Sulfuric acid is produced in the reaction:



Suppose 400 g of  $SO_2$ , 175 g of  $O_2$  and 125 g of  $H_2O$  are mixed and allows to react. Which reactant is the limiting reagent?

#### Solution

First convert the given masses to moles:

$$\text{moles of } SO_2 = \frac{400 \text{ g}}{64.06 \text{ g/mol}} = 6.24 \text{ mol } SO_2$$

$$\text{moles of } O_2 = \frac{175 \text{ g}}{31.996 \text{ g/mol}} = 5.47 \text{ mol } O_2$$

$$\text{moles of } H_2O = \frac{125 \text{ g}}{18.02 \text{ g/mol}} = 6.94 \text{ mol } H_2O$$

From the reaction equation, we see that

$$2 \text{ moles of } SO_2 \text{ yields } 2 \text{ moles of } H_2SO_4$$

or

$$1 \text{ mole of } SO_2 \text{ yields } 1 \text{ mole of } H_2SO_4$$

or

$$6.24 \text{ moles of } SO_2 \text{ yields } 6.24 \text{ moles of } H_2SO_4$$

Similarly,

1 mole of  $O_2$  yields 2 moles of  $H_2SO_4$

or

5.47 mole of  $O_2$  yields 10.94 moles of  $H_2SO_4$

and

2 moles of  $H_2O$  yields 2 moles of  $H_2SO_4$

or

1 mole of  $H_2O$  yields 1 mole of  $H_2SO_4$

or

6.94 moles of  $H_2O$  yields 6.94 moles of  $H_2SO_4$

Since  $SO_2$  yields the smallest quantity of product, it is the limiting reagent.

## Percentage yield

A balanced chemical equation tells what the *theoretical* or *ideal* yield of the reaction should be, assuming perfect completion of the reaction. In reality, the *actual* yield may be less than the theoretical yield. Reasons for this include:

1. There may be competing reactions which hinder the process under consideration.
2. External conditions may not be perfectly maintained.
3. Reactants may not be pure.

The ratio of the actual yield to the theoretical yield is a quantity known as the fractional yield:

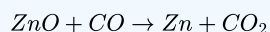
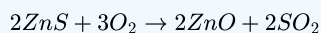
$$\text{fractional yield} = \frac{\text{actual yield}}{\text{theoretical yield}}$$

and the percentage yield is obtained from the fractional yield according to

$$\text{percentage yield} = 100\% * (\text{fractional yield})$$

### Example

Pure zinc can be produced in the following two-step process:



### Example 4.1

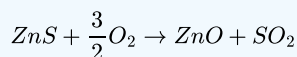
Suppose 5.32 kg of  $ZnS$  yield 3.30 kg of pure zinc. What is the percentage yield?

#### Solution

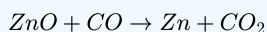
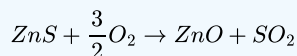
Convert the mass of  $ZnS$  to moles:

$$\text{moles } ZnS = \frac{5320 \text{ g}}{97.46 \text{ g/mol}} = 54.6 \text{ moles } ZnS$$

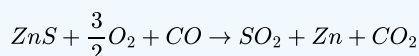
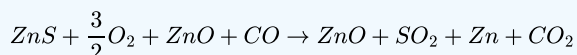
How do we figure out how many moles of  $Zn$  are produced in the two-step reaction? We need to obtain the *overall* reaction, which is just a "sum" of the individual steps. We can obtain the equation of the overall reaction by adding the equations for the individual steps. However, this addition must be carried out in a particular way. Specifically, note that the species  $ZnO$  is produced in the first step and consumed in the second step. Thus, it does not appear among the final products of the process, and for this reason, it is called an *intermediate*. The equations for the individual steps must be added in such a way that all intermediates cancel out. Since adding reaction equations works like the adding of algebraic equations, this means that the coefficients of intermediates must be the same in the individual steps. In the above process the coefficients of  $ZnO$  are different in each step. But, if the first step is divided by 2, so that the reaction equation reads:



then  $ZnO$  has the same coefficient in the first step as it does in the second and the equations can now be added:



*Adding these 2 yields :*



where  $ZnO$  has been "canceled" algebraically on both sides. From the overall reaction, we see that

*1 mole of  $ZnS$  yields 1 mole of  $Zn$*

or

*54.6 moles of  $ZnS$  yields 54.6 moles of  $Zn$*

Thus, the mass of  $Zn$  produced is

$$\text{mass of } Zn = (54.6 \text{ mol}) * (65.39 \text{ g/mol}) = 3570 \text{ g} = 3.57 \text{ kg}$$

This is the theoretical yield predicted by the reaction equations. The actual yield is only  $(3.30 \text{ kg})$ , so that the fractional yield is

$$\text{fractional yield} = \frac{3.3 \text{ kg}}{3.57 \text{ kg}} = 0.924 = 92.4\%$$

In multi-step processes, it is important that each step have as high a percentage yield as possible. The reason for this is that the overall percentage yield will be a product of the percentage yields of each step. As an example, suppose there is a 10-step process with a 50% yield for each step:

*Step 1 — percentage yield = 50%*

*Step 2 — percentage yield = 50%*

*:*

*Step 10 — percentage yield = 50%*

The overall percentage yield would be the product of the individual percentages, or

$$(0.5)^{10} = 0.001 = 0.1\%$$

Even if the percentage yield of each step were 90%, the overall yield would be  $(0.9)^{10} = 35\%$ , which is better, but still somewhat low. If the percentage yield of each step were 95%, then the overall yield would be  $(0.95)^{10} = 60\%$ , which might make the process feasible.

## 5: The classical view of the universe and the experiments that brought about its downfall

### The Classical View

In the late 19th and early 20th centuries, the science of physics and the prevailing view of the universe changed in a truly profound manner. The change was instigated by a series of key experiments that could not be rationalized within the existing theory of classical mechanics as laid out by Newton.

Let us recall what classical mechanics implies as a world view. A classical system consisting of  $N$  particles is completely determined by specifying the positions and velocities of all particles at any point in time. See the figure below:

Figure 1:

\includegraphics[scale=0.5]{classical\_box.eps}

Since momentum  $p = mv$ , we can also specify each particle's positions  $r$  and its momentum  $p$ . When this is done for every particle, we have a set of  $N$  position vectors  $r_1, r_2, \dots, r_N$  and a set of  $N$  momentum vectors  $p_1, p_2, \dots, p_N$ . In order to follow the system in time, we clearly need to specify how each of the positions and momenta change as functions of time. This time evolution is given by Newton's second law of motion.

If  $F_1, F_2, \dots, F_N$  are the forces on particles 1, 2, ...,  $N$ , respectively due to all of the other particles in the system, then the time dependence of all of the positions and momenta will be given by solving the set of *equations of motion*

$$F_i = m_i \frac{d^2 r_i}{dt^2} \quad i = 1, \dots, N \quad (5.1)$$

In order to solve Newton's equations, all we have to do is specify all of the positions and momenta at one point in time, say at  $t = 0$ , meaning that we have to provide the following vectors  $r_1(0), \dots, r_N(0)$  and  $p_1(0), \dots, p_N(0)$ . This is called specifying the initial conditions. Once we have the initial conditions, then by solving the equations of motion, we know the time evolution of the system for all time in the future, and we can trace the history of the system infinitely far in the past. More important, if we know all of the positions and momenta at all points in time, then the outcome of *any* experiment performed on the system can be predicted with perfect precision. Moreover, if the system is initially prepared in exactly the same way, with the same initial conditions in different repetitions of the experiment, then the same outcome will result every time.

Finally, since the positions and momenta of a system are continuous and can take on any values, physical quantities can also have any value since these are always computed from the positions and momenta. In particular, the energy

$$E = \sum_{i=1}^N \frac{p_i^2}{2m_i} + V(r_1, \dots, r_N) \quad (5.2)$$

can take on any value, although once its value is set for a given set of initial conditions, it will not change because energy is conserved.

#### Example 1: "Classical Hydrogen"

Consider a hydrogen atom with the proton fixed at the origin and the electron a distance  $r$  from the proton. The potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

which gives rise to a force

$$F = -\frac{e^2}{4\pi\epsilon_0 r^3} r$$

If we solve Newton's second law for the orbit of the electron, the orbit looks as shown in the figure below:

`\includegraphics[scale=0.5]{orbit.eps}`

Figure 2:

Here, the energy  $E$  of the orbit can take on any value.

Interestingly, according to Maxwell's theory of electromagnetism, an orbiting charged particle radiates energy due to its acceleration. Thus, the classical "electron" radiates energy as it orbits the proton. As a consequence, the electron loses energy continuously over time and eventually must spiral into the nucleus. Of course, this never happens, and this is one of the indications that classical mechanics has serious deficiencies.

## Key experiments that challenged the classical world view

In this section, we will discuss three important experiments that ultimately lead to the development of the quantum theory and a radical change in how we view the universe. In fact, it is not the experiments *per se* that can be attributed to this change in world view but rather the rationalization of these experiments that were proposed by theoreticians. Thus, here we have an excellent illustration of the important role played by theory. Without the experimental data, theoreticians might not have considered overthrowing the beautiful structure embodied in classical mechanics. However, it was ultimately the new theoretical structure introduced to explain the experimental results that lead to this crucial change.

## Blackbody Radiation

The explanation of this experiment was proposed by the German physicist Max Planck in 1901. Every object emits energy from its surface in the form of electromagnetic radiation. Thus, in order to discuss this experiment, we need a little background on electromagnetic waves. Some examples of waves are:

1. Vibrations of a string
2. Sound waves
3. Electromagnetic (light) waves
4. Water waves

In general, the mathematical form of a wave in motion in one dimension is

$$A(x, t) = A_0 \cos\left(\frac{2\pi x}{\lambda} - 2\pi \nu t\right)$$

where  $A_0$  is the wave *amplitude*,  $\lambda$  is its wavelength, and  $\nu$  is its frequency. A snapshot of this wave form at  $t = 0$  is shown in the figure below:

Figure 3:

`\includegraphics[scale=0.5]{cos_form.eps}`

If we wait a time  $t = 1/4\nu$  later, the wave looks as shown below:

Figure 4:

`\includegraphics[scale=0.5]{sin_form.eps}`

Thus,  $\nu$  is the number of wave crests (maxima) that pass a given point per unit time (e.g. seconds). Thus, the units of frequency are *crests/second* or *cycles/second* = *Hz* (*Hertz*), however, it is only the inverse time that is important in dimensional analysis. Given that the time  $\tau = 1/\nu$  is the time for a wave crest to move a distance  $\lambda$ , the speed of the wave is

$$v = \frac{\lambda}{\tau} = \lambda\nu \quad (5.3)$$

Visible light, microwaves, X-rays, ultraviolet radiation,... all are forms of electromagnetic (EM) radiation. Maxwell's theory (introduced in the late 19th century) predict that such waves are composed of electric and magnetic fields, both wave-like and perpendicular to each other. Thus, a free EM wave appears as follows:

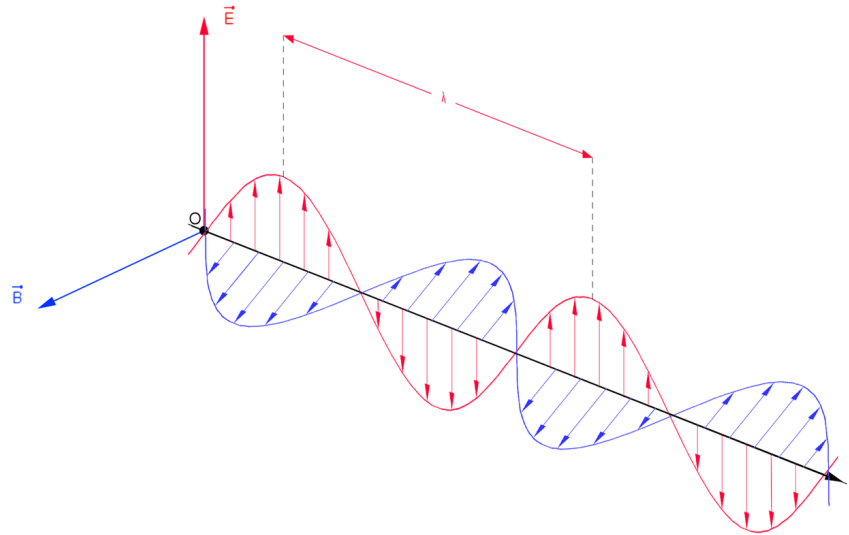


Figure 5: An electromagnetic wave consists of two waves that are oscillations of the electric (red vectors) and magnetic (blue vectors) fields. An electromagnetic wave travels in a direction that is at right angles to the oscillation direction of both fields

If the propagation occurs in the x-direction, then the electric and magnetic field components are given by

$$E(x, t) = E_0 \cos \left( \frac{2\pi x}{\lambda} - 2\pi \nu t \right)$$

$$B(x, t) = B_0 \cos \left( \frac{2\pi x}{\lambda} - 2\pi \nu t \right)$$

where  $E \perp B$ . These expressions for the electric and magnetic fields are solutions of the so-called "free-space Maxwell equations" (Maxwell's equations are the fundamental equations of the theory of electromagnetism). The speed of the wave  $c = \lambda\nu$  is the speed of light  $c = 2.9979246 \times 10^8 \text{ m/s}$ . Visible light spans  $400 \times 10^{-9} \text{ m} - 700 \times 10^{-9} \text{ m}$  or  $400 - 700 \text{ nm}$ . The lower end of this range corresponds to red light while the upper end to blue light.

Examples of blackbody radiation include heating elements on electric stoves and incandescent lightbulbs. The intensity of the radiation depends on the wavelength and on temperature. The solid curves in the figure below show the blackbody radiation spectrum (as a function of the wavelength of the radiation) for different temperatures:

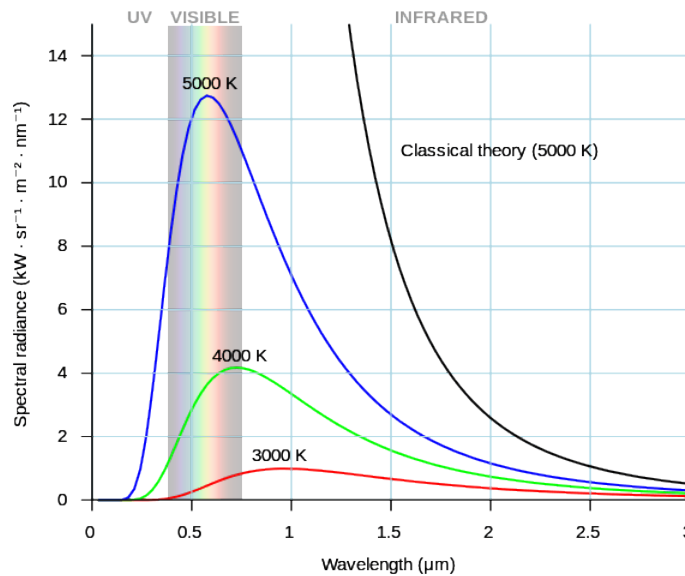


Figure 6: Planck's law (colored curves) accurately described black body radiation and resolved the ultraviolet catastrophe (black curve).

The temperature corresponding to the blue curve is higher than the temperature corresponding to the red curve. Since  $\lambda = c/\nu$ , we can also use the frequency  $\nu$  to characterize the radiation spectrum.

Classical mechanics predicts that the intensity  $I$  of emitted radiation at frequency  $\nu$  is given by

$$I(\nu) = \frac{8\pi k_B T \nu^2}{c^3} \quad (5.4)$$

where  $k_B$  is Boltzmann's constant,  $k_B = 1.38066 \times 10^{-23} \text{ J/K}$ . The classical curves in the above figure are obtained by setting  $\nu = c/\lambda$  in this expression:

$$I(\lambda) = \frac{8\pi k_B T}{c \lambda^2} \quad (5.5)$$

and are shown as the dashed curves in the figure. Note that as  $\lambda \rightarrow 0$ ,  $I \rightarrow \infty$ , which is known as the ultraviolet catastrophe.

In the classical theory, blackbody radiation is modeled as the radiation emitted from oscillating charged particles at the object's surface. These oscillations are produced by the thermal motions of the charged particles. If we treat each particle as a simple harmonic oscillator, then we can easily understand how Planck was able to explain blackbody radiation.

A simple harmonic oscillator is described by a Hooke's law force

$$F = -k(x - x_0) \quad (5.6)$$

where the force  $F$  arises from the displacement  $x$  from the equilibrium position  $x_0$  of a charged particle attached to a spring. Here  $k$  is the *spring constant*, which measures the stiffness of the spring.

Figure 7:

\includegraphics[scale=0.5]{springs.eps}

The force  $F$  is derived from the potential energy curve

$$V(x) = \frac{1}{2}k(x - x_0)^2$$

and produces the following motion in  $x$ :

$$x(t) = x_0 + A \cos(2\pi\nu t + \phi)$$

where

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

and  $\phi$  is known as the *phase angle*. Its value is determined by the initial position  $x(0)$  and initial momentum  $p(0)$  of the oscillator. The energy

$$E = \frac{p^2}{2m} + \frac{1}{2}k(x - x_0)^2$$

can take on any value, as determined by the initial conditions, but once its value is set, it does not change over time because energy is conserved.

Planck's ingenious idea was to propose the following radical hypothesis: What if the energy  $E$  could not take on just any value but only certain discrete values called "quanta" of energy. He suggested that higher frequency motion meant higher energy. By the way, in classical mechanics, the energy is only determined by the amplitude of the oscillator, not the frequency. Thus, he proposed that the energy quanta be multiplies of the frequency

$$E \propto n\nu$$

where  $n$  is an integer  $n = 0, 1, 2, \dots$ . The constant of proportionality needed to give energy units he called  $h$ , which is now known as Planck's constant. Thus, the discrete energy values were proposed to be determined by

$$E = nh\nu$$

Since there are many oscillating charged particles, we need to consider a very large number of identical oscillating systems. At Planck's time, it was known that the probability that a collection of identical systems at the same temperature  $T$  but starting from different classical initial conditions would have an energy  $E$  was proportional to the Boltzmann factor

$$probability \propto e^{-E/k_B T}$$

Let us recall the definition of a probability. Generally, given  $N$  possible events  $\epsilon_1, \dots, \epsilon_N$ , the probability that an event  $\epsilon_n$  will occur is defined to be

$$probability \text{ that } \epsilon_n \text{ occurs} \equiv P(\epsilon_n) = \frac{\text{Number of ways } \epsilon_n \text{ can occur}}{\text{Total number of ways any event can occur}}$$

Planck applied this formula to his quantized energy values. Let the event  $\epsilon_n$  be a measurement of the energy of the system at temperature  $T$  that yields an energy  $E = nh\nu$ . The probability of such an event, according to the above formula is

$$probability = \frac{e^{-nh\nu/k_B T}}{\sum_{n=0}^{\infty} e^{-nh\nu/k_B T}}$$

Note that if we sum both sides over  $n$ , we must get 1. That is, the sum over  $n$  is the probability of finding the system with any allowable energy, which, of course, must be 1. The denominator is of the form

$$\sum_{n=0}^{\infty} (e^{-h\nu/k_B T})^n$$

and since  $0 < \exp(-h\nu/k_B T) < 1$ , it follows that the sum is nothing more than a geometric series for which the following summation formula applies

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}$$

where  $|r| < 1$ . Applying this to the probability formula, we obtain

$$probability = e^{-h\nu/k_B T} (1 - e^{-h\nu/k_B T})$$

Similarly, the average energy of such a collection of systems is

$$\bar{E} = \frac{\sum_{n=0}^{\infty} n h \nu e^{-n h \nu / k_B T}}{\sum_{n=0}^{\infty} e^{-n h \nu / k_B T}}$$

These sums can be worked out (with a lot of algebra not presented here) with the result

$$\bar{E} = \frac{h \nu}{e^{h \nu / k_B T} - 1}$$

From this average energy formula, Planck was able to show that the intensity of emitted radiation from the blackbody would be given by

$$I(\nu) = \frac{8 \pi h \nu^3}{c^3} \frac{1}{e^{h \nu / k_B T} - 1}$$

or using  $\nu = c/\lambda$

$$I(\lambda) = \frac{8 \pi h}{\lambda^3} \frac{1}{e^{h c / \lambda k_B T} - 1}$$

Plotting this curve as a function of  $\lambda$  yields the solid lines in the radiation spectra shown above.

By fitting this expression to the experimental data, he was able to determine a value for  $h$ , which is now accepted to be  $h = 6.6208 \times 10^{-34} \text{ J} \cdot \text{s}$ . Planck's formula actually reduces to the classical formula in the limit that the difference between successive quantized energy values  $\Delta E = h \nu$  is small compared to  $k_B T$ , i.e.

$$\frac{h \nu}{k_B T} \ll 1$$

When this is true, the exponential can be approximated using the formula  $e^x \approx 1 + x$ , so that

$$e^{h \nu / k_B T} \approx 1 + \frac{h \nu}{k_B T}$$

In this case

$$\begin{aligned} I(\nu) &\rightarrow \frac{8 \pi h \nu^3}{c^3} \frac{1}{1 + h \nu / k_B T - 1} \\ &= \frac{8 \pi h \nu^3}{c^3} \frac{k_B T}{h \nu} \\ &= \frac{8 \pi k_B T \nu^2}{c^3} \end{aligned}$$

Planck's proposed theory about energy quantization was able to explain the blackbody radiation spectra, yet it constituted a radical departure from classical physics.

## The Photoelectric Effect

The photoelectric effect was explained by Albert Einstein in 1905. When light impinges on a metal surface, it is observed that for sufficiently high frequency light, electrons will be ejected from the surface as shown in the figure below:

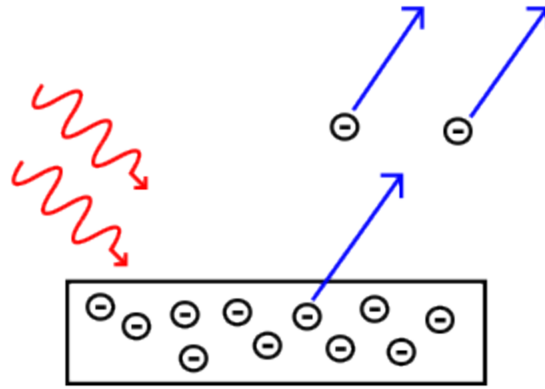


Figure 8:

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the experiment.

Einstein, borrowing Planck's hypothesis about the quantized energy of an oscillator, suggested that light comes in packets or "quanta" with energy  $E$  given by Planck's formula with  $n = 1$

$$E = h\nu$$

Since, according to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum *frequency*  $\nu_0$  needed to eject an electron with no residual energy. The corresponding energy is

$$h\nu_0 = \Phi$$

where  $\Phi$  is called the *work function* of the metal, and it is an intrinsic property of the metal. In general, if  $\nu > \nu_0$ , an electron will be ejected with some residual kinetic energy. If the electron has momentum  $p$  leaving the surface, then this kinetic energy is  $p^2/2m_e$ , and because energy is conserved, we have the relation

$$h\nu = \Phi + \frac{p^2}{2m_e}$$

The left side is the energy of the impinging light, and the right side is the sum of the minimum energy needed to extract an electron and the residual kinetic energy it has when leaving the surface.

The strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy  $E = h\nu$  can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between massive particles such as billiard balls

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## 6: Electron diffraction, postulates of quantum mechanics, the Bohr model, and the Beer-Lambert law

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### Electron diffraction

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction. It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of diffraction is the Young double slit experiment pictured below:

`\includegraphics[scale=1.0]{double-slit-wave.eps}`

Figure: From [www.lightandmatter.com](http://www.lightandmatter.com)

Here, we use water waves (pictured as waves in a plane parallel to the double slit apparatus) and observe what happens when they impinge on the slits. Each slit then becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the bottom. The intensity of the fringes is depicted in the sketch below:

Figure: From [hyperphysics.phy-astr.gsu.edu](http://hyperphysics.phy-astr.gsu.edu)

`\includegraphics[scale=1.0]{dslit.eps}`

If laser light is used, the interference pattern appears as shown below:

`\includegraphics[scale=2.0]{Laserdiffraction.eps}`

Figure 3: Laser interference through a double slit

Amazingly, if electrons are used instead of light in the double-slit experiment, and a fluorescent screen is used, one finds the same kind of interference pattern! This is shown in the electron double-slit diffraction pattern below:

`\includegraphics[scale=1.0]{electron_double_slit.eps}`

Figure 4: From [zms.desy.de](http://zms.desy.de)

Obviously, classical mechanics is not able to predict such a result. If the electrons are treated as classical particles, one would predict an intensity pattern corresponding to particles that can pass through one slit or the other, landing on the screen directly opposite the slit (i.e., no intensity maximum at the center of the screen):

`\includegraphics[scale=0.5]{classical_electron_dslit.eps}`

Figure 5: Intensity pattern for "classical" electrons

The width of each peak is a direct measure of the width of the slits. since, in classical mechanics, the electrons follow definite, deterministic, predictable paths, there can be no deviation from this pattern. For this reason, the classical explanation cannot be the correct one.

We will consider two different rationalizations of the electron double-slit experiment.

### Particle-wave picture

The first experiment, proposed by Clinton Davisson and Lester Germer in 1927, was based on a hypothesis put forth earlier by Louis de Broglie in 1922. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the

photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength  $\lambda$  to a particle with momentum  $p$  using Planck's constant as the constant of proportionality:

$$\lambda = \frac{h}{p} \quad (6.1)$$

which is called the *de Broglie wavelength*. The Davisson-Germer experiment, which produced an electron diffraction pattern from electrons scattered off a nickel crystal, confirmed the de Broglie hypothesis. However, it was not until 1961 that an experiment in which electrons impinged on a slit apparatus was performed by Claus Jönsson. This was a five-slit set-up. The double-slit experiment was finally performed in the 1970s by Pier Giorgio Merli, Giulio Pozzi and GianFranco Missiroli. The point is, however, that through such experiments, the idea that electrons can behave as waves, creating interference patterns normally associated with light, is now well-established. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the *particle-wave duality*.

In the following, we give a brief discussion of where the de Broglie hypothesis comes from. From the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relativity. In general, a particle of mass  $m$  and momentum  $p$  has an energy

$$E = \sqrt{p^2 c^2 + m^2 c^4} \quad (6.2)$$

Note that if  $p = 0$ , this reduces to the famous rest-energy expression  $E = mc^2$ . However, photons are massless particles that always have a finite momentum  $p$ . In this case, Einstein's formula becomes  $E = pc$ . From Planck's hypothesis, one quantum of electromagnetic radiation has energy  $E = h\nu$ . Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = \frac{hc}{\lambda} = pc \quad (6.3)$$

Solving for the wavelength  $\lambda$  gives

$$\lambda = \frac{h}{p} \quad (6.4)$$

Now, this relation pertains to photons not massive particles. However, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles. Hence, we associate a wavelength  $\lambda$  to a particle that has momentum  $p$ , which says that as the momentum becomes larger and larger, the wavelength becomes shorter and shorter. In both cases, this means the energy becomes larger. That is, short wavelength *and* high momentum correspond to high energy.

## Probability Waves

If particles can behave as waves, then we need to develop a theory for this type particle-wave. We will do this in detail when we study the Schrödinger wave equation. For now, suffice it to say that the theory of particle-waves has some aspects that are similar to the classical theory of waves, but by no means can a classical wave theory, like that used to describe waves on a string on the surface of a liquid, be used to formulate the theory of particle waves. To begin with, what is the very nature of a particle wave? Here, we will give only a brief conceptual answer.

A particle-wave is still described by some kind of amplitude function  $A(x, t)$ , but this amplitude must be consistent with the fact that we could, in principle, design an experiment capable of measuring the particle's spatial location or position. Thus, we seem to have arrived at a paradoxical situation: The electron diffraction experiment tells us that particle-waves can interfere with each other, yet it must also be possible to measure a particle-like property, the position, via some kind of actual experiment. The resolution of this dilemma is that the particle exhibits wave-like behavior until a measurement is performed on it that is capable of localizing it at a particular point in space. Making this leap, however, has a profound implication, namely, that the outcome of the position measurement will not be the same in each realization even if it is performed in the same way. The reason is that if it did yield the same result, then we could say that the particle was evolving in a particular way that would put it there when the measurement was made, and this negates the possibility of its ever having a wave-like character, since this is exactly how classical particles behave. Thus, if the result of a position measurement can yield different outcomes, then *the only thing we can predict is the probability that a given measurement of the position yields a particular value. The quantum world is not deterministic but rather intrinsically probabilistic.*

If we are only able to predict the probability that a measurement of position will yield a particular value, then how do we obtain this prediction. Recall that the particle-wave is described by an amplitude function  $A(x, t)$ . Let us suppose that the particle-wave reaches the screen at time  $T$  when the amplitude is  $A(x, T)$ , which we denote as  $A(x)$  (when  $T$  is fixed, the amplitude is a function of  $x$  alone). Here,  $x$  denotes the position along the screen. The screen, itself, acts as an apparatus for measuring the particle's position. The amplitude  $A(x)$  can be either positive or negative, and we could even choose it such that it is a complex number. Thus,  $A(x)$  is not a probability because it is not positive-definite, and it is not real. However, we can turn  $A(x)$  into a probability by taking the square magnitude of  $A(x)$ . We define a new function

$$P(x) = |A(x)|^2 = A^*(x)A(x)$$

where  $A^*(x)$  denotes the complex conjugate of  $A(x)$ . The function  $P(x)$  is positive-definite, and if  $A(x)$  is appropriately chosen,  $P(x)$  will satisfy the normalization condition

$$\int_a^b P(x)dx = 1$$

where  $a$  and  $b$  denote the endpoints of the screen.  $P(x)$  is an example of a probability density or probability distribution function. Because  $x$  is continuous, we cannot define a discrete probability since the probability to be at any particular value of  $x$  is zero (there are an infinite number of values for  $x$ ). What  $P(x)$  tells us is the probability to measure the particle's position on the screen within a small interval  $dx$ . In particular, the probability that a measurement of position yields a value in an interval  $dx$  centered on the point  $x_0$  is  $P(x_0)dx$ . The amplitude  $A(x)$  is called a *probability amplitude*.

So why does an interference pattern arise? Because we do not observe the particle's position until it reaches the screen, we have to consider two possibilities for the particle-wave: passage through the upper slit and passage through the lower slit, and we assign to one possibility a probability amplitude  $A_1(x)$  and other an amplitude  $A_2(x)$ . Just as with ordinary waves, we must add the amplitudes to obtain the total wave amplitude, so the total amplitude is  $A_{tot} = A_1(x) + A_2(x)$ . The probability that we observe something at a given point  $x_0$  on the screen in an interval  $dx$  is

$$\begin{aligned} P(x_0)dx &= |A_{tot}(x_0)|^2 dx \\ &= |A_1(x_0) + A_2(x_0)|^2 dx \\ &= (A_1^*(x_0) + A_2^*(x_0))(A_1(x_0) + A_2(x_0))dx \\ &= |A_1(x_0)|^2 + |A_2(x_0)|^2 + (A_1^*(x_0)A_2(x_0) + A_1(x_0)A_2^*(x_0))dx \end{aligned}$$

If the two possibilities were completely independent, then their corresponding probabilities would simply add, and we would just have the first two terms in the last expression. However, there is a cross term that is generally nonzero, and it is this cross term that gives rise to the interference between the two possibilities, which leads to the observed interference pattern. Let us look at this term in greater detail. Recall that a complex number  $A = a + ib$  can be expressed as

$$A = |A|e^{i\theta}$$

where  $|A|$  is the magnitude of the number

$$|A| = \sqrt{a^2 + b^2}$$

and  $\theta$  is the phase of the number

$$\theta = \tan^{-1} \frac{b}{a}$$

Letting

$$A_1 = |A_1|e^{i\theta_1}, \quad A_2 = |A_2|e^{i\theta_2}$$

so that

$$A_1^* = |A_1|e^{-i\theta_1}, \quad A_2^* = |A_2|e^{-i\theta_2}$$

and substituting into the probability distribution expression, we obtain

$$P(x_0) = |A_1|^2 + |A_2|^2 + (|A_1|e^{-i\theta_1}|A_2|e^{i\theta_2} + |A_1|e^{i\theta_1}|A_2|e^{-i\theta_2}) = |A_1|^2 + |A_2|^2 + |A_1||A_2|(e^{i(\theta_2-\theta_1)} + e^{-i(\theta_2-\theta_1)})$$

Recognizing that

$$e^{ix} + e^{-ix} = 2 \cos(x)$$

the probability finally becomes

$$P(x_0) = |A_1(x_0)|^2 + |A_2(x_0)|^2 + 2|A_1(x_0)||A_2(x_0)| \cos(\theta_2(x_0) - \theta_1(x_0))$$

The oscillatory nature of the cosine suggests of the oscillating pattern of bright and dark fringes in the interference pattern.

## Sum over paths picture

Let us now consider an alternative explanation of the double-slit experiment, however, due to Richard Feynman. This explanation is published in his 1965 book, *Quantum Mechanics and Path Integrals*. Feynman's explanation is closer in spirit to a classical-like picture, yet it still represents a radical departure from classical mechanics. Feynman postulated that electrons could still behave as particle in a double-slit experiment. The twist is that the particles do not follow definite paths, as they would if they were classical particles. Rather, they can trace out a myriad of possible paths that might differ considerably from the path that would be predicted by classical mechanics. In fact, electrons initialized in the same manner, will follow different paths if they are allowed to wend their way through the double-slit apparatus! This is illustrated in the figure below:

Figure 6: Illustration of the many paths an electron can follow through the double-slit apparatus

\includegraphics[scale=0.5]{quantum\_electron\_dslit.eps}

since the electron can follow any path and will follow different paths in different realizations of the experiment, physical quantities must be obtained by summing over *all* possible paths that the electron can follow. In order to carry out this sum, Feynman assigned a *weight* or *importance* to each path in the sum over paths. since each path takes the electron from the source to a point on the screen (call this point  $x$ , where  $x$  varies over the length of the screen) in a time  $t$ , the probability  $P$  associated with each path can only depend on  $x$  and  $t$ . If  $t$  is fixed, the  $P$  can only depend on  $x$ . Feynman proposed that each path could be assigned a quantity called the *action*  $S(x)$ , where  $S(x)$  has the following properties:

1.  $S(x)$  **varies only minimally for paths near the path that classical mechanics would predict the electron should follow.**
2.  $S(x)$  **varies increasingly dramatically as the paths differ increasingly from the classical path.**

He then assigned an *amplitude*  $A(x)$  to each path according to the formula

$$A(x) = e^{iS(x)/\hbar}$$

where  $i = \sqrt{-1}$  and  $\hbar = h/2\pi$ . The exponential of a complex argument has a simple expression in terms of common trigonometric functions:

$$e^{ix} = \cos(x) + i \sin(x)$$

Thus, we can also write  $A(x)$  as

$$A(x) = \cos(S(x)/\hbar) + i \sin(S(x)/\hbar)$$

however, it is generally easier to work with the exponential directly.

It is important to note that  $A(x)$  is a complex number. An amplitude is related to an actual probability  $P$  by taking the absolute value squared of the amplitude. Thus, if there were only one path with amplitude  $A(x)$ , the probability that the electron would follow that path is

$$\begin{aligned} P(x) &= A^*(x)A(x) = |A(x)|^2 \\ &= e^{-iS(x)/\hbar} e^{iS(x)/\hbar} \\ &= 1 \end{aligned}$$

as expected. This is also the probability that the electron will end up at a point  $x$  on the screen, since the single path takes the particle to a definite point  $x$ . However, in Feynman's picture, the electron can follow any path. Thus, in order to compute the probability  $P(x)$  that the particle ends up at a point  $x$  on the screen, we must sum over *all* possible paths:

$$P(x) = \left| \sum_{\text{paths}} A_{\text{path}}(x) \right|^2$$

where  $A_{\text{path}}(x)$  is the amplitude for a particle path. since we are summing over many oscillating sines and cosines, there will be an interference pattern, meaning that the paths effectively interfere with each other. Indeed, the intensity  $I(x)$  will be proportional to the probability:  $I(x) \propto P(x)$ . In fact, if we were to carry out this sum over paths (no simple feat, by the way), we would obtain an interference pattern that agrees with experiment.

Generally, a probability amplitude is a generalization of the square root of a probability that allows the amplitude to be a complex number. If  $P$  is a probability, and  $A$  is the associated probability amplitude, then if  $A$  were restricted to be real, then there would be only two possible values of  $A$ , i.e.,  $A = \sqrt{P}$  and  $A = -\sqrt{P}$ . If we let  $A$  be complex, the relation between  $A$  and  $P$  is

$$|A|^2 = A^* A = P$$

and there is an infinite number of square roots of  $P$ . To see this, consider writing  $A$  as

$$A = \sqrt{P} e^{i\theta}$$

where  $\theta$  is any number in the interval  $[0, 2\pi]$ . If we can show that  $A^* A = P$ , then it will follow that any value of  $\theta \in [0, 2\pi]$  is allowable, which means that the number of possible amplitudes is infinite. The complex conjugate of  $A$  is

$$A^* = \sqrt{P} e^{-i\theta}$$

and we find

$$\begin{aligned} A^* A &= (\sqrt{P} e^{-i\theta})(\sqrt{P} e^{i\theta}) \\ &= e^{-i\theta+i\theta} (\sqrt{P})^2 \\ &= P \end{aligned}$$

Now, suppose we have two interfering paths with amplitudes  $A_1$  and  $A_2$  (they should depend on  $x$ , but for notational simplicity, we will suppress the  $x$  dependence). The total amplitude is  $A = A_1 + A_2$ , and the corresponding probability is  $P = |A|^2$ , which gives

$$P = A^* A = (A_1^* + A_2^*)(A_1 + A_2)$$

Let  $A_1 = a_1 e^{i\theta_1}$  and  $A_2 = a_2 e^{i\theta_2}$ , where  $a_1$  and  $a_2$  are real numbers. Then

$$\begin{aligned} P &= (a_1 e^{-i\theta_1} + a_2 e^{-i\theta_2})(a_1 e^{i\theta_1} + a_2 e^{i\theta_2}) \\ &= a_1^2 + a_2^2 + a_1 a_2 (e^{-i(\theta_1-\theta_2)} + e^{i(\theta_1-\theta_2)}) \\ &= a_1^2 + a_2^2 + 2a_1 a_2 \cos(\theta_1 - \theta_2) \end{aligned}$$

The last term is known as the interference term. The presence of the cosine in that term, which oscillates, suggests the oscillation in the interference pattern observed on the screen.

At this point, several comments are in order. It is tempting to try to impose either the wave-like picture or the many-paths picture on the experiment. Indeed, both of these pictures provide a useful physical picture that helps us understand the outcome of the experiment. In the wave-like picture, we can think of each electron that leaves the source as feeling the presence of both slits simultaneously, and therefore interfering with itself (rather than with other electrons). In the many-paths picture, each electron follows not one path in the path sum but *all* possible paths at once, and these paths interfere with each other. However, the infuriating thing about quantum mechanics is that we have no way of knowing what is taking place between the source and the detector. All we have is the observation that there is an interference pattern. Feynman's picture makes this rather manifest. The implications of his picture can be summarized as

1. **Even within a particle-like interpretation of the experiment, particles do *not* have predictable positions and momenta along the paths. The reason for this is that the paths, themselves, are not predictable by any rule as they are in classical mechanics!**

2. **If we could devise an experiment for measuring the position  $x$  of the electron on the screen, we would find that different repetitions of the experiment on one electron initialized the same way would have different outcomes.**

Thus, the best we can do from theory is to predict the *probability* of a given outcome of an experiment but not the actual outcome, itself.

The rationalizations of the three experiments we have examined, blackbody radiation, the photoelectric effect, and electron diffraction, leads us to conclude that classical mechanics, with its deterministic, predictable view of the universe, must be overthrown in favor of a much more radical theory, now known as *quantum mechanics*. It is interesting to note that the idea of probabilistic outcomes of experiments and the fact that we can ONLY predict the probabilities, lead Albert Einstein ultimately to reject quantum mechanics, saying: "Gott spielt nicht Würfel" ("God does not play dice").

## Simple statement of the postulates of quantum mechanics

Below, we summarize the basic postulates of quantum mechanics and contrast them with roughly equivalent postulates of classical mechanics.

### Classical:

1. Particles are point-like objects that follow predictable, deterministic paths with well-defined positions and momenta obtained by solving Newton's laws of motion
2. The energy of a system can take on any value.
3. If the initial conditions of an experiment repeated many times are the same in each repetition, the outcome of the experiment will be the same for each repetition, and that outcome is predictable.

### Quantum:

1. Particles can exhibit wave-like or particle-like behavior, depending on the experiment. Even within the particle-like interpretation, particles do not follow well-defined, predictable paths and hence, do not have well-defined positions and momenta.
2. The energy can take on only certain discrete values.
3. Even if a system is prepared in the same way for different repetitions of an experiment, the outcome need not be the same in each repetition. All that we can predict is the probability that a given outcome will be obtained.

## Heisenberg's uncertainty principle

If particles cannot be assigned well-defined positions and momenta, then how are these two quantities related for a quantum particle? The fact that particles do not follow well-defined paths means that there must be a limit on how accurately we can determine the position and momentum of a particle and this limit is a fundamental characteristic of the particle, itself, rather than a limit on our ability to perform an accurate enough measurement.

This idea of a fundamental limit to what is knowable about a quantum particle (or collection of quantum particles) was put forth by the physicist Werner Heisenberg in 1927. His principle is now one of the fundamental postulates of quantum mechanics and is known as the *uncertainty principle* or *indeterminacy principle*. Heisenberg's principle states that there are specific pairs of physical observables that cannot be simultaneously measured to arbitrary accuracy, i.e. there will be a fundamental limit to what we can know about two such observables simultaneously. Two such observables are said to be *incompatible* with each other. Dimensionally, such pairs are related so that their product has units of energy $\cdot$ time. Thus, if  $A$  and  $B$  constitute such a pair, and if  $\Delta A$  and  $\Delta B$  are the uncertainties associated with these observables, then Heisenberg's uncertainty principle states

$$\Delta A \Delta B \geq \frac{1}{2} \hbar$$

where  $\hbar = h/2\pi$ . Here, the uncertainties can be computed from the statistical uncertainty

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

where  $\langle A^2 \rangle$  is the average of  $A^2$  over many realizations of an experiment, and  $\langle A \rangle$  is the average of  $A$  over many such realizations.

Position and momentum constitute such a pair of observables. If  $\Delta x$  and  $\Delta p$  are the corresponding uncertainties, then according to Heisenberg's principle, the best we can do in measuring  $x$  and  $p$  simultaneously is to have uncertainties in our measurements related by

$$\Delta x \Delta p \geq \frac{1}{2} \hbar$$

If we wish to determine the position of an electron, then we need to probe it with a photon, i.e. scatter a photon off of it and observe where the scattering occurred. The accuracy of the measurement will be related to the wavelength  $\lambda$  of the photon. That is, if we wish to determine the location of the scattering event to within  $10^{-12} \text{ m}$  (1% the size of an atom), then we need  $\lambda = 10^{-12} \text{ m}$ , which, according to the energy formula  $E = hc/\lambda$  is a very energetic photon.

When the photon strikes the electron, it causes the electron to change its direction, as illustrated in the figure below:

Figure 7: Electron-photon scattering events

\includegraphics[scale=0.5]{e\_photon\_scattering.eps}

If we accept that we can only predict the probability that a measurement of position will yield a particular outcome, then, of course, the same must hold for the particle's momentum. Thus, by using an energetic photon to localize the particle, we potentially also transfer a large amount of kinetic energy to the particle, which increases the range of possible momentum values that could be obtained if a subsequent measurement of momentum were to be carried out. This is why the position and momentum uncertainties must be inversely proportional:

$$\Delta p \geq \frac{\hbar}{\Delta x}$$

Feynman's many-path picture of quantum mechanics can also help us understand this fundamental indeterminacy. According to Feynman, such a picture is misleading since the electron does not follow a definite path. Rather, the electron can follow complicated paths as illustrated below:

Figure 8:

\includegraphics[scale=0.5]{electron\_photon\_paths.eps}

The more energetic the photon, the greater the spread in the possible scattered paths that electron can follow, which translates into a greater spread in the distribution of scattered momenta. since we have to sum over *all* possible paths, the uncertainty in the momentum will be quite large for such an energetic photon. So, even though we have a relatively accurate determination of the electron's location, we have a large uncertainty in the momentum, and this is why there is an inverse proportionality between  $\Delta x$  and  $\Delta p$ :

$$\Delta p \geq \frac{\hbar}{2\Delta x}$$

We stress again, that the uncertainty or indeterminacy principle is a statement about an inherent limit to what we can know about a quantum system. This limit cannot be reduced simply by defining a better experiment.

## Coulomb's Law

Given two charged particles with charges  $Q_1$  and  $Q_2$ , there is an interaction between them that behaves as follows: since charge can be positive or negative, opposite charges attract each other and like charges repel each other. The strength of the force between any pair of charges varies as the inverse square of the distance between them. These observations constitute *Coulomb's Law*. Coulomb's law is expressed as a force law of the form

Label '1' multiply defined

where  $k$  is a constant whose value is  $8.98755 \times 10^9 \text{ J} \cdot \text{m} \cdot \text{C}^{-2}$ . The direction of the force is always along the line joining the two charges. Thus, if the position of charge  $Q_1$  is  $r_1$  and the position of charge  $Q_2$  is  $r_2$ , then let  $r = r_2 - r_1$ . Here,  $r = |r|$ , and the force can be written as a proper vector quantity

Label '2' multiply defined

The force law comes from the following potential energy:

Label '3' multiply defined

and it can be easily verified that

Label '4' multiply defined

As  $r$  is varied, the energy will change, so that we have an example of a potential energy curve  $V(r)$ , as discussed in lecture 3.

If  $Q_1$  and  $Q_2$  are the same sign, then the curve appears roughly as follows:

`\begin{figure}\begin{center} \leavevmode \epsfbox{lec5_coul1.ps} {\small} \end{center}\end{figure}`

**Figure 9:**

which is a purely repulsive potential, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other. If the charges are of opposite sign, then the curve appears roughly as:

`\begin{figure}\begin{center} \leavevmode \epsfbox{lec5_coul2.ps} {\small} \end{center}\end{figure}`

**Figure 10:**

Thus, the energy decreases as the charges are brought together, implying that opposite charges attract.

## The Bohr model: An early attempt to predict the energy levels of an atom

It is observed that hydrogen will absorb and emit light at only discrete wavelengths as the figure below shows:

`\includegraphics[scale=1.0]{hydrogen-spectra.eps}`

Figure 11: From [www.solarobserving.com](http://www.solarobserving.com)

This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system. Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies of a harmonic oscillator came out of nowhere. The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as  $H$ ,  $He^+$ ,  $Li^{2+}$ ,  $Be^{3+}$ , ... Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

Consider a nucleus with charge  $+Ze$  and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant  $k$  in Coulomb's law. This constant is more commonly represented in the form

$$k = \frac{1}{4\pi\epsilon_0}$$

where  $\epsilon_0$  is known as the *permittivity of free space*, which has the numerical value  $\epsilon_0 = 8.8541878 \times 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$ . The energy of the electron (the nucleus is assumed to be fixed in space at the origin):

$$E = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The force on the electron is

$$F = -\frac{Ze^2}{4\pi\epsilon_0 r^3}r$$

and its magnitude is

$$F = |F| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

since  $F = m_e a$ , the magnitude, it follows that  $|F| = m_e |a|$ . If we assume that the orbit is circular (which is an approximation because the orbit is really elliptical), then the acceleration is purely centripetal, so

$$|a| = \frac{v^2}{r}$$

where  $v$  is the velocity of the electron. Equating force  $|F|$  to  $m_e |a|$ , we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e \frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2$$

The reason for writing the equation this way is that the quantity  $m_e v r$  is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus. He circumvented this problem by following Planck's idea and positing that the orbital angular momentum  $m_e v r$  could only take on specific values

$$m_e v r = n\hbar ; n = 1, 2, 3, \dots$$

Note that the electron must be in motion, so  $n = 0$  is not allowed.

Substituting this into the Newton's law expression above, we find

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2 (\hbar)^2$$

This expression implies that the orbits Bohr was imagining could only have certain allowed radii given by

$$\begin{aligned} r_n &= \frac{4\pi\epsilon_0 (\hbar)^2}{Ze^2 m_e} n^2 ; n = 1, 2, 3, \dots \\ &= \frac{a_0}{Z} n^2 \end{aligned}$$

where the collection of constants has been defined to be  $a_0$

$$a_0 = \frac{4\pi\epsilon_0 (\hbar)^2}{e^2 m_e}$$

a quantity that is known as the *Bohr radius*.

We can also calculate the allowed momenta since  $m_e v r = n\hbar$ , and  $p = m_e v$ . Thus,

$$p_n r_n = n\hbar$$

$$p_n = \frac{n\hbar}{r_n}$$

$$p_n = \frac{\hbar Z}{a_0 n} = \frac{Ze^2 m_e}{4\pi\epsilon_0 \hbar n}$$

From  $p_n$  and  $r_n$ , we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

Substituting in the expressions for  $p_n$  and  $r_n$  and simplifying gives

$$E_n = -\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{Z^2 e^4 m_e}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2}$$

The constant

$$\frac{e^4 m_e}{8\epsilon_0^2 \hbar^2}$$

is an energy having the value  $2.18 \times 10^{-18} \text{ J}$ . since this is a small unit, we redefine a new energy scale by defining the Rydberg as  $1 \text{ Ry} = 2.18 \times 10^{-18} \text{ J}$ . Thus, the allowed energies predicted by the Bohr model are

$$E_n = -(2.18 \times 10^{-18}) \frac{Z^2}{n^2} \text{ J} = -\frac{Z^2}{n^2} \text{ Ry}$$

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis of this problem. The energies predicted by the Bohr model are plotted in the figure below. The diagram on the right is called an *energy level diagram*.

Figure 12: Energy levels predicted by the Bohr model

\includegraphics[scale=0.3]{bohr\_energies.eps} \includegraphics[scale=0.3]{hlevels.eps}

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences.

In the final section of these notes, we discuss the Beer-Lambert law, and we will have more to say about spectroscopy later in the course. For now, let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state  $E_n$  for  $n > 1$ , i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved. Thus, if  $n_i$  is the integer that characterizes the initial (excited) state of the electron, and  $n_f$  is the final state (here we imagine that  $n_f = 1$ , but as long as  $n_f < n_i$  of the emitted light satisfies

$$E_{n_f} = E_{n_i} - h\nu$$

or

$$\nu = \frac{E_{n_f} - E_{n_i}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 \hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

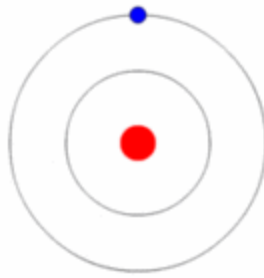


Figure used with permission from Wikipedia

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels. This is known as *emission spectroscopy*. Different values of  $n_f$  determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them. The figure below shows some of the transitions possible for different  $n_f$  and  $n_i$  values.

Figure 13: Allowed electronic transitions in an emission process

`\includegraphics[scale=0.5]{bohr_energies2.eps}`

If, on the other hand, the atom absorbs light, and ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final energy  $E_{nf}$  will be related to the initial energy  $E_{ni}$  with  $n_f > n_i$  by

$$E_{nf} = E_{ni} + h\nu$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8 \epsilon_0^2 h^3} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

## Measuring spectra: The Beer-Lambert law

The figure below shows the experimental setup for taking a spectrum:

Figure: Schematic of the experimental setup needed to record a spectrum.

`\includegraphics[scale=0.7]{Spectrum_exp_setup.eps}`

Radiation from a source is passed through a monochromator, which filters out all frequency components except one, generating *monochromatic* radiation of a single frequency  $\nu$ . The beam is then split into two by a beam-splitter. One of the two rays is allowed to pass through a cell containing the sample whose spectrum is sought. The other is allowed to pass through a reference cell, which is just the cell without the sample. We'll come back to the role of the reference cell later. Let  $I_0$  be the intensity of radiation entering the sample, and  $I_S$  be the intensity of radiation emerging from the sample. The output beam with intensity  $I_S$  is then sent to a photodetector that measures the actual intensity, the photosignal is then amplified and sent to a recording device, where a final readout of the intensity at frequency  $\nu$  is noted.

Let us first analyze what happens as the beam is sent through the sample. Let the direction of propagation of the radiation through the sample be the  $x$  direction and let the sample extend from  $x = 0$  to  $x = l$  on the  $x$  axis. Thus,  $I_0$  is the intensity at  $x = 0$ . We wish to determine the intensity  $I(x)$  as the beam passes through the sample. As it does, there will be an attenuation of intensity due to absorption events. Remember that the beam contains many many photons, and the sample contains many

molecules, so we are interested in a measure of the number of photons absorbed vs. the number of photons that pass through without being absorbed. This will give us a measure of the attenuation in the intensity, since intensity is directly proportional to the number of photons passing through a given area of the sample at any instant in time.

We expect the following. If  $I(x)$  is the intensity at point  $x$  in the sample, then the fractional loss of intensity  $-dI/I(x)$  when the beam passes through a length  $dx$  of the sample will be proportional to the concentration of the sample  $C$  as well as  $dx$ :

$$-\frac{dI}{I(x)} \propto C dx$$

The constant of proportionality is denoted  $\varepsilon'$  and is called the molar extinction coefficient:

$$-\frac{dI}{I(x)} = C\varepsilon' dx$$

(The reason for the prime will be clarified below.) The units of the molar extinction coefficient are  $L \cdot \text{mol}^{-1} \cdot \text{m}^{-1}$ . Rearranging this as a simple first-order differential equation gives

$$\frac{dI}{dx} = -C\varepsilon' I(x)$$

The solution gives us the intensity  $I(x)$  as a function of  $x$  through the sample:

$$I(x) = I(x=0)e^{-C\varepsilon'x} = I_0e^{-C\varepsilon'x}$$

Or taking the log of both sides

$$\ln\left(\frac{I(x)}{I_0}\right) = -C\varepsilon'x$$

When  $x = l$ ,  $I(x) = I_S$ , so we can write this as

$$\ln\left(\frac{I_S}{I_0}\right) = -C\varepsilon'l$$

or

$$\ln\left(\frac{I_0}{I_S}\right) = C\varepsilon'l$$

The common form of the Beer-Lambert law uses base 10 logarithms rather than natural logarithms and redefines the extinction coefficient as  $\varepsilon = \varepsilon'/2.303$ , which gives

$$\log_{10}\left(\frac{I_0}{I_S}\right) = C\varepsilon l$$

The attenuation of the beam through the sample will be due to only in part to the actual material whose spectrum is sought. There is another contribution to the cell, itself, and whatever material it is composed of. This is where the reference beam comes in. By observing the attenuation of the beam through the reference cell, we can determine how much of the attenuation is due to the cell alone. Thus, we are not interested in the ratio  $I_S/I_0$  as much as the ratio  $I_S/I_R$ , where  $I_R$  is the beam that emerges from the reference cell, partly attenuated. For the ratio  $I_S/I_R$ , we assign the molar extinction  $\varepsilon$  and write

$$\log_{10}\left(\frac{I_R}{I_S}\right) = C\varepsilon l$$

The quantity  $\log_{10}(I_R/I_S)$  is called the *absorbance*  $A$  (the quantity  $\log_{10}(I_S/I_R)$  is called the *transmittance*  $T$ ). Thus, we have finally

$$A = C\varepsilon l$$

This result is known as the *Beer-Lambert law*, and it is one of the fundamental principles of molecular spectroscopy. The extinction coefficient  $\varepsilon$  measures the extent to which the sample is able to absorb radiation at a given frequency  $\nu$  or wavelength  $\lambda$  (remember we can use either since  $\nu = c/\lambda$ ). Hence, it is an intrinsic property of the material. We will revisit the Beer-Lambert law when we cover spectroscopy in greater detail toward the end of the semester.

## Contributors and Attributions

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## 7: The Schrödinger equation- Predicting energy levels and the particle-in-a-box model

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## 8: Particles in Two-Dimensional Boxes

A quantum particle of mass  $m$  in a two-dimensional square box by a potential energy  $V(x, y)$  that is zero if  $x \in [0, L]$  and  $y \in [0, L]$  and infinite otherwise. Inside the box, the energy is entirely kinetic because  $V(x, y) = 0$ , so the classical energy is

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} = E$$

where  $p_x$  and  $p_y$  are the two components of the particle's momentum. We see that the energy naturally is expressible as a sum of kinetic energies associated with motion in the  $x$  and  $y$  directions:

$$E = \varepsilon_x + \varepsilon_y$$

Because the energy is a simple sum, the solutions of the Schrödinger equation can be expressed as simple products of the solutions of the one-dimensional [Schrödinger equation](#) for this problem. Note that it is *only* when the energy is expressible in this way that simple product solutions are rigorously correct. Thus, the wavefunction  $\psi(x, y)$  is of the form

$$\psi(x, y) = A \sin \left( \sqrt{\frac{2m\varepsilon_x}{\hbar^2}} x \right) \sin \left( \sqrt{\frac{2m\varepsilon_y}{\hbar^2}} y \right)$$

which satisfies the boundary conditions at  $x = 0$  and  $y = 0$ , namely  $\psi(0, y) = 0$  and  $\psi(x, 0) = 0$ . In order to satisfy the remaining boundary conditions  $\psi(L, y) = 0$  and  $\psi(x, L) = 0$ , we have two conditions:

$$A \sin \left( \sqrt{\frac{2m\varepsilon_x}{\hbar^2}} L \right) \sin \left( \sqrt{\frac{2m\varepsilon_y}{\hbar^2}} y \right) = 0 \quad (8.1)$$

and

$$A \sin \left( \sqrt{\frac{2m\varepsilon_x}{\hbar^2}} x \right) \sin \left( \sqrt{\frac{2m\varepsilon_y}{\hbar^2}} L \right) = 0 \quad (8.2)$$

Equation 8.1 can be satisfied if

$$\sin \left( \sqrt{\frac{2m\varepsilon_x}{\hbar^2}} L \right) = 0$$

independent of  $y$ , while Equation 8.2 can be satisfied if

$$\sin \left( \sqrt{\frac{2m\varepsilon_y}{\hbar^2}} L \right) = 0$$

independent of  $x$ . These are the same conditions that we encountered for the one-dimensional box, hence we already know the  $\sin$  function in each case can be zero in many places. In fact, these two conditions are satisfied if

$$\sqrt{\frac{2m\varepsilon_x}{\hbar^2}} L = n_x \pi$$

and

$$\sqrt{\frac{2m\varepsilon_y}{\hbar^2}} L = n_y$$

which yield the allowed values of  $\varepsilon_x$  and  $\varepsilon_y$  as

$$\varepsilon_{n_x} = \frac{\hbar^2 \pi^2}{2mL^2} n_x^2 \quad \varepsilon_{n_y} = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2$$

We need two different integers  $n_x$  and  $n_y$  because the conditions are completely independent and can be satisfied by any two different (or similar) values of these integers. The allowed values of the total energy are now given by

$$E_{n_x n_y} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2)$$

Note that the allowed energies now depend on two integers  $n_x$  and  $n_y$  rather than one. These arise from the *two* independent boundary conditions in the  $x$  and  $y$  directions. As in the one-dimensional box, the values of  $n_x$  and  $n_y$  are both restricted to the natural numbers 1, 2, 3, ... Note, therefore, that the ground state energy  $E_{11}$  is

$$E_{11} = \frac{\hbar^2 \pi^2}{mL^2}$$

is larger than for the one-dimensional box because of the contributions from kinetic energy in the  $x$  and  $y$  directions.

Once the conditions on  $\varepsilon_{n_x}$  and  $\varepsilon_{n_y}$  are substituted in, the wavefunctions become

$$\psi_{n_x n_y}(x, y) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right)$$

The constant  $A$  is now determined by the normalization condition

$$\begin{aligned} \int_0^L \int_0^L |\psi_{n_x n_y}(x, y)|^2 dx dy &= 1 \\ A^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy &= 1 \\ A^2 \frac{L}{2} \cdot \frac{L}{2} &= 1 \\ A &= \frac{2}{L} \end{aligned}$$

so that

$$\psi_{n_x n_y}(x, y) = \frac{2}{L} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right)$$

The wavefunctions are somewhat more difficult to visualize because of they are two dimensional. Nevertheless, we can still visualize them, and the figure below shows the following wavefunctions:  $\psi_{11}(x, y)$ ,  $\psi_{21}(x, y)$  and  $\psi_{22}(x, y)$ .

Figure: First few wavefunctions for a particle in a two-dimensional square box

`\includegraphics[scale=0.7]{twoD_box.eps}`

Note that the figure makes use of what we call *dimensionless* coordinates  $\bar{x}$  and  $\bar{y}$ , which are defined to be the coordinates of a particle in a *unit box*, i.e. a box with  $L = 1$ . Thus, the dimensionless coordinates are defined by

$$\bar{x} = \frac{x}{L} \quad \bar{y} = \frac{y}{L}$$

It is important to note that the wavefunctions can be either positive or negative, even though the associated probability density  $p_{n_x n_y}(x, y) = |\psi_{n_x n_y}(x, y)|^2$  is strictly positive. In the figure, the red part of the function is positive, and the blue part is negative. Unlike in the one-dimensional case, where nodes in the wavefunction are points where  $\psi_n(x) = 0$ , here entire lines can be nodal. These are called *nodal lines*. For example, in the state  $\psi_{21}(x, y)$ , there is a nodal line at  $\psi_{21}(L/2, y)$ . Along the entire line  $x = L/2$ , the wavefunction is 0 independent of the value of  $y$ . The wavefunction  $\psi_{22}(x, y)$  has two nodal lines when  $x = L/2$  and when  $y = L/2$ . The sign of the wavefunction and its nodal structure will play central roles later when we consider chemical bonding.

Note that if the box were rectangular rather than square, then instead of having a length of  $L$  on both sides, there would be two different lengths  $L_x$  and  $L_y$ . The formulas for the energies and wavefunctions become only slightly more complicated:

$$E_{n_x n_y} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$\psi_{n_x n_y}(x, y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right)$$

The definition of the dimensionless variables is also altered slightly

$$\bar{x} = \frac{x}{L_x} \quad \bar{y} = \frac{y}{L_y}$$

The fact that the wavefunction  $\psi_{n_x n_y}(x, y)$  is a product of one-dimensional wavefunctions:

$$\psi_{n_x n_y}(x, y) = \psi_{n_x}(x) \psi_{n_y}(y)$$

makes the calculation of probabilities rather easy. The probability that a measurement the particle's position will yield a value of  $x \in [a, b]$  and  $y \in [c, d]$  is

$$\begin{aligned} P(x \in [a, b] \text{ and } y \in [c, d]) &= \int_a^b dx \int_c^d dy |\psi_{n_x n_y}(x, y)|^2 \\ &= \int_a^b dx \int_c^d dy \psi_{n_x}^2(x) \psi_{n_y}^2(y) \\ &= \left[ \int_a^b \psi_{n_x}^2(x) dx \right] \left[ \int_c^d \psi_{n_y}^2(y) dy \right] \end{aligned}$$

### Example 8.1

For a particle in a two-dimensional box, if the particle is in the state  $\psi_{12}(x, y)$ , what is the probability that a measurement of the particle's position will yield  $x \in [0, L/2]$  and  $y \in [0, L/2]$ ?

#### Solution

Substituting into the above formula, we have

$$\begin{aligned} P(x \in [0, L/2] \text{ and } y \in [0, L/2]) &= \left[ \int_0^{L/2} \psi_1^2(x) dx \right] \left[ \int_0^{L/2} \psi_2^2(y) dy \right] \\ &= \left[ \frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx \right] \left[ \frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{2\pi y}{L}\right) dy \right] \\ &= \left[ \frac{2}{L} \frac{L}{4} \right] \left[ \frac{2}{L} \frac{L}{4} \right] \\ &= \frac{1}{4} \end{aligned}$$

## Contributors and Attributions

- Mark Tuckerman (New York University)

## 9: Particles in Three-Dimensional Boxes

Generalization of the results for a two-dimensional square box to a three-dimensional cubic box is straightforward. Since we live in a three-dimensional world, this generalization is an important one, and we need to be able to think about energy levels and wavefunctions in three dimensions. The potential energy  $V(x, y, z)$  for the cubic box is defined to be 0 if  $x \in [0, L]$ ,  $y \in [0, L]$  and  $z \in [0, L]$  and infinite otherwise. This means that the wavefunction  $\psi(x, y, z)$  must satisfy six boundary conditions  $\psi(0, y, z) = 0$ ,  $\psi(x, 0, z) = 0$ ,  $\psi(x, y, 0) = 0$ ,  $\psi(L, y, z) = 0$ ,  $\psi(x, L, z) = 0$  and  $\psi(x, y, L) = 0$ .

We first note that the classical energy is the sum of three terms

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} = E$$

where  $p_x$ ,  $p_y$  and  $p_z$  are the three components of the particle's momentum vector  $p$ . Thus, we can write the energy as

$$E = \varepsilon_x + \varepsilon_y + \varepsilon_z$$

corresponding to the kinetic energy in the  $x$ ,  $y$  and  $z$  directions. Because the energy is a simple sum of energies for the  $x$ ,  $y$  and  $z$  directions, the wavefunction will be a product of wavefunction forms for the one-dimensional box, and in order to satisfy the first three of the boundary conditions, we can take the  $\sin$  functions:

$$\psi(x, y, z) = A \sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right) \sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right) \sin\left(\sqrt{\frac{2m\varepsilon_z}{\hbar^2}}z\right)$$

As in the two-dimensional case, applying second three boundary conditions yields the allowed values of  $\varepsilon_x$ ,  $\varepsilon_y$  and  $\varepsilon_z$ , which now require three integers  $n_x$ ,  $n_y$  and  $n_z$ :

$$\varepsilon_{n_x} = \frac{\hbar^2 \pi^2}{2mL^2} n_x^2 \quad \varepsilon_{n_y} = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2 \quad \varepsilon_{n_z} = \frac{\hbar^2 \pi^2}{2mL^2} n_z^2$$

so that the allowed values of the total energy are

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

and the wavefunctions become

$$\psi_{n_x n_y n_z}(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

The constant  $A$  is determined from the normalization condition

$$\begin{aligned} \int_0^L \int_0^L \int_0^L |\psi_{n_x n_y n_z}(x, y, z)|^2 dx dy dz &= 1 \\ A^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy \int_0^L \sin^2\left(\frac{n_z \pi z}{L}\right) dz &= 1 \\ A^2 \frac{L}{2} \cdot \frac{L}{2} \cdot \frac{L}{2} &= 1 \\ A &= \left(\frac{2}{L}\right)^{3/2} \end{aligned}$$

Thus, the wavefunctions are

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

As with the two-dimensional box, the three integers  $n_x$ ,  $n_y$  and  $n_z$  are restricted to the natural numbers 1, 2, 3, ... Thus, the lowest energy or ground-state energy is

$$E_{111} = \frac{3(\hbar)^2 \pi^2}{2mL^2}$$

Visualizing the wavefunctions is tricky because of their high dimensionality. The most common method of visualizing functions of three variables is the use of an *isosurface*. An isosurface of a function  $f(x, y, z)$  is the complete set of points  $x, y$ , and  $z$  for which  $f(x, y, z) = C$ , where  $C$  is a chosen constant. Hence the name *isosurface* - the value of the function  $f(x, y, z)$  is the same at all points on the surface.

For wavefunctions, where the sign can be positive or negative, it is useful to base the value of  $C$  not on the wavefunction value but rather on the probability density  $p_{n_x n_y n_z}(x, y, z) = |\psi_{n_x n_y n_z}(x, y, z)|^2$ . The figure below shows two isosurfaces of the wavefunction  $\psi_{123}(x, y, z)$ . The first occurs at a probability density value of 0.64 and the other occurs at 0.04. These value then imply that the wavefunction can have a fixed positive or negative value along the surface. In one case,  $\psi_{123}(x, y, z) = \pm 0.8$ , while in the other,  $\psi_{123}(x, y, z) = \pm 0.2$ .

*Figure: Isosurfaces of  $\psi_{123}(x, y, z)$  at probability density values of 0.64 and 0.04. Red is positive and blue is negative.*

\includegraphics[scale=0.7]{threeD\_box.eps}

As in the two-dimensional case, the fact that the wavefunction  $\psi_{n_x n_y n_z}(x, y, z)$  is a product

$$\psi_{n_x n_y n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

means that the probabilities can be calculated from products of one-dimensional integrals. The probability that a measurement of a particle's position yields a value  $x \in [a, b]$ ,  $y \in [c, d]$  and  $z \in [f, g]$  is

$$\begin{aligned} P(x \in [a, b] \text{ and } y \in [c, d] \text{ and } z \in [f, g]) &= \int_a^b dx \int_c^d dy \int_f^g dz |\psi_{n_x n_y n_z}(x, y, z)|^2 \\ &= \left[ \int_a^b \psi_{n_x}^2(x) dx \right] \left[ \int_c^d \psi_{n_y}^2(y) dy \right] \left[ \int_f^g \psi_{n_z}^2(z) dz \right] \end{aligned}$$

## Contributors and Attributions

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## 10: Two Identical Particles in a Box

Let us return briefly to the particle in a box model and ask what happens if we put two identical particles in the box. If they were classical particles, they would carry an imaginary "label" that would allow us to tell the particles apart. In quantum mechanics, this is no longer possible because all we can predict is the probability that one of the particles is in a region  $dx_1$  about the point  $x_1$  and the other is in a region  $dx_2$  about the point  $x_2$ , but we cannot tell which particle is where. This fact will affect both the allowed energies and the wavefunctions.

The classical energy inside the box is, in this case

$$\frac{p_1^2}{2m} + \frac{p_2^2}{2m} = E$$

where  $p_1$  is the momentum of particle 1, and  $p_2$  is the momentum of particle 2. Because the energy is a sum of independent energies for particles 1 and 2, the energies can also be separated

$$E = \varepsilon_1 + \varepsilon_2$$

The wavefunction will depend on the positions  $x_1$  and  $x_2$ ,  $\psi(x_1, x_2)$ , and therefore, we have four boundary conditions  $\psi(0, x_2) = 0$ ,  $\psi(x_1, 0) = 0$ ,  $\psi(L, x_2) = 0$  and  $\psi(x_1, L) = 0$ . These give rise to the allowed values of  $\varepsilon_1$  and  $\varepsilon_2$  in the usual way:

$$\varepsilon_{n_1} = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2 \quad \varepsilon_{n_2} = \frac{\hbar^2 \pi^2}{2mL^2} n_2^2$$

so that the allowed values of the total energy are

$$E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2)$$

Here each particle gets an independent integer for enumerating the energy levels  $n_1$  and  $n_2$ .

Just as we did for a single particle in a two-dimensional box, we might expect the wavefunctions to be a simple product

$$\Psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1) \psi_{n_2}(x_2)$$

where  $\psi_n(x)$  is just the usual wavefunction for the particle in a box

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

However, we immediately run into two problems. First, if the particles are truly identical, how do we know whether to assign the energy level  $n_1$  to particle 1 or 2? We could do either, assigning  $n_2$  to the other, and the total energy would not change. However, the simple product wavefunction above specifies a definite assignment of  $n_1$  to particle 1 and  $n_2$  to particle 2! The second problem is that the simple product form says that there are points at which  $\Psi_{n_1 n_2}(x, x) \neq 0$ , implying that there is a nonzero probability of finding the two particles at exactly the same point in space, i.e. sitting right on top of each other!

In order to handle the first problem, we simply include two possible product forms, i.e.

$$\psi_{n_1}(x_1) \psi_{n_2}(x_2) \quad \psi_{n_2}(x_1) \psi_{n_1}(x_2)$$

and put them together to form  $\Psi_{n_1 n_2}(x_1, x_2)$ , which we can do in two ways:

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_{n_1}(x_1) \psi_{n_2}(x_2) \pm \psi_{n_2}(x_1) \psi_{n_1}(x_2)]$$

The  $1/\sqrt{2}$  is needed for proper normalization. But which combination should we take? If we take the first one:

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_{n_1}(x_1) \psi_{n_2}(x_2) + \psi_{n_2}(x_1) \psi_{n_1}(x_2)]$$

then we have not circumvented the second problem. It will still be possible for the two particles to sit at the same point in space. In fact, there are certain exotic particles in quantum mechanics that can do this (they are called *bosons*), and this possibility is what is responsible for curious phenomena such as superfluidity and superconductivity. However, the more mundane objects we care about, such as protons and electrons, cannot sit on top of each other. Thus, for these particles, we need to take the second form

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_2}(x_1)\psi_{n_1}(x_2)]$$

This form implies two things. Note first that

$$\Psi_{n_1 n_2}(x, x) = 0$$

which means that for any  $n_1$  and  $n_2$ , there is zero probability to find both particles in small regions near the same point. The other thing we see is that

$$\Psi_{nn}(x_1, x_2) = 0$$

which implies that the two particles cannot be in the same energy level. That this possibility is excluded is known as the *Pauli exclusion principle*, and it plays a key role in both the electronic configurations of atoms and molecules.

### Example 10.2:

Two particles of mass  $m$  are in a one-dimensional box of length  $L$ . What is the lowest total energy the two particle- system can have?

#### Solution

Since  $n_1 = 1, 2, 3, \dots$  and  $n_2 = 1, 2, 3, \dots$ , if we choose  $n_1 = 1$ , then, since  $n_2$  cannot be equal to  $n_1$ , the next lowest value we can choose is  $n_2 = 2$ . Thus, the lowest energy is

$$E_{12} = \frac{\hbar^2 \pi^2}{2mL^2} (1^2 + 2^2) = \frac{5\hbar^2 \pi^2}{2mL^2}$$

Notice that the calculation of probabilities changes a little because of the increased complexity of the wavefunction. Let us consider the probability that a simultaneous measurement of the position of particle 1 and of particle yields values of  $x_1$  and  $x_2$ ,  $x_1 \in [a, b]$ ,  $x_2 \in [c, d]$ . For electrons, this is given by

$$\begin{aligned} P(x_1 \in [a, b] \text{ and } x_2 \in [c, d]) &= \int_a^b dx_1 \int_c^d dx_2 |\Psi_{n_1 n_2}(x_1, x_2)|^2 \\ &= \frac{1}{2} \int_a^b dx_1 \int_c^d dx_2 [\psi_{n_1}^2(x_1)\psi_{n_2}^2(x_2) - 2\psi_{n_1}(x_1)\psi_{n_2}(x_1)\psi_{n_2}(x_2)\psi_{n_1}(x_2) + \psi_{n_2}^2(x_1)\psi_{n_1}^2(x_2)] \\ &= \frac{1}{2} \left[ \int_a^b \psi_{n_1}^2(x_1) dx_1 \right] \left[ \int_c^d \psi_{n_2}^2(x_2) dx_2 \right] \\ &\quad - \left[ \int_a^b \psi_{n_1}(x_1)\psi_{n_2}(x_1) dx_1 \right] \left[ \int_c^d \psi_{n_2}(x_2)\psi_{n_1}(x_2) dx_2 \right] \\ &\quad + \frac{1}{2} \left[ \int_a^b \psi_{n_2}^2(x_1) dx_1 \right] \left[ \int_c^d \psi_{n_1}^2(x_2) dx_2 \right] \end{aligned}$$

## Contributors and Attributions

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# 11: The Quantum Hydrogen Atom

Now that we have introduced the basic concepts of quantum mechanics, we can start to apply these concepts to build up matter, starting from its most elementary constituents, namely atoms, up to molecules, supramolecular complexes (complexes built from weak interactions such as hydrogen bonds and van der Waals interactions), networks, and bulk condensed phases, including liquids, glasses, solids,... As explore the structure of matter, itself, we should stand back and wonder at how the mathematically elegant, yet somehow not quite tangible, structure of quantum theory is able to describe so accurately all phases of matter and types of substances, ranging from metallic and semiconducting crystals to biological macromolecules, to morphologically complex polymeric materials.

We begin with the simplest system, the hydrogen atom (and hydrogen-like single-electron cations), which is the *only* atomic system (thus far) for which the Schrödinger equation can be solved exactly for the energy levels and wave functions. To this end, we consider a nucleus of charge  $+Ze$  at the origin and a single electron a distance  $r$  away from it. If we just naïvely start by writing the (total) classical energy

$$\underbrace{\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}}_{\text{Kinetic Energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}}_{\text{Potential Energy}} = E \quad (11.1)$$

where the constant  $k$  in Coulomb's Law has been rewritten as  $1/4\pi\epsilon_0$ , where  $\epsilon_0$  is the permittivity of free space, and where we have written  $r = \sqrt{x^2 + y^2 + z^2}$  in terms of its Cartesian components, then we see immediately that the energy is not a simple sum of terms involving  $(x, p_x)$ ,  $(y, p_y)$ , and  $(z, p_z)$ , and therefore, the wave function is not a simple product of a function of  $x$ , a function of  $y$  and a function of  $z$ . Thus, it would seem that we have already hit a mathematical wall. Fortunately, we are not confined to work in Cartesian coordinates. In fact, there are numerous ways to locate a point  $r$  in space, and for this problem, there is a coordinate system, known as *spherical coordinates*, that is particularly convenient because it uses the distance  $r$  of a point from the origin as one of its explicit coordinates.

## Spherical Coordinates

In Cartesian coordinates, a point in a three-dimensional space requires three numbers to locate it  $r = (x, y, z)$ . Thus, if we change to a different coordinate system, we still need three numbers to full locate the point. Figure 11.1 shows how to locate a point in the system of spherical coordinates:

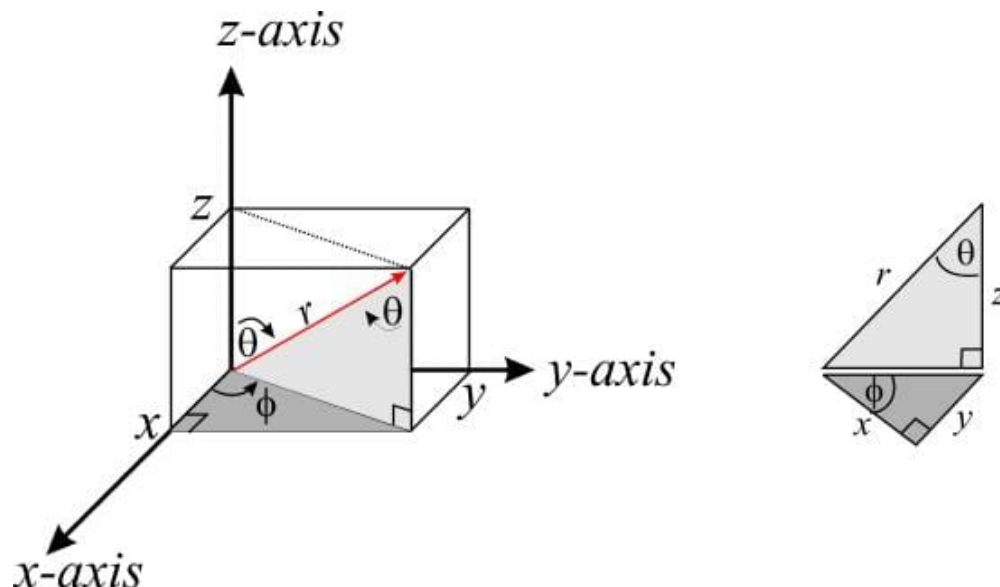


Figure 11.1: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

Thus, we use the distance  $r$  of the point from the origin, which is also the magnitude of the vector  $r$ , the angle  $\theta$  the vector  $r$  makes

with the positive  $z$ -axis, and the angle  $\phi$  between the projection of the vector  $r$  into the  $xy$  plane and the positive  $x$ -axis. The angle  $\theta$  is called the *polar angle* and the angle  $\phi$  is called the *azimuthal angle*. These three variables have the following ranges

$$r \in [0, \infty) \quad \theta \in [0, \pi] \quad \phi \in [0, 2\pi] \quad (11.2)$$

To map a point from the Cartesian representation  $r = (x, y, z)$  to spherical coordinates  $(r, \theta, \phi)$ , a coordinate transformation is needed tells us how points in the two coordinate representations are connected. To determine  $x$  and  $y$ , we need the component of  $r$  in the  $xy$  plane, which is  $r \sin \theta$ , and its projection into the  $x$  and  $y$  directions, which are

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \end{aligned}$$

Finally, to determine  $z$ , we simply need the component of  $r$  along the  $z$ -axis, which is  $r \cos \theta$ , so

$$z = r \cos \theta \quad (11.3)$$

These three relations tell us how to map the point  $(r, \theta, \phi)$  into the original Cartesian frame  $(x, y, z)$ . The inverse of this transformation tells us how to map the Cartesian numbers  $(x, y, z)$  back into spherical coordinates. It is simple algebra to show that the inverse is

$$\begin{aligned} r &= \sqrt{x^2 + y^2 + z^2} \\ \phi &= \tan^{-1} \frac{y}{x} \\ \theta &= \tan^{-1} \frac{\sqrt{x^2 + y^2}}{z} \end{aligned}$$

#### A note about vectors

Consider a two-dimensional vector  $v$  in the  $xy$  plane. The vector can be represented in terms of its two components  $v = (v_x, v_y)$ . That is, just two numbers  $v_x$  and  $v_y$  are needed, and we know everything about the vector. However, if we know the angle  $\theta$  that  $v$  makes with the  $x$ -axis, then we can also use the magnitude  $v = |v|$  and the angle as two alternative numbers that can be used to represent the vector. In this case, since  $v_x = v \cos \theta = |v| \cos \theta$  and  $v_y = v \sin \theta = |v| \sin \theta$ , then  $v$  is specified as  $v = (v \cos \theta, v \sin \theta)$ . There is still another alternative scheme for representing  $v$ . We can use the magnitude  $v = |v|$  and just one of the components of  $v$ . Suppose we wish to represent  $v$  in terms of  $v$  and  $v_x$ . since  $v = v_x^2 + v_y^2$ , the other component  $v_y$  is given by  $v_y^2 = v^2 - v_x^2$ , then  $v_y = \sqrt{v^2 - v_x^2}$ , we can write  $v = (v_x, \sqrt{v^2 - v_x^2})$ , which means we only need to know the magnitude  $v$  and one of the components to specify  $v$  entirely. This is the scheme that will be used below to represent the angular momentum, as discussed in the next section.

## Angular momentum

In spherical coordinates, the momentum  $p$  of the electron has a radial component  $p_r$ , corresponding to motion radially outward from the origin, and an angular component  $L$ , corresponding to motion along the surface of a sphere of radius  $r$ , i.e. motion perpendicular to the radial direction:

$$p = \left( p_r, \frac{L}{r} \right) \quad (11.4)$$

Note that  $L$  is, itself, still a vector, since motion along the surface of a sphere still has more than one component. Its components include motion along the  $\theta$  and along the  $\phi$  directions.

Let us step back briefly into Cartesian components to look at the angular momentum vector  $L$ . Its definition is

$$L = r \times p \quad (11.5)$$

i.e. the **vector cross product** of  $r$  and  $p$ , which is why  $L$  is perpendicular to  $r$ . In Cartesian components,  $L$  actually has three components, which are given by

$$\begin{aligned}L_x &= yp_z - zp_y \\L_y &= zp_x - xp_z \\L_z &= xp_y - yp_x\end{aligned}$$

using the definition of the cross product.

The important thing about angular momentum is that if the potential energy  $V$  depends only on  $r$ , then angular momentum is conserved. For example, suppose  $V(r)$  is the Coulomb potential, which we will write compactly as

$$V(r) = -\frac{k}{r} \quad (11.6)$$

where  $k = e^2/(4\pi\epsilon_0)$ . We will show that angular momentum is conserved within the classical mechanical description of the system. If it is true classically, it is also true in quantum mechanics.

The force on the classical electron is

$$F = -\frac{k}{r^3} r \quad (11.7)$$

Therefore, the three force components are

$$F_x = -\frac{kx}{r^3} \quad F_y = -\frac{ky}{r^3} \quad F_z = -\frac{kz}{r^3} \quad (11.8)$$

From Newton's second law:

$$F = ma = m \frac{dv}{dt} = \frac{d(mv)}{dt} = \frac{dp}{dt} \quad (11.9)$$

Now consider one of the components of the angular momentum vector, e.g.  $L_z$ . Its time derivative is

$$\begin{aligned}\frac{dL_z}{dt} &= \frac{dx}{dt} p_y + x \frac{dp_y}{dt} - \frac{dy}{dt} p_x - y \frac{dp_x}{dt} \\&= \frac{p_x}{m} p_y + x F_y - \frac{p_y}{m} p_x - y F_x \\&= \frac{p_x p_y}{m} - \frac{kxy}{r^3} - \frac{p_y p_x}{m} + \frac{kyx}{r^3} \\&= 0\end{aligned}$$

The same can be shown about  $L_x$  and  $L_y$ . Moreover, since  $L^2 = L_x^2 + L_y^2 + L_z^2$ , and the three components  $L_x$ ,  $L_y$  and  $L_z$  are all constant,  $L^2$  is constant as well.

Thus, both the energy and the angular momentum are conserved in classical mechanics, but classically, both quantities can take on any values. In quantum mechanics, the energy can have only certain allowed values, and because angular momentum is conserved, it too can only have certain allowed values, as Bohr predicted in his model of the hydrogen atom. The allowed energies are

$$E_n = -\frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^2} \frac{1}{n^2} \quad (11.10)$$

where  $n = 1, 2, 3, \dots$

What about angular momentum? In spherical coordinates, the momentum is  $p = (p_r, L/r)$ , and  $L$  only has two components, one along  $\theta$  and one along  $\phi$ . We can assign allowed values to these components separately, however, there is a compelling reason to do things a little differently. In spherical coordinates, the classical energy is given by

$$\frac{p_r^2}{2m_e} + \frac{L^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} = E \quad (11.11)$$

Thus,  $E$  separates into a purely radial part and an angular part:

$$E = \varepsilon_r + \frac{L^2}{2m_e r^2}$$

Note that the energy depends on  $L^2$ . since  $L^2$  and each of the three components  $L_x$ ,  $L_y$  and  $L_z$  are conserved, we can use the representation of  $L$  in which we choose the magnitude  $L$  and one of the components. Why just one component? Note that even though  $L$  has three Cartesian components, it really is only a two dimensional vector since it describes the motion on a two-dimensional surface. Just like the  $xy$  plane is a two-dimensional surface, the surface of a sphere is also two-dimensional, using the angles  $\theta$  and  $\phi$  to locate points on the surface.

The difference is that the surface of a sphere is not flat but curved, so we have to embed it in three-dimensional space. So as a Cartesian representation, three components are needed, but in spherical coordinates, we only need two, i.e. two numbers to represent  $L$ . Thus, we can use the magnitude  $L$  and one of its components, which by convention is taken to be the  $z$ -component  $L_z$ .  $L_z$  describes motion in the  $xy$  plane, i.e. motion in the azimuthal ( $\phi$ ) direction only. However, this is just motion on a ring, so one part of the wave function will just be the particle-on-a-ring wave functions

$$\frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (11.12)$$

where  $m = 0, \pm 1, \pm 2, \dots$ , and so the allowed values of  $L_z$  are  $m\hbar$ .

For  $L^2$ , it turns out that the allowed values are

$$L^2 \rightarrow l(l+1)\hbar^2 \quad (11.13)$$

where  $l$  is an integer that has the range  $l = 0, 1, 2, \dots, n-1$  in a given energy level characterized by  $n$ . Moreover, because  $L_z \leq |L|$ , once the value of  $l$  is specified,  $m$  cannot exceed  $l$ , so the range of  $m$  is  $m = -l, -l+1, \dots, l-1, l$ .

## Schrödinger Equation for the Hydrogen atom and hydrogen-like Cations

The Schrödinger equation for single-electron Coulomb systems in spherical coordinates is

$$-\frac{\hbar^2}{2m_e r^2} \left[ r \frac{\partial^2}{\partial r^2} (r\psi(r, \theta, \phi)) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \psi(r, \theta, \phi) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad (11.14)$$

This type of equation is an example of a *partial differential equation*, which is no simple task to solve. However, solving it gives both the allowed values of the angular momentum discussed above and the allowed energies  $E_n$ , which agree with the simpler Bohr model. Thus, we do not need to assume anything except the validity of the Schrödinger equation, and the allowed values of energy and angular momentum, together with the corresponding wavefunctions, all emerge from the solution.

Obviously, we are not going to go through the solution of the Schrödinger equation, but we can understand something about its mechanics and the solutions from a few simple considerations. Remember that the Schrödinger equation is set up starting from the classical energy, which we said takes the form

$$\frac{p_r^2}{2m_e} + \frac{L^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} = E$$

which we can write as

$$E = \varepsilon_r + \frac{L^2}{2m_e r^2}$$

where

$$\varepsilon_r = \frac{p_r^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The term  $L^2/(2m_e r^2)$  is actually dependent only on  $\theta$  and  $\phi$ , so it is purely angular. Given the separability of the energy into radial and angular terms, the wavefunction can be decomposed into a product of the form

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Solution of the angular part for the function  $Y(\theta, \phi)$  yields the allowed values of the angular momentum  $L^2$  and the z -component  $L_z$ . The functions  $Y(\theta, \phi)$  are then characterized by the integers  $l$  and  $m$ , and are denoted  $Y_{lm}(\theta, \phi)$ . They are known as *spherical harmonics*. Here we present just a few of them for a few values of  $l$ .

For  $l = 0$ , there is just one value of  $m$ ,  $m = 0$ , and, therefore, one spherical harmonic, which turns out to be a simple constant:

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

For  $l = 1$ , there are three values of  $m$ ,  $m = -1, 0, 1$ , and, therefore, three functions  $Y_{1m}(\theta, \phi)$ . These are given by

$$\begin{aligned} Y_{11}(\theta, \phi) &= -\left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{i\phi} \\ Y_{1-1}(\theta, \phi) &= \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi} \\ Y_{10}(\theta, \phi) &= \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta \end{aligned}$$

#### Note: Exponentials of Complex Numbers

Remember that

$$\begin{aligned} e^{i\phi} &= \cos \phi + i \sin \phi \\ e^{-i\phi} &= \cos \phi - i \sin \phi \end{aligned}$$

For  $l = 2$ , there are five values of  $m$ ,  $m = -2, -1, 0, 1, 2$ , and, therefore, five spherical harmonics, given by

$$\begin{aligned} Y_{22}(\theta, \phi) &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{2i\phi} \\ Y_{2-2}(\theta, \phi) &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{-2i\phi} \\ Y_{21}(\theta, \phi) &= -\left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{i\phi} \\ Y_{2-1}(\theta, \phi) &= \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{-i\phi} \\ Y_{20}(\theta, \phi) &= \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1) \end{aligned}$$

The remaining function  $R(r)$  is characterized by the integers  $n$  and  $l$ , as this function satisfies the radial part of the Schrödinger equation, also known as the *radial Schrödinger equation*:

$$-\frac{\hbar^2}{2m_e} \frac{1}{r} \frac{d^2}{dr^2}(rR_{nl}(r)) - \frac{l(l+1)\hbar^2}{2m_e r^2} R_{nl}(r) - \frac{Ze^2}{4\pi\epsilon_0 r} R_{nl}(r) = E_n R_{nl}(r)$$

Note that, while the functions  $Y_{lm}(\theta, \phi)$  are not particular to the potential  $V(r)$ , the radial functions  $R_{nl}(r)$  are particular for the Coulomb potential. It is the solution of the radial Schrödinger equation that leads to the allowed energy levels. The boundary conditions that lead to the quantized energies are  $rR_{nl}(0) = 0$  and  $rR_{nl}(\infty) = 0$ . The radial parts of the wavefunctions that emerge are given by (for the first few values of  $n$  and  $l$ ):

$$\begin{aligned}
 R_{10}(r) &= 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \\
 R_{20}(r) &= \frac{1}{2\sqrt{2}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \\
 R_{21}(r) &= \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \\
 R_{30}(r) &= \frac{2}{81\sqrt{3}} \left( \frac{Z}{a_0} \right)^{3/2} \left[ 27 - 18 \frac{Zr}{a_0} + 2 \left( \frac{Zr}{a_0} \right)^2 \right] e^{-Zr/3a_0}
 \end{aligned}$$

where  $a_0$  is the Bohr radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e} = 0.529177 \times 10^{-10} \text{ m}$$

The full wavefunctions are then composed of products of the radial and angular parts as

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

At this points, several comments are in order. First, the integers  $n, l, m$  that characterize each state are known as the *quantum numbers* of the system. Each of them corresponds to a quantity that is classically conserved. The number  $n$  is known as the *principal* quantum number, the number  $l$  is known as the *angular* quantum number, and the number  $m$  is known as the *magnetic* quantum number.

As with any quantum system, the wavefunctions  $\psi_{nlm}(r, \theta, \phi)$  give the probability amplitude for finding the electron in a particular region of space, and these amplitudes are used to compute actual probabilities associated with measurements of the electron's position. The probability of finding the electron in a small volume element  $dV$  of space around the point  $r = (r, \theta, \phi)$  is

$$\begin{aligned}
 P(\text{electron in } dV \text{ about } r, \theta, \phi) &= |\psi_{nlm}(r, \theta, \phi)|^2 dV \\
 &= R_{nl}^2(r) |Y_{lm}(\theta, \phi)|^2 dV
 \end{aligned}$$

What is  $dV$ ? In Cartesian coordinates,  $dV$  is the volume of a small box of dimensions  $dx$ ,  $dy$ , and  $dz$  in the  $x$ ,  $y$ , and  $z$  directions. That is,

$$dV = dx dy dz$$

In spherical coordinates, the volume element  $dV$  is a small element of a spherical volume and is given by

$$dV = r^2 \sin \theta dr d\theta d\phi \quad (11.15)$$

which is derivable from the transformation equations.

### Note: 3-D Integration

If we integrate  $dV$  from Equation 11.15 over a sphere of radius  $R$ , we should obtain the volume of the sphere:

$$\begin{aligned}
 V &= \left[ \int_0^R r^2 dr \right] \left[ \int_0^\pi \sin \theta d\theta \right] \left[ \int_0^{2\pi} d\phi \right] \\
 &= \left[ \frac{r^3}{3} \Big|_0^R \right] \left[ -\cos \theta \Big|_0^\pi \right] \left[ \phi \Big|_0^{2\pi} \right] \\
 &= \frac{R^3}{3} \times 2 \times 2\pi \\
 &= \frac{4}{3}\pi R^3
 \end{aligned}$$

which is the formula for the volume of a sphere of radius  $R$ .

### Example 11.1

The electron in a hydrogen atom ( $Z = 1$ ) is in the state with quantum numbers  $n = 1$ ,  $l = 0$  and  $m = 0$ . What is the probability that a measurement of the electron's position will yield a value  $r \geq 2a_0$ ?

#### Solution

The wavefunction  $\psi_{100}(r, \theta, \phi)$  is

$$\psi_{100}(r, \theta, \phi) = \frac{2}{a_0^{3/2}} \left( \frac{1}{4\pi} \right)^{1/2} e^{-r/a_0}$$

Therefore, the probability we seek is

$$\begin{aligned} P(r \geq 2a_0) &= \int_0^{2\pi} \int_0^\pi \int_{2a_0}^\infty |\psi_{100}(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi \\ &= \frac{4}{a_0^3} \frac{1}{4\pi} \left[ \int_0^{2\pi} d\phi \right] \left[ \int_0^\pi \sin \theta d\theta \right] \left[ \int_{2a_0}^\infty r^2 e^{-2r/a_0} dr \right] \\ &= \frac{1}{a_0^3 \pi} \cdot 2\pi \cdot 2 \int_{2a_0}^\infty r^2 e^{-2r/a_0} dr \end{aligned}$$

Let  $x = 2r/a_0$ . Then

$$P(r \geq 2a_0) = \frac{1}{2} \int_4^\infty x^2 e^{-x} dx$$

After integrating by parts, we find

$$P(r \geq 2a_0) = 13e^{-4} \approx 0.24 = 24\%$$

which is relatively large given that this is at least two Bohr radii away from the nucleus!

## Radial Probability Distribution Functions

The part of the probability involving the product

$$P_{nl}(r) = r^2 R_{nl}^2(r) \quad (11.16)$$

is known as the *radial probability distribution function* or simply the *radial distribution function*.  $P_{nl}(r)dr$  is the probability that a measurement of the electron's position yields a value in a radial shell of thickness  $dr$  and radius  $r$  as shown in the Figure 11.2:

## 1s orbital imagined as an onion

Concentric spherical shells

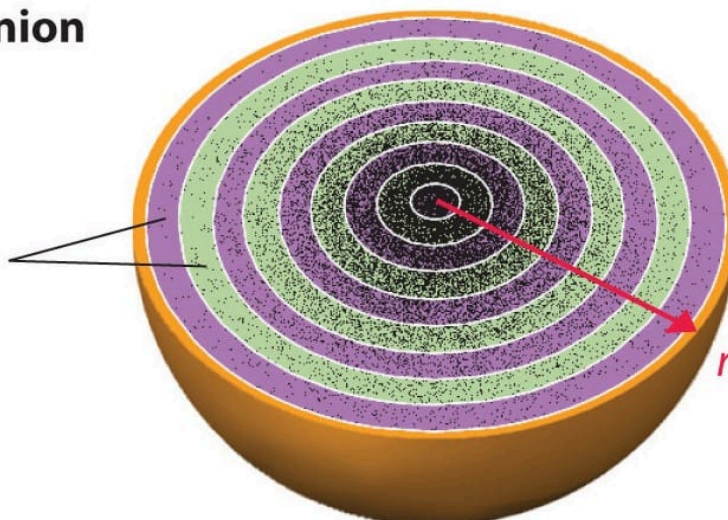


Figure 11.2 : Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing.

What the radial probability distribution shows is that the electron cannot be sucked into the nucleus because  $P_{nl}(0) = 0$ . Hence, as we shrink the radial shell into the nucleus, the probability of finding the electron in that shell goes to 0.

Another point concerns the number of allowed states for each allowed energy. Remember that each wavefunction corresponds to a probability distribution in which the electron can be found for each energy. The more possible states there are, the more varied the electronic properties and behavior of the system will be.

For  $n = 1$ , there is one energy  $E_1$  and only one wavefunction  $\psi_{100}$ .

For  $n = 2$ , there is one energy  $E_2$  and four possible states, corresponding to the following allowable values of  $l$  and  $m$

$$\begin{array}{ll} l = 0 & m = 0 \\ l = 1 & m = -1, 0, 1 \end{array}$$

Thus, there are four wavefunctions  $\psi_{200}$ ,  $\psi_{21-1}$ ,  $\psi_{210}$ , and  $\psi_{211}$ .

### Note: Degeneracy

Whenever there is more than one wavefunction corresponding to a given energy level, then that energy level is said to be *degenerate*. In the above example, the  $n = 2$  energy level of the hydrogen atom is *fourfold degenerate*.

## Physical Character of the Wavefunctions

The wavefunctions  $\psi_{nlm}(r, \theta, \phi)$  of the electron are called *orbitals*, but should not be confused these with trajectories or orbits. These are complete static objects that only give static probabilities when the electron has a well-defined allowable energy. The shapes of the orbitals are largely determined by the values of angular momentum, so we will characterize the orbitals this way.

### $l=0$ orbitals

The  $l = 0$  orbitals are called *s* (*s* for "sharp") orbitals. When  $l = 0$ ,  $m = 0$  as well, and the wavefunctions are of the form

$$\psi_{n00}(r, \theta, \phi) = R_{n0}(r)Y_{00}(\theta, \phi) = \left(\frac{1}{4\pi}\right)^{1/2} R_{n0}(r)$$

There is no dependence on  $\theta$  or  $\phi$  because  $Y_{00}$  is a constant. Thus, all of these orbitals are spherically symmetric (Figure 11.3).

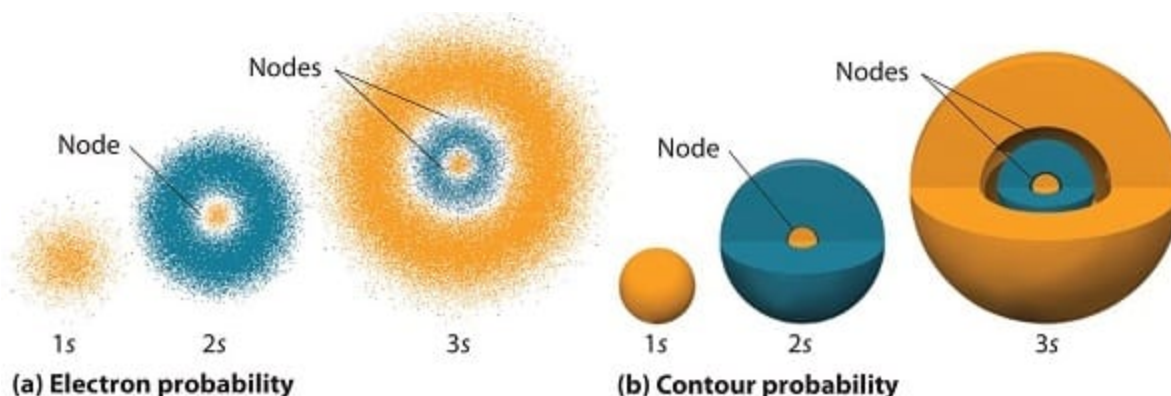


Figure 11.3: (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative.

Note several things about these orbitals. First, the density of points dies off exponentially as  $r$  increases, consistent with the exponential dependence of the functions  $R_{n0}(r)$  (Figure 11.4a).

As  $n$  increases, the exponentials decay more slowly as  $e^{-r/a_0}$  for  $n = 1$ ,  $e^{-r/2a_0}$  for  $n = 2$  and  $e^{-r/3a_0}$  for  $n = 3$ . Note, also, that the wavefunctions are peaked at  $r = 0$ , which would suggest that the amplitude is maximal to find the electron right on top of the nucleus! In fact, we need to be careful about this interpretation, since the radial probability density (Equation 11.16) contains an extra  $r^2$  factor from the volume element which goes to 0 as  $r \rightarrow 0$  (Figure 11.4b).

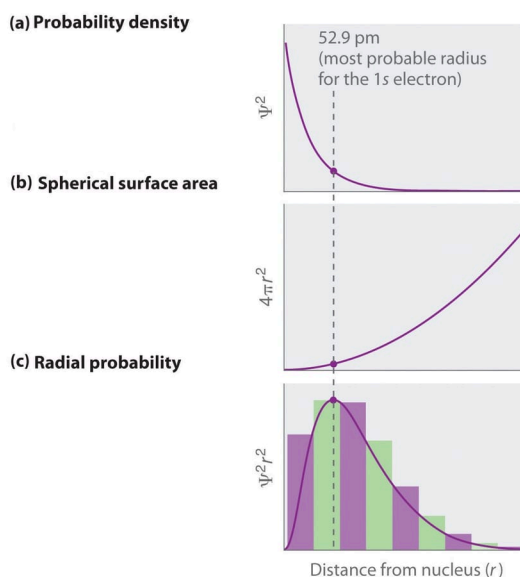


Figure 11.4 : Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) A plot of electron probability density  $\Psi^2$  versus  $r$  shows that the electron probability density is greatest at  $r = 0$  and falls off smoothly with increasing  $r$ . The density of the dots is therefore greatest in the innermost shells of the onion. (b) The surface area of each shell, given by  $4\pi r^2$ , increases rapidly with increasing  $r$ . (c) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of  $r$ . Because the surface area of each shell increases more rapidly with increasing  $r$  than the electron probability density decreases, a plot of electron probability versus  $r$  (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

Figure 11.5 compares the radial probability densities of the first three  $l = 0$  radial wavefunctions.

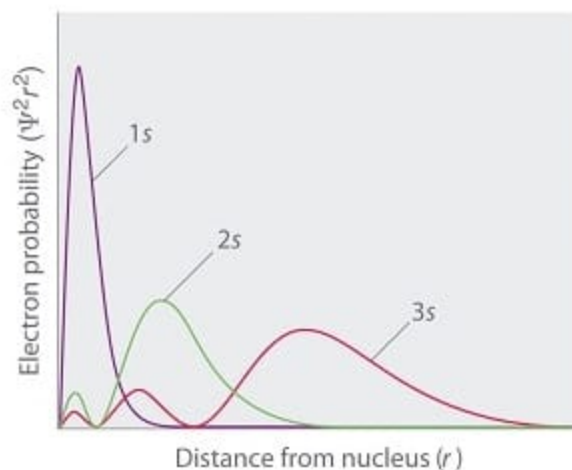
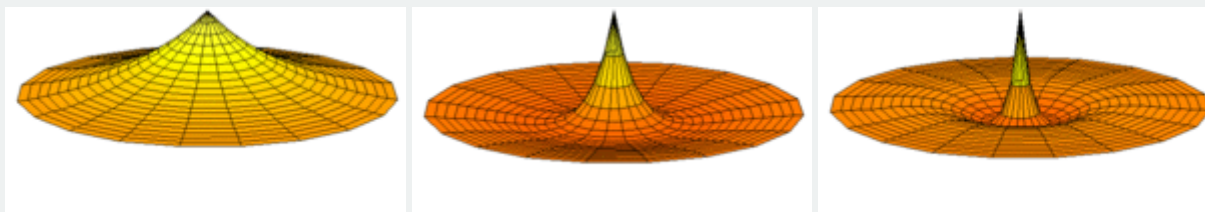


Figure 11.5: In these plots of electron probability as a function of distance from the nucleus ( $r$ ) in all directions (radial probability), the most probable radius increases as  $n$  increases, but the  $2s$  and  $3s$  orbitals have regions of significant electron probability at small values of  $r$ .

We also see that the wavefunctions have radial nodes where the electron will never be found (Figure 11.5). The number of nodes for  $R_{n0}(r)$  is  $n - 1$ .

### Note: Time Dependence

The Schrödinger Equation (11.14) is often called the *time-independent Schrödinger Equation* and is limiting case of the more complex *time-dependent Schrödinger Equation* that includes an explicit dependence to the wavefunction (where the "wave" part is most applicable). This is demonstrated in the simplified "drum" models below for the first three  $l = 0$  orbitals.



Simplified 2D drum models of the  $1s$  (left),  $2s$  (middle) and  $3s$  (left) orbitals.

In all of the modes analogous to  $s$  orbitals, it can be seen that the center of the  $r = 0$  drum vibrates most strongly.

## $l=1$ orbitals

The  $l = 1$  orbitals are known as  $p$  ("p" for "principal") orbitals. The orbitals take the form

$$\psi_{nlm}(r, \theta, \phi) = R_{n1}(r)Y_{1m}(\theta, \phi)$$

where

$$Y_{1\pm 1}(\theta, \phi) = \pm \left( \frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}$$

$$Y_{10}(\theta, \phi) = \left( \frac{3}{4\pi} \right)^{1/2} \cos \theta$$

Thus, these orbitals are *not* spherically symmetric.

The  $m = 0$  orbital is known as the  $p_z$  orbital because of the  $\cos \theta$  dependence and lack of  $\phi$  dependence. This resembles the spherical coordinate transformation for  $z$ ,  $z = r \cos \theta$ . Figure 11.6 shows the  $2p$  orbitals in more detail

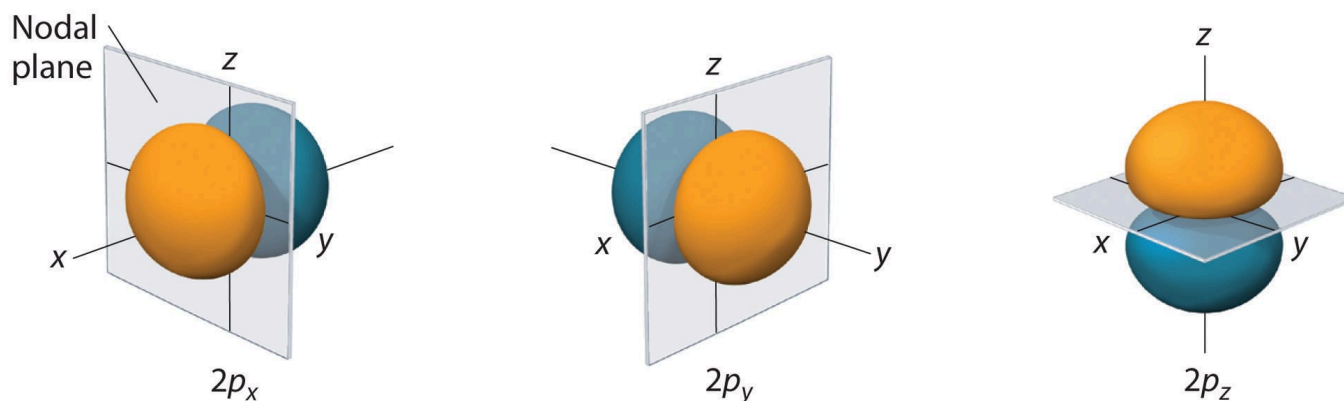


Figure 11.6: Details of the  $2p$  orbitals.

The nodal plane in the  $p$  orbital at  $\theta = \pi/2$  arises because  $\cos(\pi/2) = 0$  for all  $\phi$ , meaning that the entire  $xy$  plane is a nodal plane.

The orbitals  $\psi_{n11}(r, \theta, \phi)$  and  $\psi_{n1-1}(r, \theta, \phi)$  are not real because of the  $\exp(\pm i\phi)$  dependence of  $Y_{1\pm 1}(\theta, \phi)$ . Thus, these orbitals are not entire convenient to work with. Fortunately, because  $\psi_{n11}$  and  $\psi_{n1-1}$  are solutions of the Schrödinger equation with the same energy  $E_n$ , we can take any combination of these two functions we wish, and we still have a solution of the Schrödinger equation with the same energy. Thus, it is useful to take two combinations that give us two real orbitals. Consider, for example:

$$\begin{aligned}\tilde{\psi}_{p_x} &= \frac{1}{\sqrt{2}}[\psi_{n1-1}(r, \theta, \phi) - \psi_{n11}(r, \theta, \phi)] \\ \tilde{\psi}_{p_y} &= \frac{i}{\sqrt{2}}[\psi_{n1-1}(r, \theta, \phi) + \psi_{n11}(r, \theta, \phi)]\end{aligned}$$

which corresponds to defining new spherical harmonics:

$$\begin{aligned}Y_{p_x}(\theta, \phi) &= \frac{1}{\sqrt{2}}[Y_{1-1}(\theta, \phi) - Y_{11}(\theta, \phi)] = \left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi \\ Y_{p_y}(\theta, \phi) &= \frac{i}{\sqrt{2}}[Y_{1-1}(\theta, \phi) + Y_{11}(\theta, \phi)] = \left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi\end{aligned}$$

Again, the notation  $p_x$  and  $p_y$  is used because of the similarity to the spherical coordinate transformations  $x = r \sin \theta \cos \phi$  and  $y = r \sin \theta \sin \phi$ . These orbitals have the same shape as the  $p_z$  orbital but are rotated to be oriented along the  $x$ -axis for the  $p_x$  orbital and along the  $y$ -axis for the  $p_y$  orbital.

## $l=2$ orbitals

The  $l = 2$  orbitals are known as  $d$  ("d" for "diffuse") orbitals. Again, we seek combinations of the spherical harmonics that give us real orbitals. The combinations we arrive at are known as  $Y_{xy}$ ,  $Y_{xz}$ ,  $Y_{yz}$ ,  $Y_{z^2}$ ,  $Y_{x^2-y^2}$ , which gives us the required five orbitals we need for  $m = -2, -1, 0, 1, 2$ . The notation again reflects the angular dependence we would have if we took products  $xy$ ,  $xz$ ,  $yz$ ,  $z^2$ , and  $x^2 - y^2$  using the spherical coordinate transformation equations.

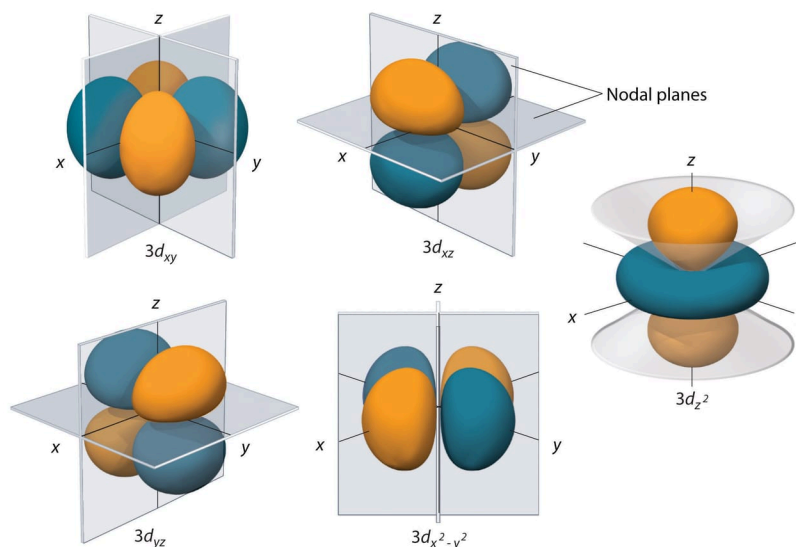


Figure 11.7: Details of the 3d orbitals.

Figure 11.7 compared the five 3d orbitals. Note the presence of two nodal planes in most of the orbitals. The exception is the  $3d_{z^2}$  orbital which has a *nodal cone*. Here, the number of radial nodes is still  $n - l - 1$ , and, as noted earlier, the overall number of nodes remains the same, so as  $l$  increases, radial nodes are exchanged for angular nodes.

For any of the wavefunctions  $\psi_{nlm}(r, \theta, \phi)$ , the result of measuring the distance of the electron from the nucleus many times yields the average value or expectation value of  $r$ , which can be shown to be

$$\begin{aligned}\langle r \rangle &= \int_0^{2\pi} \int_0^\pi \int_0^\infty |\psi_{nlm}(r, \theta, \phi)|^2 r^3 \sin \theta dr d\theta d\phi \\ &= \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \right]\end{aligned}$$

## Contributors and Attributions

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## 12: Electron spin and multi-electron atoms

### Electron spin

The quantum numbers  $n$ ,  $l$ ,  $m$  are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers  $n$ ,  $l$ ,  $m$  and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the figure 9.1:

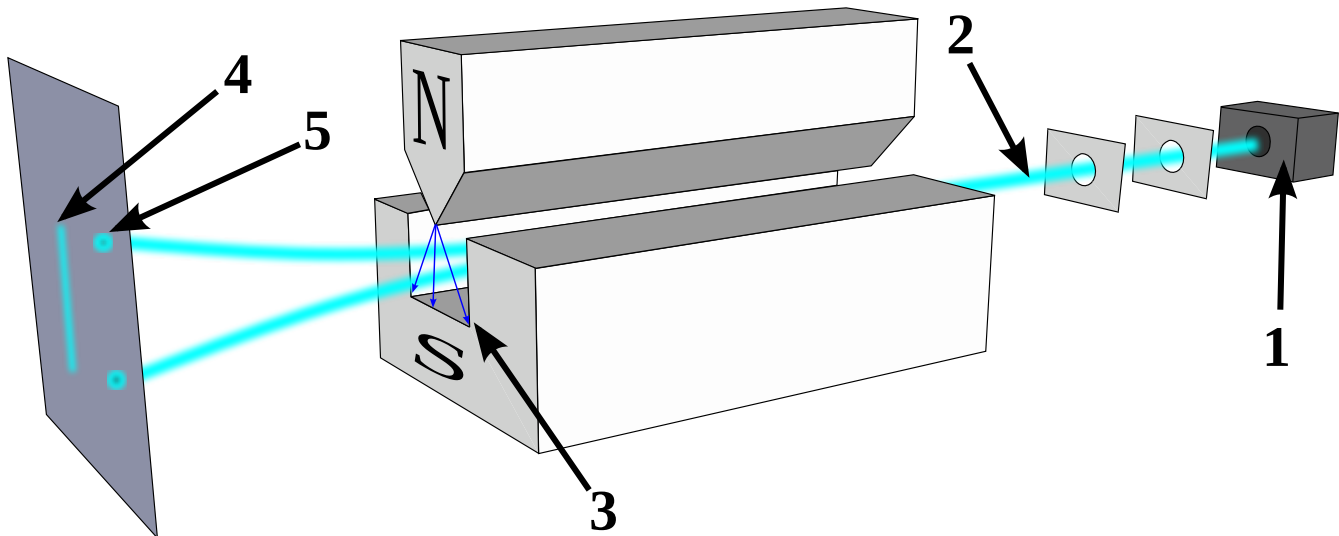


Figure 12.1: The Stern-Gerlach apparatus. (CC BY-SA 4.0; Tatoute via Wikipedia)

A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

It is known that a current loop in a nonuniform magnetic field experiences a net force. This is illustrated in Figure 9.1:

`\includegraphics[scale=0.5]{electron_current_loop1.eps}`  
`\includegraphics[scale=0.5]{electron_current_loop2.eps}`

Figure 9.1: A current loop in a magnetic field.

This force arises from an energy  $E$  given by

$$E = -\mathbf{M} \cdot \mathbf{B} \quad (9.1)$$

where  $M$  is called the *magnetic moment* of the current loop. A current loop, as the figure suggests, is caused by circulating charges. A circulating particle has an associated angular momentum  $L$ . If the charge of the particle is  $q$  and its mass is  $m$ , then the magnetic moment is given by

$$\mathbf{M} = \frac{q}{2m} \mathbf{L} \quad (9.2)$$

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment*  $M$  arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to an angular momentum and hence, must be a property that, unlike charge and mass, which are simple numbers, is a *vector property*. This property is called the *spin*,  $S$ , of the electron. As the expression above suggests, the intrinsic magnetic moment  $M$  of the electron must be proportional to the spin

$$\mathbf{M} = \gamma \mathbf{S} \quad (9.3)$$

In quantum mechanics, spin share numerous features in common with angular momentum, which is why we represent it as a vector. In particular, spin is quantized, i.e. we have certain allowed values of spin. Like angular momentum, the value of the magnitude squared  $S^2$  of spin is fixed, and one of its components  $S_z$  is as well. For an electron, the allowed values of  $S_z$  are

$$S_z \rightarrow m_s \hbar ; m_s = -\frac{1}{2}, \frac{1}{2} \quad (9.4)$$

while  $S^2$  has just one value  $3(\hbar)^2/4$ , corresponding to a general formula  $s(s+1)(\hbar)^2$ , where  $s = 1/2$ . For this reason, the electron is called a *spin-1/2* particle. The formula  $s(s+1)(\hbar)^2$  is generally valid for any spin- $s$  particle. The constant  $\gamma$  is called the *spin gyromagnetic ratio*

$$\gamma = -\frac{ge}{2m_e} \quad (9.5)$$

where  $g = 2$  for electrons. Note that  $\gamma < 0$ .

For an electron in a *uniform* magnetic field  $B$ , the energy is determined by the spin  $S$ :

$$E = -\gamma S \cdot B \quad (9.6)$$

We choose the uniform field  $B$  to be along the z-direction  $B = (0, 0, B)$ . Since the field lines flow from the north pole to the south pole, this choice of the  $B$  field means that the north pole lies below the south pole on the z-axis. In this case,

$$E = -\gamma B S_z \quad (9.7)$$

Since  $\gamma < 0$ , we see that the lowest energy configuration has  $S$  antiparallel to  $B$ . Given the two values of  $S_z$ , we have two allowed energies or two energy levels corresponding to the two values of  $m_s$ :

$$E_{1/2} = -\frac{\gamma B \hbar}{2} ; E_{-1/2} = \frac{\gamma B \hbar}{2} \quad (9.8)$$

Using the given expression for  $\gamma$ , which is negative, we obtain the two energy levels

$$E_{1/2} = \frac{eB\hbar}{2m_e} ; E_{-1/2} = -\frac{eB\hbar}{2m_e} \quad (12.1)$$

Unlike position and momentum, which have clear classical analogs, spin does not. But if we think of spin in pseudoclassical terms, we can think of a spinning charged particle, which is similar to a loop of current. Thus, if the particle spins about the z-axis, then  $S$  points along the z-axis. Since the spinning charge is negative, the left-hand rule can be applied. When the fingers of the left hand curl in the direction of the spin, the thumb points in the direction of the spin. A spinning charge produces a magnetic field similar to that of a tiny bar magnet. In this case, the spin vector  $S$  points toward the south pole of the bar magnet. Now if the spinning particle is placed in a magnetic field, it tends to align the spin vector in the opposite to the magnetic field lines, as the figure above suggests.

Now, when the electron is placed in a nonuniform magnetic field, with the field increasing in strength toward the north pole of the field source, the spin-down ( $m_s = -1/2$ ) electrons have their bar-magnet poles oriented such that the south pole points toward the north pole of the field source, and these electrons will be attracted toward the region of stronger field. The spin-up ( $m_s = 1/2$ ) electrons have their bar-magnet north poles oriented toward the north pole of the field source and will be repelled to the region of weaker field, thus causing the beam to split as observed in the Stern-Gerlach experiment.

The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number,  $m_s$  in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Note that we have added spin into the our quantum theory as a kind of *a posteriori* consideration, which seems a little contrived. In fact, the existence of the spin degree of freedom can be derived in a very natural way in the relativistic version of quantum mechanics, where it simply pops out of the relativistic analog of the Schrödinger equation, known as the *Dirac equation*.

## Spin Wavefunctions

So far, we have not explicitly considered the spin of the electrons. For the next type of approximation we will consider, the so-called *valence bond approximation*, we will need to consider spin explicitly. As we have already seen in the case of the hydrogen atom, the wavefunctions of an electron depend on the coordinates  $r = (x, y, z)$  or  $(r, \phi, \theta)$  and on the z-component of spin  $S_z$  (the total spin  $|S|$  is fixed). While the coordinates can be anything, the spin  $S_z$  can only take on two values  $\hbar/2$  and  $-\hbar/2$ . Recall that these lead to the two values of the spin quantum number  $m_s = \pm 1/2$ . The value  $m_s = 1/2$  is what we call the "spin-up" state and  $m_s = -1/2$  is what we call "spin-down".

We now define the spin wavefunctions. The spin-up wavefunction is denoted

$$\psi_{1/2}(S_z) = \psi_{\uparrow}(S_z)$$

Since  $S_z$  can take on only two values  $\pm\hbar/2$ , the spin wavefunction only have two values:

$$\psi_{\uparrow}(\hbar/2) = 1 ; \psi_{\uparrow}(-\hbar/2) = 0$$

The meaning of this wavefunction is that when the electron is in the spin-up state, the probability that a measurement of  $S_z$  will yield the value  $\hbar/2$  is  $P(S_z = \hbar/2) = |\psi_{\uparrow}(\hbar/2)|^2 = 1$  and the probability that its value will be  $-\hbar/2$  is 0. Similarly, the spin-down wavefunction is

$$\psi_{-1/2}(S_z) = \psi_{\downarrow}(S_z)$$

where

$$\psi_{\downarrow}(\hbar/2) = 0 ; \psi_{\downarrow}(-\hbar/2) = 1$$

so that the probability that a measurement of  $S_z$  yields the value  $-\hbar/2$  is 1 and that its value is  $\hbar/2$  is 0. Note that the spin wavefunctions are normalized, meaning that they satisfy

$$\sum_{S_z=-\hbar/2}^{\hbar/2} |\psi_{m_s}(S_z)|^2 = 1$$

and they are orthogonal, meaning that they satisfy

$$\sum_{S_z=-\hbar/2}^{\hbar/2} \psi_{\uparrow}(S_z)\psi_{\downarrow}(S_z) = 0$$

Now, for a hydrogen atom, there are four quantum numbers,  $n$ ,  $l$ ,  $m$ ,  $m_s$ , and the wavefunction depends on four coordinates,  $r$ ,  $\theta$ ,  $\phi$ ,  $s_z$ . While  $r$ ,  $\theta$ ,  $\phi$  are continuous,  $s_z$  takes on only two values. The wavefunction can be expressed as a simple product

$$\psi_{nlmm_s}(r, \theta, \phi, s_z) = \psi_{nlm}(r, \theta, \phi)\psi_{m_s}(s_z)$$

As a shorthand notation, we can generally represent the complete set of spatial and spin coordinates with a vector  $x$ . The spatial coordinates can be  $r, \theta, \phi$  or  $x, y, z$  or any other set of spatial coordinates useful for a given problem. For the hydrogen atom, using this notation, we would write

$$\psi_{nlmm_s}(x) = \psi_{nlm}(r, \theta, \phi)\psi_{m_s}(s_z)$$

## Many-electron atoms

The hydrogen atom is the *only* atom for which exact solutions of the Schrödinger equation exist. For any atom that contains two or more electrons, no solution has yet been discovered (so no solution for the helium atom exists!) and we need to introduce approximation schemes.

Let us consider the helium atom. The nucleus has a charge of  $+2e$ , and if we place the nucleus at the origin, there will be an electron at a position  $r_1$  with spin  $s_{z,1}$  and an electron at position  $r_2$  and spin  $s_{z,2}$ . As usual, we consider the nucleus to be fixed. The classical energy is then

$$\frac{|p_1|^2}{2m_e} + \frac{|p_2|^2}{2m_e} + \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{|r_1 - r_2|} - \frac{2}{|r_1|} - \frac{2}{|r_2|} \right] = E$$

Note that  $E$  is not simply a sum of terms for electron 1 and electron 2,  $E \neq \varepsilon_1 + \varepsilon_2$ . Therefore, it is not possible to write the wavefunction  $\Psi(x_1, x_2)$  as a simple product of the form  $\psi_1(x_1)\psi_2(x_2)$ , nor is it even possible to use the special form we introduced for identical particles

$$\frac{1}{\sqrt{2}} [\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)]$$

because these simple products are not correct solutions to the Schrödinger equation.

This means that the wavefunction  $\Psi(x_1, x_2)$  depends on the full set of 6 coordinates  $x_1, y_1, z_1, x_2, y_2, z_2$  or  $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$  if spherical coordinates are used, and 2 spin coordinates  $s_{z,1}, s_{z,2}$ , and that this dependence is not simple! In fact, as the number of electrons increases, the number of variables on which  $\Psi$  depends increases as well. For an atom with  $M$  electrons, the wavefunction  $\Psi$  depends on  $3M$  coordinates! Thus, it is clear that the wavefunction for a many-electron atom is a very unwieldy object!

As a side bar, we note that the 1998 Nobel prize in chemistry was awarded to Walter Kohn for the development of an extremely elegant theory of electronic structure known as *density functional theory*. In this theory, it is shown that the wavefunction  $\Psi$ , which depends on  $3M$  coordinates, can be replaced by a much simpler object called the electron density denoted  $\rho(r) = \rho(x, y, z)$ . This object depends on only three variables for a system of *any* number of electrons. In density functional theory, it is shown that *any* physical quantity can be computed from this electron density  $\rho(r)$ .

Consider now an imaginary form of helium in which the two electrons do not interact. For this simplified case, the energy is simply

$$\begin{aligned} E &= \frac{|p_1|^2}{2m_e} + \frac{|p_2|^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0} \left[ \frac{2}{|r_1|} + \frac{2}{|r_2|} \right] \\ &= \left[ \frac{|p_1|^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0|r_1|} \right] + \left[ \frac{|p_2|^2}{2m_e} - \frac{2e^2}{4\pi\epsilon_0|r_2|} \right] \\ &= \varepsilon_1 + \varepsilon_2 \end{aligned}$$

For this imaginary helium atom, the wavefunction can be expressed as an antisymmetric product, and because we have included spin, in the ground state, both electrons can be in the  $1s(Z=2)$  spatial orbital without having the wavefunction vanish. Recall that, when  $Z=2$ , the  $1s$  orbital is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left( \frac{2}{a_0} \right)^{3/2} e^{-2r/a_0} \equiv \psi_{1s(Z=2)}(r)$$

Multiplying this by a spin wavefunction, the wavefunction for one of the electrons is

$$\psi(x) = \psi_{1s(Z=2)}(r) \psi_{m_s}(S_z)$$

Given this form, the antisymmetrized two-electron wavefunction becomes

$$\begin{aligned} \Psi(x_1, x_2) &= \frac{1}{\sqrt{2}} [\psi_{1s(Z=2)}(r_1) \psi_{\uparrow}(S_{z1}) \psi_{1s(Z=2)}(r_2) \psi_{\downarrow}(S_{z2}) - \psi_{1s(Z=2)}(r_2) \psi_{\uparrow}(S_{z2}) \psi_{1s(Z=2)}(r_1) \psi_{\downarrow}(S_{z1})] \\ &= \frac{1}{\sqrt{2}} \psi_{1s(Z=2)}(r_1) \psi_{1s(Z=2)}(r_2) [\psi_{\uparrow}(S_{z1}) \psi_{\downarrow}(S_{z2}) - \psi_{\uparrow}(S_{z2}) \psi_{\downarrow}(S_{z1})] \end{aligned}$$

which, by virtue of the spin wavefunctions, does not vanish.

Given this wavefunction, the energy would just be the sum of the energies of two electrons interacting with a nucleus of charge  $+2e$ . We would need two quantum numbers  $n_1$  and  $n_2$  for this, and from our study of hydrogen-like atoms, the energy would be

$$E_{n_1 n_2} = -\frac{4}{n_1^2} - \frac{4}{n_2^2}$$

in Rydbergs. This comes from the fact that the energy of one electron interacting with a nucleus of charge  $+Ze$  is  $E_n = -Z^2/n^2$  in Rydbergs. So, the ground-state energy ( $n_1 = 1, n_2 = 1$ ) would be -8 Ry. In real helium, the electron-electron Coulomb repulsion

$e^2/(4\pi\epsilon_0 r_{12})$  increases the ground state energy above this value (the experimentally measured ground-state energy is -5.8 Ry). The tendency is for the electrons to arrange themselves such that the Coulomb repulsion is as small as possible.

## Hartree-Fock theory

For the helium atom, what happens if we try to use a product form as a "guess" wavefunction? Ignoring spin for the moment, we take as a guess of the solution for the ground-state wavefunction

$$\Psi_g(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)]$$

Then we know from problem set #4 that the corresponding guess of the ground-state energy

$$E_g = \int \Psi_g \hat{H} \Psi_g dV_1 dV_2 > E_0$$

where  $E_0$  is the true ground-state energy. Here,  $dV_1$  and  $dV_2$  are the volume elements of electron 1 and electron 2, respectively, and  $\hat{H}$  is the Hamiltonian

$$\hat{H} = \hat{K}_1 + \hat{K}_2 + \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{|r_1 - r_2|} - \frac{2}{|r_1|} - \frac{2}{|r_2|} \right]$$

That is, we know that this guess is *not* correct, however, we can try to optimize the form of the functions  $\psi_1(r)$  and  $\psi_2(r)$  so as to make  $E_g$  as small as possible, thereby making it approach  $E_0$ .

If we do this, we find that  $\psi_1(r)$  and  $\psi_2(r)$  satisfy a set of 2 coupled Schrödinger-like equations and that the potential energy  $V$  in each equation corresponds to what the electron would experience if we averaged over all possible positions of the other electron (think back to the classical shell model!).

If we solve these equations, we find that both  $\psi_1(r)$  and  $\psi_2(r)$  bear a strikingly resemblance to the hydrogenic function  $\psi_{100}(r, \phi, \theta) = \psi_{1s}(r, \theta, \phi)$ , the 1s wavefunction. The difference, however, is that it decays a little faster, as if its  $Z$  value were between 1 and 2. In fact, the value one obtains from an actual calculation is  $Z \approx 1.69$ . We will denote this as  $\psi_{1s(Z)}(r, \theta, \phi)$ . We can imagine one of the electrons as "occupying" the state  $\psi_1(r)$  and the other as "occupying" the state  $\psi_2(r)$ , but of course, we cannot say which electron is in which state, which is why we need the above form of the guess wavefunction. We also obtain two energies  $\epsilon_1$  and  $\epsilon_2$  that are close in energy but that the energies are lower than the energy  $E_1$  of the hydrogen atom.

Now, we see the problem with ignoring spin. If  $\psi_1$  and  $\psi_2$  are both  $\psi_{1s(Z)}$ , then the guess wavefunction becomes

$$\Psi_g(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_{1s(Z)}(r_1)\psi_{1s(Z)}(r_2) - \psi_{1s(Z)}(r_2)\psi_{1s(Z)}(r_1)] = 0$$

However, if we multiply the spatial wavefunctions by spin wavefunctions, then the two orbitals we obtain are

$$\psi_1(x) = \psi_{1s(Z)}(r)\psi_{\uparrow}(s_z) ; \psi_2(x) = \psi_{1s(Z)}(r)\psi_{\downarrow}(s_z)$$

Thus, if we substitute this into the expression for  $\Psi_g(x_1, x_2)$ , we find that we can factor out  $\psi_{1s(Z)}(r_1)\psi_{1s(Z)}(r_2)$  and we are left with the antisymmetric combination of spin wavefunctions. The only possibility for the combination of spin wavefunctions leads to

$$\Psi_g(x_1, x_2) = \frac{1}{\sqrt{2}} \psi_{1s(Z)}(r_1)\psi_{1s(Z)}(r_2) [\psi_{\uparrow}(s_{z,1})\psi_{\downarrow}(s_{z,2}) - \psi_{\uparrow}(s_{z,2})\psi_{\downarrow}(s_{z,1})]$$

Note that another possible spin wavefunction would be  $[\psi_{\uparrow}(s_{z,2})\psi_{\downarrow}(s_{z,1}) - \psi_{\uparrow}(s_{z,1})\psi_{\downarrow}(s_{z,2})]/\sqrt{2}$  however, this is different from the above wavefunction by an overall minus sign and is, therefore, not actually different.

As another shorthand notation, we can use symbols "1" and "2" to represent any of the variables of electrons 1 and 2. Thus, the guess wavefunctions can be represented simply as

$$\begin{aligned}\psi_g(1, 2) &= \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] \\ &= \frac{1}{\sqrt{2}}\psi_{1s(Z)}(1)\psi_{1s(Z)}(2)[\psi_{\uparrow}(1)\psi_{\downarrow}(2) - \psi_{\uparrow}(2)\psi_{\downarrow}(1)]\end{aligned}$$

Given that the spin wavefunctions are rather simple, we can focus on the spatial parts of the wavefunctions in the proceeding discussion. For short, we denote the electronic configuration as  $1s^2$ .

The lowest HF energy obtained for helium,  $\varepsilon_1 \approx -2.38 \text{ Ry}$ . Note how close this is to the formula  $-Z^2/n^2$  for  $n = 1$  with  $Z = 1.69$  ! The next energy  $\varepsilon_2$  is only slightly large than this value, so we see that  $\varepsilon_1 \approx \varepsilon_2$ , but strictly  $\varepsilon_1 < \varepsilon_2$ . However, the energies are so close that they can be considered as degenerate. In fact, there is a class of Hartree-Fock calculations (called "closed-shell" calculations), in which this degeneracy is assumed at the outset, and the pair of electrons is treated as a single unit or single quantum state.

Now, if we followed the same thing for lithium, we would need three functions to construct the guess wavefunction, which we could take as

$$\psi_1(x) = \phi_1(r)\psi_{\uparrow}(S_z) ; \psi_2(x) = \phi_2(r)\psi_{\downarrow}(S_z) ; \psi_3 = \phi_3(r)\psi_{\uparrow}(S_z)$$

where  $\phi_1(r)$ ,  $\phi_2(r)$ , and  $\phi_3(r)$  are arbitrary spatial wavefunctions whose shape we optimize so as to make  $E_g$  as close to the true ground state energy  $E_0$  as possible. For lithium, the Hamiltonian is

$$\hat{H} = \hat{K}_1 + \hat{K}_2 + \hat{K}_3 + \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{|r_1 - r_2|} + \frac{1}{|r_1 - r_3|} + \frac{1}{|r_2 - r_3|} - \frac{3}{|r_1|} - \frac{3}{|r_2|} - \frac{3}{|r_3|} \right]$$

The guess wavefunction we would need is

$$\begin{aligned}\Psi_g(x_1, x_2, x_3) &= \frac{1}{\sqrt{6}}[\psi_1(x_1)\psi_2(x_2)\psi_3(x_3) + \psi_1(x_3)\psi_2(x_1)\psi_3(x_2) + \psi_1(x_2)\psi_2(x_3)\psi_3(x_1) \\ &\quad - \psi_1(x_1)\psi_2(x_3)\psi_3(x_2) - \psi_1(x_3)\psi_2(x_2)\psi_3(x_1) - \psi_1(x_2)\psi_2(x_1)\psi_3(x_3)]\end{aligned}$$

and the guess energy is computed using

$$E_g = \int \Psi_g^* \hat{H} \Psi_g dx_1 dx_2 dx_3$$

where the notation  $\int dx$  means

$$\int dx = \sum_{S_i = -\hbar/2}^{\hbar/2} \int dV$$

That is, we sum over the two spin values and integrate over all space using either Cartesian ( $dV = dxdydz$ ) or spherical ( $dV = r^2 \sin\theta dr d\theta d\phi$ ) coordinates or any other coordinates we wish to use. Then, minimizing the guess energy by optimizing the shapes of the orbitals  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$ , we obtain two orbitals  $\phi_1(r)$  and  $\phi_2(r)$  that resemble  $100$  or  $1s$  hydrogen-like orbitals  $\psi_{100(Z)}(r, \phi, \theta)$  and  $\phi_3$  resembles  $\psi_{200(Z)}(r, \phi, \theta)$  but again, all of these orbitals decay faster than their counterparts for the hydrogen atom. The calculation gives an effective value of  $Z \approx 2.64$ . Thus, multiplying these by spin wavefunctions, we would obtain the three HF orbitals as

$$\begin{aligned}\psi_1(x) &= \psi_{1s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_2(x) &= \psi_{1s(Z)}(r)\psi_{\downarrow}(s_z) \\ \psi_3(x) &= \psi_{2s(Z)}(r)\psi_{\uparrow}(s_z)\end{aligned}$$

We would denote the electronic configuration as  $1s^2 2s^1$ . Here, we find  $\varepsilon_1 \approx \varepsilon_2$ , and  $\varepsilon_3 > \varepsilon_1, \varepsilon_2$ . Strictly,  $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$ . The total HF energy for the ground state is  $-14.86 \text{ Ry}$ , while the experimental value is  $-14.96 \text{ Ry}$ . Note that if we neglected the electron-electron repulsion, the energy would be

$$E_{n_1 n_2 n_3} = -\frac{9}{n_1^2} - \frac{9}{n_2^2} - \frac{9}{n_3^2}$$

with  $n_1 = n_2 = n_3 = 1$ , which gives  $-27 \text{ Ry}$ .

For Beryllium, we would obtain four orbitals, two of which resemble 1s orbitals and two of which resemble 2s orbitals. Again, these decay as if they have an effective  $Z$  value between 3 and 4. We can, therefore, represent these orbitals as

$$\begin{aligned}\psi_1(x) &= \psi_{1s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_2(x) &= \psi_{1s(Z)}(r)\psi_{\downarrow}(s_z) \\ \psi_3(x) &= \psi_{2s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_4(x) &= \psi_{2s(Z)}(r)\psi_{\downarrow}(s_z)\end{aligned}$$

We would denote the electronic configuration as  $1s^2 2s^2$ .

For Boron, we would obtain 5 orbitals, two of which would resemble 1s, two would resemble 2s, and the fifth would resemble a  $2p_x$  orbital. Again, all of these would decay as if they have an effective  $Z$  between 4 and 5. We can thus represent the 5 orbitals as

$$\begin{aligned}\psi_1(x) &= \psi_{1s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_2(x) &= \psi_{1s(Z)}(r)\psi_{\downarrow}(s_z) \\ \psi_3(x) &= \psi_{2s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_4(x) &= \psi_{2s(Z)}(r)\psi_{\downarrow}(s_z) \\ \psi_5(x) &= \psi_{2p_x(Z)}(r)\psi_{\uparrow}(s_z)\end{aligned}$$

and denote the electronic configuration as  $1s^2 2s^2 2p_x^1$ . Here the HF energies would follow the pattern  $\varepsilon_1 \approx \varepsilon_2$ ,  $\varepsilon_3 \approx \varepsilon_4$ ,  $\varepsilon_3, \varepsilon_4 > \varepsilon_1, \varepsilon_2$ , and  $\varepsilon_5 > \varepsilon_3, \varepsilon_4$ . Strictly,  $\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \varepsilon_4 < \varepsilon_5$ .

For carbon, we obtain 6 orbitals, and this time, the 6th orbital does not resemble  $2p_x$  but rather  $2p_y$ . Hence, we would represent the 6 orbitals as

$$\begin{aligned}\psi_1(x) &= \psi_{1s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_2(x) &= \psi_{1s(Z)}(r)\psi_{\downarrow}(s_z) \\ \psi_3(x) &= \psi_{2s(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_4(x) &= \psi_{2s(Z)}(r)\psi_{\downarrow}(s_z) \\ \psi_5(x) &= \psi_{2p_x(Z)}(r)\psi_{\uparrow}(s_z) \\ \psi_6(x) &= \psi_{2p_y(Z)}(r)\psi_{\uparrow}(s_z)\end{aligned}$$

These all decay as if they had an effective  $Z$  value between 5 and 6. The HF energies follow the pattern  $\varepsilon_1 \approx \varepsilon_2$ ,  $\varepsilon_3 \approx \varepsilon_4$ ,  $\varepsilon_5 \approx \varepsilon_6$ ,  $\varepsilon_3, \varepsilon_4 > \varepsilon_1, \varepsilon_2$ , and  $\varepsilon_5, \varepsilon_6 > \varepsilon_3, \varepsilon_4$ . Note that for Boron and Carbon, the energies of the  $2p$  orbitals are larger than for the  $2s$  orbitals, which is not the case for hydrogen. The electronic configuration would be  $1s^2 2s^2 2p_x^1 2p_y^1$ .

For Nitrogen, the 7th orbital would resemble a  $2p_z$  orbital, and we would just add  $\psi_7(x) = \psi_{2p_z(Z)}\psi_{\uparrow}(s_z)$ . Now, for oxygen, the 8th orbital again resembles a  $2p_x$  orbital, and we would add this to the list but with a down spin wavefunction  $\psi_8(x) = \psi_{2p_x(Z)}\psi_{\downarrow}(s_z)$ . For oxygen, we find that the 5-8 HF energies are approximately equal,  $\varepsilon_5 \approx \varepsilon_6 \approx \varepsilon_7 \approx \varepsilon_8$ , although strictly  $\varepsilon_5 < \varepsilon_6 < \varepsilon_7 < \varepsilon_8$ .

These examples illustrate a more general procedure known as *Hartree-Fock* theory or the *Hartree-Fock approximation* (named after Douglas Hartree and Vladimir Fock) developed in 1930. Hartree-Fock (HF) theory makes several important assumptions:

1. The guess wavefunction is always composed of combinations of products of single-electron functions  $\psi_1(r)$ ,  $\psi_2(r)$ ,... that properly account for the identical nature of the electrons.
2. When the shapes of these functions are optimized, each electron is subject to an effective potential  $V$  that is generated by averaging over the positions of all the other electrons. For the  $i$ th electron,  $V$  depends only on  $r_i$ .
3. For an atom,  $V$  depends only on the magnitude  $|r_i|$ , which means that the effective potential is spherically symmetric.

If an atom has  $M$  electrons, then HF theory yields  $M$  functions  $\psi_1(r)$ , ...,  $\psi_M(r)$  and  $M$  energies  $\varepsilon_1$ , ...,  $\varepsilon_M$ . These energies are *all negative*,  $\varepsilon_i < 0$ , and they are ordered such that

$$\varepsilon_1 < \varepsilon_2 < \dots < \varepsilon_M$$

We will give a physical interpretation of these energies shortly.

So how do we calculate probabilities in HF theory? What we are interested in is the probability of finding one of the  $M$  electrons in a small volume  $dV$  about the point  $r$  independent of the positions of the remaining  $M - 1$  electrons. This probability is given in terms of the electron density introduced earlier. That is

$$P(\text{electron is in } dV \text{ about } r) = \rho(r)dV$$

and the electron density can be computed from the squares of the HF orbitals:

$$\rho(r) = \sum_{S_z=-\hbar/2}^{\hbar/2} \sum_{i=1}^M |\psi_i(r, S_z)|^2$$

This is the same density that lead to the chemistry Nobel prize!

To give an idea of how well HF theory can predict the ground state energies of several atoms, consider the table below (all energies are in Ry):

Table 9.2: Hartree Fock Calculations of Ground Energies

| Atom | Hartree-Fock Energy | Experiment |
|------|---------------------|------------|
| He   | −5.72               | −5.80      |
| Li   | −14.86              | −14.96     |
| Ne   | −257.10             | −257.88    |
| Ar   | −1053.64            | −1055.20   |

The HF theory motivates the so-called "aufbau" principle for expressing/building up electron configurations in atoms. "Aufbau" is German for "building up" (*Aufbauen* = "to build up"). We see that the HF orbitals are ordered according to their energies and that as the energy increases, their shapes follow the "ladder" of wavefunctions of the hydrogen atom. Thus, as we consider atoms with more and more electrons, we simply have to "occupy" more of the HF orbitals in order of increasing energy. Since groups of these orbitals are close in energy, there are two rules we need to introduce for this procedure of occupying orbitals:

1. *Pauli exclusion principle: No two electrons in an atom can have the same set of quantum numbers.*
2. *Hund's rule: When electrons are added to a set of HF orbitals of approximately equal energy, a single electron enters each orbital before a second one can enter any orbital. The lowest energy configuration is always the one with parallel spins.*

Now, let us apply these rules to fill the orbitals in the first row elements (which are all we care about for the next two chapters). The filling will refer to the figure below:

### Figure:

Table  
of  
electronic  
configurations

Starting with hydrogen ( $Z = 1$ ), HF theory gives the exact answer because the H atom is exactly soluble. Thus, we generate the exact function  $\psi_{100}(r, \phi, \theta)$ , and we put the one electron into this orbital for the ground state. We write this as

$$1s^1$$

For Helium ( $Z = 2$ ), HF theory is no longer exact, however as we discussed, HF theory gives two orbitals  $\psi_1(r)$  and  $\psi_2(r)$ , both of which resemble  $\psi_{100}$  (but decays a little faster). The energies  $\epsilon_1$  and  $\epsilon_2$  are also very similar. Thus, we regard these orbitals as having roughly the same energy, and we place one electron into  $\psi_1$  and one into  $\psi_2$ . We regard this as placing two electrons into the single orbital  $\psi_{100}$  and assigning the electrons the same set of H-like quantum numbers  $n, l, m$ . To be consistent with Pauli's exclusion principle, they need to have one quantum number that is different, so we assign one electron  $m_s = 1/2$  and the other  $m_s = -1/2$  (see figure). We write the electron configuration as

$$1s^2$$

signifying that two electrons occupy the  $\psi_{100}$  orbital (although in reality, they occupy two different orbitals that happen to be very similar to each other).

For Lithium ( $Z = 3$ ), HF theory yields three orbitals  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$ . The first two closely resemble  $\psi_{100}$ , while the third resembles  $\psi_{200}$ . HF theory also yields three energies  $\varepsilon_1$ ,  $\varepsilon_2$  and  $\varepsilon_3$  with  $\varepsilon_1 \approx \varepsilon_2$  and  $\varepsilon_3 > \varepsilon_2 > \varepsilon_1$ . Each electron occupies an HF orbital, but we regard this as two electrons in a  $\psi_{100}$  orbital and the third in a  $\psi_{200}$  orbital (see figure). We write this as

$$1s^2 2s^1$$

Note that it takes two electrons to fill the 1s orbital, after which we move to a 2s-like orbital. In this case, we say that the 1s electrons form a *closed shell*, since we have now moved on to a different value of  $n$ , i.e.,  $n = 2$ . The 2 1s electrons are called *core electrons* and the 2s electron is called a *valence electron*.

Coming to Beryllium ( $Z = 4$ ), we have 4 HF orbitals, two of which resemble  $\psi_{100}$  and two of which resemble  $\psi_{200}$ , so we imagine that an electron in each HF orbital is equivalent to 2 in the  $\psi_{100}$  and 2 in the  $\psi_{200}$ . In each pair, the electrons have opposite spins to be consistent with the Pauli exclusion principle. We write this as

$$1s^2 2s^2$$

Now, we have two core electrons and two valence electrons.

For Boron ( $Z = 5$ ), there are 5 HF orbitals.  $\psi_1$  and  $\psi_2$  resemble  $\psi_{100}$ ,  $\psi_3$  and  $\psi_4$  resemble  $\psi_{200}$ , and  $\psi_5$  resembles  $\psi_{21m}$ , i.e. a generic p-orbital (we do not specify  $m$  because the direction of the orbital does not matter). The energies are ordered such that  $\varepsilon_1 \approx \varepsilon_2$ ,  $\varepsilon_3 \approx \varepsilon_4$ . Interestingly,  $\varepsilon_5$  is larger than all of these and not close to  $\varepsilon_4$ . Unlike in hydrogen, where orbitals with the same  $n$  but different values of  $l$  have the same energy, here orbitals with the same  $n$  but different values of  $l$  have different energies. Thus,  $\psi_5$  is at a higher energy. Hence, when we fill, we start with 1s, then 2s and finally 2p. We can choose any of the 2p orbitals, so we just start with  $2p_x$ . We thus write the electronic configuration as

$$1s^2 2s^2 2p_x^1$$

For carbon ( $Z = 6$ ), the situation is much the same. However, here we have  $\psi_5$  and  $\psi_6$  both with p-like character and similar in energy. Here, however, we need Hund's rule. We first put a spin-up electron in the  $2p_x$  orbital and then another spin-up electron in the  $2p_y$  orbital. The electronic configuration is

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

For nitrogen ( $Z = 7$ ), we would place a spin-up electron in the  $2p_z$  orbital and write  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ . When we get to oxygen  $Z = 8$ , we have now placed one electron in each of the three p-like orbitals. We now have to return to  $p_x$  and place another electron in it, which will now be spin-down to be consistent with the Pauli exclusion principle. Its electronic configuration is  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ . For fluorine  $Z = 9$ , it is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ . Finally, when we get to Neon ( $Z = 10$ ), we have  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$ , which we can write simply as  $1s^2 2s^2 2p^6$ . With Neon, as with Helium, we have completed a shell, and the next HF orbital will be like  $\psi_{300}$  and have a higher energy, thereby starting the next shell. Thus, we see that for Neon, 8 electrons are needed to complete a shell, the 2 2s electrons and the 6 2p electrons. The fact that 8 electrons close a shell for Neon lend this atom special stability and make it highly unreactive.

## Probing energy levels and the Koopmans approximation

Quantum theory successfully predicts the shell structure of atoms and can explain the observed features of the periodic table (see end of chapter 5). The shell structure and the ionization energies of atoms can be probed by a technique known as [photoelectron spectroscopy](#).

The technique works very much like the photoelectric effect in metals except that we use incident EM radiation (usually X-rays or UV rays) to knock electrons out of individual atoms, thereby leading to measures of the ionization energies. In this method, the ionization energy IE plays the same role as the work function of a metal.

Suppose a photon of energy  $h\nu$  strikes an atom or cation in order to probe one of the ionization energies  $IE_i$ . The electron will be ejected from the atom or ion and have a residual kinetic energy  $p^2/2m_e$ . Thus, by energy conservation

$$h\nu = IE_i + \frac{p^2}{2m_e}$$

Given the experimental numbers, we can compare the measured ionization energies to the orbital energies generated in a HF calculation. We find a very interesting result. If the energies are ordered according to  $\varepsilon_1 < \varepsilon_2 < \dots < \varepsilon_M$ , then the first ionization

energy  $IE_1$  is approximately equal to the negative of the highest HF energy  $-\varepsilon_M$ :

$$IE_1 \approx -\varepsilon_M$$

Similarly, the second ionization energy has the property

$$IE_2 \approx -\varepsilon_{M-1}$$

Finally, the  $M$ th ionization energy  $IE_M$  satisfies

$$IE_M \approx -\varepsilon_1$$

These relations are known as *Koopmans's approximation*.

The essential approximations made in these relations are, firstly, the approximations inherent in the HF theory. But beyond this, it is also assumed that the energies do not change much as the electrons are sequentially stripped out of the atom. Obviously, these energies *should* change, as the screening and repulsion effects of the other electrons is reduced, and the electrons are drawn closer to the positively charged nucleus, but the effects are small. This type of approximation is known as the *frozen core approximation*.

## Contributors and Attributions

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## 13: Energetics of ionic bonding and introduction to Lewis structures

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In this part of the course, we will set aside quantum mechanics briefly and discuss the so-called classical theory of chemical bonding. In our crude classical picture, electrons are viewed as point particles that move in stable classical orbits determined by Newton's second law around the atoms in a molecule. Because the nuclei are several thousand times more massive than electrons, we regard the nuclei as fixed on the time scale of significant "classical" electron motion.

Despite our crude classical picture, however, a conceptually useful definition of chemical bonding can be stated that relies on the relatively high mobility of the electrons compared to the nuclei:

### Energetic considerations of chemical bonding

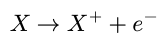
Based on our crude, conceptual definition of chemical bonding, it is clear that an important issue concerns the ability of atoms to give up electrons to or accept electrons from other atoms.

In order to quantify this notion, there are two energies that are relevant. These are:

Let us examine these in greater detail:

### Ionization energy and the shell model of the atom

Consider the reaction describing the loss of an electron by a neutral atom:



Elements toward the left of the periodic table have low electron affinities, so they tend to act as electron donors, while atoms to the right of the periodic table have high electronegativities, and they tend to act as electron acceptors.

### The Lewis dot model

When atoms are brought into some arrangement, the problem of determining the chemical bonding pattern amounts to figuring out where the electrons are and what they look like. The solution of this problem is known as *electronic structure theory* and is a quantum mechanical problem. All of chemical bonding can be explained by solving the Schrödinger wave equation, which we will discuss in the next chapter.

A simple model, developed by Lewis in 1916, exists that can be used to gain a qualitative understanding of chemical bonding and electronic structure. This is the Lewis dot model.

The Lewis model involves recognizing that not all electrons in an atom play a role in chemical bonding. Electrons that are closest to the nucleus for a set called the *core* electrons. These are generally chemically inert and not important for chemical bonding.

The outermost electrons of an atom, called the *valence electrons* are chemically, important, however, and are treated within the Lewis model.

It is worth noting that for quantitative accuracy, the effects of core electrons does need to be included in some approximate way. This can amount to a particularly difficult problem, especially in heavier elements, where the charge on the nucleus is large, and hence the forces on core electrons cause them to move at speeds near light speed. In that case, a fully relativistic treatment of core electrons is necessary, so if you thought your study of relativity theory in physics was useless, think again.

For elements in groups I-VIII in the periodic table,

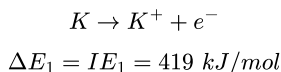
$$\# \text{ valence electrons} = \text{group \# in periodic table}$$

These atoms have multiple valencies, hence the roman numeral, which is used to distinguish between the different ions. The roman numeral is taken to be equal to the charge on the ion. The reason for the large number of valence electrons has to do with the unfilled  $d$  orbitals of these atoms (to be discussed in chapters 15 and 16) next semester.

There are several polyatomic cations and anions that are important and will be encountered later. They are:

## Energetics of ionic bonding

Consider the KF molecule. K has a low ionization energy and can act as an electron donor according to the reaction:



Chemical bonds are formed either by one atom's transferring electrons to another atom or by two atoms' sharing electrons between them, or something in between these two situations.

1. The electronegativity measures the ability of an atom to draw electrons to itself in a chemical bond. While it is reported as an atomic property, it is concerned with bonding within a molecule. One definition of electronegativity that was proposed by Mulliken in 1934 is particularly simple, being a simple arithmetical average:

$$\chi_{\text{mulliken}} \propto \frac{1}{2}(IE_1 + EA)$$

The larger the electronegativity, the greater the tendency for an atom to draw electrons to itself in a chemical bond.

In general,

- if  $IE_1$  and  $EA$  are both large, giving up an electron is unlikely, but gaining an electron is likely, and the atom tends to act as an *electron acceptor*, or is "electronegative."
- if  $IE_1$  is small, and  $EA$  is small or negative, giving up an electron is likely, but gaining an electron is unlikely, and the atom tends to act as an *electron donor*, or is "electropositive." Helium is an exception to this rule, having only 2 valence electrons.

Note that the [group 18](#) elements, known as the noble gases, have 8 valence electrons (except He, which has only 2) and are highly non-reactive. We can surmise that 8 valence electrons is a kind of magic number giving special stability to the electronic structure of the atom. We call this an *octet*, which plays an important role in the Lewis model.

As an example of identifying the number of valence electrons, consider the second period:

**Figure 2:**



For this period, we see that

$$\# \text{ core electrons} = \text{atomic number} - \# \text{ valence electrons}$$

In the Lewis dot model, valence electrons are represented by dots, while core electrons are not shown explicitly. As an example of this representation, consider the first two periods:

**Figure 3:**

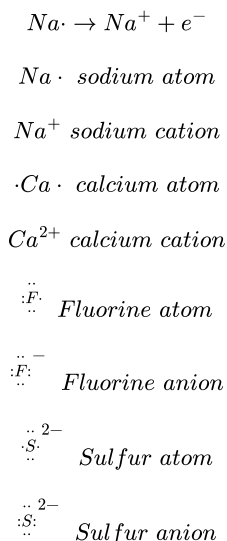


Notice how the dots are drawn as single electrons first before pairs of electrons are drawn. Again, the exception to this is Helium, whose two electrons form a *closed valence shell* and thus must be drawn as a pair. The element Ne also has a closed valence shell, but with eight electrons drawn as four pairs. Ionic bonding According to our crude, conceptual definition, chemical bonds can form either by electron transfer between atoms or by sharing of electrons. The former case constitutes a kind of bond known as an *ionic bond*. The reason for this is that if one atom transfer electrons to another, the donor is left

with a net positive charge, while the acceptor is left with a net negative charge. According to Coulomb's law, these charged species should attract each other, and this attraction is what stabilizes the bond.

When atoms lose or gain electrons, they become what are called *ions*. Loss of electrons leaves an atom with a net positive charge, and the atom is called a *cation*. Gain of electrons leaves an atom with a net negative charge, and the atom is called an *anion*.

Some examples are:



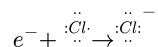
Special stability results when an atom, by losing or gaining electrons has as many valence electrons as a noble gas atom. In this case, we say that an atom or ion has a completed octet.  $Na^+$  has as many electrons as  $Ne$ , which explains why it loses only 1 electron, while  $Ca^{2+}$  also has as many electrons as  $Ne$ , but since it is a Group II, element, it must lose 2 electrons to achieve an octet configuration.

The basic assumption of the Lewis model is that atoms will tend to form chemical bonds in order to complete their valence shells and achieve completed octets (or doublets in the case of H and He). This is known as the *octet rule*.

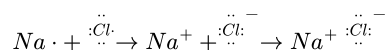
Consider the loss of an electron by sodium:



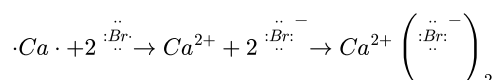
By losing the electron,  $Na$  achieves octet stability, since  $Na^+$  is isoelectronic with  $Ne$ . Similarly, chlorine favors gaining an electron:



Thus,  $Na$  can donate an electron, which  $Cl$  can accept and an ionic bond can form between them. This is expressed chemically as



which is a molecule of sodium chloride. Atoms that can lose two electrons, such as Calcium, can form molecules with two chemical bonds:



In transition metal atoms and in many heavier elements, the octet rule does not apply.

**Examples:**

$Cu^+$  ion has 10 valence electrons - copper(I) ion.

$Cu^{2+}$  ion has 9 valence electrons - copper(II) ion.

**$Fe^{3+}$  ion has five valence electrons - iron(III) ion.**

$Fe^{2+}$  ion has 6 valence electrons - iron(II) ion.

$NH_4^+$  - ammonium ion.

$H_3O^+$  - hydronium ion (important in acidic solutions).

$CO_3^-$  - carbonate ion.

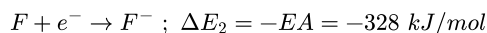
$NO_2^-$  - nitrite ion.

$NO_3^-$  - nitrate ion.

$ClO_4^-$  - perchlorate ion (forms interesting compounds with the ammonium and hydronium ions).

$OH^-$  - hydroxyl ion (important in basic solutions).

F has a high electron affinity and can accept an electron according to the reaction:



so that  $EA = 328 \text{ kJ/mol}$ . The total energy to form  $K^+$  and  $F^-$  far away from each other is just the sum of  $\Delta E_1$  and  $\Delta E_2$ :

$$\Delta E_{tot} = \Delta E_1 + \Delta E_2 = IE_1 - EA = 91 \text{ kJ/mol}$$

which implies that there is an energy cost associated with the formation of these two ions. How, then, can the ionic bond form if there is an energy cost?

The answer lies in Coulomb's law, which states that if  $K^+$  and  $F^-$  are brought near each other, there is an attraction of opposite charges. Since the charge on  $K^+$  is  $e$  and the charge on  $F^-$  is  $-e$ , if the bond length of KF is  $R_e$ , the attractive energy between them due to Coulomb's law is

$$\Delta E_{Coul} = -\frac{e^2}{4\pi\epsilon_0 R_e}$$

which is negative and tends to lower the total energy and stabilize the bond.

Let us estimate the energy needed to form the KF bond from neutral atoms, given the above information. The total energy needed to form the ionic bond should be

$$\Delta E_f \approx -\frac{e^2}{4\pi\epsilon_0 R_e} - EA + IE_1$$

where the first term is the energy gained due to the Coulomb attraction, and the second and third terms constitute the energy needed to transfer the electron from K to F to form ions. Substituting in the numbers:

$$IE_1 = 419 \text{ kJ/mol}$$

$$EA = 328 \text{ kJ/mol}$$

$$R_e = 2.17 \text{ \AA} = 2.17 \times 10^{-10} \text{ m}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

gives

$$\Delta E_f \approx -\frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(2.17 \times 10^{-10} \text{ m})} * 6.022 \times 10^{23} \text{ mol}^{-1} + 9.1 \times 10^4 \text{ J/mol}$$

gives the result  $-5.49 \times 10^5 \text{ J/mol}$  or  $-549 \text{ kJ/mol}$ . The fact that the energy is negative tells us that the bond is stabilized by the Coulomb attraction. The energy needed to dissociate the bond into neutral species  $K$  and  $F$  is just

$$\Delta E_d = -\Delta E_f$$

which is  $549 \text{ kJ/mol}$ . This is the energy needed to overcome the Coulomb attraction and transfer an electron from  $F^-$  to  $K^+$  to form neutral species.

This estimated dissociation energy is in qualitative agreement with the experimental value of  $498 \text{ kJ/mol}$ . However, it can never be quantitative agreement because the energy really needs to be computed using the rules of quantum mechanics, with a proper accounting of the electronic wave functions in the bond.

## Contributors and Attributions

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# 14: Lewis structures, covalent, and polar covalent bonding

## Covalent bonding and Lewis structures

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It is clear that as the atoms approach each other, electron density becomes decreasingly localized over each atom individually and increasingly delocalized over the entire molecule.

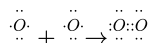
Figure 1:

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Clearly, these diagrams do not represent actual molecular geometries. In each diagram, each hydrogen has a stable doublet, while all other atoms have octets.

What does a lone pair look like? Again, we show an electron density plot for a water molecule below:

Consider, next, the molecule  $O_2$ . Since  $O$  has 6 valence electrons, if we try allowing for one shared pair, we would end up with the following Lewis structure:



Now the oxygen on the right does not have an octet. The way to rectify this is to allow a second shared pair:



Considering all shared electrons, each oxygen has an octet. The sharing of two pairs of electrons gives rise to a *double bond*, of which this is a particular example. Another way to represent it is:



What about the molecule  $N_2$ .  $N$  has 5 valence electrons, so if we try to include only 1 shared pair, the Lewis structure looks like:



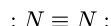
which only gives each atom 6 electrons. A double bond gives rise to:



which is only 7 electrons to each. However, sharing three pairs of electrons leads to the structure:

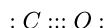


This is an example of a *triple bond*, which can be represented as



## Formal charges

Up to now, we have assumed that electrons are equally shared between the two atoms in a covalent bond. While it is true for *homonuclear* diatomic (in which the two atoms are the same species), there is no experimental basis for the assumption that this holds for *aheteronuclear* diatomic (in which the two atoms are different). To see what the consequence of this assumption is, consider the molecule  $CO$ , whose Lewis structure is easily shown to be



If the shared electrons are divided equally between the C and O atoms, then C has a total of 5 electrons (including its lone pair)



## Molecules with an odd number of electrons

The octet can only work for molecules with an even number of valence electrons. While this covers most cases, there are a few molecules that have an odd number of electrons. As an example, consider the molecule NO. N has 5 valence electrons and O has 6, giving a total of 11. Thus, one of the atoms in the Lewis structure for NO cannot have an octet. The correct Lewis structure for NO is:



which gives a formal charge of 0 to each atom. Giving an octet to N and 7 electrons to the oxygen would give higher formal charges.

## Octet deficient molecules

Some molecules are stable, even though they possess too few electrons to achieve octets for all atoms. As an example of this, consider the  $\text{BF}_3$  molecule. Applying the standard rules would lead to a Lewis structure of the form

Figure 3:

`\begin{figure}\begin{center} \leavevmode \epsfbox{lec11_fig4.ps} {\small} \end{center}\end{figure}`

which gives a double bond to Fluorine as well as a formal charge of +1. Fluorine can never have a positive formal charge, and formation of a double bond between F and B is incorrect. The way out of this mess is to deny the boron atom a full octet. Rather, we let B have a sextet, which gives a Lewis structure:

Figure 4:

`\begin{figure}\begin{center} \leavevmode \epsfbox{lec11_fig5.ps} {\small} \end{center}\end{figure}`

Although boron only has 6 electrons around it, all formal charges are 0, and the molecule is stable.

## Valence shell expansion

For molecules involving atoms in periods greater than the second, Lewis structures can become more complicated. Consider the example of the molecule  $\text{SF}_6$ .

Let us apply the rules to this case:

**Step 1:** Total valence electrons =  $6 + 6 \cdot 7 = 48$

**Step 2:** Total electrons needed for octets =  $7 \cdot 8 = 56$

**Step 3:** Total shared/bonding electrons =  $56 - 48 = 8$ .

Now we have a problem because we have 6 bonds but only 8 electrons to put in them. If each bond is to receive a pair of electrons, we would need 12 shared electrons rather than 8.

The solution to this problem is to allow for more bonding electrons. Extra bonding electrons are assigned to the central atom, S in this case, which can accommodate an *expanded valence shell* due to its relatively high atomic number. Now, step 2 becomes:

**Step 2:** Total electrons needed for 6 octets + one 12-tet = 60.

**Step 3:** Total shared/bonding electrons =  $60 - 48 = 12$ .

**Step 4:**

Figure 5:

```
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```

This example suggests that step 6 of the usual Lewis structure rules should be replaced by

**6'. Assign lone pairs to the terminal atoms to give them octets. If any electrons remain, assign them to the central atoms as lone pairs.**

Rule 5 now becomes irrelevant.

Another example is the  $I_3^-$  anion. According to the rules:

**Step 1:** Total valence electrons =  $7 \times 3 + 1 = 22$

**Step 2:** Total electrons for octets =  $8 \times 3 = 24$

**Step 3:** Total shared/bonding electrons =  $24 - 22 = 2$ .

Two electrons is not enough for the two bonds in the  $I_3^-$  ion. Thus, one of the iodines will have its valence shell expanded. We need two extra electrons, so step 2 now becomes:

**Step 2:** Total electrons for 2 octets + one 10-tet = 26.

**Step 3:** Total shared/bonding electrons =  $26 - 22 = 4$ .

The resulting Lewis structure is:

Figure 6:

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\includegraphics[scale=1.0]{ClO3+.eps}
```

Figure 7: VSEPR shapes

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\includegraphics[scale=1.0]{VSEPR_shapes.eps}
```

The reason for these assignments will become clear through a study of several examples:

**1.  $CO_2$**

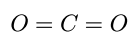
**The Lewis diagram for  $CO_2$  is**



Thus, the steric number of the central carbon is

$$SN = 2 + 0 = 2$$

and, according to the assignment table, the shape is linear:



The linear shape can be understood on the basis of the electron repulsion principle: The central carbon is surrounded by two sets of shared electron pairs, which want to achieve a maximum separation between them. The maximum separation they can achieve is at a  $180^\circ$  angle between the pairs, giving rise to the linear



# 15: Molecular geometry, coordinates, and dipole moments

## Molecular geometry and coordinates

Consider a diatomic molecule AB. Imagine fixing this molecule at a very specific spatial location, as shown below:

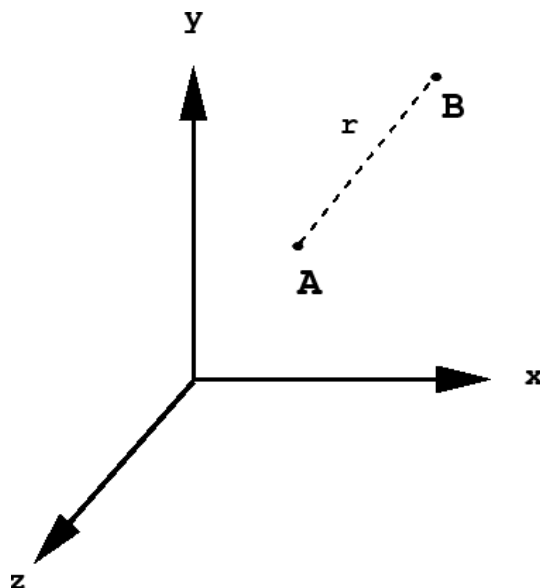


Figure 1

To locate the molecule so specifically, we would need to give the  $x$ ,  $y$ , and  $z$  coordinates of each of its atoms, i.e.,

$$\begin{aligned}(x_A, y_A, z_A) &= r_A \\ (x_B, y_B, z_B) &= r_B\end{aligned}$$

which is a total of 6 numbers.

However, we note that the molecule looks the same, no matter where in space it is located. This is called *translational invariance*, and it implies that we can give only the coordinates of one of the atoms *relative* to the other, which is equivalent to giving the vector difference between  $r_B$  and  $r_A$  (or vice-versa), which we will call the vector  $r$ :

$$r = r_B - r_A = (x, y, z)$$

which is only 3 numbers. This is the same as arbitrarily placing atom A at the origin of our  $xyz$  coordinate system.

We also note that the spatial orientation of the molecule is arbitrary, since the molecule looks the same at any viewing angle. For a diatomic, its orientation can be specified by giving two angles: the angle it makes with the  $z$ -axis and the angle of its projection onto the  $xy$  plane with the  $x$ -axis. The choice of these angles is arbitrary. This leaves only 1 number left, which is the distance between A and B, called the molecule's *bond length*.

$$\begin{aligned}r &= |r| = \sqrt{x^2 + y^2 + z^2} \\ &= |r_B - r_A| = \sqrt{(x_B - x_A)^2 + (y_B - y_A)^2 + (z_B - z_A)^2}\end{aligned}$$

This is an *internal degree of freedom* and is the only important number we need to give in order to convey the geometry of the diatomic.

In spite of this simplification, it is often necessary to specify *all* of the coordinates of the atoms in a molecule. Molecular modeling packages, which are becoming increasingly important in chemical research, require a full set of coordinates for each atom as input. Similarly, molecular data banks, such as the protein data bank (PDB) will give molecular structures as files of  $x$ ,  $y$ , and  $z$

coordinates. Thus, being able to determine a set of coordinates given only bond lengths and bond angles, and conversely being able to determine bond lengths and angles from a set of coordinates is an extremely important skill. A few examples of how to do this will be illustrated below.

### Example 1

The diatomic  $AB$ . How do we determine a set of coordinates for  $AB$  given only its bond length  $r$ . Since its absolute location in space and its orientation are arbitrary, any set of coordinates that reproduces the correct bond length will suffice. Thus, since a diatomic is linear, we may place it along one of the axes of our coordinate system with one of the atoms at the origin:

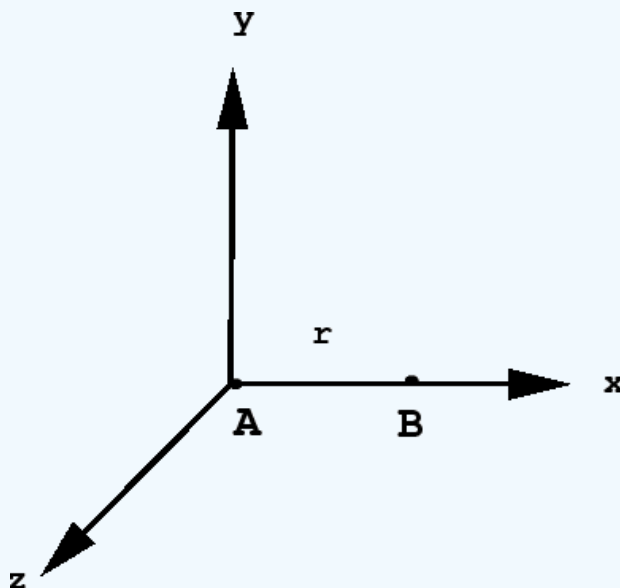


Figure 2

Now we see that the coordinates of atom  $A$  will simply be

$$r_A = (0, 0, 0)$$

and the coordinates of atom  $B$ , since  $B$  lies on the  $x$ -axis a distance  $r$  away from  $A$ , will be

$$r_B = (r, 0, 0)$$

Clearly, this set of coordinates reproduces the correct bond length:

$$|r_B - r_A| = \sqrt{r^2 + 0^2 + 0^2} = r$$

Thus, for the molecule  $HCl$ , whose bond length is  $r = 1.284 \text{ \AA}$ , a set of coordinates could be

$$\begin{aligned} r_H &= (0, 0, 0) \\ r_{Cl} &= (1.284, 0, 0) \end{aligned}$$

in  $\text{\AA}$ . This is just one possibility. We could have chosen either atom to be at the origin (or anywhere else in space for that matter), and chosen the bond to lie along any axis (or not along any particular axis), as we choose, so long as the correct bond length is reproduced.

### Example 2

Water,  $H_2O$ : The geometry of water is bent (we will see how to determine this later), with a bond angle of  $104.5^\circ$  and an  $OH$  bond length of approximately  $1.0 \text{ \AA}$ .

To determine a set of coordinates for  $H_2O$ , we note that the molecule is planar, so we may choose it to lie in the  $xy$  plane. We will place the oxygen at the origin with the hydrogens as shown below:

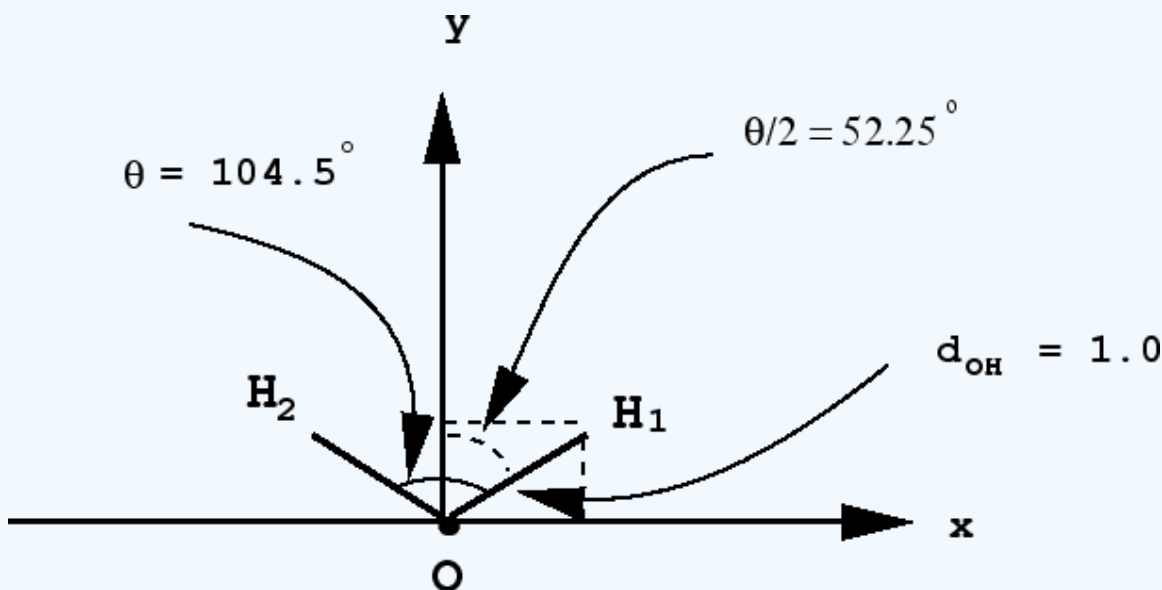


Figure 3

The coordinates of the oxygen can be written down immediately:

$$r_O = (0, 0, 0)$$

For each of the hydrogens, note that the  $y$ -axis bisects the angle, giving two right triangles. An  $OH$  bond forms the hypotenuse of one of these triangles, so that the  $x$  and  $y$  coordinates will be determined from the sine and cosine of the angle  $\theta/2$ , as can be shown using simple trigonometry:

$$\begin{aligned} r_{H_1} &= (d_{OH} \sin \theta/2, d_{OH} \cos \theta/2, 0) = (0.7907, 0.6122, 0) \\ r_{H_2} &= (-d_{OH} \sin \theta/2, d_{OH} \cos \theta/2, 0) = (-0.7907, 0.6122, 0) \end{aligned}$$

To verify that the bond lengths are correctly reproduced, we compute the magnitudes of the vector differences  $r_{H_1} - r_O$  and  $r_{H_2} - r_O$ :

$$\begin{aligned} |r_{H_1} - r_O| &= \sqrt{(0.7907)^2 + (0.6122)^2 + 0^2} = 1.0 \text{ \AA} \\ |r_{H_2} - r_O| &= \sqrt{(0.7907)^2 + (0.6122)^2 + 0^2} = 1.0 \text{ \AA} \end{aligned}$$

In order to verify that the bond angle is correct, we note that the angle between two vectors  $a$  and  $b$  is given by the formula:

$$\theta_{ab} = \cos^{-1} \left( \frac{a \cdot b}{|a||b|} \right)$$

where  $a \cdot b$  is the *dot product* of  $a$  and  $b$  defined to be

$$a \cdot b = a_x b_x + a_y b_y + a_z b_z$$

Thus, the  $H_1 - O - H_2$  angle is given by

$$\begin{aligned} \theta_{H_1-O-H_2} &= \cos^{-1} \left( \frac{(r_{H_1} - r_O) \cdot (r_{H_2} - r_O)}{|r_{H_1} - r_O| |r_{H_2} - r_O|} \right) \\ &= \cos^{-1} \left( \frac{-(0.7907)^2 + (0.6122)^2}{1.0 * 1.0} \right) \\ &= \cos^{-1}(-0.2504) = 104.5^\circ \end{aligned}$$

## Periodic trends in bond lengths and bond energies

Within a group of the periodic table, bond lengths tend to increase with increasing atomic number  $Z$ . Consider the [Group 17](#) elements:

$$\begin{array}{ll} F_2 & d = 141.7 \text{ pm} \\ Cl_2 & d = 199.1 \text{ pm} \\ Br_2 & d = 228.6 \text{ pm} \\ I_2 & d = 266.9 \text{ pm} \end{array}$$

which corresponds to an increased valence shell size, hence increased electron-electron repulsion. An important result from experiment, which has been corroborated by theory, is that bond lengths tend not to vary much from molecule to molecule. Thus, a  $CH$  bond will have roughly the same value in methane,  $CH_4$  as it will in aspirin,  $C_9H_8O_4$ .

Bond dissociation energies were discussed in the last lecture in the context of ionic bonds. There we used the symbol  $\Delta E_d$  measured in  $\text{kJ/mol}$ . This measures the energy required to break a mole of a particular kind of bond. A similar periodic trend exists for bond dissociation energies. Consider the hydrogen halides:

$$\begin{array}{lll} HF & \Delta E_d = 565 \text{ kJ/mol} & d = 0.926 \text{ pm} \\ HCl & \Delta E_d = 429 \text{ kJ/mol} & d = 128.4 \text{ pm} \\ HBr & \Delta E_d = 363 \text{ kJ/mol} & d = 142.4 \text{ pm} \\ HI & \Delta E_d = 295 \text{ kJ/mol} & d = 162.0 \text{ pm} \end{array}$$

Thus, as bond lengths increase with increasing  $Z$ , there is a corresponding decrease in the bond dissociation energy.

$CC$  bonds are an exception to the rule of constancy of bond lengths across different molecules. Because  $CC$  bonds can be single, double, or triple bonds, some differences can occur. For example, consider the  $CC$  bond in the molecules ethane ( $C_2H_6$ ), ethylene ( $C_2H_4$ ) and acetylene ( $C_2H_2$ ):

$$\begin{array}{lll} C_2H_6 & (\text{single}) & d = 1.536 \text{ \AA} \quad \Delta E_d = 345 \text{ kJ/mol} \\ C_2H_4 & (\text{double}) & d = 133.7 \text{ pm} \quad \Delta E_d = 612 \text{ kJ/mol} \\ C_2H_2 & (\text{triple}) & d = 126.4 \text{ pm} \quad \Delta E_d = 809 \text{ kJ/mol} \end{array}$$

The greater the *bond order*, i.e., number of shared electron pairs, the greater the dissociation energy. The same will be true for any kind of bond that can come in such different "flavors", e.g.,  $NN$  bonds,  $OO$  bonds,  $NO$  bonds,  $CO$  bonds, etc.

## Polar covalent bonds

Most real chemical bonds in nature are neither truly covalent nor truly ionic. Only homonuclear bonds are truly covalent, and nearly perfect ionic bonds can form between group I and group VII elements, for example,  $KF$ . Generally, however, bonds are partially covalent and partially ionic, meaning that there is partial transfer of electrons between atoms and partial sharing of electrons.

In order to quantify how much ionic character (and how much covalent character) a bond possesses, electronegativity differences between the atoms in the bond can be used. We have already seen one method for estimating atomic electronegativities, the Mulliken method. In 1936, Linus Pauling came up with another method that forms the basis of our understanding of electronegativity today.

### Pauling's method

Recall the Mulliken's method was based on the arithmetic average of the first ionization energy  $IE_1$  and the electron affinity  $EA$ . Both of these energies are properties of individual atoms, hence this method is appealing in its simplicity. However, there is no information about bonding in the Mulliken method. Pauling's method includes such information, and hence is a more effective approach.

To see how the Pauling method works, consider a diatomic  $AB$ , which is polar covalent. Let  $\Delta E_{AA}$  and  $\Delta E_{BB}$  be the dissociation energies of the diatomics  $A_2$  and  $B_2$ , respectively. Since  $A_2$  and  $B_2$  are purely covalent bonds, these two dissociation energies can be used to estimate the pure covalent contribution to the bond  $AB$ . Pauling proposed the geometric mean of  $\Delta E_{AA}$  and  $\Delta E_{BB}$ , this being more sensitive to large differences between these energies than the arithmetic average:

$$\text{pure covalent contribution} = \sqrt{\Delta E_{AA}\Delta E_{BB}}$$

If  $\Delta E_{AB}$  is the true bond dissociation energy, then the difference

$$\Delta E_{AB} - \sqrt{\Delta E_{AA}\Delta E_{BB}}$$

is a measure of the ionic contribution. Let us define this difference to be  $\Delta$ :

$$\Delta = \Delta E_{AB} - \sqrt{\Delta E_{AA}\Delta E_{BB}}$$

Then Pauling defined the electronegativity difference  $\chi_A - \chi_B$  between atoms  $A$  and  $B$  to be

$$\chi_A - \chi_B = 0.102\sqrt{\Delta}$$

where  $\Delta$  is measured in  $\text{kJ/mol}$ , and the constant  $0.102$  has units  $\text{mol}^{1/2}/\text{kJ}^{1/2}$ , so that the electronegativity difference is dimensionless. Thus, with some extra input information, he was able to generate a table of atomic electronegativities that are still used today ([Table A2](#)).

To use the electronegativities to estimate degree of ionic character, simply compute the absolute value of the difference for the two atoms in the bond. As an example, consider again the hydrogen halides:

$$\begin{array}{ll} HF & |\chi_F - \chi_H| = 1.78 \\ HCl & |\chi_{Cl} - \chi_H| = 0.96 \\ HBr & |\chi_{Br} - \chi_H| = 0.76 \\ HI & |\chi_I - \chi_H| = 0.46 \end{array}$$

As the electronegativity difference decreases, so does the ionic character of the bond. Hence its covalent character increases.

## Electric dipole moment

In a nearly perfect ionic bond, such as  $KF$ , where electron transfer is almost complete, representing the molecule as



is a very good approximation, since the charge on the potassium will be approximately  $1e$  and the charge on the fluorine will be approximately  $-1e$ . For a polar covalent bond, such as  $HF$ , in which only partial charge transfer occurs, a more accurate representation would be



where  $\delta$ , expressed in units of  $(e)$ , is known as a *partial charge*. It suggests that a fraction of an electron is transferred, although the reality is that there is simply a little more electron density on the more electronegative atom and a little less on the electropositive atom.

How much charge is actually transferred can be quantified by studying the *electric dipole moment* of the bond, which is a quantity that can be measured experimentally. The electric dipole moment of an assembly of charges  $Q_1, Q_2, \dots, Q_N$  having positions  $r_1, r_2, \dots, r_N$  is defined to be

$$\mu = Q_1r_1 + Q_2r_2 + \dots + Q_Nr_N = \sum_{i=1}^N Q_i r_i$$

Thus, for a diatomic with charges  $Q_1 = Q = \delta e$  and  $Q_2 = -Q = -\delta e$  on atoms 1 and 2, respectively, the dipole moment, according to the definition, would be

$$\begin{aligned} \mu &= Q_1r_1 + Q_2r_2 \\ &= Qr_1 - Qr_2 \\ &= Q(r_1 - r_2) \end{aligned}$$

Hence, the magnitude of the dipole moment is

$$\mu = |\mu| = Q|r_1 - r_2| = QR$$

where  $R$  is the bond length. As an example, consider  $HF$ , which has a partial charge on  $H$  of  $0.41e$ , which means  $\delta = 0.41$ , and a bond length of  $0.926 \text{ \AA}$ . Thus, the magnitude of the dipole moment is

$$|\mu| = 0.41(1.602 \times 10^{-19} C)(0.926 \times 10^{-10} m) = 6.08 \times 10^{-30} C \cdot m$$

Thus, the units of the dipole moment are Coulomb  $\cdot$  meters. However, as this example makes clear, this is a very large unit and awkward to work with for molecules. A more convenient unit is the Debye ( $D$ ), defined to be

$$1D = 3.336 \times 10^{-30} \text{ Coulomb} \cdot \text{meters}$$

1  $D$  is actually the dipole moment of two charges  $+e$  and  $-e$  separated by a distance of  $0.208 \text{ \AA}$ . Thus, for a diatomic with partial charges  $+\delta$  and  $-\delta$ , the dipole moment in  $D$  is given by

$$\mu(D) = \frac{\delta * R(\text{\AA})}{0.2082 \text{ \AA} D^{-1}}$$

and the percent ionic character is defined in terms of the partial charge  $\delta$  by

$$\text{percent ionic character} = 100\% * \delta$$

As an example, consider  $HF$  again, for which  $\delta = 0.41$ . The bond length is  $R = 0.926 \text{ \AA}$ . Thus, its dipole moment will be

$$\mu(D) = \frac{0.41 * 0.926 \text{ \AA}}{0.2082 \text{ \AA} D^{-1}} = 1.82D$$

and its percent ionic character is 41%.

## Experimental importance of the dipole moment

The electric dipole moment lies at the heart of a widely used experimental method for probing the vibrational dynamics of a system. If a system is exposed to a monochromatic electromagnetic field from a laser, then the electric dipole moment couples to the electric field component  $E(r, t)$  in such a way that the energy is

$$\mathcal{E} = -\mu \cdot \mathbf{E}(r, t)$$

In general, the electric field is a function of space and time having the general wave form

$$\mathbf{E}(r, t) = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

where  $\omega$  is the frequency of the field  $\omega = 2\pi c/\lambda$ , with  $c$  the speed of light and  $\lambda$  the wavelength, and  $k$  is called the wave vector,  $|k| = 2\pi/\lambda$ , and the direction of  $k$  is the direction of wave propagation (this will be covered in more detail next semester). In most experiments, the wavelength is long enough compared to the size of the system studied that one can take the electric field to be spatially constant and consider only the time dependence. In this case,

$$\mathcal{E} \approx -\mu \cdot E_0 \cos(\omega t)$$

Thus, the electric field varies as a simple cosine function at a single frequency  $\omega$ .

The importance of the coupling between the dipole moment and the time-dependent electric field is that the frequency of the field can be varied over a range of natural frequencies in a given chemical system. Thus, chemical bonds vibrate at a particular natural frequency, three-atom bending modes have their characteristic frequency, etc. What one seeks in this experiment is a "report" of the natural frequencies in the system, since from such a report, one can often tell one local chemical environment from another.

By sweeping through a range of frequencies, the coupling of the field to the dipole moment suggests that the local charge distribution will respond to the oscillations of the field at the field frequency. Thus, if the field frequency is "tuned" to be that of a bond stretch, the charge distribution in the bond will be stimulated and report on the frequency of the bond, etc. At each

frequency, the intensity  $I$  of the response can be measured, and a plot of  $I$  vs.  $\omega$  is produced. Such a plot is called an *infrared spectrum*. The figure below shows the infrared spectrum for liquid water (left) and for 13 M (blue) and 1 M (red) KOH solutions (right).

\includegraphics[scale=0.5]{Water\_IR.eps} \includegraphics[scale=0.5]{KOH\_IR.eps}

In the left panel, the solid curve is the water spectrum obtained from a computer simulation, while the dashed curve is the experimentally obtained spectrum. On the right, the red and blue curves are from computer simulations, while the inset at the upper right is the experimentally measured spectrum. The peaks in the spectra occur at particular vibrational frequencies in the system. The water spectrum shows very distinct bands, while the spectrum of the KOH solutions shows both bands and continuum regions. The latter arise from the fact that protons can be transferred from water to hydroxide. As the proton moves across a hydrogen bond between water and the hydroxide ion, the vibrations in the bond sweep through a range of frequencies as the proton is transferred, giving rise to the continuum. This feature in the infrared spectra of solutions of strong acids and bases is known as *Zundel polarization*. More information on how we compute these spectra and how the computer simulation are performed can be found in the following research papers:

- [H. S. Lee and M. E. Tuckerman, \*J. Chem. Phys.\* \*\*126\*\*, 164501 \(2007\)](#)
- [Z. W. Zhu and M. E. Tuckerman, \*J. Phys. Chem. B\* \*\*106\*\*, 8009 \(2002\).](#)

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## 16: The Born-Oppenheimer approximation and the hydrogen molecule ion

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*. The density functional theory referred to in the previous lecture, for which the chemistry Nobel prize was given in 1998, has had a tremendous impact in quantum chemistry, with some of the papers in this subject having acquired some 10,000 citations each since their publication. In fact, the 1998 chemistry Nobel prize was shared between Walter Kohn, one of the inventors of density functional theory and John Pople, the developer of a commonly used quantum chemistry software package.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry. It should be noted that these packages use a series of approximations to solve the Schrödinger equation because for all but the simplest of molecules, exact solutions are not available. We will discuss some of these methods, but first we need to introduce some of the underlying theory.

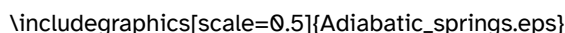
### The Born-Oppenheimer Approximation

In this section, we will discuss one of the most important and fundamental approximations in molecular quantum mechanics. This approximation was developed by Max Born and J. Robert Oppenheimer in 1927. We will consider a very general molecule with  $N$  nuclei and  $M$  electrons. The coordinates of the nuclei are  $R_1, \dots, R_N$ . The coordinates of the electrons are  $r_1, \dots, r_M$ , and their spin variables are  $S_{z,1}, \dots, S_{z,M}$ . For shorthand, we will denote the complete set of nuclear coordinates as  $R$  and the set of electrons coordinates as  $r$  and  $x$  the complete set of electron coordinates and spin variables. The total molecular wave function  $\Psi(x, R)$  depends on  $3N + 4M$  variables, which makes it a very cumbersome object to deal with. The Born-Oppenheimer approximation leads to a very important simplification of the wave function.

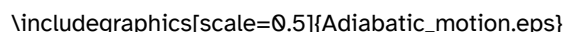
If we could neglect the electron-nuclear interaction, then the wave function would be a simple product  $\Psi(x, R) = \psi_{elec}(r)\psi_{nuc}(R)$ . However, we cannot neglect this term, but it might still be possible to write the wave function as a product. We note, first, that most nuclei are 3-4 orders of magnitude heavier than an electron. For the lightest nucleus, the proton,

$$m_p \approx 2000m_e$$

This mass difference is large enough to have important physical consequences. Let us think classically about this mass difference first. If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:



Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle, which is attached to a fixed wall by a spring. The small, light particle, which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it. The figure below (bottom panel) illustrates this:



In this illustration, when the heavy particle moves even a tiny amount, the light particle executes many oscillations around the heavy particle. Thus, we see that the light particle moves quite a bit, and we can think of the light particle as generating "on the fly" an effective potential  $V_{eff}$  for the heavy particle, at least at the present position of the heavy particle. What we can conclude, therefore, is that we can approximately fix the position of the heavy particle and just allow the light particle to move around before we advance the heavy particle to its next position.

How do the different mass scales of electrons and nuclei manifest themselves in the time-independent Schrödinger equation? Light particles, such as electrons, tend to have very diffuse, delocalized wave functions, while heavy particles, such as the nuclei, tend to have wave functions that are very localized about the classical positions. This is illustrated in the figure below:

\includegraphics[scale=0.5]{charge.eps}

Figure 1: Crude picture of matter. Nuclear wave functions are shown above the axis, electronic wave functions are shown below.

Thus, taking the idea of solving the electronic problem for fixed nuclear positions seriously, we can write the molecular wave function as

$$\Psi^{(mol)}(x, R) = \psi^{(elec)}(x, R)\psi^{(nuc)}(R)$$

which suggests that the electronic wave function  $\psi^{(elec)}(x, R)$  is solved using the nuclear positions  $R$  simply as parameters that characterize the wave function in the same way that the electron mass and electron charge do. This is not an exact wave function for the molecule but an approximate one. Hence, we call this the *Born-Oppenheimer* approximation to the wave function. The total classical energy of the molecule is

$$K_e + K_n + V_{ee}(r) + V_{en}(r, R) + V_{nn}(R) = E$$

where  $K_e$  and  $K_n$  are the electronic and nuclear kinetic energies. Therefore, the total Hamiltonian of the molecule is

$$\hat{H} = \hat{K}_e + \hat{K}_n + V_{ee}(r) + V_{en}(r, R) + V_{nn}(R)$$

where  $\hat{K}_e$  and  $\hat{K}_n$  are the kinetic energy operators that result from substituting momenta for derivatives. Thus,  $\hat{K}_e$  and  $\hat{K}_n$  contain second derivatives with respect to electronic and nuclear coordinates, respectively. The details of these operators are not that important for this discussion.

We now write the total molecular Hamiltonian as

$$\hat{H} = \hat{H}_{elec} + \hat{H}_{nucl}$$

where we assign

$$\begin{aligned}\hat{H}_{elec} &= \hat{K}_e + V_{ee}(r) + V_{en}(r, R) \\ \hat{H}_{nucl} &= \hat{K}_n + V_{nn}(R)\end{aligned}$$

If we now substitute this into the Schrödinger equation, we obtain

$$[\hat{K}_e + \hat{K}_n + V_{ee}(r) + V_{nn}(R) + V_{en}(r, R)]\psi^{(elec)}(x, R)\psi^{(nuc)}(R) = E\psi^{(elec)}(x, R)\psi^{(nuc)}(R)$$

Let us consider how the electronic and nuclear kinetic energy operators act on the wave function.  $\hat{K}_e$  contains derivatives with respect only to electronic coordinates. Thus, it has no effect on the nuclear wave function, and we can write

$$\hat{K}_e\psi^{(elec)}(x, R)\psi^{(nuc)}(R) = \psi^{(nuc)}(R)\hat{K}_e\psi^{(elec)}(x, R)$$

The operator  $\hat{K}_n$  contains derivatives with respect to nuclear coordinates, thus it affects both parts of the wave function:

$$\hat{K}_n\psi^{(elec)}(x, R)\psi^{(nuc)}(R) = \psi^{(nuc)}(R)\hat{K}_n\psi^{(elec)}(x, R) + \psi^{(elec)}(x, R)\hat{K}_n\psi^{(nuc)}(R) + \text{mixed derivate term}$$

The last term arises from an application of the product rule using the fact that  $\hat{K}_n \sim d^2/dR^2$ . What is important here is that if the nuclear wave function is highly localized, then its curvature is high in the vicinity of the nucleus, and hence,  $\hat{K}_n\psi^{(nuc)}$  is very large compared to  $\hat{K}_n\psi^{(elec)}$  since  $\psi^{(elec)}$  changes much less dramatically spatially due to the delocalized nature of the electronic wave function. Thus, we need only keep the term in the above equation that contains  $\hat{K}_n\psi^{(nuc)}$ :

$$\hat{K}_n\psi^{(elec)}(x, R)\psi^{(nuc)}(R) \approx \psi^{(elec)}(x, R)\hat{K}_n\psi^{(nuc)}(R)$$

Using this fact in the Schrödinger equation, we can write the equation as

$$\psi^{(nuc)}(R)[\hat{K}_e + V_{ee}(r) + V_{en}(r, R)]\psi^{(elec)}(x, R) + \psi^{(elec)}(x, R)[\hat{K}_n + V_{nn}(R)]\psi^{(nuc)}(R) = E\psi^{(elec)}(x, R)\psi^{(nuc)}(R)$$

or

$$\psi^{(nuc)}(R)\hat{H}_{elec}(r, R)\psi^{(elec)}(x, R) + \psi^{(elec)}(x, R)\hat{H}_{nuc}(R)\psi^{(nuc)}(R) = E\psi^{(elec)}(x, R)\psi^{(nuc)}(R)$$

We now divide both sides by  $\psi^{(elec)}(x, R)\psi^{(nuc)}(R)$ , which gives

$$\frac{\hat{H}_{elec}(r, R)\psi^{(elec)}(x, R)}{\psi^{(elec)}(x, R)} = E - \frac{\hat{H}_{nuc}\psi^{(nuc)}(R)}{\psi^{(nuc)}(R)}$$

Note that the right side depends only on the nuclear coordinates  $R$ , which means that we can write compactly as some function  $\varepsilon(R)$ . Hence, we obtain

$$\frac{\hat{H}_{elec}(r, R)\psi^{(elec)}(x, R)}{\psi^{(elec)}(x, R)} = \varepsilon(R)$$

or

$$\hat{H}_{elec}(r, R)\psi^{(elec)}(x, R) = \varepsilon(R)\psi^{(elec)}(x, R)$$

which is called the electronic Schrödinger equation. it yields a set of wave functions  $\psi_{\alpha}^{(elec)}(x, R)$  and energies  $\varepsilon_{\alpha}(R)$  characterized by a set of quantum numbers  $\alpha$ , which is the full set of quantum numbers needed to characterize the wave function, e.g.  $n, l, m$  for hydrogen. Thus, the electronic Schrödinger equation can be written as

$$\hat{H}_{elec}(r, R)\psi_{\alpha}^{(elec)}(x, R) = \varepsilon_{\alpha}(R)\psi_{\alpha}^{(elec)}(x, R)$$

Note that the potential energy  $V_{en}(r, R)$  depends on the electronic coordinates and the *fixed* nuclear coordinates  $R$ . Thus, the nuclear coordinates can be thought of as additional parameters in the potential energy. Alternatively, we can think of the nuclear as providing a fixed background potential energy in addition to the internal electron-electron repulsion  $V_{ee}(r)$  that governs the shape of the electronic wave function.

Now the nuclear part comes from setting the right side of the full Schrödinger equation equal to  $\varepsilon_{\alpha}(R)$ , which yields:

$$E - \frac{\hat{H}_{nuc}\psi^{(nuc)}(R)}{\psi^{(nuc)}(R)} = \varepsilon_{\alpha}(R)$$

and if we multiply by  $\psi^{(nuc)}(R)$ , we obtain the nuclear Schrödinger equation

$$\begin{aligned} [\hat{H}_{nuc} + \varepsilon_{\alpha}(R)]\psi^{(nuc)}(R) &= E\psi^{(nuc)}(R) \\ [\hat{K}_n + V_{nn}(R) + \varepsilon_{\alpha}(R)]\psi^{(nuc)}(R) &= E\psi^{(nuc)}(R) \end{aligned}$$

The Schrödinger equations for the electronic and nuclear part of the wave function are not exact but approximate based on the separation of electronic and nuclear degrees of freedom we assume can be made based on the mass differential.

Two interesting facts about the approximate Schrödinger equations should be noted. First, the electronic Schrödinger equation yields a set of energy levels  $\varepsilon_{\alpha}(R)$  that depend on the nuclear configuration. Thus, at each nuclear configuration we choose, we get a *different* set of energy levels. These energy levels change continuously with the nuclear configuration, in fact. At the same time, the nuclear Schrödinger equation involves a potential energy with two terms  $V_{nn}(R) + \varepsilon_{\alpha}(R)$ , i.e. the nuclear-nuclear repulsion plus the electronic energy level  $\varepsilon_{\alpha}$  as a function of  $R$ . Therefore, there is a different nuclear Schrödinger equation for *each* electronic energy level. The potential energies  $V_{nn}(R) + \varepsilon_{\alpha}(R)$  are called *Born-Oppenheimer* potential energies or *Born-Oppenheimer* surfaces. They are surfaces (or hypersurfaces) because they must be viewed as continuous functions of  $R$  (Figure 16.1):

\includegraphics[scale=5.0]{BO\_surfaces.eps}

**Figure 16.1:** Potentials energies surfaces

The potential energy  $V_{nn}(R) + \varepsilon_{\alpha}(R)$  determines the geometry of the molecule by minimization, and the nuclear probability distribution by solution of the nuclear Schrödinger equation. It also determines the nuclear dynamics if we solve the nuclear time-dependent Schrödinger equation. Thus,  $\varepsilon_{\alpha}(R)$ , the electronic energy levels, are of utmost importance in molecular quantum mechanics. For this reason, we need to understand the distributions of electrons in molecules.

Incidentally, we could now introduce a further approximation in which we treat the nuclei as classical particles with a potential energy  $V_{nn}(R) + \varepsilon_\alpha(R)$ . The nuclei would then move as classical point particles via Newton's Second Law, which would now take the form

$$M \frac{d^2 R}{dt^2} = -\frac{d}{dR} [V_{nn}(R) + \varepsilon_\alpha(R)]$$

## Solving The Hydrogen Molecule Cation Exactly

The hydrogen molecule ion  $H_2^+$  is the *only* molecule for which we can solve the electronic Schrödinger equation exactly. Note that it has just one electron! In fact, there are no multi-electron molecules we can solve exactly. Thus from  $H_2$  on up to more complicated molecules, we only have approximate solutions for the allowed electronic energies and wave functions. Before we discuss these, however, let us examine the exact solutions for  $H_2^+$  starting with a brief outline of how the exact solution is carried out.

The figure below shows the geometry of the  $H_2^+$  molecule ion and the coordinate system we will use.

`\includegraphics[scale=0.5]{H2plus.eps}`

The two protons are labeled A and B, and the distances from each proton to the one electron are  $r_A$  and  $r_B$ , respectively. Let  $R$  be the distance between the two protons (this is the only nuclear degree of freedom that is important, and the electronic wave function will depend parametrically only on  $R$ ). The coordinate system is chosen so that the protons lie on the z-axis one at a distance  $R/2$  above the  $xy$  plane and one at a distance  $-R/2$  below the  $xy$  plane (see figure). The classical energy of the electron is

$$\frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_B} \right) = E$$

The nuclear-nuclear term  $V_{nn}(R) = e^2/4\pi\epsilon_0 R$  is a constant, and we can define the potential energy relative to this quantity.

The energy is not a simple function of energies for the  $x$ ,  $y$ , and  $z$  directions, so we try another coordinate system to see if we can simplify the problem. In fact, this problem has a natural cylindrical symmetry (analogous to the spherical symmetry of the hydrogen atom) about the z-axis. Thus, we try cylindrical coordinates. In cylindrical coordinates the distance of the electron from the z-axis is denoted  $\rho$ , the angle  $\phi$  is the azimuthal angle, as in spherical coordinates, and the last coordinate is just the Cartesian  $z$  coordinate. Thus,

$$x = \rho \cos \phi \quad y = \rho \sin \phi \quad z = z$$

Using right triangles, the distance  $r_A$  and  $r_B$  can be shown to be

$$r_A = \sqrt{\rho^2 + (R/2 - z)^2} \quad r_B = \sqrt{\rho^2 + (R/2 + z)^2}$$

The classical energy becomes

$$\frac{p_\rho^2}{2m_e} + \frac{p_\phi^2}{2m_e \rho^2} + \frac{p_z^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{\sqrt{\rho^2 + (R/2 - z)^2}} + \frac{1}{\sqrt{\rho^2 + (R/2 + z)^2}} \right) = E$$

First, we note that the potential energy does not depend on  $\phi$ , and the classical energy can be written as a sum  $E = \varepsilon_{\rho,z} + \varepsilon_\phi$  of a  $\rho$  and  $z$  dependent term and an angular term. Moreover, angular momentum is conserved as it is in the hydrogen atom. However, in this case, only *one* component of the angular momentum is actually conserved, and this is the z-component, since the motion is completely symmetric about the z-axis. Thus, we have only certain allowed values of  $L_z$ , which are  $m\hbar$ , as in the hydrogen atom, where  $m = 0, \pm 1, \pm 2, \dots$ . The electronic wave function (now dropping the "(elec)" label, since it is understood that we are discussing *only* the electronic wave function), can be written as a product

$$\psi(\rho, \phi, z) = G(\rho, z)y(\phi)$$

and  $y(\phi)$  is given by

$$y_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

which satisfies the required boundary condition  $y_m(0) = y_m(2\pi)$ . Unfortunately, what is left in  $\rho$  and  $z$  is still not that simple. But if we make one more change of coordinates, the problem simplifies. We introduce two new coordinates  $\mu$  and  $\nu$  defined by

$$\mu = \frac{r_A + r_B}{R} \quad \nu = \frac{r_A - r_B}{R}$$

Note that when  $\nu = 0$ , the electron is in the  $xy$  plane. Thus,  $\nu$  is analogous to  $z$  in that it varies most as the electron moves along the  $z$ -axis. The presence or absence of a node in the  $xy$  plane will be an important indicator of wave functions that lead to a chemical bond in the molecule or not. The coordinate  $\mu$ , on the other hand, is minimum when the electron is on the  $z$ -axis and grows as the distance of the electron from the  $z$ -axis increases. Thus,  $\mu$  is analogous to  $\rho$ . The advantage of these coordinates is that the wave function turns out to be a simple product

$$\psi(\mu, \nu, \phi, R) = M(\mu)N(\nu)y(\phi)$$

which greatly simplifies the problem and allows the exact solution.

The mathematical structure of the exact solutions is complex and nontransparent, so we will only look at these graphically, where we can gain considerably insight. First, we note that the quantum number  $m$  largely determines how the solutions appear. First, let us introduce the nomenclature for designating the orbitals (solutions of the Schrödinger equation, wave functions) of the system

1. If  $m = 0$ , the orbitals are called  $\sigma$  orbitals, analogous to the  $s$  orbitals in hydrogen.
2. If  $m = 1$ , the orbitals are called  $\pi$  orbitals, analogous to the  $p$  orbitals in hydrogen.
3. If  $m = 2$ , the orbitals are called  $\delta$  orbitals, analogous to the  $d$  orbitals in hydrogen.
4. If  $m = 3$ , the orbitals are called  $\phi$  orbitals, analogous to the  $f$  orbitals in hydrogen.

These orbitals are known as *molecular orbitals* because they describe the electronic wave functions of an entire molecule. There are four designators that we use to express each molecular orbital:

- I. A greek letter,  $\sigma, \pi, \delta, \phi, \dots$  depending on the quantum number  $m$ .
- II. A subscript qualifier  $g$  or  $u$  depending on how an orbital  $\psi$  behaves with respect to a spatial reflection or *parity* operation  $r \rightarrow -r$ . If

$$\psi(-r) = \psi(r)$$

then  $\psi(r)$  is an even function of  $r$ , so we use the " $g$ " designator, where  $g$  stands for the German word *gerade*, meaning "even". If

$$\psi(-r) = -\psi(r)$$

then  $\psi(r)$  is an odd function of  $r$ , and we use the " $u$ " designator, where  $u$  stands for the German word *ungerade*, meaning "odd".

- III. An integer  $n$  in front of the Greek letter to designate the energy level. This is analogous to the integer we use in atomic orbitals ( $1s, 2s, 2p, \dots$ ).
- IV. An asterisk or no asterisk depending on the presence or absence of nodes between the nuclei. If there is significant amplitude between the nuclei, then the orbital favors a chemical bond, and the orbital is called a bonding orbital. If there is a node between the nuclei, the orbital does not favor bonding, and the orbital is called an antibonding orbital.

So, the first few orbitals, in order of increasing energy are:

$$1\sigma_g, 1\sigma_u^*, 2\sigma_g, 2\sigma_u^*, 1\pi_u, 3\sigma_g, 1\pi_g^*, 3\sigma_u$$

These orbitals are depicted in the figure below:

\includegraphics[scale=0.5]{H2P\_MOs\_1.eps} \includegraphics[scale=0.5]{H2P\_MOs\_2.eps}

The  $1\sigma_g$  and  $1\sigma_u^*$  orbitals are the lowest in energy, however, note that the  $1\sigma_u^*$  contains one more node than the  $1\sigma_g$  orbital, hence it has a higher energy. Similarly for the  $2\sigma_g$  and  $2\sigma_u^*$  orbitals. The former has two nodes while the latter has three and, therefore, it is of higher energy. The next set of orbitals are displayed in the right panel. In this set of orbitals, the  $1\pi_u$  is the lowest energy with a single node. The number of nodes increases as we go up in energy in this subset of orbitals. In addition, in all of the orbitals, the nodal structure reveals the bonding/antibonding character of each orbital. When there is significant amplitude between the nuclei, the orbital is a bonding orbital, otherwise, when there is a node there, it is an antibonding orbital.

What do bonding and antibonding orbitals mean in terms of the corresponding energy levels. Consider just the first two energy levels  $\varepsilon_0(R)$  and  $\varepsilon_1(R)$  corresponding to the  $1\sigma_g$  and  $1\sigma_u^*$  orbitals. The ground-state orbital  $1\sigma_g$  is bonding and the first excited state  $1\sigma_u^*$  is antibonding. In the figure below, we plot the energy levels  $\varepsilon_0(R)$  and  $\varepsilon_1(R)$  as functions of the internuclear separation  $R$ :

\includegraphics[scale=0.5]{H2p\_energies.eps}

The picture reveals that the curve  $\varepsilon_0(R)$  (the red curve) has a well-defined minimum, corresponding to the equilibrium bond length. This is due to the bonding character of the orbital. On the other hand, the first excited state  $\varepsilon_1(R)$  (the blue curve) has no such minimum. There is no stable bond length in this orbital, which reflects the antibonding character. Thus, exciting the molecule into this electronic state causes it to dissociate. The energy needed to do this depends on the internuclear separation  $R$ . When  $R = R_e$ , the equilibrium bond length, an energy of several  $R_y$  would be needed. At larger separations, the energy decreases as the two curves approach each other.

## Contributors and Attributions

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## 17: Linear combination of atomic orbitals

Linear combination of atomic orbitals (LCAO) is a simple method of quantum chemistry that yields a qualitative picture of the molecular orbitals (MOs) in a molecule. Let us consider  $H_2^+$  again. The approximation embodied in the LCAO approach is based on the notion that when the two protons are very far apart, the electron in its ground state will be a  $1s$  orbital of one of the protons. Of course, we do not know which one, so we end up with a Schrödinger cat-like state in which it has some probability to be on one or the other.

As with the HF method, we propose a guess of the true wave function for the electron

$$\psi_g(r) = C_A \psi_{1s}^A(r) + C_B \psi_{1s}^B(r)$$

where  $\psi_{1s}^A(r) = \psi_{1s}(r - R_A)$  is a  $1s$  hydrogen orbital centered on proton A and  $\psi_{1s}^B(r) = \psi_{1s}(r - R_B)$  is a  $1s$  hydrogen orbital centered on proton B. Recall  $\psi_{1s}(r) = \psi_{100}(r, \phi, \theta)$ . The positions  $R_A$  and  $R_B$  are given simply by the vectors

$$R_A = (0, 0, R/2) \quad R_B = (0, 0, -R/2)$$

The explicit forms of  $\psi_{1s}^A(r)$  and  $\psi_{1s}^B(r)$  are

$$\begin{aligned} \psi_{1s}^A(r) &= \frac{1}{(\pi a_0^3)^{1/2}} e^{-|r-R_A|/a_0} \\ \psi_{1s}^B(r) &= \frac{1}{(\pi a_0^3)^{1/2}} e^{-|r-R_B|/a_0} \end{aligned}$$

Now, unlike the HF approach, in which we try to optimize the shape of the orbitals themselves, in the LCAO approach, the shape of the  $\psi_{1s}$  orbital is already given. What we try to optimize here are the coefficients  $C_A$  and  $C_B$  that determine the amplitude for the electron to be found on proton A or proton B.

The guess wave function  $\psi_g(r)$  is not normalized as we have written down. Thus, our guess of the ground-state energy is given by

$$E_g = \frac{\int \psi_g \hat{H}_{elec} \psi_g dV}{\int \psi_g^2 dV}$$

where  $dV$  is the electron's volume element, and  $\hat{H}_{elec}$  is the electronic Hamiltonian (minus the nuclear-nuclear repulsion  $ke^2/R$ ):

$$\hat{H}_{elec} = \hat{K}_e - ke^2 \left( \frac{1}{|r - R_A|} + \frac{1}{|r - R_B|} \right)$$

(we will account for the nuclear-nuclear repulsion later when we consider the energies). Consider the denominator first:

$$\int \psi_g^2 dV = C_A^2 \int \psi_{1s}^2(r - R_A) dV + C_B^2 \int \psi_{1s}^2(r - R_B) dV + 2C_A C_B \int \psi_{1s}(r - R_A) \psi_{1s}(r - R_B) dV$$

Now, the  $1s$  wave function of hydrogen is normalized so

$$\int \psi_{1s}^2(r - R_A) dV = \int \psi_{1s}^2(r - R_B) dV = 1$$

In the cross term, however, the integral

$$\int \psi_{1s}(r - R_A) \psi_{1s}(r - R_B) dV$$

is not 1 because the orbitals are centered on different protons (it is only one if the two protons sit right on top of each other, which is not possible). It is also not 0 unless the protons are very far apart. We can calculate the integral analytically, however, it is not that important to do so since there is no dependence on  $C_A$  or  $C_B$ . Let us just denote this integral as  $S$ . We know that  $0 \leq S \leq 1$  and this is good enough for now. Thus, the denominator is simply

$$\int \psi_g^2 dV = C_A^2 + C_B^2 + 2SC_A C_B$$

As for the numerator

$$\int \psi_g \hat{H}_{elec} \psi_g dV = C_A^2 H_{AA} + C_B^2 H_{BB} + 2C_A C_B H_{AB}$$

where we have defined a bunch of integrals I'm too lazy to do as

$$\begin{aligned} H_{AA} &= \int \psi_{1s}^A(r) \hat{H}_{elec} \psi_{1s}^A(r) dV \\ H_{BB} &= \int \psi_{1s}^B(r) \hat{H}_{elec} \psi_{1s}^B(r) dV \\ H_{AB} &= \int \psi_{1s}^A(r) \hat{H}_{elec} \psi_{1s}^B(r) dV \end{aligned}$$

Again, these are integrals we can do, but it is not that important, so we will just keep the shorthand notation. Note that since the two nuclei are the same (they are both protons), we expect  $H_{AA} = H_{BB}$ . Since these are equal, we will just call them both  $H_{AA}$ . Hence, the guess energy becomes

$$E_g = \frac{H_{AA}(C_A^2 + C_B^2) + 2H_{AB}C_A C_B}{C_A^2 + C_B^2 + 2SC_A C_B}$$

which is just a ratio of two simple polynomials. Since we know that  $E_g > E_0$ , where  $E_0$  is the true ground-state energy, we can minimize  $E_g$  with respect to the two coefficients  $C_A$  and  $C_B$ . Thus, we need to take two derivatives and set them both to 0:

$$\frac{dE_g}{dC_A} = 0 \quad \frac{dE_g}{dC_B} = 0$$

Defining the denominator simply as  $D$ , where  $D = C_A^2 + C_B^2 + 2SC_A C_B$ , the two derivatives are

$$\begin{aligned} \frac{dE_g}{dC_A} &= \frac{2C_A H_{AA} + 2C_B H_{AB}}{D} - \frac{H_{AA}(C_A^2 + C_B^2) + 2C_A C_B H_{AB}}{D^2} (2C_A + 2SC_B) = 0 \\ \frac{dE_g}{dC_B} &= \frac{2C_B H_{AA} + 2C_A H_{AB}}{D} - \frac{H_{AA}(C_A^2 + C_B^2) + 2C_A C_B H_{AB}}{D^2} (2C_B + 2SC_A) = 0 \end{aligned}$$

Thus, we have two algebraic equations in two unknowns  $C_A$  and  $C_B$ . In fact, these will not determine  $C_A$  and  $C_B$  uniquely because they are redundant. However, we also have the normalization of  $\psi_g$  as a third condition, so we have enough information to determine the coefficients absolutely.

The equations can be solved as follows: First we write them as

$$\begin{aligned} \frac{2C_A H_{AA} + 2C_B H_{AB}}{D} &= \frac{H_{AA}(C_A^2 + C_B^2) + 2C_A C_B H_{AB}}{D^2} (2C_A + 2SC_B) \\ \frac{2C_B H_{AA} + 2C_A H_{AB}}{D} &= \frac{H_{AA}(C_A^2 + C_B^2) + 2C_A C_B H_{AB}}{D^2} (2C_B + 2SC_A) \end{aligned}$$

We now divide one equation by the other, which yields

$$\frac{C_A H_{AA} + C_B H_{AB}}{C_B H_{AA} + 2C_A H_{AB}} = \frac{C_A + SC_B}{C_B + SC_A}$$

Since we cannot solve for  $C_A$  and  $C_B$  independently, we choose, instead, to solve for the ratio  $r = C_A/C_B$ . Dividing both sides of the above by equation by  $C_B$  yields

$$\frac{rH_{AA} + H_{AB}}{H_{AA} + rH_{AB}} = \frac{r + S}{1 + rS}$$

To solve for  $r$ , we cross multiply:

$$(rH_{AA} + H_{AB})(1 + rS) = (H_{AA} + rH_{AB})(r + S)$$

Multiplying this out, we obtain

$$\begin{aligned} rH_{AA} + r^2SH_{AA} + H_{AB} + rSH_{AB} &= rH_{AA} + r^2H_{AB} + SH_{AA} + rSH_{AB} \\ r^2(SH_{AA} - H_{AB}) &= SH_{AA} - H_{AB} \\ r^2 &= 1 \end{aligned}$$

which implies  $r = \pm 1$ .

Thus, we have two solutions:  $C_A = C_B$  or  $C_A = -C_B$ . So, to simplify the notation, Let  $C_A = C$  (drop the A subscript). We, therefore, have two possible guess wave functions:

$$\begin{aligned} \psi_+(r) &= C[\psi_{1s}^A(r) + \psi_{1s}^B(r)] \\ \psi_-(r) &= C[\psi_{1s}^A(r) - \psi_{1s}^B(r)] \end{aligned}$$

The constant  $C$  can be determined for each guess wave function by imposing the normalization condition. For  $\psi_+$ , we have

$$\begin{aligned} \int \psi_+^2(r) dV &= C^2 \left[ \int \psi_{1s}^2(r - R_A) dV + \int \psi_{1s}^2(r - R_B) dV + 2 \int \psi_{1s}(r - R_A) \psi_{1s}(r - R_B) dV \right] = 1 \\ C^2[1 + 1 + 2S] &= 1 \\ C &= \frac{1}{\sqrt{2(1 + S)}} \end{aligned}$$

Similarly, one can show that for  $\psi_-$ ,  $C = 1/\sqrt{2(1 - S)}$ .

Let us now see how the two approximate solutions lead to bonding and antibonding orbitals. Consider first  $\psi_+(r)$ . We will add these two wave functions pictorially, keeping in mind that  $\psi_{1s}$  is a spherically symmetric orbital with an exponential decay. Thus,

$$\begin{aligned} \psi_{1s}^A(r) &\propto e^{-|r-R_A|/a_0} \\ \psi_{1s}^B(r) &\propto e^{-|r-R_B|/a_0} \end{aligned}$$

The figure below shows the orbitals that result from the addition or subtraction for  $\psi_+$  or  $\psi_-$ .

**Figure:** LCAO approximation to the ground ( $1\sigma_g$ ) and first excited ( $1\sigma_u^*$ ) orbitals in  $H_2^+$ .

\includegraphics[scale=0.5]{LCAO\_1s.eps}

In the bottom left panel, we show the two  $1s$  orbitals centered on protons A and B in  $\psi_+$ . In the center on the left, the result of adding them together is shown. It should be clear from the figure that  $\psi_+$  is a bonding orbital that is an approximation to the true  $1\sigma_g$  orbital that is the true ground state. This approximation is often denoted  $\sigma_{g1s}$ . On the other hand, the orbital  $\psi_-$  is the difference between  $\psi_{1s}(r - r_A)$  and  $\psi_{1s}(r - r_B)$ , which is depicted in the top left panel. This orbital has a node between the two nuclei and the amplitude between the two nuclei is generally low. This is clearly an anti-bonding orbital corresponding to  $1\sigma_u^*$ . This approximate orbital is often denoted  $\sigma_{u1s}^*$ . Since this orbital has a node, we expect that its energy will be higher than the approximate ground-state energy  $\sigma_{g1s}$ .

Concerning the energies, the figure below shows the two lowest energies curves as functions of  $R$ , comparing the results from the exact solution for  $H_2^+$  and the LCAO approximation. Note, in particular, that, in accordance with the variational principle, the exact energy curve for the ground state is always lower than the LCAO approximation.

\includegraphics[scale=0.5]{LCAO\_exact\_BO\_curves.eps}

## Energies in the LCAO method

The LCAO approach for  $H_2^+$  yields two wave functions we called  $\psi_+(r)$  and  $\psi_-(r)$ . The corresponding energies are

$$E_+(R) = \frac{H_{AA}(R) + H_{AB}(R)}{1 + S(R)} + \frac{ke^2}{R} \quad E_-(R) = \frac{H_{AA}(R) - H_{AB}(R)}{1 - S(R)} + \frac{ke^2}{R}$$

where  $E_+(R)$ , and we have indicated the explicit dependence of  $H_{AA}$ ,  $H_{AB}$ , and  $S$  on the internuclear distance  $R$ . Do not forget that both of these energies depend on the internuclear separation  $R$ . The figure below shows the two energies (adjusted to go to zero as  $R \rightarrow \infty$ ) as a function of  $\rho = R/a_0$ :

\includegraphics[scale=0.5]{H2p\_energies\_LCAO.eps}

As with the exact treatment, we see that the surface  $E_+$  (or  $\Delta E_+$  in the figure) has a minimum at the equilibrium bond length, which is consistent with the fact that  $\psi_+(r)$  is a bonding orbital.  $E_-$  (or  $\Delta E_-$  in the figure) has no such minimum and decreases monotonically, consistent with the fact that  $\psi_-(r)$  is an antibonding orbital. Since  $\psi_+(r)$  is an approximation to the true  $1\sigma_g$  orbital, we will use the notation  $\sigma_{g1s}$  for this orbital. Here, the "g" designator indicates that it is an even function, while the  $1s$  tells us that it is generated from a linear combination of  $1s$  orbitals. Similarly, the orbital  $\psi_-(r)$  is denoted  $\sigma_{u1s}^*$ , where the asterisk indicates antibonding character, and the "u" designator tells us that it is an odd function.

The following figure shows LCAO energies compare to the energies obtained by solving the Schrödinger equation exactly:

\includegraphics[scale=0.5]{H2p\_energies\_compare.eps}

Quantitatively, the LCAO predicts a bond length of  $1.32 \text{ \AA}$  while experiment and the exact solution give  $1.06 \text{ \AA}$ . The dissociation energy  $\Delta E_d$  (also denoted  $D_e$ ) from LCAO is  $1.76 \text{ eV} = 0.13 \text{ Ry}$ , while the exact value is  $2.791 \text{ eV} = 2.791 \text{ eV} = 0.21 \text{ eV}$ . This level of agreement is less than wonderful, but at the very least, LCAO gives us a correct qualitative picture that is useful for rationalizing chemical bonding situations.

The  $\sigma_{g1s}$  orbital is lower in energy than the  $\sigma_{u1s}^*$ . We can show this on an energy level diagram as well as the placement of the electron into the appropriate orbital for  $H_2^+$ . Such a diagram is called a correlation diagram. For  $H_2^+$ , the diagram appears as shown below:

**Figure 2:**  $H_2^+$  correlation diagram.

\includegraphics[scale=0.5]{H2p\_correlation.eps}

The diagram shows the two atomic orbitals (AOs) that were used to generate the corresponding MOs. These are both  $1s$  orbitals, so these are shown at the extremes of the diagram as well as the electronic configurations of each atom. Here, just one electron occupies a single  $1s$  orbital. The two MOs generated from the two AOs are also shown. Note that the  $\sigma_{g1s}$  orbital has a lower energy than the  $1s$  orbital because it has a minimum and leads to a stable bond ( $1s$ , by contrast, is monotonically decreasing). That the  $\sigma_{g1s}$  orbital is lower in energy can also be proved by comparing its energy  $(H_{AA} + H_{AB})/(1 + S)$  to the energy of the  $1s$  orbital of hydrogen. Similarly, the orbital  $\sigma_{u1s}^*$  is shown as having a higher energy because of its antibonding or destabilizing effect. That is has a higher energy than  $1s$  of hydrogen can also be seen by comparing its energy  $(H_{AA} - H_{AB})/(1 - S)$  to the energy of a  $1s$  orbital of hydrogen. In  $H_2^+$ , the electron in the  $1s$  orbital occupies the  $\sigma_{g1s}$  MO, which is also shown in the diagram.

## LCAO and the aufbau principle for molecules

The "aufbau" concept applied to the MOs produced from LCAO follows the same rules as for atoms. That is, we have to obey the Pauli exclusion principle and apply Hund's rule. Thus, for the molecule  $H_2$ , we have two electrons: Each  $H_2$  donates one in a  $1s$  orbital to the LCAO procedure. We already know that combining two  $1s$  orbitals gives us the  $\sigma_{g1s}$  and  $\sigma_{u1s}^*$  MOs, and since they are different in energy, we do not need to worry about Hund's rule. We simply place both electrons (in opposite spin configurations) into the  $\sigma_{g1s}$  orbital as the correlation diagram below illustrates:

**Figure 3:**  $H_2$  correlation diagram

\includegraphics[scale=0.5]{H2\_correlation.eps}

For the molecule  $He_2^+$ , we have three electrons. On one of the  $He$  atoms, there are two electrons both in a  $1s$  orbital, while on the  $He^+$  atom, there will be one electron in a  $1s$  orbital. Note, however, that these  $1s$  orbitals are only hydrogen-like but have a  $Z$  value of  $Z = 2$ . That is, the  $1s$  orbital is

$$\psi_{100}(r, \phi, \theta) = \left( \frac{8}{\pi a_0^3} \right)^{1/2} e^{-2r/a_0}$$

Hence, if the  $He$  nuclei are at positions  $r_A$  and  $r_B$ , the guess wave function for the LCAO procedure would take the form

$$\psi_g(r) = C_A \psi_{1s(Z=2)}(r - r_A) + C_B \psi_{1s(Z=2)}(r - r_B)$$

The procedure would still yield  $\psi_+(r)$  and  $\psi_-(r)$  orbitals, but these would also use  $Z = 2$  rather than  $Z = 1$  in their construction. Now, since only two electrons can occupy the  $\psi_+(r)$  or  $\sigma_{g1s}$  orbital that LCAO gives, the third electron must be placed in the  $\psi_-(r)$  or  $\sigma_{u1s}^*$  orbital. This gives a correlation diagram that appears as shown below:

**Figure 4:**  $He_2^+$  correlation diagram

\includegraphics[scale=0.5]{He2p\_correlation.eps}

The fact that an electron must be placed in an antibonding orbitals means that there will be some destabilization of the bond, and indeed, we find that  $He_2^+$  is more weakly bonded than  $H_2$ . Moreover, the bonding orbital  $\sigma_{g2s}$  has less electron density between the two nuclei because the decay of the  $1s(Z = 2)$  wave function is faster than that of the  $1s(Z = 1)$  wave function used to construct the MOs for  $H_2^+$  and  $H_2$ . In order to give a sense of this, consider that the bond lengths of  $H_2^+$  and  $He_2^+$  are  $1.06 \text{ \AA}$  and  $1.08 \text{ \AA}$ , which are very similar, yet the dissociation energies of these two molecules are  $276 \text{ kJ/mol}$  and  $230 \text{ kJ/mol}$ , so  $He_2^+$  is more weakly bound than  $H_2^+$ . By comparison,  $H_2$ , which has two bonding electrons has a bond length of  $0.74 \text{ \AA}$ , and a dissociation energy of  $432 \text{ kJ/mol}$ .

For the helium dimer  $He_2$ , there are four electrons, each He atom contributing 2 electrons in  $1s$  orbitals. When placing these electrons into the  $\sigma_{g1s}$  and  $\sigma_{u1s}^*$  MOs, we are forced to place two electrons into each, which means two electrons in the bonding orbital and two in the antibonding orbital. LCAO predicts that two electrons in an antibonding orbital generates as much destabilization of the bond as there is stabilization from the two bonding electrons. Thus, LCAO would predict that  $He_2$  cannot form a stable bond. In fact, a very weak bond stabilization of roughly  $10^{-8} \text{ Ry}$  exists between to helium atoms, resulting in a very weak  $He_2$  dimer with a bond length of approximately  $52 \text{ \AA}$ ! (see Grisenti *et al. Phys. Rev. Lett.* **85**, 2284 (2000)). Of course, LCAO cannot predict this. Nevertheless, LCAO gives us an easy way to estimate the stability of a chemical bond which is qualitatively reasonable (even if it misses exotic objects like the weak  $He_2$  dimer). Within LCAO, we can define a bond order

$$\text{Bond order} = \frac{1}{2} [\# \text{electrons in bonding orbitals} - \# \text{electrons in antibonding orbitals}]$$

Applying this formula, we can obtain bond orders for the molecules we have considered thus far:

$$\begin{aligned} \text{For } H_2^+ : \text{Bond order} &= \frac{1}{2} [1 - 0] = \frac{1}{2} \\ \text{For } H_2 : \text{Bond order} &= \frac{1}{2} [2 - 0] = 1 \\ \text{For } He_2^+ : \text{Bond order} &= \frac{1}{2} [2 - 1] = \frac{1}{2} \\ \text{For } He_2 : \text{Bond Order} &= \frac{1}{2} [2 - 2] = 0 \end{aligned}$$

As expected, the weaker bonds have lower bond orders.

The electronic configurations of  $H_2^+$ ,  $H_2$  and  $He_2^+$  are written in an manner analogous to the atomic case:

$$\begin{aligned} \text{For } H_2^+ : (\sigma_{g1s})^1 \\ \text{For } H_2 : (\sigma_{g1s})^2 \\ \text{For } He_2^+ : (\sigma_{g1s})^2 (\sigma_{u1s}^*)^1 \end{aligned}$$

At this point, we state the general rules for constructing MOs from AOs in the LCAO procedure:

1. Form linear combinations of the minimum number of AOs to generate MOs. The number of MOs must equal the number of AOs from which they are generated.
2. Arrange the MOs in order from lowest to highest in energy.
3. Occupy or place electrons in MOs starting from MOs of lowest energy following the Pauli exclusion principle (at most 2 electrons per MO) and Hund's rule for MOs of similar energy.

## Contrasting LCAO with other quantum chemistry methods

Before we move onto atoms in the second period of the periodic table, let us pause briefly to contrast the LCAO approach with other methods of quantum chemistry. As we have already seen, the LCAO approach is very approximate, yielding only qualitative results.

It should be noted that the Hartree-Fock method we introduced in Chapter 5 can also be used for molecules. For example, the molecule  $He_2^+$  has three electrons, and the Li atom also has three electrons. Thus, the guess wave function that you wrote down for the Li atom in the last problem set can also be used as a guess wave function for  $He_2^+$ ! As usual with Hartree-Fock, the idea is to optimize the shapes of the single-electron orbitals  $\psi_1(r)$ ,  $\psi_2(r)$  and  $\psi_3(r)$  by minimizing the guess to the ground state energy  $E_g$ . Of course, we will not get the same answer as for Li because there is a different  $V_{en}$  energy for  $He_2^+$  due to the presence of two positively charged nuclei ( $charge = +2e$ ) separated by a distance  $R$  in contrast to the single  $+3e$  charged nucleus for Li. When the shapes of the orbitals are optimized, we also obtain three energy  $\varepsilon_1$ ,  $\varepsilon_2$  and  $\varepsilon_3$ . Not unexpectedly, we find that two of the HF orbitals resemble  $1\sigma_g$  while the third resembles  $1\sigma_u^*$  and the first two energies  $\varepsilon_1$  and  $\varepsilon_2$  will be nearly equal, while the third  $\varepsilon_3$  will be noticeably higher. To contrast with the LCAO approach, in LCAO, we do not optimize the shapes of the orbitals (these are assumed *a priori* to be  $1s$  shaped). All we do is choose the mixing coefficients so as to minimize the guess to the ground-state energy  $E_g$ .

We note, finally, that the density functional theory alluded to earlier can also be used for molecules. It is often the case that density functional theory yields a more accurate description than Hartree-Fock, but this depends on the molecule. In any case, both are more accurate than LCAO. There is also a hierarchy of methods called *post Hartree-Fock* methods, all of which are based on the wave function rather than the electron density, that can be used to improve upon the HF approximation systematically. The greater the accuracy that is desired for the calculation, the more costly computationally the post HF methods become, so quantum chemistry is often a trade-off between accuracy and efficiency, an issue that becomes more critical to take into account when calculations on large molecules must be carried out!

## LCAO for second-period atoms in homonuclear diatomic molecules

A *homonuclear* diatomic is of the form XX, i.e. the two nuclei are the same. In this section we will consider homonuclear diatomics formed from the second period ( $Z = 3$  through  $Z = 10$ ) atoms.

In the LCAO approach, the most general guess wave function we could imagine constructing would be a general linear combination including  $1s$ ,  $2s$ , and  $2p$  orbitals on nuclei A and B. Fortunately, we do not need to make things so complex due to a few simple rules that we can easily understand from the quantum mechanical concepts we have developed so far.

Let us briefly consider  $H_2^+$  again and the  $\sigma_{g1s}$  orbital, which takes the form

$$\psi_+(r) = \psi_{\sigma_{g1s}}(r) = \frac{1}{\sqrt{2(1+S)}}[\psi_{1s}(r-r_A) + \psi_{1s}(r-r_B)]$$

Note that this is a Schrödinger cat type of state in which the electron is simultaneously in a  $1s$  orbital on nucleus A and in a  $1s$  orbital on nucleus B, and this remains the case unless somebody comes along and measures the position of the electron! Let us suppose, for simplicity, that the nuclei are far enough apart that we can safely set  $S = 0$  (recall that  $S$  is the integral of the product of  $\psi_{1s}(r-r_A)\psi_{1s}(r-r_B)$ ). Then,  $\psi_+(r)$  becomes

$$\psi_+(r) \approx \frac{1}{\sqrt{2}}[\psi_{1s}(r-r_A) + \psi_{1s}(r-r_B)]$$

When written in this approximation, we easily see that the probability of finding the electron in the  $1s$  orbital of atom A is  $1/2$ , and the probability of finding the electron in the  $1s$  orbital of atom B is  $1/2$ . This makes physical sense because both  $1s$  orbitals have the same energy.

Now suppose we try a guess wave function that mixes  $1s$  and  $2s$  orbitals, e.g.

$$\psi_g(r) = C_A\psi_{1s}(r-r_A) + C_B\psi_{2s}(r-r_B)$$

The  $1s$  and  $2s$  orbitals have very different energies. Thus, while we might be able to prepare a state like this under special laboratory conditions, a molecule in its equilibrium state would be very unlikely to be in a state of this character because of the disparity in energies. We would, therefore, expect that the probabilities for finding the electron in the  $1s$  and  $2s$  states would behave like  $|C_A|^2 \gg |C_B|^2$  rather than  $|C_A|^2 = |C_B|^2$ , as is the case when the energies are equal. Without significant amplitude from the  $\psi_{2s}$  orbital, we cannot expect a bond to form. So, unless the contributions from atom A and atom B are nearly equal, no bonding occurs.

Based on this consideration, we can state the following rule:

**1. Two AOs contribute significantly to bond formation only if their atomic energy levels are close to one another.**

Another important rule is one to which we have already alluded:

**2. Two AOs contribute significantly to bond formation only if they overlap significantly. This means that they must combine in such a way as to have substantial overlap in the region between the two nuclei.**

A rule such as this means that we do not need to consider the mixing of  $2p_x$  and  $2p_y$  orbitals, for example. These two rules greatly simplifies the construction of MOs within the LCAO scheme. A mixture of  $2p_x$  and  $2p_y$  orbitals have neither bonding nor antibonding character, and they do not resemble either exact solutions for  $H_2^+$  nor do they resemble any of the HF orbitals for other diatomics.

The MOs we can create, following the pattern for  $\psi_{\sigma_{g1s}}$  and  $\psi_{\sigma_{u1s}^*}$  start with the MO generated from  $2s$  AOs:

$$\psi_{\sigma_{g2s}} = \frac{1}{\sqrt{2(1+S)}} [\psi_{2s}(r-r_A) + \psi_{2s}(r-r_B)]$$

$$\psi_{\sigma_{u2s}^*}(r) = \frac{1}{\sqrt{2(1-S)}} [\psi_{2s}(r-r_A) - \psi_{2s}(r-r_B)]$$

Note that the definition of  $S$  is a different here. It is the overlap between the  $2s$  orbitals

$$S = \int \psi_{2s}(r-r_A) \psi_{2s}(r-r_B) dV$$

For the  $2p$  orbitals, we can generate MOs of  $\sigma$  character by combining the  $2p_z$  orbitals, for which the  $L_z$  quantum number  $m = 0$ . Consider first the orbital

$$\frac{1}{\sqrt{2(1-S)}} [\psi_{2p_z}(r-r_A) - \psi_{2p_z}(r-r_B)]$$

Because the  $p_z$  orbital peaks on the  $z$ -axis and is positive along the positive  $z$ -axis and negative along the negative  $z$ -axis, the difference enhances the amplitude in the region between the nuclei (see figure below - top panel):

**Figure 5:** MOs generated from  $2p_z$  AOs using the LCAO scheme

\includegraphics[scale=0.5]{LCAO\_pz.eps}

This orbital is clearly a bonding orbital and is an even function. Hence we denote it as a  $\sigma_{g2p_z}$  orbital and write:

$$\psi_{\sigma_{g2p_z}}(r) = \frac{1}{\sqrt{2(1-S)}} [\psi_{2p_z}(r-r_A) - \psi_{2p_z}(r-r_B)]$$

Here, the definition of  $S$  is:

$$S = \int \psi_{2p_z}(r-r_A) \psi_{2p_z}(r-r_B) dV$$

and clearly

$$\psi_{\sigma_{g2p_z}}(-r) = \psi_{\sigma_{g2p_z}}(r)$$

The other construction

$$\frac{1}{\sqrt{2(1+S)}} [\psi_{2p_z}(r-r_A) + \psi_{2p_z}(r-r_B)]$$

has very little amplitude in the region between the nuclei because the negative lobe of one of the  $2p_z$  orbitals cancels the positive lobe of the other (see the figure above - bottom panel). This orbital is, therefore, an antibonding orbital that is odd. We, therefore, designate it as a  $\sigma_{u2p_z}^*$  orbital and write

$$\psi_{\sigma_{u2p_z}}(r) = \frac{1}{\sqrt{2(1+S)}} [\psi_{2p_z}(r-r_A) + \psi_{2p_z}(r-r_B)]$$

For the  $2p_x$  orbitals, consider the combination

$$\frac{1}{\sqrt{2(1+S)}} [\psi_{2p_x}(r-r_A) + \psi_{2p_x}(r-r_B)]$$

This combination is pictured in the top panel of the figure below:

**Figure 6:** MOs generated from  $2p_x$  AOs using the LCAO scheme

\includegraphics[scale=0.5]{LCAO\_px.eps}

This turns out to be a bonding orbital because there is significant amplitude between the nuclei, however, the orbital is an odd function. So, we have to designate it as  $\pi_{u2p_x}$ . Note that it is a  $\pi$  orbital because  $m = \pm 1$ . Thus, we have

$$\psi_{\pi_{u2p_x}}(r) = \frac{1}{\sqrt{2(1+S)}} [\psi_{2p_x}(r-r_A) + \psi_{2p_x}(r-r_B)]$$

The different orbital becomes an antibonding orbital (see above figure - bottom panel) that happens to be an even function and is, therefore, a  $\pi_{g2p_x}^*$  orbital:

$$\psi_{\pi_{g2p_x}^*}(r) = \frac{1}{\sqrt{2(1-S)}} [\psi_{2p_x}(r-r_A) - \psi_{2p_x}(r-r_B)]$$

The same applies to the MOs constructed from  $2p_y$  AOs.

The energetic ordering of these orbitals is  $\sigma_{g2s}, \sigma_{u2s}^*, (\pi_{u2p_x}, \pi_{u2p_y})$  (these two  $\pi$  orbitals have the same energy),  $\sigma_{g2p_z}, (\pi_{g2p_x}^*, \pi_{g2p_y}^*)$ ,  $\sigma_{u2p_z}^*$  for atoms  $Li$  through  $N$ . For  $O$ ,  $F$  and  $Ne$ , the ordering is  $\sigma_{g2s}, \sigma_{u2s}^*, \sigma_{g2p_z}, (\pi_{u2p_x}, \pi_{u2p_y})$  (these two  $\pi$  orbitals have the same energy),  $(\pi_{g2p_x}^*, \pi_{g2p_y}^*)$ ,  $\sigma_{u2p_z}^*$ . The reason for this difference between the  $Z \leq 5$  and  $Z \geq 6$  elements can be understood roughly as follows: The  $\sigma_{g2p_z}$  orbital has considerable electron density along the z-axis. For  $Z \leq 5$ , the contributing  $2p_z$  orbitals are sufficiently delocalized along this axis that electrons occupying them overlap and, therefore, contribute significant Coulomb repulsion to the total energy, which raises the energy of the  $\sigma_{g2p_z}$  orbital above the  $\pi$  orbitals, for which the Coulomb repulsion is considerably less, as they do not peak along the z-axis. For  $Z \geq 6$ , however, the nuclear charge is sufficiently high that the  $2p_z$  orbitals decay more quickly, are more localized, and this reduces the overlap and Coulomb repulsion to such an extent that the energy of the  $\sigma_{g2p_z}$  orbital is now below that of the  $\pi$  orbitals. Only high level calculations could predict that this change occurs between  $Z = 5$  and  $Z = 6$ . Note that, generally, as the number of nodes in the wave function increases, so does the energy. The ordering and shapes of the orbitals are shown in the figure below, together with some example correlation diagrams for  $N_2$  and  $F_2$ :

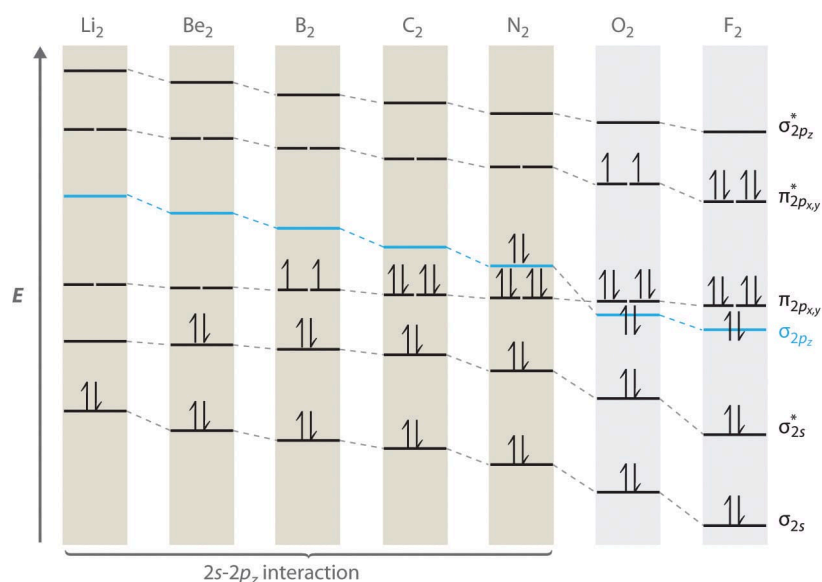
$$\frac{1}{\sqrt{2(1+S)}} [\psi_{2p_x}(r-r_A) + \psi_{2p_x}(r-r_B)]$$

This combination is pictured in the top panel of the figure below:

**Figure 7:** MOs and their ordering

\includegraphics[scale=0.5]{correlation\_diagrams.eps}

Following Pauli's exclusion principle and Hund's rule, the electronic configurations for the second-period diatomics are shown in the figure below:



\includegraphics[scale=0.5]{O2\_paramagnetism.eps}

Note the special cases of  $\text{B}_2$  and  $\text{O}_2$ , both of which contain unpaired spins because of [Hund's rule](#). Because of these unpaired spins, these molecules interact strongly with a magnetic field and can be made to align with such a field. For this reason, these molecules are called *paramagnetic*. This type of behavior can only be predicted within quantum mechanics. The classical theory of chemical bonding from Chapter 3 misses this entirely. The paramagnetic behavior of  $\text{O}_2$  means that liquid oxygen poured between the poles of a magnet will not flow through but will stick to the poles due to the ability of spins to align with a magnetic field and the forces exerted by the magnet on these spins. This is illustrated in the figure below:

#### YouTube Video

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## Contributors and Attributions

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# 18: Linear combination of atomic orbitals for heteronuclear molecules

## Heteronuclear Diatomic Molecules

In a heteronuclear diatomic molecule, there is an electronegativity difference between the atoms, which leads to an asymmetric distribution of the electronic probability density, weighted more heavily toward the element with the greater electronegativity.

Consider constructing a MO from two  $2s$  orbitals for nuclei with different  $Z$  values. Let atom A have an atomic number  $Z_A$  and atom B have an atomic number  $Z_B$ . For a single electron interacting with the two nuclei, an LCAO guess wave function could be

$$\psi_g(r) = C_A \psi_{2s(Z=Z_A)}^A(r) + C_B \psi_{2s(Z=Z_B)}^B(r)$$

Recall the energies  $H_{AA}$  and  $H_{BB}$  that were defined for LCAO in the homonuclear case:

$$H_{AA} = \int \psi_{2s(Z=Z_A)}^A(r) \hat{H}_{elec} \psi_{2s(Z=Z_A)}^A(r) dV$$

$$H_{BB} = \int \psi_{2s(Z=Z_B)}^B(r) \hat{H}_{elec} \psi_{2s(Z=Z_B)}^B(r) dV$$

For the heteronuclear case,  $H_{AA} \neq H_{BB}$ . If atom B is the more electronegative, then its  $Z$  will be larger (in the second period), and the energy will be more negative due to the large Coulomb attraction between the electrons and the nuclei. Thus, in this case  $H_{BB} < H_{AA}$  (remember  $H_{AA}$  and  $H_{BB}$  are both negative). Now, if we calculate the guess of the ground-state energy

$$E_g = \frac{\int \psi_g(r) \hat{H}_{elec} \psi_g(r) dV}{\int \psi_g^2(r) dV}$$

we find the more general result

$$E_g = \frac{H_{AA}C_A^2 + H_{BB}C_B^2 + 2H_{AB}C_AC_B}{C_A^2 + C_B^2 + 2SC_AC_B}$$

and then perform the minimization of  $E_g$ :

$$\frac{dE_g}{dC_A} = 0 \quad \frac{dE_g}{dC_B} = 0$$

we obtain the conditions

$$\frac{dE_g}{dC_A} = \frac{2C_A H_{AA} + 2C_B H_{AB}}{D} - \frac{H_{AA}C_A^2 + H_{BB}C_B^2 + 2C_AC_B H_{AB}}{D^2} (2C_A + 2SC_B) = 0$$

$$\frac{dE_g}{dC_B} = \frac{2C_B H_{BB} + 2C_A H_{AB}}{D} - \frac{H_{AA}C_A^2 + H_{BB}C_B^2 + 2C_AC_B H_{AB}}{D^2} (2C_B + 2SC_A) = 0$$

If we make the simplifying approximation that the overlap  $S \approx 0$ , then these conditions lead to the following relationship between  $C_A$  and  $C_B$ :

$$\frac{C_A}{C_B} = \frac{H_{AA} - H_{BB}}{2H_{AB}} \pm \sqrt{\frac{(H_{AA} - H_{BB})^2}{4H_{AB}^2} + 1}$$

In order to make the analysis a bit easier, let us expand the square root using the fact that

$$\sqrt{1+x} \approx 1 + \frac{1}{2}x$$

Then

$$\frac{C_A}{C_B} = \frac{H_{AA} - H_{BB}}{2H_{AB}} \pm \left[ 1 + \frac{(H_{AA} - H_{BB})^2}{8H_{AB}^2} \right]$$

Now, we know that

$$\left[ 1 + \frac{(H_{AA} - H_{BB})^2}{8H_{AB}^2} \right] > \left| \frac{H_{AA} - H_{BB}}{2H_{AB}} \right|$$

First, look at the  $\psi_+(r)$ . If  $H_{AA} > H_{BB}$ ,  $B$  is more electronegative because its energy is lower (think of the Bohr formula  $E_n = -Z^2/n^2$ , which shows that as  $Z$  increases, the energy decreases). Generally, a not so easy calculation of  $H_{AB}$  shows that  $H_{AB} < 0$ . Thus, if  $H_{AA} > H_{BB}$ , then

$$\frac{H_{AA} - H_{BB}}{2H_{AB}} < 0$$

and this means that  $C_A/C_B < 1$  or  $C_A < C_B$ , which is what we would expect if  $B$  is more electronegative. Similarly, if  $H_{AA} < H_{BB}$ ,  $A$  is more electronegative. We would then find

$$\frac{H_{AA} - H_{BB}}{2H_{AB}} > 0$$

and  $C_A/C_B > 1$ , and  $C_A > C_B$ , which is what we would expect if  $A$  is more electronegative.

Another consequence we can derive from the above result is that if  $|H_{AA}| \gg |H_{BB}|$  or  $|H_{AA}| \ll |H_{BB}|$ , then the coefficients will be very different, e.g.  $C_A \gg C_B$  or  $C_A \ll C_B$ , in which case, the resulting MO is not really an MO at all, but rather more like the AO with the larger coefficient. Thus, it is clear that  $H_{AA}$  and  $H_{BB}$  cannot be very different if we are to have a reasonable amount of mixing of the two AOs. This supports the idea that only orbitals with similar energies can be combined in the LCAO scheme.

We can no longer use the "g" and "u" designators because the orbitals have no particular symmetry when  $r \rightarrow -r$ . That is

$$\psi_+(-r) \neq \psi_+(r) \quad \psi_-(-r) \neq -\psi_-(r)$$

Thus, we denote  $\psi_+(r)$  simply as  $\sigma_{2s}$  and  $\psi_-(-r)$  simply as  $\sigma_{2s}^*$ .

Let us now construct a correlation diagram for the heteronuclear diatomic  $BO$ . Boron has an electronic configuration

$$1s^2 2s^2 2p_x$$

while oxygen's is

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

Since we are interested in the chemical bond that forms between them, we only consider the valence electrons explicitly, and these are the electrons in the  $n = 2$  shell. In  $BO$ , oxygen is the more electronegative, so its orbitals are lower in energy than those of boron. This must be indicated on the correlation diagram. Thus, the correlation diagram appears as in the figure below:

**Figure:** Correlation diagram for the heteronuclear diatomic molecule  $BO$ .

\includegraphics[scale=1.0]{BO\_correlation.eps}

Note that the ordering of the MOs follows the pattern we would expect for boron rather than oxygen. Only high-level calculations can predict this, but physically, the simple explanation is that there is only one electron in the  $\sigma_{2p_z}$  orbital, and only one of the two atoms has a large nuclear charge (unlike in  $O_2$ , where they both do). There is, therefore, insufficient Coulomb attraction for this one electron to pull the energy of the  $\sigma_{2p_z}$  orbital below the energy of the  $\pi$  bonding orbitals.

The electronic configuration of  $BO$  is, therefore

$$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^1$$

and the bond order is  $(1/2)(7 - 2) = 5/2$ . The fraction bond order indicates that the molecule is paramagnetic, as with  $O_2$ .

As another example, consider the molecule  $NO$ .  $NO$  has 11 valence electrons and has the electronic configuration:

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^2(\pi_{2p_x}^*)^1$$

The bond order is also  $5/2$ , and the molecule is paramagnetic as well.

What about the molecule  $HF$ ? Here, the  $1s$  and  $2s$  orbitals of  $F$  are so low in energy compared to the  $1s$  orbital in  $H$  that they cannot be combined to form MOs. At the same time, the  $2p_x$  and  $2p_y$  orbitals of  $F$  have an insignificant spatial overlap with the  $1s$  orbital in  $H$  (assuming that the two nuclei lie along the z-axis) that they also do not form MOs. Only the  $2p_z$  orbital of  $F$  has significant overlap with the  $1s$  orbital in  $H$  and can mix with it energetically. Thus, the LCAO guess wave function takes the form

$$\psi_+(r) = C_A\psi_{1s}^A(r) + C_B\psi_{2p_z}^B(r)$$

where atom A is  $H$  and atom B is  $F$ . If  $H$  lies to the left of  $F$ , then this orbital has antibonding character, while the orbital

$$\psi_-(r) = C_A\psi_{1s}^A(r) - C_B\psi_{2p_z}^B(r)$$

has bonding character because there is significant amplitude in the region between the nuclei. See the figure below:

**Figure:** Illustration of the overlap between the  $2s$  and  $2p$  orbitals of  $F$  with the  $1s$  of  $H$  in the molecule  $HF$ .

\includegraphics[scale=0.5]{HF\_LCAO\_orbitals.eps}

**Figure:** MOs and correlation diagram for  $HF$ .

\includegraphics[scale=0.5]{HF\_MOs.eps}

The orbital  $\psi_-$  is denoted simply as  $\sigma$  while the orbital  $\psi_+$  is denoted  $\sigma^*$  for bonding and antibonding, respectively. The  $2s$ ,  $2p_x$  and  $2p_y$  orbitals of  $F$  do not mix with anything and are, therefore, called *nonbonding orbitals*. They are denoted  $\sigma^{nb}$  and  $\pi_x^{nb}$  and  $\pi_y^{nb}$ , respectively. The orbital ordering is  $\sigma^{nb}$  (since it is a low-energy  $2s$  orbital), followed by  $\sigma$ , then the two nonbonding  $\pi$  orbitals and finally  $\sigma^*$ . Therefore, the correlation diagram for  $HF$  is as shown in the figure below:

**Figure:** Another look at the correlation diagram in  $HF$ .

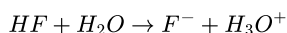
\includegraphics[scale=0.75]{HF\_correlation.eps}

The bond order of  $HF$  is easily seen to be 1.

## Frontier molecular orbitals

While we are looking at  $HF$ , it is worth digressing to discuss (briefly) the concept of frontier molecular orbitals (to which you will be exposed more in organic chemistry). The term "frontier" refers to the orbitals that are at the outer edges of a molecule. These tend to be the orbitals that are the most spatially delocalized and hence, the orbitals with the highest energies (either occupied or unoccupied). In particular, two orbitals are of particular importance. These are the *highest occupied molecular orbital* or (HOMO) and the *lowest unoccupied molecular orbital* (LUMO). "Highest" and "lowest" refer to the energies. In  $HF$ , the HOMO orbital(s) are the double degenerate  $\pi_{2p_x}$  and  $\pi_{2p_y}$  orbitals, while the LUMO is the  $\sigma_{2p_z}^*$  orbital.

The HOMO and LUMO can help us predict what will happen in a chemical reaction. Consider the reaction of  $HF$  with  $H_2O$ :



In terms of Lewis structures, the reaction can be depicted as show below:

**Figure:** Reaction of  $HF$  with  $H_2O$  in Lewis structures.

\includegraphics[scale=0.5]{HF\_H2O\_rxn.eps}

Here we see the  $H$  of  $HF$  trading the shared pair in the  $HF$  bond for one in the  $H_3O^+$  (as depicted by the arrow in the diagram).

The arrow attempts to convey that the water molecule donates one of its lone pairs to the  $HF$  molecule, causing the  $HF$  bond to rupture, thereby allowing liberated proton to attach to the water molecule.

In terms of frontier molecular orbitals, we can view the reaction as follows: The electron pair donated by the water molecule must go into the LUMO of  $HF$ . Since the LUMO is a  $\sigma_{2p_z}^*$  orbital, the occupancy of this orbital by two electrons changes the bond order of  $HF$  from 1 to 0, and this causes the bond to be destabilized and rupture, thereby freeing up the proton ( $H^+$ ) to react with the  $H_2O$ .

## Constructing MOs for the water molecule

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. The linear form clearly does not apply to  $H_2O$ , but we can still construct a reasonable argument for the energetic ordering and structure of the MOs. We first note that each  $H$  will donate a  $1s$  orbital in the LCAO scheme, and  $X$  will likely donate at least  $2s$  and possible  $2p$  orbitals, depending on its chemical identity. Let atom A be an  $H$ , let atom B be  $X$  and let atom C be  $H$ . What orbitals can we construct? Note that the molecule is symmetric about the center (the position of  $X$ ), hence the orbitals have to have the same symmetry.

As with  $HF$ , the only  $2p$  orbital of  $X$  that will overlap with  $1s$  of  $H$  is the  $2p_z$ . Hence, consider the combination

$$\psi_1(r) = |C_A|\psi_{1s}^A(r) - |C_B|\psi_{2s}^B(r) + |C_A|\psi_{1s}^C(r)$$

Note that the two coefficients in front of the  $1s$  orbitals are the same by symmetry.

How big should the  $2s$  orbital of  $X$  be compared to the  $1s$  orbital of  $H$ ? This depends on several things. First, is the nuclear charge on  $X$  and the second is the electronegativity difference between  $H$  and  $X$ . 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  $C_A$  compared to  $C_B$ . In the case of  $BeH_2$ , the  $2s$  orbital on  $Be$  multiplied by the coefficient  $C_B$  (which is smaller than that of  $H$  due to  $Be$ 's lower electronegativity) causes the  $2s$  orbital to be smaller than the  $1s$  on  $H$ . For  $H_2O$ , the  $2s$  orbital decays at about the same rate in  $r$  as does the  $1s$  orbital of  $H$ , however, the coefficient  $C_B$  will be larger than  $C_A$  because  $O$  is more electronegative. Hence, for  $O$ , the  $2s$  orbital should be larger than that of the  $1s$  on  $H$ .

However, this is a technical issue that is less important than the qualitative features of the MOs that we now seek. The orbital  $\psi_1(r)$  constructed above is purely bonding because the  $2s$  orbital is positive near the oxygen nucleus but becomes negative as we go away from the nucleus. Note that the book gets this wrong throughout Chapter 7. This orbital is also even, so we can denote it as a  $\sigma_{g2s}$  orbital signifying that it is constructed from a  $2s$  orbital of  $X$  combined with the  $1s$  orbital of  $H$  (no designator is needed for this  $1s$  orbital since this is the only orbital  $H$  can donate and hence, is obvious). The only other MO that can be constructed that has the right symmetry is

$$\psi_2(r) = |C_A|\psi_{1s}^A(r) + |C_B|\psi_{2s}^B(r) + |C_A|\psi_{1s}^C(r)$$

which will be antibonding, as shown in the figure above. The orbital is even, so we can denote it as  $\sigma_{g2s}^*$ . Next, if we combine a  $2p_z$  orbital of  $X$  with the  $1s$  of  $H$ , there are two possibilities that have the right symmetry. The first is

$$\psi_3(r) = |C_A|\psi_{1s}^A(r) - |C_B|\psi_{2p_z}^B(r) - |C_A|\psi_{1s}^C(r)$$

which is a bonding orbital as shown in the figure above. since it is odd, we can denote it as  $\sigma_{u2p_z}$ . Finally, there is

$$\psi_4(r) = |C_A|\psi_{1s}^A(r) + |C_B|\psi_{2p_z}^B(r) - |C_A|\psi_{1s}^C(r)$$

which is purely antibonding (see figure above) and odd. Hence, we denote this as  $\sigma_{u2p_z}^*$ . The orbitals  $2p_x$  and  $2p_y$  from  $X$  are nonbonding and become  $\pi_{2p_x}$  and  $\pi_{2p_y}$  nonbonding orbitals.

The figure below 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.

Figure: MOs of linear vs. bent triatomics.

```
\includegraphics[scale=0.5]{linear_bent_MOs.eps}
```

## Contributors and Attributions

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## 19: Hybrid atomic orbitals, geometry, and valence bond theory

Valence bond theory is an alternative approximation scheme for constructing many-electron wave functions. 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

$$V = V_{ee} + V_{en} + V_{nn} \\ = \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{R_{AB}} \right]$$

But as  $R_{AB} \rightarrow \infty$ , 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

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

Since the potential energy becomes a simple sum of separate energies for electrons 1 and 2, the wave function should simply be a product  $\psi_{1s}(r_1 - r_A)\psi_{1s}(r_2 - r_B)$ . But as we let  $R_{AB} \rightarrow R_e$ , 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 wave function we can construct from a product of 1s orbitals is

$$\psi_u(r_1, r_2) = C_u[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) - \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)]$$

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

$$\psi_g(r_1, r_2) = C_g[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) + \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)]$$

(where  $g$  designates that this is an even function), we violate the Pauli exclusion principle, even though such a wave function 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 wave function should change sign. Thus, we can make both wave functions above consistent with the Pauli exclusion principle by multiplying by an appropriate spin wave function. We obtain

$$\begin{aligned} \psi_u(r_1, r_2, s_1, s_2) &= \psi_u(x_1, x_2) = C_u[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) - \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) + \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \\ \psi_g(r_1, r_2, s_1, s_2) &= \psi_g(x_1, x_2) = C_g[\psi_{1s}^A(r_1)\psi_{1s}^B(r_2) + \psi_{1s}^A(r_2)\psi_{1s}^B(r_1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \end{aligned}$$

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

The fact that  $\psi_u$  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  $\psi_{1s}^A(r_1)$  and  $\psi_{1s}^B(r_1)$  have the same value for  $r_1$  in this plane, and the same for  $\psi_{1s}^B(r_2)$  and  $\psi_{1s}^A(r_2)$ . Let us assign the following values:

$$\begin{aligned} \psi_{1s}^A(r_1) &= \psi_{1s}^B(r_1) = A \\ \psi_{1s}^B(r_2) &= \psi_{1s}^A(r_2) = A' \end{aligned}$$

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 wave function has a node midway between the two atoms, it is clearly antibonding and should have a *higher energy*

than the corresponding bonding wave function  $\psi_g$ .

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 19.1: 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 wave function should be a 2-electron wave function constructed from  $2p_z$  orbitals. The bonding wave function takes the "gerade" form as in  $H_2$ :

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

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

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

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 wave functions for the bonding electrons in a Lewis structure, leaving the orbitals unused in the construction of the valence bond wave functions 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.

Historically, valence bond theory was used to explain bond 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 wave functions for the two bonding pairs in  $H_2O$ . The construction is illustrated in **Figure 19.2** below:



**Figure 19.2:** Illustration of the use of VB wave functions for  $H_2O$ .

If we consider that the molecule lies in the  $xy$  plane, then let the  $OH_1$  bond lie along the  $x$ -axis and the  $OH_2$  bond lie along the  $y$  axis. We would construct the following VB wave functions using the  $2p_x$  and  $2p_y$  orbitals of oxygen:

$$\begin{aligned} \psi_1(1, 2) &= C_1[\psi_{1s}^H(1)\psi_{2p_x}^O(2) + \psi_{1s}^H(2)\psi_{2p_x}^O(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \\ \psi_2(1, 2) &= C_2[\psi_{1s}^H(1)\psi_{2p_y}^O(2) + \psi_{1s}^H(2)\psi_{2p_y}^O(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \end{aligned}$$

This would leave the  $2s$  and  $2p_z$  orbitals of oxygen left over for the two lone pairs on the oxygen. As the figure above suggests, these wave functions would lead to a  $90^\circ$  angle between the two OH bonds, which is clearly not correct. However, the qualitative trend is right. If we consider that the two hydrogens in  $H_2O$  have positive partial charges, then Coulomb repulsion between them can be invoked to justify the fact that the angle between the two bonds is larger than  $90^\circ$ .

## Atomic 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 wave functions we would construct would be

$$\begin{aligned}\psi_1(1, 2) &= C_1[\psi_{1s}^{H_1}(1)\psi_{2s}^{Be}(2) + \psi_{1s}^{H_1}(2)\psi_{2s}^{Be}(1)][\psi_{\uparrow}(s_1)\psi_{\downarrow}(s_2) - \psi_{\uparrow}(s_2)\psi_{\downarrow}(s_1)] \\ \psi_2(1, 2) &= C_2[\psi_{1s}^{H_2}(1)\psi_{2p_z}^{Be}(2) + \psi_{1s}^{H_2}(2)\psi_{2p_z}^{Be}(1)][\psi_{\uparrow}(s_1)\psi_{\downarrow}(s_2) - \psi_{\uparrow}(s_2)\psi_{\downarrow}(s_1)]\end{aligned}$$

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 them into linear combinations that are more suitable to the construction both of valence bond wave functions *and* MOs via the LCAO procedure.

## *sp* Hybridization

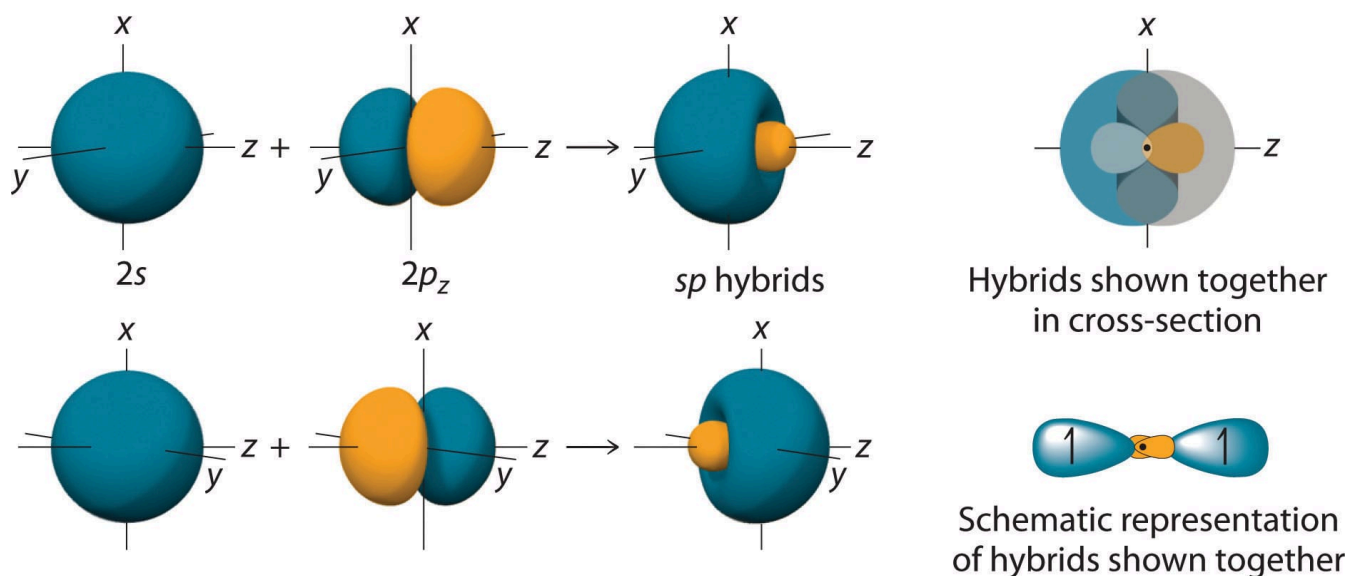
For  $Be$ , we now allow the  $s$  and  $p$  orbitals to mix and create two *hybrid* orbitals known as *sp* orbitals. There are two such orbitals we can create

$$\begin{aligned}\chi_1(r) &= \frac{1}{\sqrt{2}}[\psi_{2s}(r) + \psi_{2p_z}(r)] \\ \chi_2(r) &= \frac{1}{\sqrt{2}}[\psi_{2s}(r) - \psi_{2p_z}(r)]\end{aligned}$$

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 19.3



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 wave function of the form:

$$\begin{aligned}\psi_1(1, 2) &= C_1[\psi_{1s}^{H_1}(1)\chi_1^{Be}(2) + \psi_{1s}^{H_1}(2)\chi_1^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)] \\ \psi_2(1, 2) &= C_2[\psi_{1s}^{H_2}(1)\chi_2^{Be}(2) + \psi_{1s}^{H_2}(2)\chi_2^{Be}(1)][\psi_\uparrow(s_1)\psi_\downarrow(s_2) - \psi_\uparrow(s_2)\psi_\downarrow(s_1)]\end{aligned}$$

In the above wave functions, it is clear that  $H_1$  is on the right and  $H_2$  is on the left, based on the directionalities of  $\chi_1$  and  $\chi_2$ .

## $sp^2$ Hybrids

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  $1s^2 2s^2 2p_x 2p_y$ . 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 19.4.

\includegraphics[scale=0.5]{BH3.eps}

Figure 19.4: 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  $\phi$ . For the  $p_x$  and  $p_y$  orbitals, the  $\phi$  dependence is

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

\includegraphics[scale=0.5]{py1\_rot.eps} **Figure 19.5:** Rotation of a  $2p_y$  orbital by  $-30$  degrees.

If we rotate  $2p_y$  by  $-30$  degrees (Figure 19.5; blue is positive and red is negative), the  $\phi$  dependence becomes

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

Using the fact that

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

this rotation gives

$$\begin{aligned}\psi_{2p_y}^{(rot,1)} &\sim \sin\phi\cos30 + \cos\phi\sin30 \\ &\sim \left[ \frac{\sqrt{3}}{2}\sin\phi + \frac{1}{2}\cos\phi \right] \\ &\sim \left[ \frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x} \right]\end{aligned}$$

Similarly, consider rotating  $-\psi_{2p_y}$  by +30 degrees (Figure 19.6). This gives

$$\begin{aligned}-\psi_{2p_y}^{(rot,2)} &\sim -\sin(\phi - 30) \\ &\sim -\left[ \frac{\sqrt{3}}{2}\sin\phi - \frac{1}{2}\cos\phi \right] \\ &\sim -\frac{\sqrt{3}}{2}\psi_{2p_y} + \frac{1}{2}\psi_{2p_x}\end{aligned}$$

`\includegraphics[scale=0.5]{py2_rot.eps}`

Figure 19.6: Rotation of a  $-2p_y$  orbital by 30 degrees.

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

$$\begin{aligned}\chi_1(r) &= a\psi_{2s}(r) - b\psi_{2p_x}(r) \\ \chi_2(r) &= c\psi_{2s}(r) + d\psi_{2p_y}^{(rot,1)}(r) \\ \chi_3(r) &= c\psi_{2s}(r) - d\psi_{2p_y}^{(rot,2)}(r)\end{aligned}$$

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

$$\begin{aligned}\int |\chi_1(r)|^2 dV &= 1 ; \quad \int \chi_1^*(r)\chi_2(r) dV = 0 \\ \int |\chi_2(r)|^2 dV &= 1 ; \quad \int \chi_1^*(r)\chi_3(r) dV = 0 \\ \int |\chi_3(r)|^2 dV &= 1 ; \quad \int \chi_2^*(r)\chi_3(r) dV = 0\end{aligned}$$

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

$$\begin{aligned}\chi_1(r) &= \frac{1}{\sqrt{3}}[\psi_{2s}(r) - \sqrt{2}\psi_{2p_x}(r)] \\ \chi_2(r) &= \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) + \sqrt{3}\psi_{2p_y}(r)] \\ \chi_3(r) &= \frac{1}{\sqrt{6}}[\sqrt{2}\psi_{2s}(r) + \psi_{2p_x}(r) - \sqrt{3}\psi_{2p_y}(r)]\end{aligned}$$

The  $sp^2$  hybrids allow bonding at  $120^\circ$  degrees, and these orbitals appear as shown in Figure 19.7:

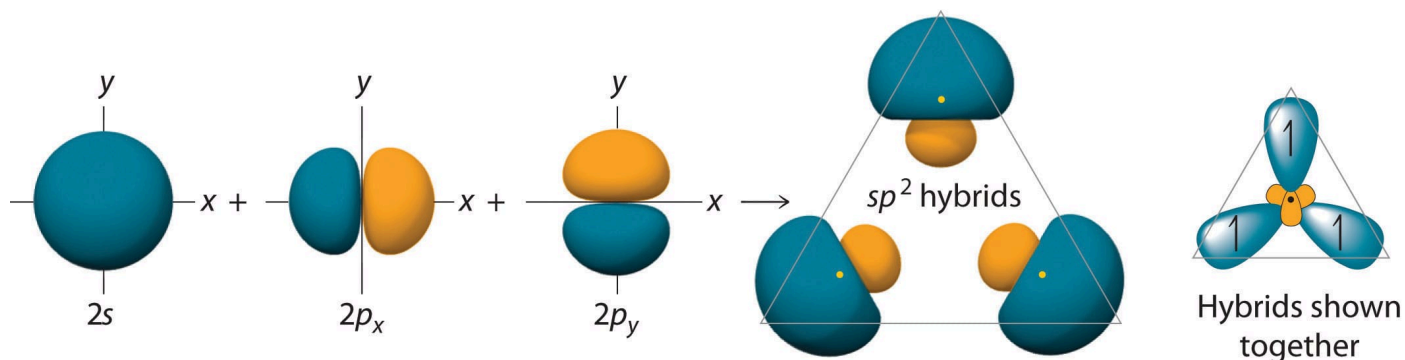


Figure 19.7: Formation of  $sp^2$  Hybrid Orbitals. Combining one  $ns$  and two  $np$  atomic orbitals gives three equivalent  $sp^2$  hybrid orbitals in a trigonal planar arrangement; that is, oriented at  $120^\circ$  to one another.

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

## $sp^3$ Hybrids

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:

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

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with  $109.5^\circ$  angles between them (Figure 19.8). Like all the hybridized orbitals discussed earlier, the  $sp^3$  hybrid atomic orbitals are predicted to be equal in energy.

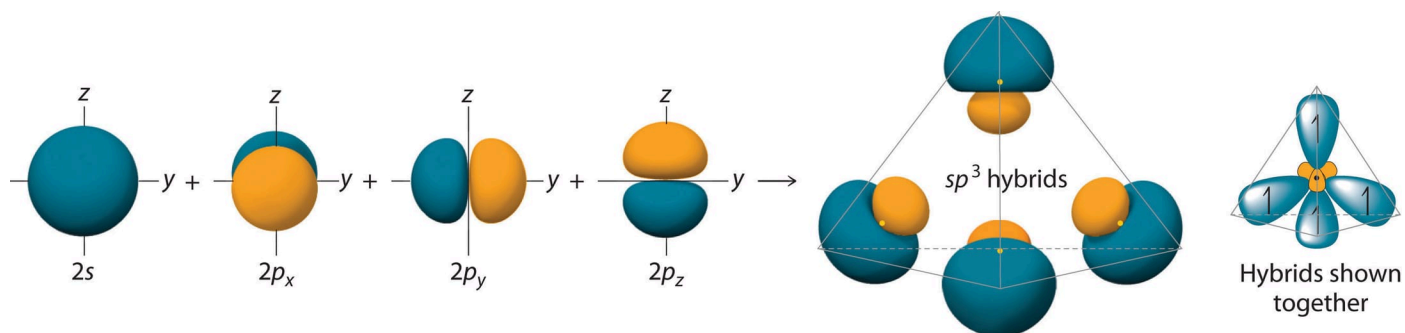


Figure 19.8: Formation of  $sp^3$  Hybrid Orbitals. Combining one  $ns$  and three  $np$  atomic orbitals results in four  $sp^3$  hybrid orbitals oriented at  $109.5^\circ$  to one another in a tetrahedral arrangement.

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.

## Contributors

- [Mark Tuckerman](#) ([New York University](#))

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## 20: Introduction to Organic Chemistry

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\includegraphics[scale=0.5]{methane.eps}  
\includegraphics[scale=0.5]{ethane.eps}

We could also combine the  $sp^3$  orbitals using LCAO theory to form  $\sigma$  and  $\sigma^*$  molecular orbitals. The appropriate combinations would be

Figure: Idealized  $Si(100) - 2 \times 1$  surface.

\includegraphics[scale=0.5]{Si\_surface.eps}

In this figure, the Si-Si dimers on this surface play a role similar to that of ethylene in the traditional Diels-Alder reaction, however, the addition of 1,3-butadiene to this surface violates the **Woodward-Hoffmann rules**.

### Contributors

Mark Tuckerman (New York University)

## 21: Overview of molecular spectroscopy, rotational and vibrational energy levels

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### Contributors and Attributions

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