CHEM 3301: Quantum Mechanics

2023

Contents

Chapter 1

Introduction and Review

1.1 Motivation for Quantization

On the macroscopic scale, most quantities can take on a continuous range of values. You can

- walk at any speed
- experience any temperature outside
- have any volume of water
- have any concentration of solution
- have any mass of a substance

However, some things are quantized. For example, at the store, you can buy only integer numbers of of fruits, vegetables, eggs, tins, etc.

At the atomic level, everything is quantized:

- only an integer number of atoms can make up a molecule or nanoparticle
- atoms have integer numbers of electrons

Given this, the mathematical description of electrons, atoms, and molecules (Quantum Mechanics, QM) must give quantized solutions and is different than that describing bulk, macroscopic properties (Classical Mechanics).

Historically, QM was developed by proposing math to explain observations such as the distinct bands in bright-line emission spectra of atoms, which revealed quantized atomic energy levels.

However, rather than introducing QM from a historical perspective, we will begin with some mathematical background.

1.2 Linear Algebra Review

Mathematically, quantized systems are commonly modeled with vectors and matrices. Two vectors can be written as $\mathbf{a} = (a_1, a_2, a_3)$ and $\mathbf{b} = (b_1, b_2, b_3)$. The dot product, $\mathbf{a} \cdot \mathbf{b}$, is

$$\mathbf{a}^T\mathbf{b} = \begin{bmatrix} a_1 & a_2 & a_3 \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = a_1b_1 + a_2b_2 + a_3b_3$$

which gives a number. Recall that the T superscript denotes the transpose of a vector or matrix. Alternatively, taking the product

$$\mathbf{a}\mathbf{b}^T = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \begin{bmatrix} b_1 & b_2 & b_3 \end{bmatrix} = \begin{bmatrix} a_1b_1 & a_1b_2 & a_1b_3 \\ a_2b_1 & a_2b_2 & a_2b_3 \\ a_3b_1 & a_3b_2 & a_3b_3 \end{bmatrix}$$

gives a matrix. To add two matrices, $\mathbf{A}$ and $\mathbf{B}$,

$$\mathbf{A} + \mathbf{B} = \begin{bmatrix} a_{1,1} & a_{1,2} & a_{1,3} \\ a_{2,1} & a_{2,2} & a_{2,3} \\ a_{3,1} & a_{3,2} & a_{3,3} \end{bmatrix} + \begin{bmatrix} b_{1,1} & b_{1,2} & b_{1,3} \\ b_{2,1} & b_{2,2} & b_{2,3} \\ b_{3,1} & b_{3,2} & b_{3,3} \end{bmatrix} = \begin{bmatrix} a_{1,1} + b_{1,1} & a_{1,2} + b_{1,2} & a_{1,3} + b_{1,3} \\ a_{2,1} + b_{2,1} & a_{2,2} + b_{2,2} & a_{2,3} + b_{2,3} \\ a_{3,1} + b_{3,1} & a_{3,2} + b_{3,2} & a_{3,3} + b_{3,3} \end{bmatrix}$$

and $\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A}$. To multiply two matrices,

$$\begin{aligned} \mathbf{AB} &= \begin{bmatrix} a_{1,1} & a_{1,2} & a_{1,3} \\ a_{2,1} & a_{2,2} & a_{2,3} \\ a_{3,1} & a_{3,2} & a_{3,3} \end{bmatrix} \begin{bmatrix} b_{1,1} & b_{1,2} & b_{1,3} \\ b_{2,1} & b_{2,2} & b_{2,3} \\ b_{3,1} & b_{3,2} & b_{3,3} \end{bmatrix} \\ &= \begin{bmatrix} a_{1,1}b_{1,1} + a_{1,2}b_{2,1} + a_{1,3}b_{3,1} & a_{1,1}b_{1,2} + a_{1,2}b_{2,2} + a_{1,3}b_{3,2} & a_{1,1}b_{1,3} + a_{1,2}b_{2,3} + a_{1,3}b_{3,3} \\ a_{2,1}b_{1,1} + a_{2,2}b_{2,1} + a_{2,3}b_{3,1} & a_{2,1}b_{1,2} + a_{2,2}b_{2,2} + a_{2,3}b_{3,2} & a_{2,1}b_{1,3} + a_{2,2}b_{2,3} + a_{2,3}b_{3,3} \\ a_{3,1}b_{1,1} + a_{3,2}b_{2,1} + a_{3,3}b_{3,1} & a_{3,1}b_{1,2} + a_{3,2}b_{2,2} + a_{3,3}b_{3,2} & a_{3,1}b_{1,3} + a_{3,2}b_{2,3} + a_{3,3}b_{3,3} \end{bmatrix} \end{aligned}$$

As a result of this definition, $\mathbf{AB} \neq \mathbf{BA}$, so the order of matrix multiplication matters and we say that it does not commute.

A square matrix ($\mathbf{A}$) has characteristic eigenvalues (λ_i) and eigenvectors ($\mathbf{x_i}$) that can be found via diagonalization.

$$\mathbf{A}\mathbf{x_i} = \lambda_i\mathbf{x_i}$$

For a 3×3 example,

$$\mathbf{A} = \begin{bmatrix} 2 & 0 & 0 \\ 1 & 2 & -1 \\ 1 & 3 & -2 \end{bmatrix}$$

We find the eigenvalues by setting

$$\det(\mathbf{A} - \lambda\mathbf{I}) = 0$$

where $\mathbf{I}$ is the identity matrix

$$\mathbf{I} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The determinant is then

$$\begin{aligned} \begin{vmatrix} 2-\lambda & 0 & 0 \\ 1 & 2-\lambda & -1 \\ 1 & 3 & -2-\lambda \end{vmatrix} &= 0 \\ -(2-\lambda)(2-\lambda)(2+\lambda) + 3(2-\lambda) &= 0 \\ (4 - 4\lambda + \lambda^2)(2+\lambda) - 6 + 3\lambda &= 0 \\ \lambda^3 - 2\lambda^2 - \lambda + 2 &= 0 \\ (\lambda - 2)(\lambda - 1)(\lambda + 1) &= 0 \end{aligned}$$

Thus, the solutions are

$$\{\lambda_1,\, \lambda_2,\, \lambda_3\} = \{2, 1, -1\}$$

and these roots are the eigenvalues. To find the eigenvectors, we need to find the solution to the system of equations

$$(\mathbf{A} - \lambda_i\mathbf{I})\mathbf{x_i} = 0$$

For the case of $\lambda_1 = 2$, we can represent the system of equations to be solved as an augmented matrix, which can be row reduced:

$$\left[\begin{array}{ccc|c} 0 & 0 & 0 & 0 \\ 1 & 0 & -1 & 0 \\ 1 & 3 & -4 & 0 \end{array}\right] = \left[\begin{array}{ccc|c} 1 & 0 & -1 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{array}\right]$$

This corresponds to a linearly dependent system of equations:

$$x - z = 0$$

$$y - z = 0$$

So picking a value of z immediately determines the values of the other two variables. If we select $z = 1$ for convenience, we then have $x = 1$ and $y = 1$ as well. Therefore, this gives an eigenvector of

$$\mathbf{x_1} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

(or any multiple of this result).

Similarly, for $\lambda_2 = 1$, we can obtain

$$\mathbf{x_2} = \begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix}$$

and, for $\lambda_3 = -1$, we have

$$\mathbf{x_3} = \begin{bmatrix} 0 \\ 1 \\ 3 \end{bmatrix}$$

Eigenvalues and eigenvectors have physical interpretations, such as the vibrational frequencies, and the corresponding vibrational modes (components in the x, y, z directions).

If the eigenvalues are taken to be a physical observable, they must be real numbers, so we are only interested in matrices that give real eigenvalues. One class of matrices that are guaranteed to give real eigenvalues are Hermitian matrices (although, as in the example above, not all matrices with real eigenvalues are Hermitian).

A matrix is Hermitian if it is equal to the transpose of its complex conjugate.

$$\mathbf{A} = \mathbf{A}^\dagger = (\mathbf{A}^*)^T$$

To prove that a Hermitian matrix has real eigenvalues, we begin with the eigenvalue equation

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$$

and take the conjugate transpose of both sides

$$\mathbf{x}^\dagger\mathbf{A}^\dagger = \lambda^*\mathbf{x}^\dagger$$

Using the Hermitian property, this becomes

$$\mathbf{x}^\dagger\mathbf{A} = \lambda^*\mathbf{x}^\dagger$$

Now we left multiply the first eigenvalue equation by $\mathbf{x}^\dagger$ to give

$$\mathbf{x}^\dagger\mathbf{A}\mathbf{x} = \lambda\mathbf{x}^\dagger\mathbf{x}$$

and right multiply the second eigenvalue equation by $\mathbf{x}$ to give

$$\mathbf{x}^\dagger\mathbf{A}\mathbf{x} = \lambda^*\mathbf{x}^\dagger\mathbf{x}$$

Subtracting the two equations,

$$(\lambda - \lambda^*)\mathbf{x}^\dagger\mathbf{x} = 0$$

which requires

$$\lambda = \lambda^*$$

so the eigenvalues are real.

Another important property of Hermitian matrices is that their eigenvectors are orthogonal:

$$\mathbf{x}_j^\dagger \mathbf{x}_i = 0$$

Typically the eigenvectors are also chosen to be normalized, such that

$$\mathbf{x}_j^\dagger \mathbf{x}_i = \delta_{ij}$$

Here, δ_{ij} is the Kronecker delta function, which is 1 for $i = j$ (normalization) and 0 for $i \neq j$.

$$\boxed{\delta_{ij} = \begin{cases} 1\,, & \text{if } i = j \\ 0\,, & \text{if } i \neq j \end{cases}}$$

Finally, the eigenvectors form a complete set, meaning that we can express any arbitrary vector, $\mathbf{y}$, in terms of these basis vectors:

$$\mathbf{y} = \sum_i c_i \mathbf{x}_i$$

where the c_i's are expansion coefficients

$$c_i = \mathbf{x}_i^\dagger \mathbf{y}$$

This requires

$$\sum_i \mathbf{x}_i \mathbf{x}_i^\dagger = 1$$

which is known as the completeness (or closure) relation.

Can we represent quantized properties without using matrices? As we will see, we can instead use Hermitian operators that share many properties with Hermitian matrices, but are based on calculus instead of linear algebra.

1.3 Review of Differential Equations

Let's consider a second-order differential equation of the form

$$-\frac{d^2}{dx^2} f(x) = \lambda f(x)$$

where λ is a real number, which resembles our matrix eigenvalue equation. Here, $-\frac{d^2}{dx^2}$ is termed an operator, $f(x)$ is an eigenfunction, and λ is once again the eigenvalue.

Our second-order differential equation can be re-written as

$$\frac{d^2}{dx^2}f(x) + \lambda f(x) = 0$$

When solving differential equations, a common approach is to propose the form of a solution, and then demonstrate that it works. To solve the above equation, we propose

$$f(x) = \mathrm{e}^{ax}$$

$$\frac{d}{dx}f(x) = a\mathrm{e}^{ax}$$

$$\frac{d^2}{dx}f(x) = a^2\mathrm{e}^{ax}$$

Substituting this into the differential equation, it becomes

$$a^2\mathrm{e}^{ax} + \lambda\mathrm{e}^{ax} = 0$$

$$(a^2 + \lambda)\mathrm{e}^{ax} = 0$$

For a non-trivial solution, this requires

$$a^2 = -\lambda$$

Let us consider the cases of $\lambda < 0$ and $\lambda > 0$ separately.

If $\lambda < 0$, $a = \pm\sqrt{|\lambda|}$ and the general solution is

$$f(x) = A\mathrm{e}^{\sqrt{|\lambda|}x} + B\mathrm{e}^{-\sqrt{|\lambda|}x}$$

where A and B are some arbitrary constants.

If $\lambda > 0$, $a = \pm\mathrm{i}\sqrt{\lambda}$ and the general solution is

$$f(x) = A\mathrm{e}^{\mathrm{i}\sqrt{\lambda}x} + B\mathrm{e}^{-\mathrm{i}\sqrt{\lambda}x}$$

Using Euler's identity

$$\begin{aligned} f(x) &= A\left[\cos\left(\sqrt{\lambda}x\right) + \mathrm{i}\sin\left(\sqrt{\lambda}x\right)\right] + B\left[\cos\left(-\sqrt{\lambda}x\right) + \mathrm{i}\sin\left(-\sqrt{\lambda}x\right)\right] \\ &= A\left[\cos\left(\sqrt{\lambda}x\right) + \mathrm{i}\sin\left(\sqrt{\lambda}x\right)\right] + B\left[\cos\left(\sqrt{\lambda}x\right) - \mathrm{i}\sin\left(\sqrt{\lambda}x\right)\right] \\ &= (A+B)\cos\left(\sqrt{\lambda}x\right) + (A-B)\,\mathrm{i}\sin\left(\sqrt{\lambda}x\right) \\ &= C\cos\left(\sqrt{\lambda}x\right) + D\sin\left(\sqrt{\lambda}x\right) \end{aligned}$$

for two new constants C and D.

The solution gives all possible sine and cosine functions, which are orthogonal and form a basis, as expected for a Hermitian operator. Any well-behaved, single-valued function can be written as a sum of many sines and cosines with different frequencies, which is the basis of the Fourier series expansion.

1.4 Definite Integrals

To evaluate many QM quantities, we will need to determine the values of definite integrals of functions. A definite integral is evaluated over a specified range, from an initial value, i, to a final value, f:

$$I = \int_i^f g'(x)dx = g(f) - g(i)$$

As an example, let us evaluate the definite integral

$$I = \int_0^1 xdx = \frac{1}{2}x^2\Big|_0^1 = \frac{1}{2}(1^2 - 0^2) = \frac{1}{2}$$

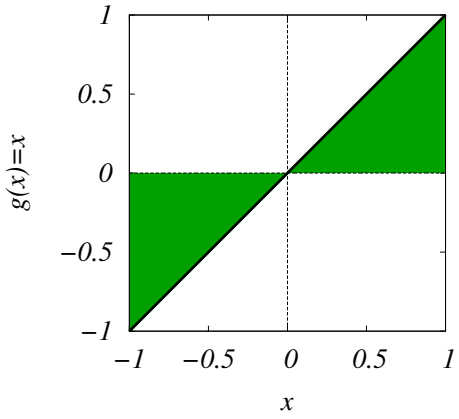
A particularly useful property is that the integral of an odd function, (i.e. $g(-x) = -g(x)$) over a symmetric interval (i.e. from $-a$ to a) is zero. This makes intuitive sense, since half of the area is negative and half positive.

As an example, consider

$$I = \int_{-1}^1 xdx$$

this is an integral of an odd function over a symmetric interval, so we can say that it is zero by inspection.
To show this

$$I = \int_{-1}^1 xdx = \frac{1}{2}x^2\Big|_{-1}^1 = \frac{1}{2}(1^2 - (-1)^2) = 0$$

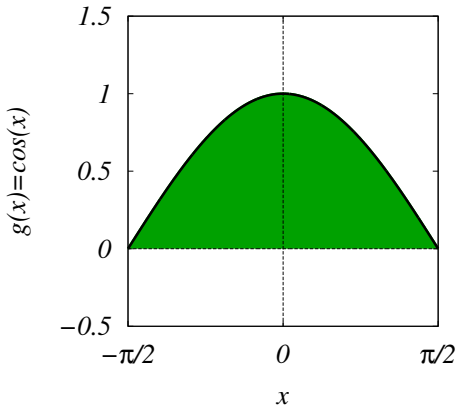


Also, the integral of an even function (i.e. $g(-x) = g(x)$) over a symmetric interval is

$$\int_{-a}^a g(x)dx = 2\int_0^a g(x)dx$$

As an example, consider

$$\begin{aligned} I &= \int_{-\pi/2}^{\pi/2} \cos(x)dx \\ &= \sin(x)\Big|_{-\pi/2}^{\pi/2} \\ &= \sin(\pi/2) - \sin(-\pi/2) \\ &= 1 - (-1) \\ &= 2 \end{aligned}$$



which is equivalent to

$$\begin{aligned} I &= 2\int_{0}^{\pi/2} \cos(x)dx \\ &= 2\sin(x)\Big|_{0}^{\pi/2} \\ &= 2\sin(\pi/2) - \sin(0) \\ &= 2(1-0) \\ &= 2 \end{aligned}$$

Finally, the product of an even function and an odd function is an odd function, so for the more complicated integral

$$I = \int_{-1}^{1} x\cos(x)\sin^2(x)dx$$

we can see that the integrand is an odd function and the integral is zero.

Most commonly, we will be evaluating definite integrals over the range $(0,\infty)$ or $(-\infty,\infty)$. Tables of definite integrals are available and should be used whenever possible. Some common definite integrals are:

$$\begin{aligned} \int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx &= \frac{a}{2} \\ \int_0^a x\sin^2\left(\frac{n\pi}{a}x\right)dx &= \frac{a^2}{4} \\ \int_0^a x^2\sin^2\left(\frac{n\pi}{a}x\right)dx &= \left(\frac{a}{2\pi n}\right)^3\left(\frac{4\pi^3n^3}{3} - 2n\pi\right) \\ \int_0^\infty x^n e^{-ax}dx &= \frac{n!}{a^{n+1}} \end{aligned}$$

$$\begin{aligned}
\int_0^\infty \mathrm{e}^{-ax^2}\,dx &= \frac{1}{2}\sqrt{\frac{\pi}{a}} \\
\int_0^\infty x\mathrm{e}^{-ax^2}\,dx &= \frac{1}{2a} \\
\int_0^\infty x^2\mathrm{e}^{-ax^2}\,dx &= \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \\
\int_0^\infty x^3\mathrm{e}^{-ax^2}\,dx &= \frac{1}{2a^2} \\
\int_0^\infty x^4\mathrm{e}^{-ax^2}\,dx &= \frac{3}{8}\sqrt{\frac{\pi}{a^5}}
\end{aligned}$$

1.5 Unit Conversion

A useful table of conversion factors is:

	J	kJ/mol	eV	a.u.	cm^{-1}	Hz
1 J	1	6.022×10^{20}	6.242×10^{18}	2.294×10^{17}	5.035×10^{22}	1.509×10^{33}
1 kJ/mol	1.661×10^{-21}	1	1.036×10^{-2}	3.089×10^{-4}	83.60	2.506×10^{12}
1 eV	1.602×10^{-19}	96.48	1	3.675×10^{-2}	8065	2.418×10^{14}
1 a.u.	4.359×10^{-18}	2625	27.21	1	2.195×10^{5}	6.580×10^{15}
1 cm^{-1}	1.986×10^{-23}	1.196×10^{-2}	1.240×10^{-4}	4.556×10^{-6}	1	2.998×10^{10}
1 Hz	6.616×10^{-34}	3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

Chapter 2

Waves in One Dimension

2.1 Kinetic and Potential Energies

The total energy (E) of a physical system,

$$E = T + V,$$

is a sum of kinetic (T) and potential (V) energies. The kinetic energy can be written in terms of the momentum, $p = mv$, which is a product of mass (m) and velocity (v):

$$T = \frac{p^2}{2m},$$

while the potential energy is generally a function of only position, $V = V(x)$. This gives the total energy as

$$E = \frac{p^2}{2m} + V(x).$$

For a free particle or wave in the absence of a potential, $V(x) = 0$, and the energy is dependent only on the momentum.

2.2 The Classical Wave Equation

Let us consider a uniform string stretched between two points and a localized wave pulse moving down the string.

The classical wave equation describes how this wave evolves with time:

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\Psi(x,t)$$

where $\Psi(x,t)$ gives the amplitude of the wave at position x and time t. Here, v is the velocity of the wave's propagation, which can be related to the wavelength (λ) and frequency (ν):

$$v = \lambda\nu$$

It is common to make a change of variables and define the wavenumber as

$$k = \frac{2\pi}{\lambda}$$

and the angular frequency as

$$\omega = 2\pi\nu$$

such that the velocity is

$$v = \frac{\omega}{k}.$$

The wave equation can be solved using the method of separation of variables. We propose a solution

$$\Psi(x,t) = \psi(x)f(t)$$

Substituting this into the wave equation gives

$$f(t)\frac{\partial^2}{\partial x^2}\psi(x) = \frac{1}{v^2}\psi(x)\frac{\partial^2}{\partial t^2}f(t)$$

Rearranging to group all the x-dependent terms on one side and the t-dependent terms on the other:

$$\frac{1}{\psi(x)}\frac{\partial^2}{\partial x^2}\psi(x) = \frac{1}{v^2}\frac{1}{f(t)}\frac{\partial^2}{\partial t^2}f(t) = k^2$$

The two sides can only be equal for all values of x, t if they are each equal to a constant, which we will pick to be k^2.

This gives two differential equations to solve, with each now being a function of a single variable:

$$\frac{\partial^2}{\partial x^2}\psi(x) - k^2\psi(x) = 0$$

$$\frac{\partial^2}{\partial t^2}f(t) - \omega^2 f(t) = 0$$

where $\omega = kv$. These both have the form we saw previously and, if k is a real number, then the solutions are sinusoidal functions. The general solutions are

$$\psi(x) = \mathrm{e}^{\pm \mathrm{i}kx}$$

$$f(t) = \mathrm{e}^{\pm \mathrm{i}\omega t}$$

2.3 From the Wave Equation to the Time-Dependent Schrödinger Equation

The time-dependent Schrödinger Equation is the fundamental equation in quantum mechanics. It can be motivated from the classical wave equation with some additional assumptions regarding energy quantization.

The general solutions of the 1D wave equation can be written as

$$\Psi(x,t) = \mathrm{e}^{\mathrm{i}(kx-\omega t)}$$

if we combine the position- and time-dependent terms into a single exponential.

Following Planck, we take the energy as being quantized and proportional to the angular frequency,

$$E = \frac{p^2}{2m} = \hbar\omega$$

where $\hbar$ is the reduced Planck constant. Solving for ω gives

$$\omega = \frac{p^2}{2m\hbar}$$

Also, de Broglie postulated that the momentum is related to the wavelength

$$p = \frac{h}{\lambda} = \left(\frac{h}{2\pi}\right)\left(\frac{2\pi}{\lambda}\right) = \hbar k$$

where h is Planck's constant and $\hbar = h/2\pi$. Substituting, this gives

$$\omega = \frac{\hbar k^2}{2m}$$

Using this relation, the wavefunction becomes

$$\Psi(x,t) = \exp\left[\mathrm{i}\left(kx - \frac{\hbar}{2m}k^2 t\right)\right]$$

Due to the k-dependence of the exponential, we can related the first derivative with respect to t to the second derivative with respect to x:

$$\frac{\partial^2\Psi}{\partial x^2} = (\mathrm{i}k)^2\Psi = -k^2\Psi$$

$$\frac{\partial\Psi}{\partial t} = -\frac{\mathrm{i}\hbar}{2m}k^2\Psi$$

Combining these results gives:

$$\frac{\mathrm{i}\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{\partial\Psi}{\partial t}$$

Multiplying through by $i\hbar$ gives the more common form of

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \mathrm{i}\hbar\frac{\partial\Psi}{\partial t}}$$

which is the time-dependent Schrödinger equation in one dimension.

The time-dependent Schrödinger equation is not a result that can be rigorously derived. Rather, it can be motivated by arguments like the one above and is shown to be valid based on the accuracy of the resulting predictions.

2.4 From the Wave Equation to the Time-Independent Schrödinger Equation

While the time-dependent Schrödinger equation is the starting point for QM, it is not the key equation in quantum chemistry. Here, we are primarily interested in the ground states of atoms and molecules, which are stable and do not depend on time, so we instead turn to the time-independent Schrödinger equation. As we will see, this equation can be derived from the time-dependent result, but it can also be motivated from the wave equation.

Let us return to the wave equation

$$\frac{\partial^2}{\partial x^2}u(x,t) = \frac{1}{v^2}\frac{\partial^2}{\partial t^2}u(x,t)$$

and propose the solution

$$u(x,t) = \psi(x)\cos(\omega t).$$

This simplifies the differential equation

$$\begin{aligned}
\frac{\partial^2}{\partial x^2}\psi(x)\cos(\omega t) &= \frac{1}{v^2}\psi(x)\frac{\partial^2}{\partial t^2}\cos(\omega t)\\
\frac{\partial^2}{\partial x^2}\psi(x)\cos(\omega t) &= -\frac{\omega^2}{v^2}\psi(x)\cos(\omega t)\\
\frac{\partial^2}{\partial x^2}\psi(x) &= -\frac{\omega^2}{v^2}\psi(x)\\
\frac{\partial^2}{\partial x^2}\psi(x) &= -k^2\psi(x)
\end{aligned}$$

Additionally, we can rearrange the total energy expression

$$E = \frac{p^2}{2m} + V(x)$$

to solve for the momentum:

$$\begin{aligned} p^2 &= 2m\left[E - V(x)\right] \\ \hbar^2 k^2 &= 2m\left[E - V(x)\right] \\ k^2 &= \frac{2m}{\hbar^2}\left[E - V(x)\right] \end{aligned}$$

where we have used the de Broglie relation.

Inserting this result into the differential equation gives

$$\frac{\partial^2}{\partial x^2}\psi(x) = -\frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x)$$

Finally, rearranging, we obtain

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

This is more compactly written as

$$\boxed{\mathcal{H}\psi(x) = E\psi(x)}$$

which has a form of an eigenvalue problem. Here, the operator

$$\boxed{\mathcal{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)}$$

is termed the Hamiltonian. The Hamiltonian is the total energy operator,

$$\mathcal{H} = T + V$$

and allows us to assign the kinetic energy operator in 1D as

$$\boxed{T = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}}$$

2.5 Eliminating Time Dependence via Separation of Variables

Finally, we can obtain the time-independent Schrödinger equation from the time-dependent one via the method of separation of variables, provided that the potential does not depend on time (i.e. $V = V(x)$).

Our general time-dependent Schrödinger equation is

$$\boxed{\mathcal{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}}$$

which reduces to the form obtained above for the case of $V = 0$.

We propose the solution

$$\Psi(x,t) = \psi(x)f(t)$$

which gives

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}f + V\psi f = \mathrm{i}\hbar\frac{df}{dt}\psi$$

Dividing through by ψf gives

$$\frac{1}{\psi}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi\right] = \frac{1}{f}\left[\mathrm{i}h\frac{df}{dt}\right] = C$$

where both sides must equal some constant, C, to ensure equality for all x, t.

The position-dependent result is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = C\psi$$

which is almost the time-independent Schrödinger equation, but we need to determine the value of the constant, C. By dimensional analysis, V has units of energy, so C must also have units of energy and it makes sense that $C = E$.

To show this more rigorously, we return to the time-dependent result:

$$\frac{1}{f}\left[\mathrm{i}\hbar\frac{df}{dt}\right] = C$$

This differential equation is separable, since we can group together like terms,

$$\frac{df}{f} = \frac{C}{\mathrm{i}\hbar}dt$$

We can then integrate both sides of the differential equation

$$\int\frac{1}{f}df = \frac{C}{\mathrm{i}\hbar}\int dt$$

Integrating gives

$$\ln(f) = \frac{C}{i\hbar}t$$

and we take the exponential of both sides to eliminate the natural logarithm

$$f(t) = \exp\left(-\mathrm{i}\frac{C}{\hbar}t\right)$$

This is a sinusoidal function with frequency $\omega = C/\hbar$, or $C = \hbar\omega$. Recalling Planck's energy quantization, $E = \hbar\omega$, so we have simply $C = E$.

Thus, replacing the value of C in the position-dependent result gives

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

or, more compactly,

$$\mathcal{H}\psi = E\psi$$

which is the time-independent Schrödinger equation.

As long as the potential is time-independent, it is trivial to go from the solution to the TISE to the TDSE. Time-dependent potentials are not common, so the TISE is normally all we care about in quantum chemistry.

Chapter 3

The Basics of Quantum Mechanics

Quantum mechanics is usually presented by introducing a series of postulates, the validity of which is confirmed by the excellent quantitative accuracy of QM predictions.

3.1 The Wavefunction

Postulate 1: The state of a QM system is completely specified by the wavefunction, Ψ, which depends on the positions of all particles in the system, and on time.

In quantum chemistry, we are primarily interested in the time-independent wavefunction, ψ, which is a function of position only. The wavefunction can be used to predict observable properties of the system, such as the energy.

As the wavefunction can be a complex function, it does not correspond to a measurable quantity itself. However, the real quantity

$$|\psi|^2 = \psi^* \psi$$

can be interpreted as a probability density. The wavefunction gives a probability, P, of finding a particle within a particular region when integrated over the volume of interest, V. In the case of a 1D system, this is

$$P = \int_V |\psi|^2 dx$$

and in the case of 3D, this is

$$P = \iiint_V |\psi|^2 dx\, dy\, dz$$

The total probability of finding a particle with wavefunction ψ anywhere in space is unity. This gives rise to the normalization constraint

$$\boxed{\int_{-\infty}^{\infty} |\psi|^2 dx = 1}$$

$$\boxed{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2 dx\, dy\, dz = 1}$$

depending on whether we are working in 1D or 3D. For any bound state, the wavefunction is always normalizable.

There is a discrete spectrum of bound wavefunctions, ψ_i, with energies, E_i (where i is a labeling index), that are the solutions to the time-independent Schrödinger equation.

$$\boxed{\mathcal{H}\psi_i = E_i\psi_i}$$

These are the stationary states (independent of time).

The wavefunctions for different energies are orthonormal

$$\boxed{\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij}}$$

and the set of wavefunctions form a complete set, spanning the space of functions. This means that any well-behaved function, f, in the same space can be written as a linear combination of the wavefunctions with coefficients, c_i:

$$\boxed{f = \sum_i c_i \psi_i}$$

3.2 Operators

Postulate 2: For every observable in classical mechanics, there is a corresponding Hermitian operator in quantum mechanics.

Hermitian operators share the same properties as Hermitian matrices, that their eigevalues are real – corresponding to real physical observables. It also is the Hermitian property that guarantees that the eigenfunctions (the wavefunctions) are orthogonal and form a complete basis (see Section 1.2).

The total energy operator is the Hamiltonian

$$\boxed{\mathcal{H} = T + V}$$

The potential energy operator, V, is system dependent, but is usually a function only of position (time dependence is uncommon and will not be considered in this course). The position operator itself is simply x in 1D or $\mathbf{r} = (x, y, z)$ in 3D.

As we have seen previously, the kinetic energy operator, T, is

$$T = \frac{p^2}{2m}$$

where m is the mass of the particle and p is the momentum. In 1D, we have

$$\boxed{T = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}$$

and in 3D, we have

$$\boxed{T = -\frac{\hbar^2}{2m}\nabla^2}$$

where ∇^2 is the Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Given the relation between the kinetic energy and momentum, we can write the square of the momentum operator as

$$p^2 = -\hbar^2\frac{d^2}{dx^2}$$

The 1D momentum operator itself is

$$p = -\mathrm{i}\hbar\frac{d}{dx}$$

Postulate 3: For any measurement of some observable property corresponding to the operator A, the result will be one of the eigenvalues of A.

The key example of this is the energy, which must be some eigenvalue of $\mathcal{H}$:

$$\mathcal{H}\psi_i = E_i\psi_i$$

The only possible results of energy measurements for a single particle are E_1, E_2, E_3, etc.

Postulate 4: If a system is a state described by the normalized wavefunction ψ, then the average value of a measurement corresponding to observable A is

$$\langle A\rangle = \int \psi^* A\psi d\tau$$

Here, the integral is a definite integral over all space and $d\tau$ is the appropriate volume element (dx in 1D or $dx\,dy\,dz$ in 3D). So, for the 1D case, this is

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^* A \psi dx$$

The physical interpretation here is that, if you have a large ensemble of particles in state ψ, any one measurement will have to give some eigenvalue a_i, but the average value over the whole ensemble is $\langle A \rangle$ and is called the expectation value.

If ψ is an eigenstate of A, then the expectation value is simply the corresponding eigenvalue. To show this, let

$$A\psi = a\psi$$

Then, the expectation value is

$$\begin{aligned} \langle A \rangle &= \int_{-\infty}^{\infty} \psi^* A \psi dx \\ &= \int_{-\infty}^{\infty} \psi^* a \psi dx \\ &= a \int_{-\infty}^{\infty} \psi^* \psi dx \\ &= a \end{aligned}$$

where

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

due to normalization of the wavefunction.

If ψ is not itself an eigenfunction of A, we can expand it in terms of the eigenfunctions. Let the eigenfunctions and eigenvalues of A be given by

$$Af_i = a_i f_i$$

Due to completeness, we can write ψ as a linear combination of the eigenfunctions, f_i, with coefficients c_i:

$$\psi = \sum_i c_i f_i = \sum_i \left(\int_{-\infty}^{\infty} f_i^* \psi dx \right) f_i$$

The coefficients are found by projecting the wavefunction onto to the eigenfunctions. The

resulting expectation value is

$$\begin{aligned}
\langle A \rangle &= \int_{-\infty}^{\infty} \psi^* A \psi dx \\
&= \int_{-\infty}^{\infty} \left(\sum_i c_i^* f_i^* \right) \left(A \sum_j c_j f_j \right) dx \\
&= \int_{-\infty}^{\infty} \left(\sum_i c_i^* f_i^* \right) \left(\sum_j c_j a_j f_j \right) dx \\
&= \sum_{ij} \int_{-\infty}^{\infty} c_i^* c_j a_j f_i^* f_j dx \\
&= \sum_{ij} c_i^* c_j a_j \delta_{ij} \\
&= \sum_i |c_i|^2 a_i
\end{aligned}$$

The final result is

$$\boxed{\langle A \rangle = \sum_i |c_i|^2 a_i}$$

which is a weighted average of the eigenvalues. Therefore, the probability of measuring a particular eigenvalue, a_i is

$$\boxed{P(a_i) = |c_i|^2}$$

Expectation values in quantum mechanics satisfy the same equations that their analogous quantities satisfy in classical mechanics. For example, the total energy is the sum of kinetic and potential terms

$$\langle \mathcal{H} \rangle = \langle T \rangle + \langle V \rangle$$

Another example of this is that the expectation values satisfy Newton's laws of motion

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt}$$

which is a statement of Ehrenfest's theorem.

There are two further postulates in Quantum Mechanics. The first of these is that the state of the system evolves in time according to the time-dependent Schrödinger equation, which we met in Chapter 2. The second concerns the antisymmetry property of the wavefunction for many-electron systems, which we will discuss in Chapter 9.

3.3 Dirac's Bra-Ket Notation

Much of what we have just written can be simplified by using Dirac's Bra-Ket (bracket) notation. Here, functions are written as a "ket"

$$f = |f\rangle$$

their complex conjugates are written as a "bra"

$$f^* = \langle f|$$

and integrals involve both a bra and ket. Orthonormality is given by

$$\langle \psi_i | \psi_j \rangle = \int \psi_i^* \psi_j d\tau = \delta_{ij}$$

and expectation values are given by

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \int \psi^* A \psi d\tau$$

The expansion of ψ in terms of a set of eigenfunctions would be

$$|\psi\rangle = \sum_i c_i |f_i\rangle = \sum_i \langle f_i | \psi \rangle | f_i \rangle$$

so that $c_i = \langle f_i | \psi \rangle$ and the completeness relation is given by

$$\sum_i |f_i\rangle\langle f_i| = 1$$

Using Dirac notation, the correspondences between Hermitian operations and Hermitian matrices and between eigenfunctions and eigenvectors become more clear.

3.4 Commutators

One property of matrices that is shared by QM operators is that the order of action matters. When multiplying two matrices, it is common for

$$\mathbf{AB} - \mathbf{BA} \neq 0$$

As an example, let

$$\mathbf{A} = \begin{bmatrix} 1 & 1 \\ 0 & 1 \end{bmatrix} \text{ and } \mathbf{B} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

Then,

$$\begin{aligned}\mathbf{AB - BA} &= \begin{bmatrix}1 & 1\\ 0 & 1\end{bmatrix}\begin{bmatrix}0 & 0\\ 1 & 0\end{bmatrix} - \begin{bmatrix}0 & 0\\ 1 & 0\end{bmatrix}\begin{bmatrix}1 & 1\\ 0 & 1\end{bmatrix}\\ &= \begin{bmatrix}1 & 0\\ 1 & 0\end{bmatrix} - \begin{bmatrix}0 & 0\\ 1 & 1\end{bmatrix}\\ &= \begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\end{aligned}$$

Similarly, when acting on a wavefunction with two (or more) operators, it is possible that

$$A(B\psi) - B(A\psi) \neq 0$$

The quantity on the left is termed the commutator, $[A, B]$, whose action on the wavefunction is

$$[A, B]\psi = A(B\psi) - B(A\psi)$$

If the two operators commute, then

$$A(B\psi) = B(A\psi)$$

and $[A, B] = 0$

It can be shown that two operators share a common set of eigenfunctions if and only if they commute. To show the first part of this, we let two operators, A and B, have a common set of eigenfunctions:

$$A\psi_i = a_i\psi_i$$
$$B\psi_i = b_i\psi_i$$

Now we evaluate the action of their commutator on an arbitrary function, f, which we can expand in terms of these eigenfunctions:

$$f = \sum_i c_i\psi_i$$

The commutator is:

$$\begin{aligned}[A, B]f &= \sum_i c_i[A, B]\psi_i\\ &= \sum_i c_i\left(AB\psi_i - BA\psi_i\right)\\ &= \sum_i c_i\left(a_ib_i - b_ia_i\right)\psi_i\\ &= 0\end{aligned}$$

and since the commutator is zero, the operators commute.

Not all QM operators commute, however. A common example is the case of the position and momentum operators. In this case,

$$\begin{aligned}[x,p]\psi &= x\left(-\mathrm{i}\hbar\frac{d\psi}{dx}\right)+\mathrm{i}\hbar\frac{d}{dx}(x\psi)\\ &= -\mathrm{i}\hbar x\frac{d\psi}{dx}+\mathrm{i}\hbar\left(\psi+x\frac{d\psi}{dx}\right)\\ &= \mathrm{i}\hbar\psi\end{aligned}$$

and therefore the commutator is $[x,p]=\mathrm{i}\hbar$. This means that the position and momentum operators do not commute, and hence do not share a common set of eigenfunctions.

3.5 Variance of Expectation Values and Uncertainty

The variance of an expectation value, $\langle A\rangle$, is given by

$$\boxed{\sigma_A^2=\langle A^2\rangle-|\langle A\rangle|^2}$$

For the case of real eigenvalues for operator A, this is

$$\sigma_A^2=\langle A^2\rangle-\langle A\rangle^2$$

where σ_A is the standard deviation or spread in the measurements of the observable A for an ensemble of particles in state ψ.

If ψ is an eigenfunction of A, then the variance is zero. To show this,

$$\begin{aligned}\sigma_A^2 &= \langle\psi|A^2|\psi\rangle-\langle\psi|A|\psi\rangle^2\\ &= a^2\langle\psi|\psi\rangle-a^2\langle\psi|\psi\rangle^2\\ &= a^2-a^2\\ &= 0\end{aligned}$$

However, if ψ is not an eigenfunction of A, then $\sigma_A\neq 0$ and you will obtain a distribution of values from measurements on an ensemble.

Heisenberg's uncertainty principle relates the variances in the position and momentum operators:

$$\sigma_p\sigma_x\geq\frac{\hbar}{2}$$

This has the consequence that one can never make precise measurements of both a particle's position and momentum simultaneously, which makes sense since they do not share a common set of eigenfunctions.

A more general statement of the uncertainty principle is, for two operators, A and B, that do not commute, the product of their variances is

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4}\langle\psi|[A,B]|\psi\rangle^2$$

For the particular case of position and momentum, we have

$$\begin{aligned}\sigma_p^2\sigma_x^2 &\geq -\frac{1}{4}\langle\psi|\mathrm{i}\hbar|\psi\rangle^2 \\ &\geq -\frac{1}{4}(-\hbar^2)\langle\psi|\psi\rangle^2 \\ &\geq \frac{\hbar^2}{4}\end{aligned}$$

and taking the square root of both sides gives the Heisenberg uncertainty principle above.

3.6 Distributive Properties of Expectation Values

The Hamiltonian is a sum of two operators, kinetic and potential energies

$$\mathcal{H} = T + V$$

The expectation value can also be written as a sum:

$$\begin{aligned}\langle\mathcal{H}\rangle &= \langle\psi|\mathcal{H}|\psi\rangle \\ &= \langle\psi|T+V|\psi\rangle \\ &= \langle\psi|T|\psi\rangle + \langle\psi V|\psi\rangle \\ &= \langle T\rangle + \langle V\rangle\end{aligned}$$

This is a general distributive property for expectation values:

$$\boxed{\langle A+B\rangle = \langle A\rangle + \langle B\rangle}$$

However, in the case of a product of two operators,

$$\langle AB\rangle \neq \langle A\rangle\langle B\rangle$$

in general.

As an example, let us consider whether $\langle A^2\rangle$ is equivalent to $\langle A\rangle^2$. From the definition of the variance:

$$\sigma_A^2 = \langle A^2\rangle - \langle A\rangle^2$$

and rearranging,

$$\langle A^2 \rangle = \langle A \rangle^2 + \sigma_A^2$$

so the distributive property for multiplication only holds here if the variance is zero.

In general, the distributive property $\langle AB \rangle = \langle A \rangle \langle B \rangle$ only holds if the wavefunction is an eigenfunction of both A and B. Letting the resulting eigenvalues be a and b, respectively, we can show this as follows:

$$\begin{aligned} \langle AB \rangle &= \langle \psi | AB | \psi \rangle \\ &= ab \langle \psi | \psi \rangle \\ &= ab \end{aligned}$$

and similarly

$$\begin{aligned} \langle A \rangle \langle B \rangle &= \langle \psi | A | \psi \rangle \langle \psi | B | \psi \rangle \\ &= a \langle \psi | \psi \rangle b \langle \psi | \psi \rangle \\ &= ab \end{aligned}$$

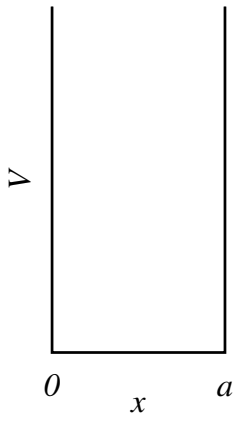
Now that we have introduced the basic framework of quantum mechanics, we are ready to apply it to some simple model systems. It is only possible to solve the Schrödinger equation exactly for certain systems in QM, so we will focus on a few such systems that we can relate to atoms and molecules.

Chapter 4

The Particle in a Box

4.1 Solutions for the Wavefunctions and Energies

The particle in a box is the simplest model system for which the Schrödinger equation can be solved exactly. It is very useful as an illustration of QM concepts. In chemistry, it can be used as a model for translation of atoms or molecules, as well as for electrons confined in molecules.



Consider a particle in a 1D box of width a with infinitely high walls such that

$$V = \begin{cases} 0\,, & \text{if } 0 \leq x \leq a \\ \infty\,, & \text{if } x < 0 \text{ or } x > a \end{cases}$$

This potential serves to confine the particle to the box, as it cannot be outside the box where the potential is infinite.

Inside the box, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

We make the change of variable

$$k^2 = \frac{2mE}{\hbar^2}$$

so that the Schrödinger equation becomes

$$\frac{d^2}{dx^2}\psi + k^2\psi = 0$$

The general solution to this differential equation ($k^2 > 0$) is

$$\psi = A\cos(kx) + B\sin(kx)$$

To determine acceptable values of k, we must apply the boundary conditions. We know that ψ must be a continuous, well-behaved function and that ψ is zero outside the box. Therefore, it must also be zero at the edges and

$$\psi(x) = 0 \text{ for } x = 0 \text{ or } x = a$$

At $x = 0$,

$$\psi = A\cos(0) + B\sin(0) = A = 0$$

so the coefficient of the cosine term must be zero.

At $x = a$,

$$\psi = B\sin(ka) = 0$$

for which there are two possible solutions. The first is that $B = 0$, which is the trivial solution. Since this would mean that $\psi = 0$ everywhere, and that there is no particle in the system, we will disregard it. The second solution is

$$\sin(ka) = 0 \Rightarrow ka = \pi, 2\pi, \ldots$$

This means that

$$ka = n\pi \text{ or } k = \frac{n\pi}{a} \text{ for } n = 1, 2, \ldots$$

so the solutions are

$$\psi_n = B\sin\left(\frac{n\pi}{a}x\right)$$

Note that $n = 0$ is not included as a solution, since it would again give $\psi = 0$ everywhere.

Recall that

$$k^2 = \frac{2mE}{\hbar^2}$$

so solving for E yields a series of solutions

$$\boxed{E_n = \frac{\hbar^2\pi^2n^2}{2ma^2}}$$

This can also be written as

$$\boxed{E_n = n^2 E_1 \text{ with } E_1 = \frac{\hbar^2 \pi^2}{2ma^2}}$$

where E_1 is the ground-state energy.

We still need to determine the value of the parameter B. To do this, we apply the constraint that the wavefunctions be normalized.

$$\begin{aligned} \langle \psi | \psi \rangle &= 1 \\ \int_{-\infty}^{\infty} \psi_n^2 dx &= 1 \end{aligned}$$

Since the particle is confined, we can adjust the integration limits to the box dimensions

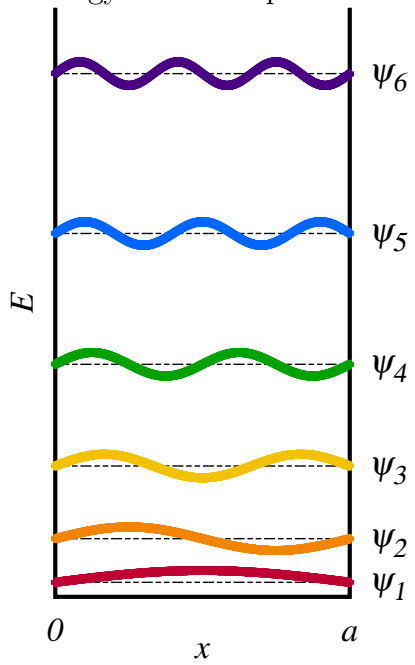
$$\begin{aligned} \int_0^a \psi_n^2 dx &= 1 \\ B^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx &= 1 \\ B^2 \left(\frac{a}{2}\right) &= 1 \\ B^2 &= \frac{2}{a} \\ B &= \sqrt{\frac{2}{a}} \end{aligned}$$

where we used our list of definite integrals in Section 1.4. This integral can also be evaluated easily using the double-angle formula: $\cos(2\theta) = 1 - 2\sin^2\theta$.

The final solutions for the particle in a box are

$$\boxed{\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \text{ with } E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}}$$

The first few wavefunctions and energy levels are plotted below:

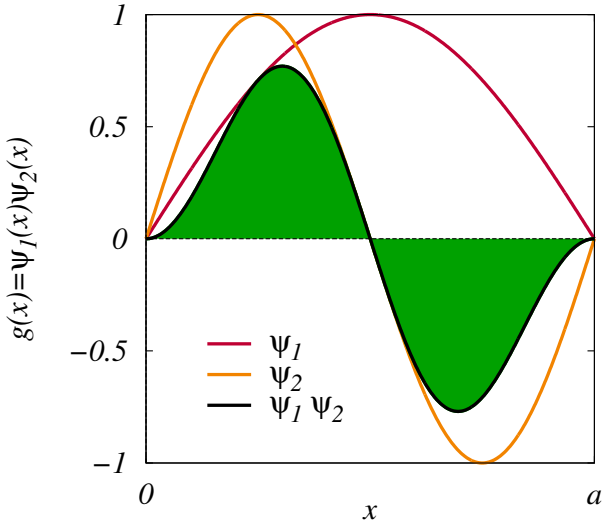


From looking at the overlaps of the various wavefunctions, it is clear that they are orthogonal:

$$\langle \psi_m | \psi_n \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) = \delta_{mn}$$

It is straightforward to demonstrate this for any combination of m, n using integrals of sine functions.

To highlight this for the case of $m = 1$, $n = 2$, a plot of the integrand, which is the product of the two sine function is shown below.



4.2 Some Examples

Let's consider only the ground state of the particle in a box and evaluate the expectation values of position and momentum. For position,

$$\begin{aligned}\langle x\rangle &= \langle\psi_1|x|\psi_1\rangle \\ &= \frac{2}{a}\int_0^a x\sin^2\left(\frac{\pi}{a}x\right)dx \\ &= \frac{2}{a}\left(\frac{a^2}{4}\right) \\ &= \frac{a}{2}\end{aligned}$$

where we used our list of definite integrals in Section 1.4. So, on average the particle is in the middle of the box, which makes sense due to symmetry.

For momentum,

$$\begin{aligned}\langle p\rangle &= \langle\psi_1|p|\psi_1\rangle \\ &= \langle\psi_1|-\mathrm{i}\hbar\frac{d}{dx}|\psi_1\rangle \\ &= -\mathrm{i}\hbar\frac{2}{a}\int_0^a \sin\left(\frac{\pi}{a}x\right)\left[\frac{d}{dx}\sin\left(\frac{\pi}{a}x\right)\right]dx \\ &= -\mathrm{i}\hbar\frac{2}{a}\int_0^a \sin\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right)dx \\ &= 0\end{aligned}$$

where we have again used our list of definite integrals. This integral can also be evaluated easily by using the double-angle formula: $\sin(2\theta) = 2\sin\theta\cos\theta$. So, the average momentum is zero, which makes sense since it is equally likely that the particle is moving to the left, or to the right, within the box.

To get an idea of the magnitude of the energies, let's consider the excitation energy of an electron in the ethylene molecule (C_2H_4) from the ground state ($n = 1$) to the first electronic excited state ($n = 2$). We will take the box length as twice the C=C bond length of 1.4 Å $= 2.8 \times 10^{-10}$ m. The excitation energy is

$$\begin{aligned}\Delta E &= E_2 - E_1 \\ &= \frac{\hbar^2\pi^2}{2ma^2}(2^2 - 1^2) \\ &= \frac{3(1.055\times10^{-34})^2(3.142)^2}{2(9.109\times10^{-31})(2.8\times10^{-10})^2} \\ &= 2.3\times10^{-18}\ \text{J} \\ &= 14.4\ \text{eV}\end{aligned}$$

which is roughly twice the energy corresponding to the experimental $\lambda_{\max}$ from UV-vis measurements, indicating our estimate of the "box" length was too small, although it does provide the correct order of magnitude. If we use the longest H–H distance in ethylene (3.1 Å), then our estimate improves to 11.7 eV.

4.3 Extension to 2D

The particle in a box model can be extended to 2D systems (such as for electrons in graphene sheets). Let us consider a particle confined to a 2D box of width a and length b with infinitely high walls. The potential is given by

$$V = \begin{cases} 0\,, & \text{if } 0 \leq x \leq a \text{ and } 0 \leq y \leq b \\ \infty\,, & \text{if } x < 0, x > a \text{ or } y < 0, y > b \end{cases}$$

Inside the box, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi = E\psi$$

and we assume that the wavefunction is separable, such that it can be written as product of the form

$$\psi(x, y) = X(x)Y(y)$$

Inserting this into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m}\Big[X''(x)Y(y) + X(x)Y''(y)\Big] = EX(x)Y(y)$$

where the $''$ notation indicates the second derivative. Dividing through by XY, we obtain

$$-\frac{\hbar^2}{2m}\frac{X''}{X} - \frac{\hbar^2}{2m}\frac{Y''}{Y} = E$$

For this equation to be valid for all values of x and y, we require that both ratios on the left-hand side are constants, which we write as E_x and E_y:

$$-\frac{\hbar^2}{2m}\frac{X''}{X} = E_x$$

$$-\frac{\hbar^2}{2m}\frac{Y''}{Y} = E_y$$

such that

$$E = E_x + E_y$$

The two differential equations above have the same form as the Schrödinger equation for the 1D particle in a box:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X = E_x X$$
$$-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y = E_y Y$$

Thus, the solutions are

$$X_{n_x} = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi}{a}x\right) \text{ with } E_{n_x} = \frac{\hbar^2\pi^2 n_x^2}{2ma^2}$$

$$Y_{n_y} = \sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi}{b}y\right) \text{ with } E_{n_y} = \frac{\hbar^2\pi^2 n_y^2}{2mb^2}$$

So the total wavefunction and energy are

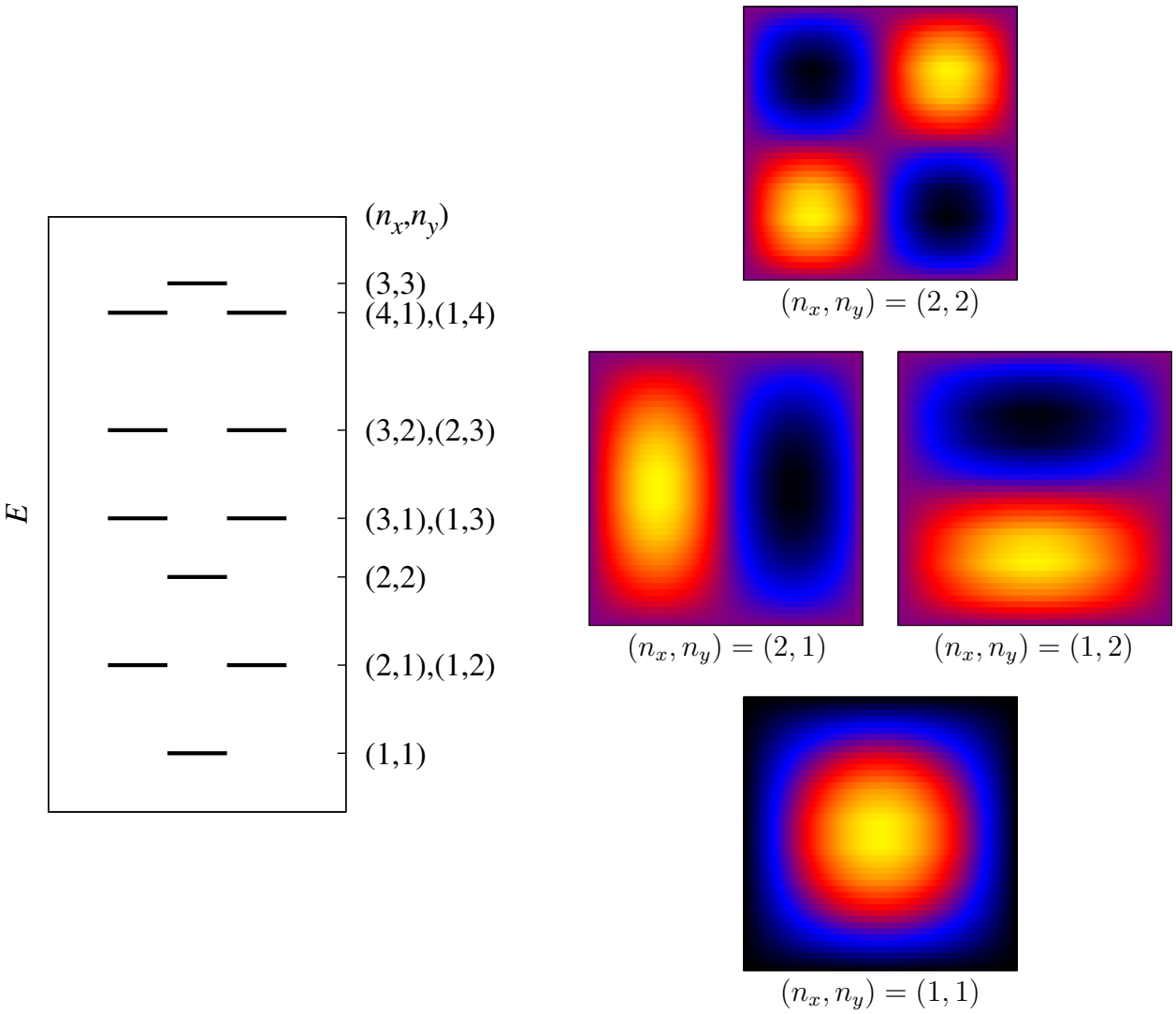
$$\boxed{\psi = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{b}y\right) \text{ with } E = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right)}$$

In the special case of a square box, $a = b$, and this simplifies to

$$\boxed{\psi = \frac{2}{a}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right) \text{ with } E = \frac{\hbar^2\pi^2}{2ma^2}\left(n_x^2+n_y^2\right)}$$

Some of the solutions, such as $(n_x, n_y) = (1, 2)$ and $(n_x, n_y) = (2, 1)$, will have equal energies and are termed "degenerate".

The energy level diagram and illustrations of the few lowest-energy wavefunctions are shown below:



4.4 Extension to 3D

Further extension of the particle in a box model to 3D follows the same logic as in the 2D case. We take the box dimensions to be a, b, and c in the x, y, and z dimensions, respectively.

Inside the box, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

and we assume that the wavefunction is separable, such that it can be written as product of

the form

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

The solutions can be shown to be

$$X_{n_x} = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right) \text{ with } E_{n_x} = \frac{\hbar^2 \pi^2 n_x^2}{2ma^2}$$

$$Y_{n_y} = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b} y\right) \text{ with } E_{n_y} = \frac{\hbar^2 \pi^2 n_y^2}{2mb^2}$$

$$Z_{n_z} = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi}{c} z\right) \text{ with } E_{n_z} = \frac{\hbar^2 \pi^2 n_z^2}{2mc^2}$$

The total wavefunction and energy are

$$\boxed{\psi = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}}\sqrt{\frac{2}{c}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{b} y\right) \sin\left(\frac{n_z \pi}{c} z\right) \text{ with } E = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)}$$

In the special case of a cubic box, $a = b = c$, and this simplifies to

$$\boxed{\psi = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_y \pi}{a} z\right) \text{ with } E = \frac{\hbar^2 \pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)}$$

Even more combinations of solutions, such as $(n_x, n_y, n_z) = (1,1,2)$, $(n_x, n_y, n_z) = (1,2,1)$, and $(n_x, n_y, n_z) = (2,1,1)$, will be degenerate.

Let's use the 3D particle in a box to approximate the energy levels for translation of an O_2 molecule (molar mass of roughly 32 g/mol) in the atmosphere. For a temperature of 0°C and 1 atm pressure, one mole of molecules takes up a volume of 22.4 L, according to the ideal gas law. Dividing by Avogadro's number, this corresponds to a cubic "box" with sides of 3.3×10^{-9} m per molecule. We will take this as the "box" length.

The energy difference between the ground translational state and first excited state is:

$$\begin{aligned}
\Delta E &= E_2 - E_1 \\
&= \frac{\hbar^2 \pi^2}{2ma^2}(2^2 + 1^2 + 1^2 - 1^2 - 1^2 - 1^2) \\
&= \frac{3(1.055 \times 10^{-34})^2 (3.142)^2}{2(32 \times 10^{-3}/6.022 \times 10^{23})(3.3 \times 10^{-9})^2} \\
&= 2.8 \times 10^{-25} \text{ J} \\
&= 1.7 \times 10^{-4} \text{ kJ/mol}
\end{aligned}$$

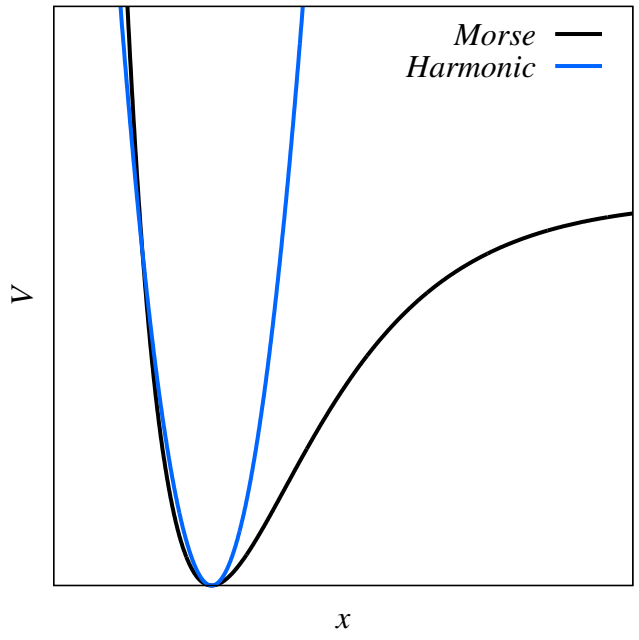
So the energy levels are separated by an extremely small amount of energy, compared to the available thermal energy of $RT = 2.3$ kJ/mol. This is why we can approximate translational energy levels as being continuous and not quantized in thermodynamics.

Chapter 5

The Harmonic Oscillator

5.1 Wavefunctions and Energies

The harmonic oscillator is a simple model for the vibration of chemical bonds. We can approximate the Morse potential that is characteristic of the potential energy curve of a diatomic molecule by a parabolic potential for the region near the equilibrium bond length.



While we can't use a parabolic potential to model bond dissociation, it is a good model for bond vibrations where the bond distorts about its equilibrium value.

For the harmonic oscillator, the form of the parabolic potential is

$$\boxed{V = \frac{1}{2}kx^2}$$

where k is the "spring constant" of the oscillator. It can be related to the reduced mass, μ, and the vibrational frequency, ω, as

$$\omega = \sqrt{\frac{k}{\mu}}$$

The reduced mass for two atoms with masses m_1 and m_2 is

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

The time-independent Schrödinger equation for the 1D harmonic oscillator is

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\psi + \frac{1}{2}kx^2\psi = E\psi$$

The solution of this differential equation is not straightforward. We will show how to solve for the energies using raising and lowering operators in Section 5.3. For now, we will assume a form for the ground state and demonstrate that it is a solution. Let's take

$$\psi = \exp(-Cx^2)$$

and determine the value for C.

Substituting this result into the Schrödinger equation, we have

$$\begin{aligned}
-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\mathrm{e}^{-Cx^2} + \frac{1}{2}kx^2\mathrm{e}^{-Cx^2} &= E\mathrm{e}^{-Cx^2} \\
-\frac{\hbar^2}{2\mu}\frac{d}{dx}\left(-2Cx\mathrm{e}^{-Cx^2}\right) + \frac{1}{2}kx^2\mathrm{e}^{-Cx^2} &= E\mathrm{e}^{-Cx^2} \\
-\frac{\hbar^2}{2\mu}\left(-2C\mathrm{e}^{-Cx^2} + 4C^2x^2\mathrm{e}^{-Cx^2}\right) + \frac{1}{2}kx^2\mathrm{e}^{-Cx^2} &= E\mathrm{e}^{-Cx^2} \\
\left(\frac{\hbar^2}{\mu}C - E\right)\mathrm{e}^{-Cx^2} + \left(\frac{1}{2}k - \frac{2\hbar^2}{\mu}C^2\right)x^2\mathrm{e}^{-Cx^2} &= 0
\end{aligned}$$

For this to be true for all values of x, we require both terms in parentheses to be zero. Thus, we can solve for C by setting

$$\begin{aligned}
\frac{2\hbar^2}{\mu}C^2 &= \frac{1}{2}k \\
C^2 &= \frac{\mu k}{4\hbar^2} \\
C &= \frac{\sqrt{\mu k}}{2\hbar}
\end{aligned}$$

We obtain the corresponding energy as

$$\begin{aligned} E &= \frac{\hbar^2}{\mu} C \\ &= \frac{\hbar^2}{\mu} \frac{\sqrt{\mu k}}{2\hbar} \\ &= \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2} \hbar\omega \end{aligned}$$

The (not yet normalized) ground-state solution for the harmonic oscillator is

$$\psi_0 = \exp\left(-\frac{\sqrt{\mu k}}{2\hbar} x^2\right) \text{ with } E_0 = \frac{1}{2}\hbar\omega$$

It can be shown that general solution for the harmonic oscillator wavefunctions is

$$\boxed{\psi_n = N_n H_n(q) \exp\left(-\frac{1}{2}q^2\right) \text{ where } q^2 = \frac{\sqrt{\mu k}}{\hbar} x^2}$$

and the corresponding energies are

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega \text{ with } n = 0, 1, 2, \ldots}$$

All the energy levels are evenly spaced, and are separated by $\Delta E = \hbar\omega$.

In the general form of the wavefunction, the functions $H_n(q)$ are the physicist's Hermite polynomials. These form a set of special functions

$$H_n(q) = (-1)^n \exp(q^2) \frac{d^n}{dq^n} \exp(-q^2)$$

such that

$$\begin{aligned} H_0(q) &= 1 \\ H_1(q) &= 2q \end{aligned}$$

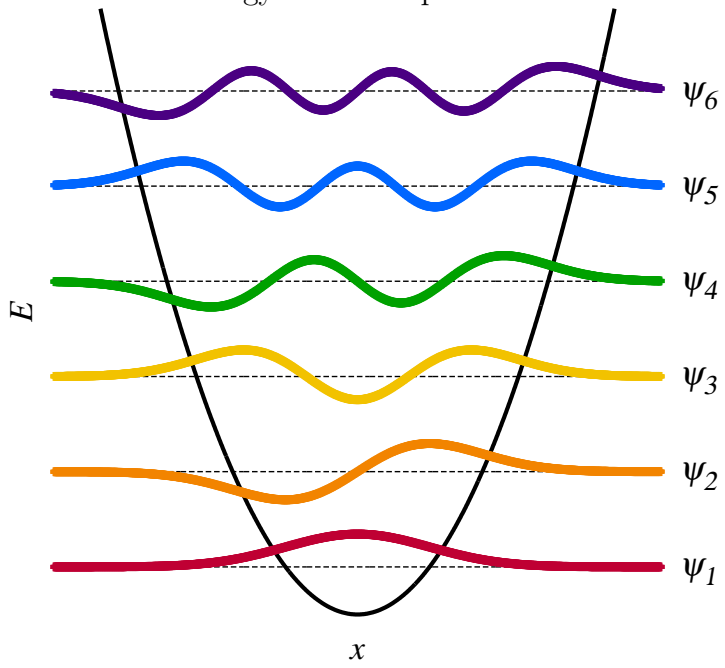
and higher-order forms are obtained from the recursion relation

$$\boxed{H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q)}$$

Finally, N_n is a normalization constant of the form

$$N_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{\sqrt{\mu k}}{\hbar \pi} \right)^{\frac{1}{4}}$$

The first few wavefunctions and energy levels are plotted below:



5.2 Some Examples

For the harmonic oscillator ground state, the expectation value of position is

$$\langle x \rangle = \langle 0 | x | 0 \rangle$$

where we introduce the notation $|n\rangle$ to denote state ψ_n. Substituting the ground-state wavefunction, this gives

$$\langle x \rangle = \left(\frac{\sqrt{\mu k}}{\hbar \pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x \exp\left(-\frac{\sqrt{\mu k}}{\hbar} x^2 \right) dx$$

but this is the integral of an odd function over all space, so $\langle x \rangle = 0$. This means that the average displacement of the oscillator is the equilibrium bond length, which makes sense due to symmetry.

Returning to our example of the O_2 molecule, its vibrational frequency is 1580 cm^{-1}. The energy difference between vibrational levels is

$$\Delta E = \hbar \omega$$

and converting units gives $\Delta E = 18.9$ kJ/mol. This is considerably higher than the available thermal energy at room temperature ($RT = 2.5$ kJ/mol), so only the ground vibrational state is likely to be occupied. At elevated temperatures, or for lower vibrational frequencies, more vibrational levels will be occupied.

5.3 Raising and Lowering Operators

Let us define two new operators that allow us to move up and down the "ladder" of harmonic oscillator states:

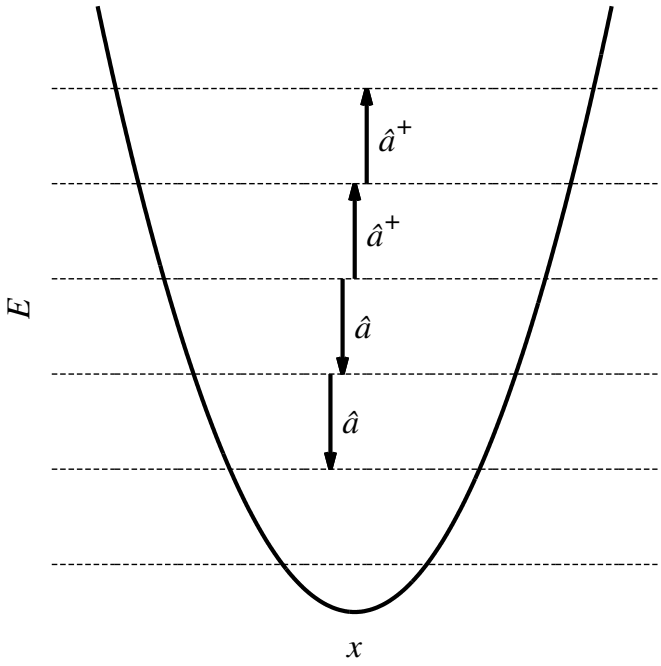
Lowering operator: $a^- \psi_n = \sqrt{n}\psi_{n-1}$

Raising operator: $a^+ \psi_n = \sqrt{n+1}\psi_{n+1}$

In Dirac notation, these are

Lowering operator: $a^- |n\rangle = \sqrt{n}|n-1\rangle$

Raising operator: $a^+ |n\rangle = \sqrt{n+1}|n+1\rangle$



All of the wavefunctions can be obtained from the ground-state wavefunction using the raising operator

$$\psi_n = \frac{1}{\sqrt{n!}} \left(a^+\right)^n \psi_0$$

We can also consider sequential application of a^- and a^+:

$$\begin{aligned} a^- a^+ |n\rangle &= \sqrt{n+1}\; a^- |n+1\rangle = (n+1)|n\rangle \\ a^+ a^- |n\rangle &= \sqrt{n}\; a^+ |n-1\rangle = n|n\rangle \end{aligned}$$

Subtracting these two equations gives the commutator

$$[a^-, a^+] = (n+1) - n = 1$$

It is not obvious what the exact forms of the raising and lowering operators should be and they depend on the system. The operators used here for the harmonic oscillator are different

than the raising and lowering operators that we will use for angular momentum for the rigid rotor problem in Chapter 7. Ultimately, a definition was proposed and we will show that it works.

We will define the raising and lowering operators as

$$\boxed{a^- = \sqrt{\frac{\mu\omega}{2\hbar}}\left(x + \frac{\mathrm{i}}{\mu\omega}p\right)}$$

$$\boxed{a^+ = \sqrt{\frac{\mu\omega}{2\hbar}}\left(x - \frac{\mathrm{i}}{\mu\omega}p\right)}$$

With this definition, it is straightforward to show that

$$\boxed{x^2 = \frac{\hbar}{2\mu\omega}\left(a^- + a^+\right)^2}$$

$$\boxed{p^2 = -\frac{\hbar\mu\omega}{2}\left(a^- - a^+\right)^2}$$

To solve for the harmonic oscillator energies using raising and lowering operators, we first need to re-write the Hamiltonian.

$$\begin{aligned}
\mathcal{H} &= -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \\
&= \frac{p^2}{2\mu} + \frac{1}{2}kx^2 \\
&= -\frac{1}{2\mu}\frac{\hbar\mu\omega}{2}\left(a^- - a^+\right)^2 + \frac{1}{2}k\frac{\hbar}{2\mu\omega}\left(a^- + a^+\right)^2 \\
&= -\frac{\hbar\omega}{4}\left(a^- - a^+\right)^2 + \frac{\hbar\mu\omega^2}{4\mu\omega}\left(a^- + a^+\right)^2 \\
&= \frac{\hbar\omega}{4}\left[\left(a^- + a^+\right)^2 - \left(a^- - a^+\right)^2\right] \\
&= \frac{\hbar\omega}{2}\left(a^-a^+ + a^+a^-\right)
\end{aligned}$$

We can also use the commutator to simplify this slightly further. Since

$$[a^-, a^+] = a^-a^+ - a^+a^- = 1$$

then

$$a^-a^+ = a^+a^- + 1$$

Making this substitution, the harmonic oscillator Hamiltonian is

$$\boxed{\mathcal{H} = \left(a^+ a^- + \frac{1}{2}\right)\hbar\omega}$$

This form allows rapid evaluation of the harmonic oscillator energies:

$$\begin{aligned}\mathcal{H}|n\rangle &= \left(a^+ a^- + \frac{1}{2}\right)\hbar\omega|n\rangle \\ &= \left(n + \frac{1}{2}\right)\hbar\omega|n\rangle\end{aligned}$$

since $a^+ a^-|n\rangle = n|n\rangle$. Thus, the eigenvalues are

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega}$$

Finally, we can demonstrate that our definition of the a^- and a^+ operations gives the expected raising and lowering action.

Recall that the Hamiltonian is

$$\mathcal{H} = \frac{\hbar\omega}{2}\left(a^- a^+ + a^+ a^-\right)$$

Using the commutator, we can then write the Hamiltonian as either

$$\mathcal{H} = \left(a^+ a^- + \frac{1}{2}\right)\hbar\omega$$

$$\mathcal{H} = \left(a^- a^+ - \frac{1}{2}\right)\hbar\omega$$

Starting from the first equation for $\mathcal{H}$, the Schrödinger equation for state $|n\rangle$ is

$$\mathcal{H}|n\rangle = E_n|n\rangle$$

$$\left(a^+ a^- + \frac{1}{2}\right)\hbar\omega|n\rangle = E_n|n\rangle$$

We left multiply both sides by a^- to obtain

$$\begin{aligned}\left(a^- a^+ a^- + \frac{1}{2}a^-\right)\hbar\omega|n\rangle &= E_n a^-|n\rangle \\ \left(a^- a^+ + \frac{1}{2}\right)\hbar\omega a^-|n\rangle &= E_n a^-|n\rangle\end{aligned}$$

Now, subtract $\hbar\omega a^-|n\rangle$ from both sides

$$\left(a^-a^+ - \frac{1}{2}\right)\hbar\omega a^-|n\rangle = (E_n - \hbar\omega)a^-|n\rangle$$

$$\mathcal{H}a^-|n\rangle = (E_n - \hbar\omega)a^-|n\rangle$$

Therefore, $a^-|n\rangle$ is an eigenfunction with eigenvalue $E_n - \hbar\omega = E_{n-1}$, (because the quantum harmonic oscillator's energy spacing is $\hbar\omega$) so this has the action of the lowering operator.

Similarly, starting from the second equation for $\mathcal{H}$, the Schrödinger equation for state $|n\rangle$ is

$$\mathcal{H}|n\rangle = E_n|n\rangle$$

$$\left(a^-a^+ - \frac{1}{2}\right)\hbar\omega|n\rangle = E_n|n\rangle$$

We left multiply both sides by a^+ to obtain

$$\begin{aligned}\left(a^+a^-a^+ - \frac{1}{2}a^+\right)\hbar\omega|n\rangle &= E_n a^+|n\rangle \\ \left(a^+a^- - \frac{1}{2}\right)\hbar\omega a^+|n\rangle &= E_n a^+|n\rangle\end{aligned}$$

Now, add $\hbar\omega a^+|n\rangle$ to both sides

$$\left(a^+a^- + \frac{1}{2}\right)\hbar\omega a^+|n\rangle = (E_n + \hbar\omega)a^+|n\rangle$$

$$\mathcal{H}a^+|n\rangle = (E_n + \hbar\omega)a^+|n\rangle$$

Therefore, $a^+|n\rangle$ is an eigenfunction with eigenvalue $E_n + \hbar\omega = E_{n+1}$, so this has the action of the raising operator.

5.4 Selection Rules for Vibrational Spectroscopy

Using raising and lowering values can also greatly simplify evaluation of expectation values involving functions of position and momentum.

As an example, we can evaluate the expectation value of position for any state, n:

$$\begin{aligned}
\langle x \rangle &= \langle n|x|n\rangle \\
&= \sqrt{\frac{\hbar}{2\mu\omega}}\langle n|a^- + a^+|n\rangle \\
&= \sqrt{\frac{\hbar}{2\mu\omega}}\langle n|\left(\sqrt{n}|n-1\rangle + \sqrt{n+1}|n+1\rangle\right) \\
&= \sqrt{\frac{\hbar}{2\mu\omega}}\left(\sqrt{n}\langle n|n-1\rangle + \sqrt{n+1}\langle n|n+1\rangle\right) \\
&= \sqrt{\frac{\hbar}{2\mu\omega}}\left(\sqrt{n}\delta_{n,n-1} + \sqrt{n+1}\delta_{n,n+1}\right) \\
&= 0
\end{aligned}$$

due to orthogonality of the wavefunctions.

For molecular vibrations to be observed in IR spectroscopy, they must result in a net change in dipole moment. For a transition from state n to state n', this requirement is that the transition dipole moment

$$\boxed{x_{nn'} = \langle n|x|n'\rangle}$$

is non-zero for an allowed transition. In the IR spectrum, the intensity of the peak is proportional to $x_{nn'}^2$.

For the harmonic oscillator,

$$\begin{aligned}
x_{nm} &= \langle n|x|n'\rangle \\
&= \sqrt{\frac{\hbar}{2\mu\omega}}\langle n|a^- + a^+|n'\rangle \\
&= \sqrt{\frac{\hbar}{2\mu\omega}}\left(\sqrt{n'}\delta_{n,n'-1} + \sqrt{n'+1}\delta_{n,n'+1}\right)
\end{aligned}$$

so, $x_{nn'}$ will be zero unless either $n = n' - 1$ or $n = n' + 1$ due to orthogonalitry.

Thus, allowed transitions occur between states with $\Delta n = \pm 1$ or $\Delta E = \pm\hbar\omega$.

In IR spectroscopy, we generally observe the fundamental vibration, where the molecule is excited from the ground state ($n = 0$) to the first excited vibrational state ($n = 1$).

Chapter 6

Approximation Methods

It is not always possible to solve the Schrödinger equation exactly for a given system, and indeed having an exactly solvable system is the exception, rather than the rule, in QM. Here, we will consider two different approximation methods.

6.1 Perturbation Theory

Perturbation theory works when the system under study is very similar to a known model system, but not quite the same. Common examples are for applying an electric or magnetic field to an atom or molecule.

Assume we have solved the Schrödinger equation for our known model system, with Hamiltonian $\mathcal{H}^\circ$, and the solutions are

$$\mathcal{H}^\circ \psi_n^\circ = E_n^\circ \psi_n^\circ$$

Now we introduce a small perturbation term to the Hamiltonian, $\mathcal{H}'$, which will result in a different set of wavefunctions and energies. We cannot solve the problem exactly for this new Hamiltonian but, because the contribution of $\mathcal{H}'$ is assumed to be small, the solution should be similar to that for $\mathcal{H}^\circ$.

The new (perturbed) problem to be solved is

$$\mathcal{H}\psi_n = E_n\psi_n \quad \text{where} \quad \mathcal{H} = \mathcal{H}^\circ + \lambda\mathcal{H}'$$

and λ is a coupling strength parameter used to keep track of the level of approximation.

$$\mathcal{H}(\lambda = 0) = \mathcal{H}^\circ$$

$$\mathcal{H}(\lambda = 1) = \mathcal{H}$$

The method of solution is to postulate

$$E_n = E_n^\circ + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$
$$\psi_n = \psi_n^\circ + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots$$

where we add a series of correction terms to the zeroth-order solution.

Substituting into the SE gives

$$(\mathcal{H}^\circ + \lambda\mathcal{H}')(\psi_n^\circ + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots) = (E_n^\circ + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\psi_n^\circ + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots)$$

This must be true for every value of λ between 0 and 1, so it must be true order by order.

To order λ^0: $\mathcal{H}^\circ\psi_n^\circ = E_n^\circ\psi_n^\circ \leftarrow$ idealized problem, known solution

To order λ^1: $\mathcal{H}^\circ\psi_n^{(1)} + \mathcal{H}'\psi_n^\circ = E_n^\circ\psi_n^{(1)} + E_n^{(1)}\psi_n^\circ \quad (*)$

To order λ^2: $\mathcal{H}^\circ\psi_n^{(2)} + \mathcal{H}'\psi_n^{(1)} = E_n^\circ\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^\circ$

To find the first-order correction to the energy, multiply $(*)$ by ψ_n° and integrate. This gives

$$\langle\psi_n^\circ|\mathcal{H}^\circ|\psi_n^{(1)}\rangle + \langle\psi_n^\circ|\mathcal{H}'|\psi_n^\circ\rangle = E_n^\circ\langle\psi_n^\circ|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_n^\circ|\psi_n^\circ\rangle$$

but $\langle\psi_n^\circ|\mathcal{H}^\circ|\psi_n^{(1)}\rangle = E_n^\circ\langle\psi_n^\circ|\psi_n^{(1)}\rangle$ and $\langle\psi_n^\circ|\psi_n^\circ\rangle = 1$. Thus

$$\boxed{E_n^{(1)} = \langle\psi_n^\circ|\mathcal{H}'|\psi_n^\circ\rangle}$$

is the first-order energy correction.

For the first-order correction to the wavefunction, we let

$$\psi_n^{(1)} = \sum_m c_{mn}\psi_m^\circ$$

Recall that we can write any function as a linear combination of the zeroth-order wavefunctions, since they are complete and form a basis.

We substitute this definition into $(*)$ to give

$$(\mathcal{H}^\circ - E_n^\circ)\sum_m c_{mn}\psi_m^\circ = -(\mathcal{H}' - E_n^{(1)})\psi_n^\circ$$

Next, we multiply through by ψ_ℓ° and integrate

$$\begin{aligned}
\sum_m c_{mn}\langle\psi_\ell^\circ|(\mathcal{H}^\circ - E_n^\circ)|\psi_m^\circ\rangle &= -\langle\psi_\ell^\circ|(\mathcal{H}' - E_n^{(1)}|\psi_n^\circ\rangle \\
\sum_m c_{mn}(E_\ell^\circ - E_n^\circ)\langle\psi_\ell^\circ|\psi_m^\circ\rangle &= -\langle\psi_\ell^\circ|\mathcal{H}'|\psi_n^\circ\rangle + E_n^{(1)}\langle\psi_\ell^\circ|\psi_n^\circ\rangle \\
c_{\ell n}(E_\ell^\circ - E_n^\circ) &= -\langle\psi_\ell^\circ|\mathcal{H}'|\psi_n^\circ\rangle + E_n^{(1)}\delta_{\ell n}
\end{aligned}$$

This gives two cases. If $\ell = n$, we recover the first-order energy correction. If $\ell \neq n$,

$$c_{\ell n} = -\frac{\langle \psi_\ell^\circ | \mathcal{H}' | \psi_n^\circ \rangle}{E_\ell^\circ - E_n^\circ}$$

Returning to our definition of $\psi_n^{(1)}$, the first-order correction to the wavefunction is

$$\boxed{\psi_n^{(1)} = \sum_{m,m\neq n} \frac{\langle \psi_m^\circ | \mathcal{H}' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} \psi_m^\circ}$$

Similarly, for the second-order correction to the energy, we consider the order-λ^2 equation, multiply through by ψ_n° and integrate:

$$\begin{aligned}
\langle \psi_n^\circ | \mathcal{H}^\circ | \psi_n^{(2)} \rangle + \langle \psi_n^\circ | \mathcal{H}' | \psi_n^{(1)} \rangle &= E_n^\circ \langle \psi_n^\circ | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^\circ | \psi_n^{(1)} \rangle + E_n^{(2)} \langle \psi_n^\circ | \psi_n^\circ \rangle \\
E_n^\circ \langle \psi_n^\circ | \psi_n^{(2)} \rangle + \langle \psi_n^\circ | \mathcal{H}' | \psi_n^{(1)} \rangle &= E_n^\circ \langle \psi_n^\circ | \psi_n^{(2)} \rangle + E_n^{(1)}(0) + E_n^{(2)}(1) \\
E_n^{(2)} &= \langle \psi_n^\circ | \mathcal{H}' | \psi_n^{(1)} \rangle
\end{aligned}$$

Thus, the second-order energy correction is

$$E_n^{(2)} = \sum_{m,m\neq n} \frac{\langle \psi_m^\circ | \mathcal{H}' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} \langle \psi_n^\circ | \mathcal{H}' | \psi_m^\circ \rangle$$

$$\boxed{E_n^{(2)} = \sum_{m,m\neq n} \frac{|\langle \psi_m^\circ | \mathcal{H}' | \psi_n^\circ \rangle|^2}{E_n^\circ - E_m^\circ}}$$

It is often useful to evaluate the second-order energy correction approximately. If we replace all the energy differences $E_n^\circ - E_m^\circ$ by their average value, ΔE, then

$$E_n^{(2)} = \frac{1}{\Delta E} \sum_{m,m\neq n} \langle \psi_n^\circ | \mathcal{H}' | \psi_m^\circ \rangle \langle \psi_m^\circ | \mathcal{H}' | \psi_n^\circ \rangle$$

If we add and subtract the $m = n$ term, this becomes

$$E_n^{(2)} = \frac{1}{\Delta E} \sum_m \langle \psi_n^\circ | \mathcal{H}' | \psi_m^\circ \rangle \langle \psi_m^\circ | \mathcal{H}' | \psi_n^\circ \rangle - \frac{1}{\Delta E} \langle \psi_n^\circ | \mathcal{H}' | \psi_n^\circ \rangle \langle \psi_n^\circ | \mathcal{H}' | \psi_n^\circ \rangle$$

but the wavefunctions form a complete set, so we can use the closure relation

$$\sum_m |\psi_m^\circ\rangle \langle \psi_m^\circ| = 1$$

Then, the second-order energy correction simplified to

$$E_n^{(2)} = \frac{1}{\Delta E} \Big(\langle \psi_n^\circ | \mathcal{H}'^2 | \psi_n^\circ \rangle - \langle \psi_n^\circ | \mathcal{H}' | \psi_n^\circ \rangle^2 \Big)$$

which is given in terms of just the ground state and we only need the average excitation energy. This is called the closure approximation. It is valid for the ground state when all excited states are much higher in energy.

6.2 An Example of Perturbation Theory

A harmonic oscillator is perturbed by an electric field of strength ε in the x-direction. We want to determine the perturbation correction to the energy through second order, assuming the oscillating mass has a charge e.

The perturbation is

$$\mathcal{H}' = \varepsilon e x$$

The first-order correction is

$$\begin{aligned} E_n^{(1)} &= \langle n|\mathcal{H}'|n\rangle \\ &= \varepsilon e\langle n|x|n\rangle \\ &= 0 \end{aligned}$$

The second-order correction is

$$\begin{aligned} E_n^{(2)} &= \sum_{m,m\neq n} \frac{|\langle\psi_m^\circ|\mathcal{H}'|\psi_n^\circ\rangle|^2}{E_n^\circ - E_m^\circ} \\ &= \sum_{m,m\neq n} \frac{\varepsilon^2 e^2|\langle\psi_m^\circ|x|\psi_n^\circ\rangle|^2}{E_n^\circ - E_m^\circ} \end{aligned}$$

However, from our discussion of the harmonic oscillator selection rules, we know that

$$\langle n|x|m\rangle = 0 \text{ unless } m = n \pm 1$$

$$\langle n|x|n-1\rangle = \sqrt{\frac{\hbar}{2\mu\omega}}\sqrt{n}$$

$$\langle n|x|n+1\rangle = \sqrt{\frac{\hbar}{2\mu\omega}}\sqrt{n+1}$$

Therefore, we only need to consider these two states in the sum and the second-order energy correction is

$$\begin{aligned} E_n^{(2)} &= \varepsilon^2 e^2 \left(\frac{\hbar}{2\mu\omega}\right)\left[\frac{n}{E_n^\circ - E_{n-1}^\circ} + \frac{n+1}{E_n^\circ - E_{n+1}^\circ}\right] \\ &= \varepsilon^2 e^2 \left(\frac{\hbar}{2\mu\omega}\right)\left[\frac{n}{\hbar\omega} - \frac{n+1}{\hbar\omega}\right] \\ &= -\frac{\varepsilon^2 e^2}{2\mu\omega^2} \end{aligned}$$

The total energy, to second order, for the harmonic oscillator in the electric field is

$$E = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{\varepsilon^2 e^2}{2\mu\omega^2}$$

and we see that the energy decreases with the square of the field strength.

6.3 The Variational Principle

An alternative to perturbation theory is to make use of the variational principle. This allows us to propose flexible forms for the wavefunction with adjustable parameters to be optimized.

The Variational Principle: For a time-independent Hamiltonian with ground-state energy E_0, if ϕ is any normalized, well-behaved function of the electron coordinates and satisfies the boundary conditions, then

$$\boxed{E = \langle\phi|\mathcal{H}|\phi\rangle \geq E_0}$$

This gives an upper bound to the ground-state energy.

To prove the variational principle, we expand ϕ in terms of the eigenfunctions of $\mathcal{H}$

$$\phi = \sum_i a_i\psi_i \quad \text{where} \quad \mathcal{H}\psi_i = E_i\psi_i$$

then

$$\begin{aligned}
\langle\phi|\mathcal{H}|\phi\rangle &= \sum_i\sum_j a_i^* a_j\langle\psi_i|\mathcal{H}|\psi_j\rangle \\
&= \sum_i\sum_j a_i^* a_j E_j\langle\psi_i|\psi_j\rangle \\
&= \sum_i\sum_j a_i^* a_j E_j\delta_{ij} \\
&= \sum_j |a_j|^2 E_j
\end{aligned}$$

and since E_0 is the ground-state energy, $E_j \geq E_0$

$$\therefore \langle\phi|\mathcal{H}|\phi\rangle \geq \sum_j |a_j|^2 E_0$$

and ϕ is normalized, so $\sum_j |a_j|^2 = 1$

$$\therefore \langle\phi|\mathcal{H}|\phi\rangle \geq E_0$$

Note that, if ϕ is not normalized, this becomes

$$\frac{\langle\phi|\mathcal{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_0$$

If the wavefunction, ϕ, depends on an adjustable parameter, A, then the energy is minimized when

$$\frac{\partial E}{\partial A} = 0$$

6.4 An Example using the Variational Principle

Let's consider a quartic oscillator, with potential

$$V = cx^4$$

Without attempting to solve the Schrödinger equation for this potential, we can approximate the ground-state energy by using a trial wavefunction with the same form as the harmonic oscillator ground state

$$\phi = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(-\frac{a}{2}x^2\right)$$

which is already normalized.

The expectation value for the energy is

$$\begin{aligned} E &= \langle\phi|\mathcal{H}|\phi\rangle \\ &= \sqrt{\frac{a}{\pi}}\int_{-\infty}^{\infty} \mathrm{e}^{-\frac{a}{2}x^2}\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + cx^4\right)\mathrm{e}^{-\frac{a}{2}x^2}dx \end{aligned}$$

Evaluating the second derivative,

$$\frac{d^2}{dx^2}\mathrm{e}^{-\frac{a}{2}x^2} = -a\mathrm{e}^{-\frac{a}{2}x^2} + a^2x^2\mathrm{e}^{-\frac{a}{2}x^2}$$

The energy is then

$$\begin{aligned} E &= \sqrt{\frac{a}{\pi}}\int_{-\infty}^{\infty}\left(\frac{\hbar^2}{2\mu}a\mathrm{e}^{-ax^2} - \frac{\hbar^2}{2\mu}a^2x^2\mathrm{e}^{-ax^2} + cx^4\mathrm{e}^{-ax^2}\right)dx \\ &= \sqrt{\frac{a}{\pi}}\left(\frac{\hbar^2}{2\mu}a\sqrt{\frac{\pi}{a}} - \frac{\hbar^2}{2\mu}a^2\frac{1}{2}\sqrt{\frac{\pi}{a^3}} + c\frac{3}{4}\sqrt{\frac{\pi}{a^5}}\right) \\ &= \frac{\hbar^2 a}{4\mu} + \frac{3c}{4a^2} \end{aligned}$$

where we have used our table of definite integrals.

Now, to find the value of the a parameter to minimize the energy, we take

$$\begin{aligned} \frac{dE}{da} &= 0 \\ \frac{d}{da}\left(\frac{\hbar^2 a}{4\mu} + \frac{3c}{4a^2}\right) &= 0 \\ \frac{\hbar^2}{4\mu} - \frac{3c}{2a^3} &= 0 \\ \frac{3c}{a^3} &= \frac{\hbar^2}{2\mu} \\ a &= \left(\frac{6c\mu}{\hbar^2}\right)^{1/3} \end{aligned}$$

Finally, the minimum energy itself is

$$\begin{aligned} E &= \frac{\hbar^2}{4\mu}\left(\frac{6c\mu}{\hbar^2}\right)^{1/3} + \frac{3c}{4}\left(\frac{\hbar^2}{6c\mu}\right)^{2/3} \\ &= \frac{\hbar}{2}\left(\frac{3\hbar c}{4\mu^2}\right)^{1/3} + \frac{\hbar}{4}\left(\frac{3\hbar c}{4\mu^2}\right)^{1/3} \\ &= \frac{3\hbar}{8}\left(\frac{3\hbar c}{4\mu^2}\right)^{1/3} \end{aligned}$$

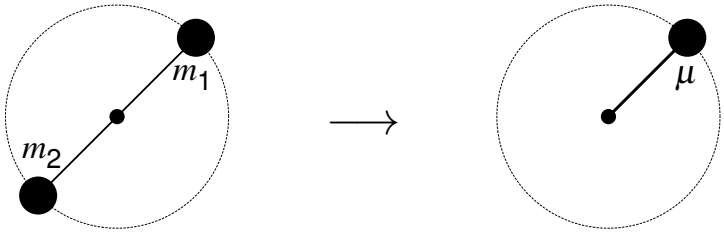
which we know is an upper bound to the true ground state energy.

Chapter 7

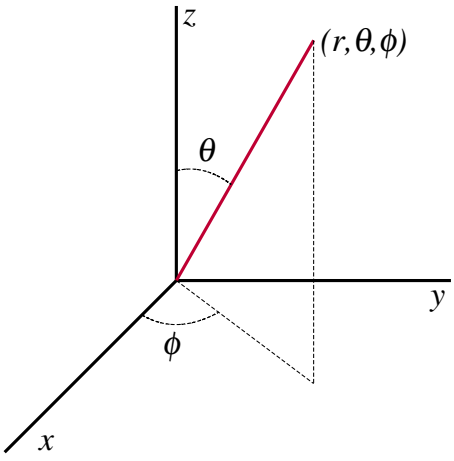
The Rigid Rotor

7.1 Wavefunctions and Energies

The rigid rotor is a model for the rotation of a molecule about its fixed centre of mass. This can be related to rotation of a single particle with reduced mass μ about a fixed origin.



This problem is solved most naturally in spherical polar coordinates:



Conversion between spherical and Cartesian coordinates:

$$\begin{aligned} x &= r\sin\theta\cos\phi & r &= (x^2+y^2+z^2)^{1/2} \\ y &= r\sin\theta\sin\phi & \cos\theta &= z/r \\ z &= r\cos\theta & \tan\phi &= y/x \end{aligned}$$

The volume element for integration is

$$dx\,dy\,dz = r^2\sin\theta dr\,d\theta\,d\phi$$

In 3D, the time-independent Schrödinger equation is

$$\mathcal{H}\psi = \left(-\frac{\hbar^2}{2\mu}\nabla^2 + V\right)\psi = E\psi$$

where ∇^2 is the Laplacian operator.

In Cartesian coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Using partial derivatives, it can be shown that, in spherical coordinates

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\end{aligned}$$

These two forms differ only in the $\partial/\partial r$ terms and either can be used depending on which is more convenient.

The Schrödinger equation is solved by separation of variables. We postulate that the wavefunction can be written as a product of separate radial and angular terms:

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

This is valid for a central potential, meaning that $V = V(r)$ only and is not also a function of angle.

For the rigid rotor problem, we have $V = 0$. All of the energy is kinetic energy of rotation related to the angular momentum. Also, as we are considering rotation of a rigid molecule (fixed bond length), r is the constant distance between the reduced mass and center of rotation.

Since r is constant, $\partial/\partial r = 0$ and the Hamiltonian is therefore

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

To highlight that we are dealing with a constant distance, we will define the moment of inertia as

$$I = \mu r^2$$

and write the Hamiltonian as

$$\mathcal{H} = \frac{\mathcal{L}^2}{2I}$$

where we define the angular momentum operator as

$$\mathcal{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

We also assume a further separation of angular variables, such that

$$Y(\theta, \phi) = P(\theta)\Phi(\phi)$$

The Schrödinger equation to be solved is

$$\frac{1}{2I}\mathcal{L}^2 P(\theta)\Phi(\phi) = EP(\theta)\Phi(\phi)$$

Where we have taken $R(r) = 1$ for simplicity. We know that $R(r)$ must be a constant since the Hamiltonian does not depend on r and the particular value does not matter since we require the whole wavefunction to be normalized.

Using the definition of $\mathcal{L}^2$ above,

$$\begin{aligned} -\frac{\hbar^2}{2I} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] P\Phi &= EP\Phi \\ \Phi \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial P}{\partial\theta} \right) + P \frac{1}{\sin^2\theta} \frac{\partial^2\Phi}{\partial\phi^2} &= -\frac{2IE}{\hbar^2} P\Phi \end{aligned}$$

Next, we multiply through by $\sin^2\theta$ and divide through by $P\Phi$

$$\begin{aligned} \frac{\sin\theta}{P} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial P}{\partial\theta} \right) + \frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} &= -\frac{2IE}{\hbar^2} \sin^2\theta \\ \frac{\sin\theta}{P} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial P}{\partial\theta} \right) + \frac{2IE}{\hbar^2} \sin^2\theta &= -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} \end{aligned}$$

As the left-hand side depends only on θ and the right-hand side depends only on ϕ, both sides must equal a constant, which we will take as m^2. This gives us two differential equations:

$$\frac{\sin\theta}{P} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial P}{\partial\theta} \right) + \frac{2IE}{\hbar^2} \sin^2\theta = m^2$$

$$-\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} = m^2$$

The second of these can be rewritten as

$$\frac{\partial^2\Phi}{\partial\phi^2} + m^2\Phi = 0$$

which has solutions

$$\Phi = A\mathrm{e}^{\pm \mathrm{i}m\phi}$$

We apply the boundary condition that Φ is a continuous, single-valued function so

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

This means that

$$\begin{aligned} A\mathrm{e}^{\pm \mathrm{i}m(\phi+2\pi)} &= A\mathrm{e}^{\pm \mathrm{i}m\phi} \\ \mathrm{e}^{\pm \mathrm{i}2\pi m} &= 1 \\ \cos(2\pi m) \pm \mathrm{i}\sin(2\pi m) &= 1 \end{aligned}$$

which requires $m = 0, \pm 1, \pm 2, \ldots$

To find the value of the normalization constant, A,

$$\begin{aligned} \int_0^{2\pi} \Phi^* \Phi d\phi &= 1 \\ A^2 \int_0^{2\pi} \mathrm{e}^{\mathrm{i}m\phi}\mathrm{e}^{-\mathrm{i}m\phi} d\phi &= 1 \\ A^2 \int_0^{2\pi} d\phi &= 1 \\ A^2(2\pi) &= 1 \\ A &= \frac{1}{\sqrt{2\pi}} \end{aligned}$$

Therefore, the solution is

$$\boxed{\Phi_m = \frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}m\phi} \text{ with } m = 0, \pm 1, \pm 2, \ldots}$$

The solutions to the other differential equation, involving P, are a set of special functions termed the Legendre polynomials (for $m = 0$) and the associated Legendre functions (for $m \neq 0$). These are denoted $P_{\ell,m}$. Together, the total wavefunctions are

$$\boxed{Y_{\ell,m}(\theta, \phi) = N_{\ell,m} P_{\ell,m}(\theta)\mathrm{e}^{\mathrm{i}m\phi} \text{ with } \ell = 0, 1, 2, \ldots \text{ and } m = 0, \pm 1, \ldots, \pm \ell}$$

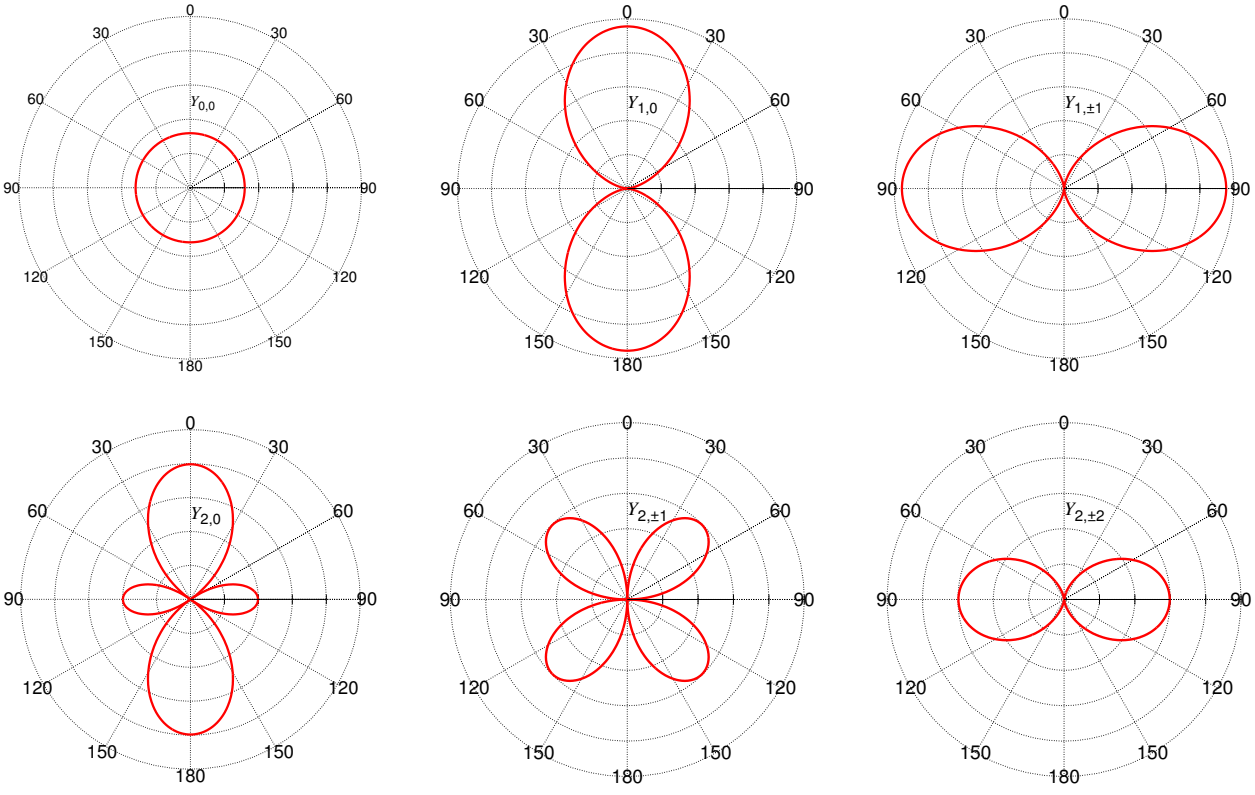
where $N_{\ell,m}$ is a normalization constant. These are termed the spherical harmonics.

The range of allowable values for m is bounded, and the spherical harmonic functions would go to zero for $m > \ell$ or $m < -\ell$.

The first few spherical harmonic functions are:

$$
\begin{aligned}
Y_{0,0} &= \sqrt{\frac{1}{4\pi}} \\
Y_{1,0} &= \sqrt{\frac{3}{4\pi}}\cos\theta \\
Y_{1,1} &= \sqrt{\frac{3}{8\pi}}\sin\theta \mathrm{e}^{\mathrm{i}\phi} \\
Y_{1,-1} &= \sqrt{\frac{3}{8\pi}}\sin\theta \mathrm{e}^{-\mathrm{i}\phi}
\end{aligned}
\qquad
\begin{aligned}
Y_{2,0} &= \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right) \\
Y_{2,1} &= \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta \mathrm{e}^{\mathrm{i}\phi} \\
Y_{2,-1} &= \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta \mathrm{e}^{-\mathrm{i}\phi} \\
Y_{2,2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta \mathrm{e}^{2\mathrm{i}\phi} \\
Y_{2,-2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta \mathrm{e}^{-2\mathrm{i}\phi}
\end{aligned}
$$

These are difficult to visualize due to the imaginary components. Polar plots showing the θ dependence of the first few spherical harmonics are shown below and reveal their characteristic shapes.

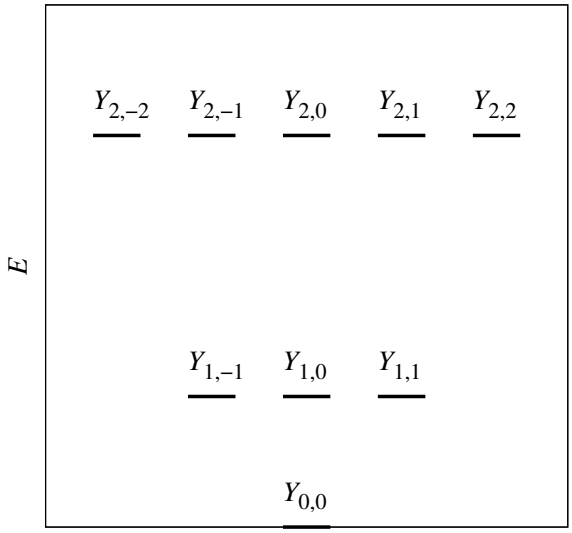


With these wavefunctions, it can be shown that the energy eigenvalues are

$$\boxed{E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1)}$$

However, it is easier to derive this result using raising and lowering operators, similar to what we did for the harmonic oscillator.

Finally, the energy level diagram for the rigid rotor is shown below. Note that there are many degenerate levels since the energy depends only on ℓ, and not on m.



7.2 Example for Molecular Rotation

Returning to our O_2 example, the two atomic masses are 16.0 g/mol, so the reduced mass is 8.0 g/mol or 1.33×10^{26} kg per molecule. Also, the bond length is 1.21 Å or 1.21×10^{-10} m. The spacing between the first two rotational levels is

$$\begin{aligned}
\Delta E &= E_{1,0} - E_{0,0} \\
&= \frac{\hbar^2}{2\mu r^2}\left[1(1+1) - 0(0+1)\right] \\
&= \frac{(1.055 \times 10^{-34})^2}{(1.33 \times 10^{-26})(1.21 \times 10^{-10})^2} \\
&= 5.7 \times 10^{-23}\ \text{J} \\
&= 0.034\ \text{kJ/mol}
\end{aligned}$$

The spacing of the rotational energy levels is greater than for the translational energy levels. However, it is still small compared to the thermal energy at room temperature ($RT = 2.5$ kJ/mol), so the rotational levels can be treated classically in thermodynamics.

7.3 Angular Momentum Operators and Commutators

Here, we define various angular momentum operators. Classically, the angular momentum is the cross product of position and momentum, and we will use this same relation for the QM operators.

$$(\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z) = (x, y, z) \times (p_x, p_y, p_z)$$

Recall that there are two types of vector products. The usual dot product is

$$(a, b, c) \cdot (u, v, w) = au + bv + cw$$

and is a scalar (single number). The cross product is

$$(a, b, c) \times (u, v, w) = (bw - cv, cu - aw, av - bu)$$

and is a vector that is perpendicular to both of the two input vectors.

Therefore, the components of the angular momentum are

$$\begin{aligned} \mathcal{L}_x &= yp_z - zp_y \\ \mathcal{L}_y &= zp_x - xp_z \\ \mathcal{L}_z &= xp_y - yp_x \end{aligned}$$

The individual components of the angular momentum operator do not commute and

$$\begin{aligned} [\mathcal{L}_x, \mathcal{L}_y] &= \mathrm{i}\hbar\mathcal{L}_z \\ [\mathcal{L}_y, \mathcal{L}_z] &= \mathrm{i}\hbar\mathcal{L}_x \\ [\mathcal{L}_z, \mathcal{L}_x] &= \mathrm{i}\hbar\mathcal{L}_y \end{aligned}$$

To show this for the case of $[\mathcal{L}_x, \mathcal{L}_y]$,

$$\begin{aligned} [\mathcal{L}_x, \mathcal{L}_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= [yp_z, zp_x] - 0 - 0 + [zp_y, xp_z] \\ &= yp_x[p_z, z] + xp_y[z, p_z] \\ &= yp_x(-\mathrm{i}\hbar) + xp_y(\mathrm{i}\hbar) \\ &= \mathrm{i}\hbar(xp_y - yp_x) \\ &= \mathrm{i}\hbar\mathcal{L}_z \end{aligned}$$

The square of the total angular momentum is

$$\boxed{\mathcal{L}^2 = \mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2}$$

$\mathcal{L}^2$ commutes with any of the individual angular momentum components

$$\boxed{[\mathcal{L}^2, \mathcal{L}_x] = [\mathcal{L}^2, \mathcal{L}_y] = [\mathcal{L}^2, \mathcal{L}_z] = 0}$$

To show this for the case of $\mathcal{L}_z$,

$$\begin{aligned}
[\mathcal{L}^2, \mathcal{L}_z] &= [\mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2, \mathcal{L}_z] \\
&= [\mathcal{L}_x^2, \mathcal{L}_z] + [\mathcal{L}_y^2, \mathcal{L}_z] + [\mathcal{L}_z^2, \mathcal{L}_z] \\
&= (\mathcal{L}_x^2\mathcal{L}_z - \mathcal{L}_z\mathcal{L}_x^2) + (\mathcal{L}_y^2\mathcal{L}_z - \mathcal{L}_z\mathcal{L}_y^2) + 0 \\
&= (\mathcal{L}_x^2\mathcal{L}_z - \mathcal{L}_x\mathcal{L}_z\mathcal{L}_x + \mathcal{L}_x\mathcal{L}_z\mathcal{L}_x - \mathcal{L}_z\mathcal{L}_x^2) + (\mathcal{L}_y^2\mathcal{L}_z - \mathcal{L}_y\mathcal{L}_z\mathcal{L}_y + \mathcal{L}_y\mathcal{L}_z\mathcal{L}_y - \mathcal{L}_z\mathcal{L}_y^2) \\
&= \mathcal{L}_x(\mathcal{L}_x\mathcal{L}_z - \mathcal{L}_z\mathcal{L}_x) + (\mathcal{L}_x\mathcal{L}_z - \mathcal{L}_z\mathcal{L}_x)\mathcal{L}_x + \mathcal{L}_y(\mathcal{L}_y\mathcal{L}_z - \mathcal{L}_z\mathcal{L}_y) + (\mathcal{L}_y\mathcal{L}_z - \mathcal{L}_z\mathcal{L}_y)\mathcal{L}_y \\
&= \mathcal{L}_x[\mathcal{L}_x, \mathcal{L}_z] + [\mathcal{L}_x, \mathcal{L}_z]\mathcal{L}_x + \mathcal{L}_y[\mathcal{L}_y, \mathcal{L}_z] + [\mathcal{L}_y, \mathcal{L}_z]\mathcal{L}_y \\
&= \mathcal{L}_x(-\mathrm{i}\hbar\mathcal{L}_y) + (-\mathrm{i}\hbar\mathcal{L}_y)\mathcal{L}_x + \mathcal{L}_y(\mathrm{i}\hbar\mathcal{L}_x) + (\mathrm{i}\hbar\mathcal{L}_x)\mathcal{L}_y \\
&= 0
\end{aligned}$$

Since they commute, it is possible to have a simultaneous set of eigenfunctions for $\mathcal{L}^2$ and $\mathcal{L}_z$. However, since $\mathcal{L}_z$ does not commute with $\mathcal{L}_x$ and $\mathcal{L}_y$, these will not be eigenfunctions of the other two angular momentum components.

Let $Y_{\ell,m} = |\ell, m\rangle$ be an eigenfunction of $\mathcal{L}^2$ and $\mathcal{L}_z$. We write

$$\boxed{\mathcal{L}^2|\ell, m\rangle = \ell(\ell+1)\hbar^2|\ell, m\rangle \text{ for } \ell = 0, 1, 2, \ldots}$$

$$\boxed{\mathcal{L}_z|\ell, m\rangle = m\hbar|\ell, m\rangle \text{ for } m = 0, \pm 1, \ldots, \pm\ell}$$

The powers of $\hbar$ make sense based on dimensional analysis. The actual eigenvalues can be found using raising and lowering operators, although the proof is rather lengthy.

7.4 Selection Rules for Rotational Spectroscopy

Similar to the use of infrared light in vibrational spectroscopy, far-infrared or microwave radiation can be used to measure the rotational spectrum of a molecule. For transitions between rotational states ℓ and ℓ' to be observed, the transition dipole moment must be non-zero:

$$\boxed{\langle \ell m|z|\ell' m'\rangle \neq 0}$$

(assuming z-polarized radiation) and the molecule must also have a permanent dipole moment.

Using commutators of the angular momentum operators, it can be shown that rotational transitions must obey the selection rule

$$\boxed{\Delta\ell = \pm 1}$$

to have a non-zero transition dipole. This means that the energy difference between rotational levels ℓ and $(\ell+1)$ is

$$\begin{aligned}\Delta E &= E_{\ell+1} - E_\ell \\ &= \frac{\hbar^2}{2I}\big[(\ell+1)(\ell+2) - \ell(\ell+1)\big] \\ &= \frac{\hbar^2}{2I}(2\ell+2) \\ &= \frac{\hbar^2}{I}(\ell+1)\end{aligned}$$

In microwave spectroscopy, it is common to give the absorption frequency of the transition as

$$\omega = 2B(\ell+1)$$

where we have used $\Delta E = \hbar\omega$. B is called the rotational constant of the molecule and is defined as

$$B = \frac{\hbar^2}{2I}$$

As we saw in our previous example, the spacing between rotational energy levels is much smaller than between vibrational energy levels. However, rotation gives fine structure to the vibrational spectrum. The resulting rotational-vibrational spectra typically have two symmetric branches for each vibrational transition. The higher-frequency is called the R branch and corresponds to the $\Delta\ell = +1$ transitions, while the lower-frequency is called the P branch and corresponds to the $\Delta\ell = -1$ transitions.

7.5 Ro-Vibrational Spectroscopy

The vibrational spectrum of a diatomic molecule will have a fine structure associated with rotational transitions. The combined vibrational and rotational energies, using the harmonic oscillator and rigid rotor models are:

$$E_{\text{vib,rot}} = \left(n + \frac{1}{2}\right)\hbar\omega + \frac{\hbar^2}{2I}\ell(\ell+1)$$

For an IR adsorption spectrum, only the $n = 0$ to $n = 1$ transition is observed. Also, the rotational selection rules require $\Delta\ell = \pm 1$. These two options give energies for the ro-vibrational transitions of

$$\Delta E = \begin{cases} \hbar\omega + \frac{\hbar^2}{I}(\ell+1) & \text{for } \ell = 0, 1, 2, \ldots \\ \hbar\omega - \frac{\hbar^2}{I}\ell & \text{for } \ell = 1, 2, 3, \ldots \end{cases}$$

The top result corresponds to $\Delta\ell = 1$ and gives the R branch of the spectrum, while the bottom result corresponds to $\Delta\ell = -1$ and gives the P branch. The relative intensities of the ro-vibrational peaks can be approximated using the populations in each level, ℓ, from which the transition originates. Here,

$$N_\ell = N_0(2\ell + 1)\exp\left[-\frac{B\ell(\ell+1)}{k_B T}\right]$$

where k_B is Boltzmann's constant and T is absolute temperature.

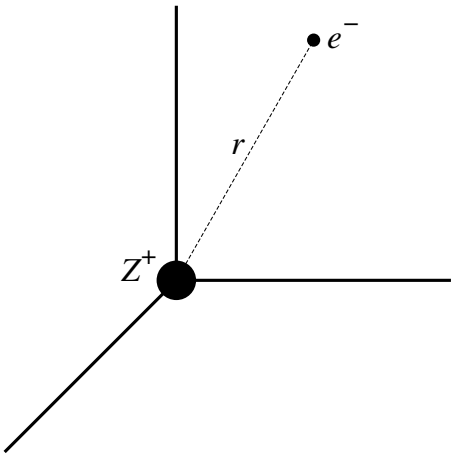
Chapter 8

The Hydrogen Atom

8.1 Wavefunctions and Energies

For a hydrogen-like atom, we consider how the electron moves in the central potential due to the nucleus.

If the electron has charge $-e$, we take the nuclear charge to be Ze, where Z is the atomic number. $Z = 1$ for the particular case of hydrogen, but can be greater for other hydrogen-like atoms, such as He^+.



The potential is

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

and arises from the electrostatic attraction between the electron and nucleus.

The $4\pi\epsilon_0$ term in the denominator is the "vacuum permittivity".

Therefore, the hydrogen-atom Hamiltonian is

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

where m_e is the electron mass (not the reduced mass since we considering motion of a

single electron about the fixed nucleus). Substituting the definition of the Laplacian and $\mathcal{L}^2$ operators,

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2m_e r^2}\mathcal{L}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The Schrödinger equation is solved using separation of variables. Let the wavefunction be

$$\psi(r,\theta,\phi) = R(r)Y_{\ell,m}(\theta,\phi)$$

We use the spherical harmonics for the angular part, since the angular part of the Hamiltonian is the same as for the rigid rotor problem.

Therefore, the time-independent Schrödinger equation for the radial term of the H atom wavefunction is:

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2}R - \frac{Ze^2}{4\pi\epsilon_0 r}R = ER$$

We will solve this equation for the H-atom ground state by proposing a solution and demonstrating that it works. We let

$$R = A\mathrm{e}^{-ar}$$

Then, the required derivatives are

$$\frac{dR}{dr} = -Aa\mathrm{e}^{-ar} = -aR$$

$$\frac{d^2R}{dr^2} = Aa^2\mathrm{e}^{-ar} = a^2R$$

Also, for the ground state, $\ell = 0$, so the Schrödinger equation becomes

$$\begin{aligned}
-\frac{\hbar^2}{2m_e}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}R &= E_0 R \\
-\frac{\hbar^2}{2m_e}\left(a^2R - \frac{2a}{r}R\right) - \frac{Ze^2}{4\pi\epsilon_0 r}R &= E_0 R \\
\left(\frac{\hbar^2 a}{m_e} - \frac{Ze^2}{4\pi\epsilon_0}\right)\frac{R}{r} &= \left(\frac{\hbar^2 a^2}{2m_e} + E_0\right)R
\end{aligned}$$

For this to be true for all values of r, both terms in parentheses must be zero, so we can write

$$E_0 = -\frac{\hbar^2 a^2}{2m_e}$$

and

$$\begin{aligned}\frac{\hbar^2 a}{m_e} &= \frac{Ze^2}{4\pi\epsilon_0} \\ a &= \frac{Ze^2 m_e}{4\pi\epsilon_0\hbar^2}\end{aligned}$$

For simplicity, the Bohr radius is defined as

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

so that $a = Z/a_0$. Substituting this result back into the energy for the ground state of the H atom

$$\boxed{E_0 = -\frac{\hbar^2 Z^2}{2m_e a_0^2}}$$

General solution of the Schrödinger equation for the radial term for all excited states, n, is not at all trivial and, like for the harmonic oscillator and rigid rotor, involves a set of special functions. It can be shown that the general solution for the H-atom energies is

$$\boxed{E_n = -\frac{\hbar^2 Z^2}{2m_e a_0^2 n^2}}$$

The corresponding wavefunctions are

$$\boxed{\psi_{n,\ell,m} = R_{n\ell}(r)Y_{\ell,m}(\theta,\phi) \text{ with } n = 1, 2, \ldots, \ell = 0, 1, \ldots (n-1), \text{ and } m = 0, \pm 1, \ldots, \pm\ell}$$

and the radial functions are

$$R_{n,\ell} = -\sqrt{\frac{(n-\ell-1)!}{2n[(n+1)!]^3}}\left(\frac{2Z}{na_0}\right)^{\ell+3/2} r^\ell \exp\left(-\frac{Zr}{na_0}\right) L_{n+1}^{2\ell+1}\left(\frac{2Zr}{na_0}\right)$$

where the set of special functions $L_{n+1}^{2\ell+1}\left(\frac{2Zr}{na_0}\right)$ are the associated Laguerre functions.

The first few H-atom wavefunctions ($n = 1, 2$) are given by

$$\begin{aligned}\psi_{100} &= \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp\left(-\frac{Zr}{a_0}\right) \\ \psi_{200} &= \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right) \\ \psi_{210} &= \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)\cos\theta \\ \psi_{21\pm1} &= \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)\sin\theta \mathrm{e}^{\pm \mathrm{i}\phi}\end{aligned}$$

The pattern of energy level is

	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	
$n=4$	— $4s$	— $4p$	— $4d$	— $4f$	7 f states, $m=0,\pm1,\pm2,\pm3$
$n=3$	— $3s$	— $3p$	— $3d$		5 d states, $m=0,\pm1,\pm2$
$n=2$	— $2s$	— $2p$			3 p states, $m=0,\pm1$
$n=1$	— $1s$				1 s states, $m=0$

All the H-atom energies depend only on n and all different ℓ, m values are degenerate. However, the ℓ, m degeneracy is broken in the presence of electric or magnetic fields, and in multi-electron atoms.

8.2 Hartree Atomic Units

Carrying around constants such as $\hbar$, m_e, e, a_0, and $4\pi\epsilon_0$ complicates equations and can lead to errors in solving numerical problems. To eliminate these constants, we define a new set of units, called Hartree atomic units. Here

$$\boxed{\hbar = m_e = e = 4\pi\epsilon_0 = 1}$$

This choice causes the Bohr radius to also be $a_0 = 1$ and the H-atom energies are simply

$$\boxed{E_n = -\frac{1}{2n^2}}$$

From atomic units (abbreviated a.u.), conversion factors to SI units are

Quantity	Atomic units	SI units
Mass	$m_e = 1$	9.1091×10^{-31} kg
Charge	$e = 1$	1.6021×10^{-19} C
Length	$a_0 = 1$	5.2617×10^{-11} m
Momentum	$\hbar = 1$	1.0545×10^{-34} Js
Permittivity	$4\pi\epsilon_0 = 1$	1.1126×10^{-10} C^2/Jm
Energy	$e^2/(4\pi\epsilon_0 a_0) = 1$	4.3594×10^{-18} J

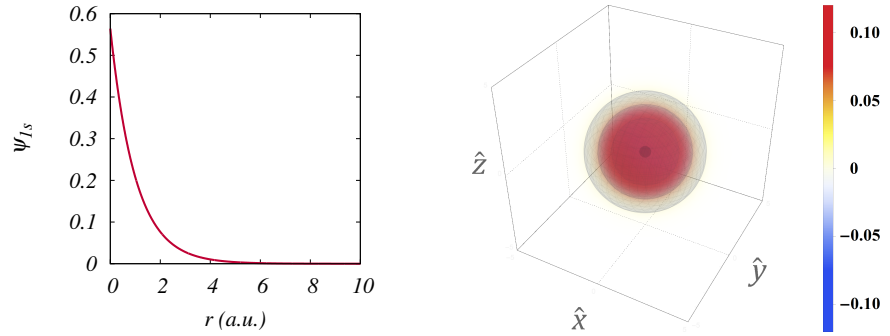
It is generally more practical to carry out QM calculations in atomic units and convert to SI at the end then trying to work in SI units throughout.

8.3 Visualizing the Hydrogen Atomic Orbitals

What do the H-atom wavefunctions look like? The real functions can be easily plotted in 3D as shown below and are called the atomic orbitals.

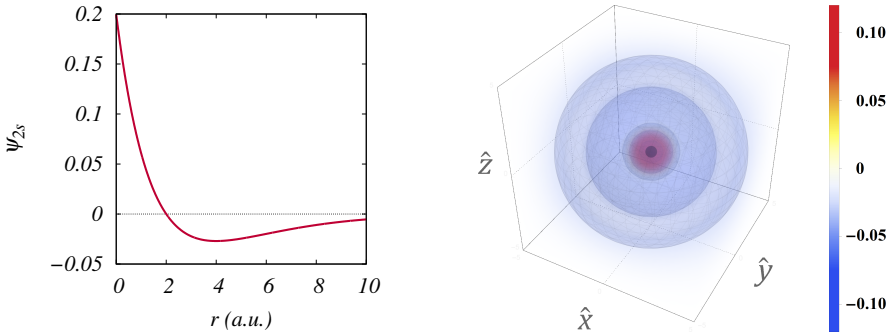
$$\psi_{1s} = \psi_{100} \sim \mathrm{e}^{-r}$$

This is a spherically symmetric function with a maximum at the nucleus.



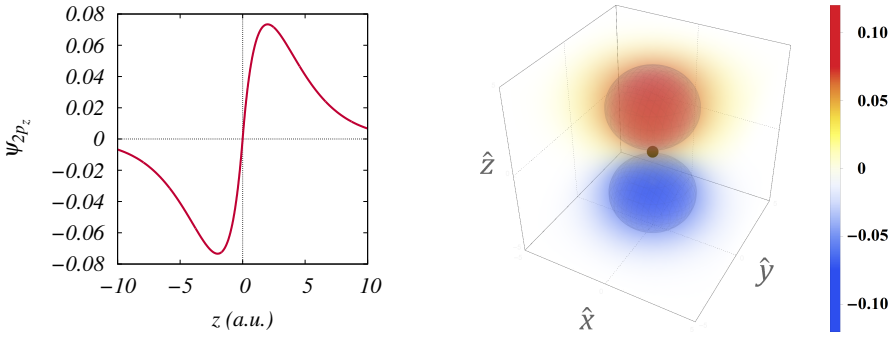
$$\psi_{2s} = \psi_{200} \sim (2 - r)\mathrm{e}^{-r/2}$$

This is also spherically symmetric, but the radial component changes sign as $\psi_{2s} = 0$ at $r = 2$. Where the wavefunction is zero is called a "node."



$$\psi_{2p_z} = \psi_{210} \sim r\cos\theta\mathrm{e}^{-r/2} = ze^{-r/2}$$

This orbital is aligned along along the z axis and has a node in the xy plane.



However, the next two H-atom wavefunctions are

$$\psi_{21\pm1} \sim r\sin\theta \mathrm{e}^{\pm \mathrm{i}\phi}\mathrm{e}^{-r/2}$$

which have complex values and cannot be plotted in real space.

To obtain real orbitals from these complex wavefunctions, we take linear combinations of ψ_{211} and ψ_{21-1}.

For the positive linear combination, we have:

$$\begin{aligned}
\frac{1}{\sqrt{2}}\left(\psi_{211}+\psi_{21-1}\right) &= \frac{1}{\sqrt{2}}\frac{1}{\sqrt{64\pi}} r\sin\theta\left(\mathrm{e}^{\mathrm{i}\phi}+\mathrm{e}^{-\mathrm{i}\phi}\right)\mathrm{e}^{-r/2} \\
&= \frac{1}{\sqrt{2}}\frac{1}{\sqrt{64\pi}} r\sin\theta\big[\cos\phi+\mathrm{i}\sin\phi+\cos(-\phi)+\mathrm{i}\sin(-\phi)\big]\mathrm{e}^{-r/2} \\
&= \frac{1}{\sqrt{32\pi}} r\sin\theta\cos\phi\mathrm{e}^{-r/2} \\
&= \frac{1}{\sqrt{32\pi}} x\mathrm{e}^{-r/2} \\
&= \psi_{2p_x}
\end{aligned}$$

and similarly for the negative linear combination, we have:

$$\begin{aligned}
-\frac{i}{\sqrt{2}}\left(\psi_{211}-\psi_{21-1}\right) &\sim -\frac{i}{\sqrt{2}}\frac{1}{\sqrt{64\pi}} r\sin\theta\left(\mathrm{e}^{\mathrm{i}\phi}-\mathrm{e}^{-\mathrm{i}\phi}\right)\mathrm{e}^{-r/2} \\
&= -\frac{i}{\sqrt{2}}\frac{1}{\sqrt{64\pi}} r\sin\theta\big[\cos\phi+\mathrm{i}\sin\phi-\cos(-\phi)-\mathrm{i}\sin(-\phi)\big]\mathrm{e}^{-r/2} \\
&= \frac{1}{\sqrt{32\pi}} r\sin\theta\sin\phi\mathrm{e}^{-r/2} \\
&= \frac{1}{\sqrt{32\pi}} y\mathrm{e}^{-r/2} \\
&= \psi_{2p_y}
\end{aligned}$$

Thus, the $2p_x$ and $2p_y$ orbitals are linear combinations of ψ_{211} and ψ_{21-1} and they are not true eigenstates of the $\mathcal{L}_z$ angular momentum operator. Similarly, for the d orbitals, $\psi_{3dz^2} = \psi_{320}$ but the other four real d orbitals are linear combinations of the complex H-atom wavefunctions and are not eigenfunctions of $\mathcal{L}_z$.

The expectation value, $\langle \mathcal{L}_z \rangle$, for an electron in either a $2p_x$ or $2p_y$ orbital would be zero:

$$\begin{aligned}
\langle \psi_{2p_z} | \mathcal{L}_z | \psi_{2p_x} \rangle &= \left\langle \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) \middle| \mathcal{L}_z \middle| \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) \right\rangle \\
&= \frac{1}{2} \langle \psi_{211} | \mathcal{L}_z | \psi_{211} \rangle + \frac{1}{2} \langle \psi_{21-1} | \mathcal{L}_z | \psi_{21-1} \rangle \\
&= \frac{1}{2} \langle \psi_{211} | \hbar \psi_{211} \rangle + \frac{1}{2} \langle \psi_{21-1} | - \hbar \psi_{21-1} \rangle \\
&= \frac{1}{2} \hbar - \frac{1}{2} \hbar \\
&= 0
\end{aligned}$$

A measurement of $\mathcal{L}_z$ would yield either $m = 1$ or $m = -1$, each with 50% probability.

8.4 Some Expectation Values

The expectation value, $\langle r \rangle$, is useful as a rough measure of orbital size. Because the spherical harmonic functions are normalized and do not depend on r, this expectation value (in a.u.) can be shown to be

$$\begin{aligned}
\langle r \rangle &= \langle n\ell m | r | n\ell m \rangle \\
&= \int_0^\infty R_{n\ell}(r) r R_{n\ell}(r) r^2 dr \\
&= \int_0^\infty r^3 R_{n\ell}(r) dr \\
&= \frac{n^2}{Z} \left[1 + \frac{1}{2} \left(1 - \frac{\ell(\ell+1)}{n^2} \right) \right]
\end{aligned}$$

So the orbital size increases with the principle quantum number, n, and also decreases slightly with increasing angular momentum quantum number, ℓ.

It can also be shown that

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2}$$

and the expectation value of the potential is

$$\langle V \rangle = -Z \left\langle \frac{1}{r} \right\rangle = -\frac{Z^2}{n^2}$$

For a general hydrogen-like atom with nuclear charge Z, the energies are

$$E_n = -\frac{Z^2}{2n^2}$$

so we have the result that

$$\boxed{\langle V \rangle = 2\langle E \rangle}$$

The result that $\langle V \rangle = 2\langle E \rangle$ is called the virial theorem. It is valid for any Coulombic potential energy (i.e. $V \sim {}^1\!/_r$), so it is valid for all atoms and molecules.

8.5 The Hydrogen Atomic Spectrum

For a H atom, the energy levels (in a.u.) are

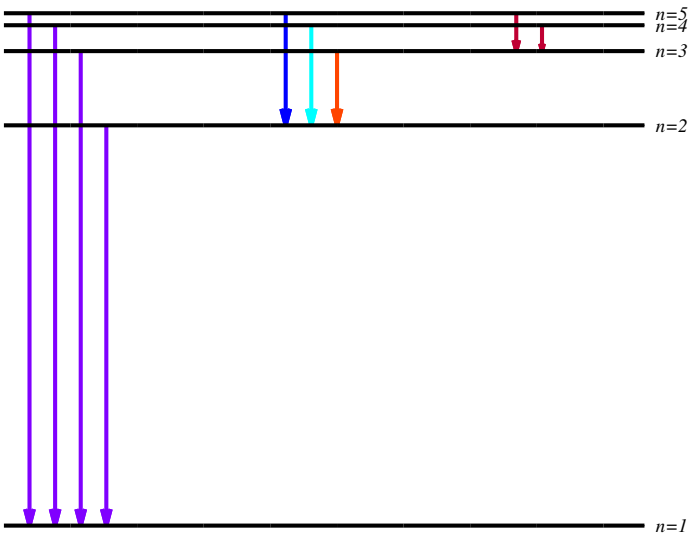
$$E_n = -\frac{1}{2n^2}$$

The spectrum arises from transitions between states. For the transition from state n' to state n, the frequency of emitted radiation is

$$\omega = \frac{1}{2}\left(\frac{1}{n'^2} - \frac{1}{n}\right)$$

For a given n, the set of transitions from $n' = n+1, n+2, \ldots$ constitute a series of bright lines, located in different regions of the electromagnetic spectrum.

$n = 1$	Lyman series	UV
$n = 2$	Balmer series	visible
$n = 3$	Paschen series	IR



Not all transitions between states are allowed. The selection rules require a non-zero transition dipole moment

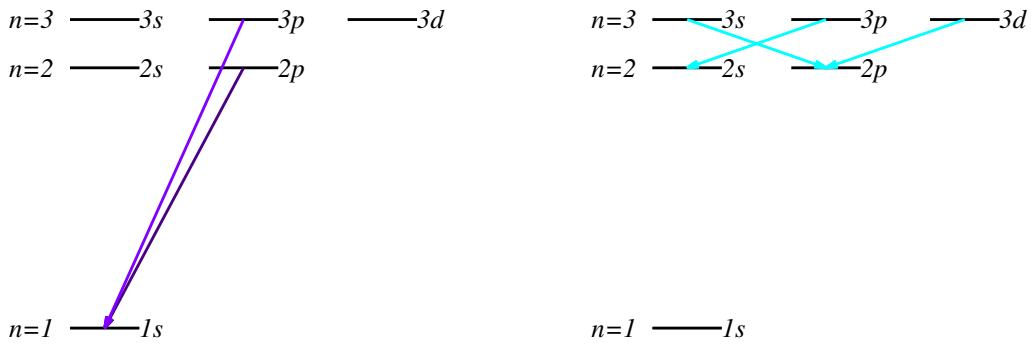
$$\langle n\ell m|z|n'\ell'm'\rangle \neq 0$$

for an allowed transition. As discussed for the rigid rotor, this requires $\Delta\ell = \pm 1$. It also requires $\Delta m = 0, \pm 1$. Therefore, spontaneous transitions between different energy levels of

a H atom are only possible with

$$\boxed{\Delta\ell = \pm 1 \text{ and } \Delta m = 0, \pm 1}$$

Allowed transitions for the Lyman and Balmer series are:



Chapter 9

Spin and Many-Electron Atoms

9.1 Electron Spin

One further level of quantization in atoms and molecules is electron "spin". An electron has a spin angular momentum of

$$|s| = \frac{1}{2}\hbar$$

The QM treatment of spin ($\mathcal{S}$) is identical to the treatment of orbital angular momentum ($\mathcal{L}$). The eigenvalue equations are

$$\boxed{\mathcal{S}^2|\chi\rangle = s(s+1)\hbar^2|\chi\rangle}$$

$$\boxed{\mathcal{S}_z|\chi\rangle = m_s\hbar^2|\chi\rangle}$$

For an electron, $s = 1/2$ and $m_s = \pm 1/2$.

The spin is independent of the spatial coordinates, (r, θ, ϕ), so we cannot write out the eigenfunctions in coordinate space. Common representations for the spin eigenfunctions are

$$|\alpha\rangle \text{ or } |\uparrow\rangle \text{ for } m_s = \frac{1}{2}$$

$$|\beta\rangle \text{ or } |\downarrow\rangle \text{ for } m_s = -\frac{1}{2}$$

The spin functions are orthonormal so that

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$$

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$$

Due to spin, the states of the H atom are all doubly degenerate (spin up or spin down). The spatial orbitals are represented as $\psi_{n\ell m_\ell}$ or $|n\ell m_\ell\rangle$ and can be occupied by 2 electrons. The spin orbitals are represented as $\psi_{n\ell m_\ell m_s}$ or $|n\ell m_\ell m_s\rangle$ and only be occupied by a single electron.

Taking spin into account, it is possible to define another set of eigenstates, involving the total (orbital plus spin) angular momentum. We take their vector sum as

$$\mathcal{J} = \mathcal{L} + \mathcal{S}$$

and the square of the total angular momentum is

$$\mathcal{J}^2 = \mathcal{L}^2 + \mathcal{S}^2 + 2\mathcal{L}\cdot\mathcal{S}$$

The eigenvalue equations are

$$\mathcal{J}^2|n\ell j m_j\rangle = j(j+1)\hbar^2|n\ell j m_j\rangle$$

$$\mathcal{J}_z|n\ell j m_j\rangle = m_j\hbar^2|n\ell j m_j\rangle$$

Wavefunctions can be written in terms of either $n\ell m_\ell m_s$ or $n\ell j m_j$ quantum numbers and conversion between the two is done using tables of Clebsh-Gordon coefficients, although this is beyond the scope of this course.

Consideration of different spin states is important for heavy elements due to spin-orbit coupling, and when considering the effect of a magnetic field on atomic energy levels, as in NMR or ESR spectroscopy.

9.2 The Pauli Exclusion Principle

Before we can consider multi-electron systems, there is one further constraint we must impose on the wavefunction that arises from the indistinguishability of identical particles.

For a system of n identical particles, the wavefunction depends on their positions and spins. We will define the vector $\mathbf{q} = (x, y, z, m_s)$ to give the spatial and spin coordinates. The wavefunction can then be written as

$$\psi = \psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_n)$$

We also define the permutation operator, $\mathcal{P}_{ij}$ that interchanges the coordinates (both space and spin) of particles i and j so that

$$\mathcal{P}_{12}\psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_n) = \psi(\mathbf{q}_2, \mathbf{q}_1, \ldots, \mathbf{q}_n)$$

Since the labeling is arbitrary, this permutation cannot affect the physical state of the system.

Two wavefunctions that correspond to the same state must be identical, to within a constant phase factor

$$\mathcal{P}_{ij}\psi = c\psi$$

so ψ is an eigenfunction of $\mathcal{P}_{ij}$. Also, application of $\mathcal{P}_{ij}$ twice recovers the original wavefunction, so

$$\mathcal{P}_{ij}^2\psi = \psi$$

However,

$$\mathcal{P}_{ij}^2\psi = \mathcal{P}_{ij}(c\psi) = c^2\psi$$

Equating these two results means that $c^2 = 1$, so $c = \pm 1$. Therefore, the wavefunction must be either symmetric on antisymmetric with respect to interchange of any two particles.

To illustrate the consequences of this constraint, let's consider two non-interacting particles in a 1D box of width a. The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right)\psi = E\psi$$

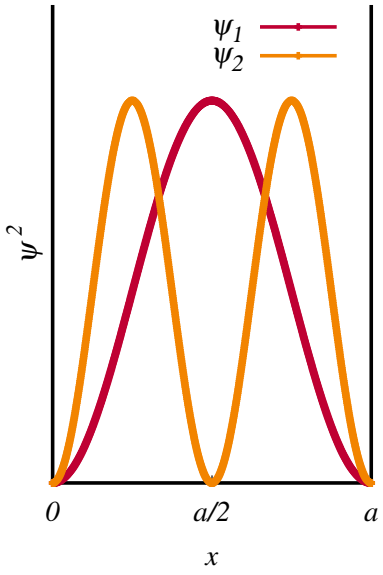
and the solution is a product of two particle in a box wavefunctions

$$\psi_{mn}(x_1, x_2) = \psi_m(x_1)\psi_n(x_2)$$

For the specific case of the particles being in the first two energy states,

$$\psi_{12}(x_1, x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_1}{a}\right)$$

The probability of finding particle 1 at $x_1 = a/4$ and particle 2 at $x_2 = a/2$ is zero because $\psi_2(a/2) = 0$. However, the probability of finding particle 1 at $x_1 = a/2$ and particle 2 at $x_2 = a/4$ is non-zero. This is not physically meaningful since the particles are indistinguishable. The wavefunction must be either symmetric or antisymmetric with respect to interchange.

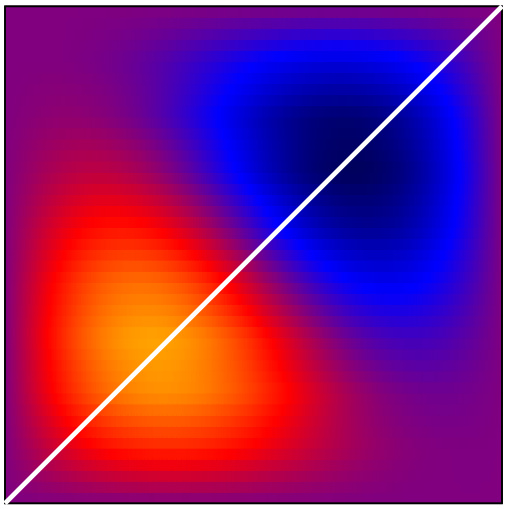


Symmetric and antisymmetric wavefunctions can be constructed from the individual particle in a box wavefunctions for each particle and are

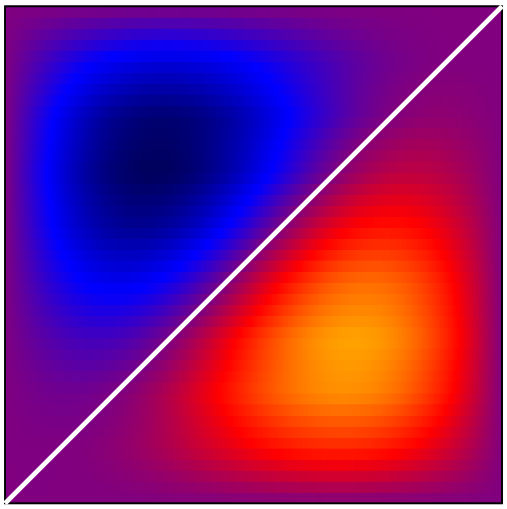
$$\psi_{mn}^{\mathrm{S}} = \frac{1}{\sqrt{2}}\left[\psi_m(x_1)\psi_n(x_2) + \psi_m(x_2)\psi_n(x_1)\right]$$

$$\psi^{\mathrm{A}}_{mn} = \frac{1}{\sqrt{2}}\left[\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1)\right]$$

For the cases of ψ^{S}_{12} and ψ^{A}_{12}, the resulting probability densities are



ψ^{S}_{12}: high probability of finding both particles at the same point.



ψ^{A}_{12}: zero probability of finding both particles at the same point.

Experiment shows that there are two types of fundamental particles, with one type having each of the behaviours shown above:

- Fermions - antisymmetric with respect to interchange
- Bosons - symmetric with respect to interchange

and electrons are Fermions.

The **Pauli Exclusion Principle** states that the wavefunction of a system of electrons must be antisymmetric with respect to interchange of any two electrons. This is also the 6th and final postulate of QM.

An important consequence of this principle can be seen by considering the value of a wavefunction when two electrons have the same space and spin coordinates (i.e. $\mathbf{q}_i = \mathbf{q}_j$). Then,

$$\psi = \psi(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_i, \mathbf{q}_i, \ldots, \mathbf{q}_n)$$

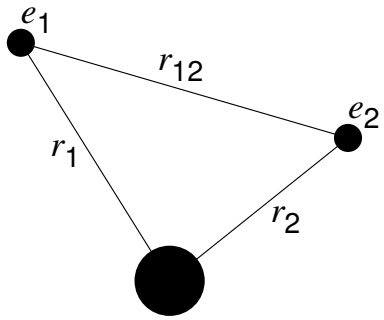
but ψ must be antisymmetric with respect to interchange of i and j. This leads to $\psi = -\psi$, and this can only be true for $\psi = 0$.

Therefore, another statement of the **Pauli Exclusion Principle** is that two electrons with the same spin have zero probability of being found at the same point in space.

9.3 The Helium Atom Ground State

The He-atom Hamiltonian, in atomic units, is

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$



The first two terms are the kinetic energies of electrons 1 and 2, respectively. The next two terms are the attractive electrostatic interactions of electrons 1 and 2 with the nucleus (charge $Z = 2$). The last term is the repulsive electrostatic interaction between the two electrons.

This resembles a repetition of the H-atom problem for electrons 1 and 2, except that the last term

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

is not separable into functions of the individual electron coordinates. This means that the Schrödinger equation cannot be solved analytically for this system and approximate methods must be used. This is true for all atoms or molecules with two or more electrons.

We can use perturbation theory to solve this by treating the $1/r_{12}$ as the perturbation.

$$\mathcal{H}' = \frac{1}{r_{12}}$$

Thus, our unperturbed Hamiltonian will be

$$\begin{aligned} \mathcal{H}^\circ &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \\ &= \mathcal{H}_1^\circ + \mathcal{H}_2^\circ \end{aligned}$$

which is the sum of two hydrogen-like Hamiltonians, one for each electron. This would be exact if the electrons did not interact with each other.

The unperturbed spatial wavefunctions are the product of the hydrogen-like orbitals. For the ground state, this is

$$\psi^\circ = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) = 1s(1)1s(2)$$

We must also take spin into account (since there is more than one electron) and multiply this spatial wavefunction by a spin eigenfunction.

We will use the notation $\alpha(i)$ or $\beta(i)$ to indicate a state in which electron i is spin up or spin down, respectively.

There are four normalized spin eigenfunctions that satisfy the requirement of being either symmetric or antisymmetric with respect to exchange:

$$\boxed{\text{symmetric, "triplet" spin functions } \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\big[\alpha(1)\beta(2)+\alpha(2)\beta(1)\big] \end{cases}}$$

$$\boxed{\text{antisymmetric, "singlet" spin function } \begin{cases} \frac{1}{\sqrt{2}}\big[\alpha(1)\beta(2)-\alpha(2)\beta(1)\big] \end{cases}}$$

According to the Pauli principle, the total wavefunction must be antisymmetric with respect to exchange. The spatial part is $1s(1)1s(2)$, which is symmetric. Therefore, the spin part must be antisymmetric and

$$\psi^\circ = 1s(1)1s(2)\frac{1}{\sqrt{2}}\big[\alpha(1)\beta(2)-\alpha(2)\beta(1)\big]$$

However, the spin terms will not affect the energy (since the Hamiltonian does not depend on spin), so we need consider only the spatial part. To show this:

$$\begin{aligned}
E &= \langle\psi|\mathcal{H}|\psi\rangle \\
&= \left\langle 1s(1)1s(2)\frac{1}{\sqrt{2}}\big[\alpha(1)\beta(2)-\alpha(2)\beta(1)\big]\middle|\mathcal{H}\middle|1s(1)1s(2)\frac{1}{\sqrt{2}}\big[\alpha(1)\beta(2)-\alpha(2)\beta(1)\big]\right\rangle \\
&= \langle 1s(1)1s(2)|\mathcal{H}|1s(1)1s(2)\rangle\frac{1}{2}\langle\alpha(1)\beta(2)-\alpha(2)\beta(1)|\alpha(1)\beta(2)-\alpha(2)\beta(1)\rangle \\
&= \langle 1s(1)1s(2)|\mathcal{H}|1s(1)1s(2)\rangle\frac{1}{2}\big[\langle\alpha(1)|\alpha(1)\rangle\langle\beta(2)|\beta(2)\rangle-\langle\alpha(1)|\beta(1)\rangle\langle\beta(2)|\alpha(2)\rangle- \\
&\quad \langle\beta(1)|\alpha(1)\rangle\langle\alpha(2)|\beta(2)\rangle+\langle\beta(1)|\beta(1)\rangle\langle\alpha(2)|\alpha(2)\rangle\big] \\
&= \langle 1s(1)1s(2)|\mathcal{H}|1s(1)1s(2)\rangle\frac{1}{2}(1-0-0+1) \\
&= \langle 1s(1)1s(2)|\mathcal{H}|1s(1)1s(2)\rangle
\end{aligned}$$

The energy using the zeroth-order wavefunction is

$$\begin{aligned}
E^\circ &= \langle\psi^\circ|\mathcal{H}^\circ|\psi^\circ\rangle \\
&= \left\langle 1s(1)1s(2)\middle| -\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{2}{r_1}-\frac{2}{r_2}\middle|1s(1)1s(2)\right\rangle \\
&= \left\langle 1s(1)1s(2)\middle| -\frac{1}{2}\nabla_1^2-\frac{2}{r_1}\middle|1s(1)1s(2)\right\rangle + \left\langle 1s(1)1s(2)\middle| -\frac{1}{2}\nabla_2^2-\frac{2}{r_2}\middle|1s(1)1s(2)\right\rangle \\
&= \left\langle 1s(1)\middle| -\frac{1}{2}\nabla_1^2-\frac{2}{r_1}\middle|1s(1)\right\rangle\langle 1s(2)|1s(2)\rangle + \left\langle 1s(2)\middle| -\frac{1}{2}\nabla_2^2-\frac{2}{r_2}\middle|1s(2)\right\rangle\langle 1s(1)|1s(1)\rangle \\
&= \left\langle 1s(1)\middle| -\frac{1}{2}\nabla_1^2-\frac{2}{r_1}\middle|1s(1)\right\rangle + \left\langle 1s(2)\middle| -\frac{1}{2}\nabla_2^2-\frac{2}{r_2}\middle|1s(2)\right\rangle
\end{aligned}$$

Each of these terms is the expectation value of the energy for a hydrogen-like atom with a nuclear charge $Z = 2$ for the ground state ($n = 1$). Since the energies of a hydrogen-like atom are $E = -Z^2/2n^2$, the energy is simply:

$$E = -\frac{2^2}{2} - \frac{2^2}{2} = -4$$

So the uncorrected energy is $E^\circ = -4$ a.u.

Next, we evaluate the first-order correction. Recall that the perturbation is

$$\mathcal{H}' = \frac{1}{r_{12}}$$

so the first-order energy correction is

$$\begin{aligned} E^{(1)} &= \langle \psi^\circ | \mathcal{H}' | \psi^\circ \rangle \\ &= \left\langle 1s(1)1s(2) \middle| \frac{1}{r_{12}} \middle| 1s(1)1s(2) \right\rangle \end{aligned}$$

This quantity is called the Coulomb integral, J. This is a 6D integral over the spatial coordinates (r_1, θ_1, ϕ_1) for electron 1 and (r_2, θ_2, ϕ_2) for electron 2. It can be shown that this integral is

$$J = \frac{5Z}{8}$$

for the $1s$ orbitals of a general hydrogen-like atom with nuclear charge Z. Thus, for the helium atom, we have $E^{(1)} = {}^5\!/_4$ a.u.

To first order, the total ground-state energy of He is predicted to be

$$E = E^\circ + E^{(1)} = -4 + \frac{5}{4} = -\frac{11}{4} = -2.75 \text{ a.u.}$$

This is in fair agreement with the exact result (obtained from numerical solution) of $E_{\text{He}} = -2.903724$ a.u. However, the error is 0.154 a.u. or ~ 400 kJ/mol, which is on the order of covalent bond strengths! It is not surprising that our result is not that accurate, since electron-electron repulsion is not a small perturbation. Much more accurate approximations must be used for quantitative predictions.

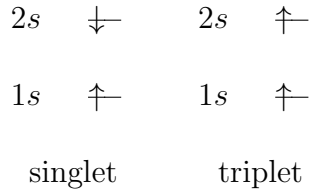
More sophisticated, numerical approaches are needed and will be discussed in CHEM 4301/5301.

9.4 Helium Atom Excited States

The lowest-lying excited states for He have the electron configuration $1s^1 2s^1$. The spatial parts of these wavefunctions are

$$\psi_{\text{singlet}} = \frac{1}{\sqrt{2}}\big[1s(1)2s(2) + 1s(2)2s(1)\big]$$

$$\psi_{\text{triplet}} = \frac{1}{\sqrt{2}}\big[1s(1)2s(2) - 1s(2)2s(1)\big]$$



where ψ_{singlet} would be paired with the singlet spin function and ψ_{triplet} could be paired with any of the three triplet spin functions.

We will write a general form of the spatial wavefunction as

$$\psi = \frac{1}{\sqrt{2}}\big[1s(1)2s(2) \pm 1s(2)2s(1)\big]$$

The corresponding zeroth-order energy is the sum of the two H-atom orbital energies

$$\begin{aligned} E^\circ &= -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} \\ &= -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \\ &= -\frac{2^2}{2}\left(\frac{1}{1^2} + \frac{1}{2^2}\right) \\ &= -\frac{5}{2} \text{ a.u.} \end{aligned}$$

The first-order energy correction is

$$\begin{aligned} E^{(1)} &= \langle\psi|\mathcal{H}'|\psi\rangle \\ &= \frac{1}{2}\left\langle 1s(1)2s(2) \pm 1s(2)2s(1)\left|\frac{1}{r_{12}}\right|1s(1)2s(2) \pm 1s(2)2s(1)\right\rangle \\ &= \left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle \pm \left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(2)2s(1)\right\rangle \\ &= J \pm K \end{aligned}$$

The first term is called the Coulomb integral (J) and the second is called the exchange integral (K).

The energy, to first order, is then

$$\begin{aligned} E_{\text{singlet}} &= -\frac{5}{2} + J + K \\ E_{\text{triplet}} &= -\frac{5}{2} + J - K \end{aligned}$$

Since both J and K are positive (due to electron-electron repulsion), the triplet state will be lower in energy. This is because, in the triplet, $\psi = 0$ when $r_1 = r_2$, so there is zero probability of finding the electrons at the same point in space. It is this additional stability that gives rise to Hund's rule of maximum electron unpairing for degenerate energy levels.

9.5 Many-Electron Atoms

The approach for He can be generalized to many-electron atoms. For example, the Hamiltonian for the Li atom is

$$\mathcal{H} = \sum_{i=1}^{3} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}$$

Treating the $1/r_{ij}$ terms as a perturbation, we would predict that the zeroth-order approximation for the spatial part of the ground-state wavefunction is $1s(1)1s(2)1s(3)$. However, this violates the Pauli exclusion principle as we only have twofold degeneracy for the $1s$ orbital – α or β spin. The correct zeroth-order approximation would be of the form $1s(1)1s(2)2s(3)$.

We must also ensure that the total wavefunction is antisymmetric with respect to exchanging any two electron indices. The solution is to write the wavefunction as a Slater determinant.

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

$2s$ $\uparrow$–

$1s$ $\uparrow\downarrow$

Properties of determinants ensure this wavefunction is antisymmetric with respect to exchange (recall that the sign of determinants flip if columns or rows exchange order). The $1/\sqrt{6}$ prefactor ensures normalization.

In general, for a N-electron atom, the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}$$

The zeroth-order wavefunction can be written as a Slater determinant

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

where $\phi_1, \phi_2, \ldots, \phi_N$ are spin orbitals, the order of which is chosen according to the AUFBAU (filling) principle.