1 Introduction: The Wavefunction

The state of a particle is described by a complex continuous wave function \( \psi(q) \) of some coordinates \( q \). In this brief summary the coordinates \( q \) are typically chosen to be \((x,t)\), and other coordinates can be added for a more complete description, e.g., the particle’s total spin and spin projection. Examples of wavefunctions include

- \( \psi(x) = \sqrt{2/L} \sin(n\pi x / L) \) (\( n \) integer) describes a particle confined to a one-dimensional box in the interval \([0, L]\).
- \( \psi(x,t) = e^{i(p x - iE)t\hbar / \sqrt{V}} \) describes a free particle in a box of volume \( V \) with momentum \( p \), including time dependence.
- \( \psi(r,\theta,\phi) = \frac{1}{\pi a_0^3} e^{-r/a_0} \), where \( a_0 \) is the Bohr radius, describes the ground state of a hydrogen atom.

Wavefunctions are normalized so that

\[
\int \psi^*(x,t)\psi(x,t)dx = 1
\]

i.e., total probability = 1. The connection between wavefunction and probability is explored in the next subsection.
1.1 Wavefunction and Probability

\[ dP = |\psi(q)|^2 dq \] represents the probability of finding a particle with coordinates \( q \) in the interval \( dq \) (assuming that \( q \) is a continuous variable, like coordinate \( x \) or momentum \( p \)). Thus \( |\psi(q)|^2 \) is a probability density. In the free particle example above, the probability for the particle having \( x,y,z > 0 \) is

\[ P = \int_{x,y,z>0} |\psi(x,t)|^2 d^3x = \int_{\Delta V} d^3x / V = 1 / 8. \]

For the particle in the one dimensional box, the probability of the particle in its ground state \( (n = 1) \) being found in the first third of the box is

\[ P = (2 / L) \int_0^{L/3} \sin^2 (\pi x / L) dx = 0.1956. \]

Only probabilities and observables (see below) can be measured, not \( \psi \) itself.

1.2 Superposition of Wavefunctions

If \( \psi_1(q) \) describes some physical state 1 and \( \psi_2(q) \) describes a physical state 2, then the wavefunction \( \psi(q) = \alpha \psi_1(q) + \beta \psi_2(q) \) describes a new physical state that is called the superposition of the two states 1 and 2. If the states are normalized and orthogonal (“orthonormal”), then

\[ |\alpha|^2 + |\beta|^2 = 1. \]

1.3 Wavefunction Evolution and Measurement

The notion of an experiment (observation) is a key concept in understanding quantum mechanics: only by conducting an experiment one can localize a particle with probabilities calculated from \( \psi(q) \). Before an experiment is conducted, the particle cannot be said to be at a given coordinate. But neither does the wavefunction describe some kind of smeared distribution of matter. QM describes the deterministic evolution of \( \psi(q) \), which gives probabilistic predictions for experiment outcomes. For example, quantum mechanics can predict the angular distribution of electrons scattered through a narrow slit (the angular distribution is a probability distribution), but cannot determine the trajectory of any given electron.

The equation describing the (nonrelativistic) time evolution of \( \psi \) is called the Schrödinger equation, after the physicist who first described it. It can be written as

\[ i \frac{\partial}{\partial t} \psi(q) = \hat{H} \psi(q) \]

where \( \hat{H} \) is a hamiltonian operator, which in most cases is \( \hat{H} = \hat{p}^2 / 2m + U \), where \( \hat{p} \) is the momentum operator and \( U \) is the potential. It has been empirically shown that the QM probabilistic description cannot be reduced to some deterministic, but hidden parameters.\(^1\)

1.4 Stationary states

Most physical potentials are time independent, so the Hamiltonian operator has no explicit time dependence. This suggests that we use separation of variables and write the wavefunction as the product of a spatial part and a time part \( \psi(x,t) = \psi(x) T(t) \). Substituting this in the Schrödinger equation and dividing by \( \psi T \) gives
\[-i\hbar \frac{T'}{T} = \hat{H}\psi / \psi\]

The left and right sides of the equation are functions of different variables, thus each must be constant. We call the constant \(E\) (it has units of energy) and obtain \(\psi(x,t) = \psi(x)e^{-iEt/\hbar}\), where \(\psi(x)\), the non-time part of the wavefunction, is a “stationary state”. Thus all time independent potentials reduce to the simplified Schrödinger equation

\[\hat{H}\psi(x) = E\psi(x)\]

### 1.5 Eigenvalues and Eigenstates

Consider a QM operator \(\hat{g}\). If a wavefunction \(\psi_g(q)\) exists such that

\[\hat{g}\psi_g(q) = g\psi_g(q)\]

where \(g\) is an ordinary (complex) number, we say that \(\psi_g(q)\) is an eigenstate of \(\hat{g}\) with eigenvalue \(g\). The following examples should help explain the idea.

- In the time-independent Schrödinger equation, the time dependent part of the wavefunction \(\psi_t = e^{-iEt/\hbar}\) is an eigenstate of the time evolution operator \(\hat{T} = i\hbar \frac{\partial}{\partial t}\) with eigenvalue \(E\) (energy): \(\hat{T}\psi_t = E\psi_t\).

- The free particle wavefunction \(\psi = e^{ipx/\hbar}\) is an eigenstate of the momentum operator \(\hat{p}_x = -i\hbar \frac{\partial}{\partial x}\) with eigenvalue \(p\) (momentum): \(\hat{p}_x e^{ipx/\hbar} = pe^{ipx/\hbar}\).

- The wavefunction \(e^{im\phi}\) is an eigenstate of the \(z\) angular momentum operator \(\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}\) with eigenvalue \(m\) (\(m\hbar\) is \(z\) component of angular momentum): \(\hat{L}_z e^{im\phi} = m\hbar e^{im\phi}\).

### 2 Expectation Value

Consider a QM operator \(\hat{g}\). For any wavefunction \(\psi(q)\) the expectation value of \(\hat{g}\) for that wavefunction is defined as

\[\langle \psi | \hat{g} | \psi \rangle \equiv \int \psi^* (q) \hat{g}\psi(q) dq\]

Since \(|\psi(q)|^2 dq\) is the probability density, the expectation value can be considered to be the usual statistical notion of expectation value. However, the order \(\psi^*, \hat{g}, \psi\) is important because \(\hat{g}\) is an operator and typically operates to the right, as is the case for differential operators. Note that if the wavefunction is an eigenstate of \(\hat{g}\) with eigenvalue \(g\), then the expectation value is merely \(g\).
Let’s calculate the momentum expectation value for a particle in a one dimensional box with infinite potential walls (Section 3). The wavefunction is $\psi(x) = \sqrt{2/L} \sin \left( \frac{n\pi x}{L} \right)$. The expectation value is

$$\langle \psi | \hat{p} | \psi \rangle = \frac{2}{L} \int \sin \left( \frac{n\pi x}{L} \right) \left( -i\hbar \frac{d}{dx} \right) \sin \left( \frac{n\pi x}{L} \right) dx = 0$$

A value of zero is expected because $\sin kx \sim e^{ikx} - e^{-ikx}$, which is an equal combination of a particle moving to the right and a particle moving to the left with the same momentum. We can also work out the expectation of the momentum squared operator

$$\langle \psi | \hat{p}^2 | \psi \rangle = \frac{2}{L} \int \sin \left( \frac{n\pi x}{L} \right) \left( -\hbar^2 \frac{d^2}{dx^2} \right) \sin \left( \frac{n\pi x}{L} \right) dx = \frac{n^2 \pi^2 \hbar^2}{L^2}$$

This is nonzero because the wavefunction has separate components moving to the left and the right.

## 3 Schrödinger Equation Examples

### 3.1 Particle in a box with infinite walls: one dimension

The particle in a 1-D box neatly illustrates how quantization arises when a potential is present. The idea is a particle confined to a region of length $L$, which we accomplish with the following potential:

$$U(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{Otherwise} \end{cases}$$

Classically, a particle within the region can have any positive energy, bouncing back and forth between the walls with a momentum depending on the energy. In the QM picture, we write the stationary state Schrödinger equation inside the region as

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

which can be rearranged into the form of a standard second order differential equation

$$\psi''(x) + \frac{2mE}{\hbar^2} \psi(x) = 0$$

Although in principle the energy $E$ can have any value, the value must allow the wavefunction to be 0 at the two boundaries of the region to maintain continuity with the vanishing wave function outside the region. We first try negative energies, or $2mE = -\hbar^2 k^2$, for which the general solution is $\psi(x) = Ae^{ikx} + Be^{-ikx}$, where $A$ and $B$ are constants. However, the condition that $\psi(0) = 0$ and $\psi(L) = 0$ force $A = B = 0$, so no nontrivial solution with negative energy exists.
We next try positive energies or \( 2mE = \hbar^2 k^2 \), with solution \( \psi(x) = A \sin(kx) + B \cos(kx) \). The boundary condition \( \psi(0) = 0 \) forces \( B = 0 \), while \( \psi(L) = 0 \) leads to \( \sin(kL) = 0 \) as the only non-trivial solution. This can be satisfied only if \( kL \) is a multiple of \( \pi \), e.g. \( k = n\pi / L \), for any non-zero integer \( n \). The boundary conditions thus lead us to wavefunctions of the form
\[
\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)
\]
with energy \( E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} \). Normalizing to unit probability
\[
\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1 \quad \text{gives} \quad A = \sqrt{2/L}.
\]
Thus the only solutions to the Schrodinger equation of a particle in an infinitely high box are:
\[
\psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-iE_n t / \hbar} \quad n \geq 1
\]
\[
E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}
\]
i.e., only a countable number of solutions and their corresponding energies are possible. This is actually an amazing result, that a potential plus boundary conditions are sufficient to select particular wavefunctions with particular energies. This quantization of wavefunctions and energies (as well as other quantities such as angular momentum) is a hallmark of almost all potentials in quantum mechanics, including the hydrogen atom which we will consider later. The probability distributions and energies are summarized in Figure 1.

![Particle in a box probability distributions (shifted by energy)](image)

**Figure 1:** Probability distributions and energies for the 1-D particle in a box
3.2 Harmonic oscillator: one dimension

The harmonic oscillator potential is \( U(x) = \frac{1}{2}kx^2 \), familiar to us from classical mechanics where Newton’s second law applied to a harmonic oscillator potential (spring, pendulum, etc.) gives the equation \( m\ddot{x} = -kx \) or \( \ddot{x} + \omega^2 x = 0 \), where \( \omega = \sqrt{k/m} \) is the angular frequency of sinusoidal oscillations. For a given total energy \( E \) the particle oscillates in the range

\[
-\sqrt{\frac{E}{m\omega^2}} \leq x \leq \sqrt{\frac{E}{m\omega^2}}
\]

The Schrödinger equation for the harmonic oscillator can be written

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \right) \psi(x) = E \psi(x)
\]

where we use \( \omega \) rather than \( k \) in the equation. The process for obtaining wavefunction solutions is more involved than we want to describe in this brief summary. The main result is that the requirement of wavefunction normalizability imposes a severe restriction on the allowable wavefunctions and their energies. The normalized wavefunctions and energies are found to be

\[
\psi(x) = \frac{1}{\sqrt{2^n n! \sqrt{\alpha \pi} \sqrt{2}}} H_n \left( \frac{x}{a} \right) e^{-x^2/2a^2} e^{-x^2/2a^2}
\]

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

where \( n \) is an integer satisfying \( n \geq 0 \) and \( H_n \) are \( n \)th order Hermite polynomials. A plot of the probability distribution is shown in Figure 2 for \( n = 0, 1, 2, 3, 4 \). A feature of the harmonic oscillator solutions is that the energies are evenly spaced with the ground state energy being \( E_0 = \frac{1}{2} \hbar \omega \).

The harmonic oscillator is an important quantum system because any potential with a minimum \( U_0 \) will look parabolic in a small region around the minimum, which allows its lowest lying energy levels to be approximated by \( U_0 \) plus the lowest harmonic oscillator energies (how would these energies be modified for a 3-D harmonic oscillator?).
3.3 Particle in a box with infinite walls: three dimensions

The solution to the 3-D particle in a cubical box with infinite potential walls is an easy extension of the one-dimensional case. The potential is

\[ U(x, y, z) = \begin{cases} 0 & 0 \leq x, y, z \leq L \\ \infty & \text{Otherwise} \end{cases} \]

Inside the box the 3-D Schrödinger equation is

\[-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) \equiv -\frac{1}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E \psi(x, y, z)\]

To solve this equation we resort again to separation of variables

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

Taking the derivatives and dividing both sides by \( X Y Z \), we obtain the differential equation

\[ \frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} + \frac{2mE}{\hbar^2} = 0 \]
Because each of the first three terms depends on a separate variable and sum to a constant, each term must be separately constant, or

\[ X'' + c_x X = 0 \]
\[ Y'' + c_y Y = 0 \]
\[ Z'' + c_z Z = 0 \]

where the \( c_i \) are constants and \( 2mE = \hbar^2 \left( c_x + c_y + c_z \right) \). As in the one-dimensional case, we apply boundary conditions for each coordinate, which as before only allows positive values for the constants (e.g., \( c_x = k_x^2 \)), with sinusoidal solutions and quantized values for the constants (e.g., \( k_x = n_x \pi / L \)). The normalized general solution is the product of the sine terms:

\[ \psi(x,y,z,t) = \sqrt{\frac{8}{V}} \sin \left( \frac{n_x \pi x}{L} \right) \sin \left( \frac{n_y \pi y}{L} \right) \sin \left( \frac{n_z \pi z}{L} \right) e^{-iEt/\hbar} \]

\[ E = \frac{\left( n_x^2 + n_y^2 + n_z^2 \right) \hbar^2 \pi^2}{2mL^2} \quad n_x, n_y, n_z \geq 1 \]

where \( V = L^3 \) is the volume of the region.

The solution exhibits some interesting properties. First, the wavefunctions are labeled by three independent positive integers, with the total energy being proportional to the sum of the squares of the integers. Labeling the solutions by \( (n_x, n_y, n_z) \), we see that the ground state \((111)\) has energy \( 3E_0 \), where \( E_0 = \pi^2 \hbar^2 / 2mL^2 \). This brings us to the second point, namely that the excited states \( \psi_{211}, \psi_{121} \) and \( \psi_{112} \), which are orthogonal to one another, have the same energy \( 6E_0 \).

We say that these wavefunctions have a degeneracy of 3. (What is the degeneracy of \( \psi_{123} \)?) Any linear combination of these states will also have the same energy, i.e., the states defined by \( \psi = \alpha \psi_{211} + \beta \psi_{121} + \gamma \psi_{112} \), with \( |\alpha|^2 + |\beta|^2 + |\gamma|^2 = 1 \), are properly normalized and have energy \( 6E_0 \). It is possible to find other degeneracies with different integer combinations.

Obviously, there is nothing sacred about having a box with identical sides, and the solutions are modified trivially by replacing the length \( L \) for a particular side by the correct value. The energy for each state is also modified in a straightforward way.

\[ E = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad n_x, n_y, n_z \geq 1 \]
3.4 The hydrogen atom: using spherical coordinates

3.4.1 Classical treatment

Before taking up the quantum mechanical treatment, it’s worthwhile to consider the classical motion of a particle around a central potential $U$ depending only on $r$. The Newtonian equations of motion are

$$m\ddot{r} - mr\dot{\theta}^2 = -\frac{dU(r)}{dr}$$

$$mr\ddot{\theta} + 2m\dot{r}\dot{\theta} = 0$$

where the second equation expresses conservation of the angular momentum $L = mr^2\dot{\theta}$. The kinetic energy can be written as a sum of radial and angular momentum components:

$$K = \frac{1}{2}mr^2 + \frac{1}{2}mr^2\dot{\theta}^2$$

$$= \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$$

Integrating the first Newtonian equation of motion yields the familiar result that the total energy $E = K + U$ is constant. For the electrostatic potential

$$U(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} = -\frac{\alpha\hbar c}{r}$$

the total energy is

$$E = -\frac{\alpha\hbar c}{2a}$$

where $a$ is the semimajor axis of the conic section describing the orbit (circle, ellipse, parabola or hyperbola). The angular momentum $L$ is also a constant of the motion. Note that $E$ and $L$ can have arbitrary values, in contrast to the situation in quantum mechanics, which we take up next.

3.4.2 Quantum mechanical treatment: Basic outline

The hydrogen atom presents a fundamentally interesting case, and its solution shows how quantization can arise from the nature of the potential and the requirement of normalizable wavefunctions and continuity. A basic outline of the solution is shown here; more details can be found in the Appendix.

Let’s first consider the general case of a time-independent radial potential $U(r)$. Clearly, it’s best to write the three dimensional Schrodinger equation using spherical coordinates.
\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + U(r) \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)
\]
\[
\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}
\]
Comparing this expression with the classical version shows that
\[
\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]
is the quantum mechanical operator corresponding to \( \hat{L}^2 \). The Schrödinger equation becomes
\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} + U(r) \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)
\]
We again try separation of variables, with \( \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \). Substituting this expression for the wavefunction, multiplying out the \( r^2 \) factor, and dividing by \( R \Theta \Phi \), we obtain three equations as before. The details are complex and require more time than we want to devote to the topic in this chapter (see Appendix for more details). The results can be summarized as follows.

1. The potential function and total energy only appear in the radial equation. The angular equations can thus be solved independently and identically for any radial potential, just like in the classical case.
2. Solving the angular equations and requiring that the solutions be normalizable and exhibit continuity (\( \Phi(\phi) = \Phi(\phi + 2\pi) \)) leads to two integer quantum numbers: \( l \geq 0 \), which describes the total angular momentum, and \( -l \leq m \leq l \), which measures the \( z \) component of angular momentum.
3. The radial equation depends on the constant \( l(l+1) \) where \( l \) is the angular momentum integer found in the angular solution. The requirement that the radial solution be normalizable severely restricts the possible solutions and introduces another quantum number \( n \), where \( n > l \) is known as the “principal quantum number”. The total energy of a hydrogen atom state described by \( n \) is \( \sim E_0 / n^2 \), independent of angular momentum \( l \).

The full hydrogen atom wavefunction is thus characterized by three quantum numbers and can be written in the separated form \( \psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_{lm}(\theta) \Phi_m(\phi) \), where \( n, l \) and \( m \) are integers satisfying \( n > 0 \), \( l < n \) and \( -l \leq m \leq l \). These quantum numbers are already familiar to you from the study of orbitals in chemistry:

- **1s state** \( \psi_{100} \)
- **2s state** \( \psi_{200} \)
• 2p states \( \psi_{21-1}, \psi_{210}, \psi_{211} \)
• 3d states \( \psi_{32-2}, \psi_{32-1}, \psi_{320}, \psi_{321}, \psi_{322} \)

Notice that each orbital momentum \( l \) has \( 2l + 1 \) possible states, each with a different angular momentum \( z \) component.\(^1\)

Finally, the energy of a hydrogen state with principal quantum number \( n \) is independent of \( l \):

\[
E_n = -\frac{\alpha^2 mc^2}{2n^2} \equiv -\frac{E_0}{n^2} = -\frac{13.6}{n^2} \text{ eV}
\]

A few radial probability distributions are shown in Figure 3 while some angular probability distributions are graphed in Figure 4.

Figure 3: The first few hydrogen atom radial probability distributions

---

\(^1\) Note that each orbital can actually accommodate 2 electrons because there is an additional spin quantum number (not discussed here) where one electron has spin up and the other has spin down. Thus there are two electrons in the \( s \) state, six in the \( p \) state, etc.
The Uncertainty Principle in Quantum Mechanics

One of the most famous predictions of quantum mechanics is the “uncertainty principle”, which states that simultaneous measurements of a particle’s space coordinate and momentum along the same direction cannot both be arbitrarily accurate but must satisfy the inequality

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

Thus as a coordinate measurement improves, the corresponding momentum measurement worsens, and vice versa. As a simple illustration of the process, consider an experiment in which one directs a short wavelength photon beam on a particle to measure its location to within a wavelength. Because the photon momentum is inversely proportional to its wavelength, a measurement of particle’s momentum would show an uncertainty inversely proportional to the wavelength.

A precise derivation of the uncertainty principle shows that the uncertainties $\Delta x$ and $\Delta p_x$ are actually the standard deviations of each variable which can be calculated from a wavefunction.
4.1 Uncertainty principle and ground state energy

4.1.1 One dimensional particle in a box

Consider the particle in the 1-D box that we solved in Section 3.1. Without solving the Schrödinger equation, we can estimate the ground state energy using the uncertainty principle. If the particle is confined to a box of length $L$, its position uncertainty is of order $L/2$. Thus the momentum uncertainty is $\Delta p_x \geq \frac{1}{2} \frac{\hbar}{L/2} \sim \frac{\hbar}{L}$. The corresponding energy is then

$$E = \frac{p^2}{2m} \sim \frac{\hbar^2}{2mL^2},$$

which is not far from the actual answer of $\frac{\pi^2\hbar^2}{2mL^2}$. We can try a better estimation that the particle is uniformly distributed throughout $L$, which gives a standard deviation $\Delta x = L/\sqrt{12}$ from which the uncertainty principle predicts $\Delta p_x \geq \frac{1}{2} \frac{\hbar}{L/\sqrt{12}} = \sqrt{3} \frac{\hbar}{L}$ corresponding to a ground state energy of $E \sim 3\hbar^2 / 2mL^2$. Finally, we can use the actual ground state wavefunction $\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$ from which we can calculate the standard deviation of the position:

$$\Delta x = \sqrt{\left(\frac{x - L/2}{L}\right)^2} = \frac{1}{\sqrt{12}} - \frac{1}{2\pi^2} L = 0.18 L$$

which yields $\Delta x \Delta p_x = 0.568 \hbar$, which is larger than $\frac{1}{2} \hbar$. Of course, the real beauty of this method is that one is able to estimate the ground state energy knowing only the size of the region.

4.1.2 Energy and size of the ground state of a harmonic oscillator potential

We can apply this method to estimating the ground state energy of the harmonic oscillator where the potential is $V = \frac{1}{2} kx^2$. The ground state energy is the lowest energy consistent with the sum of kinetic and potential energy. Clearly if $\Delta x$ shrinks, then the average potential energy gets smaller and the kinetic energy increases because of the increase in average momentum. So we want to minimize the total energy

$$E = \frac{1}{2m} \left( \frac{\hbar}{2\Delta x} \right)^2 + \frac{1}{2} k\Delta x^2$$

the minimum energy occurs at $E = \frac{1}{2} \hbar \sqrt{k/m}$ which turns out to be the exact answer, a fortuitous answer given the approximate nature of the method.

4.2 Finding the approximate size of an atom

The solution of the $1/r$ potential for the hydrogen atom yields an average radius of the ground state

$$a_0 = \frac{\hbar c}{\alpha mc^2}$$

where $a_0$ is known as the Bohr radius. We can obtain a similar answer using the following argument. Imagine an electron confined to a region of average radius $r$ around the proton. Then the total energy is the sum of the kinetic and potential energies:
\[ E \approx \frac{3}{2m} \left( \frac{\hbar}{2r} \right)^2 - \frac{\alpha \hbar c}{r} \]

where the factor of 3 accounts for momentum uncertainties in all dimensions. Minimizing the ground state energy by varying \( r \) gives a radius of

\[ r \approx \frac{3 \cdot \hbar c}{4 \alpha mc^2} \]

which is very close to the Bohr radius. Thus a consideration of the uncertainty principle plus knowledge of the potential energy variation allows one to find the approximate ground state energy and size of the system.

5 Appendix: More Details of the Hydrogen Atom Solution

We provide here some further details in the solution of the hydrogen atom, showing how separation of variables and normalizability leads to a full solution. We do not include the full details of the calculation which are normally covered in a full course in quantum mechanics.

Starting with the Schrödinger equation in spherical coordinates which we wrote in the previous subsection, separation of variables \( \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \), leads to the equation, after dividing by \( R \Theta \Phi \)

\[
\left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{2m(E-U)}{\hbar^2} r^2 - \frac{L^2(\Theta \Phi)}{\hbar^2 \Theta \Phi} \right] = 0
\]

As before, the radial and the angular terms add to a constant which forces each of them to be constant.

\[
\frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{2m(E-U)}{\hbar^2} r^2 - c_r = 0
\]

\[
L^2 (\Theta \Phi) = c_r \hbar^2 \Theta \Phi
\]

where \( c_r \) is a constant. As noted previously: (1) the potential energy function and the total energy appear only in the radial equation and (2) the angular equation is independent of the potential and the total energy, exactly the same result we saw in the classical treatment.

Now things get interesting. Without going into details, it turns out that to get a normalizable angular wavefunction, i.e. \( \int |\Theta(\theta)\Phi(\phi)|^2 d\cos \theta d\phi = 1 \), that \( c_r \) must be of the form \( c_r = l(l+1) \), where \( l \) is an integer satisfying \( l \geq 0 \) and is known as the “total angular momentum” quantum number. Separation of the angular equation using the two angular functions and applying the continuity criterion \( \Phi(\phi) = \Phi(\phi + 2\pi) \) leads to \( \Phi(\phi) = e^{im\phi} \), where \( m \) is an integer satisfying \( -l \leq m \leq l \). \( m \) is known as the \( z \) component of the angular momentum. Thus for any value \( l \) of the total angular momentum there are \( 2l + 1 \) possible wavefunctions, each with a different value of \( m \). We usually write the angular products as spherical harmonic functions \( Y_l^m(\theta, \phi) \) which are orthonormal eigenfunctions of \( \hat{L}^2 \)
\[ \hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi) \]
\[ \int Y_l^{m*}(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) \, d\Omega = \delta_{l\mu} \delta_{mm'} \]

Using the angular solution, we write the radial equation as

\[ R'' + \frac{2}{r} R' + \left[ \frac{2m(Er^2 + \alpha \hbar c r)}{\hbar^2} - l(l+1) \right] \frac{R}{r^2} = 0 \]

The requirement that the radial wavefunction solutions of this equation be normalizable, i.e. \( \int_0^{\infty} r^2 R(r) \, dr = 1 \), severely restricts the possible solutions and introduces another integer quantum number \( n > 0 \). The general radial solutions are of the form

\[ R_{nl}(r) \propto \rho^l L_{n+l}^{2l+1}(\rho) e^{-\rho/2} \]

where \( l < n \) and \( \rho \) is the dimensionless radial coordinate \( \rho = 2r / na_0 \), where \( a_0 \) is the “Bohr radius”

\[ a_0 = \frac{\hbar c}{\alpha mc^2} = 0.0529 \text{ nm} \]

\( L_l^i(x) \) are known as “Laguerre polynomials”. The total energy depends only on \( n \)

\[ E_n = -\frac{\alpha^2 mc^2}{2n^2} = -\frac{13.6}{n^2} \text{ eV} \]

which is a familiar result from the Bohr model.

**References**

1 A good article about hidden variables and quantum mechanics can be found in [http://en.wikipedia.org/wiki/Hidden_variable_theory](http://en.wikipedia.org/wiki/Hidden_variable_theory)

2 A good discussion of the harmonic oscillator details can be found in [http://en.wikipedia.org/wiki/Quantum_harmonic_oscillator](http://en.wikipedia.org/wiki/Quantum_harmonic_oscillator)