CHAPTER 11 LECTURE NOTES

11.1-3 Electromagnetic Radiation and Old Quantum Theory

- Electromagnetic radiation is characterized by two fundamental characteristics: amplitude, or the “height” of the wave, and frequency. Mathematically, we may represent a wave in terms of these properties as

\[ y = A \sin(\omega t + \delta) \]  

(11.5)

where \( A \) is the amplitude, the frequency \( \nu \), is expressed as the angular frequency \( \omega = 2\pi(\text{rad})\nu(\text{s}^{-1}) \), and the factor \( \delta \) is called the phase of the wave. The expression of Eq. (11.5) is one possible solution to the classical wave equation

\[ \frac{d^2y}{dt^2} = -\omega^2 y. \]  

(11.8)

- Frequency is related to the wavelength \( \lambda \) as \( \lambda \nu = c \), where \( c \) is the velocity of light.

- The beginnings of quantum mechanics can be traced back to the empirical expression derived by Max Planck in 1900 to account for the shape of the black-body spectrum. This expression contained a constant \( h \), now called Planck’s constant, and the underlying assumption leading to the expression was that radiation was absorbed and emitted in packets, or “quanta”, whose energy content was given by \( E = h\nu \).

- The “reality” of energy quanta was not established until the explanation for the photoelectric effect was provided by Einstein in 1905. Einstein showed that the observed phenomena could be explained only by invoking the concept of the energy quanta.

- In 1913, Neils Bohr offered the idea of “quantization” as the basis for the stability of the nuclear model of the Hydrogen atom. The nuclear model, in which the positive charge of the atom is assumed to reside in an extremely small “nucleus,” was required to explain the experimental observations made by Rutherford in 1911.

- Bohr’s model assumed that the angular momentum \( L \) (given by mass \( \times \) linear velocity \( \times \) orbital radius = \( mur \)) of the single electron in the atom is quantized:

\[ L = mur = nh; \quad n = 1, 2, \ldots \]  

(11.39)

where \( h = h/(2\pi) \) and \( n \) is called the principal quantum number.

- Based on Bohr’s analysis (see Section 11.2), the following results were obtained:
The orbital radius is related to the principal quantum number in terms of the permittivity of vacuum, \( \varepsilon_0 \), the rest mass of the electron \( m_e \), the unit of electric charge \( e \), and the atomic number \( Z \), as
\[
r = \frac{n^2}{Z} \left( \frac{\hbar^2 \varepsilon_0}{\pi m_e e^2} \right) = \frac{n^2}{Z} a_0,
\]
where the definition of \( a_0 \), the Bohr radius, is obvious.

The total energy of the electron in the atom is given by
\[
E = -\frac{Z^2 e^2}{8 \pi \varepsilon_0 a_0} \times \frac{1}{n^2}.
\]
(11.49)

The energy difference between two energy levels can be calculated using Eq. (11.49) and can be used to account for the observed lines in the hydrogen emission spectrum. In fact, Bohr was able to provide the explanation for the fact that atomic spectra consisted of discrete lines and also to predict the existence of various other sets of lines that were subsequently observed.

An “explanation” for why only the quantized orbits were possible for the electron was provided by de Broglie, who extended the wave property of radiation to matter, starting from the equation \( E = p \lambda \nu \), where \( p \) is the photon momentum. Since \( E = h \nu \), we get \( \lambda = h/p \) for radiation. By extension, for a material particle of rest mass \( m \),
\[
\lambda = \frac{h}{mu}.
\]

By requiring the circumference of each allowed orbit to accommodate an integral number of wavelengths \( (2\pi r = n\lambda) \), de Broglie showed that stable, standing waves would result. Non-integral number of wavelengths would lead to destructive interference of the waves and thus the non-existence of that orbit. Moreover, de Broglie’s suggestion automatically leads to the Bohr quantization condition for the angular momentum.

Unfortunately, Heisenberg soon showed that it was impossible, even in principle, to obtain measurements with sufficient accuracy to verify the existence of Bohr’s orbits because of the Uncertainty Principle (see Section 11.3). As a result, the “old quantum theory” had to be abandoned and a new theory constructed to take its place. This was primarily the work of Erwin Schrödinger. This “new” theory will be the basis of our discussions for the rest of this course.
11.4. The Schrödinger Equation

The Schrödinger equation is a second order differential equation whose solutions describe the behavior of the quantum system we are interested in. The physical parameters of the system are incorporated into the equation in the form of the mass(es) of the particle(s), the potential energy function, and the boundary conditions imposed on the solutions.

A hand-waving type of “derivation” of the Schrödinger equation for a “free” particle can be done starting with the classical wave equation (in one dimension, for simplicity):

\[
\frac{\partial^2 y}{\partial t^2} = \frac{1}{c^2} \frac{\partial^2 y}{\partial x^2},
\]

where \( y(x,t) \) is the displacement from the origin, \( x \) is the coordinate, \( t \) is the time, and \( c \) is the velocity of light. We now do the following:

- Replace \( y(x,t) \) with \( \Psi(x,t) \), and assume that \( \Psi(x,t) \) has the form
  \[
  \Psi(x,t) = C \exp\left[ 2\pi i \left( \frac{x}{\lambda} - vt \right) \right].
  \]
  \((11.67-69)\)

- Based on the de Broglie hypothesis, we set \( \lambda = \hbar/mu = \hbar/p_x \), and based on the quantum hypothesis, we set \( \nu = E/\hbar \). Substituting above, we get
  \[
  \Psi(x,t) = C \exp\left[ i \left( xp_x - Et \right) \right],
  \]
  where we have used the definition \( \hbar = h/2\pi \).

- Differentiating \( \Psi(x,t) \) with respect to \( t \), we get
  \[
  \frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E \Psi = -\frac{i}{\hbar} E \Psi(x,t),
  \]
  \((11.73)\)
  which can be re-written as
  \[
  -\frac{\hbar}{i} \frac{\partial \Psi}{\partial \hat{\sigma}} = E \Psi.
  \]
  \((11.74)\)

- Differentiating \( \Psi(x,t) \) with respect to \( x \), we get
  \[
  \frac{\partial \Psi}{\partial x} = i \frac{\hbar}{p_x} \Psi.
  \]
  \((11.77)\)

- Differentiating once again with respect to \( x \), we get (note that \( \hat{i}^2 = -1 \))
  \[
  \frac{\partial^2 \Psi}{\partial x^2} = -\left( \frac{p_x}{\hbar} \right)^2 \Psi.
  \]
Since we are dealing with a “free” particle, i.e., a particle not influenced by any fields or forces, all of the energy is in the form of kinetic energy. In other words, \( E = E_k = p_x^2/2m \). Therefore, \( p_x^2 = 2mE_k \). The equation above is, therefore, equivalent to

\[
\frac{\hat{\partial}^2 \Psi}{\partial x^2} = -\frac{2mE_k}{\hbar^2} \Psi, \quad \text{or} \quad \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = E_k \Psi
\]

From Eq. (11.74) above, therefore, we can write

\[
\frac{-\hbar}{i} \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2},
\]

which is the Schrödinger equation for a free particle. If the particle is moving under the influence of a potential energy function \( E_p(x,t) \), the equation becomes

\[
\frac{-\hbar}{i} \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + E_p(x,t) \Psi(x,t).
\]

(11.80)

For the special case where the potential energy function is independent of time, i.e., \( E_p(x,t) = E_p(x) \), we can write

\[
\frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + E_p(x) \psi(x) = E \psi(x),
\]

(11.85)

where we have used the notation \( \Psi(x,t) = \psi(x) \exp(-iEt/\hbar) \).

We now make several extremely important points:

- Eqs. (11.74), (11.77) and the one that follows it above, are of the form \( \hat{A} \Psi = a \Psi \), where the \( \hat{A} \) with a “hat” on it is an operator that operates on the function \( \Psi(x,t) \):
  \( \hat{A} = \frac{-\hbar}{i} \frac{\partial}{\partial t} \) or \( \frac{\partial}{\partial x} \), etc., and \( a \) is a constant. When an operator and a function satisfy an equation of this type, the function is called an eigenfunction of the operator and the constant is called an eigenvalue.

- The operator \( \frac{-\hbar}{i} \frac{\partial}{\partial t} \) acting on the solution to the Schrödinger equation yields the total energy of the system. Therefore, this is the “energy” operator.

- Similarly, the operator \( \frac{\hbar}{i} \frac{\partial}{\partial x} \) is the momentum operator \( \hat{\rho} \) and \( \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \) is the kinetic energy operator.
• The Schrödinger equation (11.85), thus, amounts to the statement that the kinetic energy operator and the potential energy operator acting on the solution $\psi(x)$ yields the total energy times $\psi(x)$.

• This can be stated more succinctly in an operator form by defining the “Hamiltonian” operator (in one dimension) as

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + E_p(x),$$

so that Eq. (11.85) can be written as

$$\hat{H}\psi(x) = E\psi(x). \quad (11.86)$$

• In other words, solutions of the Schrödinger equation are eigenfunctions of the Hamiltonian operator, and the eigenvalue is the total energy of the system.

• The solutions of the Schrödinger equation are also called wave functions. Not all solutions of the Schrodinger equation are “acceptable” wave functions. An acceptable wave function should (a) be continuous, (b) have a continuous first derivative, (c) have a non-vanishing second derivative, and (d) be “square integrable,” i.e.,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} \psi(x)^*\psi(x) dx < \infty,$$

where $\psi^*(x)$ is the complex conjugate of $\psi(x)$, obtained by substituting $-i$ in the place of $i$ in $\psi(x)$.

• An interpretation of the wave function was given by Max Born in 1926. For a one-dimensional system, the magnitude $|\psi(x)|^2 dx$ gives the probability of finding the system in the element $(x, x+dx)$. The probability of finding the system somewhere (anywhere) in space is then given by the integral of this quantity over all space:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} \psi(x)^*\psi(x) dx = 1. \quad (11.89)$$

• The integral is required to be equal to unity because we are certain to find the system somewhere in space if it exists. This requirement, that the integral in (11.89) be equal to unity, is called the normalization condition. So, a proper wave function must be an eigenfunction of the Hamiltonian operator and satisfy the normalization condition.

11.5: Refer to handout “Introduction to Quantum Mechanics.”
11.6. Quantum Mechanics of Simple Systems

The Free Particle

Consider a particle of mass $m$ moving in one dimension without any constraining potentials acting on it, i.e., $E_p(x) = 0$. The Schrödinger equation for this particle is

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi(x). \tag{11.124}
\]

So, the solution is an eigenfunction of the kinetic energy operator. Possible candidates are

\[
\begin{align*}
\psi(x) &= A \sin(kx) \\
\psi(x) &= B \cos(kx) \quad \text{where } A, B, C, D \text{ and } k \text{ are constants.} \\
\psi(x) &= Ce^{\pm ikx} \\
\psi(x) &= De^{\pm ikx}
\end{align*}
\]

Each of these functions will satisfy the Schrödinger equation but only the first three will remain finite as $x \to \pm \infty$. In other words, only the first three are “square integrable,” in the sense that

\[
\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx < \infty.
\]

Substituting any of these functions into the Schrödinger equation yields the energy of the particle as

\[
E = \frac{\hbar^2 k^2}{2m} \quad \text{or} \quad k = \sqrt{2mE / \hbar}
\]

From the definition of kinetic energy [recall that $E_p(x) = 0$], we get

\[
\frac{p_x^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \text{or} \quad p_x = \pm \hbar k = \pm \sqrt{2mE}. \tag{11.134}
\]

Note that the energy $E$ and, therefore, the momentum, can take on any value in this case. Therefore, unlike the case of the Bohr model of the hydrogen atom, the energy levels are not quantized. We will see below that the quantization of energy levels, whereby the system is allowed to exist only at certain discrete energies, is a consequence of being “bound” or confined to a region of space by a potential energy function.
Particle on a Line

Consider a particle confined to a finite region of space, say \(0 \leq x \leq a\). We will assume that \(E_p(x) = 0\) within this line segment but \(E_p(x) = \infty\) outside of it. Therefore, in the region \(0 \leq x \leq a\), the Schrödinger equation for this system is identical to that of the free particle. So, the three candidate eigenfunctions identified above are solutions to the Schrödinger equation for this system also, as long as we stay within the \((0,a)\) interval.

**Boundary Conditions:**

Since the particle will require infinite energy to leave the line segment, it goes without saying that \(|\psi(x)|^2 = 0\) outside this line segment. The requirement that wave functions be continuous then leads to the requirement that \(\psi(0) = \psi(a) = 0\). These *boundary conditions* were not present for the “free particle” case where the particle was free to move from one end of the Universe to the other.

**Quantization:**

Now, examining the three eigenfunctions of the kinetic energy operator from above, we see that only the first one, \(\psi(x) = A \sin(kx)\), will satisfy the condition \(\psi(0) = 0\). In order for this function to also satisfy the condition \(\psi(a) = 0\) for arbitrary values of \(a\), it is necessary to require that \(k = n\pi/a\), where \(n = 1, 2, 3, ...\) so that

\[
\psi(x) = A \sin\left(\frac{n\pi}{a} x\right).
\]

Substituting this definition of \(k\) into the energy expression above, we get

\[
E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2 = \frac{n^2 \hbar^2}{8ma^2}; n = 1, 2, 3...
\]

(11.145)

where we have explicitly indicated the dependence of the energy on the integer \(n\). It is obvious that only certain values of \(k\) corresponding to integer values of \(n\) can satisfy the boundary conditions of the problem. This leads to the *quantization* of energy, i.e., the phenomenon by which the energy of a system can only take on certain discrete values. It is extremely important to note and remember that quantization of energy arises from *boundary conditions imposed on the wave function* and that boundary conditions are present only when particles are “bound” or confined to a finite portion of space. In the case of the free particle, by contrast, \(k\) and therefore the energy could take on any value.
Normalization:

The solution given above still has an undefined constant $A$. This constant is defined by normalizing the wave function; in other words, we require that
\[
\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = |A|^2 \int_{0}^{a} \sin^2 \left( \frac{n\pi}{a}x \right) \, dx = 1,
\]
which leads to
\[
|A|^2 \left( \frac{a}{2} \right) = 1 \quad \text{or} \quad A = \pm \sqrt{\frac{2}{a}}.
\]

We therefore write the complete solution to the particle on a line problem as
\[
\psi(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a}x \right).
\]

Orthogonality:

Another important property of a wave function is orthogonality. This means that
\[
\left( \frac{2}{a} \right) \int_{0}^{a} \sin \left( \frac{m\pi}{a}x \right) \sin \left( \frac{n\pi}{a}x \right) \, dx = \begin{cases} 
0 & \text{if } m \neq n \\
1 & \text{if } m = n
\end{cases}.
\]

This is a general property of all acceptable solutions to any Hamiltonian operator. Since the first equality above signifies orthogonality and the second equality is just the normalization condition, we say that acceptable solutions are orthonormal.

Potential “well” of finite depth

Consider the particle on a line problem with the following modification: at $x = 0$ and $x = a$, the potential goes to a finite ($< \infty$) value, say, $V$. Now, the Schrödinger equation in the regions $x < 0$ and $x > a$ is written as
\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi(x) = E\psi(x), \quad \text{or} \quad \frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} (V - E)\psi(x).
\]

Since $V$ is a constant, a possible solution to this equation is $\psi(x) = B \exp(-\kappa|x|)$, where $\kappa = \sqrt{2m(V - E)}/\hbar$. The absolute value of the variable $x$ is taken to ensure that the solution exponentially decays as $|x|$ increases, so that the solution remains “acceptable.” The solution within the interval $0 \leq x \leq a$ now does not have to go to zero at $x = 0$ and $x = a$ but, rather, have to smoothly join the solution above for the regions $x < 0$ and $x > a$. Qualitatively, this leads to a solution which oscillates like a wave in the interval $0 \leq x \leq a$ and exponentially decays to zero outside it.
The Harmonic Oscillator

The harmonic oscillator is the model for a “perfect” spring connecting two masses which, like the “ideal” gas, is a nonexistent entity. The Schrödinger equation for the oscillator is written as

\[ \mathcal{H}\psi(x) = -\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi(x) = E \psi(x), \]  

(11.152)

where \( x \) is the “displacement” \( r - r_e \) from the equilibrium length \( r_e \) of the spring and \( \mu \) is the reduced mass. At any given total energy \( E \), the system’s energy is divided between the kinetic energy \( E_k(x) \) and potential energy \( E_p(x) \).

The classical picture that we obtain for the behavior of the harmonic oscillator is as follows. During the vibrations of the spring, the spring extends outwards or compresses inwards from its equilibrium length until \( E = E_p(x) \), which occurs when \( E = \frac{1}{2} k x^2 \). The values of \( x \) for which this occurs are called the classical turning points, because the spring reverses itself at these points and starts to travel in the opposite direction. Let us denote these points by \( \pm a = (2E/k)^{1/2} \).

Classically, the spring cannot access the regions \( x < -a \) or \( x > a \). Therefore, we call these the classically forbidden regions. Quantum mechanically, however, these regions are very similar to the \( x < 0 \) and \( x > a \) regions just discussed for the finite potential well problem. In these regions, \( E < E_p(x) \) and, therefore, we expect the solution to exhibit exponentially decaying behavior whereas in the interval \(-a \leq x \leq a\), we expect wave-like oscillatory behavior. Acceptable solutions of the harmonic oscillator problem behave exactly in this fashion as can be verified from Fig. 11.12 of the textbook. The major difference between these and the solutions of the particle on a line bounded by infinite potentials is that the harmonic oscillator solutions have non-zero amplitude in the classically forbidden [i.e., \( E < E_p(x) \)] regions. Therefore, there is a non-zero probability that the system described by the harmonic oscillator can access these regions.

The quantized energy levels corresponding to the acceptable solutions of the harmonic oscillator problem are given by

\[ E_n = \left(n + \frac{1}{2}\right) \hbar \nu_0, \text{ where } n = 0, 1, 2, \ldots \text{ and} \]

\[ \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k \hbar}{m}}. \]

The quantity \( \nu_0 \) is called the harmonic frequency of the oscillator.

It is very important to note that the lowest possible energy of the quantum oscillator is not zero, but rather \( \frac{1}{2} \hbar \nu_0 \), which is called the zero point energy of the oscillator. The solutions of the Schrödinger equations for this case is written as

\[ \psi_n(x) = C_n H_n(x)e^{-\alpha x^2}, \]

where \( C_n \) is the normalization constant, \( H_n(x) \) are a class of orthogonal polynomials called Hermite polynomials, and \( \alpha \) is a constant that can be expressed as a function of the other constants in the problem.
Particle in a box

The three dimensional “box” problem satisfies the Schrödinger equation

\[ -\frac{\hbar^2}{2\mu} \nabla^2 \psi(x, y, z) = E\psi(x, y, z), \]

for \(0 \leq x \leq a, 0 \leq y \leq b,\) and \(0 \leq z \leq c.\) The solution is exactly zero beyond these limits, i.e., outside the “box.” By a technique known as separation of variables (to be discussed in class), it can be shown that the solution to this equation is

\[ \psi_{n_x,n_y,n_z}(x, y, z) = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x\pi}{a} x\right) \sin\left(\frac{n_y\pi}{b} y\right) \sin\left(\frac{n_z\pi}{c} z\right), \]

corresponding to the energy

\[ E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \frac{\hbar^2}{8m}. \]

with \(n_x, n_y, n_z = 1, 2, 3,\ldots\) If the box is a cube, i.e., \(a = b = c,\) we get

\[ \psi_{n_x,n_y,n_z}(x, y, z) = \left(\frac{8}{a}\right)^{3/2} \sin\left(\frac{n_x\pi}{a} x\right) \sin\left(\frac{n_y\pi}{a} y\right) \sin\left(\frac{n_z\pi}{a} z\right) \]
\[ E_{n_x,n_y,n_z} = (n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2}{8ma^2}. \]

In this case, it is easy to see that the same combination of quantum numbers can give rise to the same energy. For example, \((n_x, n_y, n_z) = (2, 1, 1)\) and \((1, 2, 1),\) and \((1, 1, 2)\) all give rise to the same energy of \(6\hbar^2/8ma^2.\) However, these are three different states corresponding to three different types of motion of the particle within the box. If the same energy level accommodates multiple states, that energy level is said to be degenerate. The number of states at the energy level is called the degeneracy of the energy level. In the above example, we say that the degeneracy of the energy level is three, or that the energy level is triply degenerate. Note that degeneracy is a property of an energy level, not a quantum state.
11.9-10. Particle on a ring, particle on a sphere, and angular momentum

Let us consider the quantum mechanics of a particle of mass $\mu$ constrained to move on the surface of a sphere of fixed radius $r$. The potential energy of the particle is taken to be zero, i.e. $E_p = 0$. Since the motion is three-dimensional, the Schrödinger equation is written as (see Eqs. 11.81 and 11.85)

$$\hat{H}\psi(x, y, z) = -\frac{\hbar^2}{2\mu} \nabla^2 \psi(x, y, z) = E\psi(x, y, z).$$

Because of the nature of the system, this equation is far simpler to solve if we transform the coordinates to spherical polar coordinates, which are shown and defined in Fig. 11.13. In spherical polar coordinates, the above equation becomes

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

Now, since $r$ is held constant (radius of the sphere), the first term drops out and we are left with the second and third term, and a solution that depends on the angles $\theta$ and $\phi$. After considering a couple of related issues, we will return to this equation and its solution.

Angular momentum of the particle moving on the sphere is a vector quantity defined as the cross-product of the position vector $\mathbf{r}$ pointing to the particle from the origin of the sphere, and the linear momentum vector $\mathbf{p}$ which lies in a plane tangential to the surface of the sphere at the end of $\mathbf{r}$:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix}
\hat{i} & \hat{j} & \hat{k} \\
x & y & z \\
p_x & p_y & p_z
\end{vmatrix},$$

where the first row of the determinant contains the unit vectors in the $x$, $y$, and $z$ directions respectively. The angular momentum vector points in the direction perpendicular to the plane defined by the vectors $\mathbf{r}$ and $\mathbf{p}$. If the rotation is counterclockwise, our convention is to assume that $\mathbf{L}$ points “up” along the positive $Z$ axis and that it points “down” if the rotation is clockwise (see Fig. 11.17).

Now consider a “molecule” made up of two atoms of masses $m_1$ and $m_2$ separated by a distance $r$, rotating about the center of mass which is located at a distance $r_1$ from $m_1$ and $r_2$ from $m_2$. It can be shown (homework assignment # 5) that the moment of inertia of such a system can be expressed as

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r^2,$$

which describes the rotation of a particle of mass $\mu$ at a distance $r$ from the axis of rotation. In rotational motion, angular momentum plays the role of linear momentum in linear motion and the moment of inertia plays the role of mass. Therefore, since the kinetic energy of a particle moving along a line is defined by $E_k = p^2/2m$, we deduce that the kinetic energy of the rotating particle can be written as

$$E_k = \frac{L^2}{2I}.$$
To obtain a quantum mechanical operator for the kinetic energy of the rotating molecule, let us first consider the components of the angular momentum vector. These can be identified by expanding the determinant:

\[
L = i(y_p z - z p_y) - j(x_p z - z p_x) + k(x_p y - y p_x)
\]

so that

\[
L^2 = L_x^2 + L_y^2 + L_z^2.
\]

The quantum mechanical operators corresponding to \(L^2\) and its components can now be derived by replacing the momentum components above with the respective momentum operators (see for example, Eq. 11.193). If we further replace the cartesian components with their spherical polar counterparts, we see that the operators corresponding to \(L^2\) and its \(Z\)-component, \(L_z\), are particularly simple in form:

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

(11.194 & 196)

\[
\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}.
\]

The reason for the simple form for \(L_z\) is due to our decision to define the angle \(\phi\) in the \(XY\) plane so that a variation in \(\phi\) represents rotation about the \(Z\)-axis (see Fig. 11.13; p. 516).

Let us now consider two simple cases: (a) particle on a ring, where the ring lies in the \(XY\) plane, and (b) particle on a sphere.

**Particle on a ring:**

Since the motion is confined to the \(XY\) plane (rotation about the \(Z\) axis, \(\theta = \pi/2\)), the Schrödinger equation is simply

\[
\hat{H} \Phi(\phi) = \frac{\hat{L}^2}{2I} \Phi = -\hbar^2 \frac{\partial^2 \Phi}{\partial \phi^2} = E \Phi(\phi),
\]

where, in keeping with convention, we have chosen to represent the solution using the upper case Greek letter \(\Phi\). It is important to note and understand the difference between the solution \(\Phi\), and the angle \(\phi\). The boundary condition to be imposed on the solution is that the solution must be continuous, i.e., \(\Phi(0) = \Phi(2\pi)\). Such a solution is given by

\[
\Phi(\phi) = B \exp(i m \phi), \text{where } m = 0, \pm 1, \pm 2, \pm 3, \ldots.
\]

The normalization of the solution yields

\[
|B|^2 \int_0^{2\pi} e^{-i m \phi} e^{i m \phi} d\phi = 1, \text{ or } B = \frac{1}{\sqrt{2\pi}}.
\]

The allowed energies of such a particle, of course, are \(E_m = m^2 \hbar^2/(2I)\) with \(m = 0, \pm 1, \pm 2, \ldots\)
Particle on a sphere:

The Schrödinger equation is written as

\[
-\frac{\hbar^2}{2I} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] Y(\theta, \phi) = E Y(\theta, \phi),
\]

where, once again, we have followed convention and expressed the solution as \( Y \). We attempt a separation of variables by defining \( Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \), where \( \Phi(\phi) = e^{im\phi} \sqrt{2\pi} \). After some manipulations, we obtain the following equation

\[
-\frac{h^2}{2I} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{m^2}{\sin^2 \theta} \Theta \right] = E \Theta,
\]

with the boundary condition that \( \Theta(0) = \pm \Theta(\pi) \). Note that the solutions depend on \(|m|\). The solutions turn out to be a class of polynomials called associated Legendre polynomials, commonly denoted as \( P_l^m(\cos \theta) \), and the energy eigenvalues are given by

\[
E_l = l(l+1) \frac{\hbar^2}{2I}; \quad l = 0, 1, 2, \ldots
\]

However, for the polynomials \( P_l^m(\cos \theta) \) to satisfy the boundary conditions \( \Theta(0) = \pm \Theta(\pi) \), \( m \) can only have values \( m = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l \). Higher values of \( m \) for a given \( l \) value lead to solutions that have discontinuities and hence cannot be accepted. The normalized solutions to the particle on a sphere problem, \( Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \), are called spherical harmonics, and are written as

\[
Y_l^m(\theta, \phi) = C_{lm} P_l^m(\cos \theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}.
\]

A few normalized associated Legendre polynomials for specified values of \( m \) are presented in Table 11.3 on page 520.

The energy of the particle on the sphere depends only on the \( l \) quantum number. However, there are \((2l+1)\) states, corresponding to different values of \( m \), for each value of \( l \). Therefore, each energy level has a degeneracy of \((2l+1)\).

In order to understand the nature of the wave functions for the hydrogen atom, it is very important to understand the nature of the spherical harmonics. So, we will spend some time in class analyzing their shapes, orientations, and their nodal structure. This material, unfortunately, is not given in the textbook.
Space Quantization:

We have seen how the application of boundary conditions for “bound” systems can lead to the quantization of energy levels. We now examine the unique case of the angular momentum of a quantum mechanical system which shows that under an applied field, only certain orientations of the angular momentum vector (or certain planes of rotation for the rotating/orbiting body) are allowed. This results in a quantization of space!

To see how this result comes about, we start with Fig. 11.17 (p. 529). Note that the vector $\mathbf{L}$ is perpendicular to the plane of rotation. Its length is given by $|\mathbf{L}| = \sqrt{\mathbf{L} \cdot \mathbf{L}} = \sqrt{L^2}$, which, in the quantum mechanical case, is given by

$$|\mathbf{L}| = \sqrt{\langle L^2 \rangle} \sqrt{l(l+1)} \hbar.$$ 

The Z-component of the vector is given by $\langle L_z \rangle = mh$.

Now, in the absence of an applied field, any direction in space is no different from any other and so it does not make sense to talk about a “Z-component.” However, if a magnetic or electric field is applied, the field direction is taken to be the Z-axis. In such a case, the angular momentum vector can only exist in various states specified by the $(l,m)$ quantum numbers, as in Fig. 11.18; p. 532.
11.7. The Central Force Problem: Hydrogenic Atoms

The potential energy function in the case of the Hydrogen-like atom is determined by the laws of electrostatics. For two charges \(Ze\) (the nucleus with \(Z\) protons) and \(-e\) (the electron) separated by a distance \(r\), the potential energy is given by

\[
E_p(r) = \frac{(Ze)(-e)}{4\pi\varepsilon_0 r} = \frac{-Ze^2}{4\pi\varepsilon_0 r}
\]

where \(\varepsilon_0\) is the permittivity of vacuum, and the \(4\pi\varepsilon_0\) factor is needed to enforce SI units (see the inside of the back cover of the textbook for the units).

Strictly speaking, in the Schrödinger equation for this two particle problem (nucleus and the electron), we should use the reduced mass \(\mu = \frac{m_H m_e}{m_H + m_e}\) but, since the mass of the nucleus is much larger than that of the electron, \(\mu \approx m_e\). Therefore, we write the Schrödinger equation as

\[
-\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2m_e r^2} R(r) - \frac{Ze^2}{(4\pi\varepsilon_0 r)} \psi = E \psi.
\]

Since the only part that depends on the angles \(\theta\) and \(\phi\) is the \(L^2\) operator, the solution has to be of the form

\[
\psi(r, \theta, \phi) = D_{lm} R(r) Y^m(\theta, \phi),
\]

where the \(D_{lm}\) are constants, \(R(r)\) is a radial function to be determined by solving the equation, and the \(Y^m\) are the spherical harmonics we have already seen. Substituting this form for \(\psi(r, \theta, \phi)\) into the Schrödinger equation above and simplifying, we get

\[
-\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2m_e r^2} R(r) - \frac{Ze^2}{(4\pi\varepsilon_0 r)} R(r) = ER(r). \tag{11.167}
\]

Note that the solutions \(R(r)\) will depend on the value of the angular momentum quantum number \(l\). The solutions belong to a class of polynomials known as \textit{associated Laguerre polynomials}. Some of them, including the normalization constants, are tabulated in Table 11.4, p. 521. The proper boundary conditions imposed on these functions, \(R(0) = 0\) and \(\lim_{r \to \infty} R(r) = 0\), give rise to a quantum number \(n\), which can have values \(n = 1, 2, 3, \ldots\). Also, since the solutions depend on \(l\), the value of \(l\) is now limited so that \(l = 0, 1, 2, \ldots, (n-1)\). The complete solutions of the hydrogen atom problem are thus

\[
\psi_{nlm}(r, \theta, \phi) = N_{nl} R_{nl}(r) Y^m_l(\theta, \phi);
\]

\[
E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0} \times \frac{1}{n^2}.
\]

\(n = 0, 1, 2, \ldots, \infty\)

\(l = 0, 1, 2, \ldots, (n-1)\)

\(m = 0, \pm 1, \pm 2, \ldots, \pm l\).

Note that the energy levels depend only on \(n\). Here, \(n\) is called the \textbf{principal} quantum number, \(l\) is the \textbf{angular momentum} quantum number, and \(m\) is called the \textbf{magnetic} quantum number.

The solutions for a given set of \((n,l,m)\) quantum numbers are called \textbf{atomic orbitals}.
11.8. Physical Significance of the Orbital Quantum Numbers

It is customary to associate letter symbols to various values of $l$ as in

<table>
<thead>
<tr>
<th>Value of $l$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Letter symbol</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
</tr>
</tbody>
</table>

so that we would refer to the orbitals with $n = 1$, $l = 0$ as the 1s, that with $n = 3$, $l = 1$ as the 3p and so on.

The probability of finding the electron in the ground state of a hydrogen atom in a small element of space defined by $[(r, r + dr); (\theta, \theta + d\theta)$, and $(\phi + d\phi)]$ is given by

$$\int |\psi_{1s}(r, \theta, \phi)|^2 r^2 dr \sin \theta d\theta d\phi = \int |\psi_{1s}(r)|^2 r^2 dr \sin \theta d\theta d\phi$$

(Note that $dxdydz = r^2 dr \sin \theta d\theta d\phi$). In the second equality above, we explicitly take into account the fact that the 1s wave function does not depend on the angles (see Table 11.5; p. 522). Let us now integrate this function over the angles to obtain the probability as a function of the distance from the nucleus:

$$\int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^r \psi_{1s}(r) |^2 r^2 dr = 4\pi r^2 \int_0^r \psi_{1s}(r) |^2 dr = P_{1s}(r) dr.$$ 

This quantity is called the **radial probability distribution function** [denoted by $P_{nl}(r)$] and gives the probability of finding the electron in a spherical shell of radius $r$ and thickness $dr$. The maximum in a plot of the radial distribution function vs. $r$ is the **most probable distance** of the electron. For the ground state of the hydrogen atom, that value happens to be exactly equal to the Bohr radius, $a_0$ (verify this!).

The average distance of the 1s electron from the nucleus is given by the expectation value

$$\langle r_{1s} \rangle = 4\pi \int_0^\infty \psi_{1s}^*(r) \psi_{1s}(r) r^2 dr$$

$$= \int_0^\infty r P_{1s}(r) dr$$

$$= \frac{3}{2} a_0.$$ 

A more general result is

$$\langle r_{nl} \rangle = \int_0^\infty r P_{nl}(r) dr$$

$$= \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{l(l+1)}{n^2} \right] \right\}.$$ 

which leads to the conclusion that the excited state electrons, on average, are further away from the nucleus.
Nodal structure:
The number of angular nodes in a given wave function is the same as the number of angular nodes in the corresponding spherical harmonic, i.e., equal to $l$. Therefore, an $s$ orbital will have no angular nodes, a $p$ orbital will have 1 and a $d$ orbital will have 2, regardless of the value of $n$. The number of radial nodes is given by $n - l - 1$. So, a $1s$ orbital ($n = 1$, $l = 0$) will have no radial nodes, a $2s$ orbital will have 1 and a $3s$ orbital will have 2 radial nodes. By the same token, a $2p$ and a $3d$ orbital will have no radial nodes but a $3p$ and a $4d$ orbital will each have one radial node.

Magnetic Moment:
The electron in an atomic orbital $\psi_{nlm}$ responds to magnetic fields because the orbiting electron generates its own magnetic field. The magnetic dipole moment of an orbiting electron is related to its orbital angular momentum. For a directional magnetic field, the field direction is generally taken to be the $Z$-direction. The operator that describes the interaction of a one-electron atom with a magnetic field is $\hat{\mu}_z B = -\frac{eB}{2m_e} \hat{L}_z$, where $B$ is the magnetic flux density. [Strictly speaking, we should write this as a dot product of two vectors, $\mu \cdot B$, where $\mu$ has Cartesian components $\mu_x$, $\mu_y$, $\mu_z$.] Therefore, the Schrödinger equation for a hydrogen atom subject to a magnetic field is

\[
(\hat{H} + \hat{\mu}_z B)\psi_{nlm} = (\hat{H} + \hat{\mu}_z B)N_{nl}R_{nl}(r)Y_l^m(\theta, \phi) = E_n\psi_{nlm} + N_{nl}R_{nl}(r)\left(-\frac{eB}{2m_e} \hat{L}_z\right) Y_l^m(\theta, \phi) = \left(E_n - \frac{eh}{2m_e}Bm\right)\psi_{nlm}.
\]

Therefore, the energy of the orbital depends on the magnetic quantum number $m$. The quantity $(eh / 2m_e)$ is known as the Bohr magneton.

11.11. Spin quantum numbers
Experiments with high magnetic fields revealed the existence of another type of magnetic moment in the electron. Goudsmit and Uhlenbeck proposed in 1925 that an electron has an intrinsic angular momentum $S$ (called the “spin” angular momentum) and an accompanying magnetic moment $\mu_s$. They further proposed that

(a) the length of the vector $S$ is $|S| = [s(s+1)]^{1/2}\hbar$, where $s \equiv \frac{1}{2}$ [therefore, $|S| = (\sqrt{3}/2)\hbar$], and

(b) the $Z$-component $S_z$ of this “spin” angular momentum is $m_s\hbar$; $m_s = \pm\frac{1}{2}$.

Therefore, the complete specification of the state of an electron in an atom requires that four quantum numbers, $n$, $l$, $m$ and $m_s$, be specified. The wave function labeled by these four quantum numbers corresponds to a specific spin state of the electron and is called a spin orbital.

11.12. Many electron Atoms (Reading assignment)
11.3. Approximate methods

It is very hard, if not impossible, to directly solve the Schrödinger equation for most systems of chemical interest. Therefore, methods for obtaining approximate solutions are very valuable. Most of the quantum mechanical calculations for atoms and molecules are done in what are known as **atomic units** (au):

- **Energy**: 
  \[ 1 \text{ Hartree} = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.36 \times 10^{-18} \text{ J} = 27.2114 \text{ eV} \]
- **Length**: 
  \[ 1 \text{ Bohr} = a_0 = 5.29177 \times 10^{-11} \text{ m} \]
- **Mass**: 
  \[ 1 m_e = 9.109 \times 10^{-31} \text{ kg} \]
- **Time**: 
  \[ 1 \text{ au} = 2.42 \times 10^{-17} \text{ s} \]

In these units, \( \hbar = 1 \text{ Hartree au.} \) Therefore, the ground state energy of the hydrogen atom in atomic units is given by

\[ E_1 = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0} \times \frac{1}{1^2} = -\frac{1}{2} \text{ Hartree.} \]

This means that if we supplied \( \frac{1}{2} \) Hartree energy to the electron, it would become a “free particle,” leaving behind a proton. Therefore, the **ionization potential** for hydrogen is \( \frac{1}{2} \) Hartree.

If we calculate the energy of the \( 2s \) electron in the lithium atom, using \( Z = 3 \) and \( n = 2 \) above, we get

\[ E_2 = -\frac{9}{2} \times \frac{1}{4} = -1.125 \text{ Hartree} \]

The experimental value is \(-0.198 \) Hartree, an error of 468%! Clearly, neglecting the presence of the 2 electrons in the \( 1s \) orbital is a very bad assumption. We can deduce that one of the effects of the \( 1s \) electrons is to alter the effective nuclear charge experienced by the \( 2s \) electron.

Therefore, let us write

\[ E_2 = -\frac{Z_{\text{eff}}^2 e^2}{2} \times \frac{1}{2^2} = -0.198 \text{ Hartree,} \]

which gives us the effective nuclear charge \( Z_{\text{eff}} = 1.26 \). The wave function corresponding to the \( 2s \) electron may (approximately, since we are neglecting the presence of the other two!) be written as

\[ \psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z_{\text{eff}}}{a_0} \right)^{3/2} (2 - \frac{Z_{\text{eff}}r}{a_0}) e^{-Z_{\text{eff}}r/a_0}. \]

One way to think about this is that \( Z_{\text{eff}} \) is an adjustable parameter in the approximate wave function (or trial function). Finding the “best” value of this parameter will yield the “best” energy for the system.

The **Variation Method** is a systematic way of finding the best value of the parameters in a trial function.
The Variation Method

The basic idea in the variational method is to

(a) calculate the energy functional using the trial function $\varphi$,

(b) minimize the energy function with respect to the adjustable parameters,

(c) get the optimum value of the parameters,

(d) calculate the “best” energy using the optimum value of the parameters.

The energy functional is simply

$$ W = \frac{\int \varphi^* \hat{H} \varphi \, dt}{\int \varphi^* \varphi \, dt}, $$

where the denominator is unity if $\varphi$ is already normalized. An example of the application of this strategy is problem 11.47:

The trial function $\varphi = \frac{1}{\sqrt{\pi}} \left( \frac{Z_{\text{eff}}}{a_0} \right)^{3/2} e^{-Z_{\text{eff}} a_0}$ when substituted into Eq. (11.223) where the Hamiltonian operator is for the Helium atom, gives

Step (a): $W = \frac{e^2}{a_0} \left( Z_{\text{eff}}^2 - \frac{27}{8} Z_{\text{eff}} \right)$.

Step (b): $\frac{\partial W}{\partial Z_{\text{eff}}} = 0 = \frac{e^2}{a_0} \left( 2Z_{\text{eff}} - \frac{27}{8} \right)$

Step (c): Therefore, $Z_{\text{eff}} = 27/16 = 1.688$.

Step (d): $W = -2.85$ Hartree