A. Background on Wave Equations

- DeBroglie’s hypothesis of a wave-particle duality, brought to bear on the problem of atomic-level mechanics an impressive computational machinery built up in classical physics to treat wave mechanics. Specifically the wave function becomes an important tool in quantum mechanics. Here we review classical wave mechanics with a view to familiarize the reader with the idea of wave functions, eigenfunctions, and eigenvalues.

- In classical mechanics, wave functions are obtained by solving a differential equation. For example, the one-dimensional wave equation for a vibrating string with linear mass $\rho$ (units of kg/m) and tension $T$ (units of force) is

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} - \frac{T}{\rho} \frac{\partial^2 \Psi(x,t)}{\partial t^2} = 0 \quad (3.1)$$

where the wave velocity is given by $c = \sqrt{\frac{T}{\rho}}$. In this problem the wave function $\Psi(x,t)$ quantifies the vertical displacement $x$ of the string at a time $t$.

- It can be shown that any wave function of the form

$$\Psi_n(x,t) = A_n f_n(t) \psi_n(x) = A_n \cos\left(\frac{2\pi n t}{T}\right) \sin\left(\frac{2\pi n x}{\lambda_n}\right) \quad (3.2)$$

is a solution of the wave equation (3.1), where the specific forms for the wave frequency $\nu_n$ and the wavelength $\lambda_n$ are determined by the details of the problem. For example, for a harmonically vibrating string, fixed at $x=0$ and $x=L$ (i.e. $\Psi(0,t) = \Psi(L,t) = 0$). These boundary conditions impose the following requirements on the frequency and wavelength:

$$\nu_n = \frac{nc}{2L} \quad \text{and} \quad \lambda_n = \frac{2L}{n} \quad \text{for } n = 1, 2, 3, \ldots \quad (3.3)$$

The frequencies $\nu_n$ are the harmonic frequencies of the vibrating string. Note $n$ must be an integer to obey the boundary conditions.
• If $\Psi_n(x,t) \ n = 1, 2, 3, \ldots$ individually solve the wave equation, any linear combination of wave functions

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t)$$

(where $c_n$ is a constant) is also a solution to the wave equation. A wave equation that satisfies this property is said to be linear.

• Separation of Variables: The solution in Equation (3.2) to the Wave equation (3.1) is obtained by a process called separation of variables. One assumes the wave function has a special form

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

• When this assumption is used, the wave equation can be decomposed into two equations: one that determines $f(t)$ and one that determines $\psi(x)$. In quantum chemistry, we are mostly interested in the equation for $\psi(x)$ because this function tells us about the spatial distribution of a particle that has wave-like properties.

• A wave function $\psi(x)$ that is independent of time is called a stationary wave. The differential equation for the stationary wave in (3.5) is

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \alpha \psi(x) = 0$$

(3.6)

where $\alpha$ is a constant. If the boundary conditions are $\psi(0) = \psi(L) = 0$ any function of the form

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

(3.7)

is a solution if $\alpha_n = \left( \frac{n \pi}{L} \right)^2$. Any linear combination of functions of the form (3.7) is also a solution.

**B. Schroedinger’s Equation: The Quantum Mechanical Wave Equation**

• The quantum mechanical wave equation is called Schroedinger’s equation.

• Schroedinger’s wave equation must have the following properties
  o It must obey the quantum properties $\lambda = h/\rho \ \text{or} \ \ p = h k )$ and $E = h\nu$
  o Schroedinger’s equation must be consistent with $E = \frac{p^2}{2m} + V$
  o Schroedinger’s equation must be linear as in (3.4)
  o In general $V$ is a function of $x$ and $t$… i.e. $V(x,t)$. For the case in which $V$ is constant $V_0$, the solution to Schroedinger’s equation is a sinusoidal wave with constant $\nu$ and $\lambda$.

• Combine properties one and two: $E = \frac{p^2}{2m} + V \rightarrow h\nu = h\omega = \frac{h^2 k^2}{2m} + V$
Assume the equation is linear so that $\hbar \omega \Psi(x,t) = \frac{\hbar^2 k^2}{2m} \Psi(x,t) + V \Psi(x,t)$

Assume the case we mentioned $\Psi(x,t) = \cos(kx - \omega t) + i \sin(kx - \omega t)$

Note $i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hbar \omega \Psi(x,t)$ and $-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{\hbar^2 k^2}{2m} \Psi(x,t)$ if $i^2 = -1$

Putting it all together the quantum mechanical wave equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

Assuming that $\Psi(x,t) = f(t) \psi(x)$ the stationary Schroedinger wave equation is

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

C. Postulates of Quantum Mechanics

As a result of de Broglie’s wave-particle hypothesis, physicists realized that particle waves could be obtained using the mathematics of wave equations.

Deriving rigorously the quantum mechanical wave equation is beyond the scope of this course. We chose instead to take an approach similar to that used to introduce thermodynamics in Chemistry 452: a set of postulates are stated without proof that guide our efforts to describe systems with quantized properties. In thermodynamics the postulates are called the laws of thermodynamics. We give here three of the Postulates of Quantum Mechanics that we will use in this course. Other postulates that are less used will be discussed in homework.

Postulate I: Wave Functions

a) Any state of a system of N particles is described as fully as possible by a wave function $\Psi(x_1, x_2, \ldots, x_N, t) = \psi(x_1, x_2, \ldots, x_N) f(t)$. If there is only one particle $\Psi(x, t) = \psi(x)/f(t)$

b) The product $\Psi \Psi^* dx_1 \ldots dx_N$ is the probability that at time t particle 1 is between $x_1$ and $dx_1$, particle 2 is between $x_2$ and $dx_2$, etc. Given a stationary wave function for a single particle, $\psi(x) \psi^*(x) dx$ is the probability of finding the particle between x and $x+dx$.

c) Because $\Psi \Psi^* dx_1 \ldots dx_N$ is a probability we require that $\Psi$ be normalized, i.e.

$$\int_{all \ space} \cdots \int_{all \ space} \Psi \Psi^* dx_1 \ldots dx_N = 1.$$ Again… for a single particle described by a stationary wave function $\psi(x)$:

$$\int_{all \ space} \psi(x) \psi^*(x) dx = 1$$

d) Wave functions for different n must be orthogonal. This means that given two wave functions $\psi_n(x)$ and $\psi_m(x)$ if m and n are not equal then $\int \psi_m^*(x) \psi_n(x) dx = 0$

Postulate II: Observable Properties
a) For every observable property of the system there corresponds a linear operator $\hat{O}$, and the physical properties of the observable can be inferred (i.e. calculated) from the mathematical properties of its operator.

b) A linear operator has the property $\hat{O}\left(\sum_n \psi_n(x)\right) = \sum_n \hat{O}\psi_n(x)$

c) Linear operators that represent observable properties have other properties that we will not discuss extensively. But not only must operators used in quantum chemistry be linear, but they also must be Hermitian. Consequences of this property will be discussed shortly.

c) Rigorously determining which operators represent which physical properties is a mathematically challenging task. So we give guidelines for three important cases:

- **Time t**: Time is the same in classical and quantum mechanical calculations;
- **Spatial coordinates (e.g. x, y, z, r, $\theta$, $\phi$, etc.):** Also the same in classical and quantum mechanical calculations
- **Momentum p in Cartesian coordinates:**

$$p_x = -i\hbar \frac{\partial}{\partial x}; \quad p_y = -i\hbar \frac{\partial}{\partial y}; \quad p_z = -i\hbar \frac{\partial}{\partial z}$$

- **Energy**: Represented by the operator called the Hamiltonian $\hat{H}$.

$$\hat{H} = K(p_x, p_y, p_z) + V(x, y, z)$$

$$= \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(x, y, z) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

Then

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

d) The average value of a observable $\langle \hat{O}\rangle$ that is only dependent on x can be calculated from the stationary wave function: $\langle \hat{O}(x)\rangle = \frac{\int \psi^*(x)\hat{O}\psi(x)dx}{\int \psi^*(x)\psi(x)dx}$

Postulate III: The dependence of the wave function $\Psi(x, t)$ on x and t is obtained by solving the time dependent Schrödinger wave equation:

$$\frac{\hbar}{2\pi} \frac{\partial \Psi(x, y, z, t)}{\partial t} = \hat{H}\Psi(x, y, z, t)$$

a) Using the definition of the Hamiltonian from Postulate II the Schroedinger equation becomes:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x, y, z, t) + V(x, y, z)\Psi(x, y, z, t) = \frac{i\hbar}{2\pi} \frac{\partial \Psi(x, y, z, t)}{\partial t}$$
b) Like the classical wave equation, Schrödinger’s wave equation can be separated into two equations. For example, assume $\Psi(x,t) = \psi(x)f(t)$. Then as before

Schrödinger’s stationary wave equation is

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

(3.8)

Note the wave functions $\psi_n(x)$ that are solutions of this equation are independent of time, and are called stationary or standing particle waves, in analogy to classical standing waves in a vibrating string.

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

(3.9)

where

$$\hat{H} = -\frac{\hbar^2}{8\pi^2m} \frac{\partial^2}{\partial x^2} + V(x)$$

(3.10)

Equation (3.9) is called an eigenvalue problem. The energy $E$ is called an eigenvale and is real, which is a consequence of the Hamiltonian be a Hermitian. Hermitian operators have real eigenvalues. Like the classical wave equation, boundary conditions will impose specific forms on $E$ and the wave function. In general the wave function will have the form

$$\psi(x) = \sum_n c_n \psi_n(x)$$

(3.11)

where $\psi_n(x)$ are called eigenfunctions. The eigenfunctions individually are solutions to Equation (3.9):

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

(3.12)

where $E_n$ is called an eigenvalue.