Quantum Chemistry Supplement

Part I: Before Schrödinger:
A few years ago, Macintosh ran some ads on TV that said ‘Think Different’. This is what we will ask you to do in the quantum chemistry portion of the course. Quantum chemistry (aka quantum mechanics and quantum theory) is a relatively young field of chemistry; most of the breakthrough concepts occurred in the first 30 years of the 20th century. Giants like Planck, Bohr, Heisenberg, Schrödinger, Einstein and others, most of whom won Nobel prizes, changed the way we as scientists think about chemistry, physics, and the world in general. These scientists were rebels in the true sense of the word—think of Picasso inventing cubism, Stravinsky’s Rite of Spring, Dylan plugging in…

So what is it that made quantum such a radical and surprising theory? To fully appreciate this, we first have to put ourselves in the mindset of an early 20th century physicist. In other words, we have to ask ourselves, “What behavior would have been expected if there was no such thing as quantum mechanics?” The physics that preceded quantum mechanics is referred to as classical physics. One of the tenets of classical physics is that values of a particular quantity (e.g. velocity, energy, momentum,...) are continuous. That is, any outcome is possible. For example, the velocity of a car can be any value between 50 and 51 mph; it could be 50.3 mph, or 50.5 mph, or 50.5004 mph. This is not true in quantum mechanics. In quantum mechanics, the value is quantized, which means only certain values are allowed. For example, 50 and 51 mph might be allowed, but nothing in between; e.g. 50.3 mph might be forbidden. Quantization was surprising. It required these scientists to Think Different.

There are helpful metaphors for thinking about quantization, but keep in mind that they can never be perfect. One that I like is a series of shelves in a cupboard. You can place a cup on shelf 1, 2 or 3, but you can’t place it halfway between 1 and 2. Another metaphor is digital media. Computers, CDs, and DVDs are made up of bits of data that are binary: they have values of 0 or 1 only. You may be wondering, “OK, so there is a strange, radical set of ideas that developed about 100 years ago, and I’m excited to learn about them, but why weren’t they developed earlier?” The answer is that quantization is only noticeable when studying really small (microscopic) things, like an atom or an electron; it is hidden (although not absent) in large (macroscopic) things, like a baseball or a person. It was only when scientists started doing experiments on atoms that these startling observations were made. Because Chemistry is the molecular science, we can’t ignore quantum theory.

Our book does a nice job of presenting many of the breakthroughs in quantum mechanics. Many of these were grounded in an expectation-failure relationship. Physicists had expectations of what should have happened in a given experiment according to their classical physics worldview at the time, and when these failed they were forced to come up with better, more complete

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1 These notes are meant to supplement chapter 6 of Brown, Lemay and Bursten (BLB). A brief introduction to the nature of quantum theory is provided. More detailed explanation of some of the introductory material is available in BLB. The introduction is followed by an emphasis on the Schrödinger wave equation (SWE), as applied to a particle in a box and the hydrogen atom; much of this portion is not in BLB. Please also note that there is other material covered in chapter 6 of the book only that you are also responsible for.
explanations to explain reality. First, let’s look at quantization. If you pass white light through a prism, a continuum of wavelengths is observed (you’ve probably seen the Dark Side of the Moon cover). Thus, the expectation for the spectrum of light from dilute gaseous atoms of an element was a continuum. Nothing could have been further from the truth. As you will see in lecture, only certain wavelengths were seen (e.g. see Fig 6.12 in BLB); this is referred to as a line spectrum. As we will see below, line spectra arise because only certain energy levels are ‘allowed’ and transitions occurring between these levels give rise to lines. Each element has different energy levels, and so has a different line spectrum (Fig 6.12).

One idea from classical physics is that light (electromagnetic radiation) is a wave. You should read section 6.1 of your text now. This is a perfectly rational expectation (and is part of the truth—see below). For example, Young showed that when a collimated beam of light is passed through a double slit, many (much more than 2—the light-as-a-particle expectation) bright and dark spots are observed on a screen. This behavior is grounded in the wave phenomena of diffraction and interference. However, a number of other observations required us to think of light as a mass-less particle (or a photon). Here are three:

1.) A Geiger counter ‘clicks’ in a random fashion: Click….Click..Click……Click…Click, with the number of clicks/unit time reflecting intensity. This observation suggests that light (here gamma radiation) is made up of particles hitting the detector at random intervals. The expectation, if light were a wave, is that there should be a constant hum that should increase in volume with intensity of the beam. Clearly, light cannot be thought of only as a wave.

2.) Einstein explained the photoelectric effect by describing light as a particle. The photoelectric effect is the electricity conducted when light impinges upon a metal; the photoelectric effect is what allows the detector (photomultiplier tube) in the Geiger counter to conduct electricity. Classically, the expectation was that at low energy (e.g. red light), current would be seen and that it would increase with the intensity of the red light. Nothing could have been further from the truth. Instead, no current was found until the wavelength was below a certain value, corresponding to energy being above a minimum threshold value. This observation is consistent with the particle view of light, with sufficiently energetic particles needed to eject the electron from the surface of the metal. (Einstein won the Nobel Prize in Physics 1921 for explaining the Photoelectric Effect.)

3.) When solids are heated they emit a light, referred to as blackbody radiation. Classical physics predicted that the intensity of a radiating blackbody would increase exponentially with frequency. In reality, intensity levels off and goes to zero at high frequencies. The failure of classical physics to explain blackbody radiation, was so disappointing, physicists called it the ultraviolet catastrophe! The breakthrough concept was made by Max Planck in 1900, who proposed a quantum hypothesis to derive the blackbody radiation law. Central to this hypothesis was that the energy of light is quantized in units of $h\nu$ (E=$nh\nu$, where $h$ is a proportionality constant, $\nu$ is frequency, and $n=1, 2, 3, \ldots$). These quanta of light are referred to as photons. The proportionality constant became known as Planck’s constant. Its value is small ($6.626 \times 10^{-34}$ J s). That’s why we don’t notice quantization in objects with large energy—the spacings
are too small relative the absolute value to see. In summary, light is neither a particle nor a wave; it is both. This idea is manifest in Planck’s equation, \( E = h \nu = \frac{hc}{\lambda} \), which relates the energy of a photon (a particle) to its wavelength. The dual properties of light are referred to as the wave-particle duality.

In class, we will go through the Bohr model of the atom. Bohr said the energies of the atom are quantized. He also postulated that the electron ‘orbits’ the nucleus, having fixed orbits a certain distance from the nucleus. For obvious reasons, this is called the planetary model of the atom. It has limitations, however, the most important of which is that it does not account for the wave behavior of electrons. WAIT! Did you just say electrons are waves? Yes! Not only is light a particle and a wave, but massive particles are waves too! deBroglie said that all particles with a mass, \( m \), and velocity, \( v \), have a wavelength (\( \lambda \)) associated with them according to:

\[ \lambda = \frac{h}{mv} \]

Clearly, \( \lambda \) will be very small for massive particles. Thus, wave behavior is not noticeable for big things like people and baseballs. But it is for light things like an electron. This is the basis of the electron microscope (see Fig 6.14), which allows high resolution imaging of very small things like viruses. See below for an advanced derivation of the deBroglie equation.

**Part II: After Schrödinger:**

It was Schrödinger (in 1926) who postulated the model of the atom that we still use today. The Schrödinger wave equation (SWE) changed how chemists think about reactions; it marks a division of sorts between classical and modern chemistry—hence the division of this handout into the two parts. Schrödinger’s description of the atom involves some fairly high level mathematics; most high-level quantum chemistry books begin and end with the SWE. The SWE can only be solved exactly for one-electron atoms, like H, He\(^+\), Li\(^2+\),…, although good approximations can be made for more complex atoms and molecules. If you go on to take more chemistry, you will do more with solving and approximating solutions to the equation (in Physical Chemistry), and using the outcomes of the solutions (orbitals) to predict chemical reactions (in Organic Chemistry).

Before we look at the math behind the SWE, let’s discuss some of the qualitative features of it. The SWE is a differential equation that requires calculus to solve. The solutions are wave functions, or orbitals, given the symbol \( \Psi \) (‘psi’, pronounced like ‘sigh’), which have their own unique quantized energies, \( E \). These orbitals can hold two electrons with opposite spin. Thus, like the Bohr model of the atom, the energies of the electrons are fixed; but, unlike the Bohr model, the Schrödinger model accounts for the wave behavior of electrons (which are matter—they have mass). To get a feel for the SWE, we will solve it exactly for the simplest system possible: a particle (an electron) in a 1-dimensional box (a line). Doing this will teach a number of things: 1.) How to confirm the correctness of solutions to a linear second-order differential equation (=the 1-dimensional SWE), 2.) The information content of the solution

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2 It is important that any new theory not only explain new observations but have limits that reduce to the old theory. You will see this for the deBroglie wavelength below.

3 Don’t confuse \( v \) (velocity) and \( \nu \) (frequency).
(Ψ, E, n (a quantum number, which leads to quantization)), 3.) That we can’t say with certainty where the electron will be—but we can talk about where it is likely to be and where it cannot be. 4.) Where line spectra come from.

Recall that energy consists of the sum of kinetic energy and potential energy:
\[ E = KE + PE. \]
In classical physics, these are the energies of motion and position, respectively; in classical chemistry, we referred to these as being proportional to temperature and intermolecular attractions, respectively. The SWE has KE and PE terms too.

The SWE, in its simplest form looks like this:
\[ HΨ = EΨ \]
where \( H \) is the Hamiltonian operator, \( Ψ \) is a wavefunction, and \( E \) is energy. (No, you cannot divide through by \( Ψ \) and end up with \( H=E \). Why? Because \( H \) is an operator.) As we shall see, the construction of \( H \) is not difficult. Solving it, however, can be a different matter. Let’s return for a moment to a classical physics Hamiltonian. Since \( p = mv \), \( KE = p^2/2m \). PE is typically represented with the symbol \( V \). For a classical object moving in one dimension (x), \( H_{cl} \) is given by
\[ H_{cl} = \frac{p^2}{2m} + V(x) \]

In turns out that the momentum (\( p^\wedge \)) operator in the SWE is given by
\[ p^\wedge = -i\frac{h}{2\pi} \frac{d}{dx} \]
where \( h \) is Planck’s constant and \( i = \sqrt{-1} \), an imaginary number—see deBroglie Box below for more about imaginary and complex numbers. Substituting, we then have the SWE for a particle moving along 1-dimension:
\[ H = \frac{-h^2}{8\pi^2 m} \frac{d^2}{dx^2} + V(x) \]

Let’s now solve the SWE for a particle in a 1-dimensional box. The form of the potential function will be that \( V=0 \) in the box and \( ∞ \) outside the box. This is a fancy way of saying the particle can move freely in the box but it can’t get out; sort of like being locked in a 1-dimensional jail. We will give our box a length of \( L \). Thus, the particle has to be somewhere between \( x=0 \) and \( x=L \). The SWE for the particle then looks like

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4 Recall that an operator is a symbol that tells us how to carry out a mathematical operation. You are already familiar with one: ‘p’, which means apply ‘–log’ to something. e.g. pH = –log [H\(^+\)], pOH = –log [OH\(^–\)], … Another operator is d/dx, which tells us to take the first derivative with respect to x of something.
5 Where \( p \) is momentum and \( KE = 1/2 mv^2 \).
6 ‘\( H_0 \)’ is being used to denote the classical physics Hamiltonian. If no subscript is used, then the SWE Hamiltonian is implied.
\[-\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \Psi = E \Psi\]

The solution to this equation is a set of wavefunctions of the form

\[\Psi(x) = A \sin kx + B \cos kx\]

where A, B, and k are constants we will determine below.

Let’s now solve for E. First, let’s take the 2\textsuperscript{nd} derivative of \(\Psi\).

\[\frac{d^2}{dx^2} \Psi(x) = \frac{d^2}{dx^2} (A \sin kx + B \cos kx)\]

\[= -k^2 (A \sin kx + B \cos kx)\]

\[= -k^2 \Psi(x)\]

Since \(H\Psi = E\Psi\),

\[-\frac{\hbar^2}{8\pi^2 m} (-k^2) \Psi = E \Psi\]

or

\[E = \frac{k^2 \hbar^2}{8\pi^2 m}\]

Now, we need to determine the values of our 3 constants: k, A and B. To do this, we will apply boundary conditions (bc’s). These are conditions we imposed by our choice of experimental setup.

**bc1:** \(\Psi(0) = 0\)

\[\Psi(0) = A \sin 0 + B \cos 0 = B\]

\[\therefore B = 0\]

**bc2:** \(\Psi(L) = 0\)

\[\Psi(L) = A \sin kL = 0\]

\[\therefore kL = n\pi, \text{ where } n = 1, 2, \ldots\]

(The other solution of bc2, A=0, is a trivial solution since \(\Psi\) would then = 0 and we would have no orbital. Thus, we reject that solution.)

_Something really important just happened here!_ We introduced multiple solutions (\(\Psi_1(x), \Psi_2(x), \ldots\)) that are related by a _quantum number_, n.

**bc3:** \(\int_0^L \Psi^2(x)dx = 1\)

Recall that the probability of finding the particle inside the box is 1 (=100\%) and outside is 0. The mathematical formulation of probability is given by the Born postulate, which states that the probability of finding the particle between positions x and x+dx is proportional to the square of the wavefunction, \(\Psi\), and the intervening distance, dx, or \(P = \Psi^2 dx\). Thus, if we integrate \(\Psi^2 dx\)
between 0 to L, the answer must be 1. Setting this equality to be true is also known as normalizing the wavefunction.

\[ A^2 \int_0^L \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1 \]

This integral is tricky, so here is the answer.

\[ A = \frac{\sqrt{2}}{L} \]

Thus, we started with \( \Psi(x) = A \sin kx + B \cos kx \), and ended up with,

\[ \Psi(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right); n = 1, 2, 3... \] (1)

These solutions are a series of wavefunctions. We will show in class that they have different number of nodes, or values of \( x \) (other than \( \Psi(0) \) and \( \Psi(L) \)) where \( \Psi(x) = 0 \). See the table below.

Here is a picture of the solutions. ref: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/pbox.html

According to the Born postulate, these are positions (nodes) where there is zero possibility of finding the particle:
Now that we have a complete expression for $\Psi(x)$, let’s complete our expression for $E$. Substituting $n\pi/L$ for $k$ in the expression for $E$ gives

$$E = \frac{n^2\hbar^2}{8mL^2}$$

(2)

where $n = 1, 2, 3…$

Thus, we see that $E$ is quantized; i.e. only certain energies are allowed! It turns out that when our particle, typically an electron moves to a higher energy state (i.e. $n$ increases), a photon (or quanta) is absorbed whose energy is exactly equal to the energy between the two levels. It follows then that when electron moves to a lower energy state (i.e. $n$ decreases), a photon is emitted whose energy is exactly equal to the energy between the two levels. Transitions can happen between any two levels. The energy difference, $\Delta E$, between the two levels is given by $\Delta E = E_{\text{final}} - E_{\text{init}}$. A special case is absorption of a photon to go from level $n$ to $n+1$. In this case,

$$\Delta E = E_{n+1} - E_n = \frac{\hbar^2}{8mL^2} [(n+1)^2 - n^2]$$

$$= \frac{\hbar^2}{8mL^2}(2n + 1)$$

It should be noted that the change in energy is inversely proportional to the mass of the particle and the length of the box squared. In other words, for massive particles like baseballs, $\Delta E$ will be so small that it will look like a continuum. Also, for large boxes, $\Delta E$ will be small and therefore $\lambda$ will be large (recall that $E = mc/\lambda$).

**Question:** How will spacing change if the particle is a proton?

**Answer:** The energy levels will be about 1000 times closer together than for an electron since $m_p \approx 1000m_e$.

Lastly, note that for the particle in a box, since $PE = V = 0$, $E = KE + PE = KE$. When more complex potentials are taken into account, such as the radial potential of an atom (see below), $PE$ varies with distance, and so is not equal to 0; in this case, $KE$ will increase as $PE$ decreases, and vice versa. Note also that for any potential, total energy is never equal to 0.

In summary, the particle in a box showed us how to set up and solve the SWE, and that the solutions are wavefunctions with quantum numbers. Probability is proportional to $\Psi^2$, and nodes are regions where the particle never is found. Energy is quantized and only certain energies can be absorbed and emitted. Although the particle in the box is simple, it was useful in that it gave
us these insights. (Actually, the particle in a box has some practical applications too, especially for molecules that are long and straight and have conjugated bonds. Stay tuned in class for examples.)

To apply the SWE to more complicated systems, like atoms, we simply need to write down the new potential function. Let’s start with the simplest of atoms, one electron atoms (e.g. H, He+, Li2+, …). Recall that for the particle in a box, V(x)=0. What is V for this system? It is simply given by Coulomb’s Law, which we have already seen in class in lattice energies. The electrostatic attraction between the electron (charge of –e) and the nucleus (charge of +Ze, where Z is the atomic number) is given by

\[ V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r} \]

where r is the distance between the electron and the nucleus and \( \epsilon_0 \) is the permittivity. Since atoms exist in 3-dimensions, we need a 3D coordinate system. Since atoms are spherically symmetric, we choose radial coordinates (more in class). The SWE is now in three dimensions and the Hamiltonian looks like this:

\[ H = \frac{-\hbar^2}{8\pi^2 m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{-Ze^2}{4\pi\epsilon_0 r} \]

This equation is solvable, but it is a bear. Schrödinger solved it himself in 1927! You only need to know how to set up the Hamiltonian, what the solutions look like, and how to plot them. Basically, we end up with a series of wave functions that have 3 associated quantum numbers n, l, and m_l (three this time due to 3-dimensions). The 3 quantum numbers are as follows: \( n = 1, 2, 3, \ldots; l = 0, 1, 2, \ldots, n-1 \), and \( m_l = -l \) to \( l \). Let’s examine Schrödinger’s solutions to the one electron atom, beginning with the energies.

\[ E = \frac{-Z^2 R h}{n^2}, n = 1, 2, \ldots \]

where R is the Rydberg constant, \( R = 3.28984 \times 10^{15} \) Hz.

Note that, unlike the particle in a box, potential varies with position for an atom. To be precise, as the electron moves closer to the nucleus, the PE becomes increasingly negative, as a consequence, the KE increasingly positive (since PE+KE=E, a constant). As KE increases, momentum increases (KE=p^2/2m), and as p increases, \( \lambda \) decreases (\( \lambda = h/p \)). A wave picture of an electron in an atom looks like:
Table of orbitals and associated energies for a one electron atom.

<table>
<thead>
<tr>
<th>n (shell)</th>
<th>l (subshell)</th>
<th>m_l (orbital)</th>
<th>E</th>
<th>number of orbitals^7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-Z^2Rh</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-Z^2Rh/4</td>
<td>4 (=1+3 = n^2)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-1, 0, 1</td>
<td>-Z^2Rh/4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-Z^2Rh/9</td>
<td>9 (=1+3+5=n^2)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-1, 0, 1</td>
<td>-Z^2Rh/9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-2, -1, 0, 1</td>
<td>-Z^2Rh/9</td>
<td></td>
</tr>
</tbody>
</table>

where l=0, 1, 2, 3, 4 … corresponds to s, p, d, f, g, ...

Here are a few of the wavefunctions for the hydrogen atom. You will see others in the practice problems that follow.

\[
\Psi_{1s} = \left( \frac{1}{\pi a_o} \right)^{1/2} e^{-r/a_o}
\]

\[
\Psi_{2s} = -\frac{1}{4} \left( \frac{1}{2\pi a_o} \right)^{1/2} \left( 2 - \frac{r}{a_o} \right) e^{-r/2a_o}
\]

The radial portion of a wavefunction is the part that is a function of r, the distance from the nucleus. We are interested in plotting this, and will do so in class. At this point, you should be able to show that \(\Psi_{1s}\) is an exponential decay with no nodes, while \(\Psi_{2s}\) has a node at \(r=2a_o\), where \(a_o\) is the Bohr radius and is equal to 0.5292Å. These nodes end up being spherical nodes; i.e. in the 2s orbital, there is a sphere of radius 2a_o centered at the nucleus where the electron can never be. We will show in class the following relationship for nodes:

^7 The book tells you to think of this as \(n^2\), which is not incorrect. But it may be clearer if you see that it comes from the sum of the number of orbitals for each l. e.g. When n=2, the number is 1 + 3=4; n=3, the number is 1+3+5=9, and so on.
Introduction to complex numbers and an advanced derivation of the deBroglie equation:

In this box, we show how the deBroglie relationship (provided in Part I) for a free traveling particle (i.e. a particle not confined to a box) follows from the general solutions to the Schrödinger wave equation (SWE) for a particle in a box. However, this time, when it comes time to put in the constants, we won’t be able to use boundary conditions (because there are no boundaries on a free traveling particle); instead, we will postulate that $\lambda$ is given by the deBroglie relationship, $\lambda = h/mv = h/p$. We will then be able to show that the resulting wavefunctions satisfy the momentum operator used to build the SWE.

Wave functions can be complex numbers. Thus, we begin with a bit more background on complex numbers. The symbol $i = \sqrt{-1}$ will be used with the understanding that $i^2 = -1$. Any number with the symbol $i$ in it is an imaginary number, e.g. $\sqrt{-16} = \sqrt{16}\sqrt{-1} = 4i$. But $i^2 = -1$ is a real number. We will also need combinations of real and imaginary numbers, e.g. $i + 5$. In general, the term complex number is used to refer to any possibility, e.g. $4i$, $-1$, and $i + 5$ are all complex numbers. The complex conjugate of a complex number is obtained by changing the sign of $i$. For example, if $z = x + iy$, then its complex conjugate, given the symbol $z^*$, is given by $z^* = x - iy$. Euler’s formula (not derived here) is

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

OK, now let’s return to the general solutions to the particle in a box:

$$\Psi(x) = A \sin kx + B \cos kx$$

Let’s try the constants $A = i$, $B = 1$, this gives:

$$\Psi(x) = \cos kx + i \sin kx = e^{ikx}$$
$$\Psi^*(x) = \cos kx - i \sin kx = e^{-ikx}$$

Note that $\Psi\Psi^* = 1$, a real number. (You can show this easily by multiplying the exponential representations together.) Classically, $\Psi\Psi^*$ is the energy of the wave. Thus, it is good that $\Psi\Psi^*$ is real. Note also, that we could make $\Psi\Psi^*$ any scalar we choose simply by multiplying $\Psi$ by a constant, and that that $\Psi$ would still satisfy the momentum operator equations below.
According to the particle in a box, \( kL = n\pi \), or \( k = n\pi/L \). For a freely traveling particle, there is \( 2\pi \) radians for every cycle (=wavelength traveled). Thus, \( k = 2\pi/\lambda \). Using the deBroglie relationship, we have \( k = 2\pi(h/p) = 2\pi p/h \). Substituting, we have,

\[
\Psi(x) = e^{\frac{2\pi x}{h}}
\]

A quantum mechanical operator is a mathematical function that operates on a wavefunction and returns that wavefunction multiplied by a constant (=a scalar). The wavefunctions that satisfy this relationship are called eigenfunctions and the scalars are called eigenvalues. We can therefore say that the following must be true for momentum

\[
p^\Psi = p\Psi
\]

where \( p^\Psi \) is the momentum operator and \( p \) is the momentum, a scalar.

If we apply \( p^\Psi \) (given above) to our \( \psi(x) \), we have

\[
p^\Psi \psi = -i \frac{h}{2\pi} \frac{d}{dx} \psi = -i \frac{h}{2\pi} \frac{d}{dx} e^{\frac{2\pi x}{h}}
\]

\[
= -i \frac{h}{2\pi} \frac{2\pi p}{h} e^{\frac{2\pi x}{h}} = pe^{\frac{2\pi x}{h}} = p\psi
\]

Thus, these \( \psi \)'s are good eigenfunctions of \( p^\Psi \). Thus, the deBroglie relationship follows from (and satisfies) the SWE.
Chem 12H
Enrichment Problems for Quantum Chemistry

1.) Set up the Schroedinger Wave Equation for Li. Hint: Don’t forget to consider electron-electron interactions.

How many terms represent the screening felt by the 2s electron? Which terms are they?

2.) Given the following equation for the 3pz orbital for a 1-electron atom, sketch the radial portion of the wave function.

\[ \Psi_{3pz} = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a_o} \right)^{5/2} (6 - \frac{Zr}{a_o})r e^{-Zr/3a_o} \cos \theta \]

At what distance r (in terms of \( a_o \), the Bohr radius) is there a node for H? For Li\(^{2+} \). Show your work.

3.) Sketch the 3s wave function for the hydrogen atom given the following equation:

\[ \Psi_{3s} = \frac{1}{81(3\pi)^{1/2}} \left( \frac{Z}{a_o} \right)^{3/2} \left( 27 - 18 \frac{Zr}{a_o} + 2 \frac{Z^2r^2}{a_o^2} \right)e^{-Zr/3a_o} \]
At what two distances (in terms of $a_o$) are there nodes?

4.) a) For the particle in a box, what is the potential energy of an electron with $n=1$? $n=2$?

b) For the same box, what is the kinetic energy of an electron with $n=1$? $n=2$?

c) When an electron (=a particle with mass) has an energy increase from $n=1$ to 2, does that energy come from something with a mass or without a mass? What is that something?

d.) Based on your answer to d), can energy be transferred from mass-containing to mass-less things? If so, is energy conserved?

5.) a.) For particle in a box, how many nodes are in the $n=4$ wave function?

b.) Using the de Broglie relationship, and solving for $v$, does an $n=4$ electron have more or less velocity than an $n=1$ electron? Based on this, check your answer to 4 b and re-think if necessary.

6.) a.) For the particle in a box, assuming a fixed box size, how does the wavefunction ($n=1$) for a proton compare to that for an electron ($n=1$)?
b.) What about energy levels?

7.) For an electron in a box, how does the amplitude of the n=1 wave function change as the box is stretched out?

What about the energy level?

Knowing that ground states of molecules are the lowest energy states, is a long molecule, which simulates a long box, more or less stable than a molecule that simulates a short box?

8.) a.) Derive an equation for the spacing in energy levels (i.e. from n to n+1) for the particle in a box in terms of h, m, L, n.

b.) Based on your equation, are energy levels closer together are farther apart for a baseball compared to an electron? Based on this, are the steps in the quantized energy noticeable for a baseball?

c.) What happened to the spacing between the energy levels for an electron as you stretch out the box? Based on this, is quantization more important for very small boxes or very big ones?
9.) Sketch the 4pz orbital, include algebraic signs.

10.) Consider an isoelectronic series of ions, O\(^{2-}\), F\(^-\), Ne, Na\(^+\), Mg\(^{2+}\).

a.) Using the rules of thumb for screening from class, calculate \(Z_{\text{eff}}\) for the valence electrons and tabulate

b.) Write down an equation for \(r\) in units of \(a_0\) and add to your table.

c.) Arrange these ions in size from largest to smallest.