Chapter 14. Multidimensional Quantum Mechanics and Rotation

We have focused on single dimensional systems thus far in our discussion of quantum mechanics. However, the Universe is three-dimensional, and as such we need to study 3D quantum mechanics. To begin this chapter we will show that the inclusion of extra dimensionality causes an unfortunate increase in complexity of the kinetic energy operator. And while this is not terribly difficult for a particle in a box problem (or we should rather say particle in a cube), it can become onerous once we start to work with spherical objects such as atoms. You will see when we start describing rotating quantum particles in the 2nd half of this chapter. Regardless of the nature of our model problems, one of the most important results is the fact that multidimensionality introduces energetic degeneracy (two or more quantum states with the same energy). Degeneracies have significant impact on many areas of science as they have a substantial effect on the physical properties of chemicals and materials.

14.1 Multidimensional Free waves and the Particle in a Cube. We begin our understanding on multidimensional quantum mechanics with the kinetic energy operator $\frac{-\hbar^2}{2 \cdot \text{mass}} \frac{\partial^2}{\partial x^2}$, as most of the complexity of quantum mechanics originates from here as we saw back in Ch. 12. The operator must be augmented with additional terms, likely the same expression except with y: $\frac{-\hbar^2}{2 \cdot \text{mass}} \frac{\partial^2}{\partial y^2}$ and z: $\frac{-\hbar^2}{2 \cdot \text{mass}} \frac{\partial^2}{\partial z^2}$. Now the question is how- are these terms added into the operator? Or do they all multiply? Let's use an analogy- recalling the equipartition theorem from your earlier introduction to thermodynamics, the energy of a particle increases by $\frac{1}{2 \times \text{k}_B}$ T for every degree of freedom that particle has. The ability of a particle to move in x, y and z counted as three degrees of freedom, and as a result all the $\frac{1}{2 \times \text{k}_B}$ T energies were summed. This leads us to conclude that the kinetic energy operator must likewise sum energies for each accessible dimension, which is:

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

This expression is the full 3D kinetic energy operator, and we will use it to revisit our old problems of the freewave and particle in a box once we know a little bit more about how to solve the wavefunctions.

14.1.1. Multidimensional wavefunctions and separability in the 3D freewave problem. With the kinetic energy operator in hand, let's solve a simple system such as the freewave in 3D, which describes a particle that moves in any direction, forever, without encountering any potential energy. The Schrodinger equation for the 3D freewave is then:

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

To make further progress we must know more about the total wavefunction $\Psi(x, y, z)$. Could it be a simple summation of "mini" wavefunctions in different dimensions: $\Psi(x, y, z) = \Psi_x(x) + \Psi_y(y) + \Psi_z(z)$ or perhaps they multiply: $\Psi(x, y, z) = \Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)$? Instead of guessing, we can review some mathematical principles of differential equations to resolve between the two possibilities.

Separability is a method for solving differential equations, and what it means is that the Hamiltonian can be cast into a form whereby distinct terms that contain only an x, y or z are added or subtracted. A separable Hamiltonian is significantly easier to solve, and fortunately most (but not all) operators are in fact separable. To check for separability, first act on a wavefunction to the right of the Hamiltonian: $\hat{H}\Psi$ and then divide it out on the left: $\frac{1}{\Psi}\hat{H}\Psi$. What you are trying to see is if you can write out the Hamiltonian as:

$$\frac{1}{\Psi_{x}(x) \cdot \Psi_{y}(y) \cdot \Psi_{z}(z)} \widehat{H} \Psi_{x}(x) \cdot \Psi_{y}(y) \cdot \Psi_{z}(z) = -\{x \text{ terms}\} + \{y \text{ terms}\} + \{z \text{ terms}\}$$

and, if so, then the total wavefunction is: $\Psi(x, y, z) = \Psi_x(x) \cdot \Psi_y(y) \cdot \Psi_z(z)$.

Separability has two consequences. First, the wavefunction *cannot* look like $\Psi(x, y, z) \approx \sin(k_x x + k_y y + k_z z)$ or $e^{i \cdot k_x \cdot x} + e^{i \cdot k_y \cdot y} + e^{i \cdot k_z \cdot z}$. Second, the method of separability gives us a way to solve the Schrodinger equation as each of the terms becomes a smaller and easier differential equation. Beginning with the definition of separability:

$$\begin{split} \frac{1}{\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z)} &\left(\frac{-\hbar^{2}}{2m}\right) \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \frac{\partial^{2}}{\partial z^{2}}\right) \Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z) = \\ \frac{1}{\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z)} &\left(\frac{-\hbar^{2}}{2m}\right) \frac{\partial^{2}}{\partial x^{2}} \Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z) + \\ \frac{1}{\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z)} &\left(\frac{-\hbar^{2}}{2m}\right) \frac{\partial^{2}}{\partial y^{2}} \Psi(x)\cdot\Psi(y)\cdot\Psi(z) + \\ \frac{1}{\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z)} &\left(\frac{-\hbar^{2}}{2m}\right) \frac{\partial^{2}}{\partial z^{2}} \Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z) \end{split}$$

One simple rule of calculus is concerning derivatives is that functions of other variables are not "caught up" by the derivative operation, i.e. $\frac{\partial}{\partial x} f(x)f(y) = f(y)\frac{\partial f(x)}{\partial x}$. When we apply that to the 1st term above we find:

$$\frac{1}{\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z)}\left(\frac{-\hbar^{2}}{2m}\right)\frac{\partial^{2}}{\partial x^{2}}\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z) = \frac{\Psi_{y}(y)\cdot\Psi_{z}(z)}{\Psi_{x}(x)\cdot\Psi_{y}(y)\cdot\Psi_{z}(z)}\left(\frac{-\hbar^{2}}{2m}\right)\frac{\partial^{2}}{\partial x^{2}}\Psi_{x}(x)$$

which simplifies to $\frac{1}{\Psi_{x}(x)} \left(\frac{-\hbar^{2}}{2m}\right) \frac{\partial^{2} \Psi(x)}{\partial x^{2}}$. Appling these across-the-board yields:

$$\left\{\frac{1}{\Psi_{x}(x)}\left(\frac{-\hbar^{2}}{2m}\right)\frac{\partial^{2}\Psi_{x}(x)}{\partial x^{2}}\right\} + \left\{\frac{1}{\Psi_{y}(y)}\left(\frac{-\hbar^{2}}{2m}\right)\frac{\partial^{2}\Psi_{y}(y)}{\partial y^{2}}\right\} + \left\{\frac{1}{\Psi_{z}(z)}\left(\frac{-\hbar^{2}}{2m}\right)\frac{\partial^{2}\Psi_{z}(z)}{\partial z^{2}}\right\}$$

Success! We see three distinct terms, whereby only an x appears in the 1st one and so on. Furthermore, each term is now a min-Schrodinger equation to be solved. The last step is to realize that all three terms add up to the energy. You can see this starting with: $\hat{H}\Psi = E\Psi$ and dividing out the wavefunction on the left $\frac{1}{\Psi}\hat{H}\Psi = \frac{1}{\Psi}E\Psi = \frac{\Psi}{\Psi}E = E$. Since each term adds to a constant (the energy), then each term must be a constant in its own right. As a result, we divide the energy into three parts, one for x, for y and for z as: $E = E_x + E_y + E_z$, and then give each energy to the corresponding term (and using a little algebra to bring the wavefunctions to the right):

$$\begin{split} &\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\Psi_x(x) = E_x\Psi_x(x)\\ &\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial y^2}\Psi_y(y) = E_y\Psi_y(y)\\ &\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial z^2}\Psi_z(z) = E_z\Psi_z(z) \end{split}$$

Each of these are simply freewave Schrodinger equations. We know from the last chapter that the solutions are: $\Psi_x(x) = e^{\pm i \cdot k_x \cdot x}$, etc., which means that the full solution is:

$$\Psi(\mathbf{x},\mathbf{y},\mathbf{z}) = \mathrm{e}^{\pm \mathrm{i}\cdot \mathbf{k}_{\mathcal{X}}\cdot\mathbf{x}} \cdot \mathrm{e}^{\pm \mathrm{i}\cdot \mathbf{k}_{\mathcal{Y}}\cdot\mathbf{y}} \cdot \mathrm{e}^{\pm \mathrm{i}\cdot \mathbf{k}_{\mathcal{Z}}\cdot\mathbf{z}}$$

It is interesting to note that three separate momentum components now add to the total like a vector: $k^2 = k_x^2 + k_z^2 + k_z^2$. This is especially apparent if you use the wavefunction to calculate the total energy:

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_z^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}$$



Figure 14.1. Particle in a box potential surfaces from 1D to 3D.

If for some reason the individual wavevectors were not of equal magnitude, then it would have to be true that the total energy wasn't divided equally between the three dimensions: $E_x \neq E_y \neq E_z$. This is a very unlikely scenario, but if it was true you would be aware of it due to the fact that you must have some basic understanding of the system under study. Or, if you are solving a problem this information would be given to you as an initial condition of the system.

14.1.2. The Particle in a 3D Box and Degeneracy. The quantum particle in a box can be extended to multiple dimensions as visually represented in Figure 14.1. From the last chapter, this problem was defined by a potential that is 0 inside the box and infinite outside. Boundary conditions allow us to define the wavefunctions: $\Psi = \sin\left(\frac{n\pi}{L}x\right)$ with the quantum number n=1,2,3... that characterize the number of nodes and the energy. Extending this to multiple dimensions is straightforward. Given the previous discussion the total wavefunction is just the multiple of individual particle in a box functions for x, y and z:

$$\begin{split} \Psi_{2D}(x,y,z) &= N_{2D} \cdot \sin(k_x x) \cdot \sin(k_y y) \qquad \Psi_{3D}(x,y,z) = N_{3D} \cdot \sin(k_x x) \cdot \sin(k_y y) \cdot \sin(k_z z) \\ \text{where the normalization constants are } N_{2D} &= \frac{2}{\sqrt{L_x L_y}}, N_{3D} = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}}, \text{ and } k_x = \frac{n_x \pi}{L_x}, k_y = \frac{n_y \pi}{L_y}, \text{ and } k_z = \frac{n_z \pi}{L_z}. \end{split}$$

wavefunction back into the particle in a box Hamiltonian reveals the energy to be:

$$E = \frac{\hbar^2}{2m} \left(k_x^2 + k_y^2 + k_z^2 \right) = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$



Figure 14.2. How the particle in a box wavefunctions change with increasing dimensionality.

which can be simplified to $E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$ if all the box lengths are the same. As in the one-dimensional particle in a box problem, the quantum numbers are limited to whole numbers: $n_{x,y,z} = 1,2,3...$ due to the need to satisfy boundary conditions imposed by infinite potential energies past the barriers. Various wavefunctions are depicted in Figure 14.2, where we have made the simplification that $L = L_x = L_y = L_z$. It can be seen that there is only one wavefunction that gives the lowest energy ground state for which $n_{x,y,z} = 1$. However, there are three potential 1st and 2nd excited states; since for example:

$$\mathbf{E} = \frac{\hbar^2 \pi^2}{2\mathbf{m} \cdot \mathbf{L}^2} \{ (\mathbf{n}_{\mathbf{x}} = 2)^2 + 1^2 + 1^2 \} = \frac{\hbar^2 \pi^2}{2\mathbf{m} \cdot \mathbf{L}^2} \{ \mathbf{1}^2 + (\mathbf{n}_{\mathbf{y}} = 2)^2 + 1^2 \} = \frac{\hbar^2 \pi^2}{2\mathbf{m} \cdot \mathbf{L}^2} \{ \mathbf{1}^2 + 1^2 + (\mathbf{n}_{\mathbf{z}} = 2)^2 \}$$

This is referred to as a degeneracy, multiple distinct states that all have the same energy. One way to recognize degeneracy is if you can rotate the wavefunctions such that they all look the same.

There isn't much more to say about these simple multidimensional systems. For example, one can generate interesting problems by mixing and matching potential surfaces in different dimensions- a freewave surface in x and a parabolic (spring) potential in y. However, the solutions are rather trivial, as the total wavefunction in this example is just the freewave in x times the harmonic oscillator function in y. Such problems are left for your effort at the end of the chapter, and as such we move on to discuss a quantum particle rotating.

14.2. Rotational Quantum Mechanics: Introduction. In chemistry, we are deeply concerned about electrons and how they can bunch up (bond), or not (antibond), between atomic nuclei; this is how molecules form. Unfortunately, atoms are round and their electrons may orbit the nucleus like the Moon rotates about the Earth. This means that electrons have angular momentum and rotational kinetic energy. We must use quantum mechanics to understand how rotation works for light particles such as electrons. Rotational quantum mechanics also applies to rotational spectroscopy of molecules, which is in the microwave region of the electromagnetic spectrum.

The most important thing about rotational energy is to determine the rotational kinetic energy operator. You may be thinking, "how is rotational kinetic energy different than translational kinetic energy?" This indeed sounds like a very difficult question; fortunately, the answer is that *it isn't different*. Meaning, the kinetic energy Hamiltonian we discussed above: $\frac{-\hbar^2}{2 \cdot \text{mass}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right), \text{ hasn't changed at all! However, there is one slight problem- Cartesian coordinates are not very useful for round objects like atoms. Rather, we want to use either cylindrical or spherical coordinates. Thus, changing the kinetic energy operator from Cartesian (x, y, z) into cylindrical (r, <math>\phi$, z) or spherical (r, ϕ , θ) coordinates is our first objective.

14.2.1 Cylindrical Coordinate Transformation. If you don't recall how cylindrical and spherical coordinates work see the Example box on the next page. Once you are comfortable with these trigonometric equations, we can start on transforming the coordinate system by describing an object rotating exclusively in the x-y plane using cylindrical variables. This means that x, $y \rightarrow r$, ϕ , while z remains z. Our first model is for a quantum mechanical particle that rotates in a flat x-y plane with a fixed radius; this is referred to as a 2D rigid rotor. Since the object does not move in the z direction we can leave the z coordinate out of the kinetic energy operator as so:

$$\widehat{H}_{2D} = \frac{-\hbar^2}{2 \cdot \text{mass}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

This simplifies our transformation problem. The first step is to use the product rule to relate $x \rightarrow r$ as follows:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r}$$



Figure 14.3. Visualization of the polar (θ) and azimuthal (ϕ) angles.

The transformation of Cartesian to cylindrical or spherical coordinates is a dreadful task of recalling high school trigonometry. Rather than reviewing how sine and cosine work and defining the "hypotenuse" (which is, in fact, a large semi-aquatic mammal native to sub-Saharan Africa), instead we simply list the relevant identities without derivations below. Concerning cylindrical coordinates:

$$r = \sqrt{x^2 + y^2}, \varphi = \operatorname{atan}\left(\frac{y}{x}\right), z = z$$

where ϕ is the azimuthal angle. Likewise:

 $x = r \cdot cos(\phi), y = r \cdot sin(\phi), z = z$

Spherical coordinates introduce the θ (polar) angle as follows:

$$r = \sqrt{x^2 + y^2 + z^2}, \varphi = \operatorname{atan}\left(\frac{y}{x}\right), \theta = \operatorname{acos}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right) = \operatorname{acos}\left(\frac{z}{r}\right)$$

Likewise:

$$x = r \cdot \sin(\theta)\cos(\phi), y = r \cdot \sin(\theta)\sin(\phi), z = r \cdot \cos(\theta)$$

However, since x is a function of both r and ϕ we must include the ϕ dependency as well:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

Consequently, the transformation requires us to evaluate $\frac{\partial r}{\partial x}$ and $\frac{\partial \phi}{\partial x}$. Based on the relationships on the previous page, we see that $r = \sqrt{x^2 + y^2}$ and thus:

$$\frac{\partial r}{\partial x} = \frac{\partial (x^2 + y^2)^{\frac{1}{2}}}{\partial x} = \frac{1}{2} (x^2 + y^2)^{-\frac{1}{2}} \cdot \frac{\partial x^2}{\partial x} = \frac{1}{2} \frac{2x}{(x^2 + y^2)^{\frac{1}{2}}} = \frac{x}{(x^2 + y^2)^{\frac{1}{2}}}$$

Recall that we are not here to represent anything with x and y, rather r and ϕ . Thus, we must recognize that $\frac{1}{(x^2+y^2)^{\frac{1}{2}}} = \frac{1}{r}$ and $x = r \cdot \cos(\phi)$. Putting this altogether we see:

$$\frac{\partial \mathbf{r}}{\partial \mathbf{x}} = \frac{\mathbf{x}}{(\mathbf{x}^2 + \mathbf{y}^2)^{\frac{1}{2}}} = \frac{1}{\mathbf{r}}\mathbf{r} \cdot \cos(\phi) = \cos(\phi)$$

Likewise, we evaluate $\frac{\partial \Phi}{\partial x}$ as:

$$\frac{\partial \Phi}{\partial x} = \frac{\partial \tan \left(y/x \right)}{\partial x} = -\frac{\sin(\Phi)}{r}$$

Tying this all together reveals:

$$\frac{\partial}{\partial x} = \cos(\phi)\frac{\partial}{\partial r} - \frac{\sin(\phi)}{r}\frac{\partial}{\partial \phi}$$

A similar derivation for the y-coordinate reveals:

$$\frac{\partial}{\partial y} = \sin(\phi)\frac{\partial}{\partial r} + \frac{\cos(\phi)}{r}\frac{\partial}{\partial \phi}$$

The way to transform the kinetic energy operator is to evaluate $\frac{\partial^2}{\partial x^2}$ and $\frac{\partial^2}{\partial y^2}$ using the relationships above. The algebra involved isn't difficult but there are a very large number of steps; regardless, the end result is:

$$\widehat{H} = \frac{-\hbar^2}{2 \cdot \text{mass}} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \to \frac{-\hbar^2}{2 \cdot \text{mass} \cdot r^2} \cdot \frac{\partial^2}{\partial \phi^2}$$

14.2.2 2D rigid rotor. For this model problem, called the 2D rigid rotor, we assume that a light particle circulates on a flat potential in the x and y plane with a fixed z coordinate. The radius of the motion is fixed, so the particle travels around and around a completely flat track. We will begin by making an analogy to the particle in a box problem, which will allow us to introduce concepts important to rotation and to calculate the energy. To this end we create a visual representation of what the wavefunctions should look like by drawing the particle in a box



Figure 14.4. A. Particle in a box states (including n=0) provide insight into allowed 2D rigid rotor wavefunctions simply by folding the potential surface over onto itself as seen in **B**.

states on a piece of paper as shown in Figure 14.4 A. There is one additional n = 0 state that has no kinetic energy; please note that the particle in a box doesn't have a n = 0 state due to its zeropoint energy. Next, we fold the paper over to see how each wavefunction bites its own tail as seen in Figure 14.4 B. Doing so allows us to see whether the wavefunction is smooth and continuous at the seam, for which we can that is the case for the n = 0 and n = 2 states. As a result, these are valid 2D rigid rotor wavefunctions. In contrast, the n = 1 and n = 3 are continuous but they are not smooth, and as such they are not valid 2D rigid rotor wavefunctions. If we analyze the other states we find that odd symmetry ones are ok, while the symmetric ones are not.

We can now calculate the de Broglie wavelength for the allowed states, which provides the momentum and thus the k vectors for the wavefunctions and allows us to calculate the energy. We can see from the figure that the allowed n=0 state has an infinite wavelength and that the n = 2 has a wavelength $\lambda = C$. We can assume that the other allowed states are n = 4 which has $\lambda = \frac{C}{2}$ and n = 6 for which $\lambda = \frac{C}{4}$. From here we can generate an empirical relationship: $\lambda = \frac{L}{m}$, where m

= 0, 1, 2, ... and appears to act like a quantum number. As it is not proper to express this wavelength as a function of the circumference of the track (C, same as the length of the particle in a box), rather its radius, for which we substitute $2\pi r = C$. We see that the wavelengths for allowed 2D rigid rotor states are: $\lambda = \frac{2\pi r}{m}$. The de Broglie momenta are then:

$$\frac{h}{\lambda} = \frac{hm}{2\pi r} = \frac{\hbar m}{r}$$

and the energy is momentum squared over mass:

$$\mathbf{E} = \frac{\hbar^2 \mathbf{m}^2}{2 \cdot \mathrm{mass} \cdot \mathbf{r}^2}$$

where $\hbar = \frac{h}{2\pi}$. Despite the unconventional approach we have taken the equation for energy above is correct and reveals the existence of a new quantum number "m" for 2D rotation. To finish out this section we introduce some terminology. We are describing is a component of orbital rotational angular momentum which is typically given the symbol " l_z ". It is important to note this here because later we will see that there is another quantity called the spin angular momentum that has to be added to calculate the total. Discussion on these topics are forthcoming; as it applies to the 2D rigid rotor and the energy of rotational motion is:

$$\mathbf{E} = \frac{l_z^2}{2\mathbf{I}}$$

where $I = mass \cdot r^2$ and is called the moment of inertia. From the analogy to the equation for energy above we can see that $l_z = \hbar m$, and thus rotational momenta are quantized due to the need for the wavefunction to "bite its tail", i.e. be smooth and continuous.

14.2.2.1 2D Rigid Rotor Wavefunctions. The above is a fine start to demonstrate the principles of rotational quantum mechanics; however here we will employ more rigorous mathematics. We first find the wavefunctions which can be used to calculate the energies and evaluate other properties. This is accomplished by defining the angular momentum operator:

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

which makes potential-free Hamiltonian: $\hat{H} = \frac{\hat{L}_z^2}{2I} = \frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$. Now the eigenvalue (Schrodinger) equation can be defined as:

$$\frac{-\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\Psi(\phi) = \mathbf{E}\cdot\Psi(\phi)$$

where, as before, I is the moment of inertia. The wavefunction solution to the above is:

$$\Psi(\Phi) = e^{i \cdot m \cdot \phi}$$

where "m" is a constant that must be determined using boundary conditions. As you recall the same approach allowed us to determine all the details of the particle in a box. Concerning boundary conditions, we can see from Figure 14.4 B that the wavefunctions must be continuous at the "seam", which is defined where $\phi = 0$ meets $\phi = 2\pi$. Thus, $\Psi(\phi) = \Psi(\phi + 2\pi)$, which when applied to the wavefunction:

$$e^{i \cdot m \cdot (\phi+0)} = e^{i \cdot m \cdot (\phi+2\pi)} = e^{i \cdot m \cdot \phi} e^{i \cdot m \cdot 2\pi}$$

This only works if $e^{i \cdot m \cdot 2\pi} = 1$, which means that m = ..., -2, -1, 0, 1, 2, ... using identities for complex exponentials. As before, we have a new integer quantum number defined in exactly the same way as was found using our earlier approach to explore the 2D rigid rotor. One difference between the m quantum number and earlier examples is that it can be negative. This actually has a simple meaning; a positive m is for a quantum particle rotating clockwise while a negative value is for a particle rotating counterclockwise. If the 2D rigid rotor decides not to rotate at all, then m=0.

The rotational energy is:

$$\frac{\hat{L}_z^2}{2\mathrm{I}}\Psi(\phi) = \frac{-\hbar^2}{2\mathrm{I}}\frac{\partial^2}{\partial\phi^2}\Psi(\phi) = \frac{\hbar^2\mathrm{m}^2}{2\mathrm{I}}\cdot\Psi(\phi)$$

and is exactly the same result derived previously. As usual we should normalize the state(s) via:

$$\int_{0}^{2\pi} N^{2} \cdot e^{-i \cdot m \cdot \varphi} \cdot e^{i \cdot m \cdot \varphi} \, \partial \varphi = N^{2} \cdot \varphi]_{0}^{2\pi} = N^{2} 2\pi = 1$$

which reveals that the proper normalized wavefunction is:

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\mathbf{i} \cdot \mathbf{m} \cdot \phi}$$

There isn't much more to say about this rather simple introduction to rotation, and as such we now move onto a particle that isn't trapped in the x-y plane as discussed below. Before we do so, you should know that you will see the 2D rigid rotor once more when the wavefunctions for the hydrogen atom are calculated. In fact, this is where we get our notion for p_x, p_y and p_z orbitals; these are revealed in Ch. 15.

14.2.3 The 3D rigid rotor. For exploring rotational motion in three dimensions we will create the most simple model possible by stating that a quantum particle rotates with a fixed

radius on a 3D track that has no potential energy. As with the 2D case we first develop the kinetic energy operator. To this end we convert coordinates x, y, $z \rightarrow r$, ϕ , θ step by step beginning with:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta}$$

and then the same for $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$. With these worked out we can then convert the kinetic energy operator into the same using spherical coordinates. Unfortunately, the algebra to do so is extraordinarily tedious and as a result we will simply provide the end result here:

$$\widehat{H} = \frac{-\hbar^2}{2 \cdot \text{mass}} \cdot \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \rightarrow \frac{-\hbar^2}{2I} \cdot \left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)$$

where the moment of inertial is defined as before: $I = mass \cdot r^2$. The above Hamiltonian is usually simplified as: $\hat{H} = \frac{\hat{L}^2}{2I}$, where \hat{L} is the total (3D) orbital angular momentum operator. Regardless of the notation, the Hamiltonian in spherical coordinates appears pretty fearsome and there isn't much we can do about that other than to begin to solve it using the method of separability. First, we assume that the solution has the form:

$$\psi(\phi,\theta) = \psi(\phi)\psi(\theta)$$

This separated wavefunction is applied to the Hamiltonian: $\hat{H} \psi(\phi)\psi(\theta)$:

$$\frac{-\hbar^2}{2I} \cdot \left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)\psi(\phi)\psi(\theta) = E \cdot \psi(\phi)\psi(\theta)$$

Moving the constants to right side makes this look a little easier:

$$\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right)\psi(\phi)\psi(\theta) = \frac{-2\mathbf{I}\cdot\mathbf{E}}{\hbar^2}\cdot\psi(\phi)\psi(\theta)$$

And now we divide out the wavefunction on the left side:

$$\frac{1}{\psi(\phi)\psi(\theta)} \left(\frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right) \psi(\phi)\psi(\theta) = \frac{1}{\psi(\phi)\psi(\theta)} \frac{-2I \cdot E}{\hbar^2} \cdot \psi(\phi)\psi(\theta)$$

If you are slow and methodical you find that the process of solving the above is fairly straightforward. For example, the $\frac{\partial}{\partial \theta}$ derivative captures $\psi(\theta)$ yet allows $\psi(\phi)$ to pass through (and vice versa); after some algebra we see that:



$$\frac{1}{\psi(\phi) \cdot \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \psi(\phi) + \frac{1}{\psi(\theta) \cdot \sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \psi(\theta) = \frac{-2I \cdot E}{\hbar^2}$$

At this point there is a problem with separation because the first part:

$$\frac{1}{\psi(\phi)\cdot\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\psi(\phi)$$

containing mostly ϕ terms but also has a pesky $\frac{1}{\sin^2(\theta)}$ term. To remove the problem we multiply everything by $\sin^2(\theta)$:

$$\frac{1}{\psi(\phi)}\frac{\partial^2}{\partial\phi^2}\psi(\phi) + \frac{\sin(\theta)}{\psi(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) = \frac{-2\mathbf{I}\cdot\mathbf{E}}{\hbar^2}\sin^2(\theta)$$

Now we have a clean separation of ϕ and θ terms into mini-Schrodinger equations, although it is interesting to note that the energy is on the θ side:

$$\left(\frac{1}{\psi(\phi)}\frac{\partial^2}{\partial\phi^2}\psi(\phi)\right) + \left(\frac{\sin(\theta)}{\psi(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2\mathbf{I}\cdot\mathbf{E}}{\hbar^2}\sin^2(\theta)\right) = 0$$

To solve this, we assume that the solution to the ϕ mini-Schrodinger equation (left side) is the same as the 2D rigid rotor that we worked on previously: $\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i \cdot m \cdot \phi}$. As a result:

Example Problem 14.1

Let's verify that $Y_{l=1,m_l=0} = \psi(\theta) = \sqrt{\frac{3}{4\pi}}\cos(\theta) \cdot e^{i\cdot \cdot \cdot \cdot \phi} = \sqrt{\frac{3}{4\pi}}\cos(\theta)$ is an eigenfunction of the

3D rigid rotor Schrodinger equation:

$$\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2\mathbf{I}\cdot\mathbf{E}}{\hbar^2}\sin^2(\theta)\psi(\theta) = \mathbf{m}^2\psi(\theta)$$

Since m=0 the above simplifies to:

$$\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2\mathbf{I}\cdot\mathbf{E}}{\hbar^2}\sin^2(\theta)\cdot\psi(\theta) = 0$$

To solve the problem on the left we apply the derivative: $\frac{\partial}{\partial \theta} \cos(\theta) = -\sin(\theta)$ and insert the

expression for energy $E = l(l+1)\frac{\hbar^2}{2I} = \frac{\hbar^2}{I}$ because l = 1:

$$-\sin(\theta)\frac{\partial}{\partial\theta}\sqrt{\frac{3}{4\pi}}\sin^2(\theta) + 2\sin^2(\theta)\cdot\psi(\theta)$$

Since we know that $\frac{\partial}{\partial \theta} \sin^2(\theta) = 2\sin(\theta)\cos(\theta)$ we find that the left term is:

$$-\sin(\theta)\frac{\partial}{\partial\theta}\sqrt{\frac{3}{4\pi}}\sin^2(\theta) = -2\sin^2(\theta)\left\{\sqrt{\frac{3}{4\pi}}\cos(\theta)\right\} = -2\sin^2(\theta)\cdot\psi(\theta)$$

Putting this altogether:

$$-2\sin^2(\theta) \cdot \psi(\theta) + 2\sin^2(\theta) \cdot \psi(\theta) = 0$$

which is proof that the Y_{1,0} is a valid solution for the 3D Rigid Rotor Hamiltonian.

$$\frac{1}{\psi(\phi)}\frac{\partial^2}{\partial\phi^2}\psi(\phi) = \sqrt{2\pi} \cdot e^{-i \cdot m \cdot \phi} \frac{\partial^2}{\partial\phi^2} \frac{1}{\sqrt{2\pi}} e^{i \cdot m \cdot \phi} = -m^2$$

which when inserted into the full equation above we find that:

$$\frac{\sin(\theta)}{\psi(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2\mathbf{I}\cdot\mathbf{E}}{\hbar^2}\sin^2(\theta) = \mathbf{m}^2$$

One of the most interesting aspects of quantum mechanics is that this differential equation was solved in 1782 by Pierre Simon de Laplace, who was called the "Newton of France" and was one of Napoleon Bonaparte's teachers. The solutions are called the spherical harmonics and are listed in Table 14.1. The wavefunctions are classified by a new quantum number l, which as usual can only have integer values: $l = 0, 1, 2, 3 \dots$ There are 2l + 1 wavefunctions associated with each l quantum number, which are due to the 2D rigid rotor m quantum number that will now be

abbreviated as m_l . They can take on integer values $m_l = l$, (l - 1), ... $0 \dots - l$, and it is important to note that there are 2l + 1 possibilities. The wavefunctions are thus abbreviated as Y_{l,m_l} to designate the *l* and sub- m_l quantum states. Now that we know the wavefunctions we can use the to calculate the total orbital angular momentum using the \hat{L}^2 operator, which returns a function based on the *l* quantum number:

$$\hat{\mathbf{L}}^2 \mathbf{Y}_{l,\mathbf{m}_l} = l(l+1)\hbar^2 \cdot \mathbf{Y}_{l,\mathbf{m}_l}$$

This allows to calculate the energy of the 3D rigid rotor:

$$E = l(l+1)\frac{\hbar^2}{2mr^2} = l(l+1)\frac{\hbar^2}{2l}$$

which are 2l + 1 degenerate as discussed above.

The spherical harmonics are important to a very large number of scientific fields and are often abbreviated as $Y_{l,m_l}(\phi, \theta)$. We will now examine them as a function of the *l* quantum number, which may look surprisingly similar to the wavefunctions you learned about for the hydrogen atom in Freshman chemistry.

14.4 Wavefunctions, the s-state.

Laplace's wavefunctions are probably familiar to most physical chemistry students already. For example, the lowest energy solution l = 0, $m_l = 0$ has the solution:

$$Y_{l=0, m_l=0}(\phi, \theta) = \frac{1}{\sqrt{4\pi}}$$



This lowest energy state is referred to as the s-state and it has no dependence on angle. To **Figure 14.5.** The lowest energy s-state $Y_{0,0}$. plot this wavefunction we will use what is called a "probability isosurface", which is a picture of where all the probabilities $|Y_{l,m_l}(\phi, \theta)|^2$ have a specific value, such as $|Y_{l,m_l}(\phi, \theta)|^2 = 0.95$. When applied to $Y_{0,0}$ we see a sphere as shown in Figure 14.5. What is interesting to note is that, while it is intuitive to describe a particle with a wavefunction as clearly circulating the origin this is in fact not the case as the rotational energy is:

$$E = l(l+1)\frac{\hbar^2}{2I} = 0$$
 J



Figure 14.6. There are three p-states due to the triple degeneracy of l = 1. While the $m_l = 0$ state likely looks like a hydrogen p_z orbital, the $m_l = \pm 1$ states are probably less familiar.

The proper way to see this fact is that the wavefunction has no nodes, which is how quantum mechanics always imparts kinetic energy including rotational.

14.4.1. P- and d-states. Now let's climb the rotational kinetic energy ladder and examine the p-states. There must be three l = 1 wavefunctions given the m_l level degeneracy (m_l = -1,0,1), and they are plotted in Figure 14.6. We expect that we may see hydrogen-like p_z, p_x and p_y states, and in fact the m_l = 0 sure looks like p_z! However, the two m_l = ±1 wavefunctions do not look anything like p_x or p_y!

The reason why you aren't seeing the expected p_x and p_y "dumbbells" is that the spherical harmonics with finite values of the m quantum number have $e^{\pm i \cdot m \cdot \phi}$ terms, which are complex (i.e. it contains real and imaginary numbers). Such functions are travelling waves; however, we would prefer stationary waves if possible. It turns out that we can remove the travelling wave components simply by making linear combinations of the spherical harmonics, which is valid because the sum of two Hamiltonian wavefunctions is still a valid wavefunction.



Figure 14.7. Linear combinations of $m_l = \pm 1$ spherical harmonic wavefunctions return states that appear as the familiar p_x and p_y .

In this endeavor, let's see what happens if we do this: $Y_{1,1} + Y_{1,-1}$, which is an attempt to remove the m_l dependence. Looking up the functions from the table yields:

$$Y_{1,1} + Y_{1,-1} = \sqrt{\frac{3}{8\pi}}\sin(\theta)e^{i\cdot\phi} + \sqrt{\frac{3}{8\pi}}\sin(\theta)e^{-i\cdot\phi}$$

Next, collecting terms and using the identity $e^{-i\cdot\phi} + e^{i\cdot\phi} \sim \cos(\phi)$ yields:

•

 $Y_{1,-1} + Y_{1,1} \sim \sin(\theta) \cos(\varphi)$

If we recall that, for spherical coordinates: $x = \sin(\theta)\cos(\varphi)$, which makes $Y_{1,1} + Y_{1,-1}$ equal to the p_x orbital. Following the same idea we find that the difference of the two spherical harmonics $Y_{1,1} - Y_{1,-1}$ can be simplified using $e^{i\cdot\varphi} - e^{-i\cdot\varphi} \sim \sin(\varphi)$ to:

$$Y_{1,1} - Y_{1,-1} \sim \sin(\theta) \sin(\phi)$$

and since $y = sin(\theta)sin(\phi)$ then $Y_{1,1} + Y_{1,-1}$ is the py orbital. In fact, when we plot the isosurfaces of these functions in Figure 14.7 we see that is indeed the case.

Running through the same arguments for the five l = 2 d-states yields familiar hydrogenlike results as shown in Figure 14.8, and similarly for the seven f states. We will see these functions again when studying the hydrogen atom in the next chapter. Furthermore, the periodic table is arranged based on the *l* quantum number. Hopefully you learned in Freshman chemistry that l = 1 is the main block, l = 2 are for the transition metals and l = 3 are the trans-uranium elements.



Figure 14.8. Hydrogenic d-orbitals are created from linear combinations of spherical harmonics.

14.5. Spin Angular Momentum. You should recall from your many other classes that electrons are "spin one-half" and can either be spin up or spin down. You applied these facts when creating the electron configuration of transition metals in your inorganic chemistry class; an example for the 16-electron tetrahedral compound nickel carbonyl is shown in Figure 14.9.

Why only spin up or down? Because, if the angular momentum of an electron is $l = \frac{1}{2}$, then the allowed m_l values are $+\frac{1}{2}$ and $-\frac{1}{2}$. More important is to understand what spin angular momentum is. While it is tempting to state that the electron is spinning on its axis like the earth, akin to the type of angular motion that was discussed in the previous sections, unfortunately this is not the case. The reason is that there are many other subatomic





Figure 14.9. The spin up / spin down of electron configurations is due to spin angular momentum.

particles that have the same half spin momentum, including the proton, neutron, and quarks. Given that "normal" angular momentum is proportional to mass, and a proton is $\sim 2000 \times$ heavier than an electron, how could they possibly have the exact same spin from classical rotational motion? The conclusion is that spin is a type of angular momentum, but it doesn't originate from the type of rotational motion that we are accumtomed to.

Unfortunately no one really knows what spin angular momentum is other than its existence can be demonstrated by integrating Einstein's theory of relativity with quantum mechanics. As a result, it is considered important to distinguish spin angular momentum from "normal" orbital angular momentum discussed here. To do so, spin angular momentum is designated with "s" as the quantum number (similar to *l* for orbital angular momentum). There is a spin angular momentum operator \hat{S} that, when applied to the spin wavefunction $\psi = \alpha$ or $\psi = \beta$ yields:

$$\hat{S}^2 \alpha = s(s+1)\hbar^2 \cdot \alpha$$

likewise $\hat{S}^2\beta = s(s+1)\hbar^2 \cdot \beta$. Thus, the total angular momentum is $\hbar\sqrt{s(s+1)} = \sqrt{\frac{3}{4}}\hbar$ for either the α or β state. There are sub-m_S states designated with the s_z quantum number, which is known as the "magnetic spin". This name comes about because the magnetic properties of electrons are due to spin, which is the source of the magnetism used in power plant turbine electrical generators. The magnetic spin operator \hat{S}_z has the following properties when applied to the spin α and β wavefunctions:

$$\hat{S}_z \alpha = \frac{1}{2}\hbar \alpha$$
 and $\hat{S}_z \beta = -\frac{1}{2}\hbar \beta$

which allows us to distinguish them. The names "up" for α and "down" for β came about because, if you accelerate an electron in a magnetic field, you will see the electrons either deflect upwards or downwards depending on the magnetic spin quantum number. Spin is also the source of magnetism of protons and neutrons that makes certain elements and isotopes NMR active. This type of nuclear magnetism is however much weaker than the fields created by electrons.

The wavefunctions are orthonormal: $\int \alpha^* \alpha = \int \beta^* \beta = 1$ while $\int \alpha \beta = 0$, which is important when we discuss the hydrogen atom next chapter. At this point you are probably expecting to see some kind of function for the α and β states, maybe a complex exponential or a sine or cosine; however, we don't really know what spin is so there is no mathematical definition for it as a result. What the spin wavefunctions allow us to do is to satisfy the Pauli principle,

which you may recall is why you fill atomic orbitals with spin up electrons first and then spin down. The Pauli principle states that no two electrons can be in the same state at the same time, and the fact that electrons have spin is why you can have two occupy the same atomic orbital but not violate that rule at the same time.



Figure 14.10. The angular momentum vector is like the axel of a wheel that follows the right-hand rule.

14.6. Angular Momentum Operators. Angular momentum is defined as:

$$\vec{L} = \vec{r} \times \vec{p}$$

where \vec{r} is the position of the particle, \vec{p} is momentum and reveals the direction of motion, and \vec{L} is the angular momentum vector. As everything is a vector the angular momentum can be decomposed into x, y and z components, i.e. $\vec{L} = \hat{L}_x + \hat{L}_y + \hat{L}_z$ (this will be important later). While understanding angular momentum can be intimidating, if you look at Figure 14.10 you see that it is basically the axel of a wheel as defined by the rotation of a particle. As shown in the figure the only nuance is that the right-hand rule dictates whether the vector is up or down depending on the direction that the particle is rotating. The relationship $\vec{L} = \vec{r} \times \vec{p}$ was part of your learning of classical mechanics; likely you learned about it Physics I or even in high school. To create a

quantum mechanical operator for angular momentum, we simply insert \hat{r} as the position operator and $\hat{p} = \frac{\hbar}{i} \left\{ \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right\}$ as the momentum operator into $r \times p$. The cross product simplifies into relationships for angular momentum as projected into x, y and z as:

$$\hat{L}_{x} = \frac{\hbar}{i} \Big\{ y \cdot \frac{\partial}{\partial z} - z \cdot \frac{\partial}{\partial y} \Big\}, \ \hat{L}_{y} = \frac{\hbar}{i} \Big\{ z \cdot \frac{\partial}{\partial x} - x \cdot \frac{\partial}{\partial z} \Big\}, \text{ and } \ \hat{L}_{z} = \frac{\hbar}{i} \Big\{ x \cdot \frac{\partial}{\partial y} - y \cdot \frac{\partial}{\partial x} \Big\}$$

Next, we insert x, y, and z in spherical coordinates. You may recall we already showed how to covert $\frac{\partial}{\partial x}$ etc.: $\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta}$ and likewise: $\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \varphi}{\partial y}\frac{\partial}{\partial \varphi} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta}$. These simplify to:

$$\frac{\partial}{\partial x} = \sin(\theta)\cos(\phi)\frac{\partial}{\partial r} + \frac{\cos(\theta)\cos(\phi)}{r}\frac{\partial}{\partial \theta} - \frac{\sin(\phi)}{r \cdot \sin(\theta)}\frac{\partial}{\partial \phi}$$

and:

$$\frac{\partial}{\partial y} = \sin(\theta)\sin(\phi)\frac{\partial}{\partial r} + \frac{\cos(\theta)\sin(\phi)}{r}\frac{\partial}{\partial \theta} + \frac{\cos(\phi)}{r \cdot \sin(\theta)}\frac{\partial}{\partial \phi}$$

Hence the angular momentum in the z direction is: $\hat{L}_z = \frac{\hbar}{i} \left\{ x \cdot \frac{\partial}{\partial y} - y \cdot \frac{\partial}{\partial x} \right\} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial y} \cdot \frac{\partial}{\partial y} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial y} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} = \frac{\hbar}{i} \cdot \frac{\partial}{\partial x} + \frac{\hbar}{i} \cdot \frac{\partial}{$

$$\{r \cdot \sin(\theta)\cos(\varphi) \cdot \sin(\theta)\sin(\varphi)\frac{\partial}{\partial r} + r \cdot \sin(\theta)\cos(\varphi) \cdot \frac{\cos(\theta)\sin(\varphi)}{r}\frac{\partial}{\partial \theta} + r \cdot \sin(\theta)\cos(\varphi) \cdot \frac{\cos(\varphi)}{r \cdot \sin(\theta)}\frac{\partial}{\partial \varphi} - r \cdot \sin(\theta)\sin(\varphi) \cdot \frac{\cos(\theta)\cos(\varphi)}{r}\frac{\partial}{\partial \theta} + r \cdot \sin(\theta)\sin(\varphi) \cdot \frac{\sin(\varphi)}{r \cdot \sin(\theta)}\frac{\partial}{\partial \varphi} \}$$

While this looks overwhelming, note how the first two terms on each line cancel, leaving:

$$\hat{L}_{z} = \frac{\hbar}{i} \cdot \left\{ r \cdot \sin(\theta) \cos(\varphi) \cdot \frac{\cos(\varphi)}{r \cdot \sin(\theta)} + r \cdot \sin(\theta) \sin(\varphi) \cdot \frac{\sin(\varphi)}{r \cdot \sin(\theta)} \right\} \frac{\partial}{\partial \varphi} = \frac{\hbar}{i} \cdot \left\{ \cos^{2}(\varphi) + \sin^{2}(\varphi) \right\} \frac{\partial}{\partial \varphi} = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$$

Very simple! Along the same lines you find that:

$$\hat{L}_{x} = \frac{\hbar}{i} \left(-\cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi} - \sin(\phi)\frac{\partial}{\partial\theta} \right)$$

and:

$$\hat{L}_{y} = \frac{\hbar}{i} \left(-\cot(\theta)\sin(\phi)\frac{\partial}{\partial\phi} + \cos(\phi)\frac{\partial}{\partial\theta} \right)$$

The angular kinetic energy can be derived from:

$$\frac{\hat{L}^2}{2I} = \frac{\left(\hat{L}_x + \hat{L}_y + \hat{L}_z\right)^2}{2I} = \frac{-\hbar^2}{2I} \left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right)$$



Figure 14.11. The uncertainty principle means that the projection of the angular momentum vector onto the x-y plane is unknown. As a result, the exact motion of the quantum rotor is ill-defined. On the right is a common representation of the angular momentum.

which is exactly the same as shown before.

Overall is it unfortunate that all these operators are a bit complicated, but they are important because they reveal the existence of another uncertainty principle. You may recall from Ch. 13 section that, for two operators \widehat{A} and \widehat{B} if the following is true:

$$\left[\widehat{A},\widehat{B}\right] = \widehat{A} \cdot \widehat{B} - \widehat{B} \cdot \widehat{A} \neq 0$$

(the operators don't commute), then the two operators don't share the same eigenvectors. In other words, if Φ is an eigenvector of \hat{A} , then $\hat{A}\Phi = \omega\Phi$ where ω is just a constant such as \hbar or 0. However, the eigenvalue equation for won't work for the other operator: $\hat{B}\Phi \neq \omega\Phi$. Hence, whatever observable that \hat{B} describes, you can't know what that is for the state described by Φ . For example, in the previous chapter it was shown that $[\hat{x}, \hat{p}] = -i\hbar$ for operators \hat{x} and \hat{p} , so you can't know where something is and where it is going fully at the same time.

Returning to our rotational wavefunctions (the spherical harmonics), these have to be eigenfunctions of the \hat{L}^2 operator because they were solved to be the wavefunctions of rotational kinetic energy which is just \hat{L}^2 times a constant. Since it is always true that an operator commutes with its square, i.e. $[\hat{L}^2, \hat{L}] = \hat{L}^2 \hat{L} - \hat{L}\hat{L}^2 = \hat{L}^3 - \hat{L}^3 = 0$, then the spherical harmonics are all eigenfunctions of \hat{L} . If you apply \hat{L}_z , you see that all of the spherical harmonics are

eigenfunctions of \hat{L}_z too. Since \hat{L} and \hat{L}_z share a common set of eigenfunctions, then it must be true that $[\hat{L}, \hat{L}_z] = 0$. However, using the operators above you can show that: $[\hat{L}, \hat{L}_x] \neq 0$, $[\hat{L}, \hat{L}_y] \neq 0$, $[\hat{L}_z, \hat{L}_x] \neq 0$, and finally $[\hat{L}_z, \hat{L}_y] \neq 0$. Hence, when describing rotation we can know the total angular



Figure 14.12. The uncertainty principle as applied to various spin systems. The l = 1/2 system describes the spin of electrons.

momentum $\langle \hat{L} \rangle$ (the length of the "axel" in Figure 14.9) and the projection onto the z-axis $\langle \hat{L}_z \rangle$ (the tilt of the angular momentum vector), but we don't know the projection of angular momentum onto the x or y axes, i.e. $\langle \hat{L}_x \rangle$ and $\langle \hat{L}_y \rangle$. This is represented in Figure 14.11, where the motion of the quantum particle is displaced from the origin of its angular momentum vector so you can more easily see the rotation. What it means for $\langle \hat{L}_x \rangle$ and $\langle \hat{L}_y \rangle$ to be unknown is that the φ angle of the angular momentum vector is not defined. As a result, the angular momentum vector $\langle \hat{L} \rangle$ can point anywhere in the x-y plane when $m_l = 0$. If $m_l = 1$, the angular momentum vector can be anywhere on the surface of a cone as shown to the right of Figure 14.11. The cone representation on the right also includes $m_l = -1$; examples for $l = \frac{1}{2}$ and l = 2 are also provided in Figure 14.12 where again we emphasize that the L vectors lie on the surface of the cones, yet they describe rotation about those vectors like a wheel about its axel.

14.7. Addition of Angular Momentum and Term Symbols. One of the more complicated things about electronic structure is the addition of spin and "normal" orbital angular momenta. This is important because the total energy is proportional to the square of the total angular momentum. Thus far we have already introduced \hat{L} and \hat{S} operators and their associated *l* and *s* quantum numbers as defined previously. Now we define the total angular momentum operator \hat{J} :

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

A pictorial representation is shown in Figure 14.13. The total angular momentum operator returns eigenvalues via:

$$\hat{\mathbf{J}}\boldsymbol{\psi} = \hbar\sqrt{\mathbf{j}(j+1)}\cdot\boldsymbol{\psi}$$

where j is the quantum number for the total angular momentum, and likewise there are sub-total angular momentum states determined by the operator \hat{J}_z that has eigenvalues j_z . Similar to the m_l quantum numbers, the allowed values for j_z are:

The wavefunctions of the total angular momentum operators \hat{J} and \hat{J}_z are sums of the individual orbital×spin states.

An atom with both orbital (l) and spin (s) momentum angular momenta is like a gyroscope that has another gyroscope on top of it. While this sounds complicated, to sum the momentum one simply uses vector addition. However, there is a problem when it comes to quantum angular momenta because the uncertainty principle dictates that the x, y and z components of either the orbital l or spin s momentum vectors are not fully known. Furthermore, we aren't so concerned with \hat{J} , rather \hat{J}^2 as the square of the momentum gives us the energy. Fortunately, the mathematics of connecting the l orbital and s spin together to form j have been established; however this is best left to graduate-level texts on quantum mechanics. Here we will show the end result, which is that the final

j quantum number results from either constructive (addition) or destructive (subtraction) of the l and s angular momenta, which when applied to the quantum numbers results in the following relationship:

 $j = l + s, l + s - 1 \dots |l - s|$

Take for example a hydrogen atom in a $2p^1$ excited state. Here, we have to add the spin angular momentum $s = \frac{1}{2}$ with the orbital momentum l = 1. As a result, we can see that there are two possible j states:



Figure 14.13. Addition of the spin and orbital angular momentum of a 2p electron into a total angular momentum j=3/2 state.



Figure 14.14. A. A hydrogen atom with a $2p^1$ configuration has a single electron in one of possibley three p orbitals. As a result there are six possible states. **B.** Addition of the l=1 and s=1/2 angular momentum creates six possible j states.

 $j = l + s = 1 + \frac{1}{2} = \frac{3}{2}$ and $j = l - s = 1 - \frac{1}{2} = \frac{1}{2}$. We can express this information in a quantity called a term symbol: ^{2S+1}L_j; in this example there are two possible states labeled ²P_{3/2} and ²P_{1/2}. It is important to note that there are six possible states for the 2p¹ electron configuration because there are two possible spins (up or down) that can go into one of three orbitals (p_x, p_y and p_z); these are depicted in Figure 14.14. As a result, there must also be six j states, and we can find them once we consider the sub-total angular momentum states j_z.

For $j = \frac{3}{2}$ there are four sub-states $(j_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2})$, while $j = \frac{1}{2}$ has two sub-states $(j_z = \frac{1}{2}, -\frac{1}{2})$ for a total of six. It is important that we don't "lose" states when adding them together! These states are shown to the right of Figure 14.14, where you can see that the different j states are linear combinations of the singularly filled p_x , p_y and p_z orbitals. Last, we note that these states are degenerate, however there is an effect called spin orbit coupling that energetically favors the ${}^2P_{1/2}$; this is explained in the next chapter.

You might be curious about the 2S+1 part of the term symbol. This is called the multiplicity, and to explain it let's do another example of the addition of angular momentum just for spin. We run into such a problem for the excited state of helium with an electron configuration of $1s^{1}2s^{1}$ as shown in Figure 14.15. As there is no *l* angular momentum, we are simply adding the two s quantum numbers, s_{1} and s_{2} to the total angular momentum that we call



Figure 14.15. Two electrons in s-states with no orbital angular momentum add to form three S=1 (triplet) and one S=0 (singlet) spin states. While nominally degenerate, the triplet state is preferred because of exchange energy, see Ch. 15.

 s_{tot} . Following the addition rules reveals two possibilities, one of which is: $s_{tot} = s_1 + s_2 = \frac{1}{2} + \frac{1}{2} = 1$. This configuration must have a total of three sub- s_{tot} states which are:

$$s_{tot}, s_{tot} - 1, -s_{tot} = 1, 0, -1$$

You may have figured out already based on the diagram that these are the triplet states, where $\uparrow\uparrow$ is for the +1 sub-s_{tot} state, $\downarrow\downarrow$ is for -1 and $\uparrow\downarrow +\downarrow\uparrow$ is for 0. Likewise there is the singlet state with a s_{tot} = s₁ - s₂ = 0, which has the associated spin wavefunction $\uparrow\downarrow -\downarrow\uparrow$. The singlet state cannot be degenerate. Consequently, the 2S+1 part of a term symbol is meant to convey the degeneracy expected due to spin angular momentum.

Problems: Numerical

1. a. Shown here are the p-orbitals of benzene's electrons. The occupied HOMO looks like a 2D rigid rotor m=1 wavefunction, whereas the LUMO is like m=2. If this transition is responsible for the absorption of UV light, what wavelength of photon in nanometers will the electron absorb? The energy of a 2D rigid rotor is $\frac{\hbar^2 m^2}{2I}$, where I = m_er². The ring radius r can be approximated by the



C=C distance in benzene, which is 1.39 Å, and m_e is the mass of an electron (9.109 × 10⁻³¹ kg). (7 pts)

Hint: to do these conversions I usually remember the following conversion factors:

 $1 \text{ J} = 6.242 \times 10^{18} \text{ eV}$ and the wavelength in nanometers from eV is: $nm = \frac{1240}{eV}$ (i.e. divide 1240 by the energy in eV to get the the absorption in nanometers).

b. The absorption spectrum of pyrene is as shown here. It seems that the absorption is at ~340 nm. Can you calculate the radius of pyrene and show that it is greater than benzene (obviously)?
(7 pts)



Wavelength (nm)

35000

30000 25000

20000

15000 10000 5000

-cm-1

E (L-mol-

Problems: Theoretical or Explain in Words

1. Did I mention that people who are good at math are really really rich?

We will practice with differential equations of more than one variable. The purpose of this exercise is to convert the eigenvalue equation into a separable form composed of "mini-Schrodinger" differential equations that are solved separately. We will also see that the eigenvalue may become a part of only one of these mini-differential equations.

Let's say that we must solve the following differential equation called \hat{H} :

$$\widehat{H} = \frac{1}{x} \frac{\partial^2}{\partial y^2} + \frac{1}{x} \frac{\partial}{\partial x}$$

a. Let's see if the equation is separable. To do first apply a solution ψ to the right: $\hat{H}\psi = E\psi$, and then divide by the same on the left $\frac{1}{\mu}\hat{H}\psi = \frac{1}{\mu}E\psi$. Since we assume $\psi = \psi(x)\psi(y)$ the result is:

$$\frac{1}{\psi(x)\psi(y)}\widehat{H}\psi(x)\psi(y) = \frac{1}{\psi(x)\psi(y)}E\psi(x)\psi(y)$$

where E is the eigenvalue. Please do so as above and simplify whenever possible. *Hint:* here is an example of simplification: $\frac{1}{f(x)f(y)f(z)}\frac{\partial}{\partial x}\frac{\partial}{\partial y}f(x)f(y)f(z) = \frac{1}{f(x)f(y)}\frac{\partial}{\partial x}f(x)\frac{\partial}{\partial y}f(y)$ (5 pts)

b. Now to demonstrate separability you have to do some algebra on your answer from pt. a to make it look like:

$$\{terms with y\} + \{terms with x\} = 0$$

The problem with the above is that your answer form pt. a has this term: $\frac{1}{\psi(y)} \frac{1}{x} \frac{\partial^2}{\partial y^2} \psi(y)$, hence both "x" and "y" are in this same expression. This isn't allowed, please use some very simple algebra to remove "x" from this "y" term and tell us the result. Also, the eigenvalue "E" has now become part of one of the terms- which is it (the "x" or "y")? (2 pts)

c. Suppose that you somehow know that $\psi(y) = e^{iq \cdot y}$, where q is an integer. Please simplify the expression below by inserting $\psi(y) = e^{iq \cdot y}$: (3 pts)

$$\frac{1}{\psi(y)}\frac{\partial^2}{\partial y^2}\psi(y) + \frac{1}{\psi(x)}\frac{\partial}{\partial x}\psi(x) - \mathbf{E}\cdot \mathbf{x} = 0$$

d. Now we often have to solve the mini-Schrodinger "x" equation by inserting values for q. Let's say that, if q=0 then $\psi(x) = e^{x^2}$. Can you solve the equation from your answer to pt. c for the eigenvalue "E"? *Hint*: E=2. (5 pts) 2. In 2-D, the Hamiltonian of the free wave (no potential energy) is:

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

a. Show that writing the total wavefunction as: $\Psi(x, y) = \Psi(x) + \Psi(y)$ is incorrect because it is not an eigenfunction of the Hamiltonian, i.e.:

<u>....</u>

$$H\Psi(x, y) \neq E \cdot \Psi(x, y)$$
where $E = E_x + E_y$. You can assume that: $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) = E_x \cdot \Psi(x)$ and: $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \Psi(y) = E_y \cdot \Psi(y)$ and $E_x \neq E_y$. Of course $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(y) = 0$, etc. (5 pts)

b. Now you can show that a proper wavefunction has the form:

$$\Psi(\mathbf{x},\mathbf{y}) = \Psi(\mathbf{x}) \cdot \Psi(\mathbf{y})$$

because then $\widehat{H}\Psi(x, y) = E \cdot \Psi(x, y)$ where $E = E_x + E_y$.

3. a. Let's say that we have an atom with bonds in both the x- and y-directions. The Hamiltonian is:

$$\frac{-\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right\} + \frac{1}{2} k_f x^2 + \frac{1}{2} k_f y^2$$

Given that the 1-D normalized ground state wavefunction is:

$$\Psi(\mathbf{x}) = \left(\frac{1}{\pi\alpha}\right)^{\frac{1}{4}} \mathrm{e}^{\frac{-\mathbf{x}^2}{2\alpha^2}}$$

please use your instincts to write down what you think the 2D wavefunction is. Hint: You don't have to derive anything- you should be able to guess a proper wavefunction with the information provided. (4 pts)

b. I have taken a vibrational potential in the x-direction and added a y dimension. The y potential energy is flat but becomes infinite at y=0 and y=L as shown here. What do you expect the ground state wavefunction to be? *Hint:* You might have to look up one of the normalized wavefunctions we studied earlier.



Kr (

4. Here we will demonstrate that a 2D rigid rotor ("electron-on-a-string") can absorb light.

a. The 2D rigid rotor wavefunctions are: $\Psi = \frac{1}{\sqrt{2\pi}} e^{i \cdot m\varphi}$. What is the angular momentum change going from the m=1 state to the m=2 state if the rigid rotor absorbs light? Hint, the angular momentum operator is $\hat{j}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$. (5 pts)

(5 pts)

DRRO

b. The angular momentum of light is \hbar , so do you think a 2D rigid rotor can absorb light? (2 pts)

Answer: a. First, calculate the angular momentum of each state. For the m=2:

$$\frac{\hbar}{i}\frac{\partial}{\partial\varphi}\frac{1}{\sqrt{2\pi}}e^{i\cdot 2\varphi} = \frac{\hbar}{i}2i\cdot\frac{1}{\sqrt{2\pi}}e^{i\cdot 2\varphi} = 2\hbar\frac{1}{\sqrt{2\pi}}e^{i\cdot 2\varphi}$$

Therefore the angular momentum of the m=2 state is $2\hbar$. Likewise the angular momentum of the m=1 state is evaluated from: $\frac{\hbar}{i}\frac{\partial}{\partial\phi}\frac{1}{\sqrt{2\pi}}e^{i\phi} = \frac{\hbar}{i}i\cdot\frac{1}{\sqrt{2\pi}}e^{i\phi} = \hbar\frac{1}{\sqrt{2\pi}}e^{i\phi}$, and is thus \hbar .

As a result, the gain in angular momentum is $2\hbar - \hbar = \hbar$.

b. The angular momentum of light is conserved by the transition of the rigid rotor so yes the 2D rigid rotor can absorb light.

5. Now that we are working in more than one dimension, you should know that the flux operator is actually:

$$\frac{1}{2\mathrm{mi}}(\psi^*\nabla\psi-\psi\nabla\psi^*)$$

The ∇ (del) operator in cylindrical coordinates is: $\nabla = \frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial \varphi} + \frac{\partial}{\partial z}$.

a. First simplify the flux operator given that the 2D rigid rotor is not moving in r or z. (3 pts)

b. So, what is the flux of the 2D rigid rotor given $\psi = e^{i\mathbf{m}\cdot\boldsymbol{\phi}}$? (7 pts)

6. The fact that the flux isn't 0 means that the 2D rigid rotor particle with $\psi = e^{i \cdot \Phi}$ is moving, as in the previous problem. However, would the flux be for $\psi = e^{i \cdot \Phi} + e^{-i \cdot \Phi}$? This question is rather difficult, so we will break it down into parts.

a. Please evaluate
$$\psi^* \frac{\partial}{\partial \phi} \psi = (e^{-i \cdot \phi} + e^{i \cdot \phi}) \frac{\partial}{\partial \phi} (e^{i \cdot \phi} + e^{-i \cdot \phi})$$
 (5 pts)

b. Next evaluate
$$\psi \frac{\partial}{\partial \phi} \psi^* = (e^{i \cdot \phi} + e^{-i \cdot \phi}) \frac{\partial}{\partial \phi} (e^{-i \cdot \phi} + e^{i \cdot \phi})$$
 (5 pts)

c. Last, evaluate
$$\frac{1}{2\text{mir}} \left(\psi^* \frac{\partial}{\partial \phi} \psi - \psi \frac{\partial}{\partial \phi} \psi^* \right) = \frac{1}{2\text{mir}} (\text{pt. a} - \text{pt. b})$$
 (2 **pts**)

7. To solve the 3-D Hamiltonian you must show that the radial and angular wavefunctions are separable: $\Psi(\mathbf{r}, \theta, \varphi) = \Psi(\mathbf{r}) \cdot \Psi(\theta) \cdot \Psi(\varphi)$ which you do by demonstrating that the differential equation: $\frac{\partial^2}{\partial \mathbf{r}^2} + \frac{2}{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \frac{1}{\mathbf{r}^2}\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin^2(\theta)}\frac{\partial}{\partial \varphi^2}\right)$ can be separated into two smaller ones. What does that even mean? We will explain by first simplifying the equation above as:

$$\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\widehat{\Lambda}$$

where $\widehat{\Lambda}$ is an operator that has all the angles (θ, φ) in it. Next, we act on the wavefunction on the right and divide it out on the left like: $\frac{1}{\Psi} \cdot \widehat{\Theta} \cdot \Psi = \frac{1}{\Psi} \cdot E \cdot \Psi = E$

$$\frac{1}{\Psi(\mathbf{r})\cdot\Psi(\theta)\cdot\Psi(\varphi)}\left(\frac{\partial^2}{\partial \mathbf{r}^2} + \frac{2}{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \frac{1}{\mathbf{r}^2}\widehat{\Lambda}\right)\cdot\Psi(\mathbf{r})\cdot\Psi(\theta)\cdot\Psi(\varphi) = \mathbf{E}$$

a. Use the following notation: $\frac{\partial^2}{\partial r^2} \Psi(r) = \Psi''(r)$ and $\frac{\partial}{\partial r} \Psi(r) = \Psi'(r)$, show that the above can be simplified into:

$$\frac{\Psi''(r)}{\Psi(r)} + \frac{2 \cdot \Psi'(r)}{r \cdot \Psi(r)} + \frac{1}{r^2 \cdot \Psi(\theta) \cdot \Psi(\phi)} \widehat{\Lambda} \cdot \Psi(\theta) \cdot \Psi(\phi) = E$$

Hint: This is easier than it looks- just look at the number of points for this question!

(6 pts)

b. Now the equation above is **almost** separable, except that the 3rd term:

$$\frac{1}{r^2 \cdot \Psi(\theta) \cdot \Psi(\phi)} \widehat{\Lambda} \cdot \Psi(\theta) \cdot \Psi(\phi)$$

has both angles (θ, ϕ) and an $\frac{1}{r^2}$ term in it. Can you show that the equation can be separated by multiplying by r² and do some algebra to yield:

$$r^{2}\frac{\Psi''(r)}{\Psi(r)} + 2r\frac{\Psi'(r)}{\Psi(r)} + \frac{1}{\Psi(\theta)\cdot\Psi(\varphi)}\widehat{\Lambda}\cdot\Psi(\theta)\cdot\Psi(\varphi) = E\cdot r^{2}$$

Hint: Like pt. a this is easier than it looks.

8. Time for some operator practice. Please show that, if you apply a 2p wavefunction:

$$\psi = \sin(\theta) \cdot e^{i\phi}$$

to the 3D rigid rotor Hamiltonian:

$$\frac{-\hbar^2}{2I} \left\{ \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right\} \Psi = \mathbf{E} \cdot \Psi$$

we should derive:

$$\frac{\hbar^2}{2I}l(l+1)\Psi = \frac{\hbar^2}{I}\cdot\sin(\theta)\cdot\mathrm{e}^{\mathrm{i}\varphi}$$

since l = 1 for a p state. Hence, the energy of this wavefunction is $\frac{\hbar^2}{l}$. (10 pts)

Hint: Let's just leave the constants out of the derivation first, leaving you to solve:

$$\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\sin(\theta)\cdot e^{i\phi} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\cdot e^{i\phi}$$

(4 pts)

Once you power through this you can multiply the results by $\frac{-\hbar^2}{2I}$. Here is an identity you need: $\frac{(1-\cos^2(\theta))}{\sin(\theta)} = \sin(\theta)$.

9. Time for some operator practice. Please show that, if you apply a 2p wavefunction:

$$\psi = \sin(\theta) \cdot e^{-i\phi}$$

to the 3D rigid rotor Hamiltonian:

$$\frac{-\hbar^2}{2I} \left\{ \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right\} \Psi = \mathbf{E} \cdot \Psi$$

you should derive an energy of:

$$\mathbf{E} \cdot \Psi = \frac{\hbar^2}{2\mathbf{I}} l(l+1) \cdot \Psi = \frac{\hbar^2}{\mathbf{I}} \cdot \sin(\theta) \cdot \mathrm{e}^{-\mathrm{i}\phi}$$

since l = 1 for a p state. Hence, the energy of this wavefunction is $\frac{\hbar^2}{1}$.

Hint: Let's just leave the constants out of the derivation first, leaving you to solve:

$$\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\sin(\theta)\cdot e^{-i\phi} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\cdot e^{-i\phi}$$

Once you power through this you can multiply the results by $\frac{-\hbar^2}{2l}$. Here is an identity you need: $\frac{(1-\cos^2(\theta))}{\sin(\theta)} = \sin(\theta)$.

10. a. 3D Integrals! The ground state angular wavefunction of the 2pz orbital is:

$$\psi_{2p_z}(\theta, \phi) = \frac{\sqrt{3}}{2\sqrt{\pi}}\cos(\theta)$$

Can you integrate it to show that it is normalized: $\int_{0}^{2\pi} \int_{0}^{\pi} |\psi_{2p_{z}}(\theta, \phi)|^{2} \partial\theta \, \partial\phi = 1?$ (4 pts) *Hint:* it won't work.

b. The ground state angular wavefunction of the $2p_x$ orbital is:

$$\psi_{2p_{\chi}}(\theta, \phi) = \frac{\sqrt{3}}{2\sqrt{\pi}}\sin(\theta)\cos(\phi)$$

Can you integrate it to show that it is normalized: $\int_{0}^{2\pi} \int_{0}^{\pi} |\psi_{2p_{x}}(\theta, \phi)|^{2} \partial\theta \, \partial\phi = 1?$ (4 pts) *Hint:* it still won't work.

c. Now repeat your effort from pt. a to show that: $\int_0^{2\pi} \int_0^{\pi} |\psi_{2p_z}(\theta, \phi)|^2 \sin(\theta) \, \partial\theta \, \partial\phi$ (5 pts)

d. Now repeat your effort from pt. b to show that $\int_0^{2\pi} \int_0^{\pi} |\psi_{2p_x}(\theta, \phi)|^2 \sin(\theta) \,\partial\theta \,\partial\phi$ (5 pts)

(10 pts)

11. a. 3D Integrals! The ground state 1s radial wavefunction of the hydrogen atom is:

$$\psi(\mathbf{r}) = \frac{1}{\pi^{1/2} (a_0)^{3/2}} e^{-\mathbf{r}/a_0}$$

Can you integrate the wavefunction to show that it is normalized, i.e. $\int_0^\infty |\psi(r)|^2 \, \partial r = 1$? *Hint:* it won't work.

(5 pts)

b. Try to repeat your effort from pt. a to show that $\int_0^\infty |\psi(\mathbf{r})|^2 4\pi \mathbf{r}^2 \, \partial \mathbf{r} = 1$ (5 pts)

12. Can you propose why, in questions 1 and 2, the addition of $4\pi r^2 \sin(\theta)$ resulted in the wavefunctions appearing to be properly normalized? (5 pts)

Answer: This factor is a Jacobian, and it is necessary to use it in 3D integrals.

13. In class it was discussed how the p_x and p_y orbitals come about from addition or subtraction of the m=±1 spherical harmonics. Now let's do the d-orbitals. Table 1 lists the spherical harmonic (3D rigid rotor wavefunctions). Can you fill out Table 2 with the proper descriptions of d-orbital states as well as identifying them?

Hint: $x = r \cdot \cos(\phi) \sin(\theta)$, $y = r \cdot \sin(\phi) \sin(\theta)$, and $z = r \cdot \cos(\theta)$.

Table 1:

Y _{1=2,m=0}	$3 \cdot \cos^2(\theta) - 1$
$Y_{1=2,m=1}$	$\cos(\theta) \cdot \sin(\theta) \cdot e^{i\phi}$
Y _{1=2,m=-1}	$\cos(\theta) \cdot \sin(\theta) \cdot e^{-i\phi}$
Y _{1=2,m=2}	$\sin^2(\theta) \cdot e^{2i\phi}$
Y _{1=2,m=-2}	$\sin^2(\theta) \cdot e^{-2i\phi}$

Table 2:

(8 pts)

Ψ	result	d-function
$r^2 \times Y_{l=2,m=0}$	а.	а.
$r^2 \times (Y_{l=2,m=2} + Y_{l=2,m=-2})$	$r^2 \cdot sin^2(\theta) (cos^2(\phi) - sin^2(\phi))$	x ² -y ²
$r^2 \times (Y_{1=2,m=2} - Y_{1=2,m=-2})$	b.	b.
$r^2 \times (Y_{l=2,m=1} + Y_{l=2,m=-1})$	с.	с.
$r^2 \times (Y_{l=2,m=1} - Y_{l=2,m=-1})$	d.	d.

Double Hint: sin(2x) = 2sin(x) cos(x).