Physics 4261: Lectures for week 2

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2.1 Schrödinger's equation (Foot 2.1)

The Schrödinger equation is generally written

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi = E\psi.$$

For a problem in spherical coordinates, we typically write it as

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

Now let's plug the separated form $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ into the beast, dividing out by ψ as we go:

$$-\frac{\hbar^2}{2mr^2}\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}\psi + V(r) = E.$$

Now we have gotten all of the angular dependence into a few terms which have to be constants, since the sum has to work for all values of r,θ,ϕ. Then we recover

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}Y = bY,$$

for some constant b. Let us continue to use separation of variables for the remaining variables θ and ϕ, $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$. The first equation gives

$$\frac{\partial^2\Phi}{\partial\phi^2} = m^2\Phi,$$

where m is another constant I made up. Therefore the solutions are exponentials, $\Phi = e^{im\phi}$. I wrote this suggestively, because in order to satisfy the single-valuedness, we need m to be an integer. Ok, great, now we can work on θ,

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{m^2}{\sin^2\theta}\right\}\Theta = b\Theta.$$

Now, from here, you can note that substituting $x = \cos\theta$ will simplify this to the so-called *general Legendre equation* for which we can look up the solutions. Often, in simple cases when separation of variables works we will be confronted with some ODE at the end of the day. Whenever this happens, if we get stuck, we just go find some big table of functions because someone has already solved it. But here, there are actually some tricky ways of solving this equation using angular momentum operators, and that's important because if we understand angular momentum algebras, then we will have a much easier time when it comes to spin and related phenomena.

2.2 Angular momentum operators (Foot 2.1.1)

A tremendous amount can be accomplished on the angular portion of the Schrödinger equation using angular momentum operators. In spherical coordinates, the position and momentum operators can be written,

$$\hat{\mathbf{r}} = \begin{pmatrix} r \\ 0 \\ 0 \end{pmatrix}_{\text{Sph}}, \qquad \hat{\mathbf{p}} = -i\hbar\nabla = -i\hbar \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r}\frac{\partial}{\partial \theta} \\ \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi} \end{pmatrix}_{\text{Sph}},$$

with the subscript denoting spherical coordinates, and we have used the form of the ∇ operator suitable for the gradient. Thus the angular momentum operator is then

$$\begin{aligned} \hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} &= -i\hbar \begin{pmatrix} 0 \\ \frac{-1}{\sin\theta}\frac{\partial}{\partial \phi} \\ \frac{\partial}{\partial \theta} \end{pmatrix}_{\text{Sph}}, \\ &= -i\hbar \begin{pmatrix} -\cot\theta\cos\phi\frac{\partial}{\partial \phi} - \sin\phi\frac{\partial}{\partial \theta} \\ -\cot\theta\sin\phi\frac{\partial}{\partial \phi} + \cos\phi\frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{pmatrix}_{\text{xyz}}. \end{aligned}$$

It can be seen that the angular momentum squared is equal to the angular portion of the Schrödinger equation. Furthermore, the following commutation relations exist:

$$\begin{aligned} [\hat{l}_z, \hat{l}_x] &= i\hbar\hat{l}_y \text{ plus cyclic permutations} \\ [\hat{\mathbf{l}}^2, \hat{l}_i] &= 0, i = x, y, z. \end{aligned}$$

The real fun comes from introducing the operators

$$\begin{aligned} \hat{l}_+ &= \hat{l}_x + i\hat{l}_y \\ \hat{l}_- &= \hat{l}_x - i\hat{l}_y. \end{aligned}$$

As these operators are linear in $\hat{l}_x$ and $\hat{l}_y$ they commute with $\hat{\mathbf{l}}^2$. We call $\hat{l}_+$ the raising operator due to the following property as it acts on eigenstates of $\hat{l}_z$, which I denote by $|m\rangle$:

$$\hat{l}_z\left(\hat{l}_+|m\rangle\right) = \hat{l}_+\hat{l}_z|m\rangle + \hat{l}_+|m\rangle = (m+1)\left(\hat{l}_+|m\rangle\right).$$

So the effect of the raising operator is to move an eigenstate with eigenvalue m to one with eigenvalue $m+1$. It can be seen that the lowering operator moves to eigenvalue $m-1$ instead. It is also worth calculating the normalization factor

$$\langle m|\hat{l}_-\hat{l}_+|m\rangle = \langle m|\hat{\mathbf{l}}^2 - \hat{l}_z^2 - \hat{l}_z|m\rangle = \langle\hat{\mathbf{l}}^2\rangle - m(m+1).$$

Similarly for the lowering operator

$$\langle m|\hat{l}_-\hat{l}_+|m\rangle = \langle\hat{\mathbf{l}}^2\rangle - m(m-1).$$

Now we can know something about the possible eigenvalues of $\hat{l}_z$. You see, if we start at some random value of m, we can apply the raising (or lowering) operator repeatedly, until we have an eigenvalue arbitrarily large! Therefore, at some point, the raising operator must give us zero (and the same for the lowering operator), and this will limit the possible values of *both* $\hat{\mathbf{l}}^2$ and $\hat{l}_z$. Now we can establish that

$$\langle \hat{\mathbf{l}}^2 \rangle = m_{\text{max}}(m_{\text{max}}+1) = m_{\text{min}}(m_{\text{min}}-1) = (m_{\text{max}}-N)(m_{\text{max}}-N-1),$$

for integer N, leading finally to $m_{\text{max}} = N/2$. This is a bit curious from our previous differential equation work, because we see that not only are values of m allowed to be integers, but we can also have half-integer values. So for solutions to the Schrödinger equation, we have derived too much generality, but as we will see later, the half-integer solutions can be given meaning in the concept of spin. For dealing with spin, these operator methods are going to be incredibly useful.

Typically we would denote $N/2$ by the value l or j, and this can be any integer or half-integer starting from zero, with the operator $\hat{\mathbf{l}}^2$ having eigenvalue $l(l+1)$. Then, we denote $\hat{l}_z$ as having eigenvalues $-l, -l+1, \cdots l-1, l$. So for $l=2$, we have five states

$$|2,-2\rangle\ , |2,-1\rangle\ , |2,0\rangle\ , |2,1\rangle\ , |2,2\rangle\ .$$

And, for example

$$\hat{l}_+ |2,-1\rangle = \sqrt{2\,(2+1) - (-1)\,(0)} = \sqrt{6}\,|2,1\rangle\ .$$

Rather amazingly, this turns out to be all we need to do basically everything involving angular momentum, if we are clever enough.

2.3 Return to the angular Schrödinger equation

The major accomplishments of our operator algebra is that we know the spectrum. However, we might still be interested in wave-functions. The raising and lowering operators will help us find any wavefunction with the same total angular momentum but different value of m, if we can find just one. Fortunately, we can reduce this problem to a *first* order differential equation. Consider that the raising operator acting on the state with $m = m_{\text{max}}$ is

$$e^{i\phi}\left\{\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right\}\Theta(\theta)e^{im\phi} = e^{i(m+1)\phi}\left(\frac{\partial\Theta}{\partial\theta} - m\cot\theta\Theta\right) = 0.$$

This has only one solution, given by

$$\Theta(\theta) = e^{m\int\cot\theta} = (\sin\theta)^m.$$

The normalized eigenfunctions of angular momentum are called the spherical harmonics (this is because when multiplied by an appropriate power of r they satisfy the Laplace equation, and they

are denoted $Y_{l,m}$. The first few are

$$\begin{aligned}
Y_{0,0} &= \sqrt{\frac{1}{4\pi}} \\
Y_{1,\pm 1} &= \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi} \\
Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos\theta \\
Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{\pm 2i\phi} \\
Y_{2,\pm 1} &= \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, e^{\pm i\phi} \\
Y_{2,0} &= \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right).
\end{aligned}$$

Because all the $Y_{l,m}$ with given l are degenerate given an isotropic environment, linear combinations are also allowed. So sometimes it's useful to characterize them in Cartesian coordinates instead, and we also introduce the letter scheme $s = 0, p = 1, d = 2, f = 3, \ldots$. So there are s orbitals, p_x, p_y, p_z orbitals, and for d orbitals, two classes, d_{xy}, d_{yz}, d_{zx}, and $d_{x^2-y^2}, d_{2z^2-r^2}$.

2.4 Radial part of the Schrödinger equation (Foot 2.1.2)

We now return to the hydrogen atom. Recall the radial wave equation,

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial R}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left\{\frac{\hbar^2}{2\mu r^2}l(l+1) - \frac{e^2}{4\pi\epsilon_0 r}\right\}R = ER.$$

We now simplify the equation by dividing by $E < 0$ and introducing the dimensionless radius ρ given by

$$\rho = \frac{\sqrt{2\mu|E|}}{\hbar}r,$$

we obtain

$$\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R}{\partial\rho}\right) + \left\{-\frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - 1\right\}R = 0,$$

with

$$\lambda = \frac{e^2}{4\pi\epsilon_0}\sqrt{\frac{2\mu}{\hbar^2|E|}}.$$

A trick that is incredibly powerful for radial equations in three dimensions is to substitute $P(\rho) = \rho R(\rho)$, which reduces the first term,

$$\left\{\frac{\partial^2}{\partial\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - 1\right\}P = 0.$$

Now, to motivate things a bit, consider the equation in the two limits $\rho \to 0$ and $\rho \to \infty$. In the first case, we have (taking the shorthand $P' = \partial P/\partial\rho$.).

$$P'' - \frac{l(l+1)}{\rho^2}P = 0,$$
$$P = A\rho^{l+1} + B\rho^{-l}.$$

We choose $B = 0$ to keep things sane at the origin (there are some subtle points on this, but if you poke around for a bit with wavefunctions that diverge at the origin you will see that it doesn't really work out). In the second limit,

$$P'' - P = 0,$$
$$P = Ae^{-\rho} + Be^{\rho},$$

where again we put $B = 0$ for obvious reasons. So finally we guess the solution $P(\rho) = \rho^{l+1}e^{-\rho}F(\rho)$, where F is some function. It turns out F can be solved as a polynomial of order $n_r \geq 0$ as long as $\lambda/2 = 1 + l + n_r = n$. In fact F is the solution to the equation:

$$F''(\rho) + 2\left(\frac{l+1}{\rho} - 1\right)F'(\rho) + \frac{2n_r}{\rho}F(\rho) = 0.$$

This is called the associated Laguerre polynomial, and n is called the principal quantum number. n_r counts the number of nodes that occur moving from the origin to infinity. Using a series expansion for $F = \sum_n a_n\rho^n$ leads to the recurrence relation:

$$a_{n+1} = 2\frac{n - n_r}{(n+1)(n+2l+2)}.$$

Thus if n_r is a nonnegative integer the series terminates, while in other cases the value is bounded below by $e^{2\rho}$ and hence the wavefunction is not normalizable. The condition on λ finally leads to energy quantized exactly as in the Bohr model,

$$\frac{e^2}{4\pi\epsilon_0}\sqrt{\frac{2\mu}{\hbar^2|E|}} = 2n,$$
$$E = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{\mu}{2\hbar^2 n^2}.$$

2.4.1 Degeneracy

An important thing to note is that there is a huge degeneracy of levels with the same principal quantum number n. Every value of l less than n contributes $2l + 1$ degenerate levels, for a total of n^2 states, or $2n^2$ if you count spin (which we haven't discussed yet).

2.5 Transitions (Foot 2.2)

Here I deviate from the book a little bit. What we want to establish is whether or not a state radiates. Let us consider an atom which occupies a superposition of two different states $|\psi\rangle =$

$|1\rangle + |2\rangle\ e^{-i\omega t}$, where $\hbar\omega$ characterizes the energy difference, and we are putting in the explicit time dependence. Now we are interested in what the dipole radiation will be in, say, the $\mathbf{e_z}$ polarization direction. Let us treat the wavefunction of the electron as a classical charge distribution, and ask what the dipole moment is. The charge of the electron is $-e$ so that the electric dipole is given by

$$-e\int |\psi|^2(\mathbf{r}\cdot\mathbf{e_z})\,d^3r = -e\,\langle\psi|\,\hat{z}\,|\psi\rangle = -e\,\langle 1|\,\hat{z}\,|1\rangle - e\,\langle 2|\,\hat{z}\,|2\rangle - e\,\langle 2|\,\hat{z}\,|1\rangle\,e^{i\omega t} + \text{h.c.}$$

It is only the cross term which varies in time, and hence that can radiate. In principal, we note at this point that we could calculate other types of radiation (electric quadrupole for example) by this method as well, but we are not really going to. Let's start to evaluate this integral. This is where it is good to have used separation of variables. We write

$$D_{12} = \langle 1|\,\hat{\mathbf{r}}\cdot\mathbf{e_z}\,|2\rangle = \int R_{n_1,l_1}(r)Y^*_{l_1,m_1}(\theta,\phi)r\cos\theta R_{n_2,l_2}(r)Y_{l_2,m_2}d^3r.$$

Now, the radial integral is a thing. You can figure it out if you want. But it's a pretty boring calculation and it doesn't lead to much insight. It's very rarely equal to zero. The angular part, on the other hand, is interesting, and equal to zero in many cases, known as selection rules. We can quickly see that $\cos\theta$ can be written as $Y_{1,0}$. At this point we are excited and pre-factors should be tossed. We also note that $Y_{1,1}$ would correspond to a superposition of x and y dipoles which are out of phase, which is to say circular polarization. So we have a sum of three $Y_{l,m}$.

$$D_{12} \propto \int Y_{l_1,-m_1}Y_{1,m}Y_{l_2,m_2}d\Omega.$$

From the ϕ portion of the integral, we can see that we must have $m_1 = m_2 + m$. This reflects angular momentum conservation along the z axis, with the emitted photon taking away the angular momentum $\Delta m = \pm 1$, or $\Delta m = 0$. The next thing to notice is that *total* angular momentum is conserved, so that $|\delta l| \leq 1$. In fact, there is a final selection rule which forbids $\Delta l = 0$, called the parity selection rule.

2.6 Parity (Foot 2.2.3)

Parity is an extremely important concept in physics but it can be a bit tricky to understand. So let's start in 1D. In 1D, we can have a parity, which means a mirror symmetry with respect to reflecting about the center, and it's really the only kind of symmetry that makes sense. In 2D, we can have mirror symmetry on x or y, or a combined reflection over both. In even dimensions, this combined reflection can always be thought of as a rotation. In 3D, the dimension is odd again, so reflection of $x \to -x$, $y \to -y$, $z \to -z$ is odd and not equivalent to rotation (it is equivalent to rotation around an axis and then a mirror plane perpendicular to that axis). In spherical coordinates, $r \to r$, $\theta \to \pi - \theta$, and $\phi \to \pi + \phi$. The parity operator, $\hat{P}$, has $\hat{P}^2 = \mathbb{I}$, so the only possible eigenvalues are ± 1. The parity operator commutes with the Hamiltonian for electromagnetic systems and hence for atoms. The parity operator also commutes with the raising and lowering operators for angular momentum, so all of the states with a given l have the same parity. So we can look only at the state $|m_{\text{max}}\rangle$, and see that the parity of a $Y_{l,m}$ is $(-1)^l$. All things considered, we can now see why parity leads to the selection rule $\Delta l \neq 0$. The photon always has odd parity in the dipole mode, so transitions are only possible between even and odd parity states. Another way to say it is that states with non-zero dipole moment always have mixed parity.