(18) Central Potentials

1 Last Time

- Angular momentum Eigenstates and Operators

---

2 Outlook

- Today: Central Potentials
- Next Time: Hydrogen!

Remember way back at the beginning of the course when we discovered that Classical Mechanics didn't work for atoms? At the time you were promised that Quantum Mechanics would give you something that works. Well, we are almost there. In the next lecture we will work out a quantum description of Hydrogen which reproduces the Rydberg emission lines we saw in lecture 2.

But first, a little more ground work. Central Potentials!

---

3 Central Potentials

Our target for today, en-route to a good QM description of Hydrogen, the central potential. Central potentials have the nice feature of conserving angular momentum, so let's start with a quick recap of angular momentum.

Energy in Spherical Coordinates

$$\begin{aligned} \hat{E} &= \frac{\hat{p}^2}{2m} + V(\vec{r}) \\ &= \frac{1}{2m}\left(\hat{p}_r^2 + \frac{1}{r^2}\hat{L}^2\right) + V(\vec{r}) \\ \text{where} \qquad & \hat{p}_r^2 = -\hbar^2 \frac{1}{r}\partial_r^2\, r \end{aligned}$$

For a central potential, $V(\vec{r})$ depends only on $r = |\vec{r}|$

Since the potential can be separated into parts involving individual coordinates, and we already know the angular momentum eigenfunctions which solve the Schrödinger equation for a potential which does not depend on θ and ϕ, we can use separation of variable to reduce this 3D problem to a 1D problem.

Separation of Variables in Central Potential

$$\begin{aligned} \text{for} \quad V(\vec{r}) &= V(|\vec{r}|) = V(r) \\ \hat{E}\, R(r)Y_{lm}(\theta,\phi) &= \left(\frac{\hat{p}_r^2}{2m} + \frac{1}{2mr^2}\hat{L}^2 + V(r)\right) R(r)Y_{lm}(\theta,\phi) \\ \Rightarrow \hat{E}\, R(r) &= \left(\frac{\hat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right) R(r) \end{aligned}$$

We can continue to make this equation look more like 1D Schrödinger equation we are used to by defining an "effective potential" which includes the contribution of angular momentum.

Effective Potential

$$\begin{aligned} \Rightarrow \hat{E}\, R(r) &= \left(\frac{\hat{p}_r^2}{2m} + V_{\text{eff}}(r)\right) R(r) \\ \text{where} \qquad V_{\text{eff}}(r) &= V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \end{aligned}$$

Note: The effective potential does not depend on $L_z = \hbar m$, and so the energy doesn't either. This implies that energy eigenstates in a central potential have at least $2l + 1$ degeneracy!

Careful! There are two m's running around. This is not my fault! By convention mass is m, and the index of z angular momentum is also m. Fortunately, L_z does not appear in the energy, which is where we usually find the mass. (You can always tell them apart by the units.)

The strange form of $\hat{p}_r$ is the only thing preventing us from having exactly the same equation we have been working with in 1D. Fortunately, there is a little trick that can be used to fix this problem. Pay close attention...

Radial Equation Trick

$$
\begin{aligned}
\text{define} \qquad & U(r) = r\, R(r) \\
\hat{E}\, \frac{1}{r} U(r) &= \left(\frac{-\hbar^2}{2m} \frac{1}{r} \partial_r^2\, r + V_{\text{eff}}(r) \right) \frac{1}{r} U(r) \\
&= \left(\frac{-\hbar^2}{2m} \frac{1}{r} \partial_r^2\, r + V_{\text{eff}}(r) \right) \frac{1}{r} U(r) \\
&= \frac{-\hbar^2}{2m} \frac{1}{r} \partial_r^2\, U(r) + \frac{1}{r} V_{\text{eff}}(r) U(r) \\
\Rightarrow \hat{E}_U\, U(r) &= \frac{-\hbar^2}{2m} \partial_r^2\, U(r) + V_{\text{eff}}(r) U(r) \\
&= \left(\frac{-\hbar^2}{2m} \partial_r^2 + V_{\text{eff}}(r) \right) U(r)
\end{aligned}
$$

This works because the reason that $\hat{p}_r^2$ has that funny form, which originated with ∇^2, is that the surface area of a unit volume scales with radius in spherical coordinates. (And the volume of a sphere scales with r^2.) Essentially, we have just undone an unintuitive feature of spherical coordinates by talking about a radial function which has this scaling built-in. To see this, let's compute $\mathbb{P}(r)\ dr$, the probability of finding our particle between radius r and $r + dr$ (i.e., in a shell with radius r, thickness dr, and area $4\pi r^2$).

$\mathbb{P}$ between r and $r + dr$

$$
\begin{aligned}
\mathbb{P}(r)\ dr &= \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\ \left| R(r)\, Y_{lm}(\theta, \phi) \right|^2 r^2\, dr \\
&= \left| r\, R(r) \right|^2\ dr \underbrace{\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\ \left| Y_{lm}(\theta, \phi) \right|^2}_{\langle Y_{lm} | Y_{lm} \rangle = 1} \\
&= \left| U(r) \right|^2\ dr
\end{aligned}
$$

The Y_{lm} are normalized. Recall, for instance, that $Y_{00} = 1/\sqrt{4\pi}$.

With these tools in hand, let's see how some of our old friends look in 3D.

---

4 Example: Infinite Spherical Well

The infinite spherical well represents a particle trapped inside some radius L.

(Draw $V(r)$ with $r = 0$ and $r = L$ labeled.)

Infinite Spherical Well

$$\begin{aligned} V(r) &= \begin{cases} 0 & 0 < r < L \\ \infty & \text{else} \end{cases} \\ \Rightarrow V_{\text{eff}}(r) &= \begin{cases} \frac{\hbar^2 l(l+1)}{2mr^2} & 0 < r < L \\ \infty & \text{else} \end{cases} \end{aligned}$$

Due to angular momentum, however, the effective potential is not as simple as one might like.

(Draw $V_{\text{eff}}(r)$ with $l = \{0, 1, 2\}$.)

So, for now let's stick with $l = 0$.

Energy Eigenstates with $l = 0$

$$\begin{aligned} E\,U(r) &= -\frac{\hbar^2}{2m}\partial_r^2\,U(r) \\ \Rightarrow \partial_r^2\,U(r) &= -\frac{2m}{\hbar^2}E\,U(r) = -k^2\,U(r) \\ \Rightarrow U(r) &= A\sin(kr) + B\cos(kr) \end{aligned}$$

To satisfy the boundary conditions of $U(r) = 0$ at $r = 0$ and $r = L$, we have to pick $B = 0$ and a discrete set of k values that work.

EES with $l = 0$

$$\begin{aligned} U_n(r) &= A\sin(k_n r) \quad \text{for } r < L \\ \text{with } k_n &= (n+1)\pi/L \quad \text{for } n \in \{0, 1, 2, \cdots\} \\ \Rightarrow \phi_n(r) &= A\frac{\sin(k_n r)}{r} \quad \text{for } r < L \\ \text{and } E_n &= \frac{\hbar^2 k_n^2}{2m} \end{aligned}$$

Note that requiring $U(r) = 0$ at $r = 0$ does not imply $R(r) = 0$ at $r = 0$. In fact, our solution has $R(r) = Ak_n$ at $r = 0$.

Let's nail this down by computing A for a properly normalized solution.

Normalization

$$\begin{aligned} \psi_n(r, \theta, \phi, t) &= \phi_n(r) Y_{00}(\theta, \phi) e^{-iE_n t/\hbar} \\ \Rightarrow 1 &= \int_0^L r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\ |\phi_n(r) Y_{00}|^2 \\ &= \int_0^L |A\sin(k_n r)|^2\ dr \\ &= |A|^2 \frac{L}{2} \\ \Rightarrow |A| &= \sqrt{\frac{2}{L}} \end{aligned}$$

Which is what we got when we did the infinite square well in 1D!

You will find the solutions for $l > 0$ in Griffiths page 141 or Liboff page 416. If you look there, you will also discover why I'm not doing them on the board!

5 Example: Isotropic Oscillator

A few lectures back I introduced the isotropic oscillator.

Isotropic Oscillator

$$\begin{aligned} V(\vec{r}) &= \tfrac{1}{2}m\omega^2(x^2+y^2+z^2) = \tfrac{1}{2}m\omega^2 r^2 \\ \Rightarrow V_{\text{eff}}(r) &= \begin{cases} \frac{1}{2}m\omega^2 r^2 + \frac{\hbar^2 l(l+1)}{2mr^2} & r > 0 \\ \infty & r < 0 \end{cases} \end{aligned}$$

As with the infinite spherical well, the solutions get ugly for $l > 0$, while for $l = 0$ we just get our usual 1D Schrödinger equation.

Energy Eigenstates with $l = 0$

$$\begin{aligned} E\,U(r) &= \left(-\frac{\hbar^2}{2m}\partial_r^2 + \tfrac{1}{2}m\omega^2 r^2\right) U(r) \\ &\quad \text{with } U(r) = 0 \text{ for } r < 0 \\ \Rightarrow U(r) &= \text{odd solutions of the 1D QHO for } r > 0 \end{aligned}$$

Despite the mathematical difficulty of the $l > 0$ solutions, there are a few things we can say about the energy levels of this potential.

Recall the energy levels and degeneracy we found while working in rectangular coordinates.

Energies of Isotropic Oscillator

$$E_{\vec{n}} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$$

Degeneracy with E_{n_x,n_y,n_z}

$$
\begin{aligned}
E_{0,0,0} &= \frac{3}{2}\hbar\omega \quad \times 1 \\
E_{1,0,0} = E_{0,1,0} = E_{0,0,1} &= \frac{5}{2}\hbar\omega \quad \times 3 \\
\underbrace{E_{1,1,0}}_{\times 3} = \underbrace{E_{2,0,0}}_{\times 3} &= \frac{7}{2}\hbar\omega \quad \times 6 \\
E_{1,1,1} = \underbrace{E_{2,1,0}}_{\times 6} = \underbrace{E_{3,0,0}}_{\times 3} &= \frac{9}{2}\hbar\omega \quad \times 10 \\
&\vdots
\end{aligned}
$$

You will already notice something a bit odd. If the radial part of the spherical solution is just like a 1D harmonic oscillator, we should have a ground state with $E = \frac{1}{2}\hbar\omega$, but the lowest energy state we found in rectangular coordinates had $E = \frac{3}{2}\hbar\omega$. The trouble here comes from the boundary conditions, which require that $U(r = 0) = 0$. This eliminates all of the even n solutions of the 1D harmonic oscillator, including the ground state!

Energies for $l = 0$

$$E_{n,l=0} = \hbar\omega(2n + \tfrac{3}{2}) \quad \text{with} \;\; n \in \{0, 1, 2, \cdots\}$$

Increasing the total angular momentum such that $l = 1$ and $m = \{-1, 0, 1\}$ must give 3 degenerate states for each value of n. The lowest triplet will have $n = 0$, so we can guess it's energy!

Energies for $n = 0$ and $l = 1$

$$E_{n=0,l=1} = \frac{5}{2}\hbar\omega \quad \times 3 \;\; \text{since} \;\; m \in \{-1, 0, 1\}$$

We know that of the 6 degenerate states with $\frac{7}{2}\hbar\omega$, one is $E_{n=1,l=0}$. The only way to get 5 more degenerate states is with an $l = 2$ state, which has $m \in \{-2, \cdots, 2\}$ The lowest energy possibility will also have $n = 0$, so

Energies for $n = 0$ and $l = 2$

$$\underbrace{E_{n=1,l=0}}_{\times 1} = \underbrace{E_{n=0,l=2}}_{\times 5} = \frac{7}{2}\hbar\omega \qquad \times 6$$

It appears from this argument, and can be shown rigorously if you want to solve the Schrödinger equation for our energy eigenfunctions, that energy increases by $\hbar\omega$ for each increase in l.

Energies for any n and l

$$E_{n,l} = \hbar\omega(2n + l + \tfrac{3}{2}) \quad \text{with} \;\; n, l \in \{0, 1, 2, \cdots\}$$

Note that this also gives the right degeneracy for the next energy level.

Degeneracy with $2n + l = 3$

$$\underbrace{E_{n=1,l=1}}_{\times 3} = \underbrace{E_{n=0,l=3}}_{\times 7} = \frac{9}{2}\hbar\omega \qquad \times 10$$

---

6 Next Time

- Hydrogen!