Week 6

The Hydrogen Atom

6.1 Central Potentials

2/5:
- Review.
  - Definition of **central potential**.
    - In this case, we have three good observables: $\hat{H}, \hat{\vec{L}}^2, \hat{L}_z$.
  - Last Friday, we discovered that the eigenstates are characterized by three numbers n, ℓ, m that correspond to the three operators above.
    - Altogether, we have that

$$\hat{L}_z |n\ell m\rangle = \hbar m |n\ell m\rangle \qquad \hat{\vec{L}}^2 |n\ell m\rangle = \hbar^2 \ell(\ell+1) |n\ell m\rangle \qquad \hat{H} |n\ell m\rangle = E_n |n\ell m\rangle$$

  - We also defined ladder operators L_+, L_- such that

$$\hat{L}_\pm |n\ell m\rangle = \sqrt{\ell(\ell+1) - m(m \pm 1)}\, |n\ell(m \pm 1)\rangle$$

- **Central potential**: A three-dimensional potential energy distribution in which the potential depends only on the distance from the origin. *Denoted by* $\boldsymbol{V(r)}$.
- The eigenstates are well normalized, i.e.,

$$\langle n\ell m | n\ell m' \rangle = \delta_{mm'}$$

  - It follows that

$$\langle n\ell m | \hat{L}_x | n\ell m \rangle = \langle n\ell m | \frac{1}{2}(\hat{L}_+ + \hat{L}_-) | n\ell m \rangle = 0$$

  - Similarly,

$$\langle n\ell m | \hat{L}_y | n\ell m \rangle = 0$$

  - Additionally, we have that

$$\langle n\ell m | (\hat{L}_x^2 + \hat{L}_y^2) | n\ell m \rangle = \langle n\ell m | (\hat{\vec{L}}^2 - \hat{L}_z^2) | n\ell m \rangle = \hbar^2[\ell(\ell+1) - m^2]$$

    - Since the above eigenvalue must be greater than or equal to zero, $|m| \leq \ell$.
  - Recall that $\hat{L}_x, \hat{L}_y$ are incompatible with $\hat{L}_z$.
    - This is why we have an uncertainty associated with the quantity $\hbar^2[\ell(\ell+1) - m^2]$.
    - This is also why we have

$$\langle n\ell m | (\hat{L}_x^2 + \hat{L}_y^2) | n\ell m \rangle = 2 \langle n\ell m | \hat{L}_x^2 | n\ell m \rangle = 2 \langle n\ell m | \hat{L}_y^2 | n\ell m \rangle$$

- Recall expressing the wave function in polar coordinates via $\psi(r,\theta,\phi)$.
  - Solving by separation of variables, we have
$$|n\ell m\rangle = \psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\cdot Y_{\ell m}(\theta,\phi)$$
  - This has the interesting property that if we define
$$U_{n\ell}(r) = rR_{n\ell}(r)$$
    then
$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[U_{n\ell}(r)] + \underbrace{\left[\frac{\hbar^2\ell(\ell+1)}{2Mr^2} + V(r)\right]}_{V_{\text{eff}}(r)}U_{n\ell}(r) = E_{n\ell}U_{n\ell}(r)$$
  - This means that U is the solution to a one-dimensional problem in an effective potential.
- A couple of interesting comments.
  - m doesn't appear because directionality doesn't matter. We don't care which direction we project into; we only care about the total angular momentum.
    - Recall that there is a $2\ell+1$ degeneracy associated with the fact that m doesn't appear.
    - Indeed, we get energy levels within this potential.
  - Recall that M denotes the mass to avoid confusion with the quantum number m.
  - The effective potential we are considering is of the same shape as the red line in Figure 5.1.
- Recall that solving for Y, we obtain
$$\underbrace{-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{\ell m}}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{\ell m}}{\partial\phi^2}\right]}_{\hat{\vec{L}}^{\,2}Y_{\ell m}} = \hbar^2\ell(\ell+1)Y_{\ell m}$$
  - The rather complicated expression on the left above just describes $\hat{\vec{L}}^{\,2}Y_{\ell m}$ in polar coordinates.
  - We'll get as a solution
$$Y_{\ell m}(\theta,\phi) = \mathrm{e}^{im\phi}\Theta_{\ell m}(\theta)$$
  - We can therefore see that if $\hat{L}_z = -i\hbar(\partial/\partial\phi)$ then
$$\hat{L}_zY_{\ell m}(\theta,\phi) = \hbar mY_{\ell m}(\theta,\phi)$$
  - Remember that m and ℓ are both integers.
  - Simplifying the above, we get
$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta_{\ell m}}{\mathrm{d}\theta}\right) - m^2\Theta_{\ell m} + [\ell(\ell+1)\sin^2\theta]\Theta_{\ell m} = 0$$
  - Secretly, all the dependence on θ is a dependence on $\cos\theta$ since we can make substitutions like $\sin^2\theta = 1-\cos^2\theta$.
  - The solutions are then
$$\Theta_{\ell m}(u) = AP_\ell^m(u)$$
    where $u=\cos\theta$ and P_ℓ^m are the **associated Legendre functions**.
  - Finally, if we want to obtain a well-normalized solution, i.e., we need to calculate A. Computationally, this means that we need
$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\mathrm{d}r\,\mathrm{d}\theta\mathrm{d}\phi\; r^2\sin\theta|Y_{\ell m}(\theta,\phi)R_{n\ell}(r)|^2$$

- This integral splits into two.

$$\int_0^{2\pi}\int_0^{\pi} \mathrm{d}\theta\mathrm{d}\phi\ \sin\theta|Y_{\ell m}(\theta,\phi)|^2 = 1 \qquad\qquad \int_0^{\infty} \mathrm{d}r\ \underbrace{|rR_{n\ell}(r)|^2}_{|U_{n\ell}(r)|^2} = 1$$

- Note that this implies that

$$\int \mathrm{d}\phi\mathrm{d}\theta\ \sin\theta Y_{\ell m}(\theta,\phi)Y_{\ell' m'}(\theta,\phi) = \delta_{\ell\ell'}\delta_{mm'} \qquad\qquad \int \mathrm{d}r\ r^2 R_{n\ell}(r)R_{n'\ell'}(r) = \delta_{nn'}\delta_{\ell\ell'}$$

- **Rodrigues formula**: The formula given as follows. *Given by*

$$\frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}u^\ell}\left(u^2-1\right)^\ell$$

- **Legendre polynomials**: The system of complete orthogonal polynomials defined via the Rodrigues formula. *Denoted by* $\boldsymbol{P_\ell(u)}$. *Given by*

$$P_\ell(u) = \frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}u^\ell}\left(u^2-1\right)^\ell$$

- **Associated Legendre functions**: The canonical solutions of the general Legendre equation. *Denoted by* $\boldsymbol{P_\ell^m(u)}$. *Given by*

$$P_\ell^m(u) = (1-u^2)^{|m|/2}\frac{\mathrm{d}^{|m|}}{\mathrm{d}u^{|m|}}[P_\ell(u)]$$

- A couple of closing comments.
  - The normalization constant is such that *en toto*,

$$Y_{\ell m}(\theta,\phi) = (-1)^m\sqrt{\frac{(2\ell+1)}{4\pi}\cdot\frac{(\ell-m)!}{(\ell+m)!}}P_{\ell m}(\cos\theta)\mathrm{e}^{im\phi}$$

    - This is for $m \geq 0$
  - If $m < 0$, then use

$$Y_{\ell(-|m|)} = (-1)^{|m|}Y^*_{\ell|m|}(\theta,\phi)$$

    where the complex conjugate of Y just switches the exponential term at the end to $\mathrm{e}^{-im\phi}$.
  - The probability $P_{00}(\cos\theta)$ is a constant. So if we draw a circle in the zx-plane, it will not vary in intensity??
  - We also have $P_{10}(\cos\theta) = \cos\theta$. Thus, this particle will move more quickly past the x-axis and slower toward the bottom of its circular orbit, yielding a p-orbital shape. Maximum probability is moving in the perpendicular direction.
  - $P_{11}(\cos\theta) = \sin\theta$.
    - If you have a particle with angular momentum 1 and modulus 1, it moves in the xy plane in such a way that the total angular momentum points in the vertical direction and thus then it has maximum probability of being in the perpendicular plane.
    - This gives us something sideways (think p_z vs. p_x orbitals).

6.2 Midterm Exam Review

2/7:
- Format of the midterm.
  - 5 conceptual questions (multiple choice) that we should know by now.
  - Two computational problems.
    - One that appears in the problem set.
    - One that appears in the problem set but we will have to do a couple extra things.
    - Subject: One on harmonic oscillators and one on motion in potential wells.
  - If we fail the multiple choice, "something is wrong with you."
  - The exam is not curved, but the class will have a curve.
  - We can bring virtual notes.
- Conceptual things to remember for the midterm.
  - In classical mechanics, a particle is given by a path/trajectory $\vec{r}(t)$.
  - In quantum mechanics, there is no path. The best we can do is define $\langle\psi|\vec{r}|\psi\rangle(t)$, but we will always be hampered by the fact that $\sigma_{\vec{p}} \neq 0$.
    - The uncertainty in momentum comes from the Heisenberg uncertainty relation.
    - If the operator is independent of time (such as $\hat{x}, \hat{p}_x, \hat{\vec{r}}, \hat{\vec{p}}, V(\vec{r})$), then

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\langle\psi|\hat{O}|\psi\rangle\Big) = \frac{i}{\hbar}\langle\psi|[\hat{H},\hat{O}]|\psi\rangle$$

      - This means that if $[\hat{H},\hat{O}] = 0$, then the expected value of the operator is independent of time.
    - We most often deal with time-independent potentials $V(\vec{r},t) = V(\vec{r})$.
    - Recall that since $[\hat{H},\hat{H}] = 0$, $E = \langle\psi|\hat{H}|\psi\rangle$ is a good quantum number.
      - It follows that

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \qquad \hat{H}^2|\psi_n\rangle = E_n^2|\psi_n\rangle$$

      - We also have that

$$\sigma_{\hat{H}} = 0 \qquad \langle\psi_n|\hat{H}^2|\psi_n\rangle - (\langle\psi_n|\hat{H}|\psi_n\rangle)^2 = 0$$

    - It is very important to remember that

$$\begin{aligned}
|\psi\rangle &= \sum_n c_n \mathrm{e}^{-iE_nt/\hbar}|\psi_n\rangle \\
\langle\psi|\psi\rangle &= \sum_n |c_n|^2 = 1 \\
\langle\psi|\hat{H}|\psi\rangle &= \sum_n |c_n|^2 E_n \\
\langle\psi_n|\psi_m\rangle &= \int \mathrm{d}\vec{r}\ \psi_n^*\psi_m = \delta_{nm}
\end{aligned}$$

      - It follows from the bottom three statements that $|c_n|^2$ is the probability of measuring E_n.
    - We can obtain the m^{th} coefficient of ψ using the inner product formula.

$$\langle\psi_m|\psi\rangle = \sum_n c_n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{nm}} = c_m$$

      - Equivalently,

$$c_m = \int \mathrm{d}\vec{r}\ \psi_m^*(\vec{r})\psi(\vec{r})$$

- Computational things to remember for the midterm.
- The harmonic oscillator.
  - Since we are in one dimension, $\hat{p} = \hat{p}_x$
  - The Hamiltonian is
$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{k\hat{x}^2}{2}$$
  - We have that
$$[\hat{p}, \hat{x}] = -i\hbar$$
    - Note that this statement is not only true in the context of the harmonic oscillator. Indeed, $\hat{p}_x$ and $\hat{x}$ always compatibilize in this way.
  - Recall that compatibility is important because the *generic* uncertainty principle (restated as follows) requires a zero commutator in order for it to be possible for both uncertainties to be zero!
$$\sigma_{\hat{A}}^2 \sigma_{\hat{B}}^2 \geq \frac{1}{4} | \langle\psi|[\hat{A}, \hat{B}]|\psi\rangle |^2$$
  - We defined ladder operators
$$a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{p} + m\omega\hat{x}) \qquad a_- = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{p} + m\omega\hat{x})$$
  - Having defined these operators, we may write the Hamiltonian in terms of them as follows.
$$\hat{H} = \hbar\omega \left(a_+ a_- + \frac{1}{2}\right)$$
  - Defining $|n\rangle := |\psi_n\rangle$ and remembering that
$$a_+ a_- |n\rangle = n |n\rangle$$
this form of the Hamiltonian makes it obvious that
$$E_n = \hbar\omega \left(n + \frac{1}{2}\right)$$
since
$$\hat{H} |n\rangle = \hbar\omega \left(n + \frac{1}{2}\right) |n\rangle \qquad \langle n|\hat{H}|n\rangle = \hbar\omega \left(n + \frac{1}{2}\right)$$
  - The ladder operators also have distinctive actions on the energy eigenstates.
$$a_- |n\rangle = \sqrt{n} |n-1\rangle \qquad a_+ |n\rangle = \sqrt{n+1} |n+1\rangle$$
  - Don't forget that overall,
$$\langle n|m\rangle = \delta_{nm}$$
  - The ladder operators enable us to calculate the observables of a generic state ψ of the harmonic oscillator as follows.
$$\begin{aligned}\langle\psi|\hat{x}|\psi\rangle &= \sqrt{\frac{\hbar}{2M\omega}} \langle\psi|(a_+ + a_-)|\psi\rangle \\ &= \sum_{m,n} c_m^* c_n \sqrt{\frac{\hbar}{2M\omega}} \langle m|(a_+ + a_-)|n\rangle \, \mathrm{e}^{i(E_m - E_n)t/\hbar}\end{aligned}$$

$$
\begin{aligned}
&= \sum_{m,n} c_m^* c_n \sqrt{\frac{\hbar}{2M\omega}} \mathrm{e}^{i(E_m - E_n)t/\hbar} \big(\sqrt{n+1} \underbrace{\langle m|n+1\rangle}_{\delta_{m,n+1}} + \sqrt{n} \underbrace{\langle m|n-1\rangle}_{\delta_{m,n-1}} \big) \\
&= \sum_{n=0}^{\infty} c_{n+1}^* c_n \mathrm{e}^{i\omega t} \sqrt{n+1} + \sum_{n=0}^{\infty} c_{n-1}^* c_n \mathrm{e}^{-i\omega t} \sqrt{n} \\
&= \sum_{n=0}^{\infty} \left(c_{n+1}^* c_n \mathrm{e}^{i\omega t} + c_n^* c_{n+1} \mathrm{e}^{-i\omega t} \right) \sqrt{n+1}
\end{aligned}
$$

- Note that in the next to last line above, the second sum *can* go from zero to ∞ because for the $n = 0$ term, although we have an undefined c_{-1}, we also have $\sqrt{0} = 0$ so the problematic "undefined" term vanishes.
- We can expect to see a computation like this in the midterm.

– Using similar methods, we can calculate that

$$
\left\langle n \middle| \frac{k\hat{x}^2}{2} \middle| n \right\rangle = \frac{E_n}{2} = \langle n|\hat{p}^2|n\rangle = \frac{\hbar\omega}{2} \left(n + \frac{1}{2} \right)
$$

- In particular, we expand

$$
\langle n|(a_+ + a_-)^2|n\rangle = \underbrace{\langle n|a_+^2|n\rangle}_{0} + \underbrace{\langle n|a_-^2|n\rangle}_{0} + \underbrace{\langle n|a_+ a_-|n\rangle}_{n} + \langle n| \underbrace{a_- a_+}_{a_+ a_- + 1} |n\rangle = 2n + 1
$$

– Note that for the same reason discussed above,

$$
a_- a_+ |n\rangle = (n+1) |n\rangle
$$

– Since $\sigma_x^2 = \langle n|\hat{x}^2|n\rangle - (\langle n|\hat{x}|n\rangle)^2 \neq 0$ as we can verify by further calculations, there is *always* some nonzero σ_x for the harmonic oscillator.

- Final note.
  – If we want to compute $\langle \psi|\hat{x}|\psi\rangle$ for a generic potential, we must use

$$
\langle \psi|\hat{x}|\psi\rangle (t) = \sum_{m,n} c_m^* c_n \mathrm{e}^{i(E_m - E_n)t/\hbar} \langle m|\hat{x}|n\rangle
$$

  – In other words, it is only in the harmonic oscillator specifically that we can use the ladder operators.
  – If we are in a specific energy eigenstate (of a general potential), though, then we do get conservation of position and momentum because $E_m = E_n$ so $E_m - E_n = 0$ removes the time term. In particular,

$$
\langle \psi_n(x,t)|\hat{x}|\psi_n(x,t)\rangle = c_n^* c_n \mathrm{e}^{i(E_n - E_n)t/\hbar} \langle \psi_n(x)|\hat{x}|\psi_n(x)\rangle = c_n^* c_n \langle \psi_n(x)|\hat{x}|\psi_n(x)\rangle
$$

and

$$
\frac{\mathrm{d}}{\mathrm{d}t}(\langle \psi_n|\hat{x}|\psi_n\rangle) = \frac{i}{\hbar} \langle \psi_n|[\hat{H}, \hat{x}]|\psi_n\rangle = \frac{i}{\hbar} \langle \psi_n|\hat{H}\hat{x} - \hat{x}\hat{H}|\psi_n\rangle = \frac{i}{\hbar} (E_n \langle \psi_n|\hat{x}|\psi_n\rangle - E_n \langle \psi_n|\hat{x}|\psi_n\rangle) = 0
$$

so

$$
\frac{\mathrm{d}}{\mathrm{d}t}(\langle \psi_n|\hat{x}|\psi_n\rangle) = \frac{\mathrm{d}}{\mathrm{d}t}(\langle \psi_n|\hat{p}|\psi_n\rangle) = 0
$$

- Why does $\langle \psi_n|\hat{H}\hat{x}|\psi_n\rangle = E_n \langle \psi_n|\hat{x}|\psi_n\rangle$?? I thought $\hat{H}$ and $\hat{x}$ didn't commute.