

Week 6

The Hydrogen Atom

6.1 Central Potentials

2/5: • Review.

– Definition of **central potential**.

■ In this case, we have three good observables: $\hat{H}, \hat{L}^2, \hat{L}_z$.

– 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

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

– 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 $V(\mathbf{r})$.

• 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

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

■ 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

$$-\frac{\hbar^2}{2M} \frac{d^2}{dr^2} [U_{n\ell}(r)] + \underbrace{\left[\frac{\hbar^2 \ell(\ell+1)}{2Mr^2} + V(r) \right]}_{V_{\text{eff}}(r)} U_{n\ell}(r) = E_{n\ell} U_{n\ell}(r)$$

- 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

$$\underbrace{-\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y_{\ell m}}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y_{\ell m}}{\partial \phi^2} \right]}_{\hat{L}^2 Y_{\ell m}} = \hbar^2 \ell(\ell+1) Y_{\ell m}$$

- The rather complicated expression on the left above just describes $\hat{L}^2 Y_{\ell m}$ in polar coordinates.
- We'll get as a solution

$$Y_{\ell m}(\theta, \phi) = e^{im\phi} \Theta_{\ell m}(\theta)$$

- We can therefore see that if $\hat{L}_z = -i\hbar(\partial/\partial\phi)$ then

$$\hat{L}_z Y_{\ell m}(\theta, \phi) = \hbar m Y_{\ell m}(\theta, \phi)$$

- Remember that m and ℓ are both integers.
- Simplifying the above, we get

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta_{\ell m}}{d\theta} \right) - m^2 \Theta_{\ell m} + [\ell(\ell+1) \sin^2 \theta] \Theta_{\ell m} = 0$$

- 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

$$\Theta_{\ell m}(u) = A P_{\ell}^m(u)$$

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

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} dr d\theta d\phi r^2 \sin \theta |Y_{\ell m}(\theta, \phi) R_{n\ell}(r)|^2$$

- This integral splits into two.

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

- Note that this implies that

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

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

$$\frac{1}{2^\ell \ell!} \frac{d^\ell}{du^\ell} (u^2 - 1)^\ell$$

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

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

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

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

- A couple of closing comments.

- The normalization constant is such that *en toto*,

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

- 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 $e^{-im\phi}$.

- 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 $\sigma_{\vec{r}} \neq 0$.
 - The uncertainty in momentum comes from the Heisenberg uncertainty relation.
 - If the operator is independent of time (such as $\hat{x}, \hat{p}_x, \hat{r}, \hat{p}, V(\vec{r})$), then

$$\frac{d}{dt} \left(\langle \psi | \hat{O} | \psi \rangle \right) = \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{O}] | \psi \rangle$$

- 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

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

- 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,

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

- 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!

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4} |\langle \psi | [\hat{A}, \hat{B}] | \psi \rangle|^2$$

- We defined ladder operators

$$a_+ = \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{p} + m\omega\hat{x}) \quad a_- = \frac{1}{\sqrt{2\hbar m\omega}}(i\hat{p} + m\omega\hat{x})$$

- 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

$$\hat{H} |n\rangle = \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle \quad \langle n | \hat{H} | n \rangle = \hbar\omega \left(n + \frac{1}{2} \right)$$

- The ladder operators also have distinctive actions on the energy eigenstates.

$$a_- |n\rangle = \sqrt{n} |n-1\rangle \quad a_+ |n\rangle = \sqrt{n+1} |n+1\rangle$$

- 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.

$$\begin{aligned} \langle \psi | \hat{x} | \psi \rangle &= \sqrt{\frac{\hbar}{2M\omega}} \langle \psi | (a_+ + a_-) | \psi \rangle \\ &= \sum_{m,n} c_m^* c_n \sqrt{\frac{\hbar}{2M\omega}} \langle m | (a_+ + a_-) | n \rangle e^{i(E_m - E_n)t/\hbar} \end{aligned}$$

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

- 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

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

- In particular, we expand

$$\langle n | (a_+ + a_-)^2 | n \rangle = \underbrace{\langle n | a_+^2 | n \rangle}_0 + \underbrace{\langle n | a_-^2 | n \rangle}_0 + \underbrace{\langle n | a_+ a_- | n \rangle}_n + \underbrace{\langle n | a_- a_+ | n \rangle}_{a_+ a_- + 1} = 2n + 1$$

- 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

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

- 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,

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

and

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

so

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

- 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.

6.3 Midterm

- 2/9:
1. (5 pts) In quantum mechanics, a particle follows a definite path $\vec{r} = \vec{r}(t)$. The only difference with the classical case is that the energy is quantized.
 - a. True
 - b. False
 2. (5 pts) A particle can enter a region of space where the energy of the particle is smaller than the potential energy.
 - a. False
 - b. True, if it happens in a limited region of space.
 3. (5 pts) In quantum mechanics, observables are identified with Hermitian operators. These observables are conserved in time...
 - a. Only if these operators commute with the momentum operator;
 - b. Only if these operators commute with the Hamiltonian operator;
 - c. Only if these operators commute with the Hamiltonian operator and they have no explicit time dependence.

Give a short justification of your answer.

4. (5 pts) For the case of a time-independent potential, one can find eigenfunctions of the Hamiltonian operator $\psi_n(x)$ in which the energy E_n is well-defined. Being that the case, the mean values of the position and momentum in the states described by $\psi_n(x, t) = \psi_n(x)e^{-iE_nt/\hbar}$ are independent of time.
 - a. True
 - b. False

Give a short justification of your answer.

5. Given the eigenfunctions $\psi_n(x)$ of the Hamiltonian in one dimension with well-defined energies E_n ...
 - a. (5 pts) Write the form of the general solution $\psi(x, t)$, including its time dependence.
 - b. (5 pts) What is the mean value of the Hamiltonian in the state associated with this general solution, and how can this expression be interpreted in terms of the probability of measuring the particle with a given energy E_n ?
 - c. (10 pts) Write the formal expression one needs to calculate to obtain the mean values of the position and momentum, identified with the operators \hat{x} and $\hat{p}_x = -i\hbar(\partial/\partial x)$ in terms of the coefficients c_n , $\psi_n(x)$, E_n , x , and the derivatives with respect to x of ψ_n . Include the dependence on time.
6. For the harmonic oscillator, consider the ladder operators $a_{\pm} = (\mp i\hat{p} + M\omega x)/\sqrt{2\hbar M\omega}$ such that $[a_-, a_+] = 1$, where M is the mass of the particle. The Hamiltonian may be written as $\hat{H} = \hbar\omega(a_+a_- + 1/2)$, and the eigenstates of energy $E_n = \hbar\omega(n + 1/2)$ are related by $a_+\psi_n = \sqrt{n+1}\psi_{n+1}$, $a_-\psi_n = \sqrt{n}\psi_{n-1}$. Some additional useful formulae are given after Problem 7.
 - a. (5 pts) Compute the mean value of \hat{x} and \hat{p} in the energy eigenstates described by ψ_n .
 - b. (10 pts) Compute the mean value of \hat{x}^2 and \hat{p}^2 in these states.
 - c. (5 pts) Verify that the uncertainty principle is fulfilled for the energy eigenstates.
 - d. (15 pts) Write the expression for the mean value of the momentum for the general solution $\psi(x, t)$. Work it out as much as you can. What can you say about the frequency of oscillation of the momentum in a generic solution?

7. Imagine a particle in an infinite potential well

$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & x \leq 0 \text{ and } x \geq a \end{cases}$$

Some useful formulae for the solution of Problem 7 are given below.

- a. (10 pts) What are the energy eigenvalues and eigenstate wave functions in this case? Justify your answer.
- b. (15 pts) Take a superposition of two energy eigenstates with contiguous eigenvalues

$$\psi(x, t) = \frac{1}{\sqrt{2}}\psi_n(x, t) + \frac{1}{\sqrt{2}}\psi_{n+1}(x, t)$$

and compute the mean value of \hat{x} as a function of time for the wave function $\psi(x, t)$. Compute also the mean value of the momentum and demonstrate from these expressions that it is related to the mean value of \hat{x} by the expected Ehrenfest Theorem relation:

$$\frac{d}{dt}(\langle \psi | \hat{x} | \psi \rangle) = \frac{\langle \psi | \hat{p} | \psi \rangle}{M}$$

Some Useful Formulae

For the Harmonic Oscillator

$$\hat{p} = i\sqrt{\frac{\hbar M\omega}{2}}(a_+ - a_-) \qquad \hat{x} = \sqrt{\frac{\hbar}{2M\omega}}(a_+ + a_-)$$

Matrix elements: Using Dirac notation,

$$\begin{aligned} a_+ |n\rangle &= \sqrt{n+1} |n+1\rangle \\ a_- |n\rangle &= \sqrt{n} |n-1\rangle \\ \langle n | (a_+)^m | n \rangle &= \langle n | (a_-)^m | n \rangle = 0, \quad m \geq 1 \\ \langle m | a_+ | n \rangle &= \sqrt{n+1} \delta_{n+1, m} \\ \langle m | a_- | n \rangle &= \sqrt{n} \delta_{n-1, m} \\ \langle m | a_- a_+ | n \rangle &= (n+1) \delta_{n, m} \\ \langle m | a_+ a_- | n \rangle &= n \delta_{n, m} \end{aligned}$$

For the Harmonic Oscillator

Wave functions and energies:

$$\psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n x}{a}\right) e^{-iE_n t/\hbar} \qquad E_n = \frac{\hbar^2 \pi^2 n^2}{2Ma^2}$$

Useful integrals: For $n, m \in \mathbb{N}$,

$$\begin{aligned} \frac{2}{a} \int_0^a \sin\left(\frac{\pi n x}{a}\right) \sin\left(\frac{\pi m x}{a}\right) dx &= \delta_{nm} \\ \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi n x}{a}\right) dx &= \frac{a}{2} \end{aligned}$$

For $n + m$ even and $n \neq m$,

$$\frac{2}{a} \int_0^a x \sin\left(\frac{\pi n x}{a}\right) \sin\left(\frac{\pi m x}{a}\right) dx = 0$$

For $n + m$ even,

$$\int_0^a \sin\left(\frac{\pi nx}{a}\right) \cos\left(\frac{\pi mx}{a}\right) dx = 0$$

For $n + m$ odd,

$$\begin{aligned} \frac{2}{a} \int_0^a x \sin\left(\frac{\pi nx}{a}\right) \sin\left(\frac{\pi mx}{a}\right) dx &= -\frac{8anm}{\pi^2(m^2 - n^2)^2} \\ \frac{\pi m}{a} \frac{2}{a} \int_0^a \sin\left(\frac{\pi nx}{a}\right) \cos\left(\frac{\pi mx}{a}\right) dx &= \frac{4mn}{a(n^2 - m^2)} \end{aligned}$$