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
$$\hat{L}_z Y_{\ell m}(\theta,\phi) = \hbar m Y_{\ell m}(\theta,\phi)$$
  - Remember that m and ℓ are both integers.
  - Simplifying the above, we get
$$\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta_{\ell m}}{\mathrm{d}\theta}\right) - m^2\Theta_{\ell m} + [\ell(\ell+1)\sin^2\theta]\Theta_{\ell m} = 0$$
  - 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).