Week 4

Vibrational Motion and the Harmonic Oscillator

4.1 Rotational Motion

10/18:

- Consider the diatomic molecule AB at a distance r_0 apart rotating about its center of mass.

(a) Diatomic. (b) An equivalent system.

Figure 4.1: Diatomic rotation.

  - To simplify the problem, replace the two particles rotating about the center of mass with one particle of reduced mass μ rotating about the center of mass with lever arm r_0.

- Classically, the kinetic energy of the translational motion is

$$T = \frac{L^2}{2I}$$

  where $I = \mu r_0^2$ and $L = p \times r_0 = p r_0$ (for this kind of rotation; see Figure 4.1b).

- To further talk about this problem, we should introduce **spherical coordinates**.

- **Spherical coordinates**: The coordinate system (r, θ, ϕ) related to the Cartesian coordinates (x, y, z) by

$$x = r \sin\theta \cos\phi \qquad y = r \sin\theta \sin\phi \qquad z = r \cos\theta$$

- Classically, we will have

$$H = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

  in Cartesian coordinates.

- In spherical coordinates, this becomes

$$H = \frac{1}{2\mu}\left(p_r^2 + \frac{L^2}{r^2}\right) + V(r)$$

- Thus, in quantum mechanics, we get

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(x,y,z) \\ &= \frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)\end{aligned}$$

- Thus, we have in spherical coordinates that

$$\hat{T}\psi = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) + \frac{1}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi\right)\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi\right]$$

- 2D rigid rotor:
  - Let the system from Figure 4.1b be confined to rotating in two dimensions.
  - This simplifies the problem since both the $\partial/\partial r$ and $\partial/\partial\theta$ terms in the kinetic energy operator disappear (since, respectively, the particle is at a fixed distance from the center of mass and it cannot move out of the 2D plane).
  - Thus, our Schrödinger equation for this system is

$$-\frac{\hbar^2}{2\mu r_0^2}\frac{\partial^2}{\partial\phi^2}\psi(\phi) = E\psi(\phi)$$

  - Solution: Let $\psi(\phi) = \mathrm{e}^{im\phi}$; then

$$E_m = \frac{\hbar^2 m^2}{2\mu r_0^2}$$

    - $m = 0, 1, 2, \ldots$ is a new quantum number.
    - m doesn't go to infinity because $|m|$ is bounded by ℓ (the total angular momentum).
  - Remembering our original restriction, we have that this math describes the system from Figure 4.1a but confined to rotate in the xy plane with angular momentum in the z direction.
    - Thus, for example, the energies of the system from Figure 4.1a are dependent on m and $I = \mu r_0^2$.
  - Such a system occurs in physical reality when we put the diatomic in an external field, or attach to it a big functional group.
  - Zero point energy: $m = 0$ does not violate the UR since we still have $\Delta L\Delta\theta \geq \hbar/2$ (as everything is still rotating in the sense that we have equal probability of the particle being everywhere [as opposed to more localized/normal rotation with higher values of m]).
- 3D rigid rotor:
  - Assume that the potential energy is zero on the surface of the sphere (so we basically have a particle on a sphere).
  - Then

$$\hat{H} = \frac{\hat{L}^2}{2\mu r_0^2} = \frac{\hat{L}^2}{2I}$$

  - Solving $\hat{H}\psi = E\psi$ asserts that the eigenfunctions of the Hamiltonian are the spherical harmonics $Y_{\ell m}(\theta,\phi)$.
  - Energy:

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1)$$

    where $\ell = 0, 1, 2, \ldots$.
  - Recall that m corresponds to the projection of angular momentum onto the z-axis, so that

$$m = -\ell, \ldots, +\ell$$