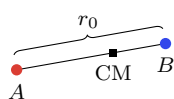


## Week 4

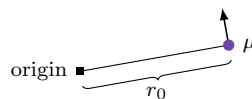
# Vibrational Motion and the Harmonic Oscillator

### 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  $\mu$  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  $L = p \times r_0 = pr_0$  (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  $(r, \theta, \phi)$  related to the Cartesian coordinates  $(x, y, z)$  by

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

- 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  $\psi(\phi) = e^{im\phi}$ ; then

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

- $m = 0, 1, 2, \dots$  is a new quantum number.
  - $m$  doesn't go to infinity because  $|m|$  is bounded by  $\ell$  (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  $\ell = 0, 1, 2, \dots$

- Recall that  $m$  corresponds to the projection of angular momentum onto the  $z$ -axis, so that

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