

University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 17 2/25/15

Recommended Reading Atkins & DePaula 9.5

A. Background in Rotational Mechanics

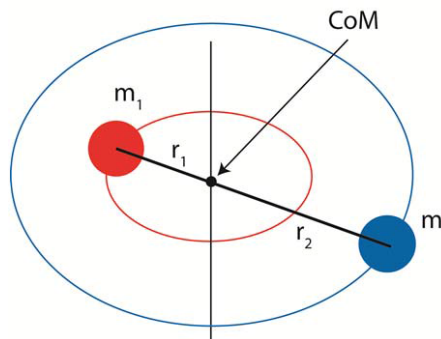
- Two masses m_1 and m_2 connected by a weightless rigid “bond” of length r rotates with angular velocity $\omega = v/r$ where v is the linear velocity. As with vibrations we can render this rotation motion in simpler form by fixing one end of the bond to the origin terminating the other end with reduced mass μ , and allowing the reduced mass to rotate freely
- For two masses m_1 and m_2 separated by r the center of mass (CoM) is defined by the condition

$$m_1 r_1 = m_2 r_2 \quad (17.1)$$

where

$$r_{1,2} = \frac{m_{2,1}}{m_1 + m_2} r \quad (17.2)$$

Figure 17.1: Location of center of mass (CoM) for two masses separated by a distance r .



- The moment of inertia I plays the role in the rotational energy that is played by mass in translational energy. The moment of inertia is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (17.3)$$

- Putting 17.3 into 17.4 we obtain

$$I = \mu r^2 \quad (17.4)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

- We can express the rotational kinetic energy K in terms of the angular momentum. The angular momentum is defined in terms of the cross product between the position vector \vec{r} and the linear momentum vector \vec{p} :

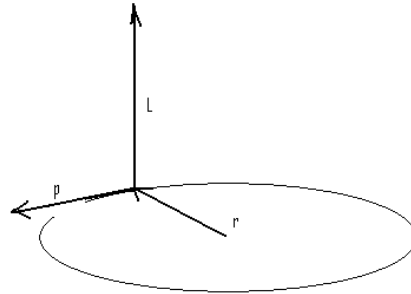
$$\begin{aligned} \vec{L} &= \vec{r} \times \vec{p} \\ &= pr \sin \theta = pr = \mu v r \end{aligned} \quad (17.5)$$

where the angle θ between \vec{p} and \vec{r} is ninety degrees for circular motion.

- As a cross product, the angular momentum vector \vec{L} is perpendicular to the plane defined by the \vec{r} and \vec{p} vectors as shown in Figure 17.2

- We can use equation 17.6 to obtain an expression for the kinetic energy in terms of the angular momentum L:

Figure 17.2: The angular momentum L is a cross product of the position r vector and the linear momentum $p=mv$ vector. L is perpendicular to the plane formed by r and p .



$$K = \frac{p^2}{2\mu} = \frac{L^2}{2\mu r^2} = \frac{L^2}{2I} \quad (17.6)$$

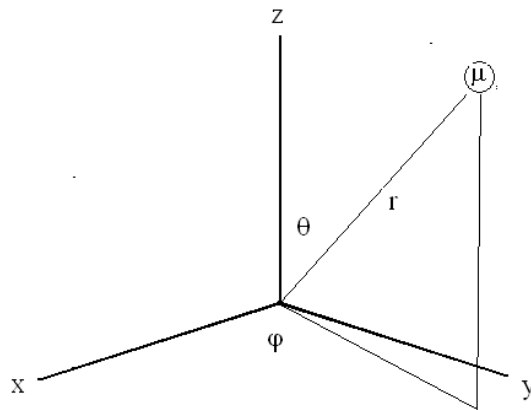
B. Quantum Planar Rigid Rotor: “Particle-on-a-Ring”

- Suppose a diatomic molecule rotates in such a way that the vibration of the bond is unaffected by the rotation. Molecular rotation is not naturally treated in Cartesian coordinates so we change to spherical coordinates

$$x = r \cos \varphi \sin \theta; y = r \sin \varphi \sin \theta; z = r \cos \theta \quad (17.7)$$

See the Figure 17.3 for the graphical relationship between the two coordinate systems.

Figure 17.3: Rotation of two mass m_1 and m_2 separated by a fixed distance r , is equivalent to rotation of a reduced mass μ at a fixed distance r about the origin



- For simplicity, assume the rigid rotor is confined to a plane such that $\theta=\pi/2$. This planar rigid rotor is not a terribly realistic model for molecular rotations, but it does illustrate an application of Schroedinger’s equation that can be worked out fairly easily.
- We imagine that the origin is the center of mass of the rigid rotor and length of the rotor is r . At r is located a reduced mass μ . Rotation occurs in the x-y plane around the z axis. As rotation occurs the angle φ changes. The notation L_z refers to the fact that because the rotation is around the z axis the angular momentum vector is parallel to the z axis. Schroedinger’s equation is:

$$\frac{p^2}{2\mu} \psi(\varphi) = \frac{p^2 R^2}{2\mu R^2} \psi(\varphi) = \frac{L_z^2}{2I} \psi(\varphi) = E \psi(\varphi) \quad (17.8)$$

- We define $L_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi} = -i\hbar \frac{\partial}{\partial \varphi}$ so that $L_z^2 = -\hbar^2 \frac{d^2}{d\varphi^2}$ and Schroedinger’s equation becomes:

$$-\frac{\hbar^2}{2I} \frac{d^2\psi(\varphi)}{d\varphi^2} = E\psi(\varphi) \Rightarrow \frac{d^2\psi(\varphi)}{d\varphi^2} = -\frac{2IE}{\hbar^2} \psi(\varphi) \quad (17.9)$$

- The resemblance of equation 17.10 to the particle in a box wave equation is obvious and for this reason the planar rigid rotor is sometimes called the particle on a ring.
- The solution is (see Figure 17.4):

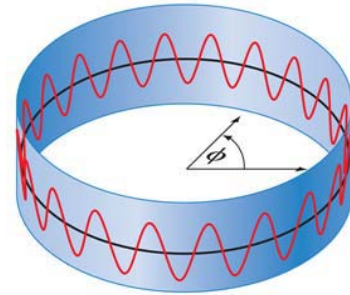
$$\psi(\varphi) = A_+ e^{im\varphi} + A_- e^{-im\varphi} = \psi_+(\varphi) + \psi_-(\varphi) \quad (17.10)$$

where $m^2 = \frac{2IE}{\hbar^2}$.

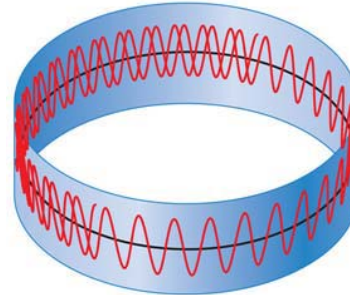
- In equation 17.11 $\psi_+(\varphi)$ corresponds to clockwise rotation and $\psi_-(\varphi)$ corresponds to counterclockwise rotation.
- We require that because the rotor is indistinguishable when it is oriented at φ versus $\varphi+2\pi$:

$$\psi(\varphi) = \psi(\varphi + 2\pi)$$

$$\text{or } \dots A_+ e^{im\varphi} + A_- e^{-im\varphi} = A_+ e^{im(\varphi+2\pi)} + A_- e^{-im(\varphi+2\pi)} \quad (17.11)$$



$m_l = \pm \text{integer}$



$m_l \neq \pm \text{integer}$

Figure 17.4: Top a wave function that satisfies 17.12 when m is a positive or negative integer. Bottom: the boundary condition in 17.12 is not fulfilled when m is not an integer.

- For this to occur we require that $e^{im2\pi} = 1$, which will only occur if $m = 0, \pm 1, \pm 2, \pm 3 \dots$. Because m is positive and negative we need only a single function to describe the wave function, which can now be normalized:

$$1 = \int_0^{2\pi} \psi^*(\varphi)\psi(\varphi) d\varphi = A^2 \int_0^{2\pi} e^{-im\varphi} e^{im\varphi} d\varphi = A^2 \int_0^{2\pi} d\varphi = 2\pi A^2 \quad (17.12)$$

$$\therefore A = \sqrt{\frac{1}{2\pi}}$$

- We substitute $\psi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$ into Schroedinger's equation 17.9 and obtain the energy quantization condition:

$$E_m = \frac{\hbar^2 m^2}{2I} \quad (17.13)$$

where $m = 0, \pm 1, \pm 2, \pm 3 \dots$

- Because $E = \frac{L_z^2}{2I}$ equation 17.13 implies that the angular momentum around the z axis is quantized according to

$$E_m = \frac{L_z^2}{2I} = \frac{\hbar^2 m^2}{2I} \Rightarrow L_z = \hbar m; \quad m = 0, \pm 1, \pm 2, \pm 3 \dots \quad (17.14)$$

- In summary, the energies of a plane rigid rotor or particle-on-a-ring appear in Figure 17.5. Above the ground state, each energy is two-fold degenerate. Note that there is no zero point energy. Zero point energies are observed in bound state systems like the particle in the box and the LHO, but the rigid rotor is not in a bound state.

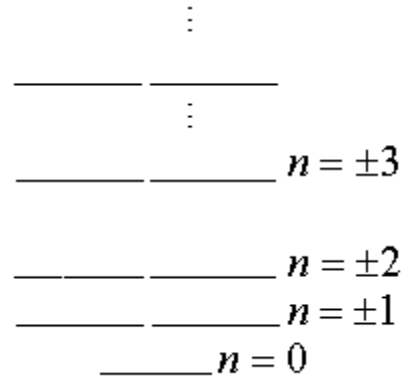


Figure 17.5: Energy levels for the Particle-on-a-Ring.

C. Applications of Particle-on-a-Ring

- There are numerous applications for the plane-rigid-rotor a.k.a. particle on a ring. A realistic physical picture of free rotation of a small molecule would require possibility of rotational motions in three dimensions. The plane rigid rotor model allows rotation only in a plane. Such a rotational model might be applicable to molecules adsorbed onto surfaces.
- A more common application is to visualize this model as describing a particle (i.e. an electron) confined to a ring-like annulus. While this seems a far-fetched notion, we can approximate the energetic of delocalized electrons in cyclic conjugated molecules (e.g. benzene) as particles in rings.