University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 18 2/27/15
Recommended Reading Atkins & DePaula 9.5

A. Rigid Rotor – Quantized Angular Momentum

- A more realistic model has a rigid linear molecule with moment of inertia I rotating through two angular dimensions, designated by θ and φ, which are the two angles used to locate a vector of length r in three dimensional space. See Figure at right which shows θ as the angle between the vector and the z axis: $z = r\cos\theta$. The angle φ is the angle between the x axis and the projection of the vector onto the x-y plane. Accordingly: $x = r\sin\theta\cos\varphi$ and $y = r\sin\theta\sin\varphi$. See Figure 18.1
- Assuming that r is constant, Schroedinger's equation becomes

$$\frac{L^2}{2I}\Psi(\theta,\varphi) = E\Psi(\theta,\varphi) \tag{18.1}$$

- where it can be shown that L^2, the total angular momentum, is:

$$L^2 = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \tag{18.2}$$

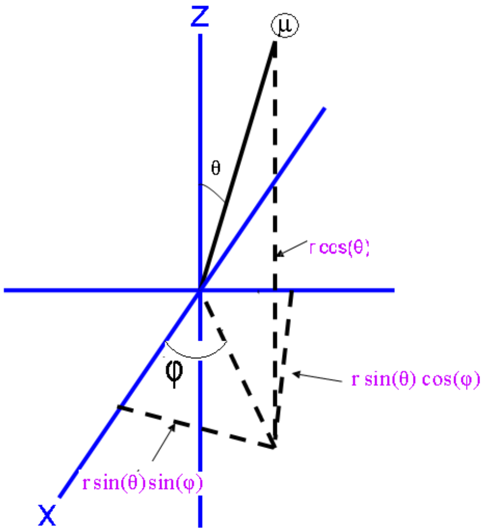


Figure 18.1: Spherical coordinate system showing definition of angles θ and φ.

- Note because the rotor is rigid r is a constant: r=R and so all derivatives with respect to r vanish. The problem becomes two dimensional and the wave function is obtained by solving (18.1) with L^2 given by (18.2).

- One dimensional problems like the particle in the one dimensional box have a single quantum number n. The particle in a three dimensional box has three quantum numbers n_x, n_y, n_z. Accordingly the rigid rotor has two quantum numbers J and m. The quantum number J quantizes total angular momentum L. The quantum number m quantizes the z component of the angular momentum J_z.

- The dependence of the wave functions on J and m is

$$\Psi_{J,m}(\theta,\varphi) = \Theta_{J,m}(\theta)\Phi_m(\varphi) \qquad (18.3)$$

- The wave functions $\Psi_{J,m}(\theta,\varphi)$ are called spherical harmonics, because they correspond to waves on the surface of a sphere. As J increases the energy increases and the wavelength decreases.
- The rigid rotor model is sometimes called “particle-on-a-sphere”. Representations of spherical harmonics for J=0, 1, and 2 are in Figure 18.2.

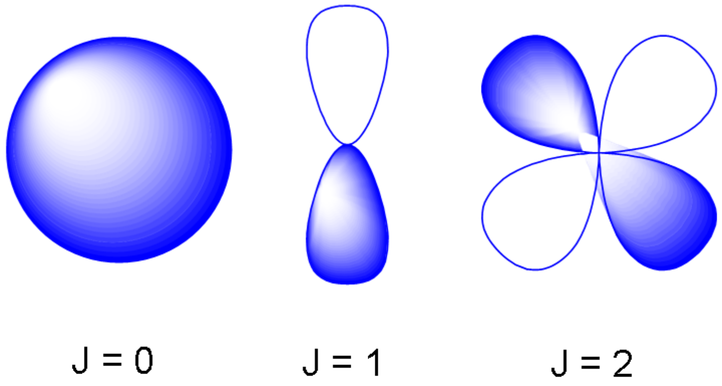


Figure 18.2: Representation of spherical harmonics for J=0, 1, 2

- The energy is a function of J only:

$$E_J = \frac{L^2}{2I} = \frac{\hbar^2}{2I}J(J+1) \qquad (18.4)$$

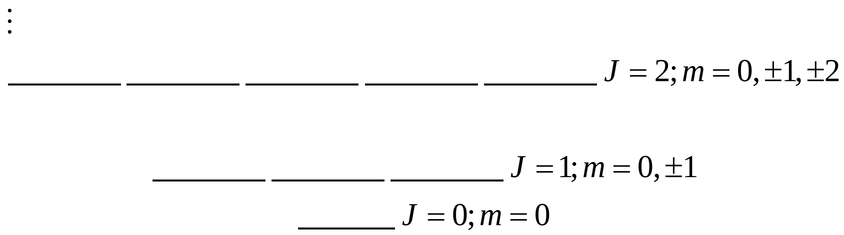
where $J = 0,1,2,3\ldots$

- For a given value of *J*, m runs from –*J* to +*J* or m=0, ±1, ±2,… ±*J*…a total of 2*J*+1 values.
- Because the energy is dependent only on *J*, there will be 2*J*+1 wavefunctions corresponding to different values of m, that will have this energy. Each rotational level will be 2*J*+1 degenerate.
  - For a rigid rotor in three dimensions each

energy level for $J \neq 0$ is $2J+1$ degenerate. For $J = 1$ the energy is three-fold degenerate.
For $J = 2$, it is five-fold degenerate, etc. Note

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right] = \frac{\hbar^2}{2I}(2J+2) \qquad (18.5)$$

so the energy level spacing also increases with increasing energy…



D. Rigid Rotor- Quantization of Total and Z Angular momentum

- Because $E_J = \frac{L^2}{2I} = \frac{\hbar^2}{2I} J(J+1)$, the total angular momentum is L quantized according to $L^2 = \hbar^2 J(J+1)$ or

$$L = \hbar\sqrt{J(J+1)} \qquad (18.6)$$

- The quantum number J has values J=0,1,2,3,4,…
- Because L_z^2 also appears in the Schroedinger equation L_z is quantized exactly as in the planar rigid rotor: $L_z^2 = \hbar^2 m^2$ or

$$L_Z = \hbar m \qquad (18.7)$$

- The total angular momentum L is related to its x, y, and z components by:

$$L^2 = L_X^2 + L_Y^2 + L_Z^2 \qquad (18.8)$$

- . Therefore in classical mechanics a freely rotating rigid, linear molecule like CO has its angular momentum vector trace out a sphere.
- In quantum mechanics, because L is quantized according to $L = \hbar\sqrt{J(J+1)}$ and Lz is also quantized by $L_Z = \hbar m$ where $m = 0, \pm1, \pm2, \ldots \pm J$. This means that instead of tracing out a sphere, for every value of ℓ there are $2J+1$ orientations of the angular momentum vector L. For m>0 the L vector point up relative to the x-y plane, for m<0 the L vector points down, and for m=0 the L vector is perpendicular to the z axis. See Figure 18.3

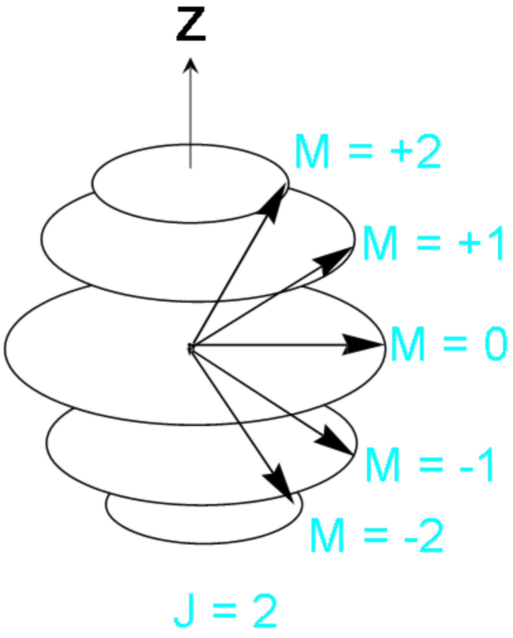


Figure 18.3: Because only L and L_z are quantized, L_x and L_y are arbitrary. So every quantized state of L and L_z corresponding to a (J,m) pair, results in a cone pattern in L_x, L_y, L_z space. An example is shown below for $J = 2$…

- For each cone the length of L is

$$L = \hbar\sqrt{J(J+1)}$$
$$= \hbar\sqrt{2(2+1)} = \hbar\sqrt{6}$$

- Each cone has a difference value of L_z corresponding to

$$L_Z = \hbar m \Rightarrow (-2\hbar, -\hbar, 0, \hbar, 2\hbar)$$

- The patterns in Figure 18.3 result from the Heisenberg Uncertainty Principle.

E. Rotational Partition Functions for the Rigid Rotor:

- To calculate the partition function for the Rigid Rotor we use the energy expression $E_J = -\frac{\hbar^2}{2I} J\left(J+1\right)$ (J=0,1,2,3...). we obtain for a diatomic molecule rotating rigidly

$$q_{rot} = \frac{1}{\sigma}\sum_{J=0}^{\infty}\left(2J+1\right)e^{-\hbar^2 J\left(J+1\right)/2Ik_BT} \qquad (18.9)$$

- The term σ is added to avoid overcounting. For a homonuclear diatomic when the molecule rotates by 180 degrees the result is indistinguishable from a rotation of zero. Therefore for homonuclear diatomics σ=2. For heteronuclear diatomics σ=1.
- In the high temperature limit where $k_BT \gg \Delta E_J = E_{J+1} - E_J = 2\left(J+1\right)\hbar^2 / 2I$, the summation can be approximated with an integral and we get

$$q_{rot} = \frac{1}{\sigma}\int_0^{\infty}\left(2J+1\right)e^{-\hbar^2 J\left(J+1\right)/2Ik_BT}dJ = \frac{2Ik_BT}{\sigma\hbar^2} = \frac{8\pi^2 Ik_BT}{\sigma h^2} \qquad (18.10).$$

- A result of equation 18.10 the internal energy and heat capacity associated with the rotation of a diatomic molecule are

$$U_{rot} = Nk_BT \text{ and } C_V = Nk_B \qquad (18.11)$$

- Note because each rotational energy state is 2J+1 fold degenerate the probability of being in the Jth energy state is:

$$P_J = \left(2J+1\right)\frac{e^{-\hbar^2 J\left(J+1\right)/2Ik_BT}}{q_{rot}} \qquad (18.12)$$

where now q_{rot} is given by equation 18.10.