University of Washington
Department of Chemistry
Chemistry 453
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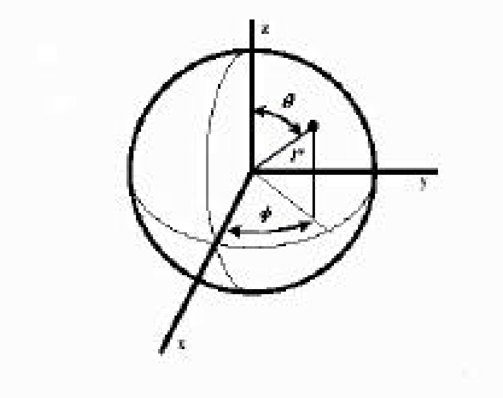
Lecture 08 1/30/12

A. Rigid Rotor – Quantized Energy

- 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 $y = r\sin\theta\sin\varphi$.



- Assuming that r is constant, Schroedinger's equation becomes

$$\frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right)\Psi(\theta,\varphi) = \frac{L^2}{2I}\Psi(\theta,\varphi) = E\Psi(\theta,\varphi) \tag{8.1}$$

where it can be shown that $p_\theta^2 = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$ *and* $p_\varphi^2 = L_z^2 = -\hbar^2\frac{\partial^2}{\partial\varphi^2}$

- Therefore L^2 is the total angular momentum:

$$L^2 = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \tag{8.2}$$

- 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 that is obtained by solving (8.1) has the form…

$$\Psi(\theta,\varphi) = \Theta(\theta)\Phi(\varphi) \tag{8.3}$$

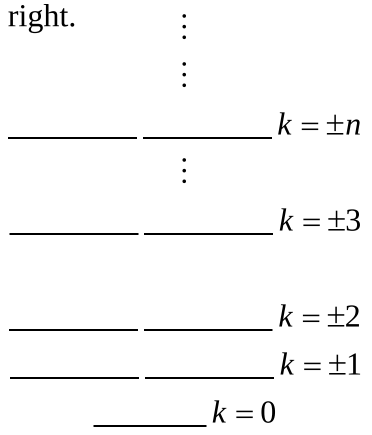
- One dimensional problems like the particle in the one dimensional box have a single quantum number n. The particle in a three dimensional box has three quantum numbers n_x, n_y, n_z. Accordingly the rigid rotor has two quantum numbers l and m. The dependence of the wave functions on l and m is

$$\Psi_{l,m}(\theta,\varphi) = \Theta_{l,m}(\theta)\Phi_m(\varphi) \tag{8.4}$$

- Schroedinger's equation can also be solved to get the energy and the wave functions.
- The energy is a function of l only: $E_l = \frac{L^2}{2I} = \frac{\hbar^2}{2I}l(l+1)$ where $\ell = 0,1,2,3\ldots$

- For a given value of *l*, m runs from –*l* to +*l* or m=0, ±1, ±2,… ±*l*…a total of 2*l*+1 values.
- Because the energy is dependent only on *l*, there will be 2*l*+1 wavefunctions corresponding to different values of m, that will have this energy. Each rotational level will be 2*l*+1 degenerate.
- Let's compare the energy level diagram for a plane rigid rotor to a rigid rotor free to rotate in three dimensional space. For a plane rigid rotor : $E_K = \dfrac{k^2\hbar^2}{2I}; k = 0, \pm 1, \pm 2\ldots$ so for $k \neq 0$ the energy levels are doubly degenerate.

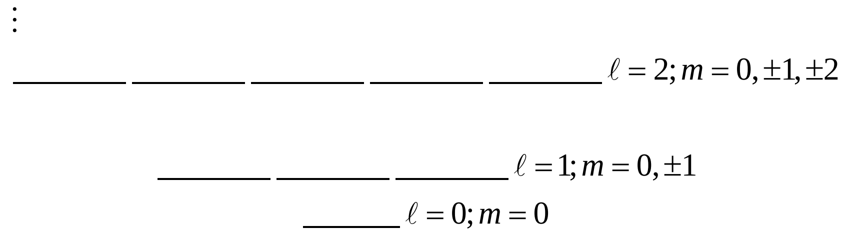
  Also $\Delta E = E_{k+1} - E_k = (2k+1)\dfrac{\hbar^2}{2I}$ so the energy levels are spread farther apart as the energy increases. See energy level scheme at the right.



- For a rigid rotor in three dimensions each energy level for $\ell \neq 0$ is $2\ell + 1$ degenerate. For $\ell = 1$ the energy is three-fold degenerate. For $\ell = 2$, it is five-fold degenerate, etc. Note

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

so the energy level spacing also increases with increasing energy…

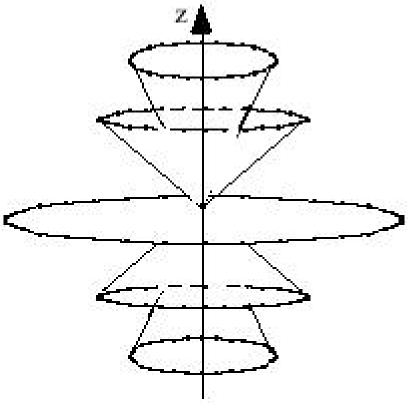


B. Rigid Rotor- Quantization of Total and Z Angular momentum

- Because $E_\ell = \dfrac{L^2}{2I} = \dfrac{\hbar^2}{2I}\ell(\ell+1)$, the total angular momentum is L quantized according to $L^2 = \hbar^2 l(l+1)$ or $L = \hbar\sqrt{\ell(\ell+1)}$
- The quantum number *l* has values *l*=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 $L_Z = \hbar m$.

- The total angular momentum L is related to its x, y, and z components by: $L^2 = L_X^2 + L_Y^2 + L_Z^2$. 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 $L = \hbar\sqrt{\ell(\ell+1)}$ and Lz is also quantized by $L_Z = \hbar m$ where $m = 0, \pm1, \pm2, \ldots \pm \ell$. This means that instead of tracing out a sphere, for every value of ℓ there are $2\ell+1$ 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.

- 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 (ℓ,m) pair, results in a cone pattern in L_x, L_y, L_z space. An example is shown below for $\ell = 2 \ldots$



- For each cone the length of L is $L = \hbar\sqrt{\ell(\ell+1)}$ $= \hbar\sqrt{2(2+1)} = \hbar\sqrt{6}$

- Each cone has a difference value of Lz corresponding to $L_Z = \hbar m \Rightarrow (-2\hbar, -\hbar, 0, \hbar, 2\hbar)$