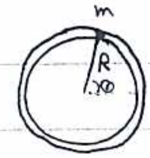
Chem. 1410
Sept. 24, 2007

Particle on a Ring



Naively: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \rightarrow -\frac{\hbar^2}{\underbrace{2mR^2}_{I}}\frac{\partial^2}{\partial \Theta^2} = \hat{H}_R$ ← "Ring"

$dx = R\,d\Theta$

More formally, for any 2-D particle in box: $\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$ + B.C.'s

Note identity: $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\frac{\partial^2}{\partial \Theta^2}$ [i.e., $\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) f(x,y) = \left(\frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\frac{\partial^2}{\partial \Theta^2}\right) f(R\cos\Theta, R\sin\Theta)$]

$x = R\cos\Theta;\ y = R\sin\Theta$

Here, R is "frozen" $\Rightarrow$ $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \rightarrow -\frac{\hbar^2}{2mR^2}\frac{\partial^2}{\partial \Theta^2}$ ✓

So, Schröd. Eq. reads:

$$-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial \Theta^2}\psi(\Theta) = E\psi(\Theta)$$

solved by: $\boxed{\psi_n(\Theta) = Ae^{in\Theta}}$; must have $\psi_n(\Theta + 2\pi) = \psi_n(\Theta)$ [to be single-valued] $\Rightarrow$ $\boxed{n = -2, -1, 0, 1, 2 \ldots}$

$\Downarrow$

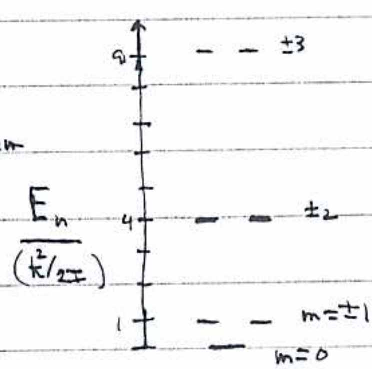
$$\boxed{E_n = \frac{\hbar^2 n^2}{2I}}$$

compute norm. factor A:

$$1 = \int_0^{2\pi} d\Theta\ \psi_n^*(\Theta)\psi_n(\Theta) = A^2\, 2\pi \Rightarrow \boxed{A = \sqrt{\frac{1}{2\pi}}}$$

Notes:

(a) energy level diagram



All levels doubly degenerate, except ground state finally, $\psi_n(\Theta)$ is eigenfunctn of $\hat{L}_z$: Classically $\underset{\sim}{L} = \underset{\sim}{r} \times \underset{\sim}{p}$, e.g. $L_z = x p_y - y p_x$

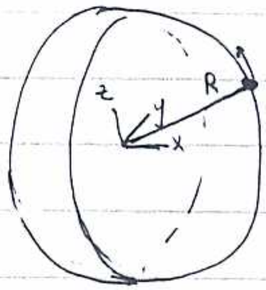
So, quantum mechanically, $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \boxed{\frac{\hbar}{i}\frac{\partial}{\partial \Theta}}$

Note: $\frac{\partial}{\partial \Theta} = \underbrace{\frac{\partial x}{\partial \Theta}}_{-r\sin\Theta = -y}\frac{\partial}{\partial x} + \underbrace{\frac{\partial y}{\partial \Theta}}_{r\cos\Theta = x}\frac{\partial}{\partial y}$

thus $\hat{L}_z e^{in\Theta} = \underbrace{\boxed{\frac{\hbar}{i}(in)}}_{\ell_z = \hbar n} e^{in\Theta}$

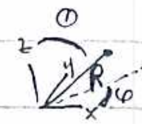
②

Particle on a Sphere [Rigid Rotor]



Same strategy as particle on ring, but details more complicated

Recall: Cartesian $\leftrightarrow$ Spherical polar coords



$$z = R\cos\Theta$$
$$x = R\sin\Theta\cos\varphi$$
$$y = R\sin\Theta\sin\varphi$$

"Laplacian" in 3-d: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Hamiltonian operator for a 3d particle: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$

Expression for Laplacian in spherical polar coords: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{R^2}\left\{\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\left(\sin\Theta\frac{\partial}{\partial\Theta}\right) + \frac{1}{\sin^2\Theta}\frac{\partial^2}{\partial\varphi^2}\right\}$

[NB: this means $\nabla^2 f(x,y,z) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial f}{\partial R}\right) + \frac{1}{R^2}\left\{\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\left(\sin\Theta\frac{\partial f}{\partial\Theta}\right) + \frac{1}{\sin^2\Theta}\frac{\partial^2 f}{\partial\varphi^2}\right\}$

$f(R\sin\Theta\cos\varphi, R\sin\Theta\cos\varphi, R\cos\Theta)$

So, for particle on sphere [R = fixed, otherwise $V=0$], S.E. reads:

$$-\frac{\hbar^2}{2m\underbrace{R^2}_{I}}\left\{\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\left(\sin\Theta\frac{\partial}{\partial\Theta}\right) + \frac{1}{\sin^2\Theta}\frac{\partial^2}{\partial\varphi^2}\right\}\psi(\Theta,\varphi) = E\,\psi(\Theta,\varphi)$$

Only fnctns. that solve the S.E. and are both finite and single-valued on sphere are

"Spherical Harmonic"

$$\psi_{l m_l}(\Theta,\varphi) = Y_{l m_l}(\Theta,\varphi) = N_{l m_l}\,\underbrace{\Theta_{l|m_l|}}_{}(\Theta)\,e^{i m_l \varphi} \quad ; \quad l = 0,1,2\ldots \quad ; \quad -l,-l+1,\ldots,l = m_l$$

"∡ momentum q.n." "Associated Legendre fnctn."

"magnetic q.n."

Typical Assoc. Legendre fnctns: $\Theta_{00} = 1$ $\leftarrow$ Note: for $m_\ell = 0$ $\Theta_{\ell 0} \to P_\ell(\cos\theta)$ = Legendre polynomial

$\Theta_{10} = \cos\theta$

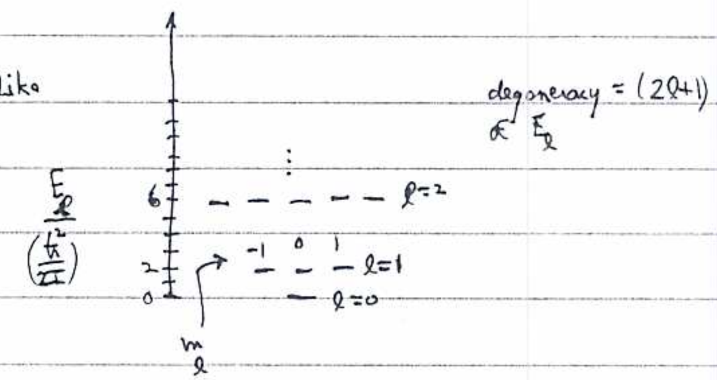
$\Theta_{11} = \sin\theta$

$\Theta_{20} = \frac{1}{2}(3\cos^2\theta - 1)$

Corresponding Energy levels:

$$E_{\ell m_\ell} = \underset{\substack{\uparrow \\ \text{independent} \\ \text{of } m_\ell\,!}}{E_\ell} = \frac{\hbar^2}{2I}\ell(\ell+1) \qquad \ell = 0, 1, 2 \ldots$$

Hence E diagram looks like



More features: (i) connection to $\not{L}$-momentum; Recall $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = y\frac{\hbar}{i}\frac{\partial}{\partial z} - z\frac{\hbar}{i}\frac{\partial}{\partial y}$

$L_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = \quad \vdots$

$L_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

It can be shown that

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + L_z^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$$

Hence $\hat{L}^2\psi_{\ell m_\ell} = \underbrace{\hbar^2\ell(\ell+1)}_{L^2}\psi_{\ell m_\ell}$ $\leftarrow$ Thus, $\psi_{\ell m_\ell}$ is also an eigenfnctn. of $\hat{L}^2$ w/ eigenvalues indicated

Furthermore, $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \Rightarrow \hat{L}_z\psi_{\ell m_\ell} = \underbrace{\hbar m_\ell}_{L_z}\psi_{\ell m_\ell}$ $\leftarrow$ Thus, $\psi_{\ell m_\ell}$ is also an eigenfnctn. of $\hat{L}_z$ w/ eigenvalues indicated

Note: $\hat{H} = \frac{\hat{L}^2}{2I}$ for rigid rotor, "as expected"

(ii) volume element; normalization: $\langle \hat{O} \rangle_\psi = \int_0^{2\pi} d\varphi \underbrace{\int_0^\pi \sin\Theta d\Theta}_{\int_{-1}^{1} d(\cos\Theta)} \psi^*(\Theta,\varphi)\, \hat{O}\, \psi(\Theta,\varphi)$

E.g. consider normalization of $\psi_{\ell m_\ell}$:

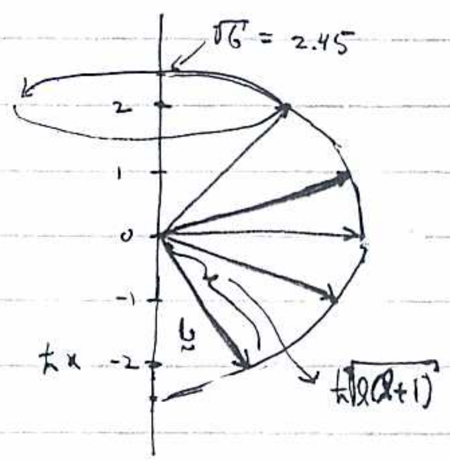
$$1 = \int_0^{2\pi} d\varphi \int_{-1}^{1} d(\cos\Theta) \left| \psi^*_{\ell m_\ell}(\Theta,\varphi) \right|^2 = 2\pi N^2_{\ell m_\ell} \int_{-1}^{1} d(\cos\Theta)\, \Theta^2_{\ell m_\ell}(\Theta)$$

For $\ell = m_\ell = 0$

$$1 = 2\pi N^2_{00} \underbrace{\int_{-1}^{1} d(\cos\Theta)}_{2} \Rightarrow N_{00} = \frac{1}{\sqrt{4\pi}}$$

(iii) Vector model of $\measuredangle$-mom [exploits fact that L^2, L_z values are precisely known]

Ex: $\ell = 2$



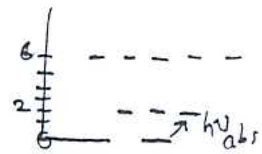
[Note L_x, L_y are "completely uncertain"]

Molecular example: microwave spectroscopy...

9/23/93

A bit of rotational ("microwave") spectroscopy

Rotational Energy levels given by $E_\ell = \dfrac{\hbar^2}{2\mu R_e^2}\,\ell(\ell+1)$; $\ell = 0, 1, 2 \ldots$ =



NB: $\mu = \dfrac{m_H m_{Cl}}{(m_H + m_{Cl})}$

Given: Lowest absorption frequency is $\nu_{abs} = 6.35E11\ Hz$

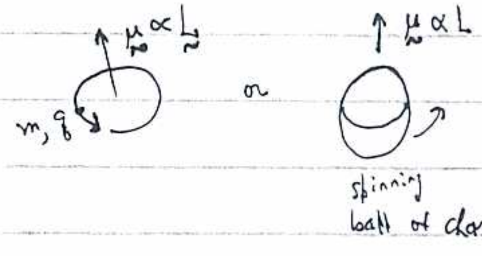
for $H^{35}Cl$ $\left(= \dfrac{6.35E11/sec}{3E10\ cm/sec} = 21.17\ cm^{-1} \right)$

What is R_e? $E_1 - E_0 = 2 \cdot \dfrac{\hbar^2}{2\mu R_e^2} = h\nu_{abs}$; $21.17\ cm^{-1} \times \left(\dfrac{1.99E{-16}\ erg}{cm^{-1}} \right) = \dfrac{(1.05E{-27}\ erg\cdot sec)^2}{\left[\left(\frac{35\cdot 1}{36}\right) \frac{1}{6.02E23}\ gm\right] R_e^2}$

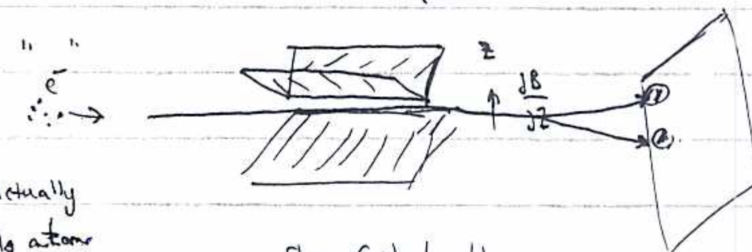
$\Rightarrow R_e = 1.27\ \mathring{A}$

"Spin" = Intrinsic ∡ momentum of the electron

Note, classically



Motion in an inhomogeneous magnetic field (B): $F \propto \mu \cdot \nabla B = \mu_z \frac{\partial B}{\partial z}$ if B changes in z direction

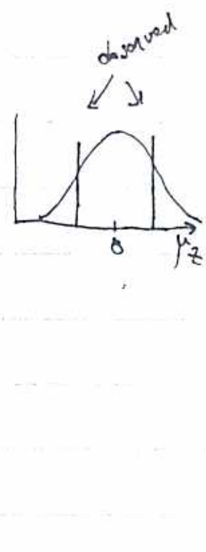


} 2 spots only

[Actually Ag atoms w/ 1 unpaired valence electron

Stern-Gerlach expt.

Analysis: (1): Classically ↑ ↗ ↙ ↑ ↖ isotropic distribution of μ expected $\Rightarrow N(\mu_z)$



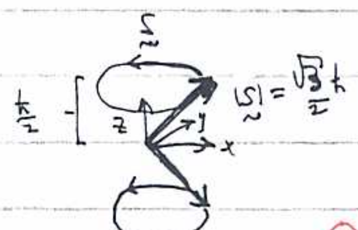
(2) Apparently $\mu_z = \pm \mu_0$, only
& μ_0 some constant
S_z

Analysis is Consistent w/ postulate that spin ∡-momentum $L \to$ "S" of an electron characterized by $\ell \to \frac{1}{2}$.

Then:

$$S_z = \pm \frac{1}{2}\hbar \; ; \; S^2 = \hbar^2 \frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}\hbar^2$$

Vector model:



← electron is "spin up", or "spin down"