Rotational Motion (Ch. 5, Levine; Ch. 4 Atkins)

<u>Previous</u> example – particle constrained to a ring:

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$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi \quad \rightarrow \quad x = R\cos\varphi$$

$$\frac{-\hbar^2}{2mR^2}\frac{\partial^2}{\partial\varphi^2}\Psi(\varphi) = E\Psi(\varphi) \qquad y = R\sin\varphi$$

$$\Psi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}$$

No dep of Ψ on R since R is const

m = 0, 1, 2, . . .   from B.C. continuity

$\Psi(0) = \Psi(2\pi)$

and substituting back: $E = m^2h^2/2I$

$I = mR^2$

moment of inertia

Meaning from

$L_z = xp_y - yp_x$

$= (-ih)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

$L_z = (-ih)\frac{\partial}{\partial\varphi}$

<u>angular momentum about z</u>

$L_z\Psi_m(\varphi) = mh\Psi_m(\varphi)$

so for this solution eigen fct of <u>ang. mom.</u> and <u>sign of m</u> indicates direction motion

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[NOTE: $\Psi(\varphi) = Ae^{-m\varphi} + Be^{+im\varphi}$ perfectly okay but not eigen fct of L_z]

same for $\sin(m\varphi)$ or $\cos(m\varphi)$

[NOTE: plotting cos $m\varphi$ **INSERT PICTURE** may look like distrib non-uniform

but $\Psi^*\Psi = 1/2\pi e^{im\varphi}e^{-im\varphi} - 1/2\pi \rightarrow$ const & uniform]

[NOTE: no zero point motion $m = 0 \rightarrow p\langle L_z\rangle = 0$, φ numbers don't need curvature to fulfill bonding coord]

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nodes increases ω/m + E_m and so does $\langle L_z\rangle$

<u>alternate up</u> – plot amplitude of Ψ as radius at angle φ

<u>symmetry</u> $\Psi(\varphi + \pi) = \frac{1}{\sqrt{2\pi}} e^{i(\varphi+\pi)m} = e^{i\pi m}\Psi = (-1)^m\Psi$

Now go to higher dimension – particle confined to <u>sphere</u>

$$H\Psi = \frac{-\hbar^2}{\partial m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\Psi = \frac{-\hbar^2}{\partial m}\nabla^2\Psi = E\Psi$$

but again since R constant can effectively reduce dimension (2 variables)

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$x = R \sin\theta \cos\varphi$
$y = R \sin\theta \sin\varphi$ (x,y,z) (R,θ,φ)
$z = R \cos\theta$

rearrangement of Laplacia (∇^2) into (R,θ,φ) coordinates

$$\nabla^2 = \left(\frac{1}{R}\right)\left[\frac{\partial^2}{\partial R^2}\right] R + \left[\frac{1}{R^2}\right]\Lambda^2$$

Legendrian:

$$\Lambda^2 = \frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial \varphi^2}\right] + \frac{1}{(\sin\theta)}\left(\frac{\partial}{\partial\theta}\right)\sin\theta\left(\frac{\partial}{\partial\theta}\right)$$

since R-fixed, terms in $\frac{\partial}{\partial R} \to 0$

$$H\Psi = \frac{-\hbar^2}{\partial m R^2}\Lambda^2\Psi = E\Psi$$

$$\Lambda^2\Psi(\theta,\varphi) = -\left[2EI/\hbar^2\right]\Psi(\theta,\varphi) \qquad I = mR^2$$

This problem is <u>separable</u>, let $\Psi(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$

$$\frac{\Theta(\theta)}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = \frac{\Theta(\varphi)}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta(\theta) = \frac{-2EI}{\hbar^2}\Theta(\theta)\Phi(\varphi)$$

divide by $\Psi(\theta,\varphi)$, mult by $\sin^2\theta$: $\frac{1}{\Phi}\frac{\partial^2}{\partial\varphi^2}\Phi(\varphi) = \frac{-\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta(\theta) - \frac{2EI}{\hbar^2}\sin^2\theta$

solve each independently
since fct of indep variables – set each equal to a const i – m

LHS: $\frac{\partial^2}{\partial\varphi^2}\Phi = -m^2\Phi$ $\qquad \Phi = \frac{1}{\sqrt{\pi}}e^{-im\varphi}$ $\qquad m = 0, 1, 2, \ldots$

just like for particle on a ring

RHS – This is more complex and involves another power series solution done Levine pp 95ff

But again this equation is one solved by LeGendre and his solution well-known (at least in 19th cent!)

$\Theta_{\ell m}(\theta) = p_\ell^{|m|}(\cos\theta)$

$p_\ell^{|m|}$ Legendre polynomial

l = 0,1,2, . . .

m = 0, 1, 2, . . ., ℓ limit on m

Normally we write $\Lambda^2 Y_{lm}(\theta,\varphi) = -\ell(\ell+1)Y_{lm}(\theta,\varphi)$

so by combining $Y_{lm}(\theta,\varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi)$ -- spherical harmonics (waves on flooded plat)

and $-\ell(\ell+1) = \frac{-2EI}{\hbar^2}$

$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1)$ only fct of ℓ not m

spacing ~($\ell^2 + \ell$)

zero E possible $\ell = 0$ solution

each ℓ level -- $(2\ell + 1)$ degenerate

plot length of vector ~ $|\Psi|^2$

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Solution: $Y_{lm}(\theta,\varphi)$

ℓ	m	
0	0	$Y\sqrt{2\pi}$
1	0	$\frac{1}{2}\left(3/\pi\right)^{1/2}\cos\theta$
	±1	$\mp\frac{1}{2}\left(3/\pi\right)^{1/2}\sin\theta\, e^{\pm i\varphi}$
2	0	$\frac{1}{4}\left(5/\pi\right)^{1/2}\left(3\cos^2\theta - 1\right)$
	±1	$\mp\frac{1}{2}\left(15/2\pi\right)^{1/2}\cos\theta\,\sin\theta\, e^{\pm i\varphi}$
	±2	$\frac{1}{4}\left(15/2\pi\right)^{1/2}\sin^2\theta\, e^{\pm 2i\varphi}$

Note: $\hat{H} = \hat{T}$, $[\hat{\pi},\hat{H}] = 0$ so expect solution to have parity

?????????

Angular Momentum

Classically $\vec{L} = \vec{r} \leftrightarrow \vec{p}$

the magnitude $|L| = I\omega$ ω – angular freq

converting to K.E.: $\frac{|I\omega|^2}{2I} = |L|^2 / 2I$

but we got q.m. $E_\ell = \hbar^2 / 2I \quad \ell(\ell+1)$

? $|L|^2 = \hbar^2 \ \ell(\ell+1)$

on <u>magnitude angular momentum</u> $\hbar\sqrt{\ell(\ell+1)}$

so <u>total ang mom</u> quantized ad operator is

$\hat{L}^2\Psi = -\hbar^2\Lambda^2 Y_{\ell m} \quad \hbar^2\ell(\ell+1)Y_{\ell m}$

from before know $\hat{L}_z = -i\hbar^2 \frac{f}{f\varphi}$

$\hat{L}_2 Y_{\ell m} = m\hbar \ Y_{\ell m}$

so both L^2 & L_z are quantized (consumed) in 2-D particle on sphere problem or Y_{lm} eigen fct of L^2 and L_z -- $[L^2, L_z] = 0$

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-- space quantization know magnitude, direction restricted to core of precession

ang momentum vector $\vec{L}$ must precess about some axis z, $|L_z|$? $|L|$

gives uncertainty in L_x, L_y

-- Clean why value of m restricted by l

*find $[L_z, L_x]$ 0 etc but $[L_x, L^2] = 0$?

(work it out ihL_y)

point one can know one component of angular momentum and the total magnitude (not omit)

How about 2 particles _

$$H_2 = \frac{-\hbar^2}{f m_1} ¾ \frac{f^2}{f x_1^2} + \frac{f^2}{f y_1^2} + \frac{f^2}{f z_1^2} √ - \frac{\hbar^2}{f m_2} ¾ \frac{f^2}{f x_2^2} + \frac{f^2}{f y_2^2} + \frac{f^2}{f z_2^2} √$$

Clearly this is separable if V = 0, no interaction between the particles means solve each independently:

$\Psi = \Psi_1(R, \theta_1, \varphi_1) \ \Psi_2(R, \theta_2, \varphi_2)$

$E = \varepsilon_1 + \varepsilon_2$

<u>Rigid Rotor</u>

Now what if we have a very high force binding the particles together at <u>specific sep'n d</u>

now only motion of interest is of m_1 w/r/t m_2 – relative motion
since d is fixed _ rotation of whole body

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Key change variables
$X = m_1x_1 + m_2x_2/M$
$Y = m_1y_1 + m_2y_2/M$ center of mass
$Z = m_1z_1 + m_2z_2/M$

$M = m_1 + m_2$
and $x = x_2 – x_1$, $y = y_2 – y_1$, $z = z_2 – z_1$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Levine 6.3

Then $H = \frac{-\hbar^2}{f M} ¾ \frac{f^2}{f X^2} + \frac{f^2}{f Y^2} + \frac{f^2}{f Z^2} √ - \frac{\hbar^2}{f \mu} ¾ \frac{f^2}{f x^2} + \frac{f^2}{f y^2} + \frac{f^2}{f z^2} √$

(Note: Still no potential, V = 0 but B.C. R = d) _ quant

6.4
Since not interested in motion of center of mass _ it is solved by 3-D place were (<u>not quant</u>)

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Transform (x,y,z) _ (r,θ,φ) but note r = d = const
then solution just
$$H_{rr}\Psi = \frac{-\hbar^2}{f \mu d^2}\Lambda^2\Psi = \frac{-\hbar^2}{f I}\Lambda^2 Y_{JM}(\theta,\varphi) = E_J Y_{JM}(\theta,\varphi)$$
this can describe rotation of rigid body $T = \mu d^2$ (linear only)

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Note: traditional to use J as angular momentum operator for rotation
$E_{\ell m} = \frac{\hbar^2}{2I} J(J+1)$ $I = \mu d^2$ $g_J = 2J + 1$
no dependence on m
$\Delta E_{J-J+1}(J+1)(\frac{\hbar^2}{I})$
levels expand and <u>spacing</u> between them increase linearly with J
Y_{JM} <u>Ang. Mom. eigen fct</u> Since some problem: $J_z Y_{JM} = Mh Y_{JM}$, $J^2 Y_{JM} = J(J + 1)h^2 Y_{JM}$

<u>Good model for molecular rotational spectroscopy</u> – molecules with ???

$\Delta E = h\nu = (J + 1)h^2/I$ for DJ = 1 selection rule

$\nu = (J + 1)h/2\pi I = 2B$ $B = h/4\pi I$ (in cm^{-1} $B = h/4\pi cI$)

increase μ on d _ I inc _ <u>ν dec</u>

– for very light molecules (H-containing)

μ ~ 1 cm, d ~ 0.1 nm

gives rise to absorptions in far-ir (10's cm^{-1})

– heavier molecules _ ν in microwave so termed <u>μ-wave spectra</u>

Spectra complex since B << kT so many J levels populated _ Thermometer

Note: measure DE _ I _ d if know μ for diatomic that is the <u>molec geometry</u>

– due to μ-wave technology this can be done with very high precision

Note: <u>polyatomic non-linear molecule</u> has another dimension (rotation of linear about axis _ no moment)

thus need another quantum number (K-momentum about the figure axis) and spectra a bit more complex

_ vib/rot ΔJ = 1 can lose energy not while gain vib handout. Check data