1. The boundary conditions for a particle in a three-dimensional rectangular box (length A, width B, and height C) lead to wave functions of the form

$$\Psi(x,y,z) = N \sin(n_x\pi x/A)\sin(n_y\pi y/B)\sin(n_z\pi z/C)$$

Show that the normalization constant is $N = \sqrt{\dfrac{8}{ABC}}$

2. Suppose that the three-dimensional wave function $\Psi(x,y,z)$ can be separated into the factors $\psi_x(x)$, $\psi_y(y)$, $\psi_z(z)$:

$$\Psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

with

$$\hat{H}_x\psi_x(x) = E_x\psi_x(x) \qquad \hat{H}_y\psi_y(y) = E_y\psi_y(y) \qquad \hat{H}_z\psi_z(z) = E_z\psi_z(z)$$

a) If $\psi_x(x)$, $\psi_y(y)$ and $\psi_z(z)$ are normalized, show that $\Psi(x,y,z)$ is normalized.

b) Give the total Hamiltonian operator and show that the total energy is $E_x + E_y + E_z$.

3. For a two-dimensional rigid rotor, all of the energy levels (except the ground level) are doubly degenerate. Why?

4. Show that the Y_{00} spherical harmonic is normalized and orthogonal to $Y_{1\pm1}$

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \qquad\qquad Y_{1\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$$

5. Spherical harmonics are eigenfunctions of the operator

$$\hat{L}_z = -\frac{ih}{2\pi}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

In spherical coordinates, show that the expression for this important operator simplifies to

$$\hat{L}_z = -\frac{ih}{2\pi}\frac{\partial}{\partial\phi}$$

Note: $x = r\sin\theta\cos\phi$ $\qquad y = r\sin\theta\sin\phi$ $\qquad z = r\cos\theta$

$r = (x^2 + y^2 + z^2)^{1/2}$ $\qquad \phi = \tan^{-1}(y/x)$ $\qquad \theta = \cos^{-1}[z/(x^2 + y^2 + z^2)^{1/2}]$

6. Derive the allowed values of L_z for the $Y_{1\pm1}$ wavefunctions.

7. Prove that $\hat{L}^2$ commutes with $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ but

$$[\hat{L}_x,\hat{L}_y]=\frac{ih}{2\pi}\hat{L}_z \qquad [\hat{L}_y,\hat{L}_z]=\frac{ih}{2\pi}\hat{L}_x \qquad [\hat{L}_z,\hat{L}_x]=\frac{ih}{2\pi}\hat{L}_y$$

Hint: Use Cartesian coordinates.

8. The $\ell = 0$ to $\ell = 1$ transition for carbon monoxide occurs at 1.1552×10^5 MHz. Calculate the bond length for CO. [h = 6.62618 x 10^{-34} J s, mass C = 1.99161 x 10^{-26} kg, mass O = 2.65464 x 10^{-26} kg]

9. Spectroscopy can be used to detect the presence of transient species whose lifetimes are too short to be detected by other methods. The OH radical (bond length 0.097 nm), for example, can be detected in the microwave region of the electromagnetic spectrum. Calculate the absorption frequency in wavenumbers for the $\ell = 0$ to $\ell = 1$ transition for OH. Also calculate the corresponding frequency for the OD radical.

10. a) Show that the ratio N_ℓ/N_0 of the number of diatomic molecules in rotational level ℓ to the number in the ground state is

$$\frac{N_\ell}{N_0} = (2\ell+1)\exp[-\ell(\ell+1)\Theta_r/T]$$

where Θ_r is an abbreviation for $h^2/(8\pi^2\mu r^2 k)$ and k is Boltzmann's constant.

b) For OH radicals at 300 K, give the frequencies in wavenumbers for the most intense bands in the P branch $(\Delta\ell = -1)$ and the R branch $(\Delta\ell = +1)$ of the fundamental absorption band.

Chemistry 331 Tutorial #6

Q1. to evaluate the normalization constant N, use:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(x,y,z)\,\psi(x,y,z)\,dx\,dy\,dz = 1$$

ψ is real, so $\psi^* = \psi$ and $\psi^*\psi = \psi^2$

ψ is zero outside the box, so the integration can be performed over $0 \le x \le A$, $0 \le y \le B$, $0 \le z \le C$

$$1 = \int_0^A\int_0^B\int_0^C N^2 \sin^2\left(\frac{n_x \pi x}{A}\right) \sin^2\left(\frac{n_y \pi y}{B}\right) \sin^2\left(\frac{n_z \pi z}{C}\right) dx\,dy\,dz$$

$$1 = N^2 \int_0^A \sin^2\left(\frac{n_x \pi x}{A}\right) dx \int_0^B \sin^2\left(\frac{n_y \pi y}{B}\right) dy \int_0^C \sin^2\left(\frac{n_z \pi z}{C}\right) dz$$

(from tables of integrals: $\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) = \frac{a}{2}$)

$$1 = N^2 \frac{A}{2}\frac{B}{2}\frac{C}{2} \qquad N^2 = \frac{8}{ABC} \qquad N = \sqrt{\frac{8}{ABC}}$$

Q2 a) $\int_{-\infty}^{\infty} \psi_x^* \psi_x\,dx = 1$ $\quad \int_{-\infty}^{\infty} \psi_y^* \psi_y\,dy = 1$ $\quad \int_{-\infty}^{\infty} \psi_z^* \psi_z\,dz = 1$

$$\iiint \Psi^*(x,y,z)\,\Psi(x,y,z)\,dx\,dy\,dz = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi_x^*(x)\psi_y^*(y)\psi_z^*(z)\,\psi_x(x)\psi_y(y)\psi_z(z)\,dx\,dy\,dz$$

$$= \int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx \int_{-\infty}^{\infty} \psi^*(y)\psi(y) \int_{-\infty}^{\infty} \psi^*(z)\psi(z)\,dz$$

$$= (1)(1)(1) = 1$$

so $\Psi(x,y,z)$ is normalized too

(2 cont.)

b) $\hat{H}_{tot}\Psi(x,y,z) = E_{tot}\Psi(x,y,z)$ $\quad \left(\hat{H}_{tot} = \hat{H}_x + \hat{H}_y + \hat{H}_z\right)$

$= \left(\hat{H}_x + \hat{H}_y + \hat{H}_z\right)\left(\psi_x(x)\,\psi_y(y)\,\psi_z(z)\right)$

$= \hat{H}_x\psi_x(x)\psi_y(y)\psi_z(z) + \hat{H}_y\psi_x(x)\psi_y(y)\psi_z(z) + \hat{H}_z\psi_x(x)\psi_y(y)\psi_z(z)$

$= \psi_y(y)\psi_z(z)\hat{H}_x\psi_x(x) + \psi_x(x)\psi_z(z)\hat{H}_y\psi_y(y) + \psi_x(x)\psi_y(y)\hat{H}_z\psi_z(z)$

$= \psi_y(y)\psi_z(z)E_x\psi_x(x) + \psi_x(x)\psi_z(z)E_y\psi_y(y) + \psi_x(x)\psi_y(y)E_z\psi_z(z)$

$= \left(E_x + E_y + E_z\right)\psi_x(x)\,\psi_y(y)\,\psi_z(z) = \left(E_x + E_y + E_z\right)\Psi(x,y,z)$

$\hat{H}_{tot}\Psi(x,y,z) = \left(E_x + E_y + E_z\right)\Psi(x,y,z) = E_{tot}\Psi(x,y,z)$

$$E_{tot} = E_x + E_y + E_z$$

Q3 for a 2 dimensional rotator,

$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ $\quad m = 0, \pm1, \pm2, \ldots$

doubly degenerate because there are 2 rotation directions, with the same energy

e.g. $m > 0$ clockwize
$m < 0$ counterclockwise rotation

Q4 $\int_0^{\pi}\int_0^{2\pi} Y_{00}^* Y_{00}\sin\theta\, d\theta\, d\phi = \int_0^{\pi}\int_0^{2\pi}\frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{4\pi}}\sin\theta\, d\theta\, d\phi$

$= \frac{1}{4\pi}\int_0^{\pi}\sin\theta\, d\theta\int_0^{2\pi}d\phi = \frac{1}{4\pi}\left(-\cos\theta\right)\Big|_0^{\pi} 2\pi$

$= \frac{1}{4\pi}\left(-\cos\pi + \cos 0\right)2\pi = \frac{1}{4\pi}(1+1)2\pi = 1$

(Q4 cont.)

4 b) $\int_0^{\pi}\int_0^{2\pi} Y^*_{1\pm1} Y_{00} \sin\theta \, d\theta \, d\phi$

$= \int_0^{\pi}\int_0^{2\pi} \sqrt{\frac{3}{8\pi}} \sin\theta e^{\mp i\phi} \frac{1}{\sqrt{4\pi}} \sin\theta \, d\theta \, d\phi$

$= \sqrt{\frac{3}{32}} \frac{1}{\pi} \int_0^{\pi} \sin^2\theta \, d\theta \int_0^{2\pi} e^{\mp i\phi} d\phi$

$= \sqrt{\frac{3}{32}} \frac{1}{\pi} \int_0^{\pi} \sin^2\theta \, d\theta \int_0^{2\pi} (\cos\phi \mp i \sin\phi) \, d\phi$

$= \sqrt{\frac{3}{32}} \frac{1}{\pi} \int_0^{\pi} \sin^2\theta \, d\theta \; \cancel{(\sin\phi \pm i\cos\phi)}\Big|_{\phi=0}^{\phi=2\pi}$ 0

$= 0$

(Q5) $\hat{L}_z f(x,y,z) = -\frac{ih}{2\pi}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) f(x,y,z) = -\frac{ih}{2\pi}\left(x\frac{\partial f}{\partial y} - y\frac{\partial f}{\partial x}\right)$

convert $\hat{L}_z$ to spherical coordinates

$df = \frac{\partial f}{\partial r} dr + \frac{\partial f}{\partial \theta} d\theta + \frac{\partial f}{\partial \phi} d\phi$

* need expressions for $\frac{\partial f}{\partial y}$, $\frac{\partial f}{\partial x}$ in spherical coordinates

divide df by dx at constant y, z:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = \left(\frac{\partial f}{\partial r}\right)_{\theta,\phi}\left(\frac{\partial r}{\partial x}\right)_{y,z} + \left(\frac{\partial f}{\partial \theta}\right)_{r,\phi}\left(\frac{\partial \theta}{\partial x}\right)_{y,z} + \left(\frac{\partial f}{\partial \phi}\right)_{r,\theta}\left(\frac{\partial \phi}{\partial x}\right)_{y,z}$$

$r = \sqrt{x^2+y^2+z^2}$ $\quad \theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$ $\quad \phi = \tan^{-1}\left(\frac{y}{x}\right)$

(Q5 cont.)

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{\partial}{\partial x}\left(x^2+y^2+z^2\right)^{1/2} = \frac{1}{2}\,\frac{2x}{\left(x^2+y^2+z^2\right)^{1/2}} = \frac{\cancel{r}\sin\theta\cos\phi}{\cancel{r}}$$

$$\left(\frac{\partial \theta}{\partial x}\right)_{y,z} = \;? \qquad \text{use} \qquad \cos\theta = \frac{z}{\sqrt{x^2+y^2+z^2}}$$

$$\left(\frac{\partial \cos\theta}{\partial x}\right)_{y,z} = -\sin\theta\left(\frac{\partial \theta}{\partial x}\right)_{y,z} = \frac{\left(-\frac{1}{2}\right)z\,2x}{\left(x^2+y^2+z^2\right)^{3/2}} = -\frac{zx}{r^3} = -\frac{r\cos\theta\, r\sin\theta\cos\phi}{r^3}$$

$$\left(\frac{\partial \theta}{\partial x}\right)_{y,z} = \frac{\cos\theta\cos\phi}{r}$$

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = \;? \qquad \text{use} \qquad \tan\phi = \frac{y}{x}$$

$$\left(\frac{\partial \tan\phi}{\partial x}\right)_{y,z} = \sec^2\phi\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = \frac{1}{\cos^2\phi}\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = \left(\frac{\partial \frac{y}{x}}{\partial x}\right)_{y,z} = -\frac{y}{x^2}$$

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{y\cos^2\phi}{x^2} = -\frac{r\sin\theta\sin\phi\cos^2\phi}{r^2\sin^2\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta}$$

$$\boxed{\frac{\partial f}{\partial x} = \sin\theta\cos\phi\,\frac{\partial f}{\partial r} + \frac{\cos\theta\cos\phi}{r}\,\frac{\partial f}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\,\frac{\partial f}{\partial \phi}}$$

$$df = \left(\frac{\partial f}{\partial r}\right)_{\theta,\phi} dr + \left(\frac{\partial f}{\partial \theta}\right)_{r,\phi} d\theta + \left(\frac{\partial f}{\partial \phi}\right)_{r,\theta} d\phi$$

divide by dy at constant x,z

(Q5 cont.)

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} = \left(\frac{\partial f}{\partial r}\right)_{\theta,\phi}\left(\frac{\partial r}{\partial y}\right)_{x,z} + \left(\frac{\partial f}{\partial \theta}\right)_{r,\phi}\left(\frac{\partial \theta}{\partial y}\right)_{x,z} + \left(\frac{\partial f}{\partial \phi}\right)_{r,\theta}\left(\frac{\partial \phi}{\partial y}\right)_{x,z}$$

$$\left(\frac{\partial r}{\partial y}\right)_{x,z} = \frac{\partial}{\partial y}(x^2+y^2+z^2)^{1/2} = \frac{1}{2}\frac{2y}{(x^2+y^2+z^2)^{1/2}} = \frac{y}{r} = \frac{\cancel{r}\sin\theta\sin\phi}{\cancel{r}}$$

$$\left(\frac{\partial \theta}{\partial y}\right)_{x,z} = \frac{\partial}{\partial y}\cos^{-1}\left(\frac{z}{(x^2+y^2+z^2)^{1/2}}\right) = \frac{-1}{\left(1-\frac{z^2}{x^2+y^2+z^2}\right)^{1/2}}\frac{-\frac{1}{2}\,z\,2y}{(x^2+y^2+z^2)^{3/2}}$$

$$\left(\frac{\partial \theta}{\partial y}\right)_{x,z} = \frac{r\cos\theta\; r\sin\theta\,\sin\phi}{\sqrt{x^2+y^2}\quad r^2} = \frac{\cos\theta\,\cancel{\sin\theta}\,\sin\phi}{\sqrt{r^2\cancel{\sin^2\theta}\cos^2\phi + r^2\cancel{\sin^2\theta}\sin^2\phi}}$$

$$\left(\frac{\partial \theta}{\partial y}\right)_{x,z} = \frac{\cos\theta\sin\phi}{r\sqrt{\sin^2\phi+\cos^2\phi}} = \frac{\cos\theta\sin\phi}{r}$$

$$\left(\frac{\partial \phi}{\partial y}\right)_{x,z} = \frac{\partial}{\partial y}\left(\tan^{-1}\frac{y}{x}\right) = \frac{1}{1+\frac{y^2}{x^2}}\frac{\partial\frac{y}{x}}{\partial y} = \frac{1}{x}\,\frac{1}{1+\frac{y^2}{x^2}}$$

$$\left(\frac{\partial \phi}{\partial y}\right)_{x,z} = \frac{1}{r\sin\theta\cos\phi}\;\frac{1}{1+\frac{\cancel{r^2}\cancel{\sin^2\theta}\sin^2\phi}{\cancel{r^2}\cancel{\sin^2\theta}\cos^2\phi}} = \frac{1}{r\sin\theta\cos\phi}\;\frac{\cos^2\phi}{\cos^2\phi+\sin^2\phi}$$

$$\left(\frac{\partial \phi}{\partial y}\right)_{x,z} = \frac{\cos\phi}{r\sin\theta}$$

$$\boxed{\left(\frac{\partial f}{\partial y}\right)_{x,z} = \sin\theta\sin\phi\left(\frac{\partial f}{\partial r}\right)_{\theta,\phi} + \frac{\cos\theta\sin\phi}{r}\left(\frac{\partial f}{\partial \theta}\right)_{r,\phi} + \frac{\cos\phi}{r\sin\theta}\left(\frac{\partial f}{\partial \phi}\right)_{r,\theta}}$$

(Q5 cont.)

$x = r\sin\theta\cos\phi \qquad y = r\sin\theta\sin\phi$

$$\hat{L}_z = -\frac{ih}{2\pi}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= -\frac{ih}{2\pi} r\sin\theta\cos\phi\left[\cancel{\sin\theta\sin\phi\frac{\partial}{\partial r}} + \cancel{\frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta}} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$+ \frac{ih}{2\pi} r\sin\theta\sin\phi\left[\cancel{\sin\theta\cos\phi\frac{\partial}{\partial r}} + \cancel{\frac{\cos\theta\cos\phi}{r}}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$= -\frac{ih}{2\pi}(\cos^2\phi + \sin^2\phi)\frac{\partial}{\partial\phi} = -\frac{ih}{2\pi}\frac{\partial}{\partial\phi} = -i\hbar\frac{\partial}{\partial\phi}$$

Q6 $\quad Y_{1\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$

$$\hat{L}_z Y_{1\pm1} = -\frac{ih}{2\pi}\frac{\partial}{\partial\phi}\left(\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}\right) = \frac{-ih}{2\pi}\sqrt{\frac{3}{8\pi}}\sin\theta(\pm i)e^{\pm i\phi}$$

$$= \frac{(\pm i)ih}{2\pi}\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi} = \frac{\mp h}{2\pi} Y_{1\pm1}$$

eigenvalues $-\frac{h}{2\pi}$ and $\frac{h}{2\pi}$ allowed values of L_z angular momentum

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Q7 in Cartesian coordinates:

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

$$= (i\hbar)(i\hbar)\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]$$

(7 cont.)

order of differentiation does'nt matter

$$\frac{\partial^2}{\partial z\partial x} = \frac{\partial^2}{\partial x\partial z} \qquad \frac{\partial^2}{\partial y\partial x} = \frac{\partial^2}{\partial x\partial y} \qquad \frac{\partial^2}{\partial y\partial z} = \frac{\partial^2}{\partial z\partial y}$$

$$[\hat{L}_x, \hat{L}_y] = -\hbar^2\Big[\cancel{yz\frac{\partial^2}{\partial z\partial x}} - \cancel{xy\frac{\partial^2}{\partial z^2}} - \cancel{z^2\frac{\partial^2}{\partial y\partial x}} + \cancel{xz\frac{\partial^2}{\partial y\partial z}} + y\frac{\partial}{\partial x}$$

$$- \cancel{yz\frac{\partial^2}{\partial x\partial z}} + \cancel{z^2\frac{\partial^2}{\partial x\partial y}} + \cancel{xy\frac{\partial^2}{\partial z^2}} - \cancel{xz\frac{\partial^2}{\partial z\partial y}} - x\frac{\partial}{\partial y}\Big]$$

$$= -\hbar^2\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) = (i\hbar)(i\hbar)\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$$

$$= i\hbar\hat{L}_x$$

similarly (permute subscripts!) :

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

show: $[\hat{L}^2, \hat{L}_z] = 0 \qquad [\hat{L}^2, \hat{L}_y] = 0 \qquad [\hat{L}^2, L_z] = 0$

in spherical coordinates

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2}\right]$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}^2\hat{L}_z = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right](-i\hbar)\frac{\partial}{\partial\phi}$$

$$= i\hbar^3\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial^2}{\partial\theta\,\partial\phi} + \frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^3}\right]$$

(7 cont.)

$$\hat{L}_z \hat{L}^2 = \left(-i\hbar \frac{\partial}{\partial \phi}\right)(\hbar^2)\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$= i\hbar^3 \frac{\partial}{\partial\phi}\left(\underbrace{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta}_{\text{independent of } \phi}\frac{\partial}{\partial\theta}\right) + i\hbar^3\left(\frac{\partial}{\partial\phi}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$= i\hbar^3\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta}\right) + \left(i\hbar^3\frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^2}\right)$$

$$= i\hbar^3\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial^2}{\partial\theta\partial\phi} + i\hbar^3\frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^2}$$

$$= \hat{L}^2\hat{L}_z$$

similarly $[\hat{L}^2, \hat{L}_y] = 0$, $[\hat{L}^2, \hat{L}_z] = 0$ (permute subscripts!)
(nothing "special" about z)

(8.) $$E_{l=1} - E_{l=0} = \Delta\left[\frac{\hbar^2}{2I}l(l+1)\right] = \frac{\hbar^2}{2I}\left[1(2) - 0(1)\right] = \frac{2\hbar^2}{2I} = h\nu$$

moment of inertia $I = \frac{\hbar^2}{h\nu} = \frac{h^2}{4\pi^2 h\nu} = \frac{h}{4\pi^2\nu} = \mu r^2$

$$r = \sqrt{\frac{h}{4\pi^2\nu\mu}} = \sqrt{\frac{h}{4\pi^2\nu}\frac{m_c+m_o}{m_c m_o}}$$

$$= \sqrt{\frac{6.62618\times10^{-34}}{4\pi^2\ 1.1552\times10^{11}}\ \frac{1.99161+2.65464}{(1.99161)(2.65464)\times10^{-26}}} = \sqrt{1.2768\times10^{-15}}\ \text{m}$$

$r = 0.11299$ nm

$$\frac{\nu_{OD}}{\nu_{OH}} = \frac{\mu_{OH}}{\mu_{OD}} = \frac{\cancel{m_O}\, m_H}{m_O + m_H}\ \frac{m_O + m_D}{\cancel{m_O}\, m_D} = \frac{1}{2}\ \frac{2.65464 + 2(0.167265)}{2.65464 + 0.167265} = 0.52964$$

(9) frequency for $l = 0$ to $l = 1$ transition for OH:

$$\Delta E = \Delta\left[\frac{\hbar^2}{2I} l(l+1)\right] = \frac{\hbar^2}{2I}(2-0) = \frac{\hbar^2}{I} = h\nu$$

frequency $\nu_{OH} = \dfrac{\hbar^2}{Ih} = \dfrac{h}{4\pi^2 \mu_{OH} r^2} = \dfrac{h\,(m_O + m_H)}{4\pi^2 r^2 m_O m_H}$

$$\nu_{OH} = \frac{6.62618\times10^{-34}\,(2.65464 + 0.167265)}{4\pi^2 (0.097\times10^{-9})^2\ (2.65464)(0.167265)10^{-26}} = 1.1337\times10^{12}\ \text{Hz}$$

($\nu_{OD} = 0.52964\,\nu_{OH} = 0.60045\times10^{12}$ Hz) (microwave)

(10) $$\frac{N_l}{N_0} = \frac{g_l}{g_0}\ \frac{e^{-E_l/kT}}{e^{-E_0/kT}} = \frac{2l+1}{1}\ \frac{e^{-\frac{\hbar^2}{2I} l(l+1)/kT}}{e^0}$$

$$\frac{N_l}{N_0} = (2l+1)\exp\left(-\frac{h^2 l(l+1)}{4\pi^2\, 2\mu r^2}\,\frac{1}{kT}\right) = (2l+1)\exp\left[-l(l+1)\,\Theta_r/T\right]$$

for OH: $\Theta_r = \dfrac{h^2}{8\pi^2 \mu r^2 k} = \dfrac{h^2}{8\pi^2 r^2 k}\ \dfrac{m_O + m_H}{m_O m_H} = 27.20$ K

at 300 K: $\dfrac{N_1}{N_0} = 3\exp[-2(27.20)/300] = 2.502$

$\dfrac{N_2}{N_0} = 5\exp[-6(27.20)/300] = 2.902$ ← $l=2$ level has the highest occupancy

$\dfrac{N_3}{N_0} = 7\exp[12(27.20)/300] = 2.358$

most intense bands:

$l = 2 \rightarrow l = 3$ R Branch fundamental $\nu_0 + 6B$

$l = 2 \rightarrow l = 1$ P Branch fundamental $\nu_0 - 4B$

B = rotational frequency spacing $\dfrac{\hbar^2}{I}\dfrac{1}{h} = 37.5\ \text{cm}^{-1}$ for OH