SOLUTIONS

PROBLEM SET 5

CHM 3411, Dr. Chatfield

1. Exercise 8C.4b

$$E_l = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2$$

$l = 0 \Rightarrow$ not rotating

$l = 1 \Rightarrow$ min. energy to start rotating

$$E = E_1 = 1(1+1)\frac{\hbar^2}{2I} \qquad I = 3.07\times10^{-45}\ kg\,m^2$$

$$= \frac{\hbar^2}{I} = \frac{(1.055\times10^{-34}\ Js)^2}{3.07\times10^{-45}\ kg\,m^2} = 3.63\times10^{-24}\ J$$

2. Exercise 8C.5b

$$\Delta E = E_3 - E_2 = 3(4)\frac{\hbar^2}{2I} - 2(3)\frac{\hbar^2}{2I} = \frac{3\hbar^2}{I}$$

$$= 3(3.63\times10^{-24}\,J) = 1.09\times10^{-23}\,J$$

3. Exercise 8C.6b

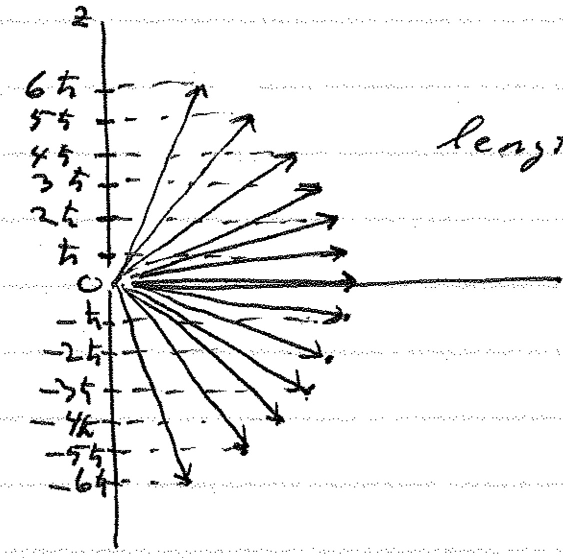
Minimum l is $\emptyset$, but this does not correspond to rotating (molecule is still).

Next value of l is 1:

ang. mom. $= \sqrt{l(l+1)}\,\hbar = \sqrt{2}\,\hbar = 1.49 \times 10^{-34}$ Js

4. Exercise 8C.7b

$l = 6 \Rightarrow m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6$



length of each vector $= 42 \frac{\hbar^2}{2I} = 21 \frac{\hbar^2}{I}$

5. Classically, $l_z = x p_y - y p_x$ $\quad \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}$ $\quad \hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$

$\Rightarrow$ QM operator $\hat{l}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

spherical polar coordinates:

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

$$\frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial}{\partial z}$$

$$\frac{\partial x}{\partial\phi} = -r\sin\theta\sin\phi = -y \qquad \frac{\partial y}{\partial\phi} = r\sin\theta\cos\phi = x \qquad \frac{\partial z}{\partial\phi} = 0$$

$$\frac{\partial}{\partial\phi} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}$$

$\Rightarrow \hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ Q.E.D.

6. To establish that $Y_{0,0}$ & $Y_{1,0}$ are orthonormal, we need to show three things:

$$\int Y_{0,0}^* Y_{0,0}\, d\tau = 1 \qquad \int Y_{1,0}^* Y_{1,0}\, d\tau = 1 \qquad \int Y_{0,0}^* Y_{1,0}\, d\tau = 0$$

where the integration is over θ & φ and $d\tau = \sin\theta\, d\theta\, d\varphi$

From Table 12.3, $Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2}$ $\quad Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$

$$\int Y_{0,0}^* Y_{0,0}\, d\tau = \int_0^{2\pi}\int_0^{\pi} \frac{1}{4\pi}\sin\theta\, d\theta\, d\varphi = \frac{1}{4\pi}\left(\int_0^{2\pi} d\varphi\right)\left(\int_0^{\pi}\sin\theta\, d\theta\right)$$

$$= \frac{1}{4\pi}\cdot 4\pi = 1 \quad \checkmark$$

$$\int Y_{1,0}^* Y_{1,0}\, d\tau = \int_0^{2\pi}\int_0^{\pi} \frac{3}{4\pi}\cos^2\theta \sin\theta\, d\theta\, d\varphi$$

$$= \frac{3}{4\pi}\underbrace{\int_0^{2\pi} d\varphi}_{2\pi}\ \underbrace{\int_0^{\pi}\cos^2\theta\sin\theta\, d\theta}_{= -\int \cos^2\theta\, d(\cos\theta) = -\frac{1}{3}\cos^3\theta\Big|_0^{\pi} = -\frac{1}{3}(-1-1) = \frac{2}{3}}$$

$$= \frac{3}{4\pi}\cdot\frac{4\pi}{3} = 1 \quad \checkmark$$

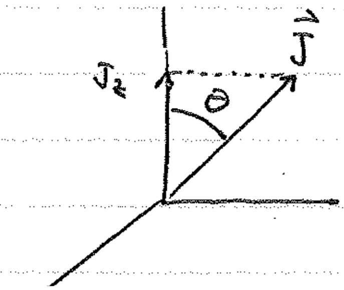
$$\int Y_{0,0}^* Y_{1,0}\, d\tau = \int_0^{2\pi}\int_0^{\pi} \frac{\sqrt{3}}{4\pi}\cos\theta\sin\theta\, d\theta\, d\varphi$$

$$= \frac{\sqrt{3}}{4\pi}\underbrace{\int_0^{2\pi} d\varphi}_{2\pi}\ \underbrace{\int_0^{\pi}\cos\theta\sin\theta\, d\theta}_{\int \sin\theta\, d(\sin\theta) = \frac{1}{2}\sin^2\theta\Big|_0^{\pi} = 0}$$

$$= 0 \quad \checkmark$$

We have shown explicitly that $Y_{0,0}$ & $Y_{1,0}$ are normalized and orthogonal. As it turns out, the entire set of functions $Y_{\ell m}$ are orthonormal; i.e. $\int Y_{\ell_1 m_1}^* Y_{\ell_2 m_2}\, d\tau = 1$ $\ell_1 = \ell_2$, $m_{\ell_1} = m_{\ell_2}$

7. (a)



$$J = |\vec{J}| = [\ell(\ell+1)]^{1/2}\hbar$$

$$J_z = |\vec{J}_z| = m_\ell \hbar$$

From definition of cosine

$$\cos\theta = \frac{J_z}{J} = \frac{m_\ell \hbar}{[\ell(\ell+1)]^{1/2}\hbar} = \frac{m_\ell}{[\ell(\ell+1)]^{1/2}}$$

$$\theta = \cos^{-1}\left(\frac{m_\ell}{[\ell(\ell+1)]^{1/2}}\right)$$

(b) $\ell = 1$ allowed angles: $\theta = \cos^{-1}\left(\frac{0}{\sqrt{2}}\right) = \frac{\pi}{2}$ radians $(90°)$

$\cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = \frac{\pi}{4}$ $(45°)$

$\cos^{-1}\left(\frac{-1}{\sqrt{2}}\right) = \frac{3\pi}{4}$ $(135°)$

$\ell = 2$ $\theta = \cos^{-1}\left(\frac{m_\ell}{\sqrt{6}}\right)$ for $m_\ell = 0, \pm 1, \pm 2$

$= \frac{\pi}{2}, 1.15, 1.99, 0.62, 2.52$ $(90°, 66°, 114°, 35°, 145°)$

$\ell = 3$ $\theta = \cos^{-1}\left(\frac{m_\ell}{\sqrt{12}}\right)$ for $m_\ell = 0, \pm 1, \pm 2, \pm 3$

$= \frac{\pi}{2}, 1.28, 1.86, 0.96, 2.18, \frac{\pi}{6}, \frac{5\pi}{6}$
$(90°, 73°, 107°, 55°, 125°, 30°, 150°)$

θ_{min} corresponds to ℓ being most nearly vertical, i.e. $m_\ell = m_\ell(\max) = \ell$

$$\theta_{min} = \cos^{-1}\left(\frac{\ell}{[\ell(\ell+1)]^{1/2}}\right) \qquad \lim_{\ell\to\infty} \theta_{min} = \cos^{-1}(1) = 0$$

8. Spartan problem: According to the Lewis definition of an acid, acidity is determined by the ability of a molecule to accept a pair of non-bonded electrons. Thus where the electrostatic potential is most positive in the vicinity of a hydrogen, we would expect the highest acidity. As shown in the figure below, where red is negative electrostatic potential and blue is positive electrostatic potential, hydrogen fluoride has the most potential to accept an electron pair at the hydrogen, and is thus the most acidic of the three, followed by water, and then ammonia. Note that the same scale was used for coloring the electrostatic potential maps in all three cases.

Electrostatic potential maps of HF, H_2O, and NH_3