$\langle L_z \rangle^2 \rightarrow \sigma_{L_x}^2 \sigma_{L_y}^2 = 0$ if only $\langle L_x \rangle = 0$, $\langle L_y \rangle = 0$

Assignment 13

1 a) $\hat{H}_{vib} = \hat{H}_{sym} + \hat{H}_{asym} + \hat{H}_{bend}$

$\hat{H}_{vib}|\Psi\rangle = E_{vib}|\Psi\rangle = (\hat{H}_{sym} + \hat{H}_{asym} + \hat{H}_{bend})|\Psi\rangle$

each mode is a Harmonic Oscillator: $E_{vib}|\Psi\rangle = (E_{sym} + E_{asym} + E_{bend})|\Psi\rangle$

$E_{vib} = E_{sym} + E_{asym} + E_{bend} = \hbar\omega_{sym}(n_{sym} + \frac{1}{2}) + \hbar\omega_{asym}(n_{asym} + \frac{1}{2}) + \hbar\omega_{bend}(n_{bend} + \frac{1}{2})$

$E_{vib,\, n=(0,0,0)} = \frac{1}{2}\hbar(\omega_{sym} + \omega_{asym} + \omega_{bend})$

b) $\Psi_0(x) = \Psi_{0,sym}(x)\, \Psi_{0,asym}(x)\, \Psi_{0,bend}(x)$

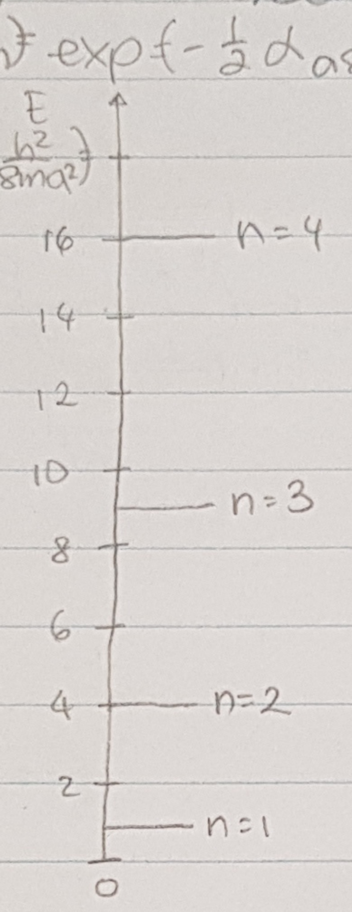
$= \exp\{-\frac{1}{2}\alpha_{sym} x_{sym}^2\} \exp\{-\frac{1}{2}\alpha_{asym} x_{sym}^2\} \exp\{-\frac{1}{2}\alpha_{bend} x_{bend}^2\}$

2) **1D box**

$E = \frac{h^2 n^2}{8ma^2}$

n	$E\ (\times \frac{h^2}{8ma^2})$
1	1
2	4
3	9

$n\uparrow \rightarrow (E_{n+1} - E_n)\uparrow$



2D box

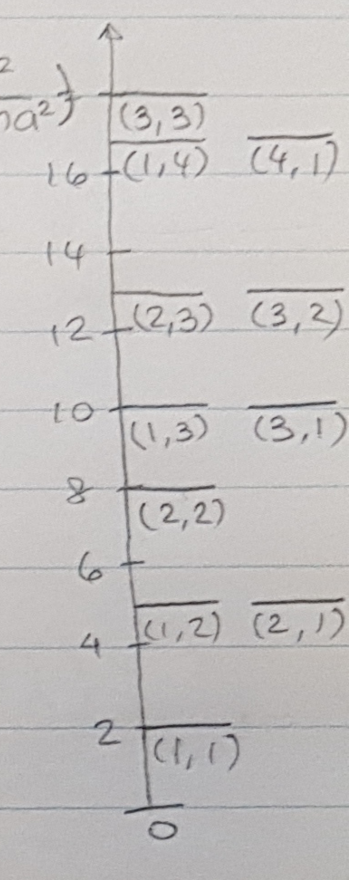
$E = \frac{h^2(n_x^2 + n_y^2)}{8ma^2}$

$n\uparrow$ ↓

$(E_{(n_x+1, n_y)} - E_{(n_x, n_y)})\uparrow$

$(E_{(n_x, n_y+1)} - E_{(n_x, n_y)})\uparrow$

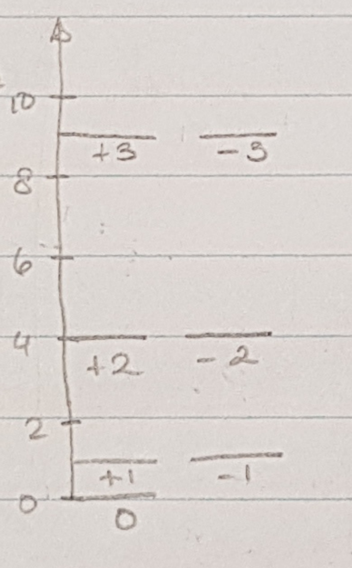
n_x	n_y	$E\ (\times \frac{h^2}{8ma^2})$
1	1	2
1	2	5
1	3	10
2	1	5
2	2	8
2	3	13
3	1	10
3	2	13
3	3	18.



Ring

$E = \frac{m_l^2 \hbar^2}{2I}$

m_l	$E\ (\times \frac{\hbar^2}{2I})$
0	0
±1	1
±2	4
±3	9

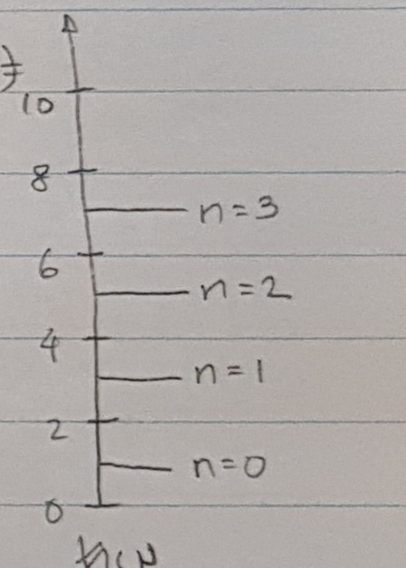


$|m_l|\uparrow \rightarrow (E_{m_l+1} - E_{m_l})\uparrow$

HO

$E = \hbar\omega(n + \frac{1}{2})$

n	$E\ (\times \frac{\hbar\omega}{2})$
0	1
1	3
2	5
3	7

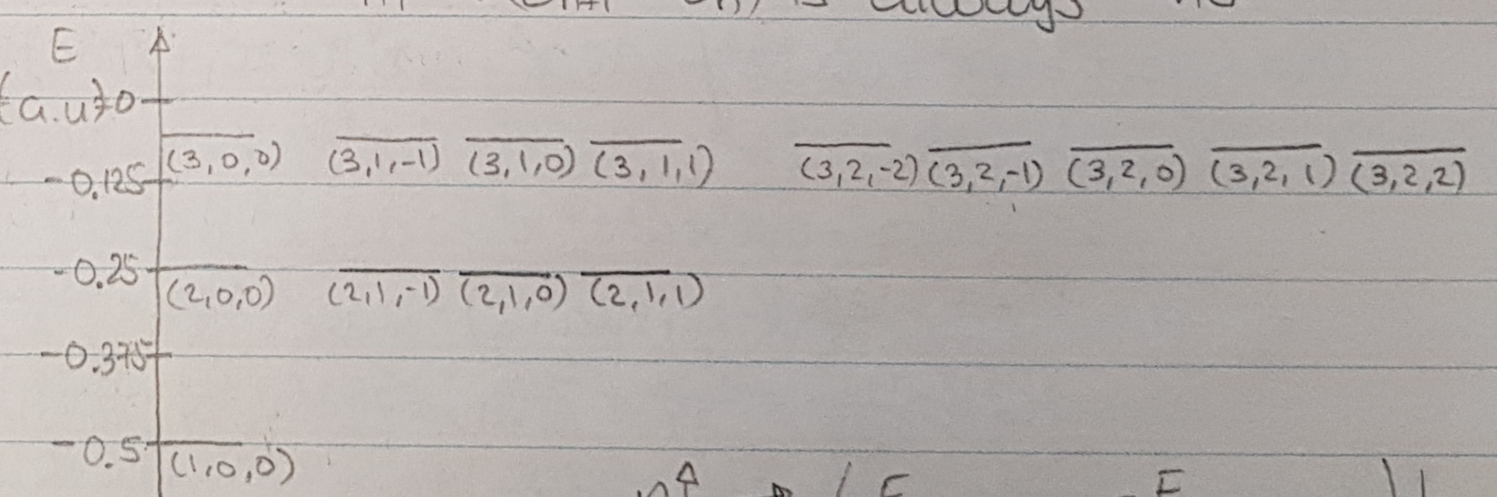


$n\uparrow \rightarrow (E_{n+1} - E_n)$ is always $\hbar\omega$

H-atom

$E = -\frac{1}{2n^2}$ a.u.

n	l	m	E (a.u.)
1	0	0	$-\frac{1}{2} \approx -0.5$
2	0	0	$-\frac{1}{8} \approx -0.125$
	1	-1, 0, 1	
3	0	0	$-\frac{1}{18} \approx -0.056$
	1	-1, 0, 1	
	2	-2, -1, 0, 1, 2	



$n\uparrow \rightarrow (E_{(n+1, l, m_l)} - E_{(n, l, m_l)})\downarrow$

3 a) $E^{(0)} = -\frac{z^2}{2n^2} - \frac{z^2}{2n^2} = -\frac{z^2}{n^2} = -\frac{4^2}{1^2} = -16$ a.u.

b) $E^{(0)} + E^{(1)} = -z^2 + \frac{5}{8}z = -16 + \frac{5}{8}(4) = -13.5$ a.u.

c) $E\{\zeta\} = -(z - 5/16)^2 = -(4 - 5/16)^2 = \sim -13.60$ a.u

4 $E = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\langle\phi|-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{k}{2}x^2|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\langle\phi|-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}|\phi\rangle + \langle\phi|\frac{k}{2}x^2|\phi\rangle}{\langle\phi|\phi\rangle}$

$= \frac{\langle\cos\lambda x|-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}|\cos\lambda x\rangle + \langle\phi|\frac{k}{2}x^2|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\langle\phi|-\frac{\hbar^2}{2\mu}(-\lambda^2)|\phi\rangle + \frac{k}{2}\langle\phi|x^2|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\frac{\lambda^2\hbar^2}{2\mu}\langle\phi|\phi\rangle + \frac{k}{2}\langle\phi|x^2|\phi\rangle}{\langle\phi|\phi\rangle}$ by parts

$= \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{2}\frac{\int x^2(\cos\lambda x)^2 dx}{\int(\cos\lambda x)^2 dx} = \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{2}\frac{\int x^2(\frac{1}{2} + \frac{\cos 2\lambda x}{2})dx}{\int(\frac{1}{2} + \frac{\cos 2\lambda x}{2})dx} = \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{2}\frac{\int\frac{x^2}{2}dx + \frac{1}{2}\int x^2\cos 2\lambda x\, dx}{\int\frac{1}{2}dx + \frac{1}{2}\int\cos 2\lambda x\, dx}$

$= \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{2}\frac{\frac{x^3}{3}\Big|_0^{\pi/2\lambda} + (\frac{1}{8\lambda^3})[(2\lambda^2x^2 - 1)\sin 2\lambda x + 2\lambda x\cos 2\lambda x]_0^{\pi/2\lambda}}{x\Big|_0^{\pi/2\lambda} + \frac{\sin 2\lambda x}{2\lambda}\Big|_{-\pi/2\lambda}^{\pi/2\lambda}} = \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{2}\frac{\frac{\pi^3}{24\lambda^3} + \frac{1}{8\lambda^3}[(\frac{\lambda^2\pi^2}{2\lambda^2} - 1)(0) + \pi(-1-1)]}{\frac{\pi}{2\lambda} + \frac{1}{2\lambda}[0]}$

$= \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{2}\left(\frac{2\lambda}{\pi}\right)\left[\frac{\pi^3}{24\lambda^3} - \frac{\pi}{4\lambda^3}\right] = \frac{\lambda^2\hbar^2}{2\mu} + \frac{k\pi^2}{24\lambda^2} - \frac{k\pi}{4\pi\lambda^2} = \frac{\lambda^2\hbar^2}{2\mu} + \frac{k}{4\lambda^2}\left[\frac{\pi^2}{6} - 1\right] = E\{\lambda\}$

$\frac{dE\{\lambda\}}{d\lambda} = \frac{\hbar^2\lambda}{\mu} + (-2)\left(\frac{k}{4\lambda^3}\right)\left[\frac{\pi^2}{6} - 1\right] = 0$

$\lambda = \left[\left(\frac{\pi^2}{12} - \frac{1}{2}\right)\frac{k\mu}{\hbar^2}\right]^{1/4}$

$E\{\lambda\} = \left(\frac{\pi^2}{3} - 2\right)^{1/2}\frac{1}{2}\hbar\left(\frac{k}{\mu}\right)^{1/2} = (1.14)\frac{1}{2}\hbar\omega$; $E_0 = \frac{1}{2}\hbar\omega$

$\Delta E = \text{error} = 0.07\hbar\omega$.

$E\{\lambda\} > E_0$, so results agree with variational principle.

5 $\phi = c_1 x(a-x) + c_2 x^2(a-x)^2$

$a^2x^2c_2^2 - 2ax^3c_2 + x^4c_2$

$E\{\lambda\} = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\langle c_1x(a-x) + c_2x^2(a-x)^2|-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}|c_1x(a-x) + c_2x^2(a-x)^2\rangle}{\langle c_1x(a-x) + c_2x^2(a-x)^2|c_1x(a-x) + c_2x^2(a-x)^2\rangle}$

$= \frac{-\frac{\hbar^2}{2m}\langle c_1x(a-x) + c_2x^2(a-x)^2|-2c_1 + 2a^2c_2^2 - 12ac_2x + 12c_2x^2\rangle}{\langle c_1x(a-x) + c_2x^2(a-x)^2|c_1x(a-x) + c_2x^2(a-x)^2\rangle} = \frac{-\frac{\hbar^2}{2m} A}{B}$

$A = \langle ac_1x - c_1x^2 + a^2c_2^2x^2 - 2ac_2x^3 + c_2x^4|(-2c_1 + 2a^2c_2^2) - 12ac_2x + 12c_2x^2\rangle$

$= \int_{-a/2}^{a/2}(ac_1x - c_1x^2 + a^2c_2^2x^2 - 2ac_2x^3 + c_2x^4)(-2c_1 + 2a^2c_2^2) - 12ac_2(ac_1x^2 - c_1x^3 + a^2c_2^2x^3 - 2ac_2x^4 + c_2x^5)$
$+ 12c_2(ac_1x^3 - c_1x^4 + a^2c_2^2x^4 - 2ac_2x^5 + c_2x^6)\, dx$

$\int_{-a}^{a}\text{odd}\{x\}\, dx = 0$; $\int_{-a}^{a}\text{even}\{x\}\, dx = 2\int_0^a \text{even}\, dx$

$= \left[\left(-\frac{c_1x^3}{3} + \frac{a^2c_2^2x^3}{3} + \frac{c_2x^5}{5}\right)(-2c_1 + 2a^2c_2^2) - 12ac_2\left(\frac{ac_1x^3}{3} - \frac{2ac_2x^5}{5}\right) + 12c_2\left(-\frac{c_1x^5}{5} + \frac{a^2c_2^2x^5}{5} + \frac{c_2x^7}{7}\right)\right][2]\Big|_0^{a/2}$

$= (-4c_1 + 4a^2c_2^2)\left(-\frac{c_1a^3}{24} + \frac{a^5c_2^2}{24} + \frac{c_2a^5}{(32)(5)}\right) - 24ac_2\left(\frac{a^4c_1}{24} - \frac{a^6c_2}{(16)(5)}\right) + 24c_2\left(-\frac{a^5c_1}{(32)(5)} + \frac{a^7c_2^2}{(32)(5)} + \frac{a^7c_2}{(128)(7)}\right)$

$= -\frac{c_1^2a^3}{6} + \frac{a^5c_1c_2^2}{6} - \frac{c_1c_2^2a^5}{6} + \frac{a^7c_2^4}{6} - \frac{c_1c_2a^5}{8(5)} + \frac{c_2^3a^7}{8(5)} - a^5c_1c_2 + \frac{3a^7c_2^2}{10} - \frac{3a^5c_1c_2}{20} + \frac{3a^7c_2^3}{20} + \frac{3a^7c_2^2}{(16)(7)}$

$= -\frac{c_1^2a^3}{6} + a^5c_1c_2\left(-\frac{47}{40}\right) + a^7c_2^2\left(\frac{c_2^2}{6} + \frac{c_2}{40} + \frac{3}{10} + \frac{3c_2}{20} + \frac{3}{112}\right) = -\frac{c_1^2a^3}{6} - \frac{47a^5c_1c_2}{40} + a^7c_2^2\left(\frac{188}{560} + \frac{7c_2}{40} + \frac{c_2^2}{6}\right)$

$B = \int(ac_1x - c_1x^2 + a^2x^2c_2^2 - 2ax^3c_2 + x^4c_2)^2 dx$

$= \int_{-a/2}^{a/2} a^2c_1^2x^2 - 2ac_1^2x^3 + 2a^3c_1c_2^2x^3 - 4a^2c_1c_2x^4 + 2ac_1c_2x^5 + c_1^2x^4 - 2a^2c_1c_2^2x^4 + 4ac_1c_2x^5 - 2c_1c_2x^6 + a^4x^4c_2^4 - 4a^3x^5c_2^3$
$+ 2a^2c_2^3x^6 + 4a^2x^6c_2^2 - 4ac_2^2x^7 + x^8c_2^2\ dx$

$= \frac{2a^2c_1^2x^3}{3} - \frac{8a^2c_1c_2x^5}{5} + \frac{2c_1^2x^5}{5} - \frac{4a^2c_1c_2^2x^5}{5} - \frac{4c_1c_2x^7}{7} + \frac{2a^4c_2^4x^5}{5} + \frac{4a^2c_2^3x^7}{7} + \frac{8a^2c_2^2x^7}{7} + \frac{c_2^2x^9}{9}\Big|_0^{a/2}$

I GIVE UP!