C474b 2007

Solutions : Problem Set #1

1. $\hat{x} \to x$; $\hat{p}_y \to \frac{\hbar}{i}\frac{\partial}{\partial y}$; $\hat{p}_z \to \frac{\hbar}{i}\frac{\partial}{\partial z}$; $\hat{p}_x \to \frac{\hbar}{i}\frac{\partial}{\partial x}$

$\Rightarrow \sqrt{\hat{y}} \to \sqrt{y}$; $\hat{t} \to t$

$$\therefore \boxed{\hat{f} = -x\hbar^2\frac{\partial^2}{\partial y^2} + e^{-t^2} - \sqrt{y}\,\frac{\hbar^3}{i}\,\frac{\partial^3}{\partial x\,\partial z^2}}$$

2. $E_n = \dfrac{n^2h^2}{8mL^2}$

$L = 10^{-10}\,m \equiv 1\,\text{Å}$

$m = 9.109\times10^{-31}\,Kg$

$h = 6.626\times10^{-34}\,J\text{-}s$

$$\therefore E_n = \frac{n^2(6.626\times10^{-34})^2}{8(9.109\times10^{-31})(10^{-10})^2} = n^2(6.025\times10^{-18})\,J.$$

a) lowest energy level is $n=1$ (not $n=0$) $\therefore E_1 = 6.025\times10^{-18}\,J$

first excited state is $n=2$ $\therefore E_2 = 4\times6.025\times10^{-18}\,J$

$= 2.41\times10^{-17}\,J$

$$\therefore \Delta E = E_2 - E_1 = (2.41\times10^{-17} - 6.025\times10^{-18})\,J = 1.8075\times10^{-17}\,J$$

b) $\Delta E = h\nu = \dfrac{hc}{\lambda} \Rightarrow \lambda = \dfrac{hc}{\Delta E} = \dfrac{(6.626\times10^{-34})(3\times10^{8}\,ms^{-1})}{1.8075\times10^{-17}}$

$= 1.1\times10^{-8}\,m = 110\,\text{Å}$

c) deep ultraviolet or vacuum ultraviolet.

3. $\Psi(x) = \sqrt{\frac{1}{5}}\,u_0(x) + \sqrt{\frac{1}{2}}\,u_2(x) + C_3\,U_3(x)$

a) $\langle\Psi|\Psi\rangle = 1$ note $\langle u_i|u_j\rangle = \delta_{ij}$

$\therefore 1 = (\frac{1}{5}) + (\frac{1}{2}) + C_3^2 \Rightarrow C_3^2 = 1 - \frac{1}{5} - \frac{1}{2} = 0.3 \quad \therefore C_3 = \sqrt{0.3}$

$\therefore \boxed{C_3 = 0.548}$

b) $\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle = \langle \psi | \hat{H} | \sqrt{\tfrac{1}{5}}\, u_0 + \sqrt{\tfrac{1}{2}}\, u_2 + \sqrt{0.3}\, u_3 \rangle$

$E_n = h\nu (n + 1/2)$

$\therefore \langle E \rangle = \langle \psi | \sqrt{\tfrac{1}{5}} \frac{h\nu}{2} u_0 + \sqrt{\tfrac{1}{2}} \left(\frac{5}{2}\right) h\nu\, u_2 + \sqrt{0.3} \left(\frac{7}{2}\right) h\nu\, u_3 \rangle$

$\because \langle u_i | u_j \rangle = \delta_{ij} \Rightarrow \langle E \rangle = \frac{1}{5} \cdot \frac{h\nu}{2} + \frac{1}{2} \cdot \frac{5}{2} h\nu + 0.3 \cdot \frac{7}{2} h\nu$

$= h\nu \left[\frac{1}{10} + \frac{5}{4} + \frac{2.1}{2} \right] = (0.1 + 1.25 + 1.04) h\nu = \boxed{2.4 h\nu}$

4 $\Omega = \sqrt{\tfrac{1}{3}}\, Y_2^1 + \sqrt{\tfrac{1}{6}}\, Y_2^2 + \sqrt{\tfrac{1}{2}}\, Y_2^{-2}$

a) - probability of finding system in state $Y_2^1 = |\langle Y_2^1 | \Omega \rangle|^2 = \frac{1}{3}$

(note: $\langle Y_\ell^m | Y_{\ell'}^{m'} \rangle = \delta_{\ell,\ell'} \delta_{m,m'}$

- in state $Y_2^2 = |\langle Y_2^2 | \Omega \rangle|^2 = \frac{1}{6}$

- in state $Y_2^{-2} = |\langle Y_2^{-2} | \Omega \rangle|^2 = \frac{1}{2}$

- in any other state, probability $= 0$

b) Recall $\hat{L}_z Y_\ell^m = m\hbar Y_\ell^m$; $\hat{L}^2 Y_\ell^m = \hbar^2 \ell(\ell+1) Y_\ell^m$

$\therefore \langle \sqrt{\tfrac{1}{3}}\, Y_2^1 + \sqrt{\tfrac{1}{6}}\, Y_2^2 + \sqrt{\tfrac{1}{2}}\, Y_2^{-2} | \hat{L}_z | \sqrt{\tfrac{1}{3}}\, Y_2^1 + \sqrt{\tfrac{1}{6}}\, Y_2^2 + \sqrt{\tfrac{1}{2}}\, Y_2^{-2} \rangle$

$= \frac{1}{3} \langle Y_2^1 | \hat{L}_z | Y_2^1 \rangle + \frac{1}{6} \langle Y_2^2 | \hat{L}_z | Y_2^2 \rangle + \frac{1}{2} \langle Y_2^{-2} | \hat{L}_z | Y_2^{-2} \rangle$

(all other terms $= 0$

$= \frac{1}{3}(1)\hbar + \frac{1}{6}(2)\hbar + \frac{1}{2}(-2)\hbar = \boxed{-\hbar/3}$

Similarly $\langle \Omega | \hat{L}^2 | \Omega \rangle = \frac{1}{3} \langle Y_2^1 | \hat{L}^2 | Y_2^1 \rangle + \frac{1}{6} \langle Y_2^2 | \hat{L}^2 | Y_2^2 \rangle + \frac{1}{2} \langle Y_2^{-2} | \hat{L}^2 | Y_2^{-2} \rangle$

$= \frac{1}{3}(2)(3)\hbar^2 + \frac{1}{6}(2)(3)\hbar^2 + \frac{1}{2}(2)(3)\hbar^2 = \boxed{6\hbar^2}$

5. a) $\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

$$\therefore \langle r\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\, r\, \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\, \underbrace{r^2\sin\theta\, dr\, d\theta\, d\phi}_{\text{volume element}}$$

$$= \frac{1}{\pi a_0^3}\int_0^\infty \underset{\text{I}}{r^3 e^{-2r/a_0}\, dr} \int_0^\pi \underset{\text{II}}{\sin\theta\, d\theta} \int_0^{2\pi} \underset{\text{III}}{d\phi}$$

I $\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}} \Rightarrow \int_0^\infty r^3 e^{-2r/a_0}\, dr = \frac{3!}{\left(\frac{2}{a_0}\right)^4}$

II $\int_0^\pi \sin\theta\, d\theta = -\cos\theta\Big|_0^\pi = -(-1)-(-1) = 2$

III $\int_0^{2\pi} d\phi = \phi\Big|_0^{2\pi} = 2\pi - 0 = 2\pi$

$$\therefore \langle r\rangle = \frac{1}{\pi a_0^3}\cdot\frac{3!\,a_0^4}{2^4}\cdot 2\cdot 2\pi = \frac{3!\,a_0}{4} = \boxed{\frac{3a_0}{2}}$$

Now $\langle \frac{1}{r}\rangle = \frac{1}{\pi a_0^3}\int_0^\infty r e^{-2r/a_0}\int_0^\pi \sin\theta\, d\theta\int_0^{2\pi} d\phi = \frac{1}{\pi a_0^3}\cdot\frac{1!\,a_0^2}{2^2}\cdot 2\cdot 2\pi = \boxed{\frac{1}{a_0}}$

b) $z = r\cos\theta \quad \therefore \langle \psi_{2p_z} | -er\cos\theta | \psi_{1s}\rangle$

$$= -e\int_0^\infty\int_0^\pi\int_0^{2\pi} \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2}\cdot\frac{1}{a_0}\, r\cos\theta\, e^{-r/2a_0}\, r\cos\theta\, \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{-e}{\sqrt{32}\,\pi a_0^4}\int_0^\infty r^4 e^{-3r/2a_0}\, dr \int_0^\pi \cos^2\theta\sin\theta\, d\theta\int_0^{2\pi} d\phi$$

Now : $\int_0^\pi \sin\theta\cos^2\theta\, d\theta$: let $x = \cos\theta \quad dx = -\sin\theta\, d\theta$

$\Rightarrow$ when $\theta = 0 \Rightarrow x = 1$; $\theta = \pi \Rightarrow x = -1$

$\therefore$ integral $= -\int_{1}^{-1} x^2 dx = \int_{-1}^{1} x^2 dx = \left.\frac{x^3}{3}\right|_{-1}^{1} = \frac{1}{3} - \left(-\frac{1}{3}\right) = \frac{2}{3}$

$$\therefore \langle \psi_{2p_z} | -er\cos\theta | \psi_{1s} \rangle = \frac{-e}{\sqrt{32}\,\pi a_0^4} \cdot \frac{2}{3} \cdot 2\pi \cdot \frac{4!}{\left(\frac{3}{2a_0}\right)^5}$$

$$= -e \cdot \frac{4 \cdot 4!}{\sqrt{32}\, 3^6} \cdot \frac{2^5 a_0^5}{a_0^4} = \boxed{-e\,(0.74 a_0)}$$

in SI units : $e = 1.602 \times 10^{-19}$ C , $a_0 = 5.291 \times 10^{-11}$ m

$\therefore$ dipole moment $= -0.74 \times 1.602 \times 10^{-19} \times 5.291 \times 10^{-11}$

$= -6.31 \times 10^{-30}$ C-m

but 1 Debye $= 3.3356 \times 10^{-30}$ C-m

$\therefore$ transition dipole moment $= \boxed{-1.9\,D}$

↳ an easy number to deal with!