Assignment (11)

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

$\Delta E = -\frac{1}{2(3)^2} - \left(-\frac{1}{2(2)^2}\right) = \frac{1}{8} - \frac{1}{18} = \frac{9-4}{72} = \frac{5}{72}\ \text{a.u.} = 3.0276\times10^{-19}\ J = hc/\lambda$

$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\ J\cdot s)(2.998\times10^{8}\ m/s)}{0.30276\times10^{-19}\ J} = 6.56\times10^{-7}\ m = 656\ nm$

b) $\Delta E = 0 \rightarrow \lambda = 0$

2. $E = \frac{-1}{2(1)^2} = \frac{-1}{2}\ \text{a.u.} = -2.179872\times10^{-18}\ J$ $\qquad \lim_{n\to\infty} E = 0$

$\Delta E = E_f - E_i = 0 - (-2.179872\times10^{-18}\ J) = 2.179872\times10^{-18}\ J$

$IE = (\Delta E)(N_A) = (2.179872\times10^{-18}\ J)(6.022\times10^{23}\ mol^{-1}) = 1.3127\times10^{6}\ J/mol = 1312.7\ kJ/mol$

3. $$\Psi_{Li}(\vec r_1, \vec r_2, \vec r_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_{1s}(\vec r_1)\alpha(1) & \psi_{1s}(\vec r_1)\beta(1) & \psi_{2s}(\vec r_1)\alpha(1) \\ \psi_{1s}(\vec r_2)\alpha(2) & \psi_{1s}(\vec r_2)\beta(2) & \psi_{2s}(\vec r_2)\alpha(2) \\ \psi_{1s}(\vec r_3)\alpha(3) & \psi_{1s}(\vec r_3)\beta(3) & \psi_{2s}(\vec r_3)\alpha(3) \end{vmatrix}$$

4. $P_{1s}(r<1\ \text{a.u.}) = \int_0^1 dr \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \left[\sqrt{\frac{z^3}{\pi}}\, e^{-zr} \cdot \sqrt{\frac{z^3}{\pi}}\, e^{-zr} \cdot r^2 \sin\theta\right] = \frac{1}{\pi}[\phi]_0^{2\pi}\left[\int_0^{\pi} \sin\theta\, d\theta\right]\left[\int_0^1 r^2 e^{-2r}\, dr\right]$

$u = r^2 \quad dv = e^{-2r}dr$; $du = 2r\,dr \quad v = (e^{-2r})/-2$

$= \frac{1}{\pi}[2\pi][2]\left[\frac{r^2 e^{-2r}}{-2}\Big|_0^1 - \int_0^1 \frac{2re^{-2r}}{-2} dr\right] = 4\left[\frac{(1)e^{-2}}{-2} + \int_0^1 re^{-2r}\, dr\right]$

$u = r \quad dv = e^{-2r}dr$; $du = dr \quad v = (e^{-2r})/-2$

$= 4\left[\frac{e^{-2}}{-2} + \left(\frac{re^{-2r}}{-2}\right)\Big|_0^1 - \int_0^1 \frac{e^{-2r}}{-2} dr\right] = 4\left[\frac{e^{-2}}{-2} + \frac{e^{-2}}{-2} - \frac{e^{-2r}}{(-2)(-2)}\Big|_0^1\right] = 4\left[-e^{-2} - \frac{e^{-2}}{4} + \frac{1}{4}\right] = 0.3233$

$P_{2s}(r<1\ \text{a.u.}) = \int_0^{\pi} \cos\theta\, d\theta \int_0^{2\pi} d\phi \int_0^1 \left(\frac{1}{2^5\pi}\right)(2-r)^2(e^{-r})(r^2)\, dr$

$= 4\pi\left(\frac{1}{2^5\pi}\right)\int_0^1 (4-4r+r^2)(r^2e^{-r})\, dr = \frac{1}{2^3}\int_0^1 4r^2e^{-r} - 4r^3e^{-r} + r^4e^{-r}\, dr$

$= \frac{1}{8}\left[\int_0^1 4r^2e^{-r}dr - \int_0^1 4r^3e^{-r}dr + \int_0^1 r^4e^{-r}dr\right] = \frac{1}{8}\left[\left(8 - \frac{20}{e}\right) - \left(24 - \frac{64}{e}\right) + \left(24 - \frac{65}{e}\right)\right]$

$= \frac{1}{8}[0.64241 - 0.45572 + 0.087836] = 0.034316$

$P_{2p}(r<1\ \text{a.u.}) = \int_0^{\pi} \cos\theta \cdot \cos\theta\, d\theta \int_0^{2\pi} d\phi \int_0^1 \left(\frac{1}{2^5\pi}\right) r^4 e^{-r}\, dr$

$= \left[\int_0^{\pi} \frac{1}{2} + \frac{\cos(2\theta)}{2}\, d\theta\right][2\pi]\left[\frac{1}{2^5\pi}\right]\left[\int_0^1 r^4e^{-r}\, dr\right]$

$= \left[\frac{1}{2}\theta + \left(\frac{1}{2}\right)(\sin(2\theta))\left(\frac{1}{2}\right)\right]_0^{\pi}\left[\frac{1}{2^4}\right]\left[24 - \frac{65}{e}\right] = \left[\frac{\pi}{2} + \frac{1}{4}(0)\right]\left[\frac{1}{2^4}\right][0.087836]$

$= 8.6233\times10^{-3}$

5. $\langle\hat T\rangle = -\frac{\hbar^2}{2\mu}\int \psi_{1s}^*(\vec r)\, \nabla^2 \psi_{1s}(\vec r)\, d\vec r$

μ is reduced mass $= \frac{m_e M}{M + m_e} = \frac{(9.10938\times10^{-31}\ kg)(1.672622\times10^{-27}\ kg)}{9.10938\times10^{-31}\ kg + 1.672622\times10^{-27}\ kg} = 9.10442\times10^{-31}\ kg = 0.99946\ \text{a.u.}$

$\langle\hat T\rangle = -\frac{\hbar^2}{2\mu}\left(\frac{1}{\pi}\right)\int e^{-r}\nabla^2 e^{-r}\, d\vec r \xrightarrow{\text{in a.u.}} = -\frac{1^2}{2(0.99946)}\left(\frac{1}{\pi}\right)\int e^{-r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{l(l+1)}{r^2}\right]e^{-r}\, d\vec r$

$l = 0$: $= -\frac{1}{2(0.99946)}\left(\frac{1}{\pi}\right)\int e^{-r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}e^{-r}\right]d\vec r$

$= -\frac{1}{2}\left(\frac{1}{0.99946}\right)\left(\frac{1}{\pi}\right)\int e^{-r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2)(-e^{-r})\right]d\vec r$

$= -\frac{1}{2}\left(\frac{1}{0.99946}\right)\left(\frac{1}{\pi}\right)\int_0^{2\pi} d\phi \int_0^{\pi}\cos\theta\, d\theta \int_0^{\infty} r^2 e^{-r}\left(\frac{1}{r^2}\right)(r^2e^{-r} - 2re^{-r})\, dr$

$= -\frac{1}{2\pi}\left(\frac{1}{0.99946}\right)(2\pi)(2)\left[\int_0^{\infty} r^2e^{-2r}\, dr - 2\int_0^{\infty} re^{-2r}\, dr\right]$

$= \left(-\frac{2}{0.99946}\right)\left[\frac{2!}{2^3} - \frac{2(1!)}{2^2}\right] = \left(-\frac{2}{0.99946}\right)(0.25 - 0.5) = 0.50027\ \text{a.u.}$

$\langle\hat V\rangle = -\frac{e^2}{4\pi\varepsilon_0}\int \psi_{1s}^*(\vec r)\left(\frac{1}{r}\right)\psi_{1s}(\vec r)\, d\vec r \xrightarrow{\text{in a.u.}} = -\int\left(\frac{1}{\pi}\right)(e^{-r})\left(\frac{1}{r}\right)(e^{-r})\, d\vec r$

$= -\frac{1}{\pi}\int_0^{2\pi} d\phi \int_0^{\pi}\cos\theta\, d\theta \int_0^{\infty} r^2\left(\frac{1}{r}\right)e^{-2r}\, dr$

$= -\frac{1}{\pi}(2\pi)(2)\int_0^{\infty} re^{-2r}\, dr$

$= -4\left[\frac{1!}{2^2}\right] = -1\ \text{a.u.}$

$\langle\hat T\rangle \approx -0.5\langle\hat V\rangle = 0.5\ \text{a.u.}$

6. $\hat H = -\frac{1}{2}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat L^2}{r^2}\right) + V(r)$

$V(r) = 0 \qquad 0 \le r \le a$

a) $\hat H = -\frac{1}{2}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat L^2}{r^2}\right)$

$\hat H\Psi_{klm}(r,\theta,\phi) = -\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat L^2}{r^2}\right]j_l(kr)\,Y_l^m(\theta,\phi)$

$= Y_l^m(\theta,\phi)\left[-\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right]j_l(kr) + j_l(kr)\frac{\hat L^2}{2r^2}Y_l^m(\theta,\phi)$

$= Y_l^m(\theta,\phi)\left[-\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right]j_l(kr) + j_l(kr)\frac{l(l+1)}{2r^2}Y_l^m(\theta,\phi)$

$= Y_l^m(\theta,\phi)\left[-\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2}\right]j_l(kr)$

$= Y_l^m(\theta,\phi)\frac{k^2}{2}j_l(kr) = \frac{k^2}{2}j_l(kr)\,Y_l^m(\theta,\phi)$

$\Psi_{klm}(r,\theta,\phi)$ is an eigenfunction of $\hat H$ and the energies are $E_{k,l} = \frac{k^2}{2}$

b) s type $\rightarrow l = 0 \longrightarrow j_0(kr) = \frac{\sin(kr)}{kr}$

* $\Psi_{klm}(r,\theta,\phi)$ must meet boundary conditions, $\Psi_{klm}(r,\theta,\phi) = 0$ at $r = a$,

meaning that $j_0(ka) = 0$;

$ka = n\pi \qquad ; n = 1, 2, 3, \ldots$

$k = \frac{n\pi}{a}$

$E_{n,l=0} = \frac{\left(\frac{n\pi}{a}\right)^2}{2} = \frac{n^2\pi^2}{2a^2} \longrightarrow E_{g.s} = \frac{1^2\pi^2}{2a^2} = \frac{\pi^2}{2a^2}$

c) Dipole-allowed transitions from the ground state are s to p transitions.
The lowest energy "p" orbital is:

$j_l(ka) = 0$

$ka = 4.493409$

$k = 4.493409/a$

$E_{k,l=1} = \frac{k^2}{2} = \frac{(4.493409)^2}{2a^2}$

$\Delta E_{1s\to2p} = \frac{(4.493409)^2}{2a^2} - \frac{\pi^2}{2a^2} = \frac{10.32112}{2a^2}$ Hartree

$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ J\cdot s)(2.998\times10^{8}\ m/s)}{680\times10^{-9}\ m} = 2.921\times10^{-19}\ J = 0.06700$ Hartree

0.06700 Hartree $= \frac{10.32112}{2a^2}$ Hartree

size of quantum dot $= a = 4.64\times10^{-10}\ m$