Chem 1410 HW #5

6-20 Prob that is electron of H is within $2a_0$ of the nucleus

$$\text{Prob} = \frac{4}{a_0^3}\int_0^{2a_0} r^2 e^{-2r/a_0}\,dr = 4\int_0^2 x^2 e^{-2x}\,dx$$

$$= 4\left[-\frac{x^2}{2}e^{-2x} - \frac{x}{2}e^{-2x} - \frac{1}{4}e^{-2x}\right]_0^2$$

$$= 1 - 13e^{-4} = 0.762$$

6-21 Radius of the sphere that encloses 50% of the probability of finding a H is e^-. Repeat for 90%.

$$\frac{4}{a_0^3}\int_0^{b'} r^2 e^{-2r/a_0}\,dr = 0.50$$

What value of b' satisfies this

$$4\int_0^b x^2 e^{-2x}\,dx = 1 - (2b^2+2b+1)e^{-2b} = 0.5$$

$$(2b^2+2b+1)e^{-2b} = 0.5 \quad \text{or} \quad \underbrace{2b^2+2b+1}_{LHS} = \underbrace{0.5e^{2b}}_{RHS}$$

can solve by successive guesses or by plotting LHS and RHS vs. b and looking for the intersection.

$b = 1.3, \quad b' = 1.3a_0$

Now for the 10% probability.

$$\left(2b^2+2b+1\right)e^{-2b}=0.1$$

$$b = 2.7 \quad , \quad b' = 2.7\,a_0$$

6-28. Calculate $\langle r \rangle$ for $n=2,\ \ell=1$ and $n=2,\ \ell=0$

$n=2,\ \ell=0$ $\quad \psi_{200} = \dfrac{1}{\sqrt{32\pi}}\dfrac{1}{a_0^{3/2}}(2-\sigma)e^{-\sigma/2}$

$$\langle r \rangle = \frac{4\pi}{32\pi}\frac{1}{a_0^3}\int_0^\infty r\,(2-\sigma)^2 e^{-\sigma} r^2\,dr$$

$$= \frac{1}{8a_0^3}\int_0^\infty r^3\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}\,dr$$

$$= \frac{1}{8a_0^3}\left\{\int_0^\infty 4r^3 e^{-r/a_0}\,dr - \frac{4}{a_0}\int_0^\infty r^4 e^{-r/a_0}\,dr + \frac{1}{a_0^2}\int r^5 e^{-r/a_0}\,dr\right\}$$

$$= \frac{1}{8a_0^3}\left\{4\cdot 3!\,a_0^4 - \frac{4}{a_0}4!\,a_0^5 + \frac{1}{a_0^2}5!\,a_0^6\right\}$$

$$= a_0\frac{48}{8} = 6a_0$$

Repeat the calculation for $n=2,\ \ell=1$

$$\psi_{210} = \frac{1}{\sqrt{32\pi}}\frac{1}{a_0^{3/2}}\,\sigma e^{-\sigma/2}\cos\theta$$

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

$$= \frac{1}{16 a_0^3}\left(\frac{2}{3}\right)\frac{1}{a_0^2}\, 5!\, a_0^6 = 5 a_0$$

So the 2s orbital is somewhat more extended than the 2p orbital. This is on account of the fact that the radial function for the 2s orbital is orthogonal to that of the 1s orbital.

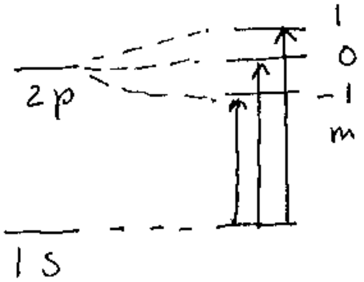
6-30 Show that $\sum_{m=-1}^{1} \psi_{21m}^2$ is spherically symmetric.

$$\frac{1}{32\pi a_0^3}\left\{\sigma^2 \cos^2\theta\, e^{-\sigma} + \sigma^2 \sin^2\theta \cos^2\phi\, e^{-\sigma} + \sigma^2 \sin^2\theta \sin^2\phi\, e^{-\sigma}\right\}$$

$$= \frac{\sigma^2 e^{-\sigma}}{32\pi a_0^3}\left\{\cos^2\theta + \sin^2\theta\left(\cos^2\phi + \sin^2\phi\right)\right\} = \frac{\sigma^2 e^{-\sigma}}{32\pi a_0^3}$$

spherically symmetrical

6-46



$$E = E_n^{(0)} + \frac{\hbar|e|}{2m_e} B_z m$$

$$\frac{\hbar|e|}{2m_e} = \frac{(1.05\times10^{-34})(1.60\times10^{-19})}{2(9.11\times10^{-31})} = 9.2\times10^{-24}\ \mathrm{J}$$

$B = 15\ \mathrm{T}$, so the energy splitting is $15\cdot(9.2\times10^{-24})\ \mathrm{J}$

$= 1.38\times10^{-22}\ \mathrm{J}$

The splitting is 1.38×10^{-22} J vs the 1.63×10^{-18} J energy associated with the electronic transition

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6-47

$\ell = 2 \ (m = -2, -1, 0, 1, 2) \rightarrow \ell = 3 \ (m = -3, -2, -1, 0, 1, 2, 3)$

$5 \times 7 = 35$ possible transitions

Now consider $\Delta m = 0$ transitions.

$$\left.\begin{array}{ll} -2 \rightarrow -2 & 1 \rightarrow 1 \\ -1 \rightarrow -1 & 2 \rightarrow 2 \\ 0 \rightarrow 0 & \end{array}\right\} \text{5 such transitions}$$

Now consider $\Delta m = \pm 1$ transitions.

$$\left.\begin{array}{l} 2 \rightarrow 1, 3 \\ 1 \rightarrow 0, 2 \\ 0 \rightarrow -1, +1 \\ -1 \rightarrow -2, 0 \\ -2 \rightarrow -3, -1 \end{array}\right\} \text{10 such transitions}$$