**Chem 20AH**

**2nd MIDTERM, November 15, 2017**

NAME________________________________________

| Problem | Points possible | Points scored |
|---|---|---|
| 1(a) | 10 | |
| 1(b) | 10 | |
| 2 (a) | 15 | |
| 2 (b) | 15 | |
| 2 (c) | 10 | |
| 3(a) | 15 | |
| 3(b) | 10 | |
| 3(c) | 8 | |
| 3(d) | 7 | |
| | 100 | |

**BE SURE TO SHOW ALL YOUR WORK, I.E., MAKE CLEAR THE REASONING BEHIND YOUR SOLUTION TO EACH PROBLEM.**

**BE CAREFUL TO WRITE UNITS FOR EVERY QUANTITY WITH DIMENSIONS, WITHOUT EXCEPTION.**

**A PERIODIC TABLE, A LIST OF FUNDAMENTAL CONSTANTS, AND SOME POSSIBLY USEFUL EQUATIONS, ARE PROVIDED ON THE LAST PAGE OF THE EXAM.**

1. (20 points) If all we know about a hydrogen atom is that its energy is $\boxed{E = -(Ryd)}$, we can conclude that it is in the state $\boxed{\psi_{E=E_1} = \psi_{1s}}$ where $\psi_{1s}$ is the top function in Table 5.2 of the textbook (and in the table on page 1 of Lecture 17/18, *and on the back page of this exam*), because this is the one and only solution to the hydrogen-atom Schroedinger equation corresponding to this energy.

But suppose, instead, that all we know is that the energy of the atom is $\boxed{E = -\frac{1}{4}(Ryd)}$; in this case the

n=2

(normalized) wave function is $\boxed{\psi_{E=E_2} = \sqrt{\frac{1}{4}}(\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})}$, where $\psi_{2s}, \psi_{2p_x}, \psi_{2p_y}$, and $\psi_{2p_z}$ are the next four wavefunctions in the table.

10 (a) (10 points) What is the value of $\psi_{E=E_2}(\vec{r})$ at the origin (nucleus)?

$\sigma = \frac{Zr}{a_0} = \frac{r}{a_0}$

$(Z=1)$

at origin, $\vec{r} = (r=0)$ regardless of angle.

From the table,

$$\psi_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$$

$$\psi_{2p_x} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$$

$$\psi_{2p_y} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$$

$$\psi_{2p_z} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$\psi_{E=E_2} = \sqrt{\frac{1}{4}}\left(\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z}\right)$$

$$= \sqrt{\frac{1}{4}}\left(\frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}(2-0)e^{0}\left(\frac{1}{4\pi}\right)^{1/2} + 0 + 0 + 0\right)$$

$\psi_{2p_x}, \psi_{2p_y}, \psi_{2p_z}$ are all proportional to $r$, so are 0 when $r=0$ (regardless of angle).

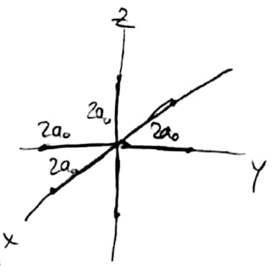
$$= \boxed{\frac{1}{4\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{1}{\pi}\right)^{1/2}}$$

substituting $a_0 = 0.529$ Å

$$= 0.259\,(\text{Å}^{-3/2})$$

heh

10 (b) (10 points) What about its values at a point on the z-axis a distance $2a_o$ from the origin? And at a similar point on the y-axis? And on the x-axis?




z-axis: $r = 2a_0, \theta = 0$, regardless of $\phi$

y-axis: $r = 2a_0, \theta = \frac{\pi}{2}, \phi = \frac{\pi}{2}$

x-axis: $r = 2a_0, \theta = \frac{\pi}{2}, \phi = 0$

$$\psi_{E=E_2}(2a_0, 0) = \sqrt{\frac{1}{4}}\left[\underbrace{\frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}(2-2)e^{-1}\left(\frac{1}{4\pi}\right)^{1/2}}_{0} + \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}(2)e^{-1}\left(\underbrace{\sin 0\cos\phi}_{0} + \underbrace{\sin 0\sin\phi}_{0} + \underbrace{\cos 0}_{1}\right)\right]$$

$$= \sqrt{\frac{1}{4}}\left(\frac{2}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}e^{-1}\right) = \boxed{\frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}e^{-1}} \quad (z\text{ axis})$$

$$\psi_{E=E_2}\left(2a_0, \frac{\pi}{2}, \frac{\pi}{2}\right) = \sqrt{\frac{1}{4}}\left[0 + \frac{2}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}e^{-1}\left(\underbrace{\sin\frac{\pi}{2}\cos\frac{\pi}{2}}_{0} + \underbrace{\sin\frac{\pi}{2}\sin\frac{\pi}{2}}_{1} + \underbrace{\cos\frac{\pi}{2}}_{0}\right)\right] = \boxed{\frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}e^{-1}} \quad (y\text{-axis})$$

$$\psi_{E=E_2}\left(2a_0, \frac{\pi}{2}, 0\right) = \sqrt{\frac{1}{4}}\left[0 + \frac{2}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}e^{-1}\left(\underbrace{\sin\frac{\pi}{2}\cos 0}_{1} + \underbrace{\sin\frac{\pi}{2}\sin 0}_{0} + \underbrace{\cos\frac{\pi}{2}}_{0}\right)\right] = \boxed{\frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}e^{-1}} \quad (x\text{-axis})$$

they're the same!

$\mathcal{A}$

2. (40 points) Consider two particles, one with mass $m_1$ and the other with mass $m_2$, in a one-dimensional (1D) box of length $L$, centered at $x = \frac{L}{2}$. If the particles do not interact at all with one another, the Schroedinger equation for this system is

$$-\frac{h^2}{8\pi^2 m_1}\frac{d^2\psi}{dx_1^2} - \frac{h^2}{8\pi^2 m_2}\frac{d^2\psi}{dx_2^2} = E\psi.$$

15pts

(a) (15 points) Show that $\psi(x_1, x_2) = \frac{2}{L}\sin\frac{\pi x_1}{L}\sin\frac{2\pi x_2}{L}$ is a solution. What is the corresponding energy?

$$\frac{d\psi}{dx_1} = \left(\frac{\pi}{L}\right)\frac{2}{L}\cos\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right) \quad \frac{d^2\psi}{dx_1^2} = -\left(\frac{\pi}{L}\right)^2\frac{2}{L}\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right)$$

$$= -\left(\frac{\pi}{L}\right)^2\psi$$

similarly $\frac{d^2\psi}{dx_2^2} = -\left(\frac{2\pi}{L}\right)^2\psi$.

So plug them in:

$$+\frac{h^2}{8\pi^2 m_1}\left(\frac{\pi}{L}\right)^2\psi + \frac{h^2}{8\pi^2 m_2}\left(\frac{2\pi}{L}\right)^2\psi$$

indeed a constant multiplied by the wavefunction!
thus $\psi(x_1, x_2)$ is a solution.

$$= \left(\frac{h^2}{8\pi^2 m_1}\left(\frac{\pi}{L}\right)^2 + \frac{h^2}{8\pi^2 m_2}\left(\frac{2\pi}{L}\right)^2\right)\psi = E\psi$$

Check boundary conditions:

$\psi(0, L) = 0 \quad \psi(L, 0) = 0$

$\psi(0, 0) = 0 \quad \psi(L, L) = 0$ ✓

Energy:

$$E = \frac{h^2}{8\pi^2 m_1}\left(\frac{\pi}{L}\right)^2 + \frac{h^2}{8\pi^2 m_2}\left(\frac{2\pi}{L}\right)^2 = \boxed{\frac{h^2\cancel{\pi^2}}{8\cancel{\pi^2}L^2}\left(\frac{1}{m_1} + \frac{4}{m_2}\right)}$$ 3

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15 pts

(b) (15 points) Derive the probability per unit length of finding particle 1 at $x_1$, independent of where particle 2 is?

Well done

$$\psi^2(x_1,x_2) = \left(\frac{2}{L}\right)^2 \sin^2\left(\frac{\pi x_1}{L}\right) \sin^2\left(\frac{2\pi x_2}{L}\right)$$

Probability density as function of the 1D positions of particles 1 & 2. ★(Has units $\frac{1}{L}$!)

To "get rid of" particle 2, integrate over all its possible positions:

$$\int_{x_2=0}^{x_2=L} \psi^2(x_1,x_2)\,dx_2 = \frac{4}{L^2}\sin^2\left(\frac{\pi x_1}{L}\right)\int_0^L \sin^2\left(\frac{2\pi x_2}{L}\right)dx_2$$

$\sin^2 x = \frac{1-\cos 2x}{2}$

$= \frac{1}{2} - \frac{1}{2}\cos 2x$

$\int_0^L \frac{1}{2} - \frac{1}{2}\cos\left(\frac{4\pi x_2}{L}\right) dx_2$

$= \int_0^L \frac{1}{2}dx_2 - \int_0^L \frac{1}{2}\cos\left(\frac{4\pi x_2}{L}\right)dx_2$

$= \left(\frac{1}{2}x_2\right)\Big|_0^L - \left(\frac{L}{8\pi}\sin\left(\frac{4\pi x_2}{L}\right)\right)\Big|_0^L$

$= \left(\frac{L}{2}-0\right) - (0-0) = \frac{L}{2}$

$$= \frac{4}{L^2}\sin^2\left(\frac{\pi x_1}{L}\right)\left(\frac{L}{2}\right)$$

$$= \boxed{\frac{2}{L}\sin^2\left(\frac{\pi x_1}{L}\right)}$$

when $x_1 = x_1$

10 pts

(c) (10 points) Show that $\psi(x_1,x_2) = \frac{2}{L}\sin\frac{\pi x_1}{L}\sin\frac{2\pi x_2}{L}$ is normalized.

If $\psi(x_1,x_2)$ is normalized, $\int_{x_1=0}^{x_1=L}\int_{x_2=0}^{x_2=L} \psi^2(x_1,x_2)\,dx_1\,dx_2 = 1$.

$$\int_{x_1=0}^{x_1=L}\int_{x_2=0}^{x_2=L} \psi^2(x_1,x_2)\,dx_1\,dx_2 = \frac{4}{L^2}\int_0^L \sin^2\left(\frac{\pi x_1}{L}\right)dx_1 \int_0^L \sin^2\left(\frac{2\pi x_2}{L}\right)dx_2$$

$\int_0^L \sin^2\left(\frac{\pi x_1}{L}\right)dx_1$

$= \int_0^L \frac{1}{2}dx_1 - \int_0^L \frac{1}{2}\cos\left(\frac{2\pi x_1}{L}\right)dx_1$

$= \left(\frac{L}{2}\right) - (0-0) = \boxed{\frac{L}{2}}$

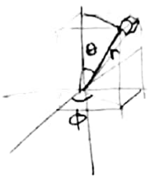
already calculated, $= \boxed{\frac{L}{2}}$

$$= \frac{4}{L^2}\left(\frac{L}{2}\right)\left(\frac{L}{2}\right) = \frac{4}{L^2}\left(\frac{L^2}{4}\right) = 1 \checkmark$$

3. (40 points)

(a) (15 points) Derive the radial probability density for the 1s orbital of an atom with atomic number $Z$, i.e., the probability per unit length of finding an electron at distance $r$ when it is in the 1s state. Be careful to include correctly all of the "normalization" constants.
HINT: Use for the 1s wavefunction the 1s orbital of a hydroden-like atom with $Z = Z_{eff}$ where $Z_{eff}$ is the effective charge on the nucleus seen by the 1s electrons, as determined by the Hartree self-consistent-field approximation.

$$\psi_{1s} = 2\left(\frac{1}{4\pi}\right)^{1/2}\left(\frac{Z_{eff}}{a_0}\right)^{3/2} e^{-Z_{eff} r/a_0}$$



radial probability density $P_{1s}(r) = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \psi^2 \, dV\left(\frac{1}{dr}\right)$

15

$$= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} 4\left(\frac{1}{4\pi}\right)\left(\frac{Z_{eff}}{a_0}\right)^3 e^{-2Z_{eff} r/a_0} r^2 dr \sin\theta \, d\theta \, d\phi \left(\frac{1}{dr}\right)$$

$$= \frac{1}{\pi}\left(\frac{Z_{eff}}{a_0}\right)^3 e^{-2Z_{eff} r/a_0} r^2 \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$(-\cos\theta)\big|_0^{\pi} = -(-1) - -(1) = 1 + 1 = 2$

$(\phi)\big|_0^{2\pi} = 2\pi - 0 = 2\pi$

Product: $2 \cdot 2\pi = 4\pi$

$\frac{\pi}{\sqrt{\pi}} = \sqrt{\pi}$

$$= \boxed{4\left(\frac{Z_{eff}}{a_0}\right)^3 \left(e^{-2Z_{eff} r/a_0}\right) r^2}$$

(b) (10 points) In part (a) you should have obtained a result for $P_{1s}^{Z}(r)$ that is proportional to $r^2 e^{-2Z_{eff} r/a_0}$, where $Z_{eff} = Z_{eff}(Z;1s)$ is the self-consistent-field value for the effective charge on the nucleus seen by a 1s electron in an atom with $Z$ protons and electrons.
Derive an expression for the most probable value of the distance $r$ for a 1s electron in an atom with atomic number $Z$, with the electronic structure of the atom treated by the self-consistent-field approximation.

leave $Z_{eff}$ as is...

For what $r$ is $P_{1s}(r)$ maximized?

10

$$\frac{d}{dr}P_{1s}(r) = 8\left(\frac{Z_{eff}}{a_0}\right)^3\left(e^{-2Z_{eff} r/a_0}\right) r + 4\left(\frac{Z_{eff}}{a_0}\right)^3\left(-\frac{2Z_{eff}}{a_0}\right)\left(e^{-2Z_{eff} r/a_0}\right) r^2$$

$$= 8\left(\frac{Z_{eff}}{a_0}\right)^3\left(e^{-2Z_{eff} r/a_0}\right) r - 8\left(\frac{Z_{eff}}{a_0}\right)^4\left(e^{-2Z_{eff} r/a_0}\right) r^2$$

$$= 8\left(\frac{Z_{eff}}{a_0}\right)^3\left(e^{-2Z_{eff} r/a_0}\right) r\left(1 - \left(\frac{Z_{eff}}{a_0}\right) r\right)$$

$$\boxed{r = \frac{a_0}{Z_{eff}}}$$

This is 0 when $r = 0$ and $r = \frac{a_0}{Z_{eff}}$. $P(0) = 0$ so $r = 0$ is a minimum, but $r = \frac{a_0}{Z_{eff}}$ gives a maximum.

(c) (8 points) For this same 1s electron, how much more likely is it to be found at a distance of $\boxed{3\frac{a_o}{Z_{eff}}}$ than at $\boxed{\frac{a_o}{Z_{eff}}}$?

compare $P(r = \frac{3a_0}{Z_{eff}})dr$ and $P(r = \frac{a_0}{Z_{eff}})dr$ ← the higher probability/length

$$\frac{P(\frac{3a_0}{Z_{eff}})dr}{P(\frac{a_0}{Z_{eff}})dr} = \frac{P(\frac{3a_0}{Z_{eff}})}{P(\frac{a_0}{Z_{eff}})}$$

$$-\frac{1}{a_0} 2Z_{eff}\left(\frac{3a_0}{Z_{eff}}\right) = -\frac{2\cdot 3}{1} = -6$$

8

$$= \frac{4\left(\frac{Z_{eff}}{a_0}\right)^3 (e^{-6})\left(\frac{3a_0}{Z_{eff}}\right)^2}{4\left(\frac{Z_{eff}}{a_0}\right)^3 (e^{-2})\left(\frac{a_0}{Z_{eff}}\right)^2}$$

$$-\frac{1}{a_0} 2Z_{eff}\left(\frac{a_0}{Z_{eff}}\right) = -2$$

$$= e^{-4}\,\frac{9\left(\frac{a_0}{Z_{eff}}\right)^2}{\left(\frac{a_0}{Z_{eff}}\right)^2} = \boxed{9e^{-4}}$$ "more" likely

$\approx \boxed{0.165}$

(d) (7points) The Hartree/self-consistent-field approximation for the 1s wavefunction of any atom is equal to $\boxed{\psi_{1s}(\bar{r}) = \frac{1}{\sqrt{\pi}}(\frac{Z_{eff}}{a_o})^{3/2} e^{-Z_{eff}r/a_o}}$, where $\boxed{Z_{eff} = Z_{eff}(Z;1s)}$ is the self-consistent-field value for the effective charge on the nucleus seen by a 1s electron in the atom (which has Z protons and Z electrons). $\psi_{1s}(\bar{r} = 0)$ is the value of the wavefunction at the nucleus.
How much bigger is this value for Neon than for Hydrogen?

$Z = 10$ $\quad Z = 1$

$Z_{eff} = 9.64$ $\quad Z_{eff} = 1$ ← values from provided table

again, r=0 when $\vec{r}=0$.

$$\frac{\psi_{1s}^{Ne}(\vec{r}=0)}{\psi_{1s}^{H}(\vec{r}=0)} = \frac{\frac{1}{\sqrt{\pi}}\left(\frac{9.64}{a_0}\right)^{3/2} e^{-9.64(0)/a_0}}{\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-1(0)/a_0}} \quad \begin{matrix}\to e^0 \\ \to e^0\end{matrix}$$

X

$$= \frac{\left(\frac{9.64}{a_0}\right)^{3/2}}{\left(\frac{1}{a_0}\right)^{3/2}} = \frac{(9.64)^{3/2}\left(\frac{1}{a_0}\right)^{3/2}}{\left(\frac{1}{a_0}\right)^{3/2}}$$

$$= (9.64)^{3/2} \approx \boxed{29.931}$$ times larger

(value of 1s wavefunction for Ne over H based on Hartree approximations)