Chemistry 455A

Final Examination
June 5, 2007

Name ______________________________

Helpful Information:

$H\Psi = E\Psi$ $\hat{H} = \hat{T} + \hat{V}(x)$ $T = \frac{\hat{p}^2}{2m}$ $\hat{p} = -i\hbar \frac{d}{dx}$ $e^{i\phi} = \cos\phi + i\sin\phi$ $1 = \sin^2\phi + \cos^2\phi$ $\sigma_x^2 \sigma_x^2 \geq \left(\frac{\hbar}{2}\right)^2$ $[p, x] = -i\hbar$	$\hbar = 1.\cdot 10^{-34}\, J-\sec$ $m_e = 1\cdot 10^{-30}\, Kg$ $c = 3\cdot 10^8\, m/\sec$ $N_A = 6\cdot 10^{23}\, {}^{molecules}/_{mole}$ $E_n = \frac{1}{2m}\left(\frac{\hbar\pi n}{a}\right)^2$ $V = \frac{q_1 q_2}{(4\pi\varepsilon_o) r}$ $E_n = -22\cdot 10^{-19}\left(\frac{Z}{n}\right)^2 J$	$\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$ $\frac{e^2}{4\pi\,\varepsilon_0 a_0} = 44\cdot 10^{-19}\, J$	$\hat{H}\phi_m = E_m \phi_m$ $\int_x \phi_n^* \phi_m dx = \delta_{m,n}$ $1 = \int_x \Psi^* \Psi dx$ $\langle A \rangle = \frac{\int_x \Psi^* \hat{A} \Psi dx}{\int_x \Psi^* \Psi dx}$ $i\hbar \frac{\partial}{\partial t}\Psi = \hat{H}\Psi$

There are 8 pages; with 10 (multi part) problems. Be sure you have all the pages before you start.
Be sure your name is on the exam before you start.
This is a timed 110 minute exam.
To receive full credit on all problems you must show your work or reasoning.

$$E_n = \hbar\omega_{os}\left(n + \tfrac{1}{2}\right)$$

$$\omega_{os} = \sqrt{\frac{k_s}{\mu}}$$

$$\langle T \rangle_n = \langle V \rangle_n$$

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}$$

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

$$\omega = ck$$

$$\lambda\nu = c$$

$$E = \hbar\omega = h\nu$$

$$E^2 = (cp)^2 + \left(mc^2\right)^2$$

$$p = \hbar k$$

$$[A, B+C] = [A,B] + [A,C]$$

$$[A, BC] = B[A,C] + [A,B]C$$

Q1) EQ20.7) A) What possible geometrical forms can the nodes in the angular function for p and d orbitals in the H atom have?

Planes or sheets or cones, which are planes rolled up.

B) What possible geometrical forms can the nodes in the radial function for p and d orbitals in the H atom have?

Spheres (hollow spheres, like the rim of a basketball)

Q2) EQ21.1) Using the Slater Determinant for the two electron wave function (for an atom with two electrons)

$$\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \quad \text{where} \quad 1s \equiv \phi_{1s}$$

A) Evaluate the Helium ground state wave function (in the determinant form given here) giving both electrons the <u>same</u> quantum numbers.

where $\alpha(1) = \beta(1)$

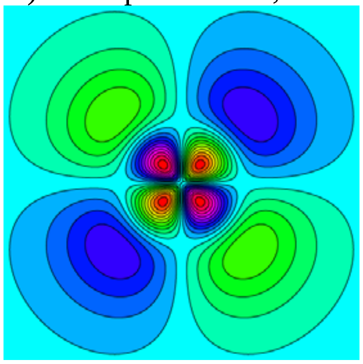
$$\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\alpha(2) \end{vmatrix} = 1s(1)\alpha(1)1s(2)\alpha(2) - 1s(2)\alpha(2)1s(1)\alpha(1)$$

$$\psi(1,2) = 0$$

B) From this result, discuss that the Slater determinant formalism automatically incorporates the Pauli Exclusion Principle.
When two orbitals are the same (and they are identified by the 4 quantum numbers, including the spin quantum number) then the (Slater) determinant will vanish.

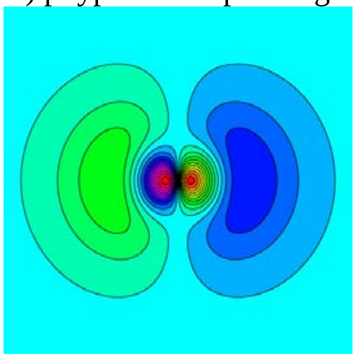
Q3) EQ21.11) Identify the orbital ($2s$, $2p_x$ and so on) from the contour plot in the x-y plane with the y axis being the vertical axis:

A) one up from a 3d, so it is a 4d orbial, and it is 4dxy because it points between axes



Explain your answer: one radial node, two angular nodes

B) p type orbital pointing on x, but a radial node so one up form 2p, so it is a 3px.



Explain your answer: One radial and one planar node.

Q4) EP21.13) A) List the allowed quantum numbers m_ℓ and m_s for the 3d subshell.

For d one has 5 orbitals, so one can hold 10 electrons

$$-\ell \le m_\ell \le \ell$$

$$m_\ell = \text{-2, -1, 0, 1, 2}$$

$$and\ m_s = -\frac{1}{2}; +\frac{1}{2}$$

$$\{\text{-2, -1, 0, 1, 2}\} \times \left\{-\frac{1}{2}\right\} \text{ and } \{\text{-2, -1, 0, 1, 2}\} \times \left\{+\frac{1}{2}\right\}$$

B) What is the maximum occupancy of this subshell? 10, two per orbital

Q5) EP21.11) Show that the charge density of the filled $n = 2,\ \ell = 1$ subshell is spherically symmetrical and that the total angular momentum . The angular distribution of the electron chare is simply the sum of the squares of the magnitude of the angular part of the wave functions for $\ell = 1$ and $m_\ell = -1, 0,$ and 1.

A) Given that the angular part of these wave functions is:

$$Y_\ell^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta \qquad Y_\ell^1(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{i\phi} \qquad Y_\ell^{-1}(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{-i\phi}$$

Write an expression for $\left|Y_\ell^0(\theta,\phi)\right|^2 + \left|Y_\ell^1(\theta,\phi)\right|^2 + \left|Y_\ell^{-1}(\theta,\phi)\right|^2$

$$\left|e^{\pm i\phi}\right|^2 = 1 \quad \left|Y_\ell^0(\theta,\phi)\right|^2 = \left(\frac{3}{4\pi}\right)\cos^2\theta \qquad \left|Y_\ell^1(\theta,\phi)\right|^2 = \left(\frac{3}{8\pi}\right)\sin^2\theta \quad \left|Y_\ell^{-1}(\theta,\phi)\right|^2 = \left(\frac{3}{8\pi}\right)\sin^2\theta$$

$$\left|Y_\ell^0(\theta,\phi)\right|^2 + \left|Y_\ell^1(\theta,\phi)\right|^2 + \left|Y_\ell^{-1}(\theta,\phi)\right|^2 = +\left(\frac{3}{4\pi}\right)\cos^2\theta + \left(\frac{3}{8\pi}\right)\sin^2\theta + \left(\frac{3}{8\pi}\right)\sin^2\theta$$

B) Show that $\left|Y_\ell^0(\theta,\phi)\right|^2 + \left|Y_\ell^1(\theta,\phi)\right|^2 + \left|Y_\ell^{-1}(\theta,\phi)\right|^2$ does not depend on θ and ϕ

$$\left|Y_\ell^0(\theta,\phi)\right|^2 + \left|Y_\ell^1(\theta,\phi)\right|^2 + \left|Y_\ell^{-1}(\theta,\phi)\right|^2$$

$$= \left(\frac{3}{8\pi}\right)\left\{2\cos^2\theta + \sin^2\theta + \sin^2\theta\right\} = \left(\frac{3}{8\pi}\right)\left\{2\cos^2\theta + 2\sin^2\theta\right\}$$

$$= \left(\frac{3}{8\pi}\right)2$$

C) Why does this result show that the charge density for the filled $n = 2,\ \ell = 1$ subshell is spherically symmetrical?

The charge density is proportional to this quantity. The radial part is the same for all three terms, and this part has no angular dependence. This is called Unsold's theorem, it is true for any subshell.

Q6) EP21.3) A) Is this wave function

$\psi(1,2) = 1s(1)\alpha(1)1s(2)\beta(2) + 1s(1)\beta(1)1s(2)\alpha(2)$ where $1s \equiv \phi_{1s}$ an eigenfunction of the $\hat{S}_z$ operator? Yes

$$\hat{S}_z = \hat{s}_{z1} + \hat{s}_{z2}$$

$$\hat{S}_z\psi(1,2) = \left(1s(1)1s(2)\right)\left(\hat{s}_{z1} + \hat{s}_{z2}\right)\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]$$

$$= \frac{\hbar}{2}\left(1s(1)1s(2)\right)\left\{\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] + \left[-\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]\right\}$$

$$= \frac{\hbar}{2}(0)$$

B) If so what is its eigenvalue M_s? $M_s = 0$

C) Is this an acceptable (or possible) wave function for 2 electrons in He? Explain. No, because it is fully symmetric, and wave functions for electrons must be anti symmetric.

Q7) EP21.7) Because the spin of the electron does not correspond to anything physical that we know of, the only representation for spin that we have is in terms of vectors and (square) matrices. The spin eigenfunctions are represented as the column vectors:

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

A) Show that these eigenfunctions are orthogonal:

$$\alpha^\dagger \beta = \begin{pmatrix} 1 \\ 0 \end{pmatrix}^\dagger \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0 + 0 = 0$$

B) The spin angular momentum operators are represented by the matrices

$$\hat{s}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{s}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \hat{s}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

Show that the commutation rule $\left[\hat{s}_x, \hat{s}_y\right] = i\hbar\,\hat{s}_z$ holds.

$$\left[\hat{s}_x, \hat{s}_y\right] = \left(\frac{\hbar}{2}\right)^2 \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] = i\left(\frac{\hbar}{2}\right)^2 \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} - \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right]$$

$$= i\left(\frac{\hbar}{2}\right)^2 \left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\right] = i2\left(\frac{\hbar}{2}\right)\left\{\left(\frac{\hbar}{2}\right)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right\}$$

$$= i\hbar\,\hat{s}_z$$

C) Show that $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \frac{\hbar^2}{4}\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$.

$$\left(\hat{s}_x\right)^2 = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \left(\hat{s}_y\right)^2 = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \hat{s}_z = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = 3\left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\hbar^2}{4}\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$$

D) Show that β is an eigenfunctions of $\hat{s}_z$ and give the eigenvalue:

$$\hat{s}_z \beta = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\beta$$

E) Show that β is an eigenfunctions of $\hat{s}^2$ and give the eigenvalue: $-\frac{\hbar}{2}$

F) Show that α is not eigenfunctions of $\hat{s}_x$:

$$\hat{s}_x \alpha = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2}\beta \neq m_s \alpha$$

Q8) EP20.18&20) The wave function for the H atom in its ground state is:

$\phi_{1s} = \frac{1}{\sqrt{4\pi}} \frac{2}{a_o^{3/2}} e^{-\frac{r}{a_o}}$, where $a_o = 53pm$ is the Bohr radius.

A) What is the total energy for the system in the ground state?

From the top page $E_{n=1} = -22 \cdot 10^{-19} \left(\frac{Z}{n}\right)^2 J = -22 \cdot 10^{-19} J$

B) Calculate the average value of the H atom potential energy in this state. [You may either evaluate the integral or use the virial theorem.]

$$\langle V \rangle = 2E = -44 \cdot 10^{-19} J$$

$$\langle V \rangle = \frac{4}{4\pi a_o^3} \left(\frac{-e^2}{4\pi \varepsilon_0} \right) \iiint_{r,\theta\phi} e^{-2\frac{r}{a_o}} \frac{1}{r} r^2 \sin\theta dr d\theta d\phi$$

$$\langle V \rangle = \frac{4}{4\pi} \left(\frac{-e^2}{4\pi \varepsilon_0 a_0} \right) \int_{y=0}^{\infty} e^{-2y} y dy 2\pi \cdot 2 = 4 \left(\frac{-e^2}{4\pi \varepsilon_0 a_0} \right) \frac{1}{2^2} = \left(\frac{-e^2}{4\pi \varepsilon_0 a_0} \right)$$

$$\langle V \rangle = \left(\frac{-e^2}{4\pi \varepsilon_0 a_0} \right) = 44 \cdot 10^{-19} J$$

C) EP20.17) In polar coordinates $z = r\cos\theta$. what would you expect for $\langle z \rangle$ [Hint: You don't need to 'do' the integral if you can explain your result.)

$$\langle z \rangle = \frac{4}{4\pi a_o^3} \iiint_{r,\theta\phi} e^{-2\frac{r}{a_o}} (r\cos\theta) r^2 \sin\theta dr d\theta d\phi$$

$\int_0^{\pi} \cos\theta \sin\theta d\theta = \int_{-1}^{1} x dx = 0$ An odd function over an even interval

$$\langle z \rangle = 0$$

The angular integral is zero, so the entire integral vanishes.

Q8-Contd

D) What would you expect for $\langle z^2 \rangle$?

$$\langle z^2 \rangle = \frac{4}{4\pi a_o^3} \iiint_{r,\theta\phi} e^{-2\frac{r}{a_o}} (r\cos\theta)^2 r^2 \sin\theta dr d\theta d\phi$$

$$\int_0^\pi \cos^2\theta \sin\theta d\theta = \frac{1}{3}2$$

$$\langle z^2 \rangle = \frac{4 \cdot 4\pi}{4\pi} \frac{1}{3} a_o^2 \iiint_{r,\theta\phi} e^{-2y} y^4 dy = \frac{4}{3} a_o^2 \frac{4!}{2^5} = a_o^2$$

The rms distance is the Bohr radius, what else would you expect?

E) Show that the most probable distance for the electron, using the probability density for the electron in the ground state, ϕ_{1s}, is the Bohr radius.

$$P(r) = r^2 (\phi_{1s})^2 = \frac{4r^2}{a_o^3} e^{-2\frac{r}{a_o}} = \frac{4}{a_o} y^2 e^{-2y} \quad \text{where} \quad y = \frac{r}{a_o}$$

$$0 = \frac{dP(r)}{dr} = \frac{dP(r)}{dy} = \frac{d}{dy}\left(y^2 e^{-2y}\right) = \left(2ye^{-2y} - 2y^2 e^{-2y}\right) = 2ye^{-2y}(1-y)$$

Therefore the maximum position is $1 = y$ or $r = a_o$

F) By contrast show that the average distance, $\langle r \rangle$, from the nucleus, for the electron is larger than the Bohr radius.

$$\langle r \rangle = \frac{4}{4\pi a_o^3} \iiint_{r,\theta\phi} e^{-2\frac{r}{a_o}} r^3 \sin\theta dr d\theta d\phi$$

$$\langle r \rangle = \frac{4}{4\pi} 4\pi a_o \int_{y=0}^{\infty} e^{-2y} y^3 dy = 4a_o \frac{3!}{2^4} = \frac{3}{2} a_o$$

Q9) Z14.5) A) Draw the Lewis Dot structure of HCN.

$HCN \qquad H \ : \ C \ ::: \ N \ :$

B) Draw a picture showing all the bonds between the atoms
[a) Indicate the hybrid orbitals or the Molecular Orbitals b) Label each bond as σ or π]

$$HCN \qquad H \ : \ C \ :\ :\ : \ N \ :$$

$$H \ \uparrow \ C \ \uparrow\uparrow\uparrow \ N \ \uparrow$$

$$H \ \sigma \ C \ \pi\sigma\pi \ N \ \sigma_{NB\_LP}$$

Q10) Z14.15) Why must all atoms of $H_2C = CH_2$ or C_2H_4 be in the same plane. Use the σ and π MO <u>or</u> hybrid orbital description in your explanation.
There are two ways to explain this structure. Either of these will be fine.
1) The HAO, has the Carbons be sp2 hybridized. This leaves a single p orbital on each C to overlap and make a pi orbital. That pi orbital locks the framework in plane, the other HAOs of the Carbons are in the common plane and bond to each H.
2) The sigma framework has a sigma MO mostly between the carbons and a sigma_ptype MO among the carbons and the hydrogens. There is also a pi type MO. Again the pi MO forces planarity.