Exam II

CH 301H Fall '10

Vanden Bout

Name: KEY

Carefully read all the problems

Show all your work on numerical problems

Clearly mark your answers

If you think a problem cannot be worked out with the information provided write "this problem can not be worked with the information provided"

Problems may contain extraneous information

Please sign at the bottom to certify that you have worked on your own.

I certify that I have worked the following exam without the help of others, and that the work I am turning in is my own.

Signed: --

Signature Date

Potentially Useful Information

e	1.602×10^{-19} C
m_e	9.109×10^{-31} kg
m_p	1.67×10^{-27} kg
m_n	1.67×10^{-27} kg
ε_0	8.854×10^{-12} $C^2\ J^{-1}\ m^{-1}$
c	2.998×10^{8} $m\ s^{-1}$
1Å	10^{-10} m

$h = 6.626 \times 10^{-34}$ J s

$E = h\nu$

$\lambda\nu = c$

1 Rhydberg 2.18×10^{-18} J

1 eV = 1.602×10^{-19} J

N_A 6.02×10^{23}

$$\lambda = \frac{h}{p}$$

Particle in a box

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})$$

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

$$\psi_n(x,y,z) = \sqrt{\frac{2}{L_x}}\sin(\frac{n_x\pi x}{L_x})\sqrt{\frac{2}{L_y}}\sin(\frac{n_y\pi y}{L_y})\sqrt{\frac{2}{L_z}}\sin(\frac{n_z\pi z}{L_z})$$

$$E_n = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

Hydrogen-like Atoms

$$E_n = -\frac{Z^2}{n^2}$$ in Rhydbergs

$$\overline{r_{n,l}} = \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$$

$a_0 = 0.529$ Å

Multi electron atoms

$$E_n \approx -\frac{Z_{eff}^2}{n^2}$$ in Rhydbergs

$$\overline{r_{n,l}} \approx \frac{n^2 a_0}{Z_{eff}(n)}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$$

Hydrogenic Wavefunctions

$$R_{1s} = 2\left(\frac{Z}{a_0}\right)\exp\left(\frac{-Zr}{a_0}\right)$$

$$R_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)\exp\left(\frac{-Zr}{2a_0}\right)$$

$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(\frac{-Zr}{2a_0}\right)$$

$$Y_S = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_{pz} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

1. True/False (3 points each/ 30 points)

[✓ T] F In a Li^{2+} ion the 4s and 4f wavefunctions have the same energy. H-like $1e^-$ atom

T [✓ F] A major problem with the Bohr model for the hydrogen atom is that it predicts the energy levels to be discrete (quantized). that is what it gets right

[✓ T] F Ultraviolet radiation has a higher energy compared to radio waves

T [✓ F] This wavefunction is anti-symmetric with respect to exchange of the electrons

$$1s(1)1s(2)[\alpha(1)\beta(2)+\alpha(2)\beta(1)]$$ this is symm

T [✓ F] K^+ is the same size as Ar iso-electronic but $Z_{eff_{K^+}} > Z_{eff\,Ar}$

[✓ T] F A 3d wavefunction has no radial nodes 2 angular nodes

T [✓ F] The 2pz wavefunction in hydrogen has a node at $\theta = 0$ node at $\theta = \pi/2$

[✓ T] F Atoms don't actually have electron orbitals ~~[illegible] it was~~ $1e^-$ orbitals are an approx.

T [✓ F] Hund's rule states you should always fill the 2px orbital first as it is lowest in energy of the 2p orbitals

[✓ T] F The probability of finding an electron at a distance of greater than 1 meter away from the nucleus in ground state of hydrogen is extremely small but finite.

Multiple Guess (5 points each/ 20 points) Write your answer on the line provided.

2. For Carbon is the Z_{eff} larger for the 2s or the 2p Hartree orbital?

A. Z_{eff}(2s) would be larger
B. Z_{eff}(2p) would be larger
C. Z_{eff}(2s) would be exactly equal to Z_{eff}(2p)
D. it depends on the spin

A

3. The most probable distance for an electron in a 1s wavefuction in Li^{2+} is at a distance that is

A. 2 times smaller than hydrogen
B. 2 times larger than hydrogen
C. 3 times smaller than hydrogen
D. 3 times larger than hydrogen
E. no way to guess exactly due to shielding effects

H-like $Z=3$

C

4. The wavelength of a neutron traveling at 10^4 m s^{-1} would be how long compared to an neutron traveling at 10^3 m s^{-1}?

A. 10 times longer
B. 10 times shorter
C. $\sqrt{10}$ times longer
D. $\sqrt{10}$ times shorter
E. neutrons don't have a wavelength

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

B

5. In a hydrogen-like atom, how many different wavefunctions are there in the n=5 level with l=4 (not taking into account the spin which is not important for a 1 electron system)?

A. 1
B. 8
C. 9
D. 14
E. 25
F. none of the above

$$l=4 \quad m = \underbrace{-4,-3,-2,-1,0,1,2,3,4}_{9}$$

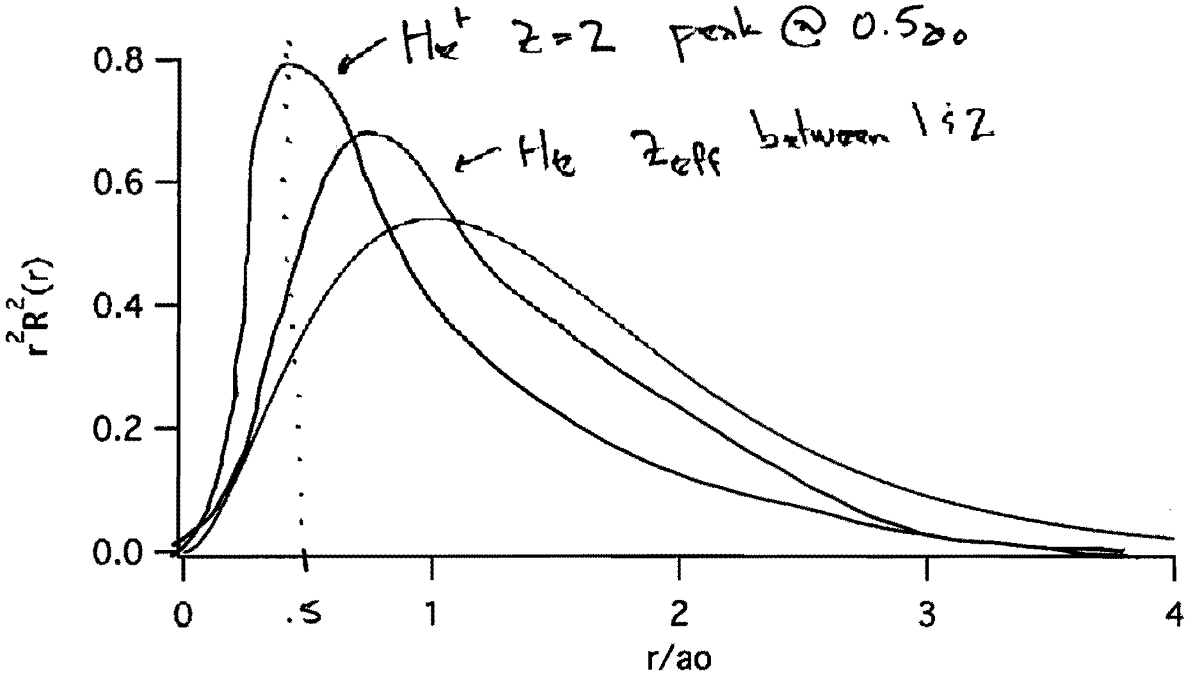
C

Shorter Problems

6. Which has a larger electron affinity Cd or Ag? Why? (10 points)

Ag has a large EA as Cd is likely zero Cd has a full 5s ; 4d shells. Ag has one less e^-.

7. Below is a plot of the radial probability density for 1s wave function in the hydrogen atom. On the same plot sketch what you think a 1s function would look like for both He and He$^+$. Try to be a quantitative as possible in your peak positions.(15 points)



8. Give the electronic configuration of the following atoms (12 points)
State whether each is paramagnetic or diamagnetic

Cf $[Rn]\,7s^2 5f^{10}$ (or $[Rn]\,7s^2 6d^1 5f^{10}$) Unpaired e^- ⇒ paramagnetic

Ga^+ $[Ar]\,4s^2 3d^{10}$ all paired e^-. diamagnetic

9. Imagine a He^+ ion with an excited electron in state described by a 5g wavefunction. What wavelength of light would be emitted if the electron fell down to a 4f state? (12 points)

$$\Delta E = \left[-\frac{Z^2}{n_f^2} - \left(-\frac{Z^2}{n_i^2} \right) \right] =$$

$$= 4 \left[\frac{1}{25} - \frac{1}{16} \right] = -0.09 \text{ Rhydbergs}$$

emission

$$0.09 \text{ Rhyd} = 1.962 \cdot 10^{-19} \text{ J}$$

$$h\nu = 1.962 \cdot 10^{-19} \text{J}$$

$$\nu = 2.96 \cdot 10^{14} \text{ s}^{-1}$$

$$\boxed{\lambda = \frac{c}{\nu} = 1.01 \cdot 10^{-6} \text{ m}}$$

10. Given that the atomic radius of Xe is approximately 1.5 times larger than that of Ar, how much larger do you think the ionization energy of Ar is compared to Xe? (you should try to calculate this rather than just guessing). (10 points)

$$1.5 = \frac{r_{Xe}}{r_{Ar}} = \frac{\frac{(5)^2 \cancel{a_0}}{Z_{eff\,Xe}} \times \left\{1 + \frac{1}{2}\left(1 - \frac{2}{5^2}\right)\right\}}{\frac{(3^2)\cancel{a_0}}{Z_{eff\,Ar}} \times \left\{1 + \frac{1}{2}\left(1 - \frac{2}{3^2}\right)\right\}} \Longrightarrow \frac{Z_{eff\,Ar}}{Z_{eff\,Xe}} = 0.51$$

$$\frac{IE_{Ar}}{IE_{Xe}} = \frac{\left(Z_{eff\,Ar}/3\right)^2}{\left(Z_{eff\,Xe}/5\right)^2} = 0.73$$

11. The work function for silver metal is 4.6 eV. If a sample of sodium is illuminated with a 0.1 W laser at a wavelength of 532 nm. [Note: a Watt (W) is a J per second]. (15 points)

About how many electrons would be emitted per second (if any)?

compare energy of photon to work function

$h\nu = 3.73 \cdot 10^{-19}\,J = 2.3\,eV$ Not high enough E.

What if the power was increased to 1 W?

$\therefore$ NO ELECTRONS EMITTED

more light will not have an effect as the energy is below the threshold. (work function).

12. Given that Z_{eff} for a 2p electron in F is 5.10, predict the 2nd ionization energy of Ne. (in Rhydbergs) (10 points)

Ne^+ is like F, but with larger Zeff.

$$Z_{eff\,Ne^+} \approx Z_{eff\,F} + 1 = 6.10$$

$$I.E. = -\mathcal{E}_n = \frac{(6.10)^2}{2^2} = \boxed{9.3 \text{ Rhydbergs}}$$

14. The periodic trend in ionization energy within a group is a decrease in I.E. from the top to bottom of the group. Imagine that the valence electrons in F experienced the same effective nuclear charge as the valence electron in Cl.

If this were the case, how much larger would the I.E. of F be compared to the I.E. of Cl? (8 points)

$$\frac{I.E_F}{I.E_{Cl}} = \frac{-\mathcal{E}_{F2p}}{-\mathcal{E}_{Cl3p}} = \frac{+\left(\frac{Z_{eff}^2}{2^2}\right)}{+\left(\frac{Z_{eff}}{3^2}\right)} = \frac{9}{4} \text{ or } 2.25$$

Given that the experimental ratio is that the I.E. of F is 1.3 times that of Cl, would you say that effective nuclear charge increases, decreases, or stays the same as you go from top to bottom in a group? Does this make sense? (8 points)

since $2.25 > 1.3$

$Z_{eff\,Cl}$ must be larger than $Z_{eff\,F}$.

this make sense since $Z_{Cl} > Z_F$

shielding is ~~not~~ less effective for e^- at larger distances from the nucleus.

Longer Problems

14. Consider a quantum mechanical particle in a box that is bound between –L/2 and L/2 (a box of length L that is centered at x=0). (25 points)

What are the boundary conditions that the wavefunction of this particle must satisfy?

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

We saw in the homework that the ground state solution for this problem is

$$\psi_1 = \sqrt{\frac{2}{L}}\cos\left(\frac{\pi x}{L}\right)$$

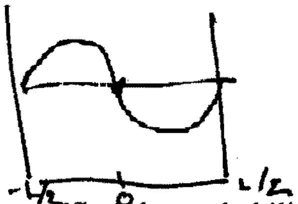
What is the wavefunction for the first excited state of this problem?

cos won't meet boundary conditions if n=2, but sin will!

$$\psi_2 = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$$

Does this first excited state wavefunction have any nodes? If so, how many and at what values of x?

1 node at x=0

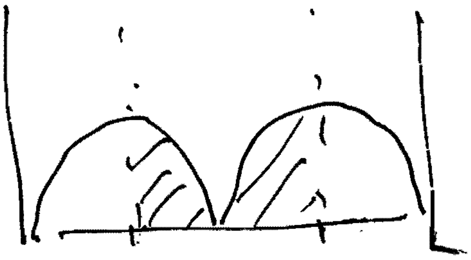


Write down and integral that you would need to solve to find the probability that the particle is located between x=-L/4 and x=+L/4 if it is described by the first excited state wavefunction.

$$\int_{-L/4}^{L/4} \psi^2 \, dx = \int_{-L/4}^{L/4} \frac{2}{L}\sin^2\left(\frac{2\pi x}{L}\right) dx$$

What is the value of this integral? You don't have to show your math. If you can't determine a number, estimate the value (more than half, roughly 0.25,...)

$$\int = 0.5$$



function is symm about $-\frac{L}{4}$: $\frac{L}{4}$

15. (25 points)
Imagine an electron in a box of length 1 pm (picometer = 10^{-12} m) on each side.

What is the zero point energy for an electron in such a box? (in Joules)

$$E_{111} = \frac{h^2}{8mL^2}\left(1^2+1^2+1^2\right) = \frac{3h^2}{8mL^2}$$

$$= \frac{3\left(6.626\cdot 10^{-34}\right)^2}{8\left(9.109\cdot 10^{-31}\right)\left(10^{-12}\right)^2} = 1.807\cdot 10^{-13}\ \mathrm{J}$$

From this what is the root mean square momentum of the electron in the box? (This is the square root of the average of the square of the momentum)

$$\text{zero point } E = K.E. = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$p^2 = 2m \times K.E. =$$

$$p = \sqrt{2\times\left(9.109\cdot 10^{-31}\right)\left(1.807\cdot 10^{-13}\right)}$$

$$p = 5.74\cdot 10^{-22}\ \mathrm{kg\ m\ s^{-1}}$$

Since the electron must be somewhere inside this box, the uncertainty in the position of the electron is at most 1 pm. Given this, what is the uncertainty in the momentum of the electron?

$$\Delta x\,\Delta p \geq \frac{\hbar}{2}$$

$$\Delta p = \frac{\hbar}{2\Delta x} = \frac{\left(6.626\cdot 10^{-34}\right)}{4\pi\left(10^{-12}\right)} = 5.27\cdot 10^{-23}\ \mathrm{kg\ m s^{-1}}$$

How does this compare to your root mean square momentum calculated from the zero point energy? They are very close to the same value!

Bonus. Not worth much. No partial credit. (3 points each)

Use your answer to the last problem to answer the following. Compare the kinetic energy of an electron that arises simply from the zeropoint energy of confinement to a cube with sides 1 pm to the potential energy of an electron and a nucleus separated by 1 pm. What does this say about the possibility of the electron "falling" down to very small distances close to the nucleus?

What is the most probable radius for an electron in a 2p wavefunction in Li^{2+}?

How would you compute the probability described in the last true false problem?