Name________________________________ Student #__________________________

Quiz 6
CHEM 3PA3; Fall 2018

This quiz has 8 problems worth 12 points each. The first four problems go together and the last three problems go together.

1. **Write the electronic Hamiltonian for a 3-electron atom with atomic number *Z* in the Born-Oppenheimer approximation. You may use atomic units.**

2. **If you neglect the electron-electron repulsion, what is the ground-state electronic energy of the 3-electron atom with atomic number *Z*? You may use atomic units.**

3. **The approximate energy in question #2 is ________ the exact energy for the 3-electron atom. (I.e., neglecting the electron-electron repulsion changes the energy in what way?)**
(a) less than (b) greater than (c) equal to (d) insufficient information to know.

4. **Suppose you neglect the electron-electron repulsion (as in question #2) and then use that wavefunction to evaluate the energy of the Hamiltonian *including* the electron-electron repulsion. This energy is __________ the exact energy for the 3-electron atom. That is, the energy expression**

$$\int \Psi^*_{\substack{\text{neglect e-e}\\ \text{repulsion}}}\left(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3\right)\hat{H}_{\substack{\text{3-electron}\\ \text{atom}}}\Psi_{\substack{\text{neglect e-e}\\ \text{repulsion}}}\left(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3\right)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

gives an energy __________ the exact energy for the 3-electron atom.
(a) less than (b) greater than (c) equal to (d) insufficient information to know.

5,6. **Fill in the eigenvalues for the total angular momentum squared, $\hat{L}^2$, and the angular momentum around the *z*-axis for a spherical Harmonic.**

$$\hat{L}^2 Y_l^m\left(\theta,\phi\right) = \underline{\hspace{6cm}}\, Y_l^m\left(\theta,\phi\right)$$

$$\hat{L}_z Y_l^m\left(\theta,\phi\right) = \underline{\hspace{6cm}}\, Y_l^m\left(\theta,\phi\right)$$

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7. Sketch the shape of the spherical harmonics associated with a *p* orbital. That is, sketch the shape (or describe in words what the shape looks like) for $Y_1^{-1}(\theta,\phi)$, $Y_1^{0}(\theta,\phi)$, and $Y_1^{+1}(\theta,\phi)$.

8. What is the degeneracy of the *n=3* state of the one-electron atom with atomic number *Z*? That is, how many different electronic states have the energy $-\frac{1}{18}Z^2$?

BONUS: (5 points) What is the *general* formula for the degeneracy of the 1-electron atom for any value of the principle quantum number *n*?

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1. **Write the electronic Hamiltonian for a 3-electron atom with atomic number *Z* in the Born-Oppenheimer approximation. You may use atomic units.**

$$\hat{H}_{\text{el}} \equiv -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{2}\nabla_3^2 - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{Z}{r_3} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|}$$

2. **If you neglect the electron-electron repulsion, what is the ground-state energy of the 3-electron atom with atomic number *Z*? You may use atomic units.**

Using the fact that the energy eigenvalues are $-\tfrac{1}{2n^2}Z^2$, put two electrons in the $n=1$ state and one in the $n=2$ state.

$$-\frac{Z^2}{2(1)^2}\cdot\left(2\text{ electrons}\right) - \frac{Z^2}{2(2)^2}\cdot\left(1\text{ electron}\right) = -Z^2\left(1+\tfrac{1}{8}\right) = -\tfrac{9}{8}Z^2 = -1.125\cdot Z^2$$

3. **The approximate energy in question #2 is ________ the exact energy for the 3-electron atom. (I.e., neglecting the electron-electron repulsion changes the energy in what way?)**
   <u>(a) less than</u> (b) greater than (c) equal to (d) insufficient information to know.

The electron-electron repulsion is a positive contribution to the energy. If you leave out a positive contribution to the energy, the energy is too small.

4. **Suppose you neglect the electron-electron repulsion (as in question #2) and then use that wavefunction to evaluate the energy of the Hamiltonian *including* the electron-electron repulsion. This energy is __________ the exact energy for the 3-electron atom. That is, the energy expression**

$$\int \Psi^*_{\substack{\text{neglect e-e}\\ \text{repulsion}}}\left(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3\right)\hat{H}_{\substack{\text{3-electron}\\ \text{atom}}}\Psi_{\substack{\text{neglect e-e}\\ \text{repulsion}}}\left(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3\right)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

   gives an energy __________ the exact energy for the 3-electron atom.
   (a) less than **<u>(b) greater than</u>** (c) equal to (d) insufficient information to know.

When an approximate wavefunction is used, the energy of the approximate wavefunction is greater than the true ground-state energy. This is the variational principle.

5,6. Fill in the eigenvalues for the total angular momentum squared, $\hat{L}^2$, and the angular momentum around the *z*-axis for a spherical Harmonic.

$$\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)$$

$$\hat{L}_z Y_l^m(\theta,\phi) = \hbar m Y_l^m(\theta,\phi)$$

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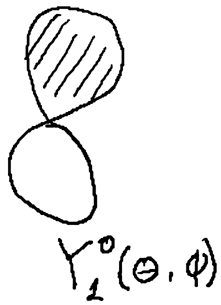
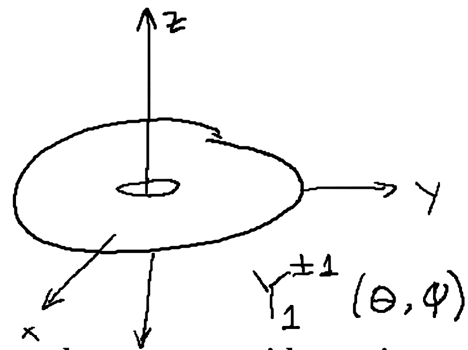
7. **Sketch the shape of the spherical harmonics associated with a *p* orbital. That is, sketch the shape (or describe in words what the shape looks like) for $Y_1^{-1}(\theta,\phi)$, $Y_1^{0}(\theta,\phi)$, and $Y_1^{+1}(\theta,\phi)$.**

The $m=0$ state is the traditional "figure-eight" *p* orbital you are used to. the $m=\pm1$ states are "donuts" (tori) and the electrons more counterclockwise or clockwise around this shape depending on whether $m=\pm1$





8. **What is the degeneracy of the *n=3* state of the one-electron atom with atomic number *Z*? That is, how many different electronic states have the energy $-\frac{1}{18}Z^2$?**

Listing the states and remembering that $l=0,1,2,\ldots n-1$

$n=3 \quad l=0 \quad m=0$

$n=3 \quad l=1 \quad m=-1,0,+1$

$n=3 \quad l=2 \quad m=-2,-1,0,+1,+2$

There are therefore *nine* orbitals which can be occupied with either an alpha- or a beta-spin electron, so there are 18 states with the same energy. I will give full credit for people who say nine states, but the correct answer is 18.

BONUS: (5 points) What is the *general* formula for the degeneracy of the 1-electron atom for any value of the principle quantum number *n*?

You could prove this mathematically but just notice the pattern: there is one orbital with *n*=1 (which can have either spin); there are four orbitals with *n*=2 (which can have either spin), etc…
So there are $2n^2$ degenerate states: n^2 spatial orbitals and 2 choices for the spin of the electron.