Quiz 3

Chemistry 3BB3; Winter 2005

1. Write the Schrödinger Equation for the Hydrogen atom in SI units. You may use the Born-Oppenheimer approximation.

2. Which of the following molecules will the Born-Oppenheimer approximation be *least* accurate for.

(a) Cl_2
(b) UF_6
(c) $NaCl$
(d) UO_2

3. Consider the ground state of the Boron atom again. Suppose we do an unrestricted Hartree-Fock (UHF) calculation and a restricted Hartree-Fock (RHF) calculation. We make some observations, which are listed below. Assign each observation to the appropriate method (RHF, UHF).

_____ The energy from this calculation is larger.

_____ The 1s orbital for an α-spin electron and a β-spin electron are the same.

4-5. For the 2-electron atom with atomic number *Z*, sketch the dependence of the effective nuclear charge on the distance from the nucleus. Label the value of Z_{eff} at the nucleus and infinitely far from the nucleus.

6-8. Denote which of the properties are associated with fermions (F) or bosons (B).

_____ The particle has spin $\frac{3}{2}$.

_____ The particle has spin 0.

_____ The wave function is symmetric with respect to exchange of identical particles.

_____ Identical particles cannot be in the same place at the same time

_____ The ground state can be modeled with ten particles occupying the lowest orbital.

_____ The wave function can be modeled with a Slater determinate.

9-10. Which of the following statements about a Slater determinant of N orthogonal and normalized orbitals is true. (There may be more than one answer.) Here, N is the number of electrons (which is equal to the number of orbitals).

(a) The normalization constant is $\frac{1}{N}$.
(b) The normalization constant is $\frac{1}{N!}$.
(c) Interchanging two rows in the Slater determinant does not change the value of the Slater determinant.
(d) Interchanging two rows in the Slater determinant always gives a determinant that is equal to -1.
(e) If two rows in the Slater determinant are the same, then the value of the determinant is zero.
(f) Interchanging two columns in the Slater determinant does not change the value of the Slater determinant.
(g) Interchanging two columns in the Slater determinant causes the determinant to be multiplied by a factor of -1.
(h) Interchanging two columns in the Slater determinant causes the determinant to equal -1.
(i) If two columns in the Slater determinant are the same, then the value of the determinant is zero.
(j) If two rows in the Slater determinant are the same *and* two columns in the Slater determinant are the same, we can delete the "extra" row and the "extra" column without changing the value of the determinant.
(k) We take a Slater determinant and rewrite it, with all the "rows" becoming "columns" in the new determinant. (This is the definition of the transpose of the matrix in the determinant.) The value of the determinant does not change.
(l) We take a Slater determinant and rewrite it, with all the "rows" becoming "columns" in the new determinant. (This is the definition of the transpose of the matrix in the determinant.) The value of the determinant changes by a factor of -1.

Quiz 3

Chemistry 3BB3; Winter 2005

1. Write the Schrödinger Equation for the Hydrogen atom in SI units. You may use the Born-Oppenheimer approximation.

$$\left(\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r})$$

2. Which of the following molecules will the Born-Oppenheimer approximation be *least* accurate for.

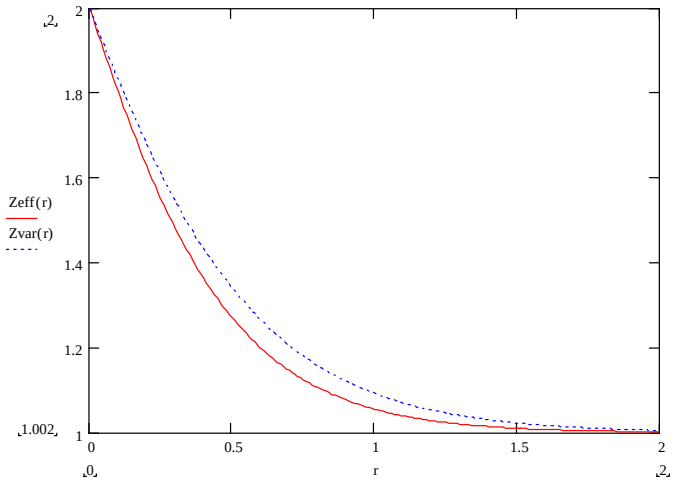
(a) Cl_2
(b) UF_6
(c) $NaCl$
(d) UO_2

3. Consider the ground state of the Boron atom. Suppose we do an unrestricted Hartree-Fock (UHF) calculation and a restricted Hartree-Fock (RHF) calculation. We make some observations, which are listed below. Assign each observation to the appropriate method (RHF, UHF).

___RHF____ The energy from this calculation is larger.

___RHF____ The 1s orbital for an α-spin electron and a β-spin electron are the same.

4-5. For the 2-electron atom with atomic number *Z*, sketch the dependence of the effective nuclear charge on the distance from the nucleus. Label the value of Z_{eff} at the nucleus and infinitely far from the nucleus.



The above figure is straight from the notes, where the effective nuclear charge is plotted for the Helium atom. The value at r=0 is, in the general case, is *Z*. The value at $r \to \infty$ is $Z-1$.

6-8. Denote which of the properties are associated with fermions (F) or bosons (B).

__F___ The particle has spin $\frac{3}{2}$.

__B___ The particle has spin 0.

__B___ The wave function is symmetric with respect to exchange of identical particles.

__F___ Identical particles cannot be in the same place at the same time

__B___ The ground state can be modeled with ten particles occupying the lowest orbital.

__F___ The wave function can be modeled with a Slater determinant.

9-10. Which of the following statements about a Slater determinant of N orthogonal and normalized orbitals is true. (There may be more than one answer.) Here, N is the number of electrons (which is equal to the number of orbitals).

(a) The normalization constant is $\frac{1}{N}$.

(b) The normalization constant is $\frac{1}{N!}$.

(c) Interchanging two rows in the Slater determinant does not change the value of the Slater determinant.

(d) Interchanging two rows in the Slater determinant always gives a determinant that is equal to -1.

(e) If two rows in the Slater determinant are the same, then the value of the determinant is zero.

(f) Interchanging two columns in the Slater determinant does not change the value of the Slater determinant.

(g) Interchanging two columns in the Slater determinant causes the determinant to be multiplied by a factor of -1.

(h) Interchanging two columns in the Slater determinant causes the determinant to equal -1.

(i) If two columns in the Slater determinant are the same, then the value of the determinant is zero.

(j) If two rows in the Slater determinant are the same *and* two columns in the Slater determinant are the same, we can delete the "extra" row and the "extra" column without changing the value of the determinant.

(k) We take a Slater determinant and rewrite it, with all the "rows" becoming "columns" in the new determinant. (This is the definition of the transpose of the matrix in the determinant.) The value of the determinant does not change.

(l) We take a Slater determinant and rewrite it, with all the "rows" becoming "columns" in the new determinant. (This is the definition of the transpose of the matrix in the determinant.) The value of the determinant changes by a factor of -1.