

Chem 332: Problem Set #9

Due in class, Monday, April 15

(1) Consider the 4 wavefunctions discussed in class for the $1s2s$ excited state of the He atom:

$$\psi_{\text{singlet}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) + 2s(1)1s(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\psi_{\text{triplet-1}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \alpha(1)\alpha(2)$$

$$\psi_{\text{triplet-2}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \beta(1)\beta(2)$$

$$\psi_{\text{triplet-3}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

For each of these 4, write the wavefunction in terms of 1 (or more) normalized Slater determinants.

(2) Find all the possible RS term symbols that arise from each of the following electron configurations. Assuming Hund's Rules apply in these cases, predict which would be the ground state in each case.

(a) $1s^2 2s^2 2p$

(b) $[\text{Ne}] 3s^2 3p 3d$

(c) $[\text{Ar}] 4s^2 3d^9 4p$

(d) $[\text{Kr}] 5p 4f$

(3) Determine the levels that belong to each of the following terms and give the number of states of each:

(a) ${}^4\text{F}$ (b) ${}^1\text{S}$ (c) ${}^3\text{P}$ (d) ${}^2\text{D}$

(4) Predict the ground state term symbol for each of the following atoms:

(a) Na, $1s^2 2s^2 2p^6 3s$ (b) As, $[\text{Ar}] 4s^2 4p^3$

(c) Zn, $[\text{Ar}] 4s^2 3d^{10}$ (d) Zr, $[\text{Kr}] 5s^2 4d^2$

- (5) Consider the following trial function for the ground state of the He atom:

$$\phi = e^{-\alpha(r_1^2 + r_2^2)}$$

In this function, α is a variational parameter.

- (a) Write down the complete expression for determining the trial energy in a variational calculation. Be sure to indicate the volume element, integration limits, and the Hamiltonian.
- (b) Suppose that the resulting expression for the trial energy is

$$E_{trial} = \frac{11}{4}\alpha - \frac{11\sqrt{\alpha}}{2}$$

What is the optimum value of α and the resulting optimum energy?