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Student Number _____
Recitation Instructor _____

Chemistry 483

Examination 3

Fall 2009

1. (40 points) Define and/or characterize

a. π bonding orbital for a homonuclear diatomic

A π bonding orbital for a homonuclear diatomic has the form $p_{xA} + p_{xB}$ where x is $\perp$ to the internuclear line. The orbital has μ symmetry & has the shape

b. Inversion Operator

$\hat{I} f(\vec{r}) = f(-\vec{r})$

c. Atomic orbital energies

Eigenvalues of the Fock operator

$\hat{f} \psi_i = \epsilon_i \psi_i$

↳ atomic orbital energies

d Spin-Orbit interaction

The interaction between the magnetic moment of the electron due to its spin and the magnetic field it experiences due to the relative motion of the nucleus & electron.

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e Term Symbol

A symbol representing the orbital, spin and total angular momentum of an atom.

$^{2S+1}L_J$; $2S+1$ = multiplicity

L = angular momentum due to orbital motion

J = total angular momentum

f Slater Determinant

Form of a wavefunction that ensures that the wavefunction is antisymmetric WRT electron exchange.

$\mathcal{A}\,\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)$; φ_i is a spin orbital

g Bond Order

$\frac{1}{2}$ (number of bonding electrons − number of antibonding)

h Electron configuration for the oxygen atom

$1s^2 2s^2 2p^4$

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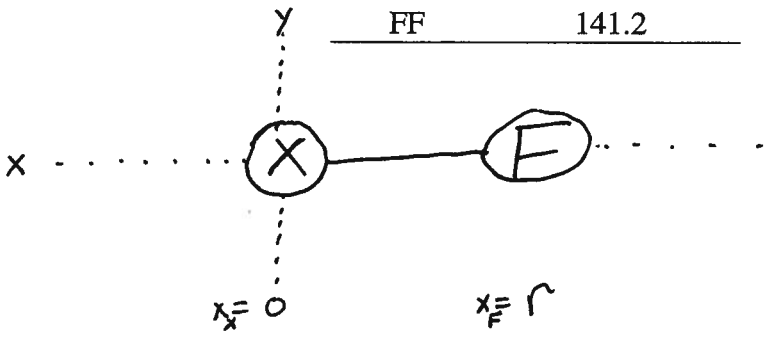
2. (15 points) An unknown diatomic molecule is being investigated. One of the atoms is fluorine, but the identity of the other atom is unknown. The dipole moment of this molecule has been experimentally measured as 1.230x10-30 C.m. Molecular orbital calculations predict a net charge of +0.05829e on the fluorine atom. From this information and the following table of bond distances determine the identity of the other atom.

Diatomic	Bond length (pm)
BF	126.3
CF	127.2
NF	131.7
OF	132.6
FF	141.2



$$\mu = e\sum_i z_i x_i = Z_x e X_x^{=0} + Z_F e X_F$$

$$1.230\times10^{-30}\,C\cdot m = 0.05829\,e\,(r)$$

$$r = \frac{1.230\times10^{-30}\,C\cdot m}{0.05829\,(1.602177\times10^{-19}\,C)}\left(\frac{1\times10^{12}\,pm}{1\,m}\right)$$

$$= 131.7\,pm$$

The unknown diatomic is NF

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3. (15 points)

a. Given that the electron configuration of a chromium atom is $[Ar](4s)^1(3d)^5$, determine the ground state term symbol for *Cr*. Be sure to include the J value.

b. What is the degeneracy of the ground state?

$\underset{4s}{\uparrow}$ $\underset{}{\uparrow}$ $\underset{}{\uparrow}$ $\underset{3d}{\uparrow}$ $\underset{}{\uparrow}$ $\underset{}{\uparrow}$ } Configuration w/ maximum M_S is ground state.

$M_S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 3$

$2S + 1 = 7$ (multiplicity)

$M_L = 0 + 2 + 1 + 0 - 1 - 2 = 0$

$L \Rightarrow S$ $\quad J = |L+S|, \ldots, |L-S| = 3$

$^{2S+1}L_J \Rightarrow {}^7S_3$ (term)

Degeneracy $= (2S+1)(2L+1) = 7 \cdot 1 = 7$

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4. (15 points) Using molecular orbital theory, predict the relative bond strengths and bond lengths of the two homonuclear diatomic molecules B_2 and C_2.

Which of these two molecules do you expect to have the largest bond force constant, k?

Electron configurations:

B_2 (10 e⁻): $(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$

C_2 (12 e⁻): $(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2$

Bond orders:

B_2 b.o. $= \frac{1}{2}(6-4) = \frac{2}{2} = 1$

C_2 b.o. $= \frac{1}{2}(8-4) = \frac{4}{2} = 2$

Relative bond strengths: C_2 has a relatively stronger bond than B_2 (since larger b.o. $\Rightarrow$ stronger bond)

Relative bond lengths: B_2 has a shorter bond length than C_2 (since smaller b.o. $\Rightarrow$ shorter bond length)

Since the magnitude of the bond force constant, k, is directly proportional to the bond order, C_2 is expected to have the larger bond force constant.

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5. (15 points) Sketch the symmetry orbitals generated by forming linear combinations ot two 1s atomic orbitals. Label each symmetry orbital with the appropriate symmetry labels and indicate which of these are/is bonding and which are/is antibonding.

2 possible linear combinations of (two) 1s AOs:

Symmetry orbitals formed:

$1s_A + 1s_B$

$\sigma_g 1s$ bonding

$1s_A - 1s_B$

$\sigma_u 1s$ antibonding