# Chemistry 651

## Problem set 3

Due: 23 May 2006

From your text,

1. 7.23
2. 7.27
3. 7.31
4. Use either your text, or the literature to define the bulleted items on page 356 (third edition).
5. Write the Hartree Fock equations for the effective one electron HF operator for the $\sigma_g 1s$ and $\pi_g 2p$ orbitals of $N_2$ using a minimal basis set (1s,2s,2p) for each atom.

# Problem set 3 : Ch 651

1. 7.23

a) $2P_{ya} + 2P_{yb} \Rightarrow \Pi_u$ bonding

b) $2P_{za} + 2P_{zb} \Rightarrow \sigma_u$ anti bonding

c) $3dz^2_a + 3dz^2_b \Rightarrow \delta_g$ angular momentum funct $Y_{20}$ bonding

d) $3dxy_a + 3dxy_b \Rightarrow \delta_g$ bonding

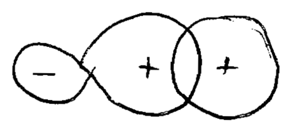
e) $3dxz_a - 3dxz_b \Rightarrow \Pi_u$ bonding

angular momentum functn $Y_{2,1}$

2. 7.27

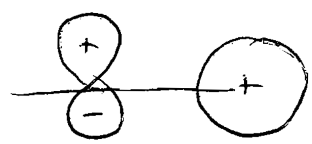
a) $\int dV \; 2P_{za} \; 1S_b$

$\neq 0$




b) $\int dV \; 2P_{ya} \; 1S_b$

$= 0$




c) $\int dV \; 2P_{za} \, 2P_{yb} = 0$

d) $\int dV \, 2P_{ya} \, 3d_{yzb} \neq 0$

e) $\int dV \; 2P_{za} \; 3d_{yz} = 0$, z-integral non-zero

y vanishes

f) $= 0$, see (b)

g) $\neq 0$ same as (a)

3. 7.31

$$1\sigma_g^2\, 1\sigma_u^2 \,\Big|\, 2\sigma_g^2\, 2\sigma_u^2 \,\Big|\, 3\sigma_g^2\, 1\pi_u^4 \,\Big|\, 1\pi_g^2 \quad \Rightarrow O_2$$

a) 4 net bonding $e^-$

b) $S = 1$

c) the bond energy increases if we lose a $\pi_g$ $e^-$ and it decreases if we lose a $3\sigma_g$ $e^-$

d) $S = 1/2$

e) $\pi_u \Rightarrow 2P_x$

5. HF equations for $N_2$

$$\phi_1 = 1s_a + 1s_b = \sigma_{g,1s}$$
$$\phi_2 = 1s_a - 1s_b$$
$$\phi_3 = 2s_a + 2s_b$$
$$\phi_4 = 2s_a - 2s_b$$
$$\phi_5 = 2p_{za} - 2p_{zb}$$
$$\phi_6 = \pi_{2p_{x},a} + \pi_{2p_{x},b} = \pi_{u\,2p}$$
$$\phi_7 = \pi_{2p_{y},a} + \pi_{2p_{y},b}$$

$$F(1) = H^{core}(1) + \sum_{j=1}^{n/2} \left(2J_j(1) - K_j(1)\right)$$

$$F(1)\,\phi(1) = \epsilon_1\,\phi(1), \qquad \hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - Z\left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}}\right)$$

$$F(1)\,\phi_1(1) = \hat{H}^{core}(1)\,\phi_1(1) + \phi_1(1)\int d2\,\phi_1^2(2)/r_{12}$$
$$+\sum_{j=2}^{n/2} \left\{ 2\phi_1(1)\int dr_2\,\frac{\phi_j(2)}{r_{12}^2} - \phi_j(1)\int dr_2\,\frac{\left(\phi_j(1)\,\phi_1(1)\right)}{r_{12}} \right\}$$
$$= \epsilon_1\,\phi_1(1)$$

Here $n = 14$, $\frac{n}{2} = 7$ occupied orbitals

note that is not integrated. This equation has derivatives and integrals

The same eq for $\phi_7$. Replace al $\phi_1$'s by $\phi_7$ ad change the sum to $\sum_{j=1}^{6}$