Question 1

14 e⁻

a) $$H = \underbrace{-\frac{1}{2M_C}\nabla_C^2 - \frac{1}{2M_O}\nabla_O^2}_{\text{nuclear kinetic energy}} \underbrace{-\sum_{i=1}^{14}\frac{1}{2}\nabla_i^2}_{\text{electronic kinetic energy}} \underbrace{-\sum_{i=1}^{14}\frac{6}{r_{iC}}}_{\text{attraction e-O}} \underbrace{-\sum_{i=1}^{14}\frac{8}{r_{iO}}}_{\text{attraction e-C}}$$

$$+ \underbrace{\sum_{i<j}^{14}\frac{1}{r_{ij}}}_{\text{repulsion between } e^-} + \underbrace{\frac{Z_O \cdot Z_C}{R_{OC}}}_{\text{repulsion between nuclei}} \quad (6\cdot 8) = T_e + T_N + V_{eN} + V_{ee} + V_{NN}$$

b) We separate this into the electronic Hamiltonian, for a fixed nuclear position, and the nuclear kinetic energy operator;

$$H = H^{(0)} + T_N$$

$$H^{(0)} = T_{el} + V \qquad V = V_{eN} + V_{ee} + V_{NN}$$

c) The molecular wavefunction is now a product of an electronic WF that depends parametrically on the nuclear coordinates, $\phi(r_i; R_N)$ and a nuclear function, that depends only on nuclear coordinates, $X(R_N)$

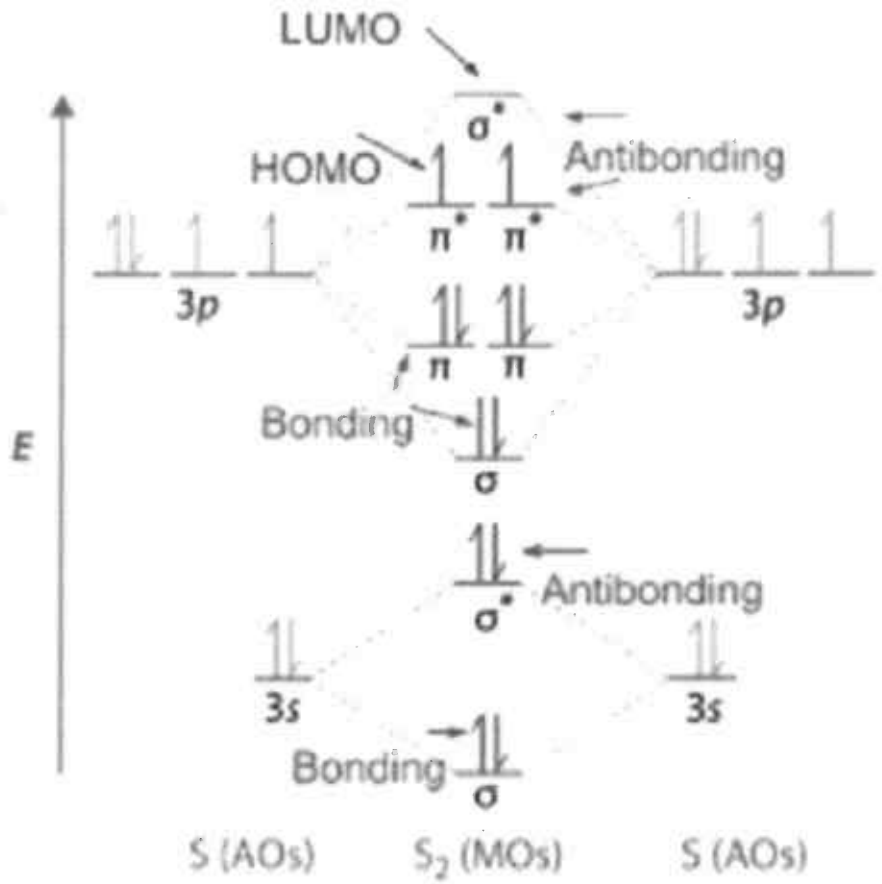
$$\psi = \phi(r_i; R_N) \cdot X(R_N)$$

d) C1: 3 regions of electron density - sp^2

C2: sp^3 (4 regions of electron density)

Question 2

a)



b)

Core-core orbitals have very little overlap (even though they are close/the same in energy) as they are 'smaller', i.e. more localized around the nuclei. 2) core-valence orbitals have a little more overlap but are typically of very different energy, therefore their contribution is insignificant.

c) S_2: $^3\Sigma_g^-$; S_2^+: $^2\Pi_g$

d) From counting electrons:

S_2: ½(8-4)=2

S_2^+: ½(8-3)=2.5

Question 3

$$H_{cc} = \varepsilon_c = -IP_c = -11.3 \text{ eV}$$

$$H_{oo} = \varepsilon_o = -IP_o = -13.6 \text{ eV}$$

$$\langle p_x^o | H | p_x^c \rangle = -1.5 \text{ eV}, \quad S = 0$$

a)

$$\begin{vmatrix} -11.3 - W & -1.5 \\ -1.5 & -13.6 - W \end{vmatrix} = 0$$

$$(-11.3 - W)(-13.6 - W) - 1.5^2 = 0$$

$$W^2 + 24.9\,W + 151.43 = 0$$

$$\frac{-24.9 \pm \sqrt{24.9^2 - 4 \cdot 151.43}}{2} = \frac{-24.9 \pm 3.78}{2} \Rightarrow$$

$$W_1 = -14.34$$

$$W_2 = -10.56$$

b). Bonding orbital - W_1

$$(-11.3 + 14.34)\,C_c - 1.5\,C_o = 0$$

$$3.04\,C_c = 1.5\,C_o$$

$$C_o = 2.03 \cdot C_c$$

If we want to normalize it, we will have

$$C_c^2 + 2.03^2 C_c^2 = 1 \Rightarrow C_c = 0.44$$

$$C_o = 0.89$$

$$\phi_{II} = 0.44 \cdot 2p_x^c + 0.89 \cdot 2p_x^o$$

As expected, because $\varepsilon_{2p_x^o}$ is lower in energy.

c) Since B is to the left of C in periodic table, we will expect a larger energy difference between the bonding orbital $2p_x$ of B and of O. Hence, the bonding orbital will have even more oxygen character.

4). a) for allowed transition: $\mu_{if} \neq 0$

$$\mu_{if} = \int \Psi_i^* \mu \Psi_f \, d\tau$$

$\mu = \mu_{el} + \mu_{nuc}$ dipole moment.

Within BO: $\Psi_i = \phi_i^{el} \cdot \chi_i^{nuc}$

$$\mu_{if} = \int \phi_i^{el*} \chi_i^{nuc*} \mu_{el} \phi_f^{el} \chi_f^{nuc} \, d\tau + \int \phi_i^{el*} \chi_i^{nuc*} \mu_{nuc} \phi_i^{el} \chi_i^{nuc} \, d\tau =$$

$$= \int \phi_i^{el*} \mu_{el} \phi_f^{el} \, d\tau_{el} \int \chi_i^{nuc*} \chi_f^{nuc} \, d\tau_{nuc} +$$

$0 = \phi_i = \phi_f$

$$+ \int \phi_i^{el*} \phi_f^{el} \, d\tau_{el} \cdot \int \chi_i^{nuc*} \mu_{nuc} \chi_i^{nuc} \, d\tau_{nuc} =$$

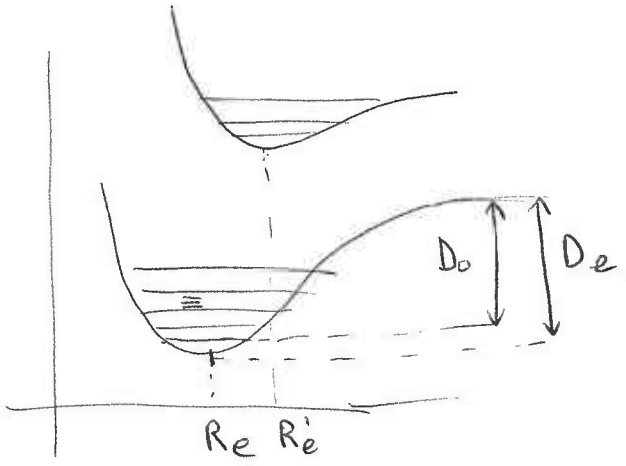
$$= \int \phi_i^{el*} \phi_f^{el} \, d\tau_{el} \cdot \int \chi_i^{nuc*} \mu_{nuc} \chi_i^{nuc} \, d\tau_{nuc}$$

should not be 0.

b). From the exam: $S_2 \Rightarrow \mu = 0$

$CO \Rightarrow \mu \neq 0$

c)



d) $D_e = 6,124\ eV$

$\omega_e = 4138\ cm^{-1}$

$\omega x_e = 89.9\ cm^{-1}$

$$\epsilon_0 = \frac{1}{2}\omega_e - \frac{1}{4}\omega x_e = 2069 - 22,5 = 2046\ cm^{-1} = 0,254\ eV$$

$$D_0 = D_e - \epsilon_0 = 6,124\ eV - 0,254\ eV = 5,87\ eV$$

e) Because $\omega_e \sim \frac{1}{\sqrt{\mu}}$, we expect ω_e for DF to be smaller (μ is mostly determined by the light atom). Hence, $\omega_e^{DF} < \omega_e^{HF}$. $\Rightarrow D_0^{DF} > D_0^{HF}$.