(1) Explain why $1s2s$ and $2p^2$ configurations can contribute to a CI calculation of the ground state of He_2 atom, but not $1s2p$.

Ground state: ^1S

$1s2s$: ^1S, ^3S

$2p^2$: ^3P, ^1D, ^1S

$1s2p$: ^3P, ^1P

(2) Evaluate the expectation value of $\hat{S}^2$ for $|1s\,2s|$.

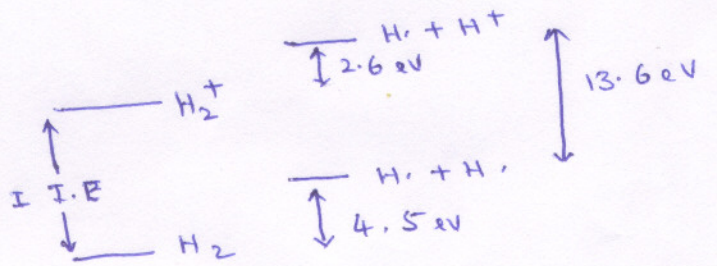
$$\hat{S}^2 = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\,\hat{S}_1 \cdot \hat{S}_2 \quad \text{(vector coupling)}$$

$$= \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z})$$

$$\langle \alpha(1)\,\alpha(2) |\, \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_{1x}\hat{S}_{2x} + 2\hat{S}_{1y}\hat{S}_{2y} + 2\hat{S}_{1z}\hat{S}_{2z} \,| \alpha(1)\,\alpha(2)\rangle$$

$$= \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) + \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) + 2\,\tfrac{1}{2}\,\tfrac{1}{2} = 2$$

(3) The D_0 value for H_2 is 4.5 eV. The D_0 value for H_2^+ is 2.6 eV. Estimate the I ionization energy of H_2.



$$I\ I.E = 13.6 - 2.6 + 4.5 = 15.5\ eV$$

(4) Write the energies of the following states in terms of 1-e and 2-e integrals.

(i) $|\phi_1 \bar{\phi}_1|$ (ii) $|\phi_1 \bar{\phi}_2|$ (iii) $|\phi_1 \phi_2|$

(iv) $|\phi_1 \bar{\phi}_1 \phi_2|$ (v) $|\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2|$

(i) $2H_{11} + J_{11}$ (ii) $H_{11} + H_{22} + J_{12}$

(iii) $H_{11} + H_{22} + J_{12} - K_{12}$

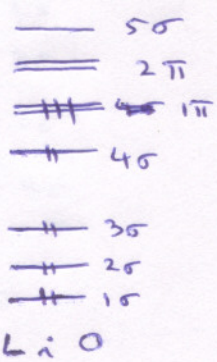
(iv) $2H_{11} + H_{22} + J_{11} + 2J_{12} - K_{12}$

(v) $2H_{11} + 2H_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$

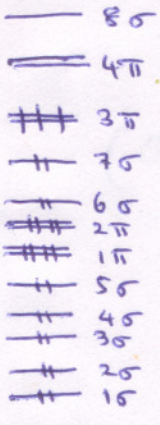
(5) State True or False: The ground state energy of Li is equal to the sum of the I I.E and two times the II I.E.

False. Neglects electron correlation.

(6) Both LiO and ClO have the spectroscopically determined ground state $^2\Pi$. Construct MO level diagrams.



LiO



ClO

(Construct approximate correlation diagrams)