

MEST - Assignment 4

Due date: 30/04/2024

(For each solution, show your work through a set of important steps.)

1. The Hartree-Fock energy expression is:

$$E^{HF} = \sum_{i=1}^N \int \chi_i(x_i) \hat{h} \chi_i(x_i) dx_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int dx_i dx_j \chi_i(x_i) \chi_j(x_j) \frac{1}{\hat{r}_{12}} \chi_i(x_i) \chi_j(x_j) - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int dx_i dx_j \chi_i(x_i) \chi_j(x_j) \frac{1}{\hat{r}_{12}} \chi_i(x_j) \chi_j(x_i)$$

Where, $\chi(x)$ are the space-spin molecular orbitals with space-spin coordinate x , \hat{h} is one electron Hamiltonian and \hat{r} is the interelectron distance and N denotes the occupied molecular orbitals respectively. Now, for restricted Hartree-Fock case deduce the HF energy expression in terms of spatial molecular orbitals only. (3 pts)

2. For the H_2 molecule at equilibrium separation, we have following bonding and anti-bonding MOs obtained using the AO basis functions $\chi_1 = \phi_{1sa}$, and $\chi_2 = \phi_{1sb}$.

$$\Psi_g = c_{11}\chi_1 + c_{12}\chi_2$$

$$\Psi_u = c_{21}\chi_1 + c_{22}\chi_2$$

where, $c_{11} = c_{12} = 0.554884228$, $c_{21} = -c_{22} = 1.21245192$. (2+2+3+3 pts)

- (a) Calculate ground and excited state orbital energies at the HF level.
- (b) Calculate total HF energy of the H_2 molecule
- (c) In this MO basis, construct the CISD (configuration interaction singles doubles) matrix with and without using the Slater-Condon rules, and check that the results are the same. Evaluate each matrix element.
- (d) Calculate CISD ground-state energy. Calculate the ratio of CISD correlation energy and HF total energy?

Use the following one and two electron integrals for calculations.

$$\langle \chi_1 | \hat{h} | \chi_1 \rangle = \langle \chi_2 | \hat{h} | \chi_2 \rangle = -1.12095946, \langle \chi_1 | \hat{h} | \chi_2 \rangle = \langle \chi_2 | \hat{h} | \chi_1 \rangle = -0.95937577$$

$$\langle \chi_1 \chi_1 | \chi_1 \chi_1 \rangle = \langle \chi_2 \chi_2 | \chi_2 \chi_2 \rangle = 0.77460594,$$

$$\langle \chi_1 \chi_2 | \chi_2 \chi_2 \rangle = \langle \chi_2 \chi_1 | \chi_2 \chi_2 \rangle = \langle \chi_2 \chi_2 | \chi_1 \chi_2 \rangle = \langle \chi_2 \chi_2 | \chi_2 \chi_1 \rangle =$$

$$\langle \chi_1 \chi_1 | \chi_1 \chi_2 \rangle = \langle \chi_1 \chi_1 | \chi_2 \chi_1 \rangle = \langle \chi_1 \chi_2 | \chi_1 \chi_1 \rangle = \langle \chi_2 \chi_1 | \chi_1 \chi_1 \rangle = 0.44459112,$$

$$\langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle = \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle = \langle \chi_2 \chi_1 | \chi_1 \chi_2 \rangle = \langle \chi_2 \chi_1 | \chi_2 \chi_1 \rangle = 0.29759055,$$

$$\langle \chi_1 \chi_1 | \chi_2 \chi_2 \rangle = \langle \chi_2 \chi_2 | \chi_1 \chi_1 \rangle = 0.56999488$$

$$\langle \chi_1 | \chi_1 \rangle = \langle \chi_2 | \chi_2 \rangle = 1.00000000$$

$$\langle \chi_1 | \chi_2 \rangle = \langle \chi_2 | \chi_1 \rangle = 0.65987312$$

3. For the ground-state of H_2^+ , the simple MO wavefunction is $\sigma_g 1s(r_1) = \phi_{1sa}(r_1) + \phi_{1sb}(r_1)$, where a and b denote the two H atoms, and $\phi_{1sa} = \frac{e^{-ra}}{\sqrt{\pi}}$ is the hydrogen AO. Using confocal elliptical coordinates (see Levine for definition), show that the overlap integral is given by $S_{ab} = e^{-R}(1 + R + \frac{R^2}{3})$. Here, R is the internuclear separation. The volume element in confocal elliptic coordinates is $dv = \frac{1}{8}R^3(\xi^2 - \eta^2)d\xi d\eta d\phi$. The following integral formula can be handy (4 pts):

$$\int_t^\infty z^n e^{-az} dz = \frac{n!}{a^{n+1}} e^{-at} \left(1 + at + \frac{a^2 t^2}{2!} + \dots + \frac{a^n t^n}{n!} \right), n = 0, 1, 2, \dots > 0$$

4. The exact nuclear-electron wavefunction can be expanded in a basis of the BO wavefunctions

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_{a\alpha} c_{a\alpha} \Phi_a(\mathbf{r}; \mathbf{R}) \chi_{a\alpha}(\mathbf{R})$$

where $\Phi_a(\mathbf{r}; \mathbf{R})$ is the a^{th} eigenfunction of \hat{H}^{el} and $\chi_{a\alpha}(\mathbf{R})$ is the α^{th} eigenfunction of nuclear Schrodinger equation for electronic surface a within BO approximation. Starting from the exact energy

$$\langle \Psi | \hat{H} | \Psi \rangle; \hat{H} = \hat{T}_N + \hat{H}_{el}$$

identify the Hamiltonian elements that should be neglected to obtain the energy expectation used in the Born-Oppenheimer approximation

$$\langle \chi_{a\alpha} | \hat{T}_N + U_a(\mathbf{R}) | \chi_{a\alpha} \rangle; U_a(\mathbf{R}) = \langle \Phi_a | \hat{H}_{el}(\mathbf{R}) | \Phi_a \rangle. \quad (4 \text{ pts})$$

5. For H_2 in a minimal basis-set, but with infinite nuclear separation and using only Φ_0 and Φ_{11}^{22} configurations, derive the CI wavefunctions corresponding to the ground and excited-states, i.e. solve for c_0 and c_1 for $\Psi = c_0 \Phi_0 + c_1 \Phi_{11}^{22}$. Comment on the ionic/covalent nature of the two CI wavefunctions by expanding the MOs of the two Slater determinants in AOs. (4 pts)
6. (a) The experimental force constants in ($N.m^{-1}$) for the diatomic molecules B_2 , C_2 , N_2 , O_2 , F_2 are 350, 930, 2260, 1140, 450 respectively. Can the trend be correctly predicted by MOT? Explain your answer.(5 pts)
- (b) Under Born-Oppenheimer Approximation the force constant of a diatomic molecule will be independent of isotopic substitution. Justify or criticise the statement.(1 pt)
7. The molecule BF is isoelectronic with CO. However, the MOs for BF are different from those of CO. (2+1+2+2+2 pts)
- (a) Construct a quantitative molecular-orbital energy-level diagram for CO in minimal basis-set using the following atomic orbital data:

Atom	Valence Orbital	Ionisation energy(in MJ/mol)
O	2s	3.116
O	2p	1.524
C	2s	1.872
C	2p	1.023

- (b) The energy ordering of the MOs for BF is $\psi(2s_B + 2p_{z,F}) < \psi(2p_{x,B} - 2p_{x,F}) < \psi(2s_B - 2p_{z,F}) < \psi(2p_{x,B} + 2p_{x,F}) < \psi(2p_{y,B})$. Explain what may be the reason for different ordering of BF than that of CO. [For further Reference: <https://doi.org/10.1021/ed100758t>]
- (c) What are the symmetry designations of the MOs for CO and BF?
- (d) What are the electron configuration of the ground state of CO and BF?
- (e) What are the bond orders for them? Are they paramagnetic or diamagnetic?