MEST - Assignment 4

Due date: 28/04/2022
(For each solution, show your work through a set of important steps.)

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1. For the H_2 molecule at equlibrium separation, we have following bonding and anit-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, $c_{11} = c_{12} = 0.554884228, \quad c_{21} = -c_{22} = 1.21245192$. (2+2+3+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) Calculate MP2 correction to HF energy. What is the ratio of MP2 correction and HF energy. In this case, will MP2 be a good approximation to correlation energy?

   (d) 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.

   (e) 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.

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

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

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

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

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

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

2. 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 $\phi_{1sa} = \frac{e^{-r_a}}{\sqrt{\pi}}$ 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):

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

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3. 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

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

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

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

4. For H_2 in a minimal basis-set, but with infinite nuclear separation and using only Φ_0 and $\Phi_{1\bar{1}}^{2\bar{2}}$ configurations, derive the CI wavefunctions corresponding to the ground and excited-states, i.e. solve for c_0 and c_1 for $\Psi = c_0\Phi_0 + c_1\Phi_{1\bar{1}}^{2\bar{2}}$. Comment on the ionic/covalent nature of the two CI wavefunctions by expanding the MOs of the two Slater determinants in AOs. (4 pts)