

## Question 1: Post-Hartree Fock methods I

This is a question from a previous exam.

We consider the  $\text{H}_2$  molecule, i.e., two protons (we call them A and B) and two electrons (we call them 1 and 2). In Hartree-Fock (HF) it is equally likely that (I) both electron 1 and 2 are simultaneously localized near nucleus A and (II) that electron 1 is near nucleus A while electron 2 is near nucleus B. This unphysical behaviour is due to the lack of electron correlation of the HF ground state wave function.

First we consider the HF ground state wave function

$$\Psi_{\text{HF,gs}} = \frac{1}{\sqrt{2}} |\phi_{\text{b}} \bar{\phi}_{\text{b}}|. \quad (1)$$

Here  $\phi_{\text{b}}$  is the ground state MO that we approximate as the normalized bonding combination of two functions of  $s$ -symmetry,  $s_{\text{A}}$  and  $s_{\text{B}}$ , centered at nucleus A and nucleus B respectively. So:

$$\phi_{\text{b}}(1) = s_{\text{A}}(1) + s_{\text{B}}(1) \quad \text{and} \quad \phi_{\text{b}}(2) = s_{\text{A}}(2) + s_{\text{B}}(2). \quad (2)$$

- 1a.** With the above approximation for  $\phi_{\text{b}}$  write down the complete HF ground state wave function as a sum of all possible products of the functions  $s_{\text{A}}$  and  $s_{\text{B}}$ , i.e. insert expression 2 into expression 1 and write down all contributions.

Answer:

$$\begin{aligned} \Psi_1 &= (s_{\text{A}}(1) + s_{\text{B}}(1))(s_{\text{A}}(2) + s_{\text{B}}(2)) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) = \\ &= (s_{\text{A}}(1)s_{\text{A}}(2) + s_{\text{A}}(1)s_{\text{B}}(2) + s_{\text{B}}(1)s_{\text{A}}(2) + s_{\text{B}}(1)s_{\text{B}}(2)) \frac{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}{\sqrt{2}} \end{aligned}$$

*One sees that all four combinations have equal weight and hence equal likelihood in the HF ground state WF.*

Next consider the HF LUMO. We approximate it with the anti-bonding combination<sup>1</sup>

$$\phi_{\text{a}}(1) = s_{\text{A}}(1) - s_{\text{B}}(1), \text{ etc.}$$

We neglect all other empty HF orbitals.

- 1b.** Build the CID wave function  $\Psi_{\text{CID}}$  consisting of two determinants and show that it allows to repair the correlation problem, i.e. that it can describe a different (higher) likelihood for the electrons split up over the protons than for both electrons residing on just a single proton.

<sup>1</sup>Note that this function in principle is only normalized if  $\langle s_{\text{A}} | s_{\text{B}} \rangle = 0$ . Here we ignore this aspect, as it is irrelevant to questions **1b** and **1c**.

Answer: *The second Slater determinant is:*

$$\Psi_2 = (s_A(1) - s_B(1))(s_A(2) - s_B(2)) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) =$$

$$(s_A(1)s_A(2) - s_A(1)s_B(2) - s_B(1)s_A(2) + s_B(1)s_B(2)) \frac{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}{\sqrt{2}}$$

*The CID WF is:*

$$\Psi_{\text{CID}} = c_1 \Psi_1 + c_2 \Psi_2$$

*Choosing, e.g.,  $c_1 = -c_2$  one sees that all terms with both electrons on a single proton can be made to vanish in the CID WF whereas the others survive. It thus has the freedom that allows to describe the correlation effect.*

- 1c.** To compute the potential energy curve for dissociation of  $\text{H}_2$ , the CID wave function with two determinants is still an approximation. An MCSCF function with the same two determinants would be better. Why?

*Answer: The real shape of the s-orbital now becomes very different from that of the HF reference as now one electron completely localizes at one nucleus (while remaining indistinguishable from the other). So the shape of the atomic orbital in the anti-bonding MO needs to be optimized independently.*

## Question 2: Post-Hartree Fock methods II

This is an easier question from a previous exam.

- 2a.** Briefly describe how to do a full CI calculation, i.e., how do you obtain the functions to build your determinants, how do you build the determinants from these functions, and how do the determinants build the wave function? Also explain how CISD differs from full CI.

*Answer: You start with HF, with a basis larger than the number of occupied MOs. So you also get empty MOs. Then you build a series of SDs, with one, two, three, four, etc. electrons excited into the empty orbitals. You make a determinant for every possible excitation. You put coefficients in front and then variationally optimize or just get these from the Schrödinger equation. In CISD you only consider all determinants with single and double excitations.*

- 2b.** In Møller-Plesset (MP) perturbation theory you do, obviously, a perturbation theory calculation. As a starting point you need an unperturbed system for which you know the exact Hamiltonian  $H_0$  and its corresponding ground state eigenfunction  $|\Phi_0\rangle$  (of course for MP3 and beyond you also need the excited states of  $H_0$ ). Explain how MP chose  $H_0$  and  $|\Phi_0\rangle$ .

Answer: MP chose  $H_0$  such that the HF wave function is  $|\Phi_0\rangle$ . So  $H_0$  is the Fock operator. [NOT REQUIRED: The Fock operator is the sum, over the occupied states, of the operator  $\hat{f}$ :

$$\hat{f}(1) = \hat{h}(1) + \sum_{l=1}^{N/2} \left\{ 2\hat{J}_l(1) - \hat{K}_l(1) \right\} \text{ where}$$

$$\hat{J}_l(1) = \int d\mathbf{r}_2 \frac{\phi_l^*(2)\phi_l(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \text{ and } \hat{K}_l(1) = \int d\mathbf{r}_2 \frac{\phi_l^*(2)\hat{P}_{12}\phi_l(2)}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

The HF (eigenvalue) equation is:

$$\hat{f}(1)\phi_k(1) = \epsilon_k\phi_k(1). \quad (3)$$

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**2c.** MCSCF methods deal with several SDs of which you independently optimize the orbitals that these SDs are made of. When is it advisable to use such methods?

Answer: In case correlation effects cannot be treated anymore as a “small” perturbation from a single HF determinant, i.e., if “static” correlations is of comparable or more significance as “dynamic” correlation. One could elaborate here on an example...