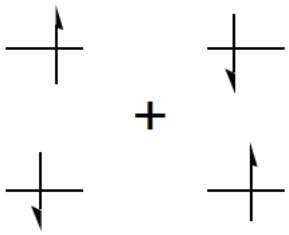
Problem Set 6

Lecture 19

Question 1. Calculate the expectation energy for the following triplet state of a He atom (Please show your detailed derivations):



$1s^1 2s^1$

Question 2. Directly write down the determinantal energy:

(a) $|\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3)\rangle$

(b) $|\psi_a(1)\alpha(1)\psi_b(2)\alpha(2)\psi_b(3)\beta(3)\rangle$

(c) $|\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3)\psi_b(4)\beta(4)\rangle$

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Question 3. (1) Please show that for a single restricted determinant $|\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\rangle$, the electron density (i.e., the probability density of finding **any** electron at $\boldsymbol{r}$) is

$$\rho(\boldsymbol{r}) = 2|\psi_a(\boldsymbol{r})|^2$$

Remark: The general result for an *N*-electron determinant is

$$\rho(\boldsymbol{r}) = \sum_{m=1}^{n} \theta_m |\psi_m(\boldsymbol{r})|^2$$

in which θ_m is the spatial-orbital occupation number for the *m*-th molecular orbital. For a doubly occupied orbital θ_m= 2; for an empty orbital θ_m= 0; for a singly occupied orbital θ_m= 1. For metals, θ_m could be a fractional number between 0 and 2 as determined by the Fermi-Dirac distribution.

(2) Show that under a set of atomic-orbital basis functions $\{\chi_\mu(\boldsymbol{r})\}$, the effective Hartree-Fock potential $\hat{v}^{\text{H-F}}(i)$ for electron *i* is a function of the density matrix elements $P_{\mu\nu}$, which satisfy

$$\rho(\boldsymbol{r}) = \sum_{\mu\nu} P_{\mu\nu}\chi_\mu^*(\boldsymbol{r})\chi_\nu(\boldsymbol{r})$$

Based on the above expression for the electron density, derive the expression for $P_{\mu\nu}$. (μ and ν are the indices for the atomic-orbital basis functions. Express your result in terms of θ_m and the linear combination coefficients $\{c_{\mu m}\}$ for the *m*-th molecular orbital.)

(3) Please write down the expression for $\hat{v}^{\text{H-F}}(i)$ in terms of $P_{\mu\nu}$.

Question 4. (1) Starting from the canonical restricted Hartree-Fock equation for spin orbitals $\{\varphi_a\}$ of an *N*-electron system,

$$\hat{F}_i\varphi_a(i) = \hat{h}_i\varphi_a(i) + \sum_{b\neq a}^{N}\left[\hat{J}_b(i) - \hat{K}_b(i)\right]\varphi_a(i) = \varepsilon_a\varphi_a(i)$$

in which ε_a is the Hartree-Fock orbital energy, please derive the *closed-shell* restricted Hartree-Fock equation for the occupied spatial orbitals $\{\psi_a\}$

$$\hat{F}_i\psi_a(i) = \hat{h}_i\psi_a(i) + \sum_{b\neq a}^{N/2}\left[2\hat{J}_b(i) - \hat{K}_b(i)\right]\psi_a(i) = \varepsilon_a\psi_a(i)$$

in which $\hat{h}_i$, $\hat{J}_b(i)$, and $\hat{K}_b(i)$ are all defined for the spatial orbitals.

Hint: For α-spin orbitals $\varphi_a(i) = \psi_a(i)\alpha(i)$ (i = 1, 2, ... N/2), let us integrate over the spin coordinate s_i first,

$$\left[\int_{s_i} ds_i\alpha^*(i)\hat{F}_i\alpha(i)\right]\psi_a(i)$$

then we shall consider the integrated Hartree-Fock equation.

(2) Based on **Question 3** (2), show that the Hartree-Fock purely electronic energy (i.e., excluding the nuclear electrostatic repulsions) for closed-shell systems

$$E_0 = \frac{1}{2}\sum_{\mu\nu} P_{\mu\nu}\left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}\right)$$

in which $H_{\mu\nu}^{\text{core}}$ is the core-Hamiltonian matrix element (under the atomic-orbital basis $\{\chi_\mu(\boldsymbol{r})\}$), $P_{\mu\nu}$ is the density matrix element, and $F_{\mu\nu}$ is the Fock matrix element.

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Question 5. Restricted Hartree-Fock theory for the H_2 molecule with the minimal basis functions (real-valued) $\chi_1 = |1s_A\rangle$, $\chi_2 = |1s_B\rangle$, in which A and B represent the nuclei:

(1) Derive the coefficients $[2(1+S_{12})]^{-1/2}$ and $[2(1-S_{12})]^{-1/2}$ in the basis-function expansion of the molecular orbitals ψ_1 and ψ_2 respectively, by requiring ψ_1 and ψ_2 to be normalized. You do *not* need to compute the overlap integral $S_{12} = \langle 1s_A|1s_B\rangle$.

(2) From the Roothaan equation, solve for the Hartree-Fock orbital energies for ψ_1 and ψ_2:

$$\varepsilon_1 = \frac{F_{11} + F_{12}}{1 + S_{12}}$$

$$\varepsilon_2 = \frac{F_{11} - F_{12}}{1 - S_{12}}$$

in which F_{11} and F_{12} are the Fock matrix elements.

(3) At the internuclear distance R_{AB} = 1.4 a.u.(i.e., 0.74 Å), the values of the integrals are (which are evaluated with the STO-3G functions): F_{11} = –0.3655 a.u., F_{12} = –0.5939 a.u., H_{11}^{core} = –1.1204 a.u. (the core-Hamiltonian matrix element), H_{12}^{core} = –0.9584 a.u., and S_{12} = 0.6593 a.u. Use the conclusion in **Question 4** (2), compute the *total* electronic energy of H_2 at R_{HH} = 1.4 a.u. (Keep five digits.)

Note: Do not forget to include the internuclear repulsion in the total electronic energy of H_2 molecule.

(4) Compute the first ionization energy (in the unit of eV), i.e., $H_2 \rightarrow H_2^+ + e^-$. Let us assume that the ionization process is ultrafast, and the H–H internuclear distance remains at 1.4 a.u. Compare your result with the experimental measurement 15.43 eV. How will you further improve your calculation?

Note: The electronic energy of a free electron is zero.

(5) Show that at the dissociation limit of the H_2 molecule (i.e., $R_{AB} \rightarrow +\infty$), the restricted Hartree-Fock theory energy is higher than the total energy of two isolated H atoms. (Please derive the energy expression for H_2 at the dissociation limit.)