TD2

H_2, a good training

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1 H_2 described by a minimal basis set

H_2 is described by a minimal basis set built on the atomic orbitals $1s$ of each hydrogen (noted a and b).

1. Give the molecular orbitals σ_g and σ_u of H_2 within this basis set.
2. Write all the 2-electron determinants that can be built with these orbitals. The following notation is assumed:
$$g \equiv \sigma_g(r)\alpha(\omega) \qquad \bar{g} \equiv \sigma_g(r)\beta(\omega)$$
$$u \equiv \sigma_u(r)\alpha(\omega) \qquad \bar{u} \equiv \sigma_u(r)\beta(\omega)$$
3. Show that these determinants are eigenvectors of the operator $\hat{\mathcal{S}}_z$, projection on the z-axis of the spin-operator $\hat{\mathcal{S}}$.
4. We aim at the eigenvectors of $\hat{S^2}$.
    - (a) Giving the definition of $\hat{S^2} = \hat{S^+}\hat{S^-} + \hat{S_z^2} - \hat{S}_z$, show that some determinants are eigenvectors of $\hat{S^2}$.
    - (b) Combine judiciously the other determinants to find eigenvectors of $\hat{S^2}$.
5. Calculate the energies of the eigenvectors of $\hat{S^2}$.
6. Give the spectroscopic states associated to these functions. Order its on a energetic diagram.
7. The previous functions can be developped in the product “space function × spin function”. Check that the space function of the triplet state is antisymmetrical whereas the one of the singlet is symmetrical.

2 Dissociation of H_2

1. Give the molecular orbitals of H_2 described in the minimal basis set (orbitals $1s$ of each hydrogen) using the previous notations.
2. Write the wave-function Ψ_0 of the ground state of H_2 described with the RHF method. Expand Ψ_0 on the basis of molecular orbitals, of atomic orbitals.
3. Discuss the behaviour of Ψ_0 along the dissociation of H_2. Conclude.

3 Unrestricted calculation

We have seen that the restricted Hartree-Fock solution doesn't describe properly thee dissociated state of H_2: $2H^\bullet$. This exercice aims at understanding the behaviour of the unrestricted solution.

1. Write the restricted solutions (namely g and u).
2. Unrestricted orbitals are defined as follow:

$$\begin{aligned} g^\alpha &= \cos\theta g + \sin\theta u \qquad & u^\alpha &= -\sin\theta g + \cos\theta u \\ g^\beta &= \cos\theta g - \sin\theta u \qquad & u^\beta &= \sin\theta g + \cos\theta u \end{aligned}$$

   (a) What is the difference between restricted and unrestricted methods ?
   (b) Show that $\theta = 0°$ match the restricted solution.
   (c) Let's consider the case of two non-interacting atoms *i.e.* $S = 0$. Show that $\theta = 45°$ describe a state of two hydrogen atoms.

3. We now consider the unrestricted determinant $|\Psi_0\rangle = |g^\alpha \bar{g^\beta}\rangle$

   (a) It can easily be shown that the energy is written:

$$\begin{aligned} E_0(\theta) = 2\cos^2\theta h_{gg} &+ 2\sin^2\theta h_{uu} + \cos^4\theta J_{gg} \\ &+ \sin^4\theta J_{uu} + 2\sin^2\theta\cos^2\theta(J_{gu} - K_{gu}) \end{aligned}$$

   and that the differential can be written:

$$\begin{aligned} E_0^{'}(\theta) &= \underbrace{4\cos\theta\sin\theta}_{A} \times \\ & \underbrace{\left(h_{uu} - h_{gg} + \sin^2\theta J_{uu} - cos^2\theta J_{gg} + (cos^2\theta - \sin^2\theta)(J_{gu} - 2K_{gu})\right)}_{B} \end{aligned}$$

   Deduce that the restricted solution is still solution of the problem.

   (b) We impose now $\theta \neq 0$. When both atoms are widely separated, show that $J_{gg} = J_{uu} = J_{gu} = K_{gu}$ et $h_{gg} = h_{uu}$ and, consequently that $\theta = 45°$.
   (c) What becomes then the wave-function written within the atomic orbitals basis set ? Is it the wave-function of an open-shell singlet ?
   (d) Show that the resulting wave-function can be written as an average of a triplet function and a singlet function:

$$\lim_{R\to\infty} |\Psi_0\rangle = \frac{1}{2}\left[|g\bar{g}\rangle - |u\bar{u}\rangle - \sqrt{2}|^3\Psi\rangle\right]$$

   This wave-function is 50% *contaminated* by the triplet function.

4 H_2: Configuration Interaction

We consider one more time the case of H_2 described with the minimal basis set $\{a, b\}$, combined into molecular orbitals g and u.

1. Write the ground state (Hartree-Fock) $|\Psi_0\rangle$, and all the excitations.
2. Which excited determinants are able to couple with $|\Psi_0\rangle$.
3. Write the configuration interaction matrix. Use the notation $2\Delta = \langle u\bar{u}|\hat{H}|u\bar{u}\rangle - \langle g\bar{g}|\hat{H}|g\bar{g}\rangle$.
4. Calculate the correlation energy E_{corr} and the wave-function $|\Psi\rangle$.
5. Discuss the behaviour of the wave-function for in the different cases.

5 Correlation and quantum chemistry methods

We give the potential energy of H_2 calculated with the Restricted Hartree-Fock (RHF) method, a DFT method and Full Configuration Interaction (Full-CI).

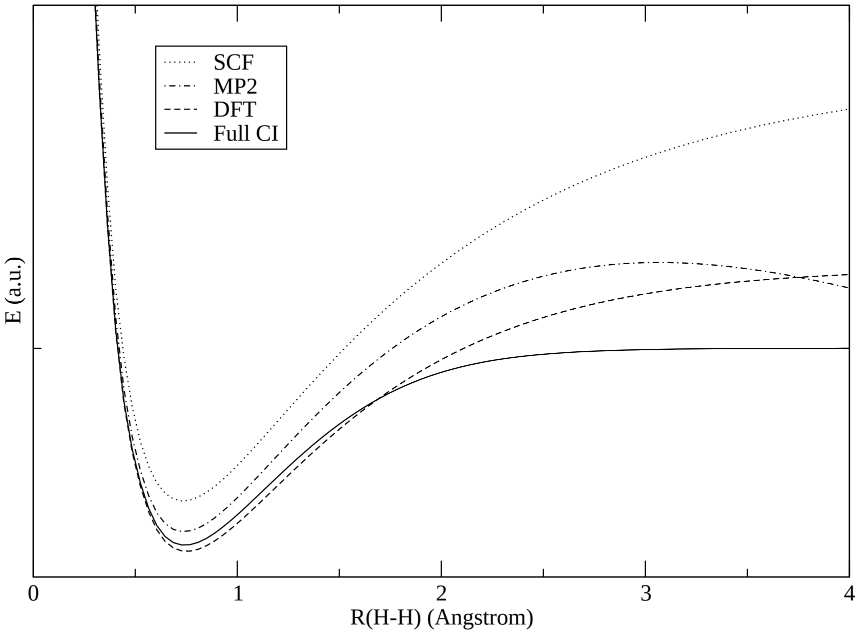

Figure 1: Potential curve of H_2 calculated with Restricted Hartree-Fock (SCF), MP2, DFT (BP86 functionnal) and Full-CI.

1. Give the concept of each method.
2. Which method is suppose to give the best result
   (a) at the equilibrium distance ?
   (b) at the dissociated state ?

3. Let’s focus on the RHF curve.
    (a) Why is it always higher than the other ?
    (b) Why the dissociation limit is that wrong ?
4. Explain the form of the MP2 curve.
5. Comment on the form of the DFT curve.