PES DISSOCIATION OF H_2 MOLECULE AS FUNCTION OF H-H DISTANCE USING STO-3G BASIS SET

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Hartree-Fock

The Hartree-Fock (HF) equations form the foundation of the HF method in quantum chemistry, describing the behavior of electrons in a molecular system within the Born-Oppenheimer approximation. These equations are derived by minimizing the total energy of the system with respect to variations in the molecular orbitals.

We have to solve,

$$FC = SC\varepsilon$$

Which is a generalized eigen value problem. On solving this equation we will get electronic energy in which we can add Vnn (nuclear-nuclear interaction energy) to get total energy.

Where

F is a Fock matrix (Fock operator)
S is overlap matrix

Fock matrix can be formulated as

$$
\begin{aligned}
F_{\mu v} &= H_{\mu v}^{core} + \sum_{a}^{N/2} \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^{*} [2(\mu v|\sigma\lambda) - (\mu\lambda|\sigma v)] \\
&= H_{\mu v}^{core} + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu v|\sigma\lambda) - \tfrac{1}{2}(\mu\lambda|\sigma v)] \\
&= H_{\mu v}^{core} + G_{\mu v}
\end{aligned}
$$

and Hcore can be formulated as one-electron operator (BO)

$$H_{\mu v}^{core} = \int dr_1 \ \phi_{\mu}^{*}(1) h(1) \phi_{v}(1)$$

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Basis set : STO-3G

The STO-3G basis set is considered minimal, containing a total of three basis functions (three Gaussian functions) for each atomic orbital, forms a contracted Gaussian function. Therefore, for the hydrogen molecule (H2), the total number of basis functions is six (three for each hydrogen atom). I have fitted the basis functions of STO-3G basis set to maximize the overlap with slater function with $\zeta = 1.24$.

SLATER FUNCTION

$$\phi_{1s}^{SF}(\zeta, \mathbf{r} - \mathbf{R}_A) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}_A|}$$

GAUSSIAN FUNCTION

$$\phi_{1s}^{GF}(\alpha, \mathbf{r} - \mathbf{R}_A) = (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2}$$

CONTRACTED GAUSSIAN FUNCTION

$$\phi_{\mu}^{CGF}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^{L} d_{p\mu}\phi_{p}^{GF}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A)$$

$$\phi_{1s}^{CGF}(\zeta = 1.24, \text{STO-3G}) = 0.444635\phi_{1s}^{GF}(0.168856) + 0.535328\phi_{1s}^{GF}(0.623913)$$
$$+ 0.154329\phi_{1s}^{GF}(3.42525) \qquad (3.225)$$

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SCF Algorithm

1. Calculate S, Hcore, Vee
2. Now we diagonalize S with a transformation matrix X i.e. X*SX = Identity matrix
3. Now make a guess at the Coefficient matrix C
4. Now we begin with SCF cycle
5. Form a density matrix P = C*C
6. Form a G matrix from Gµv = $\sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - \tfrac{1}{2}(\mu\lambda|\sigma\nu)]$
7. Now form the Fock matrix F = Hcore + G
8. Calculate the transformed Fock matrix F' = X*FX
9. Transform C, C' = inv(X)C and form $\mathbf{F'C' = C'\varepsilon}$
10. Now solve the eigen value problem $\mathbf{F'C' = C'\varepsilon}$ and obtain C' and ε
11. Calculate back the C = XC'
12. Form the new density matrix as in step 5
13. Check for the convergence, difference between the electronic energy obtained in step 10 for 2 steps of cycle less than the requirement
14. To calculate total energy Etotal = electronic energy + nuclear-nuclear energy

Because of the Born-Oppenheimer approximation, we are able to calculate electronic energy (nucleus move in an average electronic field of electrons).

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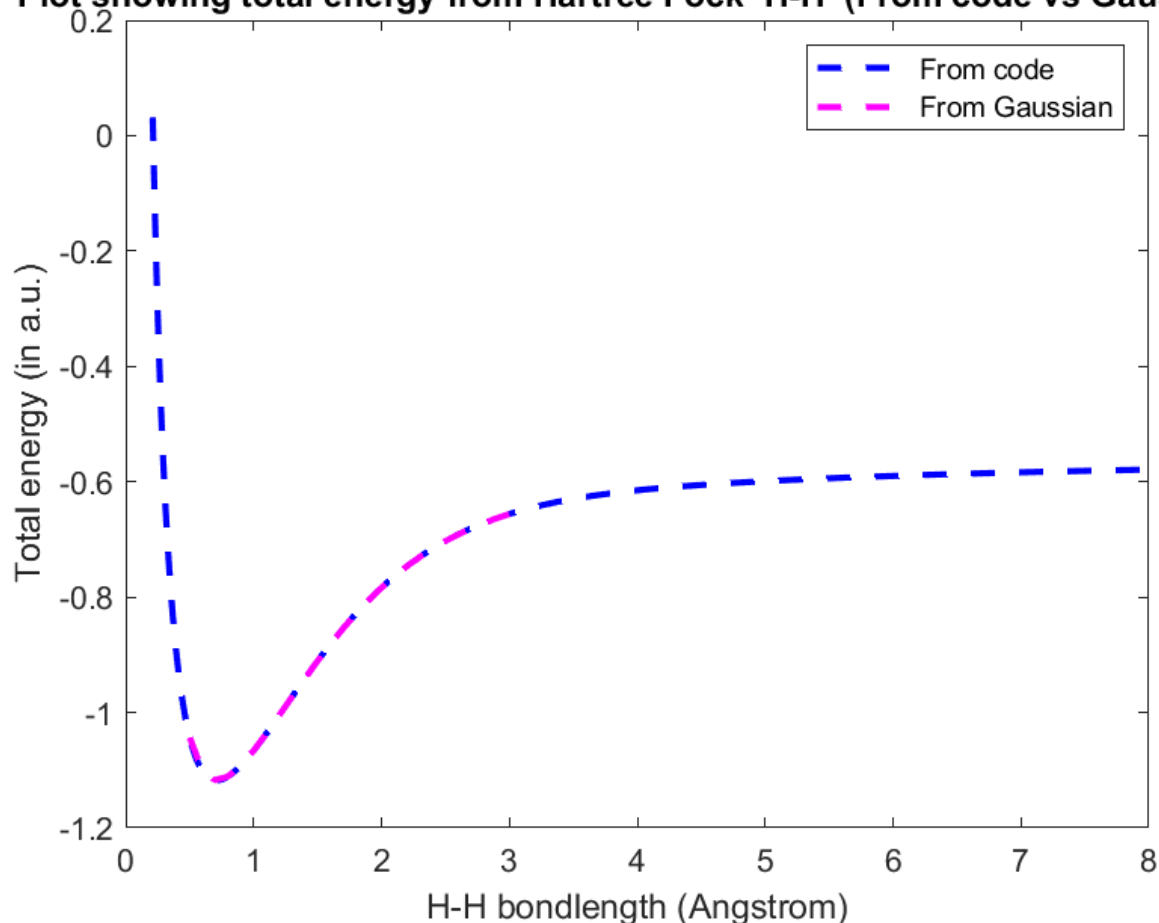
Results:

I have plotted total energy from Hartree Fock on H2 molecule. It has 2 curve, In blue is from the code and in magenta from the HF calculations from Gaussian. Both of these were performed for STO-3G basis set. These plots have total energy on their y-axis in Hartree and bond distance on x-axis in Angstrom.

It can be seen easily that both the curves coincides which tells that SCF cycle converged successfully.

The least energy bond length (A) for H-H is   **0.714388950000000**

The energy (Hartree) of this bond is   **-1.117501110858504**

Plot showing total energy from Hartree Fock H-H (From code vs Gaussian)

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