H_2 Dissociation Discussions

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1 Introduction to Dissociation problem

2 Restricted Hartree Fock Solution

For minimum basis H_2 we have two 2s orbitals, one on each H atom as our basis. i.e ϕ_A and ψ_B as atomic orbitals on hydrogen atom A and B. Let $\bar{\phi_A}$ and $\bar{\phi_B}$ denote the β spin.
Restricted Hartree Fock orbitals will be determined by pure symmetry considerations.
$\phi_\sigma = \frac{1}{\sqrt{1+S_{12}}}(\phi_A + \phi_B)$
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The determinant then is
$|\phi_\sigma \bar{\phi}_\sigma >= \frac{1}{\sqrt{2}} matrix$
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The energy of this determinant based on applying the Fock operator will be $2h_{\sigma\sigma} + J_{\sigma\sigma}$ where h is the core 1 electron part and J is the columbing 2 electron integral. Let us evaluate the energy based on atomic orbitals.
determinant -¿ To correctly describe the dissociation limit, energy of dissoiated H_2 molecule should go to two times energy of H atom. The energy calculated by RHF is an overestimation by $J_{\sigma\sigma}$. $J_{\sigma\sigma}$ should go to zero for correct description which it doesnt as shown below.
$J_{\sigma\sigma} =$

2.1 Discussion of results

If we look at equation x carefully we find that there are four determinants contributing to the molecular configuration, two of which are ionic in nature (1 and 4th). These determinants do not contribute to the correct dissociated H_2 atoms as the atomic orbitals are spacially separated. RHF molecular orbitals are unable to include this spacial separation as they include same spacial Ψ for both spin α and β. Thus we need additional degree of fredom in our orbital wavefunction to include different spacial wavefunctions for both spin states. A Unrestricted Hartree Fock (UHF) can solve this problem discussed in the next section.

3 Unrestricted Hartree Fock Solution

Restricted set of orbitals were generated purely by symmetry. Unrestricted orbitals are not generated by symmtry but through addind another parameter to make sure the spacial part of the orbitals wavefunction can be relaxed. A formulation for H_2 minimal basis case is described below.
equation for parameter addition
explaination for $\theta = 0$ and 45 case.
Let us consider the dissociated case of H_2 molecule and calculate its energy and wavefunction associated with it.

3.1 Discussion

4 Two Orbital two electron system

4.1 Spin Operator

4.2 Spin Adapted Configurations

5 Configurational Interaction Solution

5.1 Discussion

5.2 Secular Equations and its solution