

H_2 Dissociation Discussions

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1 Introduction to Dissociation problem

2 Restricted Hartree Fock Solution

A simple qualitative description of dissociation process can be made by minimal basis H_2 model using 1S orbitals on each H atom as our stomic basis. i.e ϕ_A and ψ_B as atomic orbitals on hydrogen atom A and B. Let us write α and β spin as ϕ and $\bar{\phi}$ respectively. Restricted Hartree Fock orbitals, determined by pure symmetry considerations are :

$$\begin{aligned}\phi_\sigma &= \frac{1}{\sqrt{2(1+S_{AB})}}(\phi_A + \phi_B) \\ \phi_{\sigma^*} &= \frac{1}{\sqrt{2(1-S_{AB})}}(\phi_A - \phi_B)\end{aligned}\tag{1}$$

where S_{AB} is the overlap of atomic orbitals ϕ_A and ϕ_B . The ground state staler determinant can be written as :

$$|\phi_\sigma \bar{\phi}_\sigma \rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_\sigma(1) & \bar{\phi}_\sigma(1) \\ \phi_\sigma(2) & \bar{\phi}_\sigma(2) \end{vmatrix}\tag{2}$$

The energy of this determinant based on applying the Fock operator will be $2h_{\sigma\sigma} + J_{\sigma\sigma}$ (one columbic interaction and no exchange possible between electrons of opposite spin) where h is the core 1 electron energy (kinetic and nuclear potential energy) and J is the columbing 2 electron integral. Let us write our ground state determinant in terms of atomi orbitals.

$$\begin{aligned}
|\phi_\sigma \bar{\phi}_\sigma > &= \frac{1}{\sqrt{2}} [\phi_\sigma(1) \bar{\phi}_\sigma(2) - \phi_\sigma(2) \bar{\phi}_\sigma(1)] \\
&= \frac{1}{2\sqrt{2}(1 + S_{AB})} [(\phi_A(1) + \phi_B(1))(\bar{\phi}_A(2) + \bar{\phi}_B(2)) - (\phi_A(2) + \phi_B(2))(\bar{\phi}_A(1) + \bar{\phi}_B(1))]
\end{aligned} \tag{3}$$

Expanding and rearranging, we get :

$$|\phi_\sigma \bar{\phi}_\sigma > = \frac{1}{2\sqrt{2}(1 + S_{AB})} (|\phi_A \bar{\phi}_A > + |\phi_A \bar{\phi}_B > + |\phi_B \bar{\phi}_A > + |\phi_B \bar{\phi}_B >) \tag{4}$$

Note that two out of four configurations of RHF ground state determinant show ionic bond character. These determinants are the reason of problematic behaviours in dissociation of H_2 as we shall see in the later sections. We can evaluate the total energy of this configuration by inspection. Each electron has a core kinetic and nuclear repulsion energy part $h_{\sigma\sigma}$ and the two electron have a columbic repulsion energy $J_{\sigma\sigma}$:

$$< \phi_\sigma \bar{\phi}_\sigma | H | \phi_\sigma \bar{\phi}_\sigma > = 2h_{\sigma\sigma} + J_{\sigma\sigma} \tag{5}$$

We will analyse the two parts of energy one by one to see their behavior at the dissociation limit.

$$\begin{aligned}
2h_{\sigma\sigma} &= 2(\phi_\sigma \bar{\phi}_\sigma | h | \phi_\sigma \bar{\phi}_\sigma) \\
&= \frac{2}{2(1 + S_{AB})} ((\phi_A + \phi_B)(\bar{\phi}_A + \bar{\phi}_B) | h | (\phi_A + \phi_B)(\bar{\phi}_A + \bar{\phi}_B)) \\
&= \frac{1}{1 + S_{AB}} (h_{AA} + h_{AB} + h_{BA} + h_{BB})
\end{aligned} \tag{6}$$

As $R \rightarrow \infty$ $S_{AB} \rightarrow 0$ and $h_{AB} \rightarrow 0$. Thus $2h_{\sigma\sigma} = h_{AA} + h_{BB}$ at the dissociation limit. Using eq(4) and expanding $J_{\sigma\sigma}$ in atomic orbitals at dissociation limit, we get :

$$\begin{aligned}
J_{\sigma\sigma} &= (\phi_\sigma \phi_\sigma | \phi_\sigma \phi_\sigma) \\
&= \lim_{r \rightarrow \infty} ((\phi_A \phi_A | + (\phi_A \phi_B | + (\phi_B \phi_A | + (\phi_B \phi_B |)) | \\
&\quad (|\phi_A \phi_A\rangle + |\phi_A \phi_B\rangle + |\phi_B \phi_A\rangle + |\phi_B \phi_B\rangle)) \\
&= (\phi_A \phi_A | \phi_A \phi_A) + (\phi_B \phi_B | \phi_B \phi_B) \\
&\neq 0
\end{aligned} \tag{7}$$

2.1 Discussion of results

From eq(6) and eq(7), we infer that the RHF energy of dissociated H_2 molecule is $h_{AA} + h_{BB} + J_{AA} + J_{BB}$. Dissociated H_2 molecule essentially means $2H$ atoms at ∞ distance so they cannot interact. By inspection the energy of this system should be twice

energy of H atom. Thus our RHF calculation is an overestimation of the exact energy. If we look at eq(4) we find that there are four determinants contributing to the molecular configuration, two of which are ionic in nature (1st and 4th). These determinants should not contribute to get the correct dissociated H_2 atoms as the atomic orbitals are spatially separated. RHF molecular orbitals are unable to dissociate a molecule as they have same spatial Ψ for both spin α and β . Thus we need additional degree of freedom in our orbital wavefunction to include different spatial wavefunctions for spin states. An Unrestricted Hartree Fock (UHF) can solve this problem.

3 Unrestricted Hartree Fock Solution

Restricted set of orbitals were generated purely by symmetry. Unrestricted molecular orbitals have different spatial functions for α and β spin of the same orbital. A formulation to incorporate additional degree of freedom in symmetry determined RHF molecular orbitals is to form UHF orbitals as a linear combination of RHF orbitals.

$$\begin{aligned}\phi_{\sigma}^{\alpha} &= \cos\theta\phi_{\sigma} + \sin\theta\phi_{\sigma}^{*} \\ \phi_{\sigma}^{\beta} &= \cos\theta\phi_{\sigma} - \sin\theta\phi_{\sigma}^{*}\end{aligned}\tag{8}$$

$$\begin{aligned}\phi_{\sigma}^{\alpha*} &= \cos\theta\phi_{\sigma}^{*} + \sin\theta\phi_{\sigma} \\ \phi_{\sigma}^{\beta*} &= \cos\theta\phi_{\sigma}^{*} - \sin\theta\phi_{\sigma}\end{aligned}\tag{9}$$

The added degree of freedom here is in θ which can be varied from 0 to 45° . For our purposes it is sufficient to consider the values at the 0 and 45° . As we shall see, $\theta = 0^{\circ}$ gives us RHF orbitals while $\theta \neq 0^{\circ}$ produces UHF orbitals. At 0° :

$$\begin{aligned}\phi_{\sigma}^{\alpha} &= \phi_{\sigma} \\ \phi_{\sigma}^{\beta} &= \phi_{\sigma}\end{aligned}\tag{10}$$

These are RHF ground state spin orbitals as discussed earlier. At $\theta = 45^{\circ}$ we have :

$$\begin{aligned}\phi_{\sigma}^{\alpha} &= \frac{1}{\sqrt{2}}(\phi_{\sigma} + \phi_{\sigma}^{*}) \\ \phi_{\sigma}^{\beta} &= \frac{1}{\sqrt{2}}(\phi_{\sigma} - \phi_{\sigma}^{*})\end{aligned}\tag{11}$$

In $\theta = 45^{\circ}$, taking the dissociation limit case we have $\phi_{\sigma}^{\alpha} = \phi_A$ and $\phi_{\sigma}^{\beta} = \phi_B$ which are unrestricted set of molecular orbitals. With the new set of orbitals our determinant becomes $|\phi_{\sigma}^{\alpha}\phi_{\sigma}^{\beta}\rangle = |\phi_A\bar{\phi}_B\rangle$.

Now let us calculate the energy of the ground state determinant at the dissociation limit

with our new UHF orbitals.

$$\begin{aligned}
\lim_{r \rightarrow \infty} \langle \Psi_o | H | \Psi_o \rangle &= \langle \phi_\sigma^\alpha \phi_\sigma^\beta | H | \phi_\sigma^\alpha \phi_\sigma^\beta \rangle \\
&= \langle \phi_A \phi_B | H | \phi_A \phi_B \rangle \\
&= (h_{AA} + h_{BB})
\end{aligned} \tag{12}$$

As shown here unlike RHF, UHF orbitals show correct behaviour of energy at the dissociation limit of H_2 molecule.

3.1 Discussion

We see that the energy by UHF wavefunction $\lim_{r \rightarrow \infty} \langle \Phi_o \rangle = \langle \phi_\sigma^\alpha \phi_\sigma^\beta \rangle$ goes to correct limit but the wavefunction does not, as discussed in the following sections.

4 Two Orbital two electron system

In order to understand what the correct behavior of the wavefunction at the dissociation limit be, let us consider a two electron in two orbital $\phi_1 \phi_2$ case, just like our H_2 system. Two electrons can be arranged in two orbitals in the following 6 ways.

$$|\phi_1 \bar{\phi}_1 \rangle, |\phi_2 \bar{\phi}_2 \rangle, |\phi_1 \bar{\phi}_2 \rangle, |\bar{\phi}_1 \phi_2 \rangle, |\phi_1 \phi_2 \rangle, |\phi_2 \phi_1 \rangle \tag{13}$$

In the above determinants, 3rd and 4th determinant are not pure spin state.

$$S^2 |\phi_1 \bar{\phi}_2 \rangle = \text{complete}$$

By taking a linear combination of 3rd and 4th terms, we get :

$$|\Phi^1 \rangle = \frac{1}{\sqrt{2}} (|\phi_1 \bar{\phi}_2 \rangle - |\bar{\phi}_1 \phi_2 \rangle) \quad |\Phi^3 \rangle = \frac{1}{\sqrt{2}} (|\phi_1 \bar{\phi}_2 \rangle + |\bar{\phi}_1 \phi_2 \rangle) \tag{14}$$

Thus by taking linear combinations of the above states we can form pure spin states. ground state of an N electron system. But as we shall discuss in the next section, the correct solution to H_2 dissociation at the dissociation limit is not a single determinant.

4.1 Spin Operator

Spin Operator is a vector quantity defined as follows : $\vec{s} = s_x\vec{i} + s_y\vec{j} + s_z\vec{k}$

The x, y and z components are defined as observed experimentally through the Glen Fredlich experiment. $s_x =$

$s_y =$

$s_z =$

A more convenient notation used is to define ladder operators $s_+ = s_x + is_y$

$s_- = s_x - is_y$

The action of these ladder operators can be seen as taking the spin state up the ladder through s_+ and down the ladder through s_- .

The x,y and z components of the spin operator do not commute with each other.

$$[s_x, s_y] = i[s_x, s_y] = i[s_x, s_y] = i \quad (15)$$

The action of these operators can be seen on spin states defined by α or (1,0) in matrix notation and β or (0,1). Their operators can also be defined through Pauli matrices.

$$s_x = \begin{pmatrix} 1 & 5 & 8 \\ 0 & 2 & 4 \\ 3 & 3 & -8 \end{pmatrix} s_+ s_- \quad (16)$$

The action of these matrices on the vector form of spin state gives the resulting spin state vector. Such as : $s_x|\alpha\rangle = ()() =$ Through the above action we can come up with the following relations. $s_+|\alpha\rangle = 0$ $s_-|\alpha\rangle = |\beta\rangle$ $s_+|\beta\rangle = |\alpha\rangle$ $s_-|\beta\rangle = 0$ The above definitions are valid for atomic orbitals. The following set of derivations can be made for molecular orbitals. Since S^2 commutes with H , exact molecular orbitals are also eigenfunctions of S^2 operators and called pure spin states. Since we use an approximate solution to wave function, our wavefunction Ψ can be at times not a pure spin state. In such cases we can make the wavefunction pure spin states by taking a linear combination of wavefunctions produced.

4.2 Spin Adapted Configurations

Let us consider the example of H_2 to illustrate spin adapted configurations. The ground state of H_2 will have α and β electrons in its lowest energy molecular orbital.

5 Configurational Interaction Solution

One way to look at our RHF solution of H_2 dissociation is to follow the two molecular orbitals produced ϕ_σ and ϕ_{σ^*} . The energy of configuration $|\phi_\sigma\bar{\phi}_\sigma\rangle$ is $2h_\sigma + J_{\sigma\sigma}$ and of configuration $|\phi_{\sigma^*}\bar{\phi}_{\sigma^*}\rangle$ is $2h_{\sigma^*} + J_{\sigma^*\sigma^*}$. If we expand the molecular orbitals and write the energy in terms of atomic orbitals,

$$2h_\sigma + J_{\sigma\sigma} = h_{AA} + h_{AB} + h_{BA} + h_{BB} + J_{AA} + J_{BB} \quad 2h_{\sigma^*} + J_{\sigma^*\sigma^*} = h_{AA} - h_{AB} - h_{BA} + h_{BB} - J_{AA} + J_{BB} \quad (17)$$

At the equilibrium distance, $|\phi_\sigma\rangle$ is clearly lower in energy but at the dissociation limit, $\lim_{r \rightarrow \infty} h_{AB} = h_{BA} = 0$. Thus the two states become degenerate. HF only calculating the energy of one of these states i.e ϕ_σ . The energy is even minimised by what is known as the non- dynamic correlation. One method to deal with this pseudo degeneracy is by taking a linear combination of the two states and using Configuration Interaction to solve at the dissociated state.

$$|\Phi\rangle = c_1|\phi_\sigma\bar{\phi}_\sigma\rangle + c_2|\phi_{\sigma^*}\bar{\phi}_{\sigma^*}\rangle$$

matrix equation

where the Hamiltonian coupling terms are : H_{12} all

$E = c_1 H_{11}$ We have an energy equation constrained by the normalisation equation $\langle \Phi | \Phi \rangle = 1$ which gives us $c_1^2 + c_2^2 = 1$. To solve for the minimum in energy based on the above constraint, we form the Lagrange function and find the minimum. $L =$ The above equation gives us 4 equations.

5.1 Discussion

5.2 Secular Equations and its solution