

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 atomic basis i.e ϕ_A^{1s} and ϕ_B^{1s} as atomic orbitals on hydrogen atom A and B. We will 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 Slater 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 can be written by inspection to be $2h_{\sigma\sigma} + J_{\sigma\sigma}$ (one coulombic 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 coulombic 2 electron integral. Let us write our ground state determinant in terms of atomic orbitals.

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

Expanding and rearranging, we get :

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

Note that $|\phi_A \bar{\phi}_A\rangle$ and $|\phi_B \bar{\phi}_B\rangle$ in the above configurations of Restricted Hartree Fock (RHF) ground state determinant show ionic bond character. These determinants are the reason of problematic behavior at dissociation of H_2 as we shall see in the later sections. Evaluating total energy of this configuration, each electron has one core part $h_{\sigma\sigma}$ and the two electrons have coulombic repulsion part $J_{\sigma\sigma}$, we get :

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

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} and $h_{AB} \rightarrow 0$, we get :

$$2h_{\sigma\sigma} = h_{AA} + h_{BB} \tag{7}$$

Similarly, using eq(4) and expanding $J_{\sigma\sigma}$ in atomic orbitals at dissociation limit, we get :

$$\begin{aligned}
J_{\sigma\sigma} &= (\phi_\sigma \phi_\sigma | \phi_\sigma \phi_\sigma) \\
&= \lim_{r \rightarrow \infty} ((\phi_A \phi_A | + (\phi_A \phi_B | + (\phi_B \phi_A | + (\phi_B \phi_B |)) | \\
&\quad (|\phi_A \phi_A\rangle + |\phi_A \phi_B\rangle + |\phi_B \phi_A\rangle + |\phi_B \phi_B\rangle)) \\
&= (\phi_A \phi_A | \phi_A \phi_A) + (\phi_B \phi_B | \phi_B \phi_B) \\
&\neq 0
\end{aligned} \tag{8}$$

2.1 Discussion of results

From eq(7) and eq(8), 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 two H atoms at ∞ distance so they cannot interact. The energy of this system should be twice the 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 have no contribution as the two orbitals ϕ_A and ϕ_B are spatially separated. This problem is due to the fact that RHF orbitals have the same spacial functions for α and β spin. Thus we need additional degree of freedom in our orbital wavefunction to include different spacial wavefunctions for spin states. This results in an Unrestricted Hartree Fock(UHF) method .

3 Unrestricted Hartree Fock Solution

Restricted set of orbitals were generated purely by symmetry. Unrestricted molecular orbitals have different spacial 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.

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

$$\begin{aligned}\phi_{\sigma^*}^{\alpha} &= \cos\theta\phi_{\sigma^*} + \sin\theta\phi_{\sigma} \\ \phi_{\sigma^*}^{\beta} &= \cos\theta\phi_{\sigma^*} - \sin\theta\phi_{\sigma}\end{aligned}\tag{10}$$

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 0° and 45° . At 0° :

$$\begin{aligned}\phi_{\sigma}^{\alpha} &= \phi_{\sigma} \\ \phi_{\sigma}^{\beta} &= \phi_{\sigma}\end{aligned}\tag{11}$$

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

$$\begin{aligned}
\phi_\sigma^\alpha &= \frac{1}{\sqrt{2}}(\phi_\sigma + \phi_{\sigma^*}) \\
\phi_\sigma^\beta &= \frac{1}{\sqrt{2}}(\phi_\sigma - \phi_{\sigma^*})
\end{aligned} \tag{12}$$

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 $|\phi_\sigma^\alpha \phi_\sigma^\beta\rangle = |\phi_A \bar{\phi}_B\rangle$.

Let us calculate the energy of the ground state determinant at the dissociation limit with our new UHF orbitals.

$$\begin{aligned}
\lim_{r \rightarrow \infty} \langle \Psi_o | H | \Psi_o \rangle &= \langle \phi_\sigma^\alpha \phi_\sigma^\beta | H | \phi_\sigma^\alpha \phi_\sigma^\beta \rangle \\
&= \langle \phi_A \phi_B | H | \phi_A \phi_B \rangle \\
&= h_{AA} + h_{BB}
\end{aligned} \tag{13}$$

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

3.1 Discussion

We see that the energy by UHF wavefunction $\lim_{r \rightarrow \infty} |\Psi_o\rangle = |\phi_\sigma^\alpha \phi_\sigma^\beta\rangle$ goes to correct limit but the wavefunction is incorrect. The UHF wavefunction at the dissociation limit becomes $|\phi_A \bar{\phi}_B\rangle$ in terms of atomic orbitals. This is not a pure spin state in the case where electrons occupy different spacial orbitals as in the UHF orbitals. We will discuss spin adaptation in detail in section 3. For reference, the correct wavefunction is :

$$\lim_{r \rightarrow \infty} |\Psi_o\rangle = \frac{1}{\sqrt{2}}(|\phi_A \bar{\phi}_B\rangle + |\bar{\phi}_A \phi_B\rangle) \tag{14}$$

In terms of molecular orbitals, this correct wavefunction is a multi-determinant wavefunction :

3.2 Spin Operator

Spin Operator is a vector quantity defined as follows :

$$\vec{s} = s_x \vec{i} + s_y \vec{j} + s_z \vec{k} \quad (15)$$

These spin operator components do not commute with each other and satisfy the following relations :

$$[s_x, s_y] = i s_z, [s_y, s_z] = i s_x, [s_z, s_x] = i s_y \quad (16)$$

We can derive a set of states of the spin of a particle as eigenfunctions of s^2 or one of the components of \vec{s} conventionally taken to be s_z .

$$\begin{aligned} s^2 |\phi\rangle &= s(s+1) |\phi\rangle \\ s_z |\phi\rangle &= m_s |\phi\rangle \end{aligned} \quad (17)$$

where s is the total spin of the particle and m_s is the quantum number for the z component. Since electron is a spin half system, where $m_s = \frac{1}{2}, -\frac{1}{2}$. For our convenience, we can define the two states in the matrix representation as follows :

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (18)$$

This leads us to a more convenient definition of ladder operators:

$$\begin{aligned} s_+ &= \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ s_- &= \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{aligned} \quad (19)$$

where the action of these ladder operators can be seen as taking the spin state up through s_+ and down through s_- . They are defined in terms for x and y components of \vec{s} as follows :

$$\begin{aligned} s_+ &= s_x + i s_y \\ s_- &= s_x - i s_y \end{aligned} \quad (20)$$

Using eq(17), (19) and (20) we can write the x, y and z components of our spin operator in the matrix representation as $s_k = \frac{1}{2} \sigma_k$. Here k=x, y and z and σ_k is defined as follows:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (21)$$

here 1, 2 and 3 refer to x, y and z components. This matrix formalism for spin $\frac{1}{2}$ systems was introduced by W. Pauli in 1926 and the matrices σ_k are called Pauli matrices. We can also derive an expression for s^2 in terms of components of \vec{s} using eq(15) and (16) :

$$\begin{aligned} s^2 &= s_+ s_- - s_z + s_z^2 \\ s^2 &= s_- s_+ + s_z + s_z^2 \end{aligned} \quad (22)$$

For many electron systems, the total spin angular momentum is the sum of spin vectors for each electron.

$$\vec{S} = \sum_{i=1}^N \vec{s}(i) \quad (23)$$

Thus the total squared spin operator is :

$$\begin{aligned} S^2 &= \vec{S} \cdot \vec{S} = \sum_{i=1}^N \sum_{j=1}^N \vec{s}(i) \cdot \vec{s}(j) \\ &= S_+ S_- - S_z + S_z^2 \\ &= S_- S_+ + S_z + S_z^2 \end{aligned} \quad (24)$$

Since there is no spin part in our non-relativistic H , S^2 and S_z commutes with H i.e $[H, S^2] = 0$ and $[H, S_z] = 0$. Thus the exact eigenfunctions of Hamiltonian (exact wavefunctions) are also eigenfunctions of S^2 and S_z operators.

Approximate solutions of H are not necessarily pure spin states. However we would like to convert them to spin adapted configurations to form eigenfunctions of S^2 . We will describe the process through an example in the following sections.

3.3 Two Orbital two electron system

To understand spin adapted configurations, let us consider an example of a simple case of two electrons in two orbitals $\phi_1 \phi_2$. Two electrons can be arranged in two orbitals in the following 6 ways:

$$|\phi_1 \bar{\phi}_1 >, |\phi_2 \bar{\phi}_2 >, |\phi_1 \bar{\phi}_2 >, |\bar{\phi}_1 \phi_2 >, |\phi_1 \phi_2 >, |\bar{\phi}_2 \bar{\phi}_1 > \quad (25)$$

If we calculate the S value for the above configurations, we can see that $|\phi_1\bar{\phi}_2 >$ and $|\bar{\phi}_1\phi_2 >$ are not pure spin states.

$$\begin{aligned} S^2|\phi_1\bar{\phi}_2 > &= S^2[\phi_1(1)\phi_2(2)\alpha(1)\beta(2) - \phi_1(2)\phi_2(1)\alpha(2)\beta(1)] \\ &= [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)](\alpha(1)\beta(2) + \alpha(2)\beta(1)) \end{aligned} \quad (26)$$

We can make them eigenfunctions of S^2 operator by taking a linear combination of appropriate terms

$$\begin{aligned} |^1\Psi > &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2 > + |\phi_1\bar{\phi}_2 >) \\ |^3\Psi > &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2 > - |\phi_1\bar{\phi}_2 >) \end{aligned} \quad (27)$$

As discussed here, we now have three triplet and three singlet spin adapted states from two electrons in two orbitals model. Writing in terms of H_2 case that we discussed in section (2) and (3) we have the following singlet states :

$$\begin{aligned} |^1\Psi_1 > &= |\phi_A\bar{\phi}_\sigma > \\ |^1\Psi_2 > &= |\phi_{\sigma^*}\bar{\phi}_{\sigma^*} > \\ |^1\Psi_3 > &= \frac{1}{\sqrt{2}}(|\phi_\sigma\bar{\phi}_{\sigma^*} > + |\phi_\sigma\bar{\phi}_{\sigma^*} >) \end{aligned} \quad (28)$$

Similarly the triplet states are :

$$\begin{aligned} |^3\Psi_4 > &= |\phi_\sigma\phi_{\sigma^*} > \\ |^3\Psi_5 > &= |\bar{\phi}_{\sigma^*}\bar{\phi}_\sigma > \\ |^3\Psi_6 > &= \frac{1}{\sqrt{2}}(|\phi_\sigma\bar{\phi}_{\sigma^*} > - |\phi_\sigma\bar{\phi}_{\sigma^*} >) \end{aligned} \quad (29)$$

4 Configurational Interaction Solution

Let us apply configuration Interaction method to treat the H_2 dissociation problem using the configurations developed above. The full CI wavefunction (Φ_{CI}) will include all six of the above configurations, but we can simplify the wavefunction as follows. The ground state $|^1\Psi_1 > = |\phi_A\bar{\phi}_\sigma >$ is a singlet, so we will include the three singlet configurations discussed in the above section in our CI wavefunction.

$$|\Psi_{CI} > = |^1\phi_1 > + c1|^1\phi_2 > + c2|^1\phi_3 > \quad (30)$$

We can simplify our Φ_o further by taking symmetry into consideration. Doubly excited determinant and the ground state both are of gerade symmetry and so will mix while $^1\Phi_3$ is ungerade and thus will not. We can thus simplify our Φ_{CI} as :

$$|\Phi_{CI}\rangle = |^1\phi_1\rangle + c1|^1\phi_2\rangle \quad (31)$$

Calculating the energy through this wavefunction we have :

$$\begin{aligned} E &= \langle \Phi_{CI} | H | \Phi_{CI} \rangle \\ &= \begin{pmatrix} c1 & c2 \end{pmatrix} \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c1 \\ c2 \end{pmatrix} \end{aligned} \quad (32)$$

One way to look at our HF solutions of H_2 dissociation is to follow the two molecular orbitals produced ϕ_σ and ϕ_{sigma^*} . 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,

$$2h_\sigma + J_{\sigma\sigma} = h_{AA} + h_{AB} + h_{BA} + h_{BB} + J_{AA} + J_{BB} \quad 2h_{\sigma^*} + J_{\sigma^*\sigma^*} = h_{AA} - h_{AB} - h_{BA} + h_{BB} - J_{AA} + J_{BB} \quad (33)$$

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. In HF one is 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. Thus taking a Configuration Interaction with both the states in Φ_{CI} gives the correct energy.

$$|\Phi\rangle = c1|\phi_\sigma\bar{\phi}_\sigma\rangle + c2|\phi_{\sigma^*}\bar{\phi}_{\sigma^*}\rangle$$

matrix equation

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

$E = c1H1$ We have an energy equation constrained by the normalisation equation $\langle \Phi | \Phi \rangle = 1$ which gives us $c1^2 + c2^2 = 1$. 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.

4.1 Discussion

4.2 Secular Equations and its solution