# $H_2$ 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 basis i.e $\phi_A^{1s}$ and $\phi_B^{1s}$ as atomic orbitals on hydrogen atom A and B. We will write $\alpha$ and $\beta$ spin as $\phi$ 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 $\phi_A$ and $\phi_B$. 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 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.

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

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 $R \to \infty$ $S_{AB}$ and $h_{AB} \to 0$, 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 :

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

### 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 $\infty$ 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 $\phi_A$ and $\phi_B$ are spatially separated. This problem is due to the fact that RHF orbitals have the same spacial functions for $\alpha$ and $\beta$ 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 $\alpha$ and $\beta$ 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 $\theta$ which can be varied from $0^o$ to $45^o$. For our purposes it is sufficient to consider the values at $0^o$ and $45^o$. At $0^o$ :

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

These are RHF ground state spin orbitals as discussed earlier. At $\theta = 45^o$ 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 $\theta = 45^o$, 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.

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

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 $lim_{r\to\infty}|\Psi_o\rangle = |\phi_\sigma^\alpha\phi_\sigma^\beta\rangle$ 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 :

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

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

$$Lim_{r\to\infty}|\Psi_o\rangle = \frac{1}{\sqrt{2}}(|\phi_\sigma^\alpha\phi_\sigma^\beta\rangle - |\phi_{\sigma^*}^\alpha\phi_{\sigma^*}^\beta\rangle) \tag{15}$$

### 3.2 Spin Operator

Spin Operator is a vector quantity defined as follows :

$$\vec{s} = s_x\vec{i} + s_y\vec{j} + s_z\vec{k} \tag{16}$$

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

$$[s_x, s_y] = is_z, [s_y, s_z] = is_x, [s_z, s_x] = is_y \tag{17}$$

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 $s_z$.

$$\begin{aligned} s^2|\phi\rangle &= s(s+1)|\phi\rangle \\ s_z|\phi\rangle &= m_s|\phi\rangle \end{aligned} \tag{18}$$

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 :

$$|\alpha\rangle = \binom{1}{0}, |\beta\rangle = \binom{0}{1} \tag{19}$$

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

$$\begin{aligned} s_+ &= \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ s_- &= \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{aligned} \tag{20}$$

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 :

$$\begin{aligned} s_+ &= s_x + is_y \\ s_- &= s_x - is_y \end{aligned} \tag{21}$$

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 $\sigma_k$ is defined as follows:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{22}$$

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 $\sigma_k$ 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) :

$$\begin{aligned} s^2 &= s_+ s_- - s_z + s_z^2 \\ s^2 &= s_- s_+ + s_z + s_z^2 \end{aligned} \tag{23}$$

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

$$\vec{S} = \sum_{i=1}^{N} \vec{s}(i) \tag{24}$$

Thus the total squared spin operator is :

$$\begin{aligned} S^2 = \vec{S}.\vec{S} &= \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{s}(i)\vec{s}(j) \\ &= S_+ S_- - S_z + S_z^2 \\ &= S_- S_+ + S_z + S_z^2 \end{aligned} \tag{25}$$

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 wave-functions) 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:

$$|\phi_1\bar{\phi}_1\rangle, |\phi_2\bar{\phi}_2\rangle, |\phi_1\bar{\phi}_2\rangle, |\bar{\phi}_1\phi_2\rangle, |\phi_1\phi_2\rangle, |\bar{\phi}_2\bar{\phi}_1\rangle \tag{26}$$

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

$$\begin{aligned}S^2|\phi_1\bar{\phi}_2\rangle &= S^2\big[\phi_1(1)\phi_2(2)\alpha(1)\beta(2) - \phi_1(2)\phi_2(1)\alpha(2)\beta(1)\big] \\ &= \big[\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)\big](\alpha(1)\beta(2) + \alpha(2)\beta(1))\end{aligned} \tag{27}$$

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

$$\begin{aligned}|\,{}^1\Psi\rangle &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2\rangle + |\phi_1\bar{\phi}_2\rangle) \\ |\,{}^3\Psi\rangle &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2\rangle - |\phi_1\bar{\phi}_2\rangle)\end{aligned} \tag{28}$$

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 :

$$\begin{aligned}|\,{}^1\Psi'\rangle &= |\phi_\sigma\bar{\phi}_\sigma\rangle \\ |\,{}^1\Psi''\rangle &= |\phi_{\sigma^*}\bar{\phi}_{\sigma^*}\rangle \\ |\,{}^1\Psi'''\rangle &= \frac{1}{\sqrt{2}}(|\phi_\sigma\bar{\phi}_{\sigma^*}\rangle + |\phi_\sigma\bar{\phi}_{\sigma^*}\rangle)\end{aligned} \tag{29}$$

Similarly the triplet states are :

$$\begin{aligned}|\,{}^3\Psi'\rangle &= |\phi_\sigma\phi_{\sigma^*}\rangle \\ |\,{}^3\Psi''\rangle &= |\bar{\phi}_{\sigma^*}\bar{\phi}_\sigma\rangle \\ |\,{}^3\Psi'''\rangle &= \frac{1}{\sqrt{2}}(|\phi_\sigma\bar{\phi}_{\sigma^*}\rangle - |\phi_\sigma\bar{\phi}_{\sigma^*}\rangle)\end{aligned} \tag{30}$$

# 4 Configurational Interaction Solution

One way to look at HF solutions of $H_2$ dissociation is to follow two configurations $|\phi_\sigma\bar{\phi}_\sigma\rangle$ and $|\phi_{\sigma^*}\bar{\phi}_{\sigma^*}\rangle$. 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 $2h_{\sigma^*} + J_{\sigma^*\sigma^*}$. Expanding the molecular orbitals and writing the energy in terms of atomic orbitals, we get:

$$\begin{aligned} 2h_{\sigma\sigma} + J_{\sigma\sigma} &= h_{AA} + h_{AB} + h_{BA} + h_{BB} + J_{AA} + J_{BB} \\ 2h_{\sigma^*\sigma^*} + J_{\sigma\sigma} &= h_{AA} - h_{AB} - h_{BA} + h_{BB} - J_{AA} + J_{BB} \end{aligned} \tag{31}$$

At the dissociation limit, $h_{AB} = h_{BA} = 0$ as $H_A$ and $H_B$ have no interaction. Thus the two states become degenerate. In HF we are calculating the energy of one of these states i.e $|\phi_\sigma\bar{\phi}_\sigma\rangle$. The total energy is further reduced by what is known as the non- dynamic correlation or the mixing of the two degenerate states. One can also look at this degeneracy arising in eq(15) in UHF case. Since the two states have the same energy, it should be appropriate to chose a linear combination of the two states as our ground state wavefunction and use configuration interaction (CI) method. The ground state CI wavefunction will be :

$$|\Phi_{CI}\rangle = c_1|{}^1\Psi_{\sigma^2}\rangle + c_2|{}^1\Psi_{\sigma^{*2}}\rangle \tag{32}$$

calculating the energy we have :

$$\begin{aligned} E &= \langle\Phi_{CI}|H|\Phi_{CI}\rangle \\ &= \begin{pmatrix} c_1^* & c_2^* \end{pmatrix} \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\ &= c_1^* c_1 H_{11} + c_1^* c_2 h_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22} \end{aligned} \tag{33}$$

where $H$ matrix elements are defined as follows :

$$\begin{aligned} H_{11} &= \langle\phi_\sigma\phi_\sigma|H|\phi_\sigma\phi_\sigma\rangle = 2h_{\sigma\sigma} + J_{\sigma\sigma} \\ H_{12} &= \langle\phi_\sigma\phi_\sigma|H|\phi_{\sigma^*}\phi_{\sigma^*}\rangle = (\phi_\sigma\phi_\sigma|\phi_{\sigma^*}\phi_{\sigma^*}) \\ H_{21} &= \langle\phi_{\sigma^*}\phi_{\sigma^*}|H|\phi_\sigma\phi_\sigma\rangle = (\phi_{\sigma^*}\phi_{\sigma^*}|\phi_\sigma\phi_\sigma) \\ H_{22} &= \langle\phi_{\sigma^*}\phi_{\sigma^*}|H|\phi_{\sigma^*}\phi_{\sigma^*}\rangle = 2h_{\sigma^*\sigma^*} + J_{\sigma^*\sigma^*} \end{aligned} \tag{34}$$

Normalisation condition of $\Phi_{CI}$ leads to :

$$\begin{aligned} \langle\Phi_{CI}|\Phi_{CI}\rangle &= 1 \\ c_1^* c_1\langle\Psi_{\sigma^2}|\Psi_{\sigma^2}\rangle + c_2^* c_2\langle\Psi_{\sigma^{*2}}|\Psi_{\sigma^{*2}}\rangle &= 1 \end{aligned} \tag{35}$$

To solve for the minimum in energy eq(33) based on the above constraint eq(35), we form the Lagrange function and find its minima with respect to $c_1$ and $c_2$.

$$\begin{aligned} L &= \sum_{ij} c_i^* c_j \langle\phi_i|H_{ij}|\phi_j\rangle - E(\sum_{i,j} c_i^* c_j\langle\phi_i|\phi_j\rangle - 1) \\ \delta L &= \sum_i \delta c_i^* \big[\sum_j H_{ij} c_j - E S_{ij} c_j\big] + c.c \end{aligned} \tag{36}$$

here S is the overlap matrix of our basis i.e $S_{ij} = \langle \phi_i | \phi_j \rangle$. The $\delta L$ equations are simultaneous equations in $c_1$ and $c_2$, and are called secular equations. Since the inner part of the eq(36) has to go to 0 for secular equations to vanish, thus we form the secular determinant:

$$Hc = ScE \tag{37}$$

here, $c$ is a matrix of eigenvectors and $E$ is a diagonal matrix of eigenvalues of $H$.

Our basis is orthogonal i.e $\langle \phi_\sigma | \phi_{\sigma^*} \rangle = 0$ thus we can reduce this equation to $Hc = cE$. Solving this equation in the matrix form can be done by diagonalization of $H$ as :

$$\begin{aligned} Hc &= cE \\ H &= cEc^{-1} \end{aligned} \tag{38}$$

diagonalising $H$ matrix therefore gives c as eigenvector matrix and energy in the diagonal eigenvalue matrix. Solving this equation in our example calculation we get our minimum energy at $c_1 = \frac{1}{\sqrt{2}}$ and $c_2 = -\frac{1}{\sqrt{2}}$. Our ground state wavefunction is :

$$\Phi_{CI} = \frac{1}{\sqrt{2}}\big(\Psi_{\sigma^2} - \Psi_{\sigma^{*2}}\big) \tag{39}$$

Unlike UHF and RHF, $\Phi_{CI}$ has equal contribution from both the degenerate state. Also, $E_{CI} = h_{AA} + h_{BB}$ which is the correct dissociation limit energy.

### 4.1 Discussion

### 4.2 Secular Determinant

To minimise the energy expectation value in the above section, we formed a Lagrangian function through the matrix equations eq(33) and eq(35), which led us to derive the secular determinant (eq(37)). We also showed that solving the secular determinant is equivalent to diagonalising $H$ matrix and finding the eigenvectors and eigenvalues as our solution. Another approach to come to the minimum energy of the system is to start from a trial wavefunction $\Phi$ and use functional variation to minimise the expectation value of energy. This process should lead to the same result.

Let us take and arbitrary starting wavefunction $\Phi$ as ground state wavefunction and write the energy expectation value as follows:

$$\langle\Phi|H|\Phi\rangle = \langle\Phi|E|\Phi\rangle \tag{40}$$

To find the wavefunction with the lowest energy, we can vary our wavefunction $\Phi$ by a small arbitrary amount. :

$$\Phi \to \Phi + \delta\Phi \tag{41}$$

$\Phi$ can be written in terms of basis function as :

$$|\Phi\rangle = \sum_i c_i |\phi_i\rangle \tag{42}$$

Now varying $\Phi$ is equivalent to varying coefficients associated to the basis functions $c_i's$. Thus we will minimise :

$$\langle\Phi|H|\Phi\rangle = \sum_{ij} c_i^* c_j \langle\phi_i|H|\phi_j\rangle \tag{43}$$

subject to the constraint that the trial wavefunction is normalized :

$$\begin{aligned} \langle\Phi|\Phi\rangle &= 1 \\ \sum_{ij} c_i^* c_j \langle\phi_i|H|\phi_j\rangle &= 1 \end{aligned} \tag{44}$$

We have successfully converted an eq(40) to a matrix equation where we can vary $\Phi$ as variation in coefficient matrix, similar to section 3.2. Further, we form a Lagrange function and minimise with respect to coefficients $c_i's$ as in eq(36) and eq(37) to get :

$$Hc = ScE \tag{45}$$