

H_2 Dissociation Discussions

Cheng Lab

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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 $\lim_{r \rightarrow \infty} |\Phi_o\rangle = |\phi_\sigma^\alpha \phi_\sigma^\beta\rangle$ goes to correct limit but the wavefunction is incorrect. The UHF wavefunction at the dissociation limit becomes $|\phi_A \bar{\phi}_B\rangle$. But this is not a pure spin state in the case where electrons occupy different spacial orbitals, as will be discussed in the later sections. The correct wavefunction is :

$$\lim_{r \rightarrow \infty} |\Psi_o\rangle = \frac{1}{\sqrt{2}} (|\phi_A \bar{\phi}_B\rangle + |\bar{\phi}_A \phi_B\rangle) \tag{13}$$

3.2 Spin Operator

Spin Operator is a vector quantity defined as follows :

$$\vec{s} = s_x \vec{i} + s_y \vec{j} + s_z \vec{k} \tag{14}$$

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

$$[s_x, s_y] = i s_z, [s_y, s_z] = i s_x, [s_z, s_x] = i s_y \tag{15}$$

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 .

$$\begin{aligned}
s^2 |\phi\rangle &= s(s+1) |\phi\rangle \\
s_z |\phi\rangle &= m_s |\phi\rangle
\end{aligned} \tag{16}$$

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 convinience, we can define

the two states in the matrix representation as follows :

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (17)$$

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

$$\begin{aligned} s_+ &= \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ s_- &= \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{aligned} \quad (18)$$

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

$$\begin{aligned} s_+ &= s_x + is_y \\ s_- &= s_x - is_y \end{aligned} \quad (19)$$

Using eq(18), (20) and (21) 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:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (20)$$

where 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. We can also derive an expression for s^2 in terms of components of \vec{s} using eq(15) and (16) :

$$\begin{aligned} s^2 &= s_+s_- - s_z + s_z^2 \\ s^2 &= s_-s_+ + s_z + s_z^2 \end{aligned} \quad (21)$$

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

$$\vec{S} = \sum_{i=1}^N \vec{s}(i) \quad (22)$$

Thus the total squared spin operators is :

$$\begin{aligned} S^2 &= \vec{S} \cdot \vec{S} = \sum_{i=1}^N \sum_{j=1}^N \vec{s}(i) \cdot \vec{s}(j) \\ &= S_+S_- - S_z + S_z^2 \\ &= S_-S_+ + S_z + S_z^2 \end{aligned} \quad (23)$$

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 and the correct behavior of the wavefunction at the dissociation limit be, let us consider an example of a simple case of two electrons in two orbital $\phi_1\phi_2$ case as in our minimal basis H_2 . Two electrons can be arranged in two orbitals in the following 6 ways:

$$|\phi_1\bar{\phi}_1\rangle, |\phi_2\bar{\phi}_2\rangle, |\phi_1\bar{\phi}_2\rangle, |\bar{\phi}_1\phi_2\rangle, |\phi_1\phi_2\rangle, |\bar{\phi}_2\bar{\phi}_1\rangle \quad (24)$$

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.

$$\begin{aligned} S^2|\phi_1\bar{\phi}_2\rangle &= S^2[\phi_1(1)\phi_2(2)\alpha(1)\beta(2) - \phi_1(2)\phi_2(1)\alpha(2)\beta(1)] \\ &= [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)](\alpha(1)\beta(2) + \alpha(2)\beta(1)) \end{aligned} \quad (25)$$

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

$$\begin{aligned} |^1\Psi\rangle &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2\rangle + |\bar{\phi}_1\phi_2\rangle) \\ |^3\Psi\rangle &= \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2\rangle - |\bar{\phi}_1\phi_2\rangle) \end{aligned} \quad (26)$$

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 :

$$\begin{aligned} |^1\Psi_1\rangle &= |\phi_A\bar{\phi}_\sigma\rangle \\ |^1\Psi_2\rangle &= |\phi_{\sigma^*}\bar{\phi}_{\sigma^*}\rangle \\ |^1\Psi_3\rangle &= \frac{1}{\sqrt{2}}(|\phi_\sigma\bar{\phi}_{\sigma^*}\rangle + |\phi_{\sigma^*}\bar{\phi}_\sigma\rangle) \end{aligned} \quad (27)$$

Similarly the triplet states are :

$$\begin{aligned}
|{}^3\Psi_4\rangle &= |\phi_\sigma\phi_{\sigma^*}\rangle \\
|{}^3\Psi_5\rangle &= |\bar{\phi}_{\sigma^*}\bar{\phi}_\sigma\rangle \\
|{}^3\Psi_6\rangle &= \frac{1}{\sqrt{2}}(|\phi_\sigma\bar{\phi}_{\sigma^*}\rangle - |\phi_{\sigma^*}\bar{\phi}_\sigma\rangle)
\end{aligned} \tag{28}$$

4 Configurational Interaction Solution

Let us apply configuration Interaction method to treat the H_2 dissociation problem. The ground state $|{}^1\Psi_1\rangle = |\phi_A\bar{\phi}_\sigma\rangle$ is a singlet, so we will include the three singlet configurations described in the above section in our CI wavefunction.

$$|\Phi_o\rangle = |{}^1\phi_1\rangle + c1|{}^1\phi_2\rangle + c2|{}^1\phi_3\rangle \tag{29}$$

As a next step, we can simplify our Φ_o by taking symmetry into consideration. Both Φ_o and the doubly excited determinant are gerade and will mix while ${}^1\Phi_3$ is ungerade and thus will not. So we can simplify our Φ_{CI} as :

$$|\Phi_o\rangle = |{}^1\phi_1\rangle + c1|{}^1\phi_2\rangle \tag{30}$$

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,

$$2h_\sigma + J_{\sigma\sigma} = h_{AA} + h_{AB} + h_{BA} + h_{BB} + J_{AA} + J_{BB} \quad 2h_{\sigma^*} + J_{\sigma^*\sigma^*} = h_{AA} - h_{AB} - h_{BA} + h_{BB} - J_{AA} + J_{BB} \tag{31}$$

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