H$_2$ in the minimal basis

Alston J. Misquitta

Centre for Condensed Matter and Materials Physics
Queen Mary, University of London

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Overview

- $\text{H}_2$: The 1-electron basis.
- The two-electron basis and the molecular orbitals.
- Hartree-Fock solution
- CI solution
- Density and density-matrix
- Dissociation of $\text{H}_2$. 
The system: Two H-atoms, separated by distance $R$. We will consider two cases: $R = 1.4$ Bohr (equilibrium) and $R = \infty$ (dissociation).

One electron minimal basis:

$$1s_A(r) = \frac{1}{\sqrt{\pi}} \exp(-r_A)$$

$$1s_B(r) = \frac{1}{\sqrt{\pi}} \exp(-r_B)$$

where $r_A/r_A$ are distances of electron from nucleus A/B.
1-e basis II

Symmetry-adapted atomic orbitals:

\[
\phi_1(r) = 1\sigma_g = N_g [1s_A(r) + 1s_B(r)] \\
\phi_2(r) = 1\sigma_u = N_u [1s_A(r) - 1s_B(r)]
\]

where

\[
N_g = \frac{1}{\sqrt{2(1 + S)}} \quad \text{and} \quad N_u = \frac{1}{\sqrt{2(1 - S)}}
\]

where

\[
S = \int 1s_A(r) 1s_B(r) \, dr = (1 + R + \frac{1}{3}R^2) \exp(-R).
\]
1-e basis III

All figures from: Molecular Electronic Structure Theory by Helgaker et al.
1-e basis IV

*N-electron basis:*

\[
| {^1}\Sigma_g^+ (g^2) \rangle = | 1\sigma_g^2 \rangle = a_{1\alpha}^{\dagger} a_{1\beta}^{\dagger} | \text{vac} \rangle \\
| {^1}\Sigma_g^+ (u^2) \rangle = | 1\sigma_u^2 \rangle = a_{2\alpha}^{\dagger} a_{2\beta}^{\dagger} | \text{vac} \rangle
\]

Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.
1-e basis V

Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

\[ |^{3}\Sigma_{u}^{+}\rangle = \left\{ \begin{array}{l} a_{2\alpha}^{\dagger} a_{1\alpha}^{\dagger} |\text{vac}\rangle \\ \frac{1}{\sqrt{2}}(a_{2\alpha}^{\dagger} a_{1\beta}^{\dagger} + a_{2\beta}^{\dagger} a_{1\alpha}^{\dagger}) |\text{vac}\rangle \\ a_{2\beta}^{\dagger} a_{1\beta}^{\dagger} |\text{vac}\rangle \end{array} \right\} \]

\[ |^{1}\Sigma_{u}^{+}\rangle = \frac{1}{\sqrt{2}}(a_{2\alpha}^{\dagger} a_{1\beta}^{\dagger} - a_{2\beta}^{\dagger} a_{1\alpha}^{\dagger}) |\text{vac}\rangle \]
What do these term symbols mean?
States are classified as gerade (\( g \), German for ‘even’) if they are unchanged by inversion through the centre of mass, or ungerade (\( u \), German for ‘odd’) if inversion changes the sign.
The total angular momentum of the molecular state is represented by the central term, in the above case, since we are dealing with orbitals with \( l = 0 \) only, we have \( L = 0 \) and this is represented by the \( \Sigma \).
The spin multiplicity \( 2S + 1 \) of the molecular state is indicated as a superscript on the left.
And for \( \Sigma \) states only we may additionally classify states as + if the wavefunction is unchanged on reflection in the plane containing the internuclear axis, or – otherwise. The – can only arise in open-shell \( \Sigma \) states.
See Szabo & Ostlund secs. 2.3.1 and 2.3.5

What is the matrix element: $\langle \Psi | H | \Psi \rangle$?

Notation:

$$H = h(1) + h(2) + \frac{1}{r_{12}}$$

$$= O_1 + O_2$$

where the *core-Hamiltonians* are:

$$h(1) = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}},$$

and similarly for $h(2)$. Here $A$ are all the nuclei.
We will show (in class) that:

\[ \langle \Psi | O_1 | \Psi \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle = h_{11} + h_{22}. \]

and

\[ \langle \Psi | O_2 | \Psi \rangle = \int dx_1 dx_2 \chi_1^* (x_1) \chi_2^* (x_2) \frac{1}{r_{12}} \chi_1 (x_1) \chi_2 (x_2) \]

\[ - \int dx_1 dx_2 \chi_1^* (x_1) \chi_2^* (x_2) \frac{1}{r_{12}} \chi_2 (x_1) \chi_1 (x_2) \]

and, defining

\[ \langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle \]

\[ = \int dx_1 dx_2 \chi_i^* (x_1) \chi_j^* (x_2) \frac{1}{r_{12}} \chi_k (x_1) \chi_l (x_2) \]
we get

$$\langle \Psi | O_2 | \Psi \rangle = \langle 12 | 12 \rangle - \langle 12 | 21 \rangle \equiv \langle 12 | | 12 \rangle.$$ 

The first term is the Coulomb term and the second the exchange term. The two may be written compactly as indicated by the last term.

We now write our single determinant energy — the Hartree–Fock energy — as:

$$E_{HF} = \langle \Psi | H | \Psi \rangle$$
$$= \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle.$$
Now we evaluate the HF energy for $|\Sigma^+_g (g^2)\rangle$.
Here $\chi_1 = \phi_1 \alpha$ and $\chi_2 = \phi_1 \beta$. We will integrate out the spin degrees of freedom using:

$$\int d\sigma \alpha^*(\sigma) \alpha(\sigma) = 1 = \int d\sigma \beta^*(\sigma) \beta(\sigma)$$

$$\int d\sigma \alpha^*(\sigma) \beta(\sigma) = 0 = \int d\sigma \beta^*(\sigma) \alpha(\sigma)$$

or $\langle \alpha | \beta \rangle = 0 = \langle \beta | \alpha \rangle$ etc.
Restricted HF V

\[
\langle 1| h |1 \rangle = \int dx \chi_1^*(x) h(r) \chi_1(x)
\]

\[
= \int dr d\sigma \phi_1^*(r) \alpha^*(\sigma) h(r) \phi_1(r) \alpha(\sigma)
\]

\[
= \int d\sigma \alpha^*(\sigma) \alpha(\sigma) \times \int dr \phi_1^*(r) h(r) \phi_1(r)
\]

\[
= 1 \times \langle 1| h |1 \rangle_R
\]

\[
= \langle 1| h |1 \rangle_R.
\]

Similarly show that

\[
\langle 12|12 \rangle = \langle 11|11 \rangle_R
\]

\[
\langle 12|21 \rangle = 0.
\]
Restricted HF VI

So we get the energy of the \( |^{1}\Sigma_g^+(g^2) \rangle \) state as:

\[
E(g^2) = 2\langle 1 | h | 1 \rangle_R + \langle 11 | 11 \rangle_R
\]

Q: There is no exchange term present for this state. Why not?

Because both spin orbitals in the \( |^{1}\Sigma_g^+(g^2) \rangle \) state have the same spatial part this is referred to as a restricted Hartree–Fock (RHF) state. In an unrestricted HF (UHF) state we'd allow the up and down spin electrons to reside in different spatial orbitals.
In the next two slides we see data taken from Helgaker et al. that allows us to use the energy expressions we have derived (and will derive later) to compute the numerical energies of the system.
### Table 5.1

The density-matrix elements and molecular integrals for the hydrogen molecule in a symmetry-adapted basis of hydrogenic 1s functions with exponents 1 (atomic units). Rows containing only zero elements and rows with elements that are related to those of other rows by permutational symmetry are not listed.

<table>
<thead>
<tr>
<th>Indices</th>
<th>Density elements</th>
<th>Integrals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$</td>
<td>1\sigma^2_r\rangle$</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>1111</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2222</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2211</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2121</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2112</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Kinetic and nuclear-atraction contributions: $0.4081 - 1.5937 = -1.1856$.

\(^b\)Kinetic and nuclear-atraction contributions: $1.1521 - 1.7258 = -0.5737$.

\(^c\)Kinetic and nuclear-atraction contributions: $\frac{1}{2} - 1 = -\frac{1}{2}$.
## Restricted HF IX

### Table 5.2

The electronic energies of the hydrogen molecule at an internuclear separation of $1.4a_0$ in a minimal basis of hydrogenic 1s orbitals with unit exponents ($E_h$)

<table>
<thead>
<tr>
<th>State</th>
<th>Kinetic</th>
<th>Attraction</th>
<th>Electron repulsion&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nuc. rep.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\Sigma^+_g 1\sigma^2_g$</td>
<td>0.8162</td>
<td>-3.1874</td>
<td>0.5660 + 0.0000 = 0.5660</td>
<td>0.7143</td>
<td>-1.0909</td>
</tr>
<tr>
<td>1 $\Sigma^+_g 1\sigma^2_u$</td>
<td>2.3042</td>
<td>-3.4516</td>
<td>0.5863 + 0.0000 = 0.5863</td>
<td>0.7143</td>
<td>0.1532</td>
</tr>
<tr>
<td>1 $\Sigma^+_g (\tau_0)^b$</td>
<td>0.8344</td>
<td>-3.1907</td>
<td>0.5663 - 0.0308 = 0.5354</td>
<td>0.7143</td>
<td>-1.1066</td>
</tr>
<tr>
<td>1 $\Sigma^+_g (\tau_1)^c$</td>
<td>2.2860</td>
<td>-3.4484</td>
<td>0.5861 + 0.0308 = 0.6169</td>
<td>0.7143</td>
<td>0.1688</td>
</tr>
<tr>
<td>1 $\Sigma^+<em>g (\tau</em>{\text{cov}})^d$</td>
<td>0.8452</td>
<td>-3.1926</td>
<td>0.5664 - 0.0388 = 0.5277</td>
<td>0.7143</td>
<td>-1.1055</td>
</tr>
<tr>
<td>1 $\Sigma^+<em>g (\tau</em>{\text{ion}})^e$</td>
<td>0.8452</td>
<td>-3.1926</td>
<td>0.5664 + 0.0388 = 0.6052</td>
<td>0.7143</td>
<td>-1.0279</td>
</tr>
<tr>
<td>3 $\Sigma^+_u$</td>
<td>1.5602</td>
<td>-3.3195</td>
<td>0.5564 - 0.1403 = 0.4162</td>
<td>0.7143</td>
<td>-0.6289</td>
</tr>
<tr>
<td>1 $\Sigma^+_u$</td>
<td>1.5602</td>
<td>-3.3195</td>
<td>0.5564 + 0.1403 = 0.6967</td>
<td>0.7143</td>
<td>-0.3484</td>
</tr>
</tbody>
</table>

<sup>a</sup>The electron-repulsion energy is written as the sum of the classical Coulomb contribution and the exchange and correlation contributions.

<sup>b</sup>The ground state calculated from $\tau_0 = -0.1109$.

<sup>c</sup>The excited state calculated from $\tau_1 = -0.1109 + \pi/2$.

<sup>d</sup>The covalent state calculated from $\tau_{\text{cov}} = -0.1400$.

<sup>e</sup>The ionic state calculated from $\tau_{\text{ion}} = 0.1400$. 
Using the data from table 5.2 we can write down the energies of the H$_2$ states. In particular, $E(g^2) = -1.0909$ and $E(u^2) = +0.1532$ Hartree.

So the bonding state $|^{1}\Sigma_g^{+}(g^2)\rangle$ is more strongly bound (compared with two isolated H atoms). Conversely, the anti-bonding state $|^{1}\Sigma_g^{+}(u^2)\rangle$ is even more strongly unbound.
Summary so far:

The single determinant energy — the Hartree–Fock energy — of the ket $|\psi\rangle = |\chi_1\chi_2\rangle$ is:

$$E_{HF} = \langle \psi | H | \psi \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle.$$  

The energy of the $|^{1}\Sigma_{g}^{+}(g^2)\rangle$ state is:

$$E(g^2) = 2\langle 1 | h | 1 \rangle_{R} + \langle 11 | 11 \rangle_{R}.$$
Restricted HF XII

Here are the steps we took to get here:

- Decide on the molecular geometry. In this case there was only one parameter to consider: $R$. We fix the nuclei using what is called the Born–Oppenheimer approximation.
- Decide on the atomic basis.
- Find the symmetry orbitals. This step is optional.
- Use the variational principle to combine the symmetry orbitals to form the molecular orbitals. This was not needed for $H_2$ as the high symmetry of the system and the use of a minimal basis meant that the symmetry orbitals were also the molecular orbitals.
- Place the electrons into the molecular orbitals to form molecular spin orbitals.
- With these form the approximation to the molecular wavefunction.
- Evaluate the energy of the system using this wavefunction.
Chemist’s Notation

\[ \langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int d\chi_1 d\chi_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_k(x_1) \chi_l(x_2) \]

Symmetries are clearer in this notation:

\[ (ij|kl) = (kl|ij) \]

and for real orbitals (the usual case), we additionally have:

\[ (ij|kl) = (ji|kl) = (ij|lk) = (ji|lk) \]
Density-matrices I

*The one- and two-electron density*

We first define the one- and two-electron density matrices:

$$
\gamma_1(x_1, x'_1) = N \int \psi^*(x_1, x_2, \cdots, x_N) \psi(x'_1, x_2, \cdots, x_N) dx_2 \cdots dx_N
$$

$$
\gamma_2(x_1, x_2, x'_1, x'_2) = \frac{N(N-1)}{2} \int \psi^*(x_1, x_2, x_3, \cdots, x_N) \psi(x'_1, x'_2, x_3, \cdots, x_N) dx_3 \cdots dx_N
$$

The density matrices depend on spatial and spin coordinates.
Density-matrices II

The one-electron and two-electron densities are defined to be the diagonal elements of the density matrices with the spin degrees of freedom integrated out:

\[
\rho(r_1) = \int \gamma_1(x_1, x_1) d\sigma_1
\]

\[
\rho(r_1, r_2) = \int \gamma_2(x_1, x_2, x_1, x_2) d\sigma_1 d\sigma_2
\]

*Interpretation:*

The one-electron density \( \rho(r_1) \) is proportional to the probability of finding an electron at position \( r_1 \).

The two-electron density \( \rho(r_1, r_2) \) represents the probability of simultaneously finding two electrons at positions \( r_1 \) and \( r_2 \) in the molecule.
Let's work out these terms for a 2-e single-det wavefunction:

\[
\Psi(x_1, x_2) = 2^{-1/2}(\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2))
\]

First evaluate \(\Psi^*\Psi\):

\[
\Psi^*(x_1, x_2)\Psi(x_1', x_2) = \frac{1}{2} [\chi_1^*(x_1)\chi_2^*(x_2)\chi_1(x_1')\chi_2(x_2) \\
+ \chi_2^*(x_1)\chi_1^*(x_2)\chi_2(x_1')\chi_1(x_2) \\
- \chi_1^*(x_1)\chi_2^*(x_2)\chi_2(x_1')\chi_1(x_2) \\
- \chi_2^*(x_1)\chi_1^*(x_2)\chi_1(x_1')\chi_2(x_2)] \\
= \frac{1}{2} [\chi_1^*(1)\chi_1(1')\chi_2^*(2)\chi_2(2) + \chi_2^*(1)\chi_2(1')\chi_1^*(2)\chi_1(2) \\
- \chi_1^*(1)\chi_2(1')\chi_2^*(2)\chi_1(2) - \chi_2^*(1)\chi_1(1')\chi_1^*(2)\chi_2(2)]
\]
Density-matrices IV

Therefore the one-electron density matrix is

$$\gamma_1(x_1, x'_1) = 2 \int \psi^*(x_1, x_2) \psi(x'_1, x_2) dx_2$$

$$= \chi_1^*(x_1) \chi_1(x'_1) + \chi_2^*(x_1) \chi_2(x'_1)$$

And using $\chi_i(x) = \phi_i(r) \omega_i(\sigma)$, the density is

$$\rho(r_1) = \int \gamma_1(x_1, x_1) d\sigma_1$$

$$= \phi_1^*(r_1) \phi_1(r_1) + \phi_2^*(r_1) \phi_2(r_1)$$

In general, for an $N$-electron single-det wavefunction,

$$\rho(r) = \sum_{i=1}^{N} \phi_i^*(r) \phi_i(r)$$
The two-electron density matrix is quite simply (no integration needed for the 2-electron wavefunction):

\[
\gamma_2(x_1, x_2, x'_1, x'_2) = \frac{2(2 - 1)}{2} \psi^*(x_1, x_2)\psi(x'_1, x'_2) \\
= \frac{1}{2} [\chi_1^*(1)\chi_1(1')\chi_2^*(2)\chi_2(2') + \chi_2^*(1)\chi_2(1')\chi_1^*(2)\chi_1(2') \\
- \chi_1^*(1)\chi_2(1')\chi_2^*(2)\chi_1(2') - \chi_2^*(1)\chi_1(1')\chi_1^*(2)\chi_2(2')] 
\]

So, if \(\psi\) is a singlet state with \(\chi_1 = \phi_1 \alpha\) and \(\chi_2 = \phi_2 \beta\) then the two-electron density is

\[
\rho(r_1, r_2) = \int \gamma_2(x_1, x_2, x_1, x_2) d\sigma_1 d\sigma_2 \\
= \frac{1}{2} [\phi_1^*(1)\phi_1(1)\phi_2^*(2)\phi_2(2) + \phi_2^*(1)\phi_2(1)\phi_1^*(2)\phi_1(2)]
\]
RHF: Dissociation 1

Back to $\mathrm{H}_2$: For $|1\sigma^2_g\rangle = |\phi_1\alpha, \phi_1\beta\rangle$ and $|1\sigma^2_u\rangle = |\phi_2\alpha, \phi_2\beta\rangle$:

$$\rho_{1\sigma^2_g}(r) = 2\phi_1^2(r)$$
$$\rho_{1\sigma^2_u}(r) = 2\phi_2^2(r)$$
$$\rho_{1\sigma^2_g}(r_1, r_2) = \phi_1^2(r_1)\phi_1^2(r_2)$$
$$\rho_{1\sigma^2_u}(r_1, r_2) = \phi_2^2(r_1)\phi_2^2(r_2)$$

*Interpretation:* Since the two-electron density represents the probability of simultaneously finding two electrons at positions $r_1$ and $r_2$ in the molecule, we see here is that the probability of finding an electron at $r_1$ is unaffected by the electron at $r_2$. Thus, these single-determinant (Hartree–Fock) wavefunctions do not correlate the electrons.
**Fig. 5.4.** The one- and two-electron density functions of the bonding $|1\sigma_g^2\rangle$ (upper plots) and antibonding $|1\sigma_u^2\rangle$ (lower plots) configurations of the hydrogen molecule on the molecular axis (atomic units). The
Something is wrong. The two-electron density matrix of the $1\sigma^2_g$ state suggests that the two electrons are not correlated in position: If one electron is fixed at one of the hydrogen nuclei, the other electron is not forced to be at the other nucleus. Instead, the second electron has an equal probability of being on either nucleus.

This is a problem as at dissociation we would expect one electron to reside on one nucleus, and the other electron at the other nucleus: i.e., $\text{H}_2$ should dissociate as two neutral hydrogen atoms. Let’s see what actually happens.
RHF: Dissociation IV

This has consequences for this restricted Hartree–Fock (RHF) wavefunction: it does not dissociate into two H-atoms as \( R \to \infty \). In this limit, \( S = \langle 1s_A(r)|1s_B(r) \rangle = 0 \). So

\[
\phi_1(r) = 1\sigma_g = 2^{-1/2}[1s_A(r) + 1s_B(r)]
\]
\[
\phi_2(r) = 1\sigma_u = 2^{-1/2}[1s_A(r) - 1s_B(r)].
\]

Now let’s write \( |1\sigma_g^2\rangle \) in terms of the atomic (non-symmetric) basis functions

\[
|1\sigma_g^2\rangle = |\phi_1 \alpha, \phi_1 \beta\rangle
\]
\[
= \phi_1(r_1)\phi_1(r_2) \times \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))
\]
\[
= \phi_1(r_1)\phi_1(r_2) \, 1\Sigma.
\]
Focus on the spatial part $\phi_1(r_1)\phi_1(r_2)$ and use the notation $A = 1s_A(r)$ and $B = 1s_B(r)$.

$$\phi_1(r_1)\phi_1(r_2) = \frac{1}{2} [A(1)A(2) + B(1)B(2) + A(1)B(2) + B(1)A(2)],$$

so,

$$|1\sigma^2_g\rangle = \frac{1}{2} |A^2\rangle + \frac{1}{2} |B^2\rangle + \frac{1}{\sqrt{2}} |AB\rangle.$$

Here $|A^2\rangle = A(1)A(2)^1\Sigma$ is the state with both electrons on $A$, i.e., the state $H^-$ (similarly for $B$) and $|AB\rangle = \frac{1}{\sqrt{2}} [A(1)B(2) + B(1)A(2)]^1\Sigma$ is the state with one electron on $A$ and one on $B$, i.e. the correctly dissociated state consisting of two neutral $H$ atoms.
RHF: Dissociation VI

Show that at the dissociation limit, the states $|A^2\rangle$, $|B^2\rangle$ and $|AB\rangle$ are orthonormal. You will find the result for the overlap integral of two Slater functions given at the start of this set of lecture notes useful.

Now consider the RHF energy at dissociation (all cross terms can be shown to tend to vanish as $R \to \infty$):

$$E(g^2) = \langle 1\sigma_g^2 | H | 1\sigma_g^2 \rangle$$

$$= \langle \frac{1}{2} A^2 + \frac{1}{2} B^2 + \frac{1}{\sqrt{2}} AB | H | \frac{1}{2} A^2 + \frac{1}{2} B^2 + \frac{1}{\sqrt{2}} AB \rangle$$

$$= \frac{1}{4} E(H^-) + \frac{1}{4} E(H^-) + \frac{1}{2} (2E(H))$$

$$= E(H) + \frac{1}{2} E(H^-).$$

So, as expected, we do not get $2E(H)$. 
Q: What happened to the cross terms in expression for $E(g^2)$? Show that they all vanish in the $R \to \infty$ limit.

On the previous page, how did we get from the second to the third line? Evaluate matrix elements $\langle A^2|H|A^2 \rangle$ etc. and see what mathematical steps are needed to arrive at the corresponding energies. You will find the general energy expression for a single determinant useful in filling in these gaps.
How is $\langle AB|H|AB \rangle = 2E(H)$? To show this, start with $H = H_A + H_B + V$, where $V$ includes the interaction terms between the two H-atoms. In the $R \rightarrow \infty$ limit, $V \rightarrow 0$. Use this to evaluate the matrix element and show that it is equal to $2E(H)$.

Q: Show that $\langle AA|H|AA \rangle = E(H^-) = 2\langle A|h|A \rangle_{\mathcal{R}} + \langle AA|AA \rangle_{\mathcal{R}}$. 

RHF:Dissociation VIII
Show the previous result starting from the energy expression for $|1\sigma_g^2\rangle$:

$$E(g^2) = 2\langle 1|h|1\rangle_{\mathcal{R}} + \langle 11|11\rangle_{\mathcal{R}}$$

Hint: Expand the symmetry-adapted atomic orbital $\phi_1$ in terms of the $1s_A(r)$ and $1s_B(r)$ basis functions and use

$$E(A^2) = E(H^-) = 2\langle A|h|A\rangle_{\mathcal{R}} + \langle AA|AA\rangle_{\mathcal{R}}$$

What have we done with the spin wavefunction in the above derivation? Re-derive the final result this time correctly including the spin wavefunction. Alternatively show that we can integrate out the spin early on and consider only the spatial parts of the wavefunction in the derivation.
The Configuration Interaction wavefunction:
This is a wavefunction made up of a linear combination of all allowed single determinants. For \textit{gerade} ground state of H$_2$ in this \textit{minimal} basis set this takes the simple form:

$$|^{1}\Sigma_g^+ (\tau)\rangle = \cos(\tau)|1\sigma_2^g\rangle + \sin(\tau)|1\sigma_2^u\rangle.$$ 

No other configurations are allowed to mix as the others are all of \textit{ungerade} symmetry.
There will be two orthogonal solutions, one as above and the other of the form $|^{1}\Sigma_g^+ (\tau + \pi/2)\rangle$.

\textbf{Q:} Show that $\langle^{1}\Sigma_g^+ (\tau)|^{1}\Sigma_g^+ (\tau + \pi/2)\rangle = 0.$
Now we calculate the energy of the system with the CI wavefunction:

\[|^{1\Sigma^+_g}(\tau)\rangle = \cos(\tau)|1\sigma^2_g\rangle + \sin(\tau)|1\sigma^2_u\rangle.\]

The energy of \(H_2\) now becomes (real orbitals):

\[E(\tau) = \langle ^{1\Sigma^+_g}(\tau) | H | ^{1\Sigma^+_g}(\tau) \rangle = \cos^2(\tau)E(g^2) + \sin^2(\tau)E(u^2) + 2\sin(\tau)\cos(\tau)\langle 1\sigma^2_g | H | 1\sigma^2_u \rangle\]

\[Q:\text{ Show that } \langle 1\sigma^2_g | H | 1\sigma^2_u \rangle = \langle 11 | 22 \rangle = (12 | 12).\text{ This can also be written as } (21 | 21) = g_{2121}\text{ due to symmetry of these integrals.}\]
So the energy of the CI state is

$$E(\tau) = \cos^2(\tau)E(g^2) + \sin^2(\tau)E(u^2) + \sin(2\tau)\langle 11|22 \rangle.$$ 

To find the optimum $\tau$ we minimize to get

$$\tan(2\tau) = \frac{2\langle 11|22 \rangle}{E(g^2) - E(u^2)}$$

so solutions are

$$\tau_n = \frac{1}{2} \arctan \left[ \frac{2\langle 11|22 \rangle}{E(g^2) - E(u^2)} \right] + \frac{n\pi}{2},$$

where $n$ is an integer.
From tables 5.1 and 5.2, for H$_2$ at its equilibrium separation, we get two solutions: $\tau_0 = -0.1109$ and $\tau_1 = -0.1109 + \pi/2$. Recall that the solutions must be $\pi/2$ apart to result in orthogonal states. These give (the 'e' indicates equilibrium separation):

$$|^{1}\Sigma^+_g(\tau_0)\rangle_e = 0.9939|1\sigma^2_g\rangle - 0.1106|1\sigma^2_u\rangle$$
$$|^{1}\Sigma^+_g(\tau_1)\rangle_e = 0.1106|1\sigma^2_g\rangle + 0.9939|1\sigma^2_u\rangle$$

I.e., the g.s. is dominated with the HF solution $|1\sigma^2_g\rangle$ with a weight of 98.8%.

This is calculated as $c_1^2/(c_1^2 + c_2^2)$ as the w.f. always appears quadratically in a matrix element.
CI V

Here is Table 5.2 from Helgaker et al. again:

<table>
<thead>
<tr>
<th>State</th>
<th>Kinetic</th>
<th>Attraction</th>
<th>Electron repulsion$^a$</th>
<th>Nuc. rep.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+_g 1\sigma^2_g$</td>
<td>0.8162</td>
<td>-3.1874</td>
<td>0.5660 + 0.0000 = 0.5660</td>
<td>0.7143</td>
<td>-1.0909</td>
</tr>
<tr>
<td>$^1\Sigma^+_g 1\sigma^2_u$</td>
<td>2.3042</td>
<td>-3.4516</td>
<td>0.5863 + 0.0000 = 0.5863</td>
<td>0.7143</td>
<td>0.1532</td>
</tr>
<tr>
<td>$^1\Sigma^+_g (\tau_0)^b$</td>
<td>0.8344</td>
<td>-3.1907</td>
<td>0.5663 - 0.0308 = 0.5354</td>
<td>0.7143</td>
<td>-1.1066</td>
</tr>
<tr>
<td>$^1\Sigma^+_g (\tau_1)^c$</td>
<td>2.2860</td>
<td>-3.4484</td>
<td>0.5861 + 0.0308 = 0.6169</td>
<td>0.7143</td>
<td>0.1688</td>
</tr>
<tr>
<td>$^1\Sigma^+<em>g (\tau</em>{\text{cov}})^d$</td>
<td>0.8452</td>
<td>-3.1926</td>
<td>0.5664 - 0.0388 = 0.5277</td>
<td>0.7143</td>
<td>-1.1055</td>
</tr>
<tr>
<td>$^1\Sigma^+<em>g (\tau</em>{\text{ion}})^e$</td>
<td>0.8452</td>
<td>-3.1926</td>
<td>0.5664 + 0.0388 = 0.6052</td>
<td>0.7143</td>
<td>-1.0279</td>
</tr>
<tr>
<td>$^3\Sigma^+_u$</td>
<td>1.5602</td>
<td>-3.3195</td>
<td>0.5564 - 0.1403 = 0.4162</td>
<td>0.7143</td>
<td>-0.6289</td>
</tr>
<tr>
<td>$^1\Sigma^+_u$</td>
<td>1.5602</td>
<td>-3.3195</td>
<td>0.5564 + 0.1403 = 0.6967</td>
<td>0.7143</td>
<td>-0.3484</td>
</tr>
</tbody>
</table>

$^a$The electron-repulsion energy is written as the sum of the classical Coulomb contribution and the exchange and correlation contributions.

$^b$The ground state calculated from $\tau_0 = -0.1109$.

$^c$The excited state calculated from $\tau_1 = -0.1109 + \pi/2$.

$^d$The covalent state calculated from $\tau_{\text{cov}} = -0.1400$.

$^e$The ionic state calculated from $\tau_{\text{ion}} = 0.1400$. 
Energies of these states are listed in table 5.2. We see that the CI g.s. is 1.4% lower than the $|1\sigma^2_g\rangle$ HF ground state. This may not seem like much, but it is significant. Further, the effect of the CI g.s. on the two-electron density is enormous (fig. 5.5): the small fraction of the $|1\sigma^2_u\rangle$ state introduces what is known as Left–Right correlation: the two electrons are now correlated and prefer to sit on opposite nuclei.

We will demonstrate below that this mixing of states allows the CI g.s. to correctly dissociate into two H-atoms at $R \to \infty$, whereas, as we have already shown, the HF g.s. doesn’t. The one- and two-electron densities can be calculated as for the RHF wavefunction. These are displayed on the next slide.
Fig. 5.5. The one- and two-electron density functions of the two-configuration $^1\Sigma^+_g$ ground (upper plots) and excited (lower plots) states of the hydrogen molecule on the molecular axis (atomic units). The two-elect-
Compare the CI and RHF two-electron density matrices for the $1\sigma_g^2$ state. How do they differ? Does the CI density matrix suggest that the CI wavefunction will exhibit the correct dissociation limit?

When you performed the CI calculations with NWChem you used CISD and not FCI. In CISD only singly and doubly excited determinants are included in the CI expansion. Is this appropriate for H$_2$, or does it lead to an approximation?
Work out the one- and two-electron densities of the CI wavefunction. As we will show soon, in the $R \to \infty$ limit, $\tau_0 = -\pi/4$. Write down the two-electron density in this limit and by expressing it in terms of the $1s_A(r)$ and $1s_B(r)$ orbitals, show that the CI wavefunction has indeed introduced Left–Right correlation as shown in Fig. 5.5.
Notice the following:

- There is very little change in the one-electron density from the RHF case. Here the $|1\sigma^2_g\rangle$ (i.e. RHF) state has a weight of 98.8%. The $|1\sigma^2_u\rangle$ state contributing only 1.2%.

- However, the two-electron density is vastly different. Now it indicates a vanishing probability for the electrons to be on the same atom. Instead, electrons in the CI wavefunction prefer to reside on opposite nuclei.

- This correlation is called *Left–Right correlation*. It is a *non-dynamical* correlation that arises when multiple configurations (many-electron determinants) are used to describe the state.
Dissociation of the CI wavefunction

\[ |^{1\Sigma_g^+}(\tau)\rangle = \cos(\tau)|1\sigma_g^2\rangle + \sin(\tau)|1\sigma_u^2\rangle. \]

with an energy

\[ E(\tau) = \cos^2(\tau)E(g^2) + \sin^2(\tau)E(u^2) + \sin(2\tau)\langle 11|22\rangle \]

where

\[ \tau_n = \frac{1}{2} \arctan \left[ \frac{2\langle 11|22\rangle}{E(g^2) - E(u^2)} \right] + \frac{n\pi}{2} \]
CI XII

What is $\tau$ in the dissociation limit?
For $R \to \infty$ we have (Q: Show it!):

$$E(g^2) = E(u^2) = 2h_{AA} + \frac{1}{2}\langle AA|AA\rangle$$

This degeneracy can be expected on physical grounds. Also, in the $R \to \infty$ limit

$$\langle 11|22\rangle = \frac{1}{4}\langle (A(1) + B(1))(A(2) + B(2))|(A(1) - B(1))(A(2) - B(2))\rangle$$

$$= \frac{1}{4}[\langle AA|AA\rangle + \langle BB|BB\rangle]$$

$$= \frac{1}{2}\langle AA|AA\rangle \neq 0$$

Here we have used the fact that any cross-terms involving $A$ and $B$ will vanish in the large-$R$ limit.
Consequently, for $R \to \infty$, \[ \frac{2\langle 11|22 \rangle}{E(g^2) - E(u^2)} \to -\infty \] (Q: Why $-\infty$?), so

\[ \tau_n = -\frac{\pi}{4} + \frac{n\pi}{2}. \]

The ground state is $n = 0$, or $\tau_0 = -\frac{\pi}{4}$ and we get

\[ |^{1}\Sigma^+ (\tau)\rangle \to \frac{1}{\sqrt{2}}[|1\sigma_g^2 \rangle - |1\sigma_u^2 \rangle] \]

\[ E(\tau) \to \frac{1}{2}(E(g^2) + E(u^2)) - \langle 11|22 \rangle \]

Note that in this limit the weight of the $|1\sigma_u^2 \rangle$ state is equal to that of the HF, $|1\sigma_g^2 \rangle$, state! As the system dissociates, the weights change.
Q: Show that in this limit $|^{1}\Sigma_{g}^{+}(\tau)\rangle$ correctly describes two H-atoms. I.e., show that $|^{1}\Sigma_{g}^{+}(\tau)\rangle = |AB\rangle$.

Using the results we have stated (and you have to prove) earlier, we get

$$E(-\pi/4) = \frac{1}{2}(E(g^2) + E(u^2)) - \langle 11|22 \rangle$$

$$= 2h_{AA} + \frac{1}{2}\langle AA|AA \rangle - \frac{1}{2}\langle AA|AA \rangle$$

$$= 2h_{AA} = 2E(H).$$

I.e., the CI energy correctly tends to the energy of 2 hydrogen atoms as $R \rightarrow \infty$. 
In summary:

\[ H_2(\text{RHF}) \rightarrow H + \frac{1}{2}H^- \]

\[ H_2(\text{FCI}) \rightarrow 2H \]
CI is computationally expensive. In general there are a lot of determinants possible and the variational space increases exponentially with the size of the basis. So it would be nice to have an alternative way to dissociate H\textsubscript{2}. There is one: the unrestricted Hartree–Fock (UHF) method. Here we realise that at dissociation we want the spatial parts of orbitals used by the two electrons to be different: the $\alpha$-spin electron will be associated with one hydrogen atom and the $\beta$-spin electron with the other. So we need to allow our single determinant this freedom. This leads to the UHF solution.
UHF II

Define the UHF wavefunction $|\Psi\rangle = |\chi_1^\alpha \chi_1^\beta\rangle$ where the unrestricted spin-orbitals are defined to be

$$
\chi_1^\alpha(x) = \psi_1\alpha(r)\alpha(\omega)
\chi_1^\beta(x) = \psi_1\beta(r)\beta(\omega)
$$

where

$$
\psi_1\alpha = \cos(\theta)\phi_1 + \sin(\theta)\phi_2
\psi_1\beta = \cos(\theta)\phi_1 - \sin(\theta)\phi_2
$$

Show that this choice for the spatial orbitals covers all possibilities. I.e., that for $\theta = 0$ we get the RHF solution and for $\theta = \pi/4$ we get the dissociated limit of 2 H-atoms.
Rather than solve the UHF problem for you, I will outline it and expect you to solve it completely for homework. This is an important problem so I require you to write it up and submit it to me!

Next write down the energy of this UHF wavefunction. Start from the general form for the energy of a single determinant state (we proved this at the start of this lecture):

$$E = \langle \Psi | H | \Psi \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle.$$ 

Show that the last term vanishes.

Write each of the terms in the energy expression in terms of $g = \phi_1$ and $u = \phi_2$. I will use $g$ and $u$ are short forms for these orbitals in the expressions below.
Hence show that the energy can be written as a function of the angle $\theta$:

$$E(\theta) = 2 \cos^2(\theta) h_{gg} + 2 \sin^2(\theta) h_{uu}$$

$$+ 2 \cos^4(\theta) \langle gg | gg \rangle + 2 \sin^4(\theta) \langle uu | uu \rangle$$

$$+ 2 \sin^2(\theta) \cos^2(\theta) [\langle gu | gu \rangle - 2 \langle gg | uu \rangle \] .$$

Find the extrema of $E(\theta)$. There should be two solutions.

Characterize the solutions: they are not both minima so you will need to find the second derivative of $E(\theta)$. Do this carefully.

Use integral values from table 5.1 to make a plot of the energy as a function of $\theta$ at $R_e$ and at dissociation ($R \to \infty$). Do your results agree with this plot? (use any plotting package - but Mathematica or Gnuplot may be best suited for this)
For the $\theta \neq 0$ solution: evaluate all matrix elements in the $R \to \infty$ limit and show that in this limit $\theta \to \pi/4$.

Hence show that the UHF energy in this limit is that of two H-atoms.

Solve this correctly and completely and you will have understood everything we have covered so far.