H_2 in the minimal basis

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Overview

- H_2: The 1-electron basis.
- The two-electron basis and the molecular orbitals.
- Hartree-Fock solution
- CI solution
- Desity and density-matrix
- Dissociation of H_2.

1-e basis I

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*:

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

where r_A/r_A are distances of electron from nucleus A/B.

1-e basis II

Symmetry-adapted atomic orbitals:

$$\phi_1(\mathrm{r}) = 1\sigma_{\mathrm{g}} = N_g[1\mathbf{s_A}(\mathrm{r}) + 1\mathbf{s_B}(\mathrm{r})]$$
$$\phi_2(\mathrm{r}) = 1\sigma_{\mathrm{u}} = N_u[1\mathbf{s_A}(\mathrm{r}) - 1\mathbf{s_B}(\mathrm{r})]$$

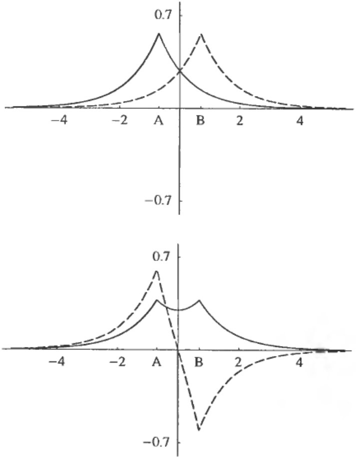
where

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

where it can be shown (see Piela, Appendix R):

$$S = \int 1\mathbf{s_A}(\mathrm{r})1\mathbf{s_B}(\mathrm{r})\mathrm{dr} = (1 + \mathrm{R} + \frac{1}{3}\mathrm{R}^2)\exp(-\mathrm{R}).$$

1-e basis III



All figures from: *Molecular Electronic Structure Theory* by Helgaker *et al.*.

1-e basis IV

N-electron basis:

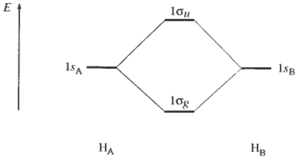


Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

With two electrons of opposite spins in either of these orbitals we get two molecular wavefunctions. Both of these are *singlet* states.

$$|{}^1\Sigma_g^+(g^2)\rangle = |1\sigma_{\rm g}^2\rangle = a^\dagger_{1\alpha}a^\dagger_{1\beta}|{\rm vac}\rangle$$
$$|{}^1\Sigma_g^+(u^2)\rangle = |1\sigma_{\rm u}^2\rangle = a^\dagger_{2\alpha}a^\dagger_{2\beta}|{\rm vac}\rangle$$

1-e basis V

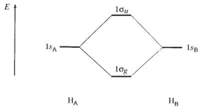


Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

And with other combinations of spins and orbitals we get two more classes of molecular wavefunctions. One is a singlet and the other class of three states is a triplet.

$$|^3\Sigma_u^+\rangle = \begin{cases} a_{2\alpha}^\dagger a_{1\alpha}^\dagger|\mathrm{vac}\rangle \\ \frac{1}{\sqrt{2}}(a_{2\alpha}^\dagger a_{1\beta}^\dagger + a_{2\beta}^\dagger a_{1\alpha}^\dagger)|\mathrm{vac}\rangle \\ a_{2\beta}^\dagger a_{1\beta}^\dagger|\mathrm{vac}\rangle \end{cases}$$

$$|^1\Sigma_u^+\rangle = \frac{1}{\sqrt{2}}(a_{2\alpha}^\dagger a_{1\beta}^\dagger - a_{2\beta}^\dagger a_{1\alpha}^\dagger)|\mathrm{vac}\rangle$$

1-e basis VI

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 Σ.

The spin multiplicity $2S + 1$ of the molecular state is indicated as a superscript on the left.

And for Σ 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 Σ states.

Restricted HF I

See Szabo & Ostlund secs. 2.3.1 and 2.3.5

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

Notation:

$$\begin{aligned} H &= h(1) + h(2) + \frac{1}{r_{12}} \\ &= \mathcal{O}_1 + \mathcal{O}_2 \end{aligned}$$

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.

Restricted HF II

We will show (in class) that:

$$\begin{aligned}\langle\Psi|\mathcal{O}_1|\Psi\rangle &= \langle 1|h|1\rangle + \langle 2|h|2\rangle \\ &= h_{11} + h_{22}.\end{aligned}$$

and

$$\begin{aligned}\langle\Psi|\mathcal{O}_2|\Psi\rangle = &\int dx_1 dx_2 \chi_1^*(x_1)\chi_2^*(x_2)\frac{1}{r_{12}}\chi_1(x_1)\chi_2(x_2) \\ &- \int dx_1 dx_2 \chi_1^*(x_1)\chi_2^*(x_2)\frac{1}{r_{12}}\chi_2(x_1)\chi_1(x_2)\end{aligned}$$

and, defining

$$\begin{aligned}\langle ij|kl\rangle &= \langle\chi_i\chi_j|\chi_k\chi_l\rangle \\ &= \int dx_1 dx_2 \chi_i^*(x_1)\chi_j^*(x_2)\frac{1}{r_{12}}\chi_k(x_1)\chi_l(x_2)\end{aligned}$$

Restricted HF III

we get

$$\langle \Psi | \mathcal{O}_2 | \Psi \rangle = \langle 12|12 \rangle - \langle 12|21 \rangle \equiv \langle 12||12 \rangle.$$

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:

$$\begin{aligned} E_{\mathrm{HF}} &= \langle \Psi | \mathcal{H} | \Psi \rangle \\ &= \langle 1|h|1 \rangle + \langle 2|h|2 \rangle + \langle 12|12 \rangle - \langle 12|21 \rangle. \end{aligned}$$

Restricted HF IV

Now we evaluate the HF energy for $|^1\Sigma_g^+(g^2)\rangle$.
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

$$
\begin{aligned}
\langle 1|h|1\rangle &= \int dx \chi_1^*(x) h(r) \chi_1(x) \\
&= \int d\mathrm{r} d\sigma \phi_1^*(\mathrm{r}) \alpha^*(\sigma) \mathrm{h}(\mathrm{r}) \phi_1(\mathrm{r}) \alpha(\sigma) \\
&= \int d\sigma \alpha^*(\sigma)\alpha(\sigma) \quad \times \quad \int d\mathrm{r} \phi_1^*(\mathrm{r}) \mathrm{h}(\mathrm{r}) \phi_1(\mathrm{r}) \\
&= \quad 1 \quad \times \quad \langle 1|h|1\rangle_{\mathcal{R}} \\
&= \langle 1|h|1\rangle_{\mathcal{R}}.
\end{aligned}
$$

Similarly show that

$$
\begin{aligned}
\langle 12|12\rangle &= \langle 11|11\rangle_{\mathcal{R}} \\
\langle 12|21\rangle &= 0.
\end{aligned}
$$

Restricted HF VI

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

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

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.

Restricted HF VII

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.

Restricted HF VIII

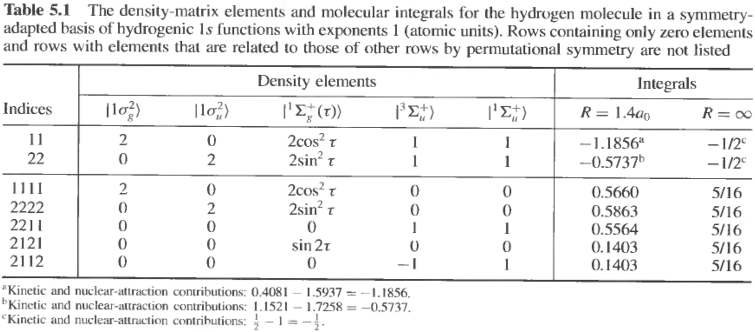


Table 5.1 The density-matrix elements and molecular integrals for the hydrogen molecule in a symmetry-adapted basis of hydrogenic 1*s* functions with exponents 1 (atomic units). Rows containing only zero elements and rows with elements that are related to those of other rows by permutational symmetry are not listed

Indices	Density elements					Integrals	
	$\lvert 1\sigma_g^2\rangle$	$\lvert 1\sigma_u^2\rangle$	$\lvert {}^1\Sigma_g^+(\tau)\rangle$	$\lvert {}^3\Sigma_u^+\rangle$	$\lvert {}^1\Sigma_u^+\rangle$	$R = 1.4a_0$	$R = \infty$
11	2	0	$2\cos^2\tau$	1	1	−1.1856[a]	−1/2[c]
22	0	2	$2\sin^2\tau$	1	1	−0.5737[b]	−1/2[c]
1111	2	0	$2\cos^2\tau$	0	0	0.5660	5/16
2222	0	2	$2\sin^2\tau$	0	0	0.5863	5/16
2211	0	0	0	1	1	0.5564	5/16
2121	0	0	$\sin 2\tau$	0	0	0.1403	5/16
2112	0	0	0	−1	1	0.1403	5/16

[a] Kinetic and nuclear-attraction contributions: 0.4081 − 1.5937 = −1.1856.

[b] Kinetic and nuclear-attraction contributions: 1.1521 − 1.7258 = −0.5737.

[c] Kinetic and nuclear-attraction contributions: $\frac{1}{2} - 1 = -\frac{1}{2}$.

Restricted HF IX

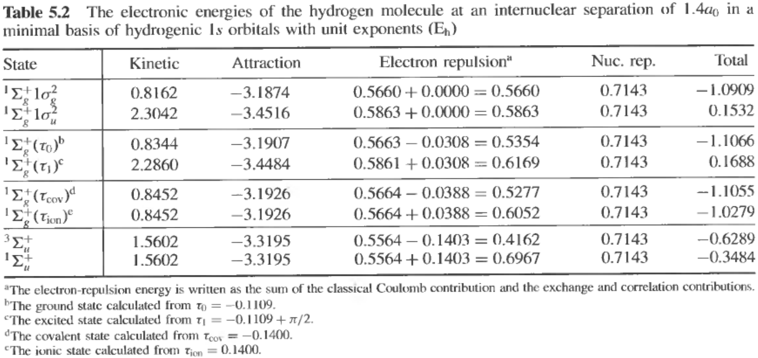


Table 5.2 The electronic energies of the hydrogen molecule at an internuclear separation of $1.4a_0$ in a minimal basis of hydrogenic 1*s* orbitals with unit exponents (E_h)

State	Kinetic	Attraction	Electron repulsion[a]	Nuc. rep.	Total
$^1\Sigma_g^+ 1\sigma_g^2$	0.8162	−3.1874	$0.5660 + 0.0000 = 0.5660$	0.7143	−1.0909
$^1\Sigma_g^+ 1\sigma_u^2$	2.3042	−3.4516	$0.5863 + 0.0000 = 0.5863$	0.7143	0.1532
$^1\Sigma_g^+(\tau_0)$[b]	0.8344	−3.1907	$0.5663 - 0.0308 = 0.5354$	0.7143	−1.1066
$^1\Sigma_g^+(\tau_1)$[c]	2.2860	−3.4484	$0.5861 + 0.0308 = 0.6169$	0.7143	0.1688
$^1\Sigma_g^+(\tau_{\text{cov}})$[d]	0.8452	−3.1926	$0.5664 - 0.0388 = 0.5277$	0.7143	−1.1055
$^1\Sigma_g^+(\tau_{\text{ion}})$[e]	0.8452	−3.1926	$0.5664 + 0.0388 = 0.6052$	0.7143	−1.0279
$^3\Sigma_u^+$	1.5602	−3.3195	$0.5564 - 0.1403 = 0.4162$	0.7143	−0.6289
$^1\Sigma_u^+$	1.5602	−3.3195	$0.5564 + 0.1403 = 0.6967$	0.7143	−0.3484

[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 $\tau_{\text{ion}} = 0.1400$.

Restricted HF X

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.

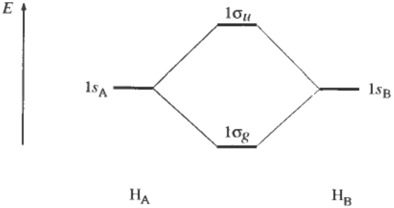


Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

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.

Restricted HF XI

Summary so far:

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

$$\begin{aligned} E_{\mathrm{HF}} &= \langle\Psi|\mathcal{H}|\Psi\rangle \\ &= \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle. \end{aligned}$$

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

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

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.

Restricted HF XIII

Chemist's Notation

$$\begin{aligned}\langle ij|kl\rangle &= \langle \chi_i\chi_j|\chi_k\chi_l\rangle \\ &= \int dx_1 dx_2 \chi_i^*(x_1)\chi_j^*(x_2)\frac{1}{r_{12}}\chi_k(x_1)\chi_l(x_2) \\ &= \int dx_1 dx_2 \chi_i^*(x_1)\chi_k(x_1)\frac{1}{r_{12}}\chi_j^*(x_2)\chi_l(x_2) \\ &= (ik|jl)\end{aligned}$$

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:

$$\rho(\mathrm{r}_1) = \int \gamma_1(x_1, x_1) d\sigma_1$$

$$\rho(\mathrm{r}_1, \mathrm{r}_2) = \int \gamma_2(x_1, x_2, x_1, x_2) d\sigma_1 d\sigma_2$$

Interpretation:
The one-electron density $\rho(\mathrm{r}_1)$ is proportional to the probability of finding an electron at position r_1.
The two-electron density $\rho(\mathrm{r}_1, \mathrm{r}_2)$ represents the probability of simultaneously finding two electrons at positions r_1 and r_2 in the molecule.

Density-matrices III

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 $\Psi^*\Psi$:

$$\begin{aligned}
&\Psi^*(x_1, x_2)\Psi(x_1', x_2) \\
&= \frac{1}{2}[\chi_1^*(x_1)\chi_2^*(x_2)\chi_1(x_1')\chi_2(x_2) \\
&\quad + \chi_2^*(x_1)\chi_1^*(x_2)\chi_2(x_1')\chi_1(x_2) \\
&\quad - \chi_1^*(x_1)\chi_2^*(x_2)\chi_2(x_1')\chi_1(x_2) \\
&\quad - \chi_2^*(x_1)\chi_1^*(x_2)\chi_1(x_1')\chi_2(x_2)] \\
&= \frac{1}{2}[\chi_1^*(1)\chi_1(1')\chi_2^*(2)\chi_2(2) + \chi_2^*(1)\chi_2(1')\chi_1^*(2)\chi_1(2) \\
&\quad - \chi_1^*(1)\chi_2(1')\chi_2^*(2)\chi_1(2) - \chi_2^*(1)\chi_1(1')\chi_1^*(2)\chi_2(2)]
\end{aligned}$$

Density-matrices IV

Therefore the one-electron density matrix is

$$\begin{aligned}\gamma_1(x_1, x_1') &= 2\int \Psi^*(x_1, x_2)\Psi(x_1', x_2)dx_2 \\ &= \chi_1^*(x_1)\chi_1(x_1') + \chi_2^*(x_1)\chi_2(x_1')\end{aligned}$$

And using $\chi_i(x) = \phi_i(\mathrm{r})\omega_\mathrm{i}(\sigma)$, the density is

$$\begin{aligned}\rho(\mathrm{r}_1) &= \int \gamma_1(x_1, x_1)d\sigma_1 \\ &= \phi_1^*(\mathrm{r}_1)\phi_1(\mathrm{r}_1) + \phi_2^*(\mathrm{r}_1)\phi_2(\mathrm{r}_1)\end{aligned}$$

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

$$\rho(\mathrm{r}) = \sum_{i=1}^{N} \phi_i^*(\mathrm{r})\phi_\mathrm{i}(\mathrm{r})$$

Density-matrices V

The two-electron density matrix is quite simply (no integration needed for the 2-electron wavefunction):

$$\begin{aligned}\gamma_2(x_1, x_2, x_1', x_2') &= \frac{2(2-1)}{2}\Psi^*(x_1, x_2)\Psi(x_1', x_2') \\ &= \frac{1}{2}[\chi_1^*(1)\chi_1(1')\chi_2^*(2)\chi_2(2') + \chi_2^*(1)\chi_2(1')\chi_1^*(2)\chi_1(2') \\ &- \chi_1^*(1)\chi_2(1')\chi_2^*(2)\chi_1(2') - \chi_2^*(1)\chi_1(1')\chi_1^*(2)\chi_2(2')]\end{aligned}$$

So, if Ψ is a singlet state with $\chi_1 = \phi_1\alpha$ and $\chi_2 = \phi_2\beta$ then the two-elecron density is

$$\begin{aligned}\rho(\mathrm{r}_1, \mathrm{r}_2) &= \int \gamma_2(x_1, x_2, x_1, x_2) d\sigma_1 d\sigma_2 \\ &= \frac{1}{2}[\phi_1^*(1)\phi_1(1)\phi_2^*(2)\phi_2(2) + \phi_2^*(1)\phi_2(1)\phi_1^*(2)\phi_1(2)]\end{aligned}$$

RHF:Dissociation I

Back to H_2: For $|1\sigma_{\mathrm{g}}^2\rangle = |\phi_1\alpha, \phi_1\beta\rangle$ and $|1\sigma_{\mathrm{u}}^2\rangle = |\phi_2\alpha, \phi_2\beta\rangle$:

$$\begin{aligned}
\rho_{1\sigma_{\mathrm{g}}^2}(\mathrm{r}) &= 2\phi_1^2(\mathrm{r}) \\
\rho_{1\sigma_{\mathrm{u}}^2}(\mathrm{r}) &= 2\phi_2^2(\mathrm{r}) \\
\rho_{1\sigma_{\mathrm{g}}^2}(\mathrm{r}_1, \mathrm{r}_2) &= \phi_1^2(\mathrm{r}_1)\phi_1^2(\mathrm{r}_2) \\
\rho_{1\sigma_{\mathrm{u}}^2}(\mathrm{r}_1, \mathrm{r}_2) &= \phi_2^2(\mathrm{r}_1)\phi_2^2(\mathrm{r}_2)
\end{aligned}$$

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.

RHF:Dissociation II

Helgaker *et al.*

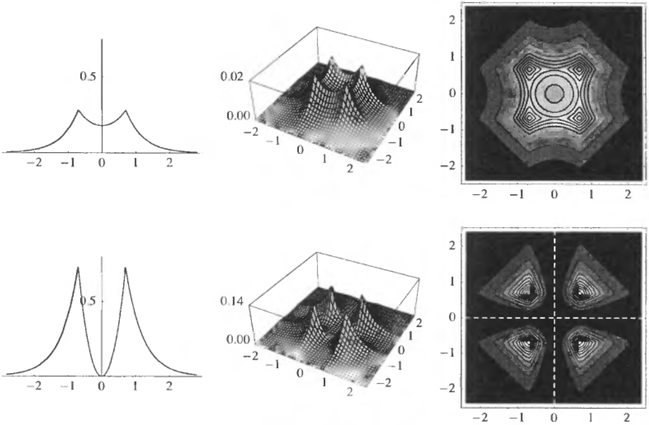


Fig. 5.4. The one- and two-electron density functions of the bonding $|1\sigma_g^2\rangle$ (upper plots) and antibonding $|1\sigma_u^2\rangle$ (lower plots) configurations of the hydrogen molecule on the molecular axis (atomic units). The

RHF:Dissociation III

Something is wrong. The two-electron density matrix of the $1\sigma_g^2$ 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., 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, $S = \langle 1\mathbf{s_A}(\mathrm{r}) | 1\mathbf{s_B}(\mathrm{r}) \rangle = 0$. So

$$\begin{aligned} \phi_1(\mathrm{r}) &= 1\sigma_{\mathrm{g}} = 2^{-1/2}[1\mathbf{s_A}(\mathrm{r}) + 1\mathbf{s_B}(\mathrm{r})] \\ \phi_2(\mathrm{r}) &= 1\sigma_{\mathrm{u}} = 2^{-1/2}[1\mathbf{s_A}(\mathrm{r}) - 1\mathbf{s_B}(\mathrm{r})]. \end{aligned}$$

Now let's write $|1\sigma_{\mathrm{g}}^2\rangle$ in terms of the atomic (non-symmetric) basis functions

$$\begin{aligned} |1\sigma_{\mathrm{g}}^2\rangle &= |\phi_1\alpha, \phi_1\beta\rangle \\ &= \phi_1(\mathrm{r}_1)\phi_1(\mathrm{r}_2) \times \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\ &= \phi_1(\mathrm{r}_1)\phi_1(\mathrm{r}_2)\ {}^1\Sigma\ . \end{aligned}$$

RHF:Dissociation V

Focus on the spatial part $\phi_1(\mathrm{r}_1)\phi_1(\mathrm{r}_2)$ and use the notation $A = 1\mathbf{s}_\mathbf{A}(\mathrm{r})$ and $B = 1\mathbf{s}_\mathbf{B}(\mathrm{r})$.

$$\phi_1(\mathrm{r}_1)\phi_1(\mathrm{r}_2) = \frac{1}{2}[A(1)A(2) + B(1)B(2) + A(1)B(2) + B(1)A(2)], \quad \text{so,}$$

$$|1\sigma_\mathrm{g}^2\rangle = \frac{1}{2}|A^2\rangle + \frac{1}{2}|B^2\rangle + \frac{1}{\sqrt{2}}|AB\rangle.$$

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

Q: Show that at the dissociation limit, the states $|A^2\rangle$, $|B^2\rangle$ and $|AB\rangle$ 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 $R \to \infty$):

$$\begin{aligned} E(g^2) &= \langle 1\sigma_{\mathrm{g}}^2|\mathcal{H}|1\sigma_{\mathrm{g}}^2\rangle \\ &= \langle \frac{1}{2}A^2 + \frac{1}{2}B^2 + \frac{1}{\sqrt{2}}AB|\mathcal{H}|\frac{1}{2}A^2 + \frac{1}{2}B^2 + \frac{1}{\sqrt{2}}AB\rangle \\ &= \frac{1}{4}E(\mathrm{H}^-) + \frac{1}{4}E(\mathrm{H}^-) + \frac{1}{2}(2E(\mathrm{H})) \\ &= E(\mathrm{H}) + \frac{1}{2}E(\mathrm{H}^-). \end{aligned}$$

So, as expected, we do not get $2E(\mathrm{H})$.

RHF:Dissociation VII

Q: What happened to the cross terms in expression for $E(g^2)$? Show that they all vanish in the $R \to \infty$ limit.

Q: On the previous page, how did we get from the second to the third line of the derivation? Evaluate matrix elements $\langle A^2|\mathcal{H}|A^2\rangle$ 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.

RHF:Dissociation VIII

Q: How is $\langle AB|\mathcal{H}|AB\rangle = 2E(\mathrm{H})$? To show this, start with $\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{V}$, where $\mathcal{V}$ includes the e-e and e-n interaction terms between the two H-atoms. In the $R \rightarrow \infty$ limit, the e-n interaction goes to zero, and as long as the electrons are on either atom (do we need to assume that this is the case?), the e-e interaction also goes to zero, so $\mathcal{V} \rightarrow 0$. Use this to evaluate the matrix element and show that it is equal to $2E(\mathrm{H})$.

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

RHF:Dissociation IX

Q: Show the previous result starting from the energy expression for $|1\sigma_{\mathrm{g}}^2\rangle$:

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

Hint: Expand the symmetry-adapted atomic orbital ϕ_1 in terms of the $1\mathbf{s_A}(\mathrm{r})$ and $1\mathbf{s_B}(\mathrm{r})$ basis functions and use

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

Q: Spin functions can often (but not always) be integrated out early in a derivation. This is usually a good idea, particularly, as is the case here, when all wavefunctions have the same spin state. Re-derive the dissociation energy of the $E(g^2)$ state by first integrating out the singlet spin function. Doing so will allow you to focus only on the spatial parts of the wavefunctions.

CI I

The Configuration Interaction wavefunction:
This is a wavefunction made up of a linear combination of all allowed single determinants. For *gerade* ground state of H_2 in this *minimal* basis set this takes the simple form:

$$|^1\Sigma_g^+(\tau)\rangle = \cos(\tau)|1\sigma_{\mathrm{g}}^2\rangle + \sin(\tau)|1\sigma_{\mathrm{u}}^2\rangle.$$

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

Q: Show that $\langle ^1\Sigma_g^+(\tau)|^1\Sigma_g^+(\tau+\pi/2)\rangle = 0$.

CI II

Now we calculate the energy of the system with the CI wavefunction:

$$|{}^1\Sigma_g^+(\tau)\rangle = \cos(\tau)|1\sigma_{\mathrm{g}}^2\rangle + \sin(\tau)|1\sigma_{\mathrm{u}}^2\rangle.$$

The energy of H_2 now becomes (real orbitals):

$$\begin{aligned} E(\tau) &= \langle {}^1\Sigma_g^+(\tau)|\mathcal{H}|{}^1\Sigma_g^+(\tau)\rangle \\ &= \cos^2(\tau)E(g^2) + \sin^2(\tau)E(u^2) + 2\sin(\tau)\cos(\tau)\langle 1\sigma_{\mathrm{g}}^2|\mathcal{H}|1\sigma_{\mathrm{u}}^2\rangle \end{aligned}$$

Q: Show that $\langle 1\sigma_{\mathrm{g}}^2|\mathcal{H}|1\sigma_{\mathrm{u}}^2\rangle = \langle 11|22\rangle = (12|12)$. This can also be written as $(21|21) = g_{2121}$ due to symmetry of these integrals.

CI III

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 τ 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.

CI IV

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):

$$|^1\Sigma_g^+(\tau_0)\rangle_e = 0.9939|1\sigma_{\mathrm{g}}^2\rangle - 0.1106|1\sigma_{\mathrm{u}}^2\rangle$$
$$|^1\Sigma_g^+(\tau_1)\rangle_e = 0.1106|1\sigma_{\mathrm{g}}^2\rangle + 0.9939|1\sigma_{\mathrm{u}}^2\rangle$$

I.e., the g.s. is dominated with the HF solution $|1\sigma_{\mathrm{g}}^2\rangle$ 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:

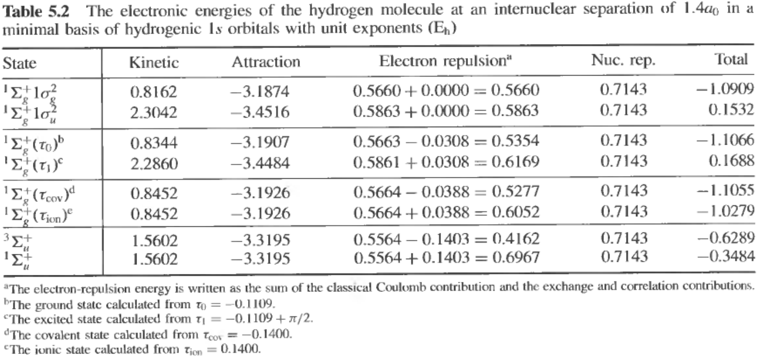


Table 5.2 The electronic energies of the hydrogen molecule at an internuclear separation of $1.4a_0$ in a minimal basis of hydrogenic $1s$ orbitals with unit exponents (E_h)

State	Kinetic	Attraction	Electron repulsion[a]	Nuc. rep.	Total
$^1\Sigma_g^+ 1\sigma_g^2$	0.8162	−3.1874	$0.5660 + 0.0000 = 0.5660$	0.7143	−1.0909
$^1\Sigma_g^+ 1\sigma_u^2$	2.3042	−3.4516	$0.5863 + 0.0000 = 0.5863$	0.7143	0.1532
$^1\Sigma_g^+(\tau_0)$[b]	0.8344	−3.1907	$0.5663 - 0.0308 = 0.5354$	0.7143	−1.1066
$^1\Sigma_g^+(\tau_1)$[c]	2.2860	−3.4484	$0.5861 + 0.0308 = 0.6169$	0.7143	0.1688
$^1\Sigma_g^+(\tau_{\mathrm{cov}})$[d]	0.8452	−3.1926	$0.5664 - 0.0388 = 0.5277$	0.7143	−1.1055
$^1\Sigma_g^+(\tau_{\mathrm{ion}})$[e]	0.8452	−3.1926	$0.5664 + 0.0388 = 0.6052$	0.7143	−1.0279
$^3\Sigma_u^+$	1.5602	−3.3195	$0.5564 - 0.1403 = 0.4162$	0.7143	−0.6289
$^1\Sigma_u^+$	1.5602	−3.3195	$0.5564 + 0.1403 = 0.6967$	0.7143	−0.3484

[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 $\tau_{\mathrm{cov}} = -0.1400$.

[e] The ionic state calculated from $\tau_{\mathrm{ion}} = 0.1400$.

CI VI

Energies of these states are listed in table 5.2. We see that the CI g.s. is 1.4% lower than the $|1\sigma_{\rm g}^2\rangle$ 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 $|1\sigma_{\rm u}^2\rangle$ 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.

CI VII

Helgaker *et al.*

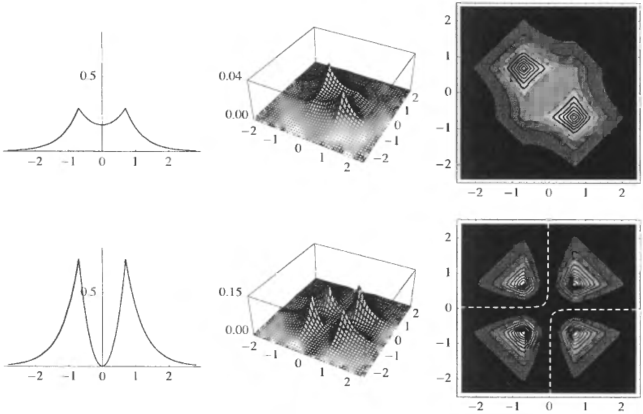


Fig. 5.5. The one- and two-electron density functions of the two-configuration $^1\Sigma_g^+$ ground (upper plots) and excited (lower plots) states of the hydrogen molecule on the molecular axis (atomic units). The two-elect-

CI VIII

Q: Compare the CI and RHF two-electron density matrices for the $1\sigma_g^2$ state in the $R \to \infty$ limit. How do they differ? Does the CI density matrix suggest that the CI wavefunction will exhibit the correct dissociation limit?

Q: 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?

CI IX

Q: 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 $1\mathbf{s_A}(\mathrm{r})$ and $1\mathbf{s_B}(\mathrm{r})$ orbitals, show that the CI wavefunction has indeed introduced Left–Right correlation as shown in Fig. 5.5.

CI X

Notice the following:

- There is very little change in the one-electron density from the RHF case. Here the $|1\sigma_{\rm g}^2\rangle$ (i.e. RHF) state has a weight of 98.8%. The $|1\sigma_{\rm u}^2\rangle$ 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.

CI XI

Dissociation of the CI wavefunction

$$|^1\Sigma_g^+(\tau)\rangle = \cos(\tau)|1\sigma_{\mathrm{g}}^2\rangle + \sin(\tau)|1\sigma_{\mathrm{u}}^2\rangle.$$

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 τ 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

$$\begin{aligned}\langle 11|22\rangle &= \frac{1}{4}\langle (A(1)+B(1))(A(2)+B(2))|(A(1)-B(1))(A(2)-B(2))\rangle \\ &= \frac{1}{4}[\langle AA|AA\rangle + \langle BB|BB\rangle] \\ &= \frac{1}{2}\langle AA|AA\rangle \neq 0\end{aligned}$$

Here we have used the fact that any cross-terms involving A and B will vanish in the large-R limit.

CI XIII

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

$$|{}^1\Sigma_g^+(\tau)\rangle \to \frac{1}{\sqrt{2}}[|1\sigma_{\mathrm{g}}^2\rangle - |1\sigma_{\mathrm{u}}^2\rangle]$$

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

Note that in this limit the weight of the $|1\sigma_{\mathrm{u}}^2\rangle$ state is equal to that of the HF, $|1\sigma_{\mathrm{g}}^2\rangle$, state! As the system dissociates, the weights change.

CI XIV

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

$$\begin{aligned} E(-\pi/4) &= \frac{1}{2}(E(g^2) + E(u^2)) - \langle 11|22\rangle \\ &= 2h_{AA} + \frac{1}{2}\langle AA|AA\rangle - \frac{1}{2}\langle AA|AA\rangle \\ &= 2h_{AA} = 2E(\mathrm{H}). \end{aligned}$$

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

CI XV

In summary:

$$\boxed{H_2(\mathrm{RHF}) \rightarrow \mathrm{H} + \frac{1}{2}\mathrm{H}^-}$$

$$\boxed{H_2(\mathrm{FCI}) \rightarrow 2\mathrm{H}}$$

UHF I

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_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 α-spin electron will be associated with one hydrogen atom and the β-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

$$\chi_1^\alpha(x) = \psi_{1\alpha}(\mathrm{r})\alpha(\omega)$$
$$\chi_1^\beta(x) = \psi_{1\beta}(\mathrm{r})\beta(\omega)$$

where

$$\psi_{1\alpha} = \cos(\theta)\phi_1 + \sin(\theta)\phi_2$$
$$\psi_{1\beta} = \cos(\theta)\phi_1 - \sin(\theta)\phi_2$$

Q: 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.

UHF III

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):

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

- 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.

UHF IV

- Hence show that the energy can be written as a function of the angle θ:

$$\begin{aligned} E(\theta) = {} & 2\cos^2(\theta) h_{gg} + 2\sin^2(\theta) h_{uu} \\ & + 2\cos^4(\theta)\langle gg|gg\rangle + 2\sin^4(\theta)\langle uu|uu\rangle \\ & + 2\sin^2(\theta)\cos^2(\theta)[\langle gu|gu\rangle - 2\langle gg|uu\rangle]. \end{aligned}$$

- 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 θ 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)

UHF V

- 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.