H_2 in a minimal basis

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Many electron basis I

The many-electron basis has two requirements:

- Spin: We need to consider spin-orbitals rather than just spatial orbitals.
- Antisymmetry: The many electron basis functions cannot simply be products of one-electron spin-orbitals. It must be antisymmetric with respect to electron exchange.

Many electron basis II

The first condition is simple enough to take care of. If we have a spatial orbital $\psi(r)$ we can construct two spin-orbitals:

$$\chi(x) = \begin{cases} \psi(r)\alpha(\omega) \\ \psi(r)\beta(\omega) \end{cases} \tag{1}$$

All wavefunctions will be constructed from these spin-orbitals.
We have assumed that there is no difference between the up and down spins states. This *restricted* solution is valid for a closed-shell systems. In general we will want to allow the spatial parts of the two spins to vary independently. This leads to what's known as an *unrestricted* solution. More later.

Many electron basis III

The antisymmetry condition puts restrictions on the kinds of trial wavefunctions we can use. Consider a two-electron case: The following trial wavefunction is not allowed for electrons

$$\Psi^{\mathrm{HP}}(x_1, x_2) = \chi_i(x_1)\chi_j(x_2)$$

This is because $\Psi^{\mathrm{HP}}(x_1, x_2) = \Psi^{\mathrm{HP}}(x_2, x_1)$. I.e., the wavefunction remains invariant on interchanging the electron labels. Such a wavefunction is suitable for bosons and is called the Hartree product (hence, the 'HP' superscript).

Many electron basis IV

To make our trial wavefunction antisymmetric we need it to be of the form:

$$\begin{aligned}\Psi(x_1, x_2) &= \frac{1}{\sqrt{2}}\left(\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right) \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2)\end{vmatrix}\end{aligned}$$

This is called a *Slater determinant*.

Many electron basis V

More generally, for N-electrons the Slater determinant takes the form

$$\Psi(x_1, x_2, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \tag{2}$$

$$\equiv |\chi_i \chi_j \cdots \chi_k\rangle \tag{3}$$

where the last equation is short-hand for writing out the determinant.

Hartree–Fock (in brief) I

So now let us describe the ground state of our N-electron system with the BO approximation using a single Slater determinant:

$$\Psi_0(x_1, x_2, \cdots, x_N) = |\chi_1 \chi_2 \cdots \chi_N\rangle \tag{4}$$

The Hartree–Fock approximation to the ground state energy is found by varying the spin-orbitals $\{\chi_i\}$ to minimize the energy:

$$E_0 \leq E^{\mathrm{HF}} = \min\langle\Psi_0|\mathcal{H}|\Psi_0\rangle \tag{5}$$

subject to the conditions that the spin-orbitals are orthonormal.

Hartree–Fock (in brief) II

As before, but with many more steps, the variational principle leads to the following equations for the spin-orbitals

$$f(i)\chi(x_i) = \epsilon\chi(x_i) \tag{6}$$

where $f(i)$ is an effective operator called the *Fock operator*

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i) \tag{7}$$

where $v^{\mathrm{HF}}(i)$ is the Hartree–Fock *effective* potential that depends on the solutions to the above equations. So we must solve these equations self-consistently: Make a guess for the solutions; construct the potential $v^{\mathrm{HF}}(i)$ from this guess; solve the Fock equations; get new solutions; and repeat till convergence.

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*:

$$
\begin{aligned}
1s_{\mathbf{A}}(\mathbf{r}) &= \frac{1}{\sqrt{\pi}} \exp(-r_A) \\
1s_{\mathbf{B}}(\mathbf{r}) &= \frac{1}{\sqrt{\pi}} \exp(-r_B)
\end{aligned}
$$

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

1-e basis II

Symmetry-adapted atomic orbitals:

$$\phi_1(\mathbf{r}) = 1\sigma_{\mathrm{g}} = N_g[1\mathsf{s}_{\mathbf{A}}(\mathbf{r}) + 1\mathsf{s}_{\mathbf{B}}(\mathbf{r})]$$
$$\phi_2(\mathbf{r}) = 1\sigma_{\mathrm{u}} = N_u[1\mathsf{s}_{\mathbf{A}}(\mathbf{r}) - 1\mathsf{s}_{\mathbf{B}}(\mathbf{r})]$$

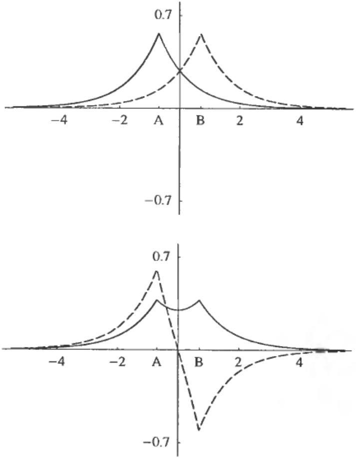
where

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

where

$$S = \int 1\mathsf{s}_{\mathbf{A}}(\mathbf{r}) 1\mathsf{s}_{\mathbf{B}}(\mathbf{r}) d\mathbf{r} = (1 + R + \frac{1}{3}R^2)\exp(-R).$$

1-e basis III



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

1-e basis IV

N-electron basis:

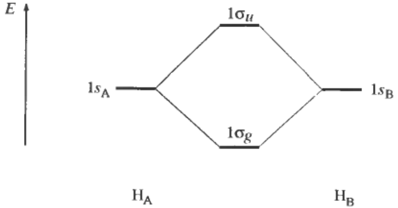


Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

$$|{}^1\Sigma_g^+(g^2)\rangle = |1\sigma_{\mathrm{g}}^2\rangle = a_{1\alpha}^\dagger a_{1\beta}^\dagger|\mathrm{vac}\rangle$$
$$|{}^1\Sigma_g^+(u^2)\rangle = |1\sigma_{\mathrm{u}}^2\rangle = a_{2\alpha}^\dagger a_{2\beta}^\dagger|\mathrm{vac}\rangle$$

1-e basis V

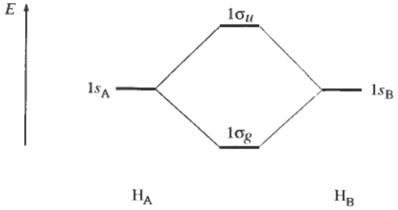


Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

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

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

1-e basis VI

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 $\langle {}^1\Sigma_g^+(\tau)|{}^1\Sigma_g^+(\tau + \pi/2)\rangle = 0$.

Matrix elements I

See Szabo & Ostlund secs. 2.3.1 and 2.3.5

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

Matrix elements 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

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

Matrix elements III

we get

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

The first term is the Coulomb term and the second the exchange term.

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

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

Matrix elements 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.

Matrix elements V

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

Similarly show that

$$
\begin{aligned}
\langle 12|12\rangle &= (11|11) \equiv g_{1111} \\
\langle 12|21\rangle &= 0.
\end{aligned}
$$

The second term on the first line is the *Chemist's notation* used by S&O and the third is the notation used by Helgaker *et al.*

Matrix elements VI

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

$$E(g^2) = 2(1|h|1) + (11|11)$$

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.

Matrix elements VII

Summary so far:

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

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

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

$$E(g^2) = 2(1|h|1) + (11|11)$$

Matrix elements VIII

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:

$$(ij|kl) = (ji|kl) = (ij|lk) = (ji|lk)$$

Matrix elements IX

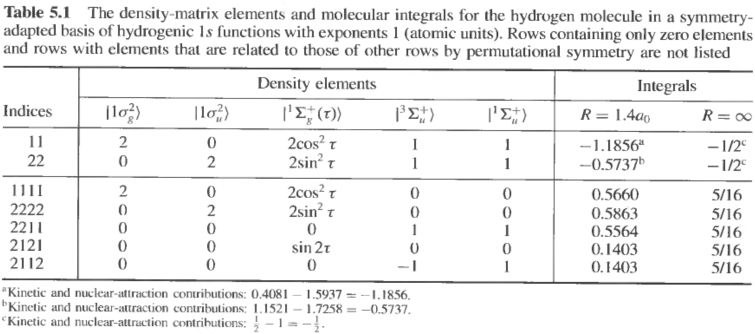


Table 5.1 The density-matrix elements and molecular integrals for the hydrogen molecule in a symmetry-adapted basis of hydrogenic 1*s* functions with exponents 1 (atomic units). Rows containing only zero elements and rows with elements that are related to those of other rows by permutational symmetry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

Indices	Density elements					Integrals	
	$\vert 1\sigma_g^2\rangle$	$\vert 1\sigma_u^2\rangle$	$\vert ^1\Sigma_g^+(\tau)\rangle$	$\vert ^3\Sigma_u^+\rangle$	$\vert ^1\Sigma_u^+\rangle$	$R = 1.4a_0$	$R = \infty$
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: $\frac{1}{2} - 1 = -\frac{1}{2}$.

Matrix elements X

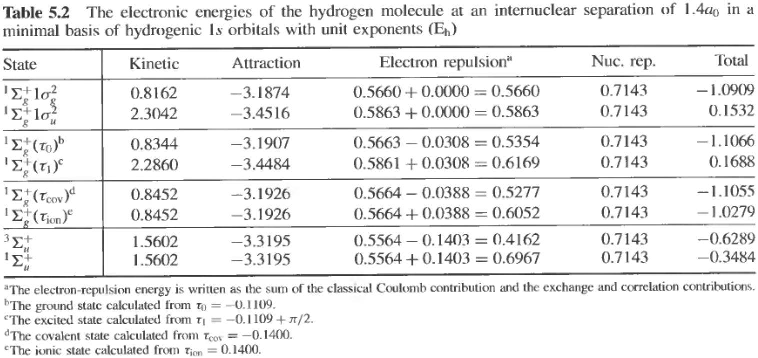


Table 5.2 The electronic energies of the hydrogen molecule at an internuclear separation of $1.4a_0$ in a minimal basis of hydrogenic 1*s* orbitals with unit exponents (E_h)

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
${}^1\Sigma_g^+(\tau_{\mathrm{cov}})$[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 $\tau_{\mathrm{ion}} = 0.1400$.

HF I

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.

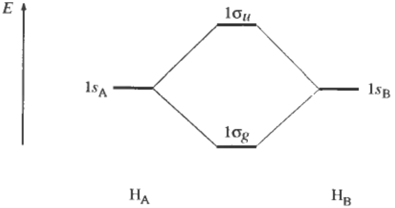


Fig. 5.3. Molecular-orbital energy-level diagram for the hydrogen molecule.

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.

HF II

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.

HF III

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:

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

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

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

HF IV

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 $\Psi^*\Psi$:

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

HF V

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 $\chi_i(x) = \phi_i(\mathbf{r})\omega_i(\sigma)$, the density is

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

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

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

HF VI

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

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

HF VII

Back to H_2: For $|1\sigma_g^2\rangle = |\phi_1\alpha, \phi_1\beta\rangle$ and $|1\sigma_u^2\rangle = |\phi_2\alpha, \phi_2\beta\rangle$:

$$\rho_{1\sigma_g^2}(\mathbf{r}) = 2\phi_1^2(\mathbf{r})$$
$$\rho_{1\sigma_u^2}(\mathbf{r}) = 2\phi_2^2(\mathbf{r})$$
$$\rho_{1\sigma_g^2}(\mathbf{r}_1, \mathbf{r}_2) = \phi_1^2(\mathbf{r}_1)\phi_1^2(\mathbf{r}_2)$$
$$\rho_{1\sigma_u^2}(\mathbf{r}_1, \mathbf{r}_2) = \phi_2^2(\mathbf{r}_1)\phi_2^2(\mathbf{r}_2)$$

Interpretation: Since the two-elecrtron density represents the probability of simultaneously finding two electrons at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ in the molecule, we see here is that the probability of finding an electron at $\mathbf{r}_1$ is unaffected by the electron at $\mathbf{r}_2$. Thus, these single-determinant (Hartree–Fock) wavefunctions do not correlate the electrons.

HF VIII

Helgaker *et al.*

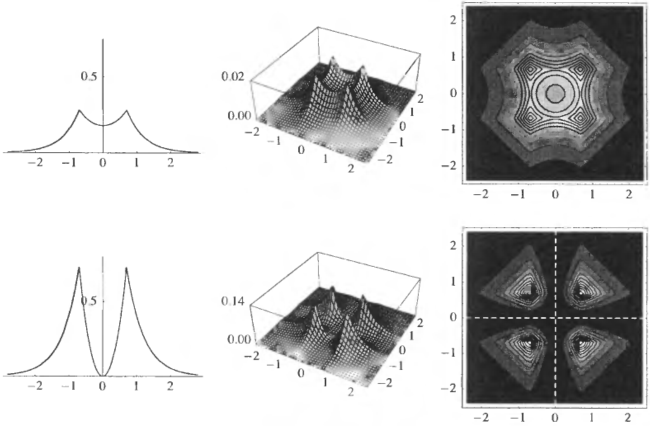


Fig. 5.4. The one- and two-electron density functions of the bonding $|1\sigma_g^2\rangle$ (upper plots) and antibonding $|1\sigma_u^2\rangle$ (lower plots) configurations of the hydrogen molecule on the molecular axis (atomic units). The

HF IX

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, $S = \langle 1\mathbf{s_A}(\mathbf{r}) | 1\mathbf{s_B}(\mathbf{r}) \rangle = 0$. So

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

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

$$\begin{aligned} |1\sigma_{\mathrm{g}}^2\rangle &= |\phi_2\alpha, \phi_2\beta\rangle \\ &= \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \times \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \end{aligned}$$

HF X

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

$$\begin{aligned}\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) &= \frac{1}{2}[A(1)A(2) + B(1)B(2) + A(1)B(2) + B(1)A(2)] \\ &= \frac{1}{2}|A^2\rangle + \frac{1}{2}|B^2\rangle + \frac{1}{\sqrt{2}}|AB\rangle.\end{aligned}$$

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

HF XI

Q: Show that the states $|A^2\rangle$, $|B^2\rangle$ and $|AB\rangle$ orthonormal.

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

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

So, as expected, we do not get $2E(H)$.

HF XII

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

$$E(g^2) = 2(1|h|1) + (11|11)$$

Hint: Expand the symmetry-adapted atomic orbital ϕ_1 in terms of the $1\mathbf{s}_{\mathbf{A}}(\mathbf{r})$ and $1\mathbf{s}_{\mathbf{B}}(\mathbf{r})$ basis functions and use

$$E(A^2) = E(H^-) = 2(A|h|A) + (AA|AA)$$

CI I

The CI wavefunction

Now we will repeat the calculation 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):

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

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

CI II

So the energy of the CI state is

$$E(\tau) = \cos^2(\tau)E(g^2) + \sin^2(\tau)E(u^2) + \sin(2\tau)(21|21).$$

To find the optimum τ we minimize to get

$$\tan(2\tau) = \frac{2(21|21)}{E(g^2) - E(u^2)}$$

so solutions are

$$\tau_n = \frac{1}{2}\arctan\left[\frac{2(21|21)}{E(g^2) - E(u^2)}\right] + \frac{n\pi}{2},$$

where n is an integer.

CI III

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%.

CI IV

Here is Table 5.2 from Helgaker *et al.* again:

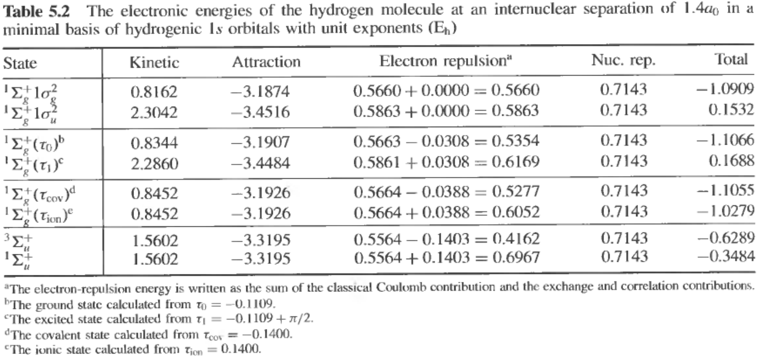


Table 5.2 The electronic energies of the hydrogen molecule at an internuclear separation of $1.4a_0$ in a minimal basis of hydrogenic 1*s* orbitals with unit exponents (E_h)

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
$^1\Sigma_g^+(\tau_{\mathrm{cov}})$[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 V

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 later demonstrate that this mixing of states allows the CI g.s. to correctly dissociate into two H-atoms at $R \rightarrow \infty$, whereas, 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 VI

Helgaker *et al.*

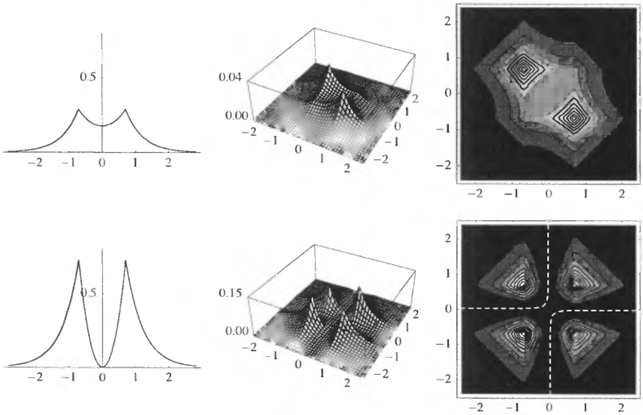


Fig. 5.5. The one- and two-electron density functions of the two-configuration $^1\Sigma_g^+$ ground (upper plots) and excited (lower plots) states of the hydrogen molecule on the molecular axis (atomic units). The two-elect-

CI VII

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 $1s_{\mathbf{A}}(\mathbf{r})$ and $1s_{\mathbf{B}}(\mathbf{r})$ orbitals, show that the CI wavefunction has indeed introduced Left–Right correlation as shown in Fig. 5.5.

CI VIII

Notice the following:

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

Dissociation of the CI wavefunction

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

with an energy

$$E(\tau) = \cos^2(\tau)E(g^2) + \sin^2(\tau)E(u^2) + \sin(2\tau)(12|12)$$

where

$$\tau_n = \frac{1}{2}\arctan\left[\frac{2(12|12)}{E(g^2) - E(u^2)}\right] + \frac{n\pi}{2}$$

CI X

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

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

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

$$\begin{aligned}(12|12) &= \frac{1}{4}((A(1)+B(1))(A(1)-B(1))|(A(2)+B(2))(A(2)-B(2))) \\ &= \frac{1}{4}[(AA|AA)+(BB|BB)] \\ &= \frac{1}{2}(AA|AA) \neq 0\end{aligned}$$

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

CI XI

Consequently, for $R \to \infty$, $\frac{2(21|21)}{E(g^2)-E(u^2)} \to -\infty$, 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

$$|{}^1\Sigma_g^+(\tau)\rangle \to \frac{1}{\sqrt{2}}[|1\sigma_{\mathrm{g}}^2\rangle - |1\sigma_{\mathrm{u}}^2\rangle]$$
$$E(\tau) \to \frac{1}{2}(E(g^2) + E(u^2)) - (12|12)$$

CI XII

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

$$\begin{aligned} E(-\pi/4) &= \frac{1}{2}(E(g^2) + E(u^2)) - (12|12) \\ &= 2h_{AA} + \frac{1}{2}(AA|AA) - \frac{1}{2}(AA|AA) \\ &= 2h_A A = 2E(\mathrm{H}). \end{aligned}$$

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

CI XIII

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

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

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):

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

- 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:

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

- 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.