VARIABLE SEPARATION FOR $\text{H}_2^+$ WAVEFUNCTION

The hamiltonian for the electronic motion in $\text{H}_2^+$ is given by

$$\hat{H}_d = -\frac{1}{2} \nabla^2 + \frac{\epsilon^2}{R} - \frac{\epsilon^2}{|R - R/2|} - \frac{\epsilon^2}{|R_+ R/2|}$$

Define two new variables

$$\xi = \frac{1}{R} \left( r_A + r_B \right) \quad \eta = \frac{1}{R} \left( r_A - r_B \right)$$

and the azimuthal angle $\phi$ in the plane $\Pi$ to the internuclear axis (the $z$-axis).

The $\nabla^2$ operator in these coordinates becomes

$$\nabla^2 = \frac{4}{R^2 (\xi^2 - \eta^2)} \left\{ \frac{1}{2} \frac{d}{d\xi} \left( \frac{\xi^2 - 1}{2} \frac{dX}{d\xi} \right) + \frac{1}{2} \frac{d}{d\eta} \left( \frac{1}{2} \frac{dY}{d\eta} \right) + \frac{\xi^2 - \eta^2}{(\xi^2 - 1) (1 - \eta^2)} \frac{d^2}{d\phi^2} \right\}$$

Note, that these variables are all dimensionless, and the spatial scale of the problem is set by the value of $R$. The range of the variables in $0 < \xi < \infty$, $-1 < \eta < 1$, $0 \leq \phi \leq 2\pi$, $1 < \xi \leq \infty$ ($\xi$, $\eta$, $\phi$).

The variables form the confocal elliptic coordinates.

Variable separation is effected by writing the wavefunction in the form

$$\Phi = X(\xi) \ Y(\eta) \ Z(\phi)$$

where $Z(\phi) = e^{i m \phi}$ $m = 0, 1, \ldots$.

The functions $X$ and $Y$ satisfy the equations

$$\frac{d}{d\xi} \left[ (\xi^2 - 1) \frac{dX}{d\xi} \right] + \frac{R^2}{2} \left( \frac{E - 1}{R} \right) \xi^2 + 2R \xi - \frac{m^2}{\xi^2 - 1} + \mu \right] X = 0$$

$$\frac{d}{d\eta} \left[ (1 - \eta^2) \frac{dY}{d\eta} \right] + \frac{R^2}{2} \left( \frac{E - 1}{R} \right) \eta^2 + \frac{m^2}{1 - \eta^2} + \mu \right] Y = 0$$

The Schrödinger equation is

$$\frac{2}{\xi} \left[ (\xi^2 - 1) \frac{d^2 \Phi}{d\xi^2} \right] + \frac{1}{\eta} \left[ (1 - \eta^2) \frac{d^2 \Phi}{d\eta^2} \right] + \left[ \frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right] \frac{\partial^2 \Phi}{\partial \phi^2}$$

$$+ \left[ \frac{R^2}{2} \left( \frac{E - 1}{R} \right) (\xi^2 - \eta^2) + 2R \xi \right] \phi = 0$$
$\mu$ is the separation constant.
The solutions are characterised by three quantum numbers $\lambda$, $\eta_x$, $\eta_y$ which are the number of zeros of the three separated functions.
A peculiarity arising out of the separation is that for a given $\lambda$, there can be two $E(R)$ curves corresponding to different pairs of $(\eta_x, \eta_y)$ which cross each other. That is, for a given $\lambda$
$$E(R; \eta_x, \eta_y) = E(R; \eta'_x, \eta'_y)$$
for some $R$.

The two equations above can be solved numerically. The curve $E(R)$ can be obtained from these for both, the $\Phi_g$ and $\Phi_u$ states.
The $E_u(R; 1s)$ curve from this calculation matches the curve which we obtained earlier by constructing $\Phi_u$ using LCAO.
The $E_g(R; 1s)$ curve lies lower and has a minimum at a smaller value of $R_0$ than the curve based on constructing $\Phi_g$ using LCAO.
WAVEFUNCTION FOR $H_2$

The Hamiltonian for the $H_2$ molecule is

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} + \frac{e^2}{|\vec{R}_2 + \vec{R}/2|} + \frac{e^2}{|\vec{R}_1 + \vec{R}/2|} - \frac{e^2}{|\vec{R}_2 + \vec{R}/2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} + \frac{e^2}{R}$$

The Schrödinger equation with this Hamiltonian cannot be solved exactly, nor is the separation of variables possible.

We therefore use an approach similar to the one that we used for atoms to obtain the approximate wavefunction.

In atoms we constructed the many-electron wavefunction by a linear combination of single electron (atomic) wavefunctions which, in combination with the correct spin wave functions, obeying Pauli's exclusion principle.

Likewise we construct the molecular wavefunctions by linear combinations of 1-electron Molecular Orbital wavefunctions, in combination with appropriate spin functions:

The spin wavefunction for a 2-electron system is either a singlet ($S=0$) or a triplet ($S=1$) corresponding to the functions

$$\chi_{00} = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) - \beta(1) \alpha(2) \right]$$

$$\chi_{10} = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) + \beta(1) \alpha(2) \right]$$

$$\chi_{11} = \alpha(1) \alpha(2)$$

$$\chi_{1-1} = \beta(1) \beta(2)$$

1-electron

Recall that the (spatial) molecular orbital wavefunctions are

$$\Phi_g(R,r) = \frac{1}{\sqrt{2}} \left( \Psi(R_A) + \Psi(R_B) \right)$$

$$\Phi_u(R,r) = \frac{1}{\sqrt{2}} \left( \Psi(R_A) - \Psi(R_B) \right)$$

and $\Phi_g$ corresponds to the lowest energy when $\Psi(R_{A,B}) = \Psi_{1s}(R_{A,B})$
MOLECULAR ORBITAL METHOD

In accordance with the exclusion principle, states corresponding to $\chi_{00}$ must have an anti-symmetric spatial part, and there are three possible linear combinations of molecular orbitals for the singlet state:

$$\Psi_A (1,2) = \Phi_g (1) \Phi_g (2) \chi_{00} (1,2)$$
$$\Psi_B = \Phi_u (1) \Phi_u (2) \chi_{00} (1,2)$$
$$\Psi_C = \frac{1}{\sqrt{2}} \left[ \Phi_g (1) \Phi_u (2) + \Phi_u (1) \Phi_g (2) \right] \chi_{00} (1,2)$$

$^1\Sigma_g^+$ state of $H_2$
$^1\Sigma_u^+$ state of $H_2$
$^1\Sigma_u^+$ state of $H_2$

and only one possibility for the triplet state with anti-symmetric spatial part:

$$\Psi_B (1,2) = \frac{1}{\sqrt{2}} \left[ \Phi_g (1) \Phi_u (2) - \Phi_g (2) \Phi_u (1) \right] \chi_{11} (1,2)$$
$$\frac{1}{\sqrt{2}} \left[ \chi_{11} (1,2) \right]$$
$$\frac{1}{\sqrt{2}} \left[ \chi_{10} (1,2) \right]$$

$^3\Sigma_u^+$ state of $H_2$

The first case corresponds to the lowest energy.

To obtain the energies corresponding to these states we re-write the Hamiltonian in the form

$$\hat{H}_0 = H_0 (1) + H_0 (2) + \sum_i \frac{1}{r_{12}}$$

where $H_0 (i) = -\frac{1}{2} \frac{V_t^2}{r_i} - \frac{1}{\left| r_i - R/2 \right|} - \frac{1}{\left| r_i + R/2 \right|} (i = 1, 2)$

$$\left( = r_{1A} \right) \quad \left( = r_{1B} \right)$$

This ensures that the 1-electron molecular orbital wavefunctions are exact solutions to

$$\hat{H}_{0i} \Phi_g, u = \left[ E_g, u - \frac{1}{R} \right] \Phi_g, u$$

The $\Phi_g, u$ are assumed normalised to 1, so that

$$E = \int \Psi_A^* \hat{H} \Psi_A \, dt_1 \, dt_2$$
$$= 2E_g (R) - \frac{1}{R} + \int \left| \Phi_g (1) \Phi_g (2) \right|^2 \, dt_1 \, dt_2$$

numerical integration
recalling that \( \Phi_g = \left[ \psi_{1s}(r_1) + \psi_{1s}(r_2) \right] / \sqrt{2} \), so that

\[
\Phi_g(1) = \psi_{1s}(r_{A1}) + \psi_{1s}(r_{B1}) \frac{1}{\sqrt{2}} \quad \Phi_g(2) = \psi_{1s}(r_{A2}) + \psi_{1s}(r_{B2}) \frac{1}{\sqrt{2}}
\]

we have

\[
\Psi_A = \frac{1}{2} \left[ \psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) + \psi_{1s}(r_{A1}) \psi_{1s}(r_{A2}) + \psi_{1s}(r_{B1}) \psi_{1s}(r_{B2}) \right] \chi_{00}(1,2)
\]

The first two terms correspond to the case when the two electrons are equally shared (associated with) between the nuclei. The second two terms correspond to the case when the two electrons are more likely associated with one nucleus than being shared. The first two terms therefore represent "covalent bonding"

\[
\Psi_{A}^\text{covalent} = \frac{1}{2} \left[ \psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) \right] \chi_{00}(1,2)
\]

while the other two represent ionic bonding

\[
\Psi_{A}^\text{ionic} = \frac{1}{2} \left[ \psi_{1s}(r_{A1}) \psi_{1s}(r_{A2}) + \psi_{1s}(r_{B1}) \psi_{1s}(r_{B2}) \right] \chi_{00}(1,2)
\]

The probability corresponding to \( \Psi_{A}^\text{ionic} \) is smaller than that for \( \Psi_{A}^\text{covalent} \). The ionic part represents the case of \( \text{H}^+ : \text{H}^- \) separated atoms limit, while the covalent part represents the \( \text{H}^0 : \text{H}^0 \) separation limit.

The \( \Psi_{A}^\text{covalent} \) wavefunction by itself is an LCAO of two atomic hydrogen wavefunctions with exchange, corresponding to the singlet state \( 1\Sigma_g^+ \).

Similarly, if we expand out the \( \Psi_D^0 \) written earlier for the \( 3\Sigma_u^+ \) state, we find that there is a similar "covalent" part

\[
\Psi_{D}^\text{cov} = \frac{1}{2} \left[ \psi_{1s}(r_{A1}) \psi_{1s}(r_{B2}) - \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) \right] \chi_{11}(3\Sigma_u^+ \text{ spin states})
\]

In both the above wavefunctions, \( \Psi_{A}^\text{cov} (1\Sigma_g^+) \) and \( \Psi_{D}^\text{cov} (3\Sigma_u^+) \), there is a direct linear combination of atomic hydrogen 1s states.
(both atoms are separately 1s). These resultant molecular orbitals are
called Valence-Bond or Heitler-London orbitals.
The corresponding energies of the $^{1}Σ^+_g$ and $^{3}Σ^+_u$ states are
given by

$$E_{g/u} = 2E_{1s} \pm \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} + \frac{1}{R}$$

where

$$I = \int \psi_{1s}(r_{A1}) \psi_{1s}(r_{B1}) \, dt_{1} = \int \psi_{1s}(r_{A2}) \psi_{1s}(r_{B2}) \, dt_{2}$$

$$J = \int |\psi_{1s}(r_{A1})|^2 |\psi_{1s}(r_{B2})|^2 \, dt_{1} \, dt_{2} \left( \frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right)$$

$$K = \int \psi_{1s}(r_{A1}) \psi(r_{B2}) \left( \frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right) \psi_{1s}(r_{A2}) \psi_{1s}(r_{B1}) \, dt_{1} \, dt_{2}$$