Molecular Electronic Structure

Quantum Supplementary Course Hilary Term 2024

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1 Bibliography

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2 Some basics

2.1 The time-independent Schrödinger equation

In studies of molecular electronic structure, we seek solutions of the time-independent Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{1}$$

where m is the mass of an electron, V is the potential and ∇^2 is the Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{2}$$

The wavefunction, ψ, must be single-valued, finite and continuous.

2.2 Born-Oppenheimer approximation

The Hamiltonian, $\hat{H}$, for a system with n electrons and N nuclei is then given by

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i^n \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_i^n\sum_a^N \frac{Z_A}{r_{iA}} + \frac{e^2}{4\pi\epsilon_0}\sum_i^n\sum_{j>i}^n \frac{1}{r_{ij}} + \frac{e^2}{4\pi\epsilon_0}\sum_A^N\sum_{B>A}^N \frac{1}{R_{AB}} \tag{3}$$

If we regard the nuclei as being fixed in space, we can factorise the total wavefunction:

$$\Theta(R,r) = \psi(r)\Omega(R) \tag{4}$$

and the electronic part becomes:

$$\hat{H}_{el}\psi = \left[-\frac{\hbar^2}{2m}\sum_i^n \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_i^n\sum_a^N \frac{Z_A}{r_{iA}} + \frac{e^2}{4\pi\epsilon_0}\sum_i^n\sum_{j>i}^n \frac{1}{r_{ij}}\right]\psi = E\psi \tag{5}$$

and the nuclear part:

$$\hat{H}_{nuc}\Omega(R) = \left[+\frac{e^2}{4\pi\epsilon_0}\sum_A^N\sum_{B>A}^N \frac{1}{R_{AB}}\right]\Omega(R) = E_{nuc}\Omega(R) \tag{6}$$

The final term, E_{nuc} is independent of the position of the electrons, and adds a constant contribution to the energy (at fixed distance). The sum of electronic and nuclear energies defines the potential energy curve (Figure 1), the electronic energy which depends parametrically on the nuclear coordinates.

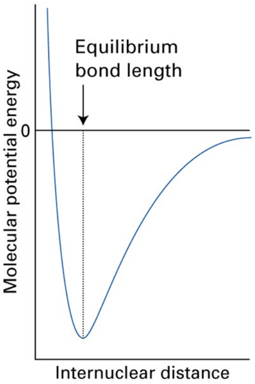


Figure 1: Potential energy surface for a diatomic molecule.

3 $\mathrm{H_2}^+$: linear variation theorem

$$\psi_{trial} = \sum_n c_n\chi_n = c_a\chi_{1sa} + c_b\chi_{1sb} \tag{7}$$

$$E_{trial} = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\langle(c_a\chi_{1sa} + c_b\chi_{1sb})|\hat{H}|(c_a\chi_{1sa} + c_b\chi_{1sb})\rangle}{\langle(c_a\chi_{1sa} + c_b\chi_{1sb})|(c_a\chi_{1sa} + c_b\chi_{1sb})\rangle}$$

Following the process set out in Prof Kirrander's 'Valence' lecture 4, minimisation of the trial wavefunction gives the following secular determinant:

$$\det(H - ES) = \begin{vmatrix} H_{aa} - ES_{aa} & H_{ba} - ES_{ba} \\ H_{ab} - ES_{ab} & H_{bb} - ES_{bb} \end{vmatrix}$$

with eigenvalues that we can formulate in terms of matrix elements

$$E_{\pm} = E_{1\sigma_g/1\sigma_u} = \frac{H_{aa} \pm H_{ab}}{1 \pm S_{ab}}$$

$$H_{aa} = \langle \chi_{1sa} | \hat{H} | \chi_{1sa} \rangle \quad H_{ab} = \langle \chi_{1sa} | \hat{H} | \chi_{1sb} \rangle \quad S_{ab} = \langle \chi_{1sa} | \chi_{1sa} \rangle$$

The molecular orbitals also emerge as the eigenfunctions of the secular equations, but in this case we can anticipate them from symmetry considerations alone:

$$\psi_{1\sigma_g/1\sigma_u} = \frac{1}{2(1 \pm S_{ab})} (\chi_{1sa} \pm \chi_{1sb})$$

We will deal exclusively with H_2 from now on, so the ‘1s’ subscript will be assumed and an orbital on hydrogen atom a referred to simply as χ_a *etc.* To make further progress we need to convert the abstract “ψ“, “H_{aa}”, “H_{ab}” *etc.* into hard numbers, and to do that we have to define $\hat{H}$!

3.1 The Hamiltonian for $H_2{}^+$:

We can expand the general expression in Equation 5 to generate the Hamiltonian for $H_2{}^+$

$$\hat{H}_{el} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_a} - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_b} \tag{8}$$

Equation 8 is given in SI units (distance in metres, mass in kg, charge in coulombs, energy in Joules). It is more convenient to express it in atomic units (distance in multiples of a_0, the Bohr radius, mass in multiples of m_e, charge in multiples of e, permittivity in multiples of $4\pi\epsilon_0$, energy in multiples of Hartrees (atomic units)).

$a_0 = 0.529 \times 10^{-10} m = 0.529$ Å

$e = 1.6022 \times 10^{-19}$ C

$m_e = 9.1095 \times 10^{-31}$ kg

1 Hartree = 1 au = $\frac{\hbar^2}{m_e a_0^2} = 4.3598 \times 10^{-18}$ J = 27.212 eV

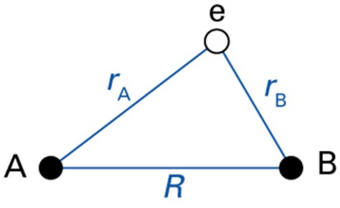


Figure 2: Components of the Hamiltonian for $H_2{}^+$.

In which case the Hamiltonian simplifies to:

$$\hat{H}_{el} = -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \tag{9}$$

and the matrix element H_{ab} to:

$$H_{ab} = \langle \chi_a | -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} | \chi_b \rangle = \langle \chi_a | -\frac{1}{2} \nabla^2 | \chi_b \rangle + \langle \chi_a | -\frac{1}{r_a} | \chi_b \rangle + \langle \chi_a | -\frac{1}{r_b} | \chi_b \rangle$$

So in order to calculate the energy for $H_2{}^+$, we $\therefore$ need to evaluate integrals of the following types, kinetic energy (T), electron-nucleus attraction (A) and overlap (S):

$$T = -\frac{1}{2} \langle \chi_a | \nabla^2 | \chi_b \rangle \quad A = -\langle \chi_a | \frac{1}{r_a} | \chi_b \rangle \quad S = \langle \chi_a | \chi_b \rangle \tag{10}$$

When we get to H_2, we will find that we also need to calculate a fourth type of integral, the electron-electron repulsion (g).

$$g = \langle \chi_a(1) \chi_a(2) | \frac{1}{r_{12}} | \chi_b(1) \chi_b(2) \rangle \tag{11}$$

4 Basis functions

In order to evaluate these integrals, we need to choose a mathematical representation of the orbitals, χ_a For discrete molecules, there are two common choices, **Slater-type** orbitals and **Gaussian-type** orbitals (Figure 3). For solid-state (periodic) calculations, there is a third choice, a basis set of plane waves, but we will not be concerned with those here.

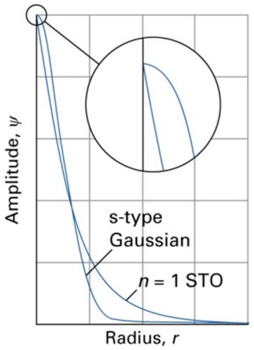


Figure 3: Slater-type and Gaussian-type basis functions.

4.1 Slater-type orbitals (STOs):

$$STO = N_1 r^{n-1} e^{-\zeta r}.Y_{lm}(\theta, \phi) \tag{12}$$

N_1 is the normalising constant. $Y_l m(\theta, \phi)$ is a spherical harmonic, controlling angular dependence ζ is a measure of how contracted the function is (larger ζ implies more contracted). In very simple (minimal) basis sets, ζ is related to Slater's effective nuclear charge, which controls radial behaviour, and can be calculated using Slater's simple empirical rules. Slater-type functions replicate the behaviour of real atomic orbitals, so they are an intuitively appealing option.

4.2 Gaussian-type orbitals (GTOs):

$$GTO = N_1 x^i y^j z^k e^{-\alpha r^2} = N_1 x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)} \tag{13}$$

Angular properties are specified by i, j, k:

$$(0,0,0) = s \quad (1,0,0) = p_x \quad (1,1,0) = d_{xy} \ etc.$$

The major difference compared to Slater functions is that the exponential decay is $e^{-\alpha r^2}$ and not $e^{-\alpha r}$, which means that the orbital decays too quickly at large r, and fails to reproduce the cusp at the nucleus found in real atomic orbitals (see Figure 3). Thus they are less accurate representations of a real atomic orbital than Slater functions. However, GTOs have two major advantages:

(1) GTOs are separable in the x, y and z directions:

$$GTO = N_1 x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)} = N_1 \left(x^i e^{-\alpha x^2}\right)\left(y^j e^{-\alpha y^2}\right)\left(z^k e^{-\alpha z^2}\right)$$

the same cannot be said of STOs:

$$STO = N_1 e^{-\zeta\sqrt{x^2+y^2+z^2}} \neq N_1 e^{-\zeta x} e^{-\zeta y} e^{-\zeta z}$$

(2) the product of two GTOs on different centres is just a different GTO centred somewhere in between (the **Gaussian Product Theorem**, or GPT for short). To illustrate this, consider the product of two s-type gaussians ($i = j = k = 0$) with equal exponents, α, one centred at $x = 0$, the other at $x = a$

$$
\begin{aligned}
&G_1 = N_1 e^{-\alpha x^2} \quad G_2 = N_2 e^{-\alpha (x-a)^2} \\
G_1 G_2 =& N_1 N_2 e^{-\alpha x^2} e^{-\alpha (x-a)^2} = N_1 N_2 e^{-\alpha (x^2 + (x-a)^2)} \\
=& N_1 N_2 e^{-\alpha (2x^2 - 2ax + a^2)} = N_1 N_2 e^{-2\alpha (x^2 - ax + \frac{a^2}{2})} \\
=& N_1 N_2 e^{-2\alpha ((x-\frac{a}{2})^2 + \frac{a^2}{4})} \\
=& N_1 N_2 e^{-\alpha \frac{a^2}{2}} e^{-2\alpha (x - \frac{a}{2})^2}
\end{aligned}
\tag{14}
$$

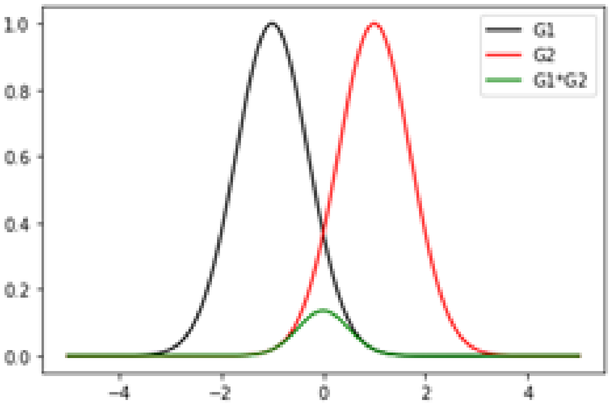


Figure 4: The product of two gaussian functions.

i.e. the product is another Gaussian with exponent 2α, centred half way between the original basis functions ($x = a/2$) and scaled by $e^{-\alpha \frac{a^2}{2}}$ (Figure 4). The GPT makes the computation of all integrals much easier for Gaussian functions than for Slater functions. It is harder, but still tractable, to calculate the 1-electron integrals (overlap, kinetic energy, electron-nucleus interaction) using a Slater-type basis, but if electron-electron repulsion integrals are needed (as they are for anything with more than 1 electron!), Slater-type functions are generally a very poor choice.

5 Evaluation of matrix elements.

5.1 Elements of the overlap matrix, S_{ab}

Example 1: an overlap integral between two s orbitals described by gaussians with exponent α on different atoms separated by a distance r:

$$
\begin{aligned}
&\chi_a = N_1 e^{-\alpha (x^2+y^2+z^2)} \quad \chi_b = N_2 e^{-\alpha (x^2+y^2+(z-r)^2)} \\
&S_{ab} = \langle \chi_a | \chi_b \rangle = N_1 N_2 \iiint_{-\infty}^{+\infty} e^{-\alpha (x^2+y^2+z^2)} e^{-\alpha (x^2+y^2+(z-r)^2)} dx dy dz
\end{aligned}
$$

First, we need to normalise each basis function.

$$\begin{aligned}
1 &= N_1^2 \iiint_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2+z^2)} e^{-\alpha(x^2+y^2+z^2)} dxdydz \\
&= N_1^2 \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx + \int_{-\infty}^{+\infty} e^{-\alpha y^2} dy + \int_{-\infty}^{+\infty} e^{-\alpha z^2} dz \\
&= N_1^2 \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} = N_1^2 \left(\frac{\pi}{2\alpha}\right)^{3/2} \\
N_1 (= N_2) &= \left(\frac{2\alpha}{\pi}\right)^{3/4}
\end{aligned}$$

where we have used the standard integral

$$\int_{-\infty}^{+\infty} e^{-bx^2} dx = \sqrt{\frac{\pi}{b}} \tag{15}$$

now return to the required overlap integral:

$$\begin{aligned}
S_{ab} &= N_1 N_2 \iiint_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2+z^2)} e^{-\alpha(x^2+y^2+(z-r)^2)} dxdydz \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\alpha}{\pi}\right)^{3/4} \int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-\alpha(z^2+(z-r)^2)} dz \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-\alpha(z^2+(z-r)^2)} dz
\end{aligned}$$

use the Gaussian product theorem (Equation 14) to deal with the integral in z:

$$\int_{-\infty}^{+\infty} e^{-\alpha(z^2+(z-r)^2)} dz = e^{-\frac{\alpha r^2}{2}} \int_{-\infty}^{+\infty} e^{-2\alpha\left(z-\frac{r}{2}\right)^2} = e^{-\alpha\frac{r^2}{2}} \left(\frac{\pi}{2\alpha}\right)^{1/2}$$

$$S_{ab} = \left(\frac{2\alpha}{\pi}\right)^{3/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} e^{-\alpha\frac{r^2}{2}} = e^{-\alpha\frac{r^2}{2}}$$

Using $r = 0.77$ Å and $\alpha = 0.4166$, we get $S_{ab} = 0.643$ (this number is relevant later: don't forget to convert the distance to atomic units: 0.77 Å = $^{0.77}/_{0.529177}$ = 1.455 au).

We can generalise this expression for the case where two s-type basis functions separated by a distance r have *different* exponents, α and β

$$S_{ab} = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} e^{-\frac{\alpha\beta}{(\alpha+\beta)} r^2} \tag{16}$$

The expression is somewhat more complicated again if p, d or f orbitals are involved.

5.2 Elements of the kinetic energy matrix, T_{ab}

Example 2: Calculate the kinetic energy of an electron in a $1s$ orbital (*i.e.* both basis functions are located on the same centre), $T_{aa} = \langle \chi_a | \hat{T} | \chi_a \rangle$

$$\chi_a = N_1 e^{-\alpha(x^2+y^2+z^2)}$$

$$\begin{aligned}
T_{aa} &= -\frac{N_1^2}{2} \langle e^{-\alpha(x^2+y^2+z^2)} | \nabla^2 | e^{-\alpha(x^2+y^2+z^2)} \rangle \\
&= -\frac{N_1^2}{2} \iiint_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2+z^2)} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) e^{-\alpha(x^2+y^2+z^2)} dxdydz
\end{aligned}$$

Taking the x component (y and z give identical contributions), we need to evaluate:

$$T_{aa}x = -\frac{N_1^2}{2} \int e^{-\alpha x^2} \frac{\partial^2}{\partial x^2} \left(e^{-\alpha x^2} \right) \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz$$

$$\frac{\partial^2}{\partial x^2} \left(e^{-\alpha x^2} \right) = \left(4\alpha^2 x^2 - 2\alpha \right) e^{-\alpha x^2}$$

So we need to evaluate 2 integrals and sum them:

$$\begin{aligned}
T_{aa}x &= -\frac{N_1^2}{2} \left[4\alpha^2 \int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz - 2\alpha \int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz \right] \\
&= -2\alpha^2 \left(\frac{2\alpha}{\pi} \right)^{3/2} \left(\frac{1}{4\alpha} \right) \left(\frac{\pi}{2\alpha} \right)^{3/2} + \alpha \left(\frac{2\alpha}{\pi} \right)^{3/2} \left(\frac{\pi}{2\alpha} \right)^{3/2} \\
&= -\frac{\alpha}{2} + \alpha = \frac{\alpha}{2}
\end{aligned}$$

where we have used a second standard integral:

$$\int_{-\infty}^{+\infty} x^2 e^{-bx^2} dx = \frac{1}{2b} \sqrt{\frac{\pi}{b}} \tag{17}$$

and because the total kinetic energy integral is symmetric in x, y, z:

$$T_{aa} = T_{aa}x + T_{aa}y + T_{aa}z = 3T_{aa}x = \frac{3\alpha}{2}$$

So for an s orbital with $\alpha = 0.4166$, we get $T_{aa} = 0.625$ (again, we use this later).

Again, we can generalise to the case for s orbitals on *different* atoms with *different* exponents:

$$T_{ab} = \left(\frac{2\alpha}{\pi} \right)^{3/4} \left(\frac{2\beta}{\pi} \right)^{3/4} \left(\frac{\pi}{\alpha + \beta} \right)^{3/2} \frac{\alpha\beta}{\alpha + \beta} \left[3 - \frac{2\alpha\beta}{\alpha + \beta} r^2 \right] e^{-\frac{\alpha\beta}{\alpha+\beta}|r_a - r_b|^2} \tag{18}$$

5.3 Elements of the nucleus-electron attraction matrix, A_{ab}

For the electron-nucleus attraction , the most complicated situation is where we have two basis functions on different atoms, χ_a and χ_b, and the nucleus on a 3rd atom, C. What we do is use the GPT to express the product of the two basis functions on $\chi_a \chi_b$ as a third gaussian, located at some point between a and b (point p in the Figure below). We then calculate the coulomb interaction between the electron distribution described by the gaussian function at p and the nucleus at C.

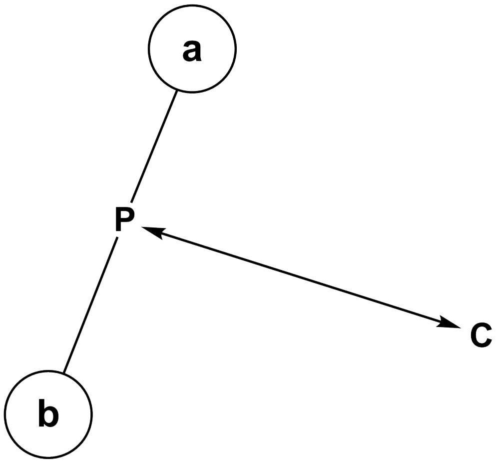


Figure 5: Positions of atoms a, b, C in the calculation of A_{ab}.

The coulomb integral is trickier than overlap or kinetic energy because of the $1/r$ terms, for which we need Fourier transform techniques. However, relatively simple closed analytical forms do exist. For interactions involving only s orbitals, the appropriate expression is:

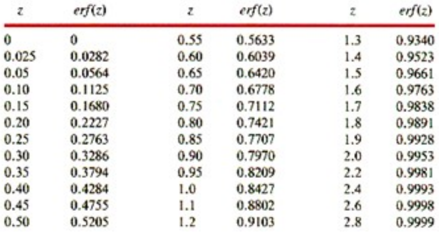
$$A_{ab} = \sum_{C}^{N} \langle \chi_a | \frac{-Z_C}{r_C} | \chi_b \rangle \tag{19}$$

$$= -\sum_{C}^{N} \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{2\pi}{\alpha+\beta}\right) Z_C \; e^{-\frac{\alpha\beta}{\alpha+\beta}|r_a - r_b|^2} F_0 \left[(\alpha+\beta)\left|\frac{r_a - r_b}{2} - r_C\right|^2\right] \tag{20}$$

where the summation runs over all N nuclei, Z_C is the charge on nucleus C and F_0 is the 'Boys' function (after Frank Boys).

$$F_0\left[t\right] = \frac{1}{2}\left(\frac{\pi}{t}\right)^{(1/2)} \; erf\left(t^{1/2}\right)$$

$$erf\left(x\right) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du \qquad\qquad F_0\left[0\right] = 1$$



z	$erf(z)$	z	$erf(z)$	z	$erf(z)$
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

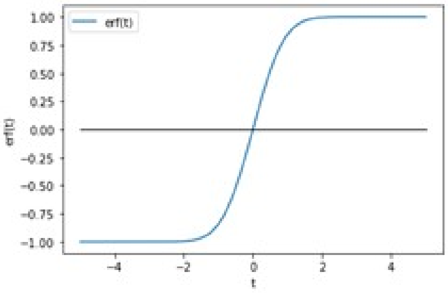


Figure 6: Error Function, $erf(t)$

The rather complicated expression in Equation 20 takes simpler forms under certain limiting cases ($r_c = 0$ or $r_c \to \infty$):

Example 3: Calculate the attraction between the nucleus in a hydrogen atom and its $1s$ electron described by a single gaussian function,

$$\chi_a = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

In this case, both basis functions and the nucleus are centred at the same place (the origin!), so:

$$\begin{aligned}
&|r_a - r_b| = 0 \quad e^{-\frac{\alpha\beta}{\alpha+\beta}|r_a-r_b|^2} = 1\\
&\left|\frac{r_a - r_b}{2} - r_c\right| = 0 \quad \therefore\ t = 0 \quad \therefore\ F_0\left[t\right] = 1\\
&A_{aa} = \langle\chi_a\left|\frac{-1}{r_a}\right|\chi_a\rangle = -\left(\frac{2\alpha}{\pi}\right)^{3/2}\left(\frac{\pi}{\alpha}\right) = -2^{3/2}\left(\frac{\alpha}{\pi}\right)^{1/2}
\end{aligned}$$

note that $T_{aa} \propto \alpha$ but $A_{aa} \propto \sqrt{\alpha}$.

Example 4: Calculate the attraction $\langle\chi_a\left|\frac{-1}{r_C}\right|\chi_a\rangle$ between the $1s$ electron on a hydrogen atom at the origin, described by a single gaussian function,

$$\chi_a = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

and a second hydrogen nucleus, C, at very large separation.

If the two basis functions are at the origin,

$$\begin{aligned}
&|r_a - r_b| = 0 \quad \therefore\ e^{-\frac{\alpha\beta}{\alpha+\beta}|r_a-r_b|^2} = 1\\
&\left|\frac{r_a - r_b}{2} - r_c\right| = r_C \quad \therefore\ t = 2\alpha\left|\frac{r_a - r_b}{2} - r_C\right|^2 = 2\alpha {r_C}^2
\end{aligned}$$

at large r_C, erf(t)$\sim$ 1 (see Figure 6).

$$\begin{aligned}
&F_0\left[t\right] = \frac{1}{2}\left(\frac{\pi}{t}\right) = \frac{1}{2}\left(\frac{\pi}{2\alpha}\right)^{1/2}\frac{1}{r_C}\\
&A_{aa} = -\langle\chi_a\left|\frac{1}{r_C}\right|\chi_a\rangle = -\left(\frac{2\alpha}{\pi}\right)^{3/2}\cdot\left(\frac{\pi}{\alpha}\right)\cdot\frac{1}{2}\cdot\left(\frac{\pi}{2\alpha}\right)^{1/2}\cdot\frac{1}{r_C} = -\frac{1}{r_C}
\end{aligned}$$

Note: this is simply the classical attraction between two point charges separated by r_c.

5.4 Electron-electron repulsion integrals, g_{abcd}

The expression for an electron-electron repulsion integral, g_{abcd}, which we need later for H_2 (and anything with more than 1 electron) is rather more complex. For one electron distributed over two s orbitals on centres a and b with exponents α and β, respectively, interacting with another electron distributed over two $1s$ orbitals on centres c and d with exponents δ and γ, respectively, the repulsion integral is given by:

$$\begin{aligned}
g_{abcd} = &\left(\frac{2\alpha}{\pi}\right)^{3/4}\left(\frac{2\beta}{\pi}\right)^{3/4}\left(\frac{2\delta}{\pi}\right)^{3/4}\left(\frac{2\gamma}{\pi}\right)^{3/4}\left(\frac{2\pi^{5/2}}{\left(\alpha+\beta\right)\left(\delta+\gamma\right)\left(\alpha+\beta+\delta+\gamma\right)^{1/2}}\right)\times\\
&e^{\left(-\frac{\alpha\beta}{\alpha+\beta}|r_a-r_b|^2-\frac{\delta\gamma}{\delta+\gamma}|r_c-r_d|^2\right)}\times F_0\left[\left(\alpha+\beta\right)\left(\delta+\gamma\right)\left(\alpha+\beta+\delta+\gamma\right)\left|r_p-r_q\right|^2\right]
\end{aligned} \tag{21}$$

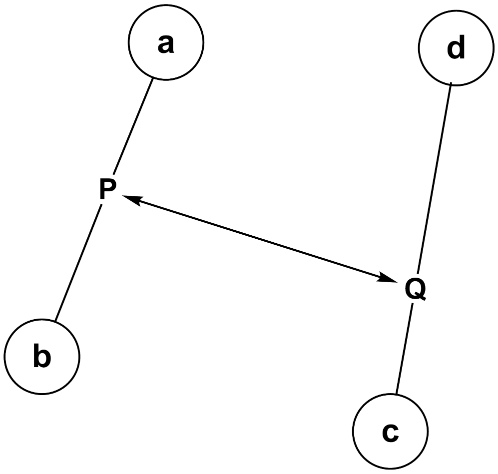


Figure 7: Positions of atoms a, b, c, d in a 2-electron integral.

where p is the midpoint of the gaussian product $\chi_a\chi_b$ and q is the midpoint of the gaussian product $\chi_c\chi_d$. See Szabo and Ostlund P416. Equivalent expressions for Slater-type functions are *much much* more complicated! See Atkins MQM.

Example 5: Calculate the coulomb repulsion, J, between two electrons in a $1s$ electron on an atom, described by a single gaussian function,

$$\chi_a = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

$$\begin{aligned}
&|r_a - r_b| = 0 \qquad |r_c - r_d| = 0 \qquad |r_p - r_q| = 0 \qquad F_0\left[t\right] = 1 \\
&e^{-\frac{\alpha\beta}{\alpha+\beta}|r_a-r_b|^2 - \frac{\delta\gamma}{\delta+\gamma}|r_c-r_d|^2} = 1 \\
&g_{abcd} = J = \left(\frac{2\alpha}{\pi}\right)^3 \left(\frac{2\pi^{5/2}}{(2\alpha)(2\alpha)(4\alpha)^{1/2}}\right) = \left(\frac{2\alpha}{\pi}\right)^3 \left(\frac{2\pi^{5/2}}{8\alpha^{5/2}}\right) = 2\left(\frac{\alpha}{\pi}\right)^{1/2}
\end{aligned} \tag{22}$$

Let's put this into practice:

Evaluate the energy of $H_2{}^+$ at $r = 0.77$ $\mathring{A}$, using a basis set composed of a single Gaussian function with $\alpha = 0.4166$ on each atom.

$$E_{\pm} = E_{1\sigma_g/1\sigma_u} = \frac{H_{aa} \pm H_{ab}}{1 \pm S_{ab}} = \frac{T_{aa} + A_{aa} \pm (T_{ab} + A_{ab})}{1 \pm S_{ab}}$$

Plugging $r = 0.77$ $\mathring{A}$ and α into equations 16, 18 and 20 gives:

Overlap (S)	S_{aa}=S_{bb}=1	S_{ab}=0.643
Kinetic energy (T)	T_{aa}=T_{bb}=0.625 au	T_{ab}=0.284 au
Nuclear attraction (A)	A_{aa}=A_{bb}=-1.676 au	A_{ab}=-1.154 au

$$\begin{aligned} E_+ = E_{1\sigma_g} &= \frac{T_{aa} + A_{aa} + (T_{ab} + A_{ab})}{1 + S_{ab}} \\ &= \frac{0.625 - 1.676 + 0.284 - 1.154}{1 + 0.643} = -1.169\ au \end{aligned}$$

we then add the nuclear-nuclear repulsion, E_{nuc}, to get the total energy of $H_2{}^+$. We can treat the nuclei classically, so E_{nuc} comes from simple electrostatics:

$$\begin{aligned} E_{nuc} &= \frac{1}{R_{ab}} = 0.687 \\ E_{tot} &= E_{1\sigma_g} + E_{nuc} = -1.169 + 0.687 = -0.481\ au \end{aligned}$$

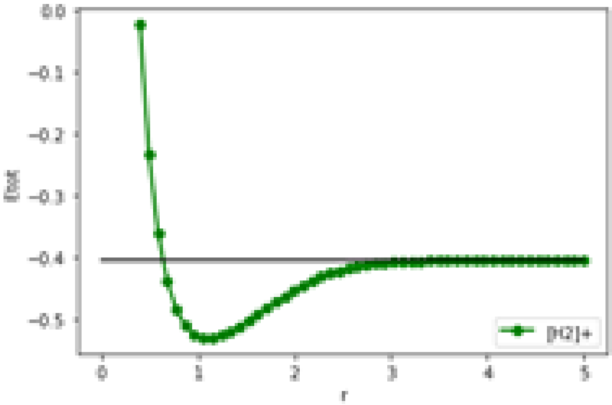


Figure 8: Potential energy surface for $H_2{}^+$.

6 Practical choices of basis set.

6.1 Linear combinations of gaussians

Despite their mathematical convenience, it remains true that GTOs provide a much worse approximation to atomic orbitals than STOs. The compromise is to use a linear combination of several GTOs to represent each atomic orbital rather than a single STO. For example, a triple-ζ basis set uses three GTOs to describe each atomic orbital. The basic philosophy is that it is easier to perform a large number of easy integrals than to perform a much smaller number of harder ones!

What can we create using just linear combinations of three Gaussian functions with different values of ζ (0.25, 0.5 and 1.0 in Figure 9)?

$$\psi = c_1 e^{-r^2} + c_2 e^{-\frac{1}{2}r^2} + c_3 e^{-\frac{1}{4}r^2}$$

If we vary the coefficients in the sum, we can get an orbital of arbitrary size (Figure 10).

And we can introduce radial nodes by using negative coefficients, Figure 11 (the coefficients are arbitrary, simply designed to illustrate how you can create different radial distribution functions from the same set of gaussian functions).

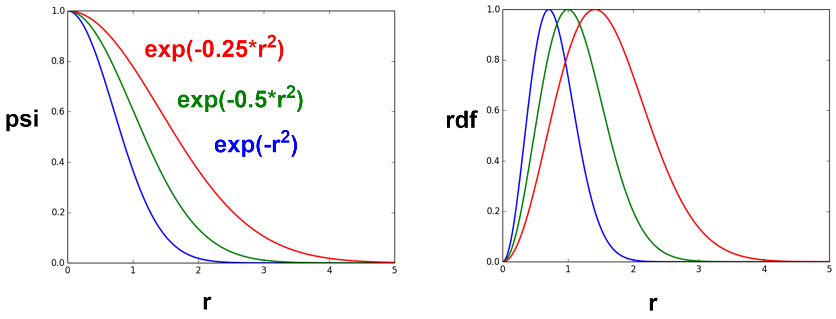


Figure 9: Three gaussian functions with increasing exponents (and so decreasing widths).

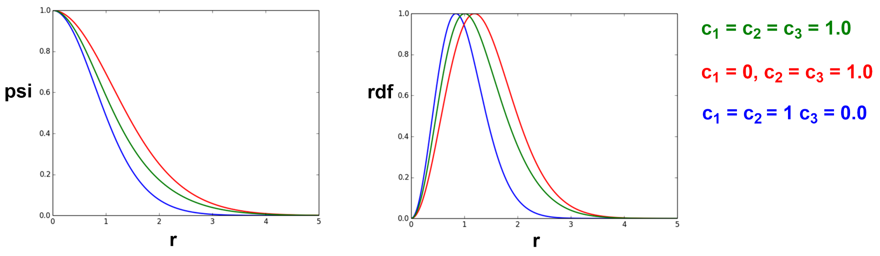


Figure 10: Linear combinations with all $c_n \geq 0$ gives a continuous spectrum of orbital sizes.

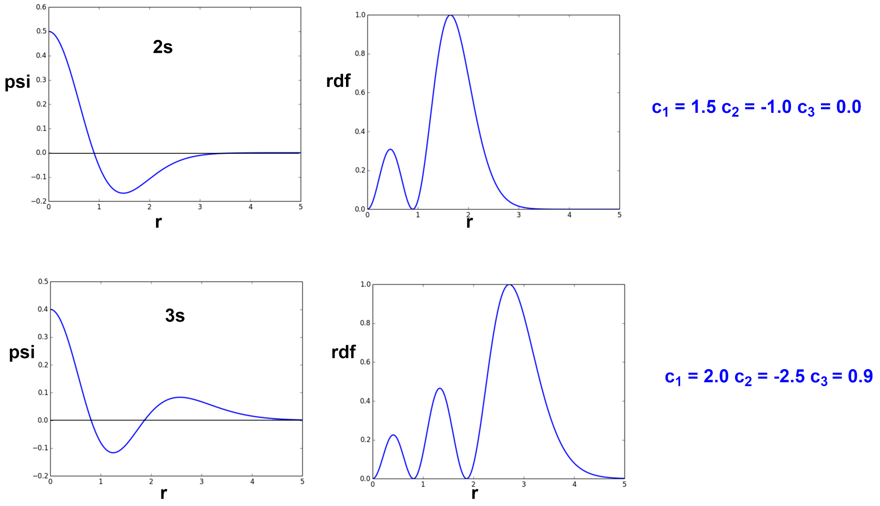


Figure 11: Linear combinations with positive and negative c_n introduce radial nodes.

6.2 Basis set libraries

All software packages have an internal database of basis sets, and many more are available in repositories like the **basis set exchange** (https://www.basissetexchange.org/). These range from very small to huge. At the simplest end, we have basis sets like STO-3G which uses 3 GTOs to represent each STO. Thus a calculation on H_2O with an STO-3G basis would involve 21 basis functions (3 for each of O $1s$, $2s$, $2p_{x,y,z}$ and H $1s$ ($\times 2$)).
Very large basis sets are commonly used now, including double, triple, quadruple... ζ forms: more than one exponent is used to describe a given orbital. Varying linear combinations allows the radial extent of the

orbital to vary (*c.f.* Figure 10). *e.g.* 6-31G

Polarisation functions: basis functions with higher angular momentum (*e.g.* *p*-symmetry functions on H, *d*-symmetry functions on B, C, N, O, F, *f*-symmetry functions on transition metals - recall the discussion of the role of *d* orbitals in *e.g.* SF_6) *e.g* 6-31G*

Diffuse functions: very low ζ – important for accurate description of weakly bound electrons (anions, for example) *e.g.* 6-31+G

The choice of an appropriate basis set is typically one of the major decisions practising computational chemists need to make.

7 Chemical bonding: what is a bond?

The chemical bond is often presented as an electrostatic phenomenon: "electrons accumulate in the internuclear region, where the potential energy is highest". But this is not true: in ${H_2}^+$, the potential energy is most favourable when the electron is at one nucleus or the other (where $^1/_r$ is infinite), not when it is in the middle! Where does this idea come from?

The virial theorem tells us that $T = -\frac{V}{2}$. Combine this with the expression for the total energy, $E = T + V = \frac{V}{2}$ and it seems that we need only to know the potential energy to know the total energy! However, we could equally well argue that $E = T + V = -T$ and that the total energy is defined entirely by the kinetic energy! Simple models of bonding focus almost exclusively on the electrostatics, but we really need to consider the balance between T and V as the H-H bond forms in ${H_2}^+$:

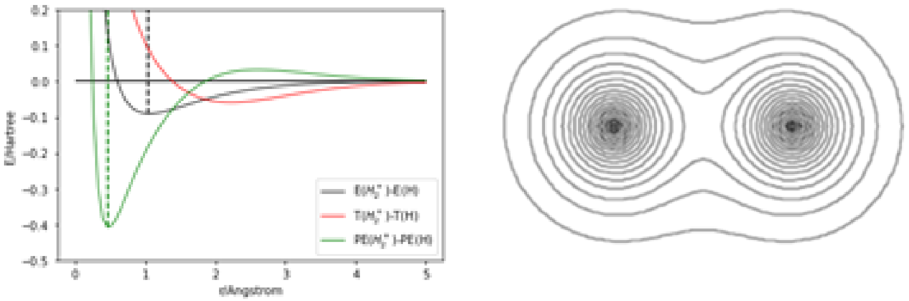


Figure 12: Variation in A, T and V across the potential energy surface for ${H_2}^+$

As the bond begins to form, the potential energy V (green curve) actually goes up, and it is the kinetic energy (black line) that causes the initial drop in total energy. The electron is no longer confined to a single atom, so is effectively in a bigger 'box', so T goes down. The increase in V comes because the electron strays further from the original nucleus. At shorter distances, the curves for V and T cross, and at equilibrium it is indeed the former that stabilises the molecule. The wavefunction contracts along the direction perpendicular to the bond (it effectively 'shrink wraps' the nuclei. So the bond, even in something as simple as ${H_2}^+$, is quite complicated!

8 Formulation of the wavefunction for systems with >1 electron.

8.1 Slater determinants

Also see *Valence* Lecture 3.
The Pauli principle: The total wavefunction must be antisymmetric under the exchange of identical particles.

Example 1: He
For He, the 2-electron wavefunction

$$\psi_{He} = 1s(1)\bar{1s}(2)$$

is not antisymmetric because

$$1s(1)\bar{1s}(2) - \neq 1s(2)\bar{1s}(1)$$

(note $1s(1)\bar{1s}(2)$ is shorthand for $1s(1)1s(2)\alpha(1)\beta(2)$)
But the linear combination

$$\psi_{He} = \frac{1}{\sqrt{2}}(1s(1)\bar{1s}(2) - 1s(2)\bar{1s}(1))$$

is antisymmetric because

$$\frac{1}{\sqrt{2}}(1s(2)\bar{1s}(1) - 1s(1)1\bar{s(2)}) = -\frac{1}{\sqrt{2}}(1s(1)\bar{1s}(2) - 1s(2)\bar{1s}(1)) = -\psi_{He}$$

Example 2: Li

$$\psi_{Li} = 1s(1)\bar{1s}(2)2s(3)$$

is not antisymmetric.

$$\psi_{Li} = \frac{1}{\sqrt{2}}(1s(1)\bar{1s}(2)2s(3) - 1s(2)\bar{1s}(1)2s(3))$$

is antisymmetric wrt exchange of electrons 1 and 2, but not wrt 1 and 3 or wrt 2 and 3.

$$\begin{aligned}\psi_{Li} =& \frac{1}{\sqrt{6}}(1s(1)\bar{1s}(2)2s(3) + 1s(2)\bar{1s}(3)2s(1) + 1s(3)\bar{1s}(1)2s(2) \\ &- 1s(1)\bar{1s}(3)2s(2) - 1s(2)\bar{1s}(1)2s(3) - 1s(3)\bar{1s}(2)2s(1))\end{aligned}$$

is antisymmetric wrt exchange of all three.

The antisymmetric wavefunctions can be written as *Slater determinants*:

$$\psi_{He} = \frac{1}{\sqrt{2}}(1s(1)\bar{1s}(2) - 1s(2)\bar{1s}(1)) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & \bar{1s}(1) \\ 1s(2) & \bar{1s}(2) \end{vmatrix}$$

$$\begin{aligned}\psi_{Li} &= \frac{1}{\sqrt{6}}(1s(1)\bar{1s}(2)2s(3) + 1s(2)\bar{1s}(3)2s(1) + 1s(3)\bar{1s}(1)2s(2) \\ &\quad - 1s(1)\bar{1s}(3)2s(2) - 1s(2)\bar{1s}(1)2s(3) - 1s(3)\bar{1s}(2)2s(1)) \\ &= \frac{1}{\sqrt{6}}\begin{vmatrix} 1s(1) & \bar{1s}(1) & 2s(1) \\ 1s(2) & \bar{1s}(2) & 2s(2) \\ 1s(3) & \bar{1s}(3) & 2s(3) \end{vmatrix}\end{aligned}$$

Note that using a single Slater determinant to represent the wavefunction is a convenient way to ensure that it conforms to the Pauli Principle, but it is by no means the only way. Any linear combination of Slater determinants will do the job, as we will see when we consider **Configuration Interaction**.

9 H_2 explicit formulation of the Hamiltonian for a 2-electron system

$$\hat{H}_{el} = -\sum_i \left(\frac{1}{2}\nabla_i^2 + V_i\right) = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{a2}} - \frac{1}{r_{b2}}\right) + \frac{1}{r_{12}} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \tag{23}$$

$\hat{H}_1$ and $\hat{H}_2$ are identical to the 1-electron Hamiltonians for ${H_2}^+$ (Equation 9). If we chose to ignore the $\frac{1}{r_{12}}$ term in the Hamiltonian (*i.e.* we assumed that electrons don't interact!), this is simply the sum of two independent one-electron ${H_2}^+$ Hamiltonians, and the problem is separable.
The resulting energy and ground-state wavefunction would be $E = 2E_{1\sigma_g}$ and $\psi = 1\sigma_g(1)1\sigma_g(2)$, a simple "Hartree product".

We have already established, however, that a wavefunction of this type is not antisymmetric wrt exchange of electrons (unsurprisingly as we chose to ignore the interaction between the electrons in deriving it!): we need to use a Slater determinant.

$$\psi_{H_2} = \frac{1}{\sqrt{2}}(1\sigma_g(1)1\bar{\sigma}_g(2) - 1\sigma_g(2)1\bar{\sigma}_g(1)) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1) & 1\bar{\sigma}_g(1) \\ 1\sigma_g(2) & 1\bar{\sigma}_g(2) \end{vmatrix}$$

Now we have a correct expression for ψ and an expression for $\hat{H}$, we can compute the expectation value: $\langle\psi|\hat{H}|\psi\rangle$

Step 1: Expand ψ

$$\begin{aligned} E = \langle\psi|\hat{H}|\psi\rangle &= \frac{1}{2}\left\langle(1\sigma_g(1)1\bar{\sigma}_g(2) - 1\sigma_g(2)1\bar{\sigma}_g(1))|\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}|(1\sigma_g(1)1\bar{\sigma}_g(2) - 1\sigma_g(2)1\bar{\sigma}_g(1))\right\rangle \\ &= \frac{1}{2}\left\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}|1\sigma_g(1)1\bar{\sigma}_g(2)\right\rangle + \frac{1}{2}\left\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}|1\sigma_g(2)1\bar{\sigma}_g(1)\right\rangle \\ &- \frac{1}{2}\left\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}|1\sigma_g(2)1\bar{\sigma}_g(1)\right\rangle - \frac{1}{2}\left\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}|1\sigma_g(1)1\bar{\sigma}_g(2)\right\rangle \end{aligned}$$

Step 2: Expand terms of $\hat{H}$ to give 12 integrals, labelled I_1-I_{12}.

$$\begin{aligned}
E =& \frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_1|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \quad I_1\\
&+\frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_2|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \quad I_2\\
&-\frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_1|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle \quad I_3\\
&-\frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_2|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle \quad I_4\\
&-\frac{1}{2}\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\hat{H}_1|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \quad I_5\\
&-\frac{1}{2}\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\hat{H}_2|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \quad I_6\\
&+\frac{1}{2}\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\hat{H}_1|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle \quad I_7\\
&+\frac{1}{2}\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\hat{H}_2|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle \quad I_8\\
&+\frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \quad I_9\\
&-\frac{1}{2}\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\frac{1}{r_{12}}|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \quad I_{10}\\
&-\frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle \quad I_{11}\\
&+\frac{1}{2}\langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\frac{1}{r_{12}}|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle \quad I_{12}
\end{aligned} \tag{24}$$

I_1-I_8 are termed '1-electron integrals' as they depend only on the coordinates of a single electron, whereas $I_9 - I_{12}$ are referred to as '2-electron integrals'. We will now look at each of $I_1 - I_{12}$ in turn and establish whether they are zero or not.

9.1 1-electron integrals, I_1-I_8

$$I_1 = \frac{1}{2}\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_1|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle$$

Note that $\hat{H}_1$ only acts on electron 1. We can therefore separate out everything to do with electron 1 from electron 2, and also separate out the spatial and spin components of the wavefunctions:

$$\begin{aligned}
I_1 &= \frac{1}{2}\langle 1\sigma_g(1)|\hat{H}_1|1\sigma_g(1)\rangle\langle 1\bar{\sigma}_g(2)|1\bar{\sigma}_g(2)\rangle\\
&= \frac{1}{2}\langle 1\sigma_g(1)|\hat{H}_1|1\sigma_g(1)\rangle\langle 1\sigma_g(2)|1\sigma_g(2)\rangle\langle\alpha(1)|\alpha(1)\rangle\langle\beta(2)|\beta(2)\rangle\\
&= \frac{1}{2}E_{1\sigma_g}\times 1\times 1\times 1 = \frac{1}{2}E_{1\sigma_g}
\end{aligned}$$

Similarly

$$\begin{aligned}
I_2 &= \frac{1}{2}\langle 1\bar{\sigma}_g(2)|\hat{H}_2|1\bar{\sigma}_g(2)\rangle\langle 1\sigma_g(1)|1\sigma_g(1)\rangle = \frac{1}{2}E_{1\sigma_g}\\
I_7 &= \frac{1}{2}\langle 1\bar{\sigma}_g(1)|\hat{H}_1|1\bar{\sigma}_g(1)\rangle\langle 1\sigma_g(2)|1\sigma_g(2)\rangle = \frac{1}{2}E_{1\sigma_g}\\
I_8 &= \frac{1}{2}\langle 1\sigma_g(2)|\hat{H}_2|1\sigma_g(2)\rangle\langle 1\bar{\sigma}_g(1)|1\bar{\sigma}_g(1)\rangle = \frac{1}{2}E_{1\sigma_g}
\end{aligned}$$

now consider I_3:

$$I_3 = \frac{1}{2}1\langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\hat{H}_1|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle$$

Separating the spatial and spin components of the wavefunctions gives:

$$\begin{aligned}
I_3 =& \frac{1}{2} \langle 1\sigma_g(1)|\hat{H}_1|1\bar{\sigma}_g(1)\rangle \langle 1\bar{\sigma}_g(2)|1\sigma_g\rangle (2) \\
=& \frac{1}{2} \langle 1\sigma_g(1)|\hat{H}_1|1\sigma_g(1)\rangle \langle 1\sigma_g(2)|1\sigma_g(2)\rangle \langle \alpha(1)|\beta(1)\rangle \langle \beta(2)|\alpha(2)\rangle \\
=& \frac{1}{2} E_{1\sigma_g} \times 1 \times 0 \times 0 = 0
\end{aligned}$$

The integral is zero due to spin orthogonality, and likewise for I_4, I_5 and I_6.
If we now add up the sum of the 1-electron integrals, I_1-I_8, we get $E_{tot} = 4 \times \frac{1}{2} E_{1\sigma_g} + 4 \times 0 = 2E_{1\sigma_g}$, as we might have guessed!

9.2 2-electron integrals, I_9-I_{12}

We now can't separate out the components in electron 1 and electron 2 because the operator acts on both, but we can still separate out the spatial and spin parts (because $\frac{1}{r_{12}}$ does not act on spin).

$$\begin{aligned}
I_9 &= \frac{1}{2} \langle 1\sigma_g(1)1\bar{\sigma}_g(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \\
&= \frac{1}{2} \langle 1\sigma_g(1)1\sigma_g(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_g(2)\rangle \langle \alpha(1)|\alpha(1)\rangle \langle \beta(2)|\beta(2)\rangle \\
&= \frac{1}{2} J_{1\sigma_g 1\sigma_g} \times 1 \times 1 = \frac{1}{2} J_{1\sigma_g 1\sigma_g}
\end{aligned} \tag{25}$$

This is the 'Coulomb integral' (note the multiple uses of the term 'Coulomb integral' in the literature).
Physically: J is the repulsion between two electrons occupying the same orbital, $1\sigma_g$.
similarly:

$$I_{12} = \frac{1}{2} \langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\frac{1}{r_{12}}|1\sigma_g(2)1\bar{\sigma}_g(1)\rangle = \frac{1}{2} J_{1\sigma_g 1\sigma_g}$$

but:

$$\begin{aligned}
I_{10} &= -\frac{1}{2} \langle 1\sigma_g(2)1\bar{\sigma}_g(1)|\frac{1}{r_{12}}|1\sigma_g(1)1\bar{\sigma}_g(2)\rangle \\
&= -\frac{1}{2} \langle 1\sigma_g(2)1\sigma_g(1)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_g(2)\rangle \langle \beta(1)|\alpha(1)\rangle \langle \alpha(2)|\beta(2)\rangle \qquad = 0
\end{aligned}$$

due to spin orthogonality, and likewise for I_{11}. So, finally, we have an expresssion for the total energy of H_2:

$$E_{tot} = 4 \times \frac{1}{2} E_{1\sigma_g} + 2 \times \frac{1}{2} J_{1\sigma_g 1\sigma_g} = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g} \tag{26}$$

i.e. what you might expect classically: twice the energy of an electron in ${H_2}^+$, plus an additional term $J_{1\sigma_g 1\sigma_g}$, capturing the destabilising effect of electron-electron repulsion.

9.3 A note on physicists' and chemists' notation

A commonly used shorthand notation for the 2-electron integral

$$\langle 1\sigma_g(1)1\sigma_g(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_g(2)\rangle$$

is

$$\langle 1\sigma_g(1)1\sigma_g(2)|1\sigma_g(1)1\sigma_g(2)\rangle$$

or more generally

$$\langle ij|ij\rangle$$

where the $\frac{1}{r_{12}}$ term is implicit. This is called the *physicists notation*. Even without the $\frac{1}{r_{12}}$ present, the 2-electron integrals can still be distinguished from overlap integrals, $\langle i|j\rangle$ because the former have 2 indices on each side rather than one. Up to 4 spin orbitals can be involved, in which case the integral is denoted $\langle ij|kl\rangle$. It is often conceptually easier (at least in the eyes of chemists, apparently!) to collect all terms relating to a given electron on the same side of the $\frac{1}{r_{12}}$ term. Writing the integrals out in full, including complex conjugation, we have:

$$J_{1\sigma_g 1\sigma_g} = \langle 1\sigma_g(1)1\sigma_g(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_g(2)\rangle = \int 1\sigma_g^*(1)1\sigma_g^*(2)|\frac{1}{r_{12}}|\sigma_g(1)1\sigma_g(2)d\tau$$

we can rearrange this so that all terms in electron 1 are on the left and all terms in electron 2 are on the right:

$$\langle ij|ij\rangle = J_{1\sigma_g 1\sigma_g} = \int 1\sigma_g^*(1)1\sigma_g(1)|\frac{1}{r_{12}}|\sigma_g(2)1\sigma_g^*(2)d\tau = [ii|jj]$$

This arrangements of terms makes it more obvious that the interaction is between a probability density defined by electron 1 ($\sigma_g^*(1)1\sigma_g(1)$) and a probability density defined by electron 2 ($\sigma_g(2)1\sigma_g^*(2)$). Note the use of a square bracket rather than a traditional 'bra'/'ket' - this is called '*chemists' notation*'. We can't use the Dirac notation because the complex conjugates have moved, and so the left and right hand sides are no longer bras and kets. Both systems of nomenclature are used in the literature, and if you are writing a code, it is vital to keep track of which one you are using.

9.4 Evaluation of molecular integrals

So far, we have developed the required integrals (S, T, A, J) in terms of the molecular orbitals, $1\sigma_g$ in this case. In order to get a numerical result (as we did for atomic H previously), we need to expand the orbitals using the LCAO ansatz.

$$1\sigma_g = \frac{1}{\sqrt{2\left(1+S_{ab}\right)}}\left(\chi_a+\chi_b\right)$$

Expanding $J_{1\sigma_g 1\sigma_g} = \langle 1\sigma_g(1)1\sigma_g(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_g(2)\rangle$ in this basis gives:

$$\begin{aligned}
J_{1\sigma_g 1\sigma_g} =& \frac{1}{4(1+S_{ab})^2}\left\langle\left(\chi_a+\chi_b\right)(1)\left(\chi_a+\chi_b\right)(2)|\frac{1}{r_{12}}|\left(\chi_a+\chi_b\right)(1)\left(\chi_a+\chi_b\right)(2)\right\rangle \\
&= \frac{1}{4(1+S_{ab})^2}\big[\\
&\langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_a(2)\rangle + \langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_b(2)\rangle \\
&+ \langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_a(2)\rangle + \langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_b(2)\rangle \\
&+ \langle\chi_a(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_a(2)\rangle + \langle\chi_a(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_b(2)\rangle \\
&+ \langle\chi_a(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_a(2)\rangle + \langle\chi_a(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_b(2)\rangle \\
&+ \langle\chi_b(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_a(2)\rangle + \langle\chi_b(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_b(2)\rangle \\
&+ \langle\chi_b(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_a(2)\rangle + \langle\chi_b(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_b(2)\rangle \\
&+ \langle\chi_b(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_a(2)\rangle + \langle\chi_b(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_b(2)\rangle \\
&+ \langle\chi_b(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_a(2)\rangle + \langle\chi_b(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_b(2)\rangle\,\big]
\end{aligned} \tag{27}$$

The 16 integrals above, separate into four distinct types:

$$\langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_a(2)\rangle = \langle aa|aa\rangle = \langle bb|bb\rangle$$

$$\langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_b(1)\chi_b(2)\rangle = \langle aa|bb\rangle = \langle bb|aa\rangle$$

$$\langle\chi_a(1)\chi_b(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_b(2)\rangle = \langle ab|ab\rangle = \langle ba|ba\rangle = \langle ab|ba\rangle = \langle ba|ab\rangle$$

$$\langle\chi_a(1)\chi_a(2)|\frac{1}{r_{12}}|\chi_a(1)\chi_b(2)\rangle = \langle aa|ab\rangle = \langle aa|ba\rangle = \langle ab|aa\rangle = \langle ba|aa\rangle = \langle ab|bb\rangle = \langle ba|bb\rangle = \langle bb|ab\rangle = \langle bb|ba\rangle$$

$$J_{1\sigma_g 1\sigma_g} = \frac{1}{4(1+S_{ab})^2}\left[2\langle aa|aa\rangle + 4\langle ab|ab\rangle + 2\langle aa|bb\rangle + 8\langle aa|ab\rangle\right]$$

The analytical formula required to calculate these integrals was given in Equation 21. Note that the corresponding equations with Slater basis sets are <u>much</u> more complicated!).

For our standard toy model of H_2 at 0.77 $\mathring{A}$ with the single Gaussian basis function ($\alpha = 0.4166$) on each atom, values are:

$$\begin{aligned}
&\langle aa|aa\rangle = 0.728\ au \quad \langle aa|bb\rangle = 0.561\ au\\
&\langle ab|ab\rangle = 0.301\ au \quad \langle aa|ab\rangle = 0.436\ au\\
&S_{ab} = 0.643\\
&J = \frac{1}{4\times 1.643^2}\left[2\times 0.728 + 2\times 0.561 + 4\times 0.301 + 8\times 0.436\right] = 0.673\ au\\
&E = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g} + E_{nuc} = 2\times -1.169 + 0.673 + 0.687 = -0.977\ au
\end{aligned} \tag{28}$$

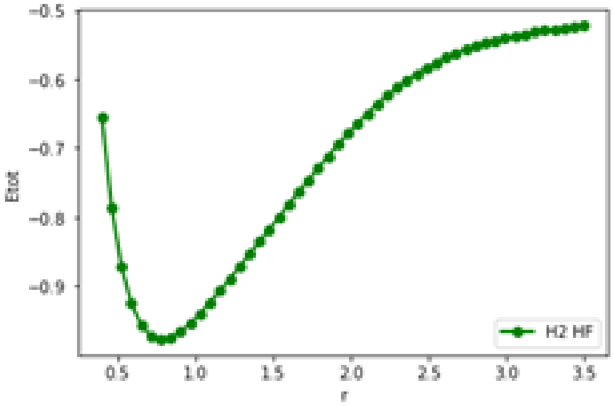


Figure 13: Potential energy surface for ${H_2}^+$.

We can expand a molecular orbital using as many functions on as many atoms as we like:

$$\psi = N\left(c_a\chi_a + c_b\chi_b + c_c\chi_c + c_d\chi_d\right)$$

If we do so, the number of integrals required increases rapidly (the number of 2-electron integrals scales as N^4 where N is the number of basis functions). Moreover, the 1- and 2-electron integrals (H, J and K) can involve atomic functions on up to four different atoms, a, b, c and d: *e.g.*

$$\langle\chi_a(1)\chi_b(2)|\frac{1}{r_{12}}\chi_c(1)\chi_d(2)\rangle = \langle ab|cd\rangle$$

The 4-centre-2-electron integrals are numerous and very time-consuming to evaluate.

9.5 Excited states of $\mathbf{H_2}$ and the exchange integral, K.

Let us perform the same analysis with the first triplet excited state of H_2,

$$\psi = \frac{1}{\sqrt{2}}(1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1))) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1) & 1\sigma_u(1) \\ 1\sigma_g(2) & 1\sigma_u(2) \end{vmatrix}$$

Expand in terms of ψ and $\hat{H}$ again gives 12 integrals, again labelled I_1-I_{12}.

$$\begin{aligned}
E =& \frac{1}{2}\langle 1\sigma_g(1)1\sigma_u(2)|\hat{H}_1|1\sigma_g(1)1\sigma_u(2)\rangle \quad I_1 \\
&+\frac{1}{2}\langle 1\sigma_g(1)1\sigma_u(2)|\hat{H}_2|1\sigma_g(1)1\sigma_u(2)\rangle \quad I_2 \\
&-\frac{1}{2}\langle 1\sigma_g(1)1\sigma_u(2)|\hat{H}_1|1\sigma_g(2)1\sigma_u(1)\rangle \quad I_3 \\
&-\frac{1}{2}\langle 1\sigma_g(1)1\sigma_u(2)|\hat{H}_2|1\sigma_g(2)1\sigma_u(1)\rangle \quad I_4 \\
&-\frac{1}{2}\langle 1\sigma_g(2)1\sigma_u(1)|\hat{H}_1|1\sigma_g(1)1\sigma_u(2)\rangle \quad I_5 \\
&-\frac{1}{2}\langle 1\sigma_g(2)1\sigma_u(1)|\hat{H}_2|1\sigma_g(1)1\sigma_u(2)\rangle \quad I_6 \\
&+\frac{1}{2}\langle 1\sigma_g(2)1\sigma_u(1)|\hat{H}_1|1\sigma_g(2)1\sigma_u(1)\rangle \quad I_7 \\
&+\frac{1}{2}\langle 1\sigma_g(2)1\sigma_u(1)|\hat{H}_2|1\sigma_g(2)1\sigma_u(1)\rangle \quad I_8 \\
&+\frac{1}{2}\langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_u(2)\rangle \quad I_9 \\
&-\frac{1}{2}\langle 1\sigma_g(2)1\sigma_u(1)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_u(2)\rangle \quad I_{10} \\
&-\frac{1}{2}\langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)\rangle \quad I_{11} \\
&+\frac{1}{2}\langle 1\sigma_g(2)1\sigma_u(1)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)\rangle \quad I_{12}
\end{aligned} \tag{29}$$

1-electron terms, I_1-I_8

$$\begin{aligned}
I_1 =& \frac{1}{2}\langle 1\sigma_g(1)|\hat{H}_1|1\sigma_g(1)\rangle \langle 1\sigma_u(2)|1\sigma_u(2)\rangle \\
&= \frac{1}{2}\langle 1\sigma_g(1)|\hat{H}_1|1\sigma_g(1)\rangle \langle 1\sigma_u(2)|1\sigma_u(2)\rangle \langle \alpha(1)|\alpha(1)\rangle \langle \alpha(2)|\alpha(2)\rangle \\
&= \frac{1}{2}E_{1\sigma_g} \times 1 \times 1 \times 1 = \frac{1}{2}E_{1\sigma_g} \\
&I_1 = I_8 = E_{1\sigma_g} \\
&I_2 = I_7 = E_{1\sigma_u} \\
&I_3 = I_4 = I_5 = I_6 = -\frac{1}{2}\langle 1\sigma_g(1)|\hat{H}_1|1\sigma_u(1)\rangle \langle 1\sigma_u(2)|1\sigma_g(2)\rangle = 0
\end{aligned}$$

note that $I_3 = I_4 = I_5 = I_6 = 0$ because now the spatial components, $1\sigma_u$ and $1\sigma_u$, are orthogonal. Contrast with the expansion of the ground state where I_3, I_4, I_5 and $I_6 = 0$ were zero because of orthogonality of the spin components.

2-electron terms:

$$\begin{aligned}
I_9 = I_{12} &= \frac{1}{2}\,\langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_u(2)\rangle \\
&= \frac{1}{2}\,\langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_u(2)\rangle\;\;\langle\alpha(1)|\alpha(1)\rangle\;\;\langle\alpha(2)|\alpha(2)\rangle \\
&= \frac{1}{2}J_{1\sigma_g 1\sigma_u} \times 1 \times 1 = \frac{1}{2}J_{1\sigma_g 1\sigma_u}
\end{aligned}$$

$J_{1\sigma_g 1\sigma_u}$ is the repulsion between an electron in $1\sigma_g$ and an electron in $1\sigma_u$.

Thus far, the expression is exactly as it was for the ground state, BUT

$$\begin{aligned}
I_{10} = I_{11} &= \frac{1}{2}\,\langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)\rangle \\
&= \frac{1}{2}\,\langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)\rangle\;\;\langle\alpha(1)|\alpha(1)\rangle\;\;\langle\alpha(2)|\alpha(2)\rangle \\
&= \frac{1}{2}K_{1\sigma_g 1\sigma_u} \times 1 \times 1 = \frac{1}{2}K_{1\sigma_g 1\sigma_u}
\end{aligned}$$

recall that in the singlet case, I_{10} and I_{11} were exactly zero because of spin orthogonality - the two spin components were $\langle\alpha(1)|\beta(1)\rangle$ and $\langle\beta(2)|\alpha(2)\rangle$. There is no such orthogonality here (both spins are the same!), so the integrals are not necessarily zero: they are known as exchange integrals, K – a purely quantum phenomenon. Note also that the integrals come into the expression with the *opposite sign* to I_9 and I_{12}.
Collecting terms:

$$E_{tot} = E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u} \tag{30}$$

J and K are both positive (I will explain why later), so K can be thought of as offsetting some of the electron-electron repulsion captured in J: this is what lies behind the general observation '*electrons with parallel spin repel each less than electrons with opposite spins*'.

Note the special case when the two orbitals are the same:

$$J = \langle ij|ij\rangle \qquad K = \langle ij|ji\rangle \tag{31}$$

$\therefore$ when $i = j$, $J = K$. This proves to be very important later when we come to manipulate expressions involving energies.

Finally, note $\hat{H}$ does not operate on spin degrees of freedom. Thus the influence of spin on the energy is exerted indirectly *via* the constraints on the spatial component of ψ imposed by the Pauli principle. The total wavefunction (spatial×spin) must be antisymmetric therefore the spin part places constraints on the spatial part, and it is the spatial part that determines the energy. If we write out the spatial part of ${}^3\psi$ to make the dependence on the *positions* of electrons 1 and 2 (r_+1 and r_2, explicitly clear, we see that the wavefunction must go to zero in the limit that the electrons are in the same place (the 'Fermi hole').

$${}^3\psi = \frac{1}{\sqrt{2}}(1\sigma_g(r_1)1\sigma_u(r_2) - 1\sigma_g(r_2)1\sigma_u(r_1)) = 0 \quad \textit{when } r_1 = r_2.$$

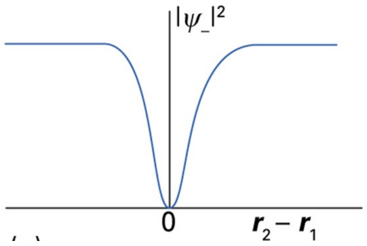


Figure 14: Fermi hole at $r_1 = r_2$ for the triplet wavefunction.

10 Hartree-Fock theory

What have we achieved so far?
We have set up the machinery that allows us to evaluate the expression $\langle\psi|\hat{H}|\psi\rangle = E$ *if we know the wavefunction in the form of an antisymmetrised product* and we know the exact mathematical form that the individual orbitals, $1\sigma_g$ in this case, take.

$$\psi = \left|1\sigma_g \quad 1\bar{\sigma}_g\right| = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1) & 1\bar{\sigma}_g(1) \\ 1\sigma_g(2) & 1\bar{\sigma}_g(2) \end{vmatrix} \tag{32}$$

In the case of minimal basis set H_2, symmetry was all we needed ($1\sigma_g$ is uniquely defined as the appropriately normalised in-phase combination of the $1s$ orbitals) but what if we didn't know, *a priori*, what the orbitals look like. In $[\mathrm{HHe}]^+$, for example, we know that the occupied orbital is an in-phase combination of $1s$ orbitals and, qualitatively, we anticipate that the bonding orbital will be polarised towards the more electronegative He atom. But how polarised? 90:10? 60:40? How do we work this out? The next section deals with Hartree-Fock theory, which provides a route, *via* the variation theorem, to find the optimum linear combination of atomic orbitals in cases where the coefficients are not determined by symmetry alone (*i.e.* the vast majority of problems!)

By analogy to the ground state of H_2, we have an expression for the total energy of $[\mathrm{HHe}]^+$:

$$E = 2E_\sigma + J_{\sigma\sigma}$$

where E_σ represents the energy of an isolated electron in the σ orbital (note there is no g/u because the molecule has $C_{\infty v}$ symmetry). We would like to minimise this energy with respect to the coefficients in the LCAO expansion of the σ orbital:

$$\psi = N\left(c_a\chi_H + c_b\chi_{He}\right)$$

We can express the ground-state wavefunction of $[\mathrm{HHe}]^+$ as a Slater determinant:

$$\psi = \left|1\sigma \quad 1\bar{\sigma}\right| = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma(1) & 1\bar{\sigma}(1) \\ 1\sigma(2) & 1\bar{\sigma}(2) \end{vmatrix}$$

If we define the coulomb and exchange operators, $\hat{J}_i$ and $\hat{K}_i$ (Equation 34) we see that in order to know the effect of J_2 on electron 1, we need to know the wavefunction for electron 2 because it is contained in the operator. Likewise, if we wish to compute the effect of J_1 on electron 2, we need to know the wavefunction for electron 1. We escape from the 'chicken and egg' situation by starting with a guess, and then *iterating* until the answer no longer changes - the so-called 'self-consistent field'.

$$\hat{J}_j\psi_i(2) = \left(\int \psi_j^*(1)\psi_j(1)\frac{1}{r_{12}}\right)\psi_i(2) \tag{33}$$

$$\hat{K}_j\psi_i(2) = \left(\int \psi_i^*(1)\psi_j(1)\frac{1}{r_{12}}\right)\psi_j(2) \tag{34}$$

The coulomb operator defines the influence of the charge cloud of electron 2, $\psi_j(2)\psi_j(2)$, on electron 1. The exchange operator defines the modification of this repulsion by spin correlation.

The formal derivation of the HF equations involves finding the condition under which E, the total energy, is a minimum, subject to the constraint that the orbitals remain orthonormal, $\langle\psi_i|\psi_j\rangle = \delta_{ij}$. The process involves the use of Lagrange multipliers – see box and MQM Ch 7 further info for a full derivation.

A reminder about Lagrange multipliers: how to find an extremum subject to a constraint.
Find the turning point of $f = 3x^2 - 2y^2$ subject to the constraint that $x + y = 2$
define $g = x + y - 2 = 0$ and so $f = f - \lambda\ g = 3x^2 - 2y^2 - \lambda(x + y - 2)$
λ is the 'Lagrange multiplier'.

$$\frac{df}{dx} = 6x - \lambda = 0 \quad \frac{df}{dy} = -4y - \lambda = 0$$
$$x = -4 \quad y = 6 \quad \lambda = -24$$

This procedure leads to the *Hartree-Fock equations*,

$$\hat{F}\psi_i = \epsilon_i\psi_i \tag{35}$$

where the Fock operator, $\hat{F}$, is defined as

$$\hat{F} = \hat{H} + \sum_j \left(2\hat{J}_j - \hat{K}_j\right) = \hat{H} + \hat{G}$$

ϵ_i is the Hartree Fock orbital energy (and also the Lagrange multiplier).
$\hat{H}$ collects together the one-electron terms for kinetic energy ($\hat{T}$) and nuclear-electron attraction ($\hat{A}$)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{H1}} - \frac{1}{r_{He1}}$$

The eigenvalues of the Hartree-Fock equations are:

$$\epsilon_i = E_i + \sum_j (2J_{ij} - K_{ij}) \tag{36}$$

Note the difference between E_i and ϵ_i: E_i is the interaction between the electron and the nuclei in the absence of the other electron (*i.e.* exactly as in H_2^+). ϵ_i is the Hartree Fock orbital energy, which represents the energy of the electron in the combined field of the nuclei and the other electron. We now have a system of linear equations where the Fock operator (a one-electron operator) defines the average field due to the nuclei (contained in $\hat{H}$) and the remaining electrons (contained in $\hat{J}$ and $\hat{K}$ operators).

What do the one-electron energies, ϵ_i, mean?
Each orbital energy contains the effects of repulsions by all other electrons, so if we sum over all occupied orbital energies, $\sum_i \epsilon_i$, the repulsions are counted twice. Therefore, to calculate the total energy we have to correct for this by subtracting the electron-electron repulsion.

$$E = \sum_i 2\epsilon_i - \sum_{i,j} (2J_{ij} - K_{ij})$$

where the sum is over doubly-occupied orbitals.
Check this works for H_2:

$$E = 2\epsilon_{1\sigma_g} - 2J_{1\sigma_g 1\sigma_g} + K_{1\sigma_g 1\sigma_g}$$

but recall that $J_{1\sigma_g 1\sigma_g} = K_{1\sigma_g 1\sigma_g}$ (Equation 31) and also that $\epsilon_{1\sigma_g} = E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$

$$\begin{aligned}\therefore \quad E &= 2\left(E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}\right) - 2J_{1\sigma_g 1\sigma_g} + -J_{1\sigma_g 1\sigma_g} \\ &= 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}\end{aligned}$$

precisely as we found in Equation 26.

10.1 Koopmans' approximation:

"The ionisation energy is approximately equal to the negative of the *Hartree Fock* orbital energy":

$$I_i \approx -\epsilon_i \tag{37}$$

Why?

$$\begin{aligned}I\left(\mathrm{H}_2\right) &= E_{\mathrm{H}_2{}^+} - E_{\mathrm{H}_2} \\ &= E_{1\sigma_g} - \left(2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}\right) \\ &= -E_{1\sigma_g} - J_{1\sigma_g 1\sigma_g} = -\epsilon_{1\sigma_g}\end{aligned}$$

The final equality comes from Equation 36. A more physical way to see this is to note that when we remove an electron from H_2 we lose the attraction to the nuclei ($E_{1\sigma_g}$) but we also relieve one unit of Coulomb repulsion, $J_{1\sigma_g 1\sigma_g}$, – precisely the components of $\epsilon_{1\sigma_g}$

10.2 Hartree-Fock-Roothaan (HFR) Equations:

These are the HF equations expressed in terms of the LCAO approximation.

$$\hat{F}\phi = \epsilon\phi \qquad \phi = \sum_n c_n \chi_n$$

$$\hat{F}\sum_n c_n \chi_n = \epsilon \sum_n c_n \chi_n$$

Pre-multiplying by $\langle \chi_m |$ and integrating gives

$$\sum_n c_n \langle \chi_m | \hat{F} | \chi_n \rangle = \epsilon \sum_n c_n \langle \chi_m | \chi_n \rangle$$

$$\sum_n c_n \left(F_{mn} - \epsilon\, S_{mn}\right) = 0$$

which has non-trivial solutions when $|F_{mn} - \epsilon\, S_{mn}| = 0$ (note similarities to secular equations, Equation 3 – more on solving these in the last 2 lectures).

Reiterate: in order to determine c_n by solving the HFR equations, we need to be able to calculate the matrix elements F_{mn} (including coulomb and exchange integrals), which in turn means that we need to already know c_n! Hence we need to start with a guess and iterate:

The flow diagram for a Hartree-Fock calculation is given in Figure 15.

10.3 The anatomy of a Hartree-Fock calculation:

Calculate the ground-state energy of $[\mathrm{HHe}]^+$ at the equilibrium separation, $R = 0.80$ $\mathring{A}$ with a minimal STO-1G basis set ($\alpha = 0.4166$ on H, $\alpha = 0.7739$ on He). The 'best' exponents are obtained by fitting to experiment, and a huge range is available at https://www.basissetexchange.org/. In this case, the larger value of ζ for He reflects the fact that the Z_{eff} should be higher and the 1s orbital should be smaller.

Expand the MOs in the form

$$\psi = c_a \chi_H \pm c_b \chi_{He}$$

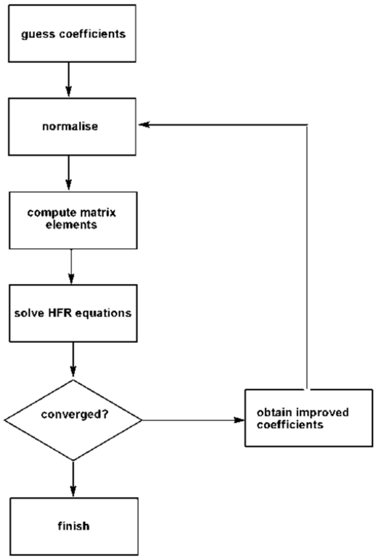


Figure 15: Flow diagram for a Hartree-Fock calculation.

where χ_H and χ_{He} are 1s orbitals centred on He and He, respectively.

The general expression for the HFR equations

$$\sum_n c_n \left(F_{mn} - \epsilon\ S_{mn}\right) = 0$$

give us:

$$\begin{aligned}(F_{aa} - \epsilon\ S_{aa})\, c_a + (F_{ab} - \epsilon\ S_{ab})\, c_b = 0\\(F_{ab} - \epsilon\ S_{ab})\, c_a + (F_{bb} - \epsilon\ S_{bb})\, c_b = 0\end{aligned}$$

$$\begin{vmatrix} F_{aa} - \epsilon\ S_{aa} & F_{ab} - \epsilon\ S_{ab} \\ F_{ab} - \epsilon\ S_{ab} & F_{bb} - \epsilon\ S_{bb} \end{vmatrix} = 0$$

We need to build this matrix using matrix elements of the Fock operator:

$$\hat{F} = \hat{H} + \sum_j \left(2\hat{J}_j - \hat{K}_j\right) = \hat{H} + \hat{G}$$

so we need numerical values for all the matrix elements (energies in Hartree units), which we can calculate using the tools set out in Section 5.

Overlap (S):	S_{aa}=$S_{bb} = 1$	$S_{ab} = 0.502$	
Kinetic energy (T)	$T_{aa} = 0.625$	$T_{bb} = 1.161$	$T_{ab} = 0.239$
Nuclear attraction (A)	$A_{aa} = -2.285$	$A_{bb} = -3.464$	$A_{ab} = -1.555$

$$\hat{H} + \hat{T} = \begin{pmatrix} -1.661 & -1.316 \\ -1.316 & -2.303 \end{pmatrix} \qquad \hat{S} = \begin{pmatrix} 1.0 & 0.502 \\ 0.502 & 1.0 \end{pmatrix}$$

We also need the matrix elements of electron-electron repulsion (note there are now 6 different ones because the molecule is no longer symmetric, so $\langle aa|aa\rangle \neq \langle bb|bb\rangle$ and $\langle aa|ab\rangle \neq \langle bb|ab\rangle$), as was the case in Equation 27:

Table 1: **Electron-electron repulsion integrals for HHe$^+$. These are obtained from Equation 21.**

$$\langle aa|aa\rangle = 0.728 \quad \langle bb|bb\rangle = 0.993 \quad \langle ab|ba\rangle = 0.585$$

$$\langle aa|ab\rangle = 0.342 \quad \langle aa|bb\rangle = 0.219 \quad \langle bb|ab\rangle = 0.436$$

Let us start the iteration with a guess for c_a and c_b.

Step 1: guess $c_b = 2c_a \quad \therefore \quad \frac{c_b}{c_a} = 2$ (a plausible guess because we anticipated that $c_b > c_a$ for the σ bonding orbital in HHe$^+$)

Step 2: normalise $\psi_{1\sigma} = c_a\chi_H + c_b\chi_{He} = c_a\chi_H + 2c_a\chi_{He}$

$$\int (c_a\chi_H + 2c_a\chi_{He})(c_a\chi_H + 2c_a\chi_{He})\, d\tau = 1$$

Step 3: Now calculate the elements of the electron-electron repulsion matrix. Here, we need to introduce the coefficients, c_a and c_b, in the bonding orbital – these determine where the electrons are, and hence what the form of $\hat{J}_j$ is.
Take the first element as an example - this expression is analogous to the one set out in Equation 9.4 for H$_2$.

$$\begin{aligned}G_{aa} = \langle a|\hat{G}|a\rangle &= 2c_a^2\left(\langle aa|aa\rangle - \frac{1}{2}\langle aa|aa\rangle\right) + 2c_ac_b\left(\langle aa|ab\rangle - \frac{1}{2}\langle aa|ab\rangle\right) + \\ &2c_bc_a\left(\langle aa|ab\rangle - \frac{1}{2}\langle aa|ab\rangle\right) + 2c_b^2\left(\langle ab|ba\rangle - \frac{1}{2}\langle aa|bb\rangle\right) \\ &= 2\times 0.143\times\frac{1}{2}\times 0.728 + 2\times 0.286\times\frac{1}{2}\times 0.342 \\ &+ 2\times 0.286\times\frac{1}{2}\times 0.342 + 2\times 0.572\times\left(0.585 - \frac{1}{2}\times 0.219\right) = 0.842\end{aligned}$$

The complete G matrix is

$$\hat{G} = \begin{pmatrix} 0.842 & 0.319 \\ 0.319 & 0.952 \end{pmatrix}$$

$$\hat{F} = \hat{H} + \hat{G} = \begin{pmatrix} -1.661 & -1.316 \\ -1.316 & -2.303 \end{pmatrix} + \begin{pmatrix} 0.842 & 0.319 \\ 0.319 & 0.952 \end{pmatrix} = \begin{pmatrix} -0.819 & -0.997 \\ -0.997 & -1.351 \end{pmatrix}$$

Step 4: solve $FC = SCE$

$$\begin{vmatrix} -0.819 - \epsilon & -0.997 - 0.502\epsilon \\ -0.997 - 0.502\epsilon & -1.351 - \epsilon \end{vmatrix} = 0 \tag{38}$$

$\epsilon_1 = -1.460\ au$ (lowest eigenvalue)
Step 5: Converged? *i.e.* is the value of ϵ_1 the same (to within a defined threshold) as the previous value.

Clearly as this is the first iteration we have nothing to compare to, and so the answer is no!
Otherwise

Step 6: solve the secular equations for c_a, c_b using $\epsilon = \epsilon_1 = -1.460\ au$

$$(F_{aa} - \epsilon\ S_{aa})\, c_a + (F_{ab} - \epsilon\ S_{ab})\, c_b = 0$$
$$(F_{ab} - \epsilon\ S_{ab})\, c_a + (F_{bb} - \epsilon\ S_{bb})\, c_b = 0$$

$$0.641c_a - 0.264c_b = 0 \ \therefore\ \frac{c_b}{c_a} = 2.43$$

and go round the cycle again..

Step 2: normalise $\psi_{1\sigma} = c_a\chi_H + c_b\chi_{He}$ with $\frac{c_b}{c_a} = 2.43$

$$c_a = 0.327\ \therefore\ c_b = 0.795$$

etc. etc.

	c_a	c_b	F_{aa}	F_{ab}	F_{bb}	ϵ_1
Initial	0.378	0.756	-0.819	-0.997	-1.351	-1.460
1st	0.327	0.795	-0.804	-0.984	-1.347	-1.449
2nd	0.319	0.801	-0.802	-0.982	-1.346	-1.448
3rd	0.318	0.802	-0.801	-0.982	-1.346	-1.447
4th	0.318	0.802	-0.801	-0.982	-1.346	-1.447
5th	0.318	0.802	-0.801	-0.982	-1.346	-1.447

Table 2: Convergence History

at self consistency: $\psi_{1\sigma} = 0.318\chi_H + 0.802\chi_{He}$. So the bonding orbital really is localised on He!

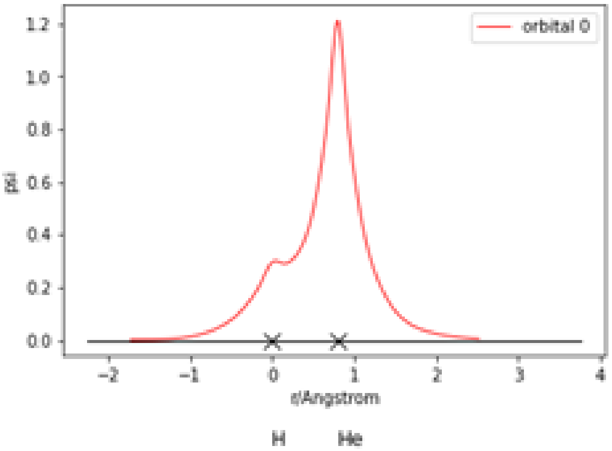


Figure 16: HOMO of HHe$^+$.

11 Electron-electron repulsions in a chemical context:

We can generalise the expression for the energy to atoms/molecules with more than 2 electrons:

$$E = \sum_i 2E_i + \sum_{i,j} (2J_{ij} - K_{ij}) \tag{39}$$

for any closed-shell molecule, where the summation runs over doubly occupied orbitals For a 4-electron system (Figure 17), for example:

$$\begin{aligned} E &= 2E_a + 2E_b + (2J_{aa} - K_{aa}) + (2J_{bb} - K_{bb}) + 2\,(2J_{ab} - K_{ab}) \\ &= 2E_a + 2E_b + J_{aa} + J_{bb} + 4J_{ab} - 2K_{ab} \end{aligned}$$

A simple 'algorithm' that works for any atom/molecule (open or closed shell):

Total energy =

- the sum of the one-electron energies
- + 1J per pairwise interaction between two electrons
- - 1K per pairwise interaction between two electrons with parallel spins.

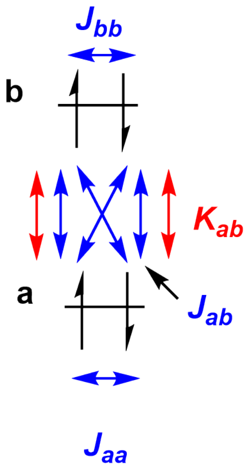


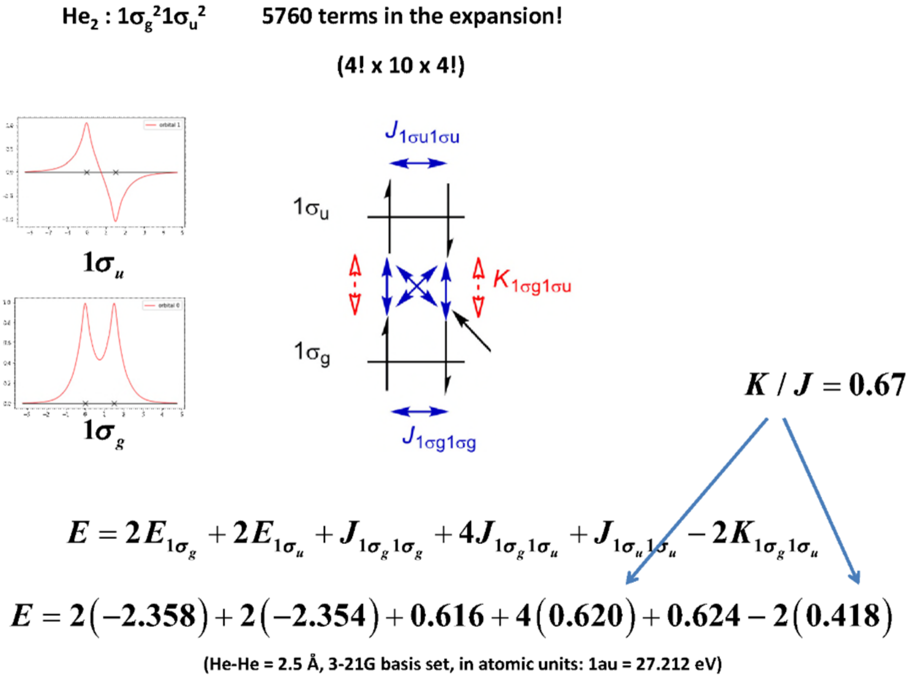
Figure 17: Coulomb and exchange contributions to the total electron-electron repulsion in a 4-electron system.

Let's look at 2 limiting cases, both with 4 electrons: He_2 and Be

He_2:

In this case, the two pairs of electrons (in σ_g and σ_u) occupy *similar* regions of space, Figure 18 (both are linear combinations of He 1s).

K is very large – it reduces the Coulomb repulsion by a factor of 2/3!



$$E = 2E_{1\sigma_g} + 2E_{1\sigma_u} + J_{1\sigma_g 1\sigma_g} + 4J_{1\sigma_g 1\sigma_u} + J_{1\sigma_u 1\sigma_u} - 2K_{1\sigma_g 1\sigma_u}$$

$$E = 2(-2.358) + 2(-2.354) + 0.616 + 4(0.620) + 0.624 - 2(0.418)$$

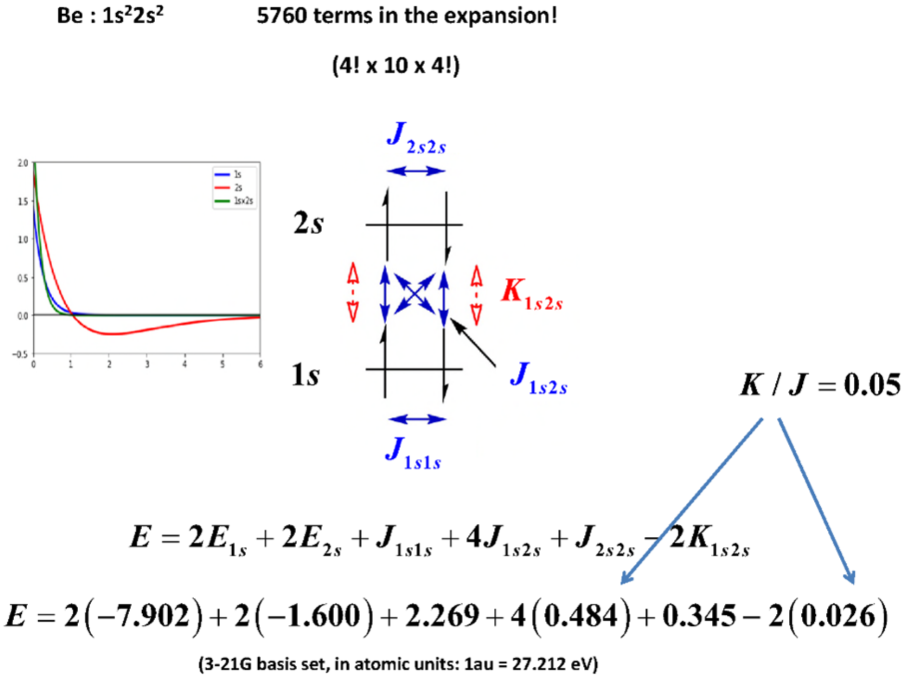
(He-He = 2.5 Å, 3-21G basis set, in atomic units: 1au = 27.212 eV)

Figure 18: Components of the total energy for a He$_2$ dimer.

Be:

Effectively the same problem (4 electrons in 2 orbitals), but now the two pairs of electrons (in 1s and 2s) occupy very *different* regions of space, Figure 19.

K is very small – it only offsets $\sim 5\%$ of the Coulomb repulsion.
Useful rule of thumb for d electrons transition metals: $K \approx 0.25 \times J$ (electrons are in similar regions of space).



$$E = 2E_{1s} + 2E_{2s} + J_{1s1s} + 4J_{1s2s} + J_{2s2s} - 2K_{1s2s}$$

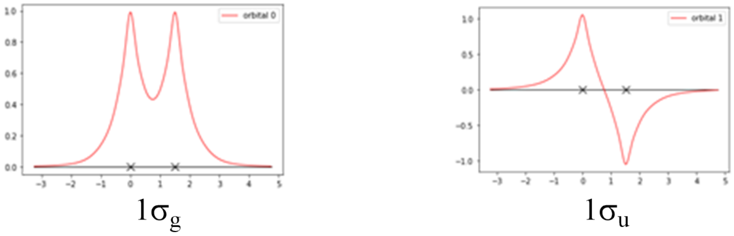
$$E = 2(-7.902) + 2(-1.600) + 2.269 + 4(0.484) + 0.345 - 2(0.026)$$

Figure 19: Components of the total energy for a Be atom.

11.1 What are the signs and magnitudes of J and K?

Recall the shapes of the orbitals in He_2:

orbitals



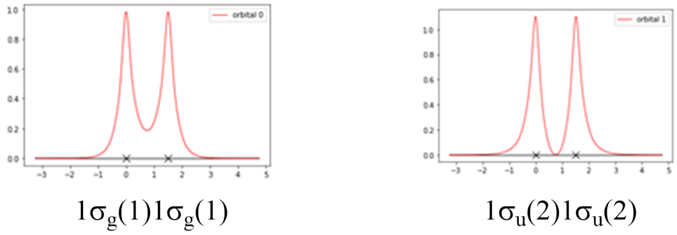
$1\sigma_g$

$1\sigma_u$

Now consider the **products** of orbitals on the left and right hand sides of the expression for J.

$$J_{1\sigma_g 1\sigma_u} = \langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(1)1\sigma_u(2)\rangle$$

Hartree products in J



$1\sigma_g(1)1\sigma_g(1)$

$1\sigma_u(2)1\sigma_u(2)$

$$1\sigma_g(1)1\sigma_g(1) \qquad\qquad 1\sigma_u(2)1\sigma_u(2)$$

$$> 0 \textbf{ everywhere} \qquad\qquad > 0 \textbf{ everywhere}$$

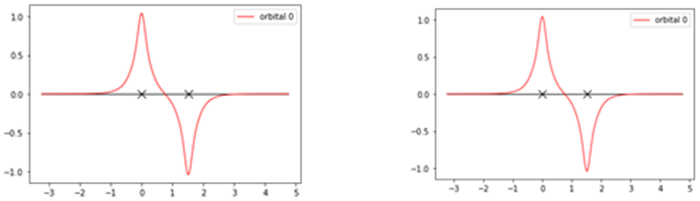
$$\frac{1}{r_{12}} > 0 \textbf{ everywhere}$$

J is the sum of terms that are all positive, so J MUST be positive (no surprise - it is a repulsion, after all!).

What about K?

$$K_{1\sigma_g 1\sigma_u} = \langle 1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)\rangle$$

Hartree products in K



$1\sigma_g(1)1\sigma_u(1)$ $1\sigma_g(2)1\sigma_u(2)$

$$1\sigma_g(1)1\sigma_u(1) \qquad\qquad 1\sigma_g(2)1\sigma_u(2)$$

$$> 0 \; on\ left, < 0 \; on\ right \qquad\qquad > 0 \; on\ left, < 0 \; on\ right$$

$$\frac{1}{r_{12}} > 0 \textbf{ everywhere}$$

The products can now be either positive or negative, depending on position in space.

If both electrons on same side of the node: $1\sigma_g(1)1\sigma_u)2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1) > 0$

If electrons on opposite sides of the node: $1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1) < 0$

Unlike J, K is the sum of some terms that are positive and some terms that are negative, so we cannot, *a priori*, predict its sign in the same way as we can for J.

However, if the electrons are on the *same* side of the node, r_{12} is necessarily small, so $1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)$ is large (and positive as established above).

In contrast, if the electrons are on *opposite* sides of the node, r_{12} is necessarily large(r), so $1\sigma_g(1)1\sigma_u(2)|\frac{1}{r_{12}}|1\sigma_g(2)1\sigma_u(1)$ is small (and negative as established above).

The summation large positive and small negative contributions means that K is positive, but generally smaller than J

In practice $K \approx 0.25J$ for electrons in the same subshell where there are no radial nodes, such as first-row atoms (C, N, O, F), first-row TMs and lanthanides.

12 The correlation problem and post-HF methods.

The Hartree-Fock wavefunction for the ground state of H_2 can be represented as:

$$\psi = \left| 1\sigma_g \quad 1\bar{\sigma}_g \right| = \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1) & 1\bar{\sigma}_g(1) \\ 1\sigma_g(2) & 1\bar{\sigma}_g(2) \end{vmatrix}$$

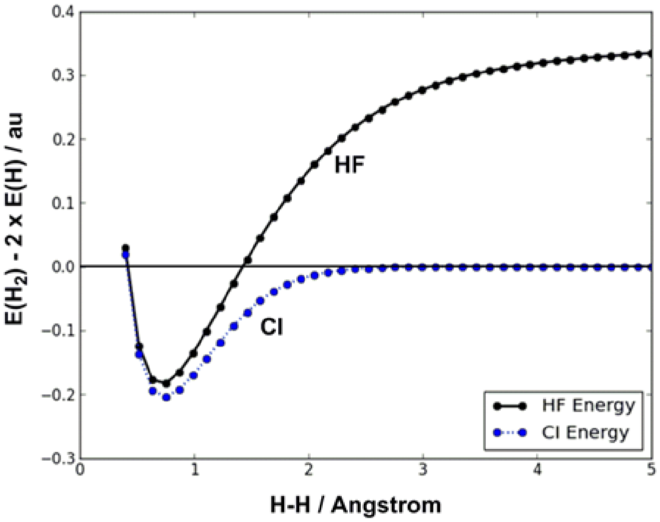


Figure 20: HF and CI potential energy curves for the H_2 dimer.

The potential energy surface obtained with this wavefunction shown in Figure 20 (blac curve) indicates that this reproduces the equilibrium geometry reasonably well, but fails to reproduce the dissociation energy: the HF energy of H_2 at the dissociation limit is ≈ 0.34 *au* higher than that of two isolated H atoms - this is a spectacular failure! To see the origin of the problem with the HF wavefunction, expand one of the Hartree products in the ground-state:

$$\begin{aligned} 1\sigma_g(1)1\sigma_g(2) &= \frac{1}{2\,(1+S)} \left(\chi_a(1) + \chi_b(1)\right)\left(\chi_a(2) + \chi_b(2)\right) \\ &= \frac{1}{2\,(1+S)} \left[\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) + \chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)\right] \\ &= H_a^- ... H_b^+ \quad + \quad H_a^+ ... H_b^- \quad + \quad H_a ... H_b . \quad + \quad H_a ... H_b \end{aligned}$$

i.e. it is an equal mixture of covalent $(H_a ... H_b)$ and ionic $(H_a^+ ... H_b^-)$ resonance structures. This is reasonable at the equilibrium geometry, where overlap is large, but unrealistic at the dissociation limit, where two neutral H atoms will be strongly favoured over $H^+ + H^-$. This problem is a consequence of the central field approximation, where one electron is influenced only by the *average* position of the other: the result is that situations where both electrons are very close to each other at any given instant have a higher weight in the wavefunction than they should have: we say that the *motion of the two electrons is not correlated.* Another way to see this is to note that if the two electrons share the same spatial wavefunction, then wherever the most probable position to find electron 1 is, it must also be the most probable position to find electron 2, and that doesn't make much sense!

12.1 Configuration interaction

The problems at the dissociation limit can be reduced by using configuration interaction – adding in extra configurations to the wavefunction. In this case we will mix the $|1\sigma_g^2|$ configuration with the doubly excited configuration $|1\sigma_u^2|$

$$\Psi_{CI} = c_1|1\sigma_g^2| + c_2|1\sigma_u^2| \tag{40}$$

Expanding one of the Hartree products for the $|1\sigma_u^2|$ configuration as we did above for $|1\sigma_g^2|$:

$$\begin{aligned}
1\sigma_u 1\sigma_u &= \frac{1}{2(1-S)}\left(\chi_a(1) - \chi_b(1)\right)\left(\chi_a(2) - \chi_b(2)\right) \\
&= \frac{1}{2(1-S)}\left[\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) - \chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2)\right] \\
&\qquad\qquad = H_a^- ... H_b^+ \quad + \quad H_a^+ ... H_b^- \quad - \quad H_a ... H_b. \quad - \quad H_a ... H_b
\end{aligned}$$

note that the ionic and covalent terms now appear with *opposite* signs.

for $\Psi_{CI} = c_1|1\sigma_g^2| + c_2|1\sigma_u^2|$

$$\begin{aligned}
&\left(\frac{c_1}{2(1+S)} + \frac{c_2}{2(1-S)}\right)\left(\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2)\right) \\
&+ \left(\frac{c_1}{2(1+S)} - \frac{c_2}{2(1-S)}\right)\left(\chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)\right)
\end{aligned}$$

An appropriate choice of coefficients (specifically $\frac{c_1}{c_2} = -\frac{1+S}{1-S}$) causes the ionic terms to vanish completely. The ratio $\frac{c_1}{c_2}$ varies from 0 to -1 at the dissociation limit. The correlation energy is defined as the difference between the energy obtained from this wavefunction and the Hartree Fock energy. Notice that in order to get a better energy, we have had to abandon the idea that electrons live in orbitals – this is a big leap!
In practice, CI is performed by constructing linear combinations of ground and excited determinants based on the Hartree-Fock orbitals. The optimum linear combination $\Phi = \sum_i C_i \Phi_i$ where Φ_i are now determinants, not orbitals, is then found using the linear variation method.
Example: $\mathbf{H_2}$:

$$\Phi = C_1\Phi_i + C_2\Phi_2$$

$$\Phi_1 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1) & 1\bar{\sigma}_g(1) \\ 1\sigma_g(2) & 1\bar{\sigma}_g(2) \end{vmatrix} \qquad \Phi_2 = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_u(1) & 1\bar{\sigma}_u(1) \\ 1\sigma_u(2) & 1\bar{\sigma}_u(2) \end{vmatrix}$$

and the secular determinant we need to solve is:

$$\begin{vmatrix} \langle\Phi_1|\hat{H}|\Phi_1\rangle - E & \langle\Phi_2|\hat{H}|\Phi_1\rangle \\ \langle\Phi_1|\hat{H}|\Phi_2\rangle & \langle\Phi_2|\hat{H}|\Phi_2\rangle - E \end{vmatrix} = 0$$

We have already encountered the matrix element $\langle\Phi_1|\hat{H}|\Phi_1\rangle$ - it is just the ground-state energy of H_2:

$$\langle\Phi_1|\hat{H}|\Phi_1\rangle = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$$

Similarly, we can show that

$$\begin{aligned}
\langle\Phi_2|\hat{H}|\Phi_2\rangle &= 2E_{1\sigma_u} + J_{1\sigma_u 1\sigma_u} \\
\langle\Phi_1|\hat{H}|\Phi_2\rangle &= \langle\Phi_2|\hat{H}|\Phi_1\rangle = K_{1\sigma_g 1\sigma_u}
\end{aligned}$$

(see Problems 1, Qu 7)
So the total energy including CI is the lowest root of

$$\begin{vmatrix} 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g} - E & K_{1\sigma_g 1\sigma_u} \\ K_{1\sigma_g 1\sigma_u} & 2E_{1\sigma_u} + J_{1\sigma_u 1\sigma_u} - E \end{vmatrix} = 0 \tag{41}$$

Solution of this determinant for different values of r gives the dashed curve in Figure 20.
Note that if the off-diagonal elements ($K_{1\sigma_g 1\sigma_u}$) in Equation 41 are zero, there is no mixing of configurations. So configuration interaction is most significant when K is large (see previous lecture for a discussion of when this is the case).
For larger molecules, many millions or even billions of excited determinants may be needed for good accuracy. The methods (acronyms CI, CID, CISD(T), CASSCF, MRCI...) can be very accurate but **very** expensive.

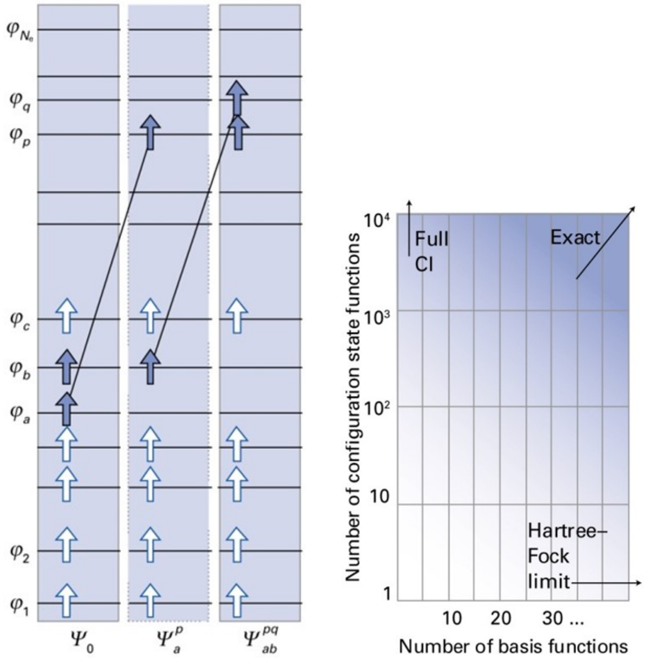


Figure 21: Singly and doubly excited configurations and the approach to the 'exact' limit.

13 Density Functional Theory

A fundamentally different approach, based on the density, ρ, (a 3-dimensional variable) rather than the wavefunction (a $3n$-dimensional entity, where n is the number of electrons). Based on Theorems by Hohenberg and Kohn (Kohn, Nobel prize 1998):

1. The energy is uniquely defined by the electron density, ρ.
2. The ground-state energy can be obtained variationally: the density that minimises the total energy is the exact ground-state density.

In principle, orbitals are not needed for DFT, but in practice it is very difficult to calculate the KE term ($-\frac{1}{2}\nabla^2$) accurately using the density alone. Kohn and Sham developed a methodology wherein the electron density is modelled as a system of fictitious non-interacting electrons which occupy the 'Kohn-Sham orbitals' and reproduce the real density. This leads to a set of 1-electron Kohn-Sham equations very similar in structure to the Hartree Fock equations:

$$\begin{gathered} \hat{H}_{KS}\phi_i = \left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\phi_i = \epsilon_i\phi_i \\ V_{eff} = V(r) + J(r) + V_{xc}(r) \end{gathered} \tag{42}$$

$V(r)$ and $J(r)$ are the electron-nuclear and coulomb potentials, precisely as in HF theory. $V_{xc}(r)$ is the so-called 'exchange-correlation' potential, which determines both the exchange and correlation effects. Notice that the influence of correlation is introduced through the Hamiltonian, rather than by expanding the wavefunction beyond the HF single determinant. Therefore it is appealing in terms of cost. The problem is that the exact form of $V_{xc}(r)$ is unknown, and there are hundreds (thousands ...) of different approximations to it (BP86, BLYP, HCTH, B3LYP, PBE, rev-PBE........ – the so-called 'functional zoo'). Nearly 30 years after it was first proposed, the most popular remains B3LYP ('everybody's favourite functional').

The simplest density functional for the exchange energy, the so-called 'local density approximation, is based on the properties of the Uniform Electron Gas:

$$E_x{}^{LDA} = -\left(\frac{3}{4}\right)\left(\frac{3}{\pi}\right)^{1/3}(4\pi)\int_0^\infty r^2\rho(r)^{4/3}dr \tag{43}$$

This turns out to be a surprisingly good approximation. Recall in Equation 22 we calculated J for two electrons in a $1s$ orbital. Also recall that if the two electrons are in the same orbital, $J = K$ and that the exchange energy is intrinsically negative. The expression for the Hartree-Fock exchange energy is then:

$$E_x{}^{HF} = -2\left(\frac{\alpha}{\pi}\right)^{1/2} = -\left(\frac{2^2}{\pi}\right)^{1/2}\alpha^{1/2} \sim -1.128\alpha^{1/2}$$

Using the expression for the orbital,

$$\chi = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

we can express the density as

$$\rho = 2\left(\frac{2\alpha}{\pi}\right)^{3/2} e^{-2\alpha r^2}$$

and plugging into equation 44, we get, with use of the standard integral in Equation 17 and some collecting of terms:

$$E_x{}^{LDA} = -\left(\frac{3^{17}}{2^{19}\pi^5}\right)^{1/6}\alpha^{1/2} \sim -0.964\alpha^{1/2}$$

The value is about 15% too low. To correct for this, Slater introduced an empirical correction factor to give the so-called 'Slater $X\alpha$' expression:

$$E_x{}^{X\alpha} = -1.05E_x{}^{LDA} \sim -1.013\alpha^{1/2} \tag{44}$$

Slater's exchange expression was used extensively, particularly in solid-state physics, for many years. More modern functionals use more complex expressions for E_x and get better agreement with experiment, but the principle is the same - the only difference is that the integral is harder!

Correlation energies can be calculated using the same principles, but the expressions are typically more complex.

14 Semi-empirical theory

The number of 2-electron integrals in a HF expansion scales as N^4 where N is the number of basis functions. Thus reducing the size of the basis set and avoiding the calculation of some of the integrals is clearly an advantageous strategy. There are two ways to do this.

1. We can parameterise (or set to zero) many of the 2-electron integrals that make up the Fock matrix (such as those in Table 1), but leave the iterative structure unchanged. Depending on the parameterisation scheme, this leads to a family of methods, CNDO, INDO, MINDO, ZINDO, AM1, AM2 *etc. etc.*. 'NDO'

is 'neglect of differential overlap'. AM1 *etc.* were developed in Austin, Texas - hence Austin model 1, 2 *etc.* These methods were popular up to the 1980's, but have now largely been supplanted by DFT. There are still some niche applications in *e.g.* electronic spectroscopy (they provide a quick way of approximating the CI matrix).

2. We can be more radical and try to guess the structure of the final Fock matrix (as in Equation 38). This removes the need to calculate any of the individual matrix elements, and also the need for iteration. Hückel theory is the ultimate extension of this approach, but a more useful middle ground is extended Hückel theory (EHT, for short). It should be emphasised that the approximations in these methods are so severe that it is not realistic to expect quantitative results. So extended Hückel theory is typically used for qualitative studies of electronic structure based on overlap and symmetry arguments, but not for the calculation of accurate energies or geometries. All of the MO diagrams and Walsh diagrams presented in the core course **Bonding in Molecules** were generated using EHT.

14.1 Hückel theory

Also see Valence lectures 7/8. The ultimate extension of semi-empirical theory - the philosophy is to eliminate the computation of matrix elements entirely by parameterisation at the Fock matrix element level. Thus it is not iterative.

- Assume complete separation of σ and π systems (contrast **Extended Hückel Theory**, later, where all valence orbitals are included)

- Assumes independent electrons: *i.e.* $\psi = \psi_1\psi_2\psi_3\psi_4..$, a simple Hartree product, and $E = E_1 + E_2 + E_3 + E_4 + ...$

- $H_{11} = \alpha$ the Coulomb integral

- $H_{12} = \beta$ (the resonance integral) if 1 and 2 are nearest neighbours, 0 otherwise

- α and β usually given symbolic values rather than assigned to real numbers.

- $S_{ij} = \delta_{ij}$
  this makes the overlap matrix equal to the identity, and simplifies the secular equations from $\hat{H}c = ScE$ to $\hat{H}c = cE$. In a typical conjugated system $S_{12} \approx 0.2$, so this seems a somewhat radical approximation. However it has little impact on the final solutions.

- Note geometry (*i.e.* bond lengths) is not considered at any point – only connectivity.

14.2 Extended Hückel theory

As with Hückel theory, the computation of matrix elements is avoided entirely by parameterisation of the Fock matrix elements: again not iterative, but no assumptions are made about $\sigma\pi$ separability: all valence electrons included. Unlike Hückel theory, geometry determines overlaps, which are calculated explicitly (ignoring π overlap might be OK, but ignoring σ overlap is not reasonable!).

- Assumes independent electrons: $\psi = \psi_1\psi_2\psi_3\psi_4..$ and $E = E_1 + E_2 + E_3 + E_4 + ...$

- S_{ij} computed as in Hartree Fock theory, using a minimal basis of Slater-type orbitals. If you want to see the details of how this is done, look at the python script EH.py in the course support materials.

- $H_{ii} = -I_i$ The ionisation energy of an electron in the appropriate orbital in the valence configuration (*e.g.* sp^3 for a tetrahedral carbon). In practice this is usually taken as the weighted average of $2s$ and $2p$ electrons in C, but the choice is not critical.

- $$H_{ij} = KS_{ij}\left[\frac{H_{ii}+H_{jj}}{2}\right] \qquad \textbf{Wolfsberg-Helmholtz formula}$$

- $K = 1.75$ reproduces rotational barrier for ethane, but the choice is not critical. Early versions used the simpler $H_{ij} = KS_{ij}$

- Solve matrix equation $Hc = ScE$ to get energies and eigenfunctions (=orbitals)

Example: $\mathbf{CH_4}$ valence orbitals: $C\ 2s$, $C\ 2p_{x,y,z}$ $H\ 1s$

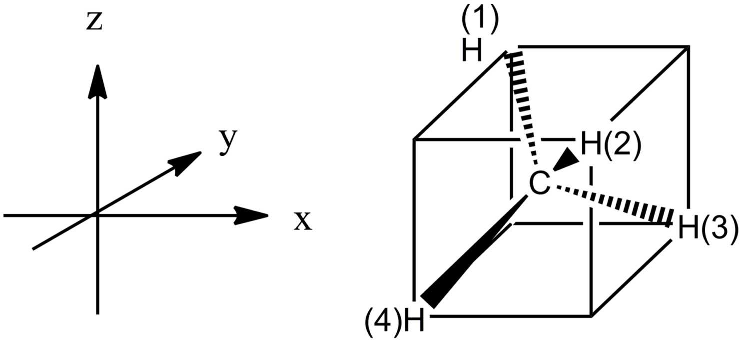


Figure 22: Definition of axis system for CH_4.

Work flow:
Construct S using geometry and form of basis functions (Table 3)

Parameters: $C : \zeta_{2s,2p} = 1.625$ $H : \zeta_{1s} = 1.20$ $C - H = 1.09$ Å (this information is only required to construct overlap matrix).

Table 3: **Overlap matrix for $\mathbf{CH_4}$**

	$C\ 2s$	$C\ 2p_z$	$C\ 2p_x$	$C\ 2p_y$	$H\ 1s(1)$	$H\ 1s(2)$	$H\ 1s(3)$	$H\ 1s(4)$
$C\ 2s$	1	0	0	0	0.5183	0.5183	0.5183	0.5183
$C\ 2p_z$	0	1	0	0	0.2819	0.2819	-0.2819	-0.2819
$C\ 2p_x$	0	0	1	0	-0.2819	0.2819	0.2819	-0.2819
$C\ 2p_y$	0	0	0	1	0.2819	-0.2819	0.2819	-0.2819
$H\ 1s(1))$	0.5183	0.2819	-0.2819	0.2819	1	0.1844	0.1844	0.1844
$H\ 1s(2)$	0.5183	0.2819	0.2819	-0.2819	0.1844	1	0.1844	0.1844
$H\ 1s(3)$	0.5183	-0.2819	0.2819	0.2819	0.1844	0.1844	1	0.1844
$H\ 1s(4)$	0.5183	-0.2819	-0.2819	-0.2819	0.1844	0.1844	0.1844	1

Insert diagonal elements H_{ii} (usually tabulated) into H
Calculate off-diagonal elements H_{ij} using Wolfsberg-Helmholtz formula. (Table 4)

Construct secular determinant and solve for E, c_n

Table 4: **Hamiltonian matrix for CH$_4$**

	C 2s	C 2p_z	C 2p_x	C 2p_y	H 1s(1)	H 1s(2)	H 1s(3)	H 1s(4)
C 2s	-19.44	0	0	0	-14.98	-14.98	-14.98	-14.98
C 2p_z	0	-10.67	0	0	-5.99	-5.99	5.99	5.99
C 2p_x	0	0	-10.67	0	5.99	-5.99	-5.99	5.99
C 2p_y	0	0	0	-10.67	-5.99	5.99	-5.99	5.99
H 1s(1)	-14.98	-5.99	5.99	-5.99	-13.6	-4.39	-4.39	-4.39
H 1s(2)	-14.98	-5.99	-5.99	5.99	-4.39	-13.6	-4.39	-4.39
H 1s(3)	-14.98	5.99	-5.99	-5.99	-4.39	-4.39	-13.6	-4.39
H 1s(4)	-14.98	5.99	5.99	5.99	-4.39	-4.39	-4.39	-13.6

Table 5: **Results (eigenvalues and eigenfunctions) of an extended Hückel calculation on CH$_4$**

orbital	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
				Eigenvalues (energies)				
E	-23.21	-14.93	-14.93	-14.93	6.06	6.06	6.06	34.0
Occup	2	2	2	2	0	0	0	0
				Eigenfunctions (MOs)				
C 2s	0.58	0	0	0	0	0	0	1.70
C 2p_z	0	-0.12	0.48	0.20	0.25	-0.31	1.09	0
C 2p_x	0	-0.28	0.12	-0.44	-0.92	0.60	0.38	0
C 2p_y	0	0.44	0.20	-0.23	-0.66	-0.95	-0.12	0
H 1s(1)	0.19	0.17	-0.10	-0.52	1.0	0.02	0.45	-0.69
H 1s(2)	0.19	0.36	0.34	0.25	-0.28	1.01	0.33	-0.69
H 1s(3)	0.19	-0.50	0.24	0.0	0.0	-0.67	-0.86	-0.69
H 1s(4)	0.19	-0.03	-0.48	0.28	-0.73	0.36	0.74	-0.69

15 Problems - 1 and 2

15.1 Problems 1

1. Write down the Slater determinant for the ground states of the following: Li, He$_2$ and Li$_2$.

2. The z component of the spin angular momentum operator is

$$\hat{S}_z = \sum_{j=1}^{n} \hat{s}_{jz}$$

. Show that

$$\Phi = \frac{1}{\sqrt{3}} \begin{vmatrix} 1s(1) & \bar{1}s(1) & 2s(1) \\ 1s(2) & \bar{1}s(2) & 2s(2) \\ 1s(3) & \bar{1}s(3) & 2s(3) \end{vmatrix}$$

is an eigenfunction of $\hat{S}_z$ and evaluate its eigenvalue.

For the next two questions, you will need the standard integrals:

$$\int_{-\infty}^{+\infty} e^{-bx^2}dx = \sqrt{\frac{\pi}{b}} \qquad \int_{-\infty}^{+\infty} x^2 e^{-bx^2}dx = \frac{1}{2b}\sqrt{\frac{\pi}{b}}$$

3. Evaluate the overlap matrix element between a normalised p-type Gaussian basis function located at the origin, χ_a, and an s-type Gaussian located at (0,0,a), χ_b. The exponent in both cases is α.

$$\chi_a = N_1 z e^{-\alpha(x^2+y^2+z^2)} \quad \chi_b = N_2 e^{-\alpha(x^2+y^2+(z-a)^2)}$$

4. Evaluate the off-diagonal matrix element of the kinetic energy operator, $T_{ab} = \langle\chi_a|\hat{T}|\chi_b\rangle$ between an s-type Gaussian basis function located at the origin, χ_a and an s-type Gaussian located at (0,0,a), χ_b. The exponent in both cases is α.

$$\chi_a = N_3 e^{-\alpha(x^2+y^2+z^2)} \quad \chi_b = N_4 e^{-\alpha(x^2+y^2+(z-a)^2)}$$

5. Show that the total energy, $T + V$, of a hydrogen atom described by a single gaussian function, $\chi_a = Ne^{-\alpha r^2}$, is minimised when $\alpha = \frac{8}{9\pi}$.

6. The total nuclear-electron attraction for an electron in an s orbital centred on one of the two nuclei in H_2^+ (χ_a) is given by:

$$A_{aa} = \sum_C \langle\chi_a|\frac{-Z_C}{r_C}|\chi_a\rangle$$

where

$$\chi_a = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

show that for $r = 0.77\ \mathring{A}$ and $\alpha = 0.4166$, $A_{aa} = -1.676\ au$.

hint: to do this you need to sum over the interaction with both nuclei, the one that the orbital is centred on and the other one. The first one is as set out in the notes ($r_c = 0$, Equation **??**) but for the second one, the distance is not large enough to ensure that $erf(t) \approx 1$. You will therefore need to estimate the value for $erf(t)$ by interpolating the values in the table given in the handout.

7. We showed in the handout (Equation 30) that for the ground state configuration of H_2,

$$\psi_1 = \frac{1}{\sqrt{2}}(1\sigma_g(1)1\bar{\sigma}_g(2) - 1\sigma_g(2)1\bar{\sigma}_g(1)) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1) & 1\bar{\sigma}_g(1) \\ 1\sigma_g(2) & 1\bar{\sigma}_g(2) \end{vmatrix}$$

$$E_1 = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$$

By expanding the expression

$$\langle\psi_2|\hat{H}|\psi_2\rangle = E = \langle\psi_2|\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}|\psi_2\rangle$$

Show that the energy of the doubly excited configuration

$$\psi_2 = \frac{1}{\sqrt{2}}(1\sigma_u(1)1\bar{\sigma}_u(2) - 1\sigma_u(2)1\bar{\sigma}_u(1)) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_u(1) & 1\bar{\sigma}_u(1) \\ 1\sigma_u(2) & 1\bar{\sigma}_u(2) \end{vmatrix}$$

$$E_2 = 2E_{1\sigma_u} + J_{1\sigma_u 1\sigma_u}$$

and also that the matrix element

$$\langle\psi_1|\hat{H}|\psi_2\rangle = K_{1\sigma_g 1\sigma_u}$$

8. The expression $E = E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}$ was derived in the handout for the first excited triplet state of H_2 (Equation 30),

$$^3\psi = \frac{1}{\sqrt{2}}(1\sigma_g(1)1\sigma_u(2) - 1\sigma_u(1)1\sigma_g(2)) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1) & 1\sigma_u(1) \\ 1\sigma_g(2) & 1\sigma_u(2) \end{vmatrix}$$

The wavefunction above is in fact the $M_S = 1$ component of the triplet state, which can also represented as

$$^3\psi(M_S = 1) = \frac{1}{\sqrt{2}}\left[1\sigma_g(1)1\sigma_u(2) - 1\sigma_u(1)1\sigma_g(2)\right]\alpha(1)\alpha(2)$$

where the spatial and spin parts have been separated. The $M_S = 0$ component of the same triplet state is:

$$^3\psi(M_S = 0) = \frac{1}{2}\left[1\sigma_g(1)1\sigma_u(2) - 1\sigma_u(1)1\sigma_g(2)\right]\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

while the $M_S = 0$ component of the corresponding open-shell *singlet* excited state is given by:

$$^1\psi(M_S = 0) = \frac{1}{2}\left[1\sigma_g(1)1\sigma_u(2) + 1\sigma_u(1)1\sigma_g(2)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

Show that these two wavefunctions can be represented as linear combinations of two Slater determinants.

$$^{1,3}\psi(M_S = 0) = \frac{1}{2}\left(\begin{vmatrix} 1\sigma_g(1) & 1\bar{\sigma}_u(1) \\ 1\sigma_g(2) & 1\bar{\sigma}_u(2) \end{vmatrix} \pm \begin{vmatrix} 1\bar{\sigma}_g(1) & 1\sigma_u(1) \\ 1\bar{\sigma}_g(2) & 1\sigma_u(2) \end{vmatrix}\right)$$

By expanding, verify that the energy of the $M_S = 0$ component of the triplet state is also

$$E_{S=1} = E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}$$

and show that the energy of the corresponding open-shell singlet state is

$$E_{S=0} = E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_u} + K_{1\sigma_g 1\sigma_u}$$

15.2 Problems 2

1. Using the following data, set up the 2×2 overlap and Hamiltonian matrices for one component of the π system (π and $\pi*$) of CO (you need only consider the p_x orbitals as the p_y are equivalent by symmetry). You may use the following overlap integral:

$$S_{C_{2p_x} O_{2p_x}} = 0.27$$

ionisation energies (=diagonal matrix elements, H_{ii}):

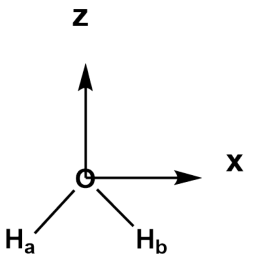
$$H_{C_{2p}C_{2p}} = -11.4\ eV \quad H_{O_{2p}O_{2p}} = -14.8\ eV$$

and the Wolfsberg-Helmholtz formula:

$$H_{ij} = 1.75 \times\ S_{ij} \times \left[\frac{H_{ii} + H_{jj}}{2}\right]$$

Solve the 2×2 determinant and calculate the coefficients in the bonding and antibonding orbitals. Comment on your results.

2. Using the following data, set up the overlap and Hamiltonian matrices for H_2O. All other overlap integrals are either 1 (S_{ii}) or zero (S_{ij}).



$$\begin{aligned}
&S_{O_{2s}H_{1s}} = 0.41\\
&S_{O_{2p_z}H_{a1s}} = S_{O_{2p_z}H_{b1s}} = -0.20\\
&S_{O_{2p_x}H_{a1s}} = -S_{O_{2p_x}H_{b1s}} = -0.30\\
&S_{H_{a1s}H_{b1s}} = 0.16
\end{aligned}$$

ionisation energies (=diagonal matrix elements, H_{ii}):

$$H_{O_{2s}O_{2s}} = -32.3\ eV \quad H_{O_{2p}O_{2p}} = -14.8\ eV \quad H_{H_{1s}H_{1s}} = -13.6\ eV$$

the Wolfsberg-Helmholtz formula:

$$H_{ij} = 1.75 \times\ S_{ij} \times \left[\frac{H_{ii} + H_{jj}}{2}\right]$$

Using the Jupyter notebook supplied, solve the 6×6 secular determinant to give the orbital energies and the corresponding coefficients in the LCAO expansion. Use the coefficients to sketch the orbitals.

16 More on DFT

$$T_{TF}\left[\rho\left(r\right)\right] = \frac{3}{10}\left(3\pi^2\right)^{2/3} \int \rho^{5/3}\left(r\right) dr$$

$$E_{TF}\left[\rho\left(r\right)\right] = \frac{3}{10}\left(3\pi^2\right)^{2/3}\int \rho^{5/3}\left(r\right)dr - Z\int \frac{\rho\left(r\right)}{r}dr + \frac{1}{2}\int \frac{\rho\left(r_1\right)\rho\left(r_2\right)}{r_{12}}dr_1 dr_2$$

$$E\left(\rho\right) = T\left(\rho\right) + E_{n-e}\left(\rho\right) + E_{e-e}\left(\rho\right)$$

$$E\left(\rho\right) = T\left(\rho\right) + E_{n-e}\left(\rho\right) + E_{coulomb}\left(\rho\right) + E_{xc}\left(\rho\right)$$

$$E_x{}^{LDA} = -\left(\frac{3}{4}\right)\left(\frac{3}{\pi}\right)^{1/3}\int_{-\infty}^{\infty}\rho(r)^{4/3}dV \tag{45}$$