

Molecular Electronic Structure

Quantum Supplementary

Hilary Term 2020

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Bibliography

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Some basics:

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

$$-\frac{\hbar}{2m}\nabla^2\varphi + V\varphi = E\varphi$$

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

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

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

Born-Oppenheimer approximation

The above equation is derived from the complete (electronic + nuclear) Schrödinger equation by regarding the nuclei as being fixed in space, and so the total wavefunction factorises as

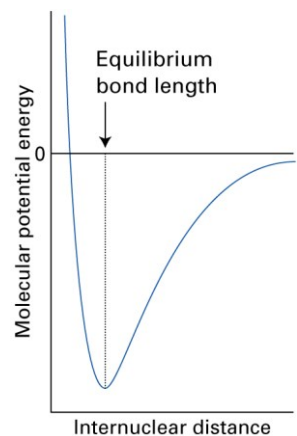
$$\Xi(R, r) = \psi(r)\Omega(R)$$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i^n \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_i^n \sum_a^N \frac{Z_a}{r_{ia}} + \frac{e^2}{4\pi\epsilon_0}\sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} + \frac{e^2}{4\pi\epsilon_0}\sum_a^N \sum_{b>a}^N \frac{1}{R_{ab}} = E\varphi$$

The final term is independent of the position of the electrons, and adds a constant contribution to the energy (at fixed distance)

This defines the potential energy curve: the electronic energy which depends parametrically on the nuclear coordinates.



Linear Combination of Atomic Orbitals (LCAO) approximation

Molecular orbitals are typically expanded as linear combinations of their atomic components:

$$\varphi = \sum_a c_a \chi_a$$

Slater determinants (see Valence Lecture 3, pp 12)

The Pauli principle: *The total wavefunction must be antisymmetric under the exchange of identical particles.*

Example: For He, the 2-electron wavefunction $\Phi = 1s(1)1\bar{s}(2)$ is **not** antisymmetric because $1s(1)1\bar{s}(2) \neq -1s(2)1\bar{s}(1)$
(note $1s(1)1\bar{s}(2)$ is shorthand for $1s(1)1s(2)\alpha(1)\beta(2)$)

But the linear combination

$\Phi = \frac{1}{\sqrt{2}}(1s(1)1\bar{s}(2) - 1s(2)1\bar{s}(1))$ is antisymmetric because

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

Example: Li $\Phi = 1s(1)1\bar{s}(2)2s(3)$ is not antisymmetric.

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

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

$$\Phi = \frac{1}{\sqrt{6}} \begin{pmatrix} 1s(1)1\bar{s}(2)2s(3) - 1s(1)1\bar{s}(3)2s(2) - 1s(2)1\bar{s}(1)2s(3) \\ + 1s(2)1\bar{s}(3)2s(1) + 1s(3)1\bar{s}(1)2s(2) - 1s(3)1\bar{s}(2)2s(1) \end{pmatrix}$$

is antisymmetric wrt exchange of all three.

The antisymmetric wavefunction can be written as a Slater determinant

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

$$\text{Li: } \Phi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & 1\bar{s}(1) & 2s(1) \\ 1s(2) & 1\bar{s}(2) & 2s(2) \\ 1s(3) & 1\bar{s}(3) & 2s(3) \end{vmatrix}$$

He (triplet excited state, $1s^1 2s^1$):

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

Note 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 also do the job, see *configuration interaction*)

H_2^+ : linear variation theorem

(n.b. only 1 electron, so Slater “determinant” is just a 1 x 1 determinant: $\Phi = |\psi|$)

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

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

Following the process set out in Prof Brouard’s ‘Valence’ lecture 4 (handout pp 18-23) or the equivalent derivation given in Appendix 1, minimisation of the trial wavefunction gives the following secular determinant:

$$\det |H - ES| = \begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{bb} - ES_{bb} \end{vmatrix} = 0$$

with eigenvalues that we can formulate in terms of matrix elements

$$E_{\pm} = \frac{(H_{aa} \pm H_{ab})}{(1 \pm S_{ab})} \text{ and } H_{aa} = \langle \chi_{1sa} | \hat{H} | \chi_{1sa} \rangle \text{ etc.}$$

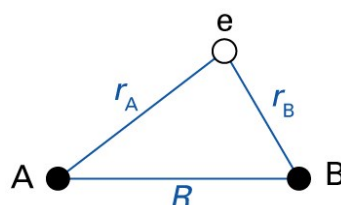
(but note we have not yet defined \hat{H} !)

and eigenfunctions that we can anticipate from symmetry considerations:

$$\psi_{\pm} = 1\sigma_{g/u} = \frac{1}{\sqrt{2(1 \pm S_{ab})}} (\chi_{1sa} \pm \chi_{1sb})$$

To make further progress we need to convert the abstract “ H_{aa} ”, “ H_{ab} ” etc. into hard numbers.

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2m} \nabla^2 + V = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_a} \right) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_b} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{R_{ab}} \right) \\ &= -\frac{\hbar^2}{2m} \nabla^2 - \frac{j_0}{r_a} - \frac{j_0}{r_b} + \frac{j_0}{R_{ab}} \\ j_0 &= \frac{e^2}{4\pi\epsilon_0} \end{aligned}$$



$\frac{j_0}{R_{ab}}$ is the repulsion between two nuclei – it is independent of the electron coordinates, so adds a constant term to the total energy. We will neglect this term in the following derivations (it can be trivially added in at the end of any energy calculation).

A note on units:

The Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_a}\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_b}\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R_{ab}}\right)$$

is given in SI units (distance in metres, mass in kg, charge in coulombs, energy in Joules).

It is also often expressed 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)).

$$a_0 = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA} \quad e = 1.6022 \times 10^{-19} \text{ C} \quad m_e = 9.1095 \times 10^{-31} \text{ kg}$$

$$1 \text{ hartree} = 1 \text{ au} = \frac{\hbar^2}{m_e a_0^2} = 4.3598 \times 10^{-18} \text{ J} = 27.21 \text{ eV}$$

In which case the Hamiltonian simplifies to $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}}$

See also 'Valence' lecture 2, P 8:

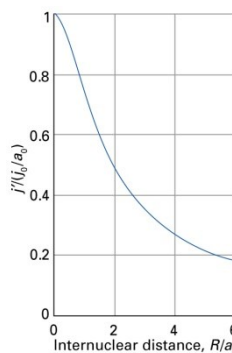
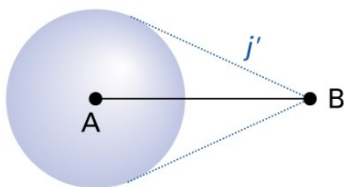
Coulomb integral: $\alpha = H_{aa} = \langle \chi_a | \hat{H} | \chi_a \rangle = \langle \chi_a | -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} | \chi_a \rangle$

We will see how to compute these integrals shortly, but for now just note that

$$\langle \chi_a | -\frac{1}{2}\nabla^2 - \frac{1}{r_a} | \chi_a \rangle = E_{1s}, \text{ the energy of an electron in a hydrogen atom.}$$

$$\therefore \alpha = E_{1s} - \langle \chi_a | \frac{1}{r_b} | \chi_a \rangle = E_{1s} - j'$$

$$j' = \langle \chi_a | \frac{1}{r_b} | \chi_a \rangle = \text{Coulomb attraction between charge density } \chi_a^2 \text{ and nucleus b}$$

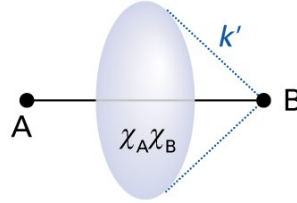


Likewise, the resonance integral: $\beta = H_{ab} = \langle \chi_a | \hat{H} | \chi_b \rangle = \langle \chi_a | -\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} | \chi_b \rangle$

$$\text{but } \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_b} \right) | \chi_b \rangle = E_{1s} | \chi_b \rangle$$

$$\therefore \beta = \langle \chi_a | \chi_b \rangle E_{1s} - \langle \chi_a | \frac{1}{r_a} | \chi_b \rangle = S E_{1s} - k'$$

$k' = \langle \chi_a | \frac{1}{r_a} | \chi_b \rangle$ = interaction between overlap charge density $\chi_a \chi_b$ and nucleus a



Sub into solutions of secular equation:

$$E_{1\sigma_g/1\sigma_u} = \frac{(\alpha \pm \beta)}{(1 \pm S)} = \frac{(E_{1s} - j' \pm (S E_{1s} - k'))}{(1 \pm S)}$$

$$E_{1\sigma_g} = E_{1s} - \frac{(j' + k')}{1 + S} \text{ or } E_{1\sigma_u} = E_{1s} - \frac{(j' - k')}{1 - S}$$

Basis functions

In order to evaluate $E_{1\sigma_g}$ or $E_{1\sigma_u}$, we need to be able to calculate the various integrals involved in the above expressions. These include the overlap integrals, $\langle \chi | \chi \rangle$, and the components of H_{ij} , which are the kinetic energy, $\langle \chi | -\frac{1}{2} \nabla^2 | \chi \rangle$, and the electron-nucleus interaction, $\langle \chi | \frac{1}{r_A} | \chi \rangle$. When we get to H_2 , we will find that we also need to calculate

electron-electron repulsion integrals of the type $\langle \chi(1)\chi(2) | \frac{1}{r_{12}} | \chi(1)\chi(2) \rangle$

To calculate these numbers we need to choose a mathematical representation of the atomic orbitals, χ . For discrete molecules, there are 2 plausible choices, *Slater-type orbitals* and *Gaussian-type orbitals*. For solid-state (periodic) calculations, there is a third choice, a basis set of *plane waves*, but we will not be concerned with that here.

Slater-type orbitals (STOs):

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

N_1 is the normalising constant.

$Y_{lm}(\theta, \phi)$ 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.

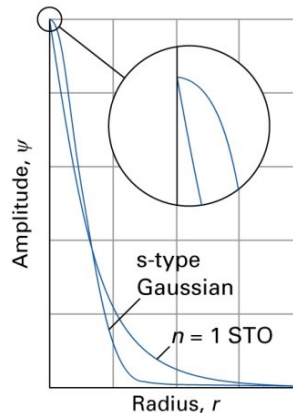
These replicate the behaviour of real atomic orbitals, so are the most intuitive option.

Gaussian-type orbitals (GTOs):

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

Angular properties are specified by i, j, k : $(0,0,0) = s$; $(1,0,0) = p_x$; $(1,1,0) = d_{xy}$ etc etc.

The major difference 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. Thus they are less accurate representations of a real atomic orbital than Slater functions.



However, GTOs have 2 major advantages:

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

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

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 2 GTOs on different centres is just a different GTO centred somewhere in between (the **Gaussian Product Theorem**).

Consider the product of two s-type gaussians ($i = j = k = 0$) with equal exponents, α , one centred at $\mathbf{x} = \mathbf{0}$, the other at $\mathbf{x} = \mathbf{a}$

$$GTO1 = N_1 e^{-\alpha x^2} \quad GTO2 = N_2 e^{-\alpha(x-a)^2}$$

$$\begin{aligned}
 GTO1 \times GTO2 &= N_1 N_2 e^{-\alpha x^2} e^{-\alpha(x-a)^2} = N_1 N_2 e^{-\alpha[x^2+(x-a)^2]} = N_1 N_2 e^{-\alpha(2x^2-2ax+a^2)} \\
 &= N_1 N_2 e^{-2\alpha(x^2-ax+\frac{a^2}{2})} = N_1 N_2 e^{-2\alpha[(x-\frac{a}{2})^2+\frac{a^2}{4}]} = e^{-\frac{\alpha a^2}{2}} N_1 N_2 e^{-2\alpha(x-\frac{a}{2})^2}
 \end{aligned}$$

i.e. the product is another Gaussian with exponent 2α centred half way between the original basis functions ($x = \frac{a}{2}$) and scaled by $e^{-\frac{\alpha a^2}{2}}$

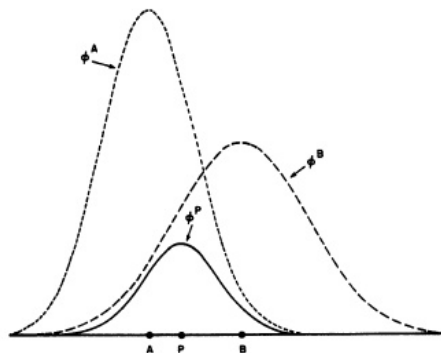


Figure 3.1 The product of two 1s Gaussians is a third 1s Gaussian.

These two features combine to make the computation of all integrals much easier for Gaussian functions than for Slater functions. It is harder, but still possible, 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 >1 electron!), Slater-type functions are a very poor choice.

Example 1: an overlap integral between two s orbitals on different atoms.

Take 2 s-type gaussians with equal exponents, one at the origin, the other at (0,0,a).

$$S = N_1 N_2 \iiint_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2+z^2)} e^{-\alpha(x^2+y^2+(z-a)^2)} dx dy dz$$

First, we need to normalise each basis function.

$$\begin{aligned}
 1 &= N_1^2 \iiint_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2+z^2)} e^{-\alpha(x^2+y^2+z^2)} dx dy dz \\
 &= N_1^2 \int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz
 \end{aligned}$$

using the standard integral

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

$$1 = N_1^2 \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} = N_1^2 \left(\frac{\pi}{2\alpha}\right)^{3/2}$$

$$N_1 (= N_2) = \left(\frac{2\alpha}{\pi}\right)^{3/4}$$

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

Using the Gaussian product theorem to deal with the integral in z :

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

$$\therefore S = \left(\frac{2\alpha}{\pi}\right)^{3/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} \left(\frac{\pi}{2\alpha}\right)^{1/2} e^{-\alpha\left(\frac{a^2}{2}\right)} = e^{-\alpha\left(\frac{a^2}{2}\right)}$$

Example 2: kinetic energy of an electron in a 1s orbital, $\langle \phi_{1s} | \hat{T} | \phi_{1s} \rangle$

$$\hat{T} = -\frac{1}{2} \nabla^2 = -\frac{1}{2} \left(\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \right)$$

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

$$N_1 N_2 \int_{-\infty}^{+\infty} e^{-\alpha x^2} \frac{d^2}{dx^2} (e^{-\alpha x^2}) dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz$$

$$\frac{d^2}{dx^2} (e^{-\alpha x^2}) = (4\alpha^2 x^2 - 2\alpha) e^{-\alpha x^2}$$

So we need to evaluate 2 integrals and sum them:

$$-2\alpha N_1 N_2 \int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz$$

and

$$4\alpha^2 N_1 N_2 \int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} dx \int_{-\infty}^{+\infty} e^{-2\alpha y^2} dy \int_{-\infty}^{+\infty} e^{-2\alpha z^2} dz$$

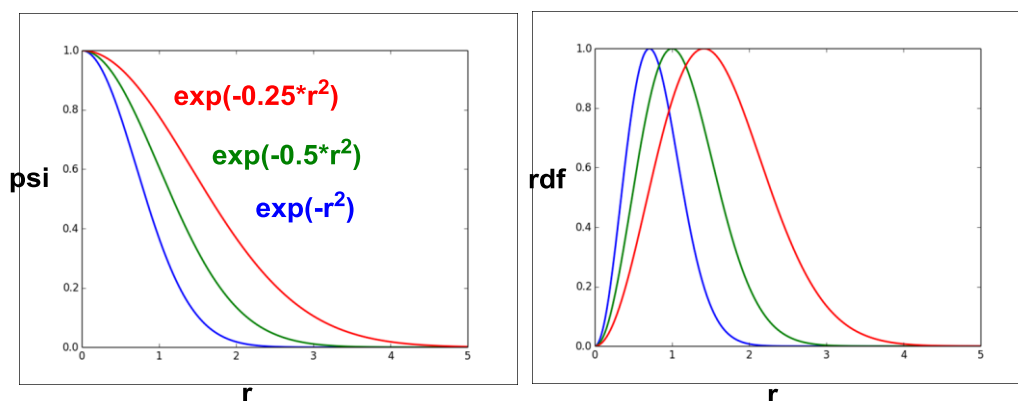
(for which we need the standard integral $\int_{-\infty}^{+\infty} x^2 e^{-bx^2} dx = \frac{1}{2b} \sqrt{\frac{\pi}{b}}$)

Attraction (to nuclei) and repulsion (with other electrons) integrals are trickier because of the $1/r$ terms, for which we need Fourier transform techniques. However, relatively simple closed analytical forms exist. The same is not true for Slater-type functions!

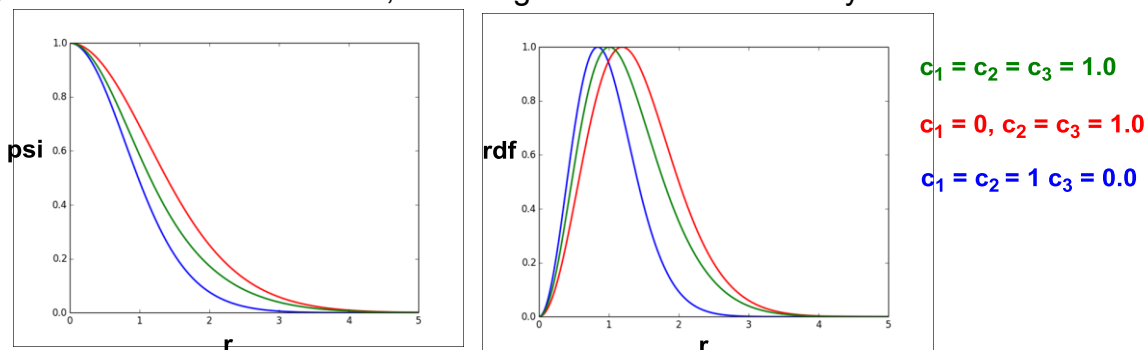
Practical choices of basis set.

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-zeta 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 small number of hard ones!

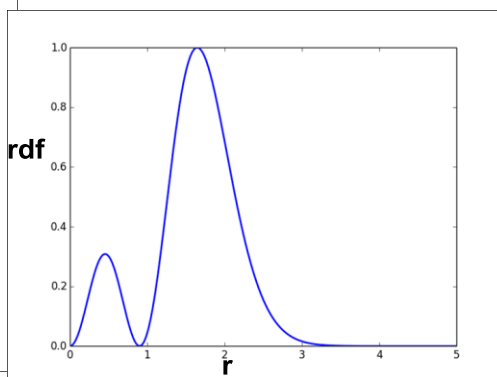
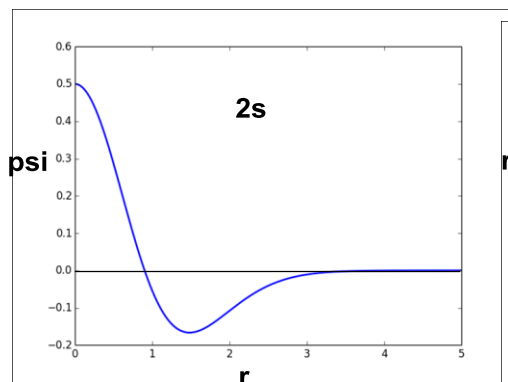
$$\varphi = c_1 e^{-r^2} + c_2 e^{-0.5*r^2} + c_3 e^{-0.25*r^2}$$



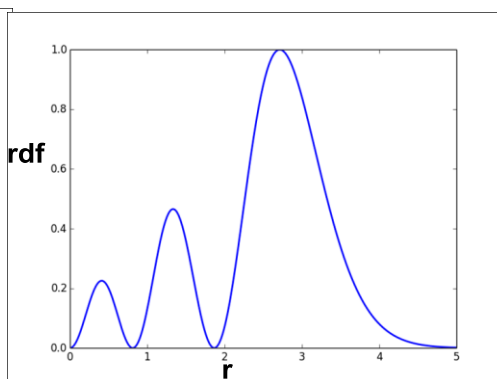
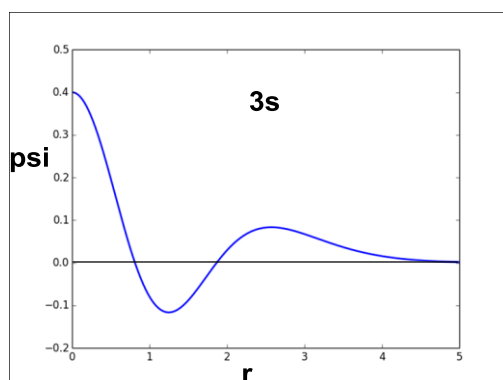
If we vary the coefficients in the sum, we can get an orbital of arbitrary size.



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



$$c_1 = 1.5 \quad c_2 = -1.0 \quad c_3 = 0.0$$



$$c_1 = 2.0 \quad c_2 = -2.5 \quad c_3 = 0.9$$

For example an STO-3G basis set uses 3 GTOs to represent each STO. Thus a calculation on H₂O with an STO-3G basis would involve 21 basis functions (3 for each of O 1s, 2s, 2p_x and H 1s (x2)).

Very large basis sets are commonly used now, including:

- 1) Double, triple, quadruple.... zeta forms: more than one exponent is used to describe a given orbital. Varying linear combinations allow radial extent of orbital to vary. e.g 6-31G
- 2) 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) e.g 6-31G* (recall the discussion of the role of d orbitals in e.g. SF₆)
- 3) Diffuse functions: very low zeta – important for accurate description of weakly bound electrons (anions, for example) e.g 6-31+G

Choice of basis is typically one of the major decisions practising computational chemists need to make.

H₂: explicit formulation of the Hamiltonian for a 2-electron system

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

Note \hat{H}_1 and \hat{H}_2 are identical to the 1-electron Hamiltonians for H₂⁺

if $\frac{1}{r_{12}}$ was ignored completely (i.e. assuming electrons don't interact), this is simply the sum of

two independent one-electron H₂⁺ Hamiltonians, and the problem is separable. The resulting energy and ground-state wavefunction would be

$$E = 2E_{1\sigma_g} \quad \Psi = 1\sigma_g(1)1\bar{\sigma}_g(2) \quad (\text{a simple "Hartree product"})$$

But we have established that a wavefunction of this type is not antisymmetric wrt exchange of electrons (unsurprisingly as we deliberately ignored the interaction between the electrons in deriving it!): we need to use a Slater determinant

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

Now we have an expression for Φ and an expression for \hat{H} , we can compute the expectation value:

$$\langle \Phi | \hat{H} | \Phi \rangle = E$$

Step 1: Expand Φ as a Slater determinant

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

Step 2: Expand terms of \hat{H} to give 12 integrals, I_{1-12}

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

Now look at each of I_{1-12} in turn:

1-electron integrals, I_{1-8}

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

(note \hat{H}_1 only acts on electron 1)

Separating the spatial and spin components of the wavefunctions gives

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

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

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

(due to spin orthogonality)

$$\begin{aligned}
 \text{Similarly } I_4 = & \langle 1\sigma_g(1)1\bar{\sigma}_g(2) | \hat{H}_2 | 1\sigma_g(2)1\bar{\sigma}_g(1) \rangle = 0 \\
 I_5 = & \langle 1\sigma_g(2)1\bar{\sigma}_g(1) | \hat{H}_1 | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle = 0 \\
 I_6 = & \langle 1\sigma_g(2)1\bar{\sigma}_g(1) | \hat{H}_2 | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle = 0
 \end{aligned}$$

2-electron integrals (terms in $1/r_{12}$), I_{9-12}

$$I_9 = \langle 1\sigma_g(1)1\bar{\sigma}_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle$$

Separating spatial and spin components:

$$\begin{aligned} &= \langle 1\sigma_g(1)1\sigma_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\sigma_g(2) \rangle \langle \alpha(1) | \alpha(1) \rangle \langle \beta(2) | \beta(2) \rangle \\ &= \langle 1\sigma_g(1)1\sigma_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\sigma_g(2) \rangle \quad \times 1 \quad \times 1 \quad = J_{1\sigma_g 1\sigma_g} \end{aligned}$$

This is the 'Coulomb integral' (note different use of the term 'Coulomb integral').

Physically: the repulsion between two electrons in the same orbital, $1\sigma_g$

Physicists' and chemists' notation

A shorthand notation for the 2-electron integral $\langle 1\sigma_g(1)1\bar{\sigma}_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle$ is

$\langle 1\sigma_g(1)1\bar{\sigma}_g(2) | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle$ or more generally $\langle ij | ij \rangle$ where the $1/r_{12}$ term is implicit. This is called the *physicists* notation. Up to 4 spin orbitals can be involved, in which case the integral is denoted $\langle ij | kl \rangle$.

It is often conceptually easier to collect all terms relating to a given electron on the same side of the $1/r_{12}$ term.

$$\begin{aligned} \langle 1\sigma_g(1)1\bar{\sigma}_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle &= \int 1\sigma_g(1)^* 1\bar{\sigma}_g(2)^* \frac{1}{r_{12}} 1\sigma_g(1)1\bar{\sigma}_g(2) = \\ \int 1\sigma_g(1)^* 1\sigma_g(1) \frac{1}{r_{12}} 1\bar{\sigma}_g(2)^* 1\bar{\sigma}_g(2) &= [ii | jj] \text{ This is called chemists' notation.} \end{aligned}$$

Note the use of a square bracket rather than a traditional 'bra'/'ket'. This is because the complex conjugates have moved (complex conjugation is implicit in $\langle \quad |$).

Returning to the expansion:

$$I_{12} = \langle 1\sigma_g(2)1\bar{\sigma}_g(1) | \frac{1}{r_{12}} | 1\sigma_g(2)1\bar{\sigma}_g(1) \rangle = J_{1\sigma_g 1\sigma_g} = I_9$$

$$\text{but } I_{10} = \langle 1\sigma_g(1)1\bar{\sigma}_g(2) | \frac{1}{r_{12}} | 1\sigma_g(2)1\bar{\sigma}_g(1) \rangle$$

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

$$= \langle 1\sigma_g(1)1\sigma_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\sigma_g(2) \rangle \quad \times 0 \quad \times 0 \quad = 0$$

$$\text{Similarly } I_{11} = \langle 1\sigma_g(2)1\bar{\sigma}_g(1) | \frac{1}{r_{12}} | 1\sigma_g(1)1\bar{\sigma}_g(2) \rangle = 0$$

$$\text{So } E = \frac{1}{2} (4E_{1\sigma_g} + 2J_{1\sigma_g 1\sigma_g}) = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$$

i.e. twice the energy of H_2^+ , plus an addition term $J_{1\sigma_g 1\sigma_g}$ for the electron-electron repulsion.

Excited states of H₂ and the exchange integral, K.

Let us perform the same analysis with the first triplet excited state of H₂,

$$\Phi = |\mathbf{1}\sigma_g \mathbf{1}\sigma_u\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{1}\sigma_g(1) & \mathbf{1}\sigma_u(1) \\ \mathbf{1}\sigma_g(2) & \mathbf{1}\sigma_u(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) - \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1))$$

Expanding Φ and \hat{H} again gives 12 integrals:

$$\begin{aligned} E = & \frac{1}{2} \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \hat{H}_1 | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle + \frac{1}{2} \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \hat{H}_2 | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle \\ & - \frac{1}{2} \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \hat{H}_1 | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle - \frac{1}{2} \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \hat{H}_2 | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle \\ & - \frac{1}{2} \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \hat{H}_1 | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle - \frac{1}{2} \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \hat{H}_2 | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle \\ & + \frac{1}{2} \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \hat{H}_1 | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle + \frac{1}{2} \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \hat{H}_2 | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle \\ & + \frac{1}{2} \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle - \frac{1}{2} \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle \\ & - \frac{1}{2} \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle + \frac{1}{2} \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle \end{aligned}$$

$$I_1 = \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \hat{H}_1 | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle = I_8 = \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \hat{H}_2 | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle = E_{1\sigma_g}$$

$$I_2 = \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \hat{H}_2 | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle = I_7 = \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \hat{H}_1 | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle = E_{1\sigma_u}$$

$$I_{3,4,5,6} = 0$$

$$I_9 = \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle = I_{12} = \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \frac{j_0}{r_{12}} | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle = J_{1\sigma_g 1\sigma_u}$$

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

thus far, all is exactly as before for the ground state, **BUT**

$$I_{10} = \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \frac{j_0}{r_{12}} | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle = I_{11} = \langle \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) \rangle$$

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

$$= \langle \mathbf{1}\sigma_g(1)\mathbf{1}\sigma_u(2) | \frac{1}{r_{12}} | \mathbf{1}\sigma_g(2)\mathbf{1}\sigma_u(1) \rangle \quad \times 1 \quad \times 1 \quad \neq 0 \quad \text{(no spin orthogonality)}$$

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

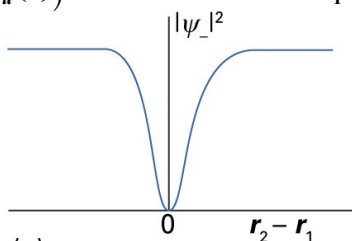
So the I_{10} (and I_{11}) integrals survive: they are known as **exchange integrals**, K – a purely quantum phenomenon.

Collecting terms: $E = E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}$

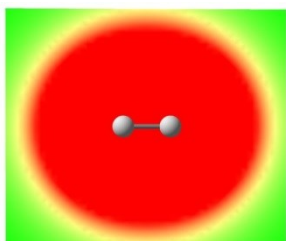
J and K are both positive (to be justified later), so K can be thought of as offsetting some of the electron-electron repulsion captured in J : electrons with parallel spin repel each less than electrons with opposite spins.

Note \hat{H} does not operate on spin degrees of freedom. Thus influence of spin on energy is exerted indirectly via the spatial constraints imposed by the Pauli principle

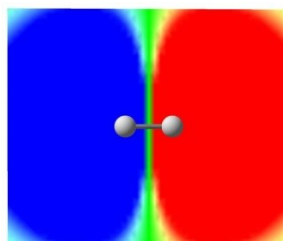
$${}^3\Phi = \frac{1}{\sqrt{2}}(1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)) = 0 \quad \text{when} \quad r_1 = r_2$$



What are the signs and magnitudes of J and K ? Consider the orbitals:



$1\sigma_g$

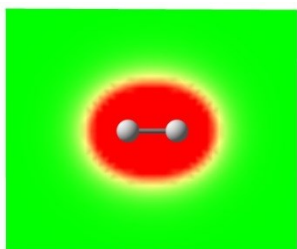


$1\sigma_u$

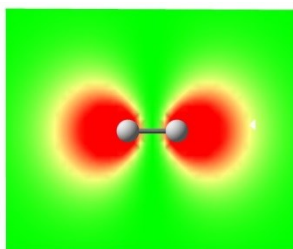
(red is positive, blue is negative)

Now consider the *products* of orbitals involved in the expressions for J and K .

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



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



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

> 0 everywhere

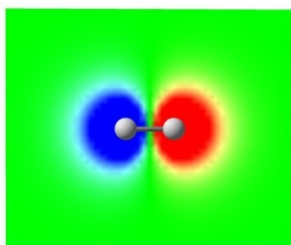
> 0 everywhere

$1/r_{12} > 0$ everywhere

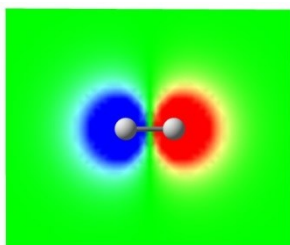
so: **J is the sum of terms that are all positive, so J *MUST* be positive**
(no surprise - it is a repulsion, after all!).

What about K ?

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



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



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

The products can 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: $1\sigma_g(1)1\sigma_u(2) \frac{1}{r_{12}} 1\sigma_g(2)1\sigma_u(1) < 0$

K is the summation 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).

Whereas if the electrons are on opposite sides of the node, r_{12} is necessarily large, 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).

Hence K is positive, but generally smaller than J (in practice ~25% smaller in cases where there are no radial such as first-row atoms (C, N, O, F), first-row TMs and lanthanides)

Conclusion: $J > K > 0$ (hence parallel spins favoured)

and note that we can trace this fact all the way back to the fact that the sign in the expansion of the wavefunction is negative:

$$\Phi = \frac{1}{\sqrt{2}} (1\sigma_g(1)1\bar{\sigma}_g(2) - 1\sigma_g(2)1\bar{\sigma}_g(1))$$

If it were positive, parallel-spin electrons would be disfavoured!

Generalised energy expressions for larger molecules.

We can generalise the expression for the energy to $E = \sum_i 2E_i + \sum_{i,j} (2J_{ij} - K_{ij})$ for any closed-shell molecule, where the summation runs over doubly occupied orbitals

Comment: expanding the ground state of H_2 using this expression gives $E = 2E_{1\sigma_g} + 2J_{1\sigma_g 1\sigma_g} - K_{1\sigma_g 1\sigma_g}$ which looks different from expression above, but note

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

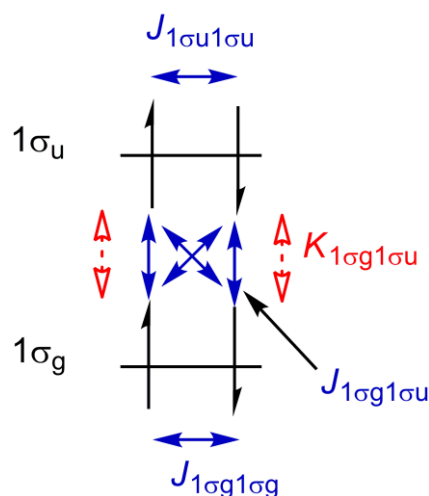
or in general $K_{ii} = J_{ii}$

so $E = 2E_{1\sigma_g} + 2J_{1\sigma_g 1\sigma_g} - K_{1\sigma_g 1\sigma_g} = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$ as on page 12

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

The total energy = sum of the one-electron energies + $1J$ per pairwise interaction between two electrons - $1K$ per pairwise interaction between two electrons *with parallel spins*.

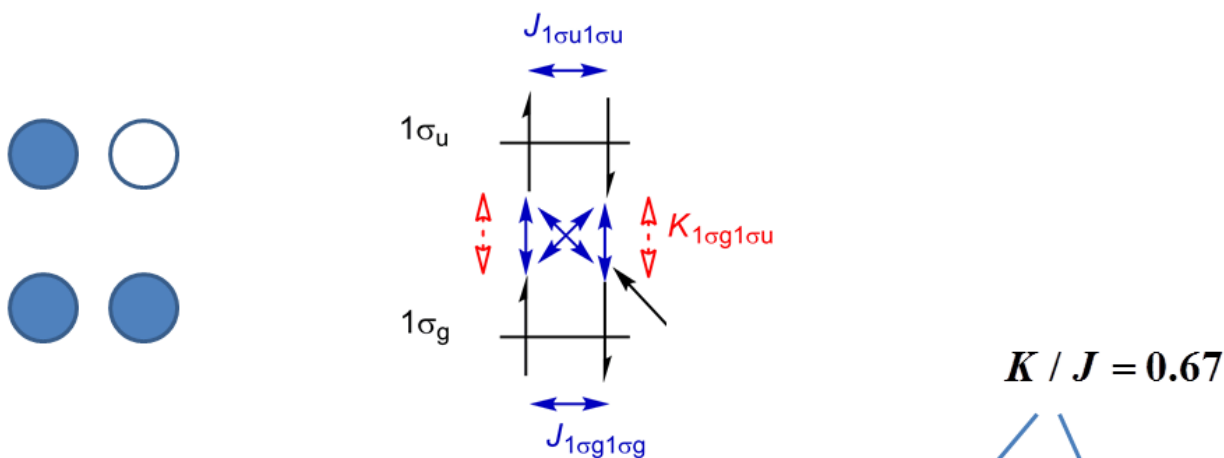
For He_2 : $E = 2E_{1\sigma_g} + 2E_{1\sigma_u} + J_{1\sigma_g 1\sigma_g} + 4J_{1\sigma_g 1\sigma_u} + J_{1\sigma_u 1\sigma_u} - 2K_{1\sigma_g 1\sigma_u}$



How important is K ?

We have established that K offsets some of the e-e repulsion in J , how much is the 'offset' worth? Let's look at 2 limiting cases, both with 4 electrons: He_2 and Be

- 1) He_2 : when the electrons (σ_g and σ_u) occupy similar regions of space

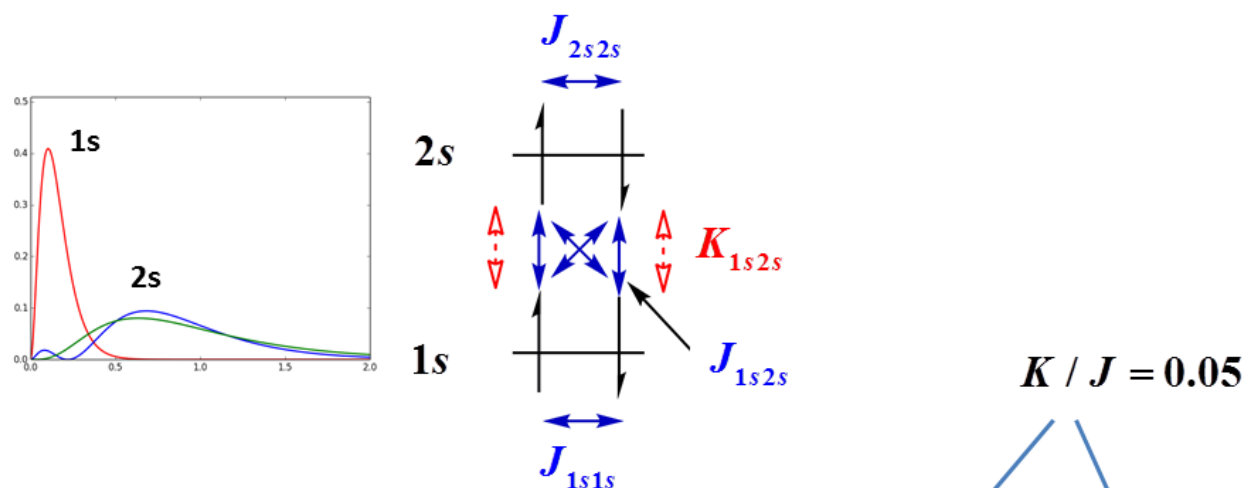


$$E = 2E_{1\sigma_g} + 2E_{1\sigma_u} + J_{1\sigma_g 1\sigma_g} + 4J_{1\sigma_g 1\sigma_u} + J_{1\sigma_u 1\sigma_u} - 2K_{1\sigma_g 1\sigma_u}$$

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

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

- 2) Be: effectively the same problem (4 electrons in 2 orbitals), but now the electrons (1s and 2s) occupy very different regions of space



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

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

K is very small – it only offsets ~ 5% of the Coulomb repulsion.

Useful rule of thumb for transition metals: $K \cong 0.25 \times J$ (electrons are in similar regions of space).

Expansion of J and K in terms of atomic basis:

We can expand $1\sigma_g = \frac{1}{\sqrt{2(1+S)}}(\chi_{1sa} + \chi_{1sb})$ $1\sigma_u = \frac{1}{\sqrt{2(1-S)}}(\chi_{1sa} - \chi_{1sb})$

$$\begin{aligned}
 J_{1\sigma_g 1\sigma_g} &= \langle 1\sigma_g(1)1\sigma_g(2) | \frac{1}{r_{12}} | 1\sigma_g(1)1\sigma_g(2) \rangle = \\
 &= \frac{1}{4(1+S)^2} \langle (\chi_a + \chi_b)(1)(\chi_a + \chi_b)(2) | \frac{1}{r_{12}} | (\chi_a + \chi_b)(2)(\chi_a + \chi_b)(1) \rangle \\
 &= \frac{1}{4(1+S)^2} \left[\langle \chi_a(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_a(1) \rangle + \langle \chi_a(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_b(1) \rangle \right. \\
 &\quad + \langle \chi_a(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_a(1) \rangle + \langle \chi_a(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_b(1) \rangle \\
 &\quad + \langle \chi_a(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_a(1) \rangle + \langle \chi_a(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_b(1) \rangle \\
 &\quad + \langle \chi_a(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_a(1) \rangle + \langle \chi_a(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_b(1) \rangle \\
 &\quad + \langle \chi_b(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_a(1) \rangle + \langle \chi_b(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_b(1) \rangle \\
 &\quad + \langle \chi_b(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_a(1) \rangle + \langle \chi_b(1)\chi_a(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_b(1) \rangle \\
 &\quad + \langle \chi_b(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_a(1) \rangle + \langle \chi_b(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_a(2)\chi_b(1) \rangle \\
 &\quad \left. + \langle \chi_b(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_a(1) \rangle + \langle \chi_b(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_b(2)\chi_b(1) \rangle \right]
 \end{aligned}$$

The 16 integrals above, I_{1-16} , separate into four distinct types:

$\langle \chi_a(1)\chi_a(2) \frac{1}{r_{12}} \chi_a(2)\chi_a(1) \rangle$	electrons 1 and 2 both on a or both on b (x2) (I_1 and I_{16})
$\langle \chi_a(1)\chi_b(2) \frac{1}{r_{12}} \chi_b(2)\chi_a(1) \rangle$	electron 1 on a, electron 2 on b or vice versa (x2) (I_7 , I_{10})
$\langle \chi_a(1)\chi_b(2) \frac{1}{r_{12}} \chi_a(2)\chi_b(1) \rangle$	overlap densities of electrons 1 and 2 (x4) ($I_{4,6,11,12}$)
$\langle \chi_a(1)\chi_a(2) \frac{1}{r_{12}} \chi_a(2)\chi_b(1) \rangle$	overlap density of electron 1 with electron 2 on a or on b, or vice versa (x8) ($I_{2,3,5,8,9,13,14,15}$)

(relatively!) simple analytical solutions are available if you use a Gaussian basis set. Much harder solutions are available for Slater orbitals (see MQM P292), but very soon become intractable for higher angular momentum basis functions (p , d , f orbitals).

Comment: expanding Φ gives 4 terms
 expanding \hat{H} splits each of these 4 into 3 components
 (2 x 1-electron + 1 x 2-electron), and the 1-electron terms further split into 1
 kinetic energy and two electron-nucleus integrals.
 expanding σ_g in terms of two atomic basis functions splits each of the each
 of the 1-e integrals into 4 components and each of the 2-e integrals terms
 into 16 components.
 = a lot of integrals!

Note that in principle we can expand a molecular orbital using as many functions on as many atoms as we like:

$$\varphi = N(\chi_a + \chi_b + \chi_c + \chi_d), \text{ for example (see 'basis sets')}$$

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.
$$\langle \chi_a(1)\chi_b(2) | \frac{1}{r_{12}} | \chi_c(1)\chi_d(2) \rangle = \langle ij | kl \rangle$$

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

What have we achieved so far?

We have illustrated the machinery that allows the expression $\langle \Phi | \hat{H} | \Phi \rangle = E$ to be evaluated if we express the total wavefunction as an antisymmetrised product:

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

and, critically, we know what the individual orbitals ($1\sigma_g$ in this case) look like. In the case of minimal basis set H_2 , symmetry is all we need ($1\sigma_g$ is the appropriately normalised in-phase combination of the 1s orbitals) but what if we don't know, *a priori*, what the orbitals look like. In 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%? 60%? 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 symmetry is not enough (*i.e.* the vast majority of problems!)

Hartree-Fock theory

We have an expression for the total energy of a closed-shell molecule:

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

where E_i represents the interaction of an isolated electron with the nuclei. The 3-body problem (2 electrons + a fixed $(H^+)_2$ unit) cannot be solved analytically because of the repulsion between the electrons.

Using the *orbital approximation* (i.e. assuming that each electron moves in an averaged potential defined by the nuclei and all other electrons - the 'mean field') we can express the ground-state wavefunction of H_2 as a Slater determinant:

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

But, in order to define the average field due to electron 1, you need to know its wavefunction (i.e. the form of the $1\sigma_g$ orbital), and likewise for electron 2. But what is the optimum form of the $1\sigma_g$ orbital? (**ans**: we don't know yet, but certainly not the same as it was in H_2^+ !).

We need to adopt an **iterative approach** - the '*self-consistent field*'.

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, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ (the process involves the use of Lagrange multipliers – see box and MQM Ch7 further info for a full derivation).

Lagrange multipliers: Finding an extremum subject to a constraint:

Find the turning point of $f = 3x^2 - 2y^2$ subject to the constraint that $x + y = 2$

Soln: define $g = x + y$ and λ so $f - \lambda g = 3x^2 - 2y^2 - \lambda(x + y)$

λ is the 'Lagrange multiplier'

$$\frac{\partial(f - \lambda g)}{\partial x} = 6x - \lambda = 0$$

$$\frac{\partial(f - \lambda g)}{\partial y} = -4y - \lambda = 0$$

Ans: $x = -4, y = 6, \lambda = -24$ n.b. $f(-4, 6) = 3x^2 - 2y^2 = -24 = \lambda$

When we do this, we arrive at the Hartree-Fock equations,

$$\hat{F}\phi_i = \epsilon_i \phi_i$$

where the Fock operator, \hat{F}_i , is defined as $\hat{F} = \hat{H} + \sum_j 2\hat{J}_j - \sum_j \hat{K}_j = \hat{H} + \hat{G}$

ε_i is the Hartree Fock orbital energy (the Lagrange multiplier and also the eigenvalue)

\hat{H} is the one-electron term $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}$

\hat{J}_j and \hat{K}_j are the Coulomb and Exchange operators, respectively

$$\hat{J}_j\phi_i(1) = \left(\int \phi_j(2)\phi_j(2) \frac{1}{r_{12}} dv_2 \right) \phi_i(1) \quad \hat{K}_j\phi_i(1) = \left(\int \phi_j(2)\phi_i(2) \frac{1}{r_{12}} dv_2 \right) \phi_j(1)$$

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

$$\text{Thus } \varepsilon_i = E_i + \sum_j (2J_{ij} - K_{ij})$$

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 the sum over all occupied orbital energies, $\sum_i \varepsilon_i$, double counts the repulsions. Therefore, to calculate the total energy we have to correct for this by *subtracting* the e-e repulsion.

$$E = \sum_i 2\varepsilon_i - \sum_{i,j} (2J_{ij} - K_{ij}) \text{ where the sum is over doubly-occupied orbitals.}$$

Check this works for H_2 :

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

but recall that $J_{1\sigma_g 1\sigma_g} = K_{1\sigma_g 1\sigma_g}$

and that

$$\varepsilon_{1\sigma_g} = E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$$

$$\therefore E = 2(E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}) - 2J_{1\sigma_g 1\sigma_g} + J_{1\sigma_g 1\sigma_g} = 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g} \text{ (as previous).}$$

Koopmans' theorem: "The ionisation energy is the negative of the Hartree Fock orbital energy": $I_i = -\epsilon_i$

Why?
$$I_{H_2} = E(H_2^+) - E(H_2) = (E_{1\sigma_g}) - (2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}) = -(E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}) = -\epsilon_{1\sigma_g}$$

Another way to see this is to note that when we remove an electron we lose the attraction to the nuclei ($E_{1\sigma_g}$) and also 1 unit of Coulomb repulsion – precisely the components of $\epsilon_{1\sigma_g}$

What do the energies of the vacant orbitals mean? Consider the σ_u orbital in H_2 .

$$\epsilon_{1\sigma_u} = E_{1\sigma_u} + \sum_i (2J_{ij} - K_{ij}) = E_{1\sigma_u} + 2J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}$$

i.e. it experiences repulsions from both electrons (unlike σ_g which only experiences repulsion from one electron (the other being 'itself')). So **beware** – it is dangerous to compare occupied and virtual HF orbital energies.

The energy of a virtual orbital in HF theory corresponds to the negative of the *electron affinity* of the atom/molecule.

$$\begin{aligned} EA_{H_2} &= E(H_2) - E(H_2^-) = (2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}) - (2E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_g} + 2J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}) \\ &= -(E_{1\sigma_u} + 2J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}) = -\epsilon_{1\sigma_u} \end{aligned}$$

Hartree-Fock-Roothaan (HFR) Equations:

These are the HF equations implemented using the LCAO approximation $\varphi = \sum_n c_n \chi_n$

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

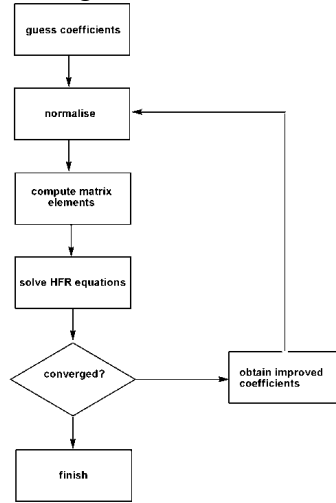
Multiply by χ_m and integrating gives $\sum_n c_n \langle \chi_m | \hat{F} | \chi_n \rangle = \epsilon_i \sum_n \langle \chi_m | c_n | \chi_n \rangle$

$$\sum_n c_n (F_{mn} - \epsilon_i S_{mn}) = 0 \text{ which have non-trivial solutions where } |F_{mn} - \epsilon_i S_{mn}| = 0$$

(note similarities to secular equations derived in Lecture 1 – 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 an *iterative* solution required:

In the context of HF theory, the flow diagram is as follows:



An example: H₂ at the equilibrium separation, R = 1.38543 a₀.

Expand the MOs in the form $\phi = c_a \chi_a + c_b \chi_b$ where χ_a, χ_b are 1s orbitals centred on the H atoms. We will use a normalised 'Slater-type' orbital of the form $\chi_{1s} = N e^{-\zeta r}$ (see '**basis functions**') with exponent $\zeta = 1.19302$ (chosen because it is the optimum value at this separation, but the choice doesn't matter for our purposes here).

The general expression for the HFR equations $\sum_n c_n (F_{mn} - \epsilon_i S_{mn}) = 0$ give us

$$\begin{aligned} (F_{aa} - \epsilon S_{aa})c_a + (F_{ab} - \epsilon S_{ab})c_b &= 0 \\ (F_{ab} - \epsilon S_{ab})c_a + (F_{bb} - \epsilon S_{bb})c_b &= 0 \end{aligned} \quad \text{and} \quad \begin{vmatrix} F_{aa} - \epsilon S_{aa} & F_{ab} - \epsilon S_{ab} \\ F_{ab} - \epsilon S_{ab} & F_{bb} - \epsilon S_{bb} \end{vmatrix} = 0$$

numerical values for matrix elements (S, H, G in Hartree units) as function of $c_{a,b}$

$$\begin{aligned} S_{aa} &= S_{bb} = 1 \\ S_{ab} &= 0.68242 \\ F_{aa} &= H_{aa} + G_{aa} = (-1.13295 + 0.74564c_a^2 + 0.89359c_a c_b + 0.81335c_b^2) au \\ F_{bb} &= H_{bb} + G_{bb} = (-1.13295 + 0.81335c_a^2 + 0.89359c_a c_b + 0.74564c_b^2) au \\ F_{ab} &= H_{ab} + G_{ab} = (-0.97475 + 0.44675c_a^2 + 0.36498c_a c_b + 0.44675c_b^2) au \end{aligned}$$

(the numbers come from well-established formulae: the details are not important but are contained in Szabo and Ostlund)

All we need to start the iteration is a guess for c_a and c_b . Clearly in this case we could guess from symmetry considerations that $c_a = c_b$ for the ground state, but to illustrate the process, let's start with an obviously incorrect guess:

Step 1: guess $c_a = 2c_b \quad \therefore \frac{c_a}{c_b} = 2$

Step 2: normalise $\phi = 2c_b\chi_a + c_b\chi_b$

$$\int (2c_b\chi_a + c_b\chi_b)(2c_b\chi_a + c_b\chi_b)d\tau = 1$$

$$\Rightarrow 5c_b^2 + 4c_b^2 S_{ab} = 1$$

$$\Rightarrow c_b = \frac{1}{\sqrt{4S_{ab} + 5}} = 0.35968$$

$$\Rightarrow c_a = 0.71936$$

Step 3: calculate matrix elements using formulae for F_{aa} , F_{ab} , F_{bb} above

$$F_{aa} = H_{aa} + G_{aa} = (-1.13295 + 0.74564(0.71936)^2 + 0.89359(0.71936)(0.35968) + 0.81335(0.35968)^2)au$$

$$= -0.4107au$$

$$\begin{vmatrix} -0.4107 - \varepsilon & -0.5913 - 0.6824\varepsilon \\ -0.5913 - 0.6824\varepsilon & -0.3844 - \varepsilon \end{vmatrix} = 0$$

Step 4: solve $\varepsilon_1 = -0.58804au$ (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

$$\left. \begin{aligned} (F_{aa} - \varepsilon S_{aa})c_a + (F_{ab} - \varepsilon S_{ab})c_b &= 0 \\ (F_{ab} - \varepsilon S_{ab})c_a + (F_{bb} - \varepsilon S_{bb})c_b &= 0 \end{aligned} \right\} \text{ for } c_a, c_b \text{ with } \varepsilon = \varepsilon_1 = -0.58804au$$

$$0.1773c_a - 0.1990c_b = 0$$

$$\frac{c_a}{c_b} = 1.0715$$

Convergence history

go round the cycle again.....

Step 2: normalise

$$c_a^2 + 2c_a c_b S + c_b^2 = 1 \Rightarrow$$

$$c_a = 0.56391$$

$$c_b = 0.52627$$

etc. etc. etc. etc.

	c_a	c_b	F_{aa}	F_{ab}	F_{bb}	ε_1	ε_2
Initial	0.71937	0.35968	-0.4107	-0.5913	-0.3844		
1st iter	0.56391	0.52627	-0.4054	-0.6001	-0.4026	-0.5880	0.6105
2nd iter	0.54711	0.54319	-0.4042	-0.6007	-0.4039	-0.5972	0.6191
3rd iter	0.54536	0.54495	-0.4041	-0.6007	-0.4041	-0.5973	0.6192
4th iter	0.54517	0.54513	-0.4041	-0.6007	-0.4041	-0.5973	0.6192
5th iter	0.54515	0.54515	-0.4041	-0.6007	-0.4041	-0.5973	0.6192

The concept of effective nuclear charge: the 4s vs 3d controversy.

For a poly-electronic electron, the full Hamiltonian for a single electron is:

$$H_{el,i} = -\frac{1}{2}\nabla^2 - \frac{Z}{r_i} + \sum_{j>i}^n \frac{1}{r_{ij}}$$

But we can simplify this by absorbing the (repulsive) electron-electron interactions into the ‘effective nuclear charge’, which is reduced from its value for the real atom:

$$H_{el,i} \approx -\frac{1}{2}\nabla^2 - \frac{Z^{eff}}{r_i}$$

We say that the reference electron (i) is ‘shielded’ from the real nuclear charge Z by the presence of the other electrons, and if we choose an appropriate value of Z^{eff} , we can recover the eigenvalues and eigenfunctions of the full Hamiltonian. There are many sets of empirical rules used to define Z^{eff} (Slater, Clementi etc).

So we really ‘hide’ the electron-electron repulsions by rolling them into a reduced positive charge at the nucleus: the ‘effective nuclear charge’. This was absolutely necessary when the concept was first thought of (ca 1930), because accurate computation of the repulsions was out of the question. Now they are routine.

Qu 1: The 4s/3d ordering debate: why is K $4s^1 3d^0$ and not $3d^1 4s^0$?

Standard answer: the 4s orbital penetrates through the core electrons, and so ‘experiences a greater effective nuclear charge’.

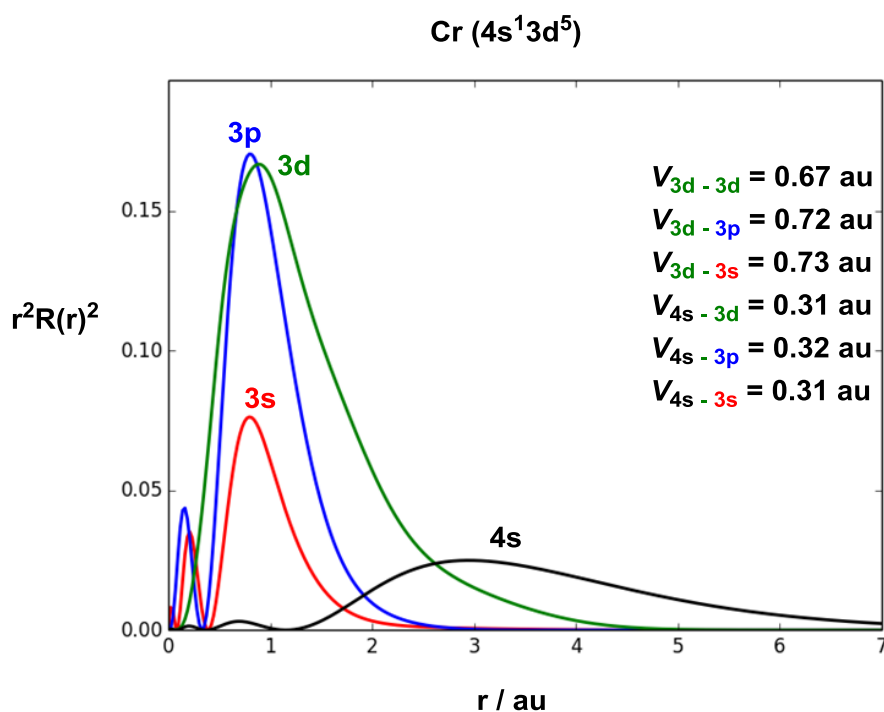
Qu 2: why is $Ti^{3+} 3d^1 4s^0$ and not $4s^1 3d^0$?

Standard answer: don’t know.

Let us consider the 7S states of the isoelectronic series Cr, Mn^+ , Fe^{2+} , where the 4s and 3d orbitals are all singly occupied (thereby avoiding the problem of comparing occupied and virtual orbital energies).

Components of the self-consistent energies of the 4s and 3d orbitals of the 7S states of Cr, Mn^+ and Fe^{2+} (in au) at the HF/VTZ level.

	T	V_{ne}	V_{ee}	E_{tot}
Cr				
4s	0.63	-8.29	7.44	-0.22
3d	4.91	-24.13	18.86	-0.36
Mn⁺				
4s	1.13	-10.96	9.28	-0.54
3d	6.50	-29.26	21.84	-0.93
Fe²⁺				
4s	1.71	-13.52	10.86	-0.95
3d	8.13	-34.25	24.47	-1.65



Components of the electron-electron repulsion in the 7S state of Cr.

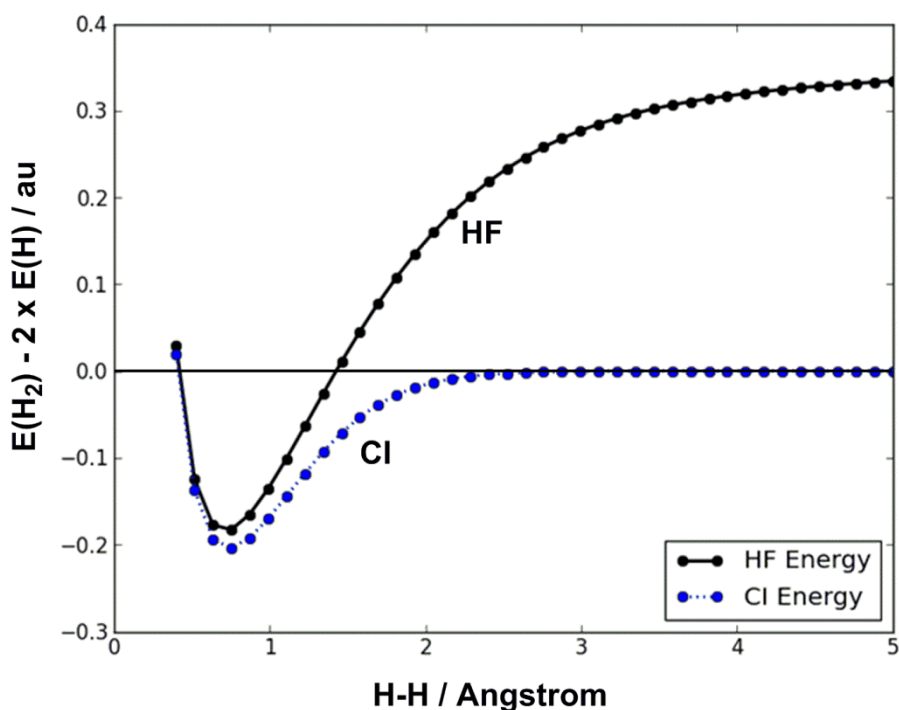
The correlation problem and post-HF methods.

We have established from MO theory that the ground state wavefunction for H₂ can be

represented as:

$$\Phi_{MO} = |\mathbf{1}\sigma_g \mathbf{1}\bar{\sigma}_g| = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{1}\sigma_g(1) & \mathbf{1}\bar{\sigma}_g(1) \\ \mathbf{1}\sigma_g(2) & \mathbf{1}\bar{\sigma}_g(2) \end{vmatrix}$$

and we used the HFR equations to find the optimum form of the orbital $\mathbf{1}\sigma_g$ in terms of the LCAO expansion. The potential energy surface shown below ('HF' = Hartree Fock) indicates that this reproduces the equilibrium geometry reasonably well, but fails to reproduce the dissociation energy: the HF energy of H₂ at the dissociation limit is ~0.34 au higher than that of two isolated H atoms (set as zero in the figure below).



To see the origin of the problem, expand the spatial part of the wavefunction:

$$\begin{aligned} \Phi_{spatial} &= \mathbf{1}\sigma_g \mathbf{1}\sigma_g = \frac{1}{2(1+S)} (\chi_a(1) + \chi_b(1)) (\chi_a(2) + \chi_b(2)) \\ &= \frac{1}{2(1+S)} (\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) + \chi_a(1)\chi_b(2) + \chi_b(1)\chi_a(2)) \\ &= \mathbf{H_a^- \dots H_b^+} + \mathbf{H_a^+ \dots H_b^-} + \mathbf{H_a^\cdot \dots H_b^\cdot} + \mathbf{H_a^\cdot \dots H_b^\cdot} \end{aligned}$$

i.e. an equal mixture of covalent ($\mathbf{H_a^\cdot \dots H_b^\cdot}$) and ionic ($\mathbf{H_a^+ \dots H_b^-}$) 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 $\mathbf{H^+ + H^-}$.

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 are more probable than they should be: 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 is also the most probable position to find electron 2, and that doesn't make much sense!

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 $(1\sigma_u)^2$

$$\Psi_{CI} = c_1 |1\sigma_g 1\bar{\sigma}_g| + c_2 |1\sigma_u 1\bar{\sigma}_u|$$

Expanding the spatial part of the second term in the same way as above gives

$$\begin{aligned}\Phi_{spatial} &= 1\sigma_u 1\sigma_u = \frac{1}{2(1-S)} (\chi_a(1) - \chi_b(1)) (\chi_a(2) - \chi_b(2)) \\ &= \frac{1}{2(1-S)} (\chi_a(1)\chi_a(2) + \chi_b(1)\chi_b(2) - \chi_a(1)\chi_b(2) - \chi_b(1)\chi_a(2))\end{aligned}$$

$$\text{Thus } \Psi_{CI} = c_1 |1\sigma_g 1\bar{\sigma}_g| + c_2 |1\sigma_u 1\bar{\sigma}_u|$$

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

Thus an appropriate choice of coefficients (specifically when $\frac{c_1}{c_2} = -\frac{(1+S)}{(1-S)}$) causes the ionic

terms to vanish completely. The ratio $\frac{c_2}{c_1}$ varies from 0 at equilibrium 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

$$\Psi = \sum_i C_i \Phi_i$$

where Φ_i are now determinants, not orbitals, is then found using the linear variation method.

Example: for H_2 : $\Psi = C_1\Phi_1 + C_2\Phi_2$

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

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 dealt with the matrix element $\langle \Phi_1 | \hat{H} | \Phi_1 \rangle$ - it is the ground-state energy of H_2 : $= 2E_{1\sigma_g} + J_{1\sigma_g 1\sigma_g}$

Similarly, we can show that

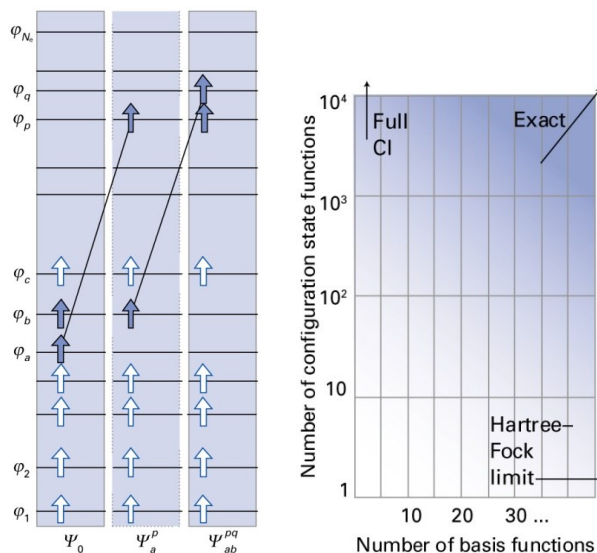
$$\langle \Phi_2 | \hat{H} | \Phi_2 \rangle = 2E_{1\sigma_u} + J_{1\sigma_u 1\sigma_u} \quad \text{and} \quad \langle \Phi_1 | \hat{H} | \Phi_2 \rangle = K_{1\sigma_g 1\sigma_u} \quad (\text{see problems sheet})$$

So the total energy including CI is the lowest root of

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

This is the dashed curve in the Figure on P 29

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...) can be very accurate but very expensive.



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):

- a) The energy is uniquely defined by the electron density, ρ .
- b) 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:

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

$V(r), J(r)$ 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, not by expanding the wavefunction beyond the HF single determinant. Therefore it is appealing in terms of cost.

Problem: $V_{xc}(r)$ is unknown, and there are hundreds (probably thousands now) of different approximations to it (BP86, BLYP, HCTH, B3LYP, PBE, rev-PBE..... – the so-called 'functional zoo'). More than 20 years after it was first proposed, the most popular remains B3LYP ('everybody's favourite functional').

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.

Hückel theory (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.

- 1) Assume complete separation of σ/π systems (contrast **EHT**, later, where all valence orbitals are included)
- 2) Assumes independent electrons: i.e. $\Phi = \phi_1\phi_2\phi_3\phi_4\dots$, a simple Hartree product, and $E = E_1 + E_2 + E_3 + E_4 + \dots$
- 3) $H_{11} = \alpha$ the Coulomb integral
- 4) $H_{12} = \beta$ (the resonance integral) if 1 and 2 are nearest neighbours, 0 otherwise
n.b α and β usually given symbolic values rather than assigned to real numbers.
- 5) $S_{12} = 0$ 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 π system $S_{12} \approx 0.2$, so this seems a radical approximation. However it has little impact on the final solutions (see problem 2.2).

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

Example: allyl radical

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

$$\text{Define } x = \left(\frac{\alpha - E}{\beta} \right) \Rightarrow \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x^3 - 2x = 0$$

$$x = 0, \pm\sqrt{2} \quad x = 0 \Rightarrow E_2 = \alpha \quad x = \pm\sqrt{2} \Rightarrow E_{1,3} = \alpha \pm \sqrt{2}\beta$$

note energy level subscripts 1-3 chosen for future convenience.

Eigenvectors: sub E_{1-3} into secular equations

$$E_2 = \alpha$$

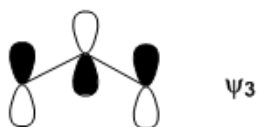
$$\left. \begin{aligned} c_1\beta + c_2(\alpha - \alpha) + c_3\beta &= 0 \Rightarrow c_3 = -c_1 \\ c_1(\alpha - \alpha) + c_2\beta &= 0 \Rightarrow c_2 = 0 \end{aligned} \right\} \quad \psi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \quad (\text{after normalisation})$$

$$E_1 = \alpha + \sqrt{2}\beta$$

$$\left. \begin{aligned} c_1(\alpha - \alpha - \sqrt{2}\beta) + c_2\beta &= 0 \Rightarrow c_2 = \sqrt{2}c_1 \\ c_1\beta + \sqrt{2}c_1(\alpha - \alpha - \sqrt{2}\beta) + c_3\beta &= 0 \Rightarrow c_3 = c_1 \end{aligned} \right\} \quad \psi_1 = \frac{1}{2}(\chi_1 + \sqrt{2}\chi_2 + \chi_3)$$

$$E_3 = \alpha - \sqrt{2}\beta$$

$$\left. \begin{aligned} c_1(\alpha - \alpha + \sqrt{2}\beta) + c_2\beta &= 0 \Rightarrow c_2 = -\sqrt{2}c_1 \\ c_1\beta - \sqrt{2}c_1(\alpha - \alpha + \sqrt{2}\beta) + c_3\beta &= 0 \Rightarrow c_3 = c_1 \end{aligned} \right\} \quad \psi_3 = \frac{1}{2}(\chi_1 - \sqrt{2}\chi_2 + \chi_3)$$



Singly occupied orbital is E_2 : the unpaired electron lies exclusively on the outer carbons.

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 σ/π separability: **all valence electrons included**.

Unlike Hückel theory, **geometry determines overlaps, which are calculated explicitly** (clearly ignoring σ overlap is not reasonable!).

Basis of method

- 1) Assumes independent electrons: $\Phi = \phi_1\phi_2\phi_3\phi_4\ldots$ and $E = E_1 + E_2 + E_3 + E_4 + \ldots$
- 2) 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.
- 3) $H_{ii} = -I_i$ 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.
- 4) $H_{ij} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} \quad K = 1.75$ Wolfsberg-Helmholtz formula
(1.75 reproduces rotational barrier for ethane, but again choice not critical)

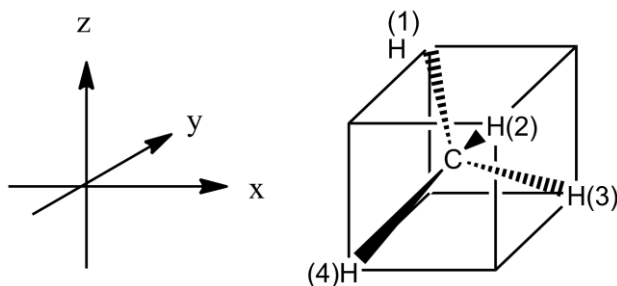
Justification: interaction will increase with overlap, and with the energies of the component orbitals (for a fixed overlap).

n.b. early versions used the simpler $H_{ij} = KS_{ij}$

- 5) Solve matrix equation $Hc = ScE$

comment: In both Hückel and extended Hückel methods we assume the electrons move independently – *i.e.* there is no explicit electron-electron repulsion term, and so a simple Hartree product, $\Phi = \phi_1\phi_2\phi_3\phi_4\ldots$ is sufficient. It is perhaps surprising that this is even remotely successful, given the lengths we go to in *ab initio* theories to compute J and K , and then in CI or DFT to include correlation. The answer is that the use of parameters based on experiment means that the effects of electron-electron repulsion are implicitly included – sometimes called ‘Nature’s correlation’.

Example: CH₄ valence orbitals: C2s, C2p_{x,y,z} H1s



- Work flow:
- 1) Construct S using geometry and form of basis functions
 - 2) Insert diagonal elements H_{ii} (usually tabulated) into H
 - 3) Calculate off-diagonal elements H_{ij} using W-H formula.
 - 4) Construct secular determinant and solve for E
 - 5) Solve for c_n

Slater exponents: **C2s = C2p = 1.625 H1s = 1.20, C-H = 1.09 Å**

(this information is required to construct overlap matrix using similar procedure to that for H₂).

- 1) Overlap matrix, S

	C2s	C2p _z	C2p _x	C2p _y	H1s(1)	H1s(2)	H1s(3)	H1s(4)
C2s	1	0	0	0	0.5183	0.5183	0.5183	0.5183
C2p _z	0	1	0	0	0.2819	0.2819	-0.2819	-0.2819
C2p _x	0	0	1	0	-0.2819	0.2819	0.2819	-0.2819
C2p _y	0	0	0	1	0.2819	-0.2819	0.2819	-0.2819
H1s(1)	0.5183	0.2819	-0.2819	0.2819	1	0.1844	0.1844	0.1844
H1s(2)	0.5183	0.2819	0.2819	-0.2819	0.1844	1	0.1844	0.1844
H1s(3)	0.5183	-0.2819	0.2819	0.2819	0.1844	0.1844	1	0.1844
H1s(4)	0.5183	-0.2819	-0.2819	-0.2819	0.1844	0.1844	0.1844	1

$$H_{C_{2s}C_{2s}} = -19.44eV$$

- 2) Parameters: $H_{C_{2p}C_{2p}} = -10.67eV$

$$H_{H_{1s}H_{1s}} = -13.60eV$$

$$H_{C_{2s}H_{1s}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(0.5833)(-19.44 - 13.6) = -14.98eV$$

- 3) $H_{C_{2p}H_{1s}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(\pm 0.2819)(-10.67 - 13.6) = \pm 5.99eV$

$$H_{H_{1s}H_{1s}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(0.1844)(-13.6 - 13.6) = -4.39eV$$

Hamiltonian matrix, H

	C2s	C2p _z	C2p _x	C2p _y	H1s(1)	H1s(2)	H1s(3)	H1s(4)
C2s	-19.44	0	0	0	-14.98	-14.98	-14.98	-14.98
C2p _z	0	-10.67	0	0	-5.99	-5.99	5.99	5.99
C2p _x	0	0	-10.67	0	5.99	-5.99	-5.99	5.99
C2p _y	0	0	0	-10.67	-5.99	5.99	-5.99	5.99
H1s(1)	-14.98	-5.99	5.99	-5.99	-13.6	-4.39	-4.39	-4.39
H1s(2)	-14.98	-5.99	-5.99	5.99	-4.39	-13.6	-4.39	-4.39
H1s(3)	-14.98	5.99	-5.99	-5.99	-4.39	-4.39	-13.6	-4.39
H1s(4)	-14.98	5.99	5.99	5.99	-4.39	-4.39	-4.39	-13.6

Jargon busting: ‘*Diagonalising the matrix*’:

The secular equations can be expressed in matrix form:

$$\begin{pmatrix} H_{aa} & H_{ab} \\ H_{ab} & H_{bb} \end{pmatrix} \begin{pmatrix} c_{a1} & c_{a2} \\ c_{b1} & c_{b2} \end{pmatrix} = \begin{pmatrix} S_{aa} & S_{ab} \\ S_{ab} & S_{bb} \end{pmatrix} \begin{pmatrix} c_{a1} & c_{a2} \\ c_{b1} & c_{b2} \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

$Hc = ScE$ a **generalised eigenvalue** problem (in a simple eigenvalue problem the overlap matrix is the identity)

When solving the Hückel and EH problems ‘by hand’, we would solve the secular determinant for E , then sub back in to the secular equations to determine the eigenfunctions (coefficients) (as in the allyl radical example above). The matrix of these coefficients, c , has the property that $c^\dagger Hc$ is diagonal, with diagonal elements equal to the eigenvalues, E .

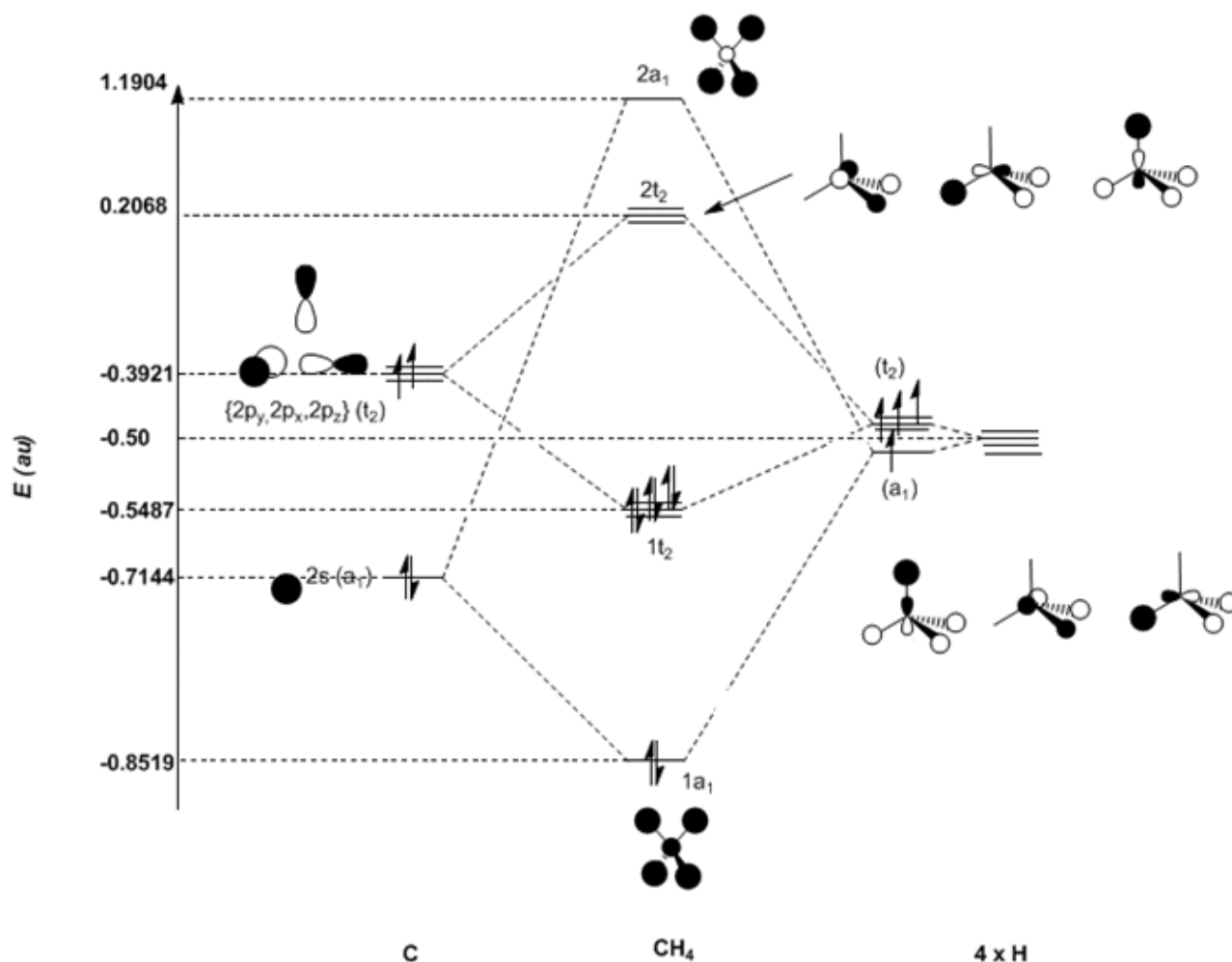
Given the matrices H and S , it then turns out to be easier (computationally) to determine the matrix c that makes $c^\dagger Hc$ diagonal than it is to expand the determinant itself. Thus we find the coefficients first and these give the energies, rather than *vice versa*. We use the expression ‘*diagonalising the matrix*’ – in effect this just means “*finding the eigenvalues and eigenvectors*”.

H-ES

	C2s	C2p_z	C2p_x	C2p_y	H1s(1)	H1s(2)	H1s(3)	H1s(4)
C2s	-19.44-E	0	0	0	-14.98-0.52E	-14.98-0.52E	-14.98-0.52E	-14.98-0.52E
C2p_z	0	-10.67-E	0	0	-5.99-0.28E	-5.99-0.28E	5.99+0.28E	5.99+0.28E
C2p_x	0	0	-10.67-E	0	5.99+0.28E	-5.99-0.28E	-5.99-0.28E	5.99+0.28E
C2p_y	0	0	0	-10.67-E	-5.99-0.28E	5.99+0.28E	-5.99-0.28E	5.99+0.28E
H1s(1)	-14.98-0.52E	-5.99-0.28E	5.99+0.28E	-5.99-0.28E	-13.6-E	-4.39-0.18E	-4.39-0.18E	-4.39-0.18E
H1s(2)	-14.98-0.52E	-5.99-0.28E	-5.99+0.28E	5.99+0.28E	-4.39-0.18E	-13.6-E	-4.39-0.18E	-4.39-0.18E
H1s(3)	-14.98-0.52E	5.99+0.28E	-5.99-0.28E	-5.99-0.28E	-4.39-0.18E	-4.39-0.18E	-13.6-E	-4.39-0.18E
H1s(4)	-14.98-0.52E	5.99+0.28E	5.99-0.28E	5.99+0.28E	-4.39-0.18E	-4.39-0.18E	-4.39-0.18E	-13.6-E

5) Results for CH₄

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)							
C2s	0.58	0	0	0	0	0	0	1.70
C2p_z	0	-0.12	0.48	0.20	0.25	-0.31	1.09	0
C2p_x	0	-0.28	0.12	-0.44	-0.92	0.60	0.38	0
C2p_y	0	0.44	0.20	-0.23	-0.66	-0.95	-0.12	0
H1s(1)	0.19	0.17	-0.10	-0.52	1.0	0.02	0.45	-0.69
H1s(2)	0.19	0.36	0.34	0.25	-0.28	1.01	0.33	-0.69
H1s(3)	0.19	-0.50	0.24	0.0	0.0	-0.67	-0.86	-0.69
H1s(4)	0.19	-0.03	-0.48	0.28	-0.73	0.36	0.74	-0.69



Mulliken population analysis: where are the electrons?

Consider a normalised orbital

$$\phi_i = c_{ai}\chi_a + c_{bi}\chi_b \text{ and } \langle \phi_i | \phi_i \rangle = c_{ai}^2 + c_{bi}^2 + 2c_{ai}c_{bi}S_{ab} = 1$$

We can define net population of atom a, q_a^i , and net overlap population between atoms a and b, p_{ab}^i , arising from this orbital as

$$q_a^i = c_{ai}^2 \quad p_{ab}^i = 2c_{ai}c_{bi}S_{ab}$$

Summing these terms over all occupied orbitals leads to the atomic populations and overlap populations between centres.

Summing atomic populations for the different orbitals on a given atom (2s, 2p_{x,y,z} on C, for example) gives the *reduced net atomic orbital* and *reduced overlap* populations.

In CH₄:

consider $\phi_1 = 0.58C_{2s} + 0.19(H_{1s}(1) + H_{1s}(2) + H_{1s}(3) + H_{1s}(4))$:

$$q_C = 0.58^2 = 0.34$$

$$q_{H(1)} = q_{H(2)} = q_{H(3)} = q_{H(4)} = 0.19^2 = 0.04$$

$$P_{CH(1)} = P_{CH(2)} = P_{CH(3)} = P_{CH(4)} = 2 \times 0.58 \times 0.19 \times 0.51 = 0.11$$

$$P_{H(1)H(2)} = P_{H(1)H(3)} = P_{H(1)H(4)} = P_{H(2)H(3)} = P_{H(2)H(4)} = P_{H(3)H(4)} = 2 \times 0.19 \times 0.19 \times 0.18 = 0.01$$

Mulliken defined gross atomic populations by dividing the overlap population equally between the two component atoms. Doing so in CH₄ leads to

	Gross Pop	Charge
C	3.966	0.034
H	1.008	-0.008

Note: Mulliken populations are notoriously basis-set dependent – only good for comparisons within closely related molecules.

Example 2 (one you can do by hand) Extended Hückel calculation on N₂.

Slater exponents: **N2s = N2p = 1.95 N-N = 1.1 Å**

1) Overlap matrix, *S*

	N1 2s	N1 2p _z	N1 2p _x	N1 2p _y	N2 2s	N2 2p _z	N2 2p _x	N2 2p _y
N1 2s	1	0	0	0	0.45	-0.44	0	0
N1 2p _z	0	1	0	0	0.44	-0.32	0	0
N1 2p _x	0	0	1	0	0	0	0.28	0
N1 2p _y	0	0	0	1	0	0	0	0.28
N2 2s	0.45	0.44	0	0	1	0	0	0
N2 2p _z	-0.44	-0.32	0	0	0	1	0	0
N2 2p _x	0	0	0.28	0	0	0	1	0
N2 2p _y	0	0	0	0.28	0	0	0	1

2) Parameters: $H_{N_{2s}N_{2s}} = -26.0eV$
 $H_{N_{2p}N_{2p}} = -13.4eV$

$$H_{N_{2s}N_{2s}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(0.45)(-2 * 26.0) = -20.3 eV$$

$$H_{N_{2pz}N_{2pz}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(-0.32)(-13.4 * 2) = 7.5 eV$$

$$3) \quad H_{N_{2px}N_{2px}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(0.28)(-13.4 * 2) = -6.5 eV$$

$$H_{N_{2pz}N_{2s}} = KS_{ij} \frac{(H_{ii} + H_{jj})}{2} = \frac{1}{2}(1.75)(\pm 0.44)(-13.4 - 26.0) = \pm 15.1 eV$$

	N1 2s	N1 2p _z	N1 2p _x	N1 2p _y	N2 2s	N2 2p _z	N2 2p _x	N2 2p _y
N1 2s	-26.0	0	0	0	-20.3	15.1	0	0
N1 2p_z	0	-13.4	0	0	-15.1	7.5	0	0
N1 2p_x	0	0	-13.4	0	0	0	-6.5	0
N1 2p_y	0	0	0	-13.4	0	0	0	-6.5
N2 2s	-20.3	-15.1	0	0	-26.0	0	0	0
N2 2p_z	15.1	7.5	0	0	0	-13.4	0	0
N2 2p_x	0	0	-6.5	0	0	0	-13.4	0
N2 2p_y	0	0	0	-6.5	0	0	0	-13.4

Solving (using linear algebra package of your choice) gives energy levels:

2σ_u: +54.0 eV

1π_g: -9.5 eV

2σ_g: -13.5 eV

note 2σ_g is above 1π_u (sp mixing)

1π_u: -15.6 eV

1σ_u: -19.9 eV

1σ_g: -32.1 eV

Problems sheet

Problems 1

1.1 Write down the Slater determinant for the ground states of the following:
Li, He₂ and Li₂.

1.2 The z component of the spin angular momentum operator is $\sum_{j=1}^n \hat{S}_{zj}$

Show that $\Phi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1) & 1\bar{s}(1) & 2s(1) \\ 1s(2) & 1\bar{s}(2) & 2s(2) \\ 1s(3) & 1\bar{s}(3) & 2s(3) \end{vmatrix}$ is an eigenfunction of S_z and evaluate the eigenvalue.

1.3 By expanding the expression $\langle \Phi | \hat{H} | \Phi \rangle = E = \langle \Phi | \hat{H}_1 + \hat{H}_2 + \frac{j_0}{r_{12}} | \Phi \rangle$

Show that the energy of the doubly excited configuration, $\Phi = |1\sigma_u 1\sigma_u\rangle$, is $E = 2E_{1\sigma_u} + J_{1\sigma_u 1\sigma_u}$

1.4 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 H₂, $\Phi = |1\sigma_g 1\sigma_u\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1) & 1\sigma_u(1) \\ 1\sigma_g(2) & 1\sigma_u(2) \end{vmatrix}$.

The wavefunction above is in fact the $M_S = 1$ component of the triplet state, also represented as $\frac{1}{\sqrt{2}} [1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)] (\alpha(1)\alpha(2))$

The $M_S = 0$ component of the same triplet state is:

$$^3\Phi = \frac{1}{2} [1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)] [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

while the $M_S = 0$ component of the corresponding open-shell singlet excited state ($(1\sigma_g)^1 (1\sigma_u)^1$) is given by:

$$^1\Phi = \frac{1}{2} [1\sigma_g(1)1\sigma_u(2) + 1\sigma_g(2)1\sigma_u(1)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

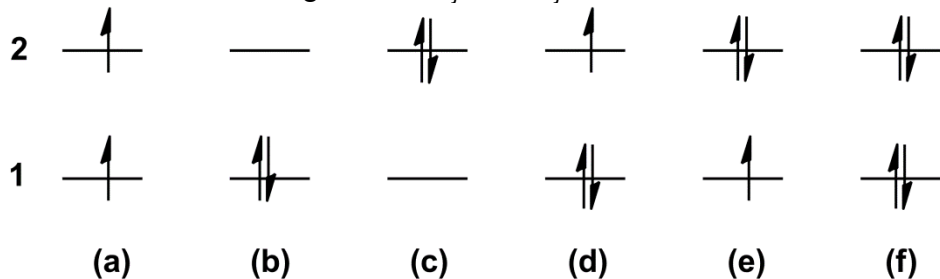
Show that these two wavefunctions can be represented as linear combinations of two Slater determinants.

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

By expanding, verify that the energy of the $M_S = 0$ component of the triplet state is also $E = E_{1\sigma_g} + E_{1\sigma_u} + J_{1\sigma_g 1\sigma_u} - K_{1\sigma_g 1\sigma_u}$.

Calculate the energy of the open-shell singlet state, $^1\Phi$.

- 1.5 (a) Give expressions for the total energy of the following configuration in terms of 1- and 2-electron integrals, E_i , J_{ij} and K_{ij} :



Note that

- (b) Express the total energies for the same species in terms of the Hartree Fock orbital energies, ϵ_i , J_{ij} and K_{ij} .
 (c) Show that the first ionization energy of Li is equal to $-\epsilon_{2s}$.

Problems 2

- 2.1 Evaluate the overlap matrix element between a normalised p-type Gaussian basis function located at the origin, ϕ_1 , and an s-type Gaussian located at (0,0,a), ϕ_2 . The exponent in both cases is α .

$$\phi_1 = N_1 z e^{-\alpha(x^2+y^2+z^2)} \quad \phi_2 = N_2 e^{-\alpha(x^2+y^2+(z-a)^2)}$$

You may use the standard integral $\int_{-\infty}^{+\infty} e^{-bx^2} dx = \sqrt{\frac{\pi}{b}}$

- 2.2 Use the Hückel approximation to set up and solve the secular determinant for the cyclobutadiene, C_4H_4 . Now introduce non-zero overlap, S , between adjacent atoms and again solve the secular equations – what impact does this have on the energy spectrum? (a typical value of S is 0.2)

- 2.3 Using the following data, set up the 2x2 overlap and Hamiltonian matrices for one component of the π system (π and π^*) of CO (you need only consider the p_x orbitals as the p_y are equivalent by symmetry)

$$S_{C_{2p_x} O_{2p_x}} = 0.27, \quad S_{C_{2p_x} C_{2p_x}} = S_{O_{2p_x} O_{2p_x}} = 1.0$$

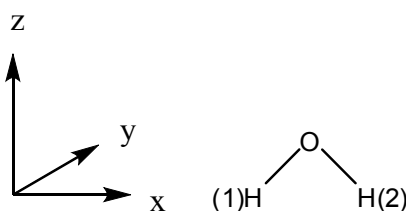
(all other overlap integrals are 1 (S_{ii}) or zero (S_{ij}))

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

$$H_{ij} = \frac{1}{2} * 1.75 * S_{ij} (H_{ii} + H_{jj})$$

Solve the 2x2 determinant and calculate the coefficients in the bonding and antibonding orbitals. Comment on your results.

- 2.4 Using the following data, set up the overlap and Hamiltonian matrices for H_2O (bond length = 1 Å, angle = 90°).



$$S_{O_{2s} H_{1s}(1)} = S_{O_{2s} H_{1s}(2)} = 0.41, \quad S_{O_{2p_z} H_{1s}(1)} = S_{O_{2p_z} H_{1s}(2)} = -0.20, \quad S_{O_{2p_x} H_{1s}(1)} = -S_{O_{2p_x} H_{1s}(2)} = -0.30, \\ S_{H_{1s}(1) H_{1s}(2)} = 0.16$$

(all other overlap integrals are either 1 (S_{ii}) or zero (S_{ij}))

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

$$H_{ij} = \frac{1}{2} K S_{ij} (H_{ii} + H_{jj}) \quad K = 1.75$$

Using an appropriate linear algebra package (octave, matlab, numpy), solve the 6x6 secular determinant to give the orbital energies and the corresponding coefficients in the LCAO expansion. Use the coefficients to sketch the orbitals.

By using appropriate normalized linear combinations of the 1s orbitals on H, show that the secular determinant can be block diagonalised into 1x1, 2x2 and 3x3 components. Solve the 2x2 component by hand (expansion coefficients not required) and show that the energies of these two orbitals are unaffected by the change in basis.

Appendix 1 (see also *Valence* lectures, pp18-23)

Linear variation theorem for H_2^+ .

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

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

$$= \frac{\langle c_a \chi_{1sa} | H | c_a \chi_{1sa} \rangle + \langle c_a \chi_{1sa} | H | c_b \chi_{1sb} \rangle + \langle c_b \chi_{1sb} | H | c_a \chi_{1sa} \rangle + \langle c_b \chi_{1sb} | H | c_b \chi_{1sb} \rangle}{\langle c_a \chi_{1sa} | c_a \chi_{1sa} \rangle + \langle c_a \chi_{1sa} | c_b \chi_{1sb} \rangle + \langle c_b \chi_{1sb} | c_a \chi_{1sa} \rangle + \langle c_b \chi_{1sb} | c_b \chi_{1sb} \rangle}$$

$$= \frac{c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}}{c_a^2 S_{aa} + 2c_a c_b S_{ab} + c_b^2 S_{bb}} \quad H_{aa} = \langle \chi_{1sa} | H | \chi_{1sa} \rangle, S_{aa} = \langle \chi_{1sa} | \chi_{1sa} \rangle \text{ etc}$$

$$\frac{\partial E}{\partial c_a} = \frac{\left[(c_a^2 S_{aa} + 2c_a c_b S_{ab} + c_b^2 S_{bb}) (2c_a H_{aa} + 2c_b H_{ab}) - (c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}) (2c_a S_{aa} + 2c_b S_{ab}) \right]}{(c_a^2 S_{aa} + 2c_a c_b S_{ab} + c_b^2 S_{bb})^2} = 0$$

$$\left(\text{using } \frac{\partial \left(\frac{f_1(x,y)}{f_2(x,y)} \right)}{\partial x} = \frac{[f_2(x,y) f_1'(x,y) - f_1(x,y) f_2'(x,y)]}{f_2(x,y)^2} \right)$$

Multiply through by $(c_a^2 S_{aa} + 2c_a c_b S_{ab} + c_b^2 S_{bb})$:

$$\frac{\partial E}{\partial c_a} = \left[(2c_a H_{aa} + 2c_b H_{ab}) - \frac{(c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb})}{(c_a^2 S_{aa} + 2c_a c_b S_{ab} + c_b^2 S_{bb})} (2c_a S_{aa} + 2c_b S_{ab}) \right] = 0$$

Note that $\frac{(c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb})}{(c_a^2 S_{aa} + 2c_a c_b S_{ab} + c_b^2 S_{bb})} = E$

$$\frac{\partial E}{\partial c_a} = \left[(2c_a H_{aa} + 2c_b H_{ab}) - E (2c_a S_{aa} + 2c_b S_{ab}) \right]$$

$$= 2 \left[c_a (H_{aa} - E S_{aa}) + c_b (H_{ab} - E S_{ab}) \right] = 0$$

Likewise $\frac{\partial E}{\partial c_b} = 2 \left[c_b (H_{bb} - E S_{bb}) + c_a (H_{ab} - E S_{ab}) \right] = 0$

$$\begin{pmatrix} H_{aa} - E S_{aa} & H_{ab} - E S_{ab} \\ H_{ab} - E S_{ab} & H_{bb} - E S_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

This system of simultaneous equations has non-trivial solutions when:

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{bb} - ES_{bb} \end{vmatrix} = 0$$

Generalising to arbitrary size: variationally optimised solution occurs when:

$$|H_{ij} - ES_{ij}| = 0$$

If we assume normalised atomic orbitals:

$$S_{aa} = S_{bb} = 1, S_{ab} = S$$

and define $H_{aa} = H_{bb} = \alpha, H_{ab} = H_{ba} = \beta$

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{bb} - ES_{bb} \end{vmatrix} = \begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\Rightarrow (\alpha - E + \beta - ES)(\alpha - E - \beta + ES) = 0$$

$$\Rightarrow E(-1 - S) + (\alpha + \beta) = 0$$

(difference of 2 squares)

$$\text{or } E(-1 + S) + (\alpha - \beta) = 0$$

$$E_{\pm} = \frac{(\alpha \pm \beta)}{(1 \pm S)} \quad (\text{note } \beta \text{ is negative})$$

These are the energies of the $1\sigma_g$ and $1\sigma_u$ orbitals of H_2^+ .

Sub E_+ back into secular equations to get c_a, c_b :

$$E_+ = \frac{(\alpha + \beta)}{(1 + S)} \Rightarrow c_a \left(\alpha - \left(\frac{\alpha + \beta}{1 + S} \right) \right) + c_b \left(\beta - \left(\frac{\alpha + \beta}{1 + S} \right) S \right) = 0$$

multiply through by $1 + S$:

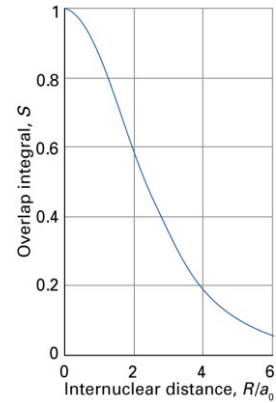
$$c_a ((1 + S)\alpha - (\alpha + \beta)) + c_b ((1 + S)\beta - (\alpha + \beta)S) = 0$$

$$\Rightarrow c_a (S\alpha - \beta) + c_b (\beta - S\alpha) = 0$$

$$\Rightarrow c_a (S\alpha - \beta) = c_b (S\alpha - \beta)$$

$$\Rightarrow c_a = c_b$$

Likewise $E_- = \frac{(\alpha - \beta)}{(1 - S)} \Rightarrow c_a = -c_b$



Normalising for $\psi_+ = c_a (\chi_{1sa} + \chi_{1sb}) = 1\sigma_g$:

$$\int c_a (\chi_{1sa} + \chi_{1sb}) c_a (\chi_{1sa} + \chi_{1sb}) d\tau = c_a^2 (1 + 1 + S + S) = 1$$

$$\Rightarrow c_a = c_b = \frac{1}{\sqrt{2(1+S)}}$$

Likewise for $\psi_- = c_a (\chi_{1sa} - \chi_{1sb}) = 1\sigma_u$

$$\Rightarrow c_a = -c_b = \frac{1}{\sqrt{2(1-S)}}$$