

CHM 673

Lecture 4: Hartree-Fock model, part 1

Suggested reading:

Chapter 3.1, 3.2 from S&O

Chapter 3.2-3.3 from Jensen

<http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/Hartree-Fock-Intro.pdf>

Electronic wavefunction

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\{\mathbf{R}\}) + \hat{V}_{eN}(\mathbf{r}; \{\mathbf{R}\}) + \hat{V}_{ee}(\mathbf{r})$$

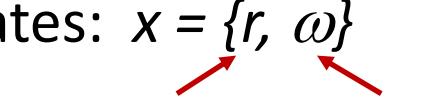
$$\hat{H}_{el}\Phi_e(\mathbf{r}; \{\mathbf{R}\}) = U(\mathbf{R})\Phi_e(\mathbf{r}; \{\mathbf{R}\})$$

"clamped-nuclei" SE; this is our "**first principle**"

Electronic SE depends only on the spatial coordinates of electrons

But electrons have spins → electronic spins need to be included in the electronic wave function

electronic coordinates: $x = \{r, \omega\}$


spatial coordinate spin coordinate

spin-functions: $\alpha(\omega)$ (spin up), $\beta(\omega)$ (spin down); ω - unspecified spin variable

Spin functions are complete and orthonormal: $\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$; $\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$

Electronic wavefunction

orbital – a wave function for a single particle, electron

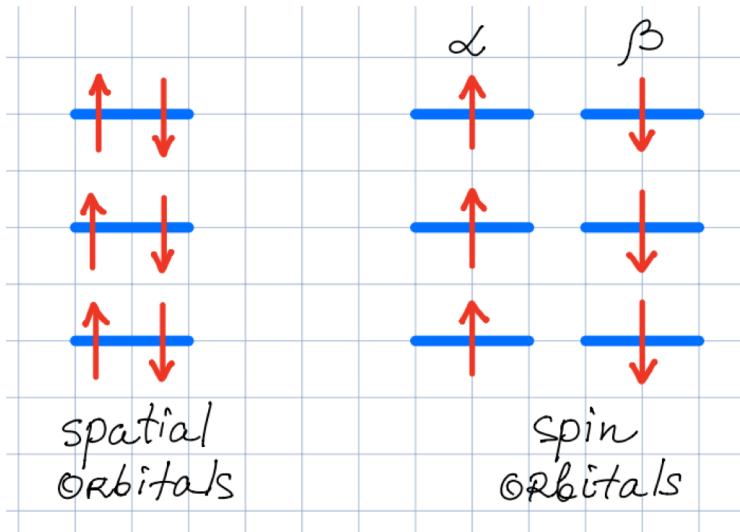
spatial orbital $\psi_i(r)$ – describes spatial distribution of an electron

probability to find electron at r : $|\psi_i(r)|^2 dr$

spatial orbitals form an orthonormal set: $\int dr \psi_i^*(r) \psi_j(r) = \delta_{ij}$

spin orbital $\chi(x)$ – describes both spatial and spin coordinates

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



K spatial orbitals
2K spin orbitals

Many-electron wavefunction

Imagine the total electronic Hamiltonian is separable into one-electron terms

$$\hat{H} = \sum_{i=1}^N \hat{h}(x_i)$$

This is true if we ignore electron-electron repulsion (lousy) OR
if $\hat{h}(x_i)$ includes electron-electron repulsion in some average way

Then for each electron: $\hat{h}(x_i)\chi_j(x_i) = \varepsilon_j\chi_j(x_i)$ or, simpler, $\hat{h}(i)\chi_j(i) = \varepsilon_j\chi_j(i)$
SE for electron i occupying spin-orbital j

Recall separation of variables? Then

$$\hat{H}\Psi^{HP} = E\Psi^{HP}$$

$$\Psi^{HP}(x_1, x_2, \dots, x_N) = \chi_i(x_1)\chi_j(x_2)\dots\chi_k(x_N)$$
 Hartree product wave function

$$E = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$
 energies of spin-orbitals $i, j, k\dots$ occupied by electrons 1,2,3...

Hartree produce wavefunction

$$\Psi^{HP}(x_1, x_2, \dots, x_N) = \chi_i(x_1) \chi_j(x_2) \dots \chi_k(x_N)$$

Let's compute probability to find electrons in space:

$$|\Psi^{HP}|^2 dx_1 dx_2 \dots dx_N = |\chi_i(x_1)|^2 dx_1 |\chi_j(x_2)|^2 dx_2 \dots |\chi_k(x_N)|^2 dx_N$$

Probability to find electron 1 in a given region of space is independent of finding electron 2 in another part of space

Hartree product is an **uncorrelated** or **independent-electron** wave function

Hartree product wave function is deficient, because

- **Electrons are indistinguishable fermions:** Electronic wave function should be antisymmetric with respect to the interchange of the space and spin coordinates of any two electrons
- **Electrons are correlated:** Coulomb repulsion → electrons repel each other

Antisymmetric wavefunction

Consider 2 electrons on two spin-orbitals

$$\Psi_{12}^{HP}(x_1, x_2) = \chi_i(x_1) \chi_j(x_2)$$

$$\Psi_{21}^{HP}(x_2, x_1) = \chi_i(x_2) \chi_j(x_1)$$

Take a linear combination of these HP wavefunctions:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} (\chi_i(x_1) \chi_j(x_2) - \chi_i(x_2) \chi_j(x_1))$$

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1) \quad \text{antisymmetric!}$$

If $\chi_i = \chi_j$, $\Psi(x_1, x_2) = 0$ ← Pauli exclusion principle

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} (\chi_i(x_1) \chi_j(x_2) - \chi_i(x_2) \chi_j(x_1)) =$$
$$\frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} \quad \text{Slater determinant}$$



John Slater
1900-1976

Slater determinant wavefunction

In general N-electron case:

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

↑ ↑
 spin-orbitals

electrons
= $|\chi_i(x_1) \chi_j(x_2) \dots \chi_k(x_N)\rangle = |\chi_i \chi_j \dots \chi_k\rangle = |ij \dots k\rangle$

short-hand notations

- normalization is implicitly assumed
- the order of electrons (x_1, x_2, x_3, \dots) is assumed

Slater determinants (SD) guarantee that

- Electrons are indistinguishable
- Antisymmetry principle is ensured
- Pauli exclusion principle is ensured

Slater determinant wavefunction

Properties of Slater determinants

- SD is completely specified by its spin-orbitals (to within a sign)
- SD is normalized
- SDs formed by different spin-orbitals are orthogonal

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \dots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \dots & \chi_k(x_2) \\ \dots & \dots & \dots & \dots \\ \chi_i(x_N) & \chi_j(x_N) & \dots & \chi_k(x_N) \end{vmatrix} = |\chi_i(x_1) \chi_j(x_2) \dots \chi_k(x_N)\rangle$$

↑ ↑
spin-orbitals

electrons

normalization

HP wavefunction – uncorrelated wavefunction

SD incorporates exchange correlation (correlation between parallel spins) – aka Fermi hole

Hartree-Fock model

Hartree-Fock model tries to find the *best variational solution* to the electronic Hamiltonian assuming that the wave function is approximated by a **single Slater determinant**.

This is the same thing as to assume *that each electron only feels an average charge distribution due to other electrons*



Douglas
Hartree

Vladimir
Fock



Variational principle

The Hartree-Fock model (as several other methods in computational chemistry) is based on variational principle

Variational principle provides a means to find increasingly better ground-state solutions of the SE, starting from a trial wavefunction

Variational principle is based on the Variational Theorem

Variational Theorem:

the exact ground state energy of any quantum system E_0 is invariably smaller than the approximate ground state energy $E_{0'}$ obtained using *any* approximate trial ground state wavefunction $\Psi_{0'}$

$$E_0 \leq E_{0'}$$

Variational principle

Variational Theorem:

the exact ground state energy of any quantum system E_0 is invariably smaller than the approximate ground state energy $E_{0'}$ obtained using *any* approximate trial ground state wavefunction $\Psi_{0'}$

$$E_0 \leq E_{0'}$$

Proof:

1. eigenstates of H are orthogonal
2. eigenstates of H form a complete set, i.e. any physically meaningful trial wavefunction can be represented as
3. $E_n = \langle n | H | n \rangle \geq E_0$

$$\begin{aligned} E_{0'} - E_0 &= \langle 0' | \hat{H} - E_0 | 0' \rangle = \int \Psi_{0'}^* (\hat{H} - E_0) \Psi_{0'} d\tau \\ &= \int \sum_{n=0}^{\infty} c_n^* \Psi_n^* (\hat{H} - E_0) \sum_{m=0}^{\infty} c_m \Psi_m d\tau = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_n^* c_m \int \Psi_n^* (\hat{H} - E_0) \Psi_m d\tau \\ &= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_n^* c_m \left(\int \Psi_n^* \hat{H} \Psi_m d\tau - \int \Psi_n^* E_0 \Psi_m d\tau \right) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_n^* c_m \left(\int \Psi_n^* E_m \Psi_m d\tau - \int \Psi_n^* E_0 \Psi_m d\tau \right) \\ &= \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_n^* c_m (E_m - E_0) \int \Psi_n^* \Psi_m d\tau = \sum_{n=0}^{\infty} c_n^* c_n (E_n - E_0) \geq 0 \end{aligned}$$

$$\Psi_{0'} = \sum_{n=0}^{\infty} c_n \Psi_n$$

Variational principle

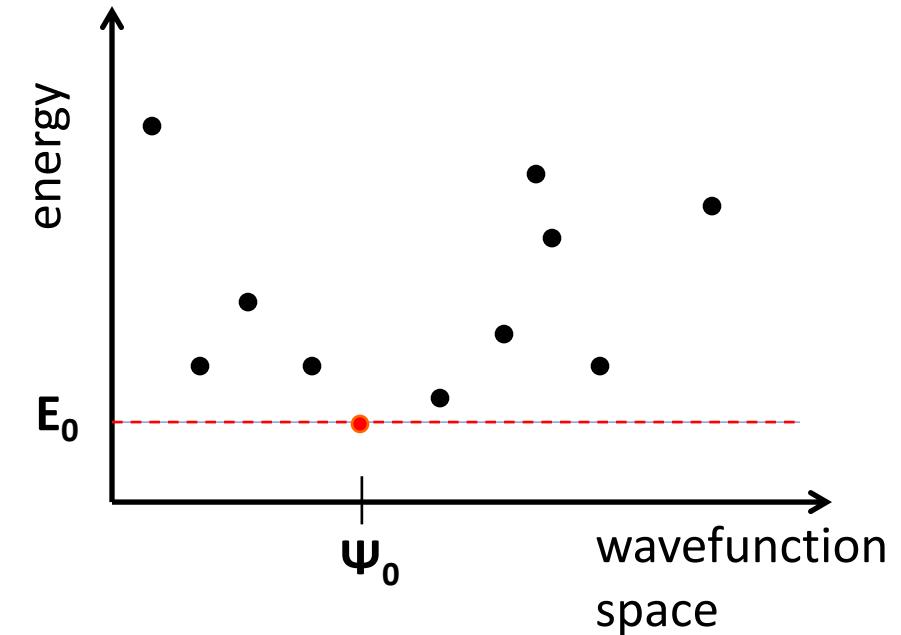
Variational Theorem:

$$E_0 \leq E_{0'}$$

Variational theorem allows us to improve the wavefunction by trying to find one that results in the lowest possible Hamiltonian expectation value (ground state energy).

Typically this is achieved by making a wavefunction a function of a parameter (or parameters) that need to be optimized to find the lowest energy.

Lower energy \leftrightarrow better (closer to the exact eigenvalue) wavefunction
The bigger the allowed wavefunction subspace \rightarrow lower energy can be found



Hartree-Fock model

Hartree-Fock model tries to find the *best variational solution* to the electronic Hamiltonian assuming that the wave function is approximated by a **single Slater determinant**: $\Psi_{HF} = \Psi_{SD}$

General strategy:

1. $E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle$ - this equation defines HF energy as a *functional* of spin-orbitals
2. Minimize E_{HF} with respect to spin-orbitals: $\delta E_{HF} \left[\{\chi_i\} \right] = 0 \rightarrow$
this equation determines optimal spin-orbitals and the variationally best (lowest) energy
3. Solve this equation for the best orbitals and energy – job done!

Notations for electronic Hamiltonian

Electronic Hamiltonian

$$\hat{H}_{el} = - \sum_i^{elec} \frac{1}{2} \nabla_i^2 - \sum_i^{elec} \sum_A^{nuc} \frac{Z_A}{r_{Ai}} + \sum_{i < j}^{elec} \frac{1}{r_{ij}} + \hat{V}_{NN}$$

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

one-electron operator:

accounts for kinetic energy of electron i and Coulomb attraction of electron i to all nuclei

$$\hat{v}(i, j) = \frac{1}{r_{ij}}$$

two-electron operator:

Coulomb repulsion between electrons i and j

$$\hat{H}_e = \sum_i \hat{h}(i) + \sum_{i < j} \hat{v}(i, j) + \hat{V}_{nn}$$

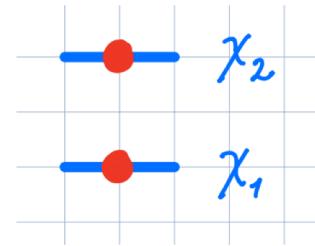
electronic Hamiltonian in these operators

Step 1. Expression for the Hartree-Fock energy

We need to compute $E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle$

Let's do it for the case of 2-electron system

$$\hat{H}_{el} = \hat{h}(r_1) + \hat{h}(r_2) + \frac{1}{r_{12}}$$



$$\Psi_{SD} = \frac{1}{\sqrt{2}} (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1))$$

1. One-electron terms:

$$\begin{aligned} \langle \Psi_{SD} | \hat{h}(r_1) | \Psi_{SD} \rangle &= \frac{1}{2} \int dx_1 dx_2 (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1))^* \hat{h}(r_1) (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) = \\ &= \frac{1}{2} \left[\begin{array}{l} \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \hat{h}(r_1) \chi_1(x_1) \chi_2(x_2) + \\ \int dx_1 dx_2 \chi_1^*(x_2) \chi_2^*(x_1) \hat{h}(r_1) \chi_1(x_2) \chi_2(x_1) + \\ - \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \hat{h}(r_1) \chi_1(x_2) \chi_2(x_1) + \\ - \int dx_1 dx_2 \chi_1^*(x_2) \chi_2^*(x_1) \hat{h}(r_1) \chi_1(x_1) \chi_2(x_2) \end{array} \right] = \\ &= \frac{1}{2} \left[\begin{array}{l} \int dx_1 \chi_1^*(x_1) \hat{h}(r_1) \chi_1(x_1) \int dx_2 \chi_2^*(x_2) \chi_2(x_2) + \\ \int dx_1 \chi_2^*(x_1) \hat{h}(r_1) \chi_2(x_1) \int dx_2 \chi_1^*(x_2) \chi_1(x_2) + \\ - \int dx_1 \chi_1^*(x_1) \hat{h}(r_1) \chi_2(x_1) \int dx_2 \chi_2^*(x_2) \chi_1(x_2) + \\ - \int dx_1 \chi_2^*(x_1) \hat{h}(r_1) \chi_1(x_1) \int dx_2 \chi_1^*(x_2) \chi_2(x_2) \end{array} \right] = \\ &= \left[\begin{array}{l} 1 \\ 1 \\ 0 \\ 0 \end{array} \right] \end{aligned}$$

The diagram shows a vertical line with four terms. Red arrows point from the second and third terms to the right, with the label '=1' below them. Red arrows point from the fourth and fifth terms to the right, with the label '=0' below them.

One-electron terms

1. One-electron terms:

$$\langle \Psi_{SD} | \hat{h}(r_1) | \Psi_{SD} \rangle = \frac{1}{2} \int dx_1 dx_2 (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1))^* \hat{h}(r_1) (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) =$$
$$\frac{1}{2} \left[\int dx_1 \chi_1^*(x_1) \hat{h}(r_1) \chi_1(x_1) + \int dx_1 \chi_2^*(x_1) \hat{h}(r_1) \chi_2(x_1) \right] = \frac{1}{2} [\langle \chi_1 | \hat{h}(1) | \chi_1 \rangle + \langle \chi_2 | \hat{h}(1) | \chi_2 \rangle]$$

This is kinetic energy and electron-nuclei interaction energy of an electron spending half-time in orbital χ_1 and half-time in orbital χ_2

Similarly, $\langle \Psi_{SD} | \hat{h}(r_2) | \Psi_{SD} \rangle = \frac{1}{2} [\int dx_2 \chi_1^*(x_2) \hat{h}(r_2) \chi_1(x_2) + \int dx_2 \chi_2^*(x_2) \hat{h}(r_2) \chi_2(x_2)] =$

$$\frac{1}{2} [\langle \chi_1 | \hat{h}(2) | \chi_1 \rangle + \langle \chi_2 | \hat{h}(2) | \chi_2 \rangle] \quad x_2 \text{ is an integration (~dummy) variable}$$
$$= \frac{1}{2} [\langle \chi_1 | \hat{h}(1) | \chi_1 \rangle + \langle \chi_2 | \hat{h}(1) | \chi_2 \rangle] = \frac{1}{2} [\langle \chi_1 | \hat{h} | \chi_1 \rangle + \langle \chi_2 | \hat{h} | \chi_2 \rangle]$$

Together, $\langle \Psi_{SD} | \hat{h}(r_1) + \hat{h}(r_2) | \Psi_{SD} \rangle = \langle \chi_1 | \hat{h} | \chi_1 \rangle + \langle \chi_2 | \hat{h} | \chi_2 \rangle = \langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle = h_1 + h_2$

For N electrons on N spin-orbitals 1,2,3...N, $\langle \Psi_{SD} | \sum_i^{Nelec} \hat{h}(i) | \Psi_{SD} \rangle = \sum_i^{Nelec} h_i$

Two-electron terms

2. Two-electron terms:

$$\left\langle \Psi_{SD} \left| \frac{1}{r_{12}} \right| \Psi_{SD} \right\rangle = \frac{1}{2} \int dx_1 dx_2 (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1))^* \frac{1}{r_{12}} (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) =$$
$$\frac{1}{2} \left[\begin{array}{l} \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_1) \chi_2(x_2) + \\ \int dx_1 dx_2 \chi_1^*(x_2) \chi_2^*(x_1) \frac{1}{r_{12}} \chi_1(x_2) \chi_2(x_1) + \\ - \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_2) \chi_2(x_1) + \\ - \int dx_1 dx_2 \chi_1^*(x_2) \chi_2^*(x_1) \frac{1}{r_{12}} \chi_1(x_1) \chi_2(x_2) \end{array} \right]$$

again, x_1 and x_2 are dummy integration variables
we can rename or switch them

$\rightarrow \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_1) \chi_2(x_2)$

$\rightarrow - \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_2) \chi_2(x_1)$

Two-electron terms

2. Two-electron terms:

$$\left\langle \Psi_{SD} \left| \frac{1}{r_{12}} \right| \Psi_{SD} \right\rangle = \frac{1}{2} \int dx_1 dx_2 (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1))^* \frac{1}{r_{12}} (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) =$$

$$\frac{1}{2} \left[\begin{array}{l} \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_1) \chi_2(x_2) + \\ \int dx_1 dx_2 \chi_1^*(x_2) \chi_2^*(x_1) \frac{1}{r_{12}} \chi_1(x_2) \chi_2(x_1) + \\ - \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_2) \chi_2(x_1) + \\ - \int dx_1 dx_2 \chi_1^*(x_2) \chi_2^*(x_1) \frac{1}{r_{12}} \chi_1(x_1) \chi_2(x_2) \end{array} \right] =$$

$$= \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_1) \chi_2(x_2) = \langle 12|12 \rangle - \langle 12|21 \rangle$$

$$= - \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \frac{1}{r_{12}} \chi_1(x_2) \chi_2(x_1) = J_{12} - K_{12}$$

Coulomb integral **J**

exchange integral **K**

More notations: $\int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_k(x_1) \chi_l(x_2) = \langle ij|kl \rangle = [ik|jl] = (ik||jl)$

Coulomb integral $J_{ij} = \langle ij|ij \rangle$

Exchange integral $K_{ij} = \langle ij|ji \rangle$

$$J_{ij} - K_{ij} = \langle ij|ij \rangle - \langle ij|ji \rangle = \langle ij || ij \rangle$$

$\langle 1^*2^*|12 \rangle$ $\langle 1^*1|2^*2 \rangle$ $\langle 1^*1|2^*2 \rangle$ for spatial orbitals

Two-electron terms

For two electrons:

$$\left\langle \Psi_{SD} \left| \frac{1}{r_{12}} \right| \Psi_{SD} \right\rangle = \frac{1}{2} \int dx_1 dx_2 (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1))^* \frac{1}{r_{12}} (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) = \\ J_{12} - K_{12}$$

For N electrons:

one Coulomb and exchange term should exist for each pair of electrons, i.e.

$$\left\langle \Psi_{SD} \left| \sum_{i < j}^{N_{elec}} \frac{1}{r_{ij}} \right| \Psi_{SD} \right\rangle = \sum_i^{N_{elec}} \sum_{j > i}^{N_{elec}} (J_{ij} - K_{ij}) = \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (J_{ij} - K_{ij})$$

Hartee-Fock energy expression

$$\hat{H}_e = \sum_i \hat{h}(i) + \sum_{i < j} \hat{v}(i, j) + \hat{V}_{nn}$$

Electronic Hamiltonian

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

one-electron operator

$$\hat{v}(i, j) = \frac{1}{r_{ij}}$$

two-electron operator

$$\text{HF energy: } E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle = \sum_i^{N_{elec}} h_i + \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (J_{ij} - K_{ij})$$

Each electron contributes a *one-electron integral*

$$\langle i | \hat{h} | i \rangle = \int dx_1 \chi_i^*(x_1) \hat{h}(r_1) \chi_i(x_1)$$

This looks like the expectation (average) value of the operator \hat{h} for an electron in orbital χ_i

Recall \hat{h} contains electron kinetic energy and potential of attraction to all nuclei

Sum over all (occupied by electrons) orbitals i gets the total electronic kinetic energy and attraction to nuclei

Hartee-Fock energy expression

$$\hat{H}_e = \sum_i \hat{h}(i) + \sum_{i < j} \hat{v}(i, j) + \hat{V}_{nn}$$

Electronic Hamiltonian

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

one-electron operator

$$\hat{v}(i, j) = \frac{1}{r_{ij}}$$

two-electron operator

$$\text{HF energy: } E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle = \sum_i^{N_{elec}} h_i + \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (J_{ij} - K_{ij})$$

Each pair of electrons (in orbitals i and j) has a *Coulomb integral*:

$$J_{ij} = \langle ij | ij \rangle = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1) \chi_j(x_2)$$

Probability electron 1 in orbital i is located at x_1

Probability electron 2 in orbital j is located at x_2

Coulomb repulsion between electron at x_1 and electron at x_2

This integral represents the Coulomb repulsion between electron 1 in orbital i and electron 2 in orbital j

Hartee-Fock energy expression

$$\hat{H}_e = \sum_i \hat{h}(i) + \sum_{i < j} \hat{v}(i, j) + \hat{V}_{nn}$$

Electronic Hamiltonian

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

one-electron operator

$$\hat{v}(i, j) = \frac{1}{r_{ij}}$$

two-electron operator

$$\text{HF energy: } E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle = \sum_i^{N_{elec}} h_i + \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (J_{ij} - K_{ij})$$

Each pair of electrons (in orbitals i and j) also has an *exchange integral*:

$$K_{ij} = \langle ij | ji \rangle = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_j(x_1) \chi_i(x_2)$$

This is like the Coulomb integral except two of the orbital indices have been exchanged:

$$J_{ij} = \langle ij | ij \rangle = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1) \chi_j(x_2)$$

No classical analogy... Physical meaning: an electron repels another electron of the same spin (so called Fermi hole). This integral is a consequence of Slater determinant (antisymmetrized) wavefunction