

For closed shell of n electrons

$$E_{HF} = 2 \sum_{i=1}^{n/2} h_{ii} + \sum_{i=1}^{n/2} J_{ii} + \sum_{i>j}^{n/2-1} \sum_{j=1}^{n/2} (4J_{ij} - 2K_{ij}) + V_{NN}$$

A more compact form is:

$$E_{HF} = 2 \sum_{i=1}^{n/2} h_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN}$$

Which works because $K_{ii} = J_{ii}$ so
there is only 1 J_{ii} for each i

Applying the Variation Principle

A minimum E is sought by varying the occupied MO's, until E is a minimum. By use of the calculus of variations, and the method of Lagrange undetermined multipliers, **the condition of minimum E requires that:**

$$\hat{F} \varphi_i(1) = 2 \sum_{i=1}^{n/2} \varepsilon_{ij} \varphi_j(1)$$

Where \mathbf{F} is the Fock Operator, given by: $\hat{F}(1) = \hat{h}(1) + \sum_j (2\hat{J}_j(1) - \hat{K}_j(1))$

Note: \mathbf{F} is a **one-electron operator!**

How does it get to be 1-electron when H has $1/r_{12}$???

Because, $\mathbf{J}_j(1)$ is repulsion an electron with $(\varphi_j)^2$, the electron charge cloud of the j^{th} MO. **Not interaction with another electron directly — just the average position.**

It is like interacting with a nucleus, except it is a smeared out electron charge

the condition of minimum E requires only that: $\hat{F} \varphi_i^{(1)} = 2 \sum_{i=1}^{n/2} \varepsilon_{ij} \varphi_j^{(1)}$

Because Any unitary transformation of the set of canonical MOs will yield the same electron density, and therefore the same energy and other properties.

One case of this is most often seen: $\hat{F} \varphi_i^{(1)} = \varepsilon_i \varphi_i^{(1)}$

obtained by diagonalizing the matrix: $\langle \varphi_i | \hat{F} | \varphi_j \rangle$

These eigenfunctions of the Fock Operator are called the **Canonical Molecular Orbitals**,

The Fock Operator:

The Fock Operator F is an effective Hamiltonian, like the one in Huckel theory, but much more versatile and accurate.

*Therefore, the **Fock Operator is physically quite transparent and easy to grasp.***

$$\hat{F}(1) = \hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j)$$

\hat{h} says that each electron (always called electron 1) has KE and attraction for all the nuclei (the one-electron part, sometime called H^{core}).

$\hat{J}_j(\mathbf{1})$ is repulsion of electron 1 with $(\varphi_j)^2$, the electron charge cloud of the j^{th} MO. Not interaction with another electron directly — **just the average position**

same is true for the K_j

$-\hat{K}_j$ reduces this repulsion between the electron in the the j^{th} MO having the same m_s as electron 1.

To see what the J operator (\hat{J}) is, we first write the expression for the J_{ij} integral:

$$J_{ij} = \int \int \varphi_i^*(1) \varphi_j^*(2) \frac{1}{r_{12}} \varphi_i(1) \varphi_j(2) d\tau_1 d\tau_2$$

We may reorder so that all the integration over electron 2 is in the center, revealing the J operator.

$$J_{ij} = \int \varphi_i^*(1) \left[\int \varphi_j^*(2) \frac{1}{r_{12}} \varphi_j(2) d\tau_2 \right] \varphi_i(1) d\tau_1$$

$$\text{where } \left[\int \varphi_j^*(2) \frac{1}{r_{12}} \varphi_j(2) d\tau_2 \right] = \hat{J}_j(1)$$

$$J_{ij} = \int \varphi_i^*(1) \hat{J}_j(1) \varphi_i(1) d\tau_1$$

Because J_{ij} is just a classical repulsion of two clouds, J_{op} can be thought of as very similar to e^2/r_{12} except that the charge is not a point, it is a cloud shaped like the square of the j^{th} molecular orbital. It is just a function of electron 1 because we integrated over electron 2.

The exchange operator requires special description:

$$K_{ij} = \int \phi_i^*(1) \int \phi_j^*(2) \phi_i(2) \frac{1}{r_{12}} d\tau_2 \phi_j(1) d\tau_1$$

or in Dirac notation:

$$K_{ij} = \langle \phi_i(1) | \langle \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2) \rangle | \phi_j(1) \rangle$$

but we want: $K_{ij} = \langle \phi_i(1) | \hat{K}_j | \phi_i(1) \rangle$

\hat{K}_j evidently must turn $\phi_i(1)$ into $\phi_j(1)$ and multiply by

$\langle \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2) \rangle$, but it does not know what ϕ_i

it will be operating on;

In all text books I have seen, this operator is just **stated** to have have the following effect:

$$\hat{K}_j |\phi_i(1)\rangle = \langle \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2)\rangle |\phi_j(1)\rangle$$

In words:

turn $|\phi_i(1)\rangle$ into $|\phi_j(1)\rangle$

and multiply by the number: $\langle \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2)\rangle$

This is just the overlap integral, which would be zero, except it is weighted by $1/r_{12}$ in the integral.

An explicit operator that will accomplish this is :

$$\hat{K}_j = \langle \varphi_j^{(2)} | \frac{1}{r_{12}} \left\{ \sum_{\mathbf{m}} | \varphi_{\mathbf{m}}^{(2)} \rangle | \varphi_j^{(1)} \rangle \langle \varphi_{\mathbf{m}}^{(1)} | \right\}$$

then

$$\begin{aligned} K_{ij} &= \langle \varphi_i^{(1)} | \left[\langle \varphi_j^{(2)} | \frac{1}{r_{12}} \left\{ \sum_{\mathbf{m}} | \varphi_{\mathbf{m}}^{(2)} \rangle | \varphi_j^{(1)} \rangle \langle \varphi_{\mathbf{m}}^{(1)} | \right\} \right] | \varphi_i^{(1)} \rangle \\ &= \langle \varphi_i^{(1)} | \hat{K}_j | \varphi_i^{(1)} \rangle \end{aligned}$$

No matter what value of i , K_j gives 0, unless $m=i$; then we get:

$$\hat{K}_j | \varphi_i^{(1)} \rangle = \langle \varphi_j^{(2)} | \frac{1}{r_{12}} \langle \varphi_i^{(2)} | \varphi_j^{(1)} \rangle | \varphi_i^{(1)} \rangle$$

Transition density operator

$|\varphi_i\rangle\langle\varphi_j|$ operating on φ_j :

$$|\varphi_i\rangle\langle\varphi_j|\varphi_i\rangle = 0$$

$|\varphi_i\rangle\langle\varphi_j|$ operating on φ_j

$$|\varphi_i\rangle\langle\varphi_j|\varphi_j\rangle = |\varphi_i\rangle$$

i.e., turned $|\varphi_j\rangle$ into $|\varphi_i\rangle$

a Raising Operator is just a sum of transition operators

Transition Density == $\phi_i^{(1)}\phi_j^{*(1)}$ i.e. a product of two different functions

Transition Density operator = $|\phi_i^{(1)}\rangle\langle\phi_j^{(1)}|$

changes $|\phi_j^{(1)}\rangle$ into $|\phi_i^{(1)}\rangle$

Raising operator

$$a = \sum_{\mathbf{m}} |\phi_{\mathbf{m}+1}^{(1)}\rangle\langle\phi_{\mathbf{m}}^{(1)}|$$

$$a |\phi_n^{(1)}\rangle = |\phi_{n+1}^{(1)}\rangle$$

$$\sum_{\mathbf{m}} |\phi_{\mathbf{m}+1}^{(1)}\rangle\langle\phi_{\mathbf{m}}^{(1)}| |\phi_n^{(1)}\rangle$$

$$= 0 \text{ unless } m = n, \text{ which gives } |\phi_{n+1}^{(1)}\rangle$$

Lowering operator

$$a^\dagger = \sum_{\mathbf{m}} |\phi_{\mathbf{m}-1}^{(1)}\rangle\langle\phi_{\mathbf{m}}^{(1)}|$$

$$a^\dagger |\phi_n^{(1)}\rangle = |\phi_{n-1}^{(1)}\rangle$$

$$\sum_{\mathbf{m}} |\phi_{\mathbf{m}-1}^{(1)}\rangle\langle\phi_{\mathbf{m}}^{(1)}| |\phi_n^{(1)}\rangle$$

$$= 0 \text{ unless } m = n, \text{ which gives } |\phi_{n-1}^{(1)}\rangle$$

Raising operator operating on $|\phi_n^{(1)}\rangle$ gives 0 unless $m=n$

$$a = \sum_{\mathbf{m}} |\phi_{\mathbf{m}+1}^{(1)}\rangle \langle \phi_{\mathbf{m}}^{(1)}|$$

$$a |\phi_n^{(1)}\rangle = |\phi_{n+1}^{(1)}\rangle$$

$$\sum_{\mathbf{m}} |\phi_{\mathbf{m}+1}^{(1)}\rangle \langle \phi_{\mathbf{m}}^{(1)}| |\phi_n^{(1)}\rangle$$

$$= 0 \text{ unless } m = n, \text{ which gives } |\phi_{n+1}^{(1)}\rangle$$

Lowering operator

$$a^\dagger = \sum_{\mathbf{m}} |\phi_{\mathbf{m}-1}^{(1)}\rangle \langle \phi_{\mathbf{m}}^{(1)}|$$

$$a^\dagger |\phi_n^{(1)}\rangle = |\phi_{n-1}^{(1)}\rangle$$

$$\sum_{\mathbf{m}} |\phi_{\mathbf{m}-1}^{(1)}\rangle \langle \phi_{\mathbf{m}}^{(1)}| |\phi_n^{(1)}\rangle$$

$$= 0 \text{ unless } m = n, \text{ which gives } |\phi_{n-1}^{(1)}\rangle$$

What does $|i\rangle\langle j| + |j\rangle\langle k| + |k\rangle\langle i|$ do ?

i, j, k are Cartesian unit vectors in x, y, z space

Orbital Energy

If $F\varphi_i = \varepsilon_i\varphi_i$ for each MO that is occupied, the energy of the Slater determinant is minimized, and

ε_i is called the “ i^{th} MO energy” = $\langle \varphi_i | F | \varphi_i \rangle$.

Where, $\langle \varphi_i | F | \varphi_i \rangle = h_{ii} + \sum_j (2J_{ij} - K_{ij})$

$\varepsilon_i = h_{ii} + J_{ii} + \text{sum of } 2J_{ij} - K_{ij} \text{ for all } j \text{ MOs for } j \text{ not equal to } i$

Physical Interpretation of “MO Energy”

Pretend you are an electron: what you have and see is your energy.
(you are in MO i)

ϵ_i is your:

Kinetic energy

+ your attraction coulombic attraction to all the nuclei,

+ the repulsion energy of your cloud of negative charge with
each of the other clouds j

- the repulsion energy of the “charges” given by the product of your
orbital (i) times those orbitals j with the same m_s that you have.

$\epsilon_i = h_{ii} + J_{ii} + \text{sum of } 2J_{ij} - K_{ij}$ for all j MOs for j not equal to i

$\epsilon_i = h_{ii} + J_{ii} + \text{sum of } 2J_{ij} - K_{ij}$ for all j MOs for j not equal to i

Is the Sum of MO Energies the Total HF Energy?

The Sum of MO Energies is NOT the Total HF Energy

The sum of MO energies is

$$\sum_{i=1}^{n/2} 2\epsilon_i = \sum_{i=1}^{n/2} 2h_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (4J_{ij} - 2K_{ij})$$

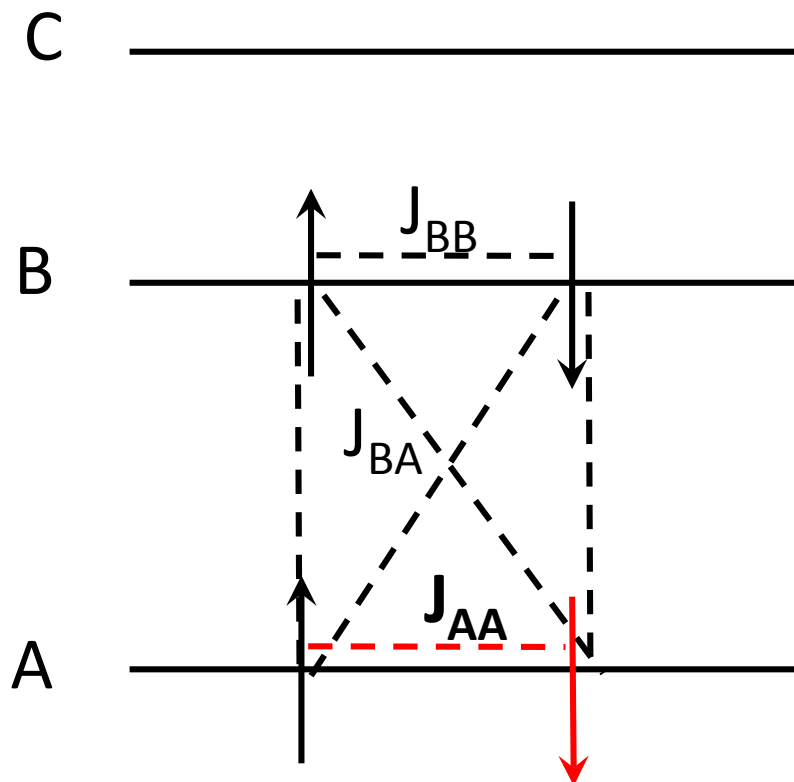
$$\text{but, } E_{HF} = \sum_{i=1}^{n/2} 2h_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

The sum of MO energies counts the electron repulsion TWICE.

$$\sum_{i=1}^{n/2} 2\varepsilon_i = \sum_{i=1}^{n/2} 2h_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (4J_{ij} - 2K_{ij})$$

$$\text{So, } E_{HF} = \sum_{i=1}^{n/2} 2\varepsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

Which is the sum of MO energies minus the total electron repulsion



Koopman's Theorem:

The i^{th} “MO Energy” = minus the ionization potential for removing an electron from the i^{th} MO

Remove one of the electrons in MO A

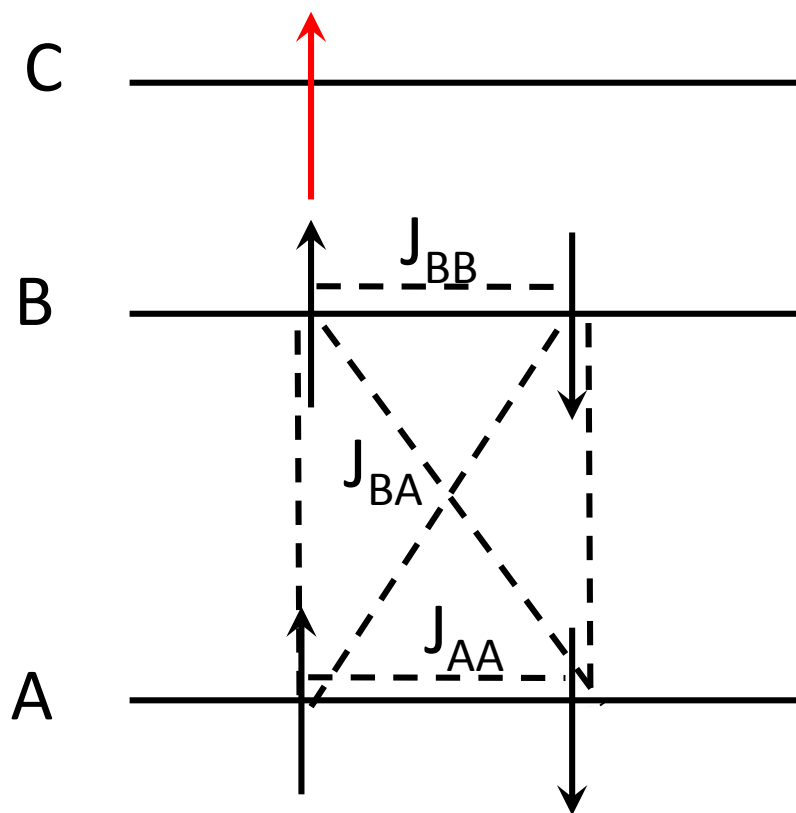
$$E_{\text{neutral}} = 2h_{AA} + 2h_{BB} + J_{AA} + J_{BB} + 4J_{BA} - 2K_{BA}$$

$$E_{\text{cation}} = h_{AA} + 2h_{BB} + J_{BB} + 2J_{BA} - K_{BA}$$

$$E_{\text{difference}} = h_{AA} + J_{AA} + 2J_{BA} - K_{BA} = \epsilon_A$$

= The ionization energy

If no relaxation due to changed electron density



Virtual (i.e., unoccupied orbitals are different!

Add an electron to MO C

The i^{th} "MO Energy" is for an electron that "sees" ALL of the occupied MO electrons

$$E_{\text{neutral}} = 2h_{AA} + 2h_{BB} + J_{AA} + J_{BB} + 4J_{BA} - 2K_{BA}$$

$$E_{\text{anion}} = 2h_{AA} + 2h_{BB} + J_{AA} + J_{BB} + 4J_{BA} - 2K_{BA} + h_{CC} + 2J_{CA} - K_{CA} + 2J_{CB} - K_{CB}$$

$$E_{\text{difference}} = h_{CC} + 2J_{CA} - K_{CA} + 2J_{CB} - K_{CB} = \epsilon_C$$

= minus the Electron Affinity

If no relaxation due to changed electron density