



2 – electron operators give

$$J_{AA} + J_{BB} + J_{CC} + 4J_{BA} + 4J_{AC} + 4J_{BC} - 2K_{BA} - 2K_{CA} - 2K_{BC}$$

Electron repulsion is reduced between electron with same m_s as seen for He(1s,2s)

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

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**,

but the previous equation shows that **they are in no way unique!**

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

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 is repulsion of electron 1 with $(\varphi_j)^2$, the electron charge cloud of the j^{th} MO.

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

But when electron 1 is in MO j , $2J(1)-K(1)$ operating on $\varphi(1)$ gives just $J_j(1)$, because $K_{jj} = J_{jj}$ (No self repulsion)

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 the following effect:

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

In words:

turn $| \varphi_i (1) \rangle$ into $| \varphi_j (1) \rangle$

and multiply by the number $\langle \varphi_j (2) | \frac{1}{r_{12}} \varphi_i (2) \rangle$

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, when m=i we get:

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