# <u>Koopman's Theorem and the Roothan Equations</u>

The HF equatios are

$F_i\varphi_i = \varepsilon_i\varphi_i \ , \ i = 1\ldots n$

$F_i = T_i + J_i - K_i$

$J_i =$Coulomb operator in the average field of j≠i electrons

$K_i =$Exchange operator in the average field of j≠i electrons

$\varepsilon_i$ are the <u>orbital energies.</u>

They are a good approximation to the magnitude of the <u>ionization</u> energy for an electron in the orbital *i*.

**"Proof"**

Clearly $\langle\varphi_i|F|\varphi_i\rangle = \varepsilon_i$, where

$$\varepsilon_i = \langle\varphi_i|h|\varphi_i\rangle + \sum_{occupied}\langle\varphi_i|T_{ij} - K_{ij}|\varphi_i\rangle$$

For electron ionization ("detachment")

I.P. = $E^N$-$E^{N-1}$ – take electron from k$^{th}$ orbital

$$= \langle\varphi_1\varphi_2\cdots\varphi_k\varphi_{k+1}\cdots|H_N|\varphi_1\varphi_2\cdots\varphi_k\varphi_{k+1}\cdots\rangle$$
$$-\langle\varphi_1\varphi_2\cdots\varphi_{k+1}\cdots|H_{N-1}|\varphi_1\varphi_2\cdots\varphi_{k+1}\cdots\rangle$$

$$= \langle\varphi_k|h|\varphi_k\rangle + \sum_j\left(J_{kj} - K_{kj}\right) = \varepsilon_k \quad \text{q.e.d.}$$

## HF Roothan equations

Return to the Hartree-Fock z electron 1s2s

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left(1s(1)2s + 1s(2)2s(1)\right)\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

$$\left[T_1 - \frac{Ze^2}{r_1} + \left\langle 2s(2)\left|\frac{e^2}{r_{12}}\right|2s(2)\right\rangle - \left\langle 2s(2)\left|\frac{e^2}{r_{12}}\right|1s(2)\right\rangle - \varepsilon_1\right]\varphi_{1s}(r_1) = 0 \qquad (1)$$

$$\left[T_1 - \frac{Ze^2}{r_2} + \left\langle 2s(1)\left|\frac{e^2}{r_{12}}\right|2s(1)\right\rangle - \left\langle 2s(1)\left|\frac{e^2}{r_{12}}\right|1s(1)\right\rangle - \varepsilon_1\right]\varphi_{2s}(r_2) = 0 \qquad (2)$$

Write
$$\varphi_{1s} = \sum_L C_L^{1s} X_L$$
$$\varphi_{2s} = \sum_L C_L^{2s} X_L$$

where $\{X_L\}$ is a complete set of functions. In atomic case these functions are orthonormal. Substitute into eqs. (1) and (2) respectively, and proceed as usual to get the linear equations which lead to diagonalization of a Hamiltonian matrix. Start with a zero order "guess" for $\varphi_{1s}$ and $\varphi_{2s}$ as usual, by choosing one coefficient C to be one and the others zero to evaluate the coulomb and exchange operators. Then diagonalize and get a new set of Cs. Use these to evaluate the coulomb and exchange operators, and diagonalize again. Continue until the process converges and the orbital energies converge.