ORBITAL ENERGIES

MINIMIZATION OF ENERGY FUNCTIONAL $\Rightarrow$ H-F EQUATIONS

$$\hat{F}\varphi_p = \varepsilon_p \varphi_p \qquad p = 1, \ldots N$$

WHEN THE OCCUPIED SPIN ORBITALS ARE KNOWN, FOCK OPERATOR IS WELL-DEFINED HERMITIAN OPERATOR WHICH HAS INFINITE NUMBER OF EIGENFUNCTIONS

$$\hat{F}\varphi_j = \varepsilon_j \varphi_j \qquad j = 1, \ldots \infty$$

N SOLUTIONS WITH THE LOWEST ENERGY = SPIN ORBITALS OCCUPIED IN Φ : $a, b, c, \ldots$

THE REMAINING INFINITE NUMBER = VIRTUAL OR UN-OCCUPIED SPIN ORBITALS : $r, s, t, \ldots$

WHAT IS THE PHYSICAL INTERPRETATION OF ε_a AND ε_r?

$$\int \varphi_i^* \Big| \; F\varphi_j = \varepsilon_j \varphi_j$$

$$\langle \varphi_i | F | \varphi_j \rangle = \varepsilon_j \langle \varphi_i | \varphi_j \rangle = \varepsilon_j \delta_{ij}$$

MATRIX REPRESENTATION OF FOCK OPERATOR

$$\varepsilon_i = \langle \varphi_i | F | \varphi_i \rangle = \langle \varphi_i | \hat{h} + \sum_b (\hat{J}_b - \hat{K}_b) | \varphi_i \rangle =$$

$$= \langle \varphi_i | h | \varphi_i \rangle + \sum_b \{ \langle \varphi_i | J_b | \varphi_i \rangle - \langle \varphi_i | K_b | \varphi_i \rangle \} =$$

$$= \langle i | h | i \rangle + \sum_b \{ \langle ib | ib \rangle - \langle ib | bi \rangle \}$$

$$\equiv \langle i | h | i \rangle + \sum_b \langle ib \| ib \rangle$$

$$\equiv \langle i | h | i \rangle + \sum_b \langle ib | ib \rangle_A$$

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b=1}^{N} \langle ab \| ab \rangle$$

$$\varepsilon_r = \langle r | h | r \rangle + \sum_{b=1}^{N} \langle rb \| rb \rangle$$

ATTRACTION TO NUCLEI + KINETIC EN.

COULOMB - EXCHANGE INTERACTION WITH N-1 ELECTRONS

$$\varepsilon_a = \langle a|h|a\rangle + \sum_{b=1}^{N}\{\langle ab|ab\rangle - \langle ab|ba\rangle\}$$

FOR $b \neq a$ SINCE $\langle aa||aa\rangle = 0$

$$\varepsilon_r = \langle r|h|r\rangle + \sum_{b=1}^{N}\{\langle rb|rb\rangle - \langle rb|br\rangle\}$$

(r - VIRTUAL)

NUCLEAR ATTRACTION + KINETIC ENERGY

COULOMB - EXCHANGE INTERACTION WITH ALL N ELECTRONS OF THE H-F GROUND STATE Φ

$$\Phi = |\varphi_1, \varphi_2, \ldots \varphi_N| \equiv |\Phi^N\rangle$$

$$|\Phi^{N-1}\rangle = a_c\,|\Phi^N\rangle$$

ELECTRON REMOVED FROM THE OCCUPIED SPIN ORBITAL φ_c

IONIZATION POTENTIAL

$$IP = {}^{N-1}E_c - {}^{N}E$$

$$\langle \Phi^N|H|\Phi^N\rangle$$

$$\langle \Phi^{N-1}|H|\Phi^{N-1}\rangle$$

ASSUMPTION: ALL SPIN ORBITALS OF Φ^{N-1} ARE THE SAME AS IN Φ^N $\equiv$ FROZEN ORBITAL APPROXIMATION

(IN SPITE THE FACT THAT THEY ARE NOT OPTIMUM SPIN ORBITALS FOR N±1 ELECTRON SYSTEM)

$$E = \sum_{i}^{occ}\langle i|h|i\rangle + \frac{1}{2}\sum_{i}^{occ}\sum_{j}^{occ}\langle ij||ij\rangle \Rightarrow$$

$${}^{N}E = \sum_{a}\langle a|h|a\rangle + \frac{1}{2}\sum_{a}\sum_{b}\langle ab||ab\rangle$$

$${}^{N-1}E_c = \sum_{a\neq c}\langle a|h|a\rangle + \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\langle ab||ab\rangle$$

$$IP = {}^{N-1}E_c - {}^{N}E =$$

$$\sum_{a\neq c}\langle a|h|a\rangle + \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\langle ab||ab\rangle -$$

$$-\sum_{a}\langle a|h|a\rangle - \frac{1}{2}\sum_{a}\sum_{b}\langle ab||ab\rangle =$$

$$= \langle c|h|c\rangle - \frac{1}{2}\sum_{a\,(b\equiv c)}\langle ab||ab\rangle - \frac{1}{2}\sum_{b\,(a\equiv c)}\langle ab||ab\rangle$$

$$= \langle c|h|c\rangle - \frac{1}{2}\sum_{a}\langle ac||ac\rangle - \frac{1}{2}\sum_{b}\langle cb||cb\rangle$$

$$= \langle c|h|c\rangle - \sum_{b}\langle cb||cb\rangle$$

BUT

$$\varepsilon_a = \langle a|h|a\rangle + \sum_{b}\langle ab||ab\rangle$$

$$\boxed{IP = {}^{N-1}E_c - {}^{N}E = -\varepsilon_c}$$

APPROXIMATE VALUES

IONIZATION POTENTIAL FOR REMOVING AN ELECTRON FROM φ_c = OCCUPIED SPIN ORBITAL ENERGY

OCCUPIED SPIN ORBITAL ENERGIES IN THE SINGLE DETERMINANT APPROXIMATION REPRESENT THE ENERGY (WITH OPPOSITE SIGN) REQUIRED TO REMOVE AN ELECTRON FROM THAT SPIN ORBITAL.

ELECTRON AFFINITY FOR ADDING AN ELECTRON TO THE VIRTUAL SPIN ORBITAL φ_r = NEGATIVE ORBITAL ENERGY OF THAT SPIN ORBITAL

$$\boxed{EA = {}^{N}E - {}^{N+1}E^{r} = -\varepsilon_r}$$

APPROXIMATE VALUES

KOOPMANS' THEOREM

HOMEWORK: SHOW THAT

$${}^{N}E - {}^{N+1}E^{r} = -\langle r|h|r\rangle - \sum_{b}\langle rb||rb\rangle$$

ANALYTICAL APPROXIMATION OF H-F MODEL

(ALGEBRAIZATION!)

WHEN IT IS IMPOSSIBLE TO SEPARATE COORDINATES (RADIAL AND ANGULAR) => H-F EQUATIONS ARE COUPLED INTEGRO-DIFFERENTIAL EQUATIONS WITH PARTIAL DERIVATIVES!!!

HARTREE-FOCK-ROOTHAAN METHOD (1951)

FOR ATOMS AND MOLECULES

$$\psi_p(i) = \sum_{l=1}^{M} C_{pl}\, X_l(i)$$

ANALYTICAL APPROXIMATION

BASIS FUNCTIONS

LINEAR COMBINATION OF KNOWN FUNCTIONS (SIMILAR TO THE RITZ METHOD)

H-F EQUATIONS

$$\hat{F}(i)\psi_p(i) = \varepsilon_p \psi_p(i) \qquad p = 1, \dots N/2$$

ALGEBRAIC EQUATIONS

$$\sum_k C_{pk}(F_{kl} - \varepsilon_p S_{kl}) = 0 \qquad l = 1, \dots M$$

(NUMBER OF BASIS FUNCTIONS)

UNKNOWN COEFFICIENTS

MATRIX ELEMENTS OF FOCK OPERATOR BETWEEN BASIS FUNCTIONS

$$F_{kl} = h_{kl} + \sum_m^M \sum_n^M \sum_p^{N/2} C^*_{pm} C_{pn} \left[2\langle km|ln\rangle - \langle km|nl\rangle \right]$$

H-F-R EQUATIONS ARE DIFFERENT FROM RITZ METHOD; WHY?

H-F $\xrightarrow{\text{ALGEBRAIZATION}}$ H-F-R

$\mathcal{E}[\Phi] \equiv \mathcal{E}[\Psi]$ — UNKNOWN FUNCTIONS

$\mathcal{E}[\Phi] \equiv \mathcal{E}[\Psi] \equiv \mathcal{E}[c_i]$ — UNKNOWN COEFFICIENTS

ITERATIVE METHODS

PRACTICAL REALIZATION

1° SCF = ITERATIONS

$\{c_1^0, c_2^0, \ldots c_M^0\} \Rightarrow \left\{ \begin{matrix} h_{kl} \\ \langle km|ln\rangle \end{matrix} \right. \Rightarrow$ EQUATIONS (ALGEBRAIC)

$\Downarrow$

$\{c_1^1, c_2^1, \ldots c_M^1\}$

$\vdots$

$\{c_1^{opt}\ c_2^{opt} \ldots c_M^{opt}\}\ E^{opt}$

SELF-CONSISTENT FIELD

2° PROBLEM WITH EVALUATION OF $\langle km|ln\rangle$ (FOR EACH ITERATION!)

$$\psi_p = \sum_{l=1}^{M} c_{pl}\chi_l$$

LONGER COMBINATION => BETTER RESULTS

$\downarrow\Downarrow$

MORE DIFFICULT TO EVALUATE THE INTEGRALS

RAPIDLY CONVERGENT EXPANSION =>

ATOMS

χ_l: HYDROGENIC ORBITALS
SLATER ORBITALS

ALWAYS ONE-CENTER INTEGRALS

MOLECULES

χ_l: ATOMIC ORBITAL OF ATOMS OF PARTICULAR MOLECULE

MO LCAO

ALWAYS MULTI-CENTER INTEGRALS
HOW TO EVALUATE THEM?
HOW TO STORE THEM?

IF THE BASIS SET IS PROPERLY CHOSEN AND ITS SIZE IS LARGE ENOUGH IT IS POSSIBLE TO OBTAIN RESULTS CLOSE TO HARTREE-FOCK SOLUTIONS!