HARTREE-FOCK EQUATIONS

- BASED ON THE VARIATIONAL PRINCIPLE
- GIVES THE BEST FUNCTION DEFINED WITHIN THE SINGLE ELECTRON APPROXIMATION:

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & & \vdots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix} = \frac{1}{\sqrt{N!}} |\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)|$$

φ_i – UNKNOWN SPIN-ORBITALS

ASSUMPTION: EACH ORBITAL IS USED TWICE TO BUILD SPINORBITAL

$$\varphi_1 = \psi_1\alpha,\ \varphi_2 = \psi_1\beta,\ \varphi_3 = \psi_2\alpha,\ \dots\quad \varphi_N = \psi_{N/2}\beta$$

$N/2 = m$ UNKNOWN FUNCTIONS (RADIAL PARTS)

VARIATIONAL PRINCIPLE $\Rightarrow$ EQUATIONS FOR $\psi_1, \psi_2, \dots \psi_m$

$$\left.\begin{aligned} H &= \sum_{i=1}^{N} H(i) + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} \\ H(i) &= -\frac{\hbar^2}{2\mu}\Delta_i + U(i) \\ U(i) &= -\sum_{\alpha=1}^{A} \frac{Z_\alpha e^2}{r_{\alpha i}} \end{aligned}\right\} \quad \varepsilon[\Phi] \equiv \varepsilon[\psi_1, \dots \psi_n] = \frac{\langle\Phi|H|\Phi\rangle}{\underbrace{\langle\Phi|\Phi\rangle}_{=1}}$$

$$\varepsilon[\Phi] = \langle|\varphi_1(1)\dots\varphi_N(N)||H||\varphi_1(1)\dots\varphi_N(N)|\rangle \quad \left(\frac{1}{N!}\ N!\ \text{PERMUTATIONS}\right)$$

ONE PARTICLE PART:

$$\langle\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)|H(1)|\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)\rangle_{d\tau_1 d\tau_2,\dots d\tau_N}$$

$$= \langle\varphi_1(1)|H(1)|\varphi_1(1)\rangle = I_1'$$

$$\sum_{i=1}^{N} H(i) \Rightarrow \sum_{i=1}^{N} I_i' = 2\sum_{p=1}^{N/2} I_p$$

(IN TERMS OF ORBITALS, EACH ONE DOUBLY OCC.)

TWO PARTICLE PART:

$$\langle \varphi_1(1)\varphi_2(2)\dots\varphi_N(N)| \frac{e^2}{r_{12}} |\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)\rangle = \int d\tau_1 d\tau_2 \dots d\tau_N$$

$$J'_{12} = \langle \varphi_1(1)\varphi_2(2)| \frac{e^2}{r_{12}} |\varphi_1(1)\varphi_2(2)\rangle$$

$$-K'_{12} = -\langle \varphi_1(1)\varphi_2(2)| \frac{e^2}{r_{12}} |\varphi_1(2)\varphi_2(1)\rangle$$

$$\sum_{i<j}^{N} \frac{e^2}{r_{ij}} \Rightarrow \sum_{i<j}^{N} J'_{ij} - K'_{ij}$$

FOR DOUBLY OCCUPIED ORBITALS

1º J'_{ij} for $\psi_i = \psi_j$, THE SAME ORBITALS:

$$J_{pp} = \langle \psi_p^{\alpha}(i)\psi_p^{\beta}(j)| \frac{e^2}{r_{ij}} |\psi_p^{\alpha}(i)\psi_p^{\beta}(j)\rangle$$

$$\sum_{p=1}^{N/2} J_{pp}$$

2º DIFFERENT ORBITALS

$$\psi_p(1)\psi_q(2) \quad \{\alpha(1)\beta(2),\ \beta(1)\alpha(2),\ \alpha(1)\alpha(2),\ \beta(1)\beta(2)\}$$

$$J_{pq} = \langle \psi_p^{\alpha}(1)\psi_q^{\alpha}(2)| \frac{e^2}{r_{12}} |\psi_p^{\alpha}(1)\psi_q^{\alpha}(2)\rangle$$

$$4\sum_{p<q=1}^{N/2} J_{pq}$$

3º $$K'_{12} = \langle \varphi_1(1)\varphi_2(2)| \frac{e^2}{r_{12}} |\varphi_1(2)\varphi_2(1)\rangle$$

SPIN FUNCTIONS MUST BE THE SAME!

$$K_{pq} = \langle \psi_p(i)\psi_q(j)| \frac{e^2}{r_{ij}} |\psi_p(j)\psi_q(i)\rangle$$

$$\psi_p(1)\psi_q(2) \quad \{\alpha(1)\alpha(2),\ \beta(1)\beta(2)\}$$

$$-2\sum_{p<q=1}^{N/2} K_{pq}$$

$$\mathcal{E} = 2\sum_{p=1}^{N/2} I_p + \sum_{p=1}^{N/2} J_{pp} + \sum_{p<q}^{N/2} (4J_{pq} - 2K_{pq})$$

$$J_{pp} = K_{pp}$$

$$+\sum_p J_{pp} - \sum_p K_{pp}$$

$$\mathcal{E} = 2\sum_{p=1}^{N/2} I_p + \sum_{p=1}^{N/2} (2J_{pp} - K_{pp}) + 2\sum_{p<q=1}^{N/2} (2J_{pq} - K_{pq})$$

$$\sum_{ij} \ldots = \sum_{i=j} \ldots + \sum_{i \neq j} \ldots = \sum_{i=j} \ldots + 2\sum_{i<j} \ldots$$

$$\boxed{\mathcal{E} = 2\sum_{p=1}^{N/2} I_p + \sum_{p,q=1}^{N/2} (2J_{pq} - K_{pq})}$$

ONE PARTICLE PART

TWO-PARTICLE PART (COULOMB INTERACTION)

ALL INTEGRALS ARE DEFINED IN THE TERMS OF UNKNOWN ORBITAL FUNCTIONS

J_{pq} – COULOMB INTEGRALS

$$J_{pq} = \langle \psi_p(1)\psi_q(2) | \frac{e^2}{r_{12}} | \psi_p(1)\psi_q(2) \rangle \equiv$$

$$\int \frac{e|\psi_p(1)|^2 \, e|\psi_q(2)|^2}{r_{12}} d\tau_{12}$$

COULOMB ENERGY

COULOMB INTERACTION BETWEEN TWO „ELECTRON CLOUDS"

K_{pq} – EXCHANGE INTEGRALS

$$K_{pq} = \langle \psi_p(1)\psi_q(2) | \frac{e^2}{r_{12}} | \psi_q(1)\psi_p(2) \rangle \equiv$$

$$\int \frac{e(\psi_p^*(1)\psi_q(1)) \, e(\psi_q^*(2)\psi_p(2))}{r_{12}} d\tau_{12}$$

RESULT FROM THE ANTISYMMETRY OF N. ELECTRON FUNCTION

CORRECTION TO THE ENERGY FOR ELECTRONS WITH THE SAME PROJECTIONS OF SPIN:

EXCHANGE ENERGY

J_{pq} $\qquad\qquad$ $J_{pq} - K_{pq}$

$r_{12}(\uparrow\downarrow) < r_{12}(\uparrow\uparrow)$: PAULI PRINCIPLE

$E_{rep}(\uparrow\downarrow) > E_{rep}(\uparrow\uparrow)$

$\Downarrow$

HUND'S RULE

$$\mathcal{E} = 2\sum_{p=1}^{N/2} I_p + \sum_{p,q=1}^{N/2}(2J_{pq} - K_{pq})$$ ENERGY FUNCTIONAL

FOR WHICH KIND OF Ψ THE ENERGY $\mathcal{E}$ IS THE BEST ?

FOR WHICH KIND OF Ψ THE ENERGY $\mathcal{E}$ IS MINIMAL ?

ARE ANY CONDITIONS REQUIRED FOR Ψ OPTIMAL ?

FUNCTIONAL VARIATION

$\mathcal{E}[\Phi]$ – FUNCTIONAL OF Φ : ITS VALUE DEPENDS ON THE FORM OF Φ

VARIATION OF Φ BY AN ARBITRARY SMALL AMOUNT

$$\Phi \to \Phi + \delta\Phi$$

RESULTS IN

$$\mathcal{E}[\Phi+\delta\Phi] = \langle \Phi+\delta\Phi | H | \Phi+\delta\Phi \rangle =$$

$$E[\Phi] + \{\langle \delta\Phi | H | \Phi \rangle + \langle \Phi | H | \delta\Phi \rangle\} + \ldots =$$

$$E[\Phi] + \delta E + \ldots$$

FIRST VARIATION IN E

ALL TERMS LINEAR IN δE

FIRST ORDER IN THE VARIATION δE

FOR WHICH Φ $E[\Phi] = \min$? :

FOR WHICH Φ THE FIRST VARIATION IN $E[\Phi]$ => IS 0

$$\boxed{\delta E = 0}$$

THIS MEANS THAT E IS STATIONARY WITH RESPECT TO ANY VARIATION IN Φ (STATIONARY POINT = MINIMUM)

MINIMIZATION OF THE ENERGY $\mathcal{E}[\psi_1, \dots \psi_n]$ WITH RESPECT TO THE SPIN ORBITALS, SUBJECT TO THE CONSTRAINT THAT THEY REMAIN ORTHONORMAL

$$S_{pq} = \langle \psi_p | \psi_q \rangle = \delta_{pq}$$

$$\delta E' = 0 \quad : \quad E' = \mathcal{E} - 2\sum_{p,q}^{N/2} S_{pq}\, \varepsilon_{pq}$$

LAGRANGE MULTIPLIERS

$\psi \rightarrow \psi + \delta\psi$ ARBITRARY INFINITESIMAL AMOUNT

THE FIRST VARIATION IN E':

$$\delta E' = \delta\mathcal{E} - 2\sum_{p,q} pq\, \varepsilon_{pq} = 0$$

$$\delta E' = 2\sum_{p=1}^{N/2} \delta I_p + \sum_{p,q}^{N/2} \left(2\delta J_{pq} - \delta K_{pq} - 2\varepsilon_{pq}\, \delta S_{pq}\right) = 0$$

VIRTUAL CHANGES CAUSED BY $\delta\psi$

NEW OPERATORS

$$\hat{J}_p(i)\psi_q(i) = \left[\int \psi_p^*(j) \frac{e^2}{r_{ij}} \psi_p(j)\, d\tau_j\right] \psi_q(i)$$

COULOMB OPERATOR

MULTIPLIFICATION OF ψ_q BY A NUMBER

$$\hat{K}_p(i)\psi_q(i) = \left[\int \psi_p^*(j) \frac{e^2}{r_{ij}} \psi_q(j)\, d\tau_j\right] \psi_p(i)$$

EXCHANGE OPERATOR

$\Downarrow$

INTEGRALS

$$J_{pq} = \int \psi_p^*(i)\, \hat{J}_q(i)\, \psi_p(i)\, d\tau_i = \int \psi_q^*(j)\, \hat{J}_p(j)\, \psi_q(j)\, d\tau_j$$

$$K_{pq} = \int \psi_p^*(i)\, \hat{K}_q(i)\, \psi_p(i)\, d\tau_i = \int \psi_q^*(j)\, \hat{K}_p(j)\, \psi_q(j)\, d\tau_j$$

HARTREE-FOCK EQUATIONS:

(COEFFICIENTS OF $\delta\psi$ HAVE TO VANISH)

$$F(i)\psi_p(i) = \sum_{q=1}^{N/2} \varepsilon_{pq}\, \psi_q(i) \qquad p=1,2,\dots N/2$$

$$\hat{F}(i) = \hat{H}(i) + \underbrace{\sum_{q=1}^{N/2} \left[2\hat{J}_q(i) - \hat{K}_q(i)\right]}$$

FOCK OPERATOR

ONE PARTICLE PART OF THE HAMILTONIAN

ALSO ONE PARTICLE OPERATOR !!!

AVERAGE POTENTIAL PRODUCED BY ALL N ELECTRONS EXCEPT ONE

$$H = \underbrace{-\frac{\hbar^2}{2\mu}\sum_i \Delta_i - \sum_i \frac{Ze^2}{r_i}}_{\sum_i H(i)} + \sum_{i<j} \frac{e^2}{r_{ij}}$$

COULOMB INTERACTION
TWO-PARTICLE OPERATOR

CENTRAL FIELD APPROXIMATION:

$$H = \sum_i \left[H(i) + U(i)\right] + \underbrace{\sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i U(i)}$$

ELECTRON CORRELATION

SMALL AS A PERTURBATION

EFFECTIVE OPERATOR

ELECTROSTATIC INTERACTION BETWEEN 1 ELECTRON AND THE REST N-1 SPREAD AROUND

$$U(i) = \sum_{q=1}^{N/2} \left[2\hat{J}_q(i) - \hat{K}_q(i)\right]$$

CENTRAL FIELD

$\Psi = RY$

$$\hat{J}_p(i)\psi_q(i) = \left[\int \psi_p^*(j) \frac{e^2}{r_{ij}} \psi_p(j)\, d\tau_j\right]\psi_q(i)$$

COULOMB OPERATOR

ONE INTEGRATION PERFORMED
AVERAGE OVER ALL N-1 ELECTRONS

$$\int \psi_q^*(i)\, d\tau_i$$

$$\int \psi_q^*(i)\hat{J}_p(i)\psi_q(i)\, d\tau_i = \iint \frac{e|\psi_p(j)|^2\, e|\psi_q(i)|^2}{r_{ij}}\, d\tau_i\, d\tau_j$$

COULOMB INTEGRAL

(CHEMICAL NOTATION) $(\overset{(i)(i)}{pp}|\overset{(j)(j)}{qq})$ OR $\langle \overset{(i)(j)}{pq}|\overset{(i)(j)}{pq}\rangle$ (PHYSICAL NOTATION)

SIMILAR BUT WITHOUT PHYSICAL INTERPRETATION

EXCHANGE OPERATOR AND EXCHANGE INTEGRAL

$$-\langle \overset{(i)(j)}{pq}|\overset{(i)(j)}{qp}\rangle$$

THE COULOMB INTERACTION

$$\frac{e^2}{r_{ij}} = e^2 \sum_k \underbrace{\frac{r_<^{\,k}}{r_>^{\,k+1}}}_{\text{RADIAL PART}} \left(C_i^{(k)} \cdot C_j^{(k)}\right)$$

SPHERICAL TENSORS

TWO-PARTICLE OPERATOR (SCALAR PRODUCT)

EXAMPLE OF MANY ELECTRON SYSTEM: $N=2$

$$\langle l^2 S M_S L M_L | (C_i^{(k)} \cdot C_j^{(k)} | l^2 S' M_S' L' M_L' \rangle =$$

(L-S COUPLING SCHEME)

PAULI EXCLUSION PRINCIPLE $\Rightarrow$ $S+L = \text{even}$

$$= \delta(SS')\delta(M_S M_S')\langle l\, l\, L M_L | (C_i^{(k)} \cdot C_j^{(k)}) | l\, l\, L' M_L \rangle =$$

IN GENERAL:

$$\langle \overset{l}{\gamma j_1} \overset{l}{j_2} \overset{L}{J} \overset{M_L}{M_J} | (T^{(k)} \cdot U^{(k)}) | \overset{l}{\gamma' j_1'} \overset{l}{j_2'} \overset{L'}{J'} \overset{M_L'}{M_J'} \rangle =$$

W-E Theorem: $\begin{pmatrix} J & 0 & J' \\ -M_J & 0 & M_J' \end{pmatrix}$

$$= (-1)^{j_1'+j_2+J} \underbrace{\delta(JJ')\delta(M_J M_J')}_{} \begin{Bmatrix} j_1' & j_2' & J \\ j_2 & j_1 & k \end{Bmatrix} \sum_{\gamma''} \langle \gamma j_1 \| T^{(k)} \| \gamma'' j_1' \rangle$$

$$\langle \gamma'' j_2 \| U^{(k)} \| \gamma' j_2' \rangle \qquad (3\text{-}36)$$

$$= \delta(SS')\delta(M_S M_S')(-1)^{2l+L}\delta(LL')\delta(M_L M_L') \begin{Bmatrix} l & l & L \\ l & l & k \end{Bmatrix} \times$$

$$\langle l \| C^{(k)} \| l \rangle \langle l \| C^{(k)} \| l \rangle$$

$$= \delta(SS')\delta(M_S M_S')\delta(LL')\delta(M_L M_L')(-1)^{L} \begin{Bmatrix} l & l & L \\ l & l & k \end{Bmatrix} \langle l \| C^{(k)} \| l \rangle^2$$

ANGULAR PART!

WHERE

$$\langle l \| C^{(k)} \| l \rangle = (-1)^l [l] \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}$$

$l+k+l = \text{even}$

FOR $l=3$ (f^2)

$$\delta(SS')\delta(M_S M_S')\delta(LL')\delta(M_L M_L')\,49(-1)^L \begin{Bmatrix} 3 & 3 & k \\ 3 & 3 & L \end{Bmatrix} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}^2$$

ALL OFF-DIAGONAL MATRIX ELEMENTS VANISH.

$$\langle f^2 S M_S L M_L | H_c | f^2 S M_S L M_L \rangle = \sum_k 49 F^{(k)} (-1)^L \begin{Bmatrix} 3 & 3 & k \\ 3 & 3 & L \end{Bmatrix} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}^2$$

THE SO-CALLED

SLATER INTEGRALS

$$F^{(k)} = e^2 \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} \left[R_{nf}(r_i) R_{nf}(r_j)\right]^2 dr_i\, dr_j$$

RADIAL INTEGRAL

„Δ" CONDITIONS FOR 6-j AND 3-j :

$$0 \leq k \leq 6 \quad \& \quad 6+k = \text{even} \Rightarrow k = \text{even}$$

SUMMATION OVER K IS LIMITED TO $k = 0, 2, 4, 6$

IN GENERAL

$$R^k(AB, CD) = \langle AB | g(r) | CD \rangle$$

$$F^{(k)}(AB) = R^k(AB, AB) = \langle AB | g(r) | AB \rangle \quad \text{COULOMB INT.}$$

$$G^{(k)}(AB) = R^k(AB, BA) = \langle AB | g(r) | BA \rangle \quad \text{EXCHANGE INT.}$$

WHEN THE RADIAL FUNCTIONS ARE UNKNOWN :

$F^{(k)}, G^{(k)}$: CONDON - SHORTLEY PARAMETERS

THE ENERGY IS EXPRESSED AS A FUNCTION OF C-S PARAMETERS (IT IS EASY TO EVALUATE THE ANGULAR PARTS).

FOR EXAMPLE: f^2

$$E(^1S) = F_0 + 60F_2 + 198F_4 + 1716F_6$$

$$E(^3P) = F_0 + 45F_2 + 33F_4 - 1287F_6$$

$$E(^1D) = F_0 + 19F_2 - 99F_4 + 715F_6$$

$$E(^3F) = F_0 - 10F_2 - 33F_4 - 286F_6$$

$\vdots$

WHERE NEW PARAMETERS ARE USED

CONDON-SHORTLEY PARAM.

$$F_2(np,np) = \frac{1}{25} F^{(2)}(np,np)$$

$$F_2(nd,nd) = 1/49\, F^{(2)}(nd,nd); \quad F_4(nd,nd) = 1/441\, F^{(4)}(nd,nd)$$

$$F_2(nf,nf) = 1/(15)^2\, F^{(2)}(nf,nf); \quad F_4(nf,nf) = 1/(33)^2\, F^{(4)}(nf,nf)$$

$$F_6(nf,nf) = 1/(85.8)^2\, F^{(6)}(nf,nf)$$

$$F_0 = F^{(0)}$$

RACAH PARAMETERS

$$\begin{cases} A = F_0(nd,nd) - 49 F_4(nd,nd) \\ B = F_2(nd,nd) - 5F_4(nd,nd) \\ C = 35 F_4(nd,nd) \end{cases}$$

$(F_0, F_2, F_4) \Rightarrow$ (A, B, C) FOR $l=d$

$$\begin{cases} E^0 = F_0(nf,nf) - 10F_2(nf,nf) - 35F_4(nf,nf) - 286 F_6(nf,nf) \\ E^1 = \frac{7}{9}[10F_2 + 33F_4 + 286F_6] \\ E^2 = \frac{1}{9}[F_2 - 3F_4 + 7F_6] \\ E^3 = \frac{1}{3}[5F_2 + 6F_4 - 91F_6] \end{cases}$$

$(F_0, F_2, F_4, F_6) \Rightarrow$ (E^0, E^1, E^2, E^3) FOR $l=f$

ab-initio CALCULATIONS: ALL INTEGRALS HAVE TO BE EVALUATED!

HYDROGENIC FUNCTIONS FOR $4f^2$ AND $5f^2$

$4f^2$:

$$\frac{F_4}{F_2} = \frac{41}{297} = 0.138$$

$$\frac{F_6}{F_2} = \frac{175}{11583} = 0.0151$$

$5f^2$:

$$\frac{F_4}{F_2} = \frac{23255}{163559} = 0.142$$

$$\frac{F_6}{F_2} = \frac{102725}{6378801} = 0.0161$$

4f, 5f - COMPLETELY DIFFERENT FUNCTIONS! STILL THE RELATIVE ENERGIES OF THE TERMS ARE EXPECTED TO BE SIMILAR

$$F(i)\psi_p(i) = \sum_{q=1}^{N/2} \varepsilon_{pq}\, \psi_q(i) \qquad p = 1, 2, \dots N/2$$

FOCK OPERATOR

THIS IS NOT CANONICAL (STANDARD) EIGENVALUE PROBLEM

$$\Phi : \quad |\varphi_1, \varphi_2, \dots \varphi_N| \Rightarrow |\psi_1, \psi_2, \dots \psi_{N/2}|$$

SLATER DET.

SPIN ORBITALS

ORBITALS (HAMILTONIAN IS INDEPENDENT OF SPIN)

CERTAIN DEGREE OF FLEXIBILITY

CHANGES OF FUNCTIONS WITHOUT CHANGING THE EXPECTATION VALUE $E = \langle \Phi | H | \Phi \rangle$

DEFINED WITH THE ACCURACY OF UNITARY TRANSFORMATION

$U^+ = U^{-1}$, $\det(U) = e^{i\varphi}$ (PHASE FACTOR)

$$\Phi' = \det(U)\,\Phi = e^{i\varphi}\Phi$$

FOCK OPERATOR IS NOT CHANGED UNDER UNITARY TRANSF. OF SPIN ORBITALS (IS INVARIANT)

LAGRANGE MULTIPLIERS ε_{pq}

$$\psi_r^* \backslash \quad F(i)\psi_p(i) = \sum_{q=1}^{N/2} \varepsilon_{pq}\, \psi_q(i)$$

$$\langle \psi_r | F | \psi_p \rangle = \sum_{q=1}^{N/2} \varepsilon_{pq} \underbrace{\langle \psi_r | \psi_q \rangle}_{\delta_{qr}}$$

$$\varepsilon_{pr} = \langle \psi_r | F | \psi_p \rangle$$

$[\varepsilon_{pr}]$ FOR ALL P AND r HERMITIAN MATRIX : $\varepsilon_{pq} = \varepsilon_{qp}^*$

ALWAYS IT IS POSSIBLE TO FIND UNITARY TRANSFORMATION U

$\varepsilon' = U^+ \varepsilon U$ THAT DIAGONALIZE ε

THE UNIQUE SET OF ORBITALS $\psi' = U\psi$ – CANONICAL ORBITALS

SPIN ORBITALS $\varphi' = U\varphi$ – CANONICAL SPIN ORB.

ARE THE SOLUTIONS OF

HARTREE-FOCK EQUATIONS

$$\boxed{F(i)\,\psi_p(i) = \varepsilon_p\,\psi_p(i)}$$

$i = 1, 2, \ldots N/2$

HARTREE-FOCK ORBITALS
CANONICAL ORBITALS

ORBITAL ENERGY
ENERGY OF AN ELECTRON THAT MOVES IN THE FIELD OF NUCLEI AND REMAINING ELECTRONS

HARTREE-FOCK EQUATIONS

IS IT AN EIGENVALUE PROBLEM?

$$F(i) = H(i) + \sum_{q=1}^{N/2}\left[2\hat{J}_q(i) - \mathcal{K}_q(i)\right]$$

SUMMATION OVER ALL ORBITALS

$$J_q(i)\,\psi_p(i) = \left[\int \psi_q^*(j)\,\frac{e^2}{r_{ij}}\,\psi_q(j)\,d\tau_j\right]\psi_p(i)$$

$$\mathcal{K}_q(i)\,\psi_p(i) = \left[\int \psi_q^*(j)\,\frac{e^2}{r_{ij}}\,\psi_p(j)\,d\tau_j\right]\psi_q(i)$$

(NON-LOCAL OPERATOR)

DEFINED BY THE SOLUTIONS OF H-F EQUATIONS!

SET OF COUPLED EQUATIONS

IS $\sum_p \varepsilon_p$ = TOTAL ENERGY?

$$F(i)\,\psi_p(i) = \varepsilon_p\,\psi_p(i)$$

$\int \psi_p$

$$\varepsilon_p = \langle \psi_p | F | \psi_p \rangle = I_p + \sum_{q=1}^{N/2}\left[2J_{pq} - \mathcal{K}_{pq}\right]$$

$$2\sum_{p=1}^{N/2}\varepsilon_p = 2\sum_{p=1}^{N/2} I_p + 2\sum_{p,q=1}^{N/2}\left[2J_{pq} - \mathcal{K}_{pq}\right]$$

BUT

$$E = 2\sum_{p=1}^{N/2} I_p + \sum_{p,q=1}^{N/2}\left[2J_{pq} - \mathcal{K}_{pq}\right]$$

$$E = 2\sum_{p=1}^{N/2}\varepsilon_p - \sum_{p,q=1}^{N/2}\left[2J_{pq} - \mathcal{K}_{pq}\right]$$

ONLY FOR THE PARTICLE-INDEPENDENT MODEL, WHEN COULOMB INTERACTION IS NEGLECTED

$$E = \sum_p^N \varepsilon_p$$

TOTAL ENERGY = HARTREE-FOCK ENERGY

HOW TO SOLVE H-F EQUATIONS?

PROBLEMS

FROM THE DERIVATION OF THE HARTREE-FOCK EQUATIONS IT IS CLEARILY SEEN THAT IN ORDER TO EVALUATE TOTAL ENERGY OF MANY ELECTRON SYSTEM, THE FOLLOWING CONTRIBUTIONS HAVE TO BE TAKEN INTO ACCOUNT:

1. I_p FOR EACH ELECTRON,
2. J_{pq} FOR EACH PAIR OF ELECTRONS WITH ANT-PARALLEL PROJECTIONS OF SPIN,
3. $J_{pq} - K_{pq}$ FOR EACH PAIR OF ELECTRONS WITH PARALLEL PROJECTIONS OF SPIN

$$E_{TOTAL} = \sum_p I_p + \sum_{\substack{\text{pairs} \\ \uparrow\downarrow}} J_{pq} + \sum_{\substack{\text{pairs} \\ \uparrow\uparrow}} (J_{pq} - K_{pq})$$

PROBLEM: ASSUMING THAT EXCHANGE INTEGRAL K_{12} IN THE CASE OF TWO ELECTRON SYSTEM IS POSITIVE, SHOW THAT THE TRIPLET STATE IS OF LOWER ENERGY THAN THE SINGLET STATE.

PROBLEM: EVALUATE THE TOTAL ENERGY OF Be ATOM WITH THE GROUND CONFIGURATION OF THE FORM

$$1s^2\, 2s^2,$$

AND EXPRESS IT IN THE TERMS OF APPROPRIATE HARTREE-FOCK ORBITAL ENERGIES.

$P(r)$ ARE THE SOLUTIONS OF THE EQUATION

$$\left(\frac{d^2}{dr^2} + \frac{2Z}{r} - 2V(r) - \frac{l(l+1)}{r^2} - E\right)P(r) = 0$$

WITH BOUNDARY CONDITIONS

$$P(0) = P(\infty) = 0$$

STURM-LIOUVILLE BOUNDARY VALUE PROBLEM

⇓ TOTAL FUNCTION : SIMPLE PRODUCT OF SPIN-ORBITALS

H-F REQUIRES: ⊛ SLATER DETERMINANT BUILT OF

$$\phi_{nlm_lm_s}(r\vartheta\varphi\sigma) = \frac{1}{r}P_{nl\ldots}(r)\,Y_{lm_l}(\vartheta\varphi)\,\chi_{m_s}(\sigma)$$

⊛ SPIN-ORBITALS FORM ORTHONORMAL SET

⊛ Φ_{TOTAL} MUST BE EIGENFUNCTION OF L^2, L_z, S^2, S_z

(USUALLY LINEAR COMBINATION OF SLATER DETERMINANTS

COUPLING OF ANGULAR MOMENTA ≡ COEFFICIENTS

3-j, 6-j, 9-j AND TOOLS OF ATOMIC SPECTROSCOPY)

RADIAL EQUATION FOR $P_{nl}(r)$

$$\left(\frac{d^2}{dr^2} + f(r) - \varepsilon_{nl}\right)P_{nl}(r) = g(r)$$

BOUNDARY CONDITIONS: $P_{nl}(0) = 0$, $P_{nl}(r) \xrightarrow[r\to\infty]{} 0$

⇓ COUPLED SYSTEMS OF EQUATIONS

IT IS IMPORTANT TO CONTROL CONVERGENCE TO THE DESIRED SOLUTION BY, FOR EXAMPLE, NODE COUNTING.

THE H-F EQUATIONS ARE THE SAME FOR

$1s2p\ ^3P$ AND $1s3p\ ^3P$

THE NUMBER OF CHANGES OF SIGN IN THE SOLUTION $P_{nl}(r)$ SHOULD BE $n-l-1$

HOW TO SOLVE H-F EQUATIONS?

1. NUMERICAL APPROACH

SCF : SELF CONSISTENT FIELD

IN ORDER TO SOLVE H-F EQUATIONS, THE FOCK OPERATOR HAS TO BE BUILT THEREFORE:

1. $\psi_1^{(0)}, \psi_2^{(0)}, \dots \psi_n^{(0)}$ – INITIAL ESTIMATES, FOR EXAMPLE HYDROGENIC WAVEFUNCTIONS
2. FOCK OPERATOR BUILT OF $\{\psi_i^{(0)}\} \Rightarrow F^{(0)}$
3. $F^{(0)}(i)\psi_q(i) = \varepsilon_q \psi_q(i) \Rightarrow$

   $\varepsilon_q^{(1)}, \psi_1^{(1)}, \dots \psi_n^{(1)}$

   ACCURACY Δ, δ
4. $F^{(1)}$
5. $F^{(1)}(i)\psi_q(i) = \varepsilon_q \psi_q(i) \Rightarrow$

   $\varepsilon_q^{(2)}, \psi_1^{(2)}, \dots \psi_n^{(2)}$

   SATISFACTORY Δ AND δ ?

   NO | **YES**

ITERATIONS

SOLUTIONS:

$\varepsilon_q^{(2)}, \psi_1^{(2)}, \dots \psi_n^{(2)}$

$q = 1, \dots n$ $\quad E_{HF}$

SELF CONSISTENT FIELD

$$\left[-\frac{1}{2}\Delta_i - \frac{Z}{r_i} + V(r_i)\right]\phi(i) = \varepsilon_i \phi(i)$$

WAVE EQUATION FOR A PARTICLE IN A CENTRAL FIELD

LIKE IN THE CASE OF HYDROGENIC EQUATION $\Rightarrow$ SEPARATION OF COORDINATES

$$\phi(r\vartheta\varphi\sigma) = \underbrace{\frac{1}{r}P(r)}_{R(r)} Y_{lm_l} \chi_{m_s}(\sigma)$$

Table: Hartree-Fock calculation for $1s2p\,3P/$

```
>HF
 Enter ATOM,TERM,Z
 Examples: O,3P,8. or Oxygen,AV,8.
>He,3P,2.
 List the CLOSED shells in the fields indicated (blank line if none)
 ... ... ... ... ... ... ... ... etc.
>
 Enter electrons outside CLOSED shells (blank line if none)
 Example: 2s(1)2p(3)
>1s(1)2p(1)
 There are   2 orbitals as follows:
   1s  2p
 Orbitals to be varied: ALL/NONE/=i (last i)/comma delimited list/H
>all
 Default electron parameters ? (Y/N/H)
>y
 Default values for remaining parameters? (Y/N/H)
>y
        WEAK ORTHOGONALIZATION DURING THE SCF CYCLE=   T
        SCF CONVERGENCE TOLERANCE (FUNCTIONS)        =1.00D-08
        NUMBER OF POINTS IN THE MAXIMUM RANGE        = 220

        ITERATION NUMBER  1
        ---------------
        SCF CONVERGENCE CRITERIA (SCFTOL*SQRT(Z*NWF)) =   2.0D-08
           EL          ED              AZ             NORM          DPM
           1s       3.5097389       5.6405312      1.0018151     4.18D-03
           2p       0.2599702       0.3599178      1.0946569     3.61D-02
           2p       0.2628234       0.3932430      0.9662618     9.78D-03
           2p       0.2629724       0.3956921      0.9973008     5.58D-04
LEAST SELF-CONSISTENT FUNCTION IS 1s: WEIGHTED MAXIMUM DPM=4.18D-03
        ITERATION NUMBER  2
        ---------------
        SCF CONVERGENCE CRITERIA (SCFTOL*SQRT(Z*NWF))=  4.0D-08
           EL          ED              AZ             NORM          DPM
           1s       3.4678763       5.6314990      0.9972158     1.85D-03
           2p       0.2631160       0.3966045      0.9984069     3.98D-04
           1s       3.4675011       5.6313578      0.9998921     4.08D-05
           2p       0.2631197       0.3966438      0.9999510     1.04D-05
LEAST SELF-CONSISTENT FUNCTION IS 1s: WEIGHTED MAXIMUM DPM=4.08D-05
```

AV = AVERAGE ENERGY OF CONFIGURATION

EXCITED CONFIGURATION

ACCURACY

NUMERICAL FUNCTIONS

Table 3.1 (continued)

```
        ITERATION NUMBER  3
        ----------------
        SCF CONVERGENCE CRITERIA (SCFTOL*SQRT(Z*NWF))=  8.0D-08
           EL          ED              AZ            NORM        DPM
           1s       3.4674906       5.6313545    0.9999972    1.02D-06
           2p       0.2631197       0.3966453    0.9999986    2.71D-07
           1s       3.4674904       5.6313545    0.9999999    2.74D-08
           2p       0.2631197       0.3966453    1.0000000    8.06D-09
LEAST SELF-CONSISTENT FUNCTION IS 1s: WEIGHTED MAXIMUM DPM=2.74D-08

        ITERATION NUMBER  4
        ----------------
        SCF CONVERGENCE CRITERIA (SCFTOL*SQRT(Z*NWF)) =   1.6D-07
           EL          ED              AZ            NORM        DPM
           1s       3.4674904       5.6313545    1.0000000    7.68D-10
           2p       0.2631197       0.3966453    1.0000000    2.49D-10

 Additional parameters ? (Y/N/H)
>n
```

HOMEWORK: B4.17

Hartree-Fock Applet

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Results

EL	ED	AZ	NORM	DPM
1s	81.0368261	70.2900869	1.0000000	4.13E-08
2s	5.6713646	17.1594347	1.0000000	2.22E-08
2p	3.1162667	38.8679801	1.0000000	1.06E-07
3s	.3639701	2.5732153	1.0000000	3.31E-08
3p	.2189625	3.9024853	1.0000000	2.92E-08

<1s|2s>=2.2E-09
<1s|3s>=7.6E-10
<2s|3s>=1.6E-08
<2p|3p>=1.7E-08

TOTAL ENERGY (a.u.)
....

Non-Relativistic	-161.82263732	Kinetic	161.82263904
Relativistic Shift	-.19886798	Potential	-323.64527636
Relativistic	-162.02150531	Ratio	-1.999999989

The End.

Plots

AtomTermZ:

Na,Av,11.

List Closed Shells:

1s 2s 2p

Electrons outside CLOSED shell:

3s(.5)3p(.5)

Orbitals to be varied

all

all

Default Electron Parameters?

Yes

Default Remaining Parameters?

Yes

RUN

Run it!

http://atoms.vuse.vanderbilt.edu/