

Self-consistent field

$$\left[-\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|r-R_n|} + \sum_{e=1}^N \int dx' |\Psi_e(x')|^2 \frac{1}{|r-r'|} \right] \Psi_k = E^k \Psi_k$$

KE

e-N

Hartree Potential

(includes self-interaction!)

Hartree (1927)

no exchange

no correlation

Born-Oppenheimer - electrons in field of fixed nuclei: Hartree-Fock N electrons
K nuclei

$$H = \underbrace{\sum_{i=1}^N -\frac{1}{2} \nabla^2}_{KE} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}}_{e-e} - \underbrace{\sum_{i=1}^N \sum_{a=1}^K \frac{z_a}{|r_i - R_a|}}_{e-N}$$

This problem cannot be solved exactly for macroscopic systems
 $N, K \sim 10^{23}$

Hartree-Fock, use simplest basis set that has the correct symmetry: 1 Slater determinant

$$\Psi(r_1, r_2, r_3, \dots, r_N) = \frac{1}{\sqrt{N!}} \sum_P \epsilon_P P \psi_1(r_1) \dots \psi_N(r_N)$$

P permutation

ϵ_P +1 even permutation -1 odd permutation

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \dots & \psi_N(r_1) \\ \psi_1(r_2) & & & \\ \vdots & & & \\ \psi_1(r_N) & \dots & \dots & \psi_N(r_N) \end{vmatrix}$$

Actually have to deal with $\chi_i(r_i, s_i)$ in many cases, where s_i is spin vector

Example: The helium atom

$$\Psi(r_1, s_1; r_2, s_2) = \phi(r_1) \phi(r_2) \frac{1}{\sqrt{2}} [\alpha(s_1) \beta(s_2) - \alpha(s_1) \beta(s_2)]$$

α spin up
 β spin-down

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + \frac{1}{|r_1 + r_2|} - \frac{2}{r_1} - \frac{2}{r_2}$$

$$H \Psi = E \Psi$$

$$\left[-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + \frac{1}{|r_1 + r_2|} - \frac{2}{r_1} - \frac{2}{r_2} \right] \phi(r_1) \phi(r_2) = E \phi(r_1) \phi(r_2)$$

Multiply by $\phi^*(r_2)$ & integrate over r_2

$$-\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + \int d^3r |\phi(r_2)|^2 \frac{1}{|r_1 - r_2|} \phi(r_1) = E' \phi(r_1)$$

Self-consistency.

Uncorrelated: $P(r_1, r_2) = P(r_1) P(r_2)$

He (contd)

$$\phi(r) = \sum C_p \chi_p(r)$$

$$\left[-\frac{1}{2} \nabla^2 - \frac{2}{r_1} + \sum_{r,s} C_r C_s \int d^3 r_2 \frac{\chi_r(r_2) \chi_s(r_2)}{|r_1 - r_2|} \right] \sum C_g \chi_g(r_1) = E' \sum C_g \chi_g(r_1)$$

Multiply by $\chi_p(r_1)$ and integrate over r_1 :

$$\sum_g \left(h_{pg} + \sum_{r,s} C_r C_s Q_{prgs} \right) C_g = E' \sum_g S_{pg} C_g$$

$p = 1, m$

$$h_{pg} = \left\langle \chi_p \left| -\frac{1}{2} \nabla^2 - \frac{2}{r} \right| \chi_g \right\rangle$$

$$Q_{prgs} = \int d^3 r_1 d^3 r_2 \frac{\chi_p(r_1) \chi_r(r_2) \chi_g(r_1) \chi_s(r_2)}{|r_1 - r_2|}$$

$$S_{pg} = \left\langle \chi_p \mid \chi_g \right\rangle$$

$$F_{pg} = h_{pg} + \sum_{r,s} Q_{prgs} C_r C_s$$

$$\sum C_p S_{pg} C_g = 1$$

$$F C = E' S C$$

Solve self-consistently: fix C_r, C_s solve generalized eigenproblem
 plug C 's back in + repeat....

$$E = 2 \sum_{p,q} C_p C_q h_{pq} + \sum_{p,q,r,s} Q_{pqrs} C_p C_q C_r C_s$$

Hartree Fock (contd)

Two particle probability density:

$$\rho(x_1, x_2) = \int dx_3 \dots dx_N \Psi$$

$$= \frac{1}{N(N-1)} \sum_{k \neq l} [|\Psi_k(x_1)|^2 |\Psi_l(x_2)|^2$$

$$- \Psi_k^*(x_1) \Psi_k(x_2) \Psi_l^*(x_2) \Psi_l(x_1)]$$

consider 2 electrons have opposite spins, $\alpha + \beta$:

$$= \underbrace{\phi_k^*(r_1) \alpha_1}_{\text{orthogonal}} \underbrace{\phi_k(r_2) \beta_2 \phi_l^*(r_2) \beta_2}_{\text{orthogonal}} \underbrace{\phi_l(r_1) \alpha_1}_{\text{orthogonal}} = 0$$

2 electrons same spin, $= 0$ if $r_1 = r_2$

Exchange: keeps like spins apart

(Exchange hole)

HF: no correlations between unlike spins (why He easy)

Hartree-Fock

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i,j} g(i,j)$$

$$g(i,j) = \frac{1}{|r_i - r_j|}$$

$$h(i) = -\frac{1}{2} \nabla_i^2 - \sum_n \frac{z_n}{|r_i - R_n|}$$

see 4.5.2

$$\langle \Psi | \sum h(i) | \Psi \rangle = \sum_k \langle \psi_k | h | \psi_k \rangle$$

$$\langle \Psi | \sum_{i,j} g(i,j) | \Psi \rangle =$$

$$\sum_{k,l} \langle \psi_k^{\alpha_1} \psi_l^{\alpha_2} | g | \psi_k^{\alpha_1} \psi_l^{\alpha_2} \rangle - \sum_{k,l} \langle \psi_k^{\alpha_1} \psi_l^{\alpha_2} | g | \psi_l^{\alpha_2} \psi_k^{\alpha_1} \rangle$$

$$\text{So } E = \sum_k \langle \psi_k | h | \psi_k \rangle + \frac{1}{2} \sum_{k,l} \left[\langle \psi_k^{\alpha_1} \psi_l^{\alpha_2} | g | \psi_l^{\alpha_2} \psi_k^{\alpha_1} \rangle - \langle \psi_k^{\alpha_1} \psi_l^{\alpha_2} | g | \psi_k^{\alpha_1} \psi_l^{\alpha_2} \rangle \right] + \sum_{n_1, n_2} \frac{z_{n_1} z_{n_2}}{|R_{n_1} - R_{n_2}|}$$

Hartree - Fock

$$J_{\kappa}(x) \psi(x) = \left[\int dx' \psi_{\kappa}^*(x') \frac{1}{r_{12}} \psi_{\kappa}(x') \right] \psi(x)$$

$$K_{\kappa}(x) \psi(x) = \int dx' \psi_{\kappa}^*(x') \frac{1}{r_{12}} \psi(x') \psi_{\kappa}(x)$$

Coulomb operator

$$J = \sum_{\kappa} J_{\kappa}$$

Exchange Operator

$$K = \sum_{\kappa} K_{\kappa}$$

[Confusion! Physics: U: Coulomb J: Exchange!]

Now:

$$E = \sum_{\kappa} \langle \psi_{\kappa} | h + \frac{1}{2}(J - K) | \psi_{\kappa} \rangle$$

Now solve $\min E$ subject to $\langle \psi_{\kappa} | \psi_{\epsilon} \rangle = \delta_{\kappa\epsilon}$

Lagrange multipliers $\Lambda_{\kappa\epsilon}$

$$\delta E - \sum_{\kappa, \epsilon} \Lambda_{\kappa\epsilon} [\langle \delta \psi_{\kappa} | \psi_{\epsilon} \rangle - \langle \psi_{\kappa} | \delta \psi_{\epsilon} \rangle]$$

$$= 0 \quad F = h + J - K$$

$$F \psi_{\kappa} = \epsilon_{\kappa} \psi_{\kappa}$$

Hartree-Fock -- Basis

So far we have not specified a basis for Ψ_e

$$\Psi_k(x) = \sum_{p=1}^M C_{pk} \chi_p(x)$$

Then:

$$FC_k = \epsilon_k SC_k$$

$$F_{pg} = h_{pg} + \sum_{\kappa} \sum_{rs} C_{r\kappa}^* C_{s\kappa} (2 \langle pr | g | gs \rangle - \langle pr | g | sg \rangle)$$

$$h_{pg} = \langle p | h | g \rangle = \int d^3r \chi_p^*(r) \left[\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|R_n - r|} \right] \chi_g(r)$$

$$\langle pr | g | gs \rangle = \int d^3r_1 d^3r_2 \chi_p^*(r_1) \chi_r^*(r_2) \frac{1}{|r_1 - r_2|} \chi_g(r_1) \chi_s(r_2)$$

Density matrix:

$$P_{pg} = 2 \sum_{\kappa} C_{p\kappa} C_{g\kappa}^*$$

Ⓞ labels state
↳ basis function

$$\rho = 2 \sum_{\kappa} |\phi_{\kappa}\rangle \langle \phi_{\kappa}|$$

Then:

$$F_{pg} = h_{pg} + \frac{1}{2} \sum_{rs} P_{rs} [2 \langle pr | g | gs \rangle - \langle pr | g | sg \rangle]$$

$$E = \sum_{pg} P_{pg} h_{pg} + \frac{1}{2} \sum_{pqr} P_{pg} P_{rs} [\langle pr | g | qs \rangle - \frac{1}{2} \langle pr | s | qs \rangle]$$

RHF vs UHF

So far Restricted Hartree Fock (spatial orbitals are independent of spin) No spin polarization $\epsilon^{\uparrow} = \epsilon^{\downarrow}$

Unrestricted Hartree Fock (UHF) (spatial orbitals are dependent on spin) Spin polarization $\epsilon^{\uparrow} \neq \epsilon^{\downarrow}$

Pople-Nesbet equations:

$$F^+ C^+ = \epsilon^+ S C^+$$

$$F^- C^- = \epsilon^- S C^-$$

$$F_{pq}^{\pm} = h_{pq} + \sum_{k^{\pm}} \sum_{rs} C_{rkt}^{\pm} C_{skt}^{\pm} [\langle pr | g | qs \rangle$$

$$- \langle pr | g | sj \rangle] + \sum_{k^{\mp}} \sum_{rs} C_{rkt}^{\mp} C_{skt}^{\mp} \langle pr | g | qs \rangle$$

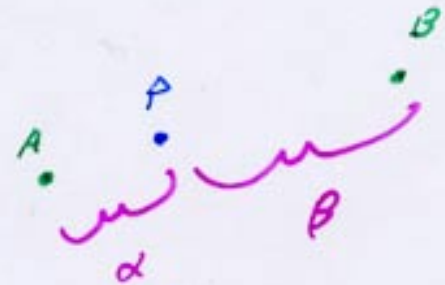
Gaussian basis

Multiplication of Gaussians:

$$P_M(x, y, z) e^{-\alpha(r-R_A)^2} Q_N(x, y, z) e^{-\beta(r-R_B)^2} \\ = R_{M+N}(x, y, z) e^{-(\alpha+\beta)(r-R_p)^2}$$

$$R_p = \frac{\alpha R_A + \beta R_B}{\alpha + \beta}$$

P_M polynomial in x, y, z degree M
 Q_N " " " " degree N
 R_{M+N} " " " " degree $M+N$



s states |

p states x
y
z

d states.

x^2
 y^2
 z^2
 xy
 yz
 xz

$x^2 + y^2 + z^2 = s\text{-state!}$

$x^2 - y^2$
 $3z^2 - r^2$

E_g

xy
 yz
 xz

T_{2g}

Contraction of Basis Functions.

We have:

$$\Psi_K = \sum_P C_{PK} \chi_P$$

Contraction:

$$\chi_P = \sum_t A_{tP} Y_t$$

Example:

χ Slater orbital $A e^{-\beta r}$

Y Gaussian $B e^{-\alpha r^2}$

Minimal basis set: 1 χ for each state

Polarization functions: add more ang. mom. l s, 3d

Breathing functions: add more radial terms 0 2p

Notation:

STO-NG N Gaussians per Slater orb

STO-31 3 Gaussians \Rightarrow 1 Slater

+ 1 extra Gaussian (radial, breathing)

STO-3* + 1 extra Gaussian (additional l)