

## • Hartree Method

### Hamiltonian for a two-electron system

The Schrodinger equation for a system of two or more electrons cannot be solved exactly. The Schrodinger equation for a He like system can be expressed as;

$$\left[ \underbrace{-\frac{h^2}{8\pi^2m}(\nabla_1^2 + \nabla_2^2)}_{\mathbf{A}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2}}_{\mathbf{B}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\mathbf{C}} \right] \Psi = E \Psi$$

**A** : Kinetic energies of electron 1 and electron 2

**B** : Potential energy of attraction of electron 1 and electron 2 to the nucleus

**C** : Potential energy of repulsion between electron 1 and electron 2

The Schrodinger equation can be expressed more succinctly in atomic units

*Length:* 1 bohr =  $a_0 = 4\pi\epsilon_0(h/2\pi)^2/me^2 = \epsilon_0 h^2/\pi m e^2 = 0.05292 \text{ nm} = 0.5292 \text{ \AA}$

*Energy:* 1 hartree =  $E_h$  (or h) =  $e^2/4\pi\epsilon_0 a_0$ ; 1 h/particle = 2625.5 kJ mol<sup>-1</sup>

$$\left( -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi = E \Psi$$

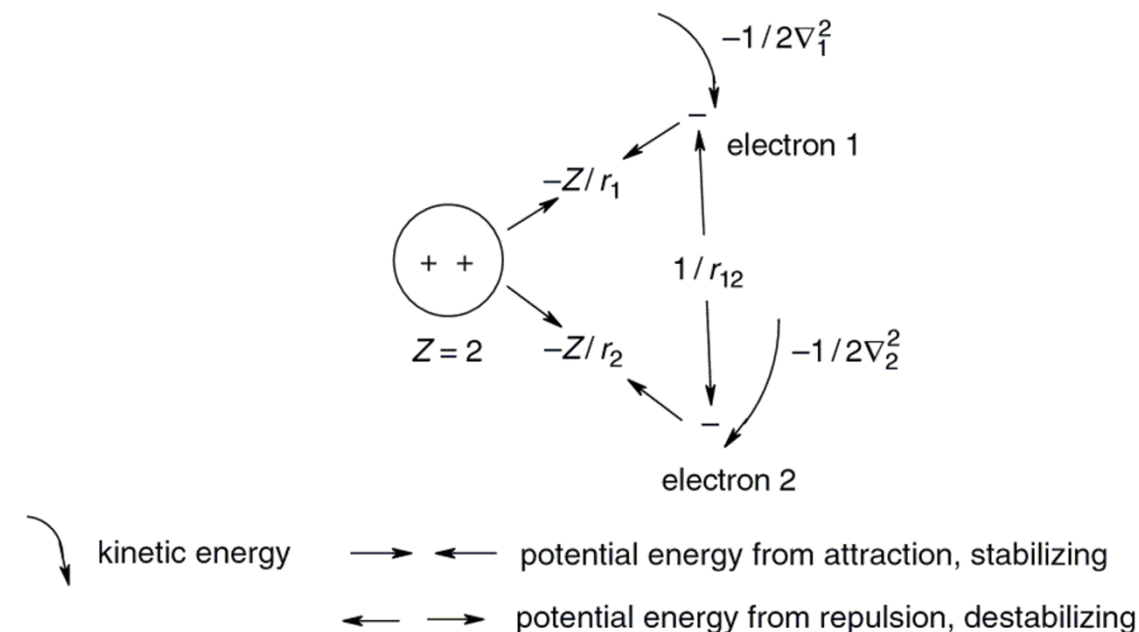
The Hamiltonian is given by;

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

The general Hamiltonian for a  $2n$  electron system is given by;

$$\hat{H} = \sum_{i=1}^{2n} -\frac{1}{2}\nabla_i^2 - \sum_{\mu,i} \frac{Z_{\mu}}{r_{\mu i}} + \sum_{i,j} \frac{1}{r_{ij}}$$

This Hamiltonian excludes effects from relativity and spin-orbit coupling (magnetic interactions)



- The Born-Oppenheimer approximation permits the separation of the nuclei kinetic terms. This Hamiltonian of focus here is thus the **electronic** Hamiltonian.

- The  $1/r_{12}$  term makes this system impossible to solve analytically.

### Hartree Wavefunction

- The Hartree method of expressing the total wavefunction as a product of one-electron wavefunctions can be used.

$$\Psi_0 = \psi_0(1)\psi_0(2)\psi_0(3) \dots \psi_0(n)$$

$\psi_0(1)$  is a function (atomic orbital) of the coordinates of electron 1

$\Psi_0$  is the initial guess for the system wavefunction

- To optimize  $\Psi_0$ , each electron is subjected to the average electrostatic field produced by all the other electrons.  $\psi_0(2), \psi_0(3), \dots, \psi_0(n)$ .

$\psi_0(1)$  is optimized to  $\psi_1(1)$ . Electron two is then treated in the same way to optimize  $\psi_0(2)$  to  $\psi_1(2)$  and so on for the other electrons until an improved molecular wavefunction is obtained;

$$\Psi_1 = \psi_1(1)\psi_1(2)\psi_1(3) \dots \psi_1(n)$$

After the second cycle, an even more improved wavefunction is obtained.

$$\Psi_2 = \psi_2(1)\psi_2(2)\psi_2(3) \dots \psi_2(n)$$

The process of MO optimization through subsection to the updated electrostatic field produced by all other electrons is the Hartree method of wavefunction optimization or also called the **Self-Consistent Field** (SCF) method

Antisymmetry and Spin

- The Hartree wavefunction does not include an important fundamental property of electrons: *Spin*.
- Pauli Exclusion: no two electron can have the same set of quantum numbers.
- Furthermore, electrons are what are called *indistinguishable particles*
  - exchange of the coordinates of any two electrons must leave their respective wavefunctions either unchanged or of opposite sign.

$$\Psi_a = f(x_1, y_1, z_1; x_2, y_2, z_2)$$

$$\Psi_b = f(x_2, y_2, z_2; x_1, y_1, z_1)$$

Symmetric       $\Psi_b = \Psi_a$

Antisymmetric       $\Psi_b = -\Psi_a$

$$|\Psi_a|^2 = |\Psi_b|^2$$

- Hartree Product is symmetric, not antisymmetric
- Electrons are actually antisymmetric with respect to exchange

Consider Helium

$$\psi_a = 1s(x_1, y_1, z_1)1s(x_2, y_2, z_2)$$

exchange       $\psi_b = 1s(x_2, y_2, z_2)1s(x_1, y_1, z_1)$

then               $\psi_a = \psi_b$

$$\psi_a = 1s(x_1, y_1, z_1)1s(x_2, y_2, z_2) - 1s(x_2, y_2, z_2)1s(x_1, y_1, z_1)$$

$$\psi_a = -\psi_b$$

$$\psi_b = 1s(x_2, y_2, z_2)1s(x_1, y_1, z_1) - 1s(x_1, y_1, z_1)1s(x_2, y_2, z_2)$$

$\psi_a$  is a proper antisymmetric wavefunction and can be represented by a determinant

Spin orbitals

- Wavefunctions can be decomposed into spatial orbital and a spin orbital part

$$\psi(\text{spin } \alpha) = \psi(\text{spatial})\alpha = \psi(x, y, z)\alpha$$

$$\psi(\text{spin } \beta) = \psi(\text{spatial})\beta = \psi(x, y, z)\beta$$

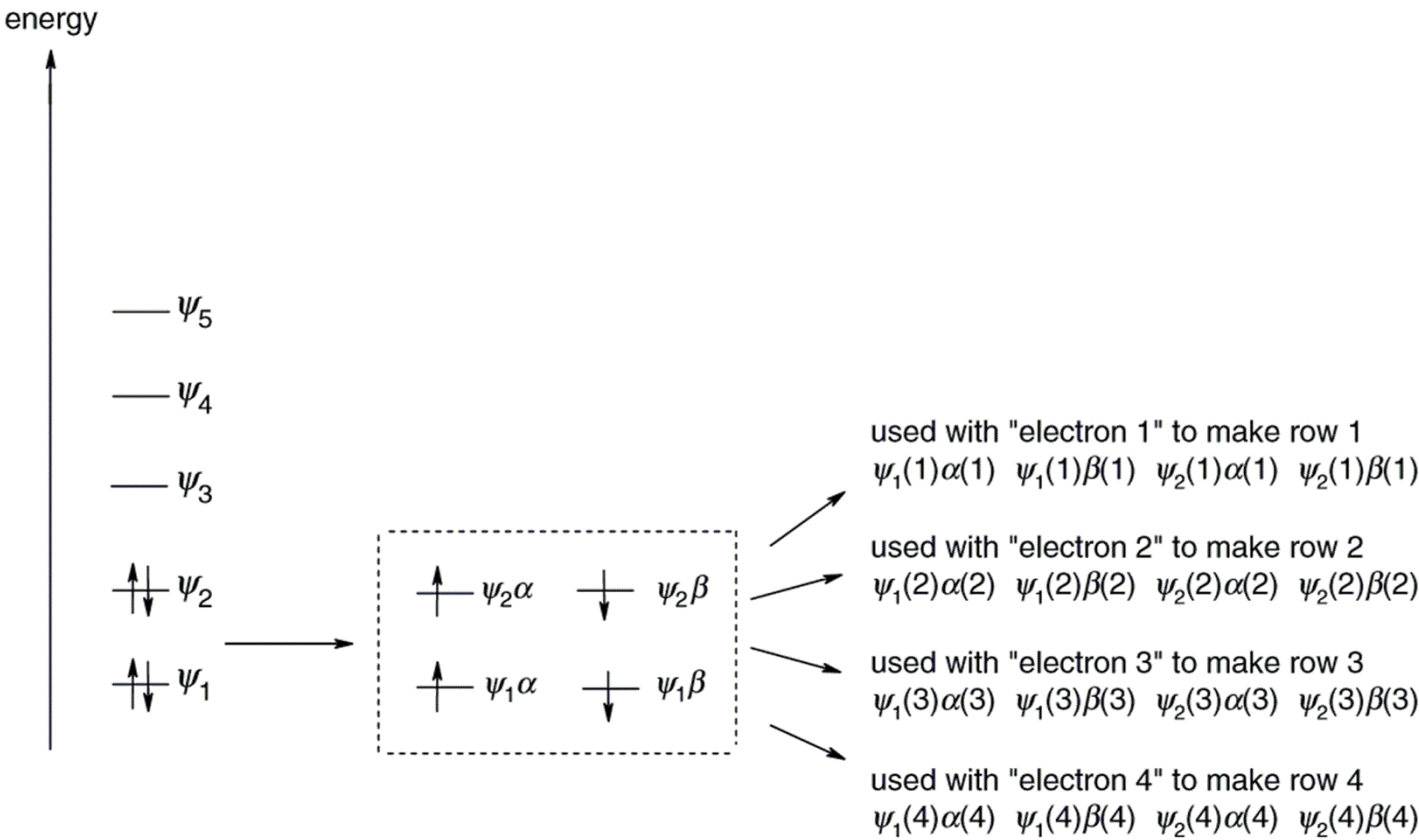
- The spin functions are associated with a spin operator  $\hat{S}_z$

$$\hat{S}_z\alpha = \frac{1}{2}(h/2\pi)\alpha$$

$$\hat{S}_z\beta = -\frac{1}{2}(h/2\pi)\beta$$

with eigenvalues  $1/2h/2\pi$  and  $-1/2h/2\pi$

Orbital diagram demonstrating spin and Pauli exclusion



The wavefunction that best describes this overall picture is best described by a **Slater Determinant**.

Slater Determinant

- Slater determinant for a 4 electron system
- $1/(4!)^{1/2}$  is a normalization factor

$$\Psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2) \\ \psi_1(3)\alpha(3) & \psi_1(3)\beta(3) & \psi_2(3)\alpha(3) & \psi_2(3)\beta(3) \\ \psi_1(4)\alpha(4) & \psi_1(4)\beta(4) & \psi_2(4)\alpha(4) & \psi_2(4)\beta(4) \end{vmatrix}$$

- The Slater determinant ensures that no more than two electrons in each spatial orbital.
- In a determinant, the exchange of two rows produces the negative of the original determinant. This property ensures antisymmetry.
- Electrons can also be assigned to columns instead of rows.

$$\Psi' = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(2)\alpha(2) & \psi_1(3)\alpha(3) & \psi_1(4)\alpha(4) \\ \psi_1(1)\beta(1) & \psi_1(2)\beta(2) & \psi_1(3)\beta(3) & \psi_1(4)\beta(4) \\ \psi_2(1)\alpha(1) & \psi_2(2)\alpha(2) & \psi_2(3)\alpha(3) & \psi_2(4)\alpha(4) \\ \psi_2(1)\beta(1) & \psi_2(2)\beta(2) & \psi_2(3)\beta(3) & \psi_2(4)\beta(4) \end{vmatrix}$$

- For a general  $2n$  electron system, the Slater determinant is;

$$\Psi_{2n} = \frac{1}{\sqrt{(2n)!}} \times \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1) & \cdots & \psi_n(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2) & \cdots & \psi_n(2)\beta(2) \\ \vdots & \vdots & \vdots & \vdots & & \\ \psi_1(2n)\alpha(2n) & \psi_1(2n)\beta(2n) & \psi_2(2n)\alpha(2n) & \psi_2(2n)\beta(2n) & \cdots & \psi_n(2n)\beta(2n) \end{vmatrix}$$

Calculate the Energy

- With our Slater determinant, we can plug that into the expectation expression for the energy.

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

With normalization;

$$\Psi^* \Psi d\tau = |\Psi|^2 d\tau = 1$$

$$E = \int \Psi^* \hat{H} \Psi d\tau$$

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

Substitute the Slater determinant in to energy expression using the following Hamiltonian;

$$\hat{H} = \sum_{i=1}^{2n} -\frac{1}{2} \nabla_i^2 - \sum_{\text{all } \mu, i} \frac{Z_\mu}{r_{\mu i}} + \sum_{\text{all } i, j} \frac{1}{r_{ij}}$$

gives; 
$$E = 2 \sum_{i=1}^n H_{ii} + \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij})$$

Nuc-Nuc repulsion is added separately 
$$V_{NN} = \sum_{\text{all } \mu, \nu} \frac{Z_\mu Z_\nu}{r_{\mu \nu}}$$

where  $H_{ij}$  is the core Hamiltonian.

$$H_{ii} = \int \psi_i^*(1) \hat{H}^{\text{core}}(1) \psi_i(1) dv$$

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{\text{all } \mu} \frac{Z_\mu}{r_{\mu 1}}$$

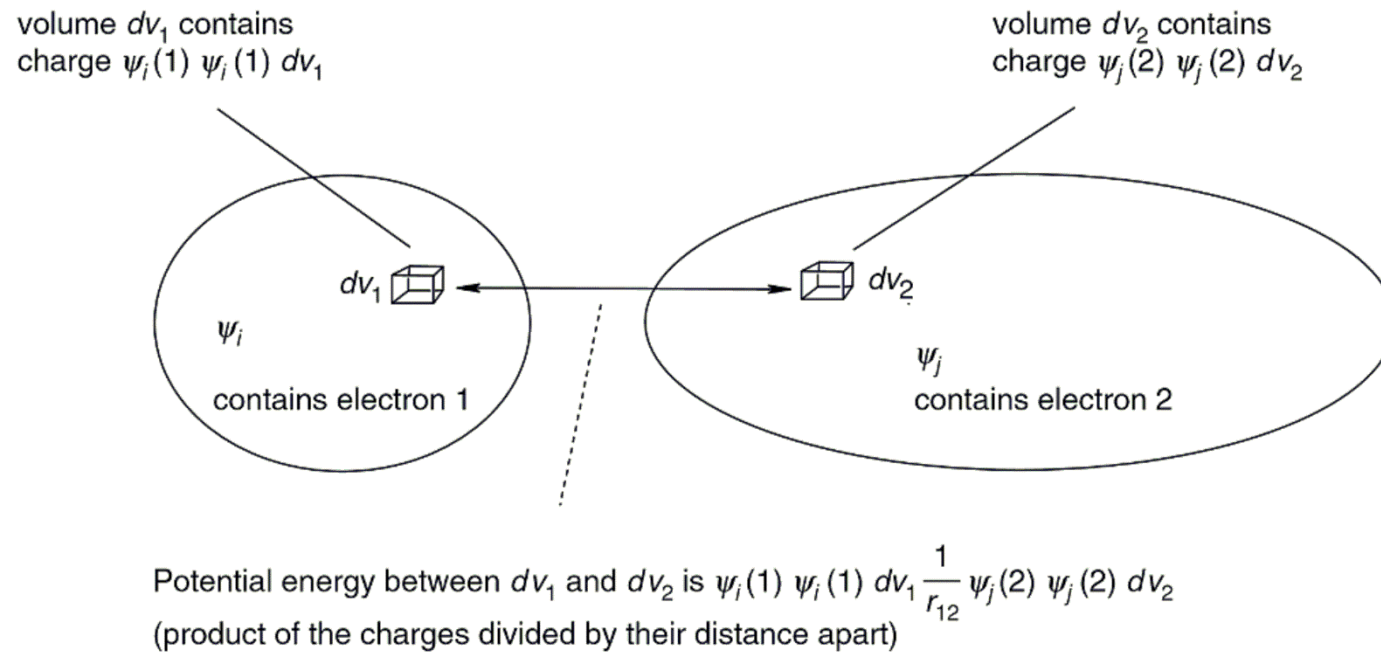
Coulomb Integral 
$$J_{ij} = \int \psi_i^*(1) \psi_i(1) \left( \frac{1}{r_{12}} \right) \psi_j^*(2) \psi_j(2) dv_1 dv_2$$

Exchange Integral 
$$K_{ij} = \int \psi_i^*(1) \psi_j^*(2) \left( \frac{1}{r_{12}} \right) \psi_i(2) \psi_j(1) dv_1 dv_2$$

## Coulomb Integral

$$J_{ij} = \int \psi_i^*(1) \psi_i(1) \left( \frac{1}{r_{12}} \right) \psi_j^*(2) \psi_j(2) dv_1 dv_2$$

Classical Coulombic repulsion



## Exchange Integral

$$K_{ij} = \int \psi_i^*(1) \psi_j^*(2) \left( \frac{1}{r_{12}} \right) \psi_i(2) \psi_j(1) dv_1 dv_2$$

- A consequence of spin and the antisymmetry of electronic wavefunctions
- Reduces the coulombic repulsion by  $K$  ( $2J - K$ )
- Accounts for the behavior that electrons of the same spin avoid each other more significantly than electrons of unlike spin.

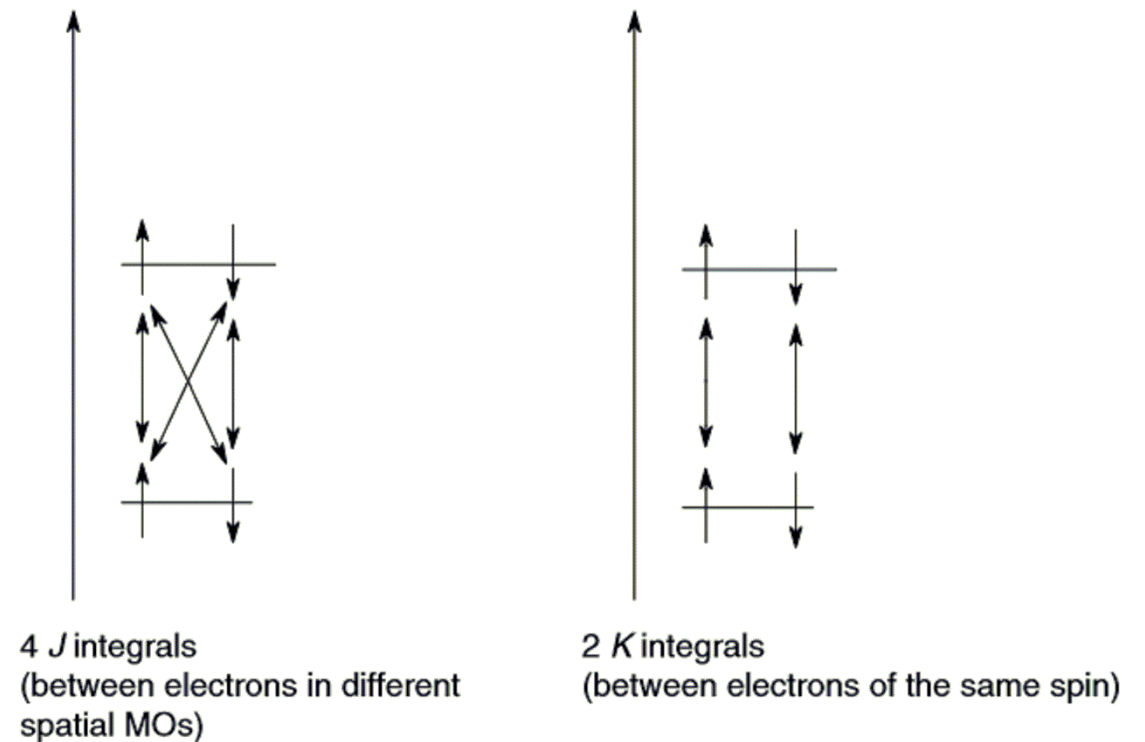
## Core Electronic Energies

$$H_{ii} = \int \psi_i^*(1) \hat{H}^{\text{core}}(1) \psi_i(1) dv$$

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{\text{all } \mu} \frac{Z_\mu}{r_{\mu 1}}$$

- $H_{ii}$  gives the energy of an electronic due to only its intrinsic kinetic energy and its attraction to all of the nuclei, in the absence of all electrons.

## Coulomb and Exchange Interactions



## • Variation Principle

- If the wavefunction and Hamiltonian are exact,  $\langle \Psi | H | \Psi \rangle$  would give the true energy of the system.
- However, we typically do not have the exact wavefunction.
- The **Variational Principle** tells us that any wavefunction that we insert into the energy expectation value equation we report back an energy that is greater than or equal to the true energy. The quality of the wavefunction is determined by how low the reported energy is.

$$E_0 \geq \frac{\int \Psi_0^* \hat{H} \Psi_0 d\tau}{\int \Psi_0^* \Psi_0 d\tau}$$

### • Energy Minimization → Hartree-Fock Equations

- Perform a similar energy minimization as was done to obtain the Secular equations in Huckel theory.
- This time, a constraint is applied to render the molecular orbitals ( $\psi$ ) orthonormal.
- The minimization subject to a constraint is done using the method of Lagrangian multipliers.
- The result is a familiar set of equations;

These are the **Hartree-Fock Equations**

$$\hat{F}\psi = \epsilon\psi$$

$$\hat{F} \begin{pmatrix} \psi_1(1) \\ \psi_2(1) \\ \psi_3(1) \\ \vdots \\ \psi_n(1) \end{pmatrix} = \begin{pmatrix} \epsilon_1 & 0 & 0 & \dots & 0 \\ 0 & \epsilon_2 & 0 & \dots & 0 \\ \vdots & \vdots & \dots & \vdots & \\ 0 & 0 & 0 & \dots & \epsilon_n \end{pmatrix} \begin{pmatrix} \psi_1(1) \\ \psi_2(1) \\ \psi_3(1) \\ \vdots \\ \psi_n(1) \end{pmatrix}$$

$$\hat{F}\psi_1(1) = \epsilon_1\psi_1(1)$$

$$\hat{F}\psi_2(1) = \epsilon_2\psi_2(1)$$

$$\hat{F}\psi_3(1) = \epsilon_3\psi_3(1)$$

$$\vdots$$

$$\hat{F}\psi_n(1) = \epsilon_n\psi_n(1)$$

Fock Operator. 
$$\hat{F} = \hat{H}^{\text{core}}(1) + \sum_{j=1}^n (2\hat{J}_j(1) - \hat{K}_j(1))$$

Coulomb Operator. 
$$\hat{J}_i(1) = \int \psi_i^*(2) \left( \frac{1}{r_{12}} \right) \psi_i(2) dv_2$$

Exchange Operator. 
$$\hat{K}_i(1)\psi_j(1) = \psi_i(1) \int \psi_i^*(2) \left( \frac{1}{r_{12}} \right) \psi_j(2) dv_2$$

The Hartree-Fock Equations are not true eigenvalue equations, unlike the Schrodinger equations. This is because the Fock operator is itself also dependent on the MOs (ie. it depends on the function by which it acts upon).

How can we improve upon the molecular wavefunction?

### Hartree-Fock Equations Interpretation.

- H-F equations are pseudoeigenvalue equations
- Each of the equations of  $\hat{F}\psi = \epsilon\psi$  is for one-electron.  $\hat{F}$  is a one-electron operator and each  $\psi$  is a one-electron spatial molecular orbital. Two electrons occupy each  $\psi$  if they have opposing spins.

$$\epsilon_i = \int \psi_i \hat{F} \psi_i dv$$

$$\epsilon_i = \int \psi_i(1) \hat{H}^{\text{core}}(1) \psi_i(1) dv + \sum_{j=1}^n (2J_{ij}(1) - K_{ij}(1))$$

$$\epsilon_i = H_{ii}^{\text{core}} + \sum_{j=1}^n (2J_{ij}(1) - K_{ij}(1))$$

- $H_{ii}^{\text{core}}$  is the energy of the electron due to its kinetic energy and attraction to the nuclear backbone
- $\sum 2J_{ij} - K_{ij}$  is the exchange corrected coulombic repulsion energy from interaction of an electron in orbital  $i$  with all the other electrons.
- A trial molecular wavefunction  $\Psi$  can be used to define the Fock operator  $\hat{F}$ .
- $\hat{F}$  is then acted on guess  $\psi_0$ 's to obtain the eigenvalues  $\epsilon_i$
- Updated  $\psi_i$ 's are then obtained as the eigenvectors
- The updated  $\psi_i$ 's are then used to construct a new  $\hat{F}$  matrix
- The process is repeated until the total energy is no longer lowered and the  $\psi_i$ 's no longer change.
- The electrostatic field produced by  $\sum \sum 2J_{ij} - K_{ij}$  will also reach consistency
- The process is self-consistent; **Self-Consistent Field Theory** (SCF)

## Roothan-Hall Equations.

- How are the  $\psi$ 's represented?
- Linear combinations of basis functions.

$$\psi_1 = c_{11}\phi_1 + c_{21}\phi_2 + c_{31}\phi_3 + \cdots + c_{m1}\phi_m$$

$$\psi_2 = c_{12}\phi_1 + c_{22}\phi_2 + c_{32}\phi_3 + \cdots + c_{m2}\phi_m$$

$$\psi_3 = c_{13}\phi_1 + c_{23}\phi_2 + c_{33}\phi_3 + \cdots + c_{m3}\phi_m$$

$$\vdots$$

$$\psi_m = c_{1m}\phi_1 + c_{2m}\phi_2 + c_{3m}\phi_3 + \cdots + c_{mm}\phi_m$$

individual basis functions

-  $i, j, k, l$  for  $\psi$ 's and  $r, s, t, u$  for  $\phi$ 's

$$\psi_i = \sum_{s=1}^m c_{si} \phi_s \quad i = 1, 2, 3, \dots, m \text{ (} m \text{ MOs)}$$

$m$  basis functions       $s$ th basis function  
 $i$ th MO       $c$  of the  $s$ th basis function of  $i$ th MO

- $x, y, z$  are the coordinates of the electron treated by  $\psi_i$
- $x_0, y_0, z_0$  are the coordinates of the nucleus

$$r = [(x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2]^{1/2}$$

## Basis set

- a set of basis functions used to describe the molecule
- a simple basis set for  $\text{CH}_4$

$$\phi(\text{C}, 1s), \phi(\text{C}, 2s), \phi(\text{C}, 2p_x), \phi(\text{C}, 2p_y), \phi(\text{C}, 2p_z)$$

$$\phi(\text{H}, 1s)$$

- This basis set would create 9 MO's which could accommodate 18 electrons
- The 10 electrons of  $\text{CH}_4$  would be used to fill the lowest energy 5 MO's

Substitution of the  $m$  basis functions into the H-F equations gives;

$$\sum_{s=1}^m c_{s1} \hat{F} \phi_{sj} = \epsilon_1 \sum_{sj=1}^m c_{s1} \phi_s$$

$$\sum_{s=1}^m c_{s2} \hat{F} \phi_s = \epsilon_2 \sum_{s=1}^m c_{s2} \phi_s$$

$$\vdots$$

$$\sum_{s=1}^m c_{sm} \hat{F} \phi_s = \epsilon_m \sum_{s=1}^m c_{sm} \hat{F} \phi_s$$

Each of the set of  $m$  equations is multiplied by  $\phi_1, \phi_2, \phi_3, \dots, \phi_m$  which is followed by integration to give  $m$  sets of equations, one for each of the basis functions,  $\phi$ .

For  $\phi_1$ 

$$\sum_{s=1}^m c_{s1} F_{1s} = \epsilon_1 \sum_{s=1}^m c_{s1} S_{1s}$$

$$\sum_{sj=1}^m c_{s2} F_{1s} = \epsilon_2 \sum_{s=1}^m c_{s2} S_{1s}$$

$$\vdots$$

$$\sum_{s=1}^m c_{sm} F_{1s} = \epsilon_m \sum_{s=1}^m c_{sm} S_{1s}$$

For  $\phi_2$ 

$$\sum_{s=1}^m c_{s1} F_{2s} = \epsilon_1 \sum_{s=1}^m c_{s1} S_{2s}$$

$$\sum_{s=1}^m c_{s2} F_{2s} = \epsilon_2 \sum_{s=1}^m c_{s2} S_{2s}$$

$$\vdots$$

$$\sum_{s=1}^m c_{sm} F_{2s} = \epsilon_m \sum_{s=1}^m c_{sm} S_{2s}$$

For  $\phi_m$ 

$$\sum_{s=1}^m c_{s1} F_{ms} = \epsilon_1 \sum_{s=1}^m c_{s1} S_{ms}$$

$$\sum_{s=1}^m c_{s2} F_{ms} = \epsilon_2 \sum_{s=1}^m c_{s2} S_{ms}$$

$$\vdots$$

$$\sum_{s=1}^m c_{sm} F_{ms} = \epsilon_m \sum_{s=1}^m c_{sm} S_{ms}$$

$$F_{rs} = \int \phi_r \hat{F} \phi_s dv \quad \text{and} \quad S_{rs} = \int \phi_r \phi_s dv$$

- Each set of  $m$  equations contains in itself  $m$  equations leading to  $m \times m$  equations
- These are the Roothan-Hall version of the H-F equations

$$\sum_{s=1}^m F_{rs} c_{si} = \sum_{s=1}^m S_{rs} c_{si} \epsilon_i \quad r = 1, 2, 3, \dots, m,$$

(for each  $i = 1, 2, 3, \dots, m$ )

Roothan-Hall equations summarized; connection between basis functions, MO's, total wavefunction and energy levels.

Using, e.g., a set of 4 basis functions:

$\{ \phi_1, \phi_2, \phi_3, \phi_4 \}$

weighted sum  
(the weighting factors are the MO coefficients  $c$ )

If there are 4 electrons in the molecule, then  $\psi_1$  and  $\psi_2$  are occupied (and  $\psi_3$  and  $\psi_4$  are virtual orbitals). The occupied orbitals are used to construct the total wavefunction, as a Slater determinant of spin orbitals.

$$\psi = \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2) \\ \psi_1(3)\alpha(3) & \psi_1(3)\beta(3) & \psi_2(3)\alpha(3) & \psi_2(3)\beta(3) \\ \psi_1(4)\alpha(4) & \psi_1(4)\beta(4) & \psi_2(4)\alpha(4) & \psi_2(4)\beta(4) \end{vmatrix}$$

Matrix Representation

- Since we have a set of  $m \times m$  equations that need to be solved, we should be able to translate the problem into a matrix format, similar to that from Huckel theory.

$FC = SC\epsilon$

- Expansion gives;

$$\begin{aligned} FC &= \begin{pmatrix} F_{11} & F_{12} & F_{13} & \cdots & F_{1m} \\ F_{21} & F_{22} & F_{23} & \cdots & F_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ F_{m1} & F_{m2} & F_{m3} & \cdots & F_{mm} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & c_{13} & \cdots & c_{1m} \\ c_{21} & c_{22} & c_{23} & \cdots & c_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ c_{m1} & c_{m2} & c_{m3} & \cdots & c_{mm} \end{pmatrix} \\ &= \begin{pmatrix} F_{11}c_{11} + F_{12}c_{21} + F_{13}c_{31} & \cdots & F_{11}c_{12} + F_{12}c_{22} + F_{13}c_{32} & \cdots & \cdots \\ F_{21}c_{11} + F_{22}c_{21} + F_{23}c_{31} & \cdots & F_{21}c_{12} + F_{22}c_{22} + F_{23}c_{32} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ F_{m1}c_{11} + F_{m2}c_{21} + F_{m3}c_{31} & \cdots & F_{m1}c_{12} + F_{m2}c_{22} + F_{m3}c_{32} & \cdots & \cdots \end{pmatrix} \\ SC\epsilon &= \begin{pmatrix} S_{11} & S_{12} & \cdots & S_{1m} \\ S_{21} & S_{22} & \cdots & S_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ S_{m1} & S_{m2} & \cdots & S_{mm} \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & \cdots & c_{1m} \\ c_{21} & c_{22} & \cdots & c_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ c_{m1} & c_{m2} & \cdots & c_{mm} \end{pmatrix} \begin{pmatrix} \epsilon_{11} & 0 & \cdots & 0 \\ 0 & \epsilon_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \epsilon_{mm} \end{pmatrix} \\ &= \begin{pmatrix} S_{11}c_{11} + S_{12}c_{21} + S_{13}c_{31} & \cdots & S_{11}c_{12} + S_{12}c_{22} + S_{13}c_{32} & \cdots & \cdots \\ S_{21}c_{11} + S_{22}c_{21} + S_{23}c_{31} & \cdots & S_{21}c_{12} + S_{22}c_{22} + S_{23}c_{32} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ S_{m1}c_{11} + S_{m2}c_{21} + S_{m3}c_{31} & \cdots & S_{m1}c_{12} + S_{m2}c_{22} + S_{m3}c_{32} & \cdots & \cdots \end{pmatrix} \epsilon \\ &= \begin{pmatrix} \epsilon_1(S_{11}c_{11} + S_{12}c_{21} + S_{13}c_{31} \cdots) & \epsilon_2(S_{11}c_{12} + S_{12}c_{22} + S_{13}c_{32} \cdots) & \cdots \\ \epsilon_1(S_{21}c_{11} + S_{22}c_{21} + S_{23}c_{31} \cdots) & \epsilon_2(S_{21}c_{12} + S_{22}c_{22} + S_{23}c_{32} \cdots) & \cdots \\ \vdots & \vdots & \ddots & \vdots \end{pmatrix} \end{aligned}$$

we can see that;

$F_{11}c_{11} + F_{12}c_{21} + F_{13}c_{31} + \cdots = \epsilon(S_{11}c_{11} + S_{12}c_{21} + S_{13}c_{31} + \cdots)$

which is shown to be generally;

$$\sum_{s=1}^m c_{si}F_{rs} = \epsilon \sum_{s=1}^m c_{si}S_{rs}$$

So the matrix treatment is a valid approach to solving the equations.

### Roothan-Hall Summary

1. Express total wavefunction  $\Psi$  as a Slater determinant
2. Electronic energy is obtained from  $\langle \Psi | H | \Psi \rangle$
3. Substitute Slater determinant into  $\langle \Psi | H | \Psi \rangle$  to get;

$$E = 2 \sum_{i=1}^n H_{ii} + \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij})$$

4. Minimize E with respect to the  $\psi$ 's to get the H-F equations

$$\hat{F}\psi = \varepsilon\psi$$

5. Substituting in the H-F equations the Roothan-Hall LCAO expansion gives;

$$\psi_i = \sum c_{si} \phi_s$$

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

### Using the Roothan-Hall Equations

The Fock matrix elements are defined by;

$$F_{rs} = \int \phi_r \hat{F} \phi_s dv$$

where the Fock operator takes the following form;

$$\hat{F} = \hat{H}^{\text{core}}(1) + \sum_{j=1}^n (2\hat{J}_j(1) - \hat{K}_j(1))$$

and substitution gives;

$$F_{rs} = \int \phi_r \left[ \hat{H}^{\text{core}}(1) + \sum_{j=1}^n (2\hat{J}_j(1) - \hat{K}_j(1)) \right] \phi_s dv$$

where the  $H^{\text{core}}$  operator is;

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{\text{all } \mu} \frac{Z_\mu}{r_{\mu 1}}$$

with the Coulomb operator;

$$\hat{J}_j(1) = \int \psi_j^*(2) \left( \frac{1}{r_{12}} \right) \psi_j(2) dv_2$$

and Exchange operator;

$$\hat{K}_i(1)\psi_j(1) = \psi_i(1) \int \psi_i^*(2) \left( \frac{1}{r_{12}} \right) \psi_j(2) dv_2$$

Obtain c's and  $\varepsilon$ 's through similar method used in EHT,

1. Overlap matrix is calculated,  $\mathbf{S}$ , followed by the orthogonalizing matrix  $\mathbf{S}^{-1/2}$

$$\mathbf{S} \rightarrow \mathbf{D} \rightarrow \mathbf{S}^{-1/2}$$

2.  $\mathbf{S}^{-1/2}$  is used to convert  $\mathbf{F}$  to  $\mathbf{F}'$

$$\mathbf{F}' = \mathbf{S}^{-1/2} \mathbf{F} \mathbf{S}^{-1/2}$$

3.  $\mathbf{F}'$  is diagonalized to obtain the MO energies

$$\mathbf{F}' = \mathbf{C}' \boldsymbol{\varepsilon} \mathbf{C}'^{-1}$$

4.  $\mathbf{S}^{-1/2}$  is used to convert  $\mathbf{C}'$  to  $\mathbf{C}$

$$\mathbf{C} = \mathbf{S}^{-1/2} \mathbf{C}'$$

The combination of Fock diagonalization with the H-F equations makes up the SCF process.

## Step 1

Specify geometry, charge and electronic state,  
e.g. CH<sub>4</sub> cartesian coordinates, charge = 0, singlet  
or CH<sub>4</sub> cartesian coordinates, charge = 0, triplet, etc.

Choose a basis set.  
Start the calculation.

## Step 2

Program calculates integrals: kinetic energy, potential energy, and  
overlap integrals.

## Step 3

Program calculates orthogonalizing matrix using overlap matrix (composed of  
overlap integrals).

## Step 4

Program calculates initial Fock matrix using kinetic energy and potential energy integrals  
and an initial guess of basis set coefficients (initial guess from, e.g., an extended  
Hückel calculation; the guess *c*'s usually have to be "projected" to the ab initio basis,  
which is almost always bigger than that used for the guess calculation).

## Step 5

Program uses orthogonalizing matrix to transform Fock matrix to one based on an  
orthonormal set of functions derived from the original atom-centered basis functions.

## Step 6

Program diagonalizes Fock matrix to get *c*'s (based on the orthonormal, derived basis  
set) and energy levels.

## Step 7

Program transforms the *c*'s to a set based on the original, atom-centered basis functions.

## Step 8

Program compares *c*'s (and/or energy, or other parameters) with the previous set; if the  
match is *not* close enough, another SCF cycle, steps 4–8, is done, using as input for  
step 4 the latest *c*'s. If the match *is* close enough, the iterations stop.

1 Define molecule



2 calculate integrals

3 calculate othogonalizing  
matrix4 calculate initial  
Fock matrix

5 transform Fock matrix



6 diagonalize Fock matrix

7 transform *c*'s8 compare parameters  
with previous ones

### Using Roothan-Hall Equations with LCAO Expansion

- The objective is to expressive all equations in terms of the basis functions and c's

Fock matrix elements look like this;

$$F_{rs} = \left\langle \phi_r(1) | \hat{H}^{\text{core}}(1) | \phi_s(1) \right\rangle + \sum_{j=1}^n [2 \langle \phi_r(1) | \hat{J}_j(1) | \phi_s(1) \rangle - \langle \phi_r(1) | \hat{K}_j(1) | \phi_s(1) \rangle]$$

with the Coulomb operator as;

$$\hat{J}_j(1) \phi_s(1) = \phi_s(1) \int \frac{\psi_j^*(2) \psi_j(2)}{r_{12}} dv_2$$

substitute LCAO expansion into  $\psi$ 's;  $\sum c_{ij}^* \phi_t^*(2) = \psi_j^*(2)$   $\sum c_{uj} \phi_u(2) = \psi_j(2)$

$$\hat{J}_j(1) \phi_s(1) = \phi_s(1) \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} \int \frac{\phi_t^*(2) \phi_u(2)}{r_{12}} dv_2$$

for insertion into  $F_{rs}$ ,  $\hat{J}_j(1) \phi_s(1)$  is multiplied by  $\phi_r(1)$  to give;

$$\langle \phi_r(1) | \hat{J}_j(1) | \phi_s(1) \rangle = \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} \int \int \frac{\phi_r^*(1) \phi_s(1) \phi_t^*(2) \phi_u(2)}{r_{12}} dv_1 dv_2$$

or more succinctly as;

$$\langle \phi_r(1) | \hat{J}_j(1) | \phi_s(1) \rangle = \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} (rs|tu)$$

where

$$(rs|tu) = \int \int \frac{\phi_r^*(1) \phi_s(1) \phi_t^*(2) \phi_u(2)}{r_{12}} dv_1 dv_2$$

analogous to

$$\langle f|g \rangle = \int f^*(q) g(q) dq$$

$$\langle rs|tu \rangle = \int (\phi_r(1) \phi_s(1))^* \phi_t(1) \phi_u(1) dv_1$$

$(rs|tu)$  is a 6-fold integral integrating over the three cartesian coordinates for electron 1 ( $x_1, y_1, z_1$ ) and the three coordinates for electron 2 ( $x_2, y_2, z_2$ )

exchange operator is;

$$\hat{K}_j(1) \phi_s(1) = \psi_j(1) \int \frac{\psi_j^*(2) \phi_s(2)}{r_{12}} dv_2$$

with similar LCAO expansion;

$$\hat{K}_j(1) \phi_s(1) = \phi_u(1) \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} \int \frac{\phi_t^*(2) \phi_s(2)}{r_{12}} dv_2$$

$$\langle \phi_r(1) | \hat{K}_j(1) | \phi_s(1) \rangle = \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} \int \int \frac{\phi_r^*(1) \phi_u(1) \phi_t^*(2) \phi_s(2)}{r_{12}} dv_1 dv_2$$

$$\langle \phi_r(1) | \hat{K}_j(1) | \phi_s(1) \rangle = \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} (ru|ts)$$

$$(ru|ts) = \int \int \frac{\phi_r^*(1) \phi_u(1) \phi_t^*(2) \phi_s(2)}{r_{12}} dv_1 dv_2$$

Substitution into above expression for  $F_{rs}$  gives the Fock matrix elements expressed exclusively in terms of  $\phi$ 's and c's

$$F_{rs} = \left\langle \phi_r(1) | \hat{H}^{\text{core}}(1) | \phi_s(1) \right\rangle + \sum_{j=1}^n \left[ 2 \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} (rs|tu) - \sum_{t=1}^m \sum_{u=1}^m c_{ij}^* c_{uj} (ru|ts) \right]$$

$$F_{rs} = H_{rs}^{\text{core}}(1) + \sum_{t=1}^m \sum_{u=1}^m \sum_{j=1}^n c_{ij}^* c_{uj} [2(rs|tu) - (ru|ts)]$$

$$H_{rs}^{\text{core}}(1) = \left\langle \phi_r(1) | \hat{H}^{\text{core}}(1) | \phi_s(1) \right\rangle$$

## Density Matrix - Compact Book Keeping of c's

The c's in  $F_{rs}$  can be organized in matrix form.

$$\mathbf{P} = \begin{pmatrix} P_{11} & P_{12} & P_{13} & \vdots & P_{1m} \\ P_{21} & P_{22} & P_{23} & \cdots & P_{2m} \\ \vdots & \vdots & \dots & \vdots & \\ P_{m1} & P_{m2} & P_{m3} & \cdots & P_{mm} \end{pmatrix}$$

$$P_{tu} = 2 \sum_{j=1}^n c_{tj}^* c_{uj} \quad t = 1, 2, \dots, m \quad \text{and} \quad u = 1, 2, \dots, m$$

$$F_{rs} = H_{rs}^{\text{core}}(1) + \sum_{t=1}^m \sum_{u=1}^m P_{tu} \left[ (rs|tu) - \frac{1}{2} (ru|ts) \right]$$

$P_{tu}$  should not be interpreted for physical meaning.

## Total H-F Energy

How can the total energy  $E_{\text{HF}}$  be calculated from the MO energy levels?

Each MO energy is determined from;

$$\varepsilon_i = H_{ii}^{\text{core}} + \sum_{j=1}^n (2J_{ij}(1) - K_{ij}(1))$$

The sum of all of the MO energies overestimates  $E_{\text{HF}}$  because of electron-electron repulsion is being counted twice.

$$E(\text{overestimated}) = 2 \sum_{i=1}^n \varepsilon_i$$

Solution is to subtract

$$\sum \sum (2J - K)$$

$$E_{\text{HF}} = 2 \sum_{i=1}^n \varepsilon_j - \sum_{i=1}^n \sum_{j=1}^n (2J_{ij}(1) - K_{ij}(1))$$

How is the energy  $E_{\text{HF}}$  expressed in terms of only  $\varepsilon$ 's and c'?

$$\sum_{i=1}^n \sum_{j=1}^n (2J_{ij}(1) - K_{ij}(1)) = \sum_{i=1}^n \varepsilon_i + \sum_{i=1}^n H_{ii}^{\text{core}}$$

$$E_{\text{HF}} = \sum_{i=1}^n \varepsilon_i + \sum_{i=1}^n H_{ii}^{\text{core}}$$

$$H_{ii}^{\text{core}} = \langle \psi_i(1) | \hat{H}^{\text{core}} | \psi_i \rangle$$

$$\psi_i = \sum_{s=1}^m c_{si} \phi_s$$

$$E_{\text{HF}} = \sum_{i=1}^n \varepsilon_i + \sum_{r=1}^m \sum_{s=1}^m \sum_{i=1}^n c_{ri}^* c_{si} H_{rs}^{\text{core}}$$

$$E_{\text{HF}} = \sum_{i=1}^n \varepsilon_i + \frac{1}{2} \sum_{r=1}^m \sum_{s=1}^m P_{rs} H_{rs}^{\text{core}}$$

$$H_{rs}^{\text{core}} = \left\langle \phi_r \left| -\frac{1}{2} \nabla^2 - \sum_{\text{all } \mu} \frac{Z_{\mu}}{r_{\mu i}} \right| \phi_s \right\rangle$$

Inclusion of nuclear-nuclear repulsion gives  $V_{NN} = \sum_{\text{all } \mu, \nu} \frac{Z_{\mu} Z_{\nu}}{r_{\mu \nu}}$

$$E_{\text{HF}}^{\text{total}} = E_{\text{HF}} + V_{NN} = \sum_{i=1}^n \varepsilon_i + \frac{1}{2} \sum_{r=1}^m \sum_{s=1}^m P_{rs} H_{rs}^{\text{core}} + V_{NN}$$