

# Hartree-Fock Method

CHEM 2430

$$\hat{H} = \frac{-\hbar^2}{2m_e} \sum \nabla_i^2 - \sum \frac{Ze^2}{r_i} + \sum \sum \frac{e^2}{r_{ij}} \quad \text{for atoms there is only one nucleus}$$

Hartree: use the trial wave function

$$\phi = g_1(r_1, \theta_1, \phi_1) g_2(r_2, \theta_2, \phi_2) \dots g_n(r_n, \theta_n, \phi_n)$$

where we find the optimal  $g_i$

$$\text{Choose } g_i = h_i(r_i) Y_{l_i}^{m_i}(\theta_i, \phi_i)$$

This neglects the antisymmetry.  
(We will deal with that later.)

The solution gives a set of equations that define the orbitals and give orbital energies. E.g.,

$$\left[ \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{Ze^2}{r_1} + V_1(r_1) \right] g_1(r_1) = \varepsilon_1 g_1(r_1)$$

There are analogous equations for the other electrons

$$\text{In these equations } V_i(r_i) = \sum_{j \neq i} \int |\phi_j|^2 \frac{1}{r_{ij}} d\vec{r}_j$$

is the potential seen by electron  $i$  due to average charge distribution of all the other electrons.

E.g., for Be atom we would solve an equation for  $g_{1s}(r)$  and  $\epsilon_{1s}$  and  $g_{2s}(r)$  and  $\epsilon_{2s}$

Now what is the total energy?

$$H = \sum_{i=1} \left[ h_i^H(r_i) + \sum_{j \neq i} \frac{e^2}{r_{ij}} - V_i(r_i) \right]$$

$$h_i^H(r_i) = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{r_i} + V_i(r_i)$$

Here the superscript  $H \Rightarrow$  Hartree

Let's look at this in more detail for Be

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} + \int g_{1s}(r_1)g_{1s}(r_2)g_{2s}(r_3)g_{2s}(r_4) \left( \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{14}} + \frac{e^2}{r_{23}} + \frac{e^2}{r_{24}} + \frac{e^2}{r_{34}} - V_1(r_1) - V_2(r_2) - V_3(r_3) - V_4(r_4) \right)$$

$$\times g_{1s}(r_1)g_{1s}(r_2)g_{2s}(r_3)g_{2s}(r_4) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} + \int g_{1s}^2(r_1) \frac{e^2}{r_{12}} g_{1s}^2(r_2) d\vec{r}_1 d\vec{r}_2 + 4 \int g_{1s}^2(r_1) \frac{e^2}{r_{13}} g_{2s}^2(r_3) d\vec{r}_1 d\vec{r}_3$$

$$+ \int g_{2s}^2(r_3) \frac{1}{r_{34}} g_{2s}^2(r_4) d\vec{r}_3 d\vec{r}_4$$

$$- \int g_{1s}^2(r_1) V(r_1) d\vec{r}_1 - \int g_{1s}^2(r_2) V(r_2) d\vec{r}_2$$

$$- \int g_{2s}^2(r_3) V(r_3) d\vec{r}_3 - \int g_{2s}^2(r_4) V(r_4) d\vec{r}_4$$

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} + \left\langle 1s1s \left| \frac{1}{r_{12}} \right| 1s1s \right\rangle + 4 \left\langle 1s2s \left| \frac{1}{r_{13}} \right| 1s2s \right\rangle + \left\langle 2s2s \left| \frac{1}{r_{34}} \right| 2s2s \right\rangle - \text{the four integrals over the } V(r_i)$$

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - J_{1s,1s} - 2J_{1s,2s} - J_{1s,1s} - 2J_{1s,2s} - J_{2s,2s} - 2J_{2s,1s} - J_{2s,2s} - 2J_{1s,2s}$$

$$E = 2\varepsilon_{1s} + 2\varepsilon_{2s} - J_{1s,1s} - J_{2s,2s} - 4J_{1s,2s}$$

Note: we could have written this down immediately if we realized that we need to eliminate the double counting in the orbital energy sum.

So far we have neglected the antisymmetry of the wavefunction.

This is accounted for in the **Hartree-Fock approximation**.

We now start with a Slater determinant trial wavefunction

$$V_i^{eff}(r_1)\phi_i(r_1) = \sum_{j \neq i} \int |\phi_j(r_2)|^2 \frac{1}{r_{12}} d\vec{r}_2 \phi_i(r_1) - \sum_{j \neq i} \int \phi_j(q_2)\phi_i(q_2) \frac{1}{r_{12}} d\tau_2 \phi_j(q_1)$$

Note, that we now only need to consider  $1/r_{12}$  and to consider integration over  $r_2$  due to the permutation of the coordinates.

However, we have to remember that the orbitals have a spin associated with them, and the exchange integral involving up and down spin orbitals is zero. This is why I switched from  $r$  to  $q$  in the exchange integrals

$$V_1^{eff}(r_1) = J_1 - K_1$$

Coulomb and exchange operators

In practice we can remove the  $j \neq i$  in the sum since if  $j = i$ , the Coulomb and exchange contributions cancel.

This has no impact on the filled orbitals but causes significant shifts of the energies of the unfilled orbitals.

This lets us obtain all orbitals from a single Fock operator

$$F\phi_i(r_1) = \varepsilon_i\phi_i(r_1)$$

Again  $E_{\text{total}}$  is not just  $\sum \varepsilon_i$  since this double counts Coulomb and exchange interactions

$$\text{For Be } E = 2\varepsilon_{1s} + 2\varepsilon_{2s} - J_{1s,1s} - J_{2s,2s} - 4J_{1s,2s} + 2K_{1s,2s}$$

Note that the numerical factor is 2" as one can only have exchange with the electron of the same spin

## Koopmans' Theorem

$$\text{IP}_i \sim -\varepsilon_i \quad \text{EA}_j = -\varepsilon_j$$

Do HF calculations on ground state neutral (assumed closed shell).

Using these orbitals calculate  $E_i^{\text{cation}} - E^{\text{neutral}}$

Where  $E_i^{\text{cation}}$  indicates that an electron is removed from orbital  $i$

E.g., for He

$$E_{\text{He}} = 2\varepsilon_{1s} - J_{1s,1s}$$

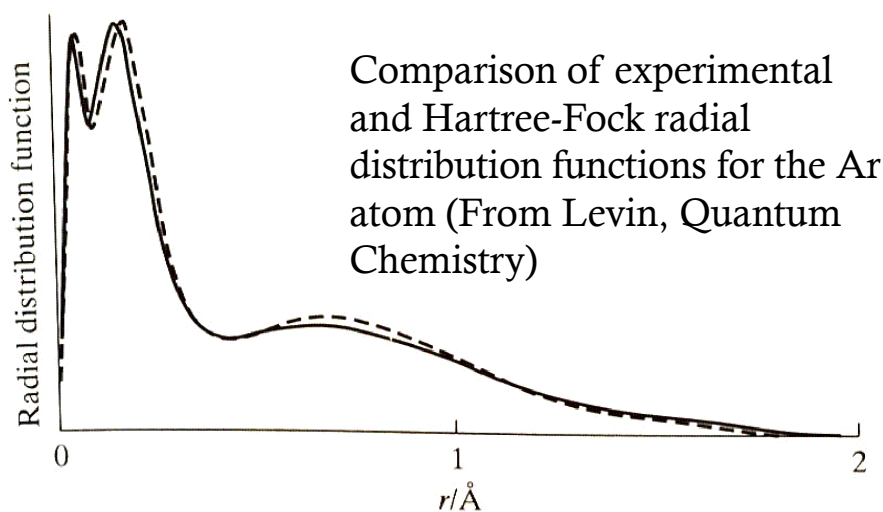
$$E_{\text{He}^+} = \varepsilon_{1s} - J_{1s,1s}$$

Not what we would get if  
we actually carried out a  
HF calculation on  $\text{He}^+$

$$\Delta E = E_{\text{He}^+} - E_{\text{He}} = \varepsilon_{1s}$$

For a single Slater determinant wave function the total charge density is simply the sum of the charge densities of the various orbitals

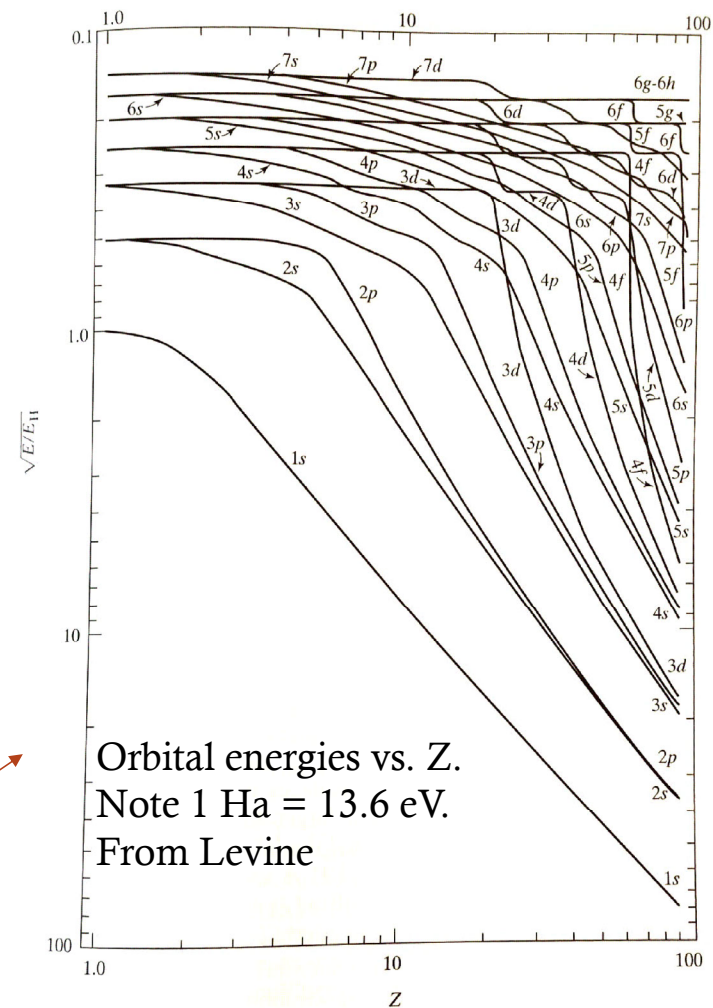
HF densities are very close to the exact densities



Radius of sphere enclosing  $\sim 98\%$  of the charge  $\approx vdW$  radius

Orbital energies alone do not allow one to determine, e.g., if  $3d^1 4s^2$  is more stable than  $3d^3$ .

Recall that the state energies also include Coulomb and exchange contributions as well as electron correlation effects





Roothaan method (1951) to solving the HF equations.

Introduce atomic basis functions :  $1s, 2s, 2p$ , etc.

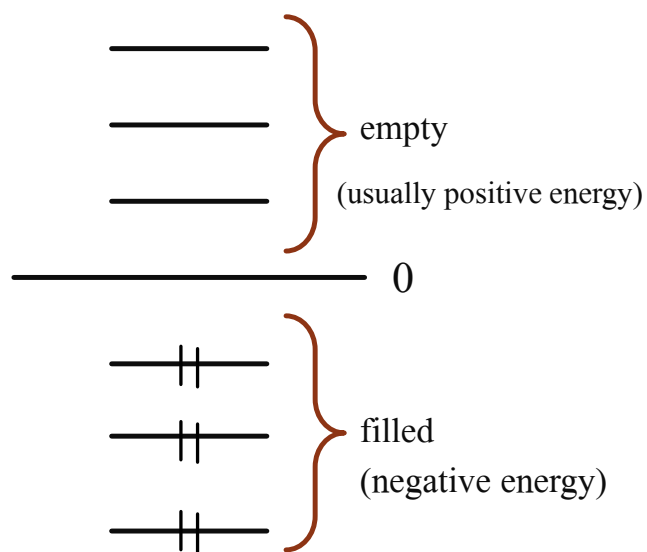
For atoms the  $\chi_i$  basis functions could be Slater functions  $r^{n-1} e^{-\zeta r/a_0} Y_\ell^m(\theta, \phi)$

$$\text{Then the HF AO's } g_j = \sum_i c_i^j \chi_i$$

For molecules it is preferable to use Gaussian functions times factors of  $x, y, z$  (to various power)

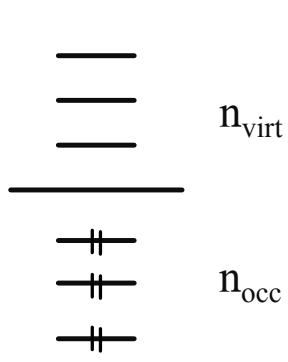
$$E_{\text{corr}} = E_{\text{nonrel}} - E_{\text{HF}}$$

HF carried out using flexible basis sets give filled and empty orbitals



Can form excited determinants by exciting electrons from filled to empty orbitals.

The wave function can then be written as a linear combination of these determinants



# Slater determinants  
(neglecting symmetry)

$$\# \text{ single excitations} \approx n_{\text{occ}} \cdot n_{\text{virt}}$$

$$\# \text{ double excitations} \approx n_{\text{occ}}^2 \cdot n_{\text{virt}}^2$$

So the # of Slater determinants grows rapidly with the # of electrons and the excitation level.

With large flexible basis sets the low-lying virtual orbitals have  $E \rightarrow 0$ .

They are actually describing (approximately) the continuum, rather than orbitals appropriate for anion states or electronically excited states

This is a major problem for multideterminant calculations using flexible basis sets.

This is a less of a problem with smaller basis sets, e.g.

2s1p for H

3s2p1d for C

etc.

} For C this would be one function for 1s and two functions for the valence 2s, 2p

## Brillouin's theorem

$$\text{Let } |0\rangle = |\psi_{HF}\rangle$$

$$\text{and } \begin{vmatrix} r \\ a \end{vmatrix} = a_r^+ a_a |0\rangle$$

represents an excitation from orbital  $a$  to orbital  $r$

$$\text{Then } \langle 0 | H \begin{vmatrix} r \\ a \end{vmatrix} = 0$$

As a result of this, the second order (MP2) method can only mix double excitations with the HF Slater determinant

$$\text{Third order PT: } \langle 0 | V | de \rangle \langle de | V | de' \rangle \langle de' | V | 0 \rangle$$

$$\begin{aligned} \text{4th order PT: } & \langle 0 | V | de \rangle \langle de | V | de' \rangle \langle de' | V | de'' \rangle \langle de'' | V | 0 \rangle \\ & \langle 0 | V | de \rangle \langle de | V | se \rangle \langle se | V | de' \rangle \langle de' | V | 0 \rangle \\ & \langle 0 | V | de \rangle \langle de | V | te \rangle \langle te | V | de' \rangle \langle de' | V | 0 \rangle \\ & \langle 0 | V | de \rangle \langle de | V | qe \rangle \langle qe | V | de' \rangle \langle de' | V | 0 \rangle \\ & \langle 0 | V | de \rangle \langle de | V | 0 \rangle \langle 0 | V | de' \rangle \langle de' | V | 0 \rangle \end{aligned}$$