

# CHM 673

## Lecture 6: Hartree-Fock model, part 3

### Hartree-Fock theorems

---

Suggested reading:

Chapter 3.3 from S&O

Chapter 3.3-3.4 from Jensen

*<http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/Hartree-Fock-Intro.pdf>*

# Hartree-Fock model

Hartree-Fock model tries to find the *best variational solution* to the electronic Hamiltonian assuming that the wave function is approximated by a **single Slater determinant**:  $\Psi_{HF} = \Psi_{SD}$

General strategy:

1.  $E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle$  - this equation defines HF energy as a *functional* of spin-orbitals

2. Minimize  $E_{HF}$  with respect to spin-orbitals:  $\delta E_{HF} \left[ \{ \chi_i \} \right] = 0 \rightarrow$

this equation determines optimal spin-orbitals and the variationally best (lowest) energy

3. Solve this equation for the best orbitals and energy – job done!

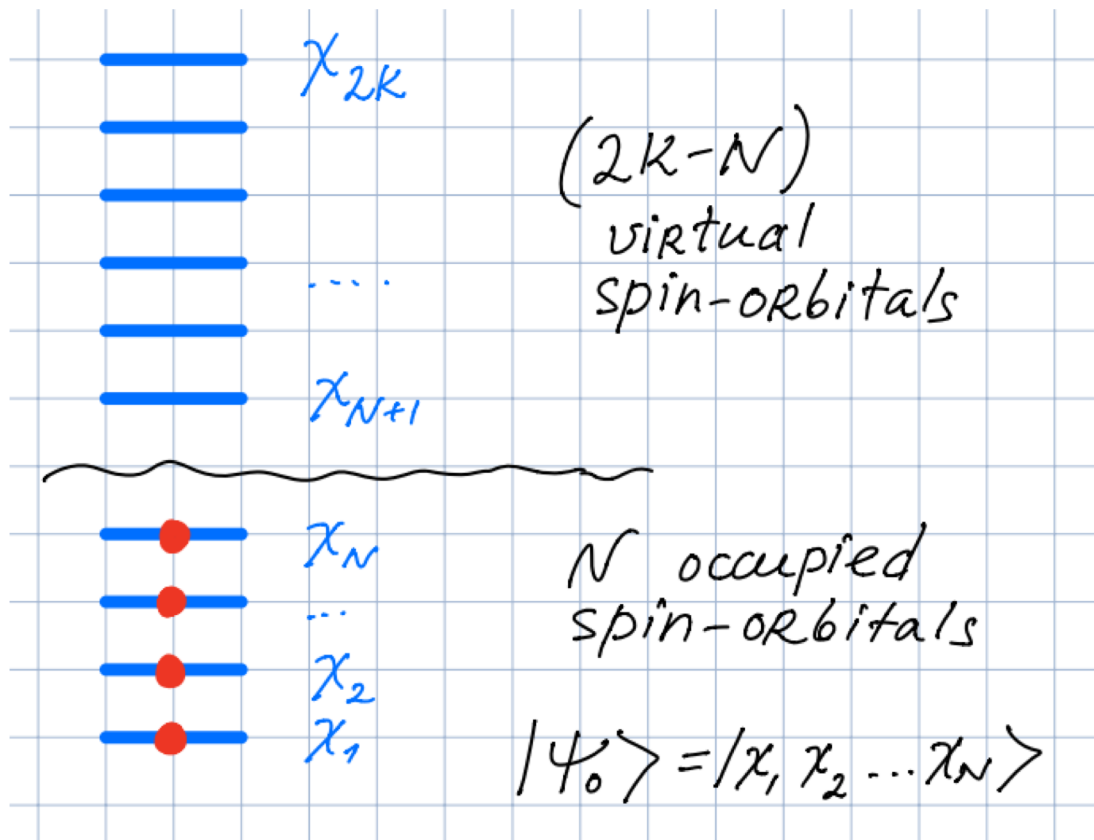
# Hartree-Fock solutions

After solving  $2K$  HF eq-ns:

$$\hat{f}_i |\chi_i\rangle = \varepsilon_i |\chi_i\rangle$$

$K$  – the total number of spatial orbitals, which is determined by the total number of basis functions – stay tuned  
 $2K$  - the total number of spin-orbitals

$2K$  orthonormal spin-orbitals  $\{\chi_i\}$  with orbital energies  $\{\varepsilon_i\}$  is produced



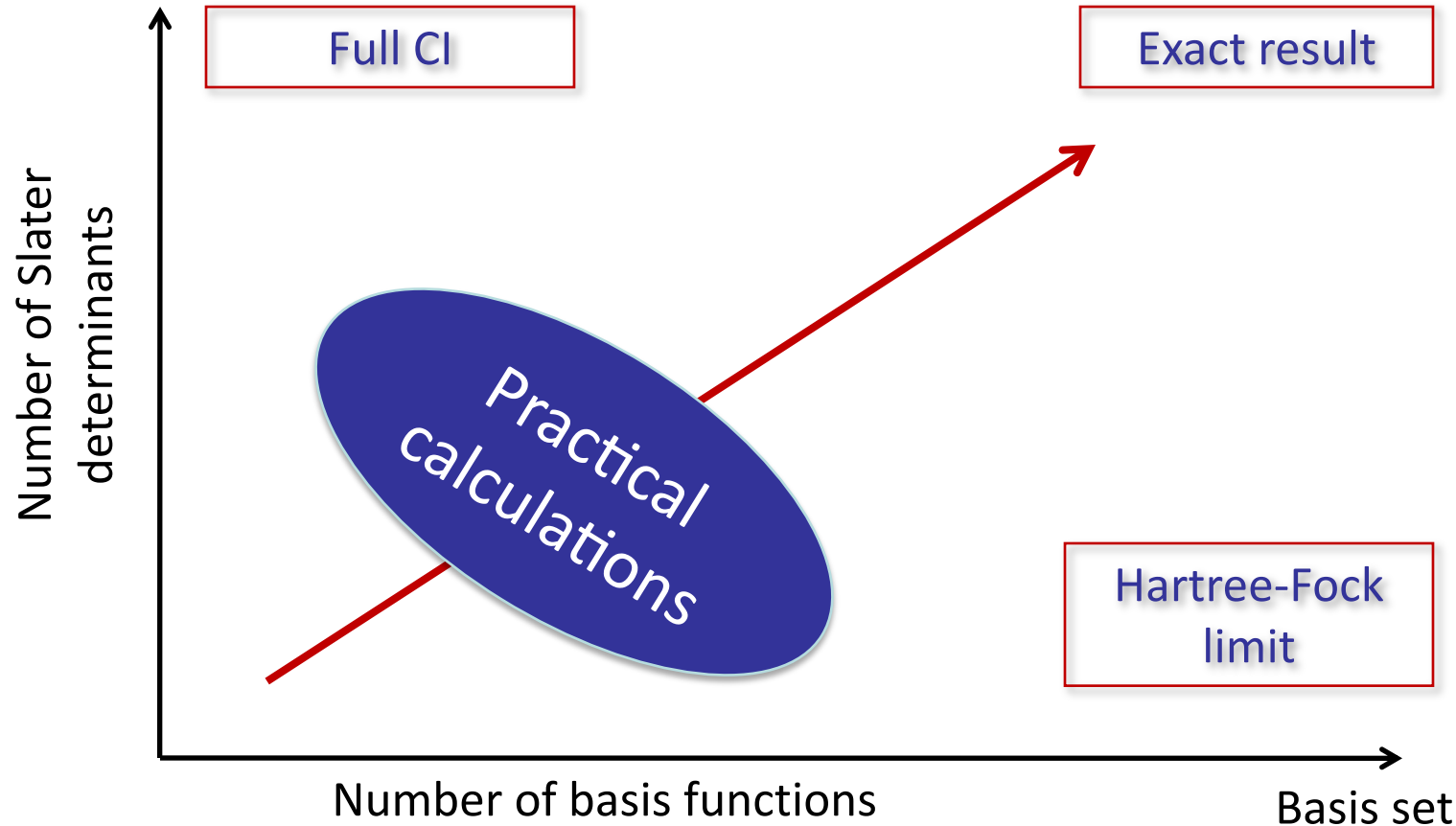
The Slater determinant formed from the  $N$  lowest occupied spin-orbitals

$|\Phi_0\rangle = |\chi_1 \chi_2 \dots \chi_N\rangle$  is the Hartree-Fock ground state wave function.

It is the best variational approximation to the ground state of the system in the single determinantal form.

# Theoretical model chemistries (John Pople)

Electron correlation



## Two approximations:

- We do not solve the exact equations → approximate treatment of electron-electron interactions (aka electron correlation)
- We do not achieve completeness in the electron expansion space (we do not solve inexact equations exactly) → basis set truncation error

# Back to the Hartree-Fock model: meaning of the Fock operator

Fock operator  $\hat{f}_i = \hat{h}_i + \sum_j^{Nelec} (\hat{J}_j - \hat{K}_j)$

Q: What is a physical meaning of the Fock operator?

Electronic Hamiltonian  $\hat{H}_{el}$  is not a sum of  $\hat{f}_i$  :

$$\hat{H}_{el} = \sum_i^{Nelec} \hat{h}_i + \frac{1}{2} \sum_{ij}^{Nelec} \frac{1}{r_{ij}} + \hat{V}_{NN}$$

Expectation value of the Fock operator is the orbital energy (aka effective one-electron energy):

$$\varepsilon_i = \langle \chi_i | \hat{f}_i | \chi_i \rangle = h_i + \sum_j^{Nelec} (J_{ij} - K_{ij})$$

$$\text{Then } E_{HF} = \sum_i^{Nelec} h_i + \frac{1}{2} \sum_{ij}^{Nelec} (J_{ij} - K_{ij}) = \sum_i^{Nelec} \varepsilon_i - \frac{1}{2} \sum_{ij}^{Nelec} (J_{ij} - K_{ij})$$

The Hartree-Fock energy is not a sum of the orbital energies!

# Physical meaning of orbital energies

Consider 2 electrons on 2 orbitals:

$$\varepsilon_i = \langle i | \hat{f}_i | i \rangle = \langle i | \hat{h} | i \rangle + \langle i | \hat{J}_j | i \rangle - \langle i | \hat{K}_j | i \rangle$$

$$\varepsilon_j = \langle j | \hat{f}_j | j \rangle = \langle j | \hat{h} | j \rangle + \langle j | \hat{J}_i | j \rangle - \langle j | \hat{K}_i | j \rangle$$

interaction of electron  $i$  with electron  $j$   
is included twice

To understand the physical meaning of the orbital energies, we need to consider the process of adding or subtracting an electron to N-electron state

The original (neutral) N-electron state:  $|\Psi_0\rangle = |\chi_i \chi_j \dots \chi_N\rangle$

Ionized (N-1) state (electron is removed from  $\chi_c$ ):  $|\Psi_0\rangle = |\chi_i \chi_j \dots \chi_{c-1} \chi_{c+1} \dots \chi_N\rangle$

(N+1) state (electron is attached to  $\chi_r$ ):  $|\Psi_0\rangle = |\chi_i \chi_j \dots \chi_N \chi_r\rangle$

# Koopmans' theorem

Koopmans' theorem:

the occupied-orbital energy  $\varepsilon_c$  is equal to a (minus) ionization potential (IP) from orbital  $\chi_c$ , in a *frozen orbital approximation*

$$\text{IP} = {}^N E_c - {}^N E_0 = -\varepsilon_c > 0$$

Usually, occupied orbitals  $\varepsilon_c$  are negative  $\rightarrow$  Ionization potentials are positive

the virtual-orbital energy  $\varepsilon_r$  is equal to a (minus) electron affinity (EA) for adding an electron to orbital  $\chi_r$ , in a *frozen orbital approximation*

$$\text{EA} = {}^N E_0 - {}^{N+1} E^r = -\varepsilon_r < 0$$

Usually, virtual orbitals  $\varepsilon_r$  are positive  $\rightarrow$  electron affinities are negative

**Frozen orbital approximation:** orbitals do not change when electron is removed or added

# Koopmans' theorem: proof

Consider ionization process in a **frozen orbital approximation**:

$${}^N E_0 = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} (\langle ij | ij \rangle - \langle ij | ji \rangle)$$

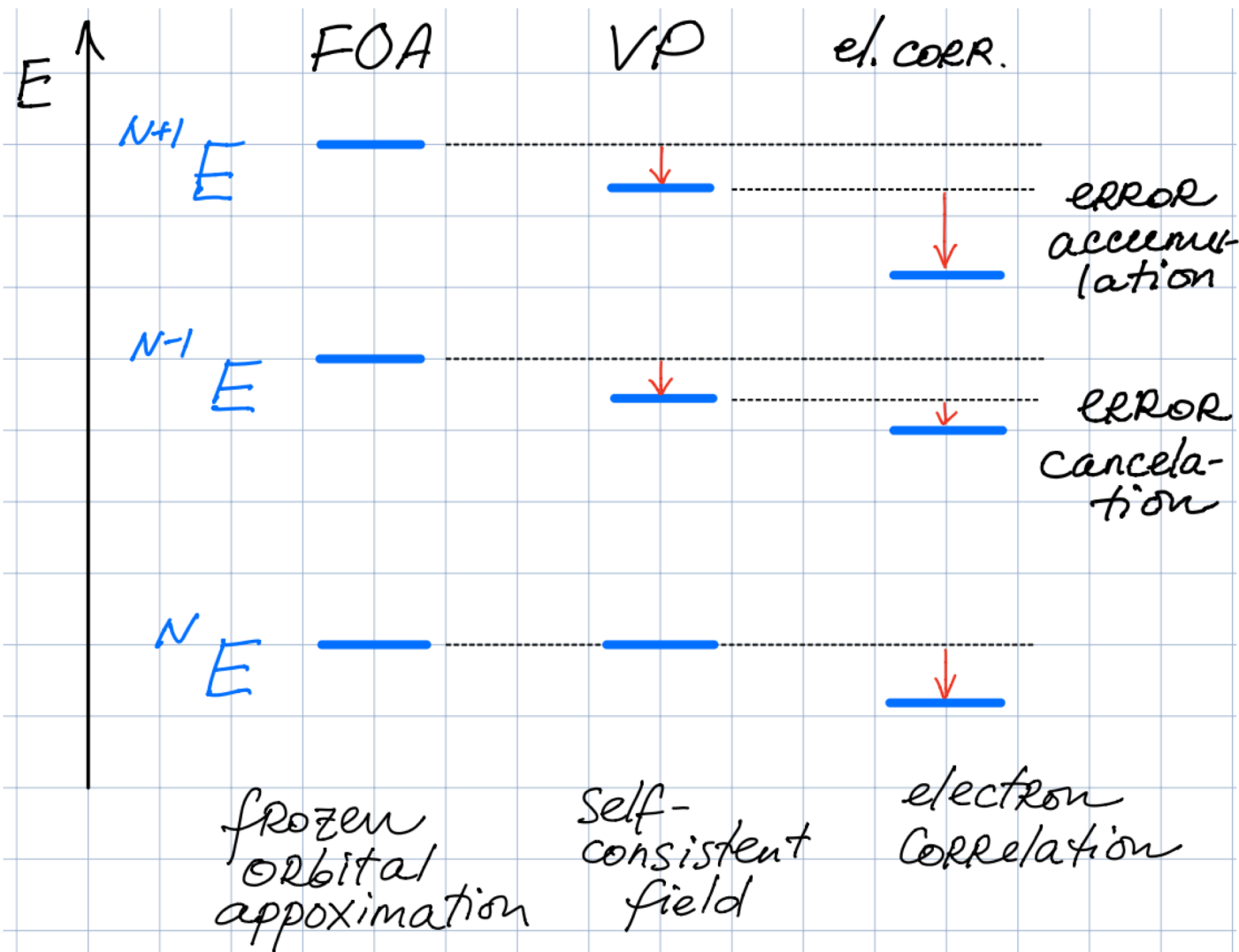
$${}^{N-1} E_c = \sum_{i \neq c} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i \neq c} \sum_{j \neq c} (\langle ij | ij \rangle - \langle ij | ji \rangle)$$

$$\begin{aligned} IP = {}^{N-1} E_c - {}^N E_0 &= - \langle c | \hat{h} | c \rangle - \frac{1}{2} \sum_i (\langle ic | ic \rangle - \langle ic | ci \rangle) - \frac{1}{2} \sum_j (\langle cj | cj \rangle - \langle cj | jc \rangle) = \\ &= - \langle c | \hat{h} | c \rangle - \sum_i (\langle ic | ic \rangle - \langle ic | ci \rangle) = -\varepsilon \end{aligned}$$

Similar proof for electron affinities



# Is Koopmans' theorem accurate?



- $N$  state ( ${}^N E$ ) is variationally optimized
- Using variational principle (SCF) lowers energies of  $N+1$  and  $N-1$  states  $\rightarrow$  relaxation
- Electron correlation further lowers (stabilizes) energies of all states
- Electron correlation is proportional to the number of electrons, i.e. is the biggest for  $N+1$  and the smallest for  $N-1$
- Correlation effects cancel relaxation error for ( $N-1$ ) state (IP) but add to the relaxation error for ( $N+1$ ) state (EA)  $\rightarrow$
- **Koopmans' IPs are reasonably accurate**
- **Koopmans' EA are pretty bad**

# Brillouin's theorem

Brillouin's theorem: Singly excited determinants  $|\Psi_i^a\rangle$  do not interact directly with a reference HF determinant  $|\Psi_0\rangle$  :

$$\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = 0$$

Proof: Similarly to how we got  $\langle \Psi_0 | \hat{H} | \Psi_0 \rangle$  (HF energy expression),

$$\langle \Psi_0 | \hat{H} | \Psi_i^a \rangle = \langle i | \hat{h} | a \rangle + \sum_j (\langle ij | aj \rangle - \langle ij | ja \rangle)$$

But  $\langle i | \hat{h} | a \rangle + \sum_j (\langle ij | aj \rangle - \langle ij | ja \rangle) = \langle i | \hat{f} | a \rangle$

$$\langle i | \hat{f} | a \rangle = \varepsilon_a \langle i | a \rangle = 0$$

Physical meaning:

Singly-excited determinants give the first variation to orbitals  $\delta\Phi$

The HF ground state is stable with respect to linear variations in orbitals  $\rightarrow$  it cannot be improved by mixing it with singly excited determinants