

CHM 673

Lecture 5: Hartree-Fock model, part 2

Suggested reading:

Chapter 2.2, 3.1, 3.2 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**.

This is the same thing as to assume *that each electron only feels an average charge distribution due to other electrons*



Douglas
Hartree

Vladimir
Fock



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!

Hartee-Fock energy expression

$$\hat{H}_e = \sum_i \hat{h}(i) + \sum_{i < j} \hat{v}(i, j) + \hat{V}_{nn}$$

Electronic Hamiltonian

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

one-electron operator

$$\hat{v}(i, j) = \frac{1}{r_{ij}}$$

two-electron operator

$$\text{HF energy: } E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle = \sum_i^{N_{elec}} h_i + \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (J_{ij} - K_{ij})$$

Each electron contributes a *one-electron integral*

$$\langle i | \hat{h} | i \rangle = \int dx_1 \chi_i^*(x_1) \hat{h}(r_1) \chi_i(x_1)$$

This looks like the expectation (average) value of the operator \hat{h} for an electron in orbital χ_i

Recall \hat{h} contains electron kinetic energy and potential of attraction to all nuclei

Sum over all (occupied by electrons) orbitals i gets the total electronic kinetic energy and attraction to nuclei

Hartee-Fock energy expression

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Each pair of electrons (in orbitals i and j) has a *Coulomb integral*:

$$J_{ij} = \langle ij | ij \rangle = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1) \chi_j(x_2)$$

Probability electron 1 in orbital i is located at x_1

Probability electron 2 in orbital j is located at x_2

Coulomb repulsion between electron at x_1 and electron at x_2

This integral represents the Coulomb repulsion between electron 1 in orbital i and electron 2 in orbital j

Hartee-Fock energy expression

$$\hat{H}_e = \sum_i \hat{h}(i) + \sum_{i < j} \hat{\nu}(i, j) + \hat{V}_{nn}$$

Electronic Hamiltonian

$$\hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

one-electron operator

$$\hat{\nu}(i, j) = \frac{1}{r_{ij}}$$

two-electron operator

$$\text{HF energy: } E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle = \sum_i^{Nelec} h_i + \frac{1}{2} \sum_i^{Nelec} \sum_j^{Nelec} (J_{ij} - K_{ij})$$

Each pair of electrons (in orbitals i and j) also has an *exchange integral*:

$$K_{ij} = \langle ij | ji \rangle = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_j(x_1) \chi_i(x_2)$$

This is like the Coulomb integral except two of the orbital indices have been exchanged:

$$J_{ij} = \langle ij | ij \rangle = \int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1) \chi_j(x_2)$$

No classical analogy... Physical meaning: an electron repels another electron of the same spin (so called Fermi hole). This integral is a consequence of Slater determinant (antisymmetrized) wavefunction

Coulomb and exchange operators

$$E_{HF} = \langle \Psi_{SD} | \hat{H}_{el} | \Psi_{SD} \rangle = \sum_i^{N_{elec}} h_i + \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (J_{ij} - K_{ij}) = \\ \sum_i^{N_{elec}} \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \sum_i^{N_{elec}} \sum_j^{N_{elec}} (\langle \chi_j | \hat{J}_i | \chi_j \rangle - \langle \chi_j | \hat{K}_i | \chi_j \rangle)$$

Coulomb operator $|\hat{J}_i | \chi_j(2) \rangle = \int d1 \chi_i^*(1) \frac{1}{r_{12}} \chi_i(1) \chi_j(2) = \left\langle \chi_i(1) \left| \frac{1}{r_{12}} \right| \chi_i(1) \right\rangle |\chi_j(2)\rangle$
Average local potential for an electron (2) in orbital χ_j due to charge distribution of an electron occupying χ_i

Exchange operator $|\hat{K}_i | \chi_j(2) \rangle = \int d1 \chi_i^*(1) \frac{1}{r_{12}} \chi_j(1) \chi_i(2) = \left\langle \chi_i(1) \left| \frac{1}{r_{12}} \right| \chi_j(1) \right\rangle |\chi_i(2)\rangle$

No classical analogue. A repulsive potential for an electron (2) due to electron (1) if they are of the same spin
(otherwise $\left\langle \chi_i(1) \left| \frac{1}{r_{12}} \right| \chi_j(1) \right\rangle = \left\langle \psi_i(1) \left| \frac{1}{r_{12}} \right| \psi_j(1) \right\rangle \langle s_i(1) | s_j(1) \rangle = 0$)

Step 2: Derivation of Hartree-Fock equations

HF energy depends on spin-orbitals.

How to find them? -> **Variational principle!**

Find minimum of energy by varying spin-orbitals:

$$\delta E_{HF} \left[\{ \chi_i \} \right] = 0$$

How to compute δE ?

Consider **trial function** Φ .

$E[\Phi]$ is **functional** of Φ :

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle$$

Vary Φ by an arbitrary small amount: $\Phi \rightarrow \Phi + \delta\Phi$

second-order in $\delta\Phi$

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

the first variation in E , includes all terms that are linear (first-order) in the variation $\delta\Phi$

Variation operator δ is similar to differential operator:

$$\delta E = \delta \langle \Phi | \hat{H} | \Phi \rangle = \langle \delta\Phi | \hat{H} | \Phi \rangle + \langle \Phi | \hat{H} | \delta\Phi \rangle$$

Lagrangian for HF energy

We are looking for Φ for which $E[\Phi]$ is a minimum (more generally, $E[\Phi]$ is stationary with respect to any small variation in Φ), i.e.

$$\delta E = \delta \langle \Phi | \hat{H} | \Phi \rangle = \langle \delta \Phi | \hat{H} | \Phi \rangle + \langle \Phi | \hat{H} | \delta \Phi \rangle = 0$$

Constraint: spin-orbitals should remain orthonormal, i.e. $\langle \chi_i | \chi_j \rangle = \delta_{ij}$

Consider functional $L[\{\chi_i\}] = E_{HF}[\{\chi_i\}] - \sum_{ij}^{N_{elec}} \lambda_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij})$

And search for $\delta L[\{\chi_i\}] = 0$

$$\delta L[\{\chi_i\}] = \delta E_{HF}[\{\chi_i\}] - \delta \sum_{ij}^{N_{elec}} \lambda_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

$$\sum_{ij}^{N_{elec}} \lambda_{ij} \delta(\langle \chi_i | \chi_j \rangle - \delta_{ij}) = \sum_{ij}^{N_{elec}} \lambda_{ij} (\langle \delta \chi_i | \chi_j \rangle + \langle \chi_i | \delta \chi_j \rangle)$$

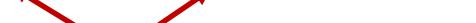
Variation of HF energy

$$\delta E_{HF}[\{\chi_i\}] = \sum_i^{N_{elec}} \delta \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \sum_{ij}^{N_{elec}} (\delta \langle \chi_j | \hat{j}_i | \chi_j \rangle - \delta \langle \chi_j | \hat{K}_i | \chi_j \rangle) =$$

$$\delta \langle \chi_i | \hat{h}_i | \chi_i \rangle = \langle \delta \chi_i | \hat{h}_i | \chi_i \rangle + \langle \chi_i | \hat{h}_i | \delta \chi_i \rangle$$

$$\delta\langle\chi_j|\hat{J}_i|\chi_j\rangle = \delta\langle\chi_i\chi_j|\chi_i\chi_j\rangle = \langle\delta\chi_i\chi_j|\chi_i\chi_j\rangle + \langle\chi_i\delta\chi_j|\chi_i\chi_j\rangle + \langle\chi_i\chi_j|\delta\chi_i\chi_j\rangle + \langle\chi_i\chi_j|\chi_i\delta\chi_j\rangle =$$

$$\langle\delta\chi_i|\hat{J}_j|\chi_i\rangle + \langle\delta\chi_j|\hat{J}_i|\chi_j\rangle + \langle\chi_i|\hat{J}_j|\delta\chi_i\rangle + \langle\chi_j|\hat{J}_i|\delta\chi_j\rangle = 2\langle\delta\chi_i|\hat{J}_j|\chi_i\rangle + 2\langle\chi_i|\hat{J}_j|\delta\chi_i\rangle$$


 same same

$$= \sum_i^{Nelec} (\langle \delta\chi_i | \hat{h}_i | \chi_i \rangle + \langle \chi_i | \hat{h}_i | \delta\chi_i \rangle) + \sum_{ij}^{Nelec} (\langle \delta\chi_i | \hat{J}_j - \hat{K}_j | \chi_i \rangle + \langle \chi_i | \hat{J}_j - \hat{K}_j | \delta\chi_i \rangle)$$

Variation of HF energy

$$\delta E_{HF}[\{\chi_i\}] = \sum_i^{N_{elec}} (\langle \delta\chi_i | \hat{h}_i | \chi_i \rangle + \langle \chi_i | \hat{h}_i | \delta\chi_i \rangle) + \sum_{ij}^{N_{elec}} (\langle \delta\chi_i | \hat{J}_j - \hat{K}_j | \chi_i \rangle + \langle \chi_i | \hat{J}_j - \hat{K}_j | \delta\chi_i \rangle) =$$

$$= \sum_i^{N_{elec}} (\langle \delta\chi_i | \hat{f}_i | \chi_i \rangle + \langle \chi_i | \hat{f}_i | \delta\chi_i \rangle)$$

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

$$\delta L[\{\chi_i\}] = \sum_i^{N_{elec}} (\langle \delta\chi_i | \hat{f}_i | \chi_i \rangle + \langle \chi_i | \hat{f}_i | \delta\chi_i \rangle) - \sum_{ij}^{N_{elec}} \lambda_{ij} (\langle \delta\chi_i | \chi_j \rangle + \langle \chi_i | \delta\chi_j \rangle) =$$

$$\sum_i^{N_{elec}} \langle \delta\chi_i | \hat{f}_i | \chi_i \rangle - \sum_{ij}^{N_{elec}} \lambda_{ij} \langle \delta\chi_i | \chi_j \rangle + \left[\sum_i^{N_{elec}} \langle \delta\chi_i | \hat{f}_i | \chi_i \rangle^* - \sum_{ij}^{N_{elec}} \lambda_{ji} \langle \delta\chi_i | \chi_j \rangle^* \right] =$$

$\langle \chi_i | \delta\chi_j \rangle = \langle \delta\chi_j | \chi_i \rangle^*$
 $\langle \chi_i | \hat{f}_i | \delta\chi_i \rangle = \langle \delta\chi_i | \hat{f}_i | \chi_i \rangle^*$
 $\lambda_{ij} = \lambda_{ji}^* \text{ Hermitian matrix}$

$$\sum_i^{N_{elec}} \langle \delta\chi_i | \hat{f}_i | \chi_i \rangle - \sum_{ij}^{N_{elec}} \lambda_{ij} \langle \delta\chi_i | \chi_j \rangle + \left[\sum_i^{N_{elec}} \langle \delta\chi_i | \hat{f}_i | \chi_i \rangle - \sum_{ij}^{N_{elec}} \lambda_{ij} \langle \delta\chi_i | \chi_j \rangle \right]^* = 0$$

← complex conjugate (c.c.)

Hartree-Fock equations

$$\delta L[\{\chi_i\}] = \sum_i^{N_{elec}} \langle \delta \chi_i | \hat{f}_i | \chi_i \rangle - \sum_{ij}^{N_{elec}} \lambda_{ij} \langle \delta \chi_i | \chi_j \rangle + c.c. = 0$$

Any variation of either $\langle \delta \chi |$ or $\langle \delta \chi |^*$ should make $\delta L = 0$. It means that

$$\hat{f}_i |\chi_i\rangle = \sum_j^{N_{elec}} \lambda_{ij} |\chi_j\rangle \quad \text{This is } N \text{ coupled equations } (\lambda_{ij} \text{ mixes } i\text{th and } j\text{th states})$$

We can find an unitary transformation U that makes λ_{ij} matrix diagonal,
i.e. $\lambda_{ij} = 0$ and $\lambda_{ii} = \varepsilon_i$:

$$\chi_i' = \sum_k \chi_k U_{ki}$$

Unitary transformation: $UU^+ = 1$ or $U^{-1} = U^+$
inverse is equal to conjugate transpose

In a new set of spin-orbitals, $\hat{f}_i |\chi_i'\rangle = \varepsilon_i |\chi_i'\rangle$ Hartree-Fock equations

A special set of spin-orbitals in which the Lagrange multiplier matrix is diagonal is called canonical molecular orbitals

Other sets of orbitals

Unitary transformation U that diagonalizes λ_{ij} matrix of Lagrange multipliers

$$\chi_i' = \sum_k \chi_k U_{ki}$$

produces **canonical molecular orbitals**,

those are solutions of **canonical HF equations** $\hat{f}_i |\chi_i'\rangle = \varepsilon_i |\chi_i'\rangle$

Note that since $|\Phi'| = |\Phi U|$, $\det(AB) = \det(A)\det(B)$, and $\det(U) = 1$,
the unitary transformation does not change the total wave function Φ

Then, different unitary transformation can produce other sets of orbitals, e.g.

- Localized orbitals (spatially localized)
- Natural orbitals (eigenvalues of the density matrix)

However, orbital energies are meaningful only for canonical molecular orbitals!

Hartree-Fock equations

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

This is a pseudo-eigenvalue problem: the Fock operator \hat{f}_i depends on solutions (the occupied spin-orbitals χ_i)!

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

Coulomb operator $|\hat{J}_i | \chi_j(2) \rangle = \langle \chi_i(1) | \frac{1}{r_{12}} | \chi_i(1) \rangle | \chi_j(2) \rangle$

Exchange operator $|\hat{K}_i | \chi_j(2) \rangle = \langle \chi_i(1) | \frac{1}{r_{12}} | \chi_j(1) \rangle | \chi_i(2) \rangle$

How to solve it? Iteratively!

Hartree-Fock procedure:

1. Make an initial guess of $2K$ spin-orbitals $\{\chi_i^{(0)}\}$
2. Calculate Fock operator for each spin-orbital $\hat{f}_i = \hat{h}_i + \sum_j^{N_{elec}} (\hat{J}_j - \hat{K}_j)$
3. Solve $\hat{f}_i |\chi_i\rangle = \varepsilon_i |\chi_i\rangle$, obtain a new set of spin-orbitals $\{\chi_i^{(1)}\}$
4. Repeat until self-consistency, i.e. until $\{\chi_i^{(k+1)}\} = \{\chi_i^{(k)}\}$

Hartree-Fock (HF) \equiv
Self Consistent Field (SCF)

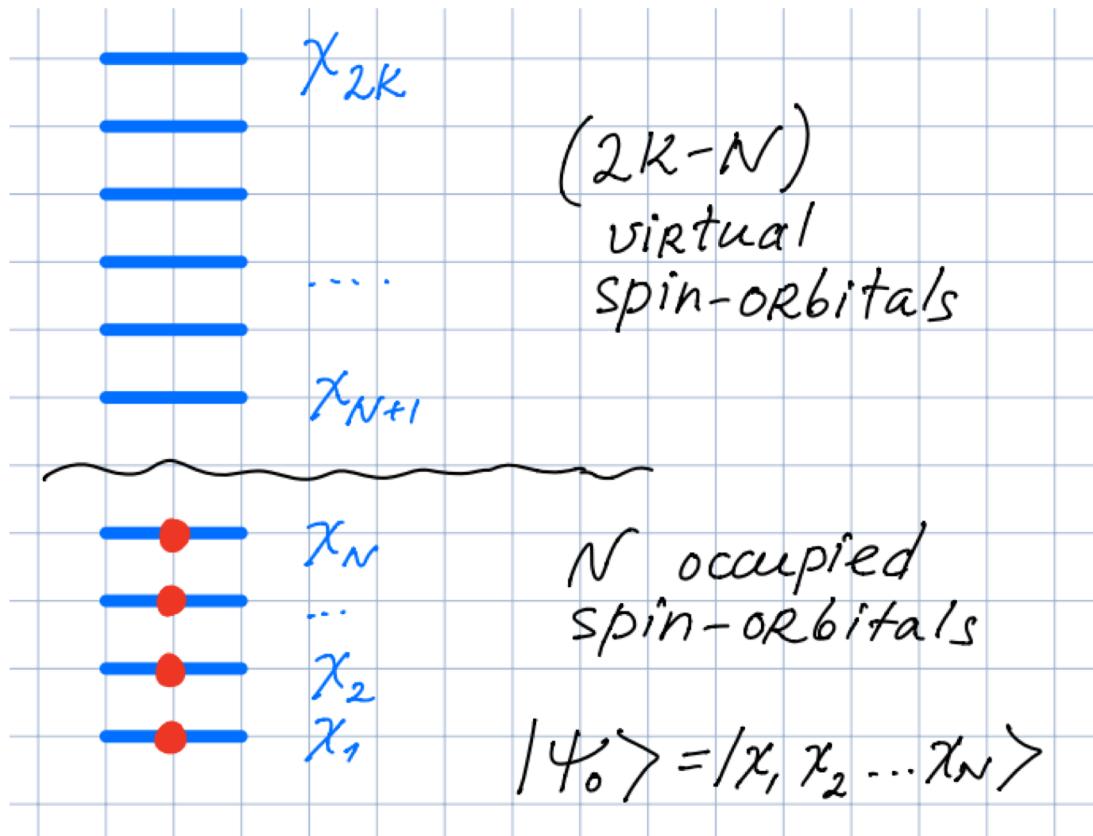
Hartree-Fock solutions

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.

Hartree-Fock solutions

$\hat{f}_i|\chi_i\rangle = \varepsilon_i|\chi_i\rangle$ 2K orthonormal spin-orbitals $\{\chi_i\}$ with orbital energies $\{\varepsilon_i\}$ is produced

Q: Is the Hartree-Fock ground state wave function the exact solution to the system?

Q: How to improve it?

The exact solution to N-electron problem

Given N electrons and 2K spin orbitals

The best solution is to combine together **all possible valid determinants** $\Psi = \sum_i c_i \Phi_i$ and use the variational principle to minimize the ground state energy.

This model is called **Full Configuration Interaction (FCI)**

FCI is the exact solution of electronic SE in a given spin-orbital basis (with given K)

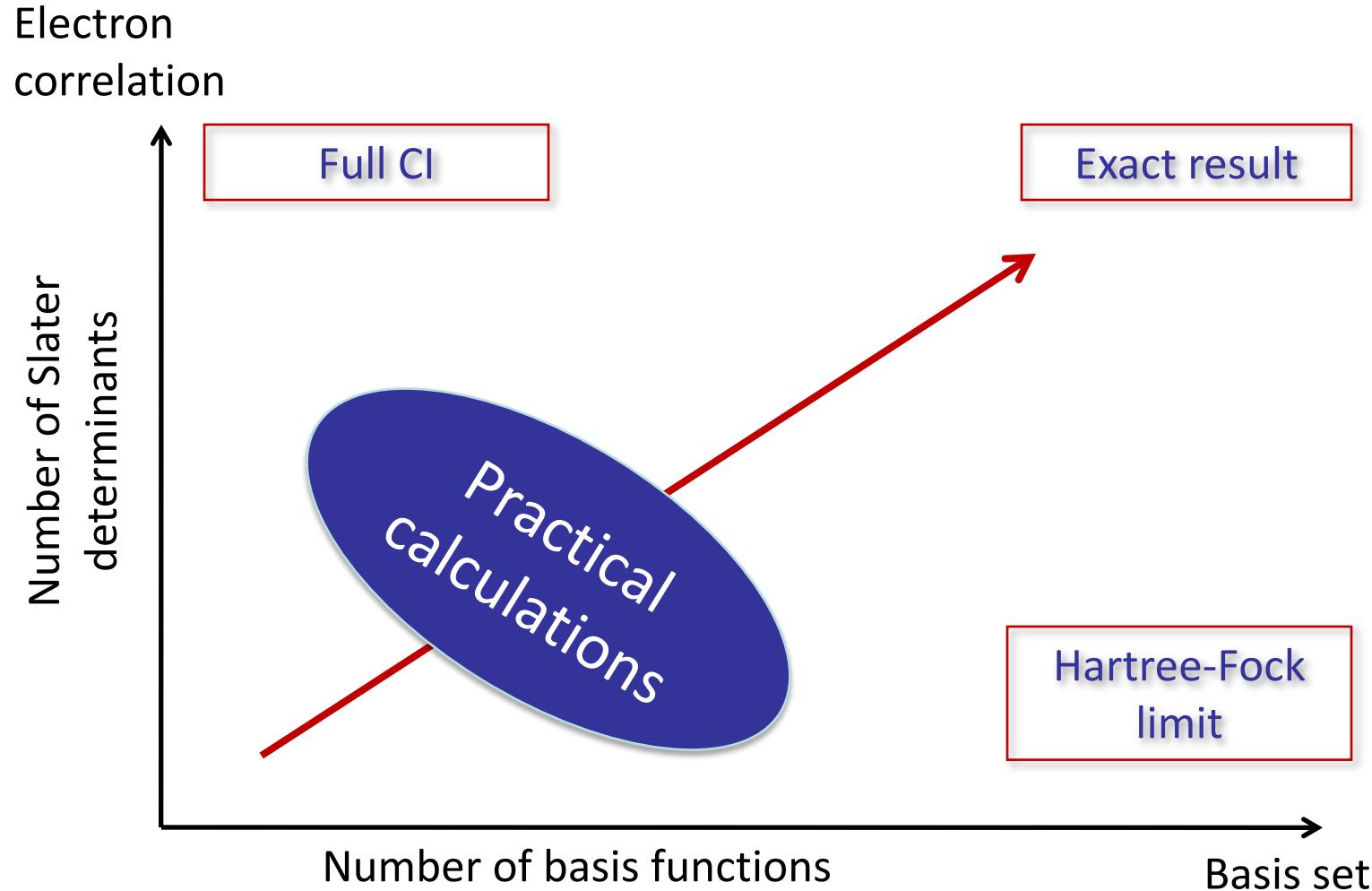
How big is a FCI wave function? The number of possible SDs is given as the number of times we can draw N spin-orbitals from a pool of 2K:

$$\# \text{configurations} = C_{2K}^N = \frac{(2K)!}{N! (2K - N)!} \approx 10^N$$

Today largest computations can deal with $\sim 10^9$ configurations

N	$2K$	C_{2K}^N
2	10	45
4	20	4845
6	30	593775
8	40	$7.7 \cdot 10^7$
10	50	$1.0 \cdot 10^{10}$
20	100	$5.4 \cdot 10^{20}$

Theoretical model chemistries (John Pople)



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

Selection of a theoretical model

Ideally, the model should be:

- Feasible when applied to the problem (scaling & timing)
- Sufficiently accurate (for meaningful results)
- Predictive (no experimental input of any sort, i.e. electrons and nuclei in, energies out. A “*black-box*” tool)
- Size-consistent (the energy of a set of identical noninteracting molecules should be proportional to their number)
- Variational