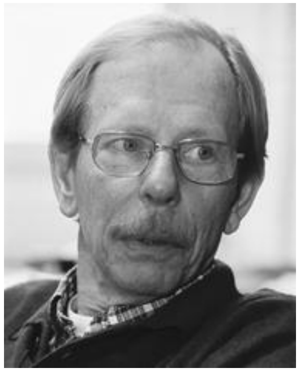

B. Roos


C. C. J. Roothaan


V. A. Fok


W. Heitler


W. Pauli


P.A.M. Dirac

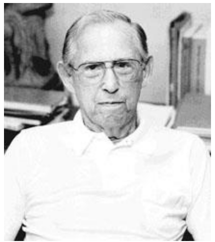

J. Čížek

Quantum Mechanics

Key Concepts, Methods and Machinery

- lecture 2 -


J. A. Pople


M. S. Plesset


W. Kohn


E. Hückel


J. C. Slater


W. Heisenberg


N. Bohr


M. Born


E. Schrödinger

and many other heroes…

Six postulates in QM

I. On quantum mechanical state

The state of the system is described by the *wavefunction* $\Psi = \Psi(r,t)$, which depends on the coordinates of particle *r* at time t. Wavefunction are in general complex functions of real variables, thus $\Psi^*(r,t)$denotes the complex conjugate of Ψ

$$P(r,t) = \Psi^*(r,t)\ \Psi(x,t)\ dV = |\Psi(r,t)|^2\ dV$$ **(probabilistic interpretation)**

II. On operator representation of mechanical quantities

The mechanical quantities that describe the particle (energy, momentum, angular momentum etc.) **are represented by linear operators acting on a *wavefunction***

The operator of the potential energy

The total energy operator, Hamiltonian: $\hat{H} = \hat{T} + \hat{V}$

The operator of the kinetic energy

Dirac notation:

$$\int \psi^* \hat{A} \phi d\tau \equiv \langle \psi | \hat{A} | \phi \rangle$$

Matrix element of the operator $\hat{A}$

$$\int \psi^* \phi d\tau \equiv \langle \psi | \phi \rangle$$

Scalar product of two wavefunctions

III. On time evolution of the state

The time evolution of the wave function is given by the equation:

$$\hat{H}\Psi(r,t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t}$$

Six postulates in QM

IV. On interpretation of experimental measurements – *not discussed here*

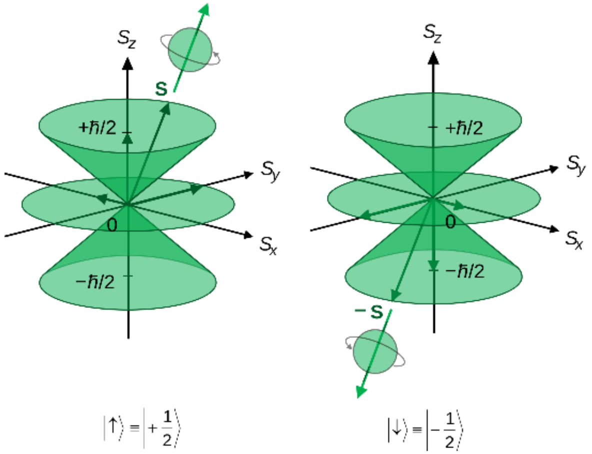
V. Spin angular momentum *(in non-relativistic formulation of QM)*

$$\hat{S}^2|\alpha\rangle = s(s+1)\hbar^2|\alpha\rangle$$

$$\hat{S}_z|\alpha\rangle = m_s\hbar|\alpha\rangle; \quad |\alpha\rangle \equiv |1/2\rangle$$

$$\hat{S}_z|\beta\rangle = m_s\hbar|\beta\rangle; \quad |\beta\rangle \equiv |-1/2\rangle$$

where the spin magnetic quantum number m_s = -s, -s+1,...,s



VI. On the permutational symmetry

$$\Psi(1,2,\ldots,i,\ldots,j,\ldots,N) = -\Psi(1,2,\ldots,j,\ldots,i,\ldots,N)$$

-fermions (electrons, ...) – non-integer spin

$$\Psi(1,2,\ldots,i,\ldots,j,\ldots,N) = \Psi(1,2,\ldots,j,\ldots,i,\ldots,N)$$

-bosons - integer spin

Probability density of finding **two identical fermions** in the same position and with the same spin coordinate equals to zero

Fermi correlation (Fermi hole)

Pauli exclusion principle

Quantum mechanics in Chemistry

- Let the **molecular system** under study contain atomic nuclei ($\boldsymbol{q}_{\text{nuclei}}$), electrons ($\boldsymbol{q}_{\text{electrons}}$) and possibly external fields.

- The key equation in quantum mechanics is the *nonrelativistic* Schrödinger equation:

$$\boxed{\hat{H}(\mathbf{q},t)\Psi(\mathbf{q},t) = i\hbar\frac{\partial\Psi(\mathbf{q},t)}{\partial t}}\ *$$

- The vector **q** collects the spatial and spin coordinates of all particles (nuclei and electrons) in the molecular system.

* *Postulate III.*

The electronic Schrödinger equation

$$\hat{H}(\mathbf{q},t)\Psi(\mathbf{q},t) = i\hbar\frac{\partial\Psi(\mathbf{q},t)}{\partial t}$$

Let the Hamiltonian be time-independent

$$\Psi(\mathbf{q},t) = \Psi(\mathbf{q})\exp\left(\frac{E_{\text{tot}}}{i\hbar}t\right); \qquad \hat{H}(\mathbf{q})\Psi(\mathbf{q}) = E_{\text{tot}}\Psi(\mathbf{q})$$

Schrödinger equation for stationary states

Born-Oppenheimer approximation

$$\Psi(\mathbf{q}) \approx \Psi(\mathbf{q}_{\text{nuclei}})\Psi(\mathbf{q}_{\text{electrons}})$$

The electronic Schrödinger equation

$$\Psi(\mathbf{q}) \approx \Psi(\mathbf{q}_{\text{nuclei}})\Psi(\mathbf{q}_{\text{electrons}})$$

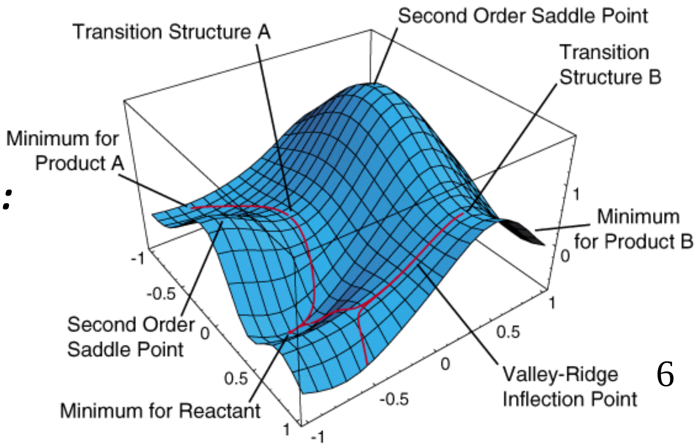
$$\downarrow$$

Nuclear-motion Schrödinger equation

$$\begin{cases} \hat{H}(\mathbf{q}) = \hat{T}_{\text{nuclei}} + \hat{H}_{\text{electrons}} \\ \left(\hat{T}_{\text{nuclei}} + E\right)\Psi(\mathbf{q}_{\text{nuclei}}) = E_{\text{tot}}\Psi(\mathbf{q}_{\text{nuclei}}) \\ \hat{H}_{\text{electrons}}\Psi(\mathbf{q}_{\text{electrons}}) = E\Psi(\mathbf{q}_{\text{electrons}}) \end{cases}$$

electronic Schrödinger equation

The concept of potential energy hypersurfaces (of dimension 3N-6):
the energy of a molecule as a function of its geometry



The Hamiltonian *(spin-dependent terms not considered)*

$$\hat{H} = \underbrace{-\sum_k \frac{\hbar^2}{2m_k}\Delta_k}_{\hat{T}_{nuclei}} \underbrace{\left[\underbrace{-\sum_i \frac{\hbar^2}{2m_e}\Delta_i}_{\hat{T}_{electrons}} \overbrace{\underbrace{-\sum_i\sum_k \frac{e^2 Z_k}{r_{ik}}}_{\hat{V}_{e-n}} \underbrace{+\sum_{i<j}\frac{e^2}{r_{ij}}}_{\hat{V}_{e-e}} \underbrace{+\sum_{k<l}\frac{e^2 Z_k Z_l}{r_{kl}}}_{\hat{V}_{n-n}}\right] \frac{1}{4\pi\varepsilon_0}}^{\text{Coulombic potential}}}_{\hat{H}_{electrons}}$$

k,l – nuclei

i,j – electrons

$$\hat{H}_{electrons} = \sum_i \hat{h}_{one-electron,i} + \sum_{i<j} \hat{h}_{two-electron,ij}$$

*Due to this term – **analytical solution** of SE is **unkonwn***

*Thus, the **numerical** solution of the **electronic** Schrödinger equation*

$$\hat{H}_{electrons}\Psi\left(\mathbf{q}_{electrons}\right) = E\Psi\left(\mathbf{q}_{electrons}\right)$$

through a favorite electronic-structure (quantum-chemical, QC) method.

QC methods are also devised to optimize the spatial configuration of nuclei, leading to E minimization - geometry optimization.

$$\boxed{\hat{H}_{electrons}\Psi\left(\mathbf{q}_{electrons}\right) = E\Psi\left(\mathbf{q}_{electrons}\right)}$$

$$\downarrow$$

$$\boxed{\frac{\left\langle \Psi \,|\, \hat{H}_{electrons} \,|\, \Psi \right\rangle}{\left\langle \Psi \,|\, \Psi \right\rangle} = E}$$

$$\Big\downarrow \quad if\ \left\langle \Psi \,|\, \Psi \right\rangle = 1$$

$$\boxed{\sum_{i}\left\langle \Psi \,|\, \hat{h}_{one-electron,i} \,|\, \Psi \right\rangle + \sum_{i<j}\left\langle \Psi \,|\, \hat{h}_{two-electron,ij} \,|\, \Psi \right\rangle = E}$$

The Many Electron Wavefunction

A form for the **electronic wavefunction** that satisfies the permutational antisymmetry (postulate VI) is the **Slater determinant (SD) or a linear combination of SDs.**

SD for two-electron system

spinorbital

$$^3\Psi_{SD} = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\alpha(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix}$$

spatial component of one-electron wave function (**molecular orbital, MO**)

spin component of one-electron wave function

SD for *N*-electron system

$$\Psi_{SD} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

Symmetry and spin-adapted **SD** or **linear combination of SDs** **= configuration state function (CSF)**

$$\hat{S}^2\Psi_{CSF} = S(S+1)\hbar^2\Psi_{CSF}$$

$$\hat{S}_z\Psi_{CSF} = M_s\hbar\Psi_{CSF}$$

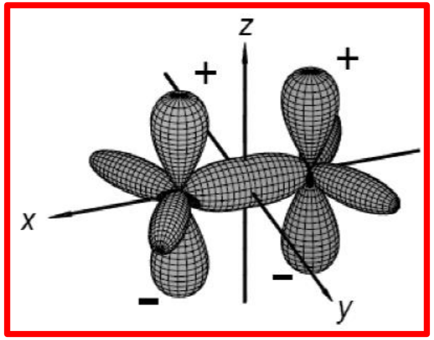
&

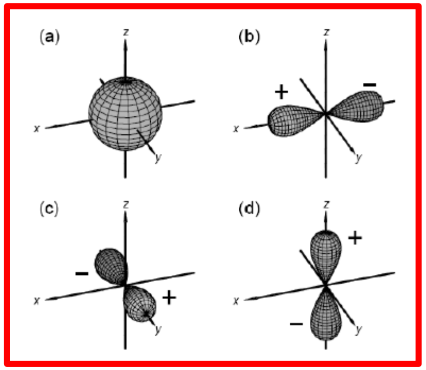
$$\hat{H}_{electrons}\Psi_{CSF} = E\Psi_{CSF}$$

Molecular orbitals, as a building elements in SD or CSF, are **constructed from atomic orbitals**:

Basis set

$$\psi_i = \sum_{a=1}^{N} c_{ai}\varphi_a$$ (Linear combination of atomic orbitals, **LCAO**)





Hydrogen-like (one-electron) AOs are always of the form:

$$\varphi(r,\theta,\vartheta)=R(r)Y_{lm}(\theta,\vartheta)$$ where *R(r)* is the radial component that decays exponentially with increasing distance from the nucleus $e^{-\zeta r}$

Since it is impossible to obtain analytic solutions in systems with two or more electrons, the exponential behavior of the AOs – **Slater-type orbitals (STOs)** – were hence the first to be used. They are characterized by an exponential factor in the radial part.

$$\varphi(r,\theta,\vartheta)=P(r)e^{-\alpha r}Y_{lm}(\theta,\vartheta)$$

STO

Drawback: difficulties associate with evaluating integrals that appear in the solution of electronic SE.

$$\varphi(r,\theta,\vartheta)=P(r)e^{-\alpha r^2}Y_{lm}(\theta,\vartheta)$$

or

$$\varphi(\alpha,l,m,n;x,y,z)=Ne^{-\alpha r^2}x^l y^m z^n$$

(Gauss-type orbital GTO)

Drawback: qualitatively incorrect behavior at the nucleus and in the asymptotic limit

Correction

Linear combination of several GTOs

$$\varphi_p^{CGTO}=\sum_a b_{ap}\varphi_a^{GTO}$$

contracted basis function

primitive

Segmented contraction scheme: each GTO contributes to exactly one CGTO

General contraction scheme: each GTO can contribute to more than one CGTO

Balanced basis set - *"More art than science"*

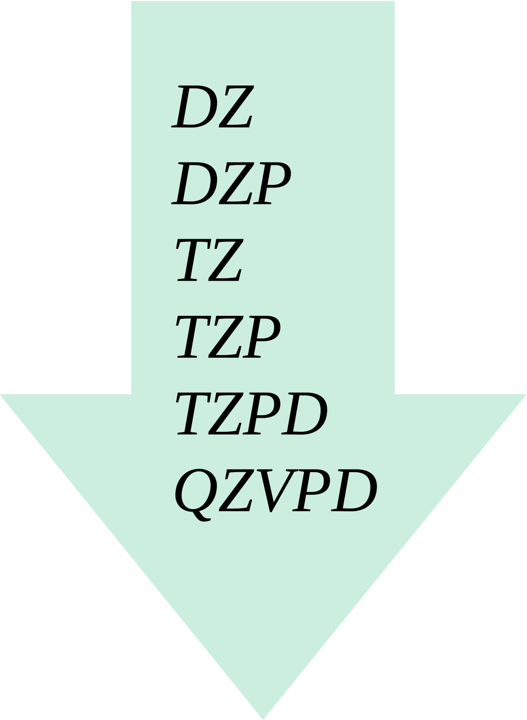
Minimal basis set -
(one STO or GTO or CGTO
for one core / valence AO)

Not very flexible

double-, triple-, quadruple n-tuple zeta basis sets

DZ, TZ, QZ …

More STO/GTO/CGTO functions describing one AO



DZ
DZP
TZ
TZP
TZPD
QZVPD

Different types of STO/GTO/CGTO functions, e.g.,

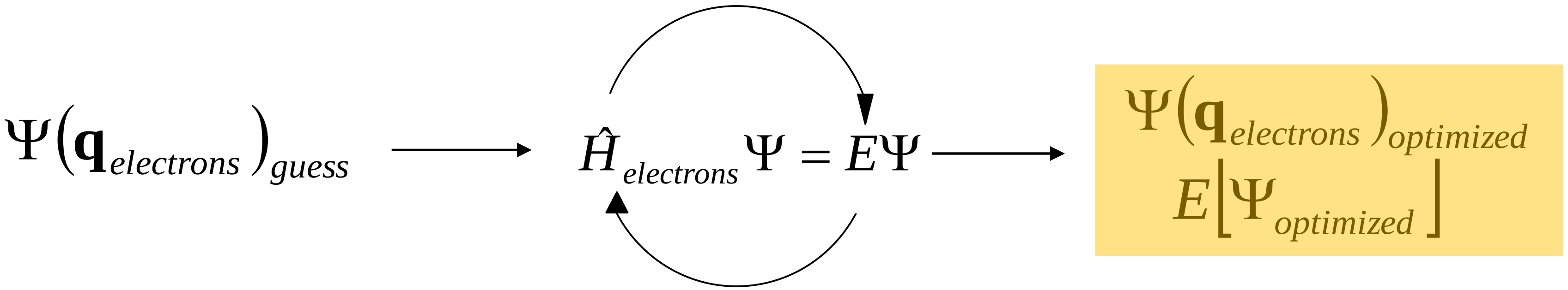
polarization functions (P):
e.g., for H atom add p functions
for Fe atom add f functions

diffuse functions (D)
(with small α in $\exp(-\alpha r^2)$ – allowing to describe electron density at larger distances from nucleus.
– suitable for anions, soft, large molecules, Rydberg states..

Infinite basis set - *N electrons in ∞ MOs – it requires ∞ AOs*
(**ideal but not realistic**)

Effective core potential: ***if the core electrons (MOs, AOs) are replaced with an approximate pseudopotential***

General strategies for solving the electronic SE



$$\Psi(\mathbf{q}_{electrons})_{guess} \longrightarrow \hat{H}_{electrons}\Psi = E\Psi \longrightarrow$$

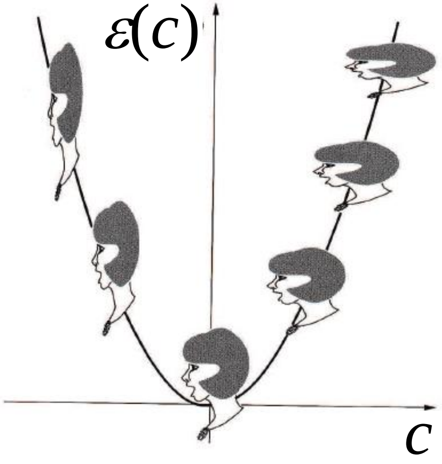
$$\Psi(\mathbf{q}_{electrons})_{optimized}$$

$$E\left[\Psi_{optimized}\right]$$

Optimize Ψ and obtain E through a variation

$$\varepsilon\left[\Psi_{guess}\right] = \frac{\left\langle \Psi_{guess} \,|\, \hat{H}_{electrons} \,|\, \Psi_{guess} \right\rangle}{\left\langle \Psi_{guess} \,|\, \Psi_{guess} \right\rangle} \geq E\left[\Psi_{opt}\right] = \frac{\left\langle \Psi_{opt} \,|\, \hat{H}_{electrons} \,|\, \Psi_{opt} \right\rangle}{\left\langle \Psi_{opt} \,|\, \Psi_{opt} \right\rangle}$$

$$\varepsilon\left[\Psi(c_0, c_1, \ldots, c_P)\right] \qquad \frac{\partial \varepsilon(c_0, c_1, .., c_P)}{\partial c_i} = 0$$



Optimize Ψ and obtain E through a perturbation

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{V}$$ Let λ be a perturbational parameter

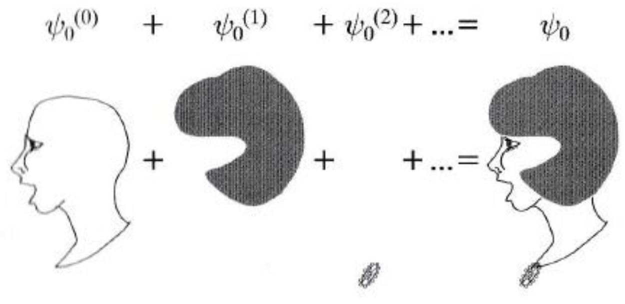
$0 \leq \lambda \leq 1$

We seek the solution in the form:

$$\Psi(\lambda) = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots$$

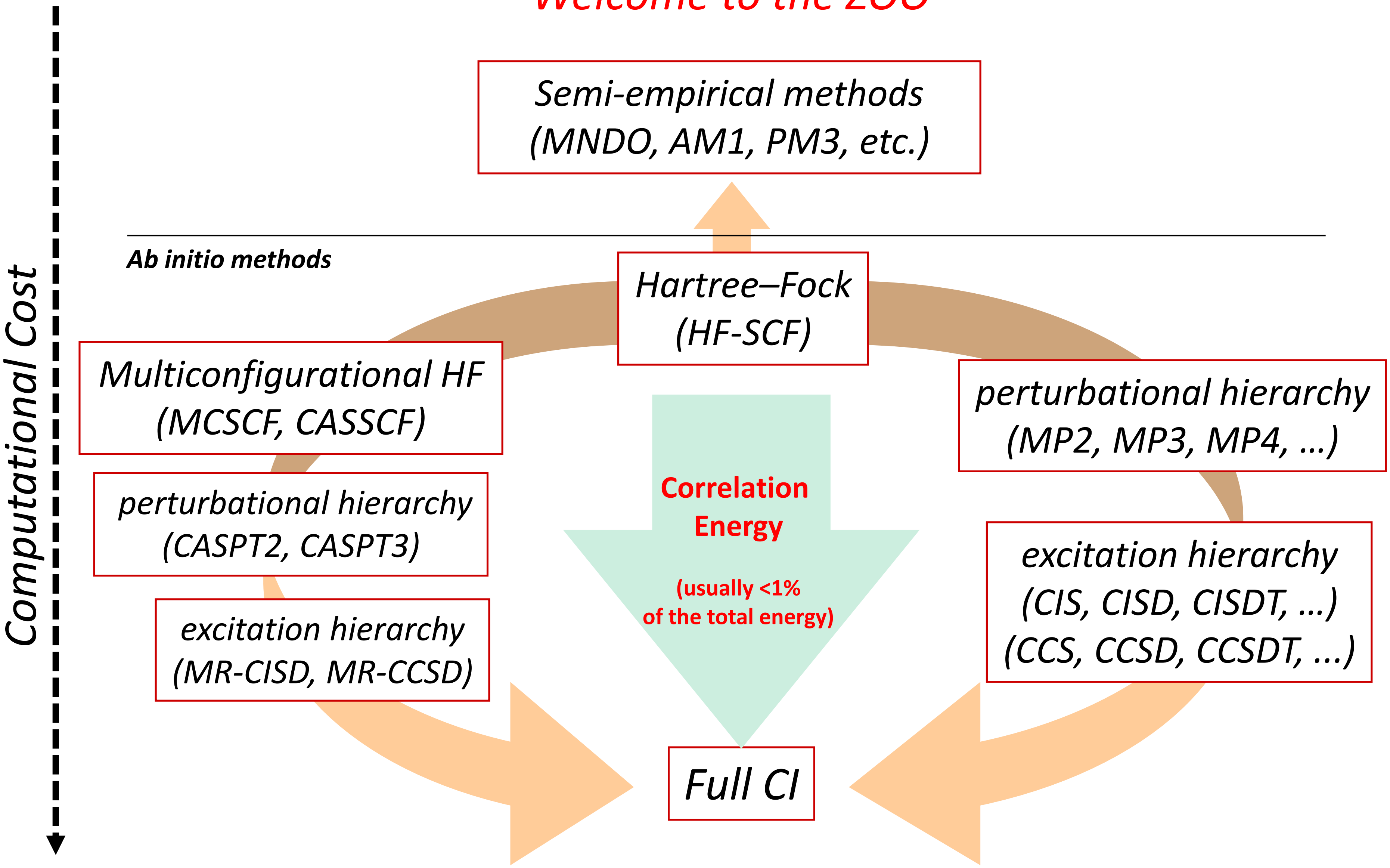
$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

Then, solving $\hat{H}(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda)$



Family of standard Wave-Function Theories (WFT) – General overview

Welcome to the ZOO



Computational Cost

Semi-empirical methods
(MNDO, AM1, PM3, etc.)

Ab initio methods

Hartree–Fock
(HF-SCF)

Multiconfigurational HF
(MCSCF, CASSCF)

perturbational hierarchy
(CASPT2, CASPT3)

excitation hierarchy
(MR-CISD, MR-CCSD)

perturbational hierarchy
(MP2, MP3, MP4, …)

excitation hierarchy
(CIS, CISD, CISDT, …)
(CCS, CCSD, CCSDT, …)

Correlation Energy

(usually <1%
of the total energy)

Full CI

Two contributions to correlation energy : *static* and *dynamic* correlation

Hartree–Fock (HF-SCF) method – the Gate to the realm of WFT

Equation from page 8:

$$E[\Psi]=\sum_i \left\langle \Psi \,|\, \hat h_{one-electron,i} \,|\, \Psi \right\rangle + \sum_{i<j} \left\langle \Psi \,|\, \hat h_{two-electron,ij} \,|\, \Psi \right\rangle$$

if $\Psi -$ ***1 Slater determinant***

spinorbitals

$$E=\sum_i \underset{\text{one-electron integrals}}{\underline{\left\langle \chi_i \,|\, \hat h_{one-electron,i} \,|\, \chi_i \right\rangle}} + \frac{1}{2}\sum_{i,j}\left\{ \underset{\text{two-electron Coulomb integrals}}{\underline{\left\langle \chi_i\chi_j \,|\, \hat h_{two-electron,ij} \,|\, \chi_i\chi_j \right\rangle}} - \underset{\text{two-electron exchange integrals}}{\underline{\left\langle \chi_i\chi_j \,|\, \hat h_{two-electron,ij} \,|\, \chi_j\chi_i \right\rangle}} \right\}$$

$$=\frac{1}{2}\sum_i \left\langle \chi_i \,|\, \hat J - \hat K \,|\, \chi_i \right\rangle$$

Condition: $\left\langle \chi_i \,|\, \chi_j \right\rangle = \delta_{ij}$ →

(inposed condition through
the method of Lagrange multipliers)

Fock equation

$$\hat F \chi_i = \varepsilon_i \chi_i$$

$$\underline{\hat F = \hat h_{one-electron} + \hat J - \hat K}$$

Fock operator = Fockian

MOs → LCAO ansatz
(and E minimized trough variational approach)

Working
Roothaan
equation:

Fock matrix
in the basis of AOs

orbital energy of j-th MO

AO-overlap matrix

Vector of LCAO coefficients
for j—th MO

$$\{\mathbf{F}(\mathbf{c}) - \varepsilon_i \mathbf{S}\}\mathbf{c}_i = 0 \longrightarrow \{\mathbf{F}'(\mathbf{c}) - \varepsilon_i \mathbf{1}\}\mathbf{c}'_i = 0$$

In fact, **F** depends on **c**:
see next page

thus, equations has to be solved
iteratively -> self-consistent field

Matrix element of the Fock matrix in the basis of AOs – explicit form (for the *restricted* Hartree-Fock method)

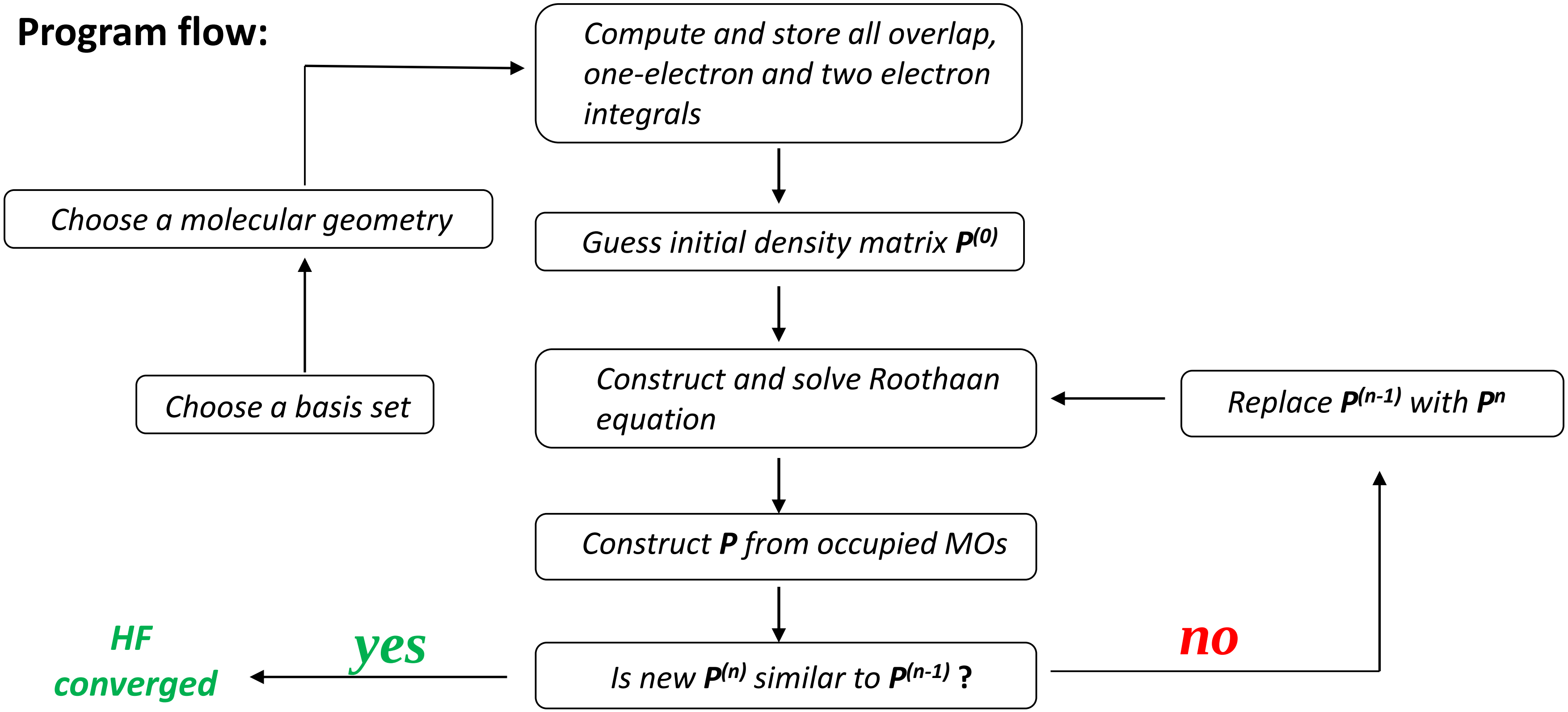
$$F_{pq} = \underbrace{\langle \varphi_p | \hat{T}_{el} | \varphi_q \rangle - \sum_{k}^{nuclei} \langle \varphi_p | \hat{V}_{e-n,k} | \varphi_q \rangle}_{h_{pq}} + \sum_{r,s} P_{rs} \left[\langle \varphi_p \varphi_r | \hat{V}_{e-e} | \varphi_q \varphi_s \rangle - \frac{1}{2} \langle \varphi_p \varphi_r | \hat{V}_{e-e} | \varphi_s \varphi_q \rangle \right]$$

AOs

density matrix = $2 \sum_{i}^{occupied} c_{ri} c_{si}$

This is what is optimized iteratively to get E minimized

Program flow:



Choose a basis set

Choose a molecular geometry

Compute and store all overlap, one-electron and two electron integrals

Guess initial density matrix ***P***$^{(0)}$

Construct and solve Roothaan equation

Construct ***P*** *from occupied MOs*

Is new ***P***$^{(n)}$ *similar to* ***P***$^{(n-1)}$ **?**

Replace ***P***$^{(n-1)}$ *with* ***P***^{n}

$$E_{HF} = \frac{1}{2} \sum_{pq}^{AO} P_{qp} \left(h_{pq} + F_{pq} \right)$$ *for restricted* Hartree-Fock method

Hartree–Fock (HF-SCF) method – Computational Remarks

- *Computational bottleneck*
  – the evaluation of two-electron (four-center) integrals

$$\left\langle \varphi_p \varphi_r \,|\, \hat{V}_{e-e} \,|\, \varphi_q \varphi_s \right\rangle$$

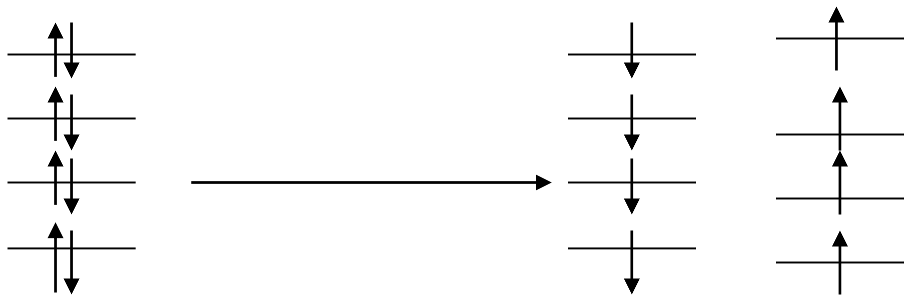
- *Approximations of such integrals through*
  ***Cholesky decomposition** (CD) or **Resolution of Identity** (RI-JK).*

- *Restricted (closed-shell / open-shell HF)*
  unrestricted HF – spin-symmetry broken

$$\left\{\mathbf{F}^{\alpha} - \varepsilon_i^{\alpha}\mathbf{S}^{\alpha}\right\}\mathbf{c}_i^{\alpha} = 0$$

$$\left\{\mathbf{F}^{\beta} - \varepsilon_i^{\beta}\mathbf{S}^{\beta}\right\}\mathbf{c}_i^{\beta} = 0$$

$$\mathbf{F}^{\beta}\left(\mathbf{c}^{\beta}, \mathbf{c}^{\alpha}\right); \;\; \mathbf{F}^{\beta}\left(\mathbf{c}^{\beta}, \mathbf{c}^{\alpha}\right)$$



$$S^2\Psi_{RHF} = \hbar^2 S(S+1)\Psi_{RHF} \qquad S^2\Psi_{UHF} \neq \hbar^2 S(S+1)\Psi_{UHF}$$

"Spin contamination"

Hartree–Fock (HF-SCF) method – Physical Remarks

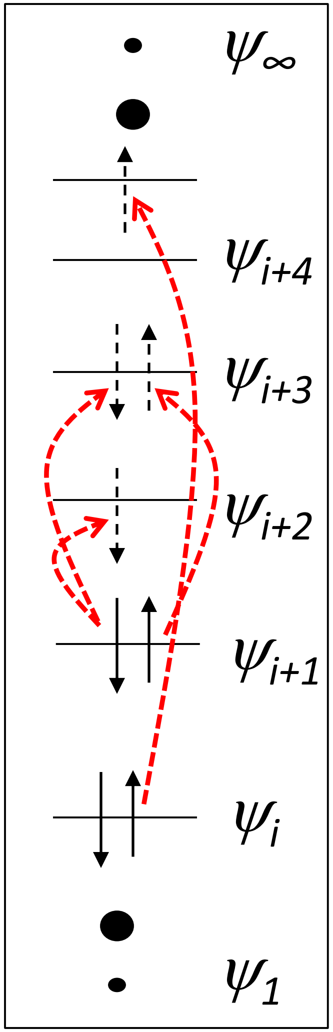
- *Each electron experiences the Coulombic repulsion of other electrons through their averaged field* ***(a mean field)***
  (the lack of dynamical correlation – see later)

- *Exchange interaction among electrons with the same spin orientation (**Fermi correlation**) – through the antisymmetric nature of the Slater determinant.*

- *One Slater determinant (SD) =* ***one "electronic configuration"***
  ("exact" wavefunction better expressed as a linear combination of many configurations - SDs).

- *Only the ground-state wavefunction and its energy is solved by HF SCF.*
  *(HF **not for excited states and their energies**)*

Exact non-realistic solution with
Full Configuration Interaction (FCI) in the infinite basis set



MOs
(being orthonormal)

Slater determinant

$$\hat{H}_{electrons}\Psi_{FCI} = E_{exact}\Psi_{FCI} \qquad \Psi_{FCI} = \sum_k C_k \Phi_{SD,k}$$

Correlation energy: $E_{corr} = E_{exact} - E_{HF}$

$$\langle \Psi_{FCI} \mid \hat{H}_{electrons} \mid \Psi_{FCI} \rangle = E_{exact} \qquad (\text{if } \langle \Psi_{FCI} \mid \Psi_{FCI} \rangle = 1)$$

$$\downarrow$$

$$\left\langle \sum_k C_k \Phi_k \mid \hat{H}_{electrons} \mid \sum_l C_l \Phi_l \right\rangle = E_{exact}$$

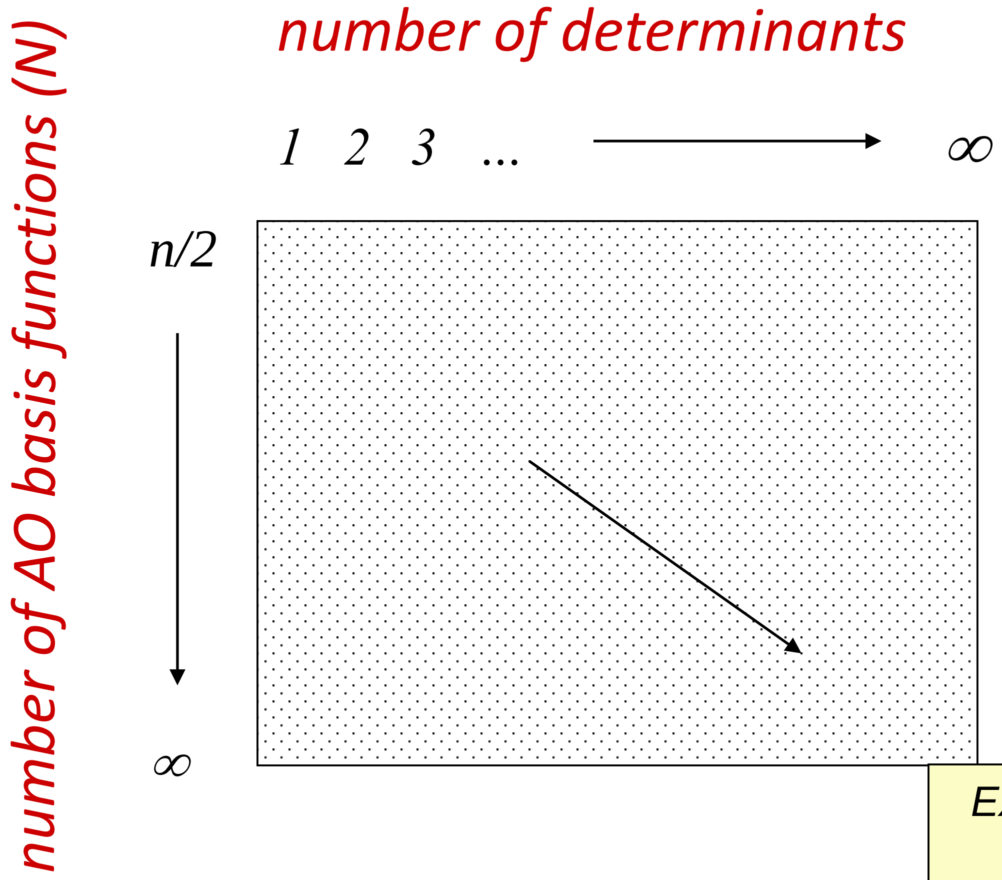
$$\downarrow$$

Slater-Condon rules → many integrals = 0

also Brillouin theorem:

$$\langle \Phi_{\mathrm{HF-SCF}} \mid \hat{\mathrm{H}}_{\mathrm{electrons}} \mid \Phi_i^a \rangle = 0$$

Exact non-realistic solution with Full Configuration Interaction (FCI) in the infinite basis set



Number of SD's:

(For 2n electrons in 2n orbitals)

2n	
2	*4*
4	*36*
6	*400*
8	*4.900*
10	*63.504*
12	*853.776*
14	*11.778.896*
16	*165.636.896*
18	*2.363.904.260*

Exact solution of electronic Schrödinger equation

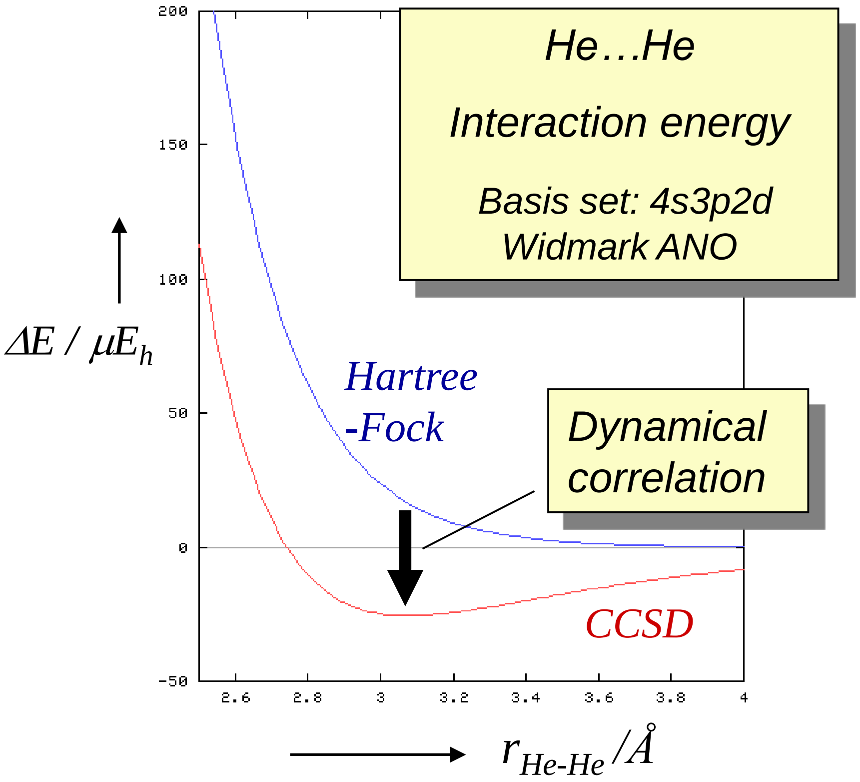
Static *versus* **dynamical** correlation?

dynamical

- **Short range effects** that arises as

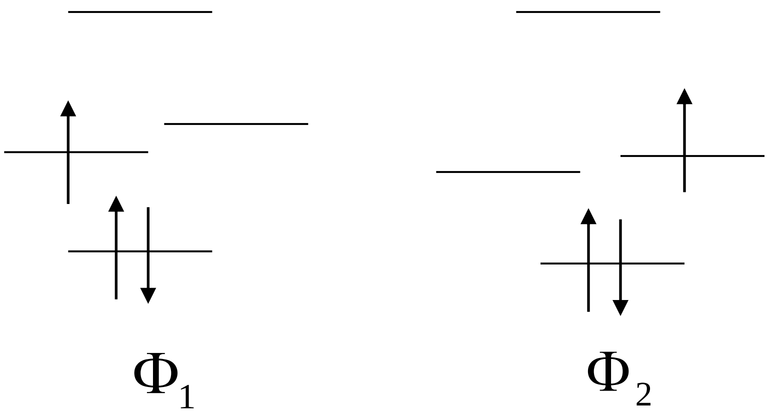
$$r_{12} \rightarrow 0$$

Dynamical correlation is related to the Coulomb hole.



Static (“non-dynamical”)

- from **configurational near-degeneracies** or from deficiencies in Hartree-Fock orbitals



$$\Psi = C_1\Phi_1 + C_2\Phi_2$$

***e.g.**, with*

$$C_1 = 0.7$$
$$C_2 = 0.3$$

Single-reference post-HF approaches
(a portion of dynamical correlation included)

Hartree–Fock
(HF-SCF)

↓

perturbational hierarchy
(MP2, MP3, MP4, …)

↓

excitation hierarchy
(CIS, CISD, CISDT, …)
(CCS, CCSD, CCSDT, …)

↓

Full CI

QC also devised for excited states and their energies

Møller-Plesset perturbation theory of *n*-th order (MPn)

$$\hat{H}(\lambda)\Psi(\lambda)=E(\lambda)\Psi(\lambda) \qquad \hat{H}(\lambda)=\underset{\text{from HF-SCF}}{\hat{H}^{(0)}}+\lambda\hat{V}$$

$$\Psi(\lambda)=\Psi^{(0)}+\lambda\Psi^{(1)}+\lambda^{2}\Psi^{(2)}+\dots$$

$$E(\lambda)=E^{(0)}+\lambda E^{(1)}+\lambda^{2}E^{(2)}+\dots$$

Truncation of perturbation to **second**-order

spinorbitals from HF-SCF

MP2:
$$E_{MP2}=E_{HF}+\sum_{k}\frac{\left|\left\langle \chi_k^{(0)}\right|\hat{V}\left|\chi_{HF}\right\rangle\right|^{2}}{E_0^{(0)}-E_0^{(k)}}$$

Truncated CI methods

$$\Psi=\underbrace{\underbrace{c_0\Phi_{HF}+\sum_{i}^{occ}\sum_{a}^{virt}c_i^{a}\Phi_i^{a}}_{CIS}+\sum_{i<j}^{occ}\sum_{a<b}^{virt}c_{ij}^{ab}\Phi_{ij}^{ab}}_{CISD}+\dots$$

Coupled-cluster methods (CC)

$$\Psi_{CC}=e^{\hat{T}}\Phi_{HF}$$

Cluster operator

$$\hat{T}=\hat{T}_1+\hat{T}_2+\hat{T}_3+\dots$$

$$e^{\hat{T}}\Phi_{HF}=\left[1+(\hat{T}_1+\hat{T}_2+..)\right]+\frac{1}{2}(\hat{T}_1+\hat{T}_2+..)^{2}+..]\Phi_{HF}$$

CCD:
$$\hat{T}=\hat{T}_2$$
$$e^{\hat{T}_2}\Phi_{HF}=(1+\hat{T}_2+\frac{1}{2}\hat{T}_2{}^{2}+..)\Phi_{HF}$$

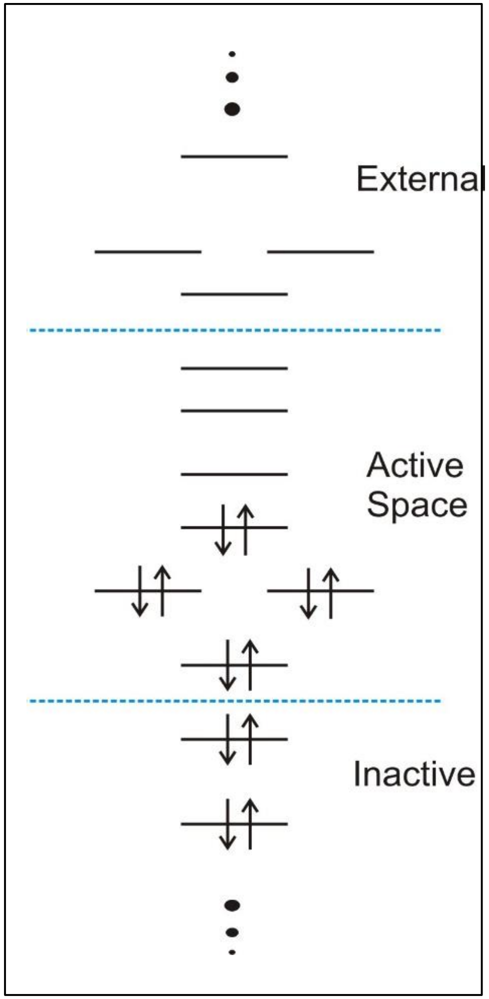
CCSD(T) – popular and often used as a golden standard method for single-reference systems (T) – triple excitations added as a perturbation

Formal scaling behavior of some single-reference QC methods

Scaling behavior	*Method(s)*
N^4	HF
N^5	MP2
N^6	MP3, CISD, MP4SDQ, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP6, CISDTQ, CCSDTQ

N – the number of basis functions

Multiconfigurational HF – MCSCF (CASSCF / RASSCF)
(a portion of static correlation included)



$$\Psi_{MCSCF} = \sum_{k} C_k \Phi_k \qquad \Psi_{MCSCF}(C,c)$$

Φ_k is a CSF ***arising from selected excitations within the active space***

- *if all possible excitations are allowed within the active space*
  -> FCI on a limited set of orbitals ***CASSCF***
- *more general approach –**RASSCF** (active space divided into subspaces – RAS1, RAS2, RAS3 – within RAS1&3 – selected excitations, within RAS2 - FCI*

Weyl's formula

$$N_{CSF} = \frac{2S+1}{n+1}\binom{n+1}{N/2-S}\binom{n+1}{N/2+S+1}$$

N= number of e^- in the active space
n = number of orbitals in the active space
S = molecular spin state

Current computational limit for CASSCF active space
~ 18-in-18

Example for S=2

	N_{CSF}
10-in-8:	420
10-in-10:	12375
10-in-11:	45375
10-in-13:	390390
10-in-14:	975975
10-in-15:	2927925

Modern approaches allowing to extent the active spaces
– Density-matrix renormalization group technology

larger active spaces within **DMRG-CASSCF** (e.g., 30-in-30)

Note on the selection of an active space

“Sometimes trivial, sometimes more difficult,
sometimes impossible”

B. Roos

Selection cannot be automatized
and depends on the particular system /problem

↓

Chemical insight is important ingredient
in choosing a proper active space

Multi-reference wavefunction approaches
(a portion of static and dynamic correlation included)

CASPT2 – PT2 on top of CASSCF

→ Popular for spectroscopy

RASPT2 – PT2 on top of RASSCF

DMRG-CASPT2 – PT2 on top of DMRG-CASSCF

→ Emerging method for "complex electronic structure" chemical transformations

MRCI(SD) – CISD on top of CASSCF

MRCC(SD) – CCSD on top of CASSCF

Higly accurate but computationally extremely demanding
→ Very small molecules

Density Functional Theory - DFT

To know the Hamiltonian, we need to know *the number of electrons and the external potential, i.e.* ***the number of electrons, the nuclear charges, and their positions****. All of these can be determined from a knowledge of the density:*

$$\int \rho(r)dr = N \qquad \frac{\partial}{\partial r_A}\bar{\rho}(r_A)|_{r_A=0} = -2Z_A\bar{\rho}(0)$$

where $\bar{\rho}$ is the spherical average of the density. The cusps of the density tell us where the nuclei are.

ρ(r) therefore determines the Hamiltonian and hence everything about the system.

Density Functional Theory - DFT

The realm of DFT methods built on two fundamental theorems:

1st Hohenberg-Kohn theorem:

shows that **electron density of an arbitrary molecular system** (in an electronically non-degenerate ground state) in the absence of external electromagnetic fields **determines unambiguously static external potential**

$$v_{ext}(r) = \sum_{k=1}^{nuclei} Z_k \left| r - R_k \right|^{-1}$$

2nd Hohenberg-Kohn theorem:

proves that the **correct ground state electron density minimizes the energy *E*[ρ]**

The total energy is represented as a functional of density:

$$E[\rho] = V_{ne}[\rho] + T[\rho] + V_{ee}[\rho] = \int \rho(r) v_{ext}(r) dr + T[\rho] + V_{ee}[\rho]$$

nucleus-electron attraction energy

kinetic energy of (interacting) electrons

electron-electron interaction energy

Kohn-Sham Density Functional Theory (KS-DFT)

$$E[\rho] = \int \rho(r)v(r)dr + T[\rho] + V_{ee}[\rho]$$

Coulomb electron-electron interaction

$$E[\rho] = \int \rho(r)v_{ext}(r)dr + T_s[\rho] + J[\rho] + \underbrace{(T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho])}$$

Kinetic energy of non-interacting electrons

$$\frac{1}{2}\int \frac{\rho(r')\rho(r)}{|r-r'|}dr'\,dr$$

$$E[\rho] = \int \rho(r)v_{ext}(r)dr + T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

Exchange-Correlation (XC) Energy

Working Kohn-Sham Equation

The idea of considering the determinantal WF
of ***N* non-interacting electrons in *N* orbitals**, then $T_s[\rho]$ is exactly given as:

$$T_s[\rho] = \sum_{i=1}^{N} \left\langle \chi_i \,|\, -\frac{\hbar^2}{2m_e}\Delta_i \,|\, \chi_i \right\rangle$$

Kohn-Sham spinorbital

& ***fulfilling condition:***

$$\rho = \sum_{i=1}^{N} \left\langle \chi_i \,|\, \chi_i \right\rangle$$

Real electron density

Then, one-electron KS equation:

$$\left(-\frac{\hbar^2}{2m_e}\Delta_i + v_{eff}(r)\right)\chi_i(r) = \varepsilon_i \chi_i(r)$$

(Fock-like equations)

with: $v_{eff} = v_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + v_{xc}(r)$

Alpha-omega in KS-DFT – exact form unknown

LCAO ansatz ↓

Roothaan-like equations

Restricted / Unrestricted Kohn-Sham equations - as in HF

↓ $\rho = \rho_\alpha + \rho_\beta$

Most common of exchange-correlation potentials

- **Local density approximation –** most popular way to do electronic structure calculations in solid state physics

- **Generalized gradient approximation (GGA) –** xc potentials are functionals of electron density and its first spatial derivatives ("gradient-corrected LDA" functionals) *PBE, BP86…*

- **Meta-GGA approximation –** extension of GGA. xc potentials are functionals of electron density, its first and second spatial derivatives and kinetic energy density *TPSS….*

- **Hybrid exchange functionals –** a portion of exact exchange from HF theory is incorporated into xc potentials. Usually, GGA hybrid and GGA approach are combined. *TPSSH, B3LYP, PBE0….*

- **Hybrid exchange and hybrid correlation (double-hybrid) functionals -** essentially extension of hybrid-GGA, which uses MP2 correction to replace part of the semi-local GGA correlation. *B2PLYP…*

Limitations of standard KS DFT methods

- **Lack of long-range correlation (dispersion)**

  empirical corrections ~$1/R^6$

  B3LYP+D3

- **Incorrect long-range exchange behavior**

  CAM-B3LYP

  e.g. incorrect energies of *charge-transfer excitations*

  (exchange should decay asymptotically as r_{12}^{-1}*; B3LYP :* $0.2r_{12}^{-1}$*)*

- **Lack of static correlation energy**

  Generally lower sensitivity of DFT to multireference character is dependent on the amount of HF exchange included in the functional

- **Self-interaction error**

  SIE interpreted as the interaction of an electron with itself.

  While the diagonal exchange terms K_{ii} cancel exactly self-interaction Coulomb terms J_{ii} in HF, it is not valid for standard KS-DFT methods.

- **Lack of systematic improvability!!!!!**

Some final notes on solving SE through WFT and DFT methods

For a given geometry – wavefunction optimization -> electronic energy *E*

(single-point calculation)

On the other hand:

QC methods can be also used to optimize geometry – algorithms allowing to evaluate (first, second) derivatives of *E* with respect to the nuclear coordinates and to search crucial points on the potential energy surface

→ **Minima & first-order stationary points (transition states)**

(**geometry optimization**)

Thus now, in principle, you are able to read the following sentence:

GGA-type PBE functional in combination with RI-*J* approximation and the DZP basis set was used for the geometry optimization, while CASPT2(10-in-8) approach combined with a larger basis set (e.g. TZVP) was employed for the final single-point energies.

APPENDIX

Properties as derivatives of the energy - Bonus

- Consider a molecule in an external electric field ε.

$$\boxed{E(\varepsilon) = E(\varepsilon = 0) + \varepsilon \left.\frac{dE}{d\varepsilon}\right|_{\varepsilon=0} + \tfrac{1}{2}\varepsilon^{2} \left.\frac{d^{2}E}{d\varepsilon^{2}}\right|_{\varepsilon=0} + \ldots}$$

  - Dipole moment (μ) $$\mu = -\left.\frac{dE}{d\varepsilon}\right|_{\varepsilon=0}$$
  - Polarizability (α) $$\alpha = -\left.\frac{d^{2}E}{d\varepsilon^{2}}\right|_{\varepsilon=0}$$
  - First hyperpolarizability (β) $$\beta = -\left.\frac{d^{3}E}{d\varepsilon^{3}}\right|_{\varepsilon=0}$$

$\frac{dE}{d\varepsilon_\alpha}$	*dipole moment; in a similar way also multipole moments, electric field gradients, etc.*
$\frac{d^2E}{d\varepsilon_\alpha d\varepsilon_\beta}$	*polarizability*
$\frac{d^3E}{d\varepsilon_\alpha d\varepsilon_\beta d\varepsilon_\gamma}$	*(first) hyperpolarizability*
$\frac{dE}{dx_i}$	*forces on nuclei*
$\frac{d^2E}{dx_i dx_j}$	*harmonic force constants; harmonic vibrational frequencies*
$\frac{d^3E}{dx_i dx_j dx_k}$	*cubic force constants; anharmonic corrections to distances and rotational constants*
$\frac{d^4E}{dx_i dx_j dx_k dx_l}$	*quartic force constants; anharmonic corrections to vibrational frequencies*
$\frac{d^2E}{dx_i d\varepsilon_\alpha}$	*dipole derivatives; infrared intensities*
$\frac{d^3E}{dx_i d\varepsilon_\alpha d\varepsilon_\beta}$	*polarizability derivatives; Raman intensities*

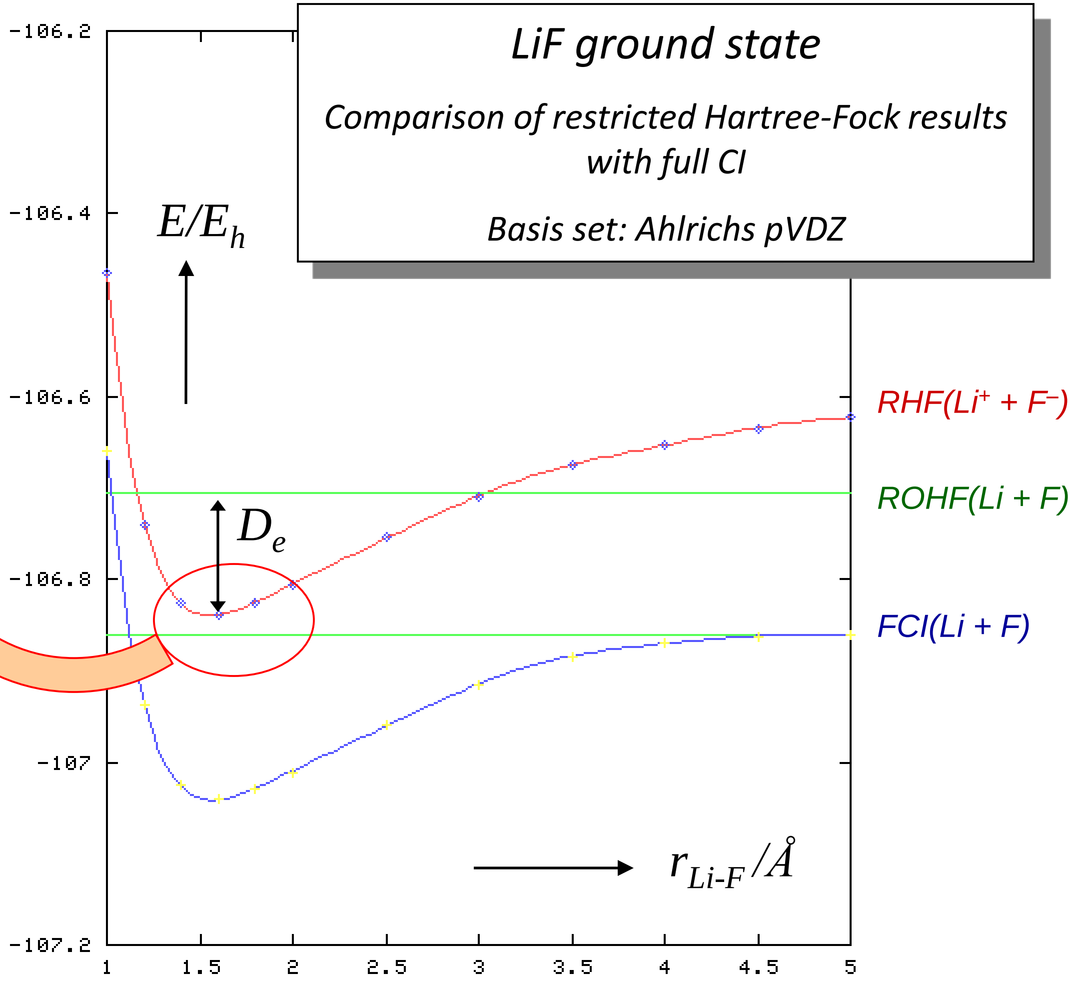
$\frac{d^2E}{dB_\alpha dB_\beta}$	*magnetizability*
$\frac{d^2E}{dI_{i_\alpha} dB_\beta}$	*nuclear magnetic shielding tensor; relative NMR shifts*
$\frac{d^2E}{dI_{i_\alpha} dI_{j_\beta}}$	*indirect spin-spin coupling constants*
$\frac{d^2E}{dB_\alpha dJ_\beta}$	*rotational g-tensor; rotational spectra in magnetic field*
$\frac{d^2E}{dI_{i_\alpha} dJ_\beta}$	*nuclear spin-rotation tensor; fine structure in rotational spectra*
$\frac{dE}{dS_\alpha}$	*spin density; hyperfine interaction constants*
$\frac{d^2E}{dS_\alpha dS_\beta}$	*electronic g-tensor*
$\dots$	*and many more ...*

Restricted Hartree–Fock (RHF) results for LiF

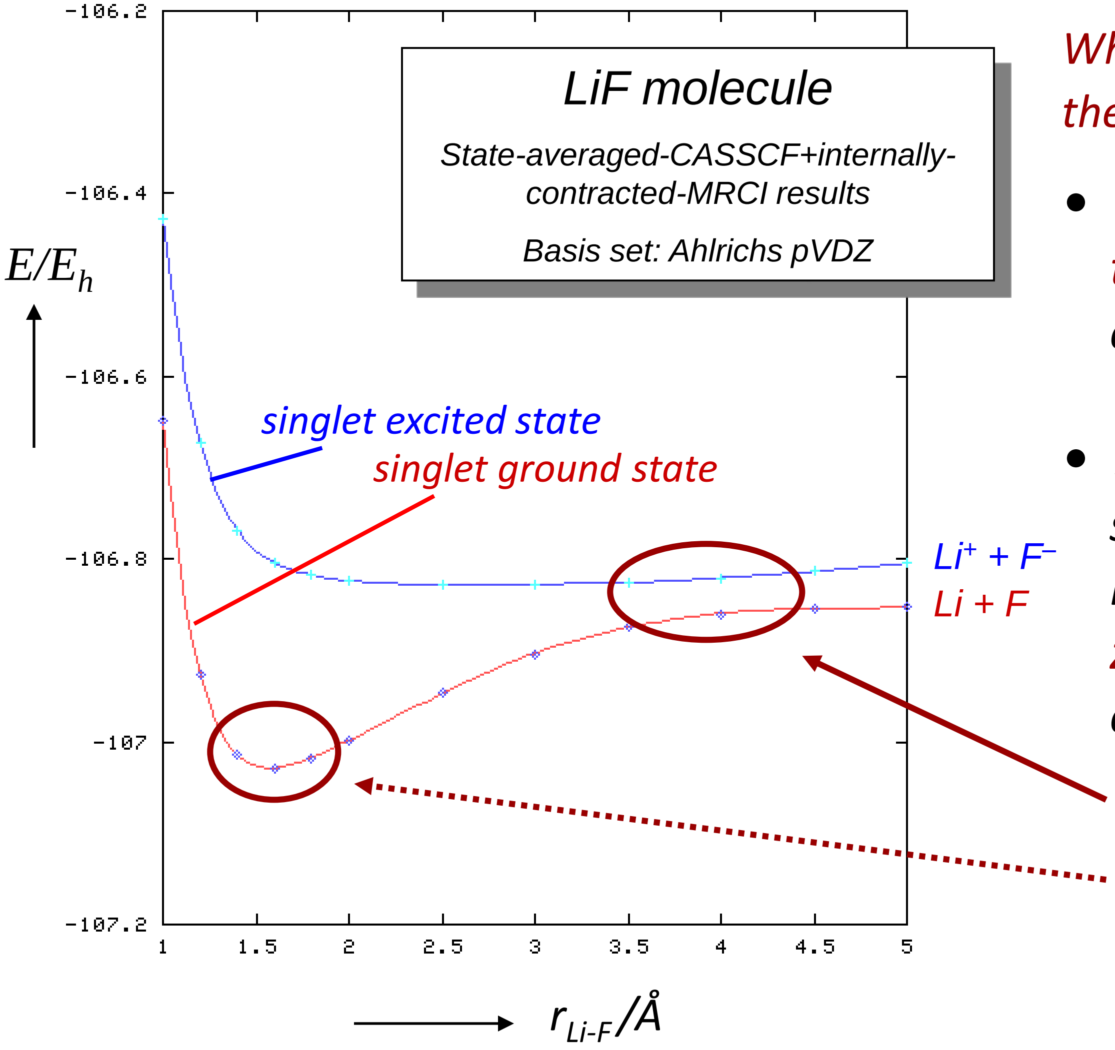
	Hartree–Fock	**Error**
r_e / Å	1.57	–0.6 %
ω_e / cm^{-1}	991	+2.5 %
μ_e / D	6.49	+3.9 %
μ'_e / DÅ^{-1}	4.14	+4.6 %
D_e / kJ mol^{-1}	352	–26 %

For LiF, the Hartree-Fock method is quite useful for calculations around the equilibrium, although the binding energy is too low by 26%.

But the RHF model dissociates incorrectly into Li$^+$ and F$^-$.



Post-Hartree-Fock for qualitative or quantitative reasons



Why do we want to go beyond the Hartree-Fock description?

- *First, we may wish to improve the accuracy of the computed energy and other properties.*
- *Second, we are dealing with a situation where the Hartree-Fock model is a very poor zeroth-order approximation of the wavefunction.*

Near-degeneracy effects

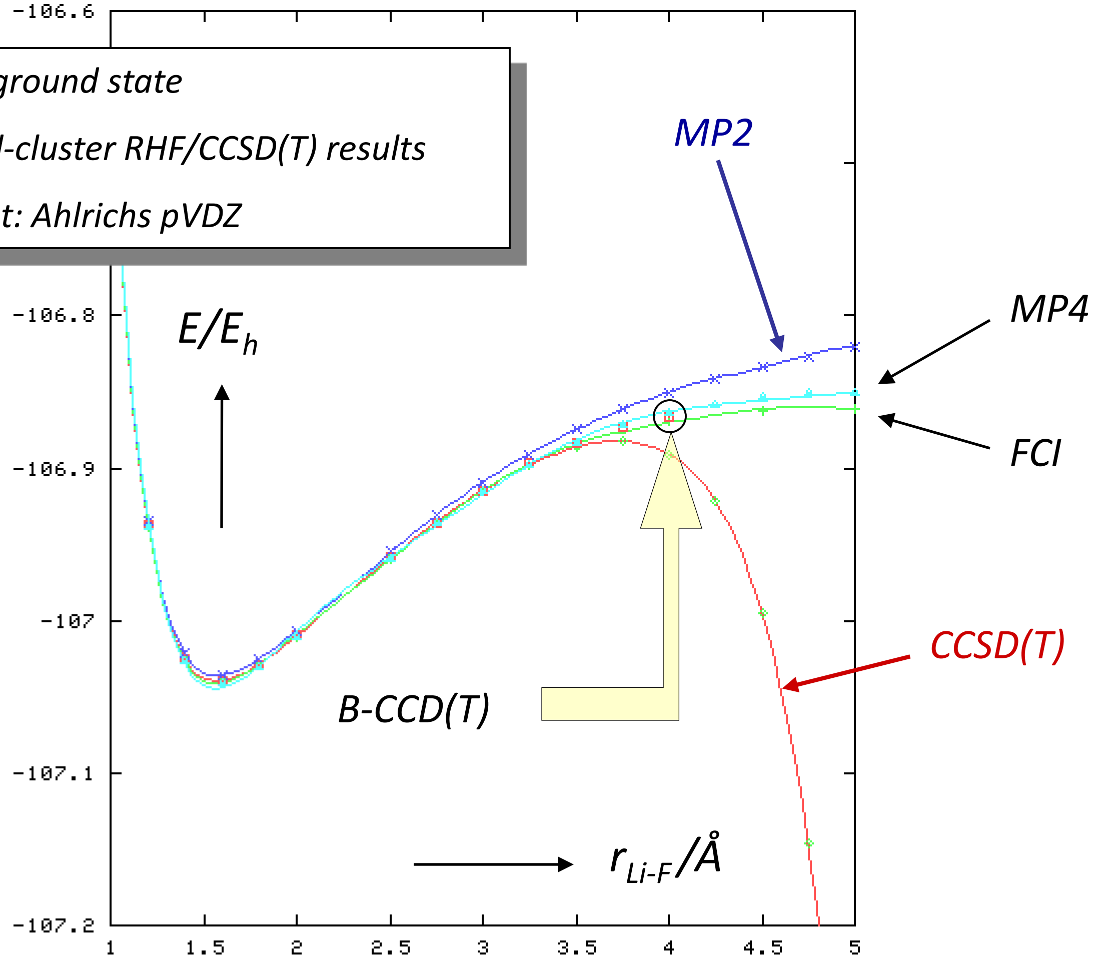
Ground-state equilibrium properties

Near-degeneracy problems of perturbation theory

LiF ground state

Closed-shell coupled-cluster RHF/CCSD(T) results

Basis set: Ahlrichs pVDZ

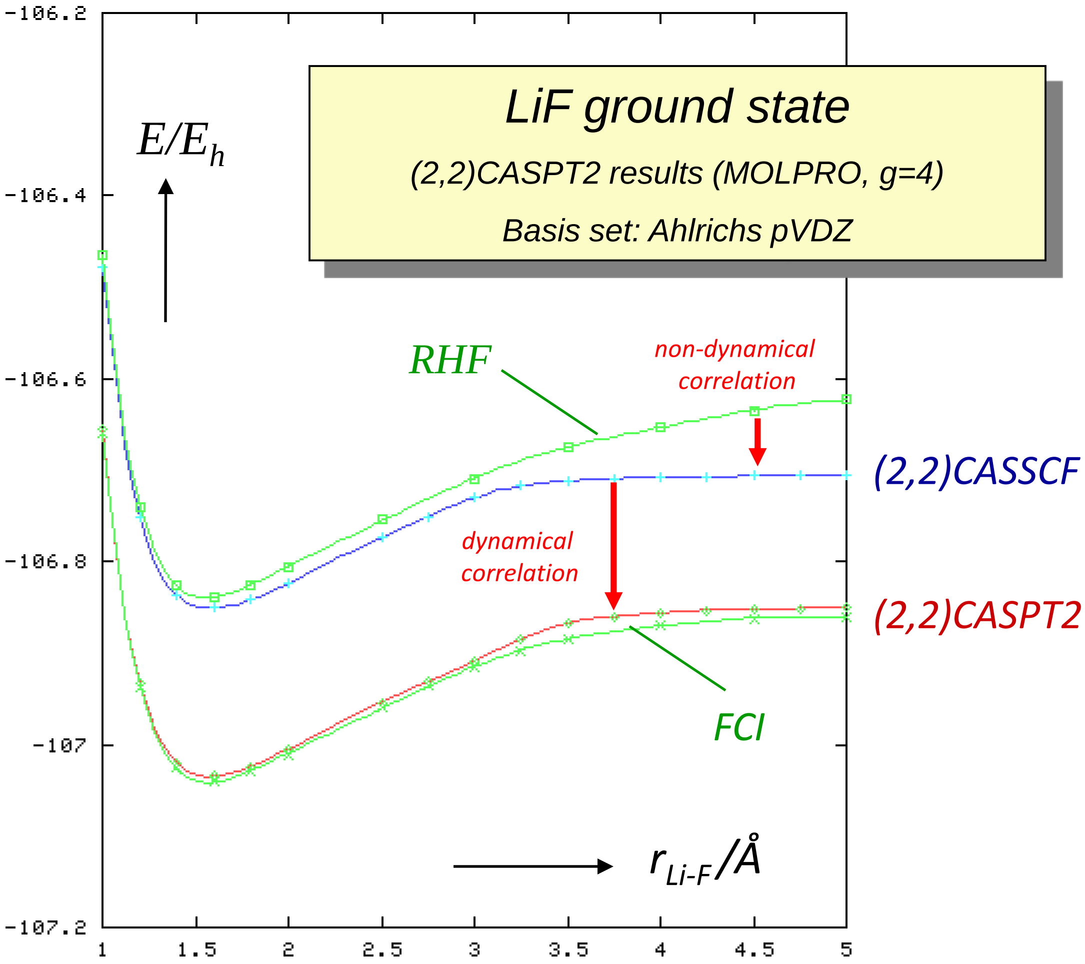


The CCSD(T) triples correction becomes very negative for distances > 3 Å.

The CCSD(T) method breaks down.

The MP4(SDTQ) energy also shows this behavior, but only at a much longer distance (> 6 Å).

Multireference perturbation theory applied to LiF



Unrestricted UCCSD(T) coupled-cluster calculations of the LiF ground state

- *The UCCSD(T) results compare favorably with the full CI potential energy curve.*
- *The expectation value* $\langle S^2 \rangle$ *is zero for the (unprojected) UHF wavefunction at distances < 3 Å, but* $\langle S^2 \rangle \approx 1.0$ *at larger distances (> 3 Å).*
- *In this example, the spin-contamination represents no real problem for the ground state energy.*
- *However, spin-contamination may make the UHF-based methods unsuitable for the study of a variety of molecular properties.*