Basics of Applied Quantum Chemistry

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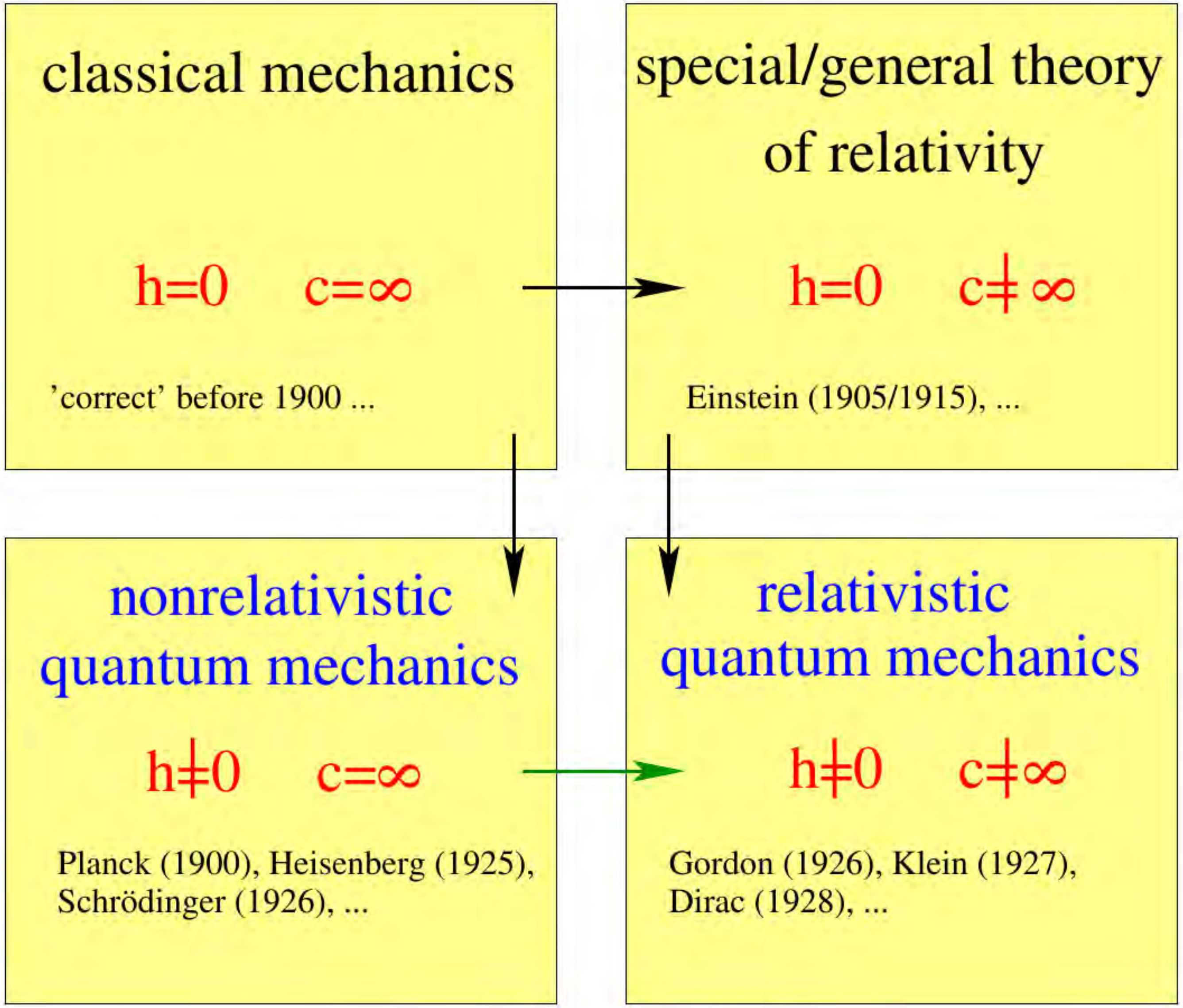
Assumption/Goals:

- You know the/some basics of quantum mechanics (QM).
- We repeat some of the things you know, but in English.
- We add some aspects to the basic knowledge in order to understand better the methods of quantum chemistry (QC)

Chapter 1

Quantum chemical description of many-electron systems

Theories of 'classical and 'modern' physics



classical mechanics

$h=0 \quad c=\infty$

'correct' before 1900 ...

special/general theory of relativity

$h=0 \quad c\neq\infty$

Einstein (1905/1915), ...

nonrelativistic quantum mechanics

$h\neq 0 \quad c=\infty$

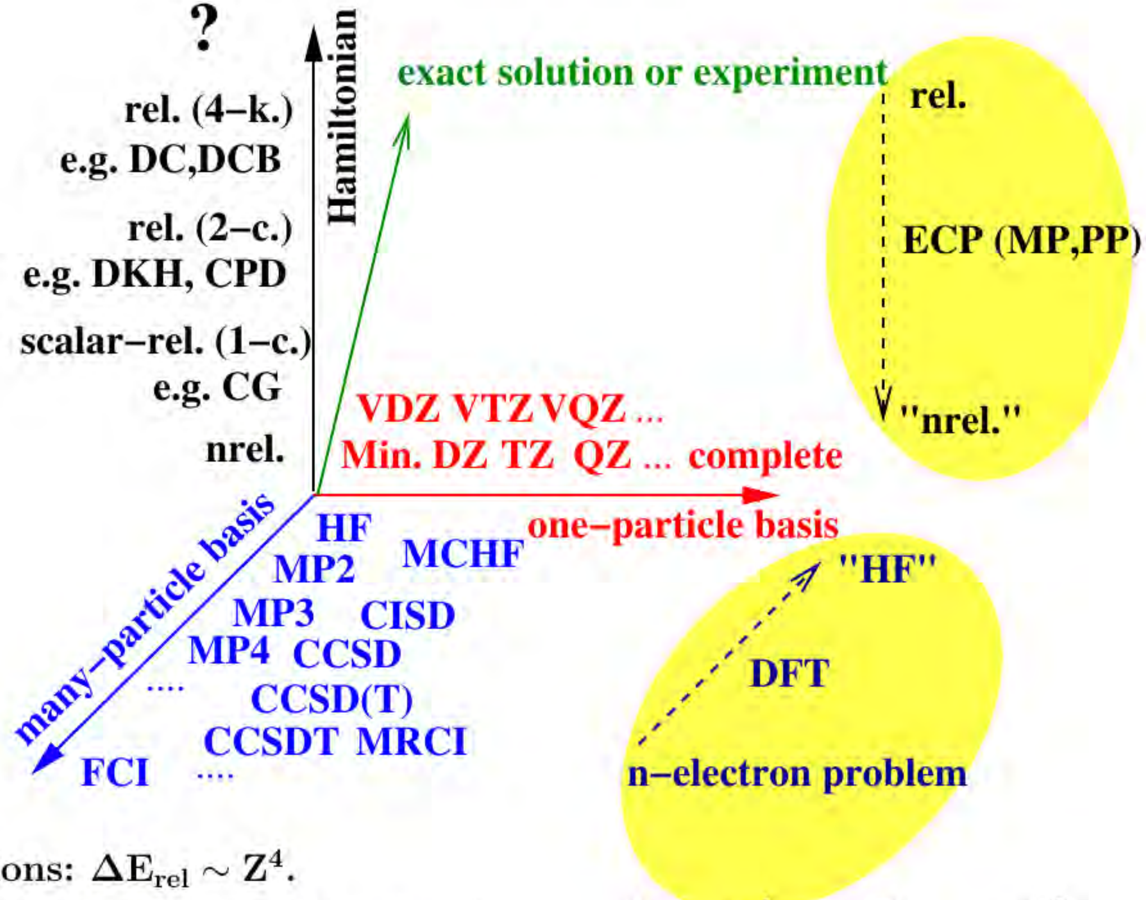
Planck (1900), Heisenberg (1925),
Schrödinger (1926), ...

relativistic quantum mechanics

$h\neq 0 \quad c\neq\infty$

Gordon (1926), Klein (1927),
Dirac (1928), ...

application to chemistry:
relativistic/nonrelativistic quantum chemistry



?

Hamiltonian

rel. (4–k.)
e.g. DC,DCB

rel. (2–c.)
e.g. DKH, CPD

scalar–rel. (1–c.)
e.g. CG

nrel.

exact solution or experiment

VDZ VTZ VQZ ...
Min. DZ TZ QZ ... complete

one–particle basis

many–particle basis

HF
MP2
MP3
MP4
....
FCI

MCHF
CISD
CCSD
CCSD(T)
CCSDT MRCI
....

rel.
ECP (MP,PP)
"nrel."

"HF"
DFT
n–electron problem

- relativistic contributions: $\Delta E_{rel} \sim Z^4$.
- correlation energy errors for standard basis set expansions: $E^{l}_{corr} - E^{\infty}_{corr} \sim 1/l^3$
  $\rightarrow$ basis set extrapolation or F12-dependent wavefunctions.
- computational effort: $t \sim n^k$ (n size of one-particle basis set, k for some standard approaches: DFT 3, HF 4, MP2 5, CISD, CCSD 6, CCSD(T) 7 ...) $\rightarrow$ low-order/linear scaling schemes.
- ECPs simplify the Hamiltonian and also lead to some reductions in the sizes of the one- and many-electron basis sets (e.g. small-core PPs plus valence-only SO terms) !
- DFT avoids costly many-determinantal wavefunctions/treatments.

Goal: Suitable compromise between accuracy and computational effort,
i.e., sufficiently accurate low-cost relativistic electronic structure calculations, also for larger systems.

The Postulates of Quantum Mechanics (QM)

- cannot be derived from classical physics (mechanics, electrodynamics)
- comparison to reality (experiments): correct → The Axioms of ....
- differing formulations in literature

Postulat/Axiom 1:

"The state of a system is completely described by a wavefunction."

- **state:** characterized by results of experimental measurements (observable quantities, observables) e.g. energy, angular momentum, spin, ...

$$\Rightarrow \quad | E, \overset{(\rightharpoonup)}{L}, \overset{(\rightharpoonup)}{S}, \ldots \rangle$$

"ket" vector

(Dirac "bra-c-ket" notation, cf. later!)

- <u>wavefunction:</u> different ways of formulation possible, i.e.

different <u>representations:</u>

- position representation
  ($\vec{r} = (x, y, z)$, $\hat{\vec{p}} =$ "derivatives wrt. x, y, z")
- momentum representation
  ($\vec{p} = (p_x, p_y, p_z)$, $\hat{\vec{r}} =$ "derivatives wrt. p_x, p_y, p_z")
- ....

We will mainly work in the position representation.

requirements for the wavefuntion:

- function $\Psi \rightarrow \Psi(\{\vec{r}_i\}, t), \Psi(\{\vec{p}_i\}, t)$

  single valued

  positions of all particles

  time

  momenta of all particles

  time

- square integrability

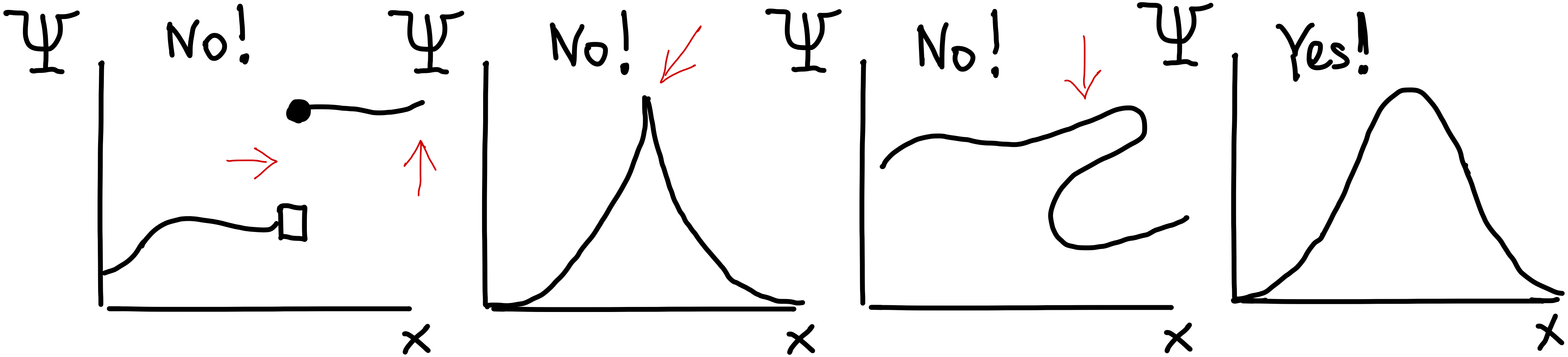
$$\int \Psi^* \Psi \, d\tau = 1$$

normalization condition

→ Born probability interpretation, cf. later!

- (twice) continously differentiable, i.e. derivatives of $\underline{\Psi}$ wrt. $x, \ldots$ or $p_x, \ldots$ must exist and be continous functions of $x, \ldots$ or $p_x, \ldots$.

examples in one dimension:



Postulat/Axiom 2:

" The squared absolute value of the wavefunction is a probability density "

Born probability density interpretation of the wavefunction

$$|\Psi|^2 = \Psi^* \Psi \quad (\geq 0)$$

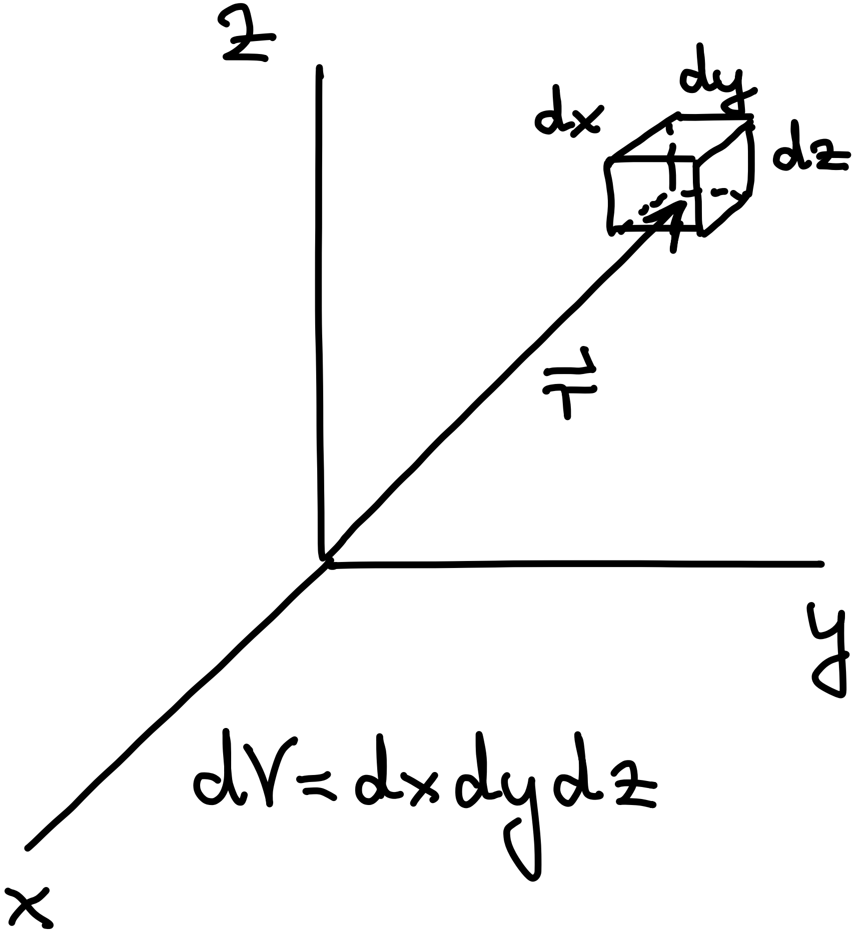
- Ψ is not an observable (it cannot be measured!)

  Ψ is a state function (it describes the state of a system completely)

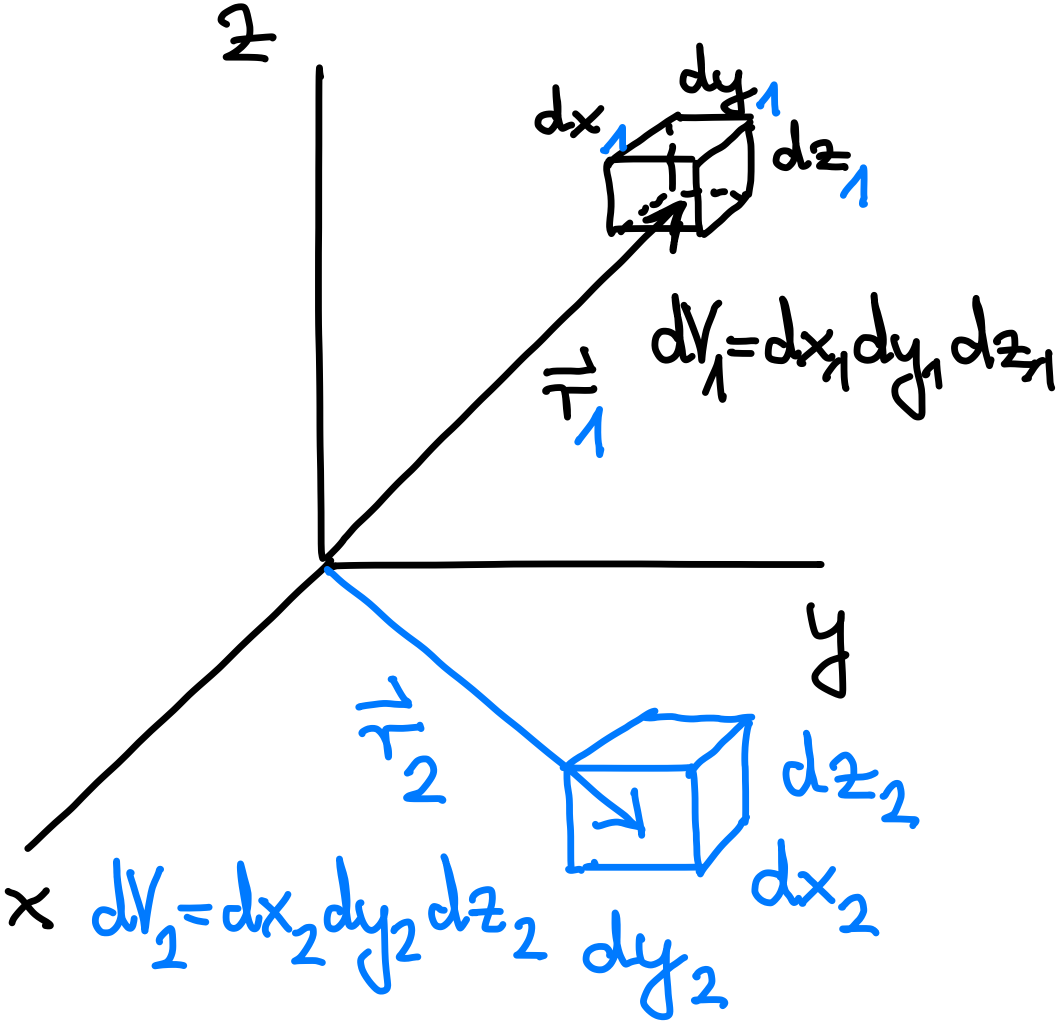
  Ψ can be written in different ways (different representations)

- $\Psi^* \Psi$ is an observable

e.g., one particle: two particles:



$dV = dx\,dy\,dz$



$dV_1 = dx_1 dy_1 dz_1$

$dV_2 = dx_2 dy_2 dz_2$

$$\int \Psi^*(\vec{r}, t_0)\,\Psi(\vec{r}, t_0)\,dV = 1 \qquad \iint \Psi^*(\vec{r}_1, \vec{r}_2, t_0)\,\Psi(\vec{r}_1, \vec{r}_2, t_0)\,dV_1 dV_2 = 1$$

- one particle:

density $\rho(\vec{r}) = \Psi^{*}\Psi$

elementary charge

e.g. electron density $\rho(\vec{r}) = e \cdot |\Psi|^2$

can be measured in experiments

$\Rightarrow |\Psi|^2$ is observable

Ψ not observable, e.g. $|-\Psi|^2 = |+\Psi|^2$

elementary charge

($\hat{=}$ negative charge of an electron)

$$e = 1.602176634 \cdot 10^{-19}\ \mathrm{C}$$

C : Coulomb

Postulat/Axiom 3:

"Measurements are represented by hermitian operators. The elementary operators of position and momentum have to fulfill the commutation relation $[\hat{x}, \hat{p}_x] = \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$."

Planck's constant (1900):

$$h = 6.62607015 \cdot 10^{-34}\, Js$$

J: Joule (energy)

s: second (time)

energy · time = action

$$\hbar = h/2\pi$$

- physical quantity A or $\vec{A}$

$\Rightarrow$ operator $\hat{A}$ or $\hat{\vec{A}}$

acts to the right side!

$\hat{A}$ means "measure A", ...

- order of measurements:

$$\underset{\text{2nd.}}{\hat{A}}\ \underset{\text{1st.}}{\hat{B}}$$

i.e. $$\underset{\text{2nd.}}{\hat{A}}\,\underset{\text{1st.}}{\hat{B}} - \underset{\text{2nd.}}{\hat{B}}\,\underset{\text{1st.}}{\hat{A}} = [\hat{A},\hat{B}]$$

commutator changes order

- $[\hat{A}, \hat{B}] = 0$ the order of the measurements does not matter, the operators $\hat{A}$ and $\hat{B}$ commute.

$[\hat{A}, \hat{B}] \neq 0$ the order of the measurements is important, the operators $\hat{A}$ and $\hat{B}$ do not commute.

e.g. $[\hat{x}, \hat{p}_x] = i\hbar$

$$\underbrace{\hat{A}}_{\text{measurement}}\,\underbrace{|\ldots\rangle}_{\text{state}} \Rightarrow \underbrace{\hat{A}}_{\text{operator}}\,\underbrace{\Psi}_{\text{state function}}$$

<u>elementary operators:</u>

position	momentum	representation
$\hat{x} = x\cdot$	$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$	position
$\hat{x} = i\hbar\frac{\partial}{\partial p_x}$	$\hat{p}_x = p_x\cdot$	momentum

$$[\hat{x},\hat{p}_x] = \hat{x}\hat{p}_x - \hat{p}_x\hat{x} \underset{\text{position representation}}{=} x\left(-i\hbar\frac{\partial}{\partial x}\right) - \underbrace{\left(-i\hbar\frac{\partial}{\partial x}\right)x} =$$

$$= i\hbar\left(-x\frac{\partial}{\partial x} + \left(1 + x\frac{\partial}{\partial x}\right)\right) = i\hbar$$

product rule: $\frac{\partial}{\partial x}(x\cdot f) = f + x\frac{\partial f}{\partial x} \leftarrow$

measurements (operators) of position and momentum do not commute!

- hermitian (hermitean) → Hermite

$$\int \Psi_1^* \hat{A} \Psi_2 \, d\tau = \left(\int \Psi_2^* \hat{A} \Psi_1 \, d\tau \right)^*$$

transpose indices

build conjugate complex

adjoint

$$\hat{A} = \hat{A}^\dagger = \left(\hat{A}^T\right)^*$$

← conjugate complex

↑ transposed

- hermitian operators have real eigenvalues, which yields real results of measurements!

$$\hat{A}\,\Psi = a \cdot \Psi$$

eigenvalue equation

operator acts on function

eigenvalue

eigenfunction

cf. later!

- construction of more complicated operators from elementary ones, e.g.

kinetic energy:

classical expression $E = \frac{1}{2}\overset{\text{mass}}{m}\underset{\text{velocity}}{v}^2 = \frac{\overset{\text{momentum}}{p}^2}{2m}$

using $p = mv$

"quantization" $p \longrightarrow \hat{\vec{p}} = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = -i\hbar\underset{\text{Nabla operator}}{\vec{\nabla}}$

$$\vec{\nabla}^2 = \underset{\text{Laplace operator}}{\Delta} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

=> kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m}\Delta \quad \text{in 3D space}$$

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad \text{in 1D space}$$

Postulat/Axiom 4:

"The average value of a measurement represented by an Operator $\hat{A}$ for a system in a state $|\Psi\rangle$ is the expectation value

$$\langle \hat{A} \rangle = \langle \overset{\downarrow}{\Psi} | \hat{A} | \Psi \rangle = \int \overset{\downarrow}{\Psi^{*}} \hat{A} \Psi \, d\tau ."$$

Dirac
"bra-c-ket"
notation

in ""
representation

$|\Psi\rangle$ "ket" vector → Ψ (behind $\hat{A}$)

$\langle\Psi|$ "bra" vector → Ψ^* (in front of $\hat{A}$)

bringing them together in a scalar product implies integration in ... representation.

$\langle\Psi|\Psi\rangle = \int \Psi^* \Psi \, d\vec{r} = 1$ normalization

$\langle\Psi|\hat{A}|\Psi\rangle = \int \Psi^* \hat{A} \Psi \, d\vec{r} = \langle\hat{A}\rangle$ expectation value

- $| \rangle$ is an eigenstate of $\hat{A}$, i.e. the measurement does not change the state of the system:

  $\hat{A}|\Psi\rangle = a \cdot |\Psi\rangle$ and

  $$\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle = \langle \Psi | a \cdot \Psi \rangle =$$

  $$= a \cdot \langle \Psi | \Psi \rangle = a$$ for normalized $|\Psi\rangle$

$\Rightarrow$ only one value a is measured!

"sharp" measurement value

- $| \;\rangle$ is not an eigenstate of $\hat{A}$, i.e. the measurement changes the state of the system:

$$\hat{A} | \underline{\Psi} \rangle = | \tilde{\underline{\Psi}} \rangle$$

$\langle \hat{A} \rangle$ is an average value of all measurements, cf. later!

Postulat/Axiom 5:

" The wavefunction is solution of the time-dependent Schrödinger equation

$$\hat{H}\,\Psi = i\hbar \frac{\partial}{\partial t}\Psi \text{ ''}.$$

[Schrödinger picture $\Psi(\ldots t)$ used here, alternatively Heisenberg picture $\hat{H}(\ldots t)$, 1925/6]

- $\hat{H}$: Hamilton operator, Hamiltonian; operator of total (= kinetic + potential) energy of the system.

  quantization of the Hamilton function $H = T + V$ with $x \to \hat{x}$, $p_x \to \hat{p}_x$, ...

- stationary states: $\hat{H} \neq \hat{H}(t)$

ansatz: $$\underset{\text{wave function}}{\Psi}(\vec{r},t) = \underset{\text{wave amplitude functio}}{\psi}(\vec{r}) \cdot e^{-iEt/\hbar}$$

=> time-independent Schrödinger equation

$$\hat{H}\psi = \overset{\text{total energy}}{E} \cdot \psi$$

- For n particles a Hamiltonian can be written as a sum over one-particle contributions $\hat{h}$ (kinetic energy, interaction with external fields) and two-particle contributions $\hat{g}$ (e.g. Coulomb interaction between charged particles):

$$\hat{H} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j)$$

Postulat/Axiom 6:

"The wavefunction of a system of identical (indistinguishable) particles is either

symmetric (for bosons, integral spin particles, → Bose)

or

antisymmetric (for fermions, half-integral spin particles → Fermi)

wrt. interchange of two particles."

- $\Psi^*\Psi$ is observable, Ψ is not observable

permutation operator $\hat{P}_{ij}$

$$\hat{P}_{ij}\,\Psi(\ldots\vec{r}_i\ldots\vec{r}_j\ldots) = \Psi(\ldots\vec{r}_j\ldots\vec{r}_i\ldots) =$$

$$= \Psi(\ldots\vec{r}_i\ldots\vec{r}_j\ldots) \quad \text{symmetric}$$

or

$$= -\Psi(\ldots\vec{r}_i\ldots\vec{r}_j\ldots) \quad \text{antisymmetric}$$

both yield $\quad |\hat{P}_{ij}\Psi|^2 = |\Psi|^2$

$\Rightarrow$ Pauli principle

An electronic wavefunction is antisymmetric wrt. an interchange of two electrons.

(Specialized:
Two electrons cannot agree in all quantum numbers ....)

Additional considerations:

- **Heisenberg uncertainty relation**

"uncertainty": $\Delta A := \sqrt{\langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle}$

with elementary operators $\hat{x}$ and $\hat{p}_x$:

$$\Delta x \, \Delta p_x \geq \frac{1}{2} \left| \langle i [\hat{x}, \hat{p}_x] \rangle \right| = \frac{\hbar}{2}$$

similar: $\Delta E \, \Delta t \geq \frac{\hbar}{2}$ (without proof)

- Hilbert space

linear space of functions, where to each pair a complex number (= scalar product) is associated.

(Extension of the Euclidian vector space to functions, however the scalar product is now complex and not commutative!)

Euclidian space	Hilbert space
$\vec{a}_i, \vec{a}_j \in V$	$f_i, f_j \in V$

$\Downarrow$ analogous!

- addition of two elements

a) $\vec{a}_i + \vec{a}_j \in V$ closedness

b) $\vec{a}_i + (\vec{a}_j + \vec{a}_k) = (\vec{a}_i + \vec{a}_j) + \vec{a}_k$ associative law

c) $\vec{a}_i + \vec{a}_j = \vec{a}_j + \vec{a}_i$ commutative law

d) $\vec{a}_i + \vec{0} = \vec{a}_i$ neutral element $\vec{0}$

e) $\vec{a}_i + (-\vec{a}_i) = \vec{0}$ inverse element $(-\vec{a}_i)$

Euclidian space   Hilbert space

⇘ analogous!

- multiplication with a scalar (… number) $c \in \mathbb{C}$

f) $c \cdot \vec{a}_i \in \mathbb{V}$

$$0 \cdot \vec{a}_i = \vec{0}, \quad c \cdot \vec{0} = \vec{0}$$

g) $c_i (c_j \vec{a}_k) = (c_i c_j) \vec{a}_k$ associative law

h) $(c_i + c_j) \vec{a}_k = c_i \vec{a}_k + c_j \vec{a}_k$ distributive

$c_k (\vec{a}_i + \vec{a}_j) = c_k \vec{a}_i + c_k \vec{a}_j$ law(s)

→ linear vector/function space!

Euclidian space	Hilbert space
i) scalar product	
$\vec{a}_i \cdot \vec{a}_j = \vec{a}_j \cdot \vec{a}_i$	$\langle f_i \vert f_j \rangle = \langle f_j \vert f_i \rangle^*$
$\vec{a}_i \cdot (c \cdot \vec{a}_j) = c \cdot (\vec{a}_i \cdot \vec{a}_j)$	$\langle c f_i \vert f_j \rangle = c^* \langle f_i \vert f_j \rangle$
$\vec{a}_i \cdot \vec{a}_i = \begin{cases} > 0 & \text{for } \vec{a}_i \neq \vec{0} \\ = 0 & \text{for } \vec{a}_i = \vec{0} \end{cases}$	$\langle f_i \vert c f_j \rangle = c \langle f_i \vert f_j \rangle$
• orthogonal vectors	• orthogonal functions
$\vec{a}_i \cdot \vec{a}_j = 0$	$\langle f_i \vert f_j \rangle = 0$

Euclidian space Hilbert space

- component representation in a complete and orthonormal set of basis vectors | functions:

orthonormality:

$$\vec{e}_i \cdot \vec{e}_j = \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \qquad \langle e_i | e_j \rangle = \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$$

completeness:

$$\mathbb{1} = \sum_i |e_i\rangle\langle e_i|$$

$$\vec{a} = \sum (\vec{a} \cdot \vec{e}_i) \cdot \vec{e}_i$$

$$|f\rangle = \sum_i \langle e_i | f \rangle |e_i\rangle$$

Euclidian space

$$\Rightarrow \vec{a} = (a_1^e, a_2^e, \ldots, a_n^e)$$

scalar product:

$$\vec{a} \cdot \vec{b} = \sum_{i=1}^{n} a_i^e b_i^e$$

Hilbert space

$$|f\rangle = (f_1^e, f_2^e, \ldots, f_n^e)$$

MO
molecular
orbital
coefficient
vector

AOs
atomic
orbital
coefficients

MO - LCAO approach

$$\langle f|g\rangle = \sum_{i=1}^{n} f_i^{e*} g_i^e$$

• Properties of hermitian operators

$$\hat{A} = (\hat{A}^T)^* = A^\dagger$$

hermitian operator $\hat{A}$

alternatively:

$$\int \psi_i^* \hat{A} \psi_j \, d\tau = \left[\int \psi_j^* \hat{A} \psi_i \, d\tau \right]^* = \int \psi_i^* \hat{A}^\dagger \psi_j \, d\tau$$

$$\langle \psi_i | \hat{A} | \psi_j \rangle = \langle \psi_j | \hat{A} | \psi_i \rangle^* = \langle \psi_i | \hat{A}^\dagger | \psi_j \rangle$$

$$\langle i | \hat{A} | j \rangle = \langle j | \hat{A} | i \rangle^* = \langle i | \hat{A}^\dagger | j \rangle$$

$$\underline{A}_{ij} = \underline{A}_{ji}^* = \underline{A}^\dagger_{ij}$$

$$\underline{A} = (\underline{A}^T)^* = \underline{A}^\dagger$$

hermitian matrix $\underline{A}$

real eigenvalues:

$\hat{A}|\psi\rangle = a|\psi\rangle \quad \rightarrow \quad \langle\psi|\hat{A}|\psi\rangle = a\langle\psi|\psi\rangle$

$$\langle\psi|\hat{A}|\psi\rangle^* = a^*\langle\psi|\psi\rangle^*$$

difference[1] $\qquad 0 = (a - a^*)\,1$

$$\Rightarrow a \in \mathbb{R}$$

[1] used: hermitian operators $\hat{A}$ and 1, normalized state $|\psi\rangle$

orthogonal eigenfunctions:

$$\hat{A}|\psi_i\rangle = a_i|\psi_i\rangle \qquad \hat{A}|\psi_j\rangle = a_j|\psi_j\rangle$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$\langle\psi_j|\hat{A}|\psi_i\rangle = a_i\langle\psi_j|\psi_i\rangle \qquad \langle\psi_i|\hat{A}|\psi_j\rangle^* = a_j^*\langle\psi_i|\psi_j\rangle^*$$

equal for hermitian operators $\hat{A}$ and 1

difference: $0 = (a_i - a_j^{(*)})\cdot\langle\psi_j|\psi_i\rangle$

If $a_i \neq a_j$ it follows that $\langle\psi_j|\psi_i\rangle = 0$

(for $a_i = a_j$ one can orthogonalize ψ_i, ψ_j)

- eigenfunctions of commuting operators

$$[\hat{A},\hat{B}] = 0$$

$$\hat{A}|\psi\rangle = a|\psi\rangle \qquad \hat{B}|\psi\rangle = |\tilde{\psi}\rangle$$

$$\hat{B}\hat{A}\underbrace{|\psi\rangle = \hat{B}a|\psi\rangle = a\hat{B}|\psi\rangle = \underline{a|\tilde{\psi}\rangle} = \hat{A}\hat{B}}_{\text{equal for commuting operators}}|\psi\rangle = \underline{\hat{A}|\tilde{\psi}\rangle}$$

$\Rightarrow$ $|\tilde{\psi}\rangle$ is eigenfunction of $\hat{A}$ with eigenvalue a, i.e. $|\tilde{\psi}\rangle \sim |\psi\rangle$ or $|\tilde{\psi}\rangle = b\cdot|\psi\rangle$ and thus $\hat{B}|\psi\rangle = b|\psi\rangle$ holds.

$\Rightarrow$ Useful to classify solutions of the Schrödinger equation according to quantum numbers of operators commuting with $\hat{H}$:

e.g. $\hat{\vec{L}}^2$, $\hat{L}_z$, $\hat{\vec{S}}^2$, $\hat{S}_z$, $\hat{\vec{J}}^2$, $\hat{J}_z$, ... and other symmetry operators

$\Longrightarrow 1s^1\ {}^2S_{1/2}$, $\pi^1\ {}^2\Pi_{1/2}$, ...

- expectation values of non-eigenstates

$$\hat{A}|\psi_i\rangle = a_i|\psi_i\rangle$$

- if the system is in an eigenstate $|\psi_i\rangle$ of the operator $\hat{A}$, the corresponding measurement will always yield the eigenvalue a_i, i.e.

$$\langle\hat{A}\rangle = \langle\psi_i|\hat{A}|\psi_i\rangle = a_i$$

- if the system is not in an eigenstate one can still expand its state in the basis of eigenstates of $\hat{A}$, which form a complete orthonormal set $\{|\psi_i\}$:

$$|\phi\rangle = \sum_i c_i |\psi_i\rangle \qquad \langle\phi|\phi\rangle = \sum_i |c_i|^2 = 1$$

$$\langle \hat{A} \rangle = \langle \phi | \hat{A} | \phi \rangle = \sum_i c_i^* c_j \langle \psi_i | \hat{A} | \psi_j \rangle =$$

$$= \sum_i c_i^* c_j a_j \langle \psi_i | \psi_j \rangle = \sum_i c_i^* c_j a_j \delta_{ij} =$$

$$= \sum_i |c_i|^2 a_i$$

$\Rightarrow$ one always measures one of the eigenvalues a_i of $\hat{A}$; a particular eigenvalue a_i is obtained with a probability $|c_i|^2$; the expectation value $\langle \hat{A} \rangle$ is a weighted sum of eigenvalues a_i; the weights correspond to the probability to "find the system in eigenstate a_i.

Angular Momentum Operators

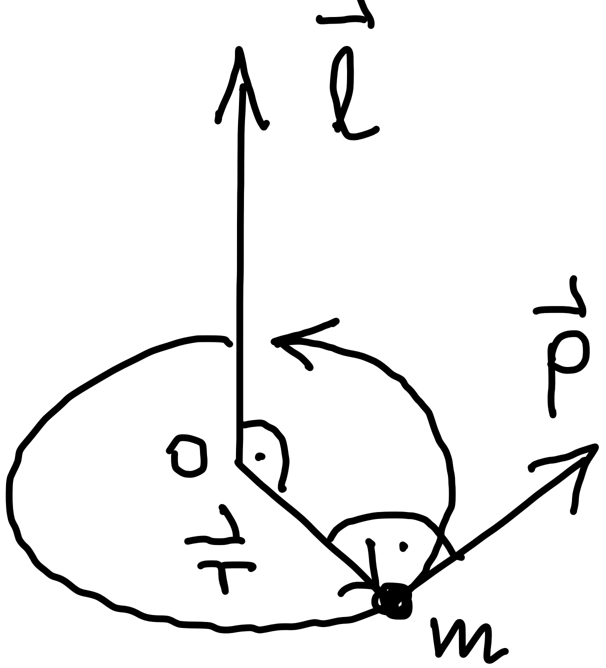
- position $x \longrightarrow \hat{x} = x\cdot$
- momentum $p_x \longrightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

(position representation)

- angular momentum

classical mechanics:

$\vec{l} := \vec{r} \times \vec{p}$



particle with mass m on a ring with radius r:

$$E_{kin} = \frac{1}{2} m v^2 = \frac{m^2 \cdot v^2}{2m} = \frac{r^2 \cdot m^2 \cdot v^2}{2m \cdot r^2} =$$

$$= \frac{l^2}{2\Theta} = \frac{\vec{l}^{\,2}}{2\Theta}$$

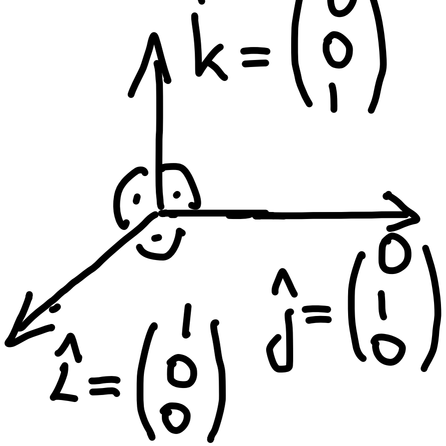
$\vec{l}$ angular momentum

Θ moment of inertia

quantization:

$$\hat{H}_{rot} = \frac{\hat{\vec{l}}^{\,2}}{2\Theta} \quad , \quad \hat{\vec{l}} = \hat{\vec{r}} \times \hat{\vec{p}}$$

$$\hat{\vec{l}} = \hat{\vec{r}} \times \hat{\vec{p}} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} =$$



$$= \begin{pmatrix} \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{pmatrix} = \begin{pmatrix} \hat{l}_x \\ \hat{l}_y \\ \hat{l}_z \end{pmatrix}$$

Using the elementary commutation relation $[\hat{x}, \hat{p}_x] = i\hbar$ one can show that

$$[\hat{\vec{l}}^{\,2}, \hat{l}_i] = 0 \quad , \quad [\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$$

$i = x, y, z$

cyclic:

$$\begin{tikzcd} x \arrow[r] & y \arrow[r] & z \arrow[ll, bend left] \end{tikzcd}$$

Rigid Rotor ($\hat{=}$ angular part H atom)

- mass m rotating on a sphere with radius r (= const.)
- analytical solution in spherical coordinates $(x, y, z \rightarrow r, \vartheta, \varphi)$
- $\hat{L}^2 \, |Y_{lm}(\vartheta, \varphi)\rangle = \hbar^2 l(l+1) |Y_{lm}(\vartheta, \varphi)\rangle$

  $\hat{L}_z \, |Y_{lm}(\vartheta, \varphi)\rangle = \hbar m |Y_{lm}(\vartheta, \varphi)\rangle$

  $l = 0, 1, 2, \ldots$ (s, p, d, ...), $m = -l, \ldots, -1, 0, +1, \ldots, +l$

$Y_{lm}(\vartheta,\varphi)$ spherical harmonics

- in QM one uses the commutation relation $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$ (cyclic) as a <u>definition</u> of an angular momentum operator $\hat{\vec{l}} = (\hat{l}_x, \hat{l}_y, \hat{l}_z)$.
- Symbols:

  H atom, atomic orbitals:

  $\hat{\vec{l}}, \hat{l}_x, \hat{l}_y, \hat{l}_z, l, m_l$

- rigid rotor:

  $\hat{\vec{J}}^2, \hat{J}_x, \hat{J}_y, \hat{J}_z, J, M_J$

$\Rightarrow$ these rotations have a classical analogue

the quantum numbers are integral

$(l, J = 0, 1, 2, \ldots ; m_l, M_J = \pm m_l, M_J, \ldots, 0)$

- experimental evidence (e.g. Stern-Gerlach experiment) or relativistic QM tells us that there exists also an angular momentum with half-integral quantum numbers and without classical analogue!

- e.g.
  - spin of an electron → $\hat{\vec{s}}$
  - total angular momentum of an electron (e.g. H atom) → $\hat{\vec{j}} = \hat{\vec{l}} + \hat{\vec{s}}$

Spin of an electron

intrinsic angular momentum, property

operators: $\hat{\vec{S}}^2, \hat{S}_x, \hat{S}_y, \hat{S}_z$

quantum numbers: $s = 1/2$, $m_s = \pm 1/2$

eigenvalue equations:

$$\hat{\vec{S}}^2 \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle = \hbar^2 \frac{3}{4} \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$$

$$\hat{S}_z \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle = \pm\hbar \frac{1}{2} \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$$

eigenfunctions: $|s, m_s\rangle = \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$

- vector/matrix representation of spin eigenfunctions/operators

spin functions:

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and}$$

$$\langle\alpha| = \begin{pmatrix} 1 & 0 \end{pmatrix} \quad , \quad \langle\beta| = \begin{pmatrix} 0 & 1 \end{pmatrix}$$

$$\Rightarrow \langle\alpha|\beta\rangle = 0 \; , \; \langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 0$$

complete orthonormal basis in 2D spin space

spin operators:

$$\hat{\vec{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$$

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\,\sigma_x$$

$$\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2}\,\sigma_y$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\,\sigma_z$$

$$\hat{\vec{S}}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

2x2 Pauli spin matrices $\sigma_x, \sigma_y, \sigma_z$

definition of angular momentum $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$ is fulfilled examples:

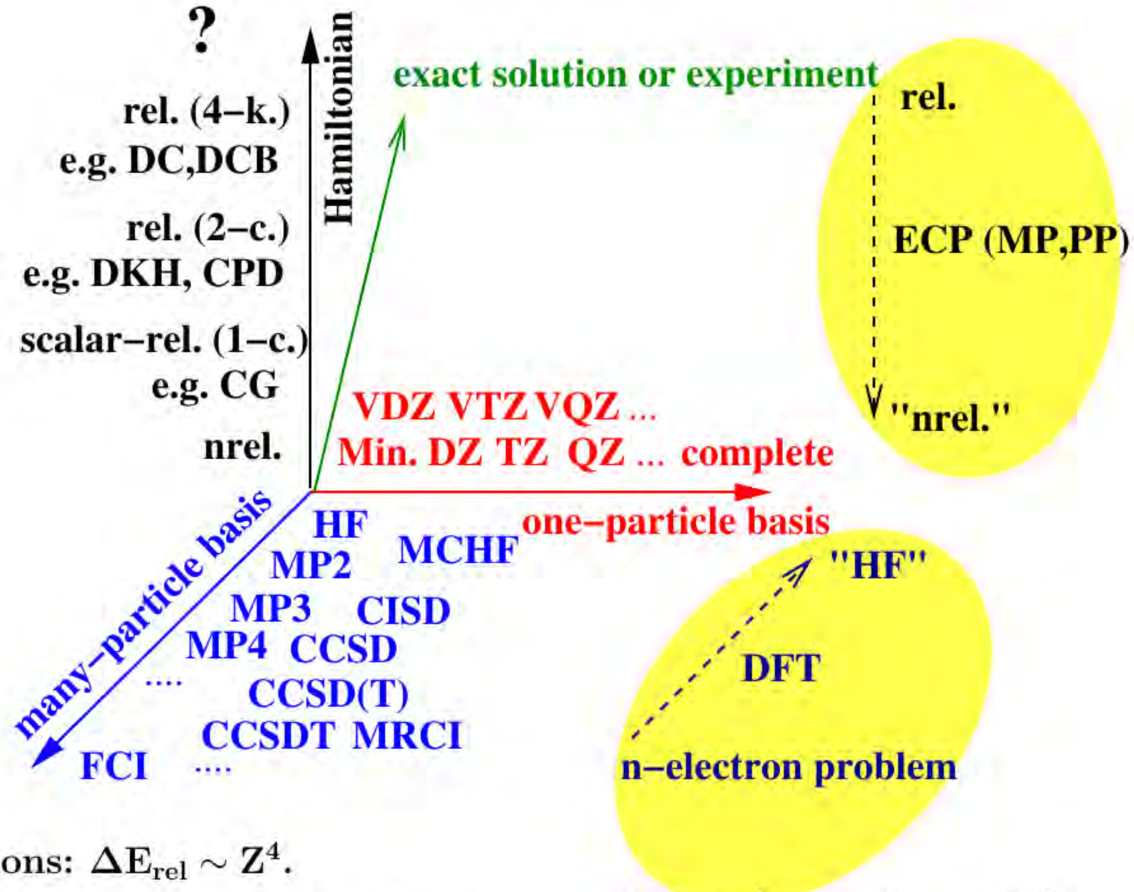
$$\hat{S}^2 |\alpha\rangle = \frac{3}{4}\hbar^2 |\alpha\rangle \Rightarrow \frac{3}{4}\hbar^2 \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix}1\\ 0\end{pmatrix}$$

$$\hat{S}_z |\beta\rangle = -\frac{1}{2}\hbar |\beta\rangle \Rightarrow \frac{1}{2}\hbar \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} = -\frac{1}{2}\hbar \begin{pmatrix}0\\ 1\end{pmatrix}$$

etc.

wavefunction:

$$\psi = \begin{pmatrix}\psi_\alpha\\ \psi_\beta\end{pmatrix} = \overset{\text{spatial part } \alpha}{\psi_\alpha} \overset{\text{spin part } \alpha}{\begin{pmatrix}1\\ 0\end{pmatrix}} + \psi_\beta \begin{pmatrix}0\\ 1\end{pmatrix}$$



?

Hamiltonian

rel. (4–k.)
e.g. DC,DCB

rel. (2–c.)
e.g. DKH, CPD

scalar–rel. (1–c.)
e.g. CG

nrel.

exact solution or experiment

VDZ VTZ VQZ ...
Min. DZ TZ QZ ... complete

one–particle basis

many–particle basis

HF
MP2
MP3
MP4
....
FCI

MCHF
CISD
CCSD
CCSD(T)
CCSDT MRCI
....

rel.
ECP (MP,PP)
"nrel."

"HF"
DFT
n–electron problem

- relativistic contributions: $\Delta E_{rel} \sim Z^4$.
- correlation energy errors for standard basis set expansions: $E^{l}_{corr} - E^{\infty}_{corr} \sim 1/l^3$ → basis set extrapolation or F12-dependent wavefunctions.
- computational effort: $t \sim n^k$ (n size of one-particle basis set, k for some standard approaches: DFT 3, HF 4, MP2 5, CISD, CCSD 6, CCSD(T) 7 ...) → low-order/linear scaling schemes.
- ECPs simplify the Hamiltonian and also lead to some reductions in the sizes of the one- and many-electron basis sets (e.g. small-core PPs plus valence-only SO terms) !
- DFT avoids costly many-determinantal wavefunctions/treatments.

Goal: Suitable compromise between accuracy and computational effort,
i.e., sufficiently accurate low-cost relativistic electronic structure calculations, also for larger systems.

Atomic units:

inconvenient, numerical problems

$$m_{0,e} = 9{,}1093837139 \cdot 10^{-31}\,\text{kg}$$

$$e = 1{,}602176634 \cdot 10^{-19}\,\text{C}$$

$$h = 6.62607015 \cdot 10^{-34}\,\text{Js}$$

by definition:

$$m_{0,e} = e = \hbar = 1 \text{ atomic unit (a.u.)}$$

length :

$$1 \text{ a.u.} = 1 \text{ Bohr} \cong 0.52918 \text{ Å}$$

energy :

$$1 \text{ a.u.} = 1 \text{ Hartree} \cong 27.2117 \text{ eV}$$

$$\cong 627.5 \text{ kcal/mol}$$

$$\cong 2625.5 \text{ kJ/mol}$$

$$\cong 219474 \text{ cm}^{-1}$$

Many-electron systems

Born-Oppenheimer approximation:

- nuclei heavy, electrons light
- uniform distribution of energy on the particles (electrons, nuclei)

  $E = \frac{1}{2} m v^2$ m large → v small
- nuclei slow, electrons fast
- electrons in the field of fixed nuclei

- Hamiltonian: BO approximation

$$\hat{H} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j)$$

$$\hat{h}(i) = -\frac{1}{2}\Delta_i - \sum_{I=1}^{N} \frac{Z_I}{r_{iI}} , \quad g(i,j) = \frac{1}{r_{ij}}$$

universal specific universal

- Schrödinger equation:

$\hat{H}\Psi = E\Psi$ → "electronic" H_{el}, E_{el}

- nuclear repulsion:

$$W = \sum_{I=J+1}^{N} \sum_{J=1}^{N-1} \frac{Z_I Z_J}{r_{IJ}}$$

const. in the
BO approximation

- total energy:

$$E_{tot}(\{\vec{R}_I\}) = E_{el} + W$$

=> potential curve,
energy hypersurface

- wavefunction:
  - no analytic solution as for the H atom possible
  - build a many-electron wavefunction from (familiar) one-electron wavefunctions (→ orbitals or spin-orbitals: one electron in the field of all others and the nuclei)

- Hartree product

$$\phi = \prod_{i=1}^{n} \varphi_i(i) = \varphi_1(1)\varphi_2(2)\dots\varphi_n(n)$$

electron index

spinorbital orbital index

- we assume $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$, so that $\langle \phi | \phi \rangle = 1$ holds
- every electron occupies its own orbital

- Slater determinant

- electrons are indistinguishable
- wavefunction must be antisymmetric wrt. exchange of two electrons

$\Rightarrow$ antisymmetrized linear combination of Hartree products

$$\Phi = \frac{1}{\sqrt{n!}} \sum_{k=1}^{n!} \hat{P}_k \, (-1)^{p_k} \prod_{i=1}^{n} \varphi_i(i) =$$

$$= \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_n(2) \\ \varphi_1(3) & \varphi_2(3) & \dots & \varphi_n(3) \\ \vdots & & & \vdots \\ \varphi_1(n) & \varphi_2(n) & \dots & \varphi_n(n) \end{vmatrix} .$$

$\hat{P}_k$ permutation operator

acts on the "diagonal" Hartree product $\varphi_1(1)\,\varphi_2(2)\,\ldots\,\varphi_n(n)$ and exchanges p_k times two electrons

→ $n!$ possible arrangements of n electrons in n orbitals, $n!$ $\hat{P}_k$ operators

→ indistinguishability of electrons

→ $(-1)^{P_k}$ leads to antisymmetry of the wavefunction (Pauli principle)

- we assume $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$, so that $\langle \phi | \phi \rangle = 1$ due to the normalization factor $\frac{1}{\sqrt{n!}}$

- properties of determinants:
  - change of sign upon exchange of two rows or two colums, corresponding to exchange of two electrons or two orbitals
  - zero if two lines or two columns are identical

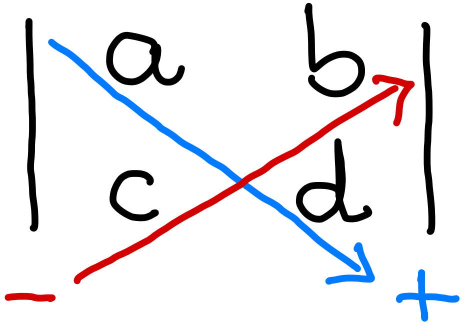
$\Rightarrow$ fulfillment of Pauli principle!

Note: a Slater determinant is not the exact solution of the Schrödinger equation!

The "best" orbitals (wrt. E) can be determined in the Hartree-Fock method. cf. later!

- how to evaluate determinants

2×2

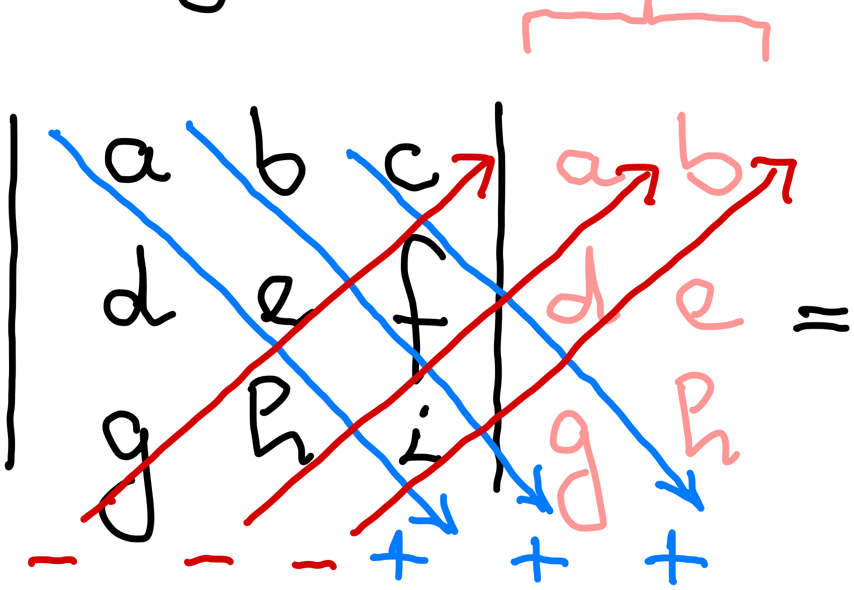


$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = \underline{ad} - \underline{bc}$$

to make it easier...

"rule of Sarrus"

3×3



$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} \begin{matrix} a & b \\ d & e \\ g & h \end{matrix} = \underline{aei} + \underline{bfg} + \underline{cdh} - \underline{gec} - \underline{hfa} - \underline{idb}$$

$n \times n \; (n \geq 2)$: expansion according to Laplace

$$\det|\underline{A}| = \begin{vmatrix} \overset{+}{a_{11}} & \overset{-}{a_{12}} & \overset{+}{a_{13}} & \cdots \\ \overset{-}{a_{21}} & \overset{+}{a_{22}} & \overset{-}{a_{23}} & \cdots \\ \overset{+}{a_{31}} & \overset{-}{a_{32}} & \overset{+}{a_{33}} & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{vmatrix}$$

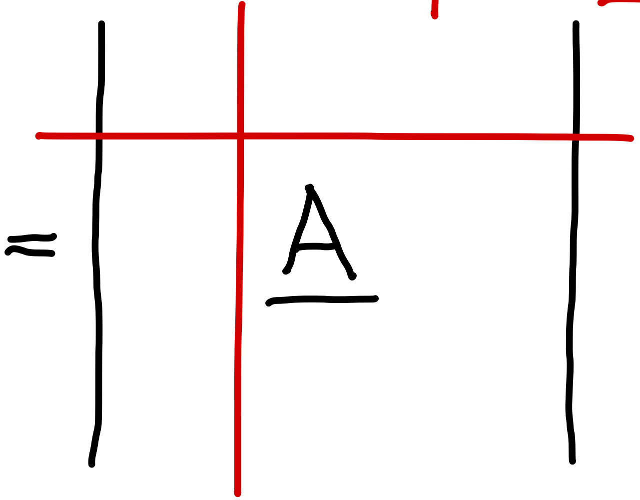
expansion wrt row l:

$$= \sum_k a_{lk} (-1)^{l+k} \cdot \det|\underline{A}^{lk}|$$

delete row l and column k from $\underline{A}$

chose row or column to expand (if possible chose those with $a_{ij} = 0$)

$$\det|\underline{A}^{lk}| =$$



example:

$$\begin{array}{ccc} + & - & + \\ \hline \end{array}$$

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11} \begin{vmatrix} \cancel{a_{11}} & \cancel{a_{12}} & \cancel{a_{13}} \\ \cancel{a_{21}} & a_{22} & a_{23} \\ \cancel{a_{31}} & a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} \cancel{a_{11}} & \cancel{a_{12}} & \cancel{a_{13}} \\ a_{21} & \cancel{a_{22}} & a_{23} \\ a_{31} & \cancel{a_{32}} & a_{33} \end{vmatrix}$$

$$+ a_{13} \begin{vmatrix} \cancel{a_{11}} & \cancel{a_{12}} & \cancel{a_{13}} \\ a_{21} & a_{22} & \cancel{a_{23}} \\ a_{31} & a_{32} & \cancel{a_{33}} \end{vmatrix} = a_{11} a_{22} a_{33} - a_{11} a_{23} a_{32}$$

$$- a_{12} a_{21} a_{33} + a_{12} a_{23} a_{31} + a_{13} a_{21} a_{32} - a_{13} a_{22} a_{31}$$

expansion wrt. column l:

$$\det|\underline{A}| = \sum_k a_{kl} (-1)^{k+l} \cdot \det|\underline{A}^{kl}|$$

Two-electron systems

$$\Phi = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) \\ \varphi_1(2) & \varphi_2(2) \end{vmatrix} =$$

$$= \frac{1}{\sqrt{2}} \left(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2) \right)$$

every electron in every orbital ✓

sign change upon electron exchange ✓

φ_i : spin orbitals

spatial part ϕ_i , spin part $\sigma_i = \begin{cases} \alpha \\ \beta \end{cases}$

there are four possibilities for ϕ:

$$\begin{array}{lllll} \varphi_1 = & \phi_1 \cdot \alpha, & \phi_1 \cdot \beta, & \phi_1 \cdot \alpha, & \phi_1 \cdot \beta \\ \varphi_2 = & \phi_2 \cdot \alpha, & \phi_2 \cdot \beta, & \phi_2 \cdot \beta, & \phi_2 \cdot \alpha \\ & 1) & 2) & 3) & 4) \end{array}$$

$$M_s = m_{s_1} + m_{s_2} = \quad 1 \quad -1 \quad 0 \quad 0$$

there is a triplet $(S=1)$ and a singlet $(S=0)$

$$\Phi_{M_S=1} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\underline{\alpha(1)} & \phi_2(1)\underline{\alpha(1)} \\ \phi_1(2)\underline{\alpha(2)} & \phi_2(2)\underline{\alpha(2)} \end{vmatrix} = \Phi_{S=1,M_S=1} =$$

$$= \frac{1}{\sqrt{2}}\, \underline{\alpha(1)}\,\underline{\alpha(2)} \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix} \qquad \uparrow\,\uparrow$$

spin part: symmetric

spatial part: anti-symmetric

<u>**triplet!**</u>

$\Phi_{M_S=-1}$ analogous $(\alpha \to \beta)$ $\downarrow\,\downarrow$

$$\phi_{M_s=0,3)} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left(\underline{\phi_1(1)}\alpha(1)\underline{\phi_2(2)}\beta(2) - \underline{\phi_2(1)}\beta(1)\underline{\phi_1(2)}\alpha(2) \right)$$

$$\phi_{M_s=0,4)} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left(\underline{\phi_1(1)}\beta(1)\underline{\phi_2(2)}\alpha(2) - \underline{\phi_2(1)}\alpha(1)\underline{\phi_1(2)}\beta(2) \right)$$

$$\frac{1}{\sqrt{2}}\left[\Phi_{M_S=0,3)} - \Phi_{M_S=0,4)}\right] = \Phi^{0s}_{S=0,M_S=0} =$$

$$= \frac{1}{2}\Big[\underline{\phi_1(1)}\alpha(1)\underline{\phi_2(2)}\beta(2) - \underline{\phi_2(1)}\beta(1)\underline{\phi_1(2)}\alpha(2)$$

$$- \underline{\phi_1(1)}\beta(1)\underline{\phi_2(2)}\alpha(2) + \underline{\phi_2(1)}\alpha(1)\underline{\phi_1(2)}\beta(2)\Big]$$

$$= \frac{1}{2}\left[\left(\underline{\phi_1(1)\phi_2(2)} + \underline{\phi_2(1)\phi_1(2)}\right)\begin{vmatrix}\alpha(1) & \beta(1)\\ \alpha(2) & \beta(2)\end{vmatrix}\right]$$

spatial part: symmetric

spin part: antisymmetric

<u>singlet</u>

$\uparrow\downarrow - \downarrow\uparrow$

$$\frac{1}{\sqrt{2}}\left[\Phi_{M_S=0,3)} + \Phi_{M_S=0,4)}\right] = \Phi_{S=1,M_S=0} =$$

$$= \frac{1}{2}\Big[\underline{\phi_1(1)}\alpha(1)\underline{\phi_2(2)}\beta(2) - \underline{\phi_2(1)}\beta(1)\underline{\phi_1(2)}\alpha(2)$$

$$+ \underline{\phi_1(1)}\beta(1)\underline{\phi_2(2)}\alpha(2) + \underline{\phi_2(1)}\alpha(1)\underline{\phi_1(2)}\beta(2)\Big]$$

$$= \frac{1}{2}\left[\big(\alpha(1)\beta(2) + \beta(1)\alpha(2)\big)\begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix}\right]$$

spin part: symmetric

spatial part: antisymmetric

<u>triplet</u>

↑ ↓ + ↓ ↑

Note:

- an open shell singlet $(\phi_1 \neq \phi_2)$ cannot be described by a single Slater determinant.
- ↑ ↓ is not an open shell singlet (wavefunction).
- $\phi_1 = \phi_2$ leads to the closed shell singlet or $\phi = 0$ for the "triplet"

$$\frac{1}{\sqrt{2}}\left[\Phi_{M_S=0,3)} - \Phi_{M_S=0,4)}\right] = \Phi^{cs}_{S=0,M_S=0}$$

$$= \frac{1}{2}\left[\left(\phi_1(1)\phi_1(2)+\phi_1(1)\phi_1(2)\right)\begin{vmatrix}\alpha(1) & \beta(1)\\ \alpha(2) & \beta(2)\end{vmatrix}\right]$$

$$\sim \frac{1}{\sqrt{2}}\phi_1(1)\phi_1(2)\begin{vmatrix}\alpha(1) & \beta(1)\\ \alpha(2) & \beta(2)\end{vmatrix}$$

closed shell singlet ⇅

$$\frac{1}{\sqrt{2}}\left[\Phi_{M_S=0,3)} + \Phi_{M_S=0,4)}\right] =$$

equal columns!

$$= \frac{1}{2}\left[\left(\alpha(1)\beta(2)+\beta(1)\alpha(2)\right)\begin{vmatrix}\phi_1(1) & \phi_1(1)\\ \phi_1(2) & \phi_1(2)\end{vmatrix}\right]$$

$$= 0$$

Pauli forbidden! ⇈

Energies of open-shell singlet and triplet:

$$\langle \Phi_{S=1,M_S=1} | \overset{\hat{h}(1)+\hat{h}(2)+\hat{g}(1,2)}{\hat{H}} | \Phi_{S=1,M_S=1} \rangle =$$

no spin dependence!!

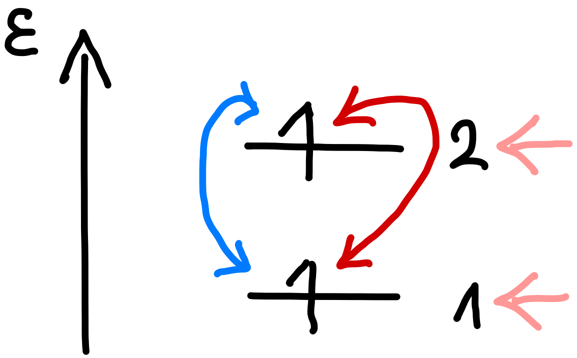
$$= \frac{1}{2} \langle \alpha(1)\alpha(2) | \alpha(1)\alpha(2) \rangle \cdot$$

$$\langle \phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2) | \hat{h}(1) + \hat{h}(2) + \hat{g}(1,2) | \ldots$$

$$\ldots \phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2) \rangle =$$

$$= \frac{1}{2}\left(2h_1 + 2h_2 + 2J_{12} - 2K_{12}\right) =$$

$$= \underbrace{h_1 + h_2}_{\text{one electron terms}} + \underbrace{J_{12} - K_{12}}_{\text{two electron terms}}$$



$$h_{\underline{1}} = \langle \phi_{\underline{1}} | \hat{h} | \phi_{\underline{1}} \rangle \ , \ h_{\underline{2}} = \langle \phi_{\underline{2}} | \hat{h} | \phi_{\underline{2}} \rangle$$

$$J_{\underline{1}\underline{2}} = \langle \phi_{\underline{1}}(1)\phi_{\underline{2}}(2) | \hat{g}(1,2) | \phi_{\underline{1}}(1)\phi_{\underline{2}}(2) \rangle \quad \text{Coulomb}$$

$$K_{\underline{12}} = \langle \phi_{\underline{1}}(1)\phi_{\underline{2}}(2) | \hat{g}(1,2) | \phi_{\underline{2}}(1)\phi_{\underline{1}}(2) \rangle \quad \text{exchange}$$

same result for $\Phi_{S=1, M_S=-1}$!

$$\left\langle \Phi^{os}_{S=0,M_S=0} \middle| \hat{H} \middle| \Phi^{os}_{S=0,M_S=0} \right\rangle =$$

$$= \frac{1}{4} \cdot \left\langle \begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix} \middle| \begin{vmatrix} \alpha(1) & \beta(2) \\ \alpha(2) & \beta(1) \end{vmatrix} \right\rangle \cdot$$

spatial part almost as for $S=1, M_S=1$!

$$\cdot \left\langle \phi_1(1)\phi_2(2) \underset{\sim}{+} \phi_2(1)\phi_1(2) \middle| \hat{h}(1) + \hat{h}(2) + \hat{g}(1,2) \middle| \right. \ldots$$

$$\ldots \left. \phi_1(1)\phi_2(2) \underset{\sim}{\pm} \phi_2(1)\phi_1(2) \right\rangle =$$

$$= \frac{1}{4} \cdot 2 \cdot \left(2h_1 + 2h_2 + 2J_{12} \underset{\sim}{\pm} 2K_{12} \right) =$$

$$= h_1 + h_2 + J_{12} \underset{\sim}{\pm} K_{12}$$

$$\langle \Phi_{S=1,M_S=0} | \hat{H} | \Phi_{S=1,M_S=0} \rangle =$$

$$= \frac{1}{4} \cdot \langle \alpha(1)\beta(2)+\beta(1)\alpha(2) | \alpha(1)\beta(2)+\beta(1)\alpha(2) \rangle \cdot$$

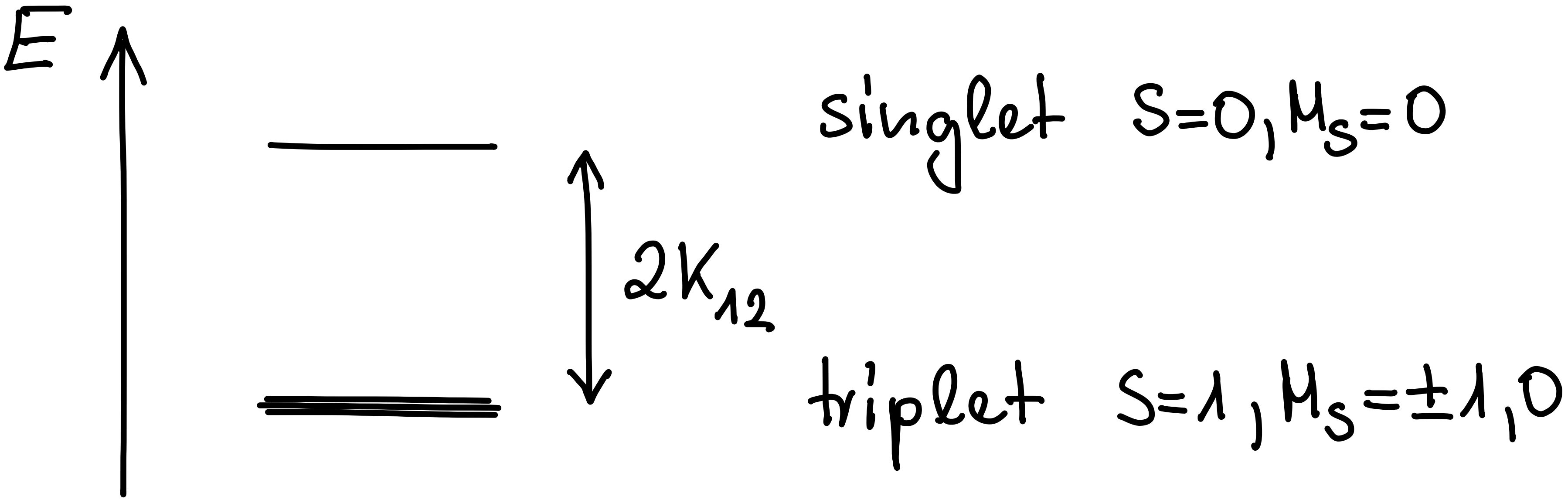
$$\cdot \langle \phi_1(1)\phi_2(2)-\phi_2(1)\phi_1(2) | \hat{h}(1)+\hat{h}(2)+\hat{g}(1,2) | \ldots$$

$$\ldots \phi_1(1)\phi_2(2)-\phi_2(1)\phi_1(2) \rangle =$$

$$= \frac{1}{4} \cdot 2 \cdot (2h_1 + 2h_2 + 2J_{12} - 2K_{12}) =$$

$$= h_1 + h_2 + J_{12} - K_{12}$$

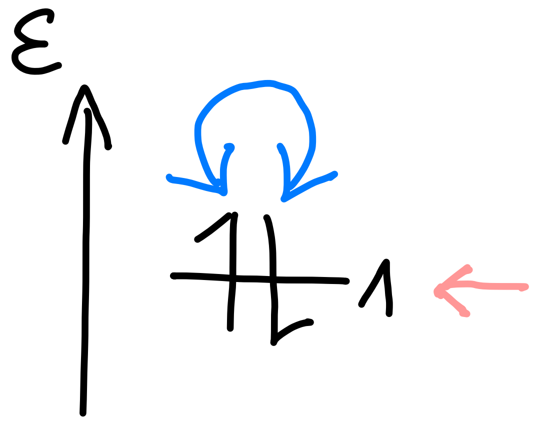
result:



The exchange integral determines the singlet-triplet splitting (open shell case)

Closed shell case:

$$\langle \Phi^{cs}_{S=0,M_S=0} | \hat{H} | \Phi^{cs}_{S=0,M_S=0} \rangle =$$

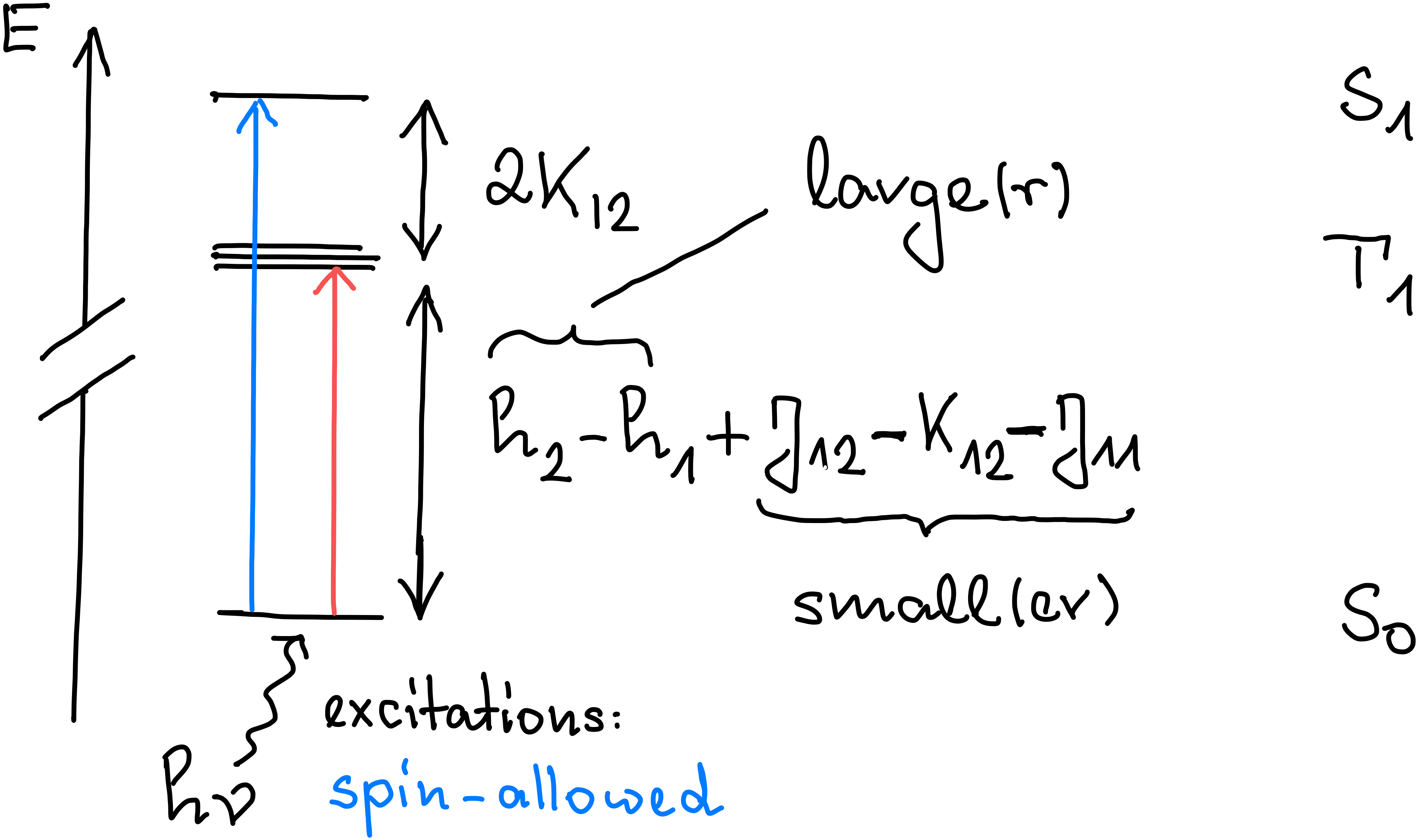


$$= \frac{1}{2} \left\langle \begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix} \middle| \begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix} \right\rangle \cdot$$

$$\cdot \langle \phi_1(1)\phi_1(2) | \hat{h}(1)+\hat{h}(2)+\hat{g}(1,2) | \phi_1(1)\phi_1(2) \rangle =$$

$$= \frac{1}{2} \cdot 2 \cdot (2h_1 + J_{11}) = \underline{2h_1} + \underline{J_{11}}$$

result:



$$\overbrace{h_2-h_1}^{\text{large(r)}}+\underbrace{J_{12}-K_{12}-J_{11}}_{\text{small(er)}}$$

excitations:

spin-allowed

spin-forbidden

Electron density and density matrices

density:

$$\rho(\vec{r}_1) = n \cdot \int\limits_1 \int\limits_2 \cdots \int\limits_n \Psi^* \, \Psi \; \underset{\text{spin}}{d\sigma_1} \; \underset{\text{space and spin}}{d\tau_2 \cdots d\tau_n}$$

- integration over all but one spatial electron coordinates
- $\int \rho(\vec{r}) \, d\vec{r} = n$ (number of electrons)
- indistinguishability of electrons: result independent of which coordinates are integrated.

$$\rho(r) = n \int_2 \cdots \int_n \left(\frac{1}{\sqrt{n!}} \sum_{k=1}^{n!} \hat{P}_k (-1)^{p_k} \prod_{i=1}^{n} \varphi_i^*(i) \right)$$

$$\left(\frac{1}{\sqrt{n!}} \sum_{k=1}^{n!} \hat{P}_k (-1)^{p_k} \prod_{i=1}^{n} \varphi_i(i) \right) dr_2 \ldots dr_n$$

electron 1 fixed to $\varphi_k^*(1)\varphi_k(1)$, $(n-1)!$ possibilities for electrons 2 to n.

$$= \frac{n}{n!} \cdot \underset{\uparrow}{(n-1)!} \left(\varphi_1^* \varphi_1 + \varphi_2^* \varphi_2 + \ldots + \varphi_n^* \varphi_n \right) =$$

$$= \rho_1(r) + \rho_2(r) + \ldots + \rho_n(r)$$

sum of densities of occupied orbitals

$$\gamma(\vec{r}_1,\vec{r}_1{}') = \int_2 \cdots \int_n \psi^*(\overbrace{\vec{r}_1}^{\text{different}},\underbrace{\dots,\vec{r}_n}_{\text{equal}})\,\psi(\vec{r}_1{}',\underbrace{\dots,\vec{r}_n}_{\text{equal}})\, d\tau_2 \dots d\tau_n$$

first order density matrix

$$\gamma(\vec{r}_1,\vec{r}_1) = \rho(\vec{r})$$

the diagonal of the first-order density matrix is the density.

higher order density matrices can be defined in analogous way; important is the pair density, which is the diagonal of the second-order density matrix:

$$\widetilde{\Pi}(\vec{r}_1, \vec{r}_2) = \Gamma(\vec{r}_1, \vec{r}_2, \vec{r}_1, \vec{r}_2)$$

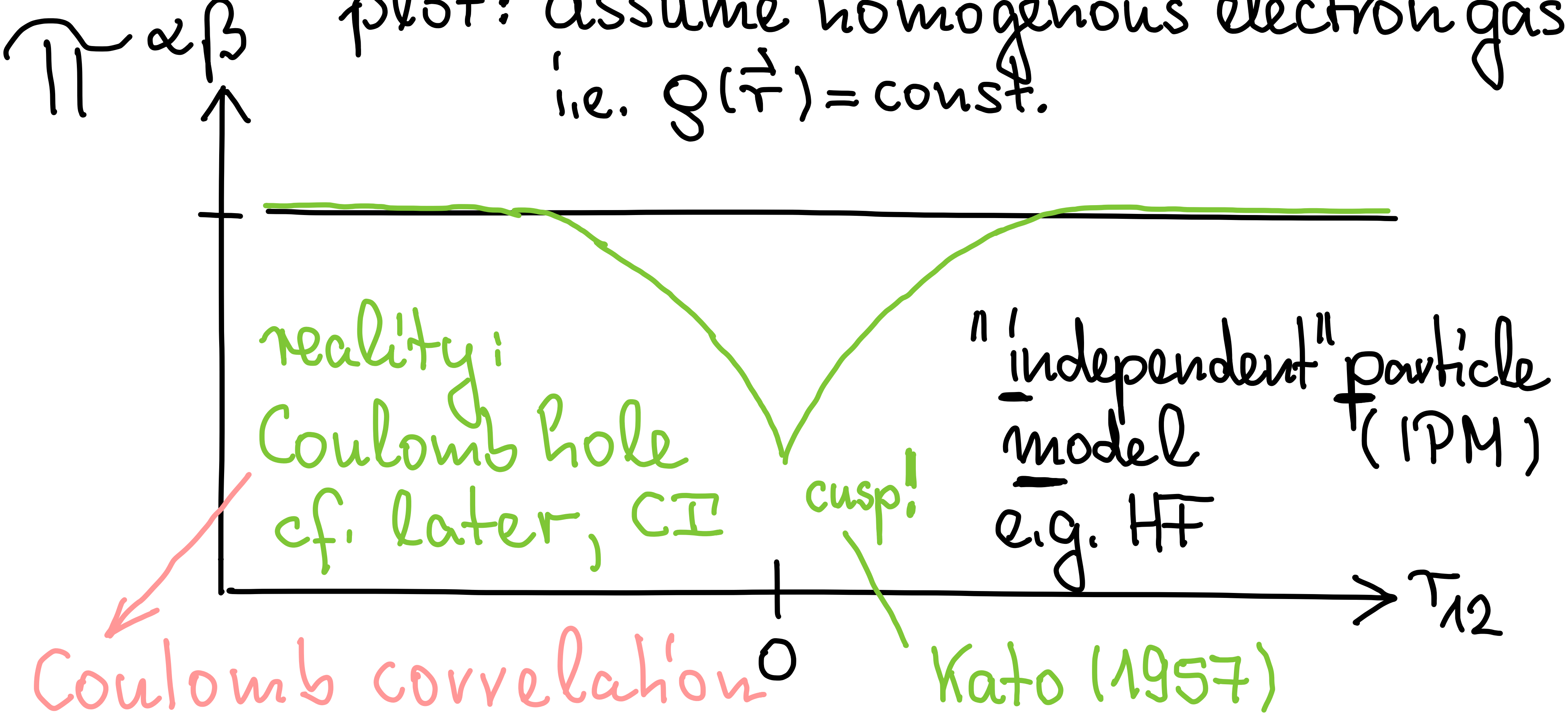
we can look at examples for the derived wave-functions of two-electron systems and distinguish between $S=0$ and $S=1$.

$$\Pi^{\alpha\beta}(\vec r_1, \vec r_2) =$$

We always integrate over <u>all</u> spin coordinates

$$\phi_1^*(1)\,\phi_1^*(2)\;\phi_1(1)\,\phi_1(2) = \rho_1(1)\cdot\rho_1(2)$$

plot: assume homogenous electron gas, i.e. $\rho(\vec r) = \text{const.}$



Kato cusp conditions (1957)

- electron-nucleus cusp

$$2 \cdot \rho(\vec{r}) \cdot Z_I = - \frac{d\rho(\vec{r})}{dr} \bigg|_{\vec{r}=\vec{R}_I} \Rightarrow$$ cf. DFT

$$\frac{\partial \psi}{\partial r_i} \bigg|_{\vec{r}_i = \vec{R}_I} = - Z_I \psi(\vec{R}_I)$$

→ You know H-type systems:

$\psi_{1s} \sim e^{-Zr}$ → fulfills the conditions $(\vec{R}_I = \vec{0})$

- electron-electron cusp

$$\left.\frac{\partial \psi}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\psi(r_{12}=0)$$

→ assume a 2-electron system so that $\psi^*\psi = \widetilde{\Pi}$ and apply the product rule for derivatives to $\psi^*\psi$! Note that $\psi(r_{12}=0)$ for α,α spin, but not for α,β spin.

→ r_{12}- or $f(r_{12})$-dependent wave-functions, e.g. F12-CCSD(T)

$$\Pi^{\alpha\alpha}(\vec{r}_1,\vec{r}_2) =$$

$$= \frac{1}{2}\left[\left(\phi_1^*(1)\phi_2^*(2) - \phi_2^*(1)\phi_1^*(2)\right)\left(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\right)\right] =$$

$$= \frac{1}{2}\Big[\rho_1(1)\rho_2(2) + \rho_2(1)\rho_1(2)$$

similar to $\Pi^{\alpha\beta}$!

$$- \phi_1^*(1)\phi_2(1)\phi_2^*(2)\phi_1(2) - \phi_2^*(1)\phi_1(1)\phi_1^*(2)\phi_2(2)\Big] =$$

$$= ?$$

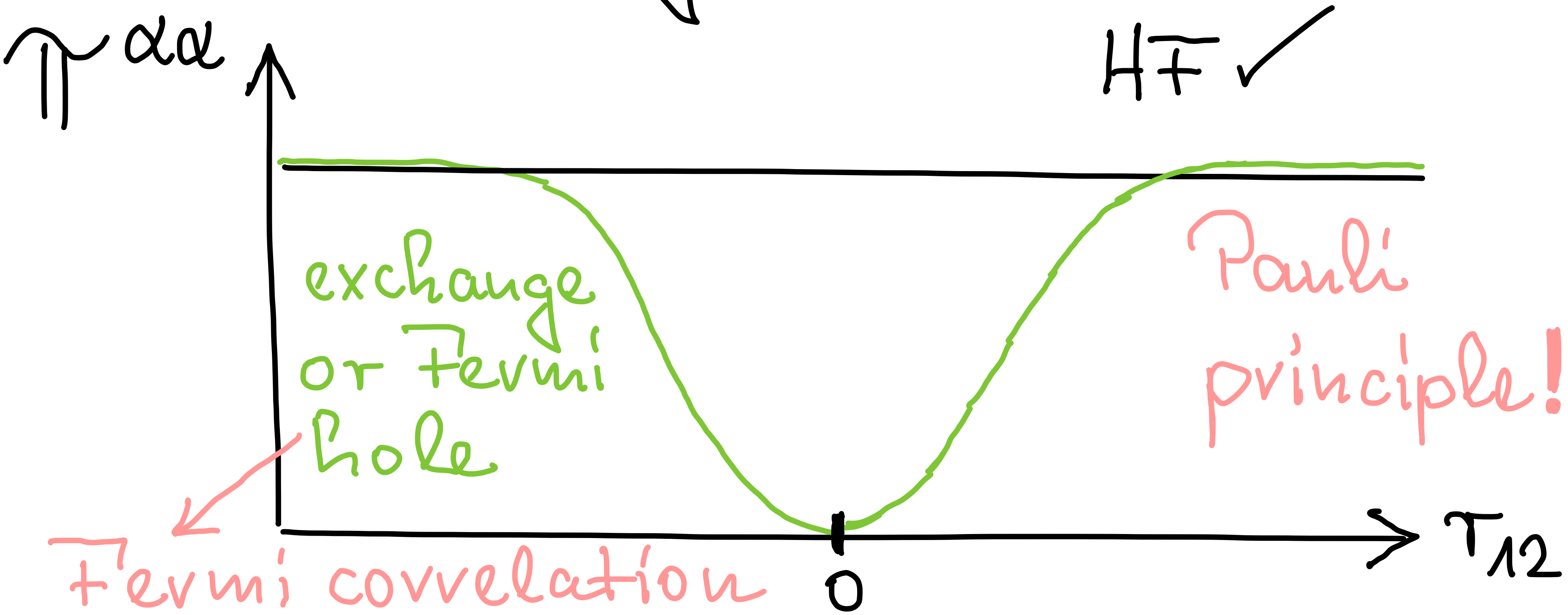
Note that $\phi_1 \neq \phi_2$

assume $\vec{r}_1 = \vec{r}_2$! then $\phi_1^*(1)\phi_1(2) = \rho_1$, etc.

$$= \frac{1}{2}\left[2\rho_1\rho_2 - \rho_1\rho_2 - \rho_2\rho_1\right] = 0$$ Pauli principle!

The pair density vanishes when two electrons with equal spin approach each other. The electrons "avoid" each other.

The pair density shows a <u>Fermi hole</u>:



Chapter 2

The Hartree-Fock (HF) method

(and beyond)

Why is the Hartree-Fock method so important for QC?

- best possible quantitative description of many-electron systems with a simple wavefunction using orbitals
- starting point for more accurate "correlation" calculations
- connection to qualitative models based on orbitals
- extension to Kohn-Sham density functional theory (HF → HFS, $X_\alpha \hat{=}$ early KSDFT)

Most important ingredients:

- Hamiltonian: variationally stable, i.e., bounded from below
- Wavefunction: Slater determinant
- Variational principle: minimize the energy to obtain the best solution
- Method of Lagrange multipliers to keep orbital orthonormalization

Hamiltonian:

$$\hat{H} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{j=i+1}^{n} \sum_{i=1}^{n-1} \hat{g}(i,j)$$

$$\hat{h}(i) = -\frac{1}{2}\Delta_i - \sum_{I=1}^{N} \frac{Z_I}{r_{Ii}}$$

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

most simple choice: non-relativistic Hamiltonian

Wavefunction: Slater determinant

$$\underset{\text{Slater determinant}}{\Phi} = \overset{\text{normalization factor}}{\frac{1}{\sqrt{n!}}} \underbrace{\sum_{k=1}^{n!} \overset{\text{permutation operator}}{\hat{P}_k} (-1)^{p_k}}_{\text{antisymmetrization operator}} \underbrace{\prod_{i=1}^{n} \overset{\text{spin-orbitals}}{\varphi}_{\underset{\text{orbital index}}{i}}(\overset{\text{electron index}}{i})}_{\text{Hartree product}}$$

$$= \frac{1}{\sqrt{n!}} \det|\varphi_1(1) \ldots \varphi_n(n)| \; ; \; \langle\varphi_i|\varphi_j\rangle = \delta_{ij}$$

Variational principle:

$$E_0^{\text{exact}} \leqslant \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = E[\tilde{\psi}]$$

- $\tilde{\psi}$ is a suitable trial wavefunction
- E_0^{exact} is the exact ground state energy
- for the exact ground state wavefunction one obtains $E_0^{\text{exact}} = E[\psi_0^{\text{exact}}]$

proof:

1. assume $\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle$ is solved!

$\{|\psi_i\rangle\}$: complete orthonormal basis, i.e.

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} \quad \text{and} \quad 1 = \sum_i |\psi_i\rangle\langle\psi_i|$$

orthonormality completeness

approximate wavefunction (normalized):

$$|\tilde{\psi}\rangle = \sum_i c_i |\psi_i\rangle$$

$$1 = \langle\tilde{\psi}|\tilde{\psi}\rangle = \sum_{i,j} c_i^* c_j \overbrace{\langle\psi_i|\psi_j\rangle}^{\delta_{ij}} = \sum_i |c_i|^2$$

$$E[\tilde{\psi}] = \langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle = \sum_{i,j} c_i^* c_j \langle\psi_i|\underbrace{\hat{H}|\psi_j\rangle}_{E_j|\psi_j\rangle} =$$

$$= \sum_{i,j} c_i^* c_j E_j \underbrace{\langle\psi_i|\psi_j\rangle}_{\delta_{ij}} = \sum_i |c_i|^2 \underbrace{E_i}_{E_i \geq E_0} \geq$$

$$\geq \sum_i |c_i|^2 E_0 = E_0 \underbrace{\sum_i |c_i|^2}_{=1} = E_0$$

$$\Rightarrow E[\tilde{\psi}] \geq E_0 = E[\psi_0]$$

q.e.d.

quod erat demonstrandum

2. assume $\hat{H}|\phi_i\rangle \overset{!}{\neq} E|\phi_i\rangle$

$\{|\phi_i\rangle\}$: complete orthonormal basis, i.e.

$$\underset{\text{orthonormality}}{\langle\phi_i|\phi_j\rangle = \delta_{ij}} \quad \text{and} \quad \underset{\text{completeness}}{1 = \sum_i |\phi_i\rangle\langle\phi_i|}$$

exact wavefunction (normalized):

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle$$

$$1 = \langle\psi|\psi\rangle = \sum_{i,j} c_i^* c_j \overbrace{\langle\phi_i|\phi_j\rangle}^{\delta_{ij}} = \sum_i |c_i|^2$$

Schrödinger equation:

$$\sum_i c_i \hat{H} |\phi_i\rangle = E \cdot \sum_i c_i |\phi_i\rangle \quad \Big| \langle\phi_j|$$

$$\sum_i c_i \underbrace{\langle\phi_j|\hat{H}|\phi_i\rangle}_{H_{ji}} = E \cdot \sum_i c_i \underbrace{\langle\phi_j|\phi_i\rangle}_{\delta_{ij}}$$

$$\sum_i c_i H_{\underset{\text{row}}{j}\,\underset{\text{column}}{i}} = E \cdot c_j$$

$$\begin{pmatrix} \\ \underset{\text{jth row}}{\underrightarrow{H_{j1}\quad H_{j2}\quad \dots\quad H_{jn}}} \\ \\ \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ \vdots \\ c_n \end{pmatrix} = E \begin{pmatrix} \\ \underset{\text{jth element}}{\boxed{H_{j1}c_1 + H_{j2}c_2 + \dots + H_{jn}c_n}} \\ \\ \end{pmatrix}$$

matrix eigenvalue problem!

(routine task for a computer (code))

one state: many states:

$$\underset{\sim}{H}\,\vec{c}_i = E_i\,\vec{c}_i \qquad \underline{H}\,\underline{C} = \underline{E}\,\underline{C} \quad \text{with} \quad \begin{array}{l} \underline{C} = (\vec{c}_1 \dots \vec{c}_n) \\ \\ \underline{E} = \begin{pmatrix} E_1 & & 0 \\ & \ddots & \\ 0 & & E_n \end{pmatrix} \end{array}$$

⇒ full configuration interaction (FCI)

- basis: all Slaterdeterminants which can be formed for a given set of (spin-orbitals) and a given number of electrons!
- exact solution! (for the underlying one-particle basis set, cf. later)

3. assume $\hat{H}|\phi_i\rangle \overset{!}{\neq} E|\phi_i\rangle$

$\{|\phi_i\rangle\}$: incomplete orthonormal basis, i.e.

$$\underset{\text{orthonormality}}{\langle\phi_i|\phi_j\rangle = \delta_{ij}} \quad \text{and} \quad \underset{\text{no completeness}}{1 \neq \sum_i |\phi_i\rangle\langle\phi_i|}$$

approximate wavefunction (unnormalized):

$$|\tilde{\psi}\rangle = \sum_i c_i |\phi_i\rangle$$

Variational principle:

$$\tilde{E}\langle\tilde{\Psi}|\tilde{\Psi}\rangle = \langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle = E[\tilde{\Psi}] \geq E_0^{exact}$$

$$\tilde{E}\sum_{ij} c_i^* c_j \underbrace{\langle\phi_i|\phi_j\rangle}_{\delta_{ij}} = \sum_{ij} c_i^* c_j \underbrace{\langle\phi_i|\hat{H}|\phi_j\rangle}_{H_{ij}}$$

$$\tilde{E}\cdot\sum_i c_i^* c_i = \sum_i c_i^* \sum_j c_j H_{ij}$$

$$\sum_i c_i^* \underbrace{\left(\sum_j c_j H_{ij} - \tilde{E} c_i\right)}_{0} = 0$$

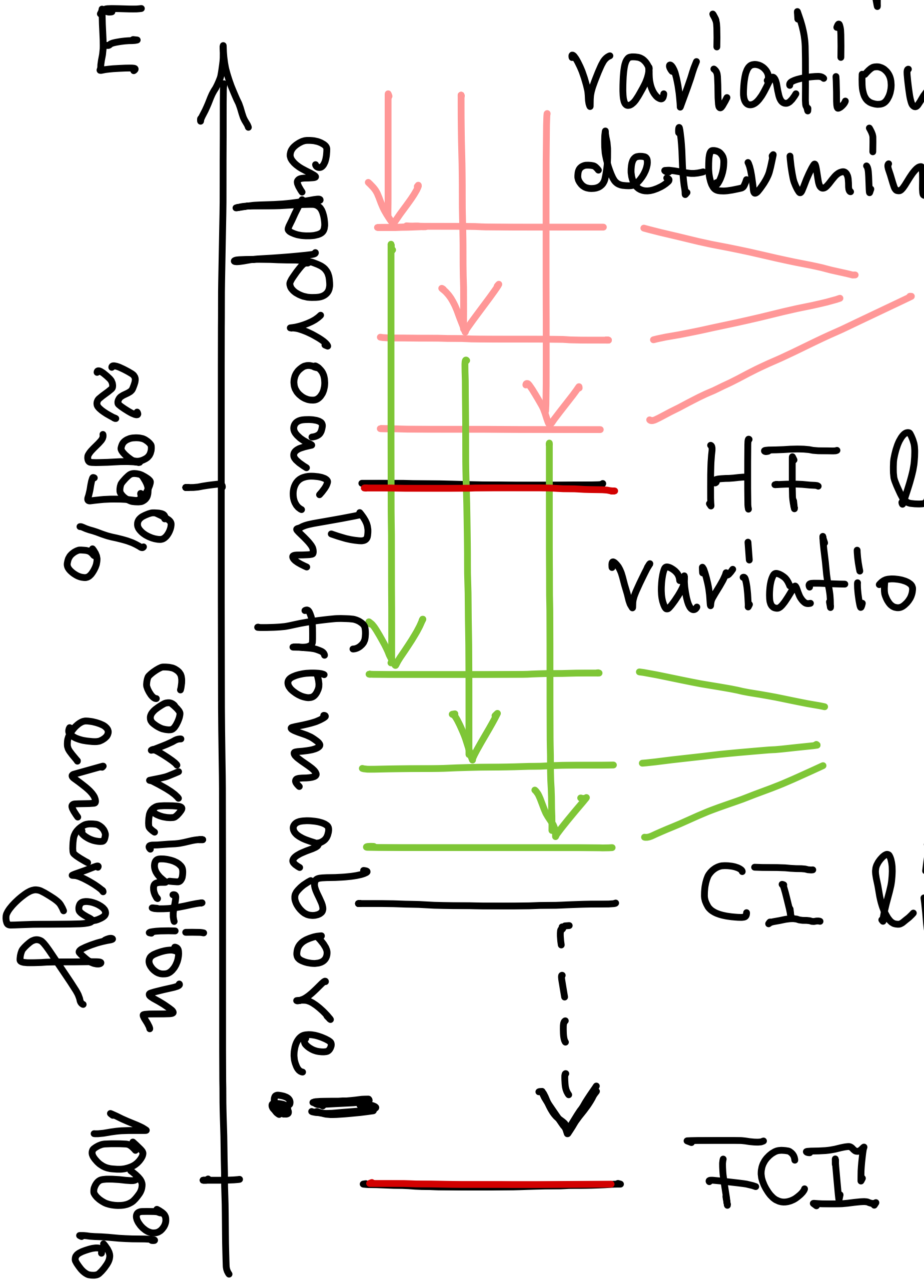
$$\sum_j c_j H_{\underset{\text{row}}{i}\,\underset{\text{column}}{j}} = \tilde{E}\cdot c_i \qquad [\text{cf. before, 2)!}]$$

$$\underline{H}\,\vec{c} = \tilde{E}\,\vec{c} \quad \text{and} \quad \underline{H}\,\underline{C} = \underline{\tilde{E}}\,\underline{C}$$

⇒ truncated **c**onfiguration **in**teraction, e.g. with **s**ingle and **do**uble excitations

CISD , and others , cf. later!

Variational principle in QC: HF, CI



variation of the orbitals in one Slater determinant

approximate HF solutions

HF limit (one determinant)

variation of coefficients of Slater determinants

approximate CI solutions

CI limit (for truncated CI)

FCI ≙ exact (for given one-electron basis set)

Hartree-Fock:

Slater determinant

Variation of $E_{HF} = \dfrac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$

wrt. orbitals ϕ_i $(\varphi_i = \sigma_i \phi_i)$ in ϕ

under the orthonormality condition

$\langle \phi_i | \phi_j \rangle = \delta_{ij}$ $(\langle \varphi_i | \varphi_j \rangle = \delta_{ij})$

$\Rightarrow$ method of Lagrange multipliers

$$E_{HF} = \langle \Phi | \hat{H} | \Phi \rangle = \langle \Phi | \sum_{i=1}^{n} \hat{h}(i) + \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j) | \Phi \rangle =$$

assume $\langle \Phi | \Phi \rangle = 1$

$$= \frac{1}{n!} \Big(\underbrace{n}_{\text{\#electrons}} \cdot \langle \det|\varphi_i(i)| \,|\, \hat{h}(\underbrace{1}_{\text{electron } 1}) \,|\, \det|\varphi_i(i)| \rangle +$$

$$\underbrace{\frac{n(n-1)}{2}}_{\text{\# pairs of electrons}} \cdot \langle \det|\varphi_i(i)| \,|\, \hat{g}(\underbrace{1,2}_{\text{electron pair } 1,2}) \,|\, \det|\varphi_i(i)| \rangle =$$

exploit the indistinguishability of the electrons!

1st term: apply Laplace expansion once

$$\det|\varphi_i(i)| \overset{\text{determinant}}{=} D = \sum_{i=1}^{n} (-1)^{i+1} \varphi_i(1)\, \overset{\text{subdeterminant}}{D^{1i}}$$

expand wrt 1st row where we have electron 1

Note: $\langle D|D\rangle = n!$, $\langle D^{ij}|D^{kl}\rangle = \delta_{ik}\delta_{jl}(n-1)!$

$$\Rightarrow \frac{1}{n!}\left(n\cdot(n-1)!\right) \sum_{i=1}^{n} \langle \varphi_i(1)|\hat{h}|\varphi_i(1)\rangle + \ldots$$

$$= \sum_{i=1}^{n} h_i + \ldots$$

for the 1st term ...

2nd term: apply Laplace expansion twice

$$\det|\varphi_i(i)| = \mathcal{D} = \sum_{i=1}^{n} (-1)^{i+1} \varphi_i(1)\, \mathcal{D}^{1i} =$$

indices for $\mathcal{D}$

1st expansion

$$\sum_{j=1}^{n-1} (-1)^{j+1} \varphi_j(2) \left(\mathcal{D}^{1i}\right)^{1j}$$

2nd expansion

indices for $\mathcal{D}^{1i}$

$$\det|\varphi_i(i)| = \mathcal{D} = \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} (-1)^{i+j} \left(\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)\right) \mathcal{D}^{1,2,i,j}$$

Note: $\langle \mathcal{D}^{i,j,k,l} | \mathcal{D}^{m,n,o,p} \rangle = \delta_{im}\delta_{jn}\delta_{ko}\delta_{lp}(n-2)!$

$$\Rightarrow \frac{1}{n!}\Bigg(\cdots \frac{n(n-1)}{2}(n-2)!\, 2 \cdot \cdots$$

$$\longrightarrow \frac{\varphi_i(1)\,\varphi_j(2)}{r_{12}}$$

$$\cdot \sum_{i=j+1}^{n}\sum_{j=1}^{n-1}\Big(\langle \underline{\varphi_i(1)}\,\underline{\varphi_j(2)} \,|\, \hat{g}(1,2) \,|\, \underline{\varphi_i(1)}\,\underline{\varphi_j(2)} \rangle -$$

exchange of indices

$$\langle \varphi_i(1)\,\varphi_j(2) \,|\, \hat{g}(1,2) \,|\, \varphi_j(1)\,\varphi_i(2) \rangle \Big)\Bigg)$$

$$= \cdots + \sum_{i=j+1}^{n}\sum_{j=1}^{n-1}\left(J_{ij} - K_{ij} \right)$$

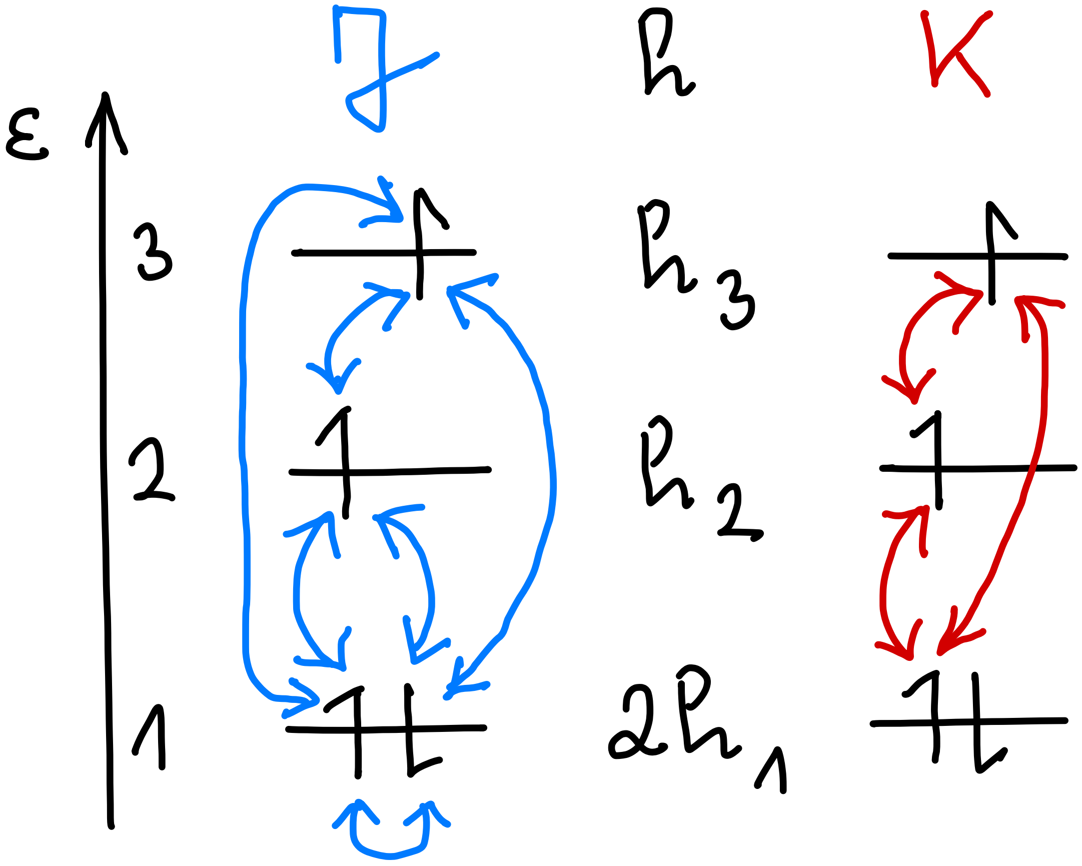
for the 2nd term ...

exchange integral

Coulomb integral

$$E_{HF} = \sum_{i=1}^{n} h_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n-1} \left(\underline{J_{ij}} - \underline{K_{ij}} \right)$$

e.g. 4 electrons in 3 orbitals with $M_S = +1$



$$E_{HF} = 2h_1 + h_2 + h_3$$
$$+ J_{11} + 2J_{12} + 2J_{13}$$
$$+ J_{23}$$
$$- K_{12} - K_{13} - K_{23}$$

Coulomb integral/operator:

$$J_{ij} = \langle \varphi_i(1)\varphi_j(2)|\hat{g}(1,2)|\varphi_i(1)\varphi_j(2)\rangle = \langle ij|ij\rangle =$$

$$= \iint \frac{\varphi_i^*(1)\varphi_j^*(2)\varphi_i(1)\varphi_j(2)}{r_{12}}\, d\tau_1\, d\tau_2$$

$$= \int \varphi_i^*(1)\,\hat{J}_j\,\varphi_i(1)\, d\tau_1$$

$$\hat{J}_j = \int \varphi_j^*(2)\,\frac{1}{r_{12}}\,\varphi_j(2)\, d\tau_2$$

classical interpretation ✓

Integration over spin "trivial":

$$\varphi_k \rightarrow \phi_k$$

$$\varphi_k^*\varphi_k \rightarrow \rho_k$$

Exchange integral / operator:

$$K_{ij} = \langle \varphi_i(1)\varphi_j(2) | \hat{g}(1,2) | \varphi_{\underline{j}}(1)\varphi_{\underline{i}}(2) \rangle = \langle ij | \underline{j}i \rangle =$$

$$= \iint \frac{\varphi_i^*(1)\varphi_j^*(2)\varphi_{\underline{j}}(1)\varphi_{\underline{i}}(2)}{r_{12}} \, d\tau_1 \, d\tau_2$$

$$= \int \varphi_i^*(1) \hat{K}_j \varphi_i(1) \, d\tau_1$$

no classical interpretation!

$$\hat{K}_j \varphi_i(1) = \int \varphi_j^*(2) \frac{1}{r_{12}} \varphi_{\underline{i}}(2) \, d\tau_2 \, \varphi_{\underline{j}}(1)$$

Note: $K_{ij} = 0$ if φ_i and φ_j have different spin!

Note: $K_{ii} = J_{ii}$, $K_{ij} = K_{ji}$, $J_{ij} = J_{ji}$

$$\Rightarrow E_{HF} = \sum_{i=1}^{n} h_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} (J_{ij} - K_{ij})$$

indices refer to spin orbitals φ_k!

special case: $\frac{n}{2}$ doubly occupied spatial orbitals

$$\Rightarrow E_{HF} = 2 \sum_{i=1}^{n/2} h_i + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})$$

indices refer to spatial orbitals ϕ_k!

Application of the method of Lagrange multipliers to the HF energy expression and the orthonormality condition:

$$
\begin{aligned}
&E_{HF}[\{\varphi_i+\underbrace{\delta\varphi_i}_{\text{infinitesimal change of orbital } \varphi_i}\}] - E_{HF}[\{\varphi_i\}] + \\
&+ \sum_{ij} \underbrace{\lambda_{ij}}_{\text{Lagrange multipliers}} \Big(\underbrace{[\delta_{ij} - \langle \varphi_i+\delta\varphi_i | \varphi_j+\delta\varphi_j \rangle]}_{=0} - \\
&\qquad - \underbrace{[\delta_{ij} - \langle \varphi_i | \varphi_j \rangle]}_{=0} \Big) \overset{\text{for assumed minimum}}{:=} 0
\end{aligned}
$$

order 0 in $\delta\varphi_i$ $\longrightarrow$ equ. (trivially) fulfilled

" 1 " " $\longrightarrow$ Fock equations

" ≥ 2 " " $\longrightarrow$ neglected

we try to derive an expression of the type

$$\langle \delta\varphi_i(1) | \boxed{\;?\;} \rangle = 0 \quad \Rightarrow \quad | \boxed{\;?\;} \rangle = |0\rangle$$

$\boxed{\;?\;}$ equations from which to obtain $\{\varphi_i\}$

in E_{HF} for h_i 2 positions and in J_{ij}, K_{ij}

4 positions for $\delta\varphi_k$!

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

$$= \underbrace{\langle \varphi_i | \hat{h} | \varphi_i \rangle}_{\text{0th order (drops out)}} + \underbrace{\langle \varphi_i | \hat{h} | \delta\varphi_i \rangle}_{\text{1st order}} + \underbrace{\langle \delta\varphi_i | \hat{h} | \varphi_i \rangle}_{\text{1st order}} + \underbrace{\dots}_{\text{neglect}}$$

$$\underbrace{\langle \delta\varphi_i | \hat{h} | \varphi_i \rangle^{*} \qquad\qquad \langle \delta\varphi_i | \hat{h} | \varphi_i \rangle}_{2\,\mathrm{Re}\,\langle \delta\varphi_i | \hat{h} | \varphi_i \rangle}$$

Hermitian operator $\hat{h}$

$$\Rightarrow \text{1st order:} \quad 2\sum_{i=1}^{n} \mathrm{Re}\,\langle \underline{\delta\varphi_i} | \hat{h} | \varphi_i \rangle$$

$$\langle \varphi_i + \delta\varphi_i \; \varphi_j + \delta\varphi_j | \hat{g} | \varphi_i + \delta\varphi_i \; \varphi_j + \delta\varphi_j \rangle =$$

$$= \langle \varphi_i \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle +$$

0th order

$$+ \langle \delta\varphi_i \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle + \langle \varphi_i \delta\varphi_j | \hat{g} | \varphi_i \varphi_j \rangle +$$

1st order

I: electron exchange 1<->2

$$\langle \delta\varphi_j \varphi_i | \hat{g} | \varphi_j \varphi_i \rangle$$

$$+ \langle \varphi_i \varphi_j | \hat{g} | \delta\varphi_i \varphi_j \rangle^* + \langle \varphi_i \varphi_j | \hat{g} | \varphi_i \delta\varphi_j \rangle^* + \ldots$$

II: hermitian operator $\hat{g}$

$$\langle \delta\varphi_i \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle^*$$

I and II

$$\langle \delta\varphi_j \varphi_i | \hat{g} | \varphi_j \varphi_i \rangle^*$$

neglect

$$\rightarrow 2\mathrm{Re}\langle \delta\varphi_i \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle + 2\mathrm{Re}\langle \delta\varphi_j \varphi_i | \hat{g} | \varphi_j \varphi_i \rangle$$

$\Rightarrow$ 2nd order :

$$2 \sum_{j=i+1}^{n} \sum_{i=1}^{n-1} \mathrm{Re}\left(\langle \delta\varphi_i \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle + \langle \delta\varphi_j \varphi_i | \hat{g} | \varphi_j \varphi_i \rangle \right) =$$

$$= 2 \sum_{i \neq j}^{n} \mathrm{Re}\langle \underline{\delta\varphi_i} \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle$$

Coulomb part

analogous derivation:

$$- 2 \sum_{i \neq j}^{n} \mathrm{Re}\langle \underline{\delta\varphi_i} \varphi_j | \hat{g} | \varphi_j \varphi_i \rangle$$

exchange part

orthonormality condition (similar h terms):

$$-2\sum_{i,j} \lambda_{ij}\, \mathrm{Re}\langle \underline{\delta\varphi_i} | \varphi_j \rangle$$

$\boxed{\;?\;}$ therefore leads to

$$\Big[\hat{h} + \sum_{j\neq i}\big(\hat{J}_j - \hat{K}_j\big)\Big]|\varphi_i\rangle = \sum_{j} \lambda_{ij} |\varphi_j\rangle$$

(using the Coulomb and exchange operators defined above!)

since $J_{ii} = K_{ii}$ resp. $\hat{J}_i|\varphi_i\rangle = \hat{K}_i|\varphi_i\rangle$ one gets one equation for all φ_i:

$$\underbrace{[\hat{h} + \sum_j (\hat{J}_j - \hat{K}_j)]}_{\substack{\hat{F} \\ \text{Fock operator}}} |\varphi_i\rangle = \sum_j \lambda_{ij} |\varphi_j\rangle$$

$$\Downarrow$$

$$\langle \varphi_l | \hat{F} | \varphi_i \rangle = \lambda_{il}$$

$$\Downarrow$$

by diagonalizing $\underline{\lambda}$ resp. $\hat{F}$ one obtains

$$[\hat{h} + \sum_j (\hat{J}'_j - \hat{K}'_j)] |\varphi'_i\rangle = \overset{\text{orbital energy}}{\varepsilon_i} |\varphi'_i\rangle$$

or: $\hat{F}|\varphi_i\rangle = \varepsilon_i|\varphi_i\rangle$

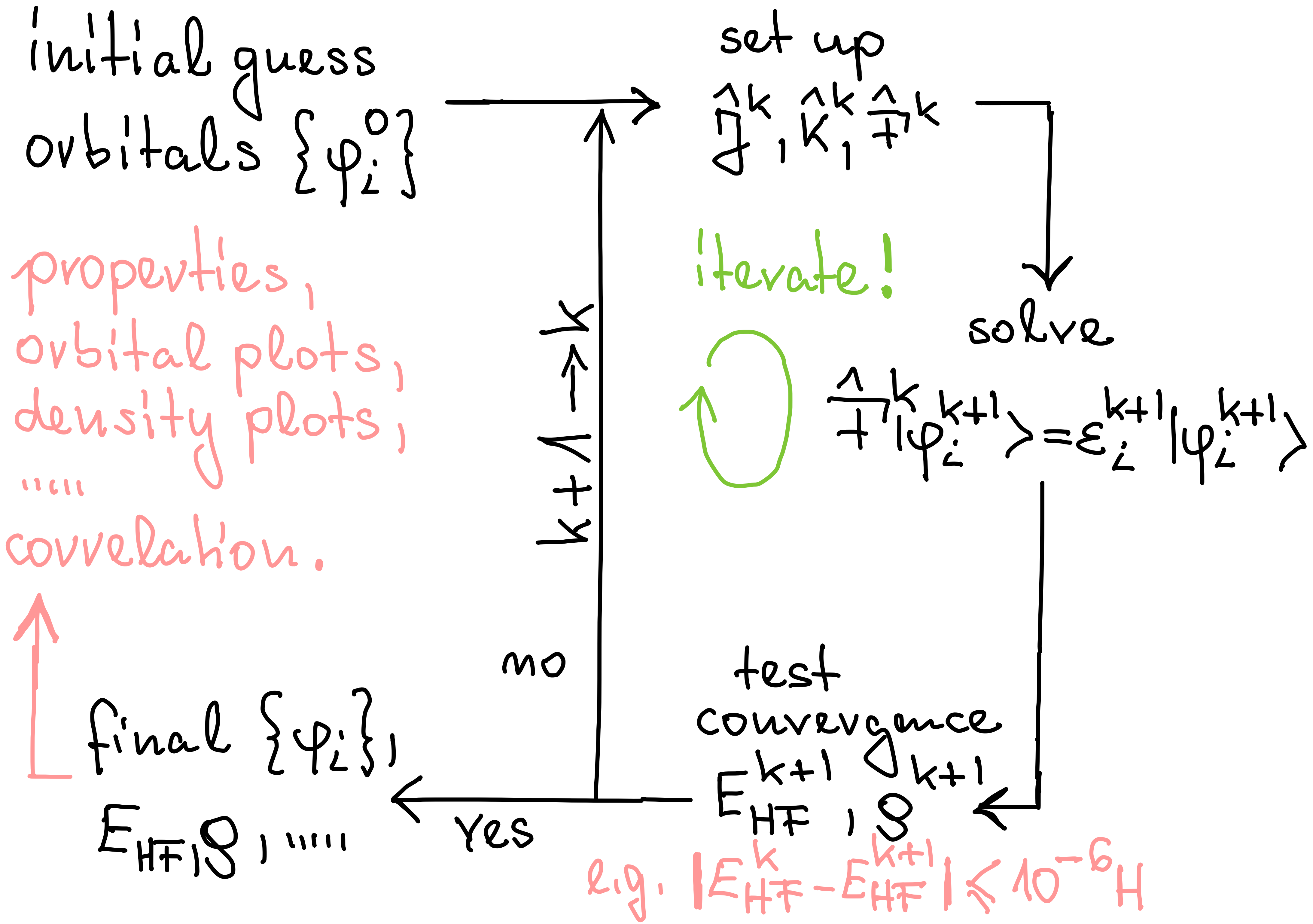
orbitals φ_i and orbital energies ε_i

"canonical" Fock equation

Since $\hat{F}[\{\varphi_i\}]$ the Fock equation depends on its own solution!

$\Rightarrow$

$\underline{\underline{\text{S}}}$elf-$\underline{\underline{\text{c}}}$onsistent $\underline{\underline{\text{f}}}$ield (SCF) method for solution (iterative).


initial guess orbitals $\{\varphi_i^0\}$
set up $\hat{J}^k, \hat{K}^k, \hat{F}^k$
iterate!
solve
$\hat{F}^k |\varphi_i^{k+1}\rangle = \varepsilon_i^{k+1} |\varphi_i^{k+1}\rangle$
test convergence
E_{HF}^{k+1}, ρ^{k+1}
e.g. $|E_{HF}^k - E_{HF}^{k+1}| \leq 10^{-6} H$
no
$k+1 \rightarrow k$
yes
final $\{\varphi_i\}$, $E_{HF}, \rho, \ldots$
properties, orbital plots, density plots, ... correlation.

How to solve the Fock equations in practise?

- atoms: spherical symmetry
  - angular part analytically: Y_{lm}
  - radial part on a grid: R_{nl}
- general molecules (and of course atoms):
  - expansion of orbitals in (usually atom-centered) basis sets
  - conversion of integro-differential equation to a matrix eigenvalue problem

Roothaan-Hall approach

$$|\phi_i\rangle = \sum_k c_{ki} |\chi_k\rangle$$

basis functions, e.g. Slater or Gaussian type functions

in Fock equation:

$$\hat{F}|\phi_i\rangle = \varepsilon_i |\phi_i\rangle$$

$$\sum_k c_{ki}\hat{F}|\chi_k\rangle = \varepsilon_i \sum_k c_{ki}|\chi_k\rangle \quad \Big|\, \langle\chi_l|$$

$$\sum_k c_{ki}\langle\chi_l|\hat{F}|\chi_k\rangle = \varepsilon_i \sum_k c_{ki}\langle\chi_l|\chi_k\rangle$$

$$\sum_k F_{\underset{\text{row}}{\ell}\,\underset{\text{column}}{k}}\, c_{\underset{\text{row}}{k}\,\underset{\text{column}}{i}} = \varepsilon_i \sum_k S_{\underset{\text{row}}{\ell}\,\underset{\text{column}}{k}}\, c_{\underset{\text{row}}{k}\,\underset{\text{column}}{i}}$$

$$\underline{F}\,\vec{c}_i = \varepsilon_i\, \underline{S}\,\vec{c}_i \quad \text{or} \quad \underline{F}\,\underset{\llcorner\, \vec{c}_i \text{ is ith column}}{\underline{C}} = \underline{\varepsilon}\,\underline{S}\,\underline{C}$$

generalized matrix eigenvalue problem

After insertion of $\underline{1} = \underline{S}^{-1/2}\,\underline{S}^{1/2}$ and multiplication from left with $S^{-1/2}$

$$\underbrace{\underline{S}^{-1/2}\,\underline{F}\,\rlap{$\overbrace{\phantom{\underline{S}^{-1/2}\,\underline{S}^{1/2}}}^{1}$}\underline{S}^{-1/2}}_{\tilde{\underline{F}}}\;\underbrace{\underline{S}^{1/2}\,\underline{C}}_{\tilde{\underline{C}}} = \underline{\varepsilon}\,\underbrace{\underline{S}^{1/2}\,\underline{C}}_{\tilde{\underline{C}}}$$

$$\tilde{\underline{F}}\;\tilde{\underline{C}} = \underline{\varepsilon}\;\tilde{\underline{C}}$$

standard matrix eigenvalue problem,
solved by diagonalization of $\tilde{\underline{F}}$
(Nontrivial solutions if $\det|\underline{F}-\underline{\varepsilon}|=0$)
ideal task for computer (code)!

Suitable basis functions:

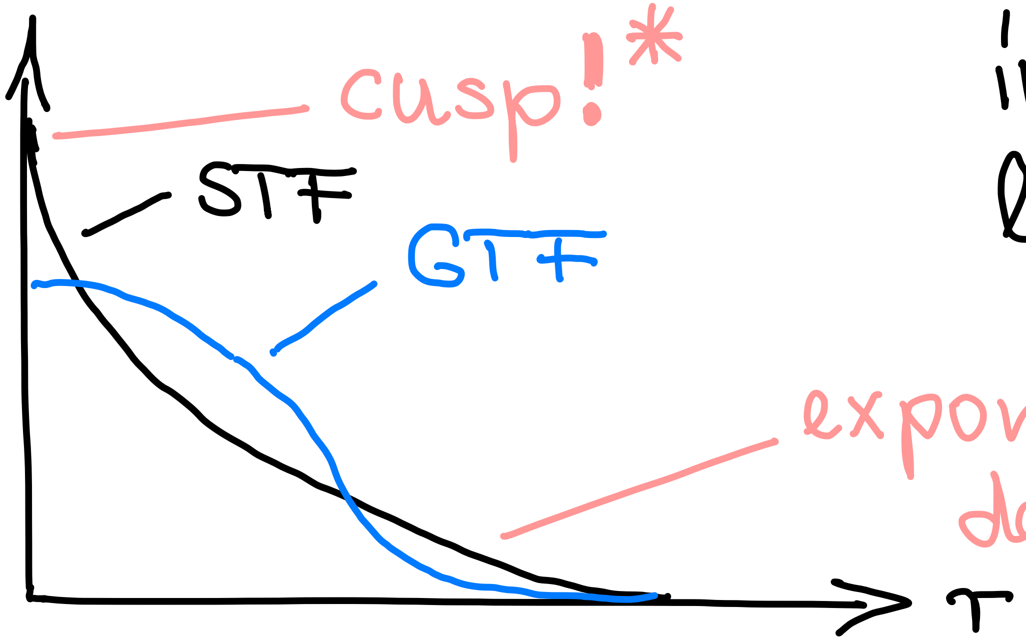
- Slater type functions (STFs)

radial part $\sim e^{-\underbrace{\zeta}_{\text{exponent ``zeta''}}(\vec{r}-\underbrace{\vec{r}_0}_{\text{nuclear position}})}$

$\Rightarrow$ corresponds to solutions of hydrogen atom resp. hydrogen like ions → accurate, but integrals over $\hat{h}$ and $\hat{g}$ very complicated resp. costly to evaluate!

- Gaussian type functions (GTF)

χ radial part $\sim e^{-\alpha(\vec{r}-\vec{r}_0)^2}$



integral evaluation less difficult | costly!

* cf. cusp conditions in Chapter 1!

to improve the accuracy use linear combinations of GTFs to approximate STFs! e.g. STO-3G, STO-4G, ... sets

STO : Slater type orbitals
GTO : Gaussian type orbitals

often used instead of STF, GTF.

- angular part

$Y_{lm}(\vartheta, \varphi)$ wrt. atomic center : spherical

$(x-x_0)^i (y-y_0)^j (z-z_0)^k$, $i+j+k=l$: cartesian

i	j	k	angular part	type
0	0	0	1	$1s$
1	0	0	$x-x_0$	$2p_x$
. . .				
1	1	0	$(x-x_0)(y-y_0)$	$3d_{xy}$
. . .				
2	0	0	$(x-x_0)^2$	$3d_{x^2-y^2}$
0	2	0	$(y-y_0)^2$	$3d_{2z^2-x^2-y^2}$
0	0	2	$(z-z_0)^2$	$\boxed{3s}$

$\llcorner x^2+y^2+z^2=r^2$

excluded in spherical basis ↗

contraction pattern: segmented

e.g. (5s)/[2s]

↑ primitives (GTOs)

↑ contractions

exponent	coefficients			
	orbital 1		orbital 2	
#1	$\neq 0$	1st contraction	0	
#2	$\neq 0$		0	
#3	$\neq 0$		0	
#4	0		$\neq 0$	2nd contraction
#5	0		$\neq 0$	

contraction pattern: generalized

e.g. (5s)/[2s]

↑ primitives (GTOs)

↑ contractions

exponent	coefficients	
	orbital 1	orbital 2
#1	$\neq 0$	$\neq 0$
#2	$\neq 0$	$\neq 0$
#3	$\neq 0$	$\neq 0$
#4	$\neq 0$	$\neq 0$
#5	$\neq 0$	$\neq 0$

1st contraction

2nd contraction

nomenclature:

- minimal basis set: one set of contractions for every occupied atomic shell, e.g.

  H $1s^1$, He $1s^2$ $\Rightarrow (\ldots s)/[1s]$

  B $1s^2 2s^2 2p^1$ $\Rightarrow (\ldots s \ldots p)/[2s1p]$

- double-, triple-, ... zeta basis set: two, three, ... contractions for every occupied shell, e.g.

H, He DZ: $(\ldots s) | [2s]$
TZ: $(\ldots s) | [3s]$
…

B DZ: $(\ldots s \ldots p) | [4s2p]$
TZ: $(\ldots s \ldots p) | [6s3p]$
…

- valence double-, triple-, … zeta basis set: minimum basis for core shells, double-, triple-, … zeta for valence shells, e.g.

B VDZ (…s…p)/[3s2p]

VTZ (…s…p)/[4s3p]

…

- augmented basis sets: a diffuse set is added to describe anions better, e.g.

B VDZ + [1s1p] ⇒ AVDZ (…s…p)/[4s3p]

VTZ + [1s1p] ⇒ AVTZ (…s…p)/[5s4p]

…

- polarized basis sets: higher angular momentum functions added to improve the description of bonding, e.g.

correlation consistent basis sets cc-pVxZ

H, He cc-pVDZ (…s…p)/[2s1p]
cc-pVTZ (…s…p…d)/[3s2p1d]
…

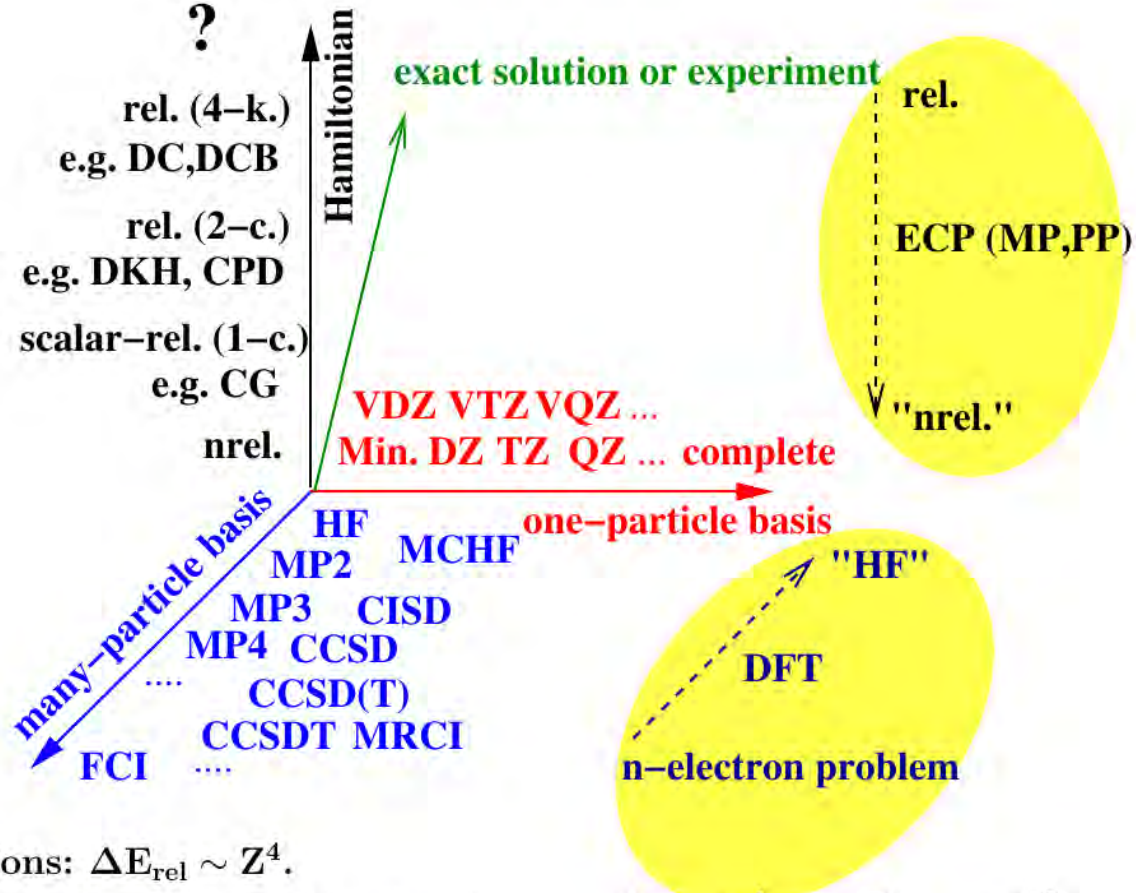
B cc-pVDZ (…s…p…d)/[3s2p1d]
cc-pVTZ (…s…p…d…f)/[4s3p2d1f]
… other schemes possible….

The larger and the more flexible the basis set, the better. Lower (HF-) energy usually indicates a better basis set.

Problem: scaling of the computational effort with system size (n basis functions)

[standard] HF $\sim n^4$, MP2 $\sim n^5$, CISD, CCSD $\sim n^6$, ...

$\Rightarrow$ compromises needed!



?

Hamiltonian

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e.g. DC,DCB

rel. (2–c.)
e.g. DKH, CPD

scalar–rel. (1–c.)
e.g. CG

nrel.

exact solution or experiment

rel.

ECP (MP,PP)

"nrel."

VDZ VTZ VQZ ...
Min. DZ TZ QZ ... complete

one–particle basis

many–particle basis

HF
MP2
MP3
MP4
....
FCI

MCHF
CISD
CCSD
CCSD(T)
CCSDT MRCI
....

"HF"

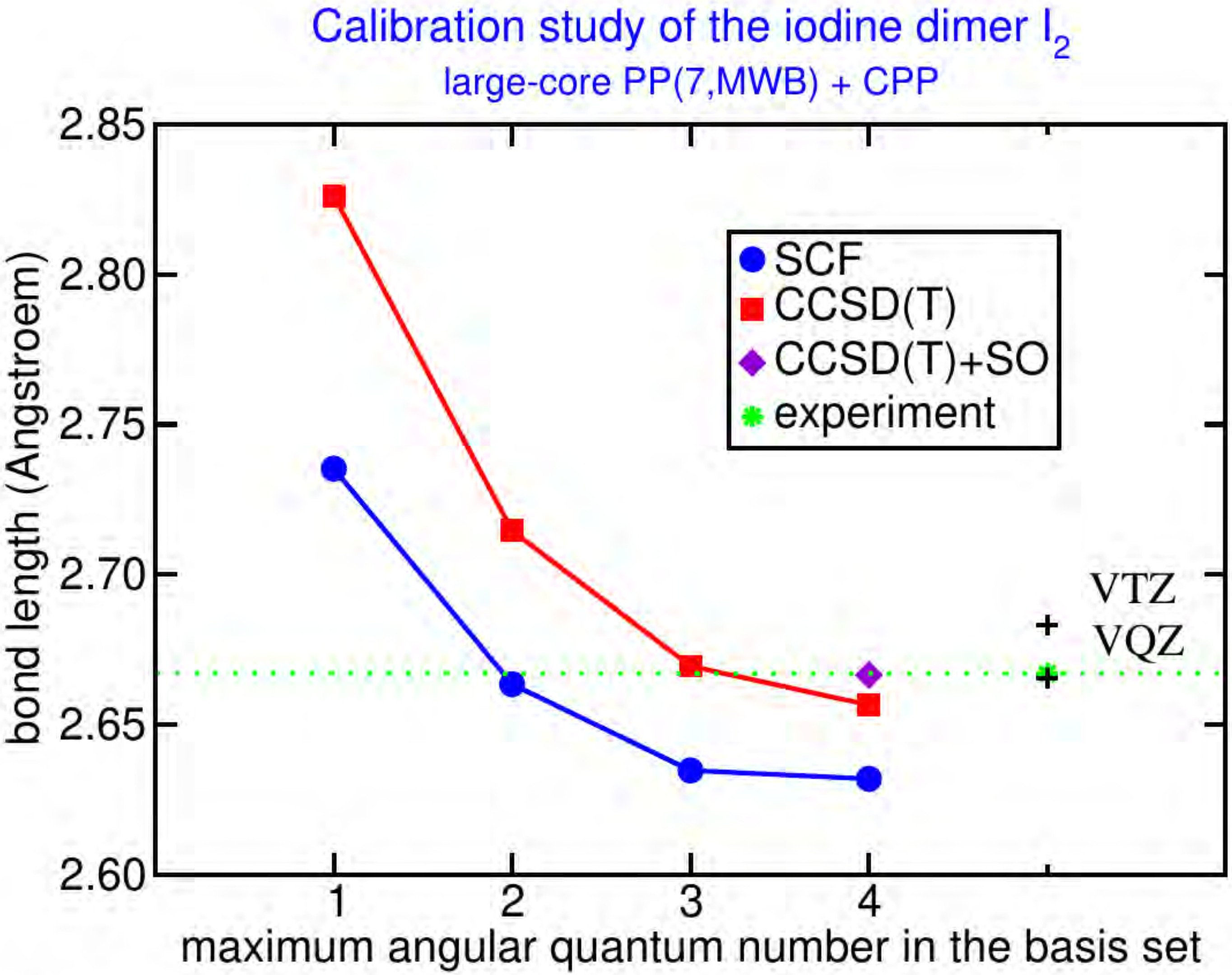
DFT

n–electron problem

- relativistic contributions: $\Delta E_{\mathrm{rel}} \sim Z^4$.
- correlation energy errors for standard basis set expansions: $E^{l}_{\mathrm{corr}} - E^{\infty}_{\mathrm{corr}} \sim 1/l^3$ → basis set extrapolation or F12-dependent wavefunctions.
- computational effort: $t \sim n^k$ (n size of one-particle basis set, k for some standard approaches: DFT 3, HF 4, MP2 5, CISD, CCSD 6, CCSD(T) 7 ...) → low-order/linear scaling schemes.
- ECPs simplify the Hamiltonian and also lead to some reductions in the sizes of the one- and many-electron basis sets (e.g. small-core PPs plus valence-only SO terms) !
- DFT avoids costly many-determinantal wavefunctions/treatments.

Goal: Suitable compromise between accuracy and computational effort,
i.e., sufficiently accurate low-cost relativistic electronic structure calculations, also for larger systems.

Basis set completeness and extrapolation



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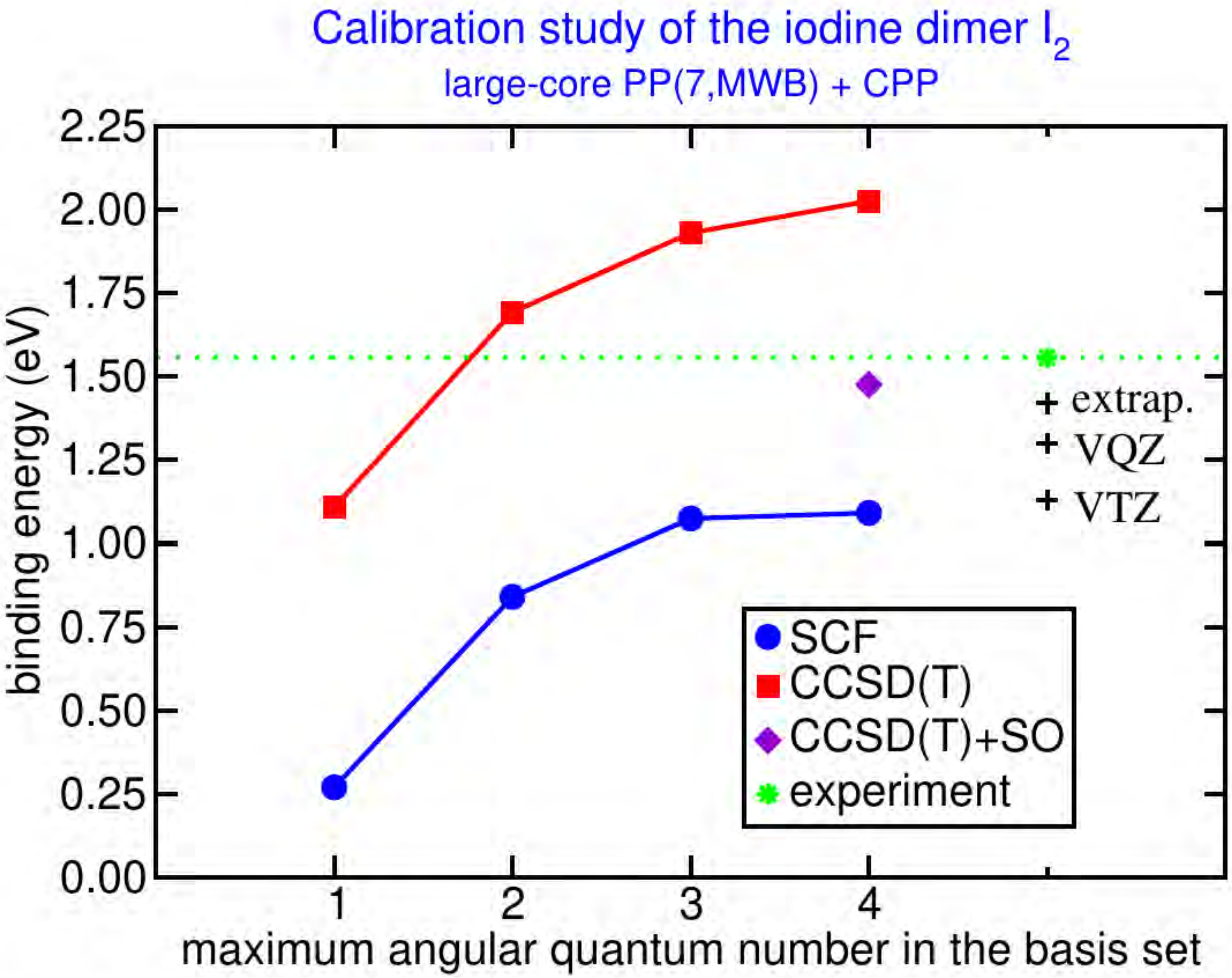

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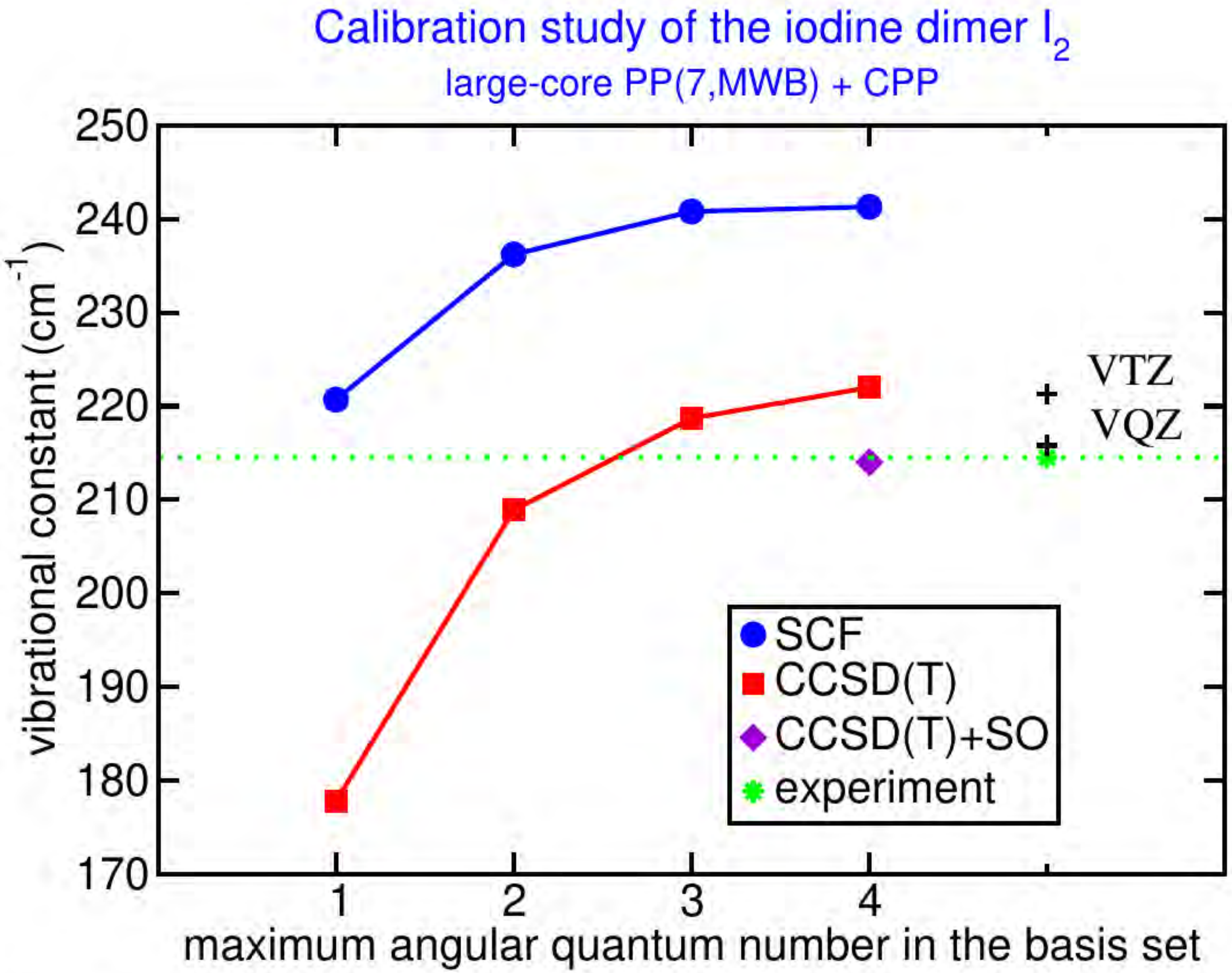

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2 types of Roothaan-Hall Hartree-Fock self-consistent field procedure:

- conventional (normal sized systems)

– evaluate $\langle \chi_i | \hat{h} | \chi_j \rangle$ and $\langle \chi_i \chi_j | \hat{g} | \chi_k \chi_l \rangle$ an store them on disk

– read integrals from disk in every iteration to set up $\underline{F}$

- disadvantage:
  for n basis functions one has $\approx n^4/4$ two-electron integrals!

- $\langle ij|kl\rangle = \langle \chi_i \chi_j | \hat{g} | \chi_k \chi_l \rangle$ short notation

  nonrelativistic case: $\hat{H}$ real $\rightarrow \Phi, \varphi_i, \ldots$ real

  "symmetries" (electron exchange, hermitian operator $\hat{g}$)

  $\langle ij|kl\rangle = \langle ji|lk\rangle = \langle lk|ji\rangle^* = \langle kl|ij\rangle^*$

  $i \leqslant k \,,\; j \leqslant l$ (spatial symmetry not exploited) store without indices: 1 dp word = 8 byte

100 bf → $(10^2)^4/4 \cdot 8$ byte ≈ 200 MB ✓

1000 bf → $(10^3)^4/4 \cdot 8$ byte ≈ 2000 GB = 2 TB ✓

10000 bf → $(10^4)^4/4 \cdot 8$ byte ≈ 20000 TB ϟ
impossible!

in addition: disk I/O is often slower than the CPU → therefore:

- direct (very large systems)

– evaluate ⟨ij|kl⟩ when needed in every iteration ("on the fly")

- integral prescreening important

e.g. $\langle ij|kl\rangle \leq \langle ij|ij\rangle^{1/2} \cdot \langle kl|kl\rangle^{1/2}$

many not so many

remiscent of the Schwarz inequality

$$|\langle i|j\rangle|^2 \leq \langle i|i\rangle\langle j|j\rangle$$

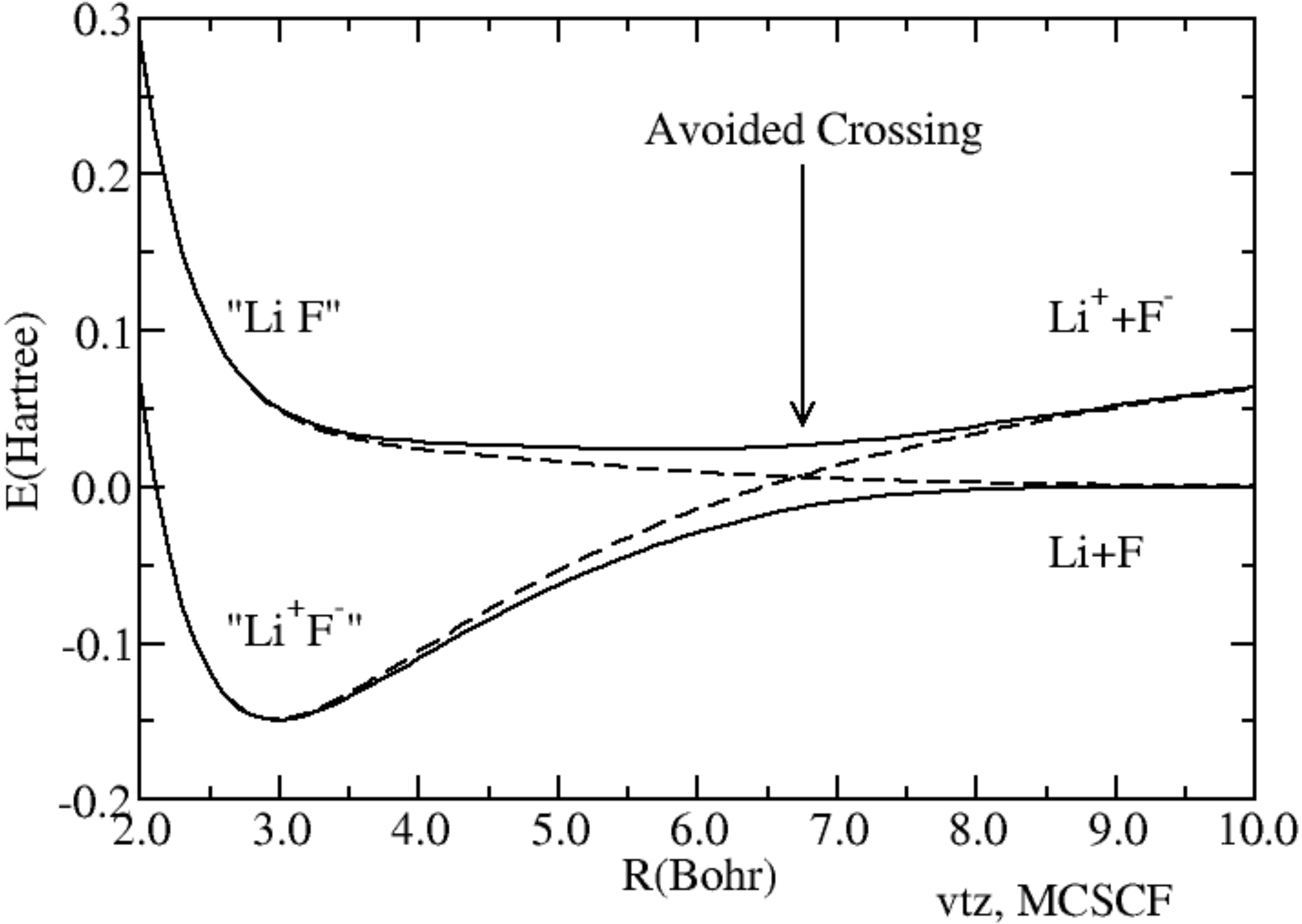
– do not calculate $\langle ij|kl\rangle$ if $\langle ij|ij\rangle\langle kl|kl\rangle$ is lower than a certain threshold

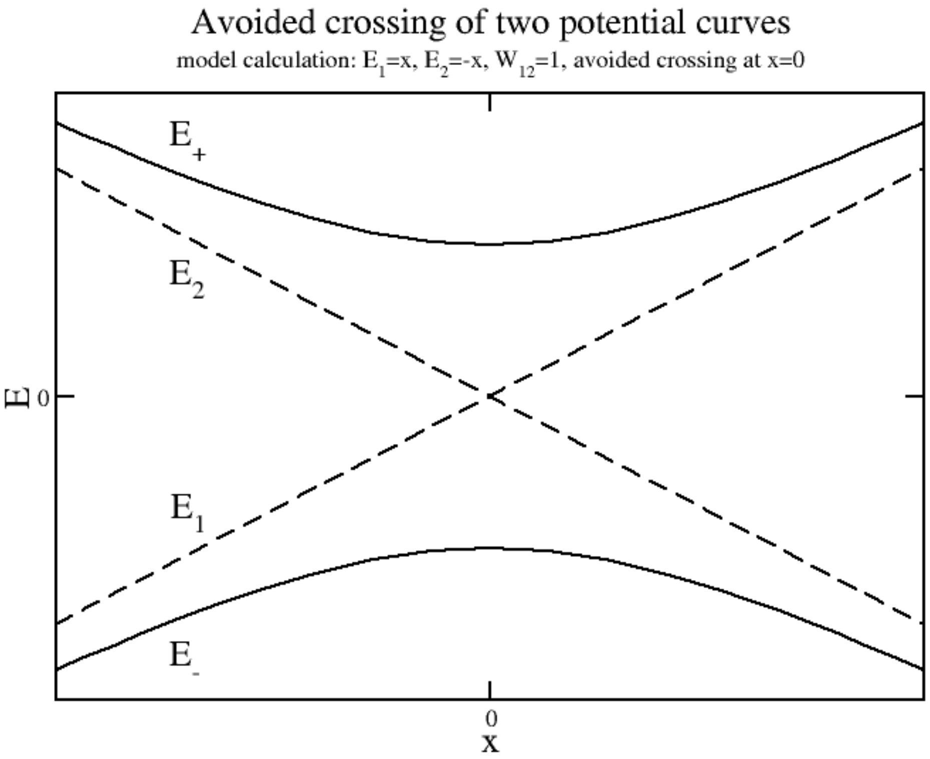
What HF can do well and what it cannot do so well:

Remember:

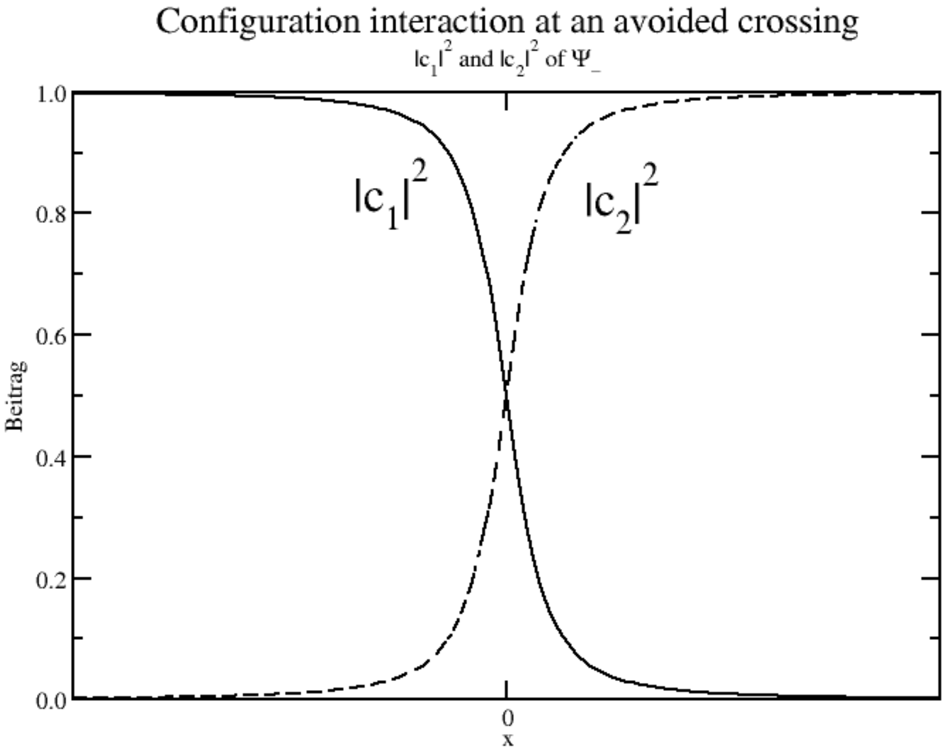
- HF is a single determinant method
  → it cannot describe situations were two or more determinants are needed, e.g. breaking of bonds

Bond breaking in LiF




Avoided crossing of two potential curves

model calculation: $E_1=x$, $E_2=-x$, $W_{12}=1$, avoided crossing at x=0


Configuration interaction at an avoided crossing

$|c_1|^2$ and $|c_2|^2$ of Ψ_-

H_2 at large distance is $\psi \sim |\sigma_g^2\rangle - |\sigma_u^2\rangle \sim$

$$\sim (1s_a(1)+1s_b(1))(1s_a(2)+1s_b(2)) - (1s_a(1)-1s_b(1))(1s_a(2)-1s_b(2))$$

$$\sim 1s_a(1)\,1s_b(2) + 1s_b(1)\,1s_a(2) \Rightarrow H\bullet + H\bullet$$ ✓

- HF does not include Coulomb correlation

  → it cannot describe interactions due to electron correlation, e.g. van der Waals bonding otherwise:

equilibrium geometries
(of covalent/ionic bonded systems)

vibrational frequencies

dipole moments etc.

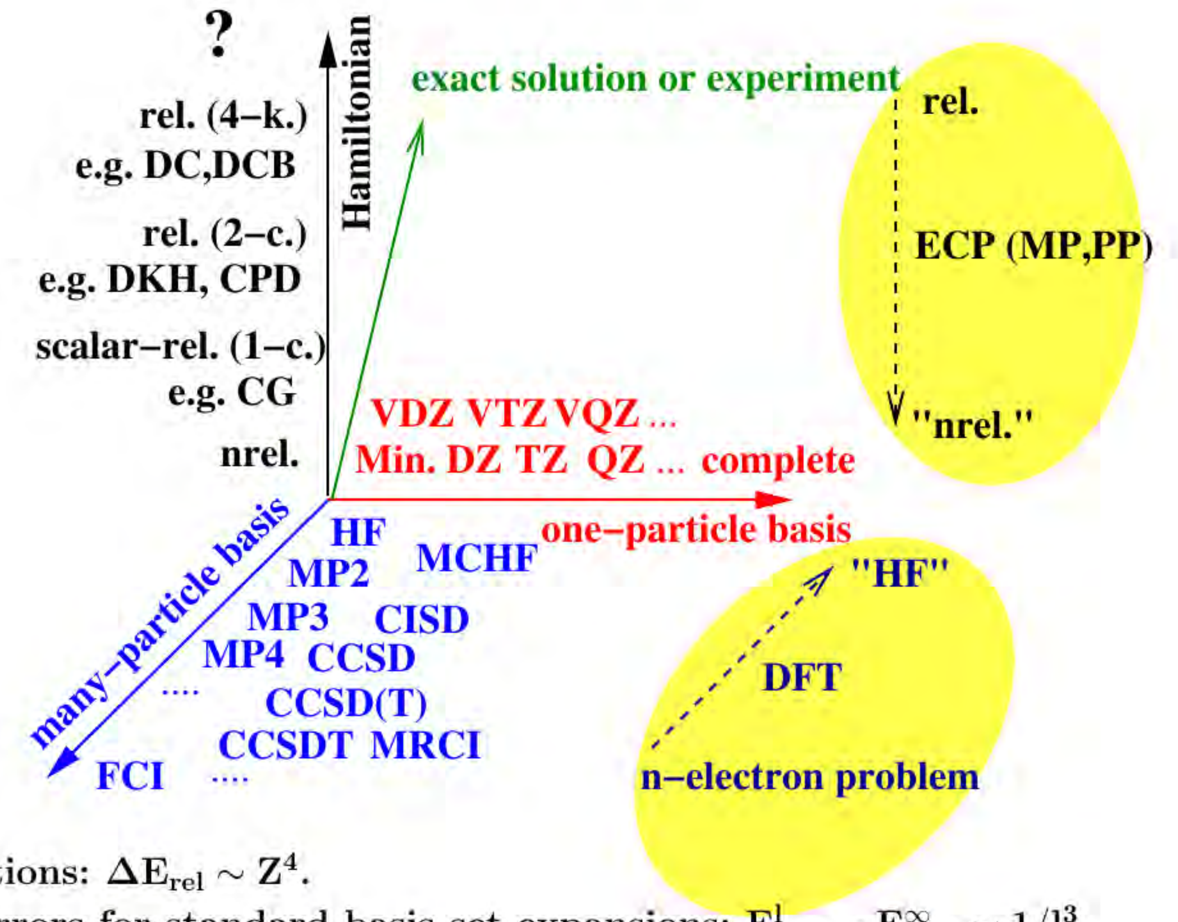
electron density

=> not extremely accurate, but
reasonable

Chapter 3

Beyond nonrelativistic Hartree-Fock theory

(correlated relativistic calculations)



?

Hamiltonian

rel. (4–k.)
e.g. DC,DCB

rel. (2–c.)
e.g. DKH, CPD

scalar–rel. (1–c.)
e.g. CG

nrel.

exact solution or experiment

rel.

ECP (MP,PP)

"nrel."

VDZ VTZ VQZ ...
Min. DZ TZ QZ ... complete

one–particle basis

many–particle basis

HF
MP2
MP3
MP4
....
FCI

MCHF
CISD
CCSD
CCSD(T)
CCSDT MRCI
....

"HF"

DFT

n–electron problem

- relativistic contributions: $\Delta E_{rel} \sim Z^4$.
- correlation energy errors for standard basis set expansions: $E^l_{corr} - E^{\infty}_{corr} \sim 1/l^3$ → basis set extrapolation or F12-dependent wavefunctions.
- computational effort: $t \sim n^k$ (n size of one-particle basis set, k for some standard approaches: DFT 3, HF 4, MP2 5, CISD, CCSD 6, CCSD(T) 7 ...) → low-order/linear scaling schemes.
- ECPs simplify the Hamiltonian and also lead to some reductions in the sizes of the one- and many-electron basis sets (e.g. small-core PPs plus valence-only SO terms) !
- DFT avoids costly many-determinantal wavefunctions/treatments.

Goal: Suitable compromise between accuracy and computational effort,
i.e., sufficiently accurate low-cost relativistic electronic structure calculations, also for larger systems.

Definition of correlation energy E^{corr} according to Löwdin:

$$E^{corr} = E^{exact} - E^{HF\text{-}limit}$$

Often neither E^{exact} nor $E^{HF\text{-}limit}$ are known* and one estimates | simplifies

$$\tilde{E}^{corr} = E^{\substack{correlated \\ method}} - E^{HF}$$

* truncated one- and many-electron basis

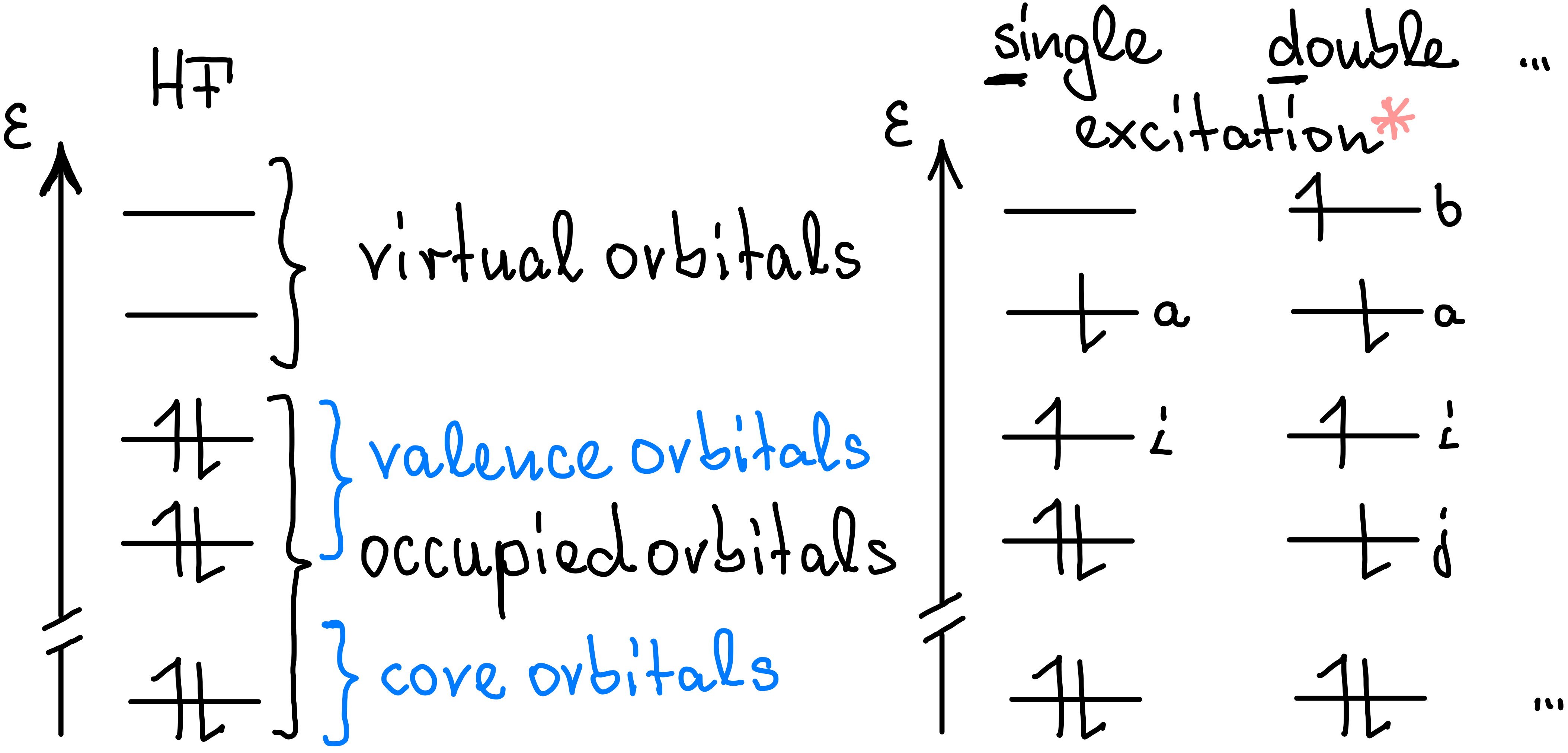
3 axes of ab initio methods coordinate system

- one-electron basis, cf. chapter 2!
- many-electron basis, cf. chapter 1!
  - Slater determinant or CSF basis

- Hamiltonian
  - nonrelativistic or relativistic
  - all-electron or valence-only
  - treatment of the environment, e.g. solvent or embedding effects

Many-electron methods beyond HF

- variational
  (e.g. CI, configuration interaction method)
- perturbative
  (e.g. MBPT, many-body perturbation theory)
- projective
  (e.g. CC, coupled cluster ansatz)
- others
  (e.g. QMC, quantum Monte Carlo)



$\Phi_{HF}, \Phi_0, |0\rangle$ $\Phi_i^a, |S\rangle$ $\Phi_{ij}^{ab}, |D\rangle$ ...

$a, b, \ldots, i, j, \ldots$ denote spin orbitals

* better: substitution

Expansion of the many-electron wavefunction

$$\Psi = \underbrace{\underbrace{\underbrace{\Phi_0}_{\text{HF}} + \sum_{i,a} c_i^a \Phi_i^a + \sum_{i,j,a,b} c_{ij}^{ab} \Phi_{ij}^{ab}}_{\text{CISD}} + \ldots}_{\text{FCI (exact)}}$$

$$|\psi\rangle = |0\rangle + \underset{\text{singles}}{|S\rangle} + \underset{\text{doubles}}{|D\rangle} + \underset{\text{triples}}{|T\rangle} + \underset{\text{quadruples}}{|Q\rangle} + \ldots$$

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$\hat{H}\big(|0\rangle + |S\rangle + |D\rangle + |T\rangle + \dots\big) = E\big(|0\rangle + |S\rangle + |D\rangle + |T\rangle + \dots\big)$$

Note: intermediate normalization is used, i.e.

$\langle 0|\psi\rangle = \langle 0|0\rangle = 1$ (standard normalization $\langle\psi|\psi\rangle = 1$)

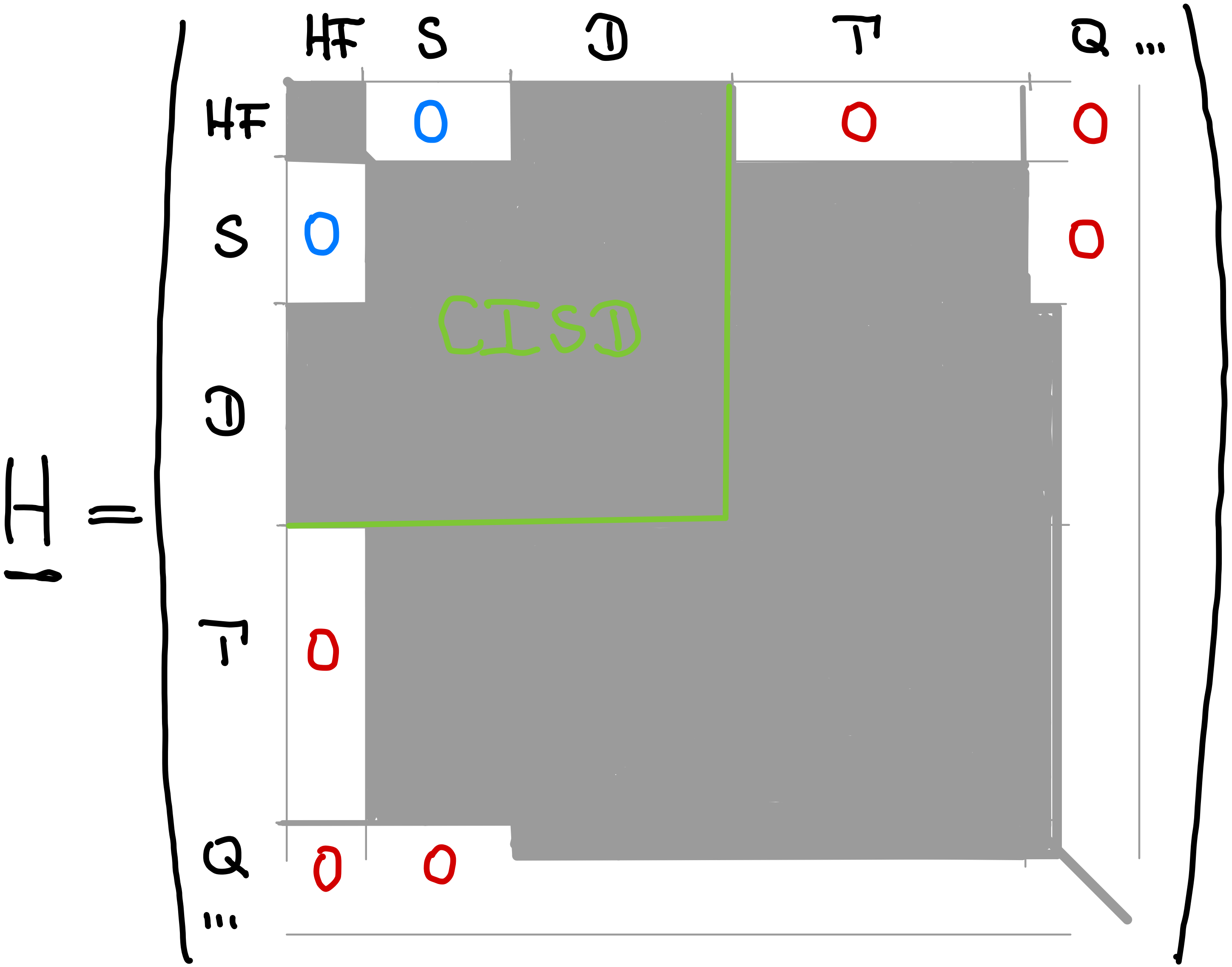
$$\langle 0| \;\Big|\; \langle 0|\hat{H}|0\rangle + \langle 0|\hat{H}|S\rangle + \langle 0|\hat{H}|D\rangle = E$$

Note: $\langle 0|S\rangle = \langle 0|D\rangle = \dots = \langle S|D\rangle = \langle S|T\rangle = \dots = 0$

$\Rightarrow$ The exact energy E is determined by a CISD expansion (with exact coefficients)!

$\Rightarrow$ This explains why most methods include single and double excitations wrt a HF reference! The remaining problem is the determination of the necessary exact coefficients!

Note: c_i^a, c_{ij}^{ab} cannot be determined from a (truncated) CISD, but have to be calculated in a FCI!



$\hat{H}$ contains one- and two-electron terms, i.e.

$$\langle \phi_k | \hat{H} | \phi_l \rangle = 0$$

if ϕ_k and ϕ_l differ by more than two orbitals.

Brilloin theorem

$$\langle \phi_{HF} | \hat{H} | \phi_i^a \rangle = 0$$

- Variational determination of $c_{i\ldots}^{a\ldots}$

  cf. chapter 1

  necessary matrix elements can be evaluated with the Slater-Condon rules:

$$\hat{h}: \langle\Phi|\sum_{i=1}^{n}\hat{h}(i)|\Phi\rangle = \sum_{i=1}^{n}\langle\varphi_i|\hat{h}|\varphi_i\rangle$$

cf. chapter 1

HF energy!

electron indices

orbital indices

$$\langle\Phi|\sum_{i=1}^{n}\hat{h}(i)|\Phi_k^a\rangle = \langle\varphi_k|\hat{h}|\varphi_a\rangle$$

$$\langle\Phi|\sum_{i=1}^{n}\hat{h}(i)|\Phi_{kl\ldots}^{ab\ldots}\rangle = 0$$

$$\hat{g}: \langle \Phi | \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j) | \Phi \rangle = \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \left(\langle \varphi_i \varphi_j | \hat{g} | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | \hat{g} | \varphi_j \varphi_i \rangle \right)$$

cf. chapter 1, HF energy!

$$\langle \Phi | \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j) | \Phi_k^a \rangle = \sum_{i=1}^{n} \left(\langle \varphi_k \varphi_i | \hat{g} | \varphi_p \varphi_i \rangle - \langle \varphi_k \varphi_i | \hat{g} | \varphi_p \varphi_i \rangle \right)$$

$$\langle \Phi | \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j) | \Phi_{kl}^{ab} \rangle = \langle \varphi_k \varphi_l | \hat{g} | \varphi_a \varphi_b \rangle - \langle \varphi_k \varphi_l | \hat{g} | \varphi_b \varphi_a \rangle$$

$$\langle \Phi | \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \hat{g}(i,j) | \Phi_{klm\ldots}^{abc\ldots} \rangle = 0$$

Now we know how to do HF + CI!

Many-body perturbation theory (MBPT)

- assume $\hat{H}_0 |\psi_i^{(0)}\rangle = E_i^{(0)} |\psi_i^{(0)}\rangle$ is solved!
- zeroth-order Hamiltonian H_0, energies $E_i^{(0)}$ and wavefunctions $\psi_i^{(0)}$
- a simple Hamiltonian is necessary!

e.g. $\hat{H}_0 = \sum_{k=1}^{n} \hat{f}(k)$, $E_i^{(0)} = \sum_{\substack{k=1 \\ k \in occ}}^{n} \varepsilon_k$,

$\Phi_i^{(0)} = \frac{1}{\sqrt{n!}} \det |\varphi_k(k)| = \Phi_{HF}$ MP0 (Møller-Plesset)

- one adds a "small" but complicated perturbation H'

perturbation parameter

$$\hat{H}^{exact} = \hat{H}_0 + \lambda \hat{H}'$$

$\lambda = 0$ "off"
no perturbation
$\lambda = 1$ "on"
full perturbation

- e.g. $\hat{H}' = \hat{H}^{exact} - \sum_{i=1}^{n} \hat{f}(i) =$

HF electron-electron interaction

exact electron-electron interaction

$$= \sum_{i=j+1}^{n} \sum_{j=1}^{n-1} \frac{1}{r_{ij}} - \sum_{i=1}^{n} \sum_{k=1}^{n} \left(\hat{J}_k(i) - \hat{K}_k(i) \right)$$

electrons

orbitals

MPn

- expansion of the (exact) energy

$$E^{exact} = \underset{\uparrow}{E^{(0)}} + \lambda \underset{\uparrow}{E^{(1)}} + \lambda^2 \underset{\uparrow}{E^{(2)}} + \dots + \lambda^n \underset{\uparrow}{E^{(n)}}$$

- expansion of the (exact) wavefunction

$$|\psi^{exact}\rangle = \underset{\substack{\uparrow \\ \text{zeroth order}}}{|\psi^{(0)}\rangle} + \lambda \underset{\substack{\uparrow \\ \text{first}}}{|\psi^{(1)}\rangle} + \lambda^2 \underset{\substack{\uparrow \\ \text{second}}}{|\psi^{(2)}\rangle} + \dots + \lambda^n \underset{\substack{\uparrow \\ \dots\ \text{nth order corrections}}}{|\psi^{(n)}\rangle}$$

- Insert the expansions in the Schrödinger equation, order wrt. λ^k and solve starting $k=0$

$$(\hat{H}_0+\lambda\hat{H}')(|\psi^{(0)}\rangle+\lambda|\psi^{(1)}\rangle+\lambda^2|\psi^{(2)}\rangle+\dots)=$$

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

$$\lambda^0: \quad \hat{H}_0|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle \quad \hat{=} \text{ assumption!}$$

$$\lambda^1: \quad \hat{H}_0|\psi^{(1)}\rangle+\hat{H}'|\psi^{(0)}\rangle = E^{(0)}|\psi^{(1)}\rangle+E^{(1)}|\psi^{(0)}\rangle$$

$$\Rightarrow \underbrace{\langle\psi^{(0)}|\hat{H}_0|\psi^{(1)}\rangle}_{0}+\langle\psi^{(0)}|\hat{H}'|\psi^{(0)}\rangle =$$

$$= E^{(0)}\underbrace{\langle\psi^{(0)}|\psi^{(1)}\rangle}_{0}+E^{(1)}\underbrace{\langle\psi^{(0)}|\psi^{(0)}\rangle}_{1}$$

"tricks": ↓ Hermitian eigenfunction

$$\langle\psi^{(0)}|\hat{H}_0|\psi^{(1)}\rangle \overset{!}{=} \langle\psi^{(1)}|\hat{H}_0|\psi^{(0)}\rangle^* \overset{!}{=} E_0\langle\psi^{(1)}|\psi^{(0)}\rangle = 0$$

$$\Rightarrow \quad \underbrace{E^{(1)}}_{\text{1st order energy correction}} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle$$

useful, e.g., to evaluate spin-orbit splittings.

e.g. in case of Møller-Plesset perturbation theory one gets

$$E^{(0)} + E^{(1)} = E^{HF} \qquad \text{MP1}$$

Up to here nothing is gained wrt. HF!

Correlation comes in in higher orders, i.e. MP2, ...

$$\lambda^2: \hat{H}_0|\psi^{(2)}\rangle + \hat{H}^{(1)}|\psi^{(1)}\rangle = E^{(0)}|\psi^{(2)}\rangle + E^{(1)}|\psi^{(1)}\rangle + E^{(2)}|\psi^{(0)}\rangle$$

$$\Rightarrow \underbrace{\langle\psi^{(0)}|\hat{H}_0|\psi^{(2)}\rangle}_{0} + \langle\psi^{(0)}|\hat{H}^{(1)}|\psi^{(1)}\rangle =$$

cf. λ^1 for "tricks"!

$$= E^{(0)}\underbrace{\langle\psi^{(0)}|\psi^{(2)}\rangle}_{0} + E^{(1)}\underbrace{\langle\psi^{(0)}|\psi^{(1)}\rangle}_{0} + E^{(2)}\underbrace{\langle\psi^{(0)}|\psi^{(0)}\rangle}_{1}$$

$$\Rightarrow E^{(2)} = \langle\psi_{\underline{i}}^{(0)}|\hat{H}^{(1)}|\psi^{(1)}\rangle = \sum_{\substack{k\\ k=\underline{i}}} c_k \langle\psi_i^{(0)}|\hat{H}^{(1)}|\psi_k^{(0)}\rangle$$

ith state

exclude ith state for $\psi^{(1)}$

$\{|\psi_i^{(0)}\rangle\}$ complete orthonormal basis set

Nice result, but from where to get the c_k?

→ c_k define the 1st-order correction $\psi^{(1)}$,

so we look at the 1st-order equation again!

$$\lambda^1: \quad \hat{H}_0|\psi^{(1)}\rangle + \hat{H}'|\psi^{(0)}\rangle = E^{(0)}|\psi^{(1)}\rangle + E^{(1)}|\psi^{(0)}\rangle$$

$$\sum_{\substack{k \\ k\neq \underline{i}}} c_k\left(\hat{H}_0 - E_{\underline{i}}^{(0)}\right)|\psi_k^{(0)}\rangle + \left(\hat{H}' - E_{\underline{i}}^{(1)}\right)|\psi_{\underline{i}}^{(0)}\rangle$$

$$= E_k^{(0)}|\psi_k^{(0)}\rangle$$

$$\langle\psi_j^{(0)}|$$

$$c_j\left(E_j^{(0)} - E_i^{(0)}\right) + \langle\psi_j^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle = 0$$

$$\Rightarrow \quad c_j = \frac{\langle \psi_j^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}}$$

1st order wavefunction:

$$|\psi_i^{(1)}\rangle = \sum_{\substack{j \\ j \neq i}} \frac{\langle \psi_j^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} |\psi_j^{(0)}\rangle$$

2nd order energy:

$$E_i^{(2)} = \sum_{\substack{j \\ j \neq i}} \frac{|\langle \psi_j^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle|^2}{E_i^{(0)} - E_j^{(0)}}$$

in general:
nth order wave-function determines 2n+1th order energy

⇒ 2nd order Rayleigh-Schrödinger perturbation theory (RS2)

the simplest (and cheapest) ab initio approach to go beyond HF!

$$\hat{H}' = \hat{H}^{exact} - \sum_{i=1}^{n} \hat{F}(i)$$

$$\left\{ \Psi_i^{(0)} = \phi_{HF}, \phi_{kl}^{ab} \right\}$$

Closed shell reference: $\langle \Phi_{HF} | \hat{H} | \Phi_k^a \rangle = 0$ [Brillouin theorem].

HF ground state Slater determinant and doubly excited Slater determinants constructed from HF orbitals

- Møller-Plesset perturbation theory

$$E_i^{(0)} = \sum_{\substack{k \\ k\in occ}} \varepsilon_k \qquad \Rightarrow \text{MP2}$$

very popular

- Epstein-Nesbet perturbation theory

$$E_i^{(0)} = \langle \psi_i^{(0)} | \hat{H} | \psi_i^{(0)} \rangle \qquad \Rightarrow \text{EN2}$$

not much used

- Higher orders can be derived, but are costly. MP4 is occasionally used.

Example: He atom $1s^2\ {}^2S$ ground state

$$|\psi_{CISD}\rangle \cong 0{,}9964\,|1s^2\rangle + 0{,}0011\,|1s^1 2s^1\rangle$$

HF

comes in by coupling to double excitations

$$-0{,}0645\,|2s^2\rangle - 0{,}0321\left(|2p_x^2\rangle + |2p_y^2\rangle + |2p_z^2\rangle\right)$$

radial correlation

angular correlation

± ııı	in eV	HF	CI	MP2	Exp.
cc-pVDZ	IP_1	23,44	24,33	24,15	
cc-pV5Z		23,45	24,58	24,44	24,59
cc-pVDZ	IP_2	54,25			
cc-pV5Z		54,42			54,42

(CPU times ≤ 1 second)

So far (CI, MBPT) we had a <u>linear</u> operator to generate excitations from the HF zeroth-order wavefunction:

$$|\Psi\rangle = (1 + \hat{T})|\Phi_0\rangle$$

$\llcorner$ $\sum$ excitation operator • coefficient

(→ singles, doubles, triples, ...)

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots$$

$$\hat{T}_1 = \sum_{\substack{i \\ \in occ}} \sum_{\substack{a \\ \in virt}} c_i^a \hat{a}_a^\dagger \hat{a}_i$$

single excitations operator

$$\hat{T}_2 = \frac{1}{4} \sum_{\substack{i,j \\ \in occ}} \sum_{\substack{a,b \\ \in virt}} c_{ij}^{ab} \hat{a}_a^{+} \hat{a}_b^{+} \hat{a}_j \hat{a}_i$$ double excitations operator

...

$\hat{a}_i, \hat{a}_j, \ldots$ annihilation operators → electrons in orbitals $i, j, \ldots$ deleted

$\hat{a}_a^{+}, \hat{a}_b^{+}, \ldots$ creation operators → electrons in orbitals $a, b, \ldots$ created

anticommutation relations obeyed:

$$\{\hat{a}_p, \hat{a}_q\} = \{\hat{a}_p^{+}, \hat{a}_q^{+}\} = 0, \{\hat{a}_p, \hat{a}_q^{+}\} = \delta_{pq}$$

commutator : $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ ✓

anticommutator : $\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ new

$\hat{a}_i, \hat{a}_j, \ldots, \hat{a}^{+}_a, \hat{a}^{+}_b, \ldots \rightarrow$ 2nd quantization

← useful "language" for many-particle theories; we will not investigate this topic further ...

Problem of truncated CI: the correlation energy does not scale correctly with system size.

Consider a system with two orbitals and two electrons and only double excitations (e.g. H_2 in a minimal basis set):

intermediate normalization!

$$|\Psi_{CID}\rangle = (1+\hat{T}_2)|\phi_{HF}\rangle = |\phi_{HF}\rangle + c_D|\phi_D\rangle$$

nrel. $\hat{H}$: all real!

$$E = \frac{\langle \phi_{HF} + c_D\phi_D|\hat{H}|\phi_{HF} + c_D\phi_D\rangle}{\langle \phi_{HF} + c_D\phi_D|\phi_{HF} + c_D\phi_D\rangle} = \frac{E^{HF} + 2c_D\langle\phi_D|\hat{H}|\phi_{HF}\rangle + c_D^2\langle\phi_D|\hat{H}|\phi_D\rangle}{1 + c_D^2}$$

check with HF code!

CID here is FCI!

Now consider two of such systems at an infinite distance from each other:

$$|\Psi_{CID}\rangle = (1+\hat{T}_{2,A}+\hat{T}_{2,B})|\Phi_{HF}\rangle \overset{\text{systems A and B}}{=}$$

$$= |\Phi_{HF}\rangle + c_{D,A}|\Phi_{D,A}\rangle + c_{D,B}|\Phi_{D,B}\rangle$$

$c_{D,A}$ and $c_{D,B}$: numerically equal

$$E = \frac{\overset{2E_{HF,A}}{E_{HF}} + 2\cdot 2c_{D,A}\langle\Phi_{D,A}|\hat{H}|\Phi_{HF}\rangle + 2\cdot c_{D,A}^{2}\langle\Phi_{D,A}|\hat{H}|\Phi_{D,A}\rangle}{1+\underline{\underline{2}}\,c_{D,A}^{2}}$$

2: A and B contribute equally; $\langle\Phi_{D,A}|\hat{H}|\Phi_{D,B}\rangle = 0$

$\Rightarrow E(2\,\text{systems}) \neq 2 \cdot E(1\,\text{system})$

- size extensivity:

$E(n\,\text{systems}) = n E(1\,\text{system})$

- CID (and other truncated CI schemes are not size extensive!
- missing is the simultaneous double excitation on A and B, i.e. $\hat{T}_{2,A} \cdot \hat{T}_{2,B}$!
(or a fourfold excitation $\hat{T}_4$ as in FCI)

We try an exponential ansatz for the excitation operator:

$$|\psi\rangle = e^{\hat{T}}|\phi_0\rangle = (\underbrace{1+\hat{T}}_{\text{as for CI}} + \underbrace{\frac{1}{2}\hat{T}^2 + \ldots}_{\text{coupled higher order excitations}})|\phi_0\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots$$

$$\hat{T}_1 = \sum_{i \in \text{occ}} \sum_{a \in \text{virt}} t_i^a \, \hat{a}_a^\dagger \hat{a}_i$$

single excitations operator

amplitude, not coefficient!

$$\hat{T}_2 = \frac{1}{4}\sum_{\substack{i,j \\ \in occ}}\sum_{\substack{a,b \\ \in virt}} t_{ij}^{ab}\,\hat{a}_a^{\dagger}\,\hat{a}_b^{\dagger}\,\hat{a}_j\,\hat{a}_i$$

double excitations operator

...

coupled higher excitations generate size extensivity

$\underbrace{\hphantom{xxxxxxxxxx}}$

products of amplitudes $t_i^a t_j^b$ yield coefficients!

Note:

CI	CC
$\hat{T}_1$	$\hat{T}_1$
$\hat{T}_2$	$\hat{T}_2 + \frac{1}{2}\hat{T}_1^2$
$\hat{T}_3$	$\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}T_1^3$
$\vdots$	$\vdots$

The exponential ansatz is the basic idea of <u>C</u>oupled <u>C</u>luster (CC) theory.

(Koester, Kümmel, 1957/1960; after ≈ 1970 also used in QC)

Problem: the underlying equations for the CC amplitudes are nonlinear and more difficult to solve than the linear ones for CI coefficients.

projective and iterative solution.

assume a "full" CC wavefunction solves the Schrödinger equation:

$$\hat{H}|e^{\hat{T}}\phi_0\rangle = E|e^{\hat{T}}\phi_0\rangle$$

then: $\langle\phi_0|\hat{H}e^{\hat{T}}\phi_0\rangle = E$

projection

$$\langle\phi_{i\ldots}^{a\ldots}|\hat{H}e^{\hat{T}}\phi_0\rangle = E\langle\phi_{i\ldots}^{a\ldots}|e^{T}\phi_0\rangle$$

equation for the energy and equations for the amplitudes!

(nonlinear, coupled)

CCSD(T) is currently considered as the "gold standard" of computational chemistry.

CCSD : Coupled cluster with single and double substitutions, nonlinear system of equations solved.

(T) : triple substitutions calculated by perturbation theory.

Attempts to combine the simplicity of CI with the higher accuracy of CC:

(only a few examples)

– ACPF	averaged coupled pair functional
– $(SC)^2CI$	self-consistent size-consistent CI
– CEPAn	coupled electron pair approximation $(n=0,\dots,3)$

Schemes for (near-) degeneracy situations

- more than one leading configuration

  → multi-reference schemes:

  - orbitals optimized for more than a single configuration:

    MCSCF (or MCHF) multi-configuration

  - if the MC wavefunction corresponds to a FCI in a so-called active orbital space:

    CASSCF complete active space

- multi-reference SCF schemes account for "static" electron correlation.

→ adding MBPT, CI, CC to MCSCF or CASSCF

- MRPT, CASPT2, ...
- MRCI (usually MRCISD)
- MRCC (several variants)

Schemes for large systems:

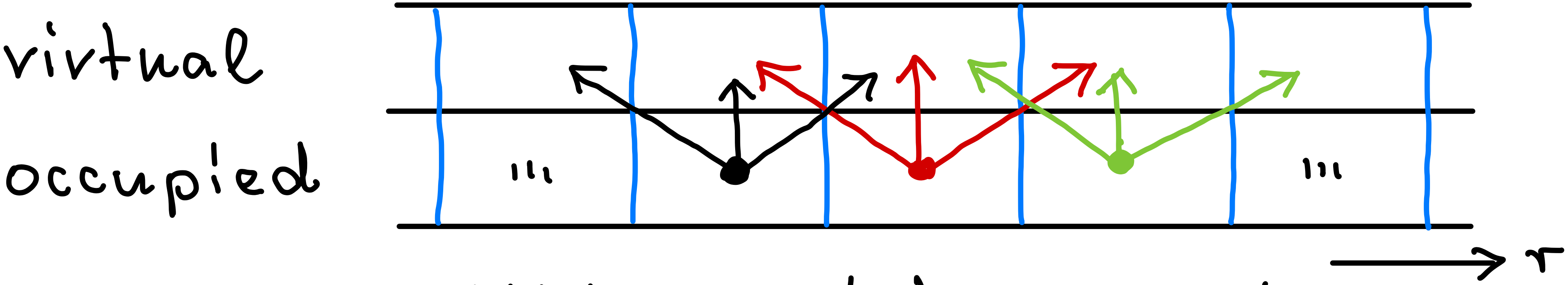
electrons
orbitals
units

- formal scaling with system size n ...

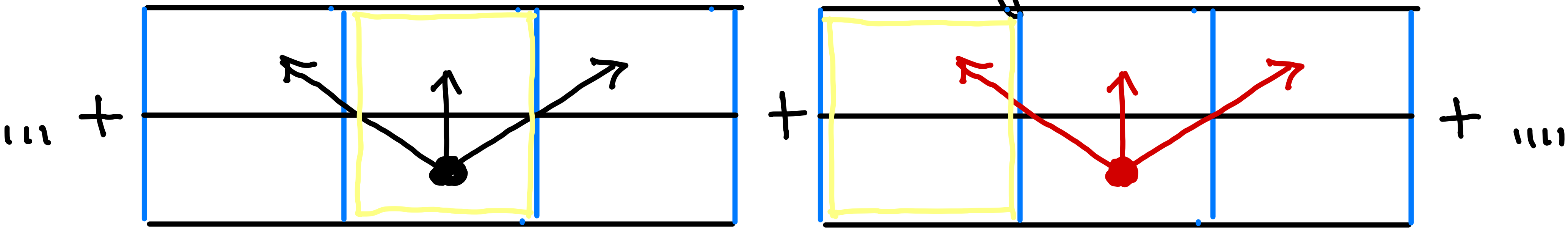
  HF $\sim n^4$, MP2 $\sim n^5$, CISD, CCSD $\sim n^6$, ...

- exploiting the locality of electron correlation (electrons have to come close to each other to "feel" their Coulomb repulsion, "near-sightedness" of electrons) $\longrightarrow$

→ localization of occupied and possibly virtual orbital, only "local" excitations included



→ partitioning into separated overlapping subsystems



usually requires size consistent electron correlation scheme, e.g. CC, MPn

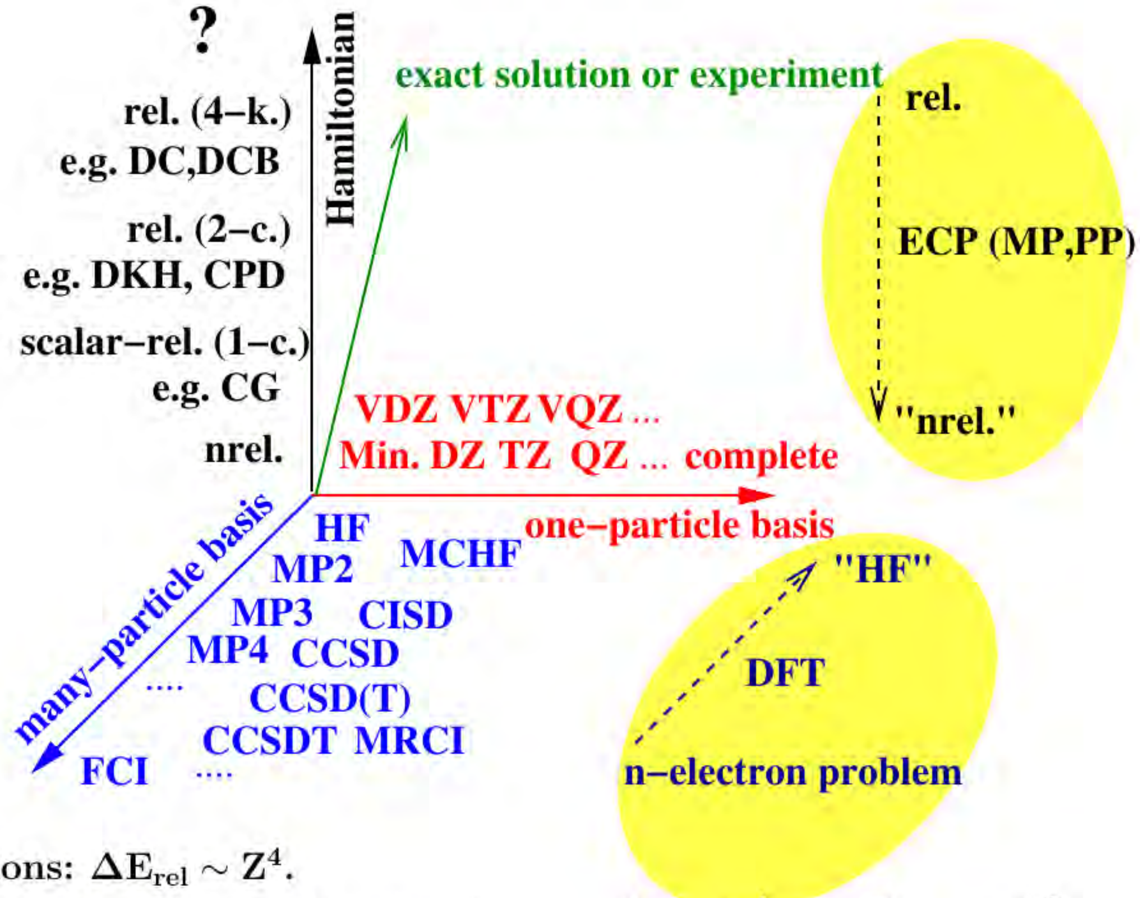
→ numerous so-called

<u>local correlation approaches</u>

- separating the system in an interesting part requiring an accurate treatment and a less interesting spectator part, e.g. <u>solvation models</u> for systems in solution (e.g. COSMO) e.g. <u>embedding schemes</u> for molecules in a solid matrix, active sites of enzymes, ... (QM/MM)

quantum mechanics

molecular mechanics



?

Hamiltonian

rel. (4–k.)
e.g. DC,DCB

rel. (2–c.)
e.g. DKH, CPD

scalar–rel. (1–c.)
e.g. CG

nrel.

exact solution or experiment

VDZ VTZ VQZ ...
Min. DZ TZ QZ ... complete

one–particle basis

many–particle basis

HF
MP2
MP3
MP4
....
FCI

MCHF
CISD
CCSD
CCSD(T)
CCSDT MRCI
....

rel.
ECP (MP,PP)
"nrel."

"HF"
DFT
n–electron problem

- relativistic contributions: $\Delta E_{rel} \sim Z^4$.
- correlation energy errors for standard basis set expansions: $E^{l}_{corr} - E^{\infty}_{corr} \sim 1/l^3$
  → basis set extrapolation or F12-dependent wavefunctions.
- computational effort: $t \sim n^k$ (n size of one-particle basis set, k for some standard approaches: DFT 3, HF 4, MP2 5, CISD, CCSD 6, CCSD(T) 7 ...) → low-order/linear scaling schemes.
- ECPs simplify the Hamiltonian and also lead to some reductions in the sizes of the one- and many-electron basis sets (e.g. small-core PPs plus valence-only SO terms) !
- DFT avoids costly many-determinantal wavefunctions/treatments.

Goal: Suitable compromise between accuracy and computational effort,
i.e., sufficiently accurate low-cost relativistic electronic structure calculations, also for larger systems.

- "Definition" of relativistic effects:

$$\Delta O^{rel} = \langle \overset{\text{many choices!}}{\psi^{rel}} | \hat{O}^{rel} | \psi^{rel} \rangle - \langle \psi^{nrel} | \hat{O}^{nrel} | \psi^{nrel} \rangle$$

- "Definition" of correlation effects:

$$\Delta O^{corr} = \langle \overset{\text{exact?}}{\psi^{corr}} | \hat{O} | \psi^{corr} \rangle - \langle \psi^{HF} | \hat{O} | \psi^{HF} \rangle$$

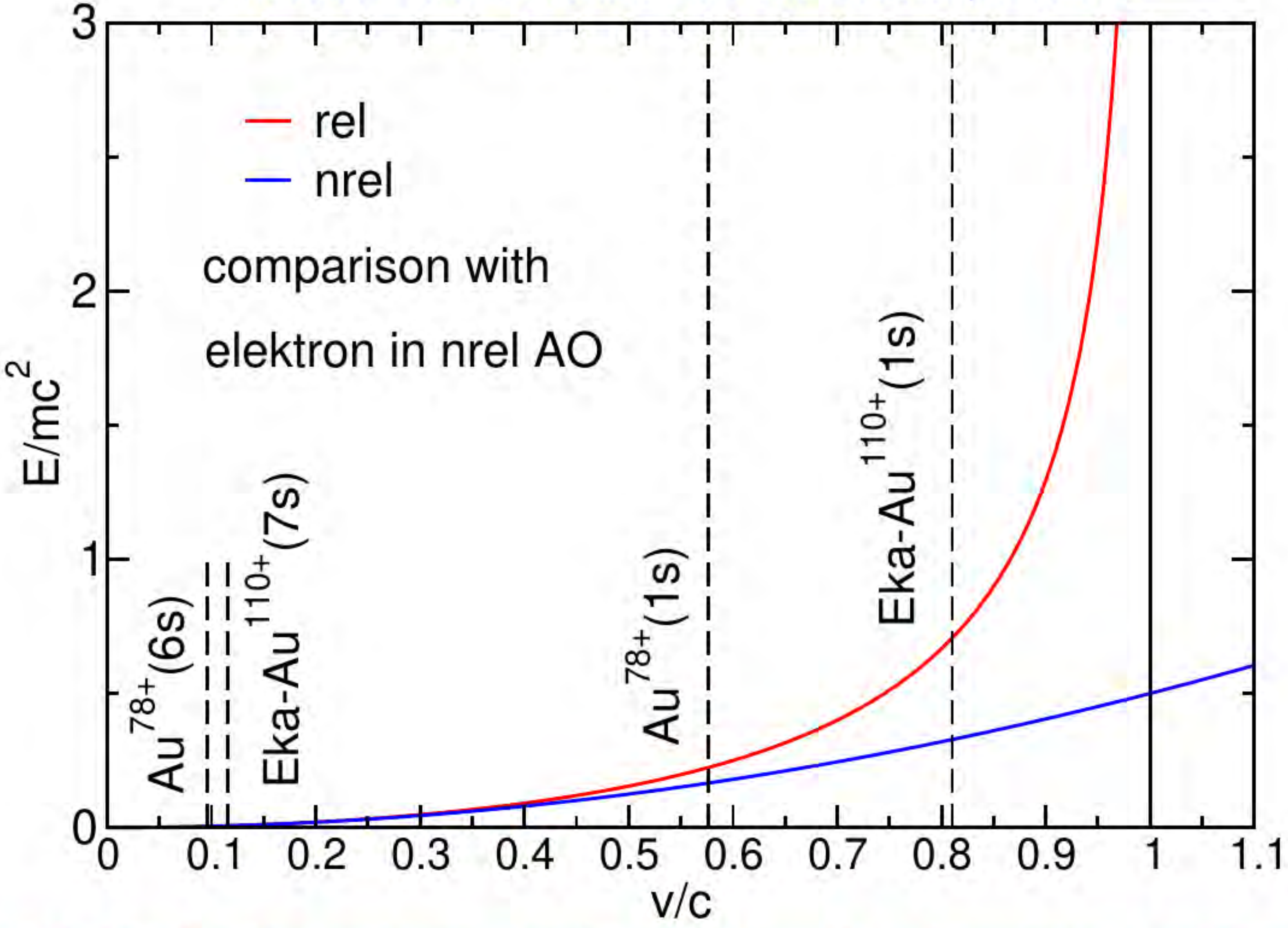
Note :

ΔO^{rel} and ΔO^{corr} are not strictly additive!

$\hat{O} = \hat{H} \Rightarrow$ energies, geometries, frequencies, ...

Kinetic energy

'classical' relativistic and nonrelativistic expressions



→ **Is relativity for the valence shells and thus for chemistry unimportant ?**
Stong relativistic contributions are to be expected for inner shells ...

$$\mathbf{E_{kin}^{nrel} = \frac{1}{2}mv^2} \qquad \mathbf{E_{kin}^{rel} = \frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}} - mc^2}$$

Relativistic Quantum Mechanics requires that the relativistic wave equation for one electron has four components:

we do not go into details here!

→ two degrees of freedom for spin (α, β)
two degrees of freedom for charge (e^-, e^+)

→ Hamilton operator contains 4x4 matrices
Wavefunction ist a 4 component vector

→ Approximate relativistic scheme keep only 2 component (α, β) or 1 component

The Dirac-Coulomb-Breit Hamiltonian

$$\hat{H} = \sum_{i=1}^{n} \hat{h}(i) + \sum_{i=j+1}^{n}\sum_{j=1}^{n-1} \hat{g}(\hat{i},\hat{j}) + W_{NN}$$

$$\hat{h}(i) = \hat{h}_D(i) = c\vec{\alpha}_i\vec{p}_i + (\beta_i - I_4)c^2 + V_N(i)$$

$$V_N(i) = \sum_{I=1}^{N}\left(-\frac{Z_I}{r_{iI}}\right)$$

finite nuclei possible!

$$\hat{g}(i,j) = \hat{g}_{CB}(i,j) = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}}\left[\vec{\alpha}_i\vec{\alpha}_j + \frac{(\vec{\alpha}_i\vec{r}_{ij})(\vec{\alpha}_j\vec{r}_{ij})}{r_{ij}^2}\right]$$

$$V_{NN} = \sum_{I=J+1}^{N} \sum_{J=1}^{N} \frac{Z_I Z_J}{r_{IJ}}$$

Dirac matrices:

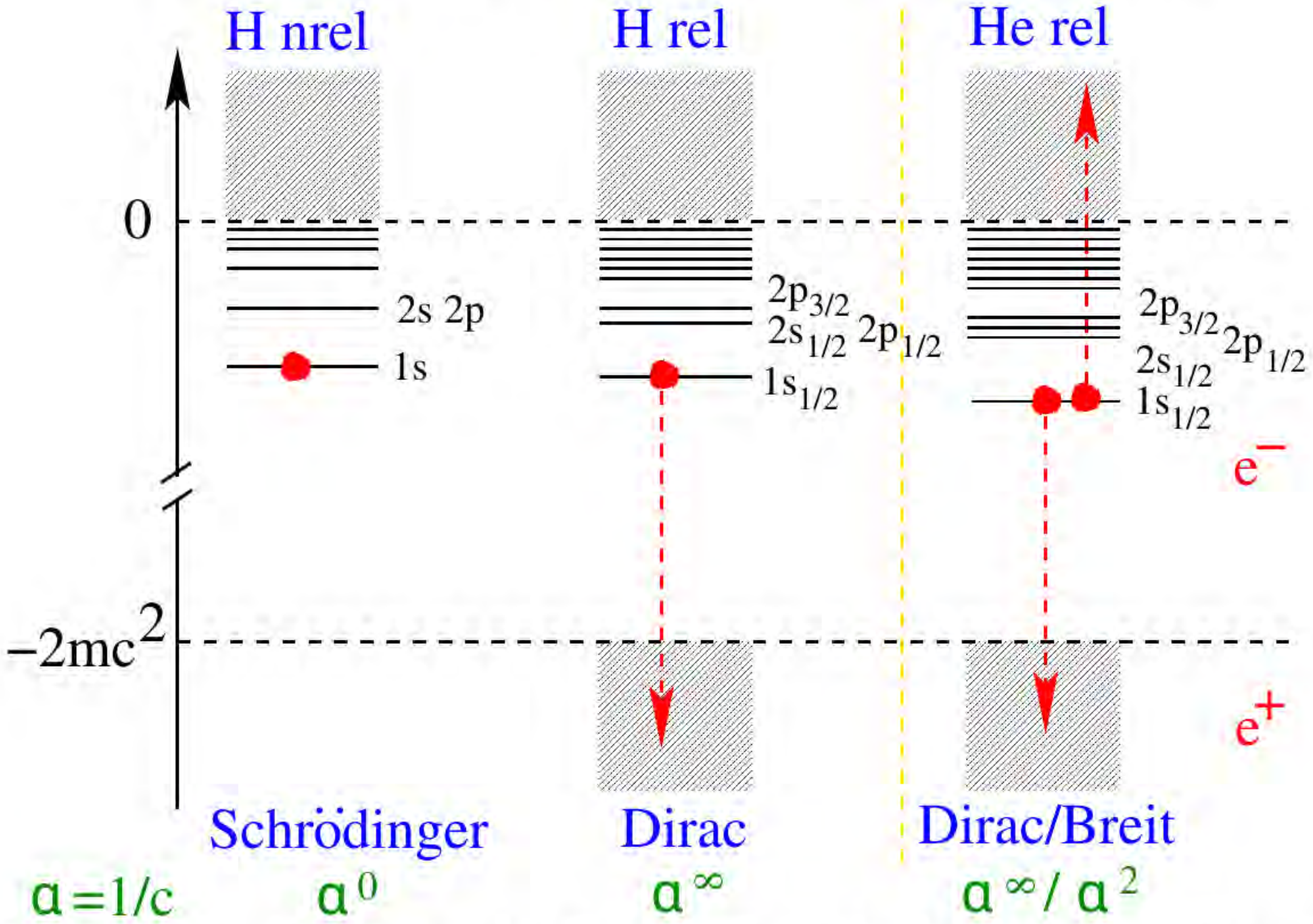
$$\alpha_k = \begin{pmatrix} 0 & i\sigma_k \\ -i\sigma_k & 0 \end{pmatrix} \text{ with } k = x, y, z, \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$$

Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, I_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

other representations possible!

One– and many–electron atoms (nrel vs. rel)



→ fundamental difficulties ('variational collapse', 'finite basis set disease', 'continuum dissolution'/'Brown-Ravenhall disease') are nowadays solved for practical calculations ('projection' on electronic states, 'kinetic balance', ...), but high computational effort is required !

→ finite difference atomic MCDHF/DC(B) calculations (e.g. GRASP, Grant et al.) are 'routine' today. Used to generate reference data for recent energy-consistent pseudopotentials.

Relativistic H-like atoms/ions energy

$$E = \frac{\overset{1\,\text{a.u.}}{\overset{\downarrow}{\underline{m}}}c^2}{\sqrt{1+\dfrac{Z^2\alpha^2}{\left(n_r+\sqrt{(j+\frac{1}{2})^2-Z^2\alpha^2}\right)^2}}}$$

$$n_r = n - j - \frac{1}{2}$$

$$\alpha = \frac{1}{c} \approx 137\ \text{a.u.}$$

fine structure constant

- assume $Z \ll c \approx 137 \Rightarrow \sqrt{(j+\frac{1}{2})^2 - Z^2\alpha^2} \approx j + \frac{1}{2}$

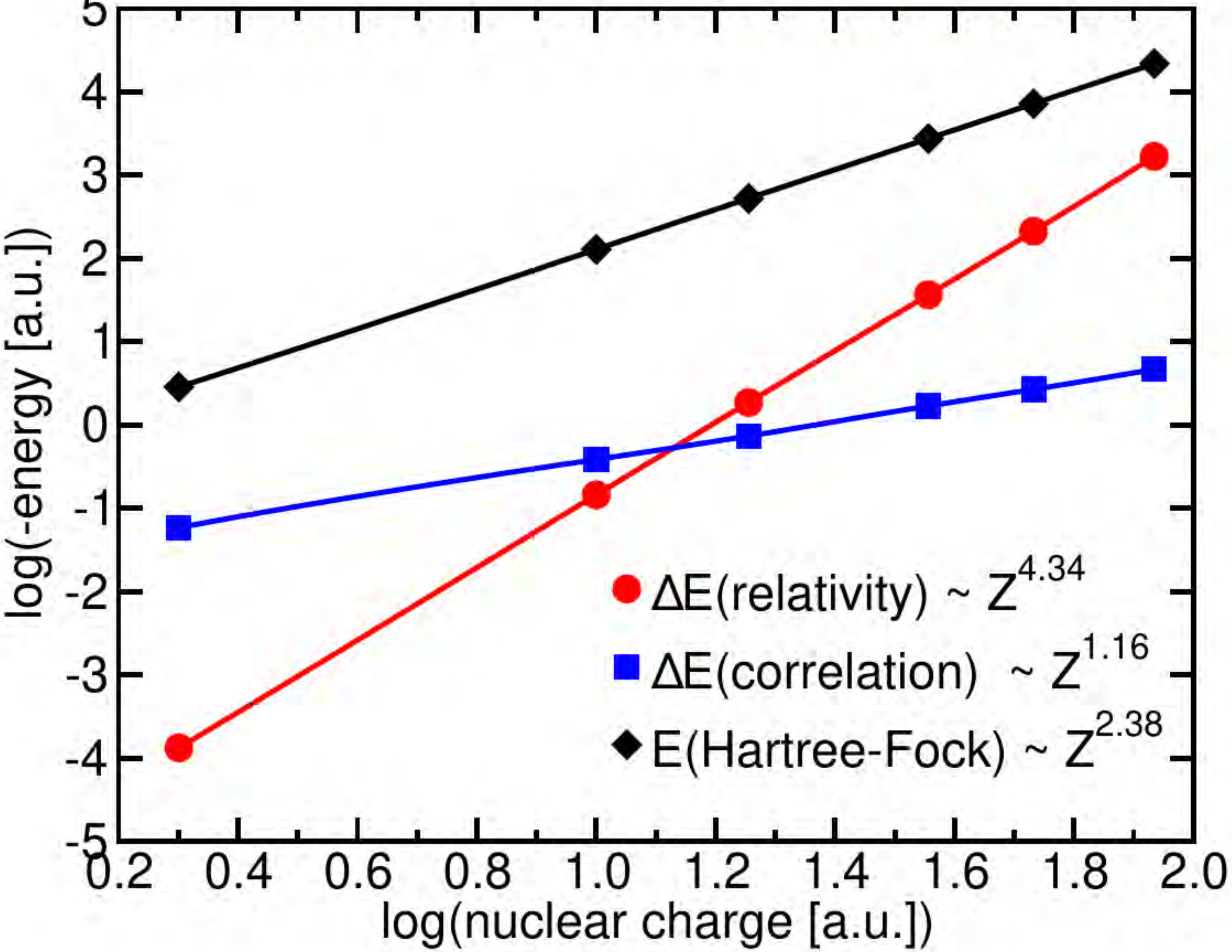
  and $n_r + \sqrt{} \approx n$

rest e. nrel.e. rel. corr.

- Taylor expansion $\dfrac{mc^2}{\sqrt{1+\frac{Z^2\alpha^2}{n^2}}} \approx mc^2 - \underset{\sim Z^2}{\dfrac{Z^2 m}{2n^2}} + \underset{\sim Z^4}{O(Z^4\alpha^2)}$

Relativistic and electron correlation contributions

HF, DHF/DC, DFT for (rare gas) atoms



Note: relativistic effects are not only important for core orbitals (high average electron velocities) but also for valence orbitals (low average electron velocities) and influence the chemical properties of heavy elements.

Quantum Mechanics of Many-Electron Systems

P. A. M. Dirac

Proc. Roy. Soc. London A 123 (1929) 714

> The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativistic ideas. These give rise to difficulties only when high speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much to complicated to be soluble.

Relativistic effects in chemistry are investigated systematically since about three decades, cf. e.g. the following early review papers on the topic:

P. Pyykkö, Adv. Quant. Chem. 11 (1978) 353.

K. S. Pitzer, Acc. Chem. Res. 12 (1979) 271.

P. Pyykkö, J.-P. Desclaux, Acc. Chem. Res. 12 (1979) 276.

Relativistic effects for atoms

- **direct effects**
  - reason: replacing $\hat{H}^{nrel}$ by $\hat{H}^{rel}$
  - result: causes contraction and stabilization of all orbitals
    - the larger the smaller n and l, i.e.
      size $1s > 2s \gtrsim 2p > 3s \gtrsim 3p \gtrsim 3d$ ....
  - result: causes spin-orbit splitting
    - the larger the smaller n and l, i.e.
      size $2p > 3p > 3d$ ...

- <u>indirect effects</u>

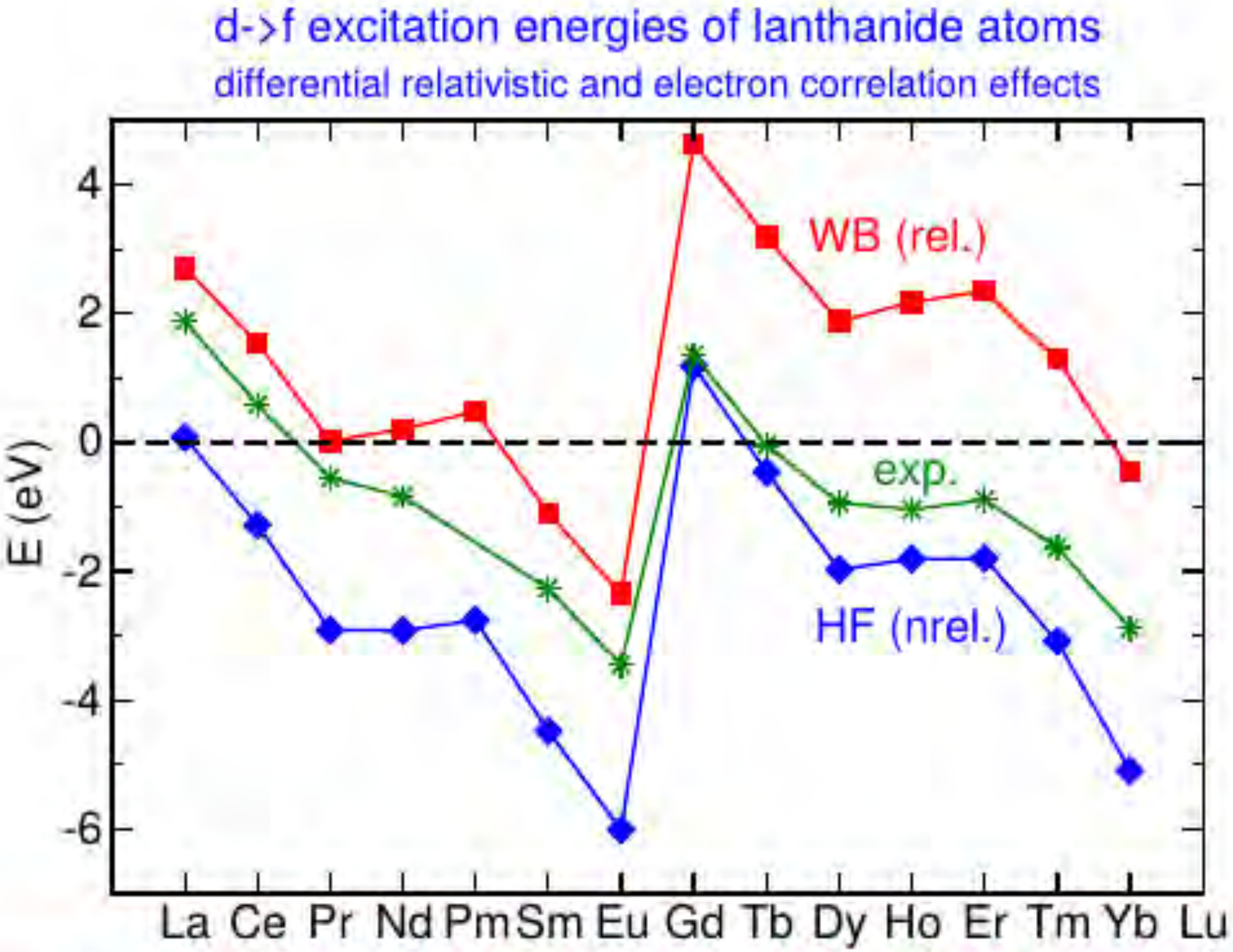
- reason: direct effects cause a contraction of inner (core) shells
- result: better screening of the nuclear charge for outer (valence) shells and thus to a destabilization and expansion.

Many-electron atoms:
<u>Both</u> effects act on <u>all</u> shells!

Result for <u>valence</u> shells:

- stabilization and contraction of s and p shells
- destabilization and expansion of d and f shells

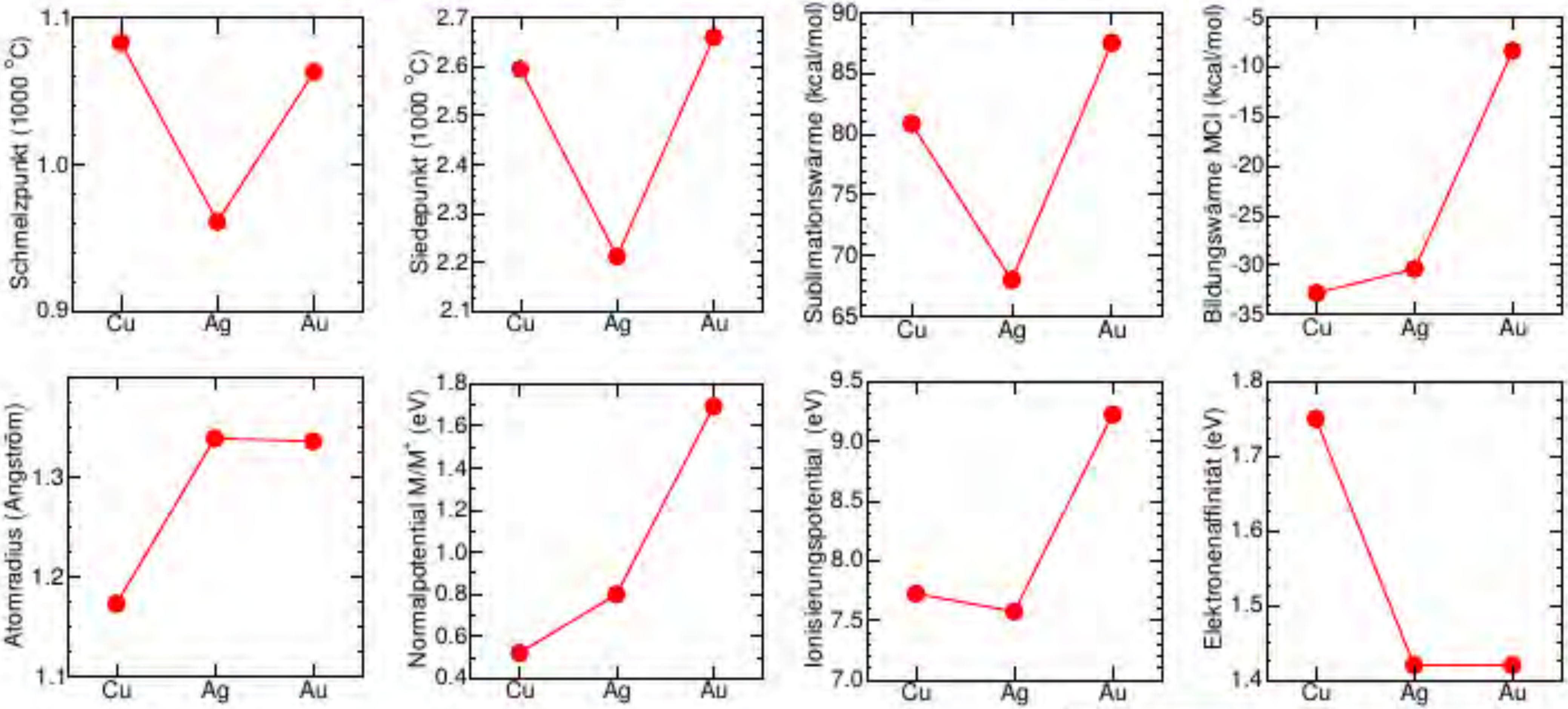
(rules of thumb!)



– Large and counteracting differential relativistic (WB vs. HF) and correlation (WB vs. Exp.) effects.

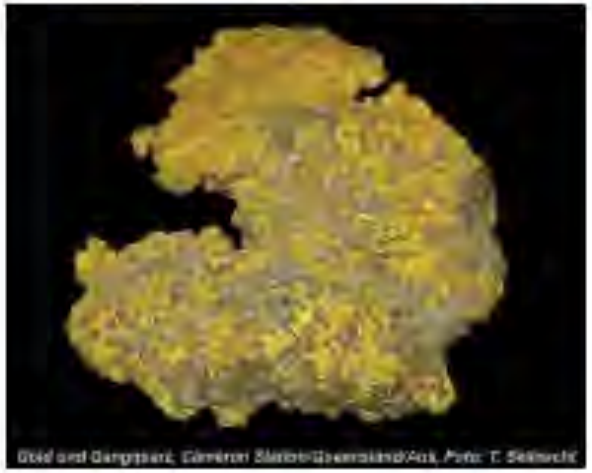
Differential relativistic and electrons correlation effects for 3d-, 4d-, 5d-transition metals are discussed in R. L. Martin, P. J. Hay, J. Chem. Phys. 75 (1981), 4539 (comparision Hartree-Fock results, Cowan-Griffin results and expimental data). Differential relativistic effects for 4f-elements can be found in M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys. 90 (1989) 1730, and for 5f-elements in W. Küchle, M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys. 100 (1994) 7535 (comparision Hartree-Fock and Wood-Boring results).

Experimentally observed trends for Cu - Ag - Au



Kupfer an Holz, USA, Foto und Copyright: T. Seilnacht

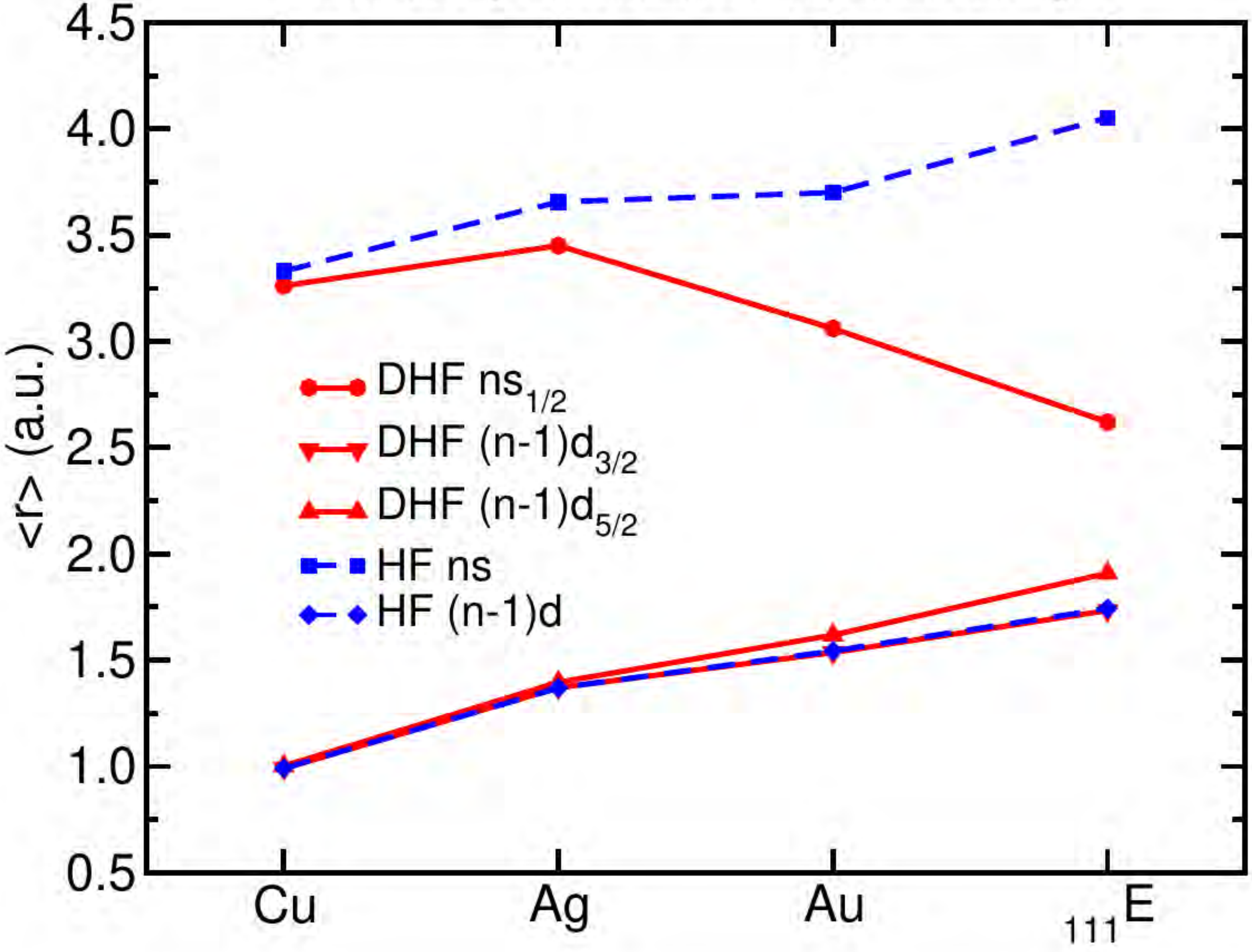
Silber gediegen, Freiberg/Sachsen, Foto und Copyright: T. Seilnacht

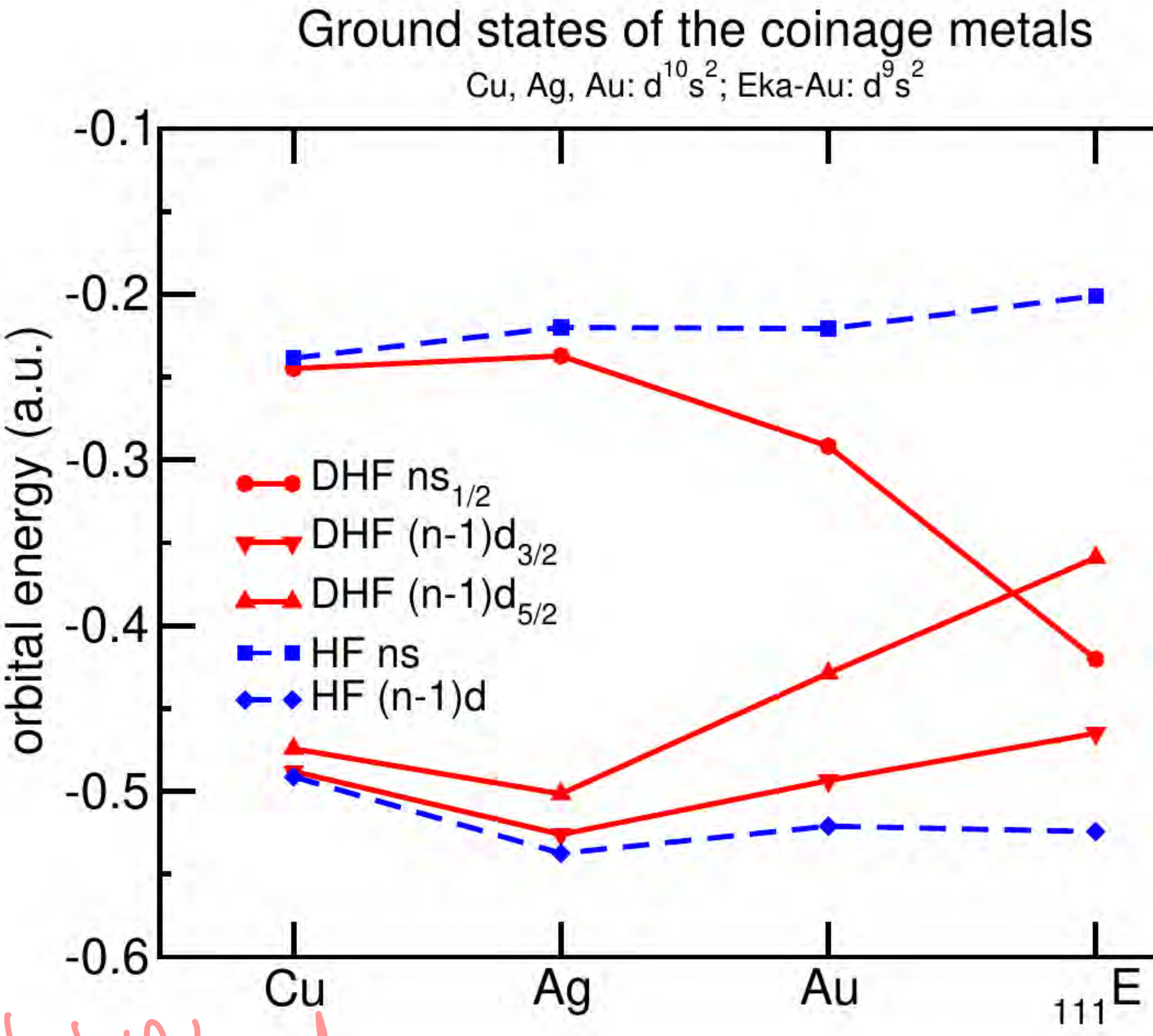


Gold und Gangquarz, Cameron Station/Queensland/Aus, Foto: T. Seilnacht

Size of the coinage metals

nrel: Cu<Ag<Au<Eka-Au; rel: Eka-Au<Au<Cu<Ag





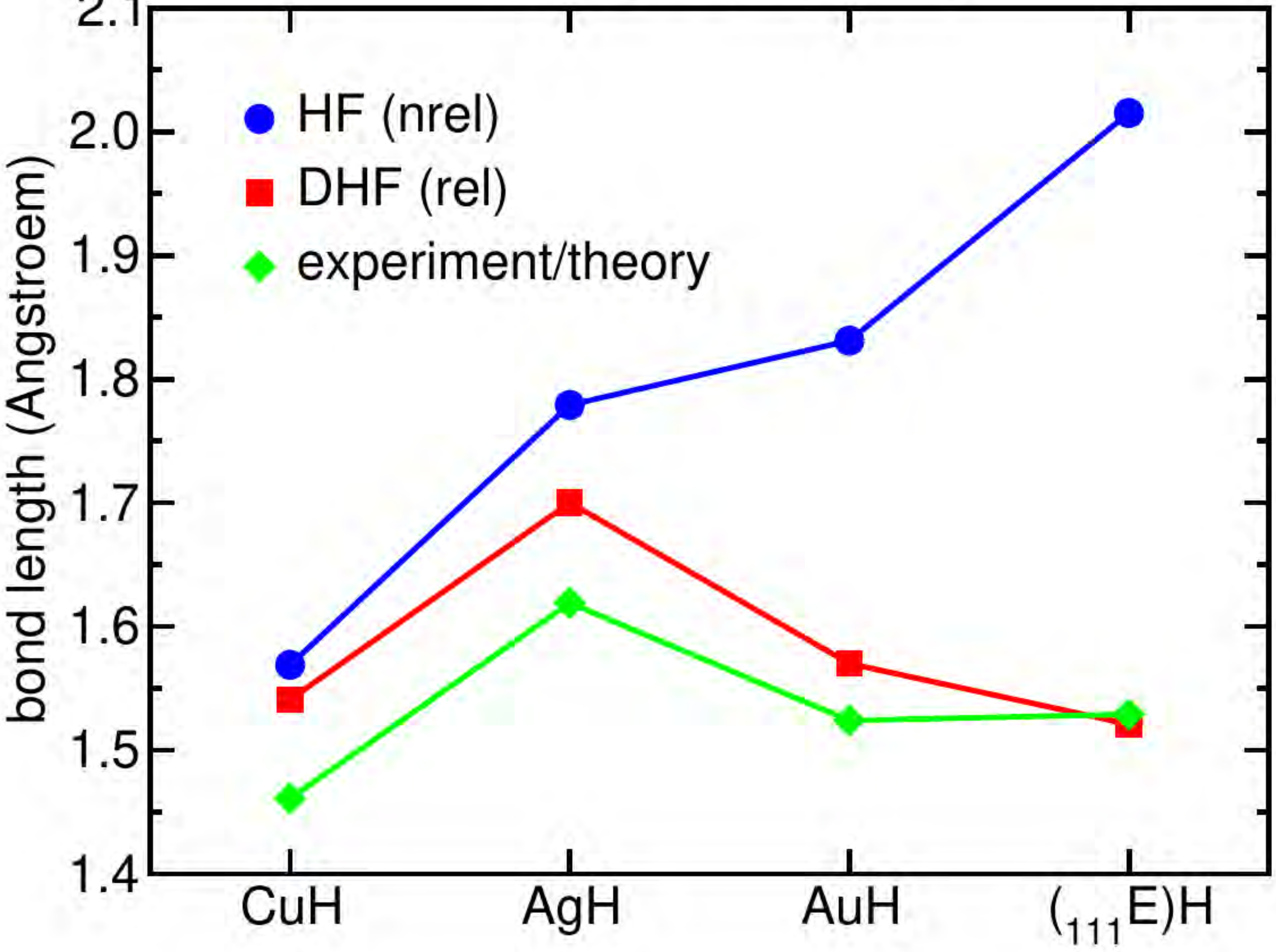
destabilized

stabilized

$d^{10}s^{1} \Longrightarrow d^{9}s^{2}$ for very large Z!

Relativistic effects in coinage metal hydrides

bond lengths (Angstroem)

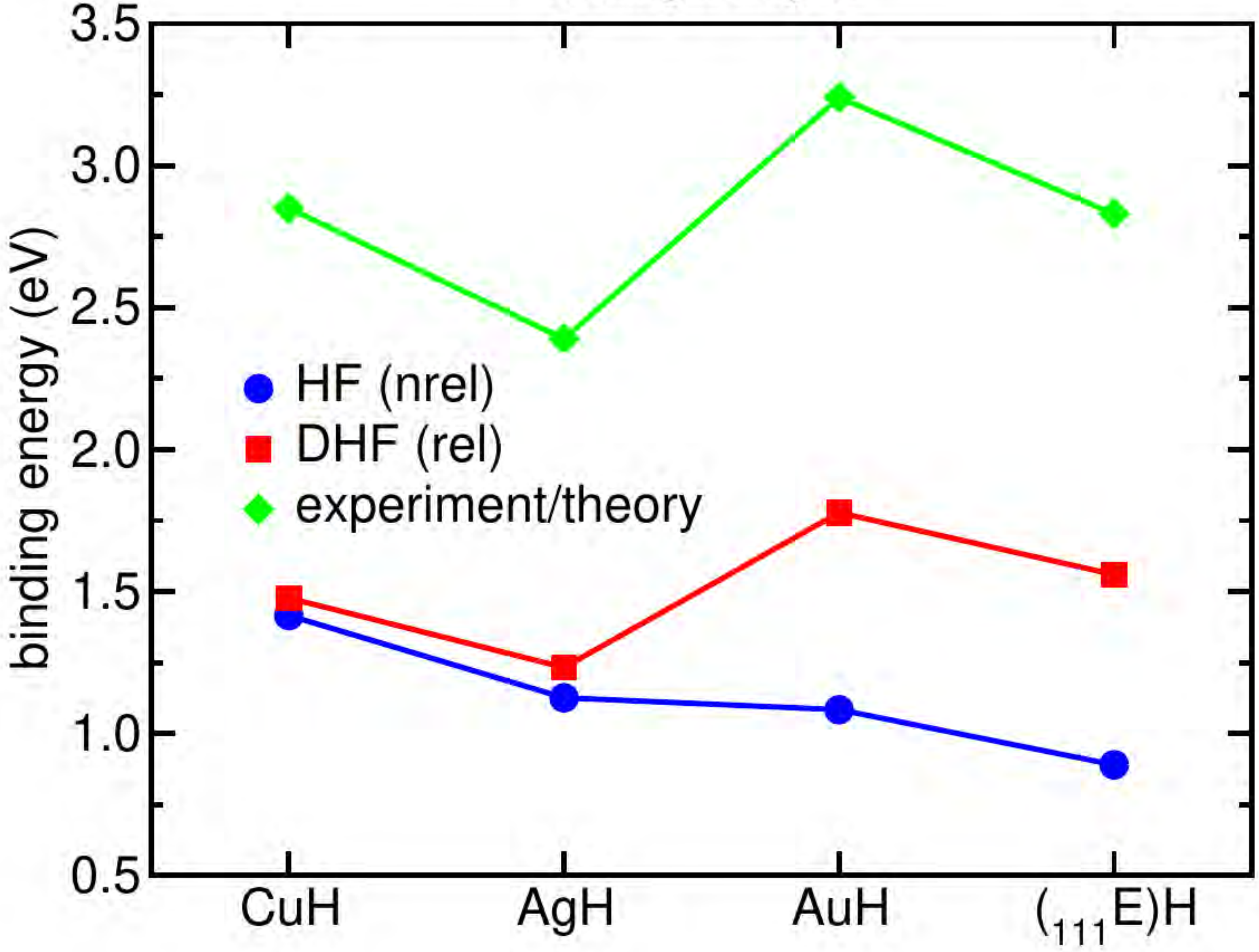


bonding orbitals contract → bond contracts

(Attention: interpretations depend on $\hat{H}$!)

Relativistic effects in coinage metal hydrides

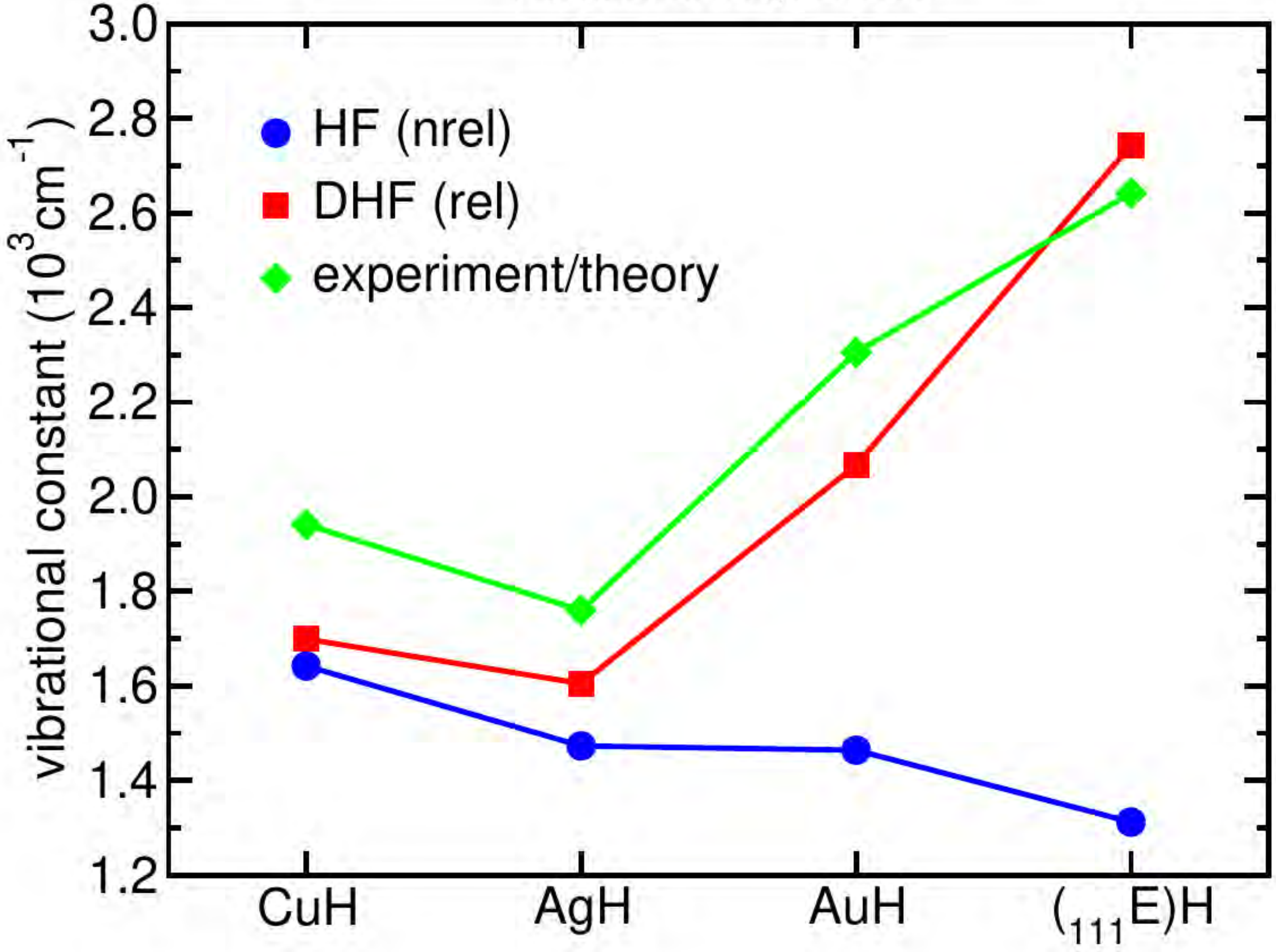
binding energies



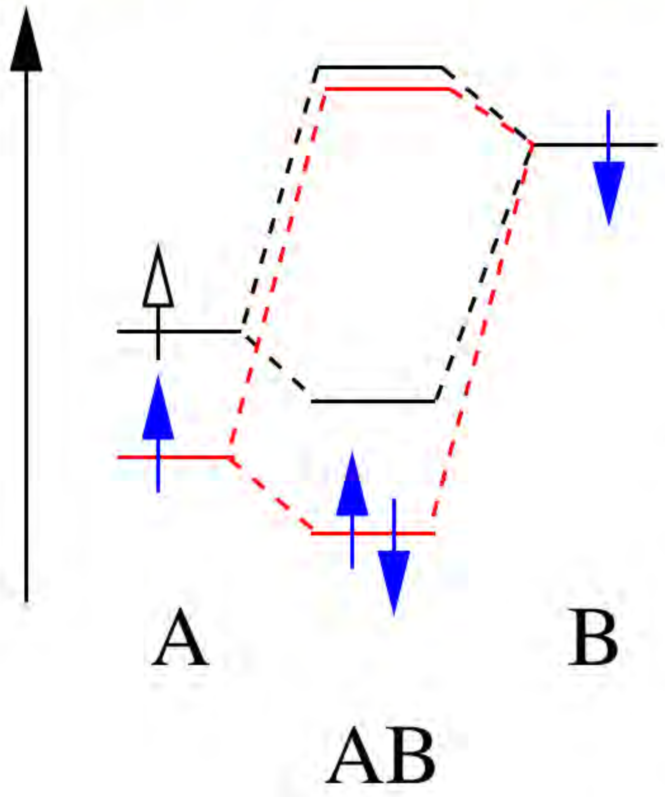
$M + H \rightarrow M^{\ominus} + H^{\oplus} \rightarrow MH$, ns^1 stabilized $\rightarrow EA\uparrow \rightarrow D_e\uparrow$

Relativistic effects in coinage metal hydrides

vibrational frequencies



Stabilization of chemical bonds



B more electropositive than A

A relativistically stabilized

=> AB stabilized

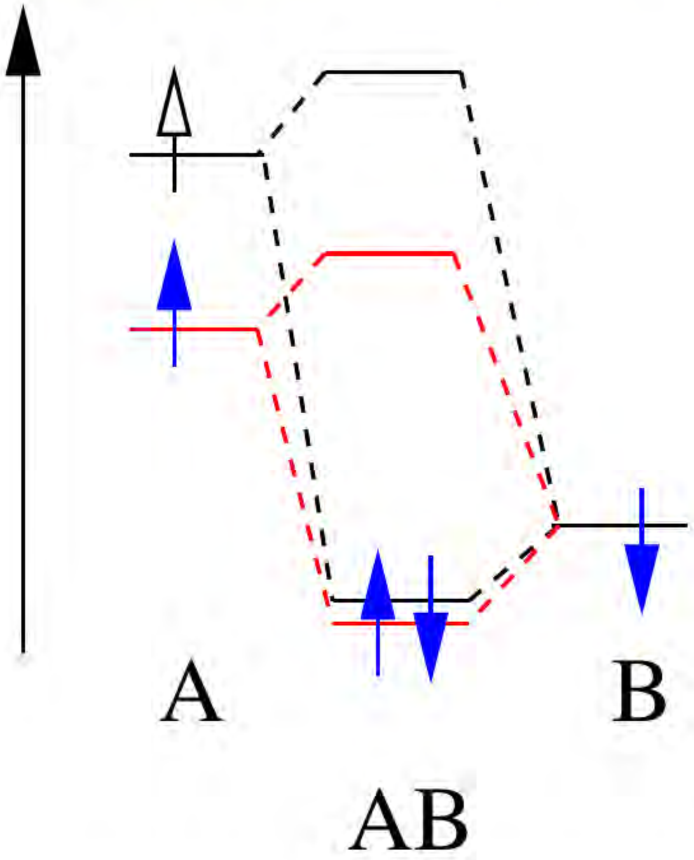
example: AuLi (Au– Li+)

stabilization

ca. 30 % of the binding energy

AuLi: Schwerdtfeger, Dolg, Schwarz, Bowmaker, Boyd, J. Chem. Phys. 91 (1989) 369.

Destabilization of chemical bonds



B more electronegative A

A relativistically stabilized

=> AB destabilized

example: AuF (Au+ F–)

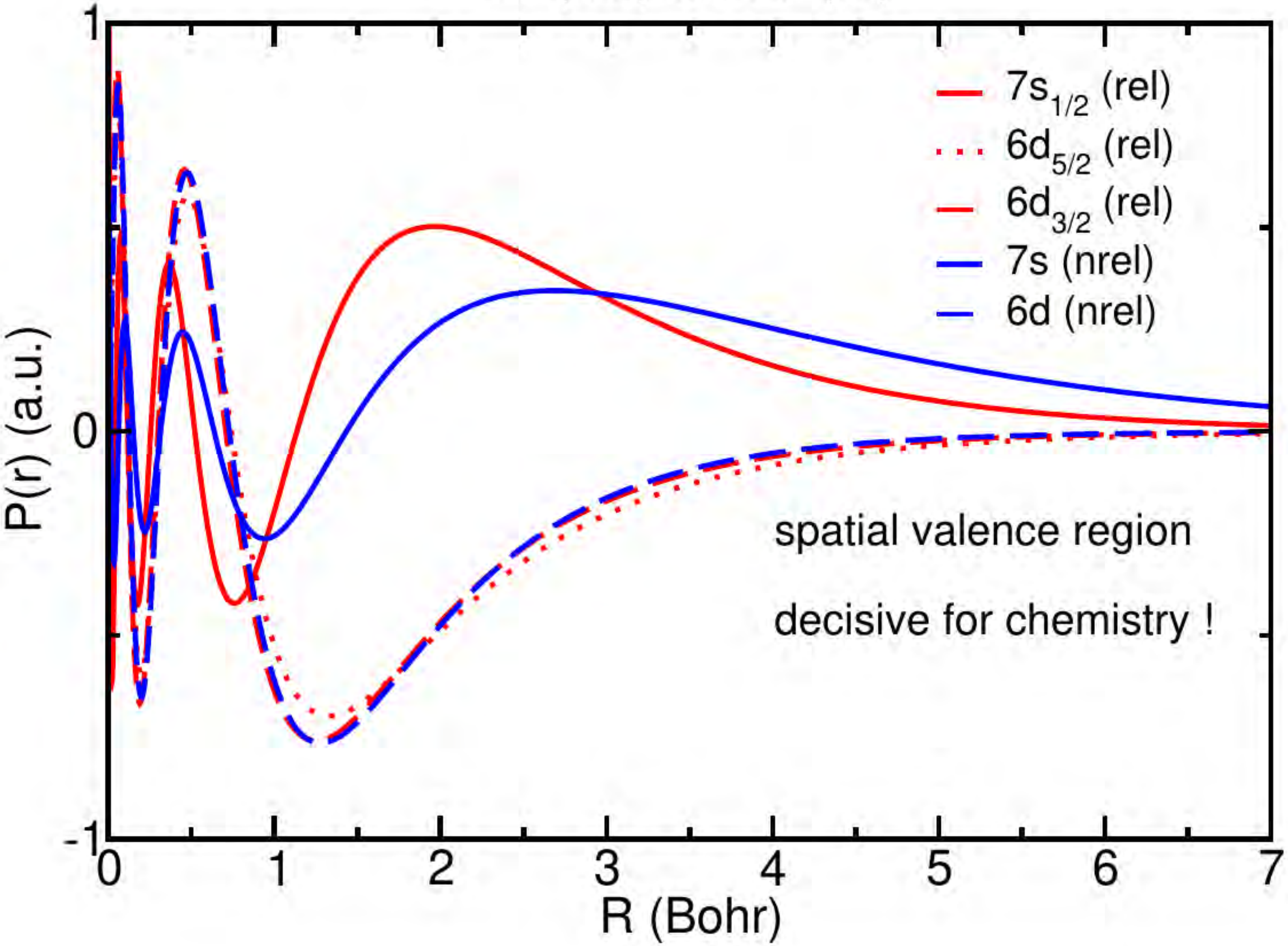
destabilization

ca. 25 % of binding energy

AuF: Schwerdtfeger, Dolg, Schwarz, Bowmaker, Boyd, J. Chem. Phys. 91 (1989) 369.

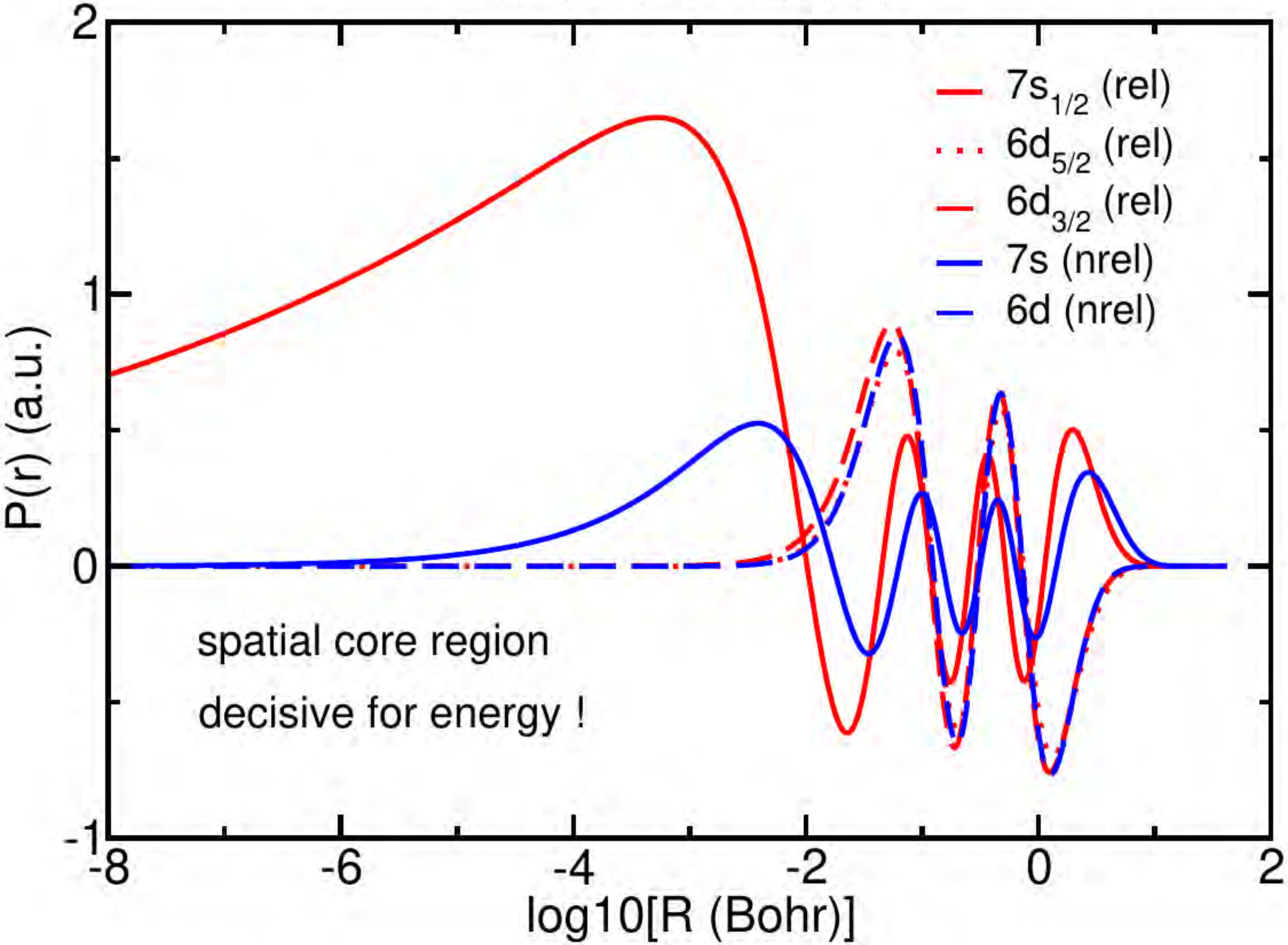
Valence orbitals of eka-gold $_{111}E$

HF (nrel) vs. DHF (rel)



Valence orbitals of eka-gold $_{111}$E

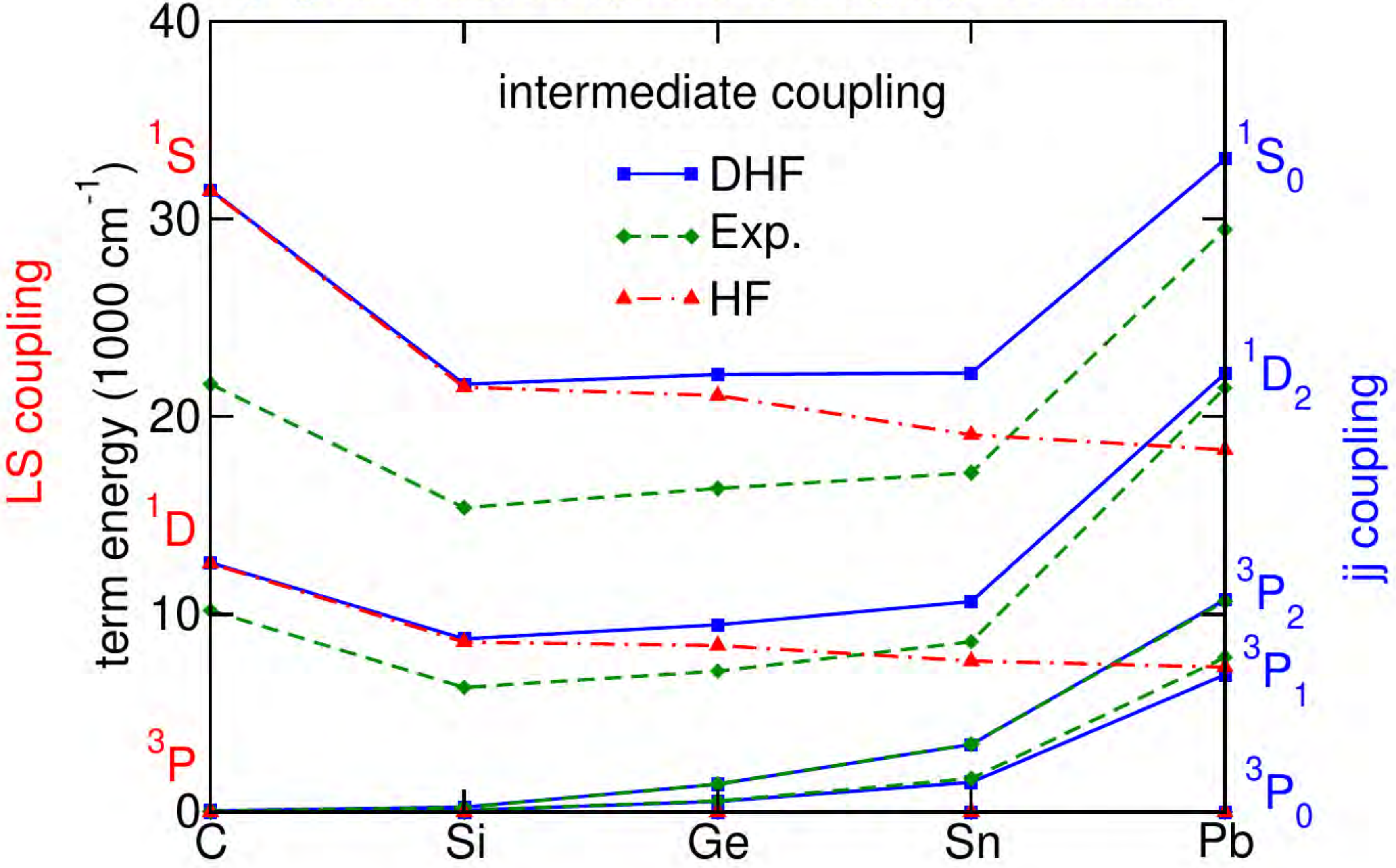
HF (nrel) vs. DHF (rel)

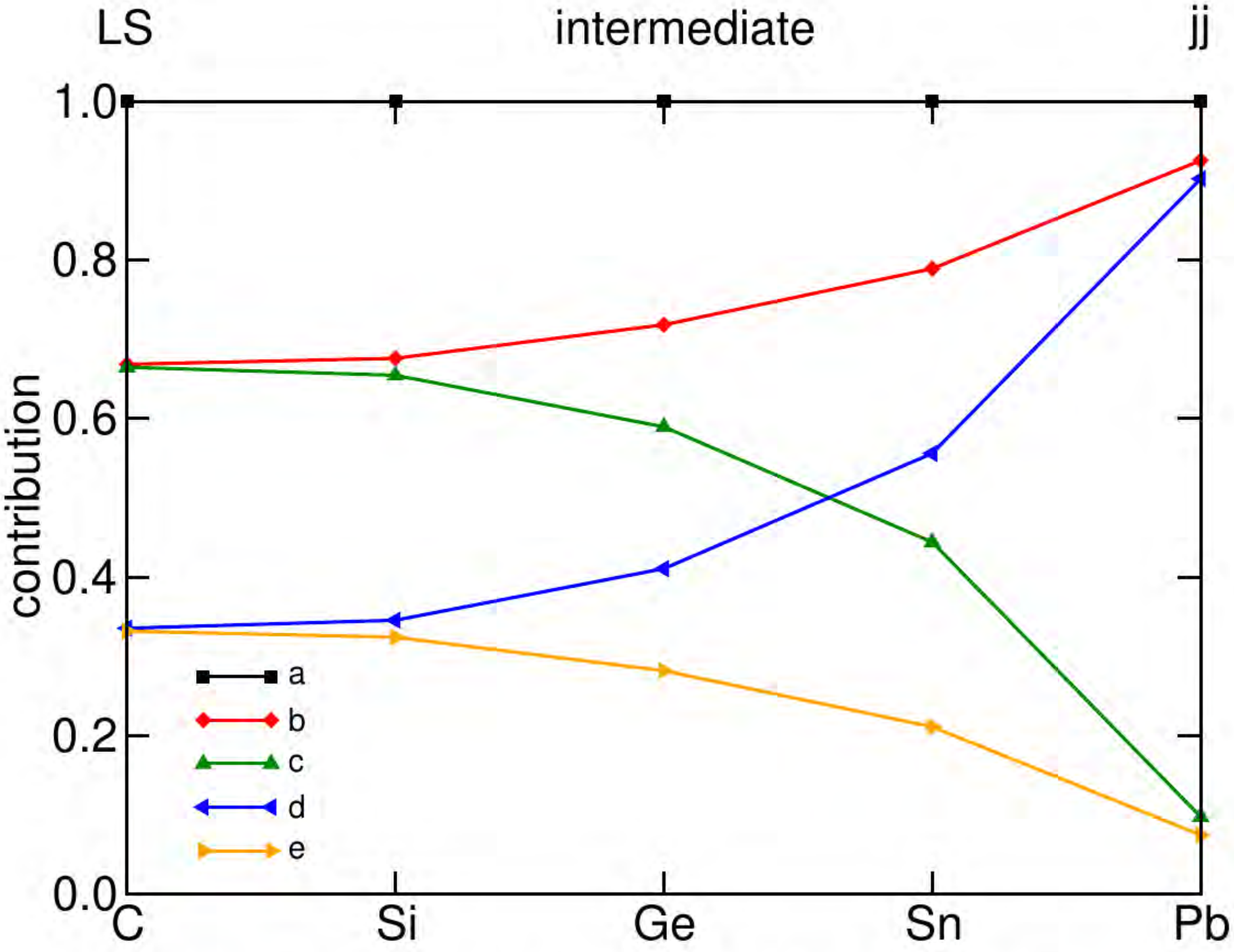


spatial core region

decisive for energy !

Term energies of states arising from the p^2 ground state configuration of the group IV elements

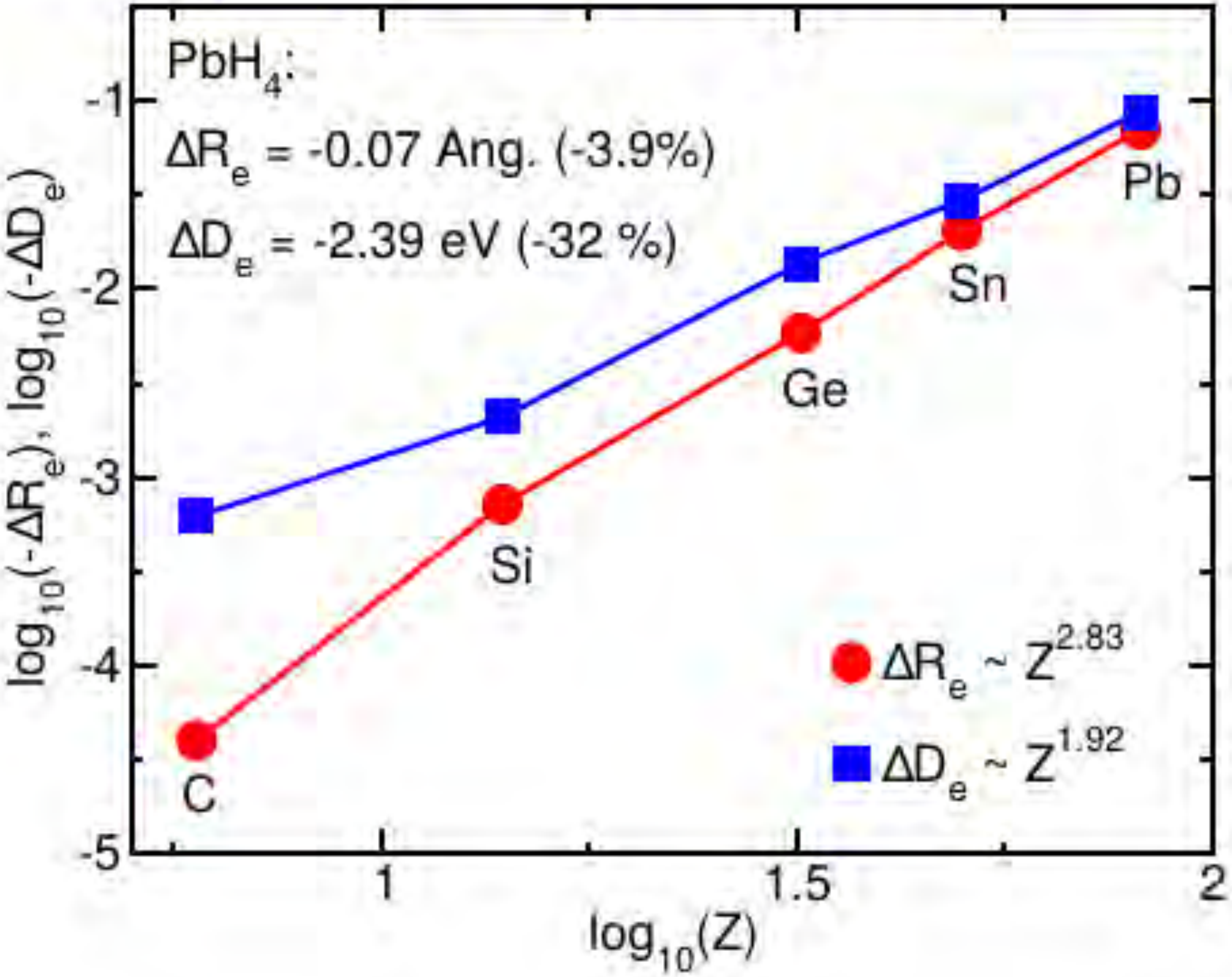




Contribution of the relativistic configuration to the LSJ levels of the p^2 ground state configurations of C, Si, Ge, Sn, Pb from average level DHF/DC calculations. a: $p^1_{1/2}p^1_{3/2}$ in $^3P_1$, b: $p^2_{1/2}$ in $^3P_0$ and $p^2_{3/2}$ in $^1S_0$, c: $p^1_{1/2}p^1_{3/2}$ in $^1D_2$ and $p^2_{3/2}$ in $^3P_2$, d: $p^1_{1/2}p^1_{3/2}$ in $^3P_2$ and $p^2_{3/2}$ in $^1D_2$, e: $p^2_{1/2}$ in $^1S_0$ and $p^2_{1/2}$ in $^3P_0$.

Relativistic effects in bond lengths and binding energies

group 4 tetrahydrides, AE DHF/DCG vs. AE HF



PbH_4:

ΔR_e = -0.07 Ang. (-3.9%)

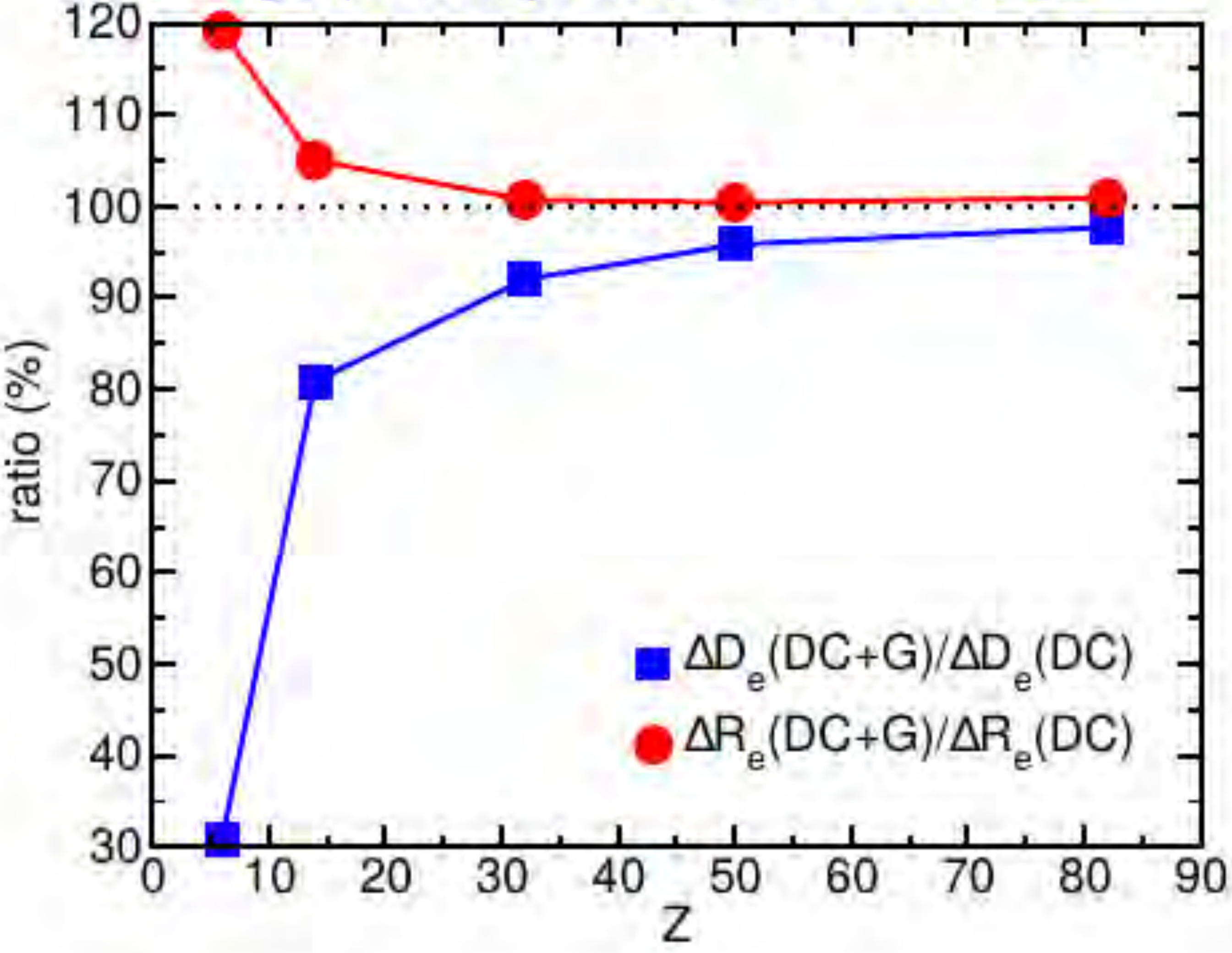
ΔD_e = -2.39 eV (-32 %)

ΔR_e (Å), ΔD_e (eV)

O.Visser, L.Visscher, P.J.C. Aerts, W.C.Nieuwpoort, Theor.Chim.Acta 81 (1992) 405.

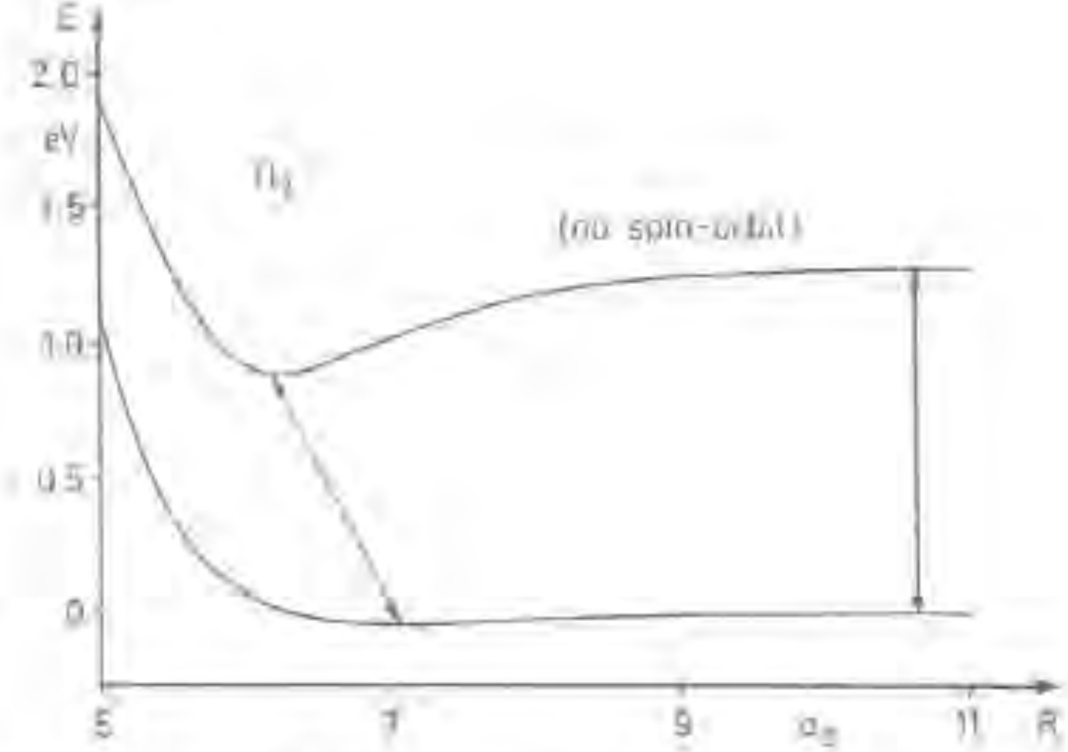
Gaunt contribution to bond lengths and binding energies

group 4 tetrahydrides, AE DHF/DCG vs. DC



Relativistic one-particle corrections are much more important than two-particle corrections.

O.Visser, L.Visscher, P.J.C. Aerts, W.C.Nieuwpoort, Theor.Chim.Acta 81 (1992) 405.



Spin-orbit coupling will usually split the atomic LS ground states and lead to a stabilization of the separated atoms. In molecules the lower symmetry leads to a partial quenching of spin-orbit coupling and a smaller stabilization compared to the atoms. Thus, usually a chemical bond is destabilized and elongated by spin-orbit coupling.

An example is Tl_2, where the experimentally observed spin-orbit splitting of the Tl $6p^1$ ^2P ground state is 7793 cm^{-1} or 0.96 eV. Thus, the Tl $6p_{1/2}$ $^2P_{1/2}$ state is lowered by about 0.64 eV and the separated atom limit of Tl_2 by about 1.28 eV.

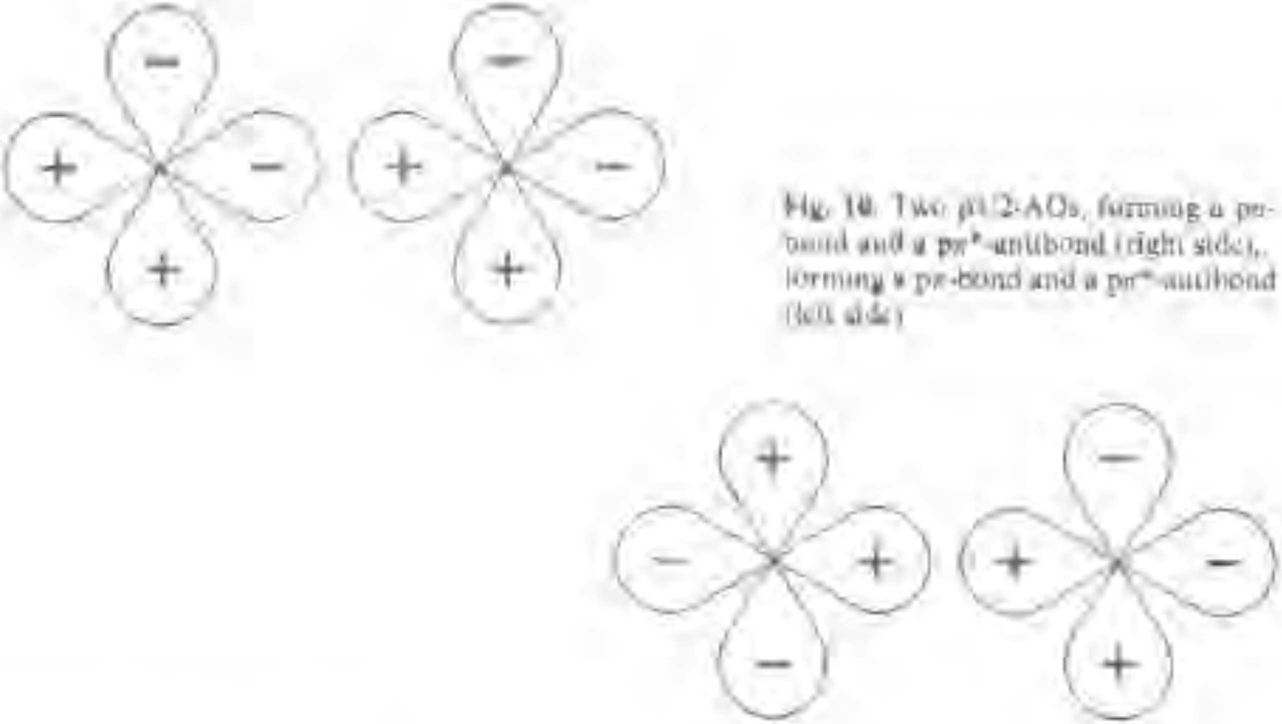


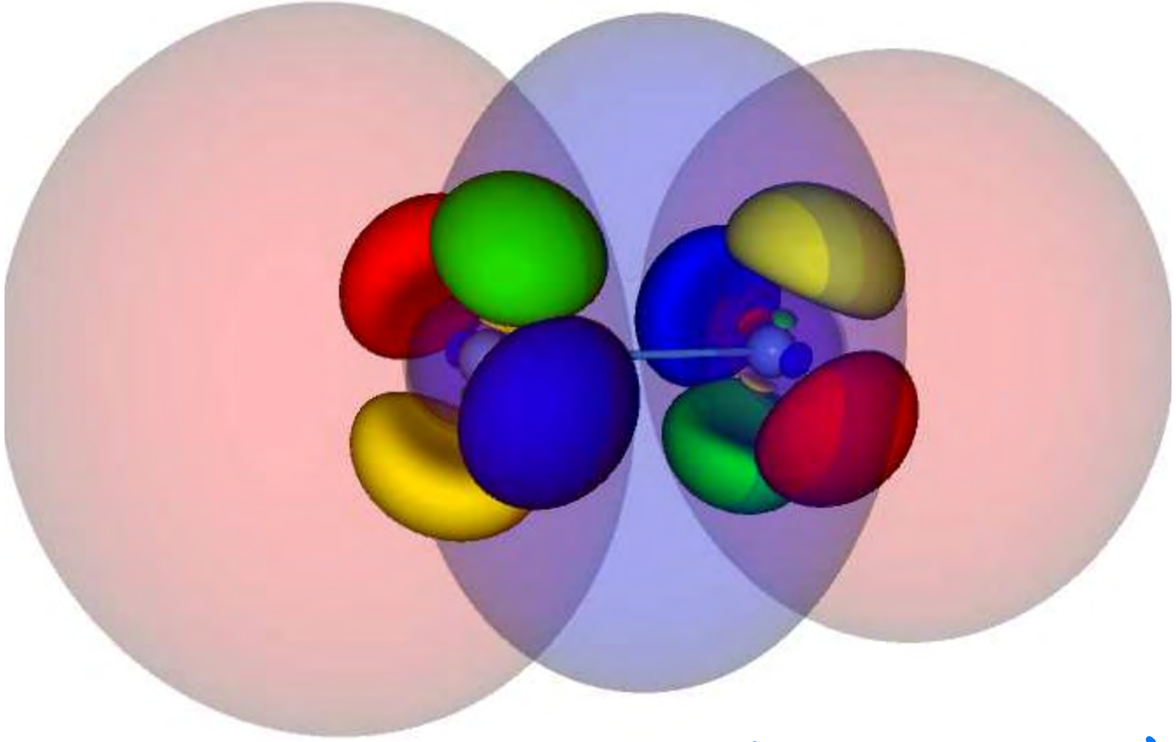
Fig. 10. Two p1/2-AOs, forming a pσ-bond and a pπ*-antibond (right side), forming a pπ-bond and a pσ*-antibond (left side)

A $p_{1/2,1/2}$ spinor can be written as

$$p_{1/2,1/2} \sim p_x\beta + ip_y\beta + p_z\alpha \sim -\sqrt{2}p_{+1}\beta + p_0\alpha$$

and has a spherical charge density. A similar relation exists for its Kramers partner $p_{1/2,-1/2}$. In a diatomic molecule aligned along the z axis a $p_{1/2}$ spinor thus has a σ and two π components. In systems like Tl_2 the $p_{1/2}$ spinors of the two Tl atoms can only form a σ bond (weight 1/3) and simultaneously a π antibond (weight 2/3), or a π bond (weight 2/3) and simultaneously a σ antibond (weight 1/3). Thus, spin-orbit coupling leads to a destabilization of the bond. Similarly, the $p_{3/2,\pm 1/2}$ spinors can form a σ antibond (weight 2/3) and simultaneously a π bond (weight 1/3) or a σ bond (weight 2/3) and simultaneously a π antibond (weight 1/3). The $p_{3/2,\pm 3/2}$ spinors do not contain the σ components and can form π bond and antibond.

Bond destabilization due to spin-orbit coupling
e.g. large/small SO energy lowering in 2Tl/Tl_2;
$\ll$
σ bonding and π antibonding in Tl—Tl
↑
?



Cover of
"Basics of Relativistic Quantum Chemistry",
X. Cao, W. Fang, M. Dolg; Science Press,
in Chinese!

All-electron case: Dirac-Coulomb-Breit Hamiltonian

$$\mathcal{H} = \sum_{i}^{n} h(i) + \sum_{i<j}^{n} g(i,j) + V_{NN}$$

$$h_D(i) = c\vec{\alpha}_i\vec{p}_i + (\beta_i - \mathbf{I}_4)c^2 + V_{Nn}$$

$$V_{Nn}(i) = \sum_{\lambda}^{N} (-\frac{Z_\lambda}{r_{\lambda i}})$$

$$g_{CB}(i,j) = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}}[\vec{\alpha}_i\vec{\alpha}_j + \frac{(\vec{\alpha}_i\vec{r}_{ij})(\vec{\alpha}_j\vec{r}_{ij})}{r_{ij}^2}]$$

$$V_{NN} = \sum_{\lambda<\mu}^{N} \frac{Z_\lambda Z_\mu}{r_{\lambda\mu}} \ .$$

possibly augmented by finite nuclear model, frequency dependence of electron interaction, vaccum polarization, electron self-energy, ...

Valence-electron-only case: pseudopotential Hamiltonian

$$\mathcal{H}_v = \sum_{i}^{n_v} h_v(i) + \sum_{i<j}^{n_v} g_v(i,j) + V_{cc} + V_{cpp}$$

$$h_v(i) = -\frac{1}{2}\Delta_i + V_{cv}(i)$$

$$V_{cv}(i) = \sum_{\lambda}^{N} (-\frac{Q_\lambda}{r_{\lambda i}} + \Delta V_{cv}^{\lambda}(\vec{r}_{\lambda i})) + \ldots$$

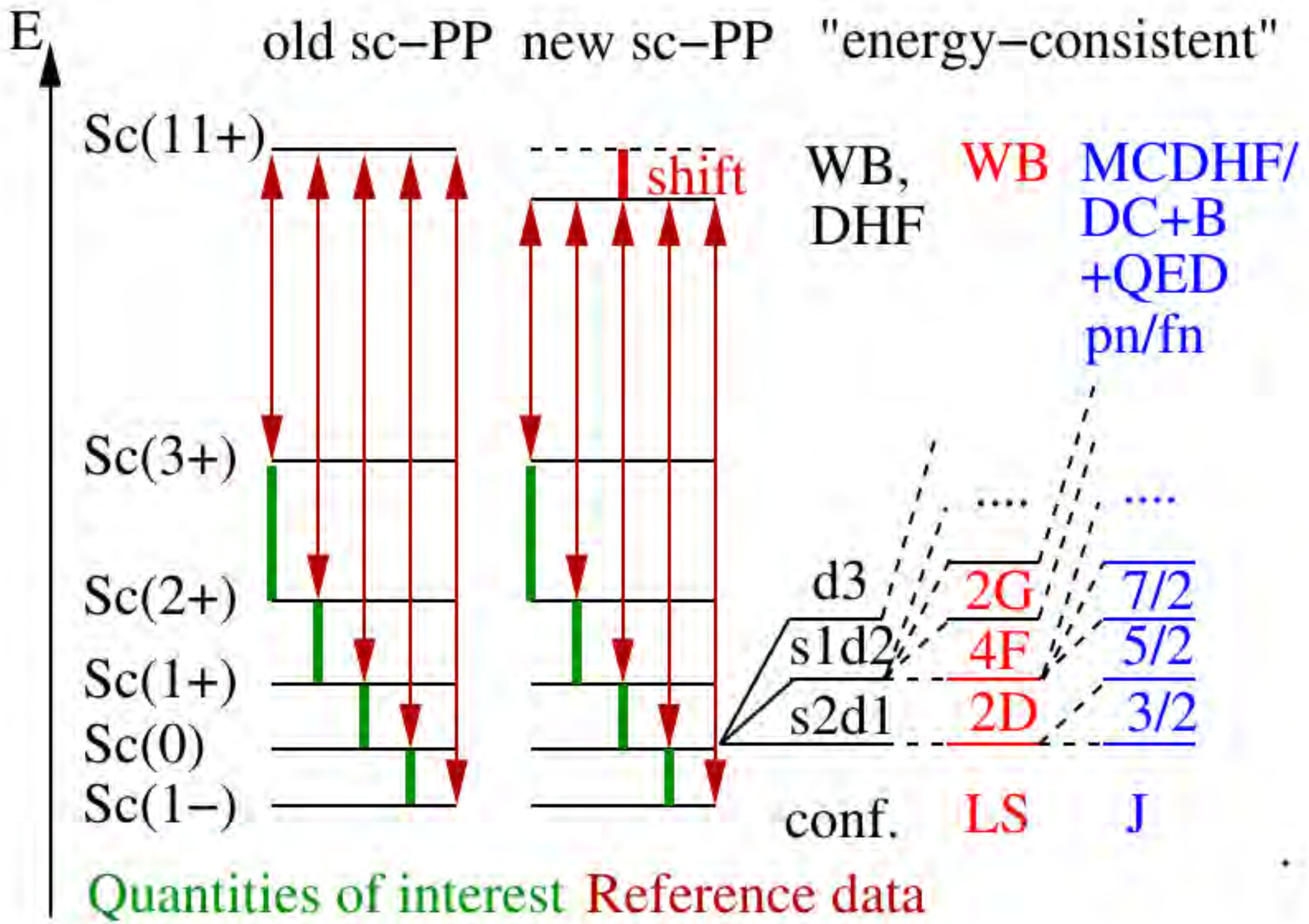
$$\Delta V_{cv}^{\lambda}(\vec{r}_{\lambda i}) = \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} (V_{lj}^{\lambda}(r_{\lambda i}) - V_{L}^{\lambda}(r_{\lambda i}))P_{lj}^{\lambda}(i) + V_{L}^{\lambda}(r_{\lambda i})$$

$$g_v(i,j) = g_C(i,j) = \frac{1}{r_{ij}}$$

$$V_{cc} = \sum_{\lambda<\mu}^{N} (\frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} + \Delta V_{cc}^{\lambda\mu}(r_{\lambda\mu}))$$

$$V_{cpp} = -\frac{1}{2}\sum_{\lambda} \alpha_\lambda \vec{f}_\lambda^{\ 2} + \sum_{\lambda,i} V^{\lambda}(r_{\lambda i})$$

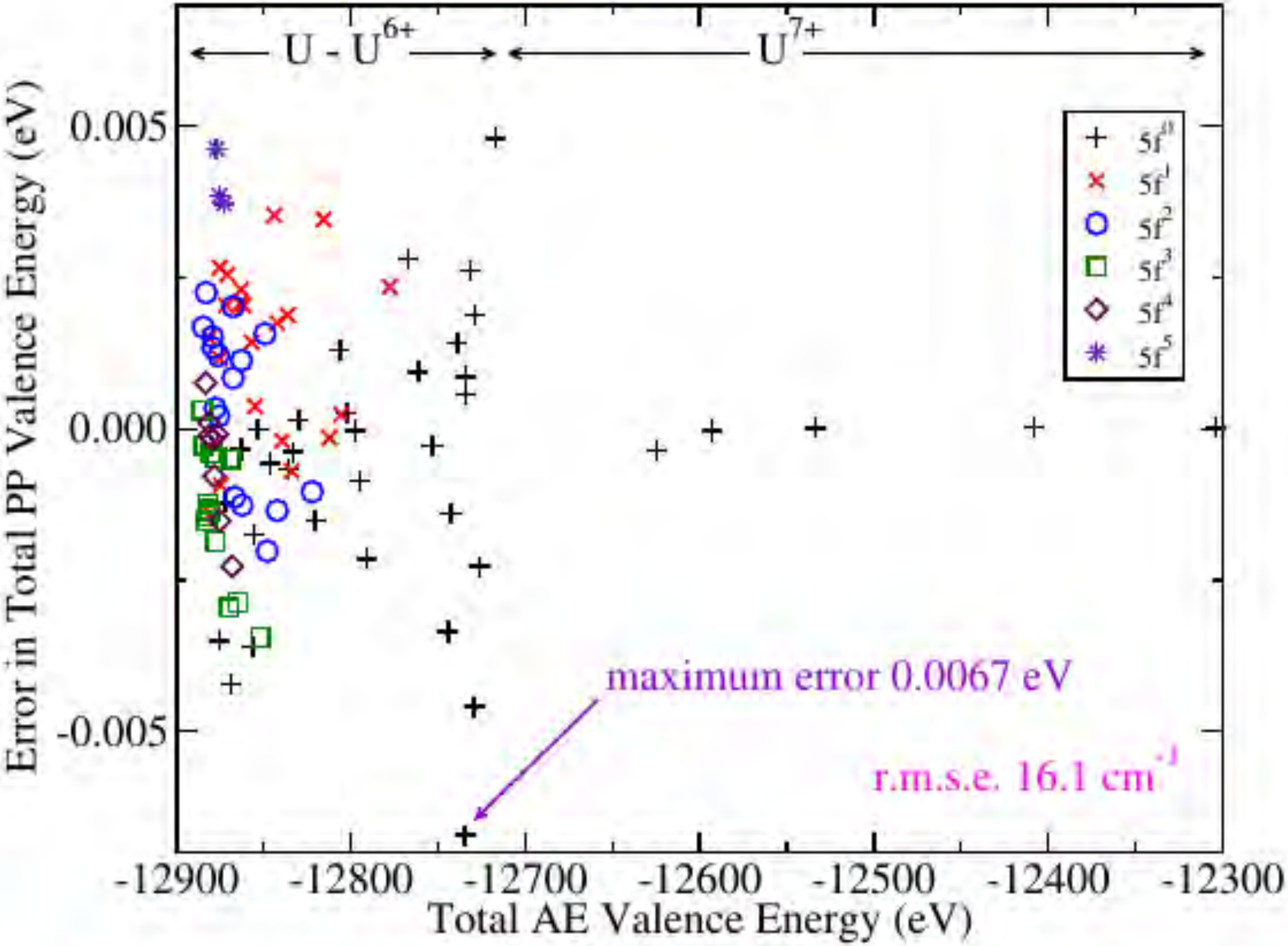
n_v, Q_λ: values to be chosen; α_λ: experimental or ab initio value; $(\Delta)V_{\gamma}^{\lambda}$, $\vec{f}_\lambda$: contain adjustable parameters



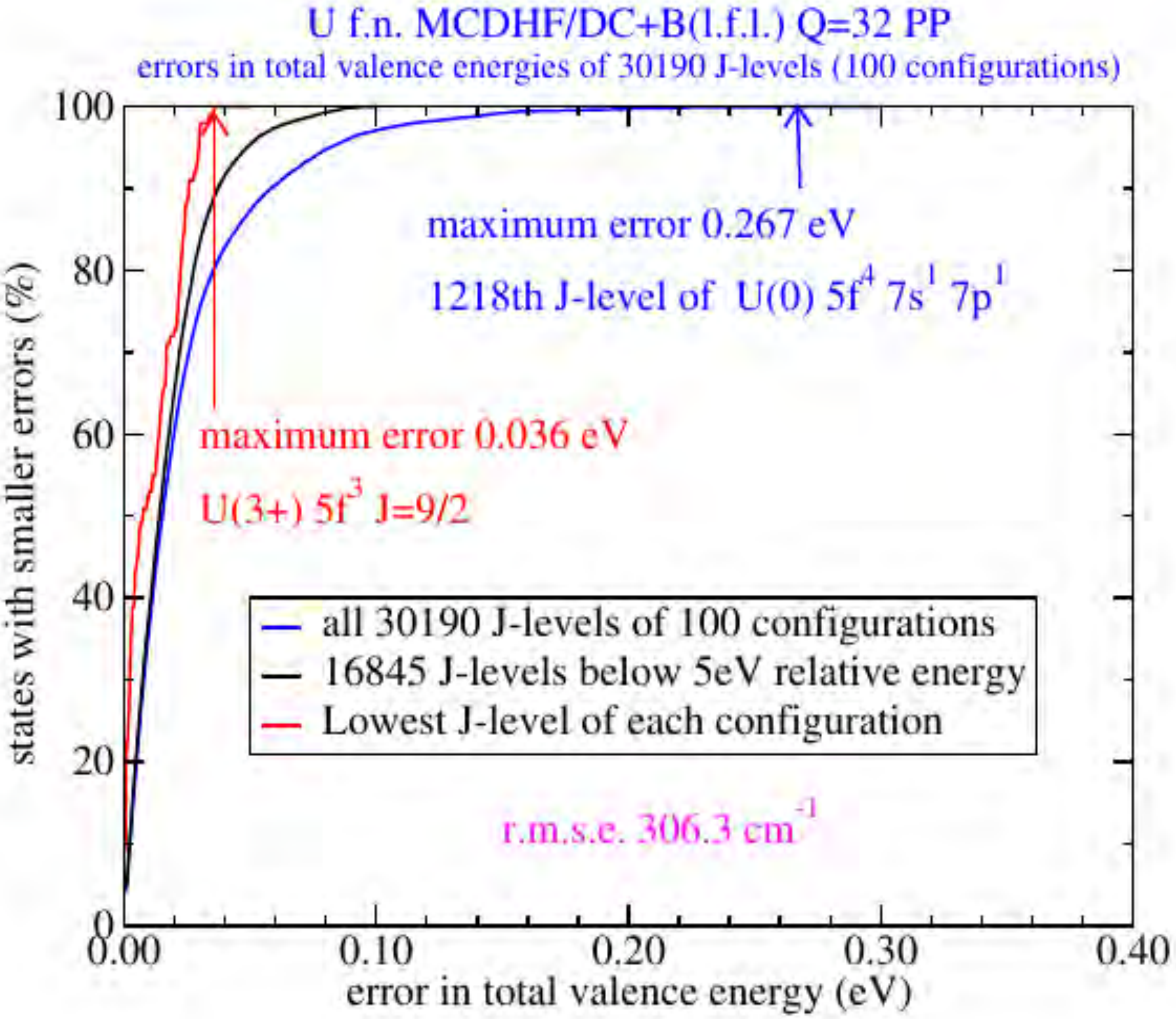
- AE: $\mathcal{H}$ [complicated] $\longrightarrow$ VO(PP): $\mathcal{H}_v$ [simple]
- Important: good energetic and spatial separation of core and valence shells!
- Parameter adjustment $\sum_I (E_I^{AE} - E_I^{PP} + \Delta E_{shift})^2 := \min$ (10^1-10^2 nrel. conf./LS-states, 10^2-10^4 J-levels)
- 'Stuttgart(-Dresden/Bonn/Cologne) PPs': SDD in GAUSSIAN, ECPxyMWB/MDF in MOLPRO, TURBOMOLE, ...
- Supplemented by 'in-house' basis sets as well as correlation-consistent (Peterson, ...) and error-balanced (Weigend, ...) basis sets.
- cf. http://www.tc.uni-koeln.de (clickable periodic system of elements: PPs and basis sets); http://basissetexchange.org.

U f.n. MCDF/DC+B(l.f.l.) PP Q=32

errors in valence energies of 100 non-relativistic configurations

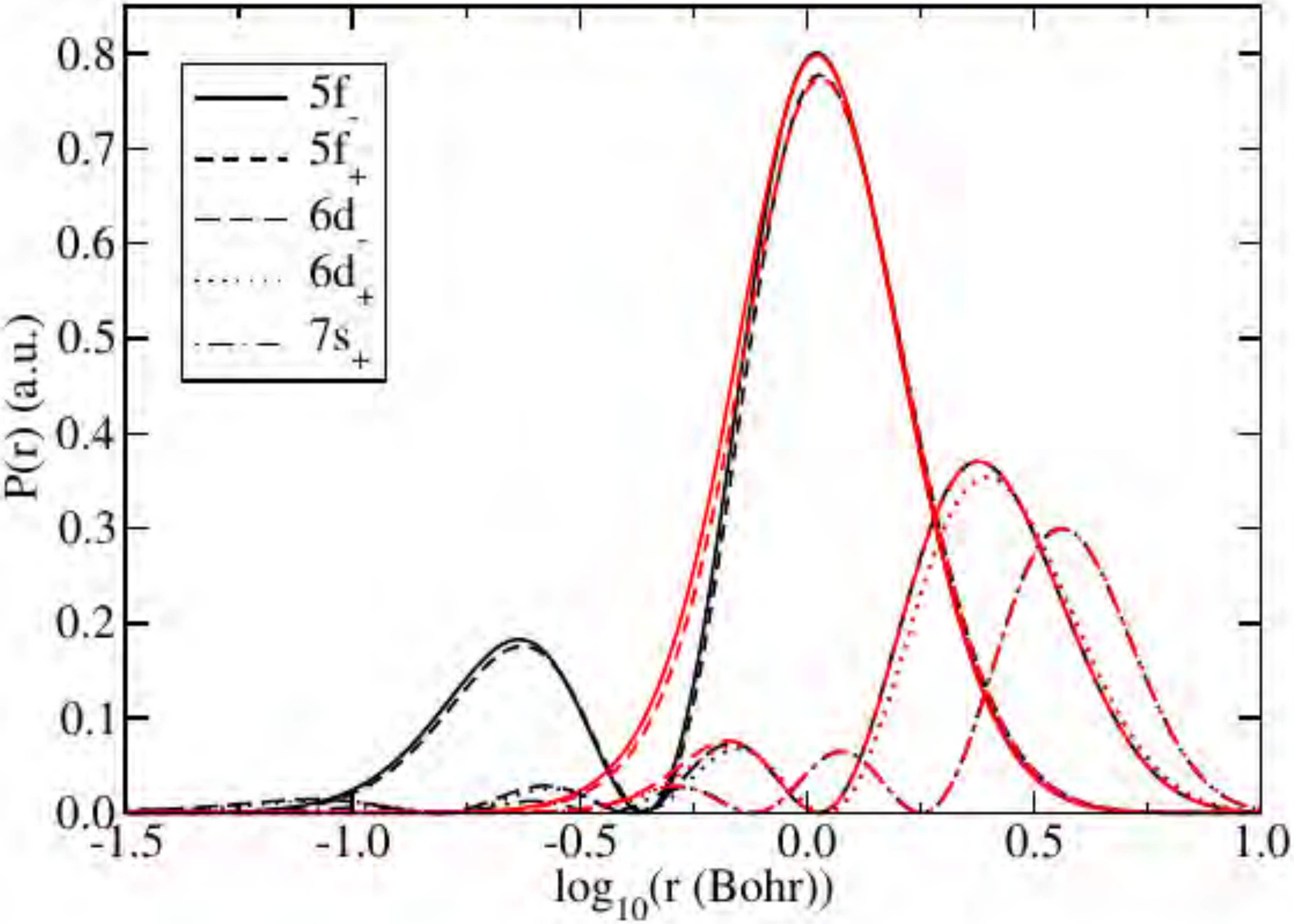


Current work: Ce - Yb, 56 - 62 configurations, m.a.e. 3.5 - 8.6 cm^{-1}, r.m.s.e. 5.3 - 11.6 cm^{-1}
Improvement on 1989 PPs more than two orders of magnitude! (NSFC project W2441007)


U f.n. MCDHF/DC+B(l.f.l.) Q=32 PP
errors in total valence energies of 30190 J-levels (100 configurations)
states with smaller errors (%)
0
20
40
60
80
100
0.00
0.10
0.20
0.30
0.40
error in total valence energy (eV)
maximum error 0.267 eV
1218th J-level of U(0) 5f^4 7s^1 7p^1
maximum error 0.036 eV
U(3+) 5f^3 J=9/2
all 30190 J-levels of 100 configurations
16845 J-levels below 5eV relative energy
Lowest J-level of each configuration
r.m.s.e. 306.3 cm^{-1}

U 5f^3 6d^1 7s^2 (AE MCDHF vs. ECP60(MCDHF/DC+B))

PP: state averaged relativistic MCHF



Term energies (cm^{-1}) of U^{4+} $5f^2$ J-Levels

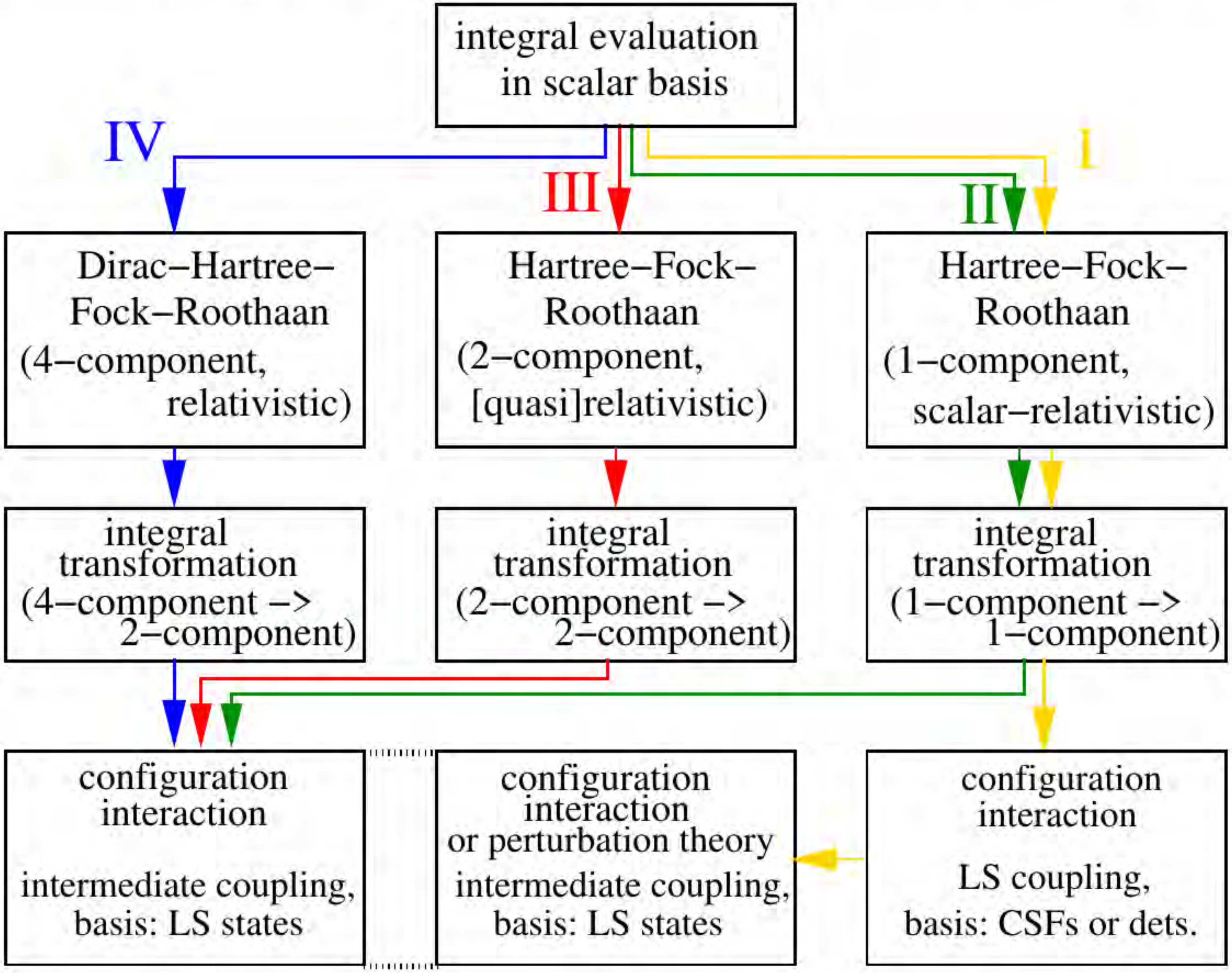
J	DCB PP[b] SO-CI	DCB PP[c] SO-CI	DCB PP[d] IH-FSCC	DCB PP[e] IH-FSCC	AE DKH[f] SO-CI	AE DCB[g] MCDF+CI	AE DCB[h] XIH-FSCC	exp.
4	0	0	0	0	0	0	0	0
2	4585	4406	3959	4233	4501	3844	4202	4161
5	6128	6162	5902	5890	6392	6012	6070	6137
3	9295	9191	8612	8825	9455	8624	8974	8984
4	9765	9583	9196	9264	9819	9278	9404	9434
6	11609	11608	11178	11144	12010	11116	11420	11514
2	*17640*	*17195*	15998	16601	*17531*	15816	16554	16465
4	*17006*	*16807*	16181	16221	*17289*	15853	16630	16656
0	18573	18532	17025	17960	18170	16199	17837	17128
1	21142	21112	19529	20420	20960	18942	20441	19819
6	23792	23065	22594	22441	23744	22131	22534	22276
2	25899	25659	24042	24799	25998	23379	24991	24653
0	46772	46583	43783	45329	46189	43847	45611	43614
m.a.e.	948	755	318	420	935	522	357	0
m.a.d.	628	436	567	162	616	802	0	357

[a] mean absolute error (m.a.e.) wrt. experimental data and mean absolute deviations (m.a.d.) wrt. AE DCB XIH-FSCC data.
[b] MCDHF/DCB PP, MRCI+DaC + SO-CI, no frozen orbitals, (14s13p10d8f6g)/[6s6p5d4f3g]
[c] MCDHF/DCB PP, IH-FSCC + SO-CI, no frozen orbitals, (14s13p10d8f6g)/[6s6p5d4f3g], LS energies from PP IH-FSCC with (16s15p12d10f8g7h7i)

[d] MCDHF/DCB PP, IH-FSCC, no frozen orbitals, (14s13p10d8f6g)/[6s6p5d4f3g]
[e] MCDHF/DCB PP, IH-FSCC, no frozen orbitals, (16s15p12d10f8g7h7i)
[f] AE DKH MRCI+DaC + AMFI SO-CI, 1s–5p frozen, 5f–6d active, (26s23p17d13f5g)/[10s9p7d5f3g] (Danilo et al., 2008)
[g] AE DCB MCDF-CI+DaC, (1s1p2d3f3g2h1i) spinors in virtual space (Seth et al., 2001)
[h] AE DCB XIH-FSCC, (37s32p24d21f12g10h9i) (Infante et al., 2007)

A. Weigand, X. Cao, V. Vallet, J.-P. Flament, M.D., J. Phys. Chem. A 113 (2009) 11509.

Relativistic and correlated ab initio calculations



integral evaluation in scalar basis

IV

III

II

I

Dirac–Hartree–Fock–Roothaan (4–component, relativistic)

Hartree–Fock–Roothaan (2–component, [quasi]relativistic)

Hartree–Fock–Roothaan (1–component, scalar–relativistic)

integral transformation (4–component –> 2–component)

integral transformation (2–component –> 2–component)

integral transformation (1–component –> 1–component)

configuration interaction

intermediate coupling, basis: LS states

configuration interaction or perturbation theory

intermediate coupling, basis: LS states

configuration interaction

LS coupling, basis: CSFs or dets.

Note: for heavy elements frozen scalar-relativistic cores may require different spin-orbit operators from those applicable to a fully variational treatment ! Similarly, when starting from scalar-relativistic orbitals different spin-orbit operators for a variational and perturbative treatment may be necessary !

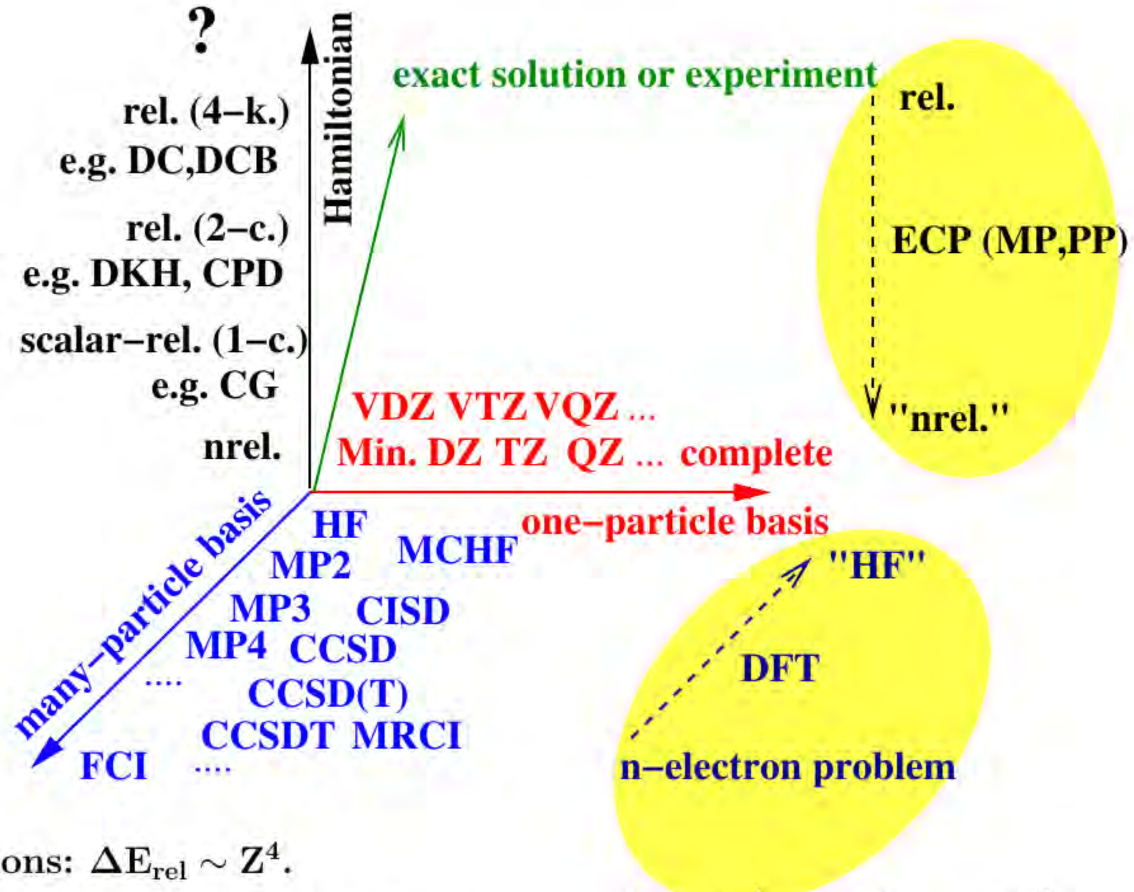
Chapter 4

Density functional theory

(DFT)

(for ground states)

Some general advice/remarks



?

Hamiltonian

rel. (4–k.)
e.g. DC,DCB

rel. (2–c.)
e.g. DKH, CPD

scalar–rel. (1–c.)
e.g. CG

nrel.

exact solution or experiment

VDZ VTZ VQZ ...
Min. DZ TZ QZ ... complete

one–particle basis

many–particle basis

HF
MP2
MP3
MP4
....
FCI

MCHF
CISD
CCSD
CCSD(T)
CCSDT MRCI
....

rel.
ECP (MP,PP)
"nrel."

"HF"
DFT
n–electron problem

- relativistic contributions: $\Delta E_{\mathrm{rel}} \sim Z^4$.
- correlation energy errors for standard basis set expansions: $E^{l}_{\mathrm{corr}} - E^{\infty}_{\mathrm{corr}} \sim 1/l^3$
  → basis set extrapolation or F12-dependent wavefunctions.
- computational effort: $t \sim n^k$ (n size of one-particle basis set, k for some standard approaches: DFT 3, HF 4, MP2 5, CISD, CCSD 6, CCSD(T) 7 ...) → low-order/linear scaling schemes.
- ECPs simplify the Hamiltonian and also lead to some reductions in the sizes of the one- and many-electron basis sets (e.g. small-core PPs plus valence-only SO terms) !
- DFT avoids costly many-determinantal wavefunctions/treatments.

Goal: Suitable compromise between accuracy and computational effort,
i.e., sufficiently accurate low-cost relativistic electronic structure calculations, also for larger systems.

- nowadays the most popular electronic structure approach in computational chemistry (basis sets usually STOs|GTOs; all-electron and valence-only treatments) and theoretical solid state physics (basis sets usually plane waves, used in combination with pseudopotentials)
- in principle (theory) exact, in practise (applications) not, unsystematic

Hohenberg-Kohn theorem proves the exactness, but does not tell how to do it correctly

→ a huge variety of approaches/functionals

- quite fast (DFT: "dirty fast trick"), since one determinant approach (Kohn-Sham formalism)
- before DFT was theoretically founded (HK theorem 1964, KS formalism 1965)

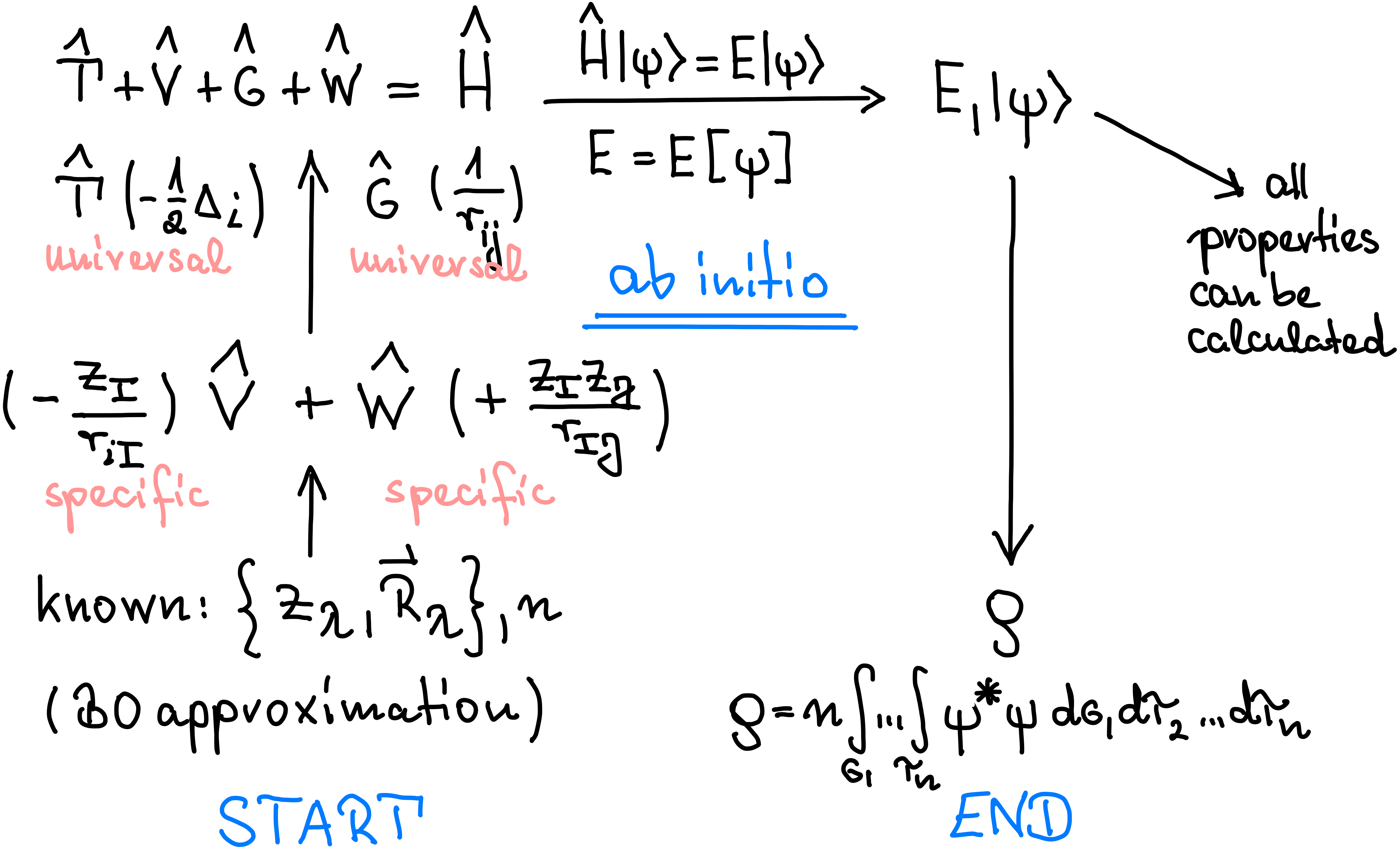
existed DFT-like methods:

- Thomas-Fermi-Dirac statistical model for atoms → "pure" DFT
- Hartree-Fock-Slater or X_α method for atoms/molecules/periodic systems → DFT KS approach with only local exchange to model/simplyfy HF

- Coupling of electrons and nuclei-possible, e.g. <u>C</u>ar-<u>P</u>arinello <u>m</u>olecular <u>d</u>ynamics (CPMD)

motivation:

ab initio treatment	first principles treatment
(HF → CI, CC, ...)	(KS DFT, ...)
$E[\psi]$ we know how it looks!	$E[\rho]$ we know that it exists, but do not know how it looks!
3n spatial and n spin coordinates, $(x_i, y_i, z_i, \sigma_i)$, $i=1,...,n$	3 spatial coordinates, (x, y, z)
→ high dimensional	→ 3-dimensional
ψ not observable	ρ observable



$$\hat{T} + \hat{V} + \hat{G} + \hat{W} = \hat{H} \xrightarrow[E = E[\psi]]{\hat{H}|\psi\rangle = E|\psi\rangle} E, |\psi\rangle$$

all properties can be calculated

$\hat{T}\left(-\frac{1}{2}\Delta_i\right)$ universal

$\hat{G}\left(\frac{1}{r_{ij}}\right)$ universal

ab initio

$\left(-\frac{Z_I}{r_{iI}}\right) \hat{V} + \hat{W} \left(+\frac{Z_I Z_J}{r_{IJ}}\right)$

specific specific

known: $\{Z_\alpha, \vec{R}_\alpha\}, n$

(BO approximation)

START

ρ

$$\rho = n \int_{\sigma_1} \cdots \int_{r_n} \psi^* \psi \, d\sigma_1 dr_2 \ldots dr_n$$

END

$$\{Z_\lambda, \overset{\uparrow}{\vec{R}_\lambda}\}, n \xleftarrow[1)\quad 2)\quad 3)]{\text{DFT}} \overset{\downarrow}{\rho}$$

1) $n = \int \rho(\vec{r})\, d\vec{r}$

2)* peaks in the electron density $\rightarrow \vec{R}_\lambda$

3)* $$\left.\frac{\partial \bar{\rho}(\vec{r})}{\partial |\vec{r} - \vec{R}_\lambda|}\right|_{\vec{r} \to \vec{R}_\lambda} = -2 Z_\lambda \bar{\rho}(\vec{R}_\lambda) \longrightarrow Z_\lambda$$

* H type ions: $\psi \sim e^{-Zr} \rightarrow \rho \sim e^{-2Zr}$

peak at $r = 0$ and $\frac{d\rho(r)}{dr} \sim -2Z\rho(r)$

cf. cusp conditions in chapter 1!

In summary:

$$\rho \longrightarrow n, \{\vec{R}_\alpha, Z_\alpha\} \longrightarrow \hat{H} \xrightarrow{*} E$$

the energy E is a functional of the electron density, $E[\rho]$

* variational search for an exact solution of $\hat{H}|\psi\rangle = E|\psi\rangle$ under the condition that $|\psi\rangle$ delivers ρ:

$$\underset{\text{ground state}}{\rho_0} \longrightarrow E_0 = E[\rho_0]$$

└ nobody knows how it looks!

questions not discussed here:

- does a wavefunction ψ exist for every electron density ρ integrating to n electrons?
  (n representability)
- does a potential V exist for every electron density ρ?
  (v representability)

→ do unreasonable/incorrect functions $\rho(\vec{r})$ exist, which should not be used in $E[\rho]$?

Theorems of Hohenberg and Kohn (1964)

assume a universal functional

$$Q[\rho] := \min \langle \psi_\rho | \hat{T} + \hat{G} | \psi_\rho \rangle$$

- universal operators: $\hat{T} = -\frac{1}{2}\sum_i \Delta_i$, $\hat{G} = \sum_{i>j} \frac{1}{r_{ij}}$
- ψ_ρ: antisymmetric wavefunction yielding ρ
- ρ : n electron density

solution yielding the minimum of $\langle \hat{T} + \hat{V} \rangle$

$$Q[\rho] = \langle \psi_\rho^{\min} | \hat{T} + \hat{G} | \psi_\rho^{\min} \rangle$$, dito for $\rho \rightarrow \rho_0$

Theorem II:

$$\int \hat{v}(\vec{r})\,\rho(\vec{r})\,d\vec{r} + Q[\rho] \geq E_0^{el}$$

external potential
Coulomb potential of nuclei

electronic ground state energy

proof:

$$\int \hat{v}(\vec{r})\,\rho(\vec{r})\,d\vec{r} + Q[\rho] = \langle \Psi_\rho^{min} | \underbrace{\hat{V} + \hat{T} + \hat{G}}_{\hat{H}_{el}} | \Psi_\rho^{min} \rangle \geq E_0^{el}$$

definitions of $Q[\rho]$ and Ψ_ρ^{min}

variational principle

$$\hat{V} = \sum_i \hat{v}_i$$

q.e.d.

Theorem II:

$$\int \hat{v}(\vec{r})\,\underset{\uparrow}{\rho_0}(\vec{r})\,d\vec{r} + Q[\underset{\uparrow}{\rho_0}] \underset{\uparrow}{=} E_0^{el}$$

proof:

$$E_0^{el} = \langle \underset{\text{exact ground state wavefunction}}{\Psi_0} | \hat{V}+\hat{T}+\hat{G} | \Psi_0 \rangle \left\{ \begin{matrix} \overset{\text{variational principle}}{\leq} \\ \\ \underset{\text{definition of } Q[\rho] \text{ and } \Psi_{\rho_0}^{min}}{\geq} \end{matrix} \right\} \langle \Psi_{\rho_0}^{min} | \hat{V}+\hat{T}+\hat{G} | \Psi_{\rho_0}^{min} \rangle$$

$\Rightarrow$ only $=$ sign fulfills both conditions!

$$\int \hat{v}(\vec{r})\,\rho_0(\vec{r})\,d\vec{r} = \langle \Psi_{\rho_0} | \hat{V} | \Psi_{\rho_0} \rangle = \text{const.}$$

q.e.d.

- The existence of a universal and variational density functional for the ground state energy has been proven.

- The theorems and their proof do <u>not</u> help to find the functional or construct suitable approximations.

A pure DFT:

Thomas-Fermi-Dirac model (1927/30)

$$E[\rho] = \underbrace{\int \hat{V}(\vec{r})\rho(\vec{r})\,d\vec{r}}_{\text{exact! } V[\rho]} + \underbrace{C_{TF}\int \rho(\vec{r})^{5/3}\,d\vec{r}}_{T[\rho] \text{ problem!}} +$$

$$+ \underbrace{\frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2}_{\text{Coulomb } J[\rho]} \underbrace{- C_x \int \rho(\vec{r})^{4/3}\,d\vec{r}}_{K[\rho] \text{ "Slater exchange"}} \pm \dots$$

→ results not good, mainly due to $T[\rho]$

Kohn-Sham formalism (1965)

$T[\rho]$ is split up in an expression for a noninteracting model system with the same density ρ (→ use orbital model!) and a correction (→ contained in the "exchange and correlation" functional $E_{xc}[\rho]$)

$$E[\rho]=\int \hat{v}(\vec{r})\rho(\vec{r})d\vec{r}+\underbrace{T_0[\{\varphi_i\}]}_{\text{0th order}}+\underbrace{E_{xc}[\rho]}_{\text{corrections to } T_0}+$$

$$+\frac{1}{2}\iint\frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1 d\vec{r}_2=V[\rho]+T_0[\{\varphi_i\}]+E_{xc}[\rho]+J[\rho]$$

This equation is the definition of $E_{xc}[\rho]$, which should contain

- exchange interaction (x)
- correlation contributions (c)
- higher-order kinetic energy corrections

Note:

- $\rho^{exact} = \sum_{i \in occ} \varphi_i^* \varphi_i$

KS (spin) orbitals

Is this generally possible for all ρ^{exact}?

- $T_0[\{\varphi_i\}] = -\frac{1}{2}\sum_{i\in occ}\langle\varphi_i|\Delta|\varphi_i\rangle$

  easy to calculate, accurate

- but this does <u>not</u> mean, e.g.

  $\psi^{exact} = \frac{1}{\sqrt{n!}}\det|\varphi_i(i)|$

  $E^{exact} = \langle\frac{1}{\sqrt{n!}}\det|\varphi_i||\hat{H}|\frac{1}{\sqrt{n!}}\det|\varphi_i|\rangle$

- φ_i^{KS} similar to φ_i^{HF}, since $\hat{T}$ and $\hat{V}$ in both KS and HF equations!

KS

HF

$$E[\rho] = T_0[\{\varphi_i\}] +$$

$$E[\Phi] = \langle \hat{T} \rangle +$$

kinetic

$$-\frac{1}{2}\sum_{i=1}^{n} \langle \varphi_i | \Delta | \varphi_i \rangle$$

equal!

$$-\frac{1}{2}\sum_{i=1} \langle \varphi_i | \Delta | \varphi_i \rangle$$

$$+ \int \hat{v}(\vec{r})\,\rho(\vec{r})\,d\vec{r} +$$

$$+ \langle \hat{V} \rangle +$$

potential

$$\int v(\vec{r}) \sum_{i=1}^{n} \varphi_i^{*}(\vec{r})\,\varphi_i(\vec{r})\,d\vec{r}$$

$$\sum_{i=1}^{n} \langle \varphi_i | \hat{v} | \varphi_i \rangle$$

$$= \sum_{i=1}^{n} \langle \varphi_i | \hat{v} | \varphi_i \rangle$$

equal!

KS

$$+\frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

HF

$$+\langle \hat{J} \rangle +$$

Coulomb

$$\sum_{i=j+1}^{n}\sum_{j=1}^{n-1}\iint \frac{\varphi_i^*(1)\varphi_j^*(2)\varphi_i(1)\varphi_j(2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

no self-interaction

$$\frac{1}{2}\iint \frac{\left(\sum_{i=1}^{n}\varphi_i^*(\vec{r}_1)\varphi_i(\vec{r}_1)\right)\left(\sum_{j=1}^{n}\varphi_j^*(\vec{r}_2)\varphi_j(\vec{r}_2)\right)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

$$=\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\iint \frac{\varphi_i^*(1)\varphi_j^*(2)\varphi_i(1)\varphi_j(2)}{|\vec{r}_1-\vec{r}_2|}\,d\vec{r}_1\,d\vec{r}_2$$

not equal!

self-interaction $(i=j)$

KS

HF

$+ \langle \hat{K} \rangle$ exchange

$+ E_{xc}[\rho]$

very different

correlation

size of contributions (absolute values!)

$$\underset{-}{\text{potential}} > \underset{+}{\text{kinetic}} > \underset{+}{\text{Coulomb}} > \underset{-}{\text{exchange}} > \underset{-}{\text{correlation}}$$

- Applying the variational principle to $E[\rho]$ wrt. φ_i:

Kohn-Sham equations

$$\Big[\underbrace{-\frac{1}{2}\Delta+\hat{v}(\vec{r})}_{\text{as for HF}}+\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,'+\frac{\delta E_{xc}}{\delta\rho(\vec{r})}\Big]|\varphi_i\rangle=\varepsilon_i|\varphi_i\rangle$$

self-interaction!

depending on the selected correlation exchange functional

- Self-consistent field procedure (cf. HF)

Types of density functionals

- LDA , <u>l</u>ocal <u>d</u>ensity <u>a</u>pproximation

$$E_{xc}[\rho] = \int \underset{\uparrow}{\varepsilon_{xc}}[\rho]\cdot\rho(\vec{r})\,d\vec{r}$$

exchange and correlation
energy per particle from
a homogenous electron gas
of density ρ

often ... $E_x^{S}[\rho] + E_c^{VWN}[\rho]$

X: analytic derivation possible

$$-c_x \int \rho(\vec{r})^{4/3} \, d\vec{r}$$ Dirac, Slater (S)

Hartree-Fock-Slater (HFS) method as simplification of HF (X_α method, since $\alpha_x = c_x$)

C: Quantum Monte Carlo results of Ceperly and Alder parametrized by Vosko, Wilk and Nusair (VWN)

LDA still very popular in solid state physics (→ relatively "homogenous" densities), but densities of atoms and molecules are not really "homogenous" →

- GGA, generalized gradient approximation inclusion of dependencies on local gradient $\nabla \rho(\vec{r})$ (besides $\rho(\vec{r})$) many functionals!

X: Becke (1988)
B88

C: Lee, Yang, Parr
LYP
C: Perdew (1986)
P86

XC: B-LYP, BP86

- meta-GGA
  inclusion of dependencies on
  $\Delta\rho$ (besides $\vec{\nabla}\rho$ and ρ)
- OPM, optimized effective potential method

$$E_{xc}[\rho] = E_x[\{\varphi_i\}] + E_c[\rho]$$

... and many other schemes

- semiempirical combinations with HF

e.g. B3LYP, ...

└ maybe the most popular DF?

hybrid functionals, e.g.

$$E_{xc}[\rho] = \underbrace{E_{xc}^{LDA}}_{S,\,VWN} + a_0\big(\underbrace{E_x^{exact}}_{K[\{\varphi_i\}]} - \underbrace{E_x^{LDA}}_{S}\big)$$

$$+ \underbrace{a_x \Delta E_x^{B88} + a_c \Delta E_c^{LYP}}_{\text{gradient corrections}}$$

The adiabatic connection (AC)

exact exchange-correlation energy expression of the Kohn-Sham formalism

$$E_{xc} = \int_0^1 U_{xc}^{\lambda} \, d\lambda$$

λ : interelectronic coupling strength parameter

→ switches $\frac{1}{r_{12}}$ on ($\lambda=1$) and off ($\lambda=0$)

$\lambda = 0$ noninteracting Kohn-Sham system

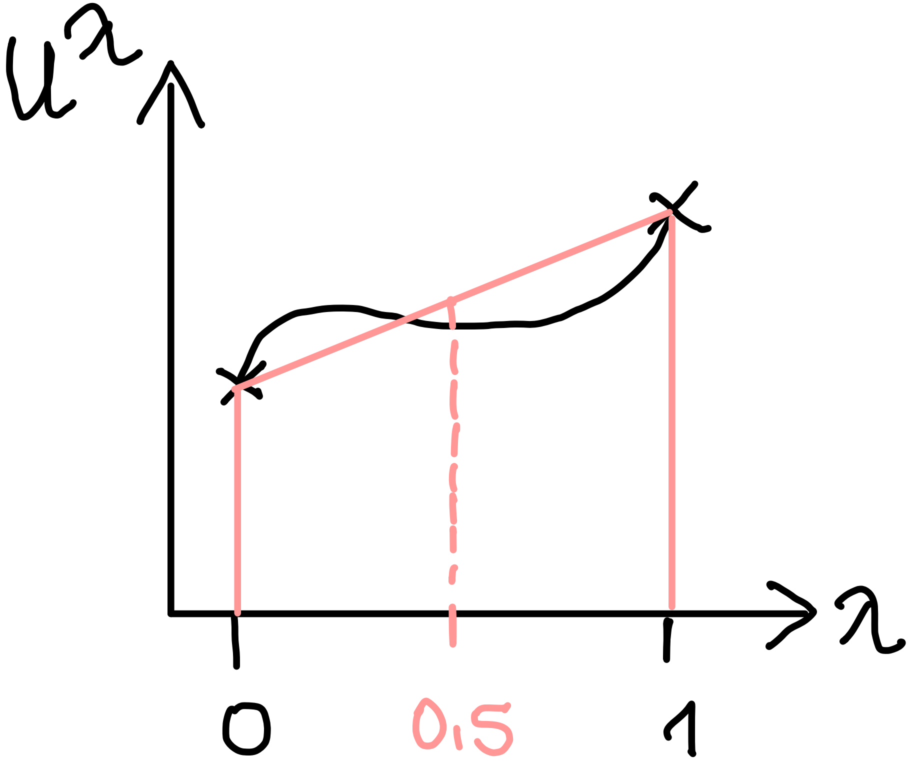
$\lambda = 1$ fully interacting real system

$0 < \lambda < 1$ "continuum" of partially interacting systems

Note: all system ($0 \leq \lambda \leq 1$) share the exact density (density of the fully interacting system)

U_{xc}^{0} pure exchange energy of the Slater determinant of the Kohn-Sham orbitals, without any dynamical correlation: E_x^{KS}

$$E_x^{KS} \approx E_x^{HF}$$



$$\int_0^1 U_{xc}^{\lambda}\, d\lambda \approx \frac{1}{2}\left(U_{xc}^{1} + U_{xc}^{0}\right) \approx$$

$$\approx \frac{1}{2} E_{xc}^{DFT} + \frac{1}{2} E_x^{HF}$$

⇒ "Half-and-half" functional of Becke (1993): BHH

⇓ Hybrid

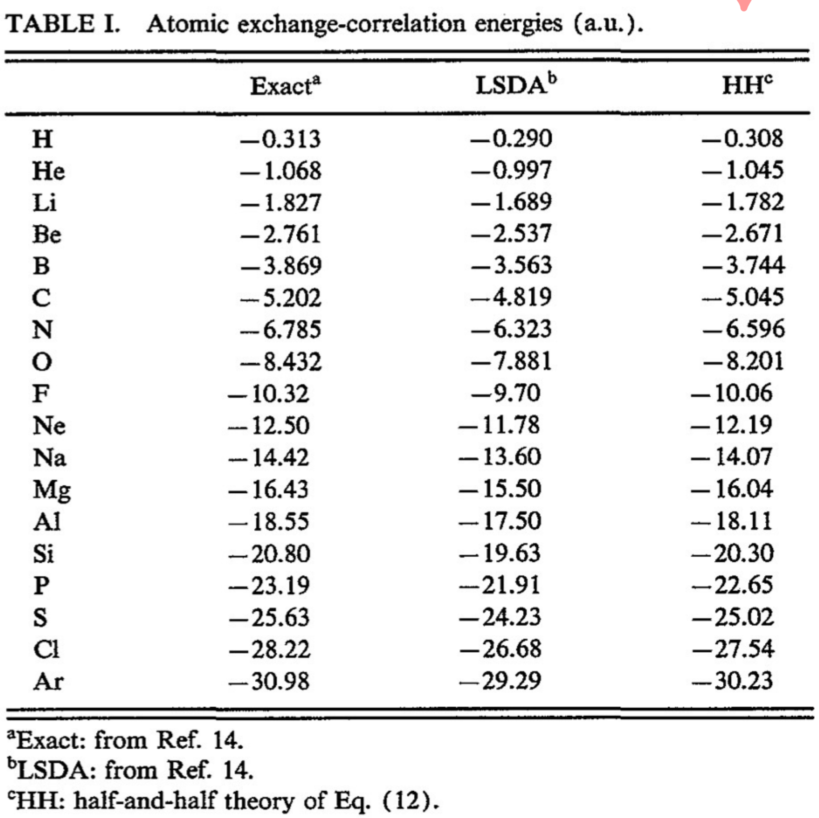


TABLE I. Atomic exchange-correlation energies (a.u.).

	Exact[a]	LSDA[b]	HH[c]
H	−0.313	−0.290	−0.308
He	−1.068	−0.997	−1.045
Li	−1.827	−1.689	−1.782
Be	−2.761	−2.537	−2.671
B	−3.869	−3.563	−3.744
C	−5.202	−4.819	−5.045
N	−6.785	−6.323	−6.596
O	−8.432	−7.881	−8.201
F	−10.32	−9.70	−10.06
Ne	−12.50	−11.78	−12.19
Na	−14.42	−13.60	−14.07
Mg	−16.43	−15.50	−16.04
Al	−18.55	−17.50	−18.11
Si	−20.80	−19.63	−20.30
P	−23.19	−21.91	−22.65
S	−25.63	−24.23	−25.02
Cl	−28.22	−26.68	−27.54
Ar	−30.98	−29.29	−30.23

[a] Exact: from Ref. 14.
[b] LSDA: from Ref. 14.
[c] HH: half-and-half theory of Eq. (12).

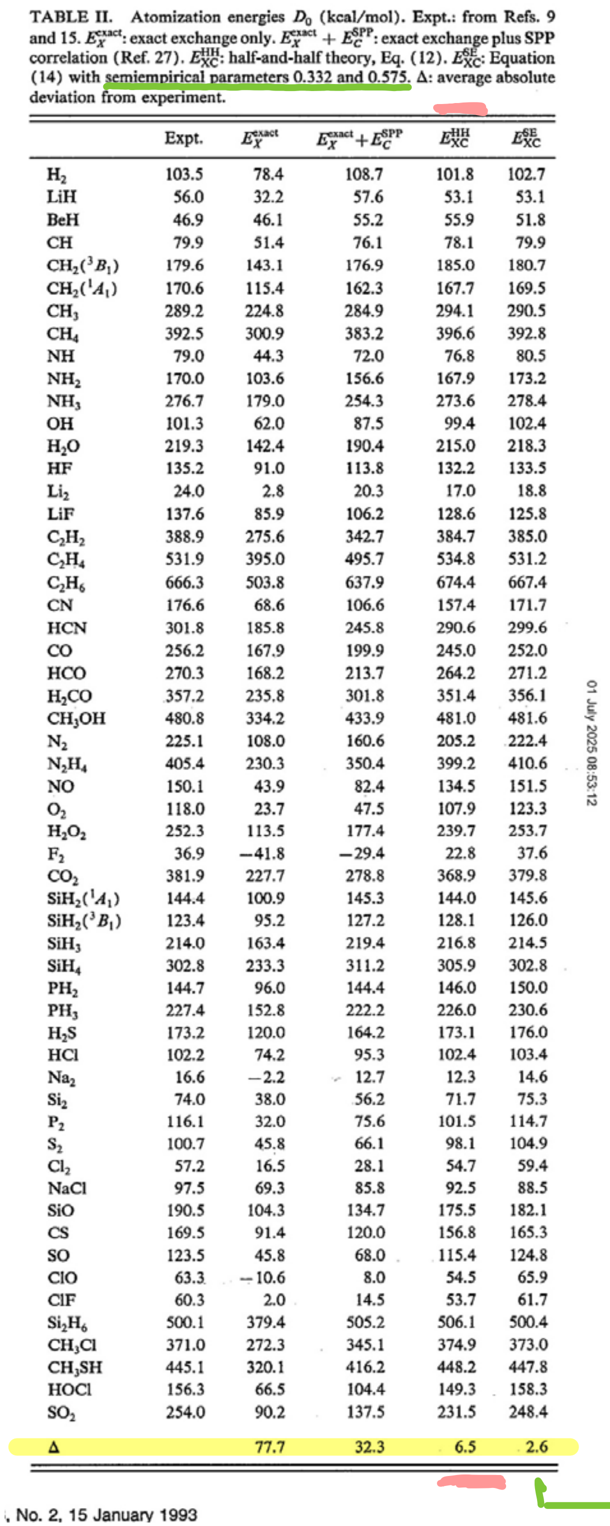


TABLE II. Atomization energies D_0 (kcal/mol). Expt.: from Refs. 9 and 15. E_X^{exact}: exact exchange only. $E_X^{\text{exact}} + E_C^{\text{SPP}}$: exact exchange plus SPP correlation (Ref. 27). E_{XC}^{HH}: half-and-half theory, Eq. (12). E_{XC}^{SE}: Equation (14) with semiempirical parameters 0.332 and 0.575. Δ: average absolute deviation from experiment.

	Expt.	E_X^{exact}	$E_X^{\text{exact}}+E_C^{\text{SPP}}$	E_{XC}^{HH}	E_{XC}^{SE}
H_2	103.5	78.4	108.7	101.8	102.7
LiH	56.0	32.2	57.6	53.1	53.1
BeH	46.9	46.1	55.2	55.9	51.8
CH	79.9	51.4	76.1	78.1	79.9
$CH_2(^3B_1)$	179.6	143.1	176.9	185.0	180.7
$CH_2(^1A_1)$	170.6	115.4	162.3	167.7	169.5
CH_3	289.2	224.8	284.9	294.1	290.5
CH_4	392.5	300.9	383.2	396.6	392.8
NH	79.0	44.3	72.0	76.8	80.5
NH_2	170.0	103.6	156.6	167.9	173.2
NH_3	276.7	179.0	254.3	273.6	278.4
OH	101.3	62.0	87.5	99.4	102.4
H_2O	219.3	142.4	190.4	215.0	218.3
HF	135.2	91.0	113.8	132.2	133.5
Li_2	24.0	2.8	20.3	17.0	18.8
LiF	137.6	85.9	106.2	128.6	125.8
C_2H_2	388.9	275.6	342.7	384.7	385.0
C_2H_4	531.9	395.0	495.7	534.8	531.2
C_2H_6	666.3	503.8	637.9	674.4	667.4
CN	176.6	68.6	106.6	157.4	171.7
HCN	301.8	185.8	245.8	290.6	299.6
CO	256.2	167.9	199.9	245.0	252.0
HCO	270.3	168.2	213.7	264.2	271.2
H_2CO	357.2	235.8	301.8	351.4	356.1
CH_3OH	480.8	334.2	433.9	481.0	481.6
N_2	225.1	108.0	160.6	205.2	222.4
N_2H_4	405.4	230.3	350.4	399.2	410.6
NO	150.1	43.9	82.4	134.5	151.5
O_2	118.0	23.7	47.5	107.9	123.3
H_2O_2	252.3	113.5	177.4	239.7	253.7
F_2	36.9	−41.8	−29.4	22.8	37.6
CO_2	381.9	227.7	278.8	368.9	379.8
$SiH_2(^1A_1)$	144.4	100.9	145.3	144.0	145.6
$SiH_2(^3B_1)$	123.4	95.2	127.2	128.1	126.0
SiH_3	214.0	163.4	219.4	216.8	214.5
SiH_4	302.8	233.3	311.2	305.9	302.8
PH_2	144.7	96.0	144.4	146.0	150.0
PH_3	227.4	152.8	222.2	226.0	230.6
H_2S	173.2	120.0	164.2	173.1	176.0
HCl	102.2	74.2	95.3	102.4	103.4
Na_2	16.6	−2.2	12.7	12.3	14.6
Si_2	74.0	38.0	56.2	71.7	75.3
P_2	116.1	32.0	75.6	101.5	114.7
S_2	100.7	45.8	66.1	98.1	104.9
Cl_2	57.2	16.5	28.1	54.7	59.4
NaCl	97.5	69.3	85.8	92.5	88.5
SiO	190.5	104.3	134.7	175.5	182.1
CS	169.5	91.4	120.0	156.8	165.3
SO	123.5	45.8	68.0	115.4	124.8
ClO	63.3	−10.6	8.0	54.5	65.9
ClF	60.3	2.0	14.5	53.7	61.7
Si_2H_6	500.1	379.4	505.2	506.1	500.4
CH_3Cl	371.0	272.3	345.1	374.9	373.0
CH_3SH	445.1	320.1	416.2	448.2	447.8
HOCl	156.3	66.5	104.4	149.3	158.3
SO_2	254.0	90.2	137.5	231.5	248.4
Δ		77.7	32.3	6.5	2.6

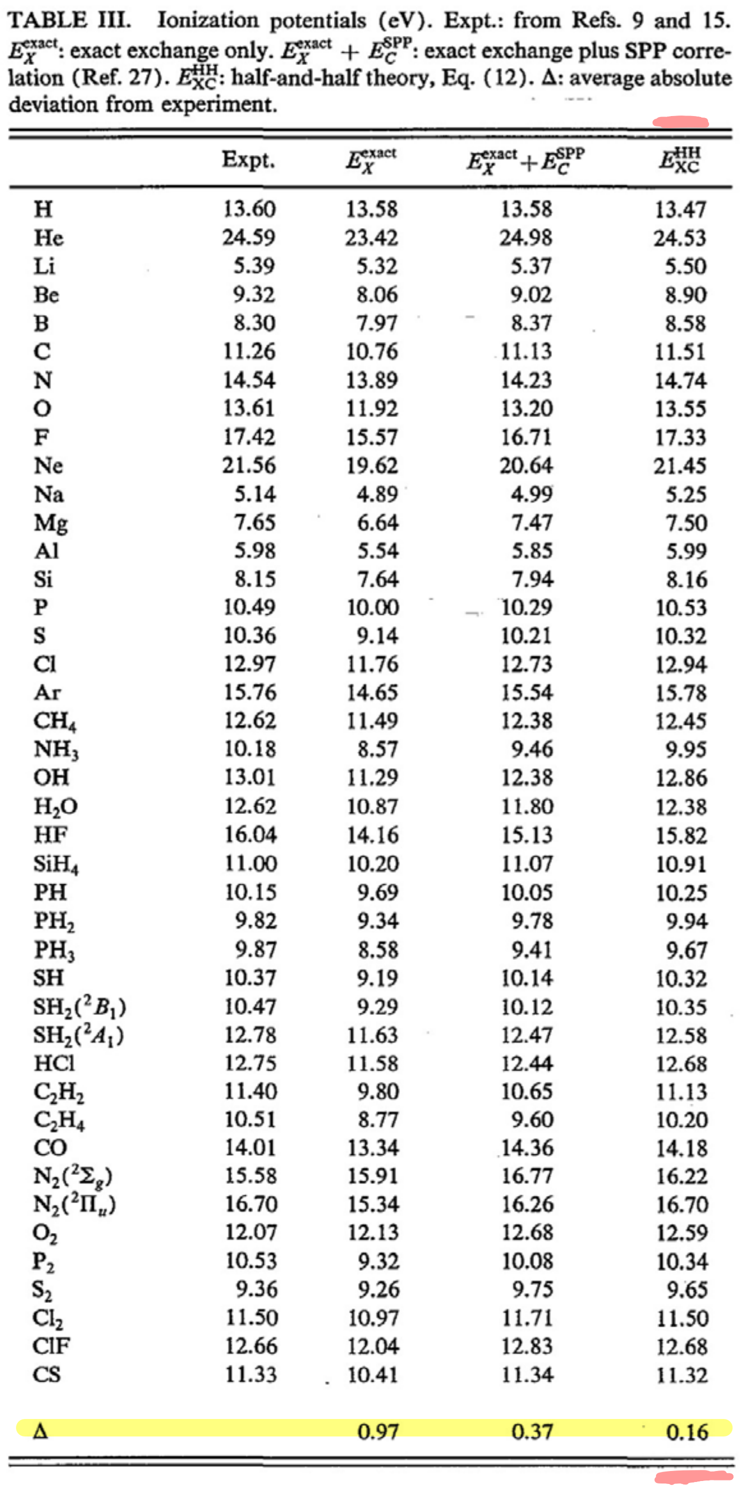


TABLE III. Ionization potentials (eV). Expt.: from Refs. 9 and 15. E_X^{exact}: exact exchange only. $E_X^{\text{exact}} + E_C^{\text{SPP}}$: exact exchange plus SPP correlation (Ref. 27). E_{XC}^{HH}: half-and-half theory, Eq. (12). Δ: average absolute deviation from experiment.

	Expt.	E_X^{exact}	$E_X^{\text{exact}}+E_C^{\text{SPP}}$	E_{XC}^{HH}
H	13.60	13.58	13.58	13.47
He	24.59	23.42	24.98	24.53
Li	5.39	5.32	5.37	5.50
Be	9.32	8.06	9.02	8.90
B	8.30	7.97	8.37	8.58
C	11.26	10.76	11.13	11.51
N	14.54	13.89	14.23	14.74
O	13.61	11.92	13.20	13.55
F	17.42	15.57	16.71	17.33
Ne	21.56	19.62	20.64	21.45
Na	5.14	4.89	4.99	5.25
Mg	7.65	6.64	7.47	7.50
Al	5.98	5.54	5.85	5.99
Si	8.15	7.64	7.94	8.16
P	10.49	10.00	10.29	10.53
S	10.36	9.14	10.21	10.32
Cl	12.97	11.76	12.73	12.94
Ar	15.76	14.65	15.54	15.78
CH_4	12.62	11.49	12.38	12.45
NH_3	10.18	8.57	9.46	9.95
OH	13.01	11.29	12.38	12.86
H_2O	12.62	10.87	11.80	12.38
HF	16.04	14.16	15.13	15.82
SiH_4	11.00	10.20	11.07	10.91
PH	10.15	9.69	10.05	10.25
PH_2	9.82	9.34	9.78	9.94
PH_3	9.87	8.58	9.41	9.67
SH	10.37	9.19	10.14	10.32
$SH_2(^2B_1)$	10.47	9.29	10.12	10.35
$SH_2(^2A_1)$	12.78	11.63	12.47	12.58
HCl	12.75	11.58	12.44	12.68
C_2H_2	11.40	9.80	10.65	11.13
C_2H_4	10.51	8.77	9.60	10.20
CO	14.01	13.34	14.36	14.18
$N_2(^2\Sigma_g)$	15.58	15.91	16.77	16.22
$N_2(^2\Pi_u)$	16.70	15.34	16.26	16.70
O_2	12.07	12.13	12.68	12.59
P_2	10.53	9.32	10.08	10.34
S_2	9.36	9.26	9.75	9.65
Cl_2	11.50	10.97	11.71	11.50
ClF	12.66	12.04	12.83	12.68
CS	11.33	10.41	11.34	11.32
Δ		0.97	0.37	0.16

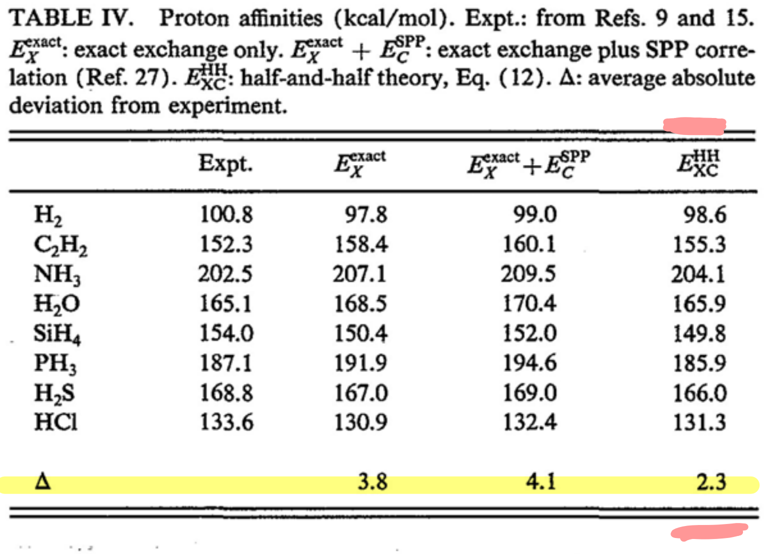


TABLE IV. Proton affinities (kcal/mol). Expt.: from Refs. 9 and 15. E_X^{exact}: exact exchange only. $E_X^{\text{exact}} + E_C^{\text{SPP}}$: exact exchange plus SPP correlation (Ref. 27). E_{XC}^{HH}: half-and-half theory, Eq. (12). Δ: average absolute deviation from experiment.

	Expt.	E_X^{exact}	$E_X^{\text{exact}}+E_C^{\text{SPP}}$	E_{XC}^{HH}
H_2	100.8	97.8	99.0	98.6
C_2H_2	152.3	158.4	160.1	155.3
NH_3	202.5	207.1	209.5	204.1
H_2O	165.1	168.5	170.4	165.9
SiH_4	154.0	150.4	152.0	149.8
PH_3	187.1	191.9	194.6	185.9
H_2S	168.8	167.0	169.0	166.0
HCl	133.6	130.9	132.4	131.3
Δ		3.8	4.1	2.3

results are very good!

⇓

improvements still possible ...

⇒ first hybrid functional by Becke, 1993:

$a_0 = 0{,}20$

$a_x = 0{,}72$

$a_c = 0{,}81$

semiempirical

3 optimized parameters

B3PW91

⇓ hybrid

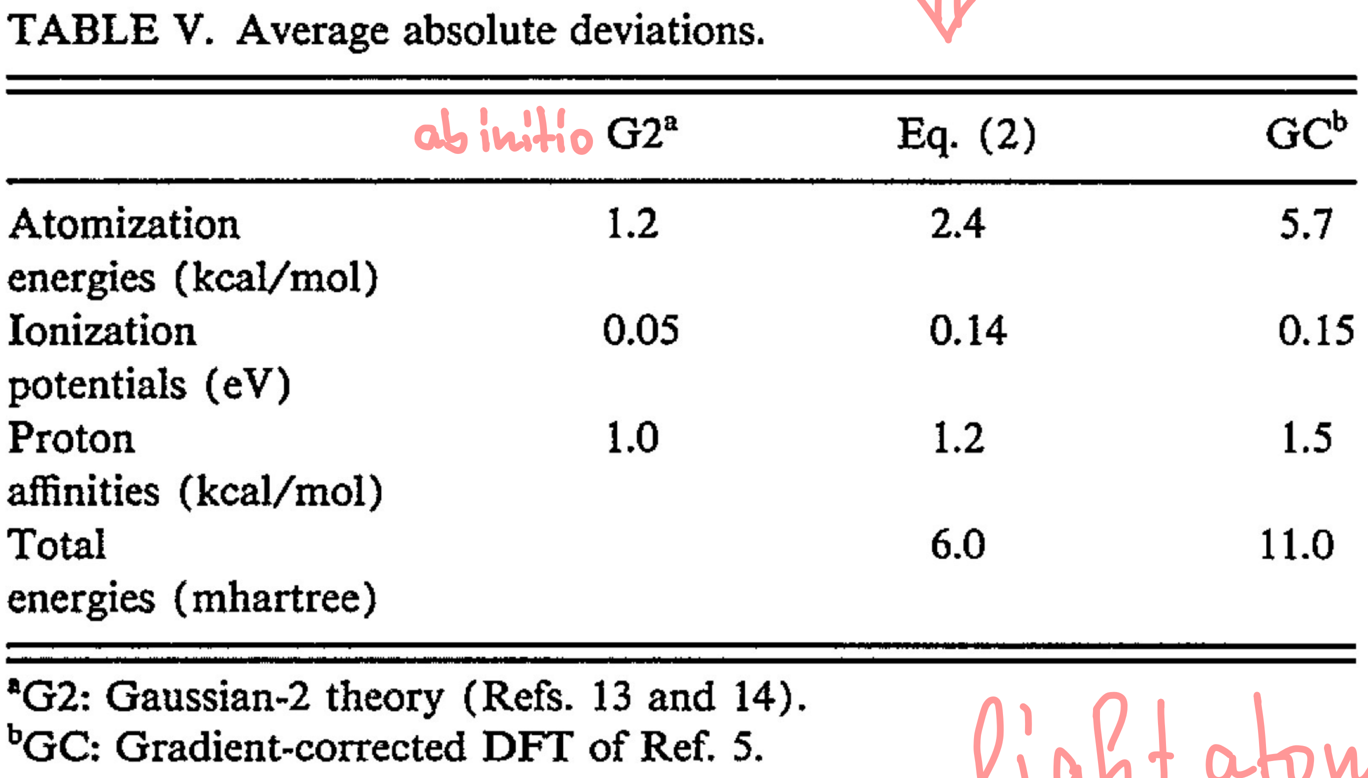


TABLE V. Average absolute deviations.

	ab initio G2[a]	Eq. (2)	GC[b] GGA
56 Atomization energies (kcal/mol)	1.2	2.4	5.7
42 Ionization potentials (eV)	0.05	0.14	0.15
8 Proton affinities (kcal/mol)	1.0	1.2	1.5
10 Total energies (mhartree)		6.0	11.0

[a] G2: Gaussian-2 theory (Refs. 13 and 14).
[b] GC: Gradient-corrected DFT of Ref. 5.

light atoms!

B3PW91

"Hybrid"

TABLE V. Average absolute deviations.

		ab initio G2[a]	Eq. (2)	GC[b] GGA
56	Atomization energies (kcal/mol)	1.2	2.4	5.7
42	Ionization potentials (eV)	0.05	0.14	0.15
8	Proton affinities (kcal/mol)	1.0	1.2	1.5
10	Total energies (mhartree)		6.0	11.0

[a] G2: Gaussian-2 theory (Refs. 13 and 14).

[b] GC: Gradient-corrected DFT of Ref. 5.

light atoms!

$\Rightarrow$ almost uncountable number $[O(10^2)]$ of possibilites/functionals!

You can almost always find a functional which produces excellent results for one property of one system, but hardly one which does this for several properties of many systems.

- Advantages DFT:
  - efficient (fast, moderate computational effort, large systems accessible)
- Disadvantages of DFT:
  - not systematically improvable (≠ ab initio)
  - one determinantal approach: problems to dissociate bonds, problems with (near-) degeneracies, problems with multiplet splittings
  - long range potential often wrong ($\hat{v}_J + \underline{\hat{v}}_x$): anions often with $\varepsilon_i > 0$ for valence shell

- p_x, $p_x + ip_y$ or $d_{2z^2-x^2-y^2}$, $d_{x^2-y^2}$ are degenerate, but have different densities
  → no degeneracy at DFT level, e.g., for Sc $3d^1\ {}^2D$ (5 levels)
- no interaction for no density overlap, e.g. van der Waals interaction is not described, e.g.

interaction

$$\underbrace{\text{He } 1s^2\ {}^1S \to 1s^1 2p^1\ {}^1P \quad \text{He } 1s^2\ {}^1S \to 1s^1 2p^1\ {}^1P}_{{}^1\Sigma_g^+}$$

The HK-theorem and the KS-formalism are for electronic ground states.

An extension to time-dependent potentials (external electromagnetic fields) allows to calculate the response of the system to these, e.g. excitation energies ⟹ time-dependent density functional theory (TDDFT)

We had a look at "standard" approaches,

HF, MBPT (MPn, ...), CI (CISD, ..., FCI),

CC (CCSD, ..., CCSD(T), ...)

DFT (LDA, GGA, meta-GGA, hybrid, ...)

There are many more approaches / variants / details / topics .... to talk about.

⟶ MSc, PhD, ... enough time to find out!

Some advice for practical work

Before you start:

- Check the literature! (WoS, Bing, ...)

- Theory <u>and</u> experiment
- Who? Which methods? Results? Problems?
- Was your problem/question already looked at or even solved?

Doing calculations:

- Use published coordinates (calculations, experiment) as starting guess; if not available start with simple/cheap methods first and increase the accuracy step by step (force field → DFT → ab initio; small basis → big basis; HF → MP2 → CI, CC)
- Make sure your chosen approach can deal with your problem

- Check by visualization your initial and your final structures for plausability (jmol, avogadro, ...)
- Check changes on atoms for plausability (Mulliken population analysis, ...)
- Check your output(s) for error messages or warnings (... not implemented; code not tested for ..., no convergence; ...)

Writing the report/paper:

- Make sure you provide the correct references in correct form (at least look at title and abstract; check autor names, journal, year, volume and page numbers (WoS,...)
- Provide all details of your calculations (Hamiltonian, basis set,

density functional/correlation method, ..., program system) → It should be possible to reproduce the work with the information provided!

Good Luck!