# Ab initio methods and density functional theory

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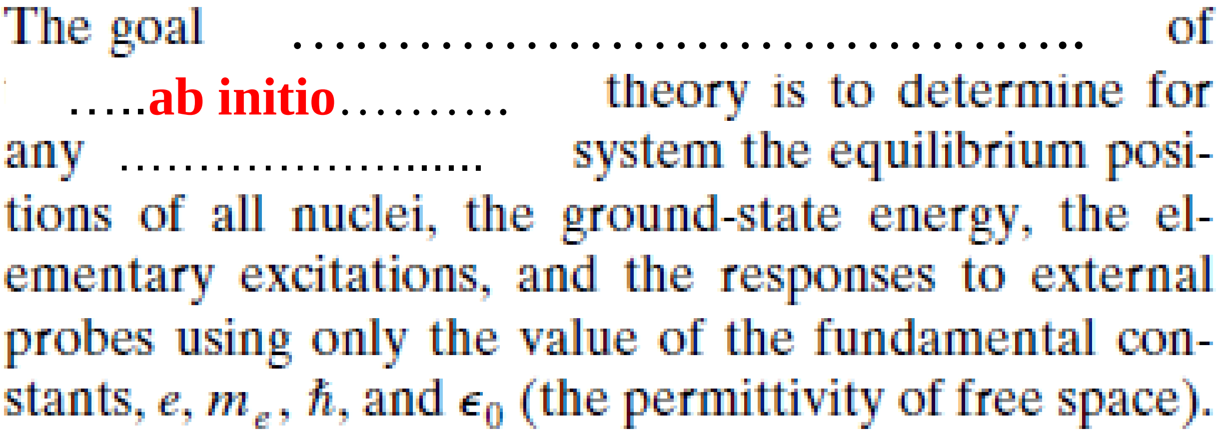
18th July 2012

# Outline

- Introduction
- Hartree-Fock and derived methods. CI and CC
- Density functional theory:
    - The fundamental theorems
    - The approximated exchange-correlation functionals
    - The van der Waals interaction
- Conclusions

# Introduction: Ab *initio* methods

T.B. Grimley, Prog. Surf. Membr. Sci. 9, 71 (1975), wrote some 37 years a clear definition of ***ab initio* methods**:



The goal …………………………………. of …..**ab initio**………. theory is to determine for any ……………....... system the equilibrium positions of all nuclei, the ground-state energy, the elementary excitations, and the responses to external probes using only the value of the fundamental constants, $e$, $m_e$, $\hbar$, and $\epsilon_0$ (the permittivity of free space).

**Thomas B. Grimley, University of Liverpool (UK) (1923- )**

- ❑ Use the **exact Hamiltonian** for atomic, molecular or solid systems within the **Born-Oppenheimer approximation**:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{ext}$$

atomic units

$$\hat{H}_1 = \sum_{\mathrm{i=1,N}} \hat{h}_\mathrm{i}; \quad \hat{h}_\mathrm{i} = -\frac{1}{2}\nabla^2_{\mathrm{r_i}} - \sum_{\alpha=1}^{M} \frac{Z_\alpha}{r_\mathrm{i} - R_\alpha}$$

$$\hat{H}_2 = \sum_{i<\mathrm{j}=1}^{N} \frac{1}{r_\mathrm{ij}}$$

.

- ❑ Determine the ground state of the system by the **variational principle** by using an N-electron **anti-symmetric wavefunction** , which results into solving a Schrödinger equation.

- ❑ **Crucial factors** :

  Development of theoretical concepts and numerical methods to obtain an **approximate wavefunction** $\Psi$ so that the binding and barrier energies are worked out close to **chemical accuracy**, defined as 1 kcal/mol = 43 meV.

  Improvements in **computational hardware**.

  Improvements in **computational software**

  **Novel theoretical concepts**, as it was density functional theory compared to wavefunction based methods.

# Hartree- Fock (HF) method

- The **self-consistent electron-electron potential energy (Hartree approach)** was introduced first by Hartree in 1928.
- **Slater** showed that Hatree’s equation could be derived variationally (1928)
- **Fock** pointed out that the wavefunction has to be **anti-symmetrized** leading to the exchange term (1930).

HIC TUTA PERENNAT

Quantum Mechanics Division

Vladimir Aleksandrovich Fock
St. Petersburg (1898-1974)

# Single Slater determinant as approximate anti-symmetric electron wavefunction

$$\Phi(q_1, q_2, \ldots\ldots q_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P u_\alpha(q_1) u_\beta(q_2) \ldots\ldots u_\nu(q_N) \; ; \quad q = \mathbf{r}, \sigma$$

**Energy functional**: $$E[\Phi] = \sum_{\lambda=1}^{N} I_\lambda + \frac{1}{2} \sum_{\lambda,\mu=1}^{N} [J_{\lambda\mu} - K_{\lambda\mu}] \; ;$$

$$\underbrace{I_\lambda = < \lambda | h_i | \lambda >;}_{\textbf{One particle;}} \qquad \underbrace{J_{\lambda\mu} = (\lambda\mu | \frac{1}{r_{\mathrm{ij}}} | \lambda\mu);}_{\textbf{Hartree-classical-direct;}} \; \underbrace{K_{\lambda\mu} = (\lambda\mu | \frac{1}{r_{\mathrm{ij}}} | \mu\lambda)}_{\textbf{Exchange term}}$$

**Variational** condition imposing **orthonormality of wavefunctions**:

$$\delta E - \sum_\lambda \varepsilon_\lambda \delta < u_\lambda | u_\lambda > = 0$$

$\varepsilon_\lambda$ are Langrange multipliers

**Hartree-Fock equation**:

$$[h_\mathrm{i} + v_H(\mathbf{r}_i) - v_x(q_i)]\, u_\lambda(q_i) = \varepsilon_\lambda u_\lambda(q_i)$$

**Self-consistent** equation whose potentials can be written after defining the first order **spinless density matrix**:

$$n(\mathbf{r}_\mathrm{i}, \mathbf{r}_\mathrm{j}) = \sum_{\mu=1}^{N} u_\mu(\mathbf{r}_\mathrm{i})\, u_\mu^*(\mathbf{r}_\mathrm{j})$$

$$v_H(\mathbf{r}_\mathrm{i}) = \int n(\mathbf{r}_\mathrm{j})\, \frac{1}{r_{ij}} d\mathbf{r}_\mathrm{j}$$

**Hartree potential**

$$v_x(q_i)u_\lambda(q_i) = \delta_{m_s^\lambda, m_s^\mu} \left[\int n(\mathbf{r}_\mathrm{i}, \mathbf{r}_\mathrm{j})\, \frac{1}{r_{ij}} u_\lambda(\mathbf{r}_\mathrm{j}) d\mathbf{r}_\mathrm{j}\right] \chi_{\frac{1}{2}\, m_s^\mu}$$

**Exchange potential**

**One obtains the ground state total energy as:**

$$E_0^{HF}[\Phi_0] = \sum_{\lambda=1}^{N} \varepsilon_\lambda - \frac{1}{2} \sum_{\lambda,\mu=1}^{N} [J_{\lambda\mu} - K_{\lambda\mu}]$$

## Hartree-Fock properties:

**Self-interaction cancels exactly**

**Koopman's theorem**: The eigenvalue of the spin-orbital $u_\lambda$ is the **ionization** energy of such electron, if no electronic rearrangement occurs between the systems with *N* and *(N-1)* electrons.

$$E_N - E_{N-1} = \varepsilon_\lambda$$

**Practical solutions** are obtained by expanding the spin orbitals on a **basis set** (BS) as a linear combinationon of a finite number (*P*>*N*) of basis set functions:

$$u_\lambda = \sum_{\nu=1}^{P} c_{\nu\lambda}\psi_\nu$$

**Wavefunctions**: **Plane waves** $exp(i\mathbf{k}\cdot\mathbf{r})$

**Slater** $exp(-\beta r)$

**Gaussian** $exp(-\alpha r^2)$

Defining the **Fock operator**:

$$\hat{F} = \hat{H}_1 + \hat{J} - \hat{K}$$

One can solve a matrix equation: **FC = ε SC**

obtaining the so called **Hartree-Fock-Roothan equation,** in which the **overlap** matrix **S** can be diagonalized by unitary transformation and the solution found self-consistently

The main limitation of the HF method is the lack of **correlation energy,** defined as

$$E_{corr} = E_{exact} - E_0^{HF} \qquad E_{corr} \leq 0$$

In HF one electron moves in the **average field** of the other electrons so that electron movements **are not correlated** to each other.

**Opposite spin correlation** not considered.

**Excited states poorly** described

# Configuration interaction (CI)

The N-electron basis functions can be written as ***excitations*** from the HF ground state wavefunction, where $\Phi_j^a$ means a Slater determinant formed by replacing the occupied spin-orbital |j> in $\Phi_0$ with virtual spin orbital |a>, namely:

$$\Psi_{CI} = \Phi_0 + \sum_{a,j} C_j^a \Phi_j^a + \sum_{j>i,a>b} C_{ji}^{ab} \Phi_{ji}^{ab} + .... + \sum_{j>i>k,a>b>c} C_{jik..N}^{abc...M} \Phi_{ji...N}^{ab...H}$$

Some of the occupied *N* orbitals are substituted by *M-N=H* virtual orbitals.

The full CI corresponds to solving Schrödinger's equation exactly within the space spanned by the selected one-electron basis.

The CI method can be expressed **variationally** so the calculated **lowest energy** eigenvalue is always **an upper bound to the exact ground state energy**.

The disadvage of the method is that it is not **size-extensive**.

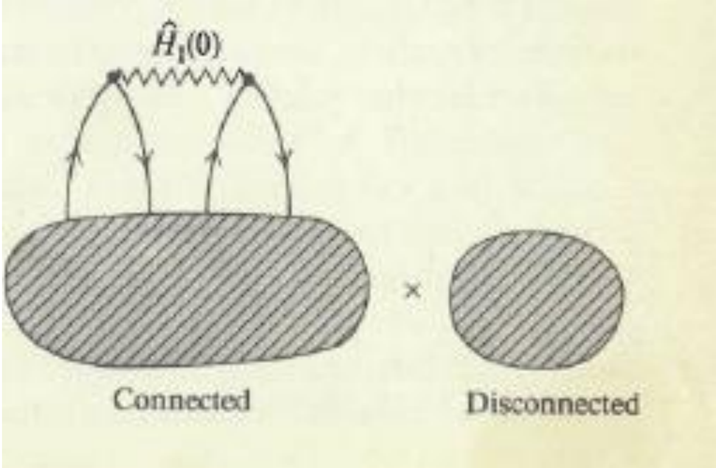
# Coupled cluster (CC) theory

CC can be explained in a diagrammatic way, e.g. similarly to Goldstone theorem, which shows cancellation of disconnected diagrams

$$E - E_0 = < \Phi_0 | \hat{H}_1 \sum_{n=0}^{\infty} \left( \frac{1}{E_0 - \hat{H}_0} \hat{H}_1 \right)^n | \Phi_0 >_{\text{connected}}$$

$$E - E_0 = \frac{< \Phi_0 | H_1 U(0,\infty) | \Phi_0 >}{< \Phi_0 | U(0,\infty) | \Phi_0 >}$$

J. Goldstone, Pr.R.Soc. A 239, 267 (1957)



# Size extensivity

$$E(AB)=E(A)+E(B), \qquad R_{AB} \longrightarrow \infty$$

$$H(AB)\,\Psi(AB)=[H(A)+H(B)]\,|AB>=[E(A)+E(B)]\,|A>|B>$$

$$|AB> \,=\, exp\,[T(A)+T(B)]\,|A_0B_0> \,=\, exp[T(A)]\,|A_0>exp[T(B)]\,|B_0>$$

➡

Exact wavefunction from a exponential operators guaranted by evaluating only linked diagrams

$$|\Psi_{cc}>= exp(\hat{T})|\Phi_0>; \quad \hat{T}=\sum_p \hat{T}_p \qquad T_p=(n!)^{-2}\sum_{ij...;ab...} t_{ij...}^{ab...}\hat{c}_a^\dagger\hat{c}_b^\dagger.....\hat{c}_j\hat{c}_i$$

$$exp(-\hat{T})\hat{H}\,exp(\hat{T})=\overline{H}$$

$$E=<\Phi_0|\overline{H}|\Phi_0>; \qquad <\Phi_{ij.....}^{ab...}|\overline{H}|\Phi_0>=0$$

# Equivalence of CC and FCI

| **CC wavefunction** | | **CI wavefunction** |
|---|---|---|
| $\vert\Psi\rangle \quad = \quad \exp(T)\ \vert 0\rangle$ | | $\Psi \quad = \quad C\ \vert 0\rangle$ |
| $T_1\ \vert 0\rangle$ | **singly excited** | $C_1\ \vert 0\rangle$ |
| $(T_2\ +\ \frac{1}{2}T_1^2)\ \vert 0\rangle$ | **doubly excited** | $C_2\ \vert 0\rangle$ |
| $(T_3\ +\ T_2T_1\ +\ \frac{1}{3!}T_1^3)\ \vert 0\rangle$ | **triply excited** | $C_3\ \vert 0\rangle$ |
| $(T_4\ +\ T_3T_1\ +\ \frac{1}{2!}T_2^2$ | **quadruply excited** | $C_4\ \vert 0\rangle$ |
| $+\ \frac{1}{2}T_1^2T_2\ +\ \frac{1}{4!}T_1^4)\ \vert 0\rangle$ | $\ldots$ | |

**matching number of parameters**

=> **CC ansatz parametrizes the exact wavefuntion**

J. Čížek, JCP 45, 4256 (1966)
G.D, Purvis and R.J. Bartlett, JCP 76, 1910 (1982)
J. ČR.J. Bartlett and M. Musial, RMP 79, 291 (2007)

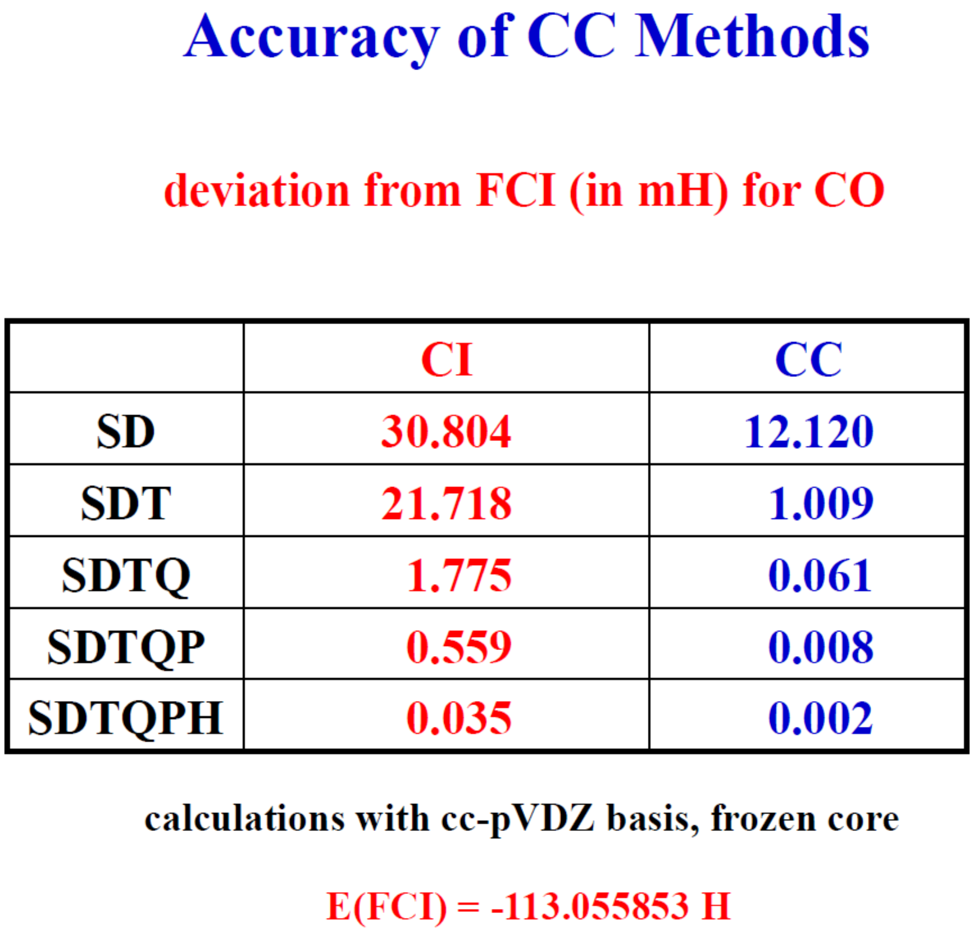
Eventually one has to solve a non-linear system of equations for the coefficients to be solved iteratively.

Unlinked diagrams cancel

Diagrams, which guarantee size extensivity, are considered differently from trunkated CI

Wavefunction in closed form

CC is applicable to infinite systems.
Correct relative energies on PES.



## Accuracy of CC Methods

deviation from FCI (in mH) for CO

| | CI | CC |
|---|---|---|
| SD | 30.804 | 12.120 |
| SDT | 21.718 | 1.009 |
| SDTQ | 1.775 | 0.061 |
| SDTQP | 0.559 | 0.008 |
| SDTQPH | 0.035 | 0.002 |

calculations with cc-pVDZ basis, frozen core

E(FCI) = -113.055853 H

**cost**

$N^6$

$N^8$

$N^{10}$

$N^{12}$

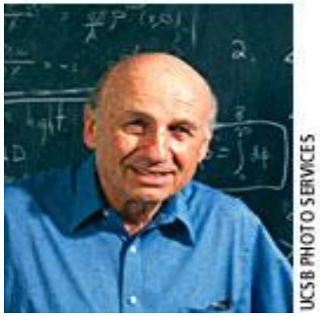
# Density functional theory (DFT)

R. M. Dreizler and E.K:U Gross, DFT, Springer-Verlag (1990)

## HK Theorem 1

P. Hohenberg and. W. Kohn, PR 136, 864 (1964)

Thus $v(\mathbf{r})$ is (to within a constant) a unique functional of $n(\mathbf{r})$; since, in turn, $v(\mathbf{r})$ fixes $H$ we see that the full many-particle ground state is a unique functional of $n(\mathbf{r})$. $v(\mathbf{r})$ is an external potential $n(\mathbf{r})$ is the ground state density



Walter Kohn,
Vienna (1923-)

## HK Theorem 2

$$F_{HK}[n(\mathbf{r})] =< \Psi|(T+V_{ee})|\Psi >$$

$$E_{\mathrm{v}}[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})dr + F_{HK}[n(\mathbf{r})] \equiv V[n(\mathbf{r})]+F_{HK}[n(\mathbf{r})]$$

has a minimum at the correct ground state density $n_0$ relative to arbitrary variations of $n$ subject to the constraint of fixed number of particles

## Kohn-Sham scheme

W. Kohn and L. Sham, PR 140, A1133 (1965)

For any interacting system there exists a local single particle potential $v_{eff}(\mathbf{r})$ such that the exact ground state charge density equals the ground state density of the auxiliary problem:

$$n_s(\mathbf{r}) = \sum_{\mathrm{i}=1,N} \varphi_i^*(\mathbf{r})\varphi_{\mathrm{i}}(\mathbf{r}) = n_0(\mathbf{r})$$

## Kohn-Sham functional

$$E_{KS}[n] = T_s[n] + V[n] + \overbrace{\frac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\,w(|\mathbf{r}-\mathbf{r}'|)\,n(\mathbf{r})\,n(\mathbf{r}')}^{J[n]} + E_{xc}[n]$$

$T_s[n]$ is the **non-interacting particle kinetic energy functional**:

$$T_s[n] = \sum_{\mathrm{i}=1,N}\int \varphi_{\mathrm{i}}^*(\mathbf{r})\left(-\frac{\hbar^2}{2m}\right)\nabla^2_{\mathbf{r}}\varphi_{\mathrm{i}}(\mathbf{r})\,d\mathbf{r} = \int\left(-\frac{\hbar^2}{2m}\right)\nabla^2_{\mathbf{r}'}n_s(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}}\,d\mathbf{r}$$

$E_{xc}[n]$ is defined as the **exchange correlation functional**

$$E_{xc}[n] = F_{HK}[n] - J[n] - T_s[n]$$

The minimization can be performed on an auxiliary functional $\Omega[\varphi]$ and in the space of the orbitals $\{|\varphi_i>\}$, subject to the **orthonormality** condition:

$$\Omega[\varphi] = E_{KS}[\varphi] - G[\varphi]; \quad G[\varphi] = \sum_{\mathrm{i}=1.N}\varepsilon_{\mathrm{i}}\,\{<\varphi_i|\varphi_i>\}$$

The variation of the functional $\delta\Omega$ in terms of $\delta n$ can be expressed in terms of the various $\delta\varphi_\mathrm{i}$ which, for real spin orbitals, amounts to the equation:

$$n + \delta n = \sum_{\mathrm{i}=1,N} |\varphi_\mathrm{i} + \delta\varphi_\mathrm{i}|^2 \simeq n + 2\sum_{\mathrm{i}=1,N} \varphi_\mathrm{i}\delta\varphi_\mathrm{i}$$

From $\delta\Omega\left[n\right] = 0$ after some manipulation, we obtain the **Kohn-Sham equation**:

$$[-\frac{1}{2}\nabla^2 + \underbrace{v(\mathbf{r}) + \mathrm{v}_H([n]\,,\mathbf{r}) + v_{xc}([n]\,,\mathbf{r})}_{v_{eff}(\mathbf{r})}]\,\varphi_\mathrm{i} = \varepsilon_\mathrm{i}\varphi_\mathrm{i}$$

We can introduce the **Kohn-Sham operator** as

$$\hat{h}_{KS} = \frac{1}{2}\nabla_\mathrm{r}^2 + v_{eff}(\mathrm{r})$$

and write:

$$\hat{h}_{KS}\varphi_\mathrm{i} = \varepsilon_\mathrm{i}\varphi_\mathrm{i}$$

**The total energy** can be written as:

G.P. Brivio and M.I. Trioni, RMP 71, 231 (1999)

$$E[n] = \sum_{\mathrm{i}=1,N} \varepsilon_{\mathrm{i}} - J[n] + E_{xc}[n] - \int v_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

## Main conclusions on the DFT-KS method

The complexity of the problem is now shifted to the term $E_{xc}[n]$ which contains both the **quantum interaction** among the electrons and **the difference term** $T - T_s$
The KS approach computes the kinetic energy $T_{\mathrm{s}}$ via the KS auxiliary orbitals,
However, recall that already for Be $T - T_s \simeq 2.0\ eV$ .

The single particle KS equations are similar to the HF ones. They can be solved **self-consistently** by an expansion of the orbitals on a suitable basis set. The non local exchange term is absent in the KS scheme since $v_{eff}(\mathbf{r})$ is a local potential.

**The KS approach is exact**: the problem regards the **exchange-correlation functional**. Various approximations are proposed for it. See the following.

Similar to the unrestricted HF method, the KS approach can be extended to magnetic systems. In this case $v_{xc}^{\alpha} \neq v_{xc}^{\beta}$

The **KS orbitals have no particular physical meaning**. They are a tool to obtain the exact charge density $n_s(\mathbf{r}) = n(\mathbf{r})$ but not the exact wavefunctions.

The KS eigenvalue are only Lagrange multipliers (no Koopman theorem exists in DFT) although they are often a good approximation to the orbital energies.

The success of the KS method is mainly due to **easier computational implementations for larger systems** than those of the HF approach and its derived methods. Also the **charge density** is an intuitive experimental measurable quantity, differently from the wavefunctions in HF.

**Excited states** are outside the reach of DFT and consequently cannot be determined *a fortiori* by the KS eigenvalues of the unoccupied states.

# The local density approximation (LDA)

Following the results for the **homogeneous electron gas (HEG)** and a similar approach to the Thomas-Fermi functional, we approximate **the exchange-correlation functional by:**

$$E_{xc}[n] \simeq E_{xc}^{LDA}[n(\mathbf{r})] = \int d\mathbf{r}\, \epsilon_{xc}(n(\mathbf{r}))\, n(\mathbf{r})$$

Where $\epsilon_{xc}(n(\mathbf{r}))$ is the **exchange-correlation energy per particle in HEG**

whose density is defined to be that appropriate to the position **r** , namely:

$$n(\mathbf{r}) = n^{HEG}$$

The **spin dependence** can be easily introduced in the KS scheme, and **the local spin density approximation** (LSDA) functional is:

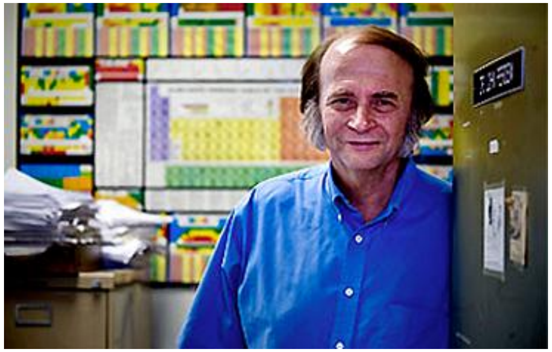
$$E^{LSDA}[n] = \sum_{\sigma} \sum_{\mathrm{i}=1,N} \varepsilon_{\mathrm{i}\sigma} - J\left[n^{\downarrow}+n^{\uparrow}\right] + E_{xc}^{LSDA}\left[n^{\downarrow},n^{\uparrow}\right] - \sum_{\sigma} \int v_{xc}^{\sigma,LSDA}(\left[n^{\downarrow},n^{\uparrow}\right]) n^{\sigma}(\mathbf{r})\, d\mathbf{r}$$

$$n = n^{\downarrow} + n^{\uparrow}$$

# The self-interaction correction

The correct number of couple interactions for a system of N electrons is given by N(N-1)/2 and for an extended system largely overcomes that of the electron self-interaction (SI) proportional to N. But for an atom or a molecule , the SI is a relevant correction.
In HF the SI is correctly zero, but in DFT the classical functional $J[n]$ contains N/2 spurious interactions.

Perdew and Zunger suggested a modified exchange functional to subtract spurious terms for each orbital

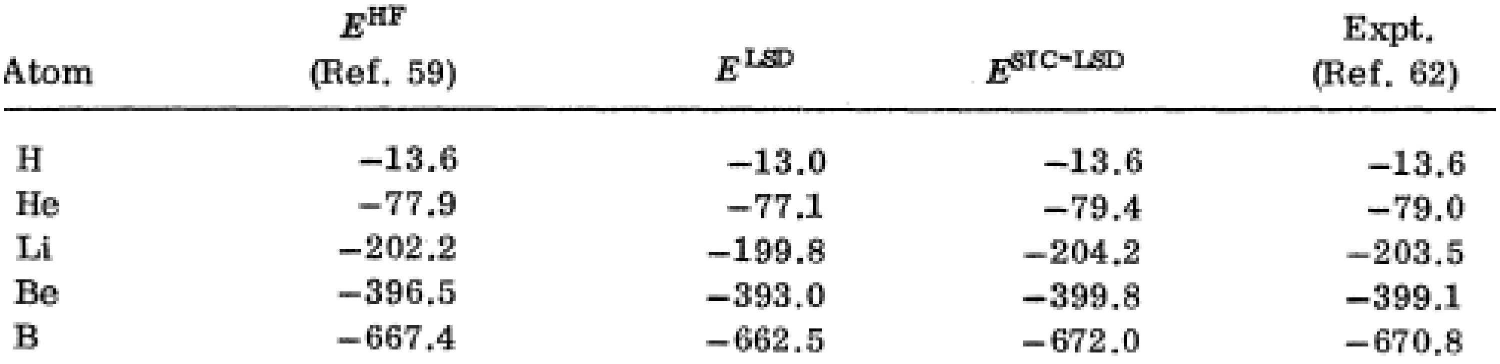


J.P. Perdew (1943- )

$$E_x^{SIC}[n] = E_x[n] - \sum_{\mathrm{i}=1,N} \left(J[n_\mathrm{i}] + E[n_\mathrm{i}]\right)$$

J.P. Perdew and A. Zunger, PRB 23, 5048 (1981))

Today with advent of new and hybrid functionals the SIC is usually ignored



| Atom | $E^{\mathrm{HF}}$ (Ref. 59) | $E^{\mathrm{LSD}}$ | $E^{\mathrm{SIC\text{-}LSD}}$ | Expt. (Ref. 62) |
|---|---|---|---|---|
| H | −13.6 | −13.0 | −13.6 | −13.6 |
| He | −77.9 | −77.1 | −79.4 | −79.0 |
| Li | −202.2 | −199.8 | −204.2 | −203.5 |
| Be | −396.5 | −393.0 | −399.8 | −399.1 |
| B | −667.4 | −662.5 | −672.0 | −670.8 |

# Fractional occupation number

We start first with the **Euler variational equation** of the energy functional with respect to the particle number *N*

$$\frac{\delta}{\delta n}\left(E_v\,[n]-\mu\int n(\mathbf{r})d\mathbf{r}=0\,,\qquad \int n(\mathbf{r})d\mathbf{r}=N\right.$$

A proper extension of the density to a **fractional number of electrons** (from a grand canonical ensemble) is given by:

$$n_\omega(\mathbf{r})=(1-\omega)\,n_N(\mathbf{r})+\omega\,n_{N+1}(\mathbf{r})\,,\quad 0\le\omega\le1$$

J.P. Perdew et al, PRL 49, 1691 (1982))

Such density may integrate to **a non integer number**. The corresponding **energy** is a **straight line segment** with derivative discontinuities at integer *N*:

$$E_v^{N+\omega}=(1-\omega)\,E_v^N+\omega\,E_v^{N+1}$$

By this approach one can prove that the Lagrange multiplier is **the chemical potential**

$$\frac{\delta E_v}{\delta n}=\frac{\partial E_v}{\partial N}=\mu$$

This is the **equivalent of Koopman's theorem for DFT** and gives the value of the **ionization potential** of the system,

$$E^{N-1} - E^{N} = -\varepsilon_H$$

J.P. Perdew and M. Levy, PRB 97, 16021 (1997)

Consider **a fractional occupation** $\omega_{\mathrm{i}}$ of the spin orbitals and define the density as:

$$\tilde{n}(\mathbf{r}) = \sum_{\mathrm{i}=1,\infty} \omega_{\mathrm{i}} |\varphi_{\mathrm{i}}(\mathbf{r})|^2; \qquad 0 \leq \omega_{\mathrm{i}} \leq 1$$

Also the energy and the orbitals are functions of $\omega_{\mathrm{i}}$ and one can prove that:

$$\frac{\partial E}{\partial \omega_{\mathrm{i}}} =< \varphi_{\mathrm{i}}(\omega_{\mathrm{i}})| -\frac{1}{2}\nabla^2 + v|\varphi_{\mathrm{i}}(\omega_{\mathrm{i}}) > + \int \left(\frac{\delta(J+E_{xc})}{\delta\tilde{n}}\right)\left(\frac{\partial\tilde{n}}{\partial\omega_{\mathrm{i}}}\right) = \varepsilon_{\mathrm{i}}$$

**Janak's Theorem**

J.F. Janak, PRB 18, 7165 (1978)

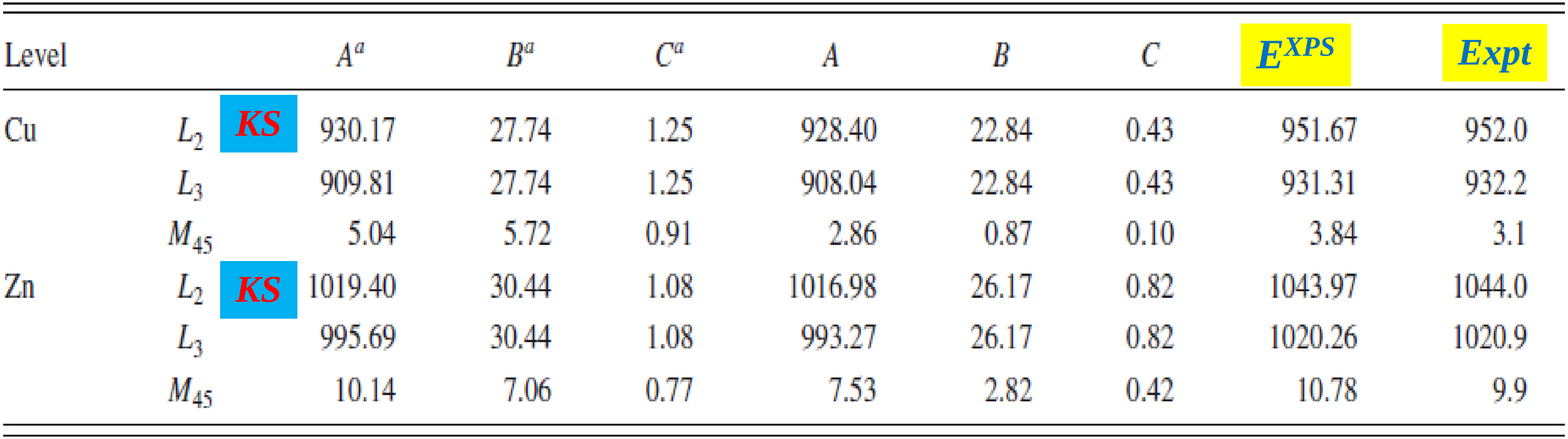
Janak’s theorem can be used to evaluate ***ab initio* photoemission (XPS) energies** by a method closely related to Slater’s transition-state theory.
We assume that the **total energy** of the system with fractional $\omega_i$ electrons removed from the level |*i*> is given **by the power expansion**:

$$E(N-\omega_i) = E(N) + A_i\omega_i + B_i\omega_i^2 + C_i\omega_i^3$$

$$-\varepsilon_i^{KS} = A_i + 2B_i\omega_i + 3C_i\omega_i^2$$

$$E_i^{XPS} = E(\mathrm{N}-1_i) - E(N) = A_i + B_i + C_i$$

**Supercell calculations**



| Level | | | $A^a$ | $B^a$ | $C^a$ | $A$ | $B$ | $C$ | $E^{XPS}$ | *Expt* |
|---|---|---|---|---|---|---|---|---|---|---|
| Cu | $L_2$ | ***KS*** | 930.17 | 27.74 | 1.25 | 928.40 | 22.84 | 0.43 | 951.67 | 952.0 |
| | $L_3$ | | 909.81 | 27.74 | 1.25 | 908.04 | 22.84 | 0.43 | 931.31 | 932.2 |
| | $M_{45}$ | | 5.04 | 5.72 | 0.91 | 2.86 | 0.87 | 0.10 | 3.84 | 3.1 |
| Zn | $L_2$ | ***KS*** | 1019.40 | 30.44 | 1.08 | 1016.98 | 26.17 | 0.82 | 1043.97 | 1044.0 |
| | $L_3$ | | 995.69 | 30.44 | 1.08 | 993.27 | 26.17 | 0.82 | 1020.26 | 1020.9 |
| | $M_{45}$ | | 10.14 | 7.06 | 0.77 | 7.53 | 2.82 | 0.42 | 10.78 | 9.9 |

G. Fratesi et al, PRB 78, 205111 (2008)

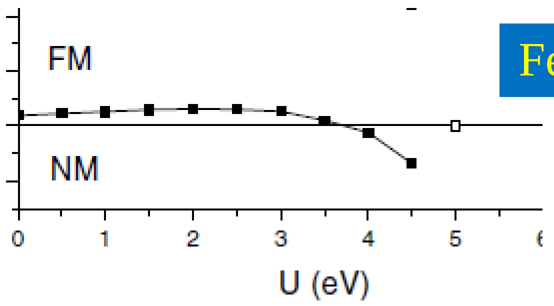
# LDA+U

V. Anisimov et al, PRB 44, 943 (1991)

It allows a treatment of strongly correlated systems. The LDA+U functional is adapted from the Hubbard model selecting a number of localized orbitals whose electronic correlation is described in a specific way:

$$E^{LDA+U}[n] = E^{LDA}[n] + E^{Hub}\left[\{n_m^{I\sigma}\}\right] + \\ -E^{DC}\left[\{n^{I\sigma}\}\right]$$

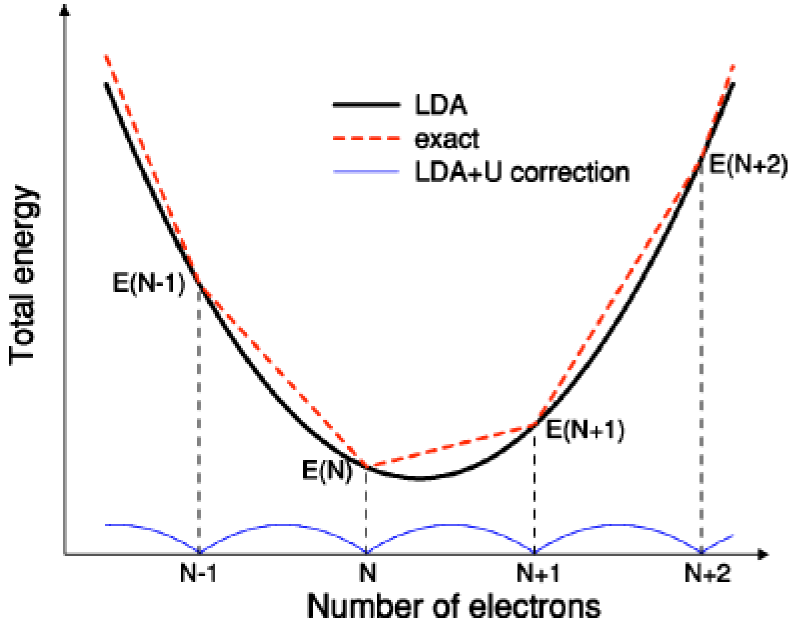
empirical U



FeAl

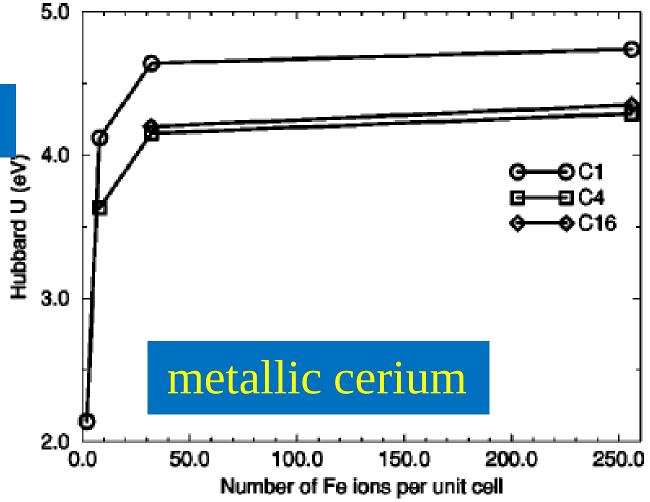
P. Mohn et al, PRL 87, 196401 (2001)

M. Cococcioni and S. de Gironcoli, PRB 71, 035105 (2005)



The curvature of the LDA energy is associated with the spurious self-interaction of fractional electrons introduced in the system and is amended by U.

U by DFT



metallic cerium

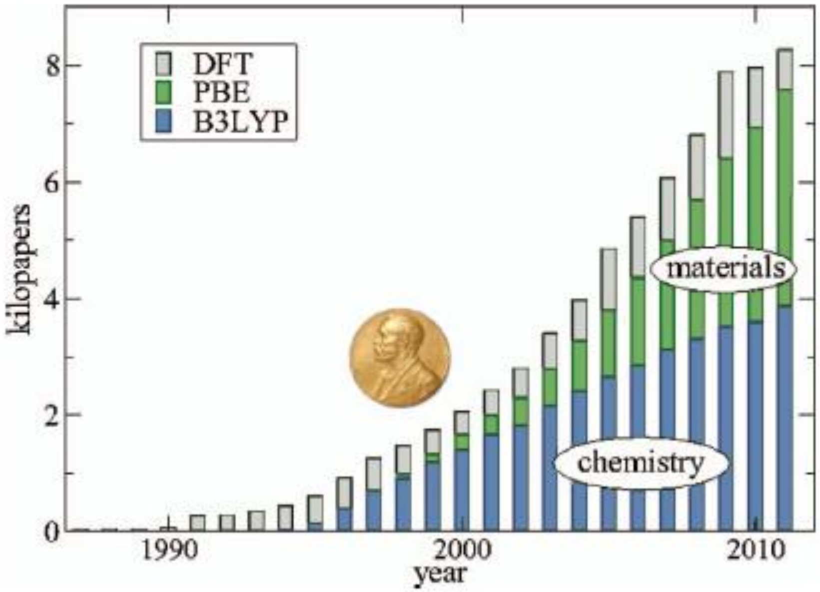
# Beyond LDA: the GGA approach

Some **non-locality** was first introduced in exchange correlation functional by a gradient expansion of the density (GEA).

J.P. Perdew, PRL 55, 1665 (1985)

Then **the generalized gradient approximation (GGA)** was proposed to set **physical constraints on the exchange and correlation holes**, satisfied by the uniform electron gas (LSDA) but not by GEA, obtaining much improved results.

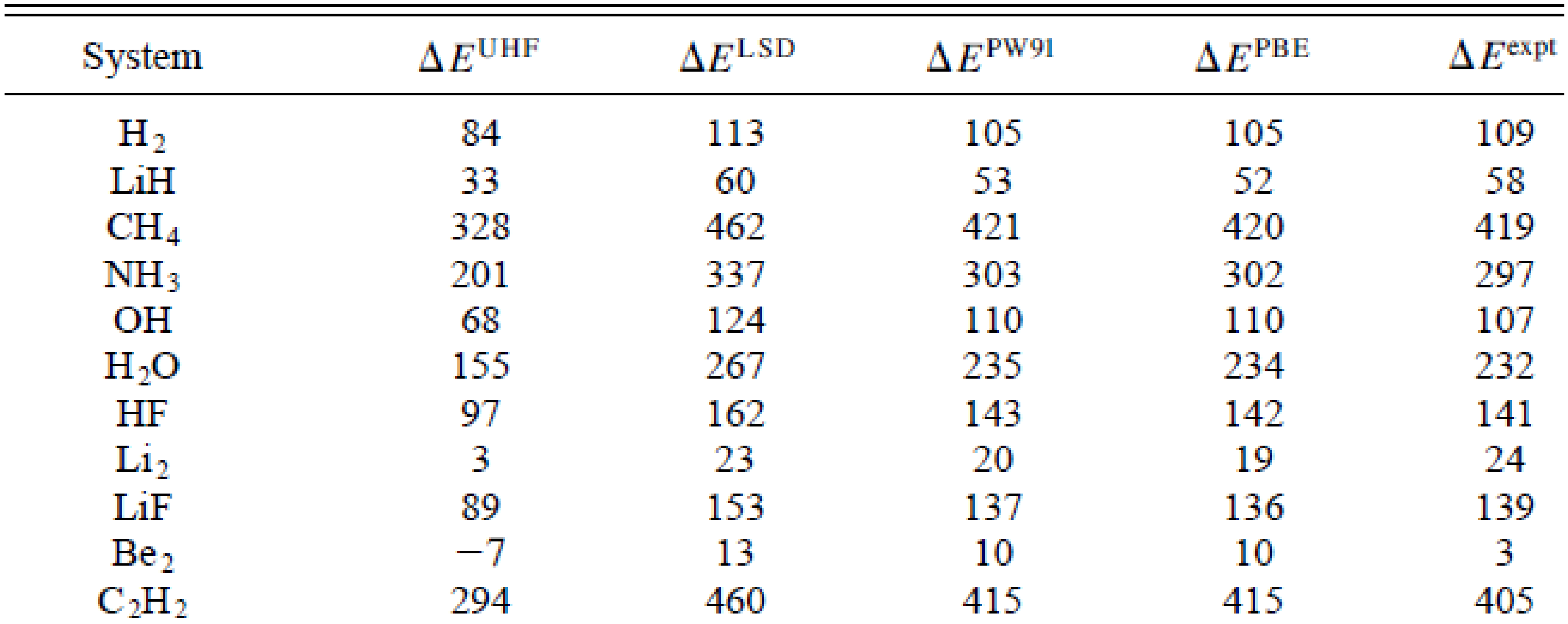
FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.



K. Burke, JCP 136, 150901 (2012)

# PBE functional

The PBE functional is based on PW91, but avoiding cumbersome features. It contains a unified real space cutoff for exchange and correlation holes to avoid spurious long range parts in the second order gradient expansion of density. PBE does not have any fitting parameters, retains correct features of LSD, combines them with the most energetically important features of gradient-corrected nonlocality.



| System | $\Delta E^{\mathrm{UHF}}$ | $\Delta E^{\mathrm{LSD}}$ | $\Delta E^{\mathrm{PW91}}$ | $\Delta E^{\mathrm{PBE}}$ | $\Delta E^{\mathrm{expt}}$ |
|---|---|---|---|---|---|
| $H_2$ | 84 | 113 | 105 | 105 | 109 |
| LiH | 33 | 60 | 53 | 52 | 58 |
| $CH_4$ | 328 | 462 | 421 | 420 | 419 |
| $NH_3$ | 201 | 337 | 303 | 302 | 297 |
| OH | 68 | 124 | 110 | 110 | 107 |
| $H_2O$ | 155 | 267 | 235 | 234 | 232 |
| HF | 97 | 162 | 143 | 142 | 141 |
| $Li_2$ | 3 | 23 | 20 | 19 | 24 |
| LiF | 89 | 153 | 137 | 136 | 139 |
| $Be_2$ | −7 | 13 | 10 | 10 | 3 |
| $C_2H_2$ | 294 | 460 | 415 | 415 | 405 |

J.P. Perdew, K. Burke and M. Erzenhof, PRL 77, 3865 (1996)

# B3LYP functional

This is a so called **GGA hybrid functional** since inclusion of the exact exchange $E_{xx}$ determines a non-local potential in the KS equation. $E_{xx}$ expressed in terms of KS orbitals.

A,D. Becke, JCP 98, 1372 (1993)

O. Salomon et al, JCP 117, 4729 (2002)

$$E_{xc}^{B3LYP} = E_x^{LSDA} + c_1 E_x^{B88} + c_2 E_c^{LYP} + (1 - c_2) E_c^{VWN} + c_3 \left[ E_{xx} - E_x^{LSDA} \right]$$

$E_x^{B88}$ Gradient correction to exchange

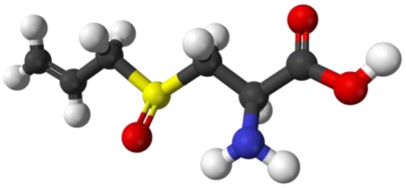
$E_c^{LYP}$ B88 exchange and correlation by gradients of HF second order density matrix and of the local kinetic energy

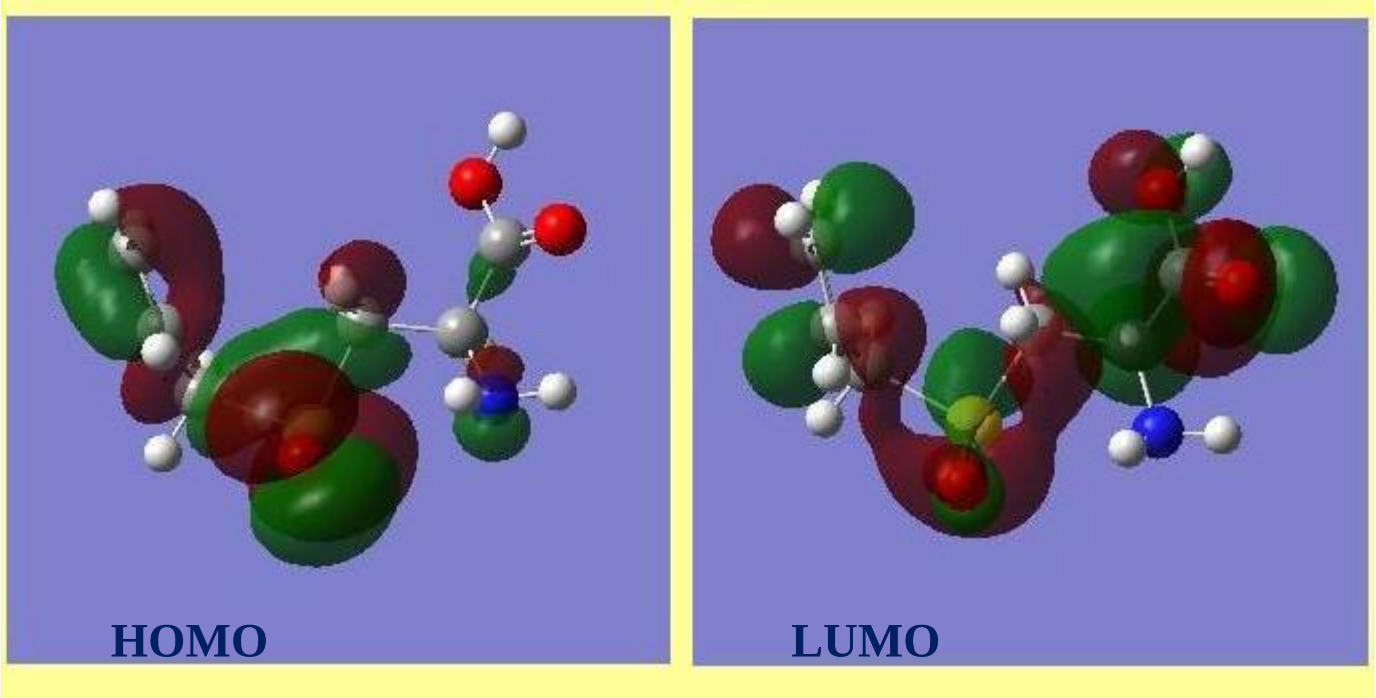
$E_c^{VWN}$ Adapted from the random phase approximation (RPA) for a uniform electron gas in the high density limit

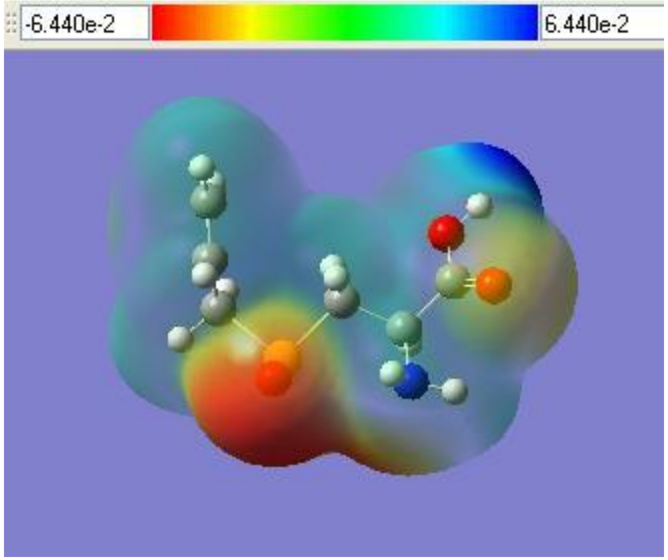
The three parameters have been taken **to reproduce** a set of atomization energies, ionization potentials, proton affinities, and total atomic energies.
The mixed character of this functional is probably one of the reasons for its success.

# Alliin molecule

C, H, S, N, O

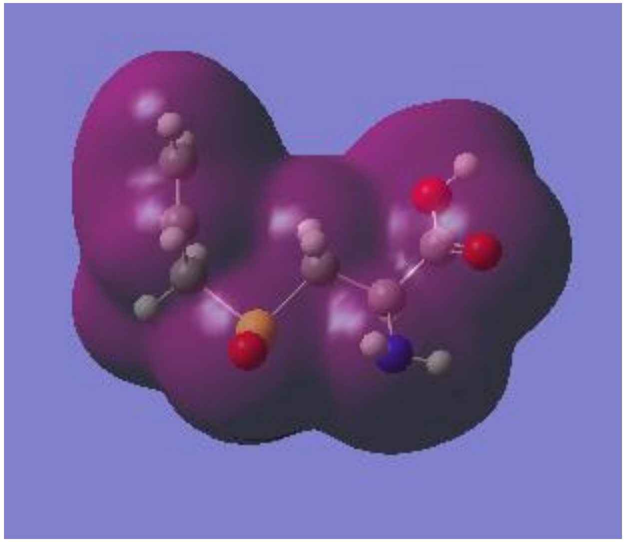






Electron total density surface coloured by ESP

From Turin University website

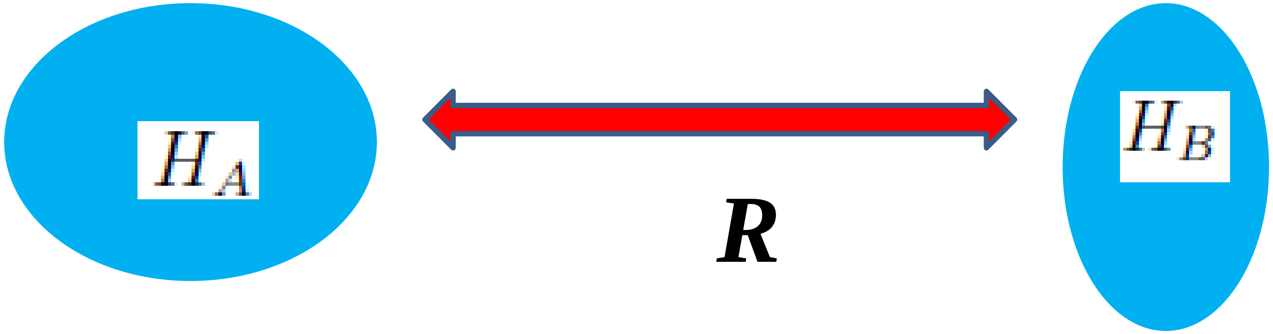


Electron total density surface

# Van der Waals (VdW) (dispersion) interaction

**vdW is fundamental** in several fields: atoms, molecules, solid state, chemistry, biology

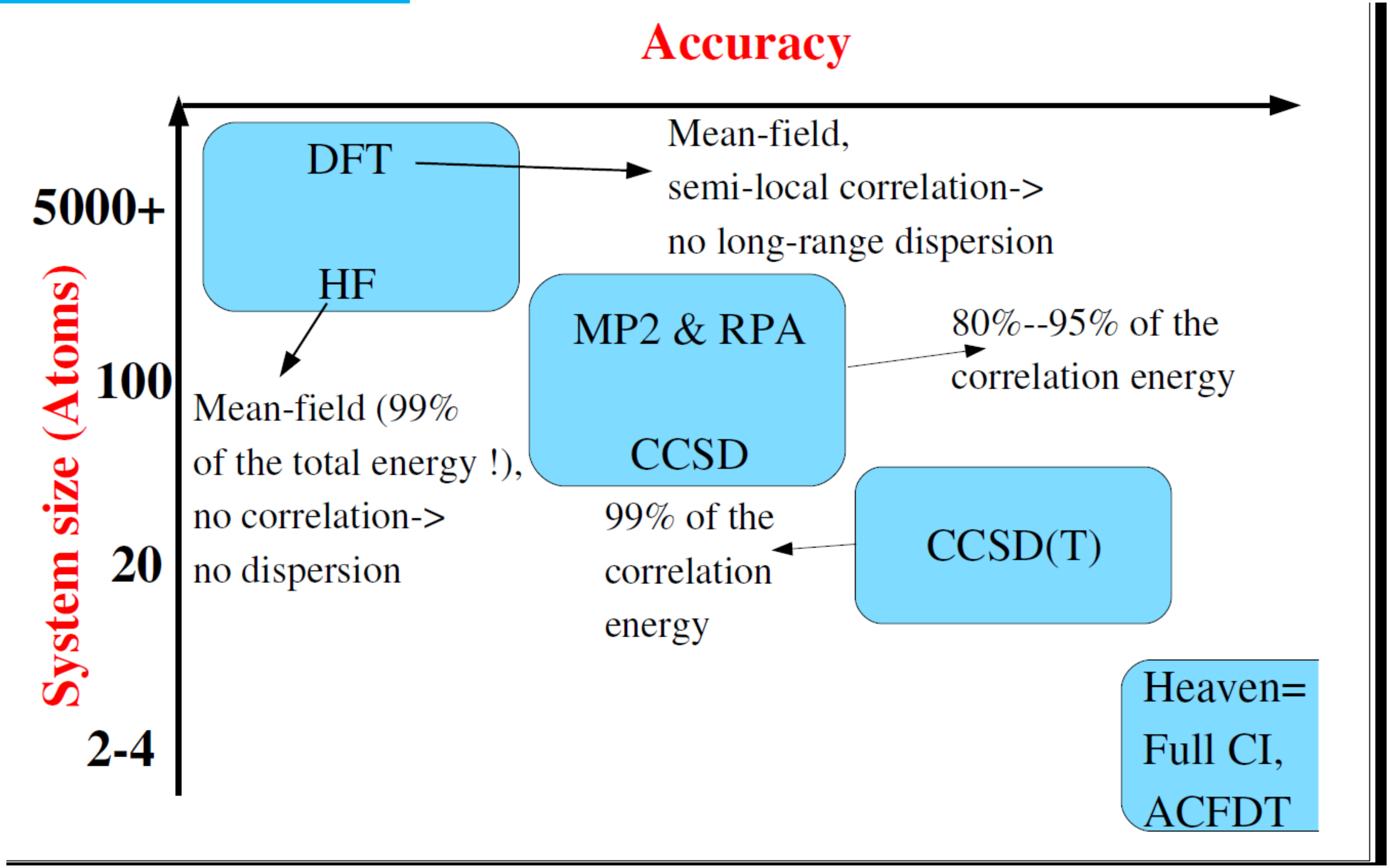
**Dispersion** (London) forces are exhibited by **nonpolar molecules** because of the **correlated motion** of the electrons in interacting molecules. For this reason, the electron density in a molecule becomes redistributed in proximity to another molecule. This is frequently described as formation of "**instantaneous dipoles**" .



$$H_A + H_B + H_1 = H \qquad E_2 = E_{vdW} = \sum_{a,b} \frac{< 00|H_1|ab >< ab|H_1|00 >}{E_{00} - E_{ab}}$$

$$E_{vdW} \simeq -f_6 \frac{C_6}{R^6} - f_8 \frac{C_8}{R^8} - f_{10} \frac{C_{10}}{R^{10}} - \dots\dots$$

# Size and accuracy



Accuracy

System size (Atoms)

5000+

100

20

2-4

DFT

HF

Mean-field,
semi-local correlation->
no long-range dispersion

Mean-field (99%
of the total energy !),
no correlation->
no dispersion

MP2 & RPA

CCSD

80%--95% of the
correlation energy

CCSD(T)

99% of the
correlation
energy

Heaven=
Full CI,
ACFDT

For materials two approaches are considered for the vdW interaction:

- **Non-local functionals**
- **Interatomic methods**

# The LL approach

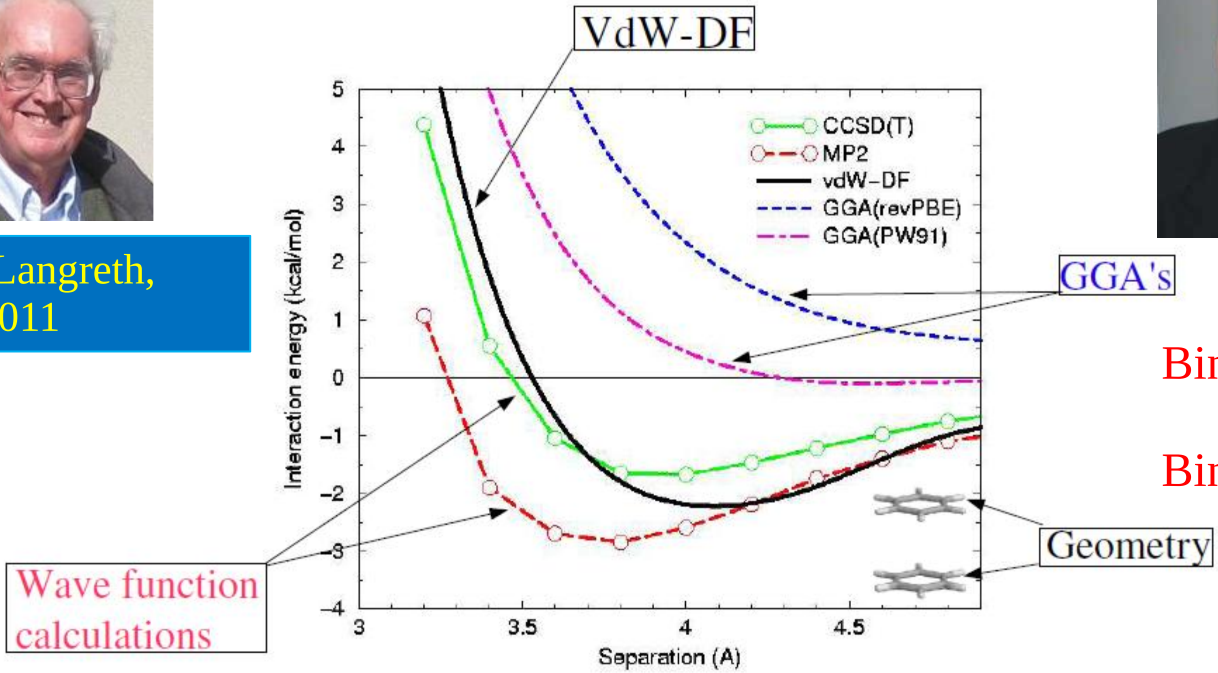
M. Dion et al, PRL 92, 246401 (2004)

Seamless DFT approach. Polarization expressed in terms of **a local dielectric function** within RPA:

$$E_c[n] = E_c^{LDA}[n] + E_c^{nl}[n]$$

Benzene-benzene interaction

David Langreth, 1937-2011



Bengt Lundquist
Chalmers University,
Sweden

Binding distance 5-10% too long

Binding energy too low 50%

# Interatomic methods

$$E_{xc} = E_x^{GGA} + E_c^{LDA-GGA} + E_{c,vdW}^{nl}$$

$$E_{vdW} \simeq -f_6\frac{C_6}{R^6} - f_8\frac{C_8}{R^8} - f_{10}\frac{C_{10}}{R^{10}} - \dots\dots$$

Fritz London,
Breslau, 1900-54

## Semi-empirical methods

A.D. Becke, JCP 107, 8554 (1997)

S. Grimme, J. Comp. Chem. 27, 1787 (2006)

Semiempirical Becke's GGA B97-D (energy functionals with gradient contributions expanded up to second order), parameterized by including **damped atom-pairwise of the form: $C_6 R^{-6}$** obtained by suitably fitting the experimental data.

S. Grimme et al J. Comp. Chem. 32, 1456 (2011)

Later the vdW correction (DFT-D3(BJ) (also with a term proportional to $C_8 R^{-8}$ ) optimized to several GGA functionals.

## The TS method

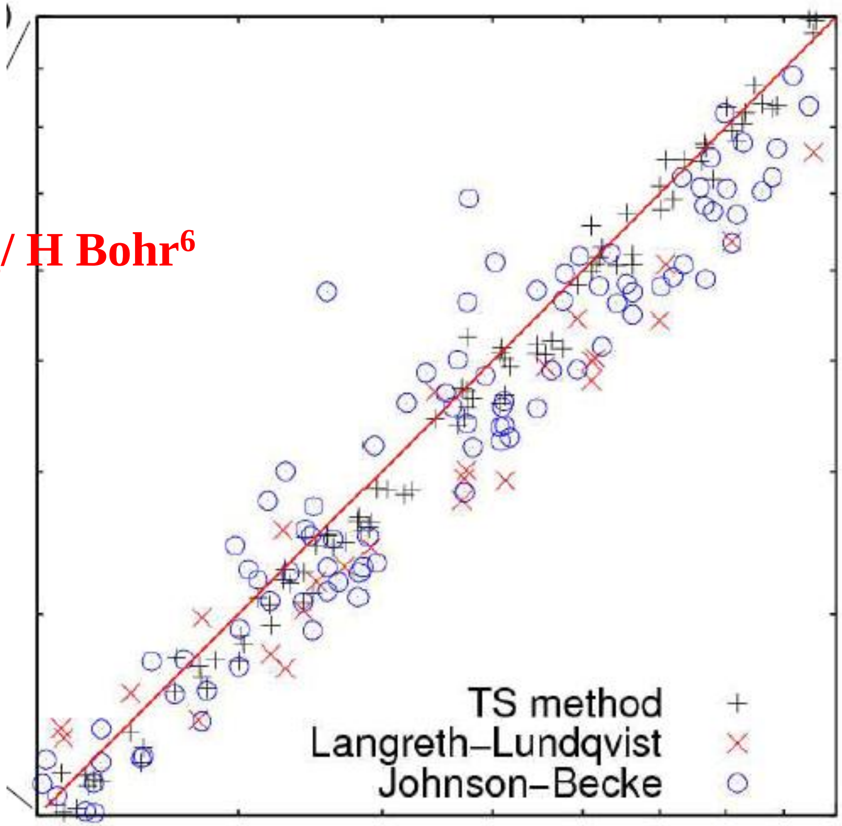
To compute the vdW interaction on firmer grounds $C_6$ and $R_0$ are derived from **the electron density of a molecule or a solid** (by DFT-GGA) and accurate reference data for the free atoms.

Pairwise summation of $C_6$ for a molecule

One parameter in the damping function

Later long range electron screening in solids and molecules (PBE+vdW)

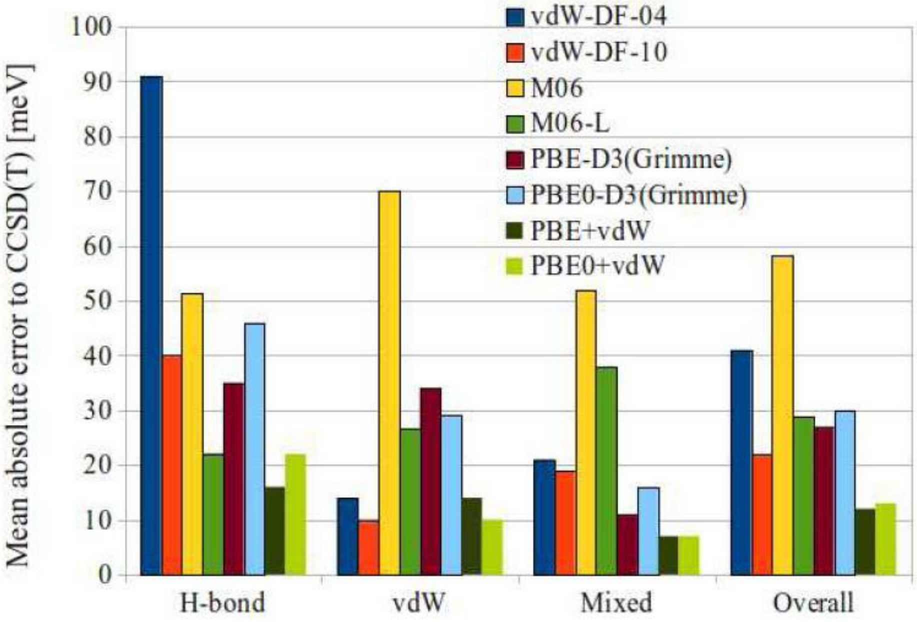
A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009)



**$C_6$/ H Bohr$^6$**

**$C_6$/ H Bohr$^6$ reference systems**

Performance of DFT+vdW for S22 (Mean Absolute Error)



A. Tkatchenko et al, PRL 102, 236402 (2012)

# Conclusions

- **First principle determination** of many-electron system properties (mainly ground state): methods, achievements, questions.

- **Excited states**, apart from HF derived methods (CI,CC), require different approaches:
  - TDDFT (**time-dependent external potential**): Excited states to be determined by the poles of the density-density correlation function

  - **Many-body perturbation theory**:
  - **Single particle** excitations by quasi-particle energy
  - **Two particle excitation** by the Bethe-Salpeter equation.

A. Abrikosov, Moscow (1928- )

E.K.U. Gross, MPI, Halle (Germany)

G. Onida et al, RMP Grimme et al J. Comp. Chem. 74, 601 (2002)

$$I_\lambda =< \lambda|h_i|\lambda >$$

$$\delta E - \sum_\lambda \varepsilon_\lambda \delta < u_\lambda|u_\lambda >= 0$$

$$\left[h_\mathrm{i} + V^d(\mathbf{r}_i) - V^{ex}(q_i)\right] u_\lambda(q_i) = \varepsilon_\lambda u_\lambda(q_i)$$

$$\varrho(\mathbf{r}_\mathrm{i}, \mathbf{r}_\mathrm{j}) = \sum_\mu u_\mu(\mathbf{r}_\mathrm{i})\, u^*_\mu(\mathbf{r}_\mathrm{j})$$

$$V^d(\mathbf{r}_\mathrm{i}) = \int \varrho(\mathbf{r}_\mathrm{j})\,\frac{1}{r_{ij}} d\mathbf{r}_\mathrm{j}$$

$$V^{ex}(q_i)u_\lambda(q_i) = \delta_{m_s^\lambda, m_s^\mu}\left[\int \rho(\mathbf{r}_\mathrm{i}, \mathbf{r}_\mathrm{j})\,\frac{1}{r_{ij}} u_\lambda(\mathbf{r}_\mathrm{j}) d\mathbf{r}_\mathrm{j}\right] \chi_{\frac{1}{2}\ m_s^\mu}$$

$$e^{\hat{T}_1+\hat{T}_2} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^{\,2}\right) + \left(\hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^{\,3}\right) + \left(\frac{1}{2}\hat{T}_2^{\,2} + \frac{1}{2}\hat{T}_2\hat{T}_1^{\,2} + \frac{1}{24}\hat{T}_1^{\,4}\right)$$