Reduced–density-matrix-functional theory: Towards an ab-initio description of strongly correlated systems

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Outline

- Basics of Reduced-Density-Matrix-Functional Theory (RDMFT)
- Approximate functionals
- RDMFT results for molecules
- RDMFT results for the e-gas
- Calculation of photo-electron spectrum within RDMFT
- RDMFT results for strongly correlated solids

Basics of Reduced Density Matrix Functional Theory

One-body reduced density matrix (1-RDM)

- for integer particle number N:

$$\gamma_N(\vec{r},\vec{r}\,') = N \cdot \int \cdots \int \Psi_N^*(\vec{r},\vec{x}_2,\ldots\vec{x}_N)\Psi_N(\vec{r}\,',\vec{x}_2,\ldots\vec{x}_N)\, d^3x_2 \ldots d^3x_N$$

- for fractional particle number $M = N_o + \omega \ \ (0 \leq \omega \leq 1)$

$$\gamma(\vec{r},\vec{r}\,') = (1-\omega)\,\gamma_{N_0}(\vec{r},\vec{r}\,') + \omega\gamma_{N_0+1}(\vec{r},\vec{r}\,')$$

Diagonalization yields the natural orbitals $\varphi_j(\vec{r})$ and their occupation numbers n_j:

$$\int \gamma\ (\vec{r},\vec{r}\,')\ \varphi_j(\vec{r}\,')\ d^3r' = n_j \varphi_j(\vec{r})$$

Central Theorem by Gilbert (1975): There is a rigorous 1-1 correspondence $\Psi_{gs}(r_1, r_2 \ldots, r_N) \longleftrightarrow \boldsymbol{\gamma(r,r')}$

- Total energy is a unique functional $E[\gamma]$ of the 1-RDM
- Ground-state energy can be calculated by minimizing $E[\gamma]$

$$E_{tot}[\gamma] = E_{kin}[\gamma] + \int v_{ext}(\vec{r})\,\gamma(\vec{r},\vec{r})\,d^3r + E_H[\gamma] + E_{xc}[\gamma]$$

Note: For given $\gamma(\vec{r},\vec{r}')$ the $\{\varphi_j(\vec{r}), n_j\}$ follow from diagonalization, i.e. $n_j = n_j[\gamma], \quad \varphi_j = \varphi_j[\gamma]$

Consequence: Any explicit functional $E\left[n_j\ ,\ \varphi_j(\vec{r})\right]$ is an implicit functional of γ

Functional Minimization

Constraints

- ★ $\sum_i n_i = N$, where N is the number of electrons.
- ★ $\int \phi_i^*(\mathbf{r})\ \phi_j(\mathbf{r})\ d^3r = \delta_{ij}$, orthonormality constraint.
- ★ $0 \le n_i \le 1$, N-representability constraint, guarantees that γ comes from a many-body wavefunction.

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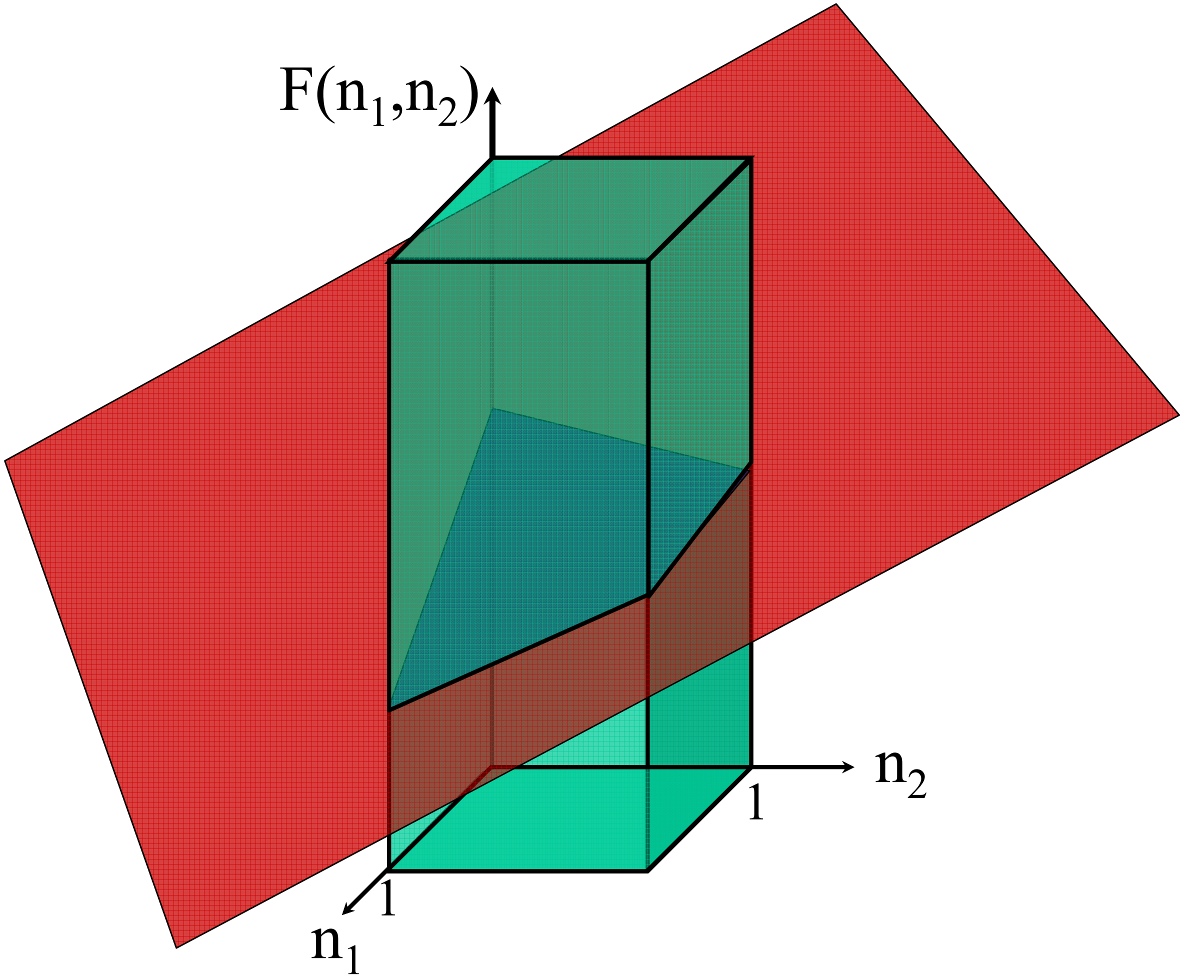
- The first two are enforced through Lagrange multipliers. The quantity to minimize becomes:

$$\mathsf{F} = E_{tot} - \mu \left(\sum_i n_i - N \right) - \sum_{ij} \varepsilon_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

μ: chemical potential.



N-representability condition $0 \leq n_j \leq 1$ generally leads to border minimum.

i.e. one can still minimize but $\frac{\partial F}{\partial n_j} \neq 0$ at minimum

Total-energy functional:

$$E_{tot}[\gamma] = E_{kin}[\gamma] + \int v_{ext}(\vec{r})\,\gamma(\vec{r},\vec{r})\,d^3r + E_H[\gamma] + E_{xc}[\gamma]$$

Three major differences to DFT

- Kinetic-energy functional is known exactly

$$E_{kin} = \int d^3r \int d^3r'\,\delta(\vec{r}-\vec{r}')\left(-\frac{\nabla^2}{2}\right)\gamma(\vec{r},\vec{r}')$$

$$= \sum_{j=1}^{\infty} n_j \left\langle \varphi_j \left| -\frac{\nabla^2}{2} \right| \varphi_j \right\rangle$$

Hence $E_{xc}[\gamma]$ does not contain any kinetic contributions, and therefore there is no adiabatic connection and no coupling-constant-integration formula for E_{xc}.

- There exists no variational equation $\frac{\delta F[\gamma]}{\delta\gamma(\vec{r},\vec{r}')} = 0$

$$\Rightarrow \quad \frac{\delta F}{\delta\gamma(\vec{r},\vec{r}')} = \sum_j \int \underbrace{\frac{\delta F}{\delta\varphi_j^*(\vec{x})}}_{0} \frac{\delta\varphi_j^*(\vec{x})}{\delta\gamma(\vec{r},\vec{r}')} d^3x + \text{c.c.} + \sum_j \frac{\partial F}{\partial n_j} \frac{\delta n_j}{\delta\gamma(\vec{r},\vec{r}')}$$

$$= \sum_j \frac{\partial F}{\partial n_j} \varphi_j^*(\vec{r})\,\varphi_j(\vec{r}') \neq 0$$

- There exists no Kohn-Sham system reproducing the interacting $\gamma(\vec{r},\vec{r}')$, because the non-interacting (KS) 1-RDM is idempotent while the interacting one is not.

FUNCTIONALS

Hartree term

$$E_H[\gamma] = \frac{1}{2}\sum_{j,k} n_j n_k \int d^3r d^3r' \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r})\varphi_k(\vec{r})\varphi_k^*(\vec{r})}{|r - r'|}$$

Approximation for the xc energy functional

$$E_{xc}[\gamma] = -\frac{1}{2}\sum_{j,k} \sqrt{n_j n_k}\,\delta_{\sigma_j\sigma_k} \int d^3r d^3r' \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r})\varphi_k(\vec{r})\varphi_k^*(\vec{r})}{|r - r'|}$$

A.M.K. Müller, Phys. Lett. 105A, 446 (1984)

$$E_H[\gamma] = \frac{1}{2}\sum_{j,k} n_j n_k \int d^3r\, d^3r' \frac{\varphi_j(\vec{r})\,\varphi_j^*(\vec{r})\,\varphi_k(\vec{r}')\,\varphi_k^*(\vec{r}')}{|r - r'|}$$

$$E_{xc}[\gamma] = -\frac{1}{2}\sum_{j,k} \sqrt{n_j n_k}\,\delta_{\sigma_j \sigma_k} \int d^3r\, d^3r' \frac{\varphi_j(\vec{r})\,\varphi_j^*(\vec{r}')\,\varphi_k(\vec{r}')\,\varphi_k^*(\vec{r})}{|r - r'|}$$

Self-interaction correction by
S. Goedecker, C.J. Umrigar, Phys. Rev. Lett. 81, 866 (1998)

$$E_H[\gamma] = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}} n_j n_k \int d^3r d^3r' \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r})\varphi_k(\vec{r}')\varphi_k^*(\vec{r}')}{|r - r'|}$$

$$E_{xc}[\gamma] = -\frac{1}{2}\sum_{\substack{j,k \\ j\neq k}} \sqrt{n_j n_k}\,\delta_{\sigma_j\sigma_k} \int d^3r d^3r' \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_k(\vec{r}')\varphi_k^*(\vec{r})}{|r - r'|}$$

All presently known approximations have the form

$$E_{xc}[\gamma] = -\frac{1}{2}\sum_{j,k} f(n_j,n_k) \int d^3r\, d^3r' \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_k(\vec{r}')\varphi_k^*(\vec{r})}{|r-r'|}$$

“power functional” $f(n_j,n_k) = (n_j n_k)^\alpha$

S. Sharma, J.K. Dewhurst, N.N. Lathiotakis and E.K.U.G., Phys. Rev. B 78 (Rapid Comm.), 201103 (2008)

$\alpha = 1$ leads to Hartree-Fock

$\alpha = 1/2$ Müller functional

The BBC functionals

- **Hierarchy of corrections to the Müller functional**
- **key idea: Distinction between strongly and weakly occupied orbitals**

O. Gritsenko, K. Pernal, E.J. Baerends, *JCP* **122**, 204102 (2005).

The BBC functionals

- **Hierarchy of corrections to the Müller functional**
- **key idea: Distinction between strongly and weakly occupied orbitals**

- BBC1: Sign change of f, if both orbitals are weakly occupied:

$$f(n_i,n_j)=\begin{cases} -\sqrt{n_i\, n_j}, & i, j \text{ weakly occupied,} \\ \sqrt{n_i\, n_j}, & \text{otherwise.} \end{cases}$$

- BBC2: Additionally, omission the square root if both orbitals are strongly occupied:

$$f(n_i,n_j)=\begin{cases} -\sqrt{n_i\, n_j}, & \text{for } i, j \text{ weakly occupied,} \\ n_i\, n_j, & \text{for } i, j \text{ strongly occupied,} \\ \sqrt{n_i\, n_j}, & \text{otherwise.} \end{cases}$$

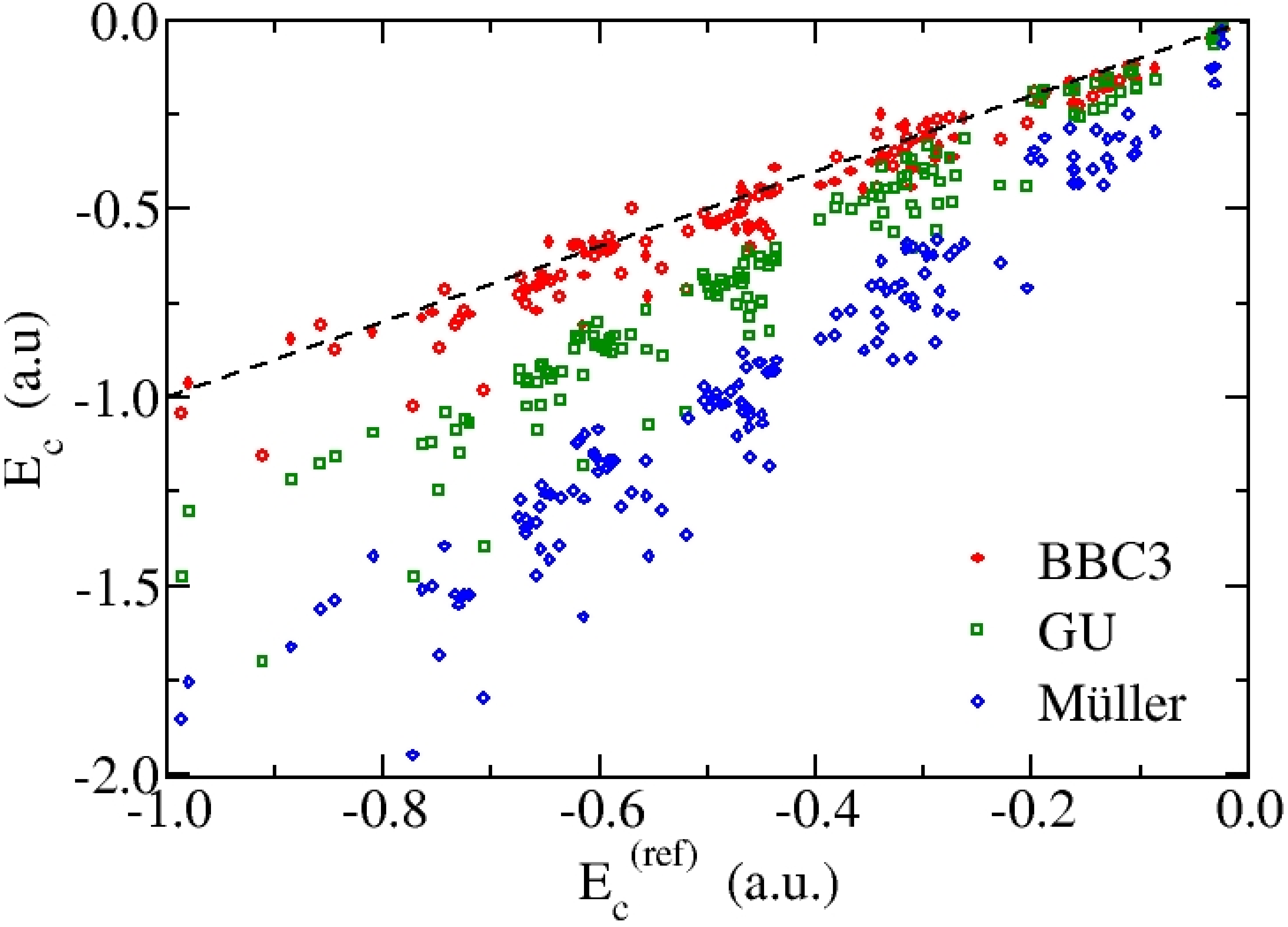
- BBC3: Inclusion of anti-bonding in the list of strongly occupied orbitals, unless it interacts with bonding.
  Removal of SI terms.

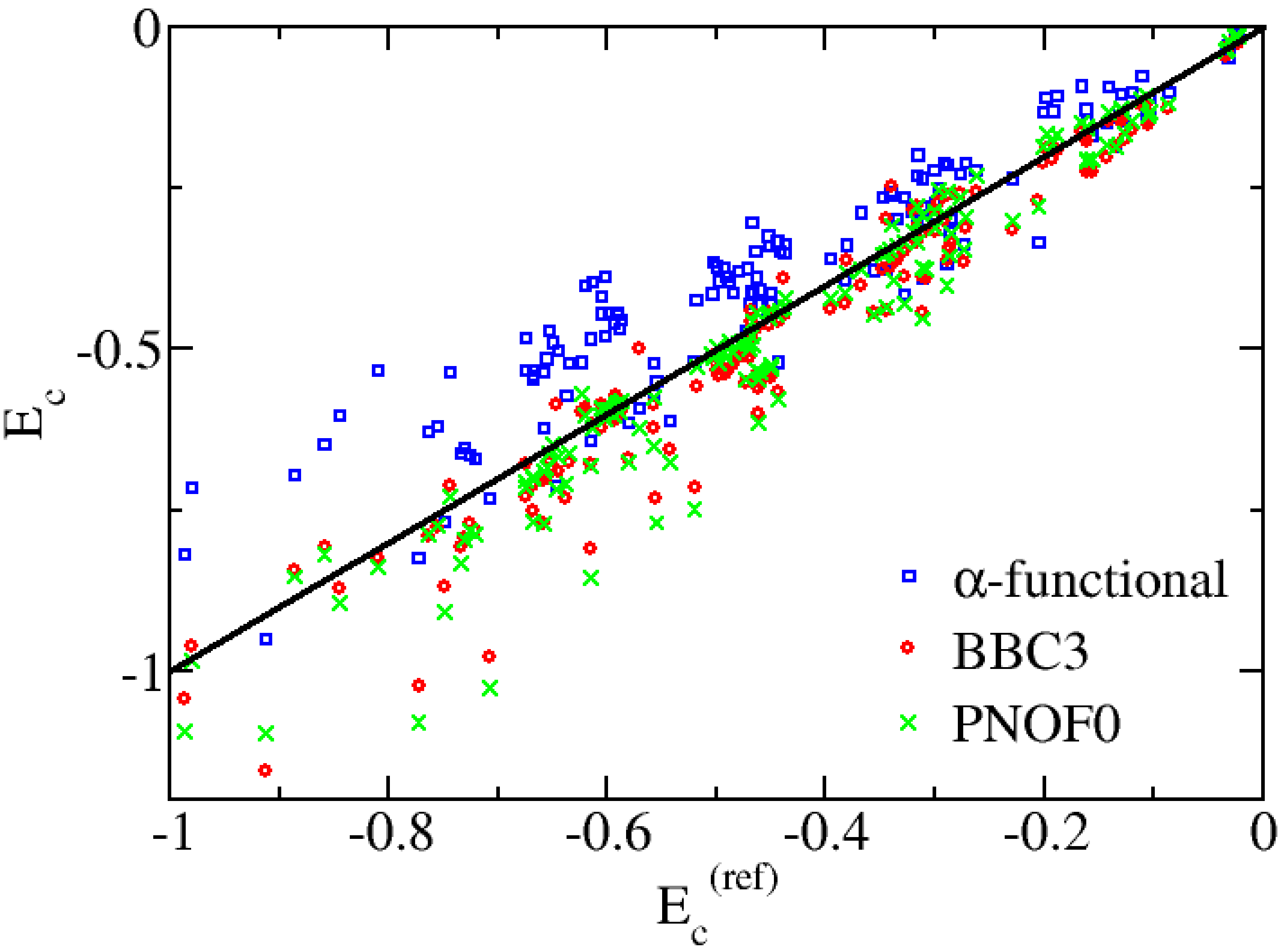
O. Gritsenko, K. Pernal, E.J. Baerends, *JCP* **122**, 204102 (2005).

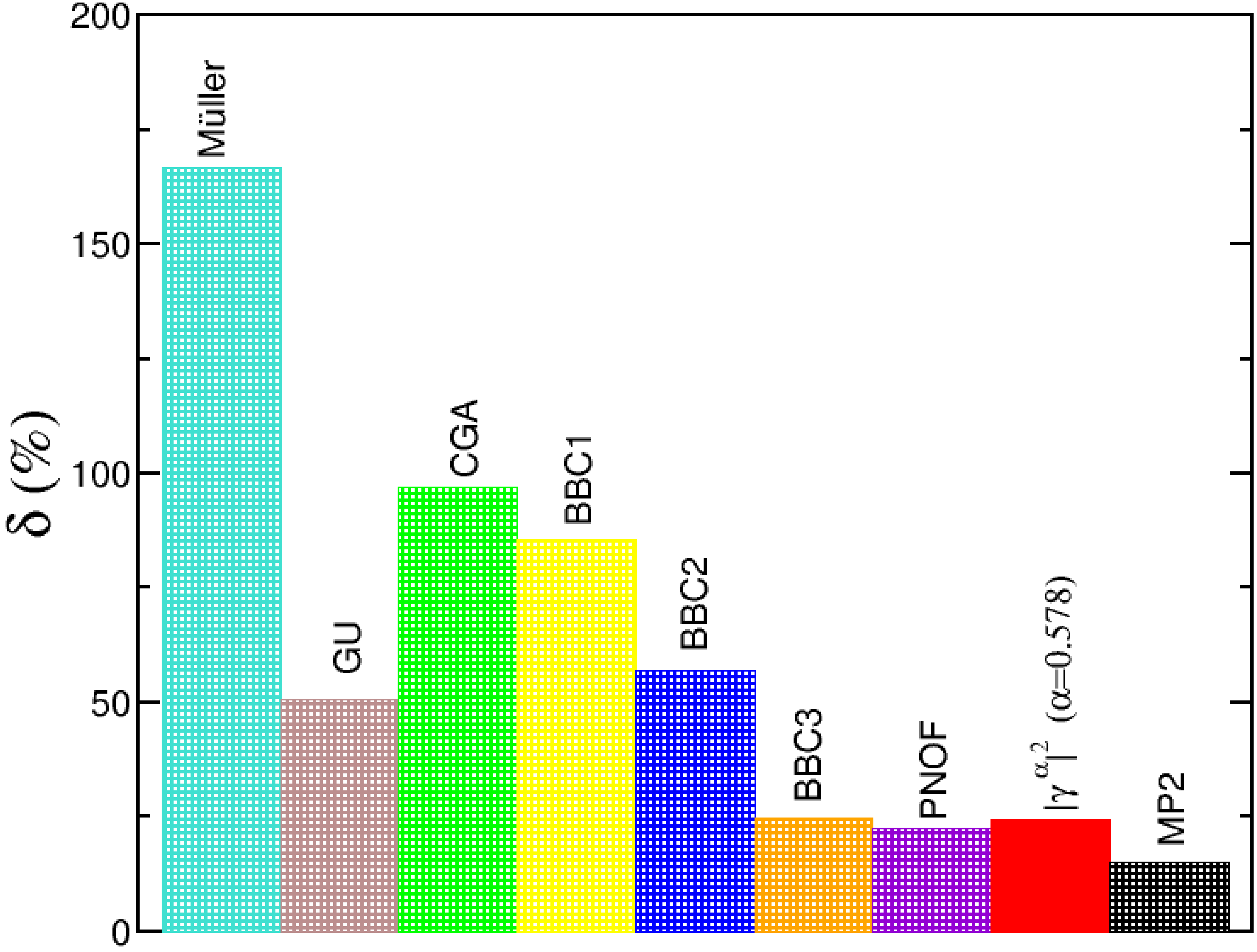
★ **G2/97 test set of molecules [1]:**
148 neutral molecules including 29 radicals, 35 non-hydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons and 15 inorganic hydrides.

★ Cartesian 6-31G* Gaussian basis-set

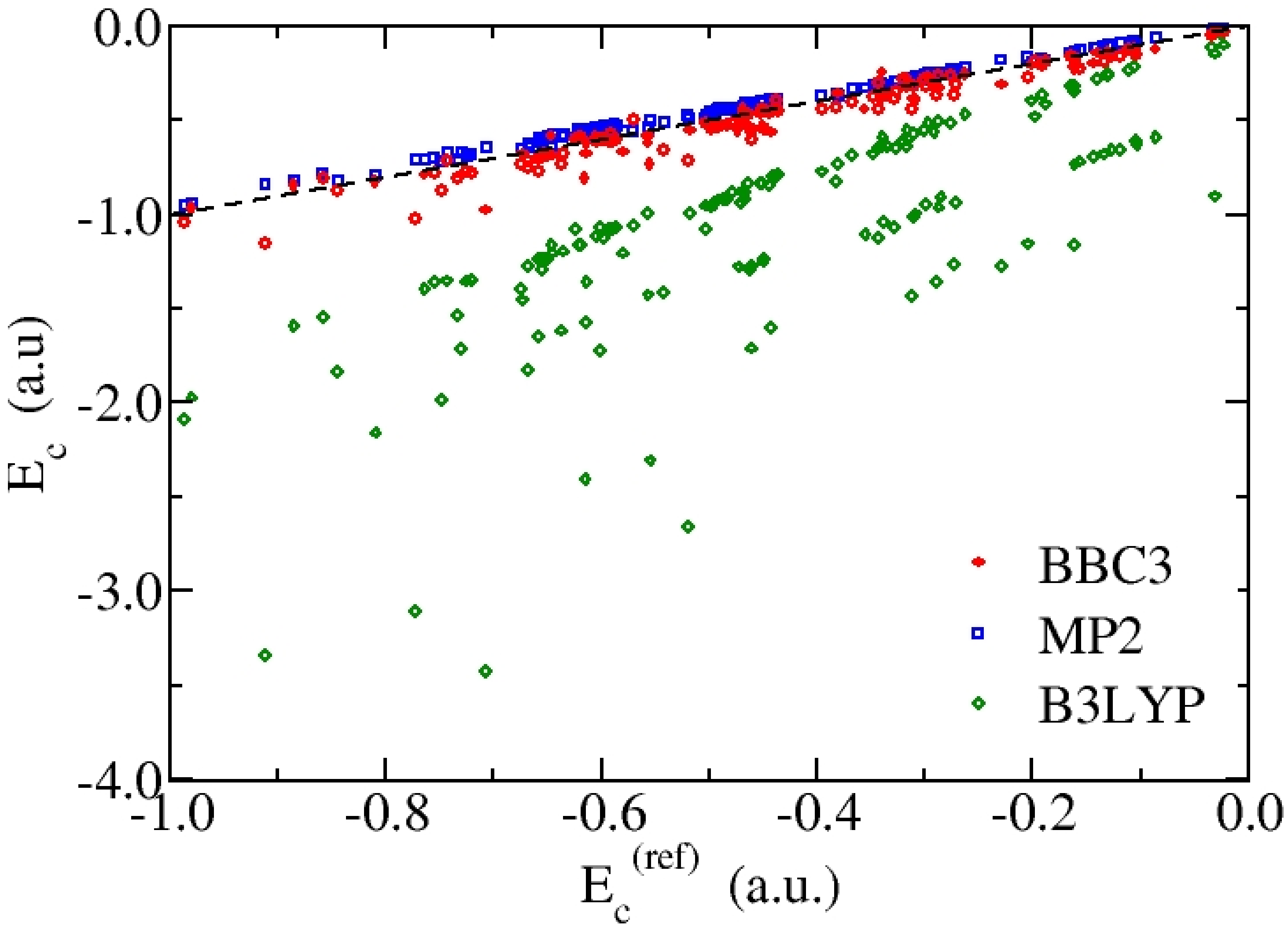
L.A. Curtiss et al., *JCP* **106**, 1063 (1997); *ibid*. **109**, 42 (1998).


0.0
-0.5
-1.0
-1.5
-2.0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E_c (a.u)
$E_c^{(ref)}$ (a.u.)
BBC3
GU
Müller

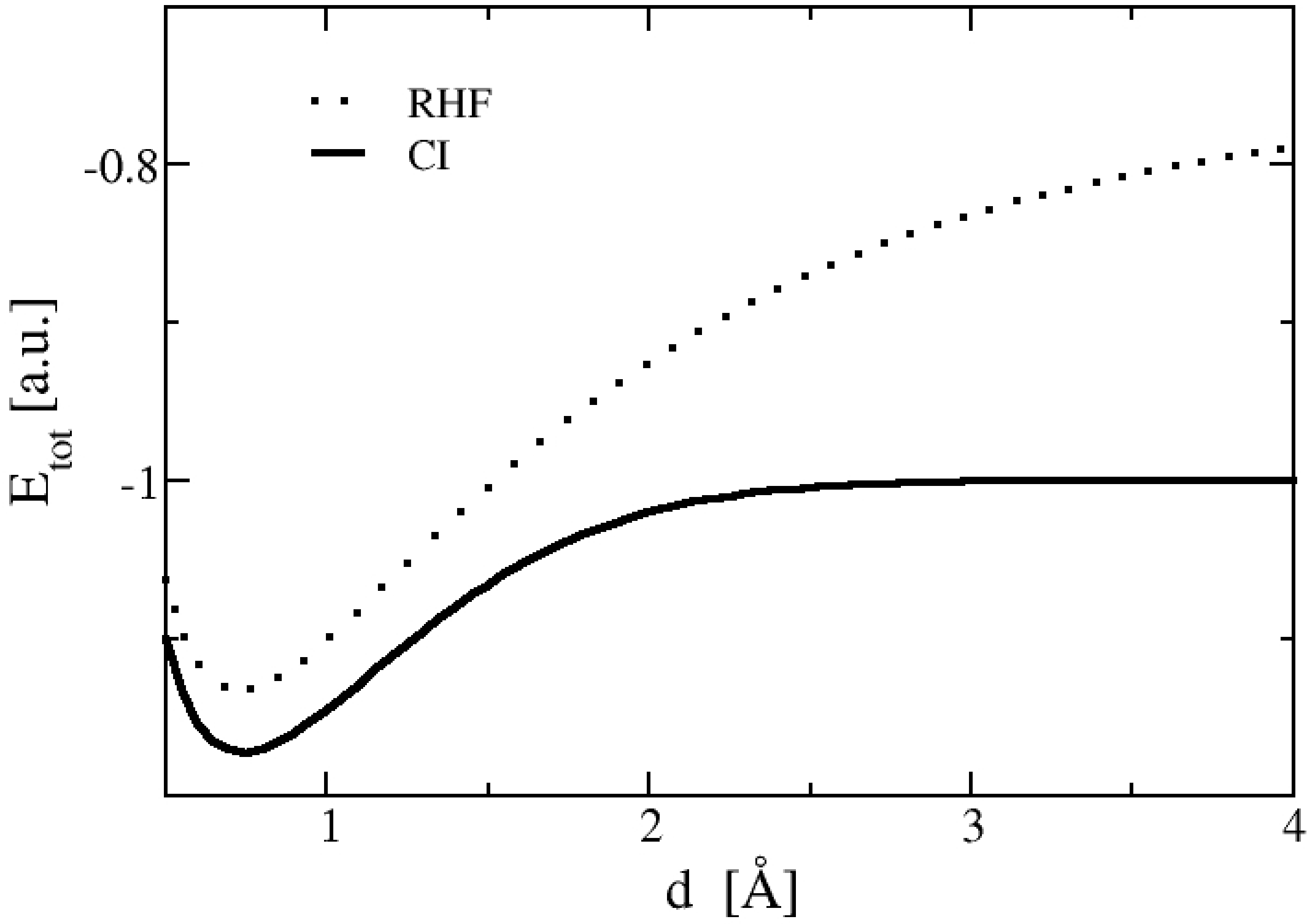

0
-0.5
-1
E_c
-1
-0.8
-0.6
-0.4
-0.2
0
$E_c^{(ref)}$
α-functional
BBC3
PNOF0



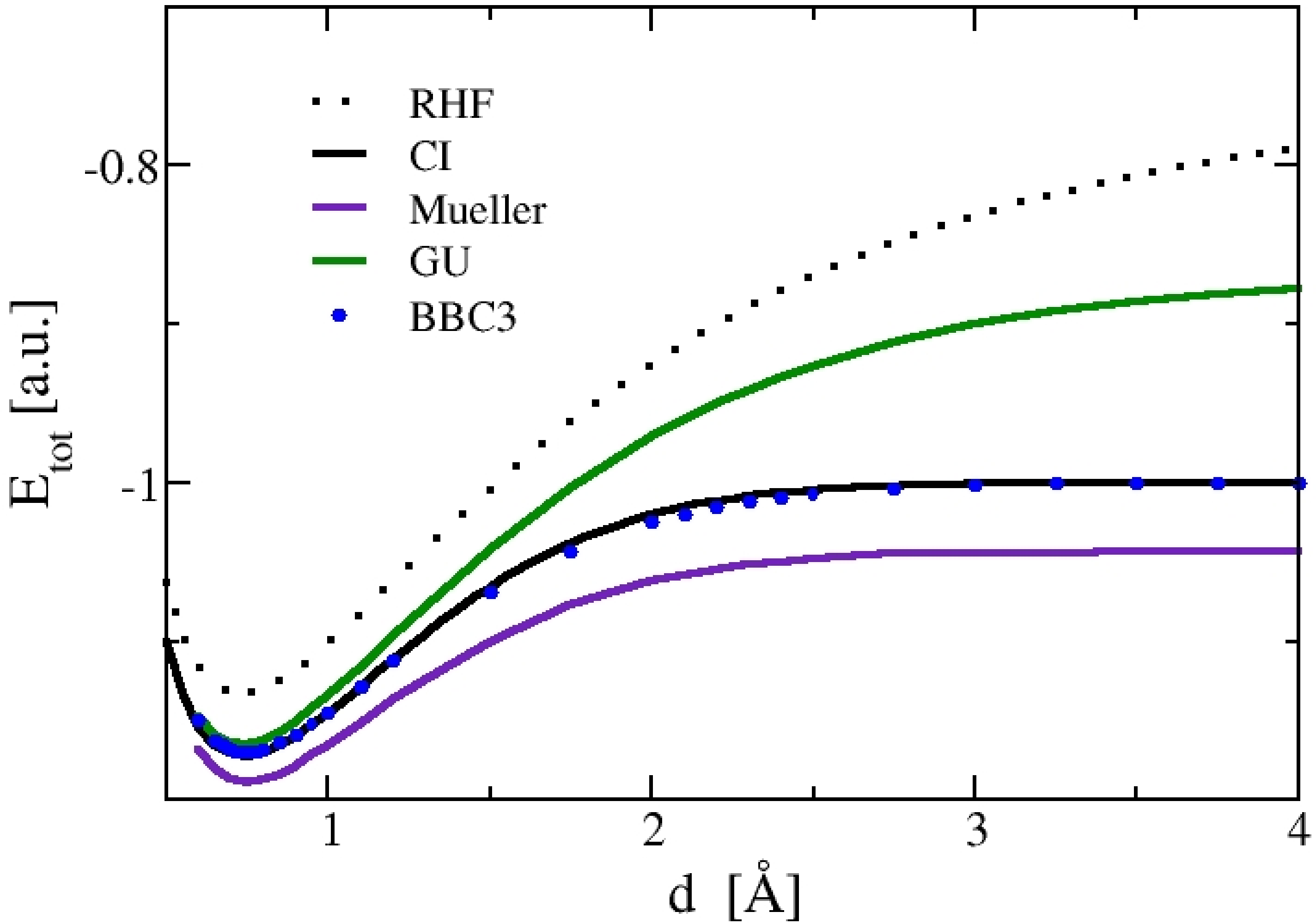
δ (%)
200
150
100
50
0
Müller
GU
CGA
BBC1
BBC2
BBC3
PNOF
$|\gamma^{\alpha}|^2$ (α=0.578)
MP2


0.0
-1.0
-2.0
-3.0
-4.0
E_c (a.u)
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
$E_c^{(ref)}$ (a.u.)
BBC3
MP2
B3LYP

Application to stretched H_2



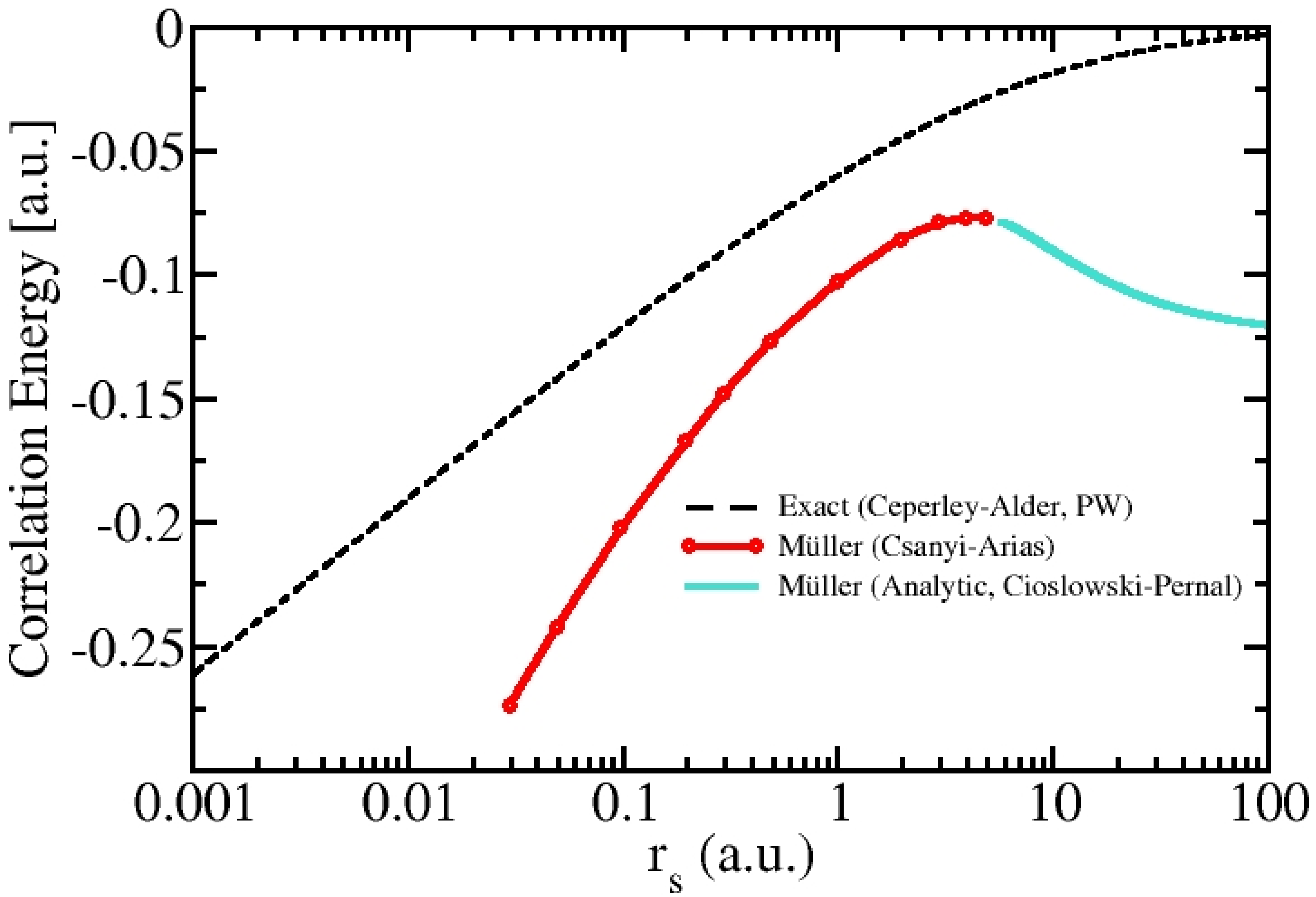
Application to stretched H_2



Results for the uniform electron gas

Numerical results for the Müller functional

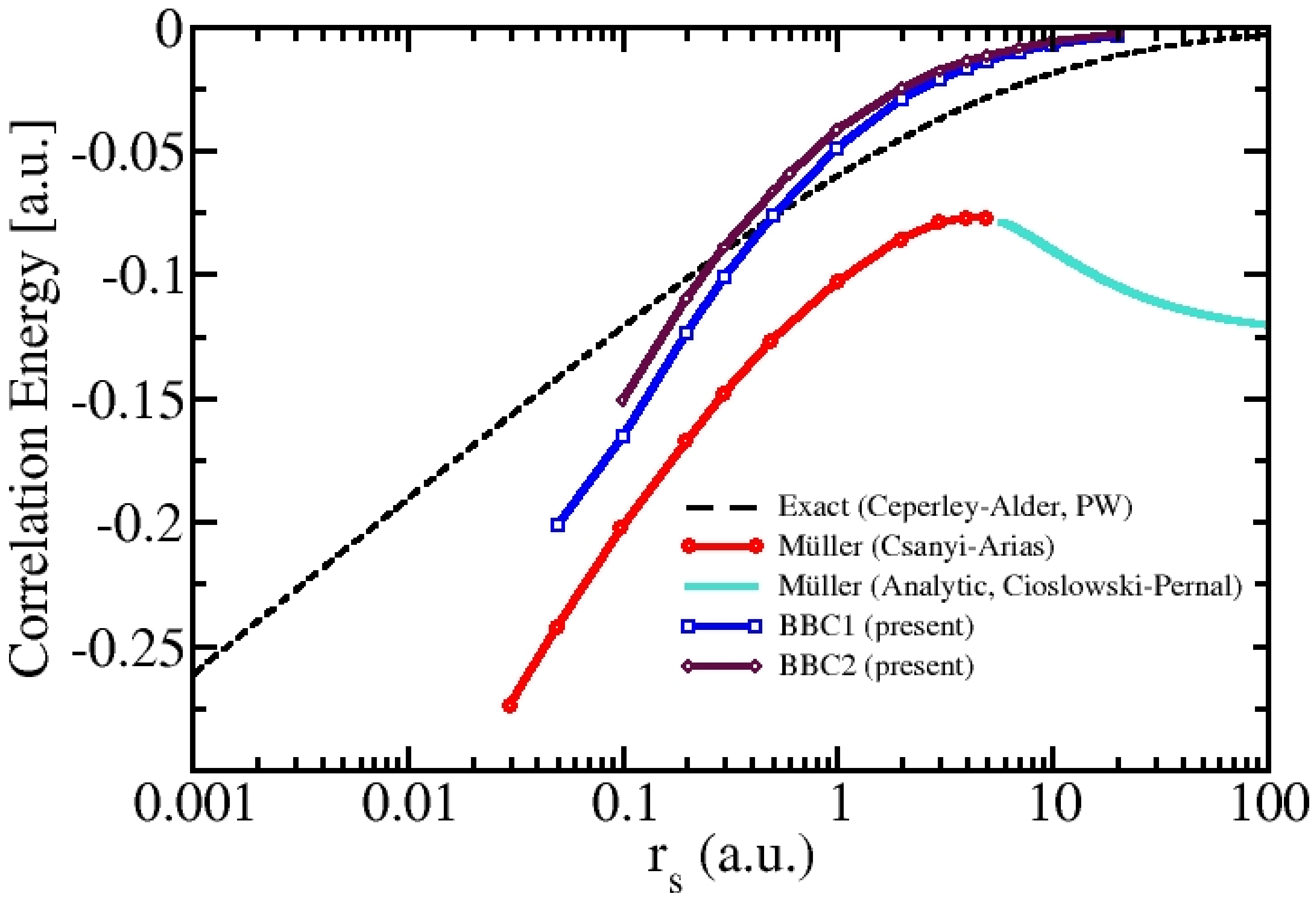
Csànyi-Arias (*PRB* **61**, 7348 (2000)):



Correlation energy of the homogeneous electron gas.

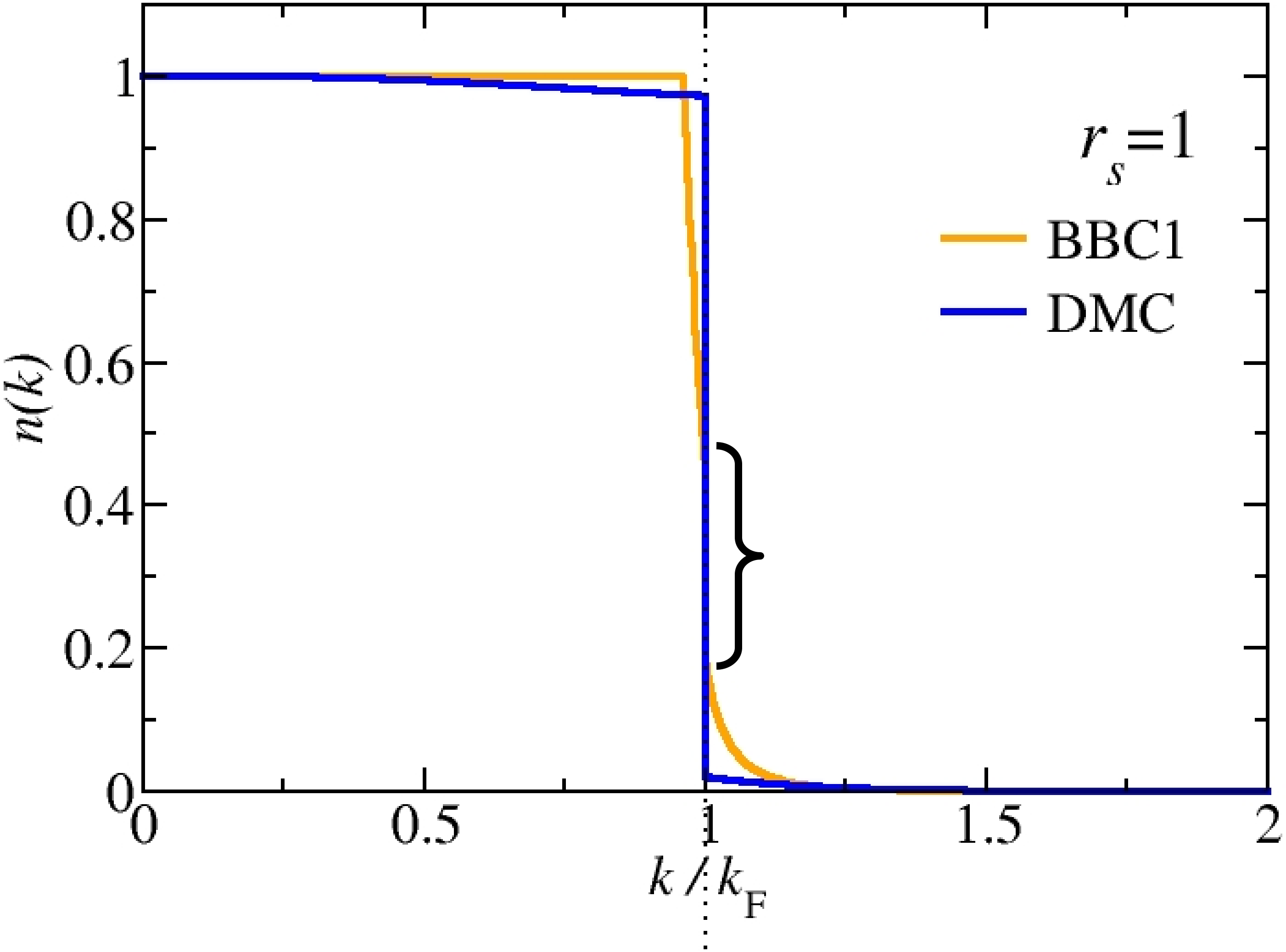
Exact: Ceperley-Alder, *PRL* **45**, 566 (1980), Perdew-Wang, *PRB* **45**, 13244 (1992).

Numerical results for BBC1 and BBC2 ($\in_c$ = Fermi energy)



Exact: Ceperley-Alder, *PRL* **45**, 566 (1980), Perdew-Wang, *PRB* **45**, 13244 (1992).

The momentum distribution



The Fundamental Gap

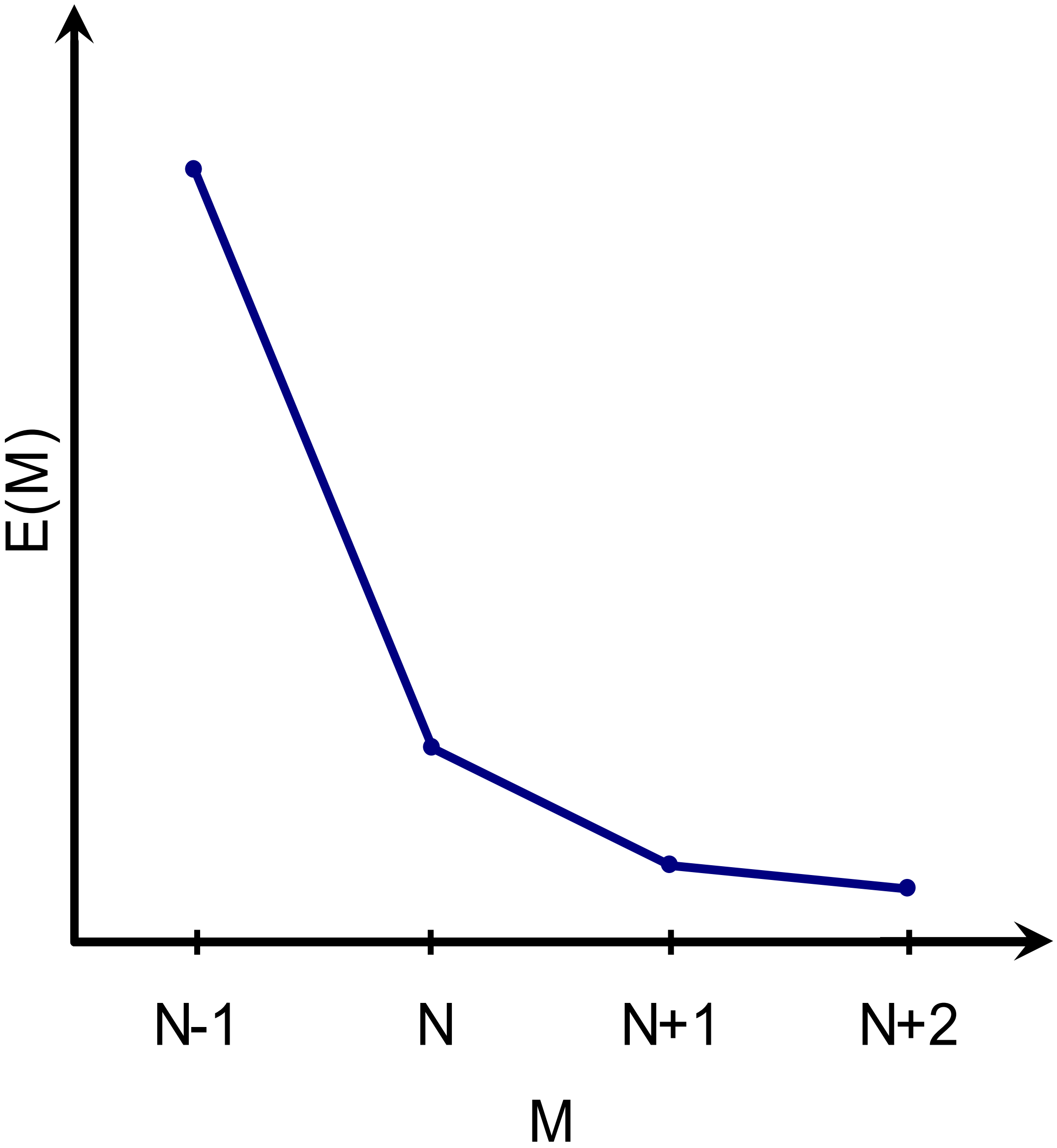
$E(M) \equiv$ ground-state energy of M-electron system

For fractional particle number M, $N_0 < M < N_0 + 1$ (with N_0 integer), the correct definition of $E(M)$ follows from the low-temperature limit of a grand-canonical ensemble

$$E(M) = \sum_{N \in \mathbb{N}} w_N \cdot E(N) \qquad M = \sum_{N \in \mathbb{N}} w_N \cdot N$$

For Coulomb systems $E(N)$ is upward convex (Lieb's conjecture). This implies

$$E(M = N_0 + \omega) = (1 - \omega) E(N_0) + \omega E(N_0 + 1) \qquad \text{for } 0 \le \omega \le 1$$


E(M)
N-1
N
N+1
N+2
M

Ionization potential:

$$I(N) \equiv E(N-1) - E(N)$$

Electron affinity:

$$A(N) \equiv E(N) - E(N+1)$$

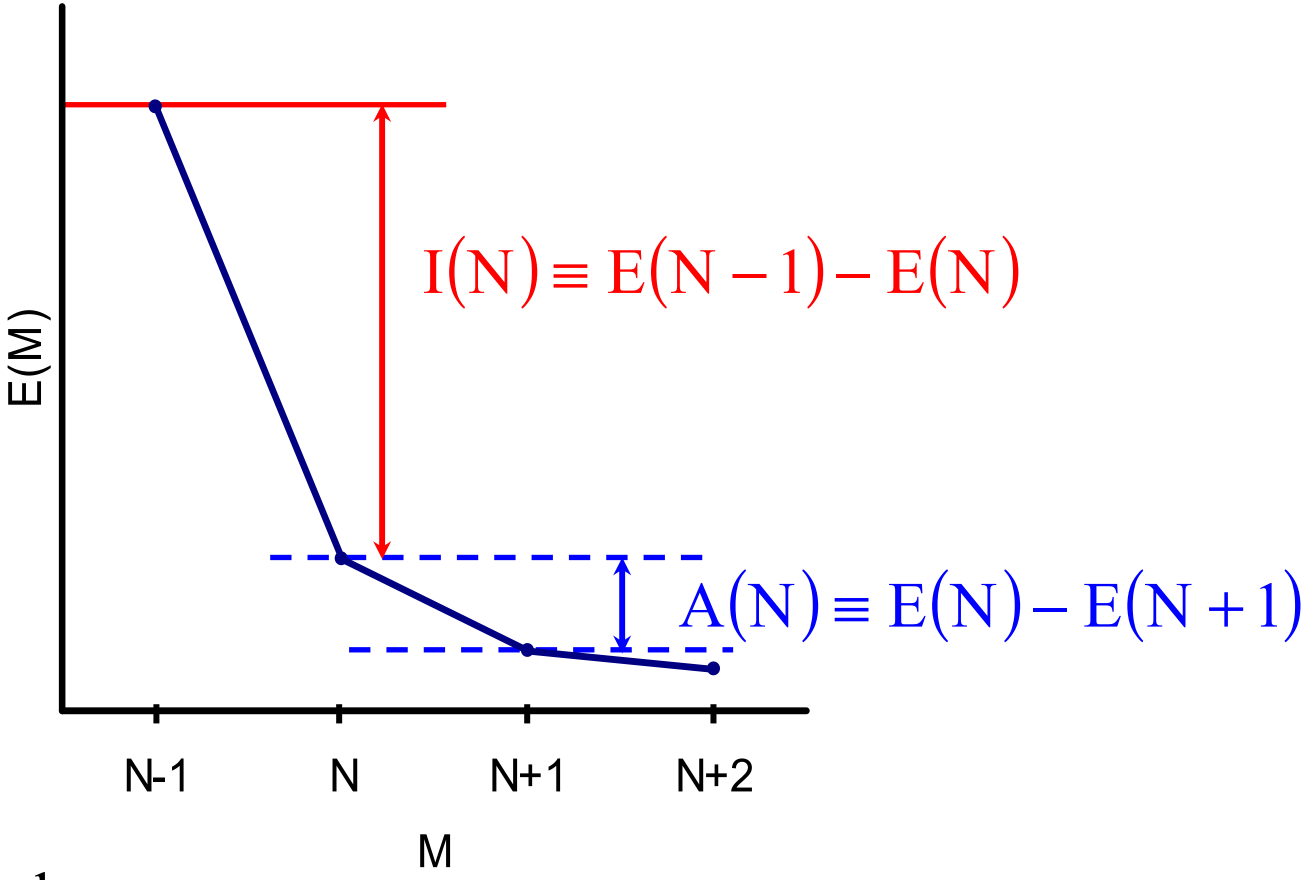
Fundamental gap:

$$\boxed{\Delta \equiv I(N) - A(N)}$$

(for charge-neutral N-electron system)

for periodic solids: $\Delta =$ quasiparticle gap

for finite systems: $\frac{\Delta}{2} =$ chemical hardness



$$I(N) \equiv E(N-1) - E(N)$$

$$A(N) \equiv E(N) - E(N+1)$$

Chemical potential:

$$\mu(M) \equiv \frac{\partial E(M)}{\partial M} = \left\{ \begin{array}{lcl} -I(N) & : & N-1 < M < N \\ -A(N) & : & N < M \leq N+1 \end{array} \right\}$$ has a jump at M=N

$$\boxed{\Delta = -A(N) + I(N) = \mu(N+\eta) - \mu(N-\eta)}$$

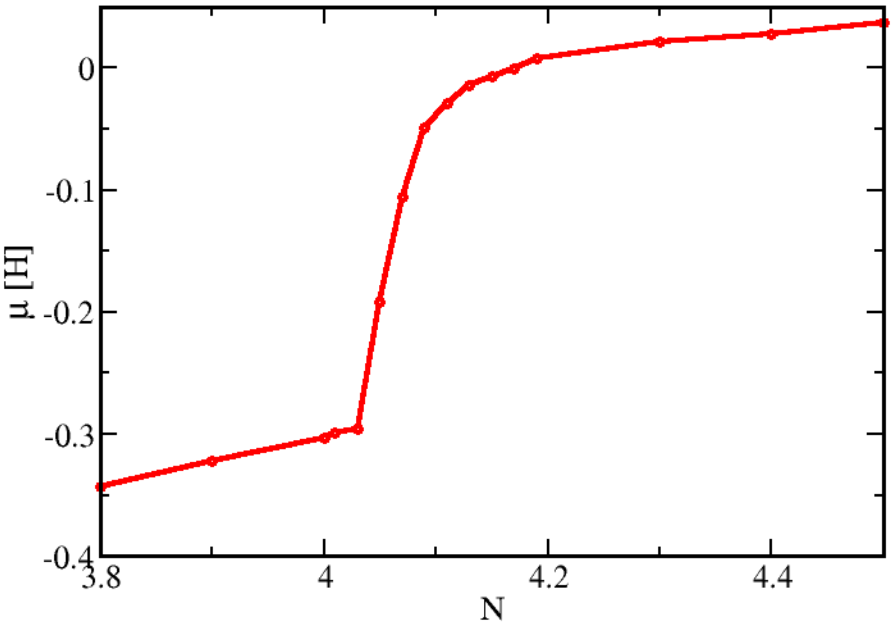
In DFT:

$$\boxed{\Delta = \underbrace{\epsilon^{KS}_{LUMO}(N) - \epsilon^{KS}_{HOMO}(N)}_{\Delta_{KS}} + \underbrace{\left[v_{xc}(N+\eta) - v_{xc}(N-\eta)\right]}_{\Delta_{xc}}}$$

In LDA/GGA:

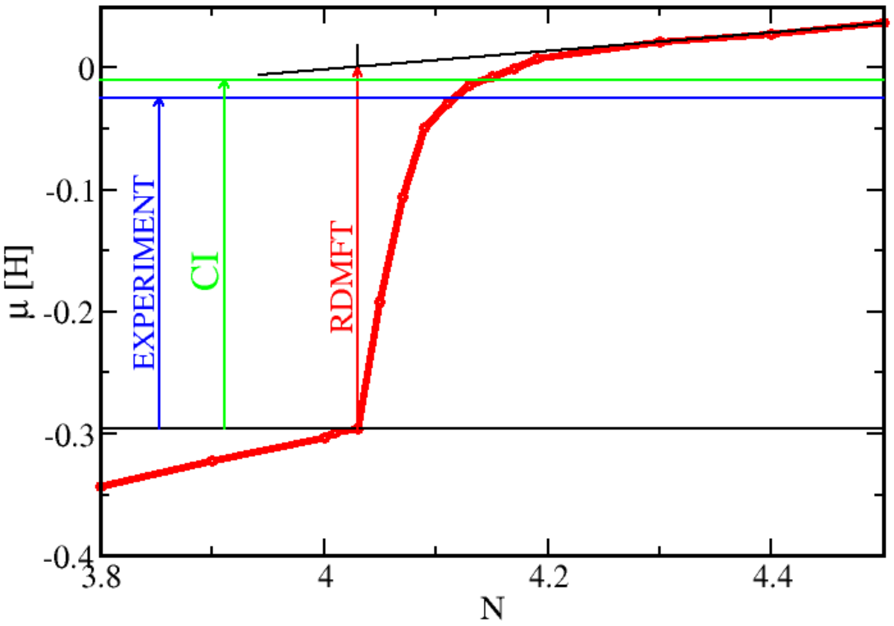
$\Delta_{xc} = 0$, $\Delta = \Delta_{KS}$ ≈ 50% too small for solids

Discontinuity of μ(M) for the LiH molecule



The discontinuity of μ(M) at N=4 electrons for LiH

Discontinuity of μ(M) for the LiH molecule



The discontinuity of μ(M) at N=4 electrons for LiH

Fundamental gap of finite systems (in a.u.)

System	RDMFT	CI	Experiment
Li atom	0.177	0.175[1]	0.175
Na atom	0.175	0.169[1]	0.169
LiH molecule	0.296	0.286[1]	0.271

The real challenge of Condensed-Matter theory: Ab-initio description of strongly correlated solids

Towards strongly correlated systems

Mott insulators in paramagnetic insulating phase
above Néel temperature: $\langle m(r)\rangle = 0$

prototype: 1D chain of hydrogen atoms

Towards strongly correlated systems

Mott insulators in paramagnetic insulating phase
above Néel temperature: <m(r)> = 0

prototype: 1D chain of hydrogen atoms

finite-temperature KS: half-filled band

⇨ KS system is metallic (independent of xc functional)

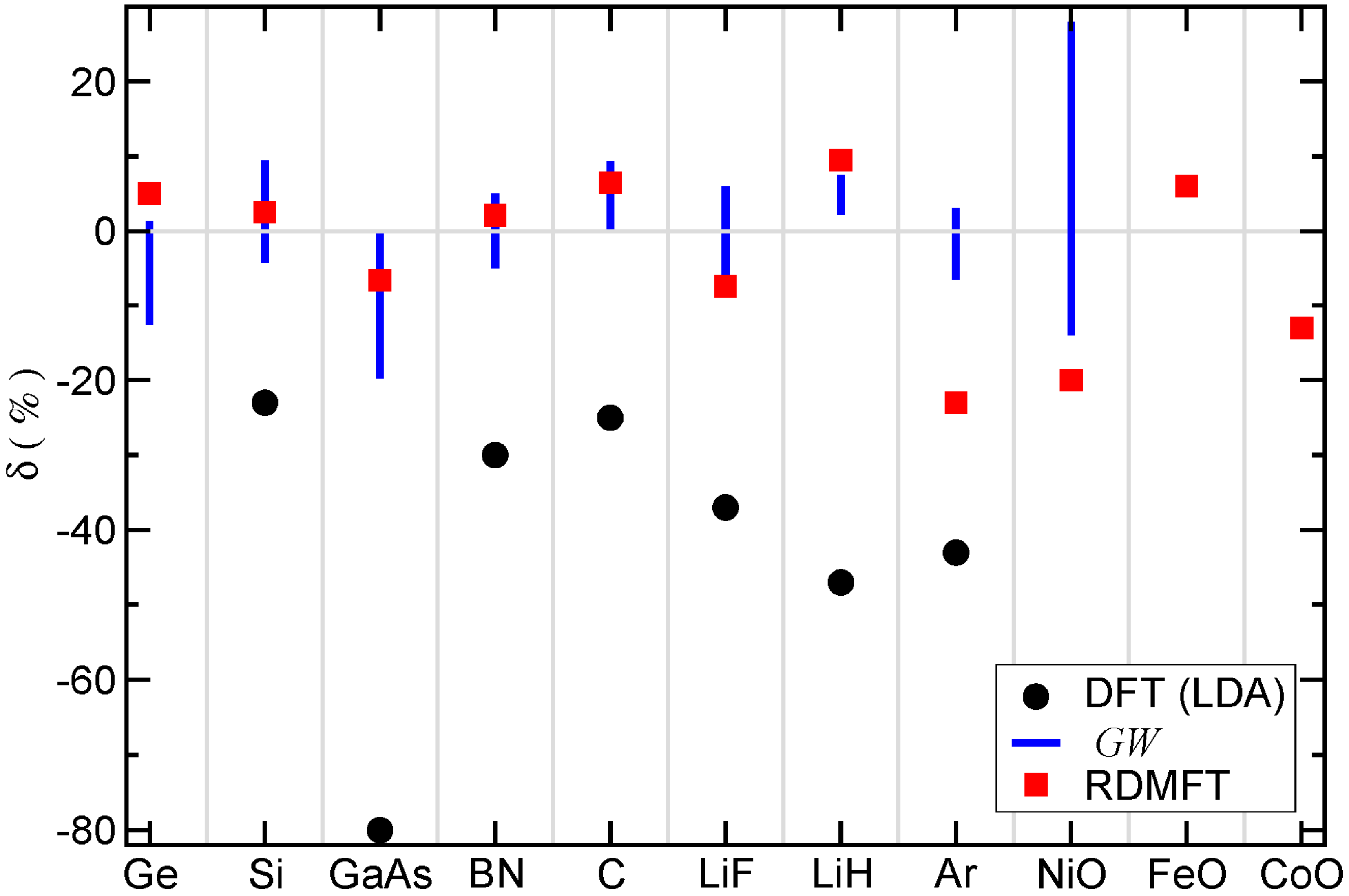
formally no problem:

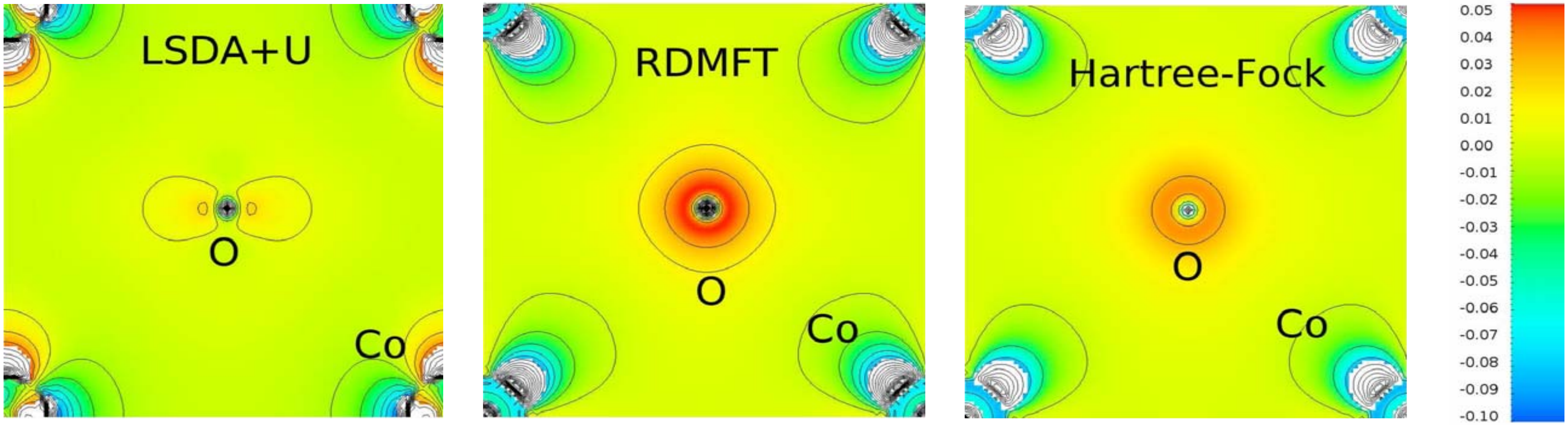
$$E_{gap} = \underbrace{E_{gap}^{KS}}_{0} + \Delta_{xc}$$

Totally unnatural
description

Fundamental gap of semiconductors and insulators

S. Sharma, J.K. Dewhurst, N.N. Lathiotakis and E.K.U.G., Phys. Rev. B **78** (Rapid Comm.), 201103 (2008)





Difference between LDA charge density and charge density calculated using RDMFT, LSDA+U and Hartree-Fock ($\rho_{\mathrm{RDMFT}}(\mathbf{r}) - \rho_{\mathrm{LDA}}(\mathbf{r})$). Positive values indicate stronger localization of charge as compared to LDA

How to calculate the quasi-particle spectrum in RDMFT?

Mimic (direct and inverse) photo-emission experiment,
i.e. remove or add an electron with well-defined momentum k
(k not necessarily in 1st BZ):

electron addition: $\varepsilon_k = E_{gs}(N) - E_{gs}(N+1_k) \;=\; E(n_k=0) - E(n_k=1)$

electron removal: $\varepsilon_k = E_{gs}(N-1_k) - E_{gs}(N) \;=\; E(n_k=0) - E(n_k=1)$

With $E(n_k) := E_{tot}[n_1\, n_2\, n_3 \dots \varphi_1\, \varphi_2\, \varphi_3 \dots]$
with all φ_i and all $n_i \neq n_k$ set to
the values corresponding to the N-electron
ground state

How to best calculate the difference E(n=1) – E(n=0)?

Stupid: Taylor expansion around n=0:

$$E(1) = E(0) + E'(0)\,\delta n + (\tfrac{1}{2})\,E''(0)\,\delta n^2 + \ldots \quad (\delta n = 1)$$

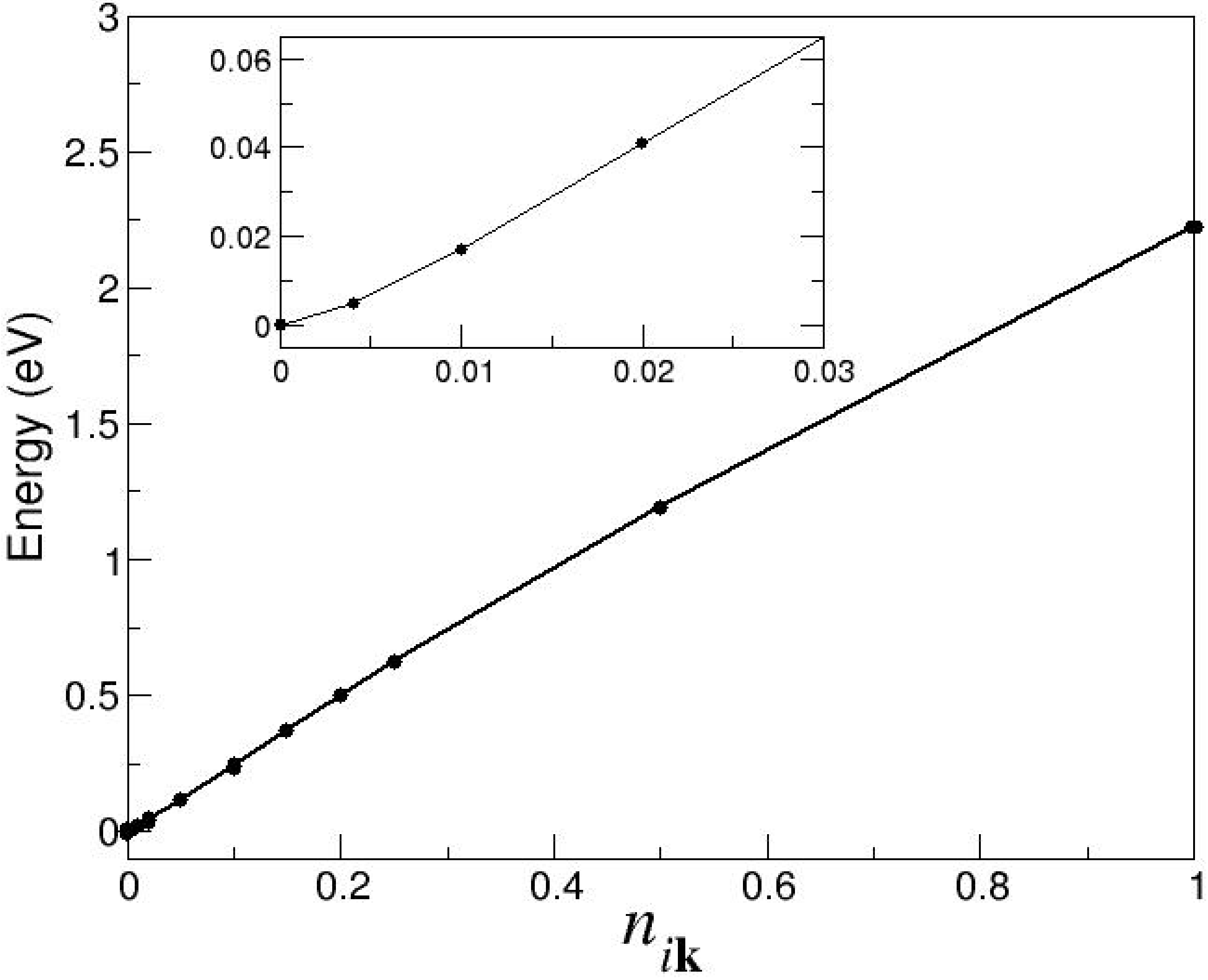
$$\Rightarrow \quad E(1) - E(0) = E'(0) + O(\delta n^2)$$

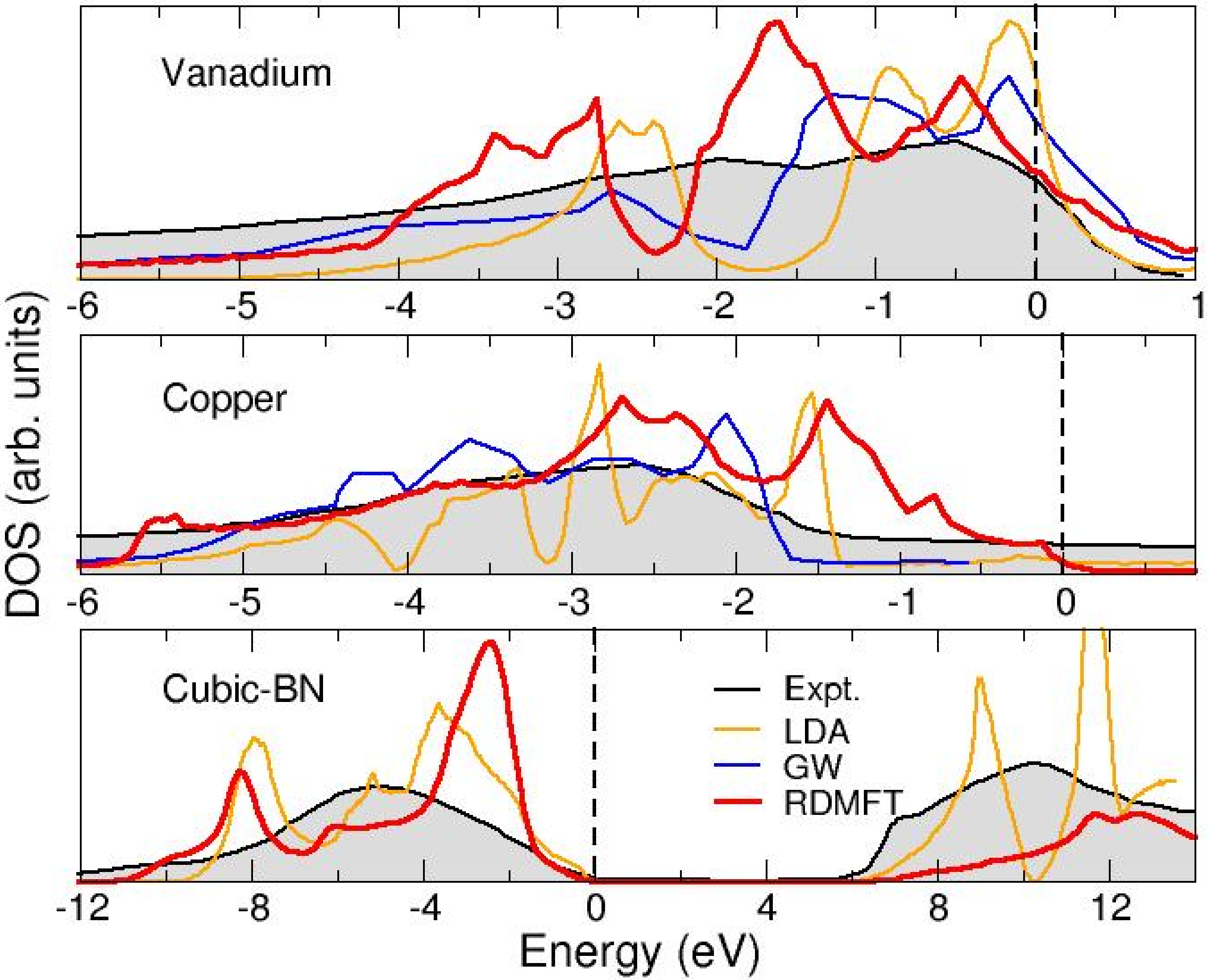
Clever: Taylor expansion around n=½:

$$E(1) = E(\tfrac{1}{2}) + E'(\tfrac{1}{2})\,\delta n + (\tfrac{1}{2})\,E''(0)\,\delta n^2 + \ldots \quad (\delta n = \tfrac{1}{2})$$
$$E(0) = E(\tfrac{1}{2}) + E'(\tfrac{1}{2})\,\delta n + (\tfrac{1}{2})\,E''(0)\,\delta n^2 + \ldots \quad (\delta n = -\tfrac{1}{2})$$

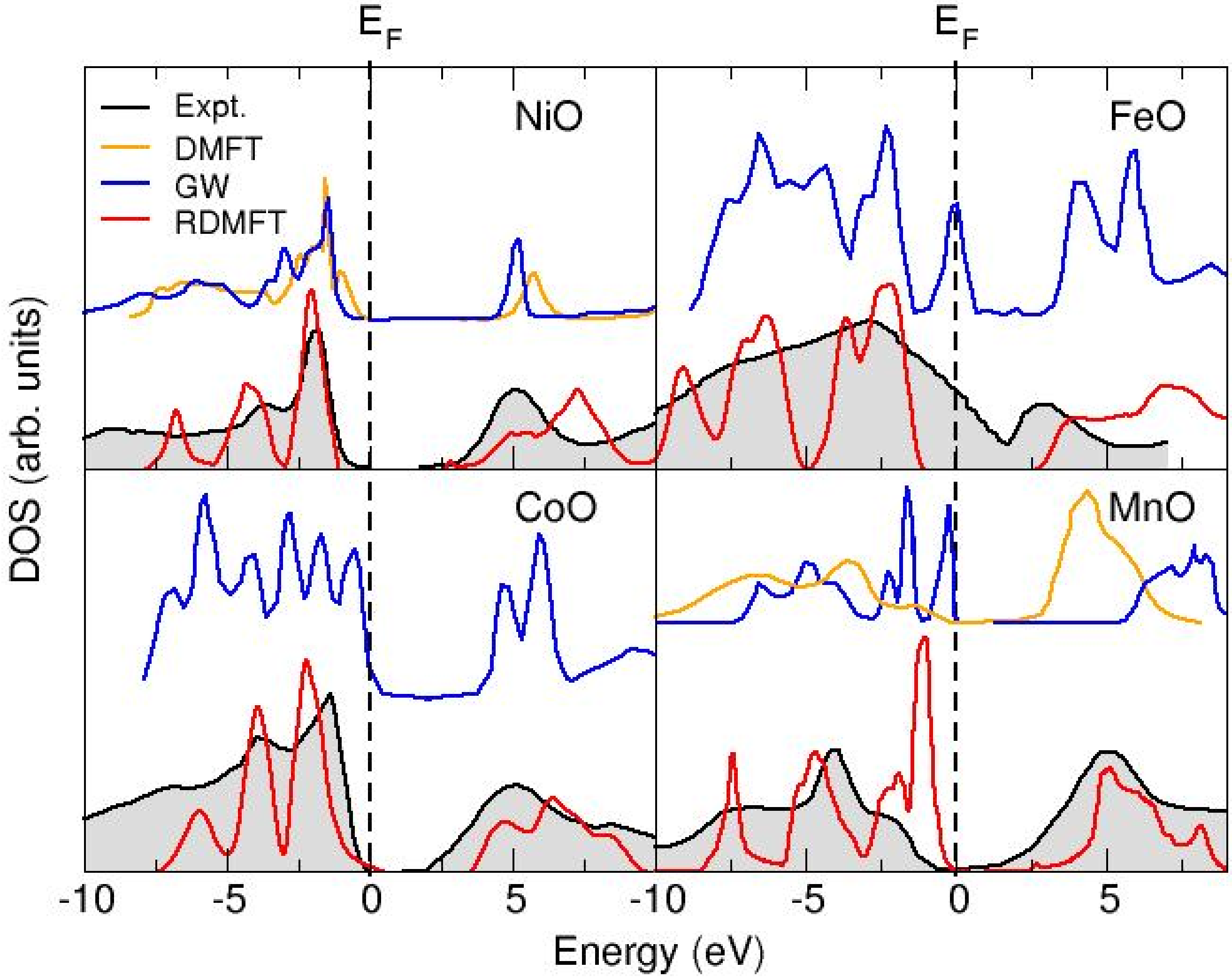
$$\Rightarrow \quad E(1) - E(0) = E'(\tfrac{1}{2}) + O(\delta n^3)$$

$$\Rightarrow \quad \boxed{\varepsilon_k \equiv \left.\frac{\partial E(n_k)}{\partial n_k}\right|_{1/2}}$$


Energy (eV)
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
$n_{i\mathbf{k}}$
0.06
0.04
0.02
0
0
0.01
0.02
0.03



S. Sharma, S. Shallcross, J.K. Dewhurst, EKUG, arXiv:0912.1118



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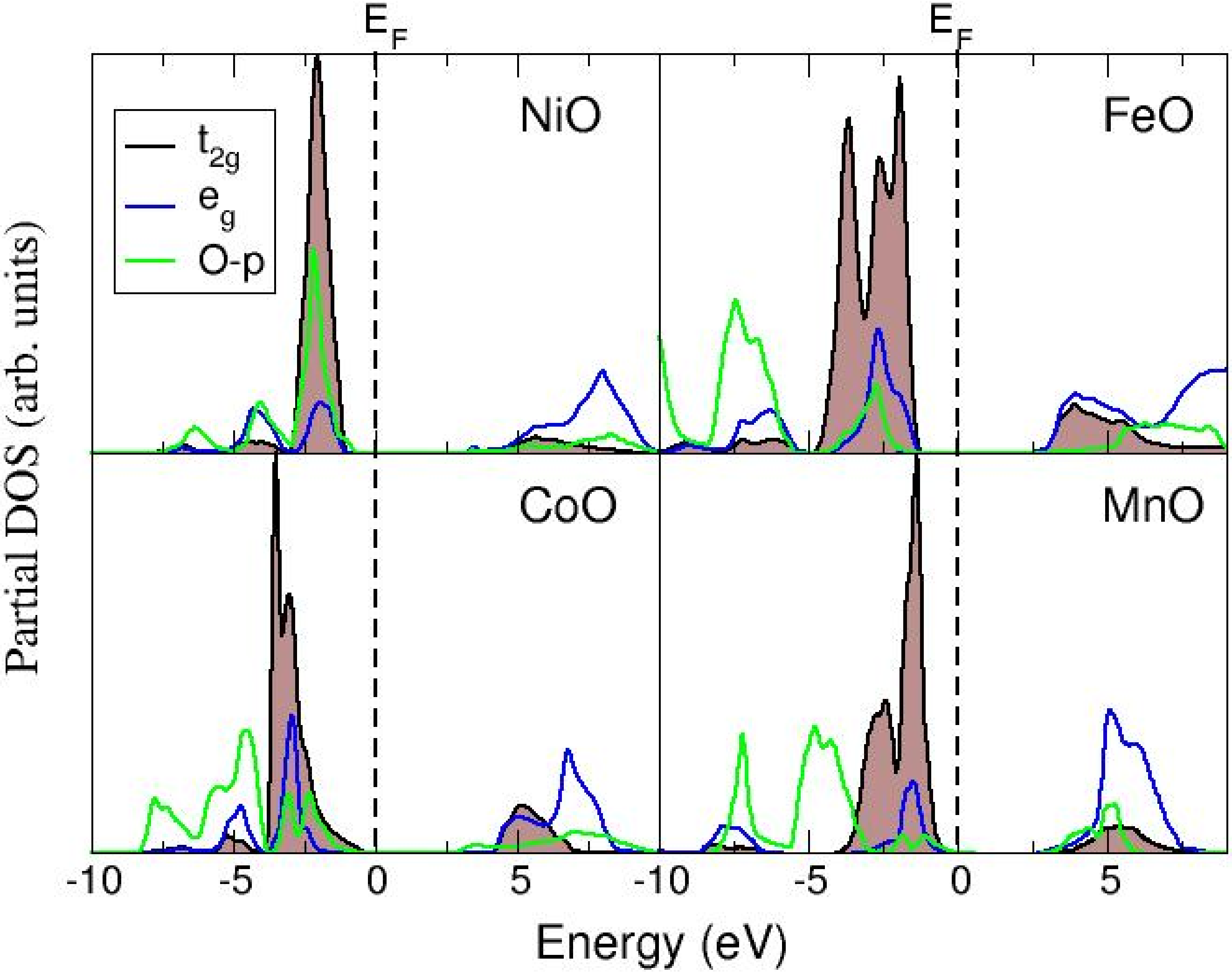
E_F
E_F
NiO
FeO
CoO
MnO
t_2g
e_g
O-p
Partial DOS (arb. units)
-10
-5
0
5
-10
-5
0
5
Energy (eV)

Thanks to

Nicole Helbig
Nektarios Lathiotakis
Angelica Zacarias

molecules

Sangeeta Sharma
Kay Dewhurst
Florian Eich
Tim Baldsiefen

solids

Deutsche Forschungsgemeinschaft
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RTN

ETSF

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