Using wave functions and DFT

A. Savin et al.

http://www.lct.jussieu.fr/pagesperso/savin/publications.html

Tokyo, August 2007

Overview

- Context
- Method coupling WF with DF ($\Psi + n$, MR−DFT, ...)
- Results for van der Waals systems
- Further steps

Context

Collaboration

- Paris: P. Gori−Giorgi, J. Toulouse
- Nancy: J. Angyán, I. Gerber
- Stuttgart: E. Goll, H. Stoll, H.−J. Werner
- Toulouse: Th. Leininger

Available methods

- QM (Ψ):universal but application to small systems only
- DF (*n*): larger systems, but not all types of interac−tions
- MM: even larger systems, but even more restrictions
- QM/MM, DF/MM, QM/DF

Objective

- Combine advantages from

  QM (Ψ): universal applicability

  DF(*n*) : larger systems

Problem with mixing: double counting

One physical effect described by both methods

Also: by none of the methods

Problem with Ψ : $N-$particle basis set

$$\Psi(1, \ldots, N) = \sum_{I=0,M} c_I \, \Phi_I(1, \ldots, N)$$

M extremely large

$M = 0$ in DFT

Problem with Ψ :1−particle basis set

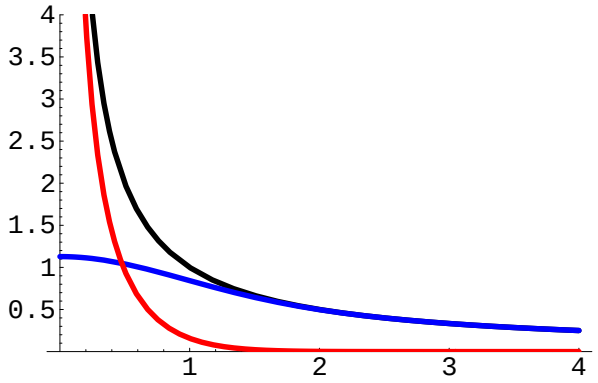
$\varphi(\boldsymbol{r}) = \sum_\mu c_\mu \chi_\mu(\boldsymbol{r})$

Φ_I need much larger sets of χ than just Φ_0 (DF)

$\Psi + n$

Splitting V_{ee}

$$1/r_{ij} = \mathrm{erf}(\mu r_{ij})/r_{ij} + \mathrm{erfc}(\mu r_{ij})/r_{ij}$$



Variation principle

$$\min_{\Psi} \{ \langle \Psi \,|\, T + V_{\mathrm{ne}} + \mathcal{W}^{\mu} \,|\, \Psi \rangle + \mathcal{F}^{\mu}[n_{\Psi}] \}$$

$$\mathcal{W}^{\mu} = \sum_{i<j} \mathrm{erf}\left(\mu \left| r_i - r_j \right|\right) \Big/ \left| r_i - r_j \right|$$

$$\mathcal{F}^{\mu}[n] = \tfrac{1}{2} \int n(r_1)\, n(r_2)\, \mathrm{erfc}\left(\mu \left| r_i - r_j \right|\right) \Big/ \left| r_i - r_j \right| + E_{\mathrm{xc}}{}^{\mu}[n]$$

Euler−Lagrange equations

$$(T + \mathcal{V}^{\mu} + \mathcal{W}^{\mu})\,\Psi^{\mu} = E^{\mu}\,\Psi^{\mu}$$

$$\mathcal{V}^{\mu} = V_{\mathrm{ne}} + \sum_{i=1,N} \delta\mathcal{F}^{\mu} / \delta\, n(r_i)$$

Approximations

- Ψ : solution of the modified Schrödinger equation (KS/HF, MP2, MCSCF, CCSD, ...)

- n : $\mathcal{F}^{\mu}$ (μ–LDA, μ–PBE, ...)

Tokyo:
Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, JCP 120, 8425 (2004)

Motivation of the approximations

- $n : \mathcal{F}^{\mu}$ (μ−LDA, μ−PBE, ...)

  where they work

Choice of μ

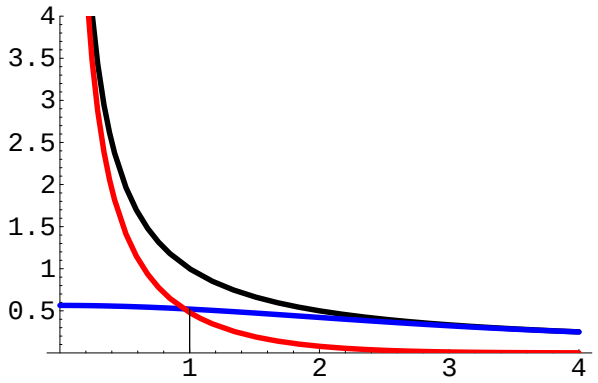
Case	μ	$\mathcal{W}$	E_{xc}^{μ}
Kohn – Sham	0	0	E_{xc}
WF	∞	V_{ee}	0

- $\mu \approx 0.5$: both erf (WF) and erfc (DF)

(cf. Ángyán, Gerber; Fromager, Jensen, Toulouse)

Choice of μ

$$1/r_{ij} = \mathrm{erf}(0.5\, r_{ij})/r_{ij} + \mathrm{erfc}(0.5\, r_{ij})/r_{ij}$$



Double counting?

Avoided (in principle) by construction:

- short−range for n
- long−range for Ψ

van der Waals dimers

J. Ángyán et al., PRA 72, 12510 (2005) #114

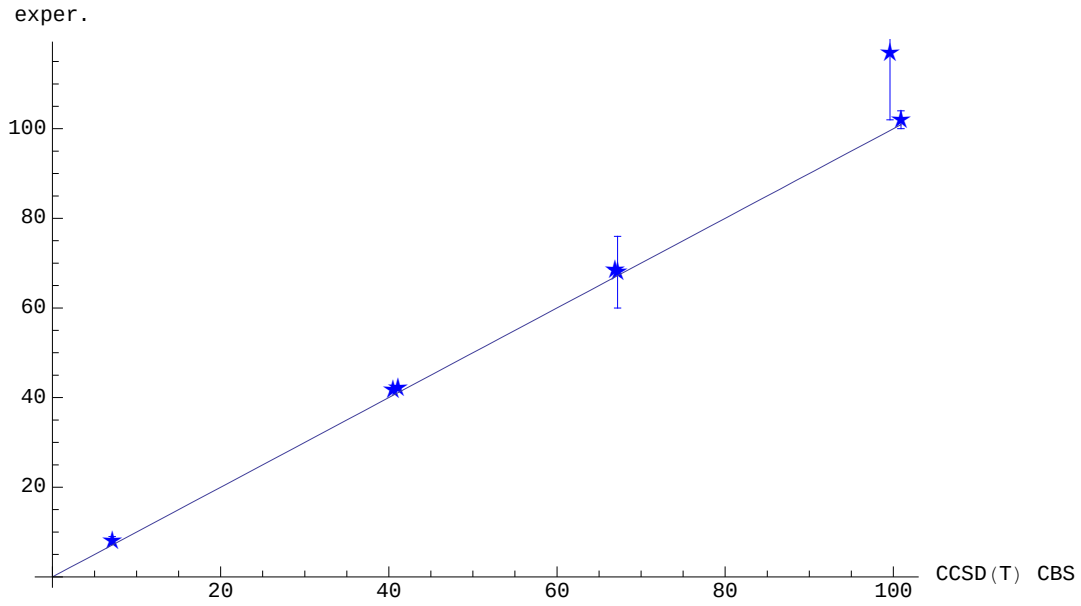
E. Goll et al., CP 329, 276 (2006) #120

Systems

- Rg_2 (Ángyán, Gerber, Toulouse)
- AmRg (Goll, Werner, Stoll, Leininger, Gori−Giorgi)

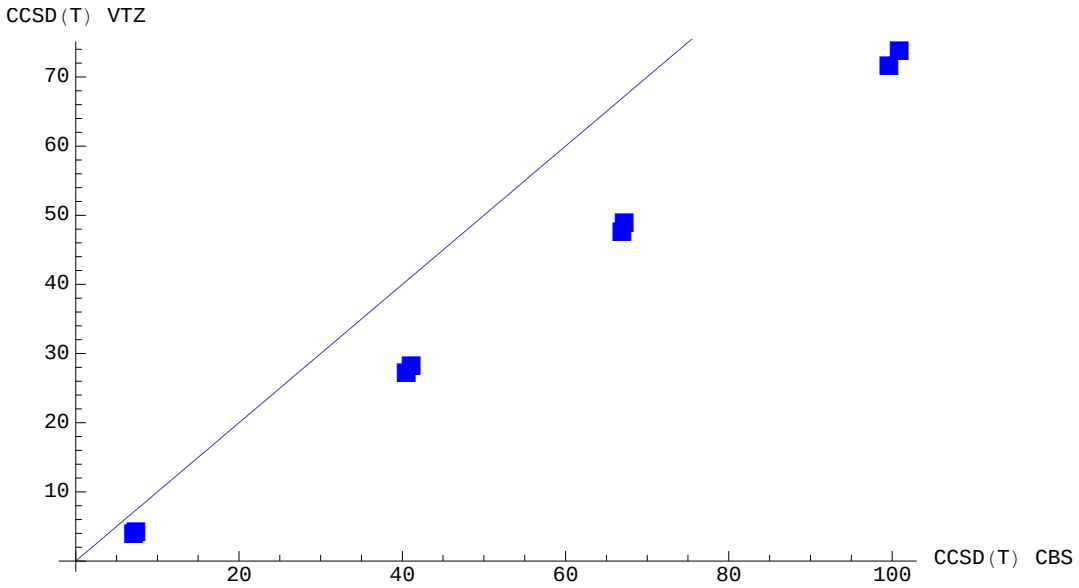
Am: alkali metal, not americium
Rg: rare gas, not roentgenium

Are reference data reliable? (D_e, cm^{-1})



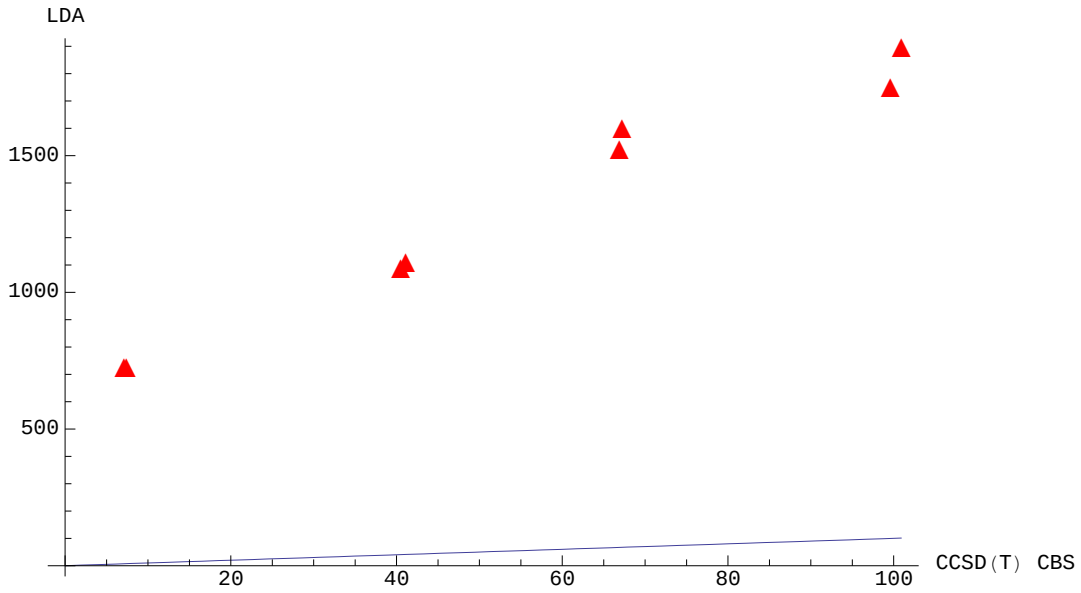
E. Goll et al., CP 329, 276 (2006) #120

Basis set effect in CCSD(T) (D_e, cm^{-1})



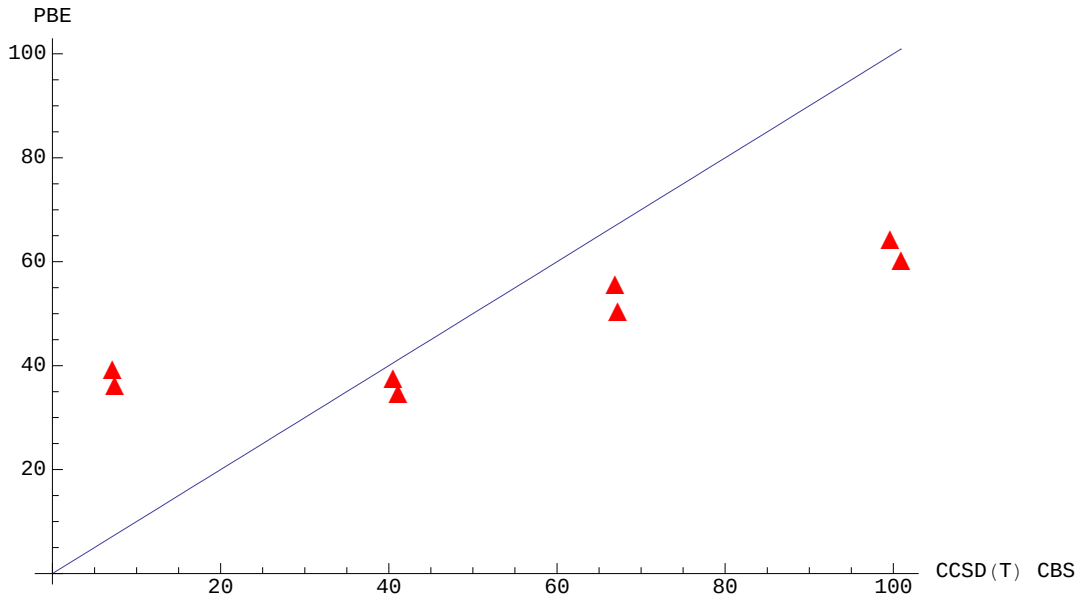
E. Goll et al., CP 329, 276 (2006) #120

Huge errors with LDA $\left(D_e, \text{cm}^{-1}\right)$



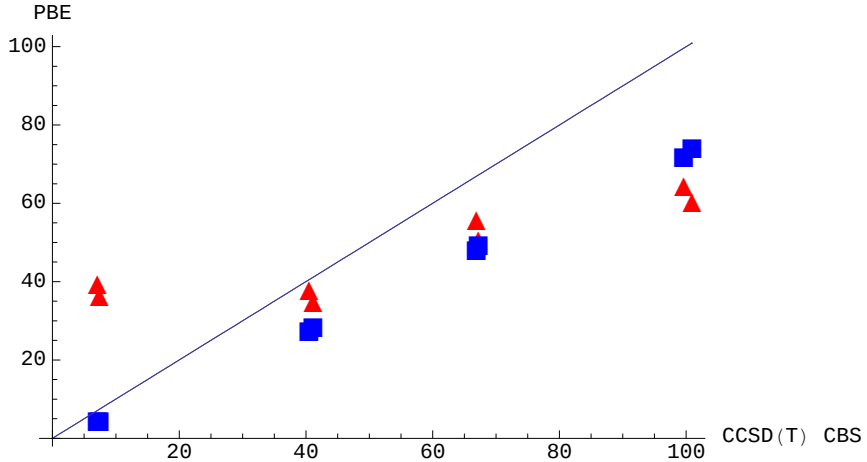
E. Goll et al., CP 329, 276 (2006) #120

PBE not sensitive (D_e, cm^{-1})



E. Goll et al., CP 329, 276 (2006) #120

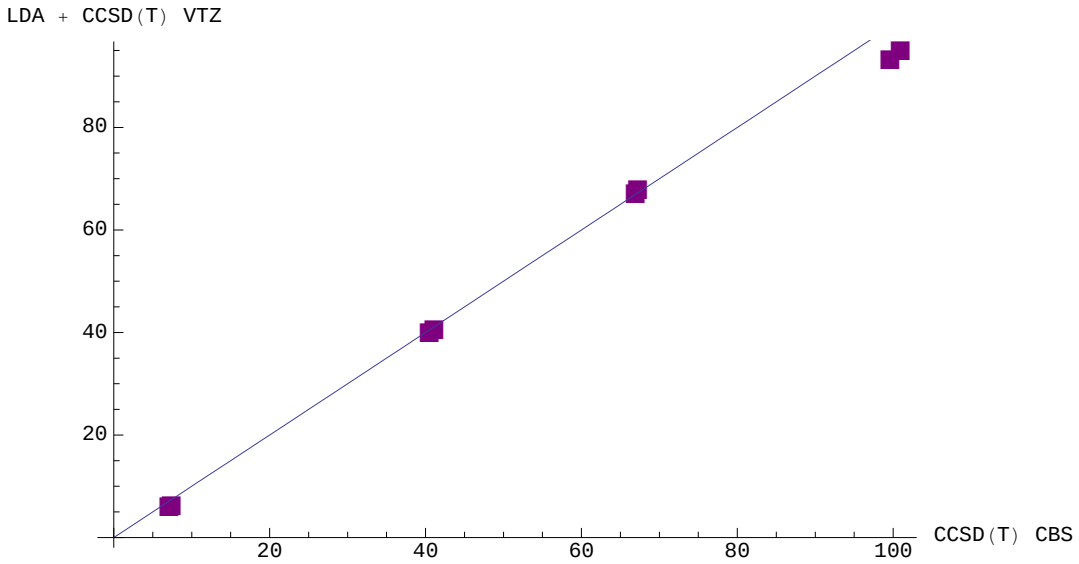
Can a mixed method work?



CCSD(T), PBE : VTZ

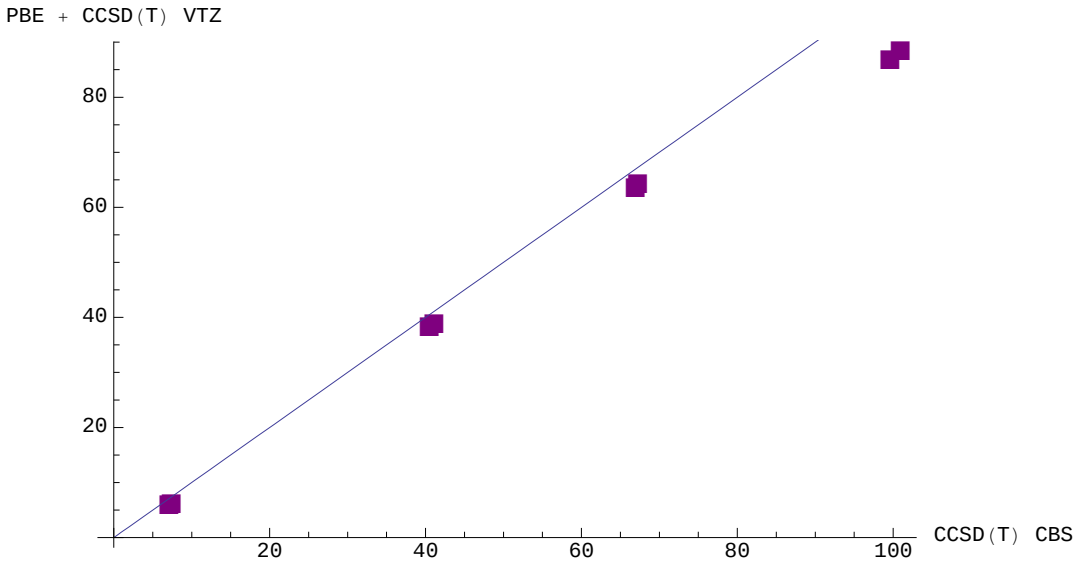
E. Goll et al., CP 329, 276 (2006) #120

CCSD(T)+LDA (VTZ) $\left(D_e, \text{cm}^{-1}\right)$



E. Goll et al., CP 329, 276 (2006) #120

CCSD(T)+PBE (VTZ) $\left(D_e, \text{cm}^{-1}\right)$



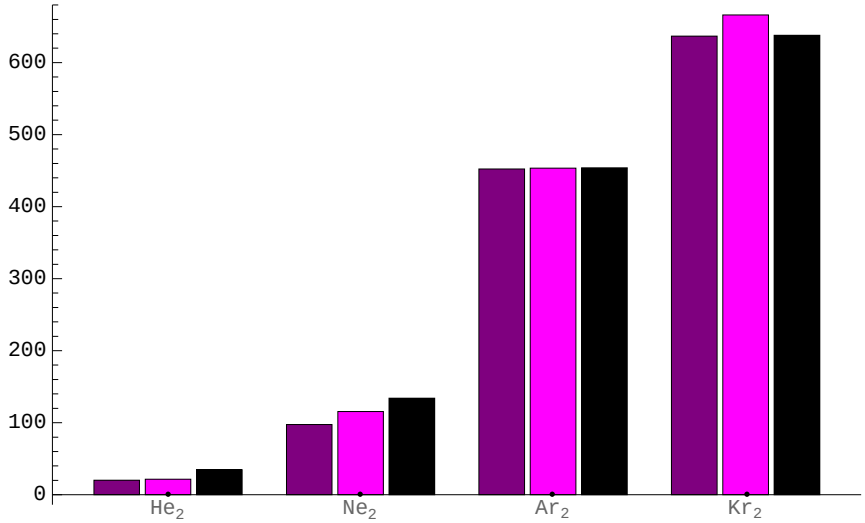
E. Goll et al., CP 329, 276 (2006) #120

Basis set effect (MAD for D_e, cm^{-1})

Method	VTZ	VQZ
CCSD (T)	16	8
PBE + CCSD (T)	5	5

E. Goll et al., CP 329, 276 (2006) #120

DF+MP2, DF+CCSD(T)



DF+MP2: J.G. Angyán, et al., PRA 72, 12510 (2005) #117
DF+CCSD(T): E. Goll, et al. , PCCP 7, 3917 (2005)

recommended: T.−H. Tang and J. P. Toennies, JCP 118, 4976 (2003)

Further steps

- Other modified Hamiltonians?
- Beyond semi−local approximations?

Modified Hamiltonians

Notation

$$H = T + V_{ne} + V_{ee} \quad \rightarrow \quad \mathcal{H} = \mathcal{T} + \mathcal{V} + \mathcal{W}$$

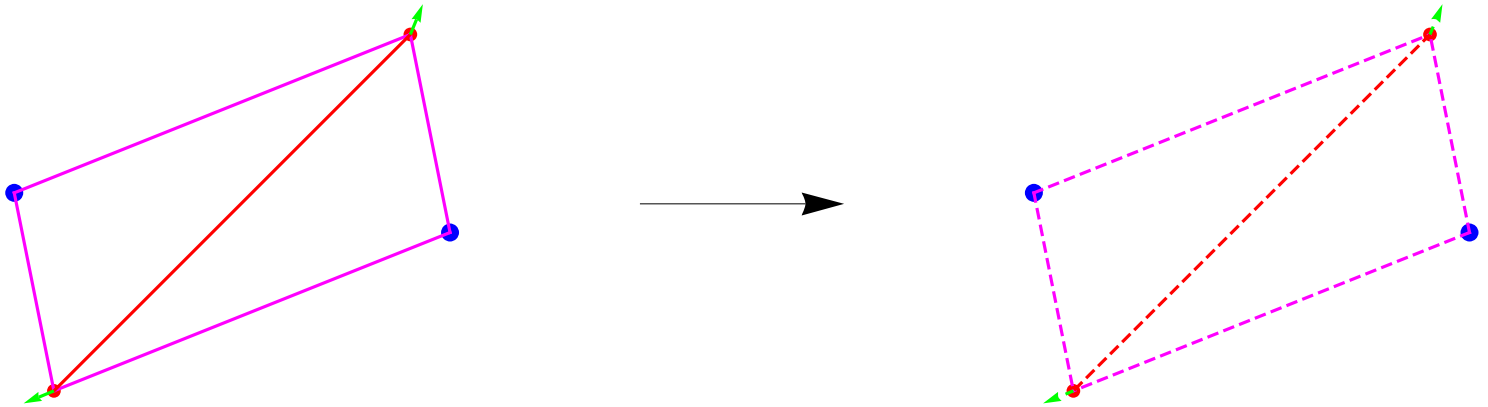
$$T = -\tfrac{1}{2} \sum_{i=1,N} \nabla_i^2 \quad \rightarrow \quad \mathcal{T} = \sum_{i=1,N} t(r_i, r_i')$$

$$V_{ne} = \sum_{i=1,N} v_{ne}(r_i) \quad \rightarrow \quad \mathcal{V} = \sum_{i=1,N} v(r_i)$$

$$V_{ee} = \sum_{1 \le i < j \le N} 1 / r_{ij} \quad \rightarrow \quad \mathcal{W} = \sum_{1 \le i < j \le N} w(r_{ij})$$

Modified Hamiltonians

e–e, e–n, e



DFT: Hohenberg–Kohn

$$\mathcal{H} = \mathcal{T} + \mathcal{V} + \mathcal{W}$$

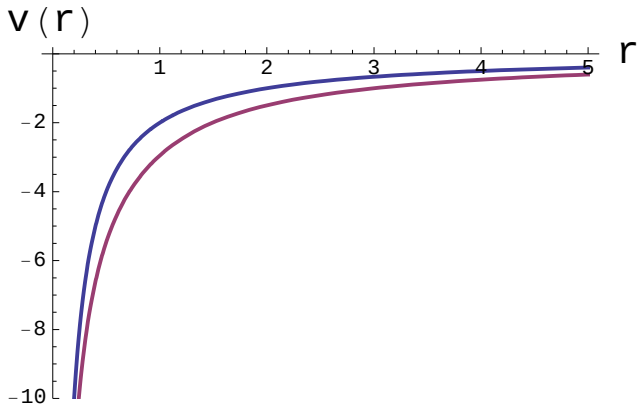
$$\Psi \rightarrow n \Rightarrow v(r) \quad (\mathcal{V})$$

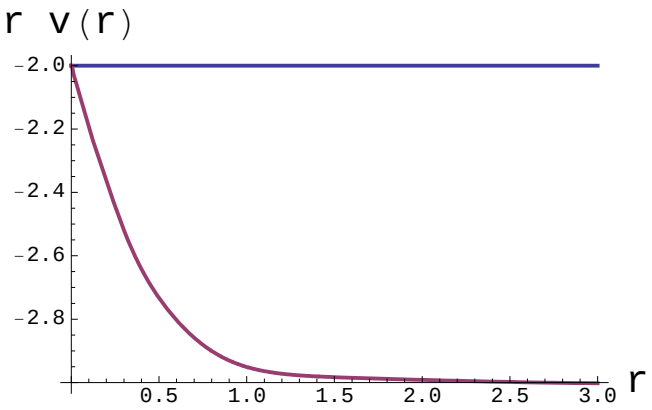
Modified Hamiltonians

$$v(r) \rightarrow n(r) = 2\,\frac{Z^3}{\pi}\,e^{-2Zr}$$

$Z = 2, \mathcal{T} = T,$

$\mathcal{W} = 0$ or $\mathcal{W} = V_{ee}$





F. Colonna, AS, J. Chem. Phys.110, 2828 (1999) #78

DFT: Hohenberg–Kohn

$$\mathcal{E}_0 = \min_\Psi \langle \Psi | \mathcal{H} | \Psi \rangle = \min_n F[n; \mathcal{T}, \mathcal{W}] + \int n\, v$$

DFT: definition of the functional

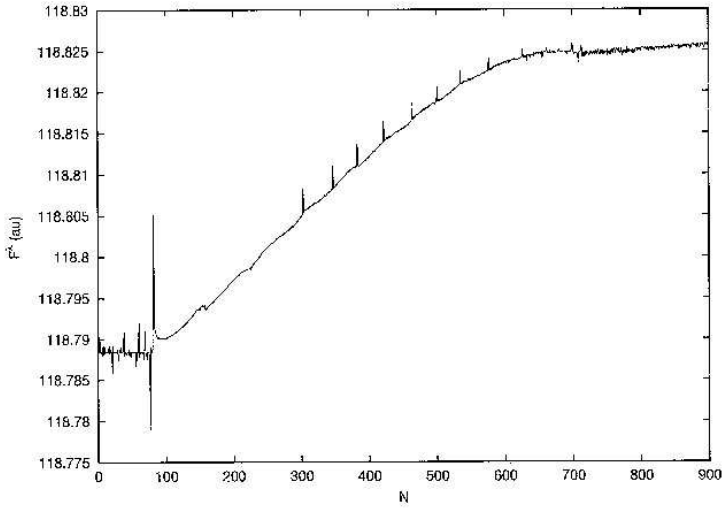
- Levy (constrained search)

$$F[n;\mathcal{T},\mathcal{W}] = \min_{\Psi\to n} \langle \Psi \,|\, \mathcal{T} + \mathcal{W} \,|\, \Psi \rangle$$

- Lieb (Legendre transform)

$$F[n;\mathcal{T},\mathcal{W}] = \sup_{v} \left\{ \left(\min_{\Psi} \langle \Psi \,|\, \mathcal{T} + V + \mathcal{W} \,|\, \Psi \rangle - \int n\, v \right) \right\}$$

Obtaining $F[n, T, V_{ee}]$ from n



R. Pollet et al. Int. J. Quantum Chem. 91, 84 (2002), #98

DFT: Kohn–Sham

$$\mathcal{T} = T \text{ and } \mathcal{W} = 0$$

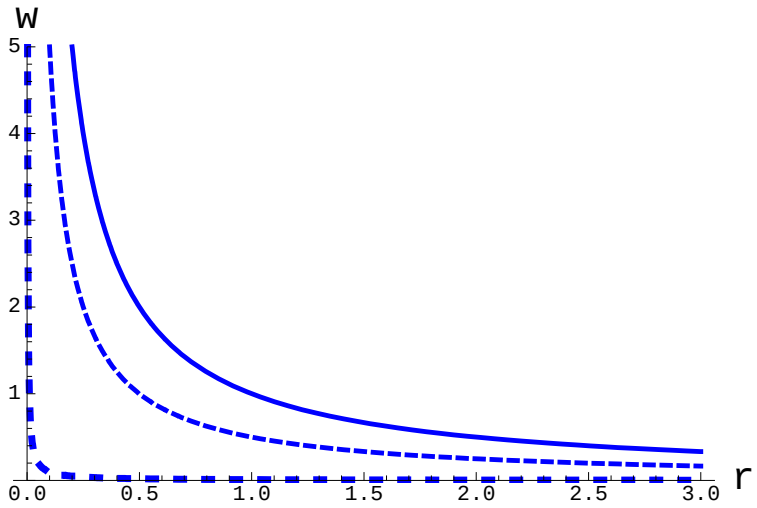
$$F[n; T, \mathcal{W} = 0] = T_s[n]$$

Obtaining $T_s[n]$ as $\sup_v$ ...

Rose and Shore, Sol. St. Commun.17, 327 (1975)

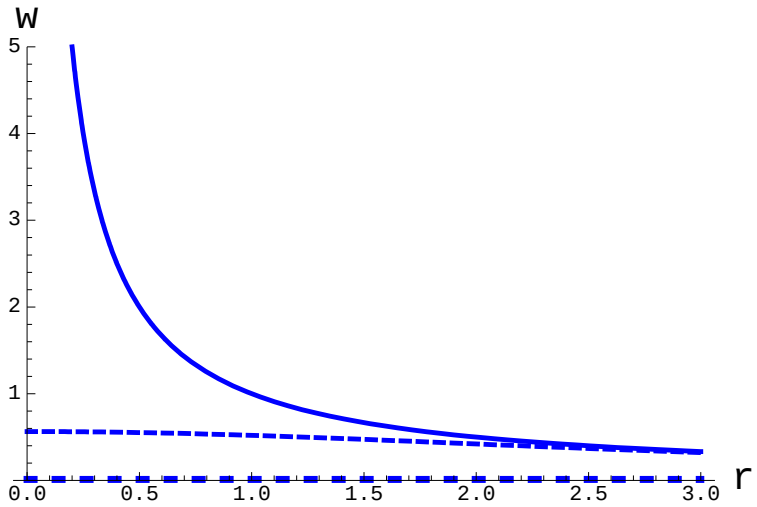
Linear switching on of V_{ee}

$$\mathcal{T} = T;\ w(r_{12};\lambda) = \lambda / r_{12},\ \lambda = 1,\ \tfrac{1}{2},\ \to 0$$



Long−range switching on of V_{ee}

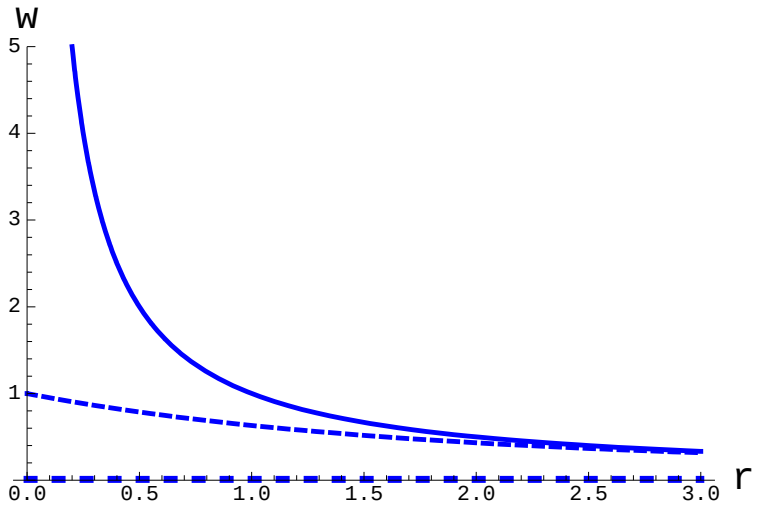
$$\mathcal{T} = T;\ w(r_{12};\mu) = \mathrm{erf}(\mu\, r_{12})/r_{12},\ \mu \to \infty,\ \tfrac{1}{2},\ \to 0$$



A.S. in: J. Seminario, ed.,... (1996) #59

Long−range switching on of V_{ee}

$$\mathcal{T} = T;\ w(r_{12};\mu) = (1 - e^{-\mu r_{12}})/r_{12},\ \mu \to \infty,\ 1,\ \to 0$$



A.S., H.−J. Flad Int. J. Quantum Chem. 56, 327 (1995) #52

Better *W*?

cf. Effective Potential eXpansion
Y. Takada, PRB 35, 6923 (1987)

Why erf($\mu\, r_{12}$) / r_{12}?

Yukawa vs. erf : similar

$$\int e^{-\alpha (r_1 - R_A)^2}\, e^{-\beta (r_2 - R_Q)^2}\, \frac{\mathrm{erf}(\mu\, r_{12})}{r_{12}} =$$

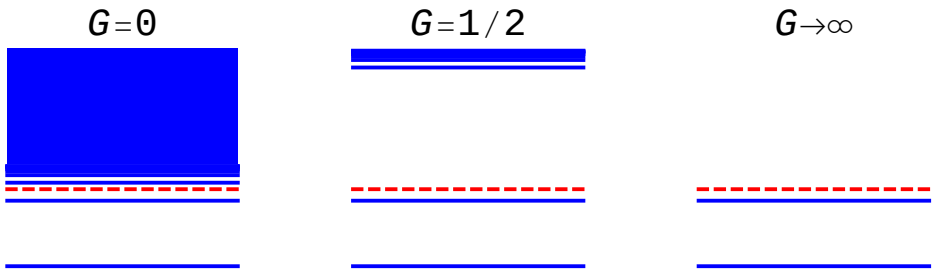
$$f(\alpha, \beta)\, \frac{1}{|R_A - R_B\}}\, \mathrm{erf}\left(\left| R_A - R_B \right| \Big/ \sqrt{\alpha^{-1} + \beta^{-1} + \mu^{-2}} \right)$$

Other integrals by recursion

McMurchie−Davidson, Obara−Saika, Gill et al., Lindh et al., ...

Orbital−space actions: gap shift

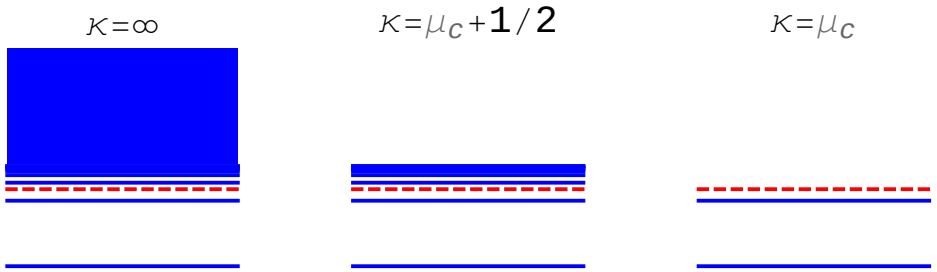
$\mathcal{T} = T + G\,\mathcal{P}_{\text{virtual}}, \mathcal{W} = V_{\text{ee}}$ (choose space!)



J.Rey, A.S., Int. J. Quantum Chemistry 69, 581 (1998) #71

Orbital−space actions: cutoff

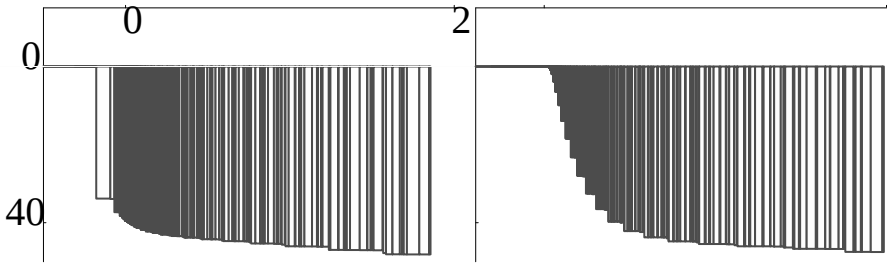
$\mathcal{T} = T + \Theta(\kappa - \varepsilon_i)$, $\mathcal{W} = V_{ee}$ (choose space!)



C. Gutlé, A.S., Phys. Rev. A 75, 032519 (2007) #122

Modified Hamiltonians

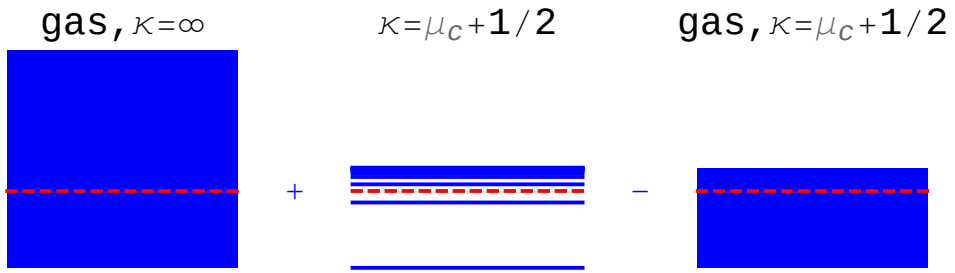
$E_c(\kappa)$: KLI and HF



C. Gutlé, A.S., Phys. Rev. A 75, 032519 (2007) #122

Modified Hamiltonians

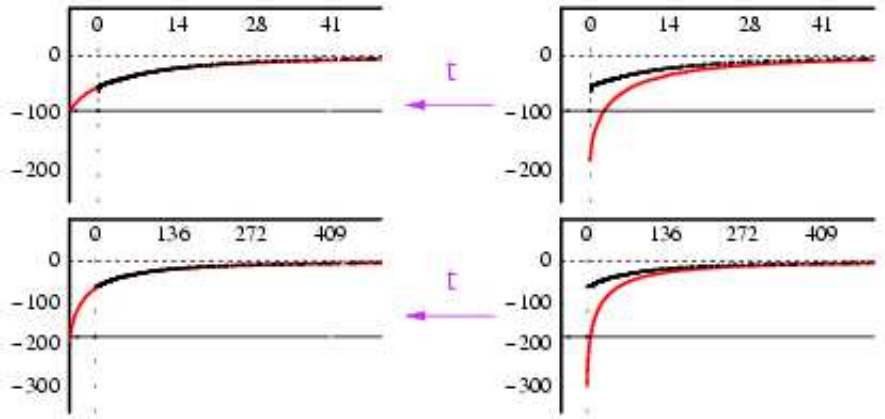
$E_c(\kappa)$: κ–LDA



C. Gutlé, A.S., Phys. Rev. A 75, 032519 (2007) #122

Modified Hamiltonians

Choice of κ ¸choice of 0



System	Origin	Origin
Be	fit	HOMO
Ne^{6+}	fit	HOMO

C. Gutlé, A.S., Phys. Rev. A 75, 032519 (2007) #122

Approximations: LDA+

Motivation

DF approximations: successful

$$\overline{E}_{\mathrm{xc}}[n; T, W = 0] \approx \int n(r)\, \varepsilon_{\mathrm{xc}}(n(r),\ |\nabla n(r)|,\ \ldots)\, d^3 r$$

LDA for given T , W

Uniform electron gas calculation with n:

$\mathcal{H} \rightarrow \mathcal{E}_0$

$H \rightarrow E_0$

Correction/electron: $\overline{\varepsilon}$

LDA correction $\int d^3 r \;\; n(r)\, \overline{\varepsilon}(n(r))$

Quantities to approximate

$$\left\langle \partial_\xi \mathcal{T}(\xi) \right\rangle_\xi$$

$$\left\langle \partial_\xi \mathcal{W} \right\rangle_\xi$$

Using reduced density matrices

$$\left\langle \partial_\xi \mathcal{T}(\xi) \right\rangle_\xi = \int\int d^3 r \; d^3 r' \left\{ \partial_\xi t(r, r'; \xi) \right\} \gamma(r, r'; \xi)$$

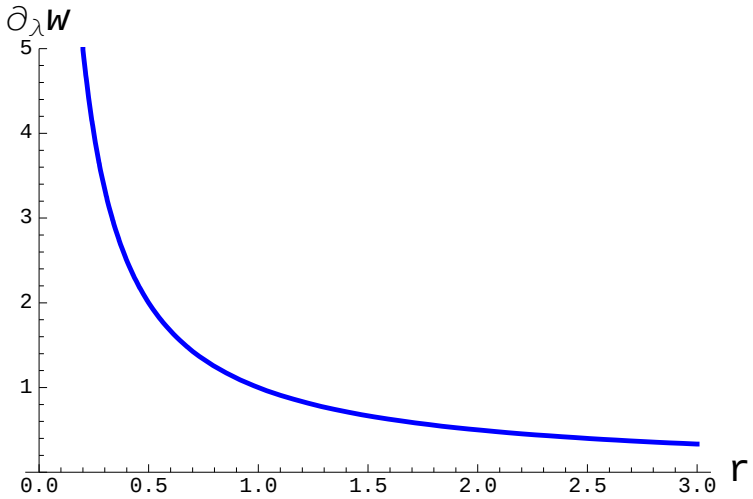
$$\left\langle \partial_\xi \mathcal{W} \right\rangle_\xi = \tfrac{1}{2} \int\int d^3 r_1 \, d^3 r_2 \, P_2(r_1, r_2; \xi) \, \partial_\xi w(r_{12}; \xi)$$

$t(r, r')$, $w(|r_1 - r_2|)$: far from (semi−)local DFAs (?)

Approximations: LDA+

$$w(r_{12}) = \lambda / r_{12}$$

$$\partial_\lambda w = 1 / r_{12}$$



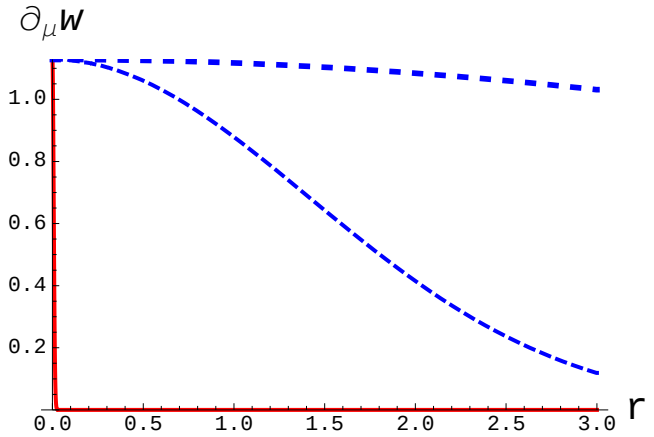
Choice of H

$$\mathcal{T} = T\,,\; w(r) = \mathrm{erf}(\mu r)/r$$

Approximations: LDA+

$$w(r_{12}) = \mathrm{erf}(\mu r_{12}) / r_{12}$$

$$\partial_\mu w = \frac{2}{\sqrt{\pi}} e^{-\mu^2 r_{12}^2}, \quad \mu \to \infty, \ \frac{1}{2}, \ \to 0$$



As $\mu \to \infty$, $\partial_\mu w$ becomes strongly local

Approximations: LDA+

$\overline{E}_x$ at large μ (1−RDM expansion)

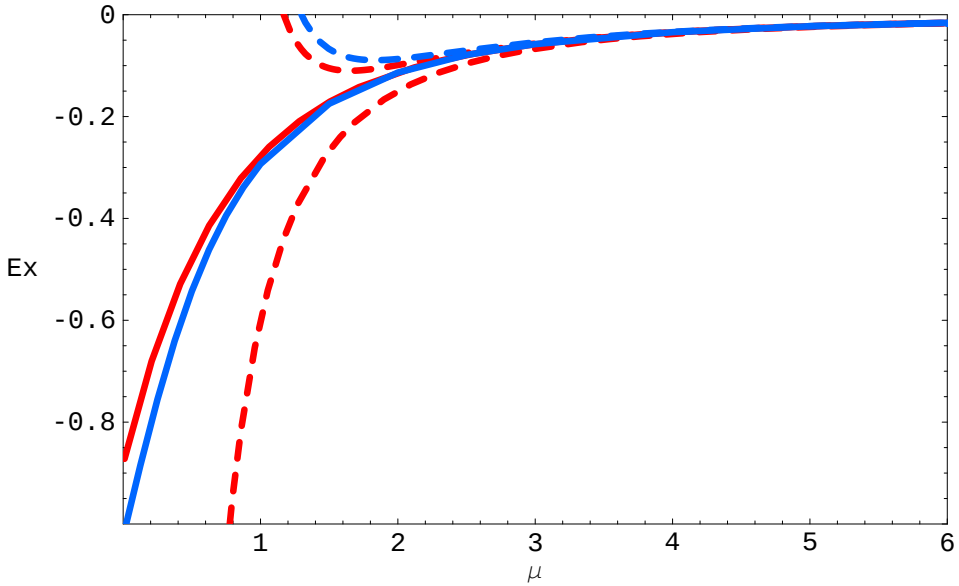
$$\overline{E}_{x,\mu}[n] = \mu^{-2} c_{-2} \int n^2 + \mu^{-4} c_{-4} \int n \left(\frac{|\nabla n|^2}{8n} + \tau \right) + \ldots$$

P. M. W. Gill, R.D. Adamson, J.A. Pople, Mol. Phys. 88, 1005 (1996);
J. Toulouse, F. Colonna, A.S., JCP 122, 14110 (2005) #108

- Exact, universal (closed shells)
- μ – LDA, μ – m – GGA, ... : systematic
- no SIC needed

Approximations: LDA+

$\overline{E}_x(\mu)$ for (He)



μ – LDA accurate

J. Toulouse, F. Colonna, AS, PRA 70, 062505 (2004) #107

Approximations: LDA+

$\overline{E}_c$ good at large μ

$$\overline{E}_{c,\mu}[n] = \mu^{-2} c_{-2} \int \left[P_2(r, r) - n(r)^2 / 2 \right] d^3 r + \mu^{-3} c_{-3} \int P_2(r, r)\, d^3 r \ldots$$

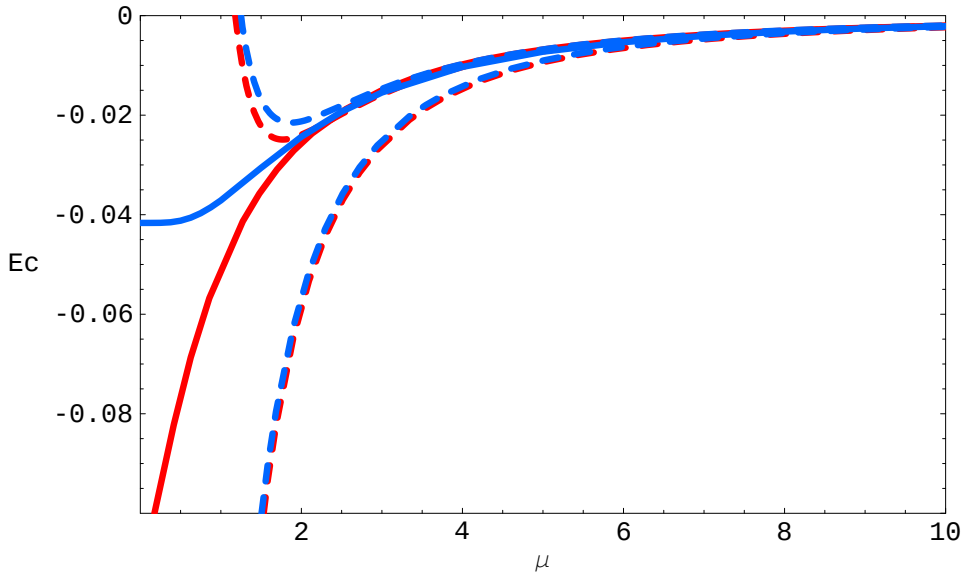
J. Toulouse, F. Colonna, AS PRA 70, 62505 (2004) #107
P. Gori−Giorgi, AS , PRA 73, 32506 (2006) #118

$P_2(r, r)$ well approximated by LDA ('system average')

J. Perdew et al

Approximations: LDA+

Behavior of $\bar{E}_c$ for large μ (He)



μ – LDA accurate

J. Toulouse, F. Colonna, AS PRA 70, 62505 (2004) #107
P. Gori−Giorgi, AS , PRA 73, 32506 (2006) #118

Beyond μ – LDA: μ – PBE

Variants

J.Toulouse,F.Colonna, A.S., PRA 70,62505 (2004) #107
E. Goll, H.−J. Werner, H. Stoll, Phys. Chem. Chem. Phys. 7,3917 (2005)

Different functionals:
Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, JCP 120, 8425 (2004)
J. Toulouse, F. Colonna, A. S., J. Chem. Phys. 122, 14110 (2005) #108

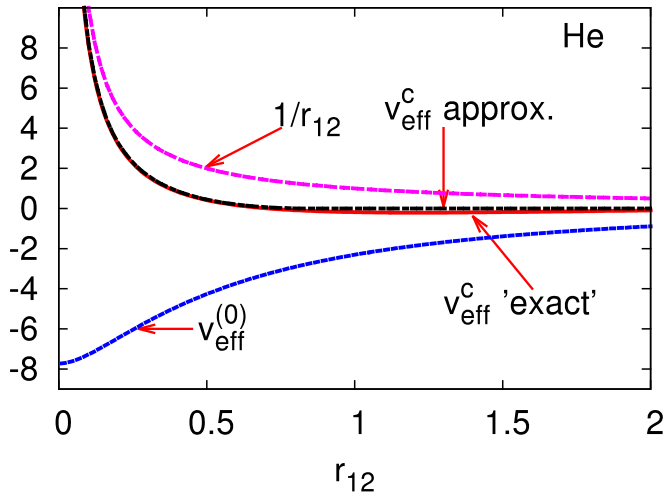
Overhauser model: Schrödinger equation → $f(r_{12})$

Uniform electron gas: A. W. Overhauser, Can. J. Phys. 73, 683 (1995),
P. Gori−Giorgi and J.P.Perdew,Phys.Rev.B 64,155102 (2001)
...
P. Gori−Giorgi, A.S., PRA 71, 32513 (2005) #110

- KS orbitals → $f^{\mu=0}(r_{12})$
- $f^{\mu=0} \rightarrow v_{\text{eff}}^{\mu=0}$
- Overhauser model: approximate correction to $v_{\text{eff}}^{\mu=0}$, $\Delta v_{\text{eff}}^{\mu}$: $v_{\text{eff}}^{\mu=0} + \Delta v_{\text{eff}}^{\mu} \approx v_{\text{eff}}^{\mu} \rightarrow f^{\mu}$

Approximations: LDA+

Overhauser model potential $\Delta v_{\mathrm{eff}}^{\mu} = v_{\mathrm{eff}}^{c,\mu}$



$$\Delta v_{\mathrm{eff}}^{\mu}(r_{12}) \approx w^{\mu}(r_{12}) - \int_{r<\bar{r}_s} \bar{n}\, w^{\mu}(|\, r - r_{12}\,|)\, d^3 r$$

P. Gori−Giorgi, AS, Phil. Mag. B 86, 2643 (2006) #116

Conclusions

Where we are

- Many of the problems of Ψ and of *n* circumvented
- Refinements?
- Simplifications?

Refinements

- Conceptual (construction of $\overline{F}[n]$, $\mathcal{H}$,...)
- Technical (multipolar character of long−range,...)

Simplifications

- Stay with single determinant?
- Construct models?