Combining methods without double counting in RDMFT context

A.Savin

Lausanne 2017

Introduction

Intuition directs us toward models:

- Can intuition give us a single model?
- Can we combine different intuitions = different models?

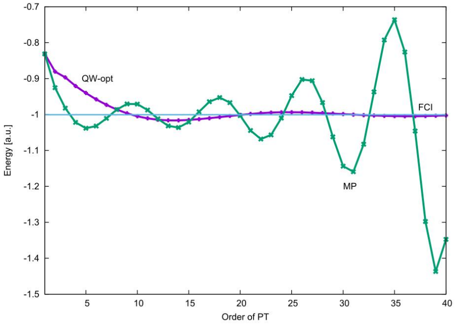
One model finally leads to the correct result

Examples:

- Variational method (full CI)
- Perturbation theory to high order (MPn)

Convergence can be slow, or not present:

H_2, $R = 3$ Å (Mihálka, Szabados, and Surján, 2017)



Model+correction, treated differently

Examples:

- Hartree + exchange-correlation density functional approximation (DFA)
- Hartree-Fock + correlation energy DFA
- Multi-configuration + dynamic correlation

Putting names on intuition

G. Frenking: “The chemical bond is like the unicorn. Everyone knows what it is, but nobody has seen it.”

Putting names on intuition

G. Frenking: “The chemical bond is like the unicorn. Everyone knows what it is, but nobody has seen it.”

True?

Putting names on intuition

G. Frenking: "The chemical bond is like the unicorn. Everyone knows what it is, but nobody has seen it."

True?

"https://www.grazia.fr/lifestyle/insolite/eh-oui-la-licorne-existe-sous-l-ocean-746356"

We can make intuition exist

. . . by introducing concepts that can lead to approximations

- producing good quality results
- easy to compute

Tooth fillings

Overview

- General frame
- Strategies
  - Adiabatic connection
  - Natural orbital occupations
  - Orbital energies

General frame

General frame

“Exact” energy:

$$E = E_\mu + \bar{E}_\mu$$

- model energy, E_μ, chosen, needs “expensive” approximation
- correction, $\bar{E}_\mu$, implicitly defined, works with “cheap” approximation

Note on nomenclature: use “correction” instead of “correlation”, . . .

Important question: what is the model that allows finding a good approximation for the correction?

Clarifications

- Double counting
- Role of operators
- Correction?
- RDMFT problems
- Families of models
- Transfer

Double counting

Double counting

- when contributions are formally not well-separated
- it is not $E < E_0$

Examples of *approximations*

- Coupled cluster: just one method
- LD*A*: E_{xc} is well-defined

Role of operators

Role of operators

- DFT: $F[\rho, T, V_{ee}] = \min_{\Psi\to\rho}\langle\Psi|T + V_{ee}|\Psi\rangle$
- RDMFT: $F[\gamma, V_{ee}] = \min_{\Psi\to\gamma}\langle\Psi|V_{ee}|\Psi\rangle$

Operators not explicit, but important source for producing models.

Example: Kohn-Sham

$$T_s[\rho] = \min_{\Psi\to\rho}\langle\Psi|T|\Psi\rangle = F[\rho, T, V_{ee} = 0]$$

Operator depending functionals

following M. Levy's constrained search

$$\begin{aligned} E_0 &= \min_{\Psi} \langle \Psi | H | \Psi \rangle \\ &= \min_{\gamma} \min_{\Psi \to \gamma} \langle \Psi | H | \Psi \rangle \\ &= \min_{\gamma} \left(\min_{\Psi \to \gamma} \langle \Psi | H_\mu | \Psi \rangle - \min_{\Psi \to \gamma} \langle \Psi | H_\mu | \Psi \rangle + \min_{\Psi \to \gamma} \langle \Psi | H | \Psi \rangle \right) \\ &= \min_{\gamma} \left(\min_{\Psi \to \gamma} \langle \Psi | H_\mu | \Psi \rangle + \bar{E}[\gamma, H, H_\mu] \right) \end{aligned}$$

If H_μ contains V_{ne}, $\bar{E}_\mu$ is *universal* (has no reference to V_{ne}):

$$\begin{aligned} \min_{\Psi \to \gamma} \langle \Psi | H | \Psi \rangle - \min_{\Psi \to \gamma} \langle \Psi | H_\mu | \Psi \rangle &= + \min_{\Psi \to \gamma} \langle \Psi | H - V_{ne} | \Psi \rangle + \int v_{ne} \gamma \\ &\quad - \min_{\Psi \to \gamma} \langle \Psi | H_\mu - V_{ne} | \Psi \rangle - \int v_{ne} \gamma \\ &= \min_{\Psi \to \gamma} \langle \Psi | H - V_{ne} | \Psi \rangle - \min_{\Psi \to \gamma} \langle \Psi | H_\mu - V_{ne} | \Psi \rangle \end{aligned}$$

Correction?

Correction?

$$E = E_\mu + \bar{E}_\mu$$

- Kohn-Sham: $\bar{E}_\mu[\rho]$

  $E_\mu[\gamma] = T_s[\gamma] + V_s[\rho]$

Perdew, Zunger, 1981

- RDMFT: $E_\mu[\gamma]$, e.g., Müller functional

  Where is $\bar{E}_\mu[\gamma]$?

RDMFT problems

RDMFT problems

- We have to model $E_\mu[\gamma]$, and we have to guess how
- A good γ needs a large basis set (for the exact T)
- . . .

Are there $\bar{E}_\mu[\gamma]$ to circumvent them?

Relationship between γ and $P_2(r, r)$

J. C. Kimball (1975): $\Psi(r_{12} \to 0)$ gives:

$$\tilde{\gamma}(k) \propto k^{-8} \int d^3r \, P_2(r, r)$$

$$\tilde{\gamma}(k) = \int d^3r \, d^3r' \, e^{i\,k\cdot(r-r')} \, \gamma(r, r')$$

$$P_2(r_1, r_2) = N(N-1) \int d^3r_3 ... \, |\Psi(r_1, r_2, \dots)|^2$$

Difficulty to construct P_2 corresponds to difficulty to construct γ.

Families of models

μ as a parameter

Families of models

μ as a parameter

Reason: change of μ to

- have less to approximate
- approach exact solution.

Needs more careful treatment. Without it, no guarantee that error decreases with increasing cost.

In literature mostly single model preferred

Transfer idea of universal functionals

Transfer idea of universal functionals

The successful approximations in Kohn-Sham theory are based upon the adiabatic connection
Ansatz using

- exact conditions (not many),
- fixed on some system (uniform electron gas, H atom, . . .), used everywhere (“universality”)

Ansatz for:

- model pair density
- model first-order density matrix ?

Approximations (semi-)local: a way to approximate size-consistency
More natural with γ?

What is to be transferred?

Quantities with universal definition, e.g.,

- kinetic energy density
- natural orbitals
- orbital energies

Adiabatic connection

Adiabatic connection

Correlation affects both the kinetic and the potential energy.

Shuffled into the potential energy by the adiabatic connection

$$H(\lambda) = T + V(\lambda) + \lambda V_{ee}$$

$$E_c = \int_0^1 d\lambda \, \frac{1}{2} \int \int P_c(r_1, r_2; \lambda) \frac{1}{r_{12}}$$

Langreth+Perdew 1975

Adiabatic connection

Correlation affects both the kinetic and the potential energy.

Shuffled into the potential energy by the adiabatic connection

$$H(\lambda) = T + V(\lambda) + \lambda V_{ee}$$

$$E_c = \int_0^1 d\lambda \, \frac{1}{2} \int \int P_c(r_1, r_2; \lambda) \frac{1}{r_{12}}$$

Langreth+Perdew 1975

Shuffled into the kinetic energy by the adiabatic connection

$$E_c = -\int_0^1 d\lambda \, \lambda^{-2} \, \frac{1}{2} \int \nabla_r \cdot \nabla_{r'} \gamma_c(r, r'; \lambda)|_{r=r'}$$

Levy+Görling 1995; S 1995

Large k contribution of $\tilde{\gamma}(k, \lambda) \propto \lambda^2 k^{-8}$

Integrands of E_c

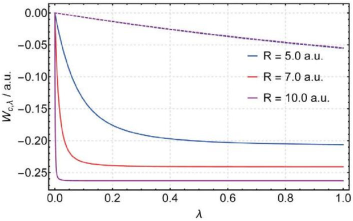
$$E_c = \int_0^1 d\lambda \, W_c(\lambda) = -\int_0^1 d\lambda \, \lambda^{-2} \, T_c(\lambda)$$

$$W_c(\lambda) = \frac{1}{2} \int \int P_c(r_1, r_2; \lambda) \frac{1}{r_{12}}$$

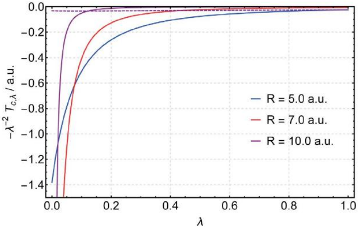
$$-\lambda^{-2} \, T_c(\lambda) = -\lambda^{-2} \, \frac{1}{2} \int \nabla_r \cdot \nabla_{r'} \gamma_c(r, r'; \lambda)|_{r=r'}$$

Integrands of E_c: H_2, different R

Teale, Helgaker, S, 2016



$$W_c(\lambda)$$



$$-\lambda^{-2} T_c(\lambda)$$

$W_c(\lambda \to \infty)$ = system-dependent constant $-\lambda^{-2} T_c(\lambda \to \infty) = 0$; week interaction limit needed.

Do RDMFT models provide it?

Strategies: Natural orbital occupations

Strategies: Natural orbital occupations

$$E = E_\mu + \bar{E}_\mu$$

E_μ: from natural orbitals with occupation number $\nu > \nu_c = \mu$
$\bar{E}_\mu$: from ρ

Motivation

- large ν: static correlation
- small ν: dynamic correlation

Steps when using natural orbitals

- Generate natural orbitals (or approximate them, e.g., from UKS, smaller CI, RDMFA, etc.)
- Use a wave function, or γ to obtain the energy within the space of natural orbitals with a occupation number smaller than an arbitrarily chosen cutoff, ν_c
- Correction $\bar{E}_{\mu=\nu_c}[\gamma(r,r)=\rho(r)]$

Approximation for $\bar{E}_{\nu_c}[\rho]$

$$E_c[\rho; \nu_c] \approx \int \rho(r)\, \epsilon_c(\rho(r))\, \phi(\rho(r), \nu_c)$$

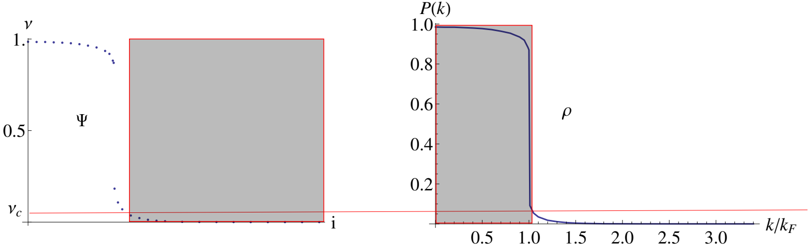
$\phi \leq 1$

- used for weakly occupied natural orbitals
- transferred from uniform electron gas (fit to electron gas data)

$$\phi \approx (\nu_c/\nu_1)^{0.329} \text{ with } \nu_c < \nu_1 = (2 + 16.9/r_s)^{-1}$$

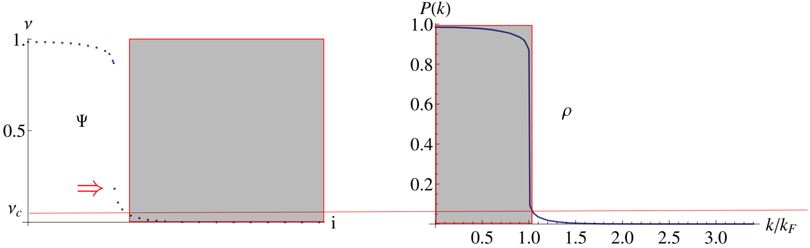
When system (molecular, ...) $\nu_i > \nu_1$
UEG cannot be used, needs another treatment (wave function, RDMFT)

Using natural orbitals



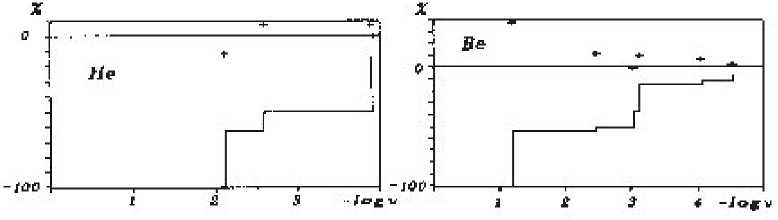
How small should be the cutoff ν_c?

Approximation starts working when occupation number in molecule is not larger than in the uniform electron gas.



How small should be the cutoff ν_c?

Approximation starts working when occupation number in molecule is not larger than in the uniform electron gas.

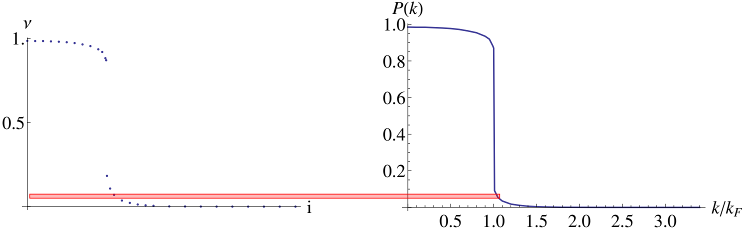


S 1988

Limitations

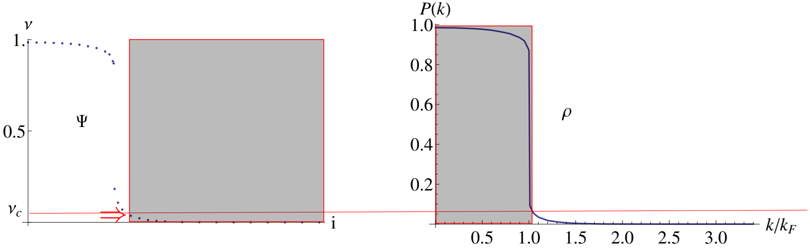
- Discrete (molecule) vs continuous (UEG) distribution of natural orbital occupation numbers
- Global ν_c is problematic in a composite system
- Discontinuities due to changes in the physical parameters (e.g., on potential energy surface)

Discrete (molecule) vs continuous (UEG) distribution of natural orbital occupation numbers



Choice of ν_c

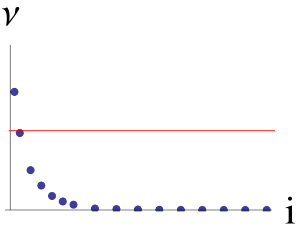
just above the first occupation number not used by the wave function:



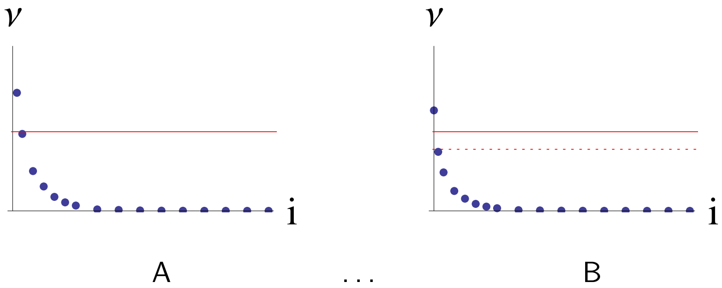
- Advantage: SIC not needed, as for 1 electron $\nu_c \to 0$
- Disadvantage: one more occupation number needed

Global ν_c is problematic in a composite system

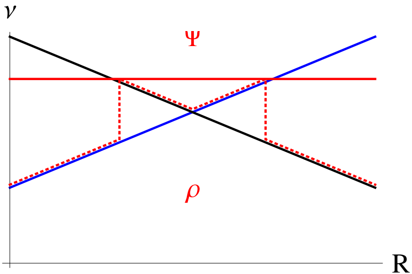
A . . . B



Defining a local ν_c



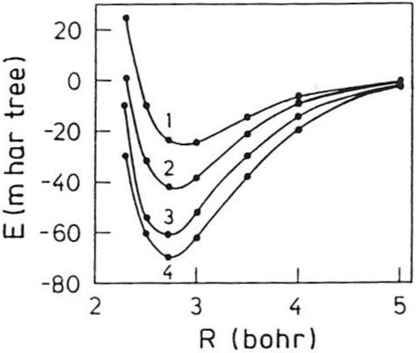
Discontinuities due to changes in the physical parameters (e.g., on potential energy surface)



Smoothing (?)

Some results using natural orbital cutoff

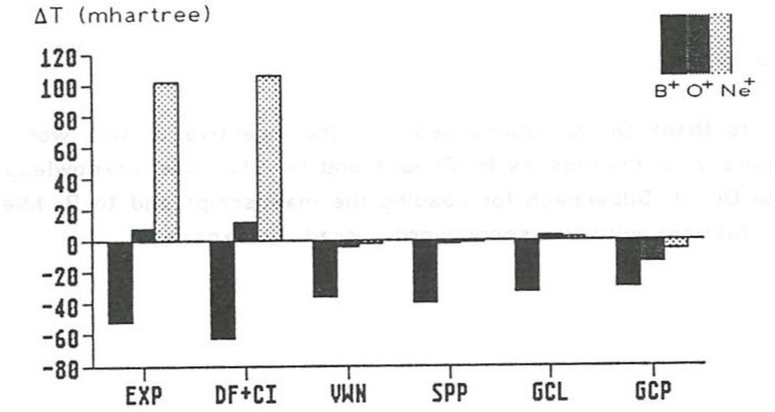
Potential energy curve of the F_2 molecule S 1991



1. MCSCF
2. natural orbital generating MR-CI
3. exact
4. CI+DF

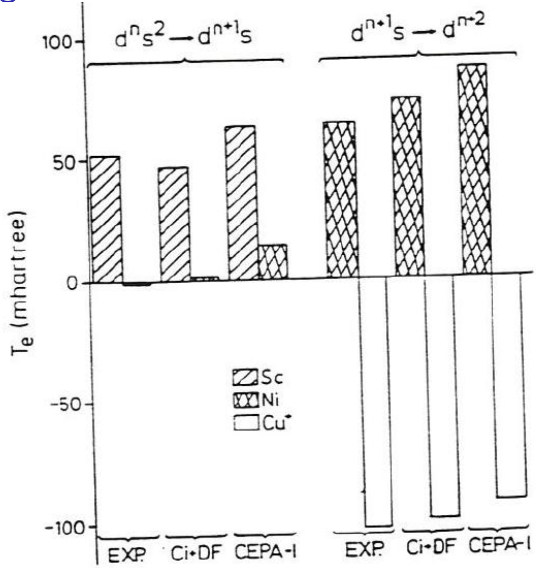
Some results using natural orbital cutoff

Correlation contributions to s → p excitation energies



S 1989

Example: Correlation contributions to $s \to d$ excitation energies



S 1991

Orbital energies

- Claudine Gutlé

- J.B. Krieger: KLI potentials
- J.L. Heully: numerical CCSD program (“accurate”)

How orbital energies get in

$$\begin{aligned} E_c &= -\int_0^1 d\lambda\, \lambda^{-2}\, \left(\langle\Psi(\lambda)|T + V_0|\Psi(\lambda)\rangle - \langle\Psi(\lambda=0)|T + V_0|\Psi(\lambda=0)\rangle\right) \\ &= \sum_i c_i \varepsilon_i(\lambda=0) \end{aligned}$$

as $\forall\lambda$, $\Psi(\lambda) \to \rho(r)$, and $\langle\Phi_J|T + V_0|\Phi_K\rangle = \delta_{JK} \sum_{i(\text{in } J)} \varepsilon_i(\lambda=0)$ for $J \neq K$

(S 1995)

Extension to RDMFT: $\langle\Psi(\lambda)|T + V_0|\Psi(\lambda)\rangle = \int h_0 \gamma(\lambda)$

How to split

- Orbitals with low-lying ε_i: to describe static correlation
- Orbitals with high-lying ε_i: to describe dynamic correlation

For RDMFT:

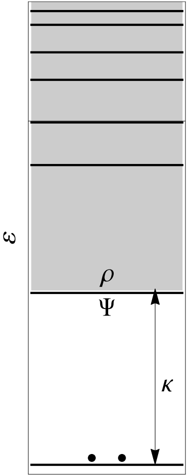
$$T + V_0 \to T + V_0 + X$$

X: one-particle, non-local operator that selects orbital space.

Using orbital energies

- Generate orbitals from KS, OEP, . . .
- Use a wave function, or RDMFT to obtain the energy within the space of orbitals with an orbital energy smaller than an arbitrarily chosen cutoff, $\mu = \kappa$, E_κ,
- Correct the energy by using a density functional that depends on the cutoff to describe the contributions of orbitals with high ε_i, $\bar{E}_\kappa$

Approximation for $\bar{E}_\kappa[\rho]$



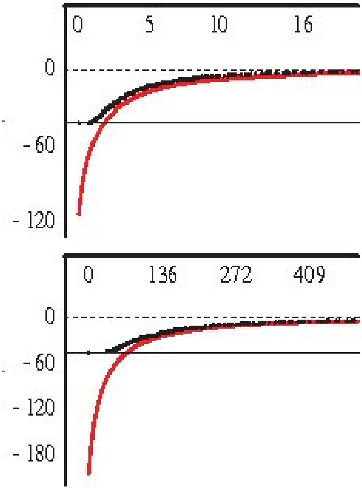
C. Gutlé+AS, 2007

Approximation for $\bar{E}_\kappa[\rho]$

$$E_\kappa[\rho] \approx \int \rho(r)\, \epsilon_c(\rho(r))\, \phi(\rho(r), \kappa)$$

ϕ transferred from uniform electron gas C. Gutlé+AS, 2007

$\bar{E}_c(\kappa)$: He and Ne^{8+}



black: accurate

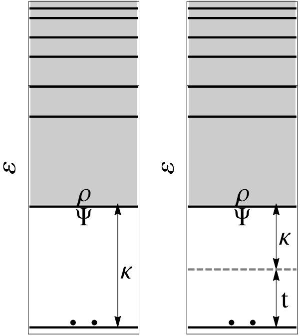
red: κ-LDA

C. Gutlé+AS, 2007

Limitations

- Discrete (molecule) vs continuous (UEG) distribution of orbital energies
- Global κ_c is problematic in a composite system

Discrete (molecule) vs continuous (UEG) distribution of orbital energies: where to choose to cutoff?



C. Gutlé+AS, 2007

Imposing invariance with change of κ

$$E_0 = \min_{\Psi}\{\langle\Psi|T + X(\kappa) + V_{ne} + V_{ee}|\Psi\rangle + \bar{E}_{\kappa}[\rho(\Psi)]\}$$

$$E_0 = E_{\kappa} + \bar{E}_{\kappa}$$

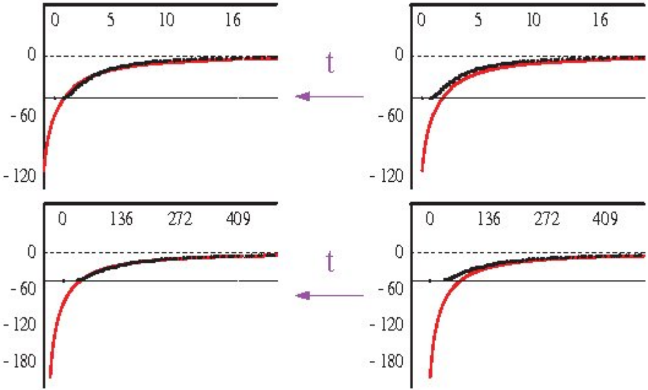
$$E_0 = E_{\kappa_1} + \bar{E}_{\kappa_1} = E_{\kappa_2} + \bar{E}_{\kappa_2}$$

Freedom to fix a parameter such that:

$$\bar{E}_{\kappa_1} - \bar{E}_{\kappa_2} = -(E_{\kappa_1} - E_{\kappa_2})$$

C. Gutlé+AS, 2007

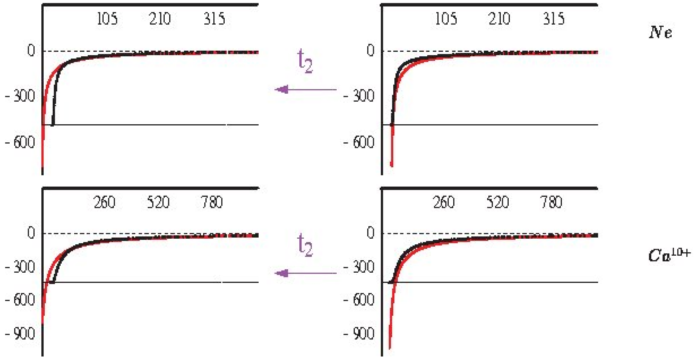
Imposing invariance with change of κ: He and Ne^{8+}



black: accurate $\bar{E}_c$ as a function of $\kappa - \varepsilon_{HOMO}$
red: κ-LDA

C. Gutlé+AS, 2007

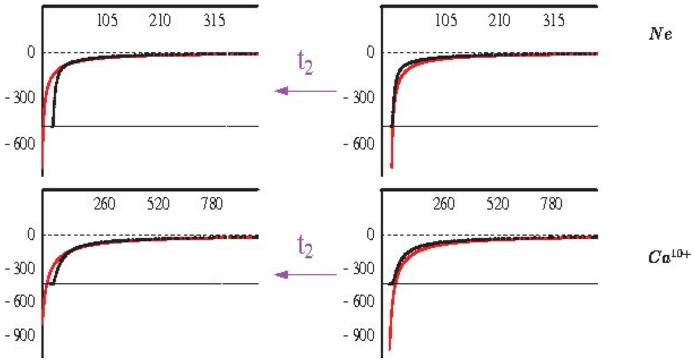
Why are Ne and Ca^{10+} problematic?



black: accurate
red: κ-LDA

C. Gutlé+AS, 2007

Why are Ne and Ca^{10+} problematic?



black: accurate
red: κ-LDA

C. Gutlé+AS, 2007

The shell structure

A local gap

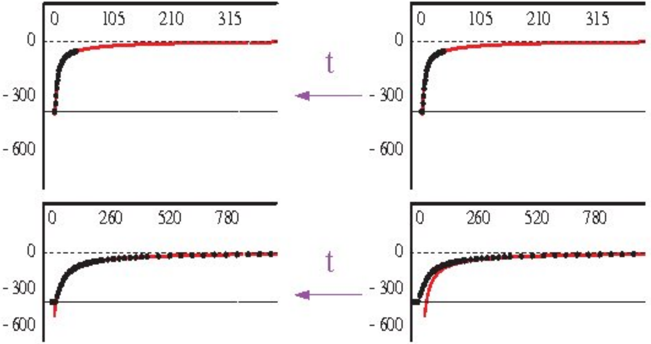
Gap is not the same for core and valence:
Valence space not accessible for correlating core electrons.

A local gap (“ionization potential”):

$$\frac{1}{8}\frac{|\nabla\rho|^2}{\rho}$$

- asymptotic decay of the density (that is exponential)
- atomic density: piecewise exponentially decaying (Parr)

A local gap ($+$ invariance): Ne and Ca^{10+}



black: accurate
red: κ-LDA

C. Gutlé+AS, 2007

Summary

Summary

$$E = E_\mu + \bar{E}_\mu$$

E_μ can be RDMFA, $\bar{E}_\mu$ can be DFA
Separation schemes for static/dynamic correlation:

- Adiabatic connection
- Natural orbital occupation numbers
- Orbital space
- . . . and many more

Much to explore