Correlation energies with one-particle operators

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Introduction
Introduction

Collaboration

• Paris: F. Colonna, C. Gutlé, J. Rey
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• Toulouse: J.L. Heully
Others

- G. E. Engel, W. E. Pickett
- M. Levy, A. Görling
Overview

Adiabatic connection

- Analysis

- Construction of density functional
Analysis

- Philosophy
- Formalism
- Examples of adiabatic connection

Analysis

Philosophy
Analysis

Correlation (energy)

Tiny missing quantity
Analysis

Common knowledge

- Correlation: only for interacting systems
  \[ \Rightarrow \text{two–particle operators needed} \]

- Correlation modifies one–particle properties
  \[ \Rightarrow \text{approximations simpler to understand?} \]
  \[ n, \gamma \]
Examples

• virial theorem $\Rightarrow$ one–particle operators

• relationship between
  – pair function $(r_{12} \to 0)$
  – momentum distribution $(k \to \infty)$
    
    Kimball (1975)

Generalization
Analysis

Formalism
Formalism: adiabatic coupling

\[ H^\lambda = T + V^\lambda + \lambda V_{ee} \]

\( V^\lambda \): to keep the density constant \((n^\lambda = n, \forall \lambda)\)

\[ E^\lambda = \min_{\Psi} \langle \Psi \mid H^\lambda \mid \Psi \rangle; \; \Psi^{\text{min}} \equiv \Psi^\lambda \]

\[ \partial_\lambda E^\lambda = \langle \Psi^\lambda \mid \partial_\lambda V^\lambda \mid \Psi^\lambda \rangle + \langle \Psi^\lambda \mid \partial_\lambda V_{ee} \mid \Psi^\lambda \rangle \]

\[ \int \partial_\lambda E^\lambda \, d \lambda = E - E^{\lambda=0} = \int_0^1 d \lambda \langle \Psi^\lambda \mid V_{ee} \mid \Psi^\lambda \rangle \]

includes correlation effects
Analysis

Formalism: models

\[ \overline{E}_c = \int_0^1 d\lambda \left( \langle \Psi^\lambda | V_{ee} | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | V_{ee} | \Psi^{\lambda=0} \rangle \right) \]

\[ = \frac{1}{2} \int \int (\int d\lambda \ P_c(r_1, r_2; \lambda)) / r_{12} \]

’Naturally’ \( V_{ee} \)

Models for \( P_c(r_1, r_2) \)

Example: uniform electron gas \( \rightarrow \) LDA
Analysis

Formalism: model Hamiltonian

\[ H^\lambda = T + V^\lambda + \lambda \ V_{ee} = \lambda (\lambda^{-1} \ T + \lambda^{-1} \ V^\lambda + V_{ee}) \]

\[ V^\lambda: \ \text{to keep the density constant} \ (n^\lambda = n, \ \forall \ \lambda) \]
\[ E^\lambda = \min_{\Psi} \langle \Psi | H^\lambda | \Psi \rangle; \ \Psi^{\min} \equiv \Psi^\lambda \]

Generalization: \[ H^\lambda = T^\lambda + V^\lambda + V_{ee} \]
Analysis

Formalism: Significance of $T^\lambda$

$T^\lambda$: non-local one particle operator

DFT: $n$ fixes $V$ (local)

$V_{ee}$: now fixed

$T^\lambda \leftrightarrow 1 \text{ RDM } (\gamma)$, like $V^\lambda_{ee} \leftrightarrow \text{ pair function}$
Analysis

Formalism: adiabatic connection

Canonical definition:
For $\lambda = 1$, $H^\lambda = H$, etc.

$$E = \langle \Psi^{\lambda=0} | T + V_{\text{ne}} + V_{\text{ee}} | \Psi^{\lambda=0} \rangle + \overline{E}_c[n]$$

Alternative definition of $\overline{E}_c$, depending on $T^\lambda$

$$\overline{E}_c = \int_0^1 d \lambda \left( \langle \Psi^{\lambda} | \partial_\lambda T^\lambda | \Psi^{\lambda} \rangle - \langle \Psi^{\lambda=0} | \partial_\lambda T | \Psi^{\lambda=0} \rangle \right)$$

needs $\gamma^\lambda(r, r')$
Analysis

Examples of choices for $T^\lambda$
Analysis

Examples of $T^\lambda$: prefactor

$$T^\lambda = \lambda^{-1} T$$

$\lambda \to 0$: $T$ dominant $\Rightarrow \Psi \to$ Kohn–Sham (limits!)

$$\overline{E}_c = -\int_0^1 d\lambda \; \lambda^{-2}(\langle \Psi^\lambda \mid T \mid \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} \mid T \mid \Psi^{\lambda=0} \rangle)$$
Analysis

Comparison: $T^\lambda$, $V_{ee}^\lambda$

$\varepsilon_c$ as function of $1/r_s \propto n^{1/3}(r)$
- 2–particle formula (curve)
- 1–particle formula, $T^\lambda = \lambda^{-1} T$ (dots)

Analysis

Examples of $T^\lambda$: prefactor, generalized

\[
\bar{E}_c = \int_0^1 d\lambda \, \lambda^{-2} \left( \langle \Psi^\lambda | T + V_{KS} | \Psi^\lambda \rangle - \langle \Psi^{\lambda=0} | T + V_{KS} | \Psi^{\lambda=0} \rangle \right)
\]

Express $\Psi^\lambda$ in basis of KS orbitals:

\[
\bar{E}_c = \bar{E}_c(\varepsilon_i(KS), P_{ii}^\lambda(KS))
\]
Analysis

Examples of $T^\lambda$: gap shift

\[ T^\lambda = T + f(\lambda) P_{\text{virt}} \]

\[ \varepsilon_i \rightarrow \begin{cases} 
\varepsilon_i & i : \text{occup.} \\
\varepsilon_i + G(\lambda) & i : \text{virtual} 
\end{cases} \]

\[ G(\lambda \rightarrow 0) \rightarrow \infty : \text{no mixing of virtual states} \]
Examples of $T^\lambda$: gap shift

One–particle spectrum (uniform electron gas)
Examples of $T^\lambda$: cutoff

\[ T^\lambda = T + f(\kappa(\lambda)) \ P_{>\kappa} \]

$\kappa(\lambda \to 0) \to 0$: no mixing of virtual states

$\kappa(\lambda \to 1) \to \infty$: all states allowed

$\varepsilon_i \to \begin{cases} 
\varepsilon_i & \varepsilon_i \leq \mu + \kappa \\
\infty & \varepsilon_i > \mu + \kappa 
\end{cases}$
Examples of $T^\lambda$: cutoff

One–particle spectrum (uniform electron gas)
Approximations

$$E_c \approx \int f(n(r), |\nabla n(r)|, ...) \, d^3 r$$

$f$: from uniform electron gas $\rightarrow$ LDA
Approach

- accurate calculations
- LDA–like approximations
Conclusions

Several possibilities to choose $T^\lambda$

As always with DFA:

the quality of the approximation decides
Construction

- Method
- Details
- Corrections to the cutoff $\kappa$
Construction

Method
Examples of $T^\lambda$: cutoff

One–particle spectrum (uniform electron gas)

$\kappa \to \infty \quad \kappa > 0$
Examples of $T^\lambda$: cutoff

Discrete spectrum
Construction

\[ \Psi + n \]
Construction

Details
Orbital choice

$\varepsilon_C(k)$: accurate calculation
Be: KLI (left), HF (right)

KLI (KS) concentrates near-degeneracy effect
Construction

Method for $E_c$ via $\Psi$

Numerical CCSD


Method for $\overline{E}_c[n; \kappa]$

LDA: local transfer from the uniform electron gas for the same value of the parameter $\kappa$.

$$E_c = \frac{E_c(\kappa)}{\Psi} + \overline{E}_c[n; \kappa]$$

$$\overline{E}_c[n] = \int n(r) \left( \varepsilon_{c,g}(n(r)) - \varepsilon_{c,g}(n(r), \kappa) \right) \text{ in LDA}$$
Uniform electron gas calculations (CC)

R.F. Bishop, K.H. Lührmann, PRB, 17, 3757 (1978)

C. Gütlé, AS, PRA 75, 32519 (2007)
Reference for $\kappa$ (or $\mu$)

HOMO
Construction

$\bar{E}_c(\kappa)$

Be series (Be, Ne$^{6+}$): accurate, LDA

C. Gutlé, AS (2007)
$\overline{E}_c(\kappa)$

He series (He, Ne$^{8+}$): accurate, LDA
Corrections to the cutoff $\kappa$
Construction

Transfer criterion for $\kappa$

Discrete spectrum: What is $\kappa$?
Construction

A condition from $\partial_\kappa$

As

$$E_c = E_c(\kappa) + \overline{E}_c[n; \kappa]$$

Transfer criterion for $\kappa$

$$\partial_\kappa E_c = 0 = \partial_\kappa E_c(\kappa) + \partial_\kappa \overline{E}_c[n; \kappa]$$

$\overline{E}_c$ not known, but $\partial_\kappa \overline{E}_c$ can be determined
$\overline{E}_c$ not known, but $\partial_{\kappa} \overline{E}_c$ can be determined
Choosing $\kappa$ for systems with gap

Transfer criterion

$$\partial_\kappa E_c = 0 = \partial_\kappa E_c(\kappa) + \partial_\kappa \overline{E}_c\left[ n; \kappa_{\text{arbitrary}} + t \right]$$
κ translation

He series (He, Ne\textsuperscript{8+}): accurate, LDA

C. Gutilé, AS (2007)
C. Gutlé, AS (2007)
$\kappa$ translation

Ne series (Ne, Ca$^{10+}$): accurate, LDA

C. Gutlé, AS (2007)
Construction

Transfer criterion for $\kappa$

Local $\kappa$?
Choice for a local $\kappa$

'Local' ionization potential: $\frac{1}{8} \left| \nabla n(r) \right| / n(r)$

Shell structure of atoms:
Construction

Local $\kappa$ and translation

He

\[ E_c = E_c - \frac{1}{8} \left| \frac{\Sigma}{\rho} \right|^2 + \kappa + t \]

\[ E_c = E_c - \frac{1}{8} \left| \frac{\Sigma}{\rho} \right|^2 + \kappa \]

C. Gutlé, AS (2007)
Construction

Local $\kappa$ and translation

$\text{Ne}^{8+}$

\[ E_C - E_C^8 \Xi \frac{\sum_{\rho}^{\Xi}}{\rho^2 + \kappa + t} \]

\[ E_C - E_C^8 \Xi \frac{1}{\rho} |\sum_{\rho}^{\Xi}|^2 + \kappa \]

C. Gutzl, AS (2007)
Construction

Local $\kappa$ and translation

Be

C. Gutlé, AS (2007)
Construction

Local $\kappa$ and translation

$\text{Ne}^{6+}$

\[ E_C - E_C^\beta |\sum \rho|^{2+\kappa+t} \]

\[ E_C - E_C^\beta |\sum \rho|^\beta + \kappa + t \]

C. Gutlé, AS (2007)
Local $\kappa$ and translation

Ne series: Ne and $\text{Ca}^{10+}$

C. Gutilé, AS (2007)
Conclusions

- DFA already show that some $\overline{E}_c[n] \approx E_c$

- More input with $\lambda$ (or $\kappa$) dependence: $\overline{E}_c[n, \kappa]$

- Stability with respect to change in $\kappa \left( \partial_\kappa \overline{E}_c \right)$ achieved locally
References (selected)

• C. Gutlé, AS, PRA 75, 032519 (2007)
• M. Levy, A. Görling, PRA 52, R1808 (1995)
• AS, PRA 52, R1805 (1995)

• G.E. Engel, W.E. Pickett, PRB 54, 8420 (1996)

$t(\text{IP})$

Ne, He, Ar, Mg, and Be series.