Beyond Conventional Functionals in DFT

Adrienn Ruzsinszky
Department of Physics
Temple University
Philadelphia, 19122

Supported by DOE

Outline

- Density functional approximations
- Failures of the approximations
- Basic Self-Interaction Correction (SIC) equations
- SIC corrections (Perdew-Zunger and Scaled-down versions), one-electron SI freedom
- Results
- Generalization of the SIC error for many-electron systems
- Derivative discontinuity and sum-rule of the open systems
- Construction of the local hybrids, range-separated hybrids
- The RPA approximation, adiabatic connection fluctuation dissipation theorem, relation to Coupled Cluster method
- RPA for atomization energies, stretched bonds,
- RPA+ method
- SOSEX and beyond RPA approximations
- Local-field effects, kernels, ultranonlocality

Basics of DFT

Theorems by Hohenberg and Kohn 1964 and Kohn and Sham 1965 showed that, in principle, the gs electron density determines the gs energy and everything else. To find the gs density and energy for *N* electrons in external potential $v(\vec{r})$, we have to minimize:

$$\delta\{E[n]-\mu\int d^3 r n(\vec{r})\}=0 \qquad \delta E/\delta n(\vec{r})=\mu$$

μ : chemical potential

Hohenberg and W. Kohn, Phys. Rev. B **136**, **B864** (1964).
W. Kohn and L.J. Sham, Phys. Rev. **140**, **A1133** (1965).
Density Functional Theory, edited by R.M. Dreizler and E.K.U. Gross, Springer, Berlin (1990).

The Hohenberg-Kohn theorem is only an existence theorem.
It tells us that the energy functional exists, but not what it is (in computable form).

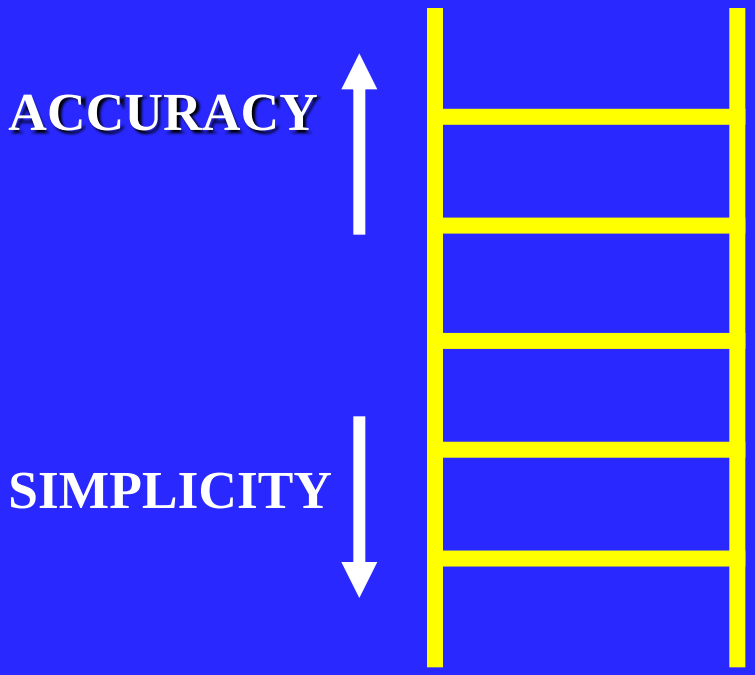
$$E[n_\uparrow,n_\downarrow]=T_s[n_\uparrow,n_\downarrow]+\sum_\sigma d^3 r v_\sigma(\vec{r})n_\sigma(\vec{r})+\frac{1}{2}\int d^3 r\int d^3 r`\frac{n(\vec{r})n(\vec{r}`)}{|\vec{r}`-\vec{r}|}+E_{xc}[n_\uparrow,n_\downarrow]$$

T_s is a large term that can be evaluated exactly from orbitals or *one-electron* wavefunctions. Then only the smaller exchange-correlation energy remains to be approximated.

Universal Approximations

$$E_{xc}[m\uparrow, n\downarrow] = E_x[m\uparrow, n\downarrow] + E_c[m\uparrow, n\downarrow] = \int d^3r\, n\, \varepsilon_{xc}(m\uparrow, n\downarrow, \nabla m\uparrow, \nabla n\downarrow, \tau\uparrow, \tau\downarrow, \ldots)$$

Heaven of the Chemical Accuracy



	RPA
ε_x	hyper-GGA
τ and/or $\nabla^2 n$	meta-GGA
∇n	GGA
n	LSDA

Hartree world

John P. Perdew, Physics, Temple University, Philadelphia

Where are semilocal functionals accurate?

(1) For an electron density that varies slowly over space, for which density gradient expansions are exact. The densities of many solids are almost slowly-varying or even almost uniform.

(2) For a density that is compact and displays no fluctuation of electron number, like the densities of atoms or typical small molecules. Here the true exchange-correlation energy density at a point arises mainly from the electron density near that point. There is often an understood error cancellation between semilocal x and semilocal c.

(3) For typical *sp* bonds in molecules and solids around the equilibrium bond lengths

"WEAK CORRELATION"

Where do semilocal functionals fail?

(1) For a density that varies rapidly over space. (But this is rare in real atoms, molecules, and solids.)

(2) For a compact density with fluctuating electron number, where the average electron number *N* is not an integer. In this case, part of the exchange-correlation hole or "personal space" around the electron in the open system is located on a distant reservoir system that shares the electrons. Semilocal information cannot recognize this situation.

This situation occurs for the valence *d* and *f* electrons in transition-metal oxides or heavy metals (strongly-correlated systems). But it also occurs in a one-electron system, bond-stretched H_2^+. It can occur in other stretched-bond situations, such as the dissociation curves of open-shell atoms or the transition states of chemical reactions. That is why semilocal functionals underestimate the energy barriers to chemical reactions.

“STRONG CORRELATION”

AJ. Cohen, P. Mori-Sanchez, and W. Yang, Science, **321**, **792** (2008).

After 1981, two roads diverged in density functional theory. **The road subsequently more traveled led from LSDA to GGA and higher-level semilocal functionals (meta-GGAs)** and eventually made DFT widely useful to chemists as well as solid state physicists.

The road subsequently less traveled led from LSDA to the self-interaction correction (SIC) and to the derivative discontinuity (and perhaps to the related LDA+U method), and to a useful treatment of strongly-correlated materials such as transition-metal oxides, lanthanides, and actinides.

Interestingly, **the strengths and weaknesses of these divergent approaches are complementary**: The semilocal functionals can be accurate for sp bonds near equilibrium, while SIC can be accurate for open-shell d or f electrons or for any stretched bonds over which electrons are shared.

Question for the Future: Is it possible to bring back the SIC on the Ladder of Approximations? Answer: Yes!

MR. Pederson and JP Perdew, Psi-k Newsletter, (2011).

The exact exchange-correlation energy and hole

$$E_{xc} = \frac{1}{2}\int d^3r \int d^3r' \quad n(\vec{r}\,)\frac{n_{xc}(\vec{r},\vec{r}\,')}{|\vec{r}\,'-\vec{r}|}$$

The exact exchange-correlation energy is the electrostatic interaction between the electron density at a point and the density of the exchange-correlation hole surrounding an electron at that point.

$n_{xc}(\vec{r},\vec{r}\,`) = \int_0^1 d\lambda n_{xc}^{\lambda}(\vec{r},\vec{r}\,`)$: is the coupling constant averaged hole density.

λ: coupling constant

The hole is created by three effects:

self-interaction correction } exchange
Pauli exclusion principle }

Coulomb repulsion — correlation

M. Levy, Phys. Rev. A **43**, 4637 (1991).

Langreth and Perdew, 1976

Exact constraints on $E_{XC}[n]$

(Langreth, Perdew, Gunnarson,Lundqvist, Levy,…)

Formally exact (but not computable) expressions for $E_{xc}[n]$ imply exact constraints on E_{XC} , e.g.,

$$E_{xc} = \frac{1}{2}\int d^3 r n(\vec{r}) \int d^3 r` \frac{n_{xc}(\vec{r},\vec{r}`)}{|\vec{r}-\vec{r}`|} = E_x + E_c$$

$n_{xc}(\vec{r},\vec{r}`) =$ density at $\vec{r}'$ of the exchange-correlation hole an electron at $\vec{r}$

$$n_x(\vec{r},\vec{r}`) \le 0$$

$$\int d^3 r' n_x(\vec{r},\vec{r}`) = -1$$

$$\int d^3 r' n_c(\vec{r},\vec{r}`) = 0.$$

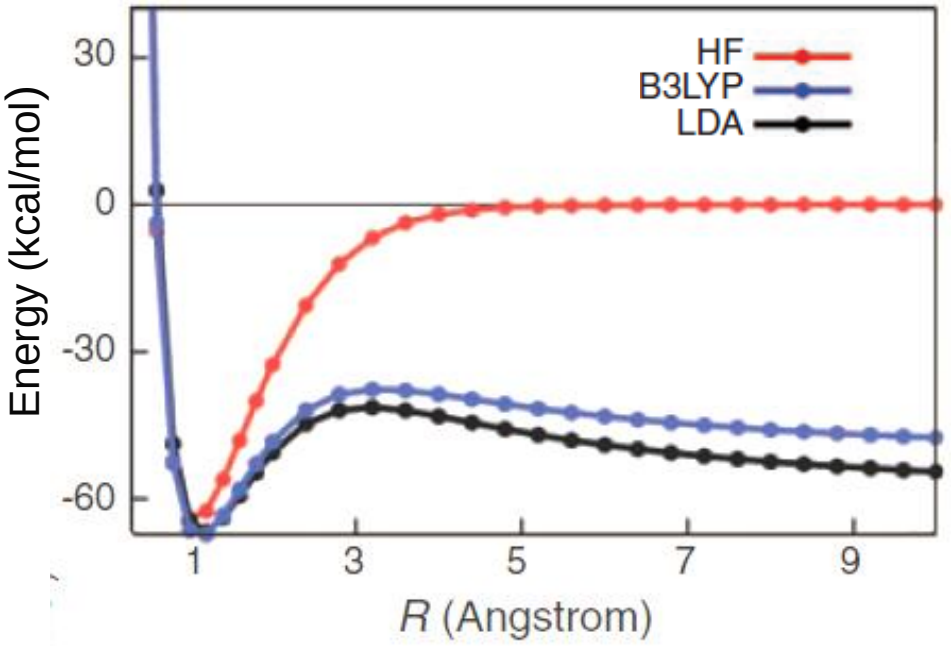
These and other exact constraints explain why LDA works better than expected, and suggests approximations beyond LDA.

Other exact constraints:

- Density gradient expansions for slowly-varying densities $n(\vec{r})$.
- Scaling relations for $E_X + E_C$ when $n(\vec{r})$ is scaled.
- Lieb-Oxford lower bound on $E_{XC}[n]$, etc.
- The higher-level approximations keep the constraints of the lower-level ones , and add more exact constraints.

Failures of the semilocal functionals for radicals–failures come from the approximate character of the exchange hole

- Symmetric charged radicals with realistic charges on the fragments display spurious energy barrier at intermediate bond length



Example: dissociation of H_2^+ in PBE

← energy of the H atom

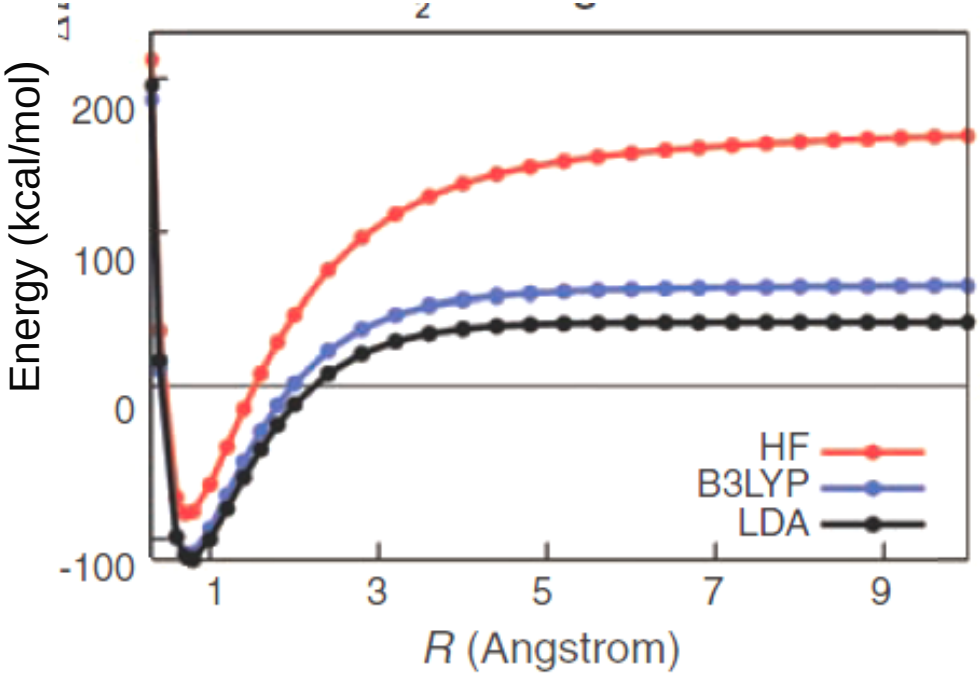
← dissociates into two $H^{+½}$

In the exact dissociation limit, all the following configurations $H^{q+} + H^{(1-q)+}$, where $0 < q < 1$ must be energetically equivalent

A. Ruzsinszky, J.P. Perdew, G.I. Csonka, O.A. Vydrov, and G.E. Scuseria, J. Chem. Phys. **126**, **104102** (2007).

Failures of the semilocal functionals for neutral homonuclear diatomics

Dissociation of H_2 molecule

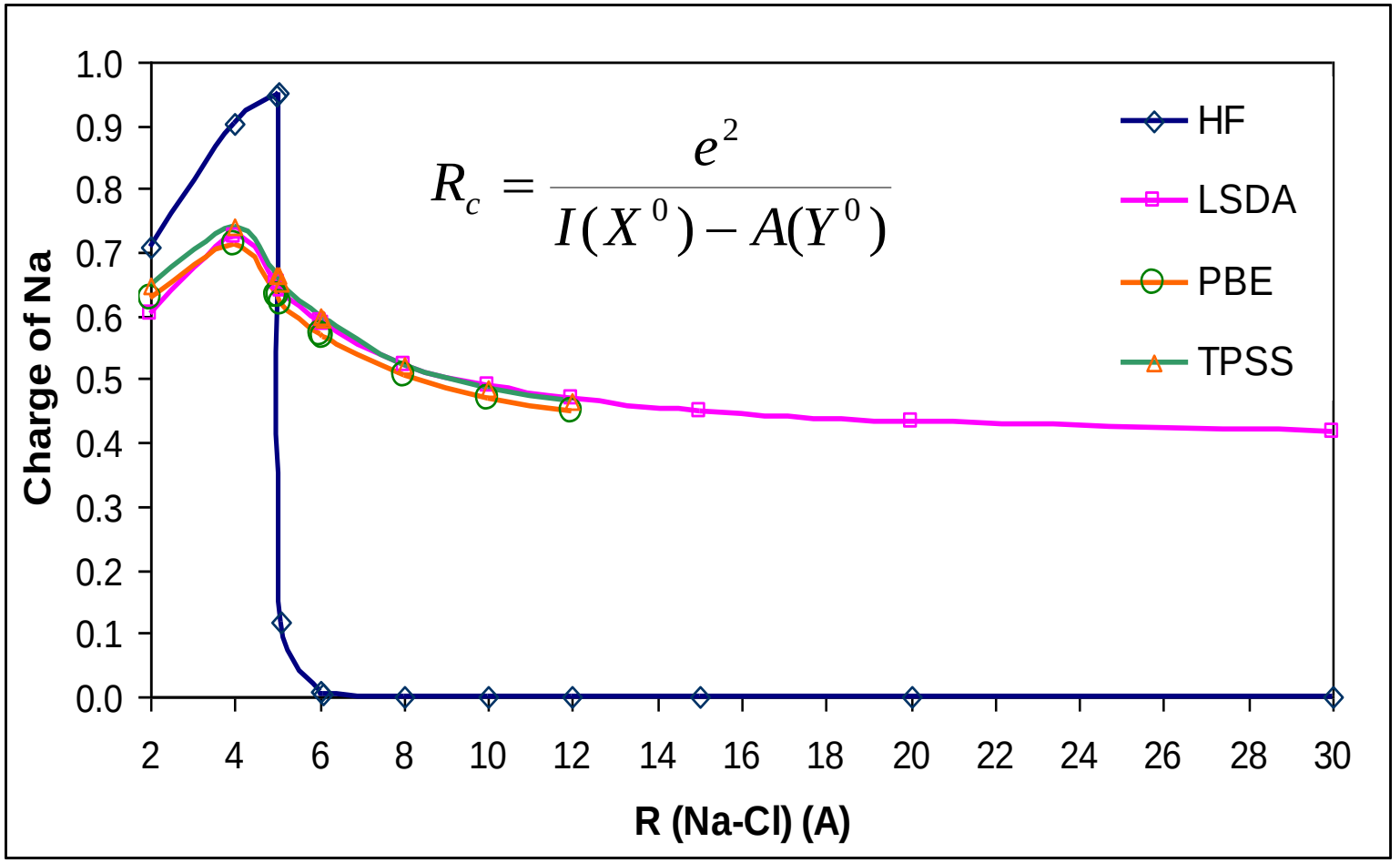


AJ. Cohen, P. Mori-Sanchez, and W. Yang, Science, **321**, **792** (2008).

Dissociation of many-electron systems

- Asymmetric neutral molecules dissociate with unrealistic fractional charges

Fractional (Mulliken) charge q on Na in NaCl as a function of bond length R (in Å).The Hartree-Fock behavior is qualitatively right.



A. Ruzsinszky, J.P. Perdew, G.I. Csonka, O.A. Vydrov, and G.E. Scuseria,. J. Chem. Phys. **125**, **194112** (2006).
A.D. Dutoi and M. Head-Gordon, Chem. Phys. Lett. **422, 230** (2006).

Requirement for the exact exchange-correlation functional in a one-electron system

The self-exchange must cancel the self-repulsion:

$$E_x[n_i,0]+U[n_i]=0$$

The correlation energy must obey:

$$E_c[n_i,0]=0$$

U[n] is the Coulomb interaction of an electron with itself

$$U[n]=\frac{1}{2}\int\int\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}drdr'$$

Basic SIC equations

The semilocal exchange-correlation hole is local, the exact hole is non-local. The SIE mimics non-dynamical correlation

Many-electron self-interaction error

SIE manifests itself not only in one-electron systems but in many-electron systems as well. It is easy to remove the spurious SI term in a one-electron system, but not easy in a many electron system.

No unique definition of SIE in many-electron systems

- Underestimation of reaction energy barriers
- Wrong description of charge transfers
- Overestimation of the electric response
- Incorrect asymptotic behavior of the xc potential; leads to wrong description of Rydberg-states
- underestimation of the binding energy of electrons

O.A. Vydrov and G.E. Scuseria, J. Chem. Phys. **121**, **8187** (2004).
A Ruzsinszky, JP Perdew, GI Csonka, GE Scuseria, OA Vydrov, Phys. Rev. A **77, 060502 (**2008).

Perdew-Zunger Self-Interaction Correction

$$E^{\mathrm{PZ}}\left[\{n_{i\sigma}\}\right] = E^{\mathrm{KS}}[n_\alpha, n_\beta] + \Delta E^{\mathrm{SIC}}\left[\{n_{i\sigma}\}\right]$$

$$\Delta E^{SIC}[\{n_{i\sigma}\}] = -\sum_{\sigma=\alpha,\beta}\sum_{i=1}^{N_\sigma}(E_{xc}[n_{i\sigma},0] + U[n_{i\sigma}])$$

where $n_{i\sigma}$ are the **orbital densities**

$$n_{i\sigma}(\vec{r}) = \left|\varphi_{i\sigma}(\vec{r})\right|^2$$

$$n_\sigma(\vec{r}) = \sum_{i=1}^{N_\sigma} n_{i\sigma}(\vec{r})$$

In the PZ-SIC localized orbitals are used to maximize the SI correction, and achieve size consistency. The SIC potential is orbital dependent.

PZ-SIC is not invariant under a unitary transformation of occupied orbitals!

J.P. Perdew and A. Zunger, Phys. Rev. B **23**, **5048** (1981).

Analogy of PZ-SIC with DFT+U

$$E_{DFA+U} = E_{DFA} + E_U = E_{DFA} + E_{Hub} - E_{dc}$$

The DFT+U approach adds an orbital-dependent term to DFT energy. In this expression the E_{Hub} term contains the detailed on-site electron-electron interactions. E_{dc} measures the corresponding electron correlation already included in the DFA, which must be subtracted from the total energy functional to avoid double-counting. The effective strength of the on-site Coulomb-repulsion is expressed by the parameter *U*.

The choice of the "*U*" parameter is not rigorously based. It can be derived from:

- solid-state calculations
- linear-response calculations

V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44, 943** (1991).
V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48, 16929** (1993).
A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52, R5467** (1995).
B. M. Cococcioni and S. Gironcoli, Phys. Rev. B **70, 235121, (**2005).

Performance of the PZ-SIC

- **Performance of PZ-SIC:**

  it improves some properties of stretched bond systems, improves Rydberg-excited states, correctly predicts the anitferromagnetic insulator state of transition-metal oxides, but it spoils thermochemistry at equilibrium

- PZ-SIC often seems to overcorrect
- The greatest inconvenience of the PZ-SIC: dependence on orbital representation
- PZ-SIC works better for LSDA than for other functionals

O.A. Vydrov and G.E. Scuseria, J. Chem. Phys. **121**, **8187** (2004).
O.A. Vydrov and G.E. Scuseria, J. Chem. Phys. **122,184107**(2005).
A. Svane, G. Gunnarson, Phys. Rev. Lett, **65**,**1148**, (1990).
Z. Szotek and W. M. Temmerman and H. Winter, Phys. Rev. B, **47**, **4019**, (1993).
G.I. Csonka and B. G. Johnson, Theor. Chem. Acc, **99, 158** (1998).
S. Patchkovskii and T. Ziegler, . Chem. Phys. **116, 7806** (2002).
A. Filipetti, N. Spaldin, Phys. Rev. B**, 67, 125109**, (2003).
J. Gräfenstein, E. Kraka and D. Cremer, J. Chem. Phys. **120, 524** (2004).
H. Gudmundsdottir, Y. Zhang, P. M. Weber and H. Jónsson J. Chem. Phys. **139, 194102** (2013).

Scaled down Self-Interaction Correction

$$E^{SIC} = -\sum_{\sigma=\alpha,\beta}\sum_{i=1}^{N\sigma}\left\{\int dr\left(\frac{\tau_\sigma^w}{\tau_\sigma}\right)^k n_{i\sigma}(r)\right\}\left(U[n_{i\sigma}]+E_{xc}[n_{i\sigma},0]\right)$$

Scaling Factor

$\mathbf{0 \le X_i \le 1}$

the same as in the PZ correction

τ^W_σ (r): is the Weizsäcker kinetic energy

$$\tau_\sigma^w(r) = \frac{|\nabla n_\sigma|^2}{8n_\sigma}$$

τ_σ(r): the kinetic energy density of σ spin electron

k: non-negative parameter

Perdew-Zunger correction is a special case when $k = 0$

The correction is scaled down in many-electron regions.

In one-electron regions the $\tau^W_\sigma(r) = \tau_\sigma(r) \longrightarrow X_i = 1.$

OA Vydrov, GE Scuseria, JP Perdew, A Ruzsinszky, GI Csonka, J. Chem. Phys. **124 (9), 094108**, (2006).

Tests of the Scaled SIC for atomization energies

- equilibrium:

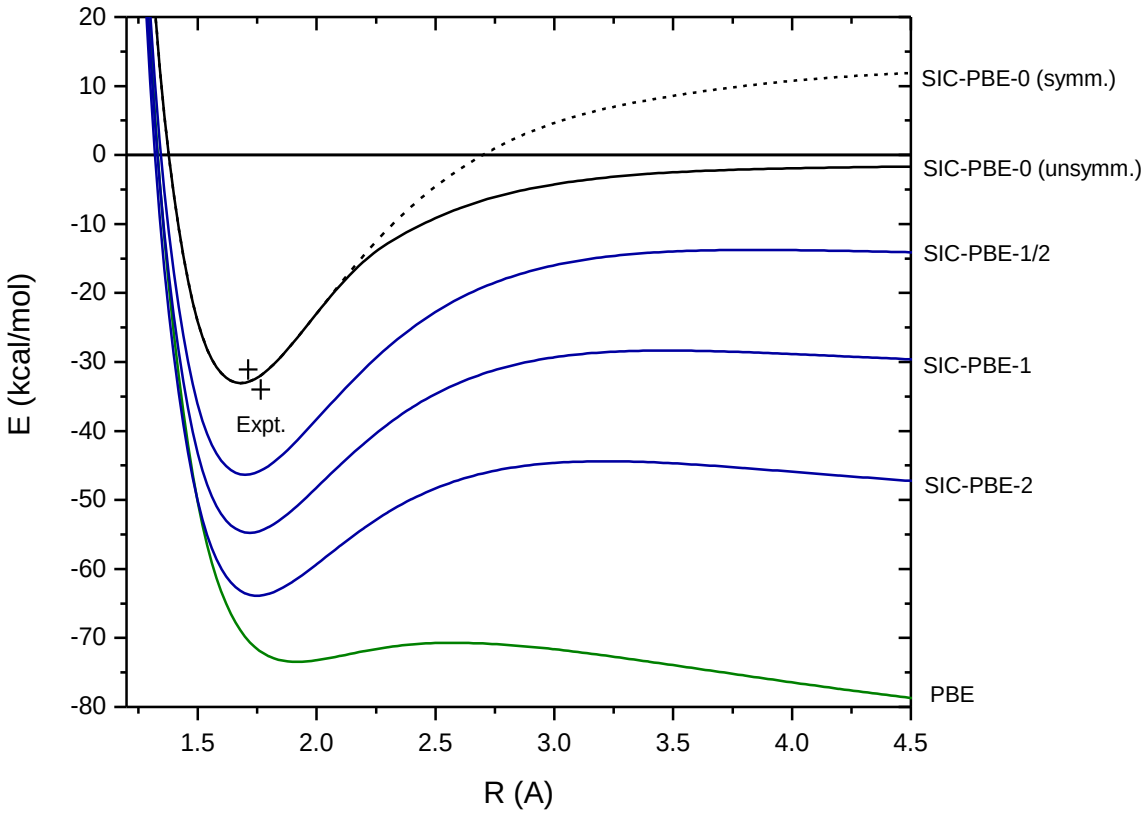
Errors in **Atomization Energies** for the AE6 test set (kcal/mol)

functional	ME	MAE	RMSE	functional	ME	MAE	RMSE
LSDA	77.3	77.3	92.2	TPSS	4.1	5.9	6.6
SIC-LSDA (k = 0)	57.7	60.3	79.4	SIC-TPSS (k = 0)	–28.8	34.7	39.2
SIC-LSDA (k = 1)	18.6	21.0	25.1	SIC-TPSS (k = 1)	1.3	9.9	10.6
SIC-LSDA (k = 2)	6.7	8.6	10.0	SIC-TPSS (k = 2)	9.4	11.3	12.4
SIC-LSDA (k = 3)	0.8	7.2	8.7	SIC-TPSS (k = 3)	11.9	12.4	14.1
PBE	12.4	15.5	17.8	PBEh	0.6	6.2	6.6
SIC-PBE (k = 0)	–13.6	17.0	21.7	SIC-PBEh (k = 0)	–19.2	19.8	25.6
SIC-PBE (k = 1)	7.8	12.6	14.7	SIC-PBEh (k = 1)	0.2	8.1	11.2
SIC-PBE (k = 2)	13.5	16.0	19.3	SIC-PBEh (k = 2)	5.1	10.3	11.9
SIC-PBE (k = 3)	14.8	17.2	20.6	SIC-PBEh (k = 3)	6.3	10.9	12.1

GI Csonka, OA Vydrov, GE Scuseria, A Ruzsinszky, JP Perdew, J. Chem. Phys. **126 (24), 244107**, (2007).
S. Klüpfel, P. Klüpfel and H. Jónsson, J. Chem. Phys. **137, 124102**, (2012)
S. Klüpfel, P. Klüpfel and H. Jónsson, Phys. Rev. A **84,050501(R)** (2011).

- dissociation

At dissociation of the many-electron systems Ne_2^+ the scaled-down SIC fails.



These errors in the open systems are not necessarily corrected either by a semilocal or a one-electron self-interaction free functional. To avoid this error, a universally-useful functional must be many-electron self-interaction free for all positive integer numbers, not only for one-electron densities.

OA Vydrov, GE Scuseria, JP Perdew, A Ruzsinszky, GI Csonka, J. Chem. Phys. **124 (9), 094108**, (2006).

Fractional (Mulliken) charge q on Na in NaCl at bond lengths R = 6 Å and 12 Å, evaluated in the HF, LSDA (k=∞) and PBE GGA (k=∞), with scaled-down self-interaction corrections (k=2 and 1), and with full Perdew-Zunger(PZ) self-interaction correction (k=0). The PZ results are qualitatively correct.

The critical bond length is: $$R_c = \frac{e^2}{I(X^0) - A(Y^0)}$$

Method	k	q (R=6Å)	q (R=12Å)
HF	-	0.01	0.00
LSDA	∞	0.59	0.47
LSD-SIC	2	0.73	0.44
LSD-SIC	1	0.83	0.33
LSD-SIC-PZ	0	0.97	0.10
PBE	∞	0.57	0.45
PBE-SIC	2	0.71	0.39
PBE-SIC	1	0.81	0.22
PBE-SIC-PZ	0	0.92	0.05

Unitarily invariant Self-Interaction Correction

There are many possible choices for a unitary transformation from KS orbitals to SIC orbitals. The standard ways to find localized orbitals is usually computationally demanding. We can restrict the unitary transformations within the occupied orbital space introducing a constraint for the orbitals constructing the SIC correction.

It is possible to choose such orbitals which are dependent on a quantity that are unitarily invariant. The Fermi orbitals satisfy this condition:

$$F_{i\sigma}(\vec{r}) = \frac{n_\sigma(a_{i\sigma},\vec{r})}{\sqrt{n_\sigma(a_{i\sigma})}} = \frac{\sum_\alpha \psi^*_{\alpha\sigma}(a_{i\sigma})\psi_{\alpha\sigma}(\vec{r})}{\sqrt{\left\{\sum_\alpha \left|\psi_{\alpha\sigma}(a_{i\sigma})\right|^2\right\}}} \equiv \sum_\alpha T^\sigma_{i\alpha}\psi_{\alpha\sigma}(\vec{r})$$

- At **r** = $a_{i\sigma}$ the absolute square of the FO orbital is identically equal to the tot al spin density. ⟶ **The FO is a localized function**!
- The absolute square of the FO is minus the x hole.

VL. Luken and DN. Beratan. Theor. Chim. Acta**, 6, 65**, (1982)
VL. Luken and JC. Culberson, Theor. Chim. Acta, **6, 79**, (1984).
MR Pederson, A Ruzsinszky, JP Perdew, J. Chem. Phys. **140**, **121103,** (2014).

Atomization energies of molecules(eV) with different approximations including SIC and FSIC.

Mol.	LSD (PW92)	GGA (PBE)	SIC-LSD	FSIC-LSD	Expt.
N_2	11.58	10.49	10.89	9.80	9.84
O_2	7.62	6.30	5.77	4.80	5.12
CO	12.94	11.65	12.02	11.00	11.32
CO_2	20.57	18.16	18.29	16.88	17.00
C_2H_2	19.93	18.01	19.81	18.93	17.52
LiF	6.75	6.01	6.17	5.61	6.03
H_2	4.91	4.51	4.97	4.97	4.77
Li_2	1.03	1.06	1.04	1.02	1.06
CH_4	20.06	18.24	20.25	20.23	18.21
NH_3	14.56	13.05	14.21	14.24	12.88
H_2O	11.64	10.27	10.68	10.71	10.10
MAE	1.62	0.41	0.94	0.62	

MR Pederson, A Ruzsinszky, JP Perdew, J. Chem. Phys. **140**, **121103,** (2014).

Generalization of the one-electron self-interaction error

Let ε_i and f_i be the orbital energy and occupation number of orbital Ψ_i.The total energy change arising from infinitesimal changes δf_i of the occupation numbers is:

$$\delta E = \sum_i \varepsilon_i \delta f_i$$

The orbitals obey the „aufbau" principle, with $f_i=1$ for $\varepsilon_i < \mu$ and $f_i=0$ for $\varepsilon_i > \mu$.
The first ionization potential and electron affinity are:

$$I(Z) = E(Z-1) - E(Z) = -\int_0^1 df \varepsilon_Z(Z-1+f)$$

$$A(Z) = E(Z) - E(Z+1) = -\int_0^1 df \varepsilon_{Z+1}(Z+f)$$

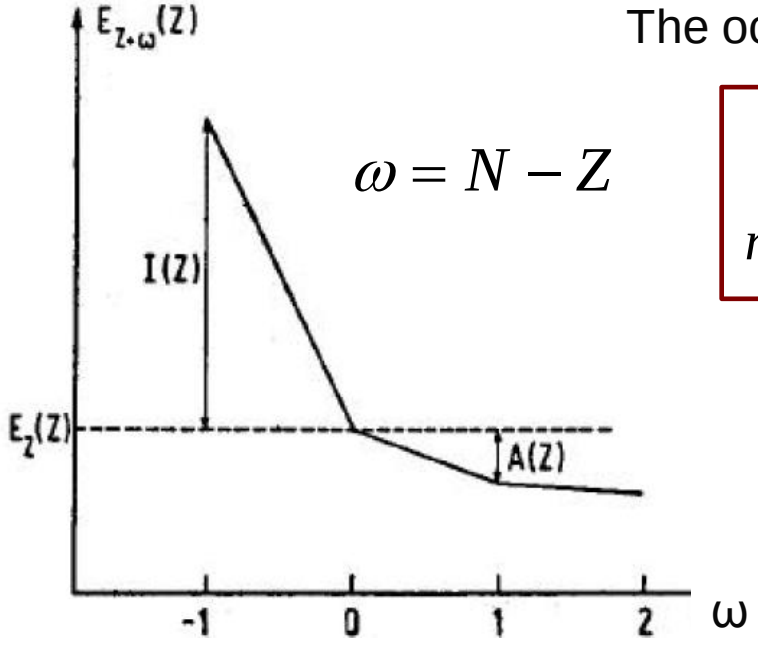
Janak's theorem makes a connection between KS and physical energy differences.

J.F. Janak, Phys. Rev. B **18,7165**,(1978)

Derivative discontinuity

The gs energy and electron density in an open system is expressed with an ensemble of the Z and Z+1 systems:

The occup. number ω follows a ground-state path



$$\omega = N - Z$$

$$E[N] = (Z-N)E(Z-1) + (N-Z+1)E(Z)$$

$$n(N;\vec{r}) = (Z-N)n(Z-1;\vec{r}) + (N-Z+1)n(Z;\vec{r})$$

According to Janak's theorem:

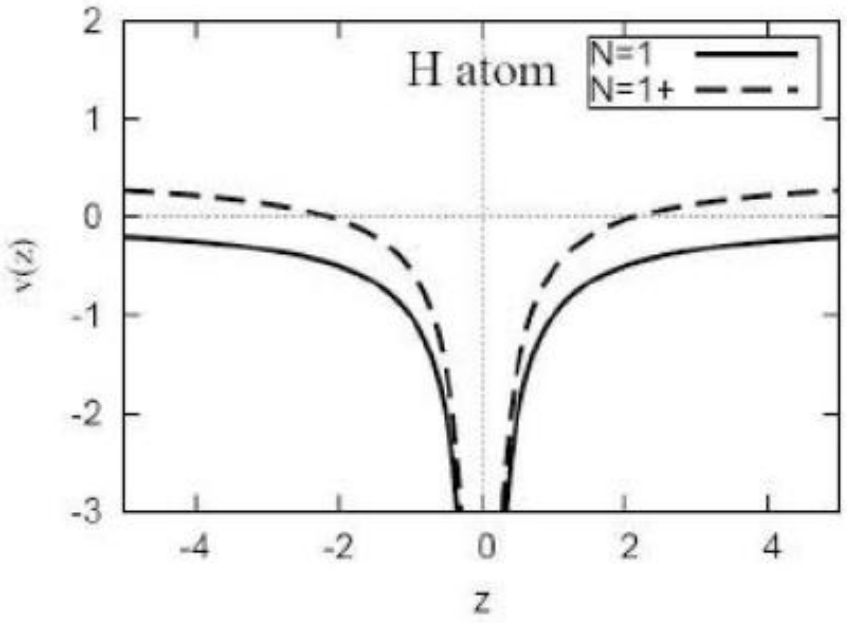
$$\mu = \frac{\delta E}{\delta N} = \begin{cases} \varepsilon_Z(N) = -I(Z) & N \le Z \\ \varepsilon_{Z+1}(N) = -A(Z) & N > Z \end{cases}$$

The energy eigenvalue of the highest partly-occupied KS orbital is the chemical potential as N crosses integer Z.

As a function of the continuous variable N the gs energy E(N) of the open system is a linkage of straight-line segments with possible derivative discontinuities at integer values of N.

What happens when N increases through the integer Z?

The effective potential can change only by an infinitesimal plus a constant C:



$$\lim_{\omega\to 0}\left[\frac{\delta E_{xc}}{\delta n(\vec{r})}\Big|_{Z+\omega} - \frac{\delta E_{xc}}{\delta n(\vec{r})}\Big|_{Z-\omega}\right] = C$$

$$I(Z) - A(Z) = \varepsilon_{Z+1}(Z) - \varepsilon_{Z}(Z) + C$$

where: $\varepsilon_Z(Z)$ and $\varepsilon_{Z+1}(Z)$ are the highest occupied (HOMO) and lowest unoccupied energy (LUMO) levels in the KS system.

The fundamental gap of any system:

$E_g = I - A$ *(= 24.6 eV for He)*

The exact Kohn-Sham gap:

ε_g^{KS} = HOMO − LUMO (= 1*s* − *2s* = *21.16 eV for He)*

These gaps are *not the same!*

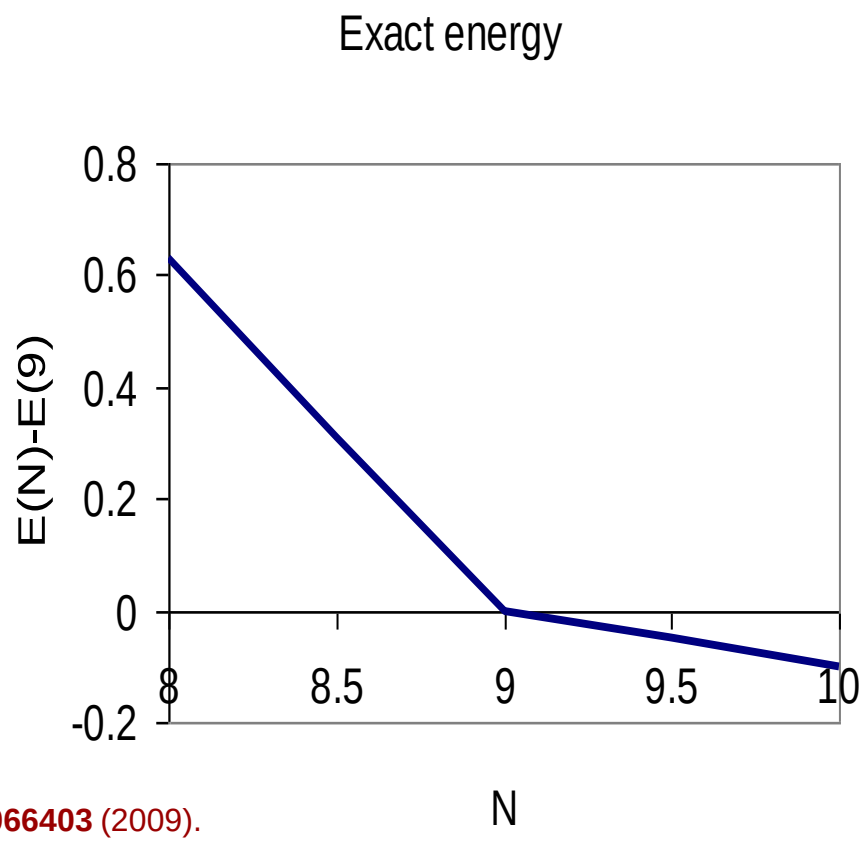
$$\varepsilon_{LUMO} = -A + \Delta_{xc}$$

Many electron self-interaction freedom

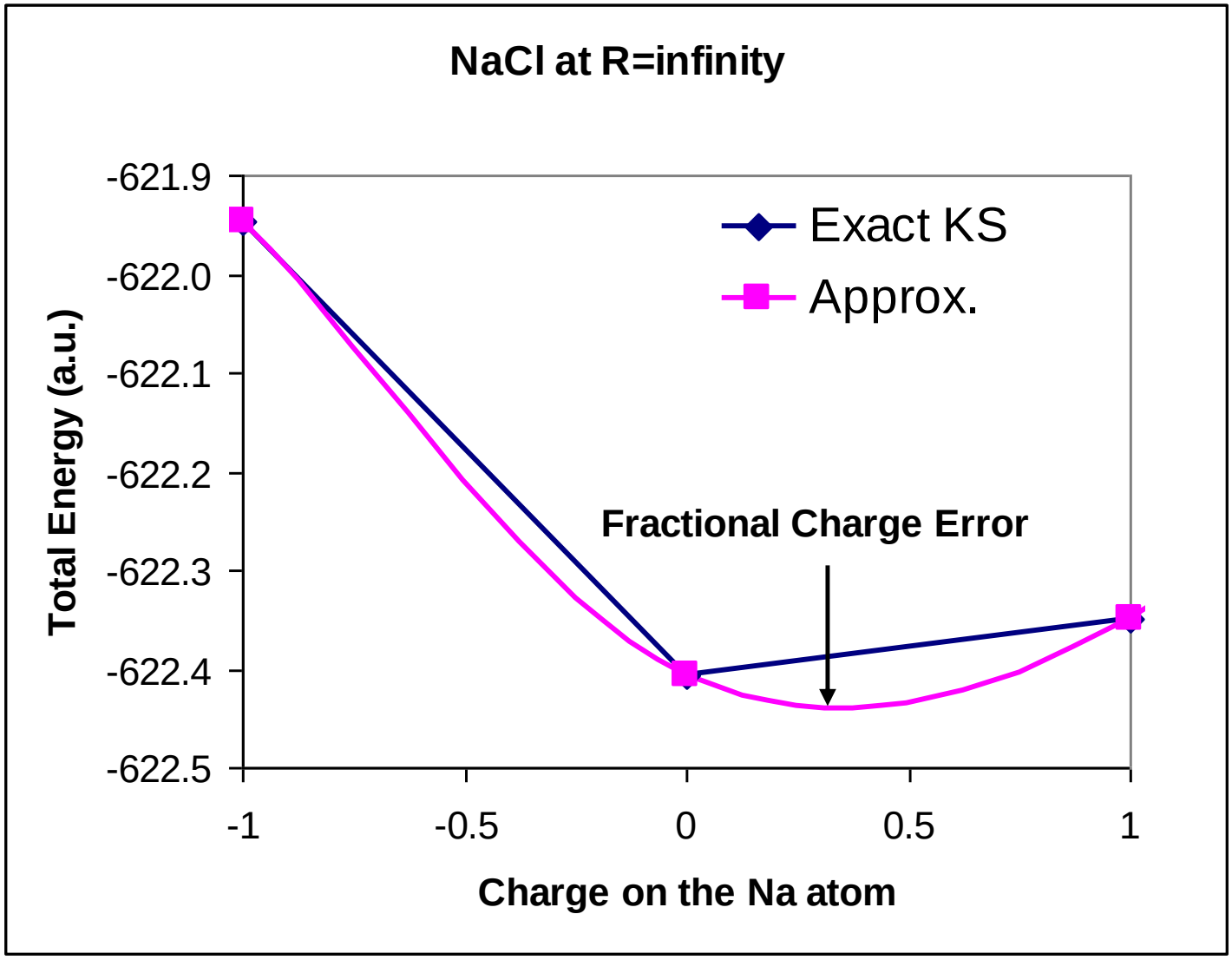
A functional is nearly "Many-electron self-interaction-free" (Z= positive integer) if its total energy for a system of fixed external potential with electron number N in the range $Z - 1 < N \leq Z$ has

(a) a realistic linear variation with N,
(b) realistic energies at integer values of Z.

The HF theory nearly satisfies condition (a), but not (b) because of the missing correlation.
Semilocal functionals satisfy condition (b), but not (a) because of the self-interaction error.



J.P. Perdew and M. Levy, Phys. Rev. Lett. **51**, **1884**(1983)
L.J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, **1888** (1983)
P. Mori-Sanchez, A. J. Cohen, and W. Yang Phys. Rev. Lett. **102**, **066403** (2009).


NaCl at R=infinity
-621.9
-622.0
-622.1
-622.2
-622.3
-622.4
-622.5
Total Energy (a.u.)
Exact KS
Approx.
Fractional Charge Error
-1
-0.5
0
0.5
1
Charge on the Na atom

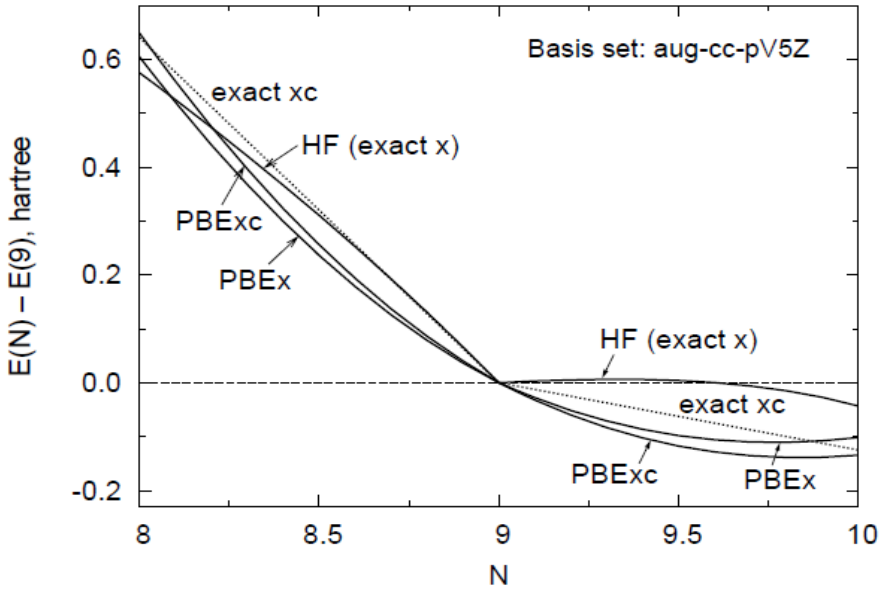
Many electron self-interaction freedom from the aspect of the sum-rule

The failure of the semilocal functionals and the Hartree-Fock method can be explained through the x and xc-hole sum rule.

Here we generalize the sum-rule expression for open systems with fluctuating number of electrons.

The x and xc-hole sum-rule is the key to construct global and local hybrids of the fourth rung of the ladder of approximations.

Electron fluctuation in an open subsystem



•The HF midpoint error is positive and less harmful than that of the semilocal x and xc energy.In the Hartree-Fock theory there is an electron fluctuation between the open subsystems. The energy minimization forces integer occupation numbers on the separated fragments, e.g., a symmetry broken $F\ldots F^{+}$ as the dissociation limit of F^{2+}.The $F^{0.5+}\ldots F^{0.5+}$ is a harmfully deep minimum for the semilocal density functionals since their midpoint error is negative .

J.P Perdew, A. Ruzsinszky, G. I Csonka, Ol. A Vydrov, G. E Scuseria, Vi. N Staroverov, J. Tao, Phys. Rev. A **76 , 040501**, (2007)

A.J. Cohen, P. Mori-Sanchez, and W. Yang J. Chem. Phys. **129**, **121104** (2008)

By the orthonormality of the orbitals in any closed or open system, the equations for the density matrix and the exchange-hole imply the **sum rule**:

$$\rho_\sigma(\vec{r},\vec{r}') = \sum_\sigma f_{\alpha\sigma}\psi_{\alpha\sigma}(\vec{r})\psi^*_{\alpha\sigma}(\vec{r}') \qquad n_x(\vec{r},\vec{r}`) = -\sum_\sigma \frac{\left|\rho_\sigma(\vec{r},\vec{r}`)\right|^2}{n(\vec{r})}$$

$$\int d\mathbf{r}' n_x(\vec{r},\vec{r}') = -\sum_\sigma \sum_\alpha f_{\alpha\sigma} n_{\alpha\sigma}(\vec{r}) / n(\vec{r})$$

where $n_{\alpha\sigma}(\mathbf{r}) = f_{\alpha\sigma}\,|\psi_{\alpha\sigma}(\mathbf{r})|^2$. Adding and subtracting the term $-1 = -\sum_{\alpha\sigma} \frac{n_{\alpha\sigma}(\vec{r})}{n(\vec{r})}$ to this equation:

$$\int d\mathbf{r}' n_x(\vec{r},\vec{r}') = -1 + \sum_{\alpha\sigma} f_{\alpha\sigma}(1 - f_{\alpha\sigma})\left|\psi_{\alpha\sigma}(\vec{r})\right|^2 / n(\vec{r})$$

When all the occupation numbers are 1 or 0, the right-hand side of the equation becomes -1, which is also the sum rule implicitly assumed by LSD, PBE, or TPSS. But, when some occupation numbers fall between 1 and 0, the right-hand side will fall between -1 and 0.

The fourth-rung: global hybrids,hyper-GGA's and range-separated hybrids

Hybrid functionals add the nonlocal exact exchange:

$$\varepsilon_x^{ex}(\vec{r}) = \frac{1}{2}\int d^3r` \frac{n_x(\vec{r},\vec{r}`)}{|\vec{r}-\vec{r}`|} \qquad n_x(\vec{r},\vec{r}`) = -\sum_\sigma \frac{|\rho_\sigma(\vec{r},\vec{r}`)|^2}{n(\vec{r})}$$

The earliest hyper-GGA's were the global hybrids:

$$E_{xc} = aE_x^{ex} + (1-a)E_x^{sl} + E_c^{sl}$$

Here "***a***" is a position independent parameter

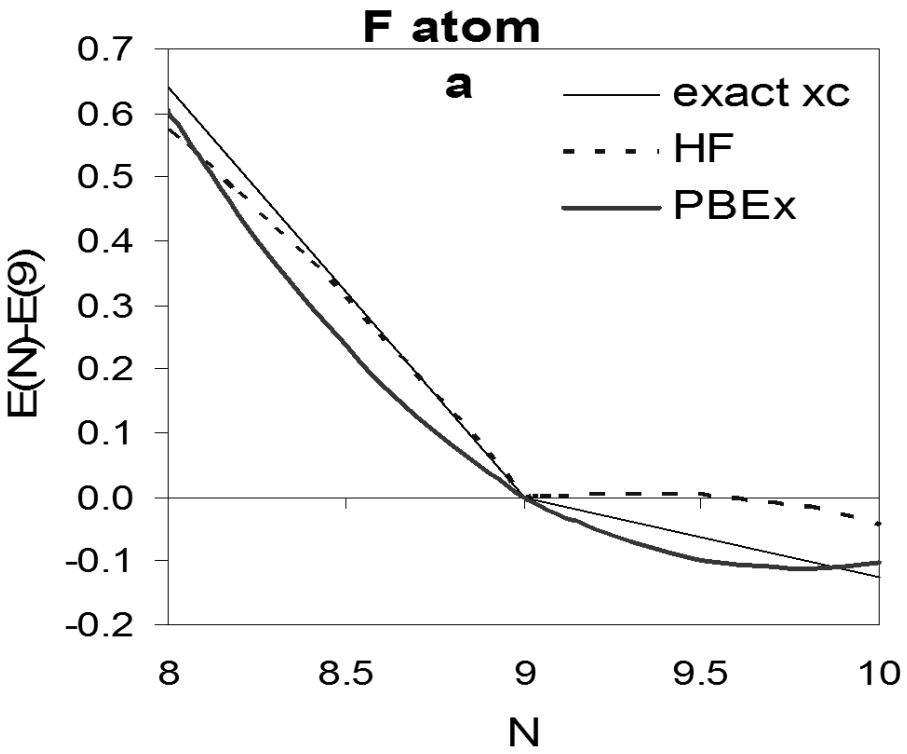
Global hybrid are very popular in chemistry (B3LYP), but some hybrids are popular in solid state physics as well.

The global hybrid form can be generalized to a **local hybrid**.

A.D. BeckeJ. Chem. Phys. **98**, **5648,** (1993).

Construction of the hyper-GGA

- The sum-rule for open systems and the concept of M-electron self-interaction freedom justify the form of the global and local hybrids.
- Some region dependent fraction of exact exchange is necessary to correct the semilocal approximations.



A mixture of the concave down semilocal exchange and concave up exact exchange are necessary to construct a global or local hybrid with the straight line between the integer electron numbers.

The local hybrid functional has the form:

$$\varepsilon_{xc}^{lh} = \varepsilon_x^{ex} + [1 - a(\vec{r})](\varepsilon_x^{sl} - \varepsilon_x^{ex}) + \varepsilon_c^{sl}$$

static correlation

$0 \le a(r) \le 1$ and sl =TPSS

J.P. Perdew, V.N. Staroverov, J. Tao and G E. Scuseria, Phys. Rev. A **78**, **052513** (2008).

Range-separated hybrids

Hybrid functionals do not fully solve the band-gap problem. Improvement is found by using the range-separated hybrid scheme (RSH).

The repulsive Coulomb potential is split into a long-range (LR) and short-range (SR) term:

$$\frac{1}{\vec{r}} = \frac{erf(\omega\vec{r})}{\vec{r}} + \frac{erfc(\omega\vec{r})}{\vec{r}}$$

A subset of RSHs is in which the SR exchange is represented by a semilocal term, while the LR part is treated by the "exact" exchange term:

$$\left(-\frac{\nabla^2}{2} + v_{ext}(\vec{r}) + v_H([n];\vec{r}) + \hat{V}_F^{lr,\omega} + v_x^{sr,\omega}([n];\vec{r}) + v_c^{sr}([n];\vec{r})\right)\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

$$\hat{V}_F^{lr,\omega}\varphi_i(\vec{r}) = -\sum_i \varphi_j(\vec{r})\int dr' \frac{erf(\omega|\vec{r}-\vec{r}'|)}{|\vec{r}-\vec{r}'|}\varphi_j^*(\vec{r}')\varphi_i(\vec{r}')$$

$v_x^{sr,\omega}([n]$ is the semilocal exchange potential

A. Savin, Recent Advances in Density Functional Methods, Part I. **129**, (1995)
T. Leininger, H. Stoll, H-J. Werner, A. Savin, Chem. Phys. Lett, **275, 151** (1997).
A. Savin, H. Flad, J.Int. Quantum Chem, **56, 327**, (1995)
J. Heyd and G.E. Scuseria,.J. Chem. Phys. **121**, **1187** (2004).
O.A. Vydrov, J. Heyd, A.V. Krukau, and G.E. Scuseria,. J. Chem. Phys. **125**, **074106** (2006).
O.A. Vydrov and G.E. Scuseria, J. Chem. Phys. **125**, **234109** (2006).
E. Livshits and R. Baer, Phys. Chem. Chem. Phys. **9**, **2932** (2007).

The RPA approximation in DFT (Langreth and Perdew, 1976)

The RPA ranks on the fifth-rung of the Ladder of density functionals and employs the unoccupied as well as the occupied Kohn-Sham orbitals in a fully nonlocal way that can potentially solve problems which remain challenges for approximate density functionals.

• By this nonlocal nature, the RPA includes the exact exchange and its correlation describes van der Waals interactions as well.

• It is even able to describe the strong static correlation in the dissociation of the H_2 molecule in a *spin-restricted* formalism.

• RPA becomes relatively exact for the uniform gas in the high-density limit.

D. Bohm and D. Pines, Phys. Rev. **92, 609** (1953).
M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106, 364**(1957).
C. Langreth and J. P. Perdew, Phys. Rev. B **15, 2884** (1977).
J. Dobson, in *Time-Dependent Density Functional Theory, edited by M.* Marques, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross, Springer, Berlin, 2006.
F. Furche, Phys. Rev. B **64, 195120** (2001).
M. Fuchs and X. Gonze, Phys. Rev. B **65, 235109** (2002).
M. Fuchs, Y. M. Niquet, X. Gonze, and K. Burke, J. Chem. Phys. **122, 094116** (2005).
H. Jiang and E. Engel, J. Chem. Phys. **127, 184108** (2007).
M. Hellgren and U. von Barth, Phys. Rev. B **76, 075107** (2007).

RPA as an approximate Coupler-Cluster method

RPA can be regarded as a simple approximate coupled-cluster method. The ring diagrams (particle–hole contractions, essentially) can be **summed to infinite order** if one solves the Riccati equation:

$$B + AT + TA + TBT = 0$$

T^{CCD}: CCD amplitude

A, B, X and Y are $ov \times ov$ (occup and unoccup. orbitals and come from the TD excitation problem:

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix}\begin{pmatrix} X & Y \\ Y & X \end{pmatrix} = \begin{pmatrix} X & Y \\ Y & X \end{pmatrix}\begin{pmatrix} \omega & 0 \\ 0 & -\omega \end{pmatrix}$$

The direct-RPA correlation energy:

$$E_c^{dRPA} = \frac{1}{2} Tr(BT^{CCD})$$

The direct-RPA accounts only for the direct correlation from symmetric Coulomb terms.
The dRPA is not self-interaction free.

G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, J. Chem. Phys.**129, 231101** (2008).
J.G. Ángyán, R.F. Liu, J. Toulouse and G. Jansen, Journal of Chem. Theory and Comp. **7, 3116** (2011).

RPA as plasmon approximation

The RPA correlation energy can be considered as a difference of electronic zero point vibrational energies.

$$E_c^{RPA} = \frac{1}{2}\sum_n \left(\Omega_n - \Omega_n^D\right)$$

Ω_n is the nth RPA excitation energy at full coupling,
Ω_n^D is the sum of the zero and first order RPA excitation energies

Significance of the zero-point vibrations in materials science:
The zero-point oscillations of the charge density in one sphere produce a long-range electric field that correlates and interacts with the zero-point oscillations of the charge density in the other sphere. This is the **van der Waals interaction**.

RPA gets the vdW qualitatively right (contains the zero-point energy of plasmons coupled by the long-ranged Coulomb interaction between subsystems).

"seamless" treatment of all forces incl. vdW, at any separation

F. Furche, J. Chem. Phys**, 129,** (2008).

The Adiabatic Connection Fluctuation Dissipation Theorem

$$\hat{H}^{\lambda} = \hat{T} + \hat{V}^{\lambda}[n] + \lambda \hat{V}_{ee}$$

$$E_{xc} = \frac{1}{2}\int d\lambda \int dr dr' \frac{n_{xc}^{\lambda}(\vec{r},\vec{r}')n(\vec{r})}{|\vec{r}_1 - \vec{r}_2|}$$

$$n_{xc}^{\lambda}(\vec{r},\vec{r}') = \frac{\langle \Psi_{\lambda} | \delta\hat{n}(\vec{r})\delta\hat{n}(\vec{r}') | \Psi_{\lambda} \rangle}{n(\vec{r})} - \delta(\vec{r} - \vec{r}')$$

$$\langle \Psi_{\lambda} | \delta\hat{n}(\vec{r})\delta\hat{n}(\vec{r}') | \Psi_{\lambda} \rangle = -\int_0^{\infty} \frac{d\omega}{\pi} \mathrm{Im}\, \chi^{\lambda}(\omega,\vec{r},\vec{r}')$$

- The adiabatic connection (AC) makes a smooth connection between the KS and interacting systems by λ
- The many-body complexity is included in the xc energy
- The λ-dependent xc hole is related to the fluctuation of the density-density correlation function
- The fluctuations are related to the response properties (FDT)

R. Kubo, Rep. Prog. Phys. **29, 255** (1966).
P. Nozières and D. Pines, Il Nuovo Cimento **[X]9, 470** (1958).
P. Nozières and D. Pines, The Theory of Quantum Liquids (Benjamin, New York, 1966).

The Random Phase Approximation in the ACFDT context

The **fluctuation-dissipation theorem** relates the density fluctuations responsible for the exchange-correlation energy to the imaginary-frequency continuation of the frequency-dependent density response:

$$E_{xc} = \frac{e^2}{2}\int_0^1 d\lambda \int d^3r \int d^3r` \frac{1}{|\vec{r}-\vec{r}`|}\left\{\left[-\frac{\hbar}{\pi}\int_0^\infty \chi^\lambda(\vec{r},\vec{r}`,\omega=iu)du\right]-n(\vec{r})\delta(\vec{r}-\vec{r}`)\right\}. \quad (*)$$

$$\chi^{\lambda=0} = \chi^{KS}$$

D.C. Langreth and J.P. Perdew, Solid State Commun. **17, 1425**, (1975)
O.Gunnarson, B.I. Lundqvist, Phys. Rev. B **13, 4274**, (1976).
F. Furche and T. Van Voorhis, J. Chem. Phys. **122**, **154106** (2005).

$$\chi^\lambda(\vec{r},\vec{r}`,\omega) = \chi^{KS}(\vec{r},\vec{r}`,\omega) + \int d^3r_1 d^3r_2 \chi^{KS}(\vec{r},\vec{r}_1,\omega)\left(\frac{e^2}{|\vec{r}_1-\vec{r}_2|} + f_{xc}(\vec{r}_1,\vec{r}_2,\omega)\right)\chi^\lambda(\vec{r}_2,\vec{r}`,\omega). \quad (**)$$

In RPA :

$$f_{xc}(\vec{r}_1,\vec{r}_2,\omega) = 0$$

In direct RPA, Eqs. (*) and (**) are combined, bootstrapping a crude approximation for the χ^λ to a more sophisticated one to E_{xc}

RPA has been applied on:

- **S22 data set**

RPA improves the binding energies considerably over semilocal functionals

H. Eshuis and F. Furche, J. Phys. Chem. Lett. **2, 983** (2011).
X. Ren, A. Tkatchenko, P. Rinke, and M. Scheffler, Phys. Rev. Lett. **106, 153003** (2011).
X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater, Sci. **47**, **7447** (2012).

• the interlayer equilibrium distance, the elastic constant, and the net layer binding energy of graphene,

S. Lebègue, J. Harl, Tim Gould, J. G. Ángyán, G. Kresse, and J. F. Dobson, Phys. Rev. Lett. **105, 196401** (2010).

excellent agreement is found with the available experimental data; however, the computed binding energy of 48 meV per atom is somewhat smaller than the one obtained by quantum Monte Carlo methods

• adsorption of organic molecules, i.e., benzene on metal surfaces, CO adsorption problem, graphene on metal surfaces

L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nature Materials **9, 741** (2010).

RPA gives the correct adsorption site and energy differences and also gives the correct $-C_3/d^3$ behavior for large molecule-surface separations

• structural phase transitions

Improvement for Si, but less satisfactory results for SiO_2

B. Xiao, J. Sun, A. Ruzsinszky, J. Feng and J.P. Perdew,. Phys. Rev. B **86**, **094109** (2012).

Some fundamental problems with the RPA correlation:

- **Stretched bonds; RPA is not self-correlation free**. This error manifests especially in the dissociation of the H_2^+ molecule.

P. Mori-Sanchez, A.J. Cohen, W.T. Yang, Phys.Rev. A **85, 042507** (2012).

For the H atom, the SIC correction is +0.02 hartree (the value also predicted by the GGA correction), but for infinitely-stretched H_2^+ the SIC correction is +0.17 hartree. This fact suggests that the correction to RPA can be highly nonlocal in stretched-bond situations.

- **Atomization energies**

Puzzlingly, the careful RPA calculations of molecular atomization energies by Furche (2003) and by Harl and Kresse (2009) found that these atomization energies were too low by typically 10 kcal/mol, in comparison to experiment.

Recent research shows that the correction to RPA in molecules requires full nonlocality of the kind found in fourth-rung or hybrid functionals. This correction is too long-ranged for LSDA and GGA, although it is still possible that the RPA hole is correct at longer range.

F. Furche, Phys. Rev. B **64, 195120** (2001).

J. Harl, L. Schimka, and G. Kresse, Phys. Rev. B **81, 115126** (2010)

The RPA has a correlation contribution, but one which may not be fully compatible with exact exchange.

The correction to the RPA is:

$$E_{xc} - E_{xc}^{RPA}$$

E_{xc} : "beyond RPA" energy

E_{xc}^{RPA} : "within RPA" energy of the same density functional

E_{xc}: semilocal or nonlocal?

A. Ruzsinszky, J.P. Perdew, and G.I. Csonka, J. Chem. Theory Comput**. 6**, **127** (2010).
A. Ruzsinszky, J.P. Perdew, and G.I. Csonka, J. Chem. Phys. **134**, **114110** (2011).

The RPA+ semilocal (*sl*) short-range correction to RPA

In many cases, RPA provides a good description of the long-range exchange-correlation hole, but it has **too much short-range correlation,** making a total-energy error of roughly -0.02 hartree/electron at high and normal electron densities. (The correction to RPA for a free atom is +0.02 hartree/electron with LSDA)

Z. Yan, J. P. Perdew and S. Kurth, Phys. Rev. B 61, 16430, (2000)
A. Ruzsinszky, J.P. Perdew, and G.I. Csonka, J. Chem. Theory Comput**. 6**, **127** (2010).

Yan, Perdew and Kurth (2000) found LSDA and GGA corrections to RPA by taking the difference between the same semilocal functional constructed beyond and within RPA. Their corrected RPA is called RPA+.

$$E_c^{RPA+}\left[n_\downarrow, n_\uparrow\right] = E_c^{RPA}\left[n_\downarrow, n_\uparrow\right] + \left\{E_c^{sl}\left[n_\downarrow, n_\uparrow\right] - E_c^{slRPA}\left[n_\downarrow, n_\uparrow\right]\right\}$$

Problems: They claimed that the correction to RPA is a short- or intermediate-range effect and thus well modeled at the semi-local level. Since RPA was expected to be exact at long range and LSDA or GGA is accurate at short range, RPA+ was expected to provide an accurate correction.

This claim is correct in the uniform electron gas, the jellium surface, and the free atom. The correction to RPA is a short-range one in an atom, but more intermediate ranged in a molecule, since the exact exchange hole in the molecule is diffuse.

The long-range cancellation between exchange and correlation holes for atomization energies

Models for the spherically- and system-averaged hole exist for many of the semilocal functionals.

$$n_{xc}(\vec{r},\vec{r}') = n(\vec{r}')[g_{xc}(\vec{r},\vec{r}') - 1]$$

The exact exchange-correlation hole is **typically deeper and more short ranged for exchange and correlation together than for exchange**, so semilocal functionals are typically more accurate for exchange and correlation together than for either separately.

- This error cancellation between semilocal exchange and semilocal correlation manifests much more strongly in the atomization energies of molecules than it does in the surface energy of jellium.

Example: exact exchange with semilocal correlation underbinds severely

Semilocal (GGA or meta-GGA) correlation works well with semilocal exchange, but poorly with exact exchange, for the atomization energies of molecules. Correlation is semilocal in the free atom, but fully nonlocal in the molecule.

For the typical molecule N_2, using PBE GGA:

	$\Delta E_{tot}=E_{tot}$(free atoms)$-E_{tot}$(molecule)	$\Delta E_c=E_c$(free atoms)$-E_c$(molecule)
PBE	**243**	**59**
Exact	**229**	**119**
PBE error:	+14	-60

Corrections to RPA beyond RPA+: SOSEX

• Exchange-like correlation terms via SOSEX (second-order screened exchange). **The "exchange" term in correlation.**

This approach makes use of the equivalence of RPA and direct-ring CCD theories. The RPA+SOSEX correlation energy uses the anti-symmetrized instead of the un-symmetrized Coulomb integrals:

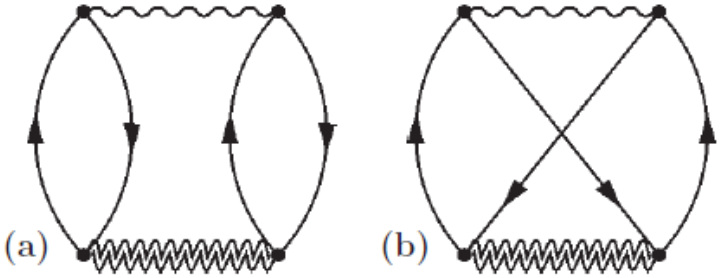
$$E_c^{SOSEX} = \frac{1}{2} Tr((B-K)T)$$

$$B_{ia,jb} = \langle ij \,|\, ab \rangle \qquad K_{ia,jb} = \langle ij \,|\, ba \rangle$$

For one-electron system:
B=K,
T: ring-CC amplitudes

D.L. Freeman, Phys. Rev. B **15,5512**, (1977).
A. Grüneis, M. Marsman, J. Harl, L. Schimka and G. Kresse, J. Chem. Phys.**131, 154115** (2009)

The leading term in RPA (a) and SOSEX (b)

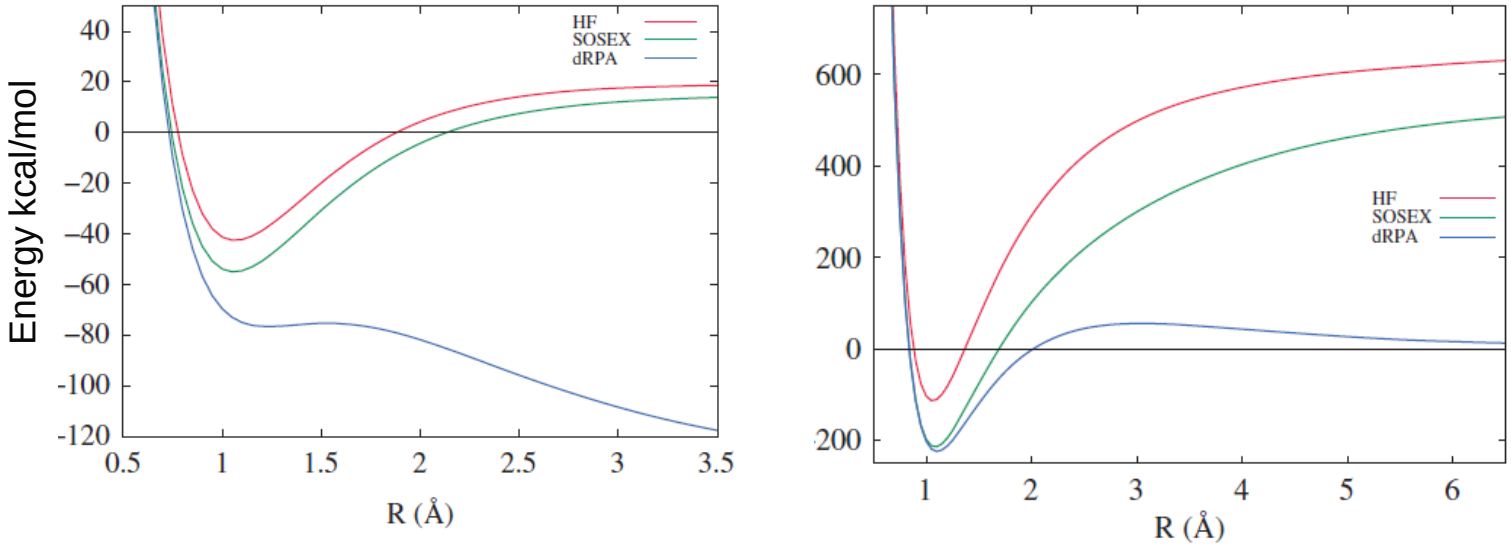


Performance of SOSEX

- SOSEX improves both total energies and energy differences simultaneously.
- Fixes the self-interaction error in the dissociation of He_2+, H_2+.
- Dissociation limit for H_2 and SOSEX yields dissociation limits that are much too large, even larger than PBE.
- Reaction barrier heights for HTBH38/NHTBH38 test sets: The performance of RPA+ is very similar to standard RPA. SOSEX correction deteriorate the performance of RPA.

J. Paier, B. G. Janesko, T. M. Henderson, G. E. Scuseria, A. Grüneis, and G. Kresse, J. Chem. Phys. **132,094103** (2010), erratum: ibid. **133, 179902** (2010).
T.M. Henderson and G.E. Scuseria, Molecular Physics, **108,2511,** (2010).
X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater, Sci. **47**, **7447** (2012).

Dissociation of He_2+ and N_2 with dRPA and SOSEX



Alternative corrections beyond RPA

- **Contribution of single excitations (SE) + SOSEX into E_{corr} of RPA.**

r2PT: improves binding energies considerably over the (EX+cRPA)@PBE results.

$$E_c^{SE} = \sum_{ia} \frac{\left| \left\langle \Psi_i \middle| \hat{f} \middle| \Psi_a \right\rangle \right|^2}{\varepsilon_i - \varepsilon_a}$$

X. Ren, A. Tkatchenko, P. Rinke, M. Scheffler,Phys. Rev. Lett., **106,153003** (2011).

- **Economical but empirical correction to the RPA**

This model is based on the Becke-Roussel exchange-hole model and gives correction for the molecules, but the correction vanishes for the atoms.

$$E_c^b - E_c^w = \int d^3 r n(\vec{r}) \left[\varepsilon_c^{bGGA}(\vec{r}) - \varepsilon_c^{wGGA}(\vec{r}) \right] \left\{ 1 - \alpha \frac{(\varepsilon_x^{mGGA}(\vec{r}) - \varepsilon_x^{exact}(\vec{r})}{\varepsilon_x^{mGGA}(\vec{r})} \right\}$$

$\alpha = 8.6$ GGA: beyond-RPA
GGA-RPA: within-RPA

A.D. Becke and M. R. Roussel, Phys. Rev. A **39, 3761**, (1989)
A. Ruzsinszky, J.P. Perdew, and G.I. Csonka, J. Chem. Phys. **134, 114110** (2011)

Local field corrections - ALDA kernel

• Local field corrections use nonzero xc kernel in the Dyson-equation. Motivated by TDDFT kernels can be derived from semilocal functionals with the adiabatic approximation. The ALDA is the next-simplest approximation for the kernel :

$$f_{xc}^{ALDA}[n](\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}')\frac{d^2[n\varepsilon_{xc}^{unif}(n)]}{dn^2}\bigg|_{n=n(\vec{r})}$$

$\varepsilon_{xc}^{unif}(n)$ is the exchange-correlation energy per particle of an electron gas of uniform density

E.K.U. Gross, W. Kohn, Adv. Quant. Chem. **21,255** (1990).

The adiabatic local density approximation (ALDA) gives reasonable accuracy for low-frequency, long-wavelength excitations, but is not the right choice for a correction to RPA.

Lein, Gross and Perdew studied the correlation energy per particle of the uniform gas using various kernels. They found that RPA and ALDA-corrected RPA make errors of about 0.5 eV, of opposite sign.

Lein, E.K.U. Gross, and J.P. Perdew, Phys. Rev. B **61**, **13431** (2000).

Exchange-correlation kernels derived from semilocal functionals yield unsatisfactory results.

• The **OEP-based RPA(EXX)** method considerably improves correlation energies, gives correct dissociation of H_2. A. Hesselmann,and A. Görling, Phys.Rev.Lett.**106, 093001** (2011)

• **PGG kernel** (approximate exact exchange kernel)
M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. 76, 1212 (1996)

• Most other kernel corrections to RPA rely on the paradigm of the uniform electron gas. Some of these efforts apply the uniform electron gas kernel to an inhomogeneous system. These efforts typically make use of the uniform gas kernel by **Moroni** and coworkers, the parametrization of the static kernel by **Corradini *et al*.** or the parametrization of the dynamic exchange-correlation kernel by **Richardson and Ashcroft**.

C.F. Richardson and N.W. Ashcroft Phys. Rev. B **50, 8170** (1994).
S. Moroni, D.M. Ceperley, and G. Senatore, Phys. Rev. Lett, **75,689** (1995).
M. Corradini, R. Del Sole, G. Onida, and M. Palummo, Phys. Rev. B **57**, **14569** (1998).
L.A. Constantin and J.M. Pitarke, Phys. Rev. B **75, 245127** (2007).

•Alternatively, the energy-optimized exchange-correlation kernels by **Dobson and collaborators** provide a more reasonable description of inhomogeneous systems J.F. Dobson and J. Wang, Phys. Rev. B, **62, 10038** (2000).

Ultranonlocality in the kernel

One of the most striking characteristics of the TDLDA kernel is that it is static and local in space.

The true exchange–correlation kernel should contain a long-range contribution. **It's Fourier-transform should have the form $1/q^2$ as $q \to 0$ in insulators or semiconductors. *This ultranonlocality is completely absent within the TDLDA, as the TDLDA* kernel tends to a constant in the limit $q \to 0$.**

Ph. Ghosez, X. Gonze, and R.W. Godby, Phys. Rev. B **56**, 1**2811** (1997).
A. Hesselmann and A. Goerling, Mol. Phys. **108**, **359** (2010).

Thank you!