

A Non-Local, Energy-Optimized Kernel for Structural Properties

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The 1st USTC-FHI workshop on the Frontiers of Advanced Electronic Structure Methods, Hefei, June 14-18, 2016

Motivation

To understand long-standing and fundamental problems in solid-state physics and materials chemistry by using the random phase approximation (RPA)

- structural phase transitions are extremely difficult (and extremely difficult to realize experimentally)
- interlayer binding (sometimes double minima is found)
- adsorption (binding and site preference)
- weak interactions in molecules, biomolecules
- reaction energies of certain kinds (self-interaction exposed)

RPA in the density functional context

- Adiabatic connection: density is constrained to physical ($\lambda=1$) value. Φ_0 is a single-determinant of Kohn-Sham orbitals

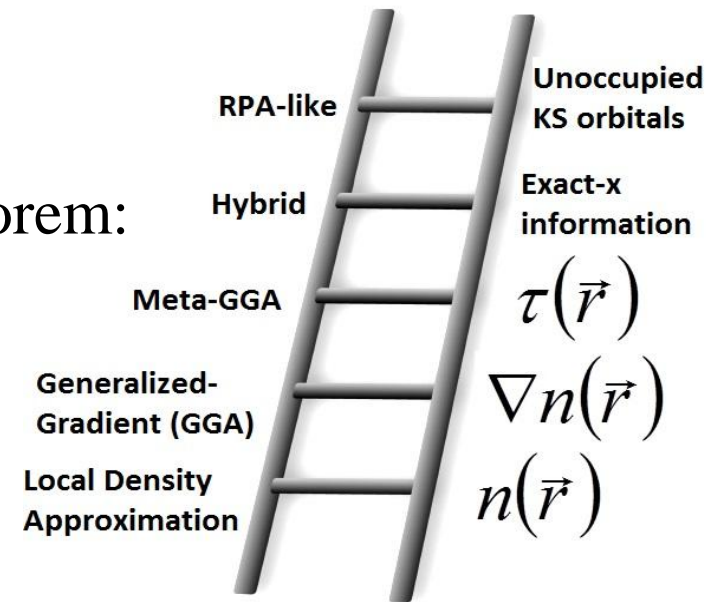
$$E[n] = \langle \Phi_0[n] | \hat{H}_{\lambda=1} | \Phi_0[n] \rangle + E_c[n]$$

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

- Zero-temperature fluctuation-dissipation theorem:

$$E_c = - \int_0^1 d\lambda \operatorname{Re} \int_0^{\infty} \frac{du}{2\pi} \langle V[\chi_{\lambda}(iu) - \chi_0(iu)] \rangle$$

χ_{λ} : Density-density response function, V : bare Coulomb interaction



The total energy is computed as $\mathbf{Exc} = \mathbf{EXX} + \mathbf{Ec}$, where E_{XX} is the Hartree-Fock exact-exchange energy evaluated using KS orbitals.

DC. Langreth, and JP. Perdew, Phys. Rev B. **15**, 2884, (1977)

Eshuis, Bates, and Furche, Theor. Chem. Acc. **131**, 1084 (2012)

Ren et al., J. Mater. Sci. **47**, 7447 (2012)

Density-density Response Function

$$\chi_{\lambda}^{-1}(\omega) = \chi_0^{-1}(\omega) - [V_{\lambda} + f_{xc}^{\lambda}(\omega)]$$
$$\chi_{\lambda} = \chi_0 + \chi_0 [V_{\lambda} + f_{xc}^{\lambda}] \chi_{\lambda}$$

- Poles of χ_{λ} at excitations of interacting system
- Exact f_{xc}^{λ} : spatially nonlocal complicated ω behavior
- Approximate f_{xc} obtained from semilocal functionals or a model

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

Petersilka, Gossmann, and Gross, Phys. Rev. Lett. **76**, 1212 (1996)

Lein, Gross, and Perdew, Phys. Rev. B **61**, 13431 (2000)

Applications of RPA

- Atomization energies were too low by typically 10 kcal/mol, in comparison to experiment.

- vdW interactions

S22 data set, adsorption of organic molecules, i.e., benzene on metal surfaces, CO adsorption problem, graphene on metal surfaces

Although RPA is known for capturing vdW interactions, binding and cohesive energies are underestimated.

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

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

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

X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci. **47**, 7447 (2012)

Question:

- How does the overall underestimation of binding by RPA affect structural properties and structural phase transitions ?
- How much a beyond RPA treatment improves these properties?

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

J.E. Bates, S. Laricchia, and A. Ruzsinszky, Phys. Rev. B, **93**, 045119, (2016)

Local field corrections

An intrinsic way to remedy the drawbacks of RPA is to restore the kernel within the ACFDT framework.

How to approach the kernel?

- derive the kernel from microscopic theory
- satisfy exact, known constraints

Most models use the paradigm of the uniform electron gas

M. Corradini, R. Del Sole, G. Onida, and M. Palumbo, *Phys. Rev. B*, **57**, 14569, (1998)

L.A. Constantin, and J.M. Pitarke, *Phys. Rev. B*, **75**, 245127, (2007)

P.E. Trevisannuto, A. Terentjevs, L.A. Constantin, V. Olevano, and F. Della Sala, *Phys. Rev. B*, **87**, 205143, (2013)

J.E. Bates, S. Laricchia, and A. Ruzsinszky, *Phys. Rev. B*, **93**, 045119, (2016)

ALDA kernel

- The ALDA is the next-simplest approximation for the kernel:

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

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

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

- ALDA is not exact for the homogeneous electron gas
- 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.
- ALDA is divergent in its correlation hole

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

F. Furche, T Van Voorhis, *J. Chem. Phys.* **122**, 164106, (2005).

What is known about the exchange-correlation kernel?

(1) Why does the ALDA kernel fail even for the uniform electron gas?

is not exact even for the static exchange-correlation kernel of the uniform electron gas.

arbitrary small density variations around the uniform density requires a two- point density functional or double integral over the three-dimensional space, while LDA is only a one-point density functional or single integral.

(2) Can a static kernel give accurate exchange-correlation energies?

Ghosez, Gonze, and Godby had shown that the static kernel in an insulator at the exchange-only level has “ultranonlocality”, decaying at large u like a negative constant over u .

(3) Can we neglect the correlation part of the kernel?

it is exact by construction in the high-density limit

(4) Error cancellation between exchange and correlation

the kernel can be ultranonlocal for insulators and molecules as well

Introducing the NEO (nonlocal energy-optimized) kernel

Three state-of-the-art features:

self-interaction correction

energy-optimization

ultranonlocality

NEO kernel: Short-range correction to the RPA correlation energy, for solid metals

Based on the knowledge of the uniform electron gas.

The exact xc kernel in the uniform electron gas is known to be nonlocal but short-ranged, and our initial version of a NEO kernel also has these features:

$$f_{xc}^{\lambda, NEO}([n_{\uparrow}, n_{\downarrow}], \vec{R}, u) = -\frac{\lambda}{u} \sum_{\sigma} \left(\frac{n_{\sigma}}{n} \right)^2 \operatorname{erfc}(-c(1 - z_{\sigma}^2) k_{F\sigma}^2 u^2)$$

$$n = n_{\uparrow} + n_{\downarrow},$$

$$k_{F\sigma} = (6\pi^2 n_{\sigma})^{1/3}, z_{\sigma} = \tau_{\sigma}^w / \tau, \tau_{\sigma}^w = |\nabla n_{\sigma}|^2 / 8n_{\sigma}$$

$$\tau_{\sigma} = 1/2 \sum_{\alpha}^{occ} |\nabla \phi_{\alpha\sigma}|^2.$$

The one -electron limit :

$$f_{xc}^{\lambda, NEO} = -\lambda / u$$

The singlet two-electron limit :

$$f_{xc}^{\lambda, NEO} = -\lambda / 2u$$

The uniform electron gas limit is:

$$(-\lambda / u) \sum_{\sigma} (n_{\sigma} / n)^2 e^{-ck_{F\sigma}^2 u^2}$$

The short-range limit:

$$(-\lambda / u) \sum_{\sigma} (n_{\sigma} / n)^2$$

The long-range limit:

$$f_{xc}^{\lambda, NEO\sigma} \rightarrow 0$$

Fitting to the second-order correlation energy

Correlation energy of the uniform electron gas:

U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972), and references therein.

$$e_c^{RPA} = -\frac{12}{\pi} \frac{\hbar^2}{m\alpha_0^2 r_s^2 a_0^2} \int_0^\infty dQ \int_0^\infty dW Q^2 [\alpha(Q, W) - \ln\{1 + \alpha(Q, W)\}] \quad Q = \frac{k}{2k_F} \quad W = \frac{\Omega}{2k_F^2}$$

$$\alpha(Q, W) \text{ is first-order in } r_s. \quad \ln(1 + \alpha) = \alpha - \frac{1}{2} \alpha^2 + \dots \quad r_s = \frac{1}{a_0} \left(\frac{3}{4\pi n} \right)^{1/3}$$

Second-order exchange energy with the local-field factor:

$$e_c^{2X} = \frac{3}{8\pi^3} \int_0^\infty dQ Q^2 \tilde{G}_x(Q) \int_0^\infty dW Q^2 \{2\beta\}^2$$

$$G(n; q, \omega) = -(q^2/4\pi) f_{xc}(n; q, \omega)$$

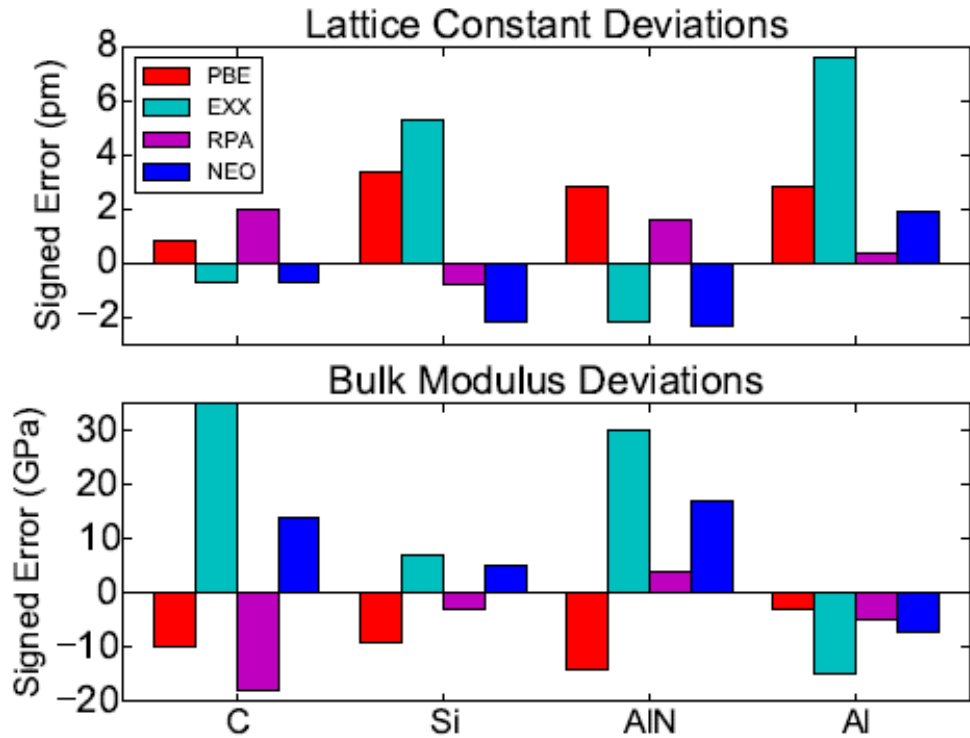
D.C. Langreth and J.P. Perdew, Solid State Commun. **17**, 1425 (1975)

The “c” parameter in NEO provides a unique fit to the exact second-order correlation energy for the spin-unpolarized electron gas. It can be evaluated from explicit expressions given by von Barth and Hedin for RPA and by Langreth and Perdew beyond RPA. **It is designed to yield the exact second-order exchange energy of the uniform gas, which is itself an average over frequencies**

J.F. Dobson and J. Wang, Phys. Rev. B, **62**, 10038 (2000).

J.E. Bates, S. Laricchia, and A. Ruzsinszky, Phys. Rev. B, **93**, 045119, (2016)

Structural parameters



Average errors:

		PBE	RPA	NEO
MD	a_0	0.025	0.008	0.004
	B	-9	-6	-1
MAD	a_0	0.025	0.012	0.012
	B	9	8	4

RPA Renormalization

$$\chi_\lambda = [1 - \chi_0 (V_\lambda + f_{xc}^\lambda)]^{-1} \chi_0$$

$\hat{\chi}_\lambda$: RPA response function

$$\chi_\lambda = \hat{\chi}_\lambda + \hat{\chi}_\lambda f_{xc}^\lambda \hat{\chi}_\lambda$$

first order approximation =
RPAr1 with the NEO kernel

Replacing $\hat{\chi}_\lambda$ by χ_0

$$\chi_\lambda = \hat{\chi}_\lambda + \chi_0 f_{xc}^\lambda \hat{\chi}_\lambda$$

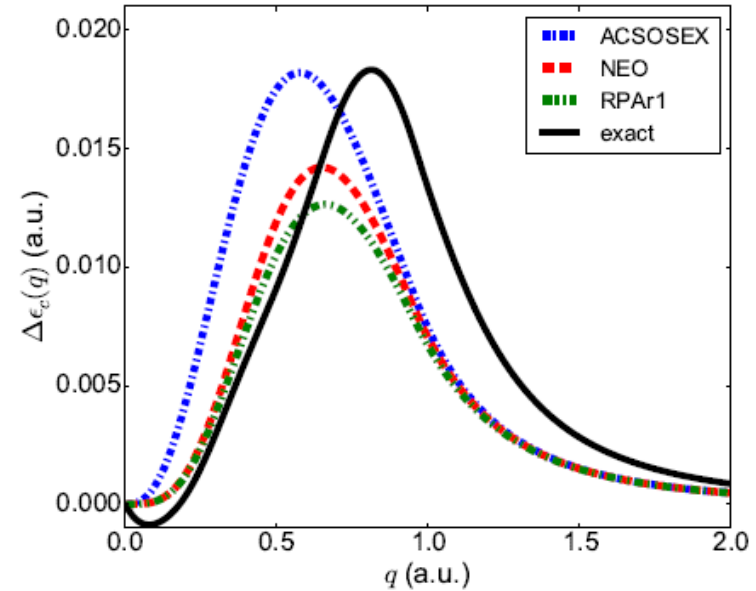
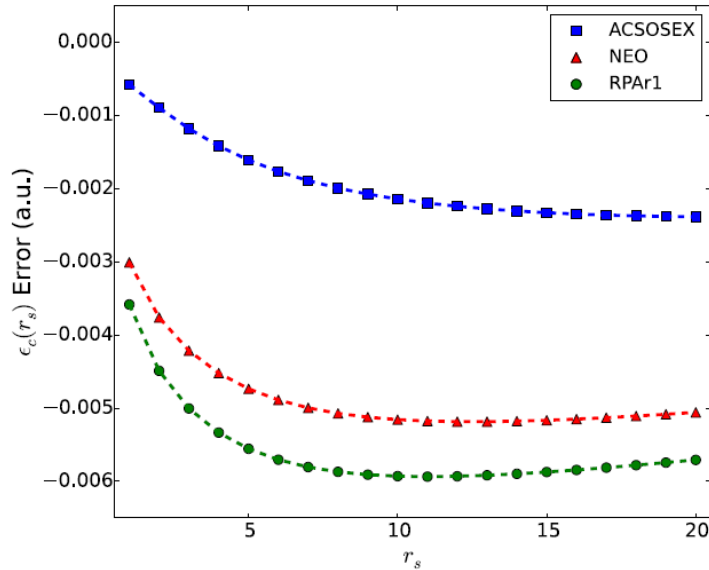
ACSOSEX with the NEO kernel

H. Jiang, and E. Engel, *J. Chem. Phys.*, **125**, 184108, (2006)

Both RPAr1 and ACSOSEX yield the exact second-order, unscreened perturbative correlation energy when the exact first-order kernel is used, but differ in their higher-order contributions.

J.E. Bates, and F. Furche, *J. Chem. Phys.*, **139**, 171103, (2013)

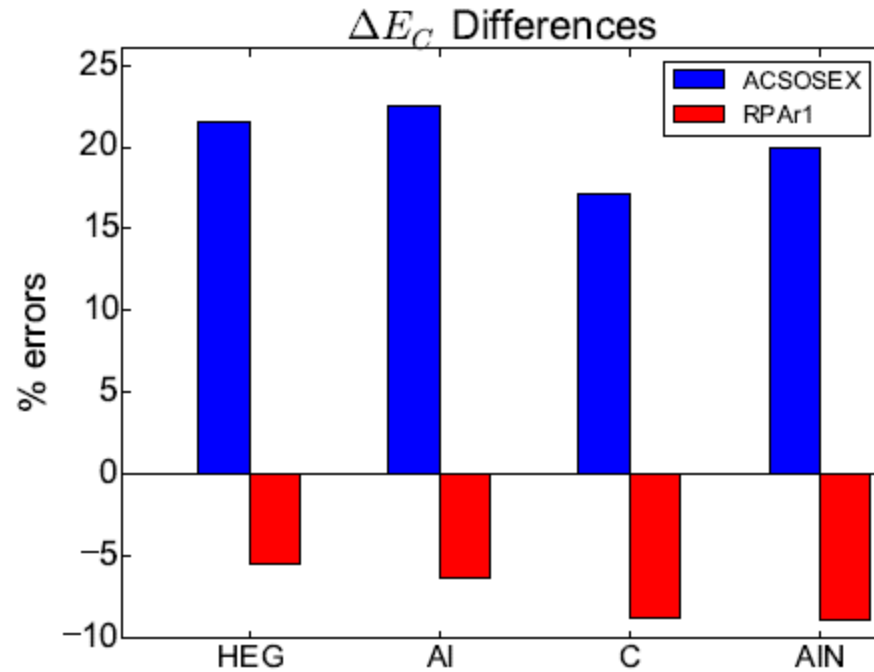
ACSOSEX vs. RPAr1: homogeneous electron gas



The error from PW92 as a function of r_s for $c = 0.264$.

- ACSOSEX overestimates, RPAr1 underestimates ΔE_C^{bRPA}
- RPAr1 systematically recovers $> 90\%$ of ∞ -order ΔE_C
- structural properties show identical trends

ACSOSEX vs. RPAr1: inhomogeneous systems



Structural properties

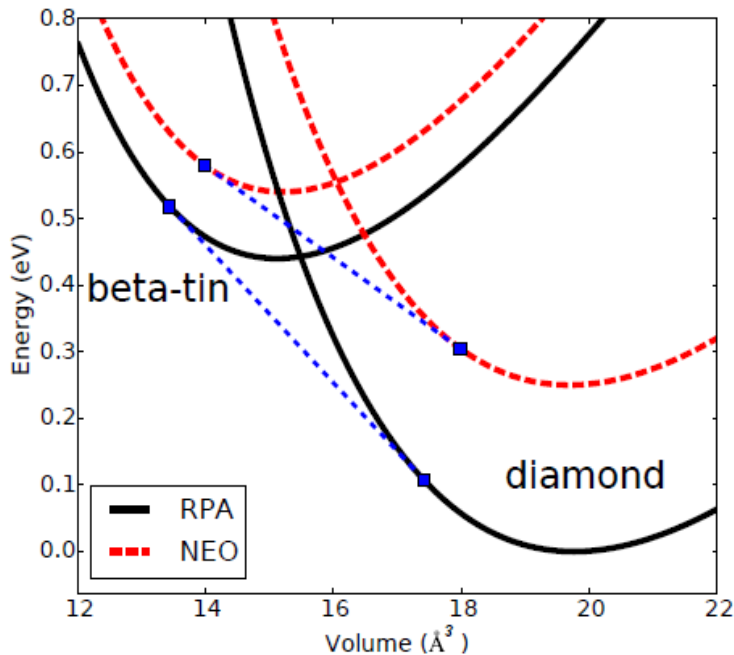
		RPA	ACSOSEX	RPAr1	NEO
MD	a_0	0.008	-0.008	0.012	0.004
	B	-6	7	-5	-1
MAD	a_0	0.012	0.018	0.014	0.012
	B	8	11	6	4

Phase Transition in Silicon from Diamond to β -tin

Equation of state:

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B_0' + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}$$

E_0 : equilibrium energy
 V_0 : equilibrium volume
 B_0 : bulk modulus
 B_0' : the pressure derivative of the bulk modulus



Method	P_t (GPa)	ΔE (eV)
PBE	9.7	0.29
RPA	13.4	0.38
ACSOSEX	7.2	0.21
RPAr1	8.8	0.25
NEO	8.0	0.23
DMC	14 ± 1	0.42
Expt	11.3–12.6	

RPAr1: NEO in RPAr1

ACSOSEX: NEO in RPAr1-ACSOSEX

J.E. Bates, N. Sengupta, and A. Ruzsinszky, in preparation.

Higher order terms (HOT)

Finite-order RPA:

$$\chi_\lambda = \hat{\chi}_\lambda + \hat{\chi}_\lambda f_{xc}^\lambda \hat{\chi}_\lambda + \hat{\chi}_\lambda f_{xc}^\lambda \hat{\chi}_\lambda f_{xc}^\lambda \hat{\chi}_\lambda + \dots$$

The n-th order RPA correction: The n-th order RPA correction is:

$$E_c = E_c^{RPA} + \sum_{n=1}^{\infty} \Delta E_c^{RPAr-n}[f_{xc}] \quad \Delta E_c^{RPAr-n}[f_{xc}] = -\int_0^1 d\lambda \int_0^\infty \frac{du}{2\pi} \left\langle V(\hat{\chi}_\lambda(iu) f_{xc}^\lambda(iu))^n \hat{\chi}_\lambda(iu) \right\rangle$$

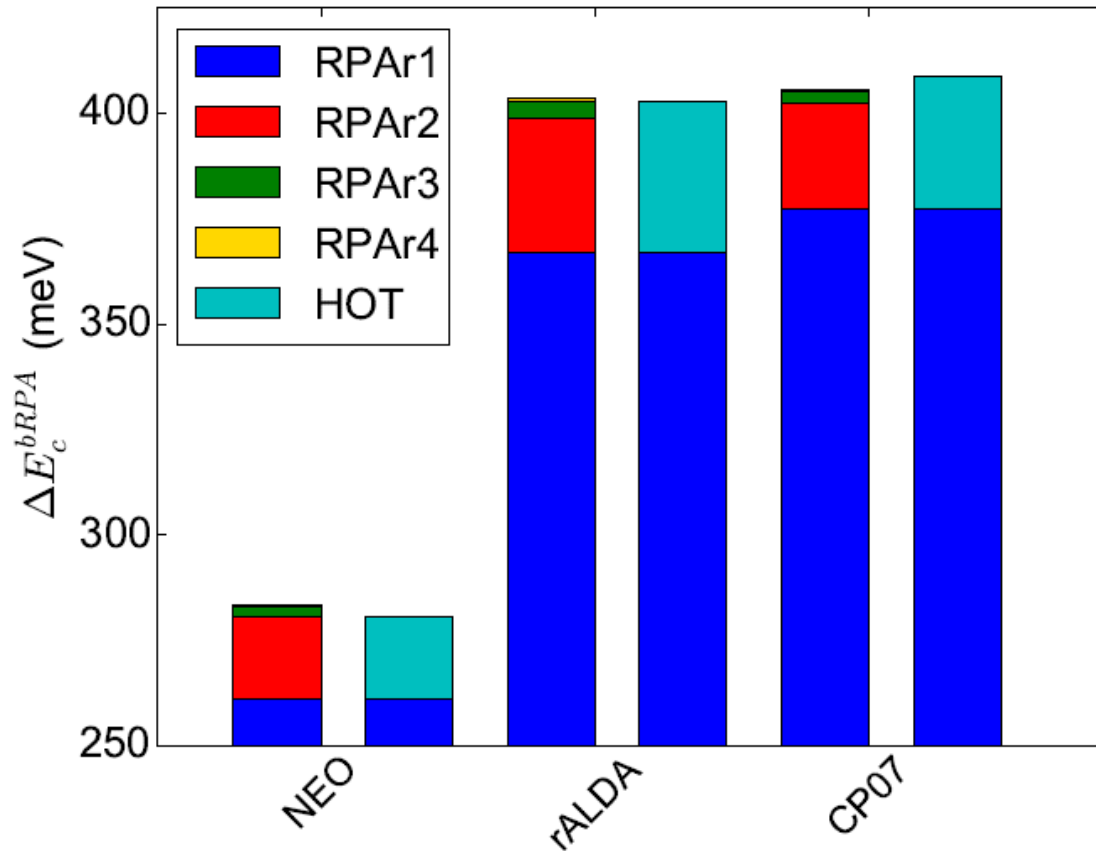
For the n-th order correction analytical integration wrt. λ is not feasible.

Solution: an approximation based on the AC formula

$$\Delta E_c^{bRPA}[f_{xc}] = \sum_{n=2}^{\infty} \Delta E_c^{RPAr-n} \approx (1 - \hat{b}) \Delta U_c^{RPAr2} \approx \frac{1}{2} \Delta U_c^{RPAr2}$$

ΔU_c^{RPAr2} can be estimated from the coupling-strength integral at $\lambda = 1$

$$E_c^{HOT}[fx] = E_c^{RPA} + \Delta E_c^{RPAr1}[fx] + \frac{1}{2} \Delta U_c^{RPAr2}[fx]$$



RPA renormalization contributions to the RPA correlation energy with NEO, rALDA and CP07 kernels for the uniform electron gas at $r_s = 4$. The HOT correction is plotted for comparison with RPAr2-4.

Another paradigm in condensed matter physics: Jellium surface

Metal surface energies can be treated within the jellium model: valence electrons are neutralized by a positive background.

The ACFDT formalism was used for the jellium surface energy by Pitarke and Eguiluz.

J.M. Pitarke, and A. Eguiluz, Phys. Rev. B, 57, 6329, (1998)

In 2000, Yan, Perdew and Kurth argued that the correction to RPA, although large (about +0.5 eV per electron), would tend to cancel almost completely out of energy differences for processes that conserve electron number.

Z. Yan, J.P. Perdew, S. Kurth, C. Fiolhais, and, L. Almeida, Phys. Rev. B, 61, 2595, (2000)

RPA can be expected to much better for the surface energy than for the bulk energy of a solid.

Jellium surface

The surface energy of jellium is the work invested to create a unit area of new surface:

$$\sigma_{xc} = \int_{-\infty}^{\infty} dz \left\{ n(z) \varepsilon_{xc}([n], z) - \bar{n} \varepsilon_{xc}^{unif}(\bar{n}) \theta(z_0 - z) \right\}$$

semi-infinite surface,
bulk contributions cancel
 $n(z)$: non-unif. electron density

The jellium slab which is the finite version of the semi-infinite jellium

Wavevector decomposition

The xc energy contributions to the slab and surface

Jellium slab:
$$\varepsilon_{xc} = \int_0^{\infty} d\left(\frac{q_{\parallel}}{2k_F}\right) \varepsilon_{q_{\parallel}}^{xc}$$

Jellium surface:
$$\sigma_{xc} = \int_0^{\infty} d\left(\frac{q_{\parallel}}{2k_F}\right) \gamma_{q_{\parallel}}^{xc}$$

q_{\parallel} : wave vector parallel to surface

z : direction of the surface

Jellium surface energy within RPA

Invoke the xc hole integral generally:

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

The q_{\parallel} wavevector analysis:

$$\gamma_{q_{\parallel}}^{xc} = \frac{k_f}{8\pi} \int dz \int dz' n(z) v_{q_{\parallel}}(|z - z'|) \int_0^1 d\lambda [n_{q_{\parallel}, \lambda}^{xc}(z, z') - \bar{n}_{q_{\parallel}, \lambda}^{xc}(|z - z'|)]$$

The xc hole density comes from the fluctuation dissipation theorem:

$$n_{q_{\parallel}, \lambda}^{xc}(z, z') = -\frac{1}{\pi n(z)} \int_0^{\infty} du \chi_{q_{\parallel}, \lambda}(z, z', iu) - \delta(z - z')$$

The density response function comes from the Dyson equation with or without the kernel:

$$\chi_{q_{\parallel}, \lambda}(z, z', \omega) = \chi_{q_{\parallel}, \lambda}^0(z, z', \omega) + \int dz_1 \int dz_2 \chi_{q_{\parallel}, \lambda}^0(z, z_1, \omega) \times [\lambda v_{q_{\parallel}}(|z_1 - z_2|) + f_{q_{\parallel}, \lambda}^{xc}(z_1, z_2, \omega)] \chi_{q_{\parallel}, \lambda}(z_2, z', \omega)$$

NEO kernel for jellium surface

NEO-I

$$f_{xc}^{\alpha, NEO}(n \uparrow, n \downarrow, \vec{R}, u) = -\frac{\lambda}{u} \sum_{\sigma} \left(\frac{n_{\sigma}}{n} \right)^2 \text{erfc}(au) \quad a = \sqrt{\tilde{c} (1 - Z_{\sigma}^2) k_{F, \sigma}^2}$$

Problem for jellium: it produces a long-ranged exchange kernel in the tail of the density of a jellium surface, since $Z \rightarrow 1$ and $k_F \rightarrow 0$ there.

The relevance of the meta-GGA ingredients

$$Z = \tau / \tau^w \quad \alpha = (\tau - \tau^w) / \tau^{unif} \quad t^{-1} = \tau / \tau^{unif}$$

1) Regions of one- and two-electron density:

$$\tau = \tau^w \quad Z = 1 \quad t^{-1} = 5s^2 / 3 \quad \alpha = 0 \quad (\text{single bonds})$$

2) Regions of uniform density:

$$\tau^w = 0 \quad Z = 0 \quad t^{-1} = 1 \quad \alpha = 1 \quad (\text{metallic bonds})$$

3) Regions of density overlap between closed shells:

$$\tau^w \approx 0 \quad Z \approx 0 \quad t^{-1} \rightarrow \infty \quad \alpha \rightarrow \infty \quad (\text{weak bonds})$$

$$\tau / \tau^{unif} \sim n / n^{5/3} \quad \text{as} \quad n \rightarrow 0 \quad t^{-1} \rightarrow \infty$$

Only α can recognize these three regions and treat them differently.

Solution: make use of our knowledge of recent meta-GGA's

Replace $(1 - Z_\sigma^2)$ by $3\alpha_\sigma - 3\alpha_\sigma^2 + \alpha_\sigma^3$. This leads to: NEO-II

$$f_{xc}^{\alpha, NEO}(n \uparrow, n \downarrow, \vec{R}, u) = -\frac{\lambda}{u} \sum_\sigma \left(\frac{n_\sigma}{n} \right)^2 \operatorname{erfc}(au) \quad a = \sqrt{\tilde{c}(\alpha_\sigma - 3\alpha_\sigma^2 + 3\alpha_\sigma^3) k_{F,\sigma}^2}$$

$$\alpha_\sigma = (\tau_\sigma - \tau_\sigma^W) / \tau_\sigma^{unif} \quad \text{properly diverges in the tail}$$

We do not refit parameter “c” when switch from NEO-I to NEO-II

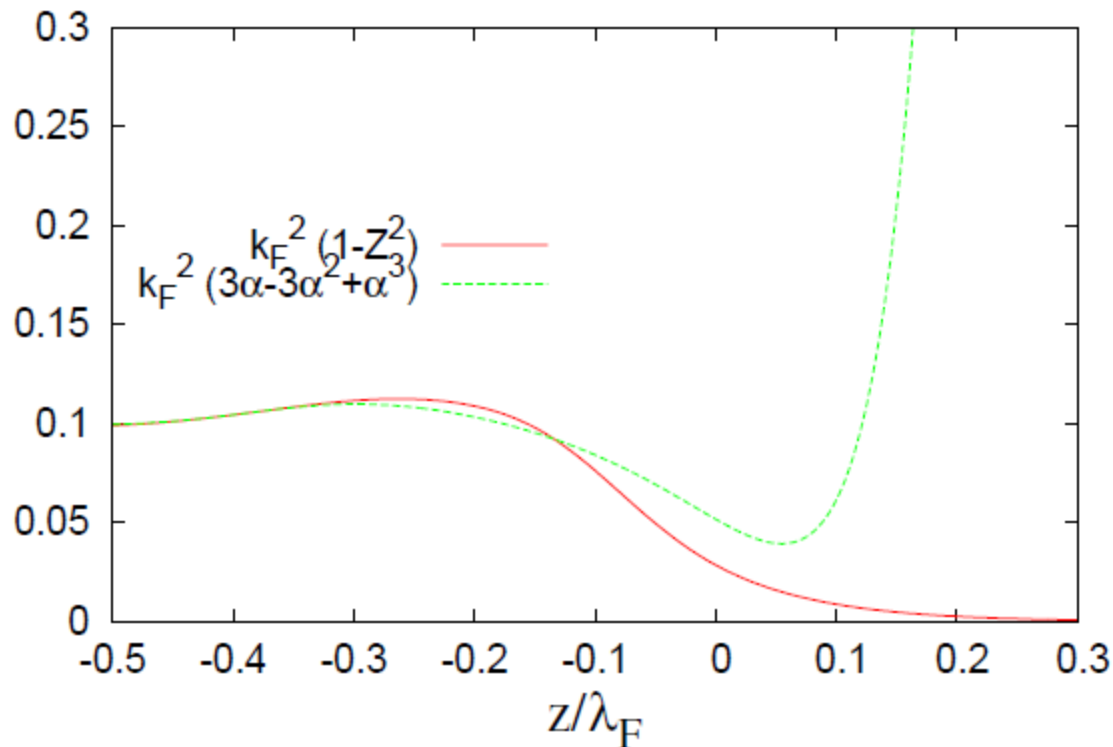
A. Ruzsinszky, L.A. Constantin, and J.M. Pitarke, to be submitted.

Correlation kernel: NEO-III

$$f_{\sigma\sigma'}^{xc}(\vec{r}, \vec{r}') = -\delta_{\sigma\sigma'} [\text{erfc}\left\{\sqrt{\frac{\tilde{c}}{1+br_s^c}} (1-Z_\sigma^2) k_{F\sigma} |\vec{r}'-\vec{r}|\right\}]$$

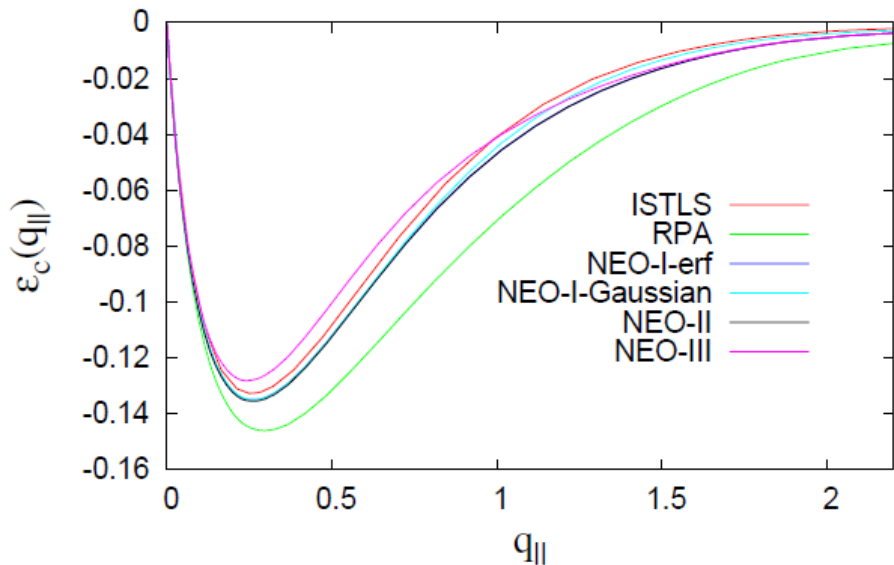
- Parameters b and c come from fitting to the uniform electron gas over a wide range of densities.
- The expression correctly reduces to the high-density limit.

NEO-II leaves unchanged the correct NEO behaviors for one- and two-electron densities ($\alpha = 0$) and slowly-varying densities ($\alpha = 1 + O(\nabla^2)$), but kills of the kernel in the tail of the surface density ($\alpha \rightarrow \infty$)



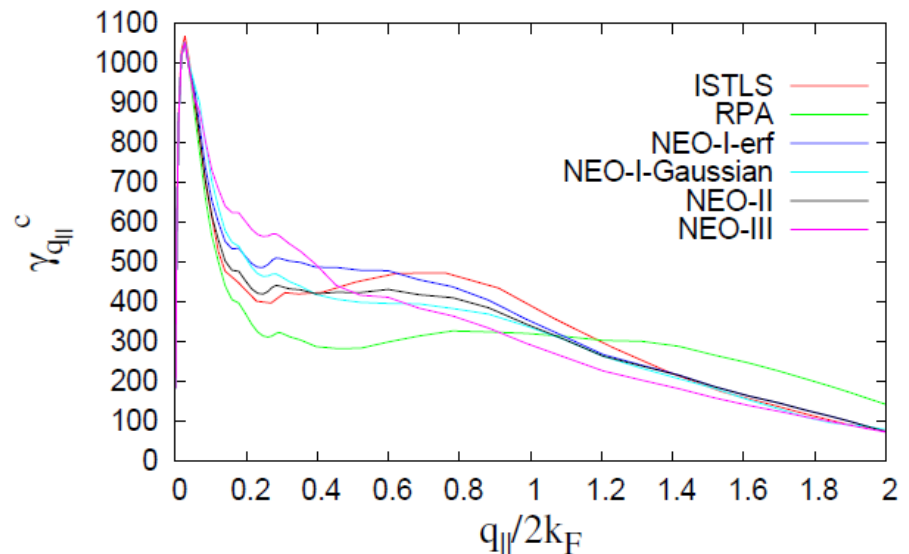
Comparison between $k_{2F} (1-Z^2)$ and $k_{2F} (\alpha - 3\alpha^2 + \alpha^3)$ at a jellium surface of bulk parameter $r_s = 6$. The surface is at $z = 0$, the bulk is at $z < 0$, and the vacuum is at $z \rightarrow \infty$

Wavevector resolution of the correlation energy for the jellium slab and surface



Two-dimensional wavevector analysis of the correlation energy per particle of the jellium slab with width $= 2.23\lambda_F$ ($\lambda_F=2\pi/k_F$), and $r_s = 2.07$ for ISTLS, RPA, and the NEO kernels.

$r_s = 2.07$ corresponds to Al(100) surface

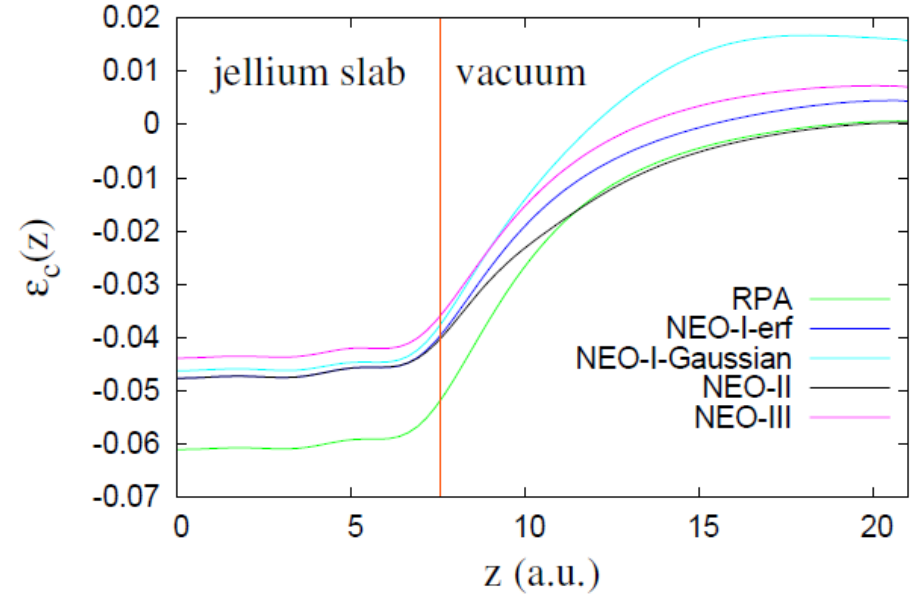
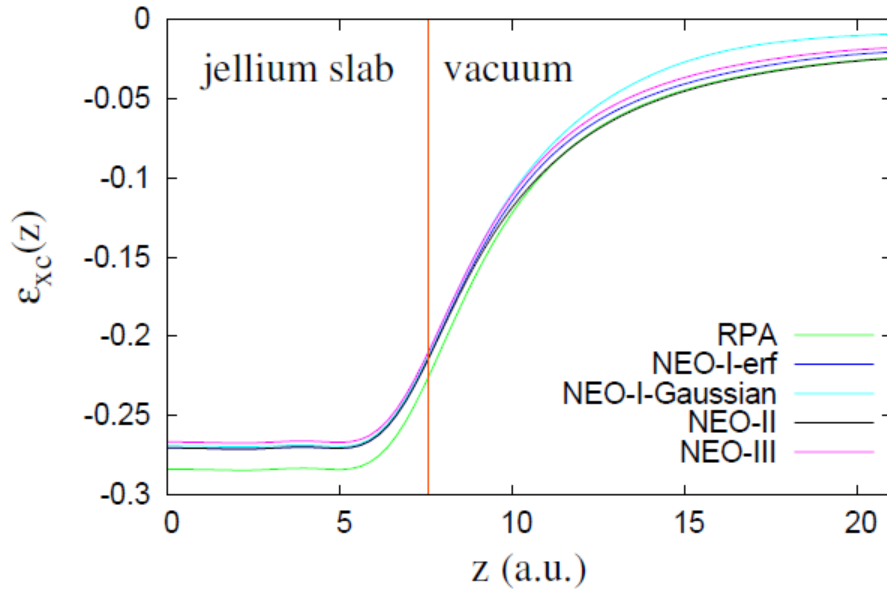


Two-dimensional wavevector analysis of the jellium surface energy with $r_s = 2.07$ for ISTLS, RPA, and the NEO kernels. Surface energy is the area below the curves.

Jellium correlation surface energies with different approaches at background parameter $r_s = 2.07$

Method	Correlation surface energy (erg/cm ²)
ISTLS	714
RPA	743
NEO-I-Gaussian	687
NEO-I-erf	723
NEO-II	678
NEO-III	698
LDA	293
PBEsol	604
DMC	697±45

Exchange-correlation and correlation energies along the “z” direction in the jellium slab

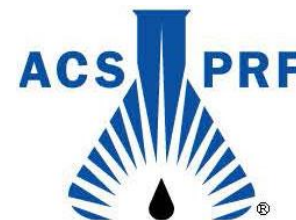


Conclusions

- RPA energies require a substantial kernel correction.
- The standard ALDA kernel used in TDDFT is as bad as no kernel at all.
- The kernel can be modelled by satisfaction of exact constraints, e.g.; the NEO kernel.
- The kernel can be included exactly to all orders, but RPA renormalization is less expensive and almost as accurate.
- The kernel has a major effect on the correlation energy of bulk jellium, but much less effect on the jellium surface energy.

Thank you and thanks to my sponsors and the support of:

- Jefferson (Jeb) Bates
- Niladri Sengupta
- Lucian A. Constantin
- J.M. (Txema) Pitarke



Alexander von Humboldt
Stiftung / Foundation

