

## PROBLEM

How to model the Exchange-Correlation (XC) energy –

The energy due to interparticle interactions within an effective single body problem, the Kohn-Sham equation

Jacob's Ladder – the standard line of attack:

- LDA – local density, HEG
- GGA – Gradient of local density
- MetaGGA – Laplacian or noninteracting KE density
- HyperGGA – general use of KS orbitals

Systematic hierarchy, Unsystematic otherwise!

A symptom of the lack of systematics – a large “GGA zoo” of GGA models (PBE, rPBE, revPBE, PBEsol, SOGGA, RGE2, VMT, BLYP, AM05, . . .) none of which is perfectly satisfying for general use in quantum chemistry.

## EXCHANGE-CORRELATION HOLE

One path to gain insight into the XC energy is the Exchange-correlation hole. It is defined as the change in ground-state expectation of the density at  $r'$  given an electron is at  $r$ :

$$n_{xc}(r, r') = n(r'|r) - n(r')$$

The interaction of an electron with its XC hole gives a useful, if not exclusive idea of the XC energy density, based on the well known trick of adiabatic integration of the Coulomb energy of the hole over coupling constant  $\lambda e^2$

$$\epsilon_{xc}(r) = n(r) \epsilon_{xc}(r);$$

$$\epsilon_{xc}(r) = \frac{1}{2} \int_0^1 d\lambda \int d^3r' \frac{n_{xc}(r, r')}{|r-r'|}$$

An integration over the energy density gives the XC energy – key theoretical input into DFT

## VARIATIONAL MONTE CARLO CALCULATIONS

- Variational Slater-Jastrow wavefunctions with e-e, e-n, up to e-e-n correlations
- Retrieve 80-85% of total correlation energy
- Pseudopotentials used to remove core electrons
- XC hole and energy density obtained by solving variationally for the ground-state wavefunction for specific e-e coupling  $\lambda$ , for several cases. Ground state density is forced to be same for all  $\lambda$  by adding a “Kohn-Sham” potential  $V_{KS}(\lambda, r)$  for  $\lambda < 1$
- Energy-per-particle versus position for given  $\lambda$  sampled stochastically as expectation of ground-state wavefunction
- Examples include: Si crystal (Hood et al. 1997), atoms, hydrocarbon molecules (Hsing 2006), CDW's (Nekovee 2001)

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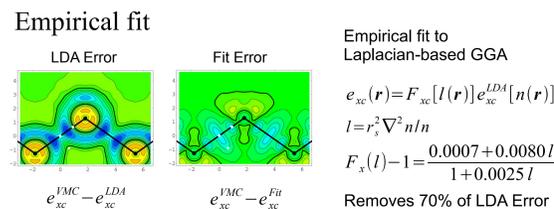
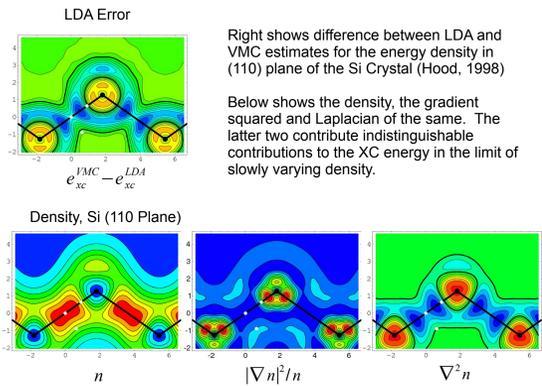
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# Laplacian-based models for the exchange-correlation energy: Revisiting the GGA in Density Functional Theory

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## VMC RESULTS – SI CRYSTAL

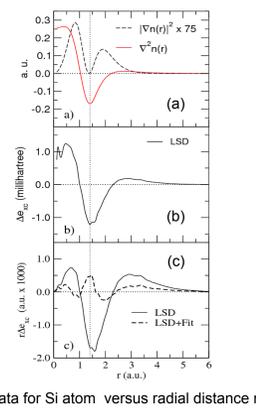


## SI ATOM (Puzder '01)

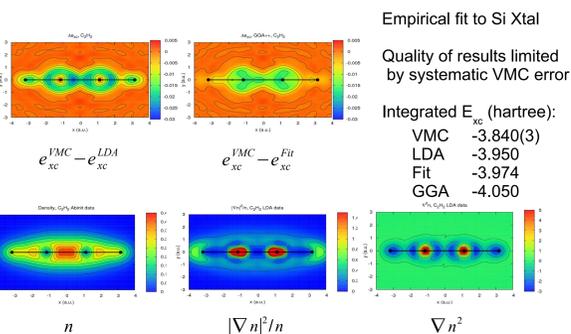
Spin polarized system using Local Spin Density approx. (LSD)

Error in LSD in (b) matches density Laplacian in (a)

Fit using *crystal-based* model better than for crystal (c)



## Data and analysis, $C_2H_2$ (Hsing 06)



## From Data Fit to DFT?

To use the insights from VMC calculations, we rethink the first step of Jacob's Ladder – the Gradient expansion. In GGA, dependence on  $|\nabla n|$  is *not necessary*:

- For a nearly homogeneous electron gas, Hohenberg and Kohn postulated a GE of the form:

$$e_{xc}[n] = e_{xc}^0[n] + [e_{xc}^{(2)}[n] \nabla^2 n + e_{xc}^{(3)}[n] |\nabla n|^2 / n] + O(\nabla^4)$$

- There are two second order terms, interchangeable under integration by parts – we have equally:

$$E_{xc}^{GEA} = \int d^3r e_{xc}^{LDA}(r, r) (1 + \mu s^2) \quad \text{with} \quad s^2 = \frac{|\nabla n|^2}{4k_F^2 n^2} \quad \text{or} \quad q = \frac{\nabla^2 n}{4k_F^2 n}$$

The normal strategy is to eliminate the Laplacian and get one gradient term.

However, use of PBE form for a GGA guarantees PBE constraints for a “GGA” using as its *any* linear combination of second order terms:

$$(1 - \alpha) |\nabla n|^2 / n + 3 \alpha \nabla^2 n$$

- This includes the slowly varying limits of both X and C, scaling laws, limits of infinite inhomogeneity, etc.

For slowly varying systems, gradient and Laplacian-based DFT's are interchangeable. The same *cannot* be said for real systems. For example, for atoms, it is well known that the Thomas Fermi approach works well for most of the atom except in two regions:

- The vicinity of the nucleus  $r < a/Z$ , where the electron density has a cusp
- The asymptotic decay of the density far from the nucleus.

As seen in the plots to the right, the gradient parameter  $s^2$  detects the second region [ $\ln(s^2) > 0$ ] indicating large inhomogeneity) but misses the first. The Laplacian-based parameter  $q$  blows up in both regions and distinguishes between the two by its sign. A related issue is the singularity in the X potential that occurs for normal GGA's in the cusp region, but not for Laplacian-based ones.

Other considerations:

- Although VMC data for the combined XC energy density is easy to model, that for X and C is not. The GEA coefficient  $\mu$  is not unambiguously obtainable from VMC data but it nearly cancels to second order.
- VMC data indicate a strong Lieb-Oxford bound for the limit of large inhomogeneity,  $|E_x^{max}| < 1.33 |E_x^{LDA}|$  as found in many molecular systems (Odashima and Capelle, 2008)
- Small  $r$  expansion of the X hole (Becke) combined with a gradient expansion for the KED suggests a “physical” choice for the mixing parameter  $\alpha$  of 0.2.

## STRATEGY FOR EXCHANGE:

Start with PBE Form:

$$e_{xc}^{GEA} = F_x[s^2] e_{xc}^{LDA}[r_s], \quad F_x(s^2) = 1 + \frac{\mu s^2}{1 + (\mu/\kappa) s^2}, \quad s^2 = \frac{|\nabla n|^2}{4k_F^2 n^2}$$

Switch out Gradient for Laplacian + Gradient mixture:

$$s^2 \rightarrow x \alpha q + \left( \frac{1 - \alpha}{3} \right) s^2, \quad q = \frac{\nabla^2 n}{4k_F^2 n}, \quad \mu \rightarrow 3\mu$$

- Small  $x$  approx:  $x \rightarrow 0, \quad F_x(x) = 1 + 3\mu x \quad (\text{GEA})$
- Large  $x$  approx:  $x \rightarrow +\infty, \quad F_x(x) = 1 + \kappa \quad (\text{Lieb-Oxford bound})$
- Parameters based on SOGGA variant of PBE:  $\mu = 10/81, \kappa = 0.552$  (optimize for solids) or APBE variant of PBE:  $\mu = 0.260, \kappa = 0.804$  (optimize for molecules)

Cure pole in enhancement for large negative Laplacian (nuclear cusp)

$$F_x(x) - 1 = \frac{3\mu x \phi^2}{\sqrt{1 + \eta Ax \phi} + (Ax \phi)^2}$$

- Workable idea:

$$\phi(x) = \left[ 1 - \exp\left(\frac{C}{Ax}\right) \right] (x < 0)$$

$$Ax \phi > -1$$

$\phi$  regulates  $q$  near cusp, avoids infinite variation of  $q$  in finite length

C and  $\eta$  obtained by optimization of curvature in potential (see left.)

## OPTIMIZATION OF THE POTENTIAL

A successful DFT based on the Laplacian needs to cope with spurious oscillations that occur in the potential due to large order derivatives coming from the minimization of the energy with respect to the Laplacian:

$$v_{xc} = \frac{\partial e_{xc}}{\partial n} - \nabla \cdot \left( \frac{\partial e_{xc}}{\partial \nabla n} \right) + \nabla^2 \left( \frac{\partial e_{xc}}{\partial \nabla^2 n} \right)$$

To do so, we consider minimization of curvature integral for a function  $\psi$

$$I = \frac{1}{2} \int |\nabla \psi|^2 dV$$

The minimum of this integral, subject to boundary conditions solves Laplace's equation  $\nabla^2 \psi = 0$

Choice for  $\psi$  to reduce unwanted curvature in the potential is:

$$\psi = \left( \frac{\partial e_{xc}[n(r)]}{\partial \nabla^2 n} \right)$$

He or Ne density can be used for “training set” with a good functional form.

## He atom test case:

Plots show DFT parameters (a), X energy-per-particle (b), and potential (c) for He atom. Includes exact density and energy from Filippi and Umrigar, PBE using SOGGA parameters and candidate DFT's using the Laplacian. Cusp region shown in (d).

Probes entire range of  $q, -\infty < q < \infty$

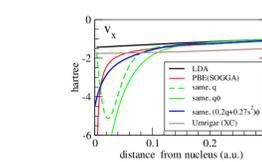
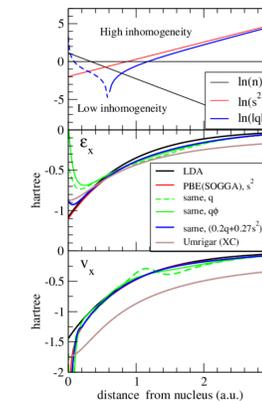
Laplacian-only models (green) notice cusp at nucleus – and gives finite potential.

Rapid oscillations in potential for simple model (dashed) due to Laplacian term in potential:

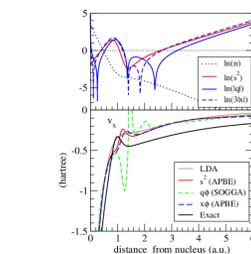
Correlates to lack of 4<sup>th</sup> order term in  $F_x(q)$ .

Hybrid model (blue) for potential, with minimization of curvature, has superior behavior at cusp and no “wiggles” elsewhere.

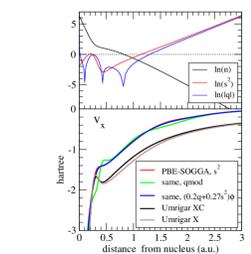
Below: Intershell region of Be with large gradients and low density gives rise to worst oscillations. Cured by use of hybrid variable.



## Be atom:



## Ne atom:



Atom	Model	Variable	$\mu$	$\kappa$	$\eta$	C	$E_c$	$V_c(0)$	I
He	LDA						-0.883	-1.509	
	SOGGA	$s^2$	10/81	0.552			-0.961	-14.88	
	APBE	$s^2$	0.26037	0.804			-1.02995	-28.77	
	ModSOGGA	$x\phi$	10/81	1.104	3.0	0.400	-0.960	-5.491	18.7e-05
	ModAPBE	$x\phi$	0.26037	1.600	3.0	0.500	-1.029	-14.42	47.4e-05
Ne	KS						-1.02457	-1.688	
	LDA						-11.021	-8.391	
	SOGGA	$s^2$	10/81	0.552			-11.621	-238.4	
	APBE	$s^2$	0.26037	0.804			-12.209	-480.3	
	ModSOGGA	$x\phi$	10/81	1.104	3.0	0.400	-11.622	-45.04	22.2e-05
	ModAPBE	$x\phi$	0.26037	1.600	3.0	0.500	-12.214	-253.8	56.4e-05
Umrigar							-7.984		
HF							-12.11		

Table 1: Exchange energy, potential at the nucleus, curvature integral for GGA's and Laplacian-based models (in hartrees).

## DISCUSSION

- Consensus of VMC data, qualitatively and quantitatively, points to primary role of Laplacian of density in explaining the energy associated with the XC hole – at least in the valence region and pseudopotential systems.
- Laplacians and Gradients of the density are interchangeable in the GGA – respecting bounds and scaling constraints equally well.
- Sensitivity of Laplacian's to structure – covalent bonds and shell structure – leads to sensitivity to *spurious* structure in DFT models, requiring more careful attention to form of correction. These can be ameliorated by minimizing the curvature in the XC potential.
- Hybrid variables with combined benefits of Laplacian and gradient can reproduce GGA calculations for small atoms and show promise to test role of Laplacian in covalent bonding.