Laplacian-based models for the exchange-correlation energy: Revisiting the GGA in Density Functional Theory
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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 – Llaplacian or noninteracting KE
- HyperGGA – general use of KS orbitals
Systematic hierarchy: Empirical/stoichiometric otherwise!
A symptom of the lack of systematics – a large "GGA zoo" of GGA models (PBE, PBE, 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 $n$ if an electron is at $r$:

$$n_r^e = n_r - n(r)$$

The interaction of an electron with its XC hole gives a useful, if not perfect, trick of adiabatic integration of the Coulomb energy of the hole over time:

$$E_{XC} = \int_{-\infty}^{\infty} n_r^e(r)\phi(r)^2 dr$$

A critical issue is the singularity in the X potential that occurs for normal $\phi(r)$
$$\lim_{r \rightarrow 0} \phi(r) = \infty$$

Below shows the density, the gradient squared and Laplacian of the same. The latter two contribute indistinguishable correlation.

Below shows the data for Si atom versus radial distance $r$ in (b) matches density Laplacian in (a)

For slowly varying systems, gradient and Laplacian-based DFTs are interchangeable. The same can 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 $r < a$, where the electron density has a cusp.
- The asymptotic decay of the density far from the nucleus.

Experiments include critical points (Hill et al, 1999) atoms, hydrocarbons molecule (Hsing, 2006), (HVS) (Valenzuela 2001).

ACKNOWLEDGEMENTS
Mickey Cho, Changpeng Hsing, Cyrus Umrigar for sharing their data
Neil Coleman, Shawn Wood for code development
Work funded by the National Science Foundation Grant DMR-08122195

BIBLIOGRAPHY

STRAIGHT FOR EXCHANGE:

Start with PBE Form
$$\rho_{PBE} = \rho_{KS} - \frac{1}{2}\int \rho^{*} \left( \frac{\nabla \rho^{*}}{\rho^{*}} \right)^{2} dV$$

Switch out Gradient for Laplacian or Gradient mixture:
$$\rho_{\text{mix}} = \rho_{KS} - \frac{1}{2} \left( \frac{\nabla^{2} \rho_{\text{mix}}}{\rho_{\text{mix}}} \right) dV$$

Small s approx: $s = 1$
Larger s approx: $s = 16$

Parameter based on SOGGA variant of PBE $s = 0.16$ or $s = 0.084$ parameters for molecules
Cure pole in enhancer for large negative Laplacian (nuclear core)

Workable idea: $s = 0.8$

$\frac{d}{dr}$ regularizes core core, avoids infinite variation of $s$ in finite length
$C$ and $s$ obtained by optimization of curvature in potential core left

OPTIMIZATION OF THE POTENTIAL

A successful DFT based on the LDA 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:

$$\frac{\partial E}{\partial \nabla^{2} \rho} = \lim_{\delta \rightarrow 0} \frac{E(\rho + \delta \nabla^{2} \rho) - E(\rho)}{\delta}$$

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

$$\min \int \left( \frac{\nabla^{2} \rho}{\rho} \right)^{2} dV$$

The minimization of this integral, subject to boundary conditions solves Laplace's equation $\nabla^{2} \rho = 0$

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

$$\frac{\nabla^{2} \rho}{\rho}$$

He or $\text{Ne}$ density can be used for “tuning” with a good functional form.

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 basis.
- Laplacians and Gradients of the density are interchangeable in the GGA – respecting bounds and scaling constraints equally well.
- Sensitivity of Laplacian to structure – covalent bonds and shell structure – leads to sensitivity to structure in DFT models, requiring more careful attention to form of correction. These can be ameliorated by modifying 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.