Beyond the local approximation to exchange and correlation: the role of the Laplacian of the density in the energy density of Si.

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We model the exchange-correlation (XC) energy density of the Si crystal and atom as calculated by variational Monte Carlo (VMC) methods with a gradient analysis beyond the local density approximation (LDA). We find the Laplacian of the density to be an excellent predictor of the discrepancy between VMC and LDA energy densities in each system. A simple Laplacian-based correction to the LDA energy density is developed by means of a least square fit to the VMC XC energy density for the crystal, which fits the homogeneous electron gas and Si atom without further effort.

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The crucial ingredient of density functional theory (DFT) is the exchange-correlation (XC) energy which incorporates the effects of many-body correlations on the ground-state energy of an electronic system into its expression as a functional of the ground-state density. The success and widespread application of DFT in solid-state physics and quantum chemistry has been due to the remarkable accuracy of simple and efficient local and “semilocal” models for this quantity, including the local density approximation (LDA) \footnote{A gradient expansion in which the variation in the density is mapped to a succession of increasingly complex local functions of the density, its gradient and related quantities.}, generalized gradient approximations (GGA’s) \footnote{Extensions of the GGA \cite{Cancio2018} with the local value of the density: n(r)}, and various further systematic improvements \footnote{A picture has been found in the context of the complex-valued functions that occur in real materials, one that is paradigmatic of all covalently bonded systems.}. These methods form a hierarchy of approximations in which this intrinsically nonlocal and as yet poorly understood functional of the density is mapped to a succession of increasingly complex local functions of the density, its gradient and related quantities. However, no systematic method for developing such corrections is known to exist, and the accuracy of current methods is not yet consistently at the level (roughly a milli-Rydberg) needed to characterize chemical reactions and other applications highly sensitive to the total energy.

A fruitful source of intuition and of mathematical constraints in the development of DFT’s has been the analysis of the XC energy in terms of the XC hole, the change in density from the mean that occurs about an electron’s position due to exchange and Coulomb correlations \cite{Slater1951}. It provides a natural interpretation for the XC energy density associated with the XC hole in the Si crystal and atom in terms of a gradient analysis of the density. We find that the deviation of the XC energy density from the LDA model is markedly correlated with the local Laplacian of the density, a quantity that has been mostly neglected in developing DFT’s, with the local gradient playing little or no role. We construct a minimal Laplacian-based model to quantify this relation with parameters fit to the crystal data. The resulting fit captures most of the discrepancy between the VMC and LDA energy densities, and fits both the homogeneous electron gas (HEG) and Si atom cases with no further effort.

A strong correlation between the Laplacian of the density and the XC energy density has previously been reported \cite{Cancio2018} for a model strongly inhomogeneous electron gas. However, the current work is the first time that such a picture has been found in the context of the complexities (covalent bonding, atomic orbitals, diamond structure) inherent in a real material, one that is paradigmatic for all covalently bonded systems. These results suggest the existence of a simple yet universal correlation between the XC hole and the local density Laplacian that should be a help in guiding future DFT models.

In DFT, the XC energy \( E_{\text{xc}} \) is usually written as an integral of a locally defined XC energy density, \( e_{\text{xc}} \):

\[
E_{\text{xc}} = \int d^3r \, e_{\text{xc}}(r; [n]);
\]

where \( e_{\text{xc}} \) is itself an unknown functional of the density \( n \). The simplest ansatz for \( e_{\text{xc}} \) is that of the LDA in which the true nonlocal functional at a given point in space is replaced by that of the homogeneous electron gas (HEG) with the local value of the density: \( e_{\text{xc}}^{\text{LDA}}(r; [n]) = e_{\text{xc}}^{\text{HEG}}(r_s(r)) \), where \( r_s = (3/4\pi n)^{1/3} \) is the Wigner-Seitz radius. Corrections to the LDA are usually based on a gradient expansion \cite{Cancio2018a} in which the variation in the density near \( r \), described by derivatives of \( n(r) \), is used to modify \( e_{\text{xc}}(r) \). GGA’s add a dependence on \( |\nabla n(r)| \),

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\]
FIG. 1: Comparison of DFT and VMC XC energy densities on the (110) plane of the Si crystal. (a) Difference in the LDA XC energy density and that of VMC data [10, 11]. (b) Difference between that of the “GGA++” model described in the text and VMC. Contours in increments of $2 \times 10^{-3}$ a.u., with thicker contour that for zero energy difference. Blue regions show negative difference and redder regions, positive.

FIG. 2: Gradient analysis of the density of crystalline Si. The density (a), its gradient squared (b), and Laplacian (c) on the (110) plane of the Si crystal. Atoms and bonds outlined in black. Shading varies from blue (lowest) to red (highest) and contours are in increments of 0.01 a.u. (a), 0.01 a.u. (b), and 0.05 a.u. (c). In (c) the zero contour is the thicker black line.

and metaGGA’s [10], on more complex local derivatives. The density Laplacian $\nabla^2 n$ occurs to the same order as $|\nabla n|$ in the gradient expansion but is less often used [6].

An intuitive picture of $e_{xc}$ is obtained from the XC hole $n_{xc}(r, r')$, which measures the change in density at $r'$ from the mean density $n(r')$, given the observation of an electron at $r$. The XC energy density may be expressed in terms of the adiabatically integrated XC hole [10]:

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

(In this paper, we use hartree atomic units.) Here, $n_{xc}$ represents the XC hole evaluated for a system with Coulomb coupling $\lambda e^2$ and the same ground-state density $n(r)$ as the true system. In this formalism, $e_{xc}(r)/n(r)$ is the sum of the potential energy due to the interaction of an electron with its own hole and the kinetic energy cost to create the hole.

Unfortunately, $e_{xc}$ is not uniquely definable – any function that integrates to zero over the system volume could be added to $e_{xc}$ in Eq (4) to generate a new “gauge” choice for the energy density, to which the energetically relevant quantity $E_{xc}$ would be invariant. This is implicitly done in GGA’s to convert any potential dependence of $e_{xc}$ upon $\nabla^2 n$ to an equivalent dependence upon $|\nabla n|^2$ alone [15]. On the other hand, the adiabatic method is a natural, easily interpreted choice for defining $e_{xc}$; moreover it is readily calculable in the VMC method from the expectation of the XC hole taken for several different values of $\lambda$ [10].

To visualize the task faced in describing $e_{xc}$ for a realistic system, we plot in Fig. 1(a) the difference $\delta e_{xc}$ between the $e_{xc}$ of the LDA and that of the VMC calculation of Hood et al. [10, 11] for the Si crystal in a pseudopotential approximation. The LDA predicts too deep an energy in the region of the Si bond, and too shallow an energy at low density, most obviously in the pseudoatom core, but also, amplified in effect since it includes a large percentage of the unit cell volume, in the interstitial regions of the crystal. The net contribution of positive and negative errors in $e_{xc}$ almost exactly cancel, so that the integrated $E_{xc}$ in the LDA is essentially the same as that of the VMC [11]. The exact functional behavior of the energy density difference is quite complex.

Figure 2 shows a gradient analysis of the Si-crystal valence electron density on the (110) plane. The gradient of the density squared $|\nabla n|^2$, shown in Fig 2(b), highlights the critical points of the density as blue regions where the
gradient is nearly zero. It is significantly nonzero around the edges of the bond between two Si atoms. The Laplacian $\nabla^2 n$, Fig. 2(c), is negative in regions of strong electron localization in the bond and positive in regions of electron depletion, such as the atom core and the interstitial regions. It has a characteristic “butterfly shape” in the bond center, caused by two regions of peak density located near the two Si atom valence shell peaks.

Upon comparison of Figs. 1(a) and 2 what is immediately evident is that the shape delineated by $\nabla^2 n$ characterizes the discrepancy between the VMC and LDA XC energies. It reliably predicts the sign of the correction needed on a point by point basis throughout the unit cell, identifies regions of maximum error (bond and atom core), and reproduces key topographic features such as the shape of the region of maximum energy error in the bond. In contrast $|\nabla n|^2$ seems to have little to do with the trends in energy density error.

VMC calculations of $\epsilon_{xc}$ have recently been performed for the valence shell of the Si atom in a pseudopotential model [12]. These allow us to verify the trends demonstrated in the gradient analysis of the crystal in a system that lacks bonds, and has significantly different boundary conditions. Shown in Fig. 3(a) are $|\nabla n|^2$ and $\nabla^2 n$ of the Si pseudo-atom electron density versus radial distance. The peak of the density, indicated by the vertical dotted line, marks the zero of $\nabla n$ and the maximum negative value of $\nabla^2 n$. The solid line in 3(b) shows the difference in $\epsilon_{xc}$ between the local spin density (LSD) [17] and VMC results. Ignoring short-wavelength statistical fluctuations that are a by-product of the Monte Carlo calculation, a dramatic correlation of $\delta \epsilon_{xc}$ with $\nabla^2 n$ is seen, with the same qualitative trends as the crystal.

These two examples (crystal and atom) demonstrate a qualitatively consistent dependence of $\epsilon_{xc}$ upon the Laplacian of the density that should be quantifiable – but not in the context of GGA’s, which do not include a dependence on $\nabla^2 n$. We consider an enhanced GGA model, a “GGA$$^{++}$$”, of the form

$$\epsilon_{xc}^{GGA^{++}}(r_s, s^2, l) = F_{xc}(r_s, s^2, l) \epsilon_{xc}^{LDA}(r_s),$$

where the correction to the LDA energy density is expressed by an enhancement factor $F_{xc}$ dependent upon the Wigner radius $r_s$ and dimensionless variables $l = r_s^2(r) \nabla^2 n(r)/n(r)$ and $s = r_s(r) |\nabla n(r)|/n(r)$. This GGA$$^{++}$$ is fit to VMC data for the Si crystal by a least-squares procedure that minimizes the variance in the energy density from the VMC value, integrated over the unit cell. The root-mean-square error of the energy density, $\delta \epsilon_{rms}$, obtained in this way is 0.442 millihartrees for the LDA, and represents the average deviation from zero for the energy-difference plot shown in Fig. 1(a).

We have found that a form for $F_{xc}$ depending only upon the dimensionless Laplacian $l$ provides the optimal fit to our data in the sense of returning the greatest degree of correction per fitting parameter. The form is given by

$$F_{xc}(l) = 1 + \frac{\alpha + \beta l}{1 + \gamma l},$$

with optimized fitting parameters $\alpha = -0.0007$, $\beta = 0.0080$, and $\gamma = 0.026$. The fitting error $\delta \epsilon_{rms}$ is thereby reduced 70% from its LDA value to 0.132 millihartrees. This form potentially satisfies several known properties of the universal $\epsilon_{xc}$, particularly recovering the correct value in the HEG limit ($s^2 = l = 0$) for $\alpha = 0$. It behaves properly under uniform scaling to infinite density [15] but fails to include a dependence of $F_{xc}$ on $r_s$ due to correlation. The smallness of the optimized value of $\alpha$ indicates that the best fit for the Si crystal simultaneously satisfies the HEG limit. This supports the validity of our model as a description of a genuine physical phenomenon rather than a mathematical anomaly specific to Si.

Shown in Fig. 1(b) is the difference in energy density between our three-parameter GGA$$^{++}$$ fit and the VMC data of Hood et al., on the same energy scale as the energy difference between LDA and VMC in (a), showing point by point what $\delta \epsilon_{rms}$ shows on average. The difference in $\epsilon_{xc}$ has been greatly reduced everywhere throughout the unit cell, with the exception of the bond center and at the antibond point behind each bond. We have also tried a 5-parameter fit including terms of order $s^2$ and forms with higher order corrections, with only minimal improvement of $\delta \epsilon_{rms}$. In every case tried the linear coefficient $\beta$ for $l$ remains at 0.008 to within 10%.

The transferability of our model can be tested by applying it to the Si atom data of Ref. 12. We have applied the Laplacian-only $F_{xc}$, obtained from our fit to the crystal data without any further adjustments as a correction to the LDA XC energy density for the Si atom. This is defined similarly to Eq. 3, by $\epsilon_{xc}^{LSD-GGA^{++}} = \frac{\epsilon_{xc}(s^2, l) - \epsilon_{xc}(s^2, 0)}{\epsilon_{xc}(s^2, 0)} = \frac{F_{xc}(l) - 1}{\alpha + \beta l}$.
$F_{xc}(s^2, l)\epsilon^{LSD}_{xc}(r_s, \zeta)$, where $\zeta = \frac{n_{\uparrow} - n_{\downarrow}}{n}$ is the local spin polarization. The result for $\delta e_{xc}$ using this model is shown in Fig. 4(b); the overall error $\delta e_{rms}$ is reduced by 70% from its LSD value, achieving the same reduction of error as for the crystal.

Our numerical results tieing $\epsilon_{xc}$ to $\nabla^2 n$ can be motivated qualitatively by reconsidering a gradient expansion, this time for $n_{xc}$. This would use as input the change in density within the length-scale of the XC hole about any position, as described by local derivatives of the density, to correct the errors inherent in the LDA assumption of a locally homogeneous environment. As the Coulomb interaction is directionally invariant, only the change in density averaged over angle should contribute to this correction. This is precisely what is measured by $\nabla^2 n$, and is unobtainable from $|\nabla n|^2$. Given an $\epsilon_{xc}$ derived from the adiabatically integrated XC hole, one could then expect the error in the LDA model of $\epsilon_{xc}$ to be dominated by the local value of $\nabla^2 n$.

The value of the Laplacian of the density in electronic structure has been noted in several other contexts. It has been used successfully as a diagnostic tool in characterizing the electronic structure of molecules. Covalent bonds have been found to be distinguished by a negative Laplacian at the bond center, denoting the build-up of charge within the bond, and non-covalent ones by a positive $\nabla^2 n$; in addition the hour-glass pattern observed in the Si crystal bond is typical of other tetrahedrally bonded systems. Secondly, studies of the XC potential of atoms have pointed out that terms in $\nabla^2 n$ are necessary to model the potential in the nuclear cusp and asymptotic regions. Thus the relevance of this quantity to DFT extends beyond the pseudopotential models studied here to all-electron calculations, and possibly from covalent to other types of chemical bonds.

The XC potential $\nu_{xc}(r) = \delta E_{xc}/\delta n(r)$, necessary for a self-consistent determination of the density is easily obtained within the plane-wave pseudopotential formalism of the DFT. Self-consistent calculations of density and structural properties of Si using our GGA$^{+\chi}$ model show no significant deviation from the already reasonably good prediction of these quantities in the LDA. Full results will be discussed in a further paper.

A caveat in regard to our results is that our model has been fit to data obtained by a variational method that underestimates the correlation energy. The true correlation energy for each system may be lower than that of the VMC by about 15%, and $E_{xc}$ lower by 1-2%. However, within the VMC approximation, the main effect of adding correlation has been to increase the match between the LDA error and $\nabla^2 n$ from that observed in the exchange-only case, shown in Fig. 6(a) of Ref. 11. The effect of the addition of the missing correlation energy might well be to reduce further the discrepancy between the actual $\epsilon_{xc}$ and a Laplacian fit.

In summary, our fit of $\epsilon_{xc}$ in terms of a Laplacian based enhancement factor $F_{xc}(l)$ provides a simple model that has a surprisingly wide range of applicability: from the HEG to covalently bonded crystal to open shell atom. This points to the potential for a Laplacian-based $F_{xc}$ to make an excellent approximation to the true, universal one for a wide range of systems. To date, the development of GGA’s and metaGGA’s has emphasized the gradient of the density as the basic departure point for the post-LDA description of DFT. Our analysis indicates rather that it may be advantageous to start with $\nabla^2 n$ as the key factor in going beyond the LDA.

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Acknowledgments

1. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
2. R. O. Jones and O. Gunnarson, Rev. Mod. Phys. 61, 689 (1989).
3. J. P. Perdew, in Electronic Structure of Solids ’91, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
4. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996); 78, 1396(E) (1997).
5. C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).
6. A. D. Becke, J. Chem. Phys. 109, 2092 (1998).
7. J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. 82, 2544 (1999).
8. J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003), cond-mat/0306203.
9. J. P. Perdew and Y. Wang, Phys. Rev. B 46, 12947 (1992); J. P. Perdew and K. Burke and Y. Wang, Phys. Rev. B 54, 16533 (1996).
10. Randolph Q. Hood et al., Phys. Rev. Lett. 78, 3350 (1997).
11. Randolph Q. Hood et al., Phys. Rev. B 57, 8972 (1998).
12. A. Puzder, M. Y. Chou, and R. Q. Hood, Phys. Rev. A 64, 022501 (2001).
13. A. C. Cancio, M. Y. Chou, and R. Q. Hood, Phys. Rev. B 64, 115112 (2001), cond-mat/0101363.
14. Maziar Nekovee, W. M. C. Foulkes and R. J. Needs, Phys. Rev. Lett. 87, 036401 (2001); Phys. Rev. B 68, 235108 (2003).
15. P. S. Svendsen and U. von Barth, Phys. Rev. B 54, 17402 (1996-II).
16. J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974); D. C. Langreth and J. P. Perdew, Solid State Commun. 17, 1425 (1975); O. Gunnarson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
17. U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).
18. M. Levy and J. P. Perdew, Phys. Rev. A 32, 2010 (1985).
19. R. F. W. Bader and H. Essen, J. Phys. Chem. 80, 1943 (1983).
20. E. Engel and S. Vosko, Phys. Rev. B 47, 13164 (1993).
21. C. J. Umrigar and X. Gonze, Phys. Rev. A 50, 3827 (1994).