4-1999

Evaluation of Gradient Corrections in Grid-Free Density Functional Theory

Kurt Raymond Glaesemann
Iowa State University

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

Evaluation of Gradient Corrections in Grid-Free Density Functional Theory

Abstract
The Almlöf–Zheng approach to grid-free density functional theory(DFT) uses the resolution of the identity (RI) instead of a finite grid to evaluate the integrals. Application of the RI can lead to stability problems, particularly when gradients are involved. The focus of the current work is on choosing a stable method of evaluating the gradient correction using the RI. A stable method is compared to several unstable methods.

Keywords
Density functional theory, Gradient approximations

Disciplines
Chemistry

Comments
The following article appeared in *Journal of Chemical Physics* 110 (1999): 6580, and may be found at doi:10.1063/1.478559.

Evaluation of gradient corrections in grid-free density functional theory

Kurt R. Glaesemann and Mark S. Gordon

Citation: The Journal of Chemical Physics **110**, 6580 (1999); doi: 10.1063/1.478559
View online: http://dx.doi.org/10.1063/1.478559
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/110/13?ver=pdfcov
Published by the AIP Publishing

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1999 issue.

NOTES

Evaluation of gradient corrections in grid-free density functional theory

Kurt R. Glaesemann and Mark S. Gordon
Chemistry Department, Iowa State University, Ames Laboratory-United States Department of Energy, Ames, Iowa 50011

(Received 21 September 1998; accepted 5 January 1999)

[S0021-9606(99)30813-8]

I. INTRODUCTION

Density functional theory (DFT), formulated in terms of the spin densities (n_α, n_β), has gained popularity for determining molecular properties and structures. Functionals were originally fit to the uniform electron gas,[1,2] but accurate energetics usually require density gradient terms.[3–8] The standard procedure is to evaluate the integrals using a numerical grid:

$$f(n_\alpha, n_\beta, \nabla n_\alpha, \nabla n_\beta)\, d\vec{r} \approx \sum_{i}^{\text{Grid points}} f(n_\alpha(i), n_\beta(i), \nabla n_\alpha(i), \nabla n_\beta(i))\, \Delta\vec{r}(i). \quad (1)$$

One grid-free approach has been developed specifically for the uniform electron gas-based $X-\alpha$ functional.[9–11] Other functionals require the more general approach proposed by Almlöf and Zheng (AZ).[12–16] The AZ grid-free approach is based on the resolution of the identity (RI).[17] The focus of the current work is on properly treating density gradient terms within the AZ approach. These terms arise within the calculation of the exchange-correlation energy and the exchange-correlation potential.

II. A GRID-FREE APPROACH TO GRADIENT CORRECTED DFT

Consider the product of two arbitrary functions, f and g. The RI can be utilized as follows, with $\{\chi\}$ being an arbitrary basis set and $\{\theta_m\}$ being a set of orthonormal functions:

$$\int \chi_i f \cdot g \chi_j \, d\vec{r} \approx \sum_m \int \chi_i f \theta_m \, d\vec{r} \cdot \int \theta_m g \chi_j \, d\vec{r}. \quad (2)$$

The foregoing expression is exact only if $\{\theta_m\}$ completely spans the $f \cdot g$ function space (often smaller than a complete basis).[15,16,18] One should therefore expect dependence of the calculation on the size of the $\{\theta_m\}$ basis set; the molecular orbitals are usually an inadequate basis.[15,18] The functions f and g must also be ''well-behaved'' in order for the decomposition in Eq. (2) to produce correct results. A well-behaved function is single-valued and defined in the entire relevant space. The relevant space of functions of n (always positive) is $\{0...\infty\}$ and of functions of the spin polarization $\xi=(n_\alpha - n_\beta)/(n_\alpha+n_\beta)$ is $\{-1...1\}$.

Application of the RI in Eq. (2) to DFT integrals will leave integrals involving functions of the spin-densities and the density gradient. The ''spectral'' resolution of the identity is used[19] to evaluate these integrals. This method [see Eq. (3)] assumes that the matrix of integrals over the density has been transformed to an orthonormal basis set in which this matrix is diagonal. No generality is lost, since this is just a basis transformation. The function of the integral is assumed to be the integral of the function:

$$\int \theta_1 f(n) \theta_j \, d\vec{r} \approx f\left(\int \theta_i n \theta_j \, d\vec{r} \right) = f(\lambda_i)\, \delta_{ij}, \quad (3)$$

where λ_i is an eigenvalue of the matrix $M[n]_{ij} = \int \theta_i n \theta_j \, d\vec{r}$. Equation (3) is exact in a complete basis, provided f is well-behaved.[15] In DFT, n is the density, although Eq. (3) does not assume this. Therefore, once the integrals over n are determined, the integrals over any well-behaved function of n can be readily obtained.

The more popular DFT functionals involve terms that depend upon the gradient of the density, to allow for ''nonlocal'' effects. The 1988 exchange functional of Becke:[20]

$$[B88X] = n^{4/3}[-c_1 y^2/(1+6\cdot c_1 \cdot y \cdot \sinh^{-1} y)],\ c_1 = 0.0042, \quad (4)$$

is a function of the dimensionless density gradient $y = |\nabla n|/n^{4/3}$ or $y^2 = (\nabla n)^2/n^{8/3}$.

The AZ papers suggest two approaches to calculating ∇n and $n^{-4/3}$ separately, then combining the results using Eq. (2). The first paper[13] suggested using the commutator relationship $(\nabla n)^2 = [[n, \nabla^2], n]$ to calculate y^2, and the second paper[14] suggested using the commutator relationship $\nabla n = [\nabla, n]$ to calculate y. Implementing these approaches causes numerical stability problems.[21] Although the ∇n terms are calculated properly, the resulting values of y are incorrect. For example, the expectation value $\langle n^{-4/3} \rangle$ is infinite for the exact hydrogen wavefunction.[22] Thus, the condition that f is well-behaved in Eq. (3) is not met for $f = n^{-4/3}$. There are reports in the literature of stability problems while evaluating the derivative this way.[12] Therefore, the ∇n and $n^{4/3}$ terms need to be calculated together as either y or y^2.

The first choice might be to directly evaluate $y^2=(\nabla n/n^{4/3})^2$, because y^2, and not y, is the dimensionless gradient originally proposed.[23] This is similar to the approach taken in the first paper by AZ and that proposed by others.[22] The RI in Eq. (2) is used in Eq. (5c)

$$\left(\frac{\nabla n}{n^{4/3}}\right)^2=9[[n^{-1/3},\nabla^2],n^{-1/3}], \tag{5a}$$

$$\int \chi_\mu\left(\frac{\nabla n}{n^{4/3}}\right)^2\chi_\nu\,d\vec{r}$$

$$=9\int \chi_\mu(2n^{-1/3}\nabla^2 n^{-1/3}-\nabla^2 n^{-2/3}-n^{-2/3}\nabla^2)\chi_\nu\,d\vec{r}, \tag{5b}$$

$$\approx 9\sum_{m,n}^{\text{Orthonormal}}\left\{\int \chi_\mu 2n^{-1/3}\theta_m\,d\vec{r}\cdot\int \theta_m\nabla^2\theta_n\,d\vec{r}\cdot\int \theta_n n^{-1/3}\chi_\nu\,d\vec{r}-\int \chi_\mu\nabla^2\theta_m\,d\vec{r}\cdot\int \theta_m n^{-2/3}\chi_\nu\,d\vec{r}-\int \chi_\mu n^{-2/3}\theta_m\,d\vec{r}\cdot\int \theta_m\nabla^2\chi_\nu\,d\vec{r}\right\}. \tag{5c}$$

The derivation can be conveniently completed in the orthonormal basis set in which n is diagonal. Since this is only a basis transformation, no generality is lost, provided that $\{\chi\}$ and $\{\theta\}$ span the same space. This must be the case in order for $\int \chi_\mu n^{-1/3}\theta_m\,d\vec{r}$ to be evaluated using the RI in Eq. (3). The eigenvalues of the matrix of $\int \chi_\mu n\chi_\nu\,d\vec{r}$ in Eq. (3) are denoted λ_ν. Equation (5c) simplifies greatly, since integrals of the type $\int \chi_\mu n^a\chi_\nu\,d\vec{r}$ are evaluated using the $\{\lambda_\nu\}$ and many indices collapse. Equation (5c) becomes:

$$\int \chi_\mu\left(\frac{\nabla n}{n^{4/3}}\right)^2\chi_\nu\,d\vec{r}$$

$$=9\left\{2\lambda_\mu^{-1/3}\cdot\int \chi_\mu\nabla^2\chi_\nu\,d\vec{r}\cdot\lambda_\nu^{-1/3}-\int \chi_\mu\nabla^2\chi_\mu\,d\vec{r}\cdot\lambda_\nu^{-2/3}-\lambda_\mu^{-2/3}\cdot\int \chi_\nu\nabla^2\chi_\nu\,d\vec{r}\right\}, \tag{6a}$$

$$=-9(\lambda_\mu^{-1/3}-\lambda_\nu^{-1/3})^2\cdot\int \chi_\mu\nabla^2\chi_\nu\,d\vec{r}. \tag{6b}$$

Clearly, $\int \chi_\nu(\nabla n/n^{4/3})^2\chi_\nu\,d\vec{r}=0$ for all ν after this application of the RI. So, the sum of all the eigenvalues of this representation of $(\nabla n/n^{4/3})^2$ is zero. But $(\nabla n/n^{4/3})^2$ is certainly positive definite, so its eigenvalues must be positive, even though this is clearly not the case after applying the RI in Eq. (5c). Thus, this application of the RI is flawed and produces an inconsistent result: increasing the size of the basis set will not converge to the correct value. The condition that f and g be well-behaved in Eq. (2) is not satisfied as applied in Eq. (5c).

Therefore, the density gradient in GAMESS[24] is evaluated using $y=|\nabla n|/n^{4/3}$ rather than $y^2=(\nabla n/n^{4/3})^2$. The commutator relationship used is similar to that proposed in Ref. 14. The RI in Eq. (2) is used in Eq. (7c):

$$\left(\frac{\nabla n}{n^{4/3}}\right)=3[n^{-1/3},\nabla], \tag{7a}$$

$$\int \chi_\mu\left(\frac{\nabla n}{n^{4/3}}\right)\chi_\nu\,d\vec{r}$$

$$=3\int \chi_\mu(n^{-1/3}\nabla-\nabla n^{-1/3})\chi_\nu\,d\vec{r}, \tag{7b}$$

$$\approx 3\sum_{m}^{\text{Orthonormal}}\left\{\int \chi_\mu n^{-1/3}\theta_m\,d\vec{r}\cdot\int \theta_m\nabla\chi_\nu\,d\vec{r}-\int \chi_\mu\nabla\theta_m\,d\vec{r}\cdot\int \theta_m n^{-1/3}\chi_\nu\,d\vec{r}\right\}. \tag{7c}$$

Choosing the orthonormal basis in which n is diagonal yields

$$\int \chi_\mu\left(\frac{\nabla n}{n^{4/3}}\right)\chi_\nu\,d\vec{r}=3\left\{\lambda_\mu^{-1/3}\cdot\int \chi_\mu\nabla\chi_\nu\,d\vec{r}-\int \chi_\mu\nabla\chi_\nu\,d\vec{r}\cdot\lambda_\nu^{-1/3}\right\}, \tag{8a}$$

$$=3(\lambda_\mu^{-1/3}-\lambda_\nu^{-1/3})\cdot\int \chi_\mu\nabla\chi_\nu\,d\vec{r}. \tag{8b}$$

Equation (8b) results in the diagonal values of $\int \chi_\mu(\nabla n/n^{4/3})\chi_\nu\,d\vec{r}$ all being zero, but $\nabla n/n^{4/3}$ and not the positive definite quantity $y=|\nabla n|/n^{4/3}$ was calculated in Eqs. (7) and (8). The RI in Eq. (2) is used to generate integrals over y^2 with all positive eigenvalues:

$$\int \chi_\mu\left(\frac{\nabla n}{n^{4/3}}\right)^2\chi_\nu\,d\vec{r}=\sum_m\int \chi_\mu\left(\frac{\nabla n}{n^{4/3}}\right)\chi_m\,d\vec{r}\cdot\int \chi_m\left(\frac{\nabla n}{n^{4/3}}\right)\chi_\nu\,d\vec{r}. \tag{9}$$

This matches the proper physics of the system. Although a large basis set is needed for accuracy, this RI does converge with an adequate auxiliary basis set.[16] This method involves integrals over $n^{-1/3}$, which is well-defined with $\langle n^{-1/3}\rangle=4.943$ for the exact hydrogen wavefunction.[22] This method was successfully used previously,[15] and it is proving useful in additional cases.[16] It is therefore recommended for implementations of the AZ grid-free approach to DFT.

ACKNOWLEDGMENTS

This work was supported in part by grants from the Air Force Office of Scientific Research and by the Ames Laboratory, US-DOE. Special thanks to W. M. Klopper, J. Hutter, and D. E. Bernhold for enlightening discussions.

[1] J. C. Slater, Adv. Quantum Chem. **6**, 1 (1972).
[2] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[3] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).
[4] M. Rasolt and D. J. W. Geldhart, Phys. Rev. B **34**, 1325 (1986).
[5] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[6] J. P. Perdew, K. Burke, and M. Ernzerhof, J. Chem. Phys. **105**, 9982 (1996).
[7] A. D. Becke, J. Chem. Phys. **104**, 1040 (1996).
[8] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1993).
[9] B. I. Dunlap, J. Phys. Chem. **90**, 5524 (1986).

[10] K. S. Werpetinski and M. Cook, Phys. Rev. A **52**, R3397 (1995).
[11] K. S. Werpetinski and M. Cook, J. Chem. Phys. **106**, 7124 (1997).
[12] G. Berghold, J. Hutter, and M. Parrinello, Theor. Chem. Acc. **99**, 344 (1998).
[13] Y. C. Zheng and J. Almlöf, Chem. Phys. Lett. **214**, 397 (1993).
[14] Y. C. Zheng and J. Almlöf, J. Mol. Struct.: THEOCHEM **288**, 277 (1996).
[15] K. R. Glaesemann and M. S. Gordon, J. Chem. Phys. **108**, 9959 (1998).
[16] K. R. Glaesemann and M. S. Gordon (unpublished).
[17] O. Vahtras, J. Almlöf, and M. W. Feyereisen, Chem. Phys. Lett. **213**, 514 (1993).
[18] D. E. Bernhold and R. J. Harrison, J. Chem. Phys. **109**, 1593 (1998).
[19] B. A. Hess, R. J. Buenker, and P. Chandra, Int. J. Quantum Chem. **29**, 737 (1986).
[20] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[21] K. R. Glaesemann and M. S. Gordon (unpublished).
[22] W. M. Klopper (personal correspondence).
[23] F. Herman, I. B. Ortenburger, and J. P. van Dyke, Int. J. Quantum Chem. **IIIS**, 827 (1970).
[24] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Mongomery Jr., J. Comput. Chem. **14**, 1347 (1993).