Theor Chem Acc (1998) 99:344–346
DOI 10.1007/s002149800m15

Theoretical
Chemistry Accounts

Letter

Grid-free DFT implementation of local and gradient-corrected XC functionals

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Received: 7 March 1998 / Accepted: 21 May 1998 / Published on line: 6 August 1998

Abstract. Following an approach to density functional theory calculations based on the matrix representation of operators, we implemented a scheme as an alternative to traditional grid-based methods. These techniques allow integrals over exchange-correlation operators to be evaluated through matrix manipulations. Both local and gradient-corrected functionals can be treated in a similar way. After deriving all the required expressions, selected examples with various functionals are given.

Key words: Grid-free – Density functional theory – Implementation

1 Introduction

Computer simulations based on density functional theory (DFT) [1] provide a powerful tool for calculating the physical and chemical properties of complex molecules and solids. The main reason is that the results of these calculations compare favourably with traditional quantum chemical methods, but with less computational effort. To overcome the problem of the unknown exchange-correlation (XC) functional, most applications make use of the local density approximation (LDA). Aiming at a more accurate description of XC effects, a variety of additional gradient corrections (GC) have been proposed [2–4]. Since all these methods involve integration over complicated algebraic expressions, it seems inevitable to have to work with numerical quadrature over a grid.

An alternative to these traditional grid-based methods was recently proposed by Zheng and Almlöf [5, 6], who use matrix techniques to calculate the required integrals analytically. The suggested approach is based on a matrix representation of the density in an auxiliary basis set. Within this representation, matrix elements of XC functionals of the density are obtained by simply calculating matrix functions. The additional use of basis set completeness relations and the spectral resolution of the identity operator allows analytical expressions for the XC energy and potential to be derived. The method is not limited to local XC functionals. Gradient-corrected functionals can be treated in a similar way, using a matrix representation of the absolute value of the gradient.

It is important to stress that such an analytical approach is not only desirable from an aesthetic point of view, it also avoids the noise resulting from numerical quadrature. Clearly, the use of a finite basis set introduces a new source of inaccuracy but the error due to basis set incompleteness is smooth, independent of the choice of coordinate system and can be eliminated in a controlled way by increasing the basis set.

The aim of this letter is to derive all the expressions required to implement this grid-free method and address a number of apparent numerical problems. Test calculations with different XC functionals show that, in the case of LDA, this technique provides an excellent alternative to grid-based methods. Working with gradient-corrected functionals is more difficult; however it is evident that this approach is feasible too. Unfortunately, large basis sets are needed to handle the apparent problems.

2 Methods

The starting point for the grid-free method is a matrix representation of the density $\rho(\mathbf{r})$. The density is defined in terms of independent Kohn-Sham orbitals

$$\rho(\mathbf{r}) = \sum_i n_i |\Psi_i(\mathbf{r})|^2 \ , \tag{1}$$

where n_i are the occupation numbers. If we expand the one-electron orbitals in a basis set (Latin letters) and use an auxiliary basis to calculate the matrix representation of the density (Greek letters) we obtain

$$M_{\alpha\beta}[\rho] = \langle\alpha|\rho|\beta\rangle = \sum_{i,j} P_{ij}(ij\alpha\beta) \ . \tag{2}$$

P_{ij} is an element of the reduced, first-order density matrix, and $(ij\alpha\beta)$ is a generalized one-electron overlap integral. Other representations of the density (e.g. in auxiliary basis set methods) require a straightforward change of Eq. (2).

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The next step is to write the XC energy in a general way

$$E_{xc} = \int \rho(\mathbf{r})\epsilon_{xc}(\rho, (|\nabla\rho|))d\mathbf{r} \ , \tag{3}$$

where ϵ_{xc} is a function of the electron density, and possibly also of the absolute value of the gradient.

To derive the required expressions for the XC energy and potential it is convenient to first consider the local part.

2.1 Local density approximation

Since ϵ_{xc} is now merely a function of the electron density, it is easy to calculate the XC energy by using the following steps:

1. Calculate the matrix representation of the density using Eq. (2).
2. Transform to an orthonormal basis

$$\tilde{M}[\rho] = XM[\rho]X \ , \tag{4}$$

where the transformation matrix X is calculated easily from the overlap matrix $S_{\alpha\beta} = (\alpha\beta)$: $X = S^{-\frac{1}{2}}$. Since we are working with real basis functions, the transformation matrix is symmetric, which means that all equations are simplified using $X = X^T$.

3. Calculate the matrix function by diagonalizing the matrix and evaluate the function of the eigenvalues

$$\epsilon_{xc}(\tilde{M}[\rho]) = Y\mathrm{diag}(\epsilon_{xc}(\lambda_1), \ldots, \epsilon_{xc}(\lambda_n))Y^T \ , \tag{5}$$

where Y is the unitary transformation that diagonalizes $\tilde{M}[\rho]$.

4. Calculate the energy

$$E_{xc}[\rho] = Tr\left[P\hat{S}X\epsilon_{xc}(\tilde{M}[\rho])X\hat{S}^T\right] \ , \tag{6}$$

where Tr denotes the trace of the matrix. $\hat{S}_{i\alpha} = (i\alpha)$ is the overlap matrix between the basis set used to expand the electron orbitals and that used to calculate the matrix representation of the density.

In order to perform a DFT calculation we also need an expression for the XC potential, which is defined as the functional derivative of the energy: $V = \frac{\delta E}{\delta\rho}$. The corresponding equation in matrix form is

$$\begin{aligned}\langle i|V|j\rangle = \frac{\partial E}{\partial P_{ij}} &= \left(\hat{S}X\epsilon_{xc}(\tilde{M}[\rho])X\hat{S}^T\right)_{ij} \\ &+ Tr\left[P\hat{S}X\frac{\partial\epsilon_{xc}(\tilde{M}[\rho])}{\partial P_{ij}}X\hat{S}^T\right] \ .\end{aligned} \tag{7}$$

The first part of Eq. (7) is straightforward to calculate, but the second part must be handled with care. The reason is that a derivation of the function which involves a diagonalization of $\tilde{M}[\rho]$ is not possible because the unitary transformation Y itself depends on P. However, we can express the matrix function in an alternative way using a line integral which includes all eigenvalues of matrix $\tilde{M}[\rho]$ [7]:

$$\begin{aligned}&\frac{\partial\epsilon_{xc}(\tilde{M}[\rho])}{\partial P_{ij}} \\ &\quad= \frac{1}{2\pi i}\frac{\partial}{\partial P_{ij}}\oint \epsilon_{xc}(z)(z\underline{1} - \tilde{M}[\rho])^{-1}dz \\ &\quad= \frac{1}{2\pi i}\oint \epsilon_{xc}(z)(z\underline{1} - \tilde{M}[\rho])^{-1}\frac{\partial\tilde{M}[\rho]}{\partial P_{ij}}(z\underline{1} - \tilde{M}[\rho])^{-1}dz \\ &\quad= Y\frac{1}{2\pi i}\oint \epsilon_{xc}(z)\left(z\underline{1} - \mathrm{diag}(\lambda_1, \ldots, \lambda_n)\right)^{-1} \\ &\qquad\times Y^T\frac{\partial\tilde{M}[\rho]}{\partial P_{ij}}Y\left(z\underline{1} - \mathrm{diag}(\lambda_1, \ldots, \lambda_n)\right)^{-1} dzY^T \ .\end{aligned} \tag{8}$$

$\underline{1}$ denotes the identity matrix. Carrying out the integration over z one obtains

$$\begin{aligned}&\frac{1}{2\pi i}\oint\frac{\epsilon_{xc}(z)}{(z-\lambda_i)(z-\lambda_j)}\,dz \\ &= \begin{cases}\mu_{xc}(\lambda_i), & \lambda_i = \lambda_j \ , \\ \frac{\epsilon_{xc}(\lambda_i)-\epsilon_{xc}(\lambda_j)}{\lambda_i-\lambda_j}, & \lambda_i \neq \lambda_j \ ,\end{cases}\end{aligned} \tag{9}$$

where μ_{xc} denotes the derivative of ϵ_{xc} with respect to ρ. Performing some trivial algebraic transformations, the second part of Eq. (7) becomes

$$\begin{aligned}&Tr\left[P\hat{S}X\frac{\partial\epsilon_{xc}(\tilde{M}[\rho])}{\partial P_{ij}}X\hat{S}^T\right] \\ &\quad= Tr\left[Y\{A,B\}Y^T\frac{\partial\tilde{M}[\rho]}{\partial P_{ij}}\right] \ ,\end{aligned} \tag{10}$$

where the matrix B_{ij} is defined through Eq. (9), $\{A, B\}$ denotes a componentwise matrix multiplication and

$$A = (\hat{S}XY)^T P(\hat{S}XY); \quad \frac{\partial\tilde{M}[\rho]}{\partial P_{ij}} = X\big((\alpha\beta ij)\big)X \ . \tag{11}$$

For the special case when the auxiliary basis coincides with the original basis the formulas can be simplified by using $\hat{S}X = X^{-1} = S^{\frac{1}{\lambda}}$.

2.2 Gradient corrections

The approach outlined earlier must be slightly modified for gradient-corrected functionals. Firstly all the non-local XC functionals that we have considered allow us to rewrite Eq. (3) using a function f depending solely on ρ and another function g depending only on a variable s

$$E_{xc}[\rho] = \int \rho(\mathbf{r})f(\rho)g(s)d\mathbf{r}; \quad s = \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \ . \tag{12}$$

This equation reads in matrix form

$$E_{xc}[\rho] = Tr\left[P\hat{S}Xf(\tilde{M}[\rho])g(\tilde{M}[s])X\hat{S}^T\right] \ . \tag{13}$$

However, what is needed is a scheme to calculate $\tilde{M}[s]$. Such a scheme has already been proposed by Zheng and Almlöf [6]. Here we obtain a matrix representation of the x-component of the gradient through

$$\tilde{M}[(\nabla\rho)_x] = \tilde{M}[(\nabla)_x]\tilde{M}[\rho] - \tilde{M}[\rho]\tilde{M}[(\nabla)_x] \ , \tag{14}$$

where the tilde denotes that we are already using an orthonormal basis set. With analogous equations for all components we derive first an expression for the absolute value of the gradient

$$\tilde{M}[|\nabla\rho|] = \sqrt{\tilde{M}[(\nabla\rho)_x]^2 + \tilde{M}[(\nabla\rho)_y]^2 + \tilde{M}[(\nabla\rho)_z]^2} \ , \tag{15}$$

and finally for the matrix representation of s

$$\tilde{M}[s] = \tilde{M}[|\nabla\rho|](\tilde{M}[\rho])^{-\frac{4}{3}} \ . \tag{16}$$

It is worth noting that working with Eq. (16) causes some problems. Firstly, $|\nabla\rho|$ and ρ interpreted as operators should commute because they are multiplicative. However, when we use a finite basis set this property is no longer true. To overcome this deficiency, we replace Eq. (16) by the corresponding anticommutator relation. Secondly, a product of two positive definite matrices is not necessarily positive definite. This means that when we diagonalize the matrix representation of s to calculate a matrix function, we cannot expect to obtain merely positive eigenvalues. Unfortunately, as discussed in the next section, the use of large basis sets appears inevitable to handle this problem.

Now to calculate the potential we get an expression resembling Eq. (7) but with a third part including the derivative $\frac{\partial g(\tilde{M}[s])}{\partial P_{ij}}$. In agreement with Eqs. (8–10) we compute this third part through repeated use of the chain rule according to the Eqs. (14–16) until we obtain nothing but terms containing the derivative $\frac{\partial\tilde{M}[\rho]}{\partial P_{ij}}$. Adding up all terms allows the straightforward calculation of the potential in a recursive way.

It is important to notice that all derived equations are exact in the limit of a complete basis set. In a practical implementation, however, we have to use a finite basis set and the effect of this restriction is discussed in the next section.

Table 1. Comparision of total and exchange-correlation (XC) energies of various molecules ([E_H]) obtained from the grid-free approach (anal.) and the numerical quadrature over a grid (num.) respectively. The XC functionals considered are a pure local density approximation (LDA) functional, an exchange functional by Becke (B), a correlation functional by Lee, Yang and Parr (LYP) and a correlation functional by Perdew (P)

Mol.	E_{xc} num.	E_{xc} anal.	E_{tot} num.	E_{tot} anal.
LDA				
H_2	−0.668071	−0.668074	−1.124706	−1.124711
N_2	−4.778431	−4.778482	−19.862484	−19.862524
O_2	−6.635701	−6.635793	−31.714852	−31.714893
H_2O	−4.135950	−4.136020	−17.105997	−17.106040
CO	−4.952923	−4.952980	−21.579077	−21.579126
CH_4	−3.079560	−3.079605	−8.025097	−8.025123
B + LYP				
H_2	−0.708794	−0.710745	−1.156783	−1.157736
N_2	−4.870245	−4.873711	−19.932737	−19.936092
O_2	−6.797641	−6.788523	−31.840368	−31.839543
H_2O	−4.236357	−4.234576	−17.185954	−17.187160
CO	−5.059707	−5.057543	−21.659556	−21.660719
CH_4	−3.150381	−3.154271	−8.073818	−8.077146
B + P				
H_2	−0.716652	−0.718191	−1.166161	− 1.167016
N_2	−4.951349	−4.960175	−20.010477	−20.020438
O_2	−6.881504	−6.887382	−31.925471	−31.931385
H_2O	−4.294198	−4.298948	−17.243376	−17.246888
CO	−5.136621	−5.138950	−21.734175	−21.736345
CH_4	−3.209921	−3.215686	−8.133744	−8.138768

3 Examples and discussion

The matrix approach has been implemented in a hybrid Gaussian and plane wave (PW) density functional scheme [8]. As in traditional PW schemes, pseudopotentials are used to eliminate the core electrons from the calculation. In addition, following an approach by Blöchl [9] we subdivide the electronic charge in atomic contributions and a smooth interstitial part. The XC energy is then also divided as $E_{xc} = \bar{E}_{xc} + E^1_{xc} - \bar{E}^1_{xc}$, into a smooth part $\bar{E}_{xc}$, which is evaluated on a regular grid using PWs, and two one-center contributions E^1_{xc} and $\bar{E}^1_{xc}$ which are evaluated according to the grid-free approach. The corresponding one-center densities are expanded, in agreement with Eq. (2), in an uncontracted Gaussian-type orbital (GTO) basis set. Experience shows that in the case of LDA this basis can be used to calculate all matrix representations. When handling the gradient-corrected functionals, however, one must use enlarged auxiliary basis sets. All calculations in Table 1 were done using 5 uncontracted *s* and *p* and 2 *d* GTO functions. The auxiliary basis consists of 7*s*, 7*p*, 4*d*, and 2*f* functions. The grid-based numerical calculations were performed using a product grid consisting of 40 radial points and an angular part with 50 points chosen according to the Lebedev method [10].

A comparison of the results obtained from our grid-free approach and the results obtained from a grid-based numerical integration is shown in Table 1. All calculations were done at fixed geometry and all energies are calculated from self-consistent densities. The XC functionals considered are a pure LDA functional in a Pade approximation [11], an exchange functional by Becke (B) [2], a correlation functional by Lee, Yang and Parr (LYP) [3] and a correlation functional by Perdew (P) [4]. It is evident that the results involving gradient-corrected functionals are less satisfactory than for the LDA case. Although the accuracy achieved is sufficient for practical purposes, we cannot completely reproduce, even with a large basis set, the results of the numerical integration.

How can such a discrepancy be explained? Firstly, it appears that the gradient of the density calculated via Eq. (14) is not well represented by small basis sets. The next point is that the calculation of the matrix representation of *s* (Eq. 16) involves a matrix representation of $\rho^{-\frac{4}{3}}$. This expression becomes unbounded for small densities and we have no appropriate representation in this region. A further problem is that when we diagonalize the matrix representation of the variable *s* (Eq. 16) in order to calculate a matrix function, using small basis sets, we obtain negative eigenvalues which are not physically meaningful. This is because a product of two positive definite matrices is not necessarily positive definite. However in our experience, with the enlarged basis sets introduced above, the appearance of negative eigenvalues is avoided and all operators are reasonably represented.

Thus it appears that the matrix approach is feasible for local as well as for gradient-corrected functionals. There is, however, a quantitative difference. In the case of LDA, we can use the original GTO basis set and the overall performance of the operator approach compares favourably with numerical integration. Unfortunately, the use of large basis sets appears inevitable for gradient corrected functionals, which questions the usefulness of such an implementation.

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