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A rotationally invariant procedure for density functional calculations

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Abstract

A simple method which is rigorously invariant under molecular rotations is presented for evaluation of the density functional exchange–correlation energy by numerical quadrature. The corresponding expressions for the first and second derivatives of the energy with respect to nuclear displacement are presented. In particular, such a scheme is necessary to remove the difficulties previously encountered in calculating Kohn–Sham harmonic vibrational frequencies for low-lying modes.

1. Introduction

Density functional theory [1–6] (DFT) has emerged in recent years as a promising alternative to conventional ab initio methods in quantum chemistry. In a number of systematic validation studies [7–15], DFT has been shown to be successful in predicting various molecular properties, often giving results of a quality comparable to or better than the MP2 perturbation theory approach. This is most encouraging, given that the computational cost of DFT is substantially less than that of traditional correlation techniques, and hence DFT may be applied to larger molecular systems. Further thorough studies of DFT methods are still required in order to obtain a better understanding of their strengths and weaknesses, but the future of DFT in practical quantum chemistry appears bright.

The Kohn–Sham (KS) formulation [2] of DFT is the most commonly employed, and is closely analogous to Hartree-Fock theory in that a set of molecular orbitals is derived from an effective one-electron potential via a self-consistent procedure. The crucial difference is that the exchange term in the Hartree-Fock energy expression is replaced by an *exchange-correlation* (XC) energy, represented as a functional of the one-electron spin densities and in many cases their derivatives as well. These functionals are of the general form

$$E_{\mathrm{XC}} = \int F(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta, \ldots)\, \mathrm{d}\mathbf{r} . \qquad (1)$$

It is generally true that the XC integrals which arise in Kohn–Sham calculations cannot be evaluated analytically, and in practice three-dimensional numerical quadrature must be employed. A number of different schemes have been advocated for this purpose

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[16–20]. Unfortunately, there are considerations particular to a grid-based approach which lead to undesirable effects if not taken into account properly in the implementation. These sorts of difficulties do not arise in methods where all integrals are evaluated analytically (such as in Hartree–Fock theory).

We focus here on the behavior of the numerical XC energy upon rigid-body rotations of the molecule. Most often the molecular quadrature grid is constructed by decomposing three-dimensional space into atomic regions which are then treated separately. In the widely used scheme due to Becke [16], this is done with nuclear weighting functions which allow the atomic contributions to be easily evaluated using standard one-center quadrature rules, which do not depend on the nuclear configuration. For a straightforward implementation in which the atomic contributions are evaluated independently, if the molecule is rotated leaving the Cartesian axes (to which the quadrature grid is referred) unaltered, the computed energy will change, i.e. the total energy does *not* possess the property of rotational invariance in the absence of external fields. This effect is entirely unphysical and originates solely from the use of a finite grid. The loss of rotational invariance also manifests itself in derivative calculations, and in particular can adversely affect calculated harmonic frequencies of low-lying vibrational modes [21].

The dilemma of rotational non-invariance in DFT grid calculations has been previously recognized. For example, randomly rotated angular grids have been employed [22] in an attempt to ameliorate the problem. This can lessen the undesirable effects by averaging out the error, but does not rigorously remove them. In this Letter, we present a simple method which is rigorously rotationally invariant, and derive expressions under this scheme for the first and second derivatives of numerical XC integrals with respect to nuclear displacement.

2. Rotationally invariant energy evaluation

The XC energy as implemented in a computer program is

$$E_{\mathrm{XC}} = \sum_{\mathrm{A}} \sum_{i} w_{\mathrm{A}i} F(\boldsymbol{r}_{\mathrm{A}i}) , \qquad (2)$$

where the first summation is over the atoms and the second is over the quadrature grid points for that particular atom. The $w_{\mathrm{A}i}$ are quadrature weights, and the grid points $\boldsymbol{r}_{\mathrm{A}i}$ are usually given by [14,23]

$$\boldsymbol{r}_{\mathrm{A}i} = \boldsymbol{R}_{\mathrm{A}} + \boldsymbol{s}_i , \qquad (3)$$

where $\boldsymbol{R}_{\mathrm{A}} = (R_{\mathrm{A}x}, R_{\mathrm{A}y}, R_{\mathrm{A}z})^{\mathrm{T}}$ is the position of nucleus A, and the $\boldsymbol{s}_i$ define the base points of a suitable three-dimensional quadrature rule centered at the origin, which is independent of the nuclear configuration.

For conciseness, from now on we shall use a condensed grid index for the atomic and single-center summations, and write

$$E_{\mathrm{XC}} = \sum_{g} f(\boldsymbol{r}_g) = \sum_{g} f_g , \qquad (4)$$

$$\boldsymbol{r}_g = \boldsymbol{R}_{\mathrm{G}} + \boldsymbol{s}_g , \qquad (5)$$

where the quadrature weights have been combined with the functional values. This does not affect the generality of the analysis.

The problem is that while the definition of the atomic grid points in (5) explicitly takes into account *translations* of the nuclei, it does not consider *rotations*. Thus, the XC energy computed with this grid is translationally invariant, but it is also clear that the angular orientation of the quadrature grid relative to the nuclei will change with rotations of the molecule. The XC energy will therefore also change, by an amount on the order of the error in the quadrature formula. The variation can be made small by using large grids, but unfortunately the magnitude of the effect is generally greater for derivative calculations [21] than for energy calculations, and in some cases is significant for all grids except those which are too large to be convenient for routine computations.

The loss of rotational invariance can be easily remedied, however, by generalizing (5) to

$$\boldsymbol{r}_g = \boldsymbol{R}_{\mathrm{G}} + O\boldsymbol{s}_g , \qquad (6)$$

where O is a 3×3 matrix which depends upon the nuclear geometry and contains the essential information about the orientation of the nuclear conformation in the present coordinate system. The matrix O is not unique, but must have certain properties. For example, O must be orthogonal, i.e.

$$O^{\mathrm{T}}O = I , \qquad (7)$$

where I is the identity matrix. Without loss of generality, it is convenient to define O implicitly via

$$O^{\mathrm{T}}MO=\Lambda\,, \tag{8}$$

where M is an appropriate real symmetric second-rank Cartesian tensor and Λ is the diagonal matrix of the eigenvalues of M. To complete the specification of O, it remains only to choose an ordering for the eigenvectors. Any well-defined criterion will do, e.g. according to increasing magnitude of the eigenvalues. The columns of O then represent a set of principal axes for a 'standard' Cartesian reference frame, which is inherent to the nuclear conformation.

The theory can be mostly developed without a need for specification of the elements of M, as long as they (and their derivatives) can be evaluated in terms of known quantities. However, in practice we will explicitly take M as the nuclear charge moment tensor

$$M=\sum_{\mathrm{A}} Z_{\mathrm{A}}\left[\,|\boldsymbol{R}_{\mathrm{A}}-\boldsymbol{T}|^2 I-(\boldsymbol{R}_{\mathrm{A}}-\boldsymbol{T})(\boldsymbol{R}_{\mathrm{A}}-\boldsymbol{T})^{\mathrm{T}}\right], \tag{9}$$

where Z_{A} is the charge of nucleus A and

$$\boldsymbol{T}=\frac{\sum_{\mathrm{A}} Z_{\mathrm{A}}\boldsymbol{R}_{\mathrm{A}}}{\sum_{\mathrm{A}} Z_{\mathrm{A}}}\,, \tag{10}$$

is the center of nuclear charge. We have recently proposed [20] a standard nuclear orientation convention which makes use of (9) to define the principal axis system through (8).

The origin of the standard coordinate system is taken as the center of nuclear charge, and hence $\boldsymbol{T}$ is equal to $\mathbf{0}$ in the standard orientation. However, the explicit inclusion of $\boldsymbol{T}$ in (9) is necessary to ensure that M is translationally invariant and to cover (infrequent) instances when energies are desired in nuclear orientations other than the standard one, such as for finite-difference derivative calculations. Also, $\boldsymbol{T}$ must be included so that this aspect of the standard orientation definition is properly differentiated when computing derivatives analytically.

This completes the specification of a grid procedure which ensures that the computed XC energy is the same for any orientation of the molecule in any Cartesian coordinate system [#1]. In itself, this is not of large consequence; in practice, single-point energy evaluations are almost always done with the nuclei in the standard orientation, so the effect of rotational non-invariance is not usually observed at this stage. However, the major significance of proper treatment of the grid orientation arises when computing derivatives of the XC energy.

3. First derivatives

In the following, it suffices to consider the case of a particularly simple quadrature grid consisting of a single point. For larger grids, the contribution from each of the individual points is treated in the same way, and hence the formulae derived for a one-point grid are trivially generalized by reinstating the summation over grid points at the end. Therefore, we shall henceforth drop the grid indices unless they are explicitly needed.

In contemplating derivatives of the XC energy, it is useful to write

$$f=f[R,\boldsymbol{r}(R)]\,, \tag{11}$$

where R denotes the set of nuclear Cartesian coordinates, to indicate that the functional depends on the nuclear positions in two ways: explicitly, and implicitly through the dependence of the grid points on R. Then, differentiating (11) gives rise to two terms:

$$f^x=f^{(x)}+\nabla_r f\cdot\boldsymbol{r}^x\,. \tag{12}$$

To avoid cluttering the notation, we have used the familiar convention of a superscript to denote differentiation, and have abbreviated with the symbol x the ith component of the position of nucleus A, i.e.

$$x\equiv R_{\mathrm{A}i}\,. \tag{13}$$

(Note that x need not represent an x coordinate.) The superscript in parentheses is used to indicate differentiation of only the explicit nuclear dependence of f, to distinguish this from differentiation of the implicit dependence, which is given by the second term in (12).

From (6) we obtain

[#1] In LCAO MO calculations, ordinarily the orbital basis functions are not rotated with the nuclei; rather, these are left aligned with the Cartesian axes. Therefore, although the present scheme preserves the orientation of the grid relative to the nuclei upon a rigid-body rotation, the grid orientation relative to the basis functions changes. This does not pose a problem, though, as the basis functions form a complete set with respect to rotations, and hence invariant quantities such as the total energy are unaffected.

$$\boldsymbol{r}^x=\delta_{\mathrm{AG}}\boldsymbol{e}_i+O^x\boldsymbol{s}\,, \qquad (14)$$

where the differentiation of $\boldsymbol{r}$ and O is on an element-by-element basis, and $\boldsymbol{e}_i$ is the unit vector in direction i. The usual definition of $\boldsymbol{r}$ in (5) gives the first term in (14) but *not* the second. It is the second term which correctly differentiates molecular rotations, and since the orientation for *any* nuclear conformation is embodied in the definition of O, this term also properly treats displacements of internal degrees of freedom. This ensures that, for example, analytically calculated derivatives are consistent with those obtained by finite difference, which is not necessarily the case when the one-center grids are merely translated to the nuclear centers without any angular re-orientation.

To complete the derivative expression, we must obtain the derivatives of the elements of O. This can be done through the relationships in (7) and (8). Differentiation of the orthogonality condition (7) yields

$$(O^x)^{\mathrm{T}}O+O^{\mathrm{T}}O^x=0\,. \qquad (15)$$

Introducing

$$P^x=O^{\mathrm{T}}O^x\,, \qquad (16)$$

which is the derivative of O expressed in the standard orientation, we see that

$$(P^x)^{\mathrm{T}}+P^x=0\,, \qquad (17)$$

i.e. the matrix P^x is antisymmetric, and thus may be written generally as

$$P^x=\begin{pmatrix} 0 & \gamma & -\beta \\ -\gamma & 0 & \alpha \\ \beta & -\alpha & 0 \end{pmatrix} \qquad (18)$$

in terms of three independent parameters. Differentiating (8) we obtain

$$\Lambda P^x-P^x\Lambda=\Lambda^x-O^{\mathrm{T}}M^xO\,, \qquad (19)$$

from which the independent parameters are readily obtained in terms of known quantities by equating the off-diagonal elements.

Note that (19) combined with (16) gives the derivative of O for an arbitrary orientation of the nuclei; in the most important case of the standard orientation ($O=I$), the independent derivatives of O with respect to nucleus A are

$$\alpha=0\,,\quad \beta=\frac{Z_{\mathrm{A}}R_{\mathrm{A}z}}{\lambda_1-\lambda_3}\,,\quad \gamma=\frac{Z_{\mathrm{A}}R_{\mathrm{A}y}}{\lambda_2-\lambda_1}\,, \qquad (20)$$

for differentiation with respect to $R_{\mathrm{A}x}$,

$$\alpha=\frac{Z_{\mathrm{A}}R_{\mathrm{A}z}}{\lambda_3-\lambda_2}\,,\quad \beta=0\,,\quad \gamma=\frac{Z_{\mathrm{A}}R_{\mathrm{A}x}}{\lambda_2-\lambda_1} \qquad (21)$$

for differentiation with respect to $R_{\mathrm{A}y}$, and

$$\alpha=\frac{Z_{\mathrm{A}}R_{\mathrm{A}y}}{\lambda_3-\lambda_2}\,,\quad \beta=\frac{Z_{\mathrm{A}}R_{\mathrm{A}x}}{\lambda_1-\lambda_3}\,,\quad \gamma=0 \qquad (22)$$

for differentiation with respect to $R_{\mathrm{A}z}$.

4. Second derivatives

The derivation of the rotationally invariant second derivative expressions follows the same approach as for first derivatives. Therefore, we will omit the algebra, which is straightforward, and merely give the results. Differentiating (12) a second time yields

$$\begin{aligned} f^{xy}&=f^{(x)(y)}+(\nabla_r f)^{(x)}\cdot\boldsymbol{r}^y+(\nabla_r f)^{(y)}\cdot\boldsymbol{r}^x \\ &\quad+(\boldsymbol{r}^x)^{\mathrm{T}}(\nabla_r^{\mathrm{T}}\nabla_r f)\boldsymbol{r}^y+\nabla_r f\cdot\boldsymbol{r}^{xy}\,, \end{aligned} \qquad (23)$$

in which the only relevant new quantities are the second derivatives of the grid points,

$$\boldsymbol{r}^{xy}=O^{xy}\boldsymbol{s}\,. \qquad (24)$$

The second derivatives of O are obtained, as before, by differentiating (7) and (8) and then solving the resulting system of linear equations for the independent elements. The expressions are

$$(P^{xy})^{\mathrm{T}}+P^{xy}=P^xP^y+P^yP^x\,, \qquad (25)$$

$$\begin{aligned} (P^{xy})^{\mathrm{T}}\Lambda+\Lambda P^{xy}&=\Lambda^{xy}-O^{\mathrm{T}}M^{xy}O+P^x\Lambda P^y+P^y\Lambda P^x \\ &\quad+P^xO^{\mathrm{T}}M^yO+P^yO^{\mathrm{T}}M^xO \\ &\quad-O^{\mathrm{T}}M^xOP^y-O^{\mathrm{T}}M^yOP^x\,, \end{aligned} \qquad (26)$$

where

$$P^{xy}=O^{\mathrm{T}}O^{xy}\,. \qquad (27)$$

The equations corresponding to the diagonal elements of (25) immediately yield the diagonal elements of P^{xy} expressed in terms of known quantities, while the off-diagonal equations place three additional constraints on the remaining elements of P^{xy}.

In conjunction with the three equations obtained from the off-diagonal elements of (26), these completely determine the desired second derivatives.

5. Results and discussion

The rotationally invariant energy and first derivative method has been implemented by one of us (BGJ) within the Q-Chem quantum chemistry program [24]. To illustrate the performance of the new method, calculations were performed on two small molecules with and without the orientation matrix producing rotationally invariant energies. Table 1 presents S-null/6-31G total energies obtained with two grids: SG-1 [20], which we have recommended for routine calculations and which has approximately 2500 points per atom, and (20, 50), which is an Euler–Maclaurin–Lebedev grid [19,25] having 1000 points per atom, more typical of the coarser grids commonly used in many programs. The energy was calculated for the same conformation of each molecule in three different orientations. Orientation I is the standard orientation, orientation II was obtained from the standard orientation by a rotation of 20° about the x axis, and orientation III was obtained from the standard orientation by successive rotations of 20° about the x axis and 30° about the y axis. The energies labeled "previous" use (5) to define the grid point positions, while the energies labeled "this work" are from the rotationally invariant method, using (6) to define the grid points.

The "previous" energies indeed demonstrate the loss of rotational invariance, as the total energies of HOF and HOOF are seen to vary with the orientation. In the case of SG-1, the magnitude of the variations for these small molecules is around 10^{-5} atomic units (au). This amount of energy is not chemically significant, but the behavior is nonetheless undesirable. Furthermore, for larger molecules the size of the variations will increase, and certainly any higher level of 'noise' in the energies would be unacceptable. For the (20, 50) grid, which is less accurate than SG-1, the variations are already at the level of 10^{-3} au, or approximately 1 kcal/mol. Errors of this magnitude arising from an artifact of the numerical algorithm clearly cannot be tolerated. In contrast, the new method gives the same energy (that of the standard orientation) for all three orientations with both grids, as it should.

As we have discussed elsewhere [21], lack of rotational invariance has more serious consequences for the derivatives of the energy. For a properly rotationally invariant energy it follows that [26]

$$\sum_{\mathrm{A}} R_{\mathrm{A}x} \frac{\partial E}{\partial R_{\mathrm{A}y}} - R_{\mathrm{A}y} \frac{\partial E}{\partial R_{\mathrm{A}x}} = 0 \qquad (28)$$

with similar relationships for yz and zx. The deviation of the left-hand side of (28) from zero can therefore be used to measure the loss of rotational invariance in first derivatives calculated by other methods. Table 2 lists these quantities for the same systems and orientations for analytically calculated gradients. (The geometries used are *not* stationary points, or otherwise (28) would be trivially satisfied.) As with

Table 1
Total molecular energies [a] for various orientations

System	Orientation [b]	SG-1		(20, 50)	
		previous [c]	this work [d]	previous	this work
HOF	I	−172.9645046	−172.9645046	−172.9651282	−172.9651282
	II	−172.9645018	−172.9645046	−172.9644639	−172.9651282
	III	−172.9645315	−172.9645046	−172.9648349	−172.9651282
HOOF	I	−274.0686706	−247.0686706	−247.0669064	−247.0669064
	II	−247.0686463	−247.0686706	−247.0666277	−247.0669064
	III	−247.0686779	−247.0686706	−247.0678356	−247.0669064

[a] S-null/6-31G, units in hartree.
[b] See text for definitions.
[c] Eq. (5) used to define the grid points.
[d] Eq. (6) used to define the grid points.

Table 2
Test for rotational invariance of energy first derivatives [a]

System	Orientation [b]	SG-1						(20, 50)					
		previous [c]			this work [d]			previous			this work		
HOF	I	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00	1.12	0.00	0.00	0.00
	II	0.00	−0.06	0.16	0.00	0.00	0.00	0.00	−0.38	1.05	0.00	0.00	0.00
	III	−0.08	−0.06	0.14	0.00	0.00	0.00	−0.52	−0.38	0.91	0.00	0.00	0.00
HOOF	I	0.08	−0.23	−0.50	0.00	0.00	0.00	−0.13	9.27	7.27	0.00	0.00	0.00
	II	0.08	−0.05	−0.54	0.00	0.00	0.00	6.08	−20.58	−6.08	0.00	0.00	0.00
	III	0.34	−0.05	−0.43	0.00	0.00	0.00	−5.12	6.23	8.60	0.00	0.00	0.00

[a] S-null/6-31G, units in mhartree/rad. Derivatives are given in the order yz, zx, xy.

[b] See text for definitions.

[c] Eq. (5) used to define the grid points.

[d] Eq. (6) used to define the grid points.

the energies, the gradients calculated by the present method rigorously obey rotational invariance, while the rotational derivatives obtained by the previous method deviate from zero. For SG-1, the deviations are at the level of 10^{-5}–10^{-4} au, while for (20, 50) they are much larger, on the order of 10^{-3}–10^{-2} au. Again, the deviations vary with the orientation.

For HOF, two of the three rotational derivatives in orientation I are zero by the previous method. This serves to illustrate how that the invariance relationships can be satisfied by symmetry for certain orientations even when they do not hold in general. In this case, the molecular plane is taken as the xy plane in the standard orientation, and the two zeros result because all three nuclei have zero z coordinates and gradients. As the molecule is rotated out of the standard orientation, these become non-zero, and the loss of rotational invariance is observed in all three components.

For molecules belonging to non-Abelian point groups, for which degenerate axes occur, some of the denominators in (20)–(22) become zero, and since in general the derivatives of the charge-moment tensor occurring in the numerator are non-zero, the corresponding derivatives of O are infinite. (It is also possible for this to occur through 'accidental degeneracy' in large C_1 molecules, though such is of course very rare). In cases where the quadrature grid does not lower the symmetry of the system, however, grid integration of the coefficient of the derivative of O in (12) produces zero by symmetry, and thus no rotational correction is necessary. In a few instances the imposition of the grid does result in symmetry lowering (e.g. the SG-1 grid has local symmetry O_h, which when combined with a C_{3v} NH_3 molecule results in an effective molecular symmetry of only C_s), in which case such a cancellation does not occur. Here, the present scheme does not apply, and must be elaborated. The simplest treatment would be to take the appropriate α, β or γ as zero (i.e. a correction is not applied). One could alternatively employ grids which preserve the molecular symmetry [17]. Note that systems examined here belong to Abelian point groups, so this problem does not arise.

For molecules where the nuclei are at or near configurations of very high symmetry, the possibility also exists that the principal axes may switch in some discontinuous manner with nuclear displacements. The resulting grid-based potential surface may therefore actually possess some discontinuities and hence will not strictly be differentiable at such high-symmetry points. Such discontinuities become smaller as the grid becomes larger, but they cannot easily be eliminated. The number of times this type of situation is encountered in practice is relatively small.

The computational cost of incorporating the orientation matrix O into XC energy and derivative calculations is negligible. From Eqs. (9) and (20)–(22), it is clear that the number of arithmetic operations involved in evaluating O and its derivatives is proportional simply to the total number of atoms. As the definition of O does not involve the grid, in first derivative calculations, for example, the application of O^x in (14) can be postponed until after the grid work has been done by accumulating the intermediate 3×3 matrix

$$V = \sum_g (\nabla_r f_g)^{\mathrm{T}} s_g , \qquad (29)$$

which is independent of x, whereupon the second term in (12) is obtained as $\mathrm{Tr}(O^x V)$. We have recently presented [27] a method for evaluating the XC energy and potential matrix which for large molecules scales only linearly with the number of basis functions. The manipulations involving O also require linear work in system size, but as this work does not depend on the basis functions indices, it is insignificant compared with the other XC work.

Finally, we note that an added benefit of the present method, above rigorously remedying the deficiencies associated with molecular rotations, is that it permits the rotational invariance relationships for derivatives to be exploited to full computational advantage. The corresponding relationships pertaining to analytical evaluation of two-electron integral derivatives have been known for some time [26,28], but are not widely used within efficient modern integral algorithms [29] as they are more awkward to apply and yield less computational savings than the analogous translational invariance relationships. This is not the case with grid-based calculations, however, where rotational invariance need not be applied until after the numerical quadrature is performed. In our DFT implementation, the innermost loops run over the quadrature points to achieve good vector performance, and thus rotational invariance can be easily handled outside the compute-intensive region.

To summarize, the method presented is a rigorous solution to the last remaining problem in the practical implementation of grid-based calculation of the XC energy and its derivatives, that of the loss of rotational invariance. We have recommended [21] for KS derivative calculations that *all* the terms which depend on the nuclear coordinates be identified and differentiated, so that the derivative formula implemented strictly corresponds to the definition of the energy. This is required for consistency with the numerical implementation of the XC energy, though virtually all derivative implementations in currently used computer programs neglect various contributions, such as the derivatives of the quadrature weights. Introducing the orientation matrix O and then *properly differentiating* it as is done here is necessary in order to rectify the problems due to loss of rotational invariance previously encountered [21] in KS frequency calculations.

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