Theor Chem Acc (2006) 115: 385–390
DOI 10.1007/s00214-006-0080-x

REGULAR ARTICLE

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Gradients of the exchange-repulsion energy in the general effective fragment potential method

Received: 31 August 2005 / Accepted: 12 December 2005 / Published online: 16 February 2006

Abstract Formulae for calculating the analytic gradients of the exchange-repulsion energy in the general effective fragment potential (EFP2) method are derived and implemented using a direct differentiation approach. The timings for the exchange repulsion gradient evaluations are approximately three times longer than the energy evaluations, orders of magnitude faster than a previous implementation. Since the direct differentiation approach is not approximate, the gradients can be used with confidence in molecular dynamics and Monte Carlo simulations with the EFP2 method.

Keywords Effective fragment potential · Exchange-repulsion · Gradient · GAMESS

1 Introduction

The general effective fragment potential (EFP2) is an ab initio based method in that all the molecular interaction parameters are obtained from preparative ab initio calculations [1,2]. In the EFP2 method, the molecular electrostatic (Coulomb) interaction is modeled with multipolar expansion points obtained from the Stone distributed multipole analysis. The induction interaction is modeled with localized orbital dipole polarizability tensors and the electric fields. The exchange repulsion is modeled with frozen localized molecular orbitals (LMO) and their intermolecular overlap, kinetic energy, Coulomb and nuclear potential integrals [2]. The dispersion interaction is modeled with LMO dynamic polarizability points obtained from time-dependent Hartree–Fock calculations [3]. Recently, an approximate formula for the intermolecular charge transfer interaction for the EFP2 method has been derived and implemented based on a second-order perturbative treatment that enables electrons to be excited from occupied orbitals of one molecule into virtual orbitals of other molecules. All of the EFP2 parameters for a molecule can be obtained from a single ab initio calculation on the molecule and can then be used for various EFP–EFP or ab initio-EFP calculations.

The EFP2 parameters for the exchange repulsion and charge transfer interaction are actually the molecular orbitals (MO) and the Fock matrix elements [2]. Once obtained, these orbitals are internally frozen in the EFPs, which can translate and rotate in the calculations. The MO integrals involved in the exchange repulsion and charge transfer calculations change when the positions and orientations of the EFPs change. To evaluate the analytic gradients of these interaction energies with respect to EFP translational and rotational displacements, the derivatives of the MO integrals are required. The gradients of the charge transfer interaction for EFP2 have been derived and implemented using a direct differentiation method, which is accurate and efficient. The time required for the charge transfer gradient evaluation is two to three times longer than that for the energy.

The exchange repulsion gradients with respect to EFP displacements have been implemented previously with an approximate treatment of the torques on the atomic orbitals (AO) [4]. The direct differentiation method was not used in that implementation, thus neither the accuracy nor the efficiency was optimized. In EFP2 calculations on small systems, the approximate exchange repulsion gradients are accurate and efficient. However, as the EFP2 method is applied to larger systems, or in molecular dynamics (MD) or Monte Carlo (MC) calculations, the impact of the approximate gradient method will become more serious, and the need for accuracy and efficiency in the gradient evaluation increases.

In this work, the direct differentiation method is applied to the evaluation of the exchange repulsion gradients in the EFP2 method. In Sect. 2, expressions are derived for the exchange repulsion gradients and the necessary integral derivatives with respect to EFP translational and rotational coordinates, as well as expressions for the gradients of pairwise-interacting molecules. After a brief description of the computational methodology in Sect. 3, the gradients calculated with the current and previous implementations and their CPU timings are compared in Sect. 4. Conclusions are presented in Sect. 5.

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2 Theory

2.1 General expression for the gradients

The exchange-repulsion energy for EFP A and B can be approximated as [2]:

$$\begin{aligned} XR^{\mathrm{AB}} = & -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} 2\sqrt{\frac{-2\ln S_{ij}}{\pi}}\,\frac{\left(S_{ij}\right)^2}{R_{ij}} \\ & -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} S_{ij}\left[\sum_k^{\mathrm{A}} F_{ik}^{\mathrm{A}} S_{kj} + \sum_l^{\mathrm{B}} F_{jl}^{\mathrm{B}} S_{li} - 2T_{ij}\right] \\ & +2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} \left(S_{ij}\right)^2\left[-\sum_J^{\mathrm{B}}\frac{Z_J}{R_{iJ}} + 2\sum_l^{\mathrm{B}}\frac{1}{R_{il}} \right. \\ & \left. -\sum_I^{\mathrm{A}}\frac{Z_I}{R_{Ij}} + 2\sum_k^{\mathrm{A}}\frac{1}{R_{kj}} - \frac{1}{R_{ij}}\right] \end{aligned} \tag{1}$$

In Eq. (1) i, k and j, l run over the LMOs of molecule A and B, respectively. I and J run over the nuclei of molecule A and B, respectively. S and T are overlap and kinetic energy integrals of the LMOs, F is the Fock matrix in the LMO basis (thus not diagonal), Z is the nuclear charge, and R are the distances between LMO centroids or the distances between LMO centroids and the nuclei.

In the EFP method, the internal geometry of a molecular fragment is frozen, leaving three degrees of translational freedom and three degrees of rotational freedom about its center of mass. Consider the forces and torques due to the exchange repulsion between molecules A and B. The forces and torques due to B acting on A are the first derivatives of XR^{AB} with respect to the translation/rotation coordinate q_{A} of A:

$$\begin{aligned} & \partial\left(XR^{\mathrm{AB}}\right)/\partial q_{\mathrm{A}} \\ & = -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}}\left(-\sqrt{\frac{2}{-\pi\ln S_{ij}}} + 4\sqrt{\frac{-2\ln S_{ij}}{\pi}}\right)\frac{S_{ij}}{R_{ij}}\left(\frac{\partial S_{ij}}{\partial q_{\mathrm{A}}}\right) \\ & +2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} 2\sqrt{\frac{-2\ln S_{ij}}{\pi}}\left(\frac{S_{ij}}{R_{ij}}\right)^2\left(\frac{\partial R_{ij}}{\partial q_{\mathrm{A}}}\right) \\ & -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}}\left(\frac{\partial S_{ij}}{\partial q_{\mathrm{A}}}\right)\cdot\left[\sum_k^{\mathrm{A}} F_{ik}^{\mathrm{A}} S_{kj} + \sum_l^{\mathrm{B}} F_{jl}^{\mathrm{B}} S_{li} - 2T_{ij}\right] \\ & -2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} S_{ij}\left[\sum_k^{\mathrm{A}} F_{ik}^{\mathrm{A}}\left(\frac{\partial S_{kj}}{\partial q_{\mathrm{A}}}\right) + \sum_l^{\mathrm{B}} F_{jl}^{\mathrm{B}}\left(\frac{\partial S_{li}}{\partial q_{\mathrm{A}}}\right) - 2\left(\frac{\partial T_{ij}}{\partial q_{\mathrm{A}}}\right)\right] \\ & +2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}} 2S_{ij}\left(\frac{\partial S_{ij}}{\partial q_{\mathrm{A}}}\right) \\ & \times\left[-\sum_J^{\mathrm{B}}\frac{Z_J}{R_{iJ}} + 2\sum_l^{\mathrm{B}}\frac{1}{R_{il}} - \sum_I^{\mathrm{A}}\frac{Z_I}{R_{Ij}} + 2\sum_k^{\mathrm{A}}\frac{1}{R_{kj}} - \frac{1}{R_{ij}}\right] \\ & +2\sum_i^{\mathrm{A}}\sum_j^{\mathrm{B}}\left(S_{ij}\right)^2\left[\begin{array}{l} \sum_J^{\mathrm{B}}\frac{Z_J}{R_{iJ}^2}\left(\frac{\partial R_{iJ}}{\partial q_{\mathrm{A}}}\right) - 2\sum_l^{\mathrm{B}}\frac{1}{R_{il}^2}\left(\frac{\partial R_{il}}{\partial q_{\mathrm{A}}}\right) \\ +\sum_I^{\mathrm{A}}\frac{Z_I}{R_{Ij}^2}\left(\frac{\partial R_{Ij}}{\partial q_{\mathrm{A}}}\right) - 2\sum_k^{\mathrm{A}}\frac{1}{R_{kj}^2}\left(\frac{\partial R_{kj}}{\partial q_{\mathrm{A}}}\right) + \frac{1}{R_{ij}^2}\left(\frac{\partial R_{ij}}{\partial q_{\mathrm{A}}}\right) \end{array}\right] \end{aligned} \tag{2}$$

Consequently, the following derivatives with respect to the translational or rotational coordinate q_{A} of A are required to evaluate Eq. (2):

$$\begin{aligned} & \frac{\partial S_{ij}}{\partial q_{\mathrm{A}}}, \frac{\partial R_{ij}}{\partial q_{\mathrm{A}}}, \frac{\partial S_{kj}}{\partial q_{\mathrm{A}}}, \frac{\partial S_{li}}{\partial q_{\mathrm{A}}}, \frac{\partial T_{ij}}{\partial q_{\mathrm{A}}}, \\ & \frac{\partial R_{iJ}}{\partial q_{\mathrm{A}}}, \frac{\partial R_{il}}{\partial q_{\mathrm{A}}}, \frac{\partial R_{Ij}}{\partial q_{\mathrm{A}}}, \frac{\partial R_{kj}}{\partial q_{\mathrm{A}}}, \frac{\partial R_{ij}}{\partial q_{\mathrm{A}}} \end{aligned} \tag{3}$$

The derivatives of the distances can be evaluated easily. The derivatives of the overlap and kinetic energy integrals can be obtained from the derivatives of the corresponding AO integrals and the derivatives of the MO coefficients. For example,

$$\begin{aligned} \frac{\partial S_{ij}}{\partial q_{\mathrm{A}}} & = \frac{\partial\left(\sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot S_{uv}\right)}{\partial q_{\mathrm{A}}} \\ & = \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot\left(\frac{\partial S_{uv}}{\partial q_{\mathrm{A}}}\right) + \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}}\left(\frac{\partial c_{ui}}{\partial q_{\mathrm{A}}}\right)\cdot S_{uv} \\ & + \sum_v^{\mathrm{B}}\left(\frac{\partial c_{vj}}{\partial q_{\mathrm{A}}}\right)\sum_u^{\mathrm{A}} c_{ui}\cdot S_{uv} \end{aligned} \tag{4}$$

Here and hereafter c refers to the MO coefficients, u and v refer to the AOs of molecules A and B, respectively.

In the following subsections, the translational and rotational gradients are discussed in detail.

2.2 Translation of A ($q_{\mathrm{A}} = x_{\mathrm{A}}, y_{\mathrm{A}}, z_{\mathrm{A}}$)

The MOs for the EFPs are frozen and the MO coefficients are constants when A translates. Consequently, the derivatives of the MO integrals can be obtained from the derivatives of the AO integrals.

For example, the derivative of the overlap integral S_{ij} [c.f., Eq. (4)] with respect to the translational motion of molecule A (molecule B is fixed) in the x direction (x_{A}) is:

$$\frac{\partial S_{ij}}{\partial x_{\mathrm{A}}} = \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot\left(\frac{\partial S_{uv}}{\partial x_{\mathrm{A}}}\right) \tag{5}$$

The overall translation of A in the x direction (x_{A}) can be decomposed into the individual atomic translations in A (x_a), so:

$$\begin{aligned} \frac{\partial S_{ij}}{\partial x_{\mathrm{A}}} & = \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot\sum_a^{\mathrm{A}}\left(\frac{\partial S_{uv}}{\partial x_a}\right) \\ & = \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot\sum_a^{\mathrm{A}}\left\langle\frac{\partial\psi_u}{\partial x_a}\middle|\psi_v\right\rangle \end{aligned} \tag{6}$$

Here a runs over the atoms of molecule A and ψ_u is a Gaussian basis function (i.e., AO) on A.

Similarly, the derivatives of the kinetic energy integrals with respect to x_{A} are:

$$\begin{aligned} \frac{\partial T_{ij}}{\partial x_{\mathrm{A}}} & = \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot\sum_a^{\mathrm{A}}\left(\frac{\partial T_{uv}}{\partial x_a}\right) \\ & = \sum_v^{\mathrm{B}} c_{vj}\sum_u^{\mathrm{A}} c_{ui}\cdot\sum_a^{\mathrm{A}}\left\langle\frac{\partial\psi_u}{\partial x_a}\middle|-\frac{\nabla^2}{2}\middle|\psi_v\right\rangle \end{aligned} \tag{7}$$

The derivatives of the basis functions can be evaluated using standard techniques.

The translational derivatives of the distances are much easier to calculate. For example (note $\partial x_{\mathrm{A}} = \partial x_i$ since i belongs to A):

$$\frac{\partial R_{ij}}{\partial x_{\mathrm{A}}} = \frac{(x_i - x_j)}{R_{ij}} \tag{8}$$

All the necessary translational derivatives in Eq. (3) can be obtained using Eqs. (6), (7) and (8). The AO overlap and kinetic energy integrals are usually calculated and stored as matrices, as are the derivatives of these integrals.

2.3 Rotation of A ($q_{\mathrm{A}} = \theta_{x\mathrm{A}}, \theta_{y\mathrm{A}}, \theta_{z\mathrm{A}}$)

When a molecule rotates about its center of mass, the AO (or nuclear) centers translate (unless an AO center is the center of mass), and the MO coefficients change. The rotational derivatives of the MO integrals can be evaluated with the translational derivatives of AO integrals and rotational derivatives of MO coefficients. For example, the derivative of S_{ij} with respect to the rotational motion in the y–z plane (denoted as $\theta_{x\mathrm{A}}$ since the angular momentum is in the x direction) about the center of mass of molecule A is,

$$\begin{aligned}\frac{\partial S_{ij}}{\partial \theta_{x\mathrm{A}}} &= \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} c_{ui} \cdot \left(\frac{\partial S_{uv}}{\partial \theta_{x\mathrm{A}}}\right) \\ &\quad + \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} \left(\frac{\partial c_{ui}}{\partial \theta_{x\mathrm{A}}}\right) \cdot S_{uv} \\ &\quad + \sum_{v}^{\mathrm{B}} \left(\frac{\partial c_{vj}}{\partial \theta_{xA}}\right) \sum_{u}^{\mathrm{A}} c_{ui} \cdot S_{uv}\end{aligned} \tag{9}$$

The overall rotation of A in the y–z plane about its center of mass can be decomposed into individual atomic rotations in the y–z plane (denoted as θ_{xa}) about the atomic centers plus individual atomic translations in the y–z plane multiplied by the distances between the atomic centers (x_a, y_a, z_a) and the center of mass ($x^{\mathrm{A}}_{\mathrm{com}}, y^{\mathrm{A}}_{\mathrm{com}}, z^{\mathrm{A}}_{\mathrm{com}}$):

$$\begin{aligned}\frac{\partial}{\partial \theta_{x\mathrm{A}}} = \sum_{a}^{\mathrm{A}} \bigg[\frac{\partial}{\partial \theta_{xa}} &+ \left(\frac{\partial}{\partial z_a}\right) \cdot \left(y_a - y^{\mathrm{A}}_{\mathrm{com}}\right) \\ &- \left(\frac{\partial}{\partial y_a}\right) \cdot \left(z_a - z^{\mathrm{A}}_{\mathrm{com}}\right) \bigg]\end{aligned} \tag{10}$$

So Eq. (9) becomes:

$$\begin{aligned}\frac{\partial S_{ij}}{\partial \theta_{x\mathrm{A}}} &= \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} c_{ui} \cdot \sum_{a}^{\mathrm{A}} \left[\begin{array}{l} + \left\langle \frac{\partial \psi_u}{\partial \theta_{xa}} \middle| \psi_v \right\rangle \\ + \left\langle \frac{\partial \psi_u}{\partial z_a} \middle| \psi_v \right\rangle \cdot \left(y_a - y^{\mathrm{A}}_{\mathrm{com}}\right) \\ - \left\langle \frac{\partial \psi_u}{\partial y_a} \middle| \psi_v \right\rangle \cdot \left(z_a - z^{\mathrm{A}}_{\mathrm{com}}\right) \end{array}\right] \\ &\quad + \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} \sum_{a}^{\mathrm{A}} \left[\begin{array}{l} + \frac{\partial c_{ui}}{\partial \theta_{xa}} \\ + \left(\frac{\partial c_{ui}}{\partial z_a}\right) \cdot \left(y_a - y^{\mathrm{A}}_{\mathrm{com}}\right) \\ - \left(\frac{\partial c_{ui}}{\partial y_a}\right) \cdot \left(z_a - z^{\mathrm{A}}_{\mathrm{com}}\right) \end{array}\right] \cdot S_{uv}\end{aligned} \tag{11}$$

The rotational derivatives of AOs and translational derivatives of MO coefficients are always zero:

$$\begin{aligned}\frac{\partial \psi_u}{\partial \theta_{xa}} &= 0 \\ \frac{\partial c_{ui}}{\partial z_a} &= 0 \\ \frac{\partial c_{ui}}{\partial y_a} &= 0\end{aligned} \tag{12}$$

So Eq. (11) further simplifies to:

$$\begin{aligned}\frac{\partial S_{ij}}{\partial \theta_{x\mathrm{A}}} &= \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} c_{ui} \cdot \sum_{a}^{\mathrm{A}} \left[\begin{array}{l} + \left\langle \frac{\partial \psi_u}{\partial z_a} \middle| \psi_v \right\rangle \cdot \left(y_a - y^{\mathrm{A}}_{\mathrm{com}}\right) \\ - \left\langle \frac{\partial \psi_u}{\partial y_a} \middle| \psi_v \right\rangle \cdot \left(z_a - z^{\mathrm{A}}_{\mathrm{com}}\right) \end{array}\right] \\ &\quad + \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} \sum_{a}^{\mathrm{A}} \left(\frac{\partial c_{ui}}{\partial \theta_{xa}}\right) \cdot S_{uv}\end{aligned} \tag{13}$$

Similarly, the rotational derivatives of the kinetic energy integrals can be obtained:

$$\begin{aligned}\frac{\partial T_{ij}}{\partial \theta_{x\mathrm{A}}} &= \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} c_{ui} \\ &\quad \cdot \sum_{a}^{\mathrm{A}} \left[\begin{array}{l} + \left\langle \frac{\partial \psi_u}{\partial z_a} \middle| -\frac{\nabla^2}{2} \middle| \psi_v \right\rangle \cdot \left(y_a - y^{\mathrm{A}}_{\mathrm{com}}\right) \\ - \left\langle \frac{\partial \psi_u}{\partial y_a} \middle| -\frac{\nabla^2}{2} \middle| \psi_v \right\rangle \cdot \left(z_a - z^{\mathrm{A}}_{\mathrm{com}}\right) \end{array}\right] \\ &\quad + \sum_{v}^{\mathrm{B}} c_{vj} \sum_{u}^{\mathrm{A}} \sum_{a}^{\mathrm{A}} \left(\frac{\partial c_{ui}}{\partial \theta_{xa}}\right) \cdot T_{uv}\end{aligned} \tag{14}$$

The rotational derivatives of the distances are also similar. For example:

$$\frac{\partial R_{ij}}{\partial \theta_{x\mathrm{A}}} = \frac{\left[\left(z_i - z_j\right) \cdot \left(y_i - y^{\mathrm{A}}_{\mathrm{com}}\right) - \left(y_i - y_j\right) \cdot \left(z_i - z^{\mathrm{A}}_{com}\right)\right]}{R_{ij}} \tag{15}$$

2.4 Derivatives of MO coefficients

Since the AOs are grouped as shells ($s, p, d, f, g, \ldots$), the rotational derivatives of the MO coefficients are simply the intra-shell linear combination of the MO coefficients. Table 1 presents the rotational derivatives of the MO coefficients for s, p, d, f and g type Cartesian Gaussian functions. For example, the derivative of the MO coefficient for the yyz component of an f type AO with respect to the rotation about the x axes is simply a linear combination of the MO coefficients for the yyy and zzy components of the same AO:

$$\frac{\partial c_f^{yyz}}{\partial \theta_x} = -3c_f^{yyy} + 2c_f^{zzy} \tag{16}$$

2.5 Pairwise gradients

Since we choose a strictly pairwise-additive form for the exchange-repulsion energy of a collection of molecular

Table 1 Derivatives of molecular orbital coefficients with respect to the rotations of atomic orbital center

AO	Components	$/\partial\theta_x$	$/\partial\theta_y$	$/\partial\theta_z$
s		0	0	0
p	∂C_x	0	$-C_z$	C_y
	∂C_y	C_z	0	$-C_x$
	∂C_z	$-C_y$	C_x	0
d	∂C_{xx}	0	$-C_{xz}$	C_{xy}
	∂C_{yy}	C_{yz}	0	$-C_{xy}$
	∂C_{zz}	$-C_{yz}$	C_{xz}	0
	∂C_{xy}	C_{xz}	$-C_{yz}$	$2C_{yy} - 2C_{xx}$
	∂C_{xz}	$-C_{xy}$	$2C_{xx} - 2C_{zz}$	C_{yz}
	∂C_{yz}	$2C_{zz} - 2C_{yy}$	C_{xy}	$-C_{xz}$
f	∂C_{xxx}	0	$-C_{yyz}$	C_{xxy}
	∂C_{yyy}	C_{yyz}	0	$-C_{yyx}$
	∂C_{zzz}	$-C_{zzy}$	C_{zzx}	0
	∂C_{xxy}	C_{xxz}	$-C_{xyz}$	$-3C_{xxx} + 2C_{yyx}$
	∂C_{xxz}	$-C_{xxy}$	$3C_{xxx} - 2C_{zzx}$	C_{xyz}
	∂C_{yyx}	C_{xyz}	$-C_{yyz}$	$3C_{yyy} - 2C_{xxy}$
	∂C_{yyz}	$-3C_{yyy} + 2C_{zzy}$	C_{yyx}	$-C_{xyz}$
	∂C_{zzx}	$-C_{xyz}$	$-3C_{zzz} + 2C_{xxz}$	C_{zzy}
	∂C_{zzy}	$-3C_{zzz} + 2C_{yyz}$	C_{xyz}	$-C_{zzx}$
	∂C_{xyz}	$2C_{zzx} - 2C_{yyx}$	$2C_{xxy} - 2C_{zzy}$	$2C_{yyz} - 2C_{xxz}$
g	∂C_{xxxx}	0	$-C_{xxxz}$	C_{xxxy}
	∂C_{yyyy}	C_{yyyz}	0	$-C_{yyyx}$
	∂C_{zzzz}	$-C_{zzzy}$	C_{zzzx}	0
	∂C_{xxxy}	C_{xxxz}	$-C_{xxyz}$	$2C_{xxyy} - 4C_{xxxx}$
	∂C_{xxxz}	$-C_{xxxy}$	$4C_{xxxx} - 2C_{xxzz}$	C_{xxyz}
	∂C_{yyyx}	C_{yyxz}	$-C_{yyyz}$	$4C_{yyyy} - 2C_{xxyy}$
	∂C_{yyyz}	$2C_{yyzz} - 4C_{yyyy}$	C_{yyyx}	$-C_{yyxz}$
	∂C_{zzzx}	$-C_{zzxy}$	$2C_{xxzz} - 4C_{zzzz}$	C_{zzzy}
	∂C_{zzzy}	$4C_{zzzz} - 2C_{yyzz}$	C_{zzxy}	$-C_{zzzx}$
	∂C_{xxyy}	C_{xxyz}	$-C_{yyxz}$	$3C_{yyyx} - 3C_{xxxy}$
	∂C_{xxzz}	$-C_{xxyz}$	$3C_{xxxz} - 3C_{zzzx}$	C_{zzxy}
	∂C_{yyzz}	$3C_{zzzy} - 3C_{yyyz}$	C_{yyxz}	$-C_{zzxy}$
	∂C_{xxyz}	$2C_{xxzz} - 2C_{xxyy}$	$3C_{xxxy} - 2C_{zzxy}$	$2C_{yyxz} - 3C_{xxxz}$
	∂C_{yyxz}	$2C_{zzxy} - 3C_{yyyx}$	$2C_{xxyy} - 2C_{yyzz}$	$3C_{yyyz} - 2C_{xxyz}$
	∂C_{zzxy}	$3C_{zzzx} - 2C_{yyxz}$	$2C_{xxyz} - 3C_{zzzy}$	$2C_{yyzz} - 2C_{xxzz}$

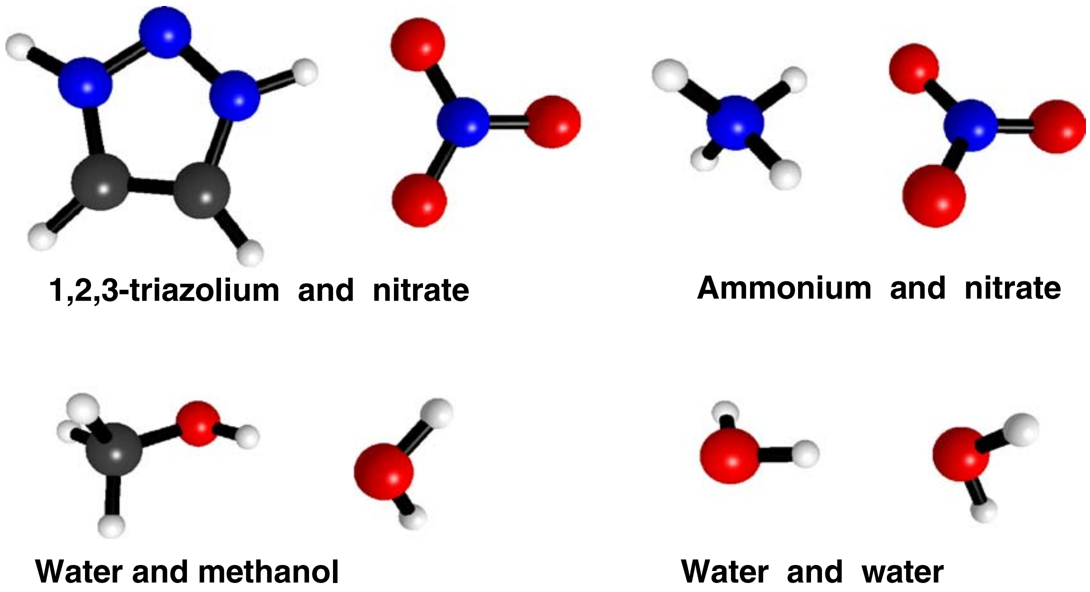

Fig. 1 The four pairs of molecules discussed in the text and in Table 2

fragments, the translational and rotational gradients of the exchange-repulsion energy are also strictly pairwise additive.

The total forces of B acting on A and A acting on B are zero in the three Cartesian directions:

$$\begin{aligned} F_x^{\mathrm{A(B)}} + F_x^{\mathrm{B(A)}} &= 0 \\ F_y^{\mathrm{A(B)}} + F_y^{\mathrm{B(A)}} &= 0 \\ F_z^{\mathrm{A(B)}} + F_z^{\mathrm{B(A)}} &= 0 \end{aligned} \tag{17}$$

Table 2 The exchange-repulsion gradients (Å) and the CPU timings (seconds) in two methods (old and new)

Method	Time	Forces			Torques		
		x	y	z	θ_x	θ_y	θ_z
1,2,3-triazolium and nitrate, aug-cc-pvDZ							
Old	9.17	0.019326118	0.010320514	−0.007950650	0.008605009	−0.000165713	0.005441934
New	0.09	0.019326117	0.010320514	−0.007950650	0.010554305	−0.012462798	0.001843728
1,2,3-triazolium and nitrate, 6-31++G(df, p)							
Old	NA	NA	NA	NA	NA	NA	NA
New	0.08	0.019090906	0.009840810	−0.006253899	0.010462815	−0.022509774	−0.004161012
1,2,3-triazolium and nitrate, 6-31++G(d, p)							
Old	4.94	0.019611113	0.010440252	−0.006684904	0.011543115	−0.022897405	−0.003169965
New	0.04	0.019611113	0.010440252	−0.006684904	0.011518631	−0.022842482	−0.003190900
1,2,3-triazolium and nitrate, 6-31+G(d, p)							
Old	4.66	0.019940843	0.010638010	−0.007000821	0.011378724	−0.023130936	−0.003452317
New	0.04	0.019940842	0.010638010	−0.007000821	0.011354214	−0.023075688	−0.003473010
Ammonium and nitrate, aug-cc-pvDZ							
Old	0.77	0.004361718	−0.036719252	−0.006535922	0.001162271	−0.003628646	0.005601252
New	0.02	0.004361718	−0.036719251	−0.006535922	0.000465569	−0.000897899	0.006178098
Ammonium and nitrate, 6-31++G(df, p)							
Old	NA	NA	NA	NA	NA	NA	NA
New	0.03	0.004200230	−0.039357771	−0.006828185	0.000730127	−0.000906337	0.006029690
Ammonium and nitrate, 6-31++G(d, p)							
Old	0.47	0.004181929	−0.039570113	−0.006845233	0.000674595	−0.000788822	0.006028449
New	0.02	0.004181929	−0.039570112	−0.006845233	0.000722296	−0.000900886	0.006006041
Ammonium and nitrate, 6-31+G(d, p)							
Old	0.44	0.004210723	−0.039989101	−0.006911544	0.000703754	−0.000809717	0.006065691
New	0.02	0.004210723	−0.039989100	−0.006911544	0.000751289	−0.000921719	0.006043244
Water and methanol, aug-cc-pvDZ							
Old	0.29	−0.000626774	−0.004549582	0.000002098	−0.001014431	0.000082082	−0.000488277
New	0.01	−0.000626774	−0.004549581	0.000002098	−0.000829586	0.000069040	−0.000486933
Water and methanol, 6-31++G(df, p)							
Old	NA	NA	NA	NA	NA	NA	NA
New	0.02	−0.000671651	−0.004719800	0.000076034	−0.000577646	0.000036956	−0.000310031
Water and methanol, 6-31++G(d, p)							
Old	0.15	−0.000698177	−0.004736755	0.000118318	−0.000721309	0.000054001	−0.000385052
New	0.02	−0.000698177	−0.004736755	0.000118318	−0.000716606	0.000054190	−0.000389025
Water and methanol, 6-31+G(d, p)							
Old	0.13	−0.000699169	−0.004662003	0.000137090	−0.000766210	0.000060396	−0.000412210
New	0.01	−0.000699169	−0.004662003	0.000137090	−0.000760624	0.000060594	−0.000416319
Water dimer, aug-cc-pvDZ							
Old	0.04	0.004376427	−0.000256661	−0.000145454	0.000008550	0.001021215	−0.000846931
New	0.02	0.004376427	−0.000256661	−0.000145454	0.000008608	0.001051125	−0.000907030
Water dimer, 6-31++G(df, p)							
Old	NA	NA	NA	NA	NA	NA	NA
New	0.01	0.004443870	−0.000103624	0.000006216	−0.000035652	−0.000028142	0.000164113
Water dimer, 6-31++G(d, p)							
Old	0.03	0.004549380	−0.000076082	0.000039854	−0.000038549	−0.000095996	0.000226995
New	0.00	0.004549380	−0.000076082	0.000039854	−0.000038538	−0.000098983	0.000230006
Water dimer, 6-31+G(d, p)							
Old	0.02	0.004539804	−0.000050902	0.000065390	−0.000042464	−0.000204941	0.000332071
New	0.00	0.004539804	−0.000050902	0.000065390	−0.000042455	−0.000207897	0.000335063

The total torques about any center point for A and B must also be zero. The total torques for the system are the sum of the torques on A about the center of mass of A, the torques on B about the center of mass of B, as well as the torques formed by the forces mutually acting on the centers of mass of A and B:

$$\begin{aligned}
&\tau_{\theta x}^{\mathrm{A(B)}}+\tau_{\theta x}^{\mathrm{B(A)}}+\left[F_y^{\mathrm{A(B)}}\cdot(z_{\mathrm{com}}^{\mathrm{A}}-z_{\mathrm{com}}^{\mathrm{B}})-F_z^{\mathrm{A(B)}}\cdot(y_{\mathrm{com}}^{\mathrm{A}}-y_{\mathrm{com}}^{\mathrm{B}})\right]=0\\
&\tau_{\theta y}^{\mathrm{A(B)}}+\tau_{\theta y}^{\mathrm{B(A)}}+\left[F_z^{\mathrm{A(B)}}\cdot(x_{\mathrm{com}}^{\mathrm{A}}-x_{\mathrm{com}}^{\mathrm{B}})-F_x^{\mathrm{A(B)}}\cdot(z_{\mathrm{com}}^{\mathrm{A}}-z_{\mathrm{com}}^{\mathrm{B}})\right]=0\\
&\tau_{\theta z}^{\mathrm{A(B)}}+\tau_{\theta z}^{\mathrm{B(A)}}+\left[F_x^{\mathrm{A(B)}}\cdot(y_{\mathrm{com}}^{\mathrm{A}}-y_{\mathrm{com}}^{\mathrm{B}})-F_y^{\mathrm{A(B)}}\cdot(x_{\mathrm{com}}^{\mathrm{A}}-x_{\mathrm{com}}^{\mathrm{B}})\right]=0
\end{aligned} \tag{18}$$

Therefore, if the forces and torques for B acting on A are obtained, the reactionary forces and torques for A acting on B can be obtained by simply using Eqs. (17) and (18) without actually calculating the derivatives.

3 Computational methodology

The efficiency of the gradient expressions outlined above is demonstrated below for several systems. All calculations have been performed with the quantum chemistry program

GAMESS [5,6], in which the codes for the calculation of the exchange-repulsion energy and derivatives are implemented.

Various basis sets have been used to perform the closed-shell SCF and corresponding EFP calculations. The molecular geometries are first optimized at the RHF/6-31+G(d, p) level of theory, in molecular pairs, and then the individual molecules (ions) are used for EFP preparative calculations with various basis sets. In the EFP calculations the internal geometries of the molecules are frozen. In general, the relative positions of the molecules are allowed to change in geometry optimization runs. However, in this work, single-point energy and gradients are evaluated using the EFP2 parameters at the geometries optimized at the RHF/6-31+G(d, p) level of theory in molecular pairs.

4 Results and discussion

Four pairs of molecules are studied: 1,2,3-triazolium–nitrate, ammonium–nitrate, water–methanol and water–water (Fig. 1). The forces and torques exerted on the molecules are calculated with the EFP2 parameters, using both the previous and the current implementations. Only electrostatic, induction and exchange repulsion are considered because the recently implemented dispersion and charge transfer terms were not available for the previous version of the method. In Table 2 the forces and torques on one molecule in each pair (i.e., 1,2,3-triazolium, ammonium, water and water, respectively) are listed. In the previous implementation, f and g type AOs were not considered. They were included in this implementation.

Identical translational gradients are produced by the two implementations. However, the rotational gradients from the two implementations are different. The differences in rotational gradients are basis set and molecular size dependent. In general, for neutral molecules with the 6-31+G(d, p) and 6-31++G(d, p) basis sets, the differences between these two methods are less than 10^{-5} Å. For larger molecules with larger basis sets the differences are more significant. The largest difference (-0.000165713 vs. -0.012462798) is found for the rotational gradient about the y direction for 1,2,3-triazolium interacting with nitrate (using the aug-cc-pvDZ basis set). Since the current implementation is based on direct differentiation, it is rigorous and the results are of double precision accuracy.

The dominant step in the exchange-repulsion energy calculation is the evaluation of the overlap and kinetic energy integrals. In the gradient calculation, the evaluation of the derivatives of these integrals is the dominant step. The CPU timings for the evaluations of single-point energy and gradients are also listed in Table 2. The new method is much more efficient than the previous method. For small molecules, the efficiency is increased by approximately ten times. For large molecules, the efficiency is increased by more than 100 times.

The CPU timing for the exchange-repulsion gradients is only two to three times longer than the CPU timing for the exchange-repulsion energy itself. For 480 water molecules described with the EFP2 parameters (only the electrostatic multipole points, polarizability tensors and exchange-repulsion parameters are included), a single-point energy evaluation requires 24.9 s on a PowerG5 processor, while a single-point energy and gradient evaluation requires 58.7 s. This efficiency is equivalent to that expected for ab initio gradient evaluations.

5 Conclusion

A direct differentiation approach is applied to calculate the gradients of the exchange repulsion with respect to molecular translations and rotations in the EFP2 method. The derivatives of the MO coefficients with respect to rotations are obtained by mixing the MO coefficients of the AOs in the same shell, and are used to evaluate the rotational derivatives of MO integrals required in the gradient calculation. In general, the rotational gradients of the exchange repulsion in the EFP2 method can be evaluated in a manner that is similar to the approach for translational gradients. The new implementation involves no approximation and is considerably faster than a previous implementation. Using the direct differentiation approach, the timings for the gradient evaluation are approximately three times longer than the energies, similar to that expected for ab initio gradient calculations. This new implementation makes the application of the EFP2 method more robust for demanding applications like MD and MC simulations, in which accurate and fast gradients are essential. The techniques used to calculate the gradients of the EFP exchange repulsion and charge transfer interaction can be used for other approximate ab initio methods in which MOs are internally frozen.

Acknowledgements This work was supported by a SciDAC (Scientific Discovery through Advanced Computing) grant from the U.S. Department of Energy via the Ames Laboratory. The authors have benefited from many help discussions with Professor Jan Jensen, Dr. Michael Schmidt and Dr. Simon Webb.

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