Theor Chem Acc (2006) 115: 354–360
DOI 10.1007/s00214-005-0063-3

REGULAR ARTICLE

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Analytical Hartree–Fock gradients with respect to the cell parameter: systems periodic in one and two dimensions

Received: 25 July 2005 / Accepted: 26 October 2005 / Published online: 17 December 2005

Abstract Analytical Hartree–Fock gradients with respect to the cell parameter have been implemented in the electronic structure code CRYSTAL, for the case of one- and two-dimensional periodicity. As in most molecular codes, Gaussian type orbitals are used to express the wavefunction. Examples demonstrate that the gradients have a good accuracy.

Keywords Hartree-Fock · Cell gradient · Periodic systems · Crystal

1 Introduction

Analytical gradients [1–7] have become a standard tool in molecular quantum chemistry. They are indispensable for the optimization of structures, and many properties can be efficiently computed with the help of analytical derivatives. The field was pioneered by Pulay [8]; the theory had already been derived earlier independently [9].

The traditional quantum chemical methods are difficult to apply to solids because of the large increase of the computational effort with the system size. After several decades of development, Hartree–Fock calculations for solids can nowadays be routinely performed with the CRYSTAL code [10, 11]. Although Hartree–Fock calculations often have large errors due to the neglect of electronic correlation, a large interest has grown in the past few years due to the success of hybrid functionals which include an admixture of exact (Fock) exchange.

Analytical gradients in the CRYSTAL code were first implemented with respect to nuclear positions [12,13], and after the implementation of a scheme for geometry optimization, an efficient structural optimization could be performed [14]. In periodic systems, the cell parameter is another variable to be optimized. The first gradients with respect to the cell parameter, at the Hartree–Fock level, were for systems periodic in one dimension [15,16]. Various groups have implemented these gradients in one dimension [17,18] (see also the recent review article [19]) or in two dimensions [20]. For the general case, a strategy to compute cell parameter derivatives (and thus the stress tensor) was suggested with point charges [21], and an algorithm for structural optimization, based on redundant internal coordinates was proposed [22]. Second analytical derivatives with respect to the cell parameter have also been implemented recently [23].

The first big step of the corresponding implementation in the CRYSTAL code was analytical Hartree–Fock gradients with respect to the cell parameter in three dimensions [24]. It is important to note that the CRYSTAL code is based on the Ewald [25,26] method in three dimensions, so that computing analytical gradients with respect to the cell parameter requires various additional derivatives: for example the reciprocal lattice vectors depend on the cell parameter, and various others. This requires additional derivatives which were not yet available with the implementation of nuclear gradients, and this has been documented in great detail [24]. The one- and two-dimensional cases are again different because different potentials are used: Parry's potential in two dimensions [27,28], and Saunders' potential in one dimension [29]. Parry's potential is similar to Ewald's potential, but modified for the case of two dimensions. Saunders' potential relies on a real space approach.

This article is intended to complement the first article on cell gradients [24]. Many parts have already been described in the first article, and therefore the main emphasis is to delineate the differences due to the dimensionality. The article consists thus of one section about the general differences to the three-dimensional case, one section about the two-dimensional case, one section about the one-dimensional case, and one section with examples.

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2 General differences with respect to the three-dimensional case

The main difference to the three-dimensional case is the way how the Coulomb energy is computed. The expression to be evaluated is the Coulomb energy per cell:

$$E^{\mathrm{coul}} = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r\,' \rho(\vec{r}) \Phi(\vec{r} - \vec{r}\,') \rho(\vec{r}\,') \qquad (1)$$

with Φ being the potential function corresponding to three dimensions (Ewald's potential function) [25,26], two dimensions (Parry's potential function) [27] or one dimension (Saunders' potential function) [29].

$\rho(\vec{r})$ is a cellular charge distribution, composed of the nuclear charges Z_a at the positions of the nuclei $\vec{A}_a$,

$$\rho^{\mathrm{nuc}}(\vec{r}) = \sum_a Z_a \delta(\vec{r} - \vec{A}_a) \qquad (2)$$

and the electronic charge distribution

$$\rho^{\mathrm{el}}(\vec{r}) = - \sum_{\vec{g},\mu,\nu} P_{\nu \vec{g} \mu \vec{0}} \phi_\mu(\vec{r} - \vec{A}_\mu) \times \phi_\nu(\vec{r} - \vec{A}_\nu - \vec{g}) \qquad (3)$$

The basis functions $\phi_\mu(\vec{r} - \vec{A}_\mu - \vec{g})$ are real spherical Gaussian type functions, $P_{\nu \vec{g} \mu \vec{0}}$ is the density matrix in real space. $\vec{A}_\mu$ denotes the nucleus where the basis function μ is centered. The implementation is done for the case of closed shell Hartree–Fock and unrestricted Hartree–Fock methods. For the sake of simplicity, the spin is ignored in the equations in this article. The extension is straightforward, as was shown for the three-dimensional case [24]. Examples for spin-polarized calculations are given in sect. 5.

The potential function enters via the nuclear-nuclear repulsion (Eq. (10) in [24]), the nuclear attraction integrals (Eq. (34) in [24]), and the field integrals (Eq. (43) in [24]). Essentially, the derivatives are computed as described in the previous article [24], there are only minor differences as described in Sect. 3 and 4.

The derivatives of the other integrals (overlap, kinetic energy, multipoles, bielectronics) and the calculation of the energy-weighted density matrix is practically identical to the three-dimensional case [24].

Finally, the correction due to the spheropole (Eq. (47) in [24]) is zero in one and two-dimensions and thus does not have to be discussed. The spheropole is a correction which arises due to the Ewald method when applied to the electronic charge distribution: the charge distribution is approximated by multipoles in the long range, and not approximated in the short range. The electrostatic potential is then computed as the sum of the Ewald potential of the multipoles and of the Coulomb potential of the charge distribution in the short range. Replacing the Ewald potential with the Coulomb potential is correct, if the difference of multipolar charge distribution and the exact charge distribution in the short range has zero charge, dipole, quadrupole, and second spherical moment [26]. The second spherical moment can also be seen as the average electrostatic potential of a charge distribution (see the discussion in Sect. 3.2 of [26]). Here, it corresponds to the average electrostatic potential of the difference of the exact and the approximated charge distribution. This term is finite and in general non-zero, in the case of periodicity in three dimensions. However, when the system has periodicity in less than three dimensions, the average electrostatic potential of a charge distribution with zero total charge, dipole and quadrupol, is zero. Therefore, there is no spheropole in less than three dimensions.

This can also be seen from Eq. (31) in [26]. The average Coulomb potential is obtained as follows:

$$\Phi = -\frac{2\pi}{3 V_{\mathrm{cell}}} \int \rho^{\mathrm{diff}}(\vec{r})\, \vec{r}^{\,2}\, \mathrm{d}^3 r \qquad (4)$$

where $\rho^{\mathrm{diff}}(\vec{r})$ corresponds here to the difference between the exact charge distribution and the multipolar charge distribution. The integral is over the whole space and finite. The prefactor involves a division by the cell volume V_{cell} of the three-dimensional cell. We might now approximate a system with periodicity in two dimensions by a system of slabs with three-dimensional periodicity, where the slabs are separated by a vacuum region. When we increase the vacuum region and thus the cell volume V_{cell}, then the integral remains essentially constant, but the prefactor becomes increasingly smaller and therefore the average Coulomb potential becomes zero, and the spheropole correction becomes zero.

It should be mentioned, that two-dimensional periodicity is implemented in the CRYSTAL code in such a way that there is only one slab which is not repeated in the third dimension. Still, the argument presented above holds in a similar way, and there is thus no spheropole correction in systems with less than three-dimensional periodicity.

The total energy is thus similar to the three-dimensional case [24], apart from the spheropole term which is zero:

$$\begin{aligned} E^{\mathrm{total}} &= E^{\mathrm{kinetic}} + E^{\mathrm{NN}} + E^{\mathrm{coul-nuc}} + E^{\mathrm{coul-el}} + E^{\mathrm{exch-el}} \\ &= \sum_{\vec{g},\mu,\nu} P_{\nu \vec{g} \mu \vec{0}} T_{\mu \vec{0} \nu \vec{g}} + \frac{1}{2} \sum_{a,b} Z_a Z_b \Phi(\vec{A}_b - \vec{A}_a) \\ &\quad - \sum_{\vec{g},\mu,\nu} P_{\nu \vec{g} \mu \vec{0}} \sum_a Z_a \int \phi_\mu(\vec{r} \\ &\quad - \vec{A}_\mu) \phi_\nu(\vec{r} - \vec{A}_\nu - \vec{g}) \Phi(\vec{r} - \vec{A}_a) \mathrm{d}^3 \mathrm{r} \\ &\quad + \frac{1}{2} \sum_{\vec{g},\mu,\nu} P_{\nu \vec{g} \mu \vec{0}} \Bigg(\sum_{\vec{h},\tau,\sigma} P_{\sigma \vec{h} \tau \vec{0}} C_{\mu \vec{0} \nu \vec{g} \tau \vec{0} \sigma \vec{h}} \\ &\quad - \sum_c \sum_{l=0}^{L} \sum_{m=-l}^{l} \eta_l^m(\rho_c; \vec{A}_c) M^m_{l \mu \vec{0} \nu \vec{g} c} \Bigg) \\ &\quad - \frac{1}{2} \sum_{\vec{g},\mu,\nu} P_{\nu \vec{g} \mu \vec{0}} \sum_{\vec{h},\tau,\sigma} P_{\sigma \vec{h} \tau \vec{0}} X_{\mu \vec{0} \nu \vec{g} \tau \vec{0} \sigma \vec{h}} \end{aligned} \qquad (5)$$

The individual terms contributing to the total energy are the kinetic energy E^{kinetic}, the nuclear–nuclear repulsion energy E^{NN}, the nuclear–electron attraction $E^{\text{coul-nuc}}$, the electron–electron repulsion $E^{\text{coul-el}}$ and the Fock exchange $E^{\text{exch-el}}$. The variables will not all be explained in order to reduce the number of formulas in this article. The reader is referred to the article on the three-dimensional case for the details where all these terms are explained [24]. The gradient with respect to the cell parameters a_{ij} is given in the following equation. As the total energy, the gradient is similar to the three-dimensional case apart from the spheropole term which is zero.

$$
\begin{aligned}
F_{a_{ij}} &= -\frac{\partial E^{\text{total}}}{\partial a_{ij}} \\
&= -\sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}\mu\vec{0}} \frac{\partial T_{\mu\vec{0}\nu\vec{g}}}{\partial a_{ij}} - \frac{\partial E^{\text{NN}}}{\partial a_{ij}} \\
&\quad -\sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}\mu\vec{0}} \frac{\partial N_{\mu\vec{0}\nu\vec{g}}}{\partial a_{ij}} \\
&\quad -\frac{1}{2}\sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}\mu\vec{0}} \Bigg\{ \sum_{\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}} \frac{\partial C_{\mu\vec{0}\nu\vec{g}\tau\vec{0}\sigma\vec{h}}}{\partial a_{ij}} \\
&\quad -\sum_{c}\sum_{l=0}^{L}\sum_{m=-l}^{l}\sum_{\vec{h},\tau\in c,\sigma} P_{\sigma\vec{h}\tau\vec{0}} \\
&\quad \times\frac{\partial}{\partial a_{ij}}\Bigg[\int \phi_\tau(\vec{r}-\vec{A}_\tau)\phi_\sigma(\vec{r}-\vec{A}_\sigma \\
&\quad -\vec{h})X_l^m(\vec{r}-\vec{A_c})\mathrm{d}^3\mathrm{r}\, M^m_{l\mu\vec{0}\nu\vec{g}c}\Bigg]\Bigg\} \\
&\quad +\frac{1}{2}\sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}\mu\vec{0}} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}} \frac{\partial X_{\mu\vec{0}\nu\vec{g}\tau\vec{0}\sigma\vec{h}}}{\partial a_{ij}} \\
&\quad -\sum_{\vec{g},\mu,\nu} \frac{\partial S_{\mu\vec{0}\nu\vec{g}}}{\partial a_{ij}} \int_{BZ} \exp(\mathrm{i}\vec{K}\vec{g}) \\
&\quad \times\sum_{n} a_{\nu n}(\vec{K})a_{\mu n}(\vec{K})\epsilon_n(\vec{K}) \\
&\quad \times\Theta(\epsilon_F-\epsilon_n(\vec{K}))\mathrm{d}^3\mathrm{k} \qquad (6)
\end{aligned}
$$

3 The two-dimensional case

In the two-dimensional case, the primitive cell is given by two vectors, with two components: $\vec{a}_1$, $\vec{a}_2$. a_{ij} are defined in such a way that $a_{11} = a_{1x}$ is the x-component of $\vec{a}_1$, $a_{12} = a_{1y}$ the y-component of $\vec{a}_1$, a_{21} is the x-component of $\vec{a}_2$, and a_{22} is the y-component of $\vec{a}_2$.

$$
\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \begin{pmatrix} a_{1x} & a_{1y} \\ a_{2x} & a_{2y} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \qquad (7)
$$

A point $\vec{g}$ of the direct lattice is defined as $\vec{g} = n_1\vec{a}_1 + n_2\vec{a}_2$, with n_1, n_2 being integer numbers. The position of an atom c in a cell at the origin (i.e. $\vec{g} = \vec{0}$) is given as $\vec{A}_c = f_{c,1}\vec{a}_1 + f_{c,2}\vec{a}_2$, and then in cell $\vec{g}$ the position will be:

$$
\vec{A}_c + \vec{g} = (f_{c,1} + n_{\vec{g},1})\vec{a}_1 + (f_{c,2} + n_{\vec{g},2})\vec{a}_2
$$

We have used an additional index, i.e. $n_{\vec{g},1}$ means factor n_1 of the lattice vector $\vec{g}$. The cartesian t component (with t being x or y) of the vector $\vec{A}_c + \vec{g}$, indicated as $A_{c,t} + g_t$, is thus

$$
A_{c,t} + g_t = \sum_{m=1}^{2}(f_{c,m} + n_{\vec{g},m})a_{mt}
$$

As all the integrals depend on the position of the nuclei, the derivatives of the nuclear coordinates with respect to the cell parameters are required:

$$
\begin{aligned}
\frac{\partial A_{c,t} + g_t}{\partial a_{ij}} &= \sum_{m=1}^{2}(f_{c,m} + n_{\vec{g},m})\delta_{im}\delta_{jt} \\
&= (f_{c,i} + n_{\vec{g},i})\delta_{jt} \qquad (8)
\end{aligned}
$$

with the Kronecker symbol δ_{jt}.

The main difference, compared to the three-dimensional case, is Parry's potential function $\Phi(\vec{r} - \vec{A}_a)$ that is used:

$$
\begin{aligned}
\Phi(\vec{r}-\vec{A}_a) &= \sum_{\vec{h}}{}' \frac{1-\mathrm{erf}(\sqrt{\gamma}|\vec{r}-\vec{A}_a-\vec{h}|)}{|\vec{r}-\vec{A}_a-\vec{h}|} \\
&\quad +\sum_{\vec{K}}{}' \frac{\exp(2\pi\mathrm{i}(K_x(x-A_{a,x})+K_y(y-A_{a,y})))}{2V|\vec{K}|} \\
&\quad \times\Bigg(\exp(2\pi|\vec{K}|(z-A_{a,z})) \\
&\quad \times\left(1-\mathrm{erf}\left(\sqrt{\gamma}(z-A_{a,z})+\frac{\pi|\vec{K}|}{\sqrt{\gamma}}\right)\right) \\
&\quad +\exp(-2\pi|\vec{K}|(z-A_{a,z})) \\
&\quad \times\left(1+\mathrm{erf}\left(\sqrt{\gamma}(z-A_{a,z})-\frac{\pi|\vec{K}|}{\sqrt{\gamma}}\right)\right)\Bigg) \\
&\quad -\frac{2\pi}{V}(z-A_{a,z})\mathrm{erf}(\sqrt{\gamma}(z-A_{a,z})) \\
&\quad -\frac{2\sqrt{\pi}}{V\sqrt{\gamma}}\exp\left(-\gamma(z-A_{a,z})^2\right) \qquad (9)
\end{aligned}
$$

where $\vec{h}$ are the direct lattice vectors, $\vec{K}$ the reciprocal lattice vectors. V is the area of the two-dimensional unit cell, γ is a screening parameter which was optimized to be $\gamma = (2.4/V^{1/2})^2$, in the two-dimensional case. Note that this is different from the three-dimensional case [26] where γ was chosen as $\gamma = (2.8/V^{1/3})^2$. The prime in the direct lattice summation indicates that the summation includes all values of the direct lattice vector $\vec{h}$, with the exception of the case when $|\vec{r} - \vec{A}_a - \vec{h}|$ vanishes. In this case, the term $\frac{1}{|\vec{r}-\vec{A}_a-\vec{h}|}$ is omitted from the sum. In the reciprocal lattice series, the prime indicates that all terms with $\vec{K} \neq \vec{0}$ are included.

The error function erf is defined as in [24], Eq. (12).

Like the Ewald potential, Parry's potential depends on the variables $\vec{A}_c$, $\vec{h}$, V, γ and $\vec{K}$. The derivative with respect to the cell parameters thus requires derivatives with respect to these variables. For the derivatives with respect to $\vec{A}_c$ and $\vec{h}$ this is like in the three-dimensional case. There are minor changes due to the two-dimensionality for the derivatives of the area V, of the $\vec{K}$-vectors with respect to a_{ij} and of the screening parameter γ.

3.1 Derivative of the area

The area is obtained as the magnitude of the cross product of the cell parameters:

$$V = |\vec{a}_1 \times \vec{a}_2| = |a_{1x}a_{2y} - a_{1y}a_{2x}| \tag{10}$$

If we assume that $a_{1x}a_{2y} - a_{1y}a_{2x}$ is positive, then the derivatives $\frac{\partial V}{\partial a_{ij}}$ are obtained as:

$$\frac{\partial V}{\partial a_{1x}} = a_{2y} \tag{11}$$

$$\frac{\partial V}{\partial a_{1y}} = -a_{2x} \tag{12}$$

$$\frac{\partial V}{\partial a_{2x}} = -a_{1y} \tag{13}$$

$$\frac{\partial V}{\partial a_{2y}} = a_{1x} \tag{14}$$

Essentially, the formulas for the three-dimensional case can be used, when setting $a_{1z} = 0$, $a_{2z} = 0$ and $\vec{a}_3 = (0, 0, 1)$. This holds also for the derivatives of the reciprocal lattice vectors, as described in the following section.

3.2 Derivative of the reciprocal lattice vectors

The reciprocal lattice vectors $\vec{K}$ can be expressed as

$$\vec{K} = n_1\vec{b}_1 + n_2\vec{b}_2 \tag{15}$$

with the primitive vectors $\vec{b}_i$ of the reciprocal lattice defined as:

$$\vec{b}_1 = \frac{2\pi}{V}(a_{2y}, -a_{2x}); \quad \vec{b}_2 = \frac{2\pi}{V}(-a_{1y}, a_{1x}) \tag{16}$$

The derivatives are thus:

$$\frac{\partial \vec{b}_1}{\partial a_{1x}} = -\frac{\partial V}{\partial a_{1x}}\frac{\vec{b}_1}{V} \tag{17}$$

$$\frac{\partial \vec{b}_1}{\partial a_{1y}} = -\frac{\partial V}{\partial a_{1y}}\frac{\vec{b}_1}{V} \tag{18}$$

$$\frac{\partial \vec{b}_1}{\partial a_{2x}} = -\frac{\partial V}{\partial a_{2x}}\frac{\vec{b}_1}{V} + \frac{2\pi}{V}(0, -1) \tag{19}$$

$$\frac{\partial \vec{b}_1}{\partial a_{2y}} = -\frac{\partial V}{\partial a_{2y}}\frac{\vec{b}_1}{V} + \frac{2\pi}{V}(1, 0) \tag{20}$$

and

$$\frac{\partial \vec{b}_2}{\partial a_{1x}} = -\frac{\partial V}{\partial a_{1x}}\frac{\vec{b}_2}{V} + \frac{2\pi}{V}(0, 1) \tag{21}$$

$$\frac{\partial \vec{b}_2}{\partial a_{1y}} = -\frac{\partial V}{\partial a_{1y}}\frac{\vec{b}_2}{V} + \frac{2\pi}{V}(-1, 0) \tag{22}$$

$$\frac{\partial \vec{b}_2}{\partial a_{2x}} = -\frac{\partial V}{\partial a_{2x}}\frac{\vec{b}_2}{V} \tag{23}$$

$$\frac{\partial \vec{b}_2}{\partial a_{2y}} = -\frac{\partial V}{\partial a_{2y}}\frac{\vec{b}_2}{V} \tag{24}$$

3.3 Derivative of the screening parameter

The derivative is straightforward, like in the three-dimensional case:

$$\frac{\partial \gamma}{\partial a_{ij}} = \frac{\partial \gamma}{\partial V}\frac{\partial V}{\partial a_{ij}} = -\frac{\gamma}{V}\frac{\partial V}{\partial a_{ij}} \tag{25}$$

As a whole, Parry's potential leads to similar terms appearing in the derivatives as in the case of the Ewald potential. This is what was to be expected, as Parry's potential is essentially obtained when Ewald's approach to treat the Coulomb interaction is applied to a system with two-dimensional periodicity.

4 The one-dimensional case

In the one-dimensional case, there is only one cell parameter: $a_{xx} = a_{11} = a = |\vec{a}|$. This case is somewhat different from the two- and three-dimensional case because a pure real space approach is used in the CRYSTAL code for the potential to describe the Coulomb interaction [29]. The potential consists of a point charge $+1$, neutralized by a uniform charge distribution of length a, with charge density $-1/a$. The uniform charge distribution is then again compensated. Up to a certain range, the summation is performed exactly. For larger distances, the summation is instead approximated with the help of the Euler–MacLaurin summation rule. As a whole, the following expression was obtained [29]:

$$\Phi(\vec{r}) = \sum_{n=-M}^{M}{}' \frac{1}{|\vec{r} - n\vec{a}|} - \frac{H(U-z,\alpha) + H(U+z,\alpha)}{a} + \xi(M, \vec{r}) + \xi(M, -\vec{r}) \tag{26}$$

The first term comprises the exact part, the next two (with the H function) the region due to the uniform charge density in the range of the exact sum (from $-M\vec{a}$ to $M\vec{a}$), the remaining two terms (the ξ-function) are the approximated part. The prime indicates that terms with $|\vec{r} - n\vec{a}| = 0$ are omitted. M is thus the number of cells, where the sum is performed exactly, and $U = a(M + 1/2)$. α is defined as $\alpha = x^2 + y^2$, with $\vec{r} = (x, y, z)$. H is the function $H(p, \alpha) = \ln(\sqrt{p^2 + \alpha} + p)$. $\xi(M, \vec{r})$ and $\xi(M, -\vec{r})$ are contributions from the long range part, which is approximated by the Euler–MacLaurin rectangle rule summation formula. For more details, see [29]. For the present purpose, it is important to note that the direct lattice vector a appears in the potential, but no screening parameter γ and no reciprocal lattice vectors $\vec{K}$ as in the two- and three-dimensional case. This means that derivatives with respect to the nuclear coordinates $\vec{A}_c$ and derivatives with respect to the direct lattice vectors $n\vec{a}$ appear, which are essentially given by the nuclear gradients, multiplied with the fractional coordinates. The derivatives with respect to a due to the H and ξ function are very lengthy, but still straightforward. They are thus not discussed here, but formulas can be derived from Saunders' article [29].

5 Examples

In this section, we give some numerical examples of the accuracy of the gradients. The tests considered are essentially identical or similar to the test cases distributed with the CRYSTAL code and with those from [14]. Note that the fractional coordinates of the atoms were not optimized.

First, two systems with one-dimensional periodicity are considered. In Table 1, SN is periodically arranged. The analytical and numerical derivative agree well up to four digits, and the minimum of the energy at $a = 4.42$ Å agrees with the place where the gradient changes its sign. In Table 2, such a comparison is done for polyglycine. The agreement of numerical and analytical gradients is similar to SN, and again the vanishing of the gradient agrees with the minimum of the energy, to at least 0.01 Å. In Table 3, ferromagnetic NiO is studied at the level of unrestricted Hartree–Fock. The agreement of numerical and analytical gradient can be improved by increasing the "ITOL"-parameters [11], as described earlier [12,24]. Indeed, when increasing them from default values to higher ones, symmetric in ITOL4 and ITOL5, then analytical and numerical gradient match better. Note that, when running at lower ITOL parameters, an inaccuracy is introduced in the total energy expression and thus in the numerical gradients as well. The fact that numerical and analytical gradients match less well at low ITOL values is thus a combination of an inaccuracy in the energy expression (which affects the numerical gradient) and an inaccuracy in the analytical gradient. Still, in all the tests performed so far, no severe error was found when using default values for the ITOL parameters. Using higher ITOL parameters is mainly useful for tests of the correctness of the code.

Table 1 SN, with one-dimensional periodicity

a [Å]	Analytical derivative [E_h/a_0]	Numerical derivative [E_h/a_0]	Energy [E_h]
4.30	0.04144	0.0414	−893.870081
4.41	0.00372	0.0037	−893.874639
4.42	0.00064	0.0006	−893.874680
4.43	−0.00238	−0.0024	−893.874663
4.500	−0.02208	−0.0221	−893.873013

A comparison of analytical and numerical gradient is done for various unit cell lengths. A [$3s2p1d$] basis set was used for S, and a [$2s1p$] basis set for N

Table 2 Polyglycine: a comparison of analytical and numerical gradient is done for various unit cell lengths

a [Å]	Analytical derivative [E_h/a_0]	Numerical derivative [E_h/a_0]	Energy [E_h]
7.30	0.01956	0.0196	−408.220173
7.42	0.00116	0.0012	−408.222495
7.43	−0.00030	−0.0003	−408.222503
7.44	−0.00175	−0.0017	−408.222484
7.50	−0.01018	−0.0102	−408.221807

Basis sets of the size [$2s1p$] were used for C, O, N and a [$1s$] basis set for H

Table 3 NiO, ferromagnetic, unrestricted Hartree–Fock

a [Å]	Analytical derivative [E_h/a_0]	Numerical derivative [E_h/a_0]	Energy [E_h]
		ITOL 6 6 6 6 12 (default)	
5.00	−0.10864	−0.1074	−1581.454974
		ITOL 6 6 6 12 12	
5.00	−0.10782	−0.1078	−1581.456358

The gradient with respect to the cell parameter is computed for two different values of the ITOL parameters. A [$5s4p2d$] basis set for Ni was used, and a [$4s3p$] basis set for O

Table 4 MgO surface, three atomic layers

a [Å]	Analytical derivative [E_h/a_0]	Numerical derivative [E_h/a_0]	Energy [E_h]
2.80	0.10544	0.1058	−823.930493
2.88	0.01035	0.0108	−823.939034
2.89	0.00006	0.0006	−823.939142
2.90	−0.00991	−0.0095	−823.939058
3.00	−0.09403	−0.0937	−823.928906

The unit cell consists of three Mg and three O atoms, with $a_{1x} = a_{2y} = a$. Basis sets of the size [$3s2p$] were used. The derivative with respect to $\frac{\partial}{\partial a} = (\partial/\partial a_{1x})(\partial a_{1x}/\partial a) + (\partial/\partial a_{2y})(\partial a_{2y}/\partial a)$ is displayed, $(\partial/\partial a_{1y})$ and $(\partial/\partial a_{2x})$ do not contribute

Table 5 Al_2O_3, six atomic layers

a [Å]	Analytical derivative [E_h/a_0]	Numerical derivative [E_h/a_0]	Energy [E_h]
4.20	0.27548	0.2757	−1400.244182
4.40	0.00590	0.0059	−1400.295000
4.41	−0.00570	−0.0060	−1400.295003
4.42	−0.01712	−0.0171	−1400.294787
4.70	−0.27847	−0.2786	−1400.211859

The unit cell consists of six Al and four O atoms, with $a_{1x} = \sqrt{3}/2 * a_{2y} = \sqrt{3}/2 * a$. Basis sets of the size [$3s2p1d$] for Al and [$2s1p$] for O were chosen. The derivative with respect to $\frac{\partial}{\partial a} = (\partial/\partial a_{1x})(\partial a_{1x}/\partial a) + (\partial/\partial a_{2y})(\partial a_{2y}/\partial a)$ is displayed, $(\partial/\partial a_{1y})$ and $(\partial/\partial a_{2x})$ do not contribute

Then, various systems with two-dimensional periodicity are considered. In Table 4, three MgO layers are considered. Numerical and analytical derivative agree to three digits, and the minimum of the energy and the vanishing of the gradient agree also well. The same accuracy is found for Al_2O_3 in Table 5, where a slab with six atomic layers is considered. In Table 6, a Cr_2O_3 slab was chosen as an example for unrestricted Hartree–Fock. The accuracy is slightly worse when comparing the numerical and the analytical gradient. This can again be improved by increasing the "ITOL"-parameters. The minimum in the energy agrees already with default "ITOL" values to at least 0.01 Å. Finally, in Table 7, LiF was arranged with two-dimensional periodicity, without symmetry, in such a way that three components of the cell gradient (a_{1x}, a_{1y}, a_{2y}) can be computed independently. This test thus demonstrates that these components are correctly computed.

In Table 8, the CPU times are displayed. The calculations were performed on a single CPU of a Compaq ES45, with a clock rate of 1 GHz. As in the three-dimensional case, we compare again the CPU time for the integrals with the time for the gradients. The CPU time for all the gradients (nuclear and cell gradients) is roughly five to ten times the CPU time for the integrals. This may become smaller in the future with further optimizations in the gradient code. Note that the CPU time for the self consistent field calculations is relatively high because a very low convergence threshold was chosen in order to ensure the accuracy of the succeeding gradient calculation (the gradient calculation is the more accurate, the more accurately the self consistent field equations are solved).

Table 6 Cr_2O_3, six atomic layers, ferromagnetic, unrestricted Hartree–Fock

a [Å]	Analytical derivative $[E_h/a_0]$	Numerical derivative $[E_h/a_0]$	Energy $[E_h]$
		ITOL 6 6 6 6 12 (default)	
4.70	0.13465	0.1379	−4622.589785
4.87	0.00426	0.0069	−4622.612278
4.88	−0.00253	0.0001	−4622.612339
4.89	−0.00921	−0.0066	−4622.612277
5.00	−0.07676	−0.0745	−4622.603638
		ITOL 6 6 6 12 12	
4.88	−0.00116	−0.0011	−4622.617935
5.00	−0.07539	−0.0754	−4622.609006

The unit cell consists of six Cr and from four O atoms, with $a_{1x} = \sqrt{3}/2 * a_{2y} = \sqrt{3}/2 * a$. Basis sets of the size [5*s*4*p*2*d*] for Cr and [3*s*2*p*] for O were chosen. The derivative with respect to $\frac{\partial}{\partial a} = (\partial/\partial a_{1x})(\partial a_{1x}/\partial a) + (\partial/\partial a_{2y})(\partial a_{2y}/\partial a)$ is displayed, $(\partial/\partial a_{1y})$ and $(\partial/\partial a_{2x})$ do not contribute

Table 7 LiF, with a unit cell of $a_{1x} = 5$ Å, $a_{2y} = 4$ Å, and an angle of 60°, resulting in $a_{1y} = 2.5$ Å

Component	Analytical derivative $[E_h/a_0]$	Numerical derivative $[E_h/a_0]$
$\frac{\partial E}{\partial a_{1x}}$	0.04045	0.0406
$\frac{\partial E}{\partial a_{1y}}$	−0.04415	−0.0441
$\frac{\partial E}{\partial a_{2y}}$	−0.01838	−0.0183

The F atoms are at ($x = 0.1$, $y = 0$ (x and y in fractional units), $z = 0.1$ Å), ($x = 0.5$, $y = 0.5$ (x and y in fractional units), $z = 0.3$ Å), the Li atoms at ($x = 0.5$, $y = 0$ (x and y in fractional units), $z = 0.2$ Å), and ($x = 0$, $y = 0.5$ (x and y in fractional units), $z = 0.4$ Å). A [2*s*1*p*] basis set was used for Li, a [4*s*3*p*] basis set for F

Table 8 CPU times for one single point calculation of the various systems

System	CPU time, in seconds		
	Integrals	SCF	Gradients
SN	1	1	6
Polyglycine	2	4	17
NiO	2	14	9
MgO	5	3	52
Al_2O_3	8	12	78
Cr_2O_3	27	153	176
LiF	3	18	20

The calculations were performed on a Compaq ES45, using a single CPU (1 GHz). The CPU times refer to the part for the integrals (all the integrals were written to disk), the self-consistent field (SCF) procedure, and to the calculation of all the gradients (i.e. nuclear gradients and cell gradients)

The CPU times thus indicate that analytical gradients can be computed at a relatively low expense. Compared to numerical gradients, it appears that analytical gradients should usually be favorable, especially because numerical gradients will depend on the step size, and often it will be necessary to break a symmetry for a finite displacement, to compute the numerical gradient. Numerical gradients require at least one additional energy evaluation for each coordinate to be optimized, which makes analytical gradients clearly favorable, if there is a large number of geometrical parameters.

6 Conclusion

A formalism for the calculation of the analytical gradient of the Hartree–Fock energy, with respect to the cell parameter, has been presented and implemented in the code CRYSTAL, for the case of systems periodic in one and two-dimensions. The implementation includes the cases of spin-restricted and unrestricted polarization. It was shown that a high accuracy can be achieved.

Acknowledgements The calculations were performed on a Compaq ES45 (computer center of the TU Braunschweig).

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