# Analytical Hartree–Fock gradients with respect to the cell parameter for systems periodic in three dimensions

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**Abstract.** Analytical Hartree–Fock gradients with respect to the cell parameter have been implemented in the electronic structure code CRYSTAL, for the case of three-dimensional periodicity. The code is based on Gaussian-type orbitals, and the summation of the Coulomb energy is performed with the Ewald method. It is shown that a high accuracy of the cell gradient can be achieved.

**Keywords:** Hartree-Fock, gradient, cell parameter, CRYSTAL

## 1 Introduction

Electronic structure codes are nowadays widely used by theoreticians and also by a growing number of experimentalists. One of the targets is the calculation of the total energy and the structural optimization of large systems. It is well known that this is greatly facilitated by the availability of analytical gradients, and thus the coding of gradients has become an important part of code development.

In the molecular case, the geometrical parameters that must be optimized are the nuclear coordinates. This field was pioneered by Pulay [1]; however, it should be mentioned that the theory had already been derived earlier independently [2]. Meanwhile, numerous review articles about analytical derivatives have appeared [3, 4, 5, 6, 7, 8, 9].

In the case of periodic systems, the cell dimensions are an additional set of parameters. Nowadays, nearly all solid-state codes compute the total energy with density functional methods. However, because of the success of hybrid functionals, which use an admixture of Fock exchange, there is growing interest in codes which compute the Fock exchange. CRYSTAL [10] was originally a

code for pure Hartree–Fock calculations. In the past decade, density functional calculations for all types of functionals have become possible as well with this code.

The code is based on Gaussian-type orbitals, and most of the contributions to the total energy rely on the Hartree–Fock formulation. Therefore, the Hartree–Fock gradients with respect to the cell parameter were the first step to make gradients with respect to the cell parameter available. In this article, we report on the implementation of gradients at the Hartree–Fock level, with respect to the cell parameter, for systems periodic in three dimensions.

The first gradients with respect to the cell parameter, at the Hartree–Fock level, were for systems periodic in one dimension [11]. Meanwhile, various groups have implemented these gradients in one dimension [12, 13] or in two dimensions [14]. For the general case, a strategy to compute cell parameter derivatives (and thus the stress tensor) was suggested with point charges [15] and an algorithm for structural optimization, based on redundant internal coordinates was proposed [16].

All these codes use a real space approach, where all the summations are performed in direct space. As an acceleration tool, the fast multipole method is applied in various cases. The cell parameter gradient is then obtained essentially by multiplying the contributions to the nuclear gradients with the appropriate factors.

In contrast, the CRYSTAL code uses, in the case of three-dimensional periodicity, the Ewald method, which is a combination of direct and reciprocal lattice summations [17]. This means, that besides some contributions which have to be multiplied with trivial factors, there will also be additional derivatives, because various parameters in the Ewald scheme, and the reciprocal lattice vectors, depend on the cell parameters. The Hartree–Fock gradients with respect to nuclear coordinates were implemented earlier [18,19], and after the implementation of a tool for structural optimization, it was demonstrated that an efficient geometry optimization of large systems with any periodicity can be performed [20].

In this article, we describe the formalism used in the CRYSTAL code for the cell parameter gradients, and

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present results from tests on various systems. The article is structured as follows. First, the variables are defined. Then the integrals and their derivatives with respect to the cell parameters are discussed, and in the following section the derivative of the total energy is given. Finally, some examples are used as an illustration of the formalism.

## 2 Variables

The primitive cell is given by three vectors, $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$, and the derivatives with respect to the cell parameters $a_{ij}$ have been coded. $a_{ij}$ 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 $\vec{a}_1$, and $a_{13} = a_{1z}$ the $z$-component of $\vec{a}_1$, i.e.,

$$
\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} = \begin{pmatrix} a_{1x}\ a_{1y}\ a_{1z} \\ a_{2x}\ a_{2y}\ a_{2z} \\ a_{3x}\ a_{3y}\ a_{3z} \end{pmatrix} = \begin{pmatrix} a_{11}\ a_{12}\ a_{13} \\ a_{21}\ a_{22}\ a_{23} \\ a_{31}\ a_{32}\ a_{33} \end{pmatrix} . \tag{1}
$$

A point $\vec{g}$ of the direct lattice is defined as $\vec{g} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, with $n_1, n_2$ and $n_3$ being integer numbers. We assume we have $N$ atoms in the unit cell. The position of an atom $c$ in a cell at the origin (i.e., $\vec{g} = \vec{0}$) is given as $\vec{A}_c = f_{c,1}\vec{a}_1 + f_{c,2}\vec{a}_2 + f_{c,3}\vec{a}_3$, and then in cell $\vec{g}$ the position will be

$$
\vec{A}_c + \vec{g} = (f_{c,1} + n_{\vec{g},1})\vec{a}_1 + (f_{c,2} + n_{\vec{g},2})\vec{a}_2 + (f_{c,3} + n_{\vec{g},3})\vec{a}_3.
$$

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 $x$, $y$ or $z$) of the vector $\vec{A}_c + \vec{g}$, indicated as $A_{c,t} + g_t$, is thus

$$
A_{c,t} + g_t = \sum_{m=1}^{3} (f_{c,m} + n_{\vec{g},m})a_{mt} .
$$

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:

$$
\frac{\partial A_{c,t} + g_t}{\partial a_{ij}} = \sum_{m=1}^{3} (f_{c,m} + n_{\vec{g},m})\delta_{im}\delta_{jt} = (f_{c,i} + n_{\vec{g},i})\delta_{jt} , \tag{2}
$$

with the Kronecker symbol $\delta_{jt}$.

In the following, we use the notation $\vec{A}_c$ to indicate the position of atom $c$. However, we also need to define basis functions $\phi_\mu$ centered at a certain nucleus, where $\mu$ runs over all the basis functions. For example, basis functions $\mu = 1, ..., 5$ might be centred at atom 1, basis functions $\mu = 6, ..., 15$ at atom 2 and so on. It is thus trivial to assign a certain atom number $c$ to the basis function $\mu$: $c = c(\mu)$. We could thus use the notation $\vec{A}_{c(\mu)}$, but will instead use the simplified notation $\vec{A}_\mu$. To avoid confusion, Greek indices are used in this case, i.e., $\vec{A}_\mu = \vec{A}_{c(\mu)} = \vec{A}_c$.

The basis functions used are real spherical Gaussian-type functions, and we will use the notation $\phi_\mu(\vec{r} - \vec{A}_\mu - \vec{g})$.

The crystalline orbitals are linear combinations of Bloch functions

$$
\Psi_n(\vec{r}, \vec{K}) = \sum_\mu a_{\mu n}(\vec{K})\psi_\mu(\vec{r}, \vec{K}) \tag{3}
$$

which are expanded in terms of real spherical Gaussian-type functions

$$
\psi_\mu(\vec{r}, \vec{K}) = \sum_{\vec{g}} \phi_\mu(\vec{r} - \vec{A}_\mu - \vec{g})e^{i\vec{K}\vec{g}} . \tag{4}
$$

The spin-free density matrix in reciprocal space is defined as

$$
P_{\mu v}(\vec{K}) = 2 \sum_n a_{\mu n}(\vec{K})a_{vn}^*(\vec{K})\Theta\left[\epsilon_F - \epsilon_n(\vec{K})\right] , \tag{5}
$$

with the Fermi energy $\epsilon_F$ and the Heaviside function $\Theta$. In the case of unrestricted Hartree–Fock [21], we use the notation

$$
\Psi_n^\uparrow(\vec{r}, \vec{K}) = \sum_\mu a_{\mu n}^\uparrow(\vec{K})\psi_\mu(\vec{r}, \vec{K}) \tag{6}
$$

$$
\Psi_n^\downarrow(\vec{r}, \vec{K}) = \sum_\mu a_{\mu n}^\downarrow(\vec{K})\psi_\mu(\vec{r}, \vec{K}) \tag{7}
$$

for the crystalline orbitals with up and down spin, respectively. We define the density matrices for spin up and spin down as follows:

$$
P_{\mu v}^\uparrow(\vec{K}) = \sum_n a_{\mu n}^\uparrow(\vec{K})a_{vn}^{*\uparrow}(\vec{K})\Theta\left[\epsilon_F - \epsilon_n^\uparrow(\vec{K})\right] \tag{8}
$$

and

$$
P_{\mu v}^\downarrow(\vec{K}) = \sum_n a_{\mu n}^\downarrow(\vec{K})a_{vn}^{*\downarrow}(\vec{K})\Theta\left[\epsilon_F - \epsilon_n^\downarrow(\vec{K})\right] . \tag{9}
$$

In the following, $P_{\mu v}$ refers to the sum $P_{\mu v}^\uparrow + P_{\mu v}^\downarrow$ in the UHF case. The density matrices in real space, $P_{\mu 0 v\vec{g}}, P_{\mu 0 v\vec{g}}^\uparrow$, and $P_{\mu 0 v\vec{g}}^\downarrow$, are obtained by Fourier transformation of the corresponding reciprocal space quantity.

## 3 Integrals and their derivatives

### 3.1 Nuclear–nuclear repulsion energy

The Ewald energy of the nuclear repulsion $E^{NN}$ is obtained as

$$
E^{NN} = \frac{1}{2} \sum_{a,b} Z_a Z_b \Phi(\vec{A}_b - \vec{A}_a) = \frac{1}{2} \sum_{a,b} Z_a Z_b \left[ -\frac{\pi}{\gamma V} \right.
$$

$$
+ \sum_{\vec{h}}' \frac{1 - \text{erf}(\sqrt{\gamma}|\vec{A}_b - \vec{A}_a - \vec{h}|)}{|\vec{A}_b - \vec{A}_a - \vec{h}|} + \frac{4\pi}{V} \sum_{\vec{K}}' \frac{1}{\vec{K}^2} \exp
$$

$$
\left. \times \left( -\frac{\vec{K}^2}{4\gamma} + i\vec{K}(\vec{A}_b - \vec{A}_a) \right) \right] , \tag{10}
$$

with the nuclear charge $Z_a$, and $\Phi(\vec{r} - \vec{A}_a)$ being the Ewald potential function $\Phi$, as defined in Ref. [22]:

$$\Phi(\vec{r}-\vec{A}_a) = -\frac{\pi}{\gamma V} + \sum_{\vec{h}}' \frac{1-\mathrm{erf}(\sqrt{\gamma}|\vec{r}-\vec{A}_a-\vec{h}|)}{|\vec{r}-\vec{A}_a-\vec{h}|}$$

$$+\frac{4\pi}{V}\sum_{\vec{K}}' \frac{1}{\vec{K}^2}\exp\left(-\frac{\vec{K}^2}{4\gamma}+i\vec{K}(\vec{r}-\vec{A}_a)\right)$$

$$= -\frac{\pi}{\gamma V} + \sum_{\vec{h}}' \Phi_{\vec{h}}(\vec{r}-\vec{A}_a) + \sum_{\vec{K}}' \Phi_{\vec{K}}(\vec{r}-\vec{A}_a) \ . \quad (11)$$

$\vec{h}$ are the direct lattice vectors, $\vec{K}$ the reciprocal lattice vectors, $V$ is the volume and $\gamma$ is a screening parameter which was optimized [22] to be $\gamma = (2.8/V^{1/3})^2$, in the three-dimensional case. 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 is defined as

$$\mathrm{erf}(p) = \frac{2}{\sqrt{\pi}}\int_0^p \exp(-u^2)\mathrm{d}u \ . \quad (12)$$

We consider the Ewald potential as being dependent on the variables $\vec{A}_c$, $\vec{h}$, $V$, $\gamma$ and $\vec{K}$. The derivative with respect to the cell parameters thus requires derivatives with respect to the centers $\vec{A}_c$ and the lattice vectors $\vec{h}$ which are similar to the nuclear gradients and have to be multiplied with a trivial factor. In addition, the Ewald potential depends on the cell parameters $a_{ij}$ through the volume $V$, the screening parameter $\gamma$, and the reciprocal lattice vectors $\vec{K}$. We obtain

$$\frac{\partial E^{\mathrm{NN}}}{\partial a_{ij}} = \sum_{c,t}\frac{\partial E^{\mathrm{NN}}}{\partial A_{c,t}}\frac{\partial A_{c,t}}{\partial a_{ij}} + \sum_{\vec{h}}'\sum_t \frac{\partial E^{\mathrm{NN}}}{\partial h_t}\frac{\partial h_t}{\partial a_{ij}}$$

$$+\frac{\partial E^{\mathrm{NN}}}{\partial V}\frac{\partial V}{\partial a_{ij}} + \frac{\partial E^{\mathrm{NN}}}{\partial \gamma}\frac{\partial \gamma}{\partial a_{ij}} + \sum_{\vec{K}}'\sum_t \frac{\partial E^{\mathrm{NN}}}{\partial K_t}\frac{\partial K_t}{\partial a_{ij}}$$

$$= \sum_c \frac{\partial E^{\mathrm{NN}}}{\partial A_{c,j}}f_{c,i} + \sum_{\vec{h}}' \frac{\partial E^{\mathrm{NN}}}{\partial h_j}n_{\vec{h},i}$$

$$+\frac{\partial E^{\mathrm{NN}}}{\partial V}\frac{\partial V}{\partial a_{ij}} + \frac{\partial E^{\mathrm{NN}}}{\partial \gamma}\frac{\partial \gamma}{\partial a_{ij}} + \sum_{\vec{K}}'\sum_t \frac{\partial E^{\mathrm{NN}}}{\partial K_t}\frac{\partial K_t}{\partial a_{ij}} \quad (13)$$

$K_t$, with $t = 1,2,3$, are the components $K_1 = K_x$, $K_2 = K_y$ and $K_3 = K_z$ of $\vec{K}$. The derivatives of the parameters $V$, $\gamma$ and $\vec{K}$ with respect to $a_{ij}$ are straightforward:

### 3.1.1 Derivative of the volume

The volume is obtained as the cross product of the cell parameters: $V = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$. Thus, the derivatives $\frac{\partial V}{\partial a_{ij}}$, are, for example, obtained as

$$\frac{\partial V}{\partial a_{1x}} = a_{2y}a_{3z} - a_{2z}a_{3y}, \quad (14)$$

$$\frac{\partial V}{\partial a_{1y}} = a_{2z}a_{3x} - a_{2x}a_{3z}, \quad (15)$$

$$\frac{\partial V}{\partial a_{2x}} = a_{3y}a_{1z} - a_{3z}a_{1y}. \quad (16)$$

The remaining components can easily be obtained by cyclic permutation: $1 \to 2, 2 \to 3, 3 \to 1$, or $x \to y$, $y \to z, z \to x$.

### 3.1.2 Derivative of the screening parameter

The derivative is straightforward:

$$\frac{\partial \gamma}{\partial a_{ij}} = \frac{\partial \gamma}{\partial V}\frac{\partial V}{\partial a_{ij}} = -\frac{2\gamma}{3V}\frac{\partial V}{\partial a_{ij}} \ . \quad (17)$$

### 3.1.3 Derivative of the reciprocal lattice vectors

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

$$\vec{K} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3 \ , \quad (18)$$

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

$$\vec{b}_1 = \frac{2\pi}{V}\vec{a}_2 \times \vec{a}_3 \ ; \vec{b}_2 = \frac{2\pi}{V}\vec{a}_3 \times \vec{a}_1 \ ; \vec{b}_3 = \frac{2\pi}{V}\vec{a}_1 \times \vec{a}_2 \ . \quad (19)$$

We thus need to evaluate the derivatives of the vectors $\vec{b}_i$ with respect to the cell parameters. A few examples are given as follows:

$$\frac{\partial \vec{b}_1}{\partial a_{1x}} = \frac{\partial}{\partial a_{1x}}\left[\frac{2\pi}{V}\begin{pmatrix} a_{2y}a_{3z} - a_{3y}a_{2z} \\ a_{2z}a_{3x} - a_{3z}a_{2x} \\ a_{2x}a_{3y} - a_{3x}a_{2y} \end{pmatrix}\right] \quad (20)$$

and thus

$$\frac{\partial \vec{b}_1}{\partial a_{1x}} = -\frac{\partial V}{\partial a_{1x}}\frac{\vec{b}_1}{V} \quad (21)$$

or

$$\frac{\partial \vec{b}_1}{\partial a_{2x}} = -\frac{\partial V}{\partial a_{2x}}\frac{\vec{b}_1}{V} + \frac{2\pi}{V}\begin{pmatrix} 0 \\ -a_{3z} \\ a_{3y} \end{pmatrix} \quad (22)$$

or

$$\frac{\partial \vec{b}_2}{\partial a_{1x}} = -\frac{\partial V}{\partial a_{1x}}\frac{\vec{b}_2}{V} + \frac{2\pi}{V}\begin{pmatrix} 0 \\ a_{3z} \\ -a_{3y} \end{pmatrix} \ . \quad (23)$$

Again, all the other derivatives can be obtained by cyclic permutation. The individual derivatives are thus

$$\frac{\partial E^{\mathrm{NN}}}{\partial V} = \frac{1}{2}\sum_{a,b}Z_aZ_b\left[\frac{\pi}{\gamma V^2} - \frac{4\pi}{V^2}\sum_{\vec{K}}'\frac{1}{\vec{K}^2}\exp\right.$$

$$\left. \times\left(-\frac{\vec{K}^2}{4\gamma}+i\vec{K}(\vec{A}_b - \vec{A}_a)\right)\right] \ , \quad (24)$$

$$\frac{\partial E^{\mathrm{NN}}}{\partial \gamma} = \frac{1}{2}\sum_{a,b}Z_aZ_b\left[\frac{\pi}{\gamma^2 V} - \sum_{\vec{h}}'\frac{1}{\sqrt{\pi\gamma}}\exp(-\gamma(\vec{A}_b - \vec{A}_a - \vec{h})^2).\right.$$

$$\left. +\frac{\pi}{\gamma^2 V}\sum_{\vec{K}}'\exp\left(-\frac{\vec{K}^2}{4\gamma}+i\vec{K}(\vec{A}_b - \vec{A}_a)\right)\right] \quad (25)$$

and

$$
\frac{\partial E^{\mathrm{NN}}}{\partial K_t} = \frac{1}{2} \sum_{a,b} Z_a Z_b \frac{4\pi}{V} \left[ \frac{-2K_t}{(\vec{K}^2)^2} \right.
$$
$$
\left. + \frac{1}{\vec{K}^2} \left( -\frac{K_t}{2\gamma} + i(A_{b,t} - A_{a,t}) \right) \right]
$$
$$
\times \exp\left[ -\frac{\vec{K}^2}{4\gamma} + i\vec{K}(\vec{A}_b - \vec{A}_a) \right] . \tag{26}
$$

The partial derivative with respect to the nuclear positions is just the nuclear gradient which is already available in the code:

$$
\frac{\partial E^{\mathrm{NN}}}{\partial A_{c,t}} = \frac{1}{2} \sum_a Z_a Z_c \left( 2 \sum_{\vec{h}}{}' (A_{c,t} - A_{a,t} - h_t) \right.
$$
$$
\times \left( -\frac{1 - \mathrm{erf}(\sqrt{\gamma}|\vec{A}_c - \vec{A}_a - \vec{h}|)}{|\vec{A}_c - \vec{A}_a - \vec{h}|^3} \right.
$$
$$
\left. - \frac{2\sqrt{\gamma}}{\sqrt{\pi}} \frac{\exp(-\gamma(\vec{A}_c - \vec{A}_a - \vec{h})^2)}{|\vec{A}_c - \vec{A}_a - \vec{h}|^2} \right)
$$
$$
+ \frac{4\pi}{V} \sum_{\vec{K}}{}' \frac{iK_t}{\vec{K}^2} \exp\left( -\frac{\vec{K}^2}{4\gamma} \right)
$$
$$
\times \left\{ \exp\left[ i\vec{K}(\vec{A}_c - \vec{A}_a) \right] \right.
$$
$$
\left. \left. - \exp\left[ -i\vec{K}(\vec{A}_c - \vec{A}_a) \right] \right\} \right) . \tag{27}
$$

The derivatives with respect to the direct lattice vectors $\vec{h}$ are obtained as

$$
\frac{\partial E^{\mathrm{NN}}}{\partial h_t} = \frac{1}{2} \sum_{a,b} Z_a Z_b (A_{b,t} - A_{a,t} - h_t)
$$
$$
\times \left( \frac{1 - \mathrm{erf}(\sqrt{\gamma}|\vec{A}_b - \vec{A}_a - \vec{h}|)}{|\vec{A}_b - \vec{A}_a - \vec{h}|^3} \right.
$$
$$
\left. + \frac{2\sqrt{\gamma}}{\sqrt{\pi}} \frac{\exp(-\gamma(\vec{A}_b - \vec{A}_a - \vec{h})^2)}{|\vec{A}_b - \vec{A}_a - \vec{h}|^2} \right) . \tag{28}
$$

## 3.2 Overlap integral

The fundamental integral is the overlap integral. It is defined as

$$
S_{\mu\vec{0}v\vec{g}} = \int \phi_\mu(\vec{r} - \vec{A}_\mu) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \mathrm{d}^3\mathrm{r}. \tag{29}
$$

Its derivative with respect to the cell parameters $a_{ij}$ is thus

$$
\frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}} = \sum_{t=1}^3 \left( \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,t}} \frac{\partial A_{\mu,t}}{\partial a_{ij}} + \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial (A_{v,t} + g_t)} \frac{\partial (A_{v,t} + g_t)}{\partial a_{ij}} \right) \tag{30}
$$

where $t$ represents the summation over $x, y, z$. Exploiting translational invariance, we obtain

$$
\frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}} = \sum_{t=1}^3 \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,t}} \left( \frac{\partial A_{\mu,t}}{\partial a_{ij}} - \frac{\partial (A_{v,t} + g_t)}{\partial a_{ij}} \right)
$$
$$
= \sum_{t=1}^3 \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,t}} \left( f_{\mu,i} - f_{v,i} - n_{\vec{g},i} \right) \delta_{jt}
$$
$$
= \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}} \left( f_{\mu,i} - f_{v,i} - n_{\vec{g},i} \right) . \tag{31}
$$

The derivative $\frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}}$ is identical to the one which is required for the calculation of the gradient with respect to nuclear positions and thus it only needs to be multiplied with a trivial factor to obtain the derivative with respect to the cell parameters.

## 3.3 Kinetic energy integrals

The evaluation of the kinetic energy integrals leads to a combination of overlap integrals:

$$
T_{\mu\vec{0}v\vec{g}} = \int \phi_\mu(\vec{r} - \vec{A}_\mu) \left( -\frac{1}{2} \Delta_{\vec{r}} \right) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \mathrm{d}^3\mathrm{r} . \tag{32}
$$

When computing the derivatives with respect to the cell parameters, we thus obtain in complete analogy to Eq. (31)

$$
\frac{\partial T_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}} = \frac{\partial T_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}} \left( f_{\mu,i} - f_{v,i} - n_{\vec{g},i} \right) . \tag{33}
$$

## 3.4 Nuclear attraction integrals

The nuclear attraction integrals are defined as

$$
N_{\mu\vec{0}v\vec{g}} = -\sum_a Z_a \int \phi_\mu(\vec{r} - \vec{A}_\mu) \Phi(\vec{r} - \vec{A}_a) \phi_v
$$
$$
\times (\vec{r} - \vec{A}_v - \vec{g}) \mathrm{d}^3\mathrm{r} . \tag{34}
$$

This has been explicitly evaluated in reference Ref. [22]. The derivative with respect to the cell parameters consists now of the following contributions: there are derivatives with respect to three centers $\vec{A}_\mu$, $\vec{A}_v + \vec{g}$ and $\vec{A}_a$. Similar to the nuclear–nuclear repulsion, derivatives with respect to $V$, $\gamma$ and $\vec{K}$ are required. These derivatives are similar to the ones appearing when evaluating the nuclear–nuclear gradient.

The derivatives with respect to the direct lattice vectors can again be obtained by using the nuclear gradients, and the rule

$$
\sum_{t=1}^3 \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,t}} \frac{\partial A_{\mu,t}}{a_{ij}} = \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}} f_{\mu,i} . \tag{35}
$$

The part of the derivative coming from the center $(\vec{A}_v + \vec{g})$ is obtained in the same way, and the derivative with respect to $\vec{A}_a$ in $\Phi(\vec{r} - \vec{A}_a)$ is obtained from translational invariance. All these nuclear gradients simply need to be multiplied with the proper factors, for $\vec{A}_\mu$, $\vec{A}_v + \vec{g}$ and $\vec{A}_a$.

We can thus view the nuclear attraction integrals $N_{\mu\vec{0}v\vec{g}}$ as a function of the variables $\vec{A}_\mu$, $\vec{A}_v + \vec{g}$, $\vec{A}_a$, $\vec{h}$, $V$, $\gamma$ and $\vec{K}$. As a whole, we obtain therefore for the derivative

$$\frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}} = \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}} f_{\mu,i} + \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial A_{v,j}} (f_{v,i} + n_{\vec{g},i})$$

$$- \left( \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}} + \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial A_{v,j}} \right) f_{a,i} - Z_a \sum_{\vec{h}}' \int$$

$$\times \phi_\mu(\vec{r} - \vec{A}_\mu) \frac{\partial \Phi_{\vec{h}}(\vec{r} - \vec{A}_a)}{\partial h_j} n_{\vec{h},i} \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \mathrm{d}^3\mathrm{r}$$

$$+ \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial V} \frac{\partial V}{\partial a_{ij}} + \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial \gamma} \frac{\partial \gamma}{\partial a_{ij}}$$

$$+ \sum_{\vec{k}}' \sum_t \frac{\partial N_{\mu\vec{0}v\vec{g}}}{\partial K_t} \frac{\partial K_t}{\partial a_{ij}} \quad . \tag{36}$$

Translational invariance can be exploited for the following contribution:

$$\int \phi_\mu(\vec{r} - \vec{A}_\mu) \frac{\partial \Phi_{\vec{h}}(\vec{r} - \vec{A}_a)}{\partial h_j} n_{\vec{h},i} \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \mathrm{d}^3\mathrm{r}$$

$$= - \int \frac{\partial \phi_\mu(\vec{r} - \vec{A}_\mu)}{\partial A_{\mu,j}} \Phi_{\vec{h}}(\vec{r} - \vec{A}_a) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) n_{\vec{h},i} \mathrm{d}^3\mathrm{r}$$

$$- \int \phi_\mu(\vec{r} - \vec{A}_\mu) \Phi_{\vec{h}}(\vec{r} - \vec{A}_a)$$

$$\times \frac{\partial \phi_v(\vec{r} - \vec{A}_v - \vec{g})}{\partial A_{v,j}} n_{\vec{h},i} \mathrm{d}^3\mathrm{r} \quad . \tag{37}$$

### 3.5 Multipolar integrals

In the expression of the total energy, a term with a factor

$$\eta_l^m(\rho_c; \vec{A}_c) = \int \rho_c(\vec{r}) X_l^m(\vec{r} - \vec{A}_c) \mathrm{d}^3\mathrm{r} \tag{38}$$

appears, with $X_l^m$ being regular solid harmonics [22]. The charge $\rho_c(\vec{r})$ is defined as

$$\rho_c(\vec{r}) = - \sum_{\vec{g}, \mu \in c, v} P_{v\vec{g}\mu\vec{0}} \phi_\mu(\vec{r} - \vec{A}_\mu) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \quad . \tag{39}$$

The expression which needs to be differentiated has the structure

$$I_{l\mu\vec{0}v\vec{g}}^m = \int \phi_\mu(\vec{r} - \vec{A}_\mu) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) X_l^m(\vec{r} - \vec{A}_\mu) \mathrm{d}^3\mathrm{r} \quad . \tag{40}$$

We can thus also write

$$\eta_l^m(\rho_c; \vec{A}_c) = - \sum_{\vec{g}, \mu \in c, v} P_{v\vec{g}\mu\vec{0}} I_{l\mu\vec{0}v\vec{g}}^m \quad . \tag{41}$$

When computing the derivative with respect to the cell parameter, this derivative is required for the expression $I_{l\mu\vec{0}v\vec{g}}^m$. The only dependence on the cell parameter is via the nuclear coordinates $\vec{A}_\mu$ and $\vec{A}_v + \vec{g}$. Thus, the derivative with respect to the cell parameters $a_{ij}$ is obtained as

$$\frac{\partial I_{l\mu\vec{0}v\vec{g}}^m}{\partial a_{ij}} = \frac{\partial I_{l\mu\vec{0}v\vec{g}}^m}{\partial A_{\mu,j}} (f_{\mu,i} - f_{v,i} - n_{\vec{g},i}) \quad . \tag{42}$$

### 3.6 Field integrals

The field integrals are defined as

$$M_{l\mu\vec{0}v\vec{g}c}^m = Z_l^m(\hat{\vec{A}}_c) \int \phi_\mu(\vec{r} - \vec{A}_\mu) \phi_v(\vec{r} - \vec{A}_v - \vec{g})$$

$$\times \left[ \Phi(\vec{r} - \vec{A}_c) - \sum_{\vec{h}}^{\text{pen}} \frac{1}{|\vec{r} - \vec{A}_c - \vec{h}|} \right] \mathrm{d}^3\mathrm{r} \quad , \tag{43}$$

with $Z_l^m(\hat{\vec{A}}_c)$ being the spherical gradient operator [22]. The penetration depth pen is a certain threshold for which the integrals are evaluated exactly [22, 23].

Similar to the nuclear attraction integrals, this integral also requires derivatives with respect to $\vec{A}_\mu$, $\vec{A}_v + \vec{g}$ and $\vec{A}_c$, $\vec{h}$ and the derivatives with respect to $V$, $\gamma$ and $\vec{K}$ because of the Ewald potential. The derivatives with respect to $\vec{A}_\mu$ and $\vec{A}_v + \vec{g}$ are already available, and the derivatives with respect to $\vec{A}_c$ are obtained from translational invariance. We obtain

$$\frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial a_{ij}} = \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial A_{\mu,j}} f_{\mu,i} + \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial A_{v,j}} (f_{v,i} + n_{\vec{g},i})$$

$$- \left( \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial A_{\mu,j}} + \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial A_{v,j}} \right) f_{c,i} + Z_l^m(\hat{\vec{A}}_c)$$

$$\times \int \phi_\mu(\vec{r} - \vec{A}_\mu) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \left( \sum_{\vec{h}}' \frac{\partial \Phi_{\vec{h}}(\vec{r} - \vec{A}_c)}{\partial h_j} n_{\vec{h},i} \right.$$

$$- \sum_{\vec{h}}^{\text{pen}} \frac{\partial}{\partial h_j} \frac{1}{|\vec{r} - \vec{A}_c - \vec{h}|} n_{\vec{h},i} \right) \mathrm{d}^3\mathrm{r}$$

$$+ \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial V} \frac{\partial V}{a_{ij}} + \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial \gamma} \frac{\partial \gamma}{\partial a_{ij}}$$

$$+ \sum_{\vec{k}}' \sum_t \frac{\partial M_{l\mu\vec{0}v\vec{g}c}^m}{\partial K_t} \frac{\partial K_t}{\partial a_{ij}} \quad . \tag{44}$$

Similar to the nuclear attraction integrals, we can exploit translational invariance:

$$\int \phi_\mu(\vec{r} - \vec{A}_\mu) \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \frac{\partial \Phi_{\vec{h}}(\vec{r} - \vec{A}_c)}{\partial h_j} n_{\vec{h},i} \mathrm{d}^3\mathrm{r}$$

$$= - \int \frac{\partial \phi_\mu(\vec{r} - \vec{A}_\mu)}{\partial A_{\mu,j}} \phi_v(\vec{r} - \vec{A}_v - \vec{g}) \Phi_{\vec{h}}(\vec{r} - \vec{A}_c) n_{\vec{h},i} \mathrm{d}^3\mathrm{r}$$

$$- \int \phi_\mu(\vec{r} - \vec{A}_\mu) \frac{\partial \phi_v(\vec{r} - \vec{A}_v - \vec{g})}{\partial A_{v,j}} \Phi_{\vec{h}}(\vec{r} - \vec{A}_c) n_{\vec{h},i} \mathrm{d}^3\mathrm{r}$$

$$\tag{45}$$

and

$$\int \phi_\mu(\vec{r}-\vec{A}_\mu)\phi_v(\vec{r}-\vec{A}_v-\vec{g})\frac{\partial}{\partial h_j}\frac{1}{|\vec{r}-\vec{A}_c-\vec{h}|}n_{\vec{h},i}\mathrm{d}^3\mathrm{r}$$

$$= -\int \frac{\partial\phi_\mu(\vec{r}-\vec{A}_\mu)}{\partial A_{\mu,j}}\phi_v(\vec{r}-\vec{A}_v-\vec{g})\frac{1}{|\vec{r}-\vec{A}_c-\vec{h}|}n_{\vec{h},i}\mathrm{d}^3\mathrm{r}$$

$$- \int \phi_\mu(\vec{r}-\vec{A}_\mu)\frac{\partial\phi_v(\vec{r}-\vec{A}_v-\vec{g})}{\partial A_{v,j}}$$

$$\times \frac{1}{|\vec{r}-\vec{A}_c-\vec{h}|}n_{\vec{h},i}\mathrm{d}^3\mathrm{r} \ . \tag{46}$$

### 3.7 Spheropole

The spheropole is a correction required because the charge distribution is approximated by a model charge distribution in the long range [22].

$$Q = \sum_c Q_c = \sum_c \frac{2\pi}{3V}\int[\rho_c(\vec{r})-\rho_c^{\mathrm{model}}(\vec{r})]|\vec{r}|^2\mathrm{d}^3\mathrm{r}$$

$$= \frac{2\pi}{3V}\sum_c\sum_{\mu\in cv\vec{g}}P_{v\vec{g}\mu\vec{0}}\int\Big[-\phi_\mu(\vec{r}-\vec{A}_\mu)\phi_v(\vec{r}-\vec{A}_v-\vec{g})$$

$$+ \int \phi_\mu(\vec{r}'-\vec{A}_\mu)\phi_v(\vec{r}'-\vec{A}_v-\vec{g})$$

$$\times X_l^m(\vec{r}'-\vec{A}_\mu)\mathrm{d}^3\mathrm{r}'\delta_l^m(\vec{A}_\mu,\vec{r})\Big]|\vec{r}|^2\mathrm{d}^3\mathrm{r} \ . \tag{47}$$

$\delta_l^m(\vec{A}_c,\vec{r})$ is a Gaussian representation of a unit point multipole [22].

There are thus dependencies on $\vec{A}_\mu$, $\vec{A}_v+\vec{g}$ and the volume $V$. We need to compute

$$\sum_c\sum_{\mu\in cv\vec{g}}P_{v\vec{g}\mu\vec{0}}\frac{\partial}{\partial a_{ij}}\frac{2\pi}{3V}\int\Big[-\phi_\mu(\vec{r}-\vec{A}_\mu)\phi_v(\vec{r}-\vec{A}_v-\vec{g})$$

$$+ \int \phi_\mu(\vec{r}'-\vec{A}_\mu)\phi_v(\vec{r}'-\vec{A}_v-\vec{g})X_l^m(\vec{r}'-\vec{A}_\mu)\mathrm{d}^3\mathrm{r}'\delta_l^m(\vec{A}_\mu,\vec{r})\Big]$$

$$\times |\vec{r}|^2\mathrm{d}^3\mathrm{r} = \sum_c\sum_{\mu\in cv\vec{g}}P_{v\vec{g}\mu\vec{0}}\frac{2\pi}{3V}\frac{\partial}{\partial A_{\mu,j}}\int\Big[-\phi_\mu(\vec{r}-\vec{A}_\mu)$$

$$\times \phi_v(\vec{r}-\vec{A}_v-\vec{g}) + \int \phi_\mu(\vec{r}'-\vec{A}_\mu)\phi_v(\vec{r}'-\vec{A}_v-\vec{g})$$

$$\times X_l^m(\vec{r}'-\vec{A}_\mu)\mathrm{d}^3\mathrm{r}'\delta_l^m(\vec{A}_\mu,\vec{r})\Big]|\vec{r}|^2\mathrm{d}^3\mathrm{r}$$

$$\times (f_{\mu,i}-f_{v,i}-n_{\vec{g},i}) - \frac{Q}{V}\frac{\partial V}{\partial a_{ij}} \ . \tag{48}$$

### 3.8 Bielectronic integrals

These are integrals of the type

$$B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}}$$

$$= \int \frac{\phi_\mu(\vec{r}-\vec{A}_\mu)\phi_v(\vec{r}-\vec{A}_v-\vec{g})\phi_\tau(\vec{r}'-\vec{A}_\tau-\vec{n})\phi_\sigma(\vec{r}'-\vec{A}_\sigma-\vec{n}-\vec{h})}{|\vec{r}-\vec{r}'|}$$

$$\times \mathrm{d}^3\mathrm{r}\mathrm{d}^3\mathrm{r}' . \tag{49}$$

The derivative with respect to the cell parameters $a_{ij}$ is straightforward, as the only dependence on the cell parameter is via the position of the centers and thus the nuclear gradients only need to be multiplied with a factor:

$$\frac{\partial B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}}}{\partial a_{ij}} = \frac{\partial B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}}}{\partial A_{\mu,j}}f_{\mu,i} + \frac{\partial B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}}}{\partial A_{v,j}}(f_{v,i}+n_{\vec{g},i})$$

$$+ \frac{\partial B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}}}{\partial A_{\tau,j}}(f_{\tau,i}+n_{\vec{n},i}) + \frac{\partial B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}}}{\partial A_{\sigma,j}}$$

$$\times (f_{\sigma,i}+n_{\vec{n},i}+n_{\vec{h},i}) \ . \tag{50}$$

As in Ref. [19], we define a Coulomb integral as

$$C_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}} = \sum_{\vec{n}}^{\mathrm{pen}} B_{\mu\vec{0}v\vec{g}\tau\vec{n}\sigma\vec{n}+\vec{h}} \tag{51}$$

and an exchange integral as

$$X_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}} = \sum_{\vec{n}} B_{\mu\vec{0}\tau\vec{n}v\vec{g}\sigma\vec{n}+\vec{h}} \ . \tag{52}$$

Using this notation, one summation over the lattice vectors is already included.

### 3.9 Energy-weighted density matrix

The contributions of the energy-weighted density matrix to the derivative with respect to $a_{ij}$

$$\frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial\vec{A}_i}\int_{\mathrm{BZ}}\exp(\mathrm{i}\vec{K}\vec{g})\sum_j\{a_{vj}^\uparrow(\vec{K})a_{\mu j}^{*\uparrow}(\vec{K})\Big[\epsilon_j^\uparrow(\vec{K})+Q\Big]$$

$$\times \Theta\Big[\epsilon_F-\epsilon_j^\uparrow(\vec{K})-Q\Big] + a_{vj}^\downarrow(\vec{K})a_{\mu j}^{*\downarrow}(\vec{K})\Big[\epsilon_j^\downarrow(\vec{K})+Q\Big]$$

$$\times \Theta\Big[\epsilon_F-\epsilon_j^\downarrow(\vec{K})-Q\Big]\}\mathrm{d}^3\mathrm{k} = \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial\vec{A}_i}\int_{\mathrm{BZ}}\cdots \tag{53}$$

require a different prefactor, compared with the case of the gradients with respect to nuclear positions:

$$\frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}}\int_{\mathrm{BZ}}\cdots = \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial A_{\mu,j}}(f_{\mu,i}-f_{v,i}-n_{\vec{g},i})\int_{\mathrm{BZ}}\cdots \tag{54}$$

## 4 Total energy and gradient

### 4.1 Total energy

The total energy, in the notation of Ref. [19], is obtained as follows:

$$E^{\mathrm{total}} = E^{\mathrm{kinetic}} + E^{\mathrm{NN}} + E^{\mathrm{Coul-nuc}} + E^{\mathrm{Coul-el}} + E^{\mathrm{exch-el}}$$

$$= \sum_{a,b}Z_aZ_b\Phi(\vec{A}_b-\vec{A}_a) + \sum_{\vec{g},\mu,v}P_{v\vec{g}\mu\vec{0}}T_{\mu\vec{0}v\vec{g}}$$

$$- \sum_{\vec{g},\mu,v}P_{v\vec{g}\mu\vec{0}}\sum_aZ_a\int\phi_\mu(\vec{r}-\vec{A}_\mu)\phi_v(\vec{r}-\vec{A}_v-\vec{g})\Phi(\vec{r}-\vec{A}_a)\mathrm{d}^3\mathrm{r}$$

$$+ \frac{1}{2}\sum_{\vec{g},\mu,v}P_{v\vec{g}\mu\vec{0}}\Big[-QS_{\mu\vec{0}v\vec{g}} + \sum_{\vec{h},\tau,\sigma}P_{\sigma\vec{h}\tau\vec{0}}C_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}}$$

$$-\sum_c \sum_{l=0}^{L} \sum_{m=-l}^{l} \eta_l^m(\rho_c; \vec{A}_c) M_{l\mu\vec{0}v\vec{g}c}^m \Bigg]$$

$$-\frac{1}{2}\sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}}^{\uparrow} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}}^{\uparrow} X_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}}$$

$$-\frac{1}{2}\sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}}^{\downarrow} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}}^{\downarrow} X_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}} . \tag{55}$$

## 4.2 Gradient of the total energy

The gradient with respect to the cell parameter is a combination of the nuclear gradients, with appropriate factors, and new derivatives with respect to parameters such as $V$, $\gamma$ and $\vec{K}$ and their derivatives with respect to the cell parameters.

$$F_{a_{ij}} = -\frac{\partial E^{\text{total}}}{\partial a_{ij}} = -\frac{\partial E^{\text{NN}}}{\partial a_{ij}} - \sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}} \frac{\partial T_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}}$$

$$-\sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}} \frac{\partial N_{\mu\vec{0}v\vec{g}}}{a_{ij}} - \frac{1}{2}\sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}} \Bigg\{ -S_{\mu\vec{0}v\vec{g}} \sum_c$$

$$\times \sum_{\vec{h},\sigma,\tau \in c} P_{\sigma\vec{h}\tau\vec{0}} \frac{\partial}{\partial a_{ij}} \frac{2\pi}{3V} \int \Bigg[ -\phi_\tau(\vec{r} - \vec{A}_\tau)\phi_\sigma(\vec{r} - \vec{A}_\sigma - \vec{h})$$

$$+ \sum_{l=0}^{L} \sum_{m=-l}^{l} \int \phi_\tau(\vec{r}' - \vec{A}_\tau)\phi_\sigma(\vec{r}' - \vec{A}_\sigma - \vec{h})$$

$$\times X_l^m(\vec{r}' - \vec{A}_c)\mathrm{d}^3\mathrm{r}'\delta_l^m(\vec{A}_c, \vec{r}) \Bigg] r^2 \mathrm{d}^3\mathrm{r} + \sum_{\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}} \frac{\partial C_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}}}{\partial a_{ij}}$$

$$-\sum_c \sum_{l=0}^{L} \sum_{m=-l}^{l} \sum_{\vec{h},\tau \in c,\sigma} P_{\sigma\vec{h}\tau\vec{0}} \frac{\partial}{\partial a_{ij}} \Bigg[ \int \phi_\tau(\vec{r} - \vec{A}_\tau)$$

$$\times \phi_\sigma(\vec{r} - \vec{A}_\sigma - \vec{h}) X_l^m(\vec{r} - \vec{A}_c)\mathrm{d}^3\mathrm{r}\, M_{l\mu\vec{0}v\vec{g}c}^m \Bigg] \Bigg\}$$

$$+ \frac{1}{2}\sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}}^{\uparrow} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}}^{\uparrow} \frac{\partial X_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}}}{\partial a_{ij}}$$

$$+ \frac{1}{2}\sum_{\vec{g},\mu,v} P_{v\vec{g}\mu\vec{0}}^{\downarrow} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}\tau\vec{0}}^{\downarrow} \frac{\partial X_{\mu\vec{0}v\vec{g}\tau\vec{0}\sigma\vec{h}}}{\partial a_{ij}}$$

$$-\sum_{\vec{g},\mu,v} \frac{\partial S_{\mu\vec{0}v\vec{g}}}{\partial a_{ij}} \int_{\text{BZ}} \exp(i\vec{K}\vec{g})$$

$$\times \sum_n \{ a_{vn}^{\uparrow}(\vec{K}) a_{\mu n}^{*\uparrow}(\vec{K}) \Big( \epsilon_n^{\uparrow}(\vec{K}) + Q \Big) \Theta\big(\epsilon_F - \epsilon_n^{\uparrow}(\vec{K}) - Q\big)$$

$$+ a_{vn}^{\downarrow}(\vec{K}) a_{\mu n}^{*\downarrow}(\vec{K}) \Big( \epsilon_n^{\downarrow}(\vec{K}) + Q \Big)$$

$$\times \Theta\big(\epsilon_F - \epsilon_n^{\downarrow}(\vec{K}) - Q\big) \} \mathrm{d}^3\mathrm{k} . \tag{56}$$

## 5 Examples

In this section, we give some numerical examples of the accuracy of the gradients. First, we consider MgO, at a lattice constant close to the equilibrium lattice constant. Numerical and analytical gradients are compared, for various values of the ITOL parameters controlling the accuracy of the calculation of the integrals in Table 1. As was explained in Ref. [18], certain parameters (ITOL2, ITOL4 and ITOL5) can introduce an asymmetry in the evaluation of the integrals, which results in inaccuracies in the gradients. Exactly the same holds for gradients with respect to the cell parameter. The accuracy for the default parameters is about $2\times10^{-4}$ au, which should be good enough for practical purposes, and by increasing the values of these parameters, the error is reduced to $10^{-5}$ au.

Various MgO supercells from $1 \times 1 \times 1$ (i.e., with one magnesium and one oxygen atom in the primitive cell) up to $5 \times 5 \times 5$ have been considered (i.e. with 125 magnesium and 125 oxygen atoms in the primitive cell) in Table 2. The results demonstrate the high stability of the gradient when larger cells are used.

Further examples in Table 3 illustrate the accuracy of the gradients. For various systems, including magnetic ones, the analytical and the numerical gradients agree reasonably well. It is again demonstrated that increasing the ITOL -parameters leads to more accurate gradients. Also, the stability with respect to the supercell size is illustrated, for $Al_2O_3$.

The total energy and the analytical gradient are displayed, around the equilibrium structure, in Table 4. We note that in all cases, the gradient changes sign around the equilibrium: for example, for MgO, the energy has its

**Table 1.** Face-centered cubic (fcc) MgO, at a lattice constant of 4.25 Å. The accuracy of the analytical gradient as a function of the truncation parameters (ITOL parameters) is displayed. Basis sets of the size [3s2p] were used for Mg and O

| ITOL | Analytical derivative ($E_{\text{h}}/a_0$) | Numerical derivative ($E_{\text{h}}/a_0$) |
|---|---|---|
| 6  6  6  6 12 (default) | −0.012737 | −0.012555 |
| 8  8  8  8 14 | −0.012589 | −0.012533 |
| 10 10 10 10 16 | −0.012522 | −0.012471 |
| 10 10 10 16 16 | −0.012496 | −0.012482 |
| 10 12 10 16 16 | −0.012505 | −0.012503 |

**Table 2.** Fcc MgO, as in Table 1. The analytical gradient is computed as a function of the supercell size to demonstrate the numerical stability (from 2 to 250 atoms per cell). The default ITOL parameters (6 6 6 6 12) are used

| Supercell size | Total energy/ MgO unit ($E_{\text{h}}$) | Analytical derivative ($E_{\text{h}}/a_0$) |
|---|---|---|
| $1 \times 1 \times 1$ | −274.6635207 | −0.01273658 |
| $2 \times 2 \times 2$ | −274.6635204 | −0.01273664 |
| $3 \times 3 \times 3$ | −274.6635205 | −0.01273668 |
| $4 \times 4 \times 4$ | −274.6635204 | −0.01273665 |
| $5 \times 5 \times 5$ | −274.6635204 | −0.01273665 |

**Table 3.** Other examples for a comparison of analytical and numerical gradients, including ferromagnetic (*FM*) and antiferromagnetic (*AF*) states. If not stated otherwise, the default ITOL parameters are used. The basis sets are in the range from [2s1p] for H in urea up to [5s4p2d] for the transition metals

| System | Space group | Cell parameters (Å) | Component | Analytical derivative ($E_h/a_0$) | Numerical derivative ($E_h/a_0$) |
|---|---|---|---|---|---|
| $Al_2O_3$ | 167 | 4.7602, 12.9933 | $-\frac{\partial E}{a_{1x}}$ | −0.19630 ($2 \times 2 \times 2$ cell: −.19630) | −0.19625 |
| $Al_2O_3$ | 167 | 4.7602, 12.9933 | $-\frac{\partial E}{a_{1z}}$ | −0.06366 ($2 \times 2 \times 2$ cell: −.06366) | −0.06361 |
| Urea | 113 | 5.565, 4.684 | $-\frac{\partial E}{a_{1x}}$ | −0.01501 | −0.01475 |
| Urea | 113 | 5.565, 4.684 | $-\frac{\partial E}{a_{3z}}$ | −0.02495 | −0.02516 |
| NiO, FM | 225 | 4.20 | $-\frac{\partial E}{a_{1z}}$ | 0.00595 | 0.00656 |
| NiO, FM (ITOL: 10 12 10 16 16) | 225 | 4.20 | $-\frac{\partial E}{a_{1z}}$ | 0.00591 | 0.00592 |
| NiO, AF | 225 | 4.20 | $-\frac{\partial E}{a_{3z}}$ | 0.01111 | 0.01234 |
| NiO, AF (ITOL: 10 12 10 16 16) | 225 | 4.20 | $-\frac{\partial E}{a_{3z}}$ | 0.01094 | 0.01109 |
| $KMnF_3$, FM | 221 | 4.19 | $-\frac{\partial E}{a_{1x}}$ | 0.01043 | 0.01095 |

**Table 4.** Other examples for a comparison of analytical and numerical gradients. The default ITOL parameters are used

| System | Cell parameter (Å) | Energy ($E_h$) | Components ($E_h/a_0$) | Gradient |
|---|---|---|---|---|
| MgO | 4.18 | −274.664192 | $\frac{\partial}{\partial a_{3x}}$ | $8.495 \times 10^{-4}$ |
|  | 4.19 | −274.664222 |  | $8.103 \times 10^{-5}$ |
|  | 4.20 | −274.664209 |  | $-6.735 \times 10^{-4}$ |
| Urea | 5.52, 4.64 | −447.683214 | $\frac{\partial}{\partial a_{1x}}, \frac{\partial}{\partial a_{3z}}$ | $7.057 \times 10^{-4}, 1.4379 \times 10^{-3}$ |
|  | 5.53, 4.63 | −447.683158 |  | $-4.045 \times 10^{-4}, 6.1033 \times 10^{-3}$ |
|  | 5.53, 4.64 | −447.683218 |  | $-7.904 \times 10^{-4}, 6.649 \times 10^{-4}$ |
|  | 5.53, 4.65 | −447.683176 |  | $-1.1725 \times 10^{-3}, -4.7011 \times 10^{-3}$ |
|  | 5.54, 4.64 | −447.683166 |  | $-2.2707 \times 10^{-3}, -1.010 \times 10^{-4}$ |
| $KMnF_3$ | 4.28 | −2047.643166 | $\frac{\partial}{\partial a_{1x}}$ | $4.098 \times 10^{-4}$ |
|  | 4.29 | −2047.643181 |  | $-5.754 \times 10^{-4}$ |
|  | 4.30 | −2047.643141 |  | $-1.5369 \times 10^{-3}$ |

**Table 5.** Optimized structures, using energies or analytical gradients. The default ITOL parameters are used. For each compound, the *upper line* refers to the structure with the lowest energy, and the *lower line* to the structure with (practically) vanishing force. The components of the forces are as in Table 3

| System | Geometry (Å) | Energy ($E_h$) | Force ($E_h/a_0$) |
|---|---|---|---|
| $KMnF_3$ | 4.288 | −2047.643182 | $-3.8 \times 10^{-4}$ |
|  | 4.284 | −2047.643179 | $1.3 \times 10^{-5}$ |
| Urea | 5.525; 4.642 | −447.683224 | $-1.2 \times 10^{-4}; -2.9 \times 10^{-5}$ |
|  | 5.524; 4.642 | −447.683224 | $2.8 \times 10^{-5}; 4.8 \times 10^{-5}$ |
| $Al_2O_3$ | 4.497; 12.111 | −1401.048515 | $-4.4 \times 10^{-4}; -1.3 \times 10^{-4}$ |
|  | 4.496; 12.111 | −1401.048515 | $2.9 \times 10^{-4}; -2.2 \times 10^{-5}$ |

minimum between 4.18 and 4.20 Å, and also the analytical gradient changes its sign. Similarly, in the other systems considered, the minimum of the energy and the zero of the analytical gradient agree to 0.01 Å, at least.

This is also demonstrated in Table 5, where the geometry has been optimized according to the minimum in energy, or the vanishing of the cell gradient (i.e., the minimum of the energy was determined, up to an accuracy of 0.001 Å, and similarly, the geometry with the smallest value for the gradients was determined, up to an accuracy of 0.001 Å). It turns out that the two minima differ at most by 0.004 Å, which is probably lower than the noise by the other parameters (basis set, choice of FIXINDEX parameter [23] and so on). Note that these calculations were done with the fractional coordinates of the atoms held fixed, by simply varying the cell parameters (an automatic optimizer which optimizes the cell dimensions and the nuclear positions simultaneously, using analytical gradients, is not yet implemented in the CRYSTAL code).

Finally, the CPU times are displayed in Table 6. The calculations were performed on a single CPU of a

**Table 6.** CPU times for the various calculations. 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)

| System | Number of symmetry operators | CPU time (s) | | |
|---|---|---|---|---|
| | | Integrals | SCF | Gradients |
| MgO ($1 \times 1 \times 1$) | 48 | 2 | 0.5 | 26 |
| MgO ($2 \times 2 \times 2$) | 48 | 11 | 18 | 152 |
| MgO ($3 \times 3 \times 3$) | 48 | 55 | 500 | 533 |
| MgO ($4 \times 4 \times 4$) | 48 | 209 | 6330 | 1662 |
| MgO ($5 \times 5 \times 5$) | 48 | 670 | 57851 | 4443 |
| $Al_2O_3$ ($1 \times 1 \times 1$) | 12 | 15 | 10 | 184 |
| $Al_2O_3$ ($2 \times 2 \times 2$) | 6 | 544 | 4681 | 3877 |
| Urea | 8 | 29 | 103 | 257 |
| NiO, FM | 48 | 12 | 6 | 128 |
| NiO, AF | 12 | 32 | 220 | 346 |
| $KMnF_3$ | 48 | 27 | 20 | 281 |

Compaq ES45, with a clock rate of 1 GHz. It is probably best to compare the CPU time for the integrals with the time for the gradients, as the code is somewhat similar for these two tasks. At present, the CPU time for all the gradients (nuclear and cell gradients) is roughly 10 times the CPU time for the integrals. This ratio is expected to be the upper limit as the gradient code is not yet fully optimized. However, the calculation of numerical gradients scales with the number of parameters to be optimized, because at least one more energy point is necessary for one additional numerical derivative. Thus, if there are enough geometrical parameters, the analytical gradients should be clearly favorable.

For the MgO supercells, one can also analyze the CPU times for the integrals and the self-consistent-field procedure as a function of the system size. When dividing by the number of iterations (which is 14, 14, 15, 15 and 18 for the cells from size $1 \times 1 \times 1$ up to $5 \times 5 \times 5$), the CPU time per iteration scales roughly with the third power of the system size, which is to be expected as the diagonalization scales with this power. The integrals scale with a somewhat lower exponent (less than 2), owing to the fact that more and more of the bielectronic integrals of the larger cells are not evaluated exactly, but with the help of a multipolar expansion.

## 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 three dimensions. The implementation includes the cases of spin-restricted and unrestricted polarization. It has been shown that high accuracy can be achieved. Future developments, such as a full structural optimization with the help of analytical gradients, now become feasible.

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