Implementation of analytical Hartree-Fock gradients for periodic systems

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Abstract

We describe the implementation of analytical Hartree-Fock gradients for periodic systems in the code CRYSTAL, emphasizing the technical aspects of this task. The code is now capable of calculating analytical derivatives with respect to nuclear coordinates for systems periodic in 0, 1, 2 and 3 dimensions (i.e. molecules, polymers, slabs and solids). Both closed-shell restricted and unrestricted Hartree-Fock gradients have been implemented. A comparison with numerical derivatives shows that the forces are highly accurate.
I. INTRODUCTION

The determination of equilibrium structure is one of the most important targets in electronic structure calculations. In surface science especially, theoretical calculations of surface structures are of high importance to explain and support experimental results. Therefore, a fast structural optimization is an important issue in modern electronic structure codes. Finding minima in energy surfaces is substantially simplified by the availability of analytical gradients. As a rule of thumb, availability of analytical gradients improves the efficiency by a factor of order $N$ with $N$ being the number of parameters to be optimized. UK’s Collaborative Computational Project 3 has therefore supported the implementation of analytical gradients in the electronic structure code CRYSTAL\textsuperscript{1}. This implementation will also be valuable for future projects which require analytical gradients as a prerequisite. Another advantage of having analytical gradients is that higher derivatives can be obtained with less numerical noise (e.g. the 2nd derivative has less numerical noise when only one numerical differentiation is necessary).

CRYSTAL is capable of performing Hartree-Fock and density-functional calculations for systems with any periodicity (i.e. molecules, polymers, slabs and solids). The periodicity is ”cleanly” implemented in the sense that, for example, a slab is considered as an object periodic in two dimensions and is not repeated in the third dimension with one slab being separated from the others by vacuum layers. The code is based on Gaussian type orbitals and the technology is therefore in many parts similar to that of molecular quantum chemistry codes. As the density-functional part of the code relies in big parts on the Hartree-Fock part, the strategy of the project was to implement Hartree-Fock gradients first.

The implementation of Hartree-Fock gradients for multicenter basis sets was pioneered by Pulay\textsuperscript{5}, the theory had already been derived earlier independently\textsuperscript{6}. Meanwhile, analytical gradients have been implemented in many molecular codes, and several review articles have appeared (see, e.g., references \textsuperscript{7–13}).

Substantial work has also been done in the case of one-dimensional periodicity: Hartree-
Fock gradients with respect to nuclear coordinates and with respect to the lattice vector have already been implemented in codes periodic in one dimension. Moreover, correlated calculations based on the MP2 scheme and MP2 gradients have been coded. Also, density functional gradients have been implemented. Even second derivatives at the Hartree-Fock level have meanwhile been coded.

The implementation of Hartree-Fock gradients with respect to nuclear coordinates in CRYSTAL is to the best of our knowledge the first implementation for the case of 2- and 3-dimensional periodicity. The aim of this article is to describe the implementation of the gradients in the code, with an emphasis on the technical aspects. Therefore, the article is supposed to complement our first article on the purely theoretical aspects. An attempt of a detailed description is made; however, as the whole code is undergoing constant changes, it can not be too detailed. For example, it did not seem advisable to give any variable names because they have already undergone major changes after the code moved to Fortran 90 with the possibility of longer variable names.

The article is structured as follows: In section II, we give a brief introduction to Gaussian and Hermite Gaussian type basis functions. The definition of the density matrix is given in section III. The individual integrals, their derivatives, and details of the implementation are discussed in section IV. Formulas for total energy and gradient are given in section V. The structure of the gradient code is explained in section VI, followed by examples in section VII and the conclusion.

II. BASIS FUNCTIONS

Two sets of basis functions are relevant for CRYSTAL: firstly, unnormalized spherical Gaussian type functions, in a polar coordinate system characterized by the set of variables ($|\vec{r}|, \vartheta, \varphi$), and centered at $\vec{A}$. They are defined as

$$S(\alpha, \vec{r} - \vec{A}, n, l, m) = |\vec{r} - \vec{A}|^{2n+l} P_l^{|m|}(\cos \vartheta) \exp(im\varphi) \exp(-\alpha|\vec{r} - \vec{A}|^2)$$

(1)
with \( P_{l}^{|m|} \) being the associated Legendre function. CRYSTAL uses real spherical Gaussian type functions defined as

\[
R(\alpha, \vec{r} - \vec{A}, n, l, 0) = S(\alpha, \vec{r} - \vec{A}, n, l, 0)
\]
\[
R(\alpha, \vec{r} - \vec{A}, n, l, |m|) = \text{Re} \ S(\alpha, \vec{r} - \vec{A}, n, l, |m|)
\]
\[
R(\alpha, \vec{r} - \vec{A}, n, l, -|m|) = \text{Im} \ S(\alpha, \vec{r} - \vec{A}, n, l, |m|)
\]

This is in the following denoted as \( \phi_{\mu}(\alpha, \vec{r} - \vec{A}_{\mu}, n, l, m) = N_{\mu} R(\alpha, \vec{r} - \vec{A}_{\mu}, n, l, m) \), with the normalization \( N_{\mu} \). \( \mu \) is an index enumerating the basis functions in the reference cell (e.g. the primitive unit cell). In fact, CRYSTAL uses only basis functions with quantum number \( n = 0 \) and angular momentum \( l=0,1 \) or \( 2 \) (i.e. \( s, p \) or \( d \) functions).

The exponents are defined by the user of the code. A huge amount of basis sets for molecular calculations is available in the literature and on the world wide web; also for periodic systems a large number of basis sets has been published. Molecular basis sets can, with a little effort, be adopted for solid state calculations. High exponents which are used to describe core electrons do not have to be adjusted, but exponents with low values (e.g. less than \( 1 \ a_0^{-2} \), with \( a_0 \) being the Bohr radius) should be reoptimized for the corresponding solid. Very diffuse exponents should be omitted because they cause linear dependence problems in periodic systems.

A second type of basis functions, which CRYSTAL uses internally to evaluate the integrals, is the Hermite Gaussian type function (HGTF) which is defined as:

\[
\Lambda(\gamma, \vec{r} - \vec{A}, t, u, v) = \left( \frac{\partial}{\partial A_x} \right)^{t} \left( \frac{\partial}{\partial A_y} \right)^{u} \left( \frac{\partial}{\partial A_z} \right)^{v} \exp(-\gamma|\vec{r} - \vec{A}|^2)
\]  

CRYSTAL uses the McMurchie-Davidson algorithm to evaluate the integrals. The basic idea of this algorithm is to map the product of two spherical Gaussian type functions on two centers onto a set of Hermite Gaussian type functions at one center.

\[
S(\alpha, \vec{r} - \vec{B}, \tilde{n}, \tilde{l}, \tilde{m})S(\alpha, \vec{r} - \vec{A}, n, l, m) = \sum_{t,u,v} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v)
\]
with $\gamma = \alpha + \tilde{\alpha}$ and $\vec{P} = \frac{\alpha \vec{A} + \tilde{\alpha} \vec{B}}{\alpha + \tilde{\alpha}}$.

The starting point $E(0, 0, 0, 0, 0, 0, 0, 0) = \exp\left(-\frac{\alpha \vec{A} + \tilde{\alpha} \vec{B}}{\alpha + \tilde{\alpha}} \right)$ is derived from the Gaussian product rule:

$$\exp\left(-\alpha |\vec{r} - \vec{A}|^2\right) \exp\left(-\tilde{\alpha} |\vec{r} - \vec{B}|^2\right) = \exp\left(-\frac{\alpha \vec{A} + \tilde{\alpha} \vec{B}}{\alpha + \tilde{\alpha}} \right) \exp\left(-\frac{(\alpha + \tilde{\alpha}) |\vec{r} - \alpha \vec{A} + \tilde{\alpha} \vec{B}|^2}{(\alpha + \tilde{\alpha})^2}\right) (4)$$

As indicated in section IV, all the integrals can be expressed with the help of the coefficients $E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v)$[24-27]. These coefficients are generated by recursion relations[24, 25]. They are zero for the case $t + u + v > 2n + 2\tilde{n} + l + \tilde{l}$ and for all negative values of $t, u$ or $v$. CRYSTAL uses only basis functions with $n = 0$. Therefore, there are $(l + \tilde{l} + 1)(l + \tilde{l} + 2)(l + \tilde{l} + 3)\frac{3!}{3!}$ coefficients $E(0, \tilde{l}, \tilde{m}, 0, l, m, t, u, v)$ for fixed values of $l, m, \tilde{l}, \tilde{m}$. As the maximum angular quantum number is $l = 2$, this results in 25 possible combinations of $m$ and $\tilde{m}$. Therefore, the maximum number of coefficients is $25 \times 35 = 875$. These coefficients are pre-programmed in the subroutine DFAC3. Pre-programming is the fastest possible way of evaluating these coefficients which is important because this is one of the key issues of the integral calculation. On the other hand, the code has become inflexible as no $E$-coefficients are available for higher quantum numbers.

Derivatives of Gaussian type functions are again Gaussian type functions. Therefore, the evaluation of gradients is closely related to the evaluation of integrals. In a similar way as all the integrals can be expressed with the help of coefficients $E$, all the derivatives of the integrals can be expressed with the help of coefficients for the gradients, $G_A^x, G_A^y, G_A^z$. These $G$-coefficients can be obtained with recursion relations derived by Saunders[22]. The recursions are similar to the ones for the $E$-coefficients. However, as the existing subroutine DFAC3 cannot compute the $G$-coefficients, the recursions were newly coded. This has in addition the advantage that, by small modifications of the new subroutines, $E$-coefficients for higher quantum numbers than $l = \tilde{l} = 2$ can now be computed by recursion. There are three sets of $G$-coefficients because of the three spatial directions. The $G$-coefficients are zero for the case $t + u + v > 2n + 2\tilde{n} + l + \tilde{l} + 1$ and for all negative values of $t, u$ or $v$. This means that for a maximum quantum number of $l = 2$, there are $3 \times 5 \times 5 \times 56 = 4200$
coefficients. Three other sets of $G$-coefficients are necessary because of the second center. However, the sets on the second center are closely related to the sets on the first center and can be derived from them in an efficient way.

III. DENSITY MATRIX

After solving the Hartree-Fock equations, the crystalline orbitals are linear combinations of Bloch functions

$$\Psi_i(\vec{r}, \vec{k}) = \sum_\mu a_{\mu i}(\vec{k}) \psi_\mu(\vec{r}, \vec{k})$$ (5)

which are expanded in terms of real spherical Gaussian type functions

$$\psi_\mu(\vec{r}, \vec{k}) = N_\mu \sum_\vec{g} R(\alpha, \vec{r} - \vec{A}_\mu - \vec{g}, n, l, m) e^{i\vec{k}\vec{g}}$$ (6)

The sum over $\vec{g}$ is over all direct lattice vectors.

In the case of closed shell, spin-restricted Hartree-Fock, the spin-free density matrix in reciprocal space is defined as

$$P_{\mu\nu}(\vec{k}) = 2 \sum_i a_{\mu i}(\vec{k}) a_{\nu i}(\vec{k}) \Theta(\epsilon_F - \epsilon_i(\vec{k}))$$ (7)

with the Fermi energy $\epsilon_F$ and the Heaviside function $\Theta$; $i$ is an index enumerating the eigenvalues.

In the case of unrestricted Hartree-Fock (UHF), we use the notation

$$\Psi_i^\uparrow(\vec{r}, \vec{k}) = \sum_\mu a_{\mu i}^\uparrow(\vec{k}) \psi_\mu(\vec{r}, \vec{k})$$ (8)

and

$$\Psi_i^\downarrow(\vec{r}, \vec{k}) = \sum_\mu a_{\mu i}^\downarrow(\vec{k}) \psi_\mu(\vec{r}, \vec{k})$$ (9)

for the crystalline orbitals with up and down spin, respectively. We define the density matrices
\[ P_{\mu\nu}^+(\vec{k}) = \sum_i a^\dagger_{\mu i}(\vec{k}) a^*_{\nu i}(\vec{k}) \Theta(\epsilon_F - \epsilon_i^+(\vec{k})) \] (10)

for up spin and

\[ P_{\mu\nu}^-(\vec{k}) = \sum_i a^\dagger_{\mu i}(\vec{k}) a^*_{\nu i}(\vec{k}) \Theta(\epsilon_F - \epsilon_i^-(\vec{k})) \] (11)

for down spin. In the following, \( P_{\mu\nu} \) refers to the sum \( P_{\mu\nu}^+ + P_{\mu\nu}^- \) in the UHF case.

The density matrices in real space \( P_{\mu\nu\vec{r}}, P_{\mu\nu\vec{r}}^+ \) are obtained by Fourier transformation.

**IV. INTEGRALS AND THEIR DERIVATIVES**

The calculation of the integrals is fundamental to all quantum chemistry programs. CRYSTAL uses two integral packages: a package derived from GAUSSIAN70 is the default for calculations when only s and sp shells are used; alternatively Saunders’ ATMOL Gaussian integral package can be used and it must be used for cases when p or d functions are involved.

The implementation of gradients has been done with routines based on the ATMOL package. This is not a restriction, and it is possible to use routines based on GAUSSIAN70 for the integrals and routines based on ATMOL for the gradients.

The calculation of the integrals is essentially controlled from MONMAD and MONIRR for one-electron integrals and from SHELLC or SHELLX for the bielelectronic integrals. SHELLC is used in the case of non-direct SCF, i.e. when the integrals are written to disk and read in each cycle. SHELLX is the direct version when the integrals are computed in each cycle without storing them on disk. The direct mode is the preferred one when the integral file is too big or when input/output to disk is too slow. The gradients are computed only once after the last iteration, when convergence is achieved. Therefore, a direct implementation of gradients has been done.

One of the bottlenecks of the CRYSTAL code is the restriction to a highest quantum number of \( l = 2 \), i.e. the code can only cope with s, p, sp and d functions, but not with basis functions with higher angular momentum. Introducing gradients, however, is similar
to increasing the quantum number from $d$ to $f$ for the corresponding basis function. This means that many subroutines had to be extended to higher quantum numbers, and array dimensions in the whole code had to be adjusted.

### A. One-electron integrals

In this section we summarize the appearing types of integrals and the corresponding gradients. We restrict the description to the x-component of the gradient; y- and z-component can be obtained in similar way. Note that the integrals depend on the dimension because of the Ewald scheme used. Therefore, there are four different routines for the one-electron integrals for the case of 0,1,2 and 3-dimensional periodicity: CJAT0, CJAT1, CJAT2 and CJAT3. Similarly, four gradient routines have been developed which have been given the preliminary names CJAT0G, CJAT1G, CJAT2G and CJAT3G. These routines calculate all the one-electron integrals except for the multipolar integrals which are computed in POLIPA (with the corresponding gradient routine OLIPAG).

#### 1. Overlap integral

The basic integral is the overlap integral:

$$S_{\mu \nu \rho \sigma} = \int \phi_{\mu}(\hat{\alpha}, \vec{r} - \vec{A}_\mu - \vec{g}_1, \tilde{n}, \tilde{l}, \tilde{m})\phi_{\nu}(\alpha, \vec{r} - \vec{A}_\nu - \vec{g}_2, n, l, m) d^3r =$$

$$\int \sum_{t, u, v} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 0) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^3r = (12)$$

The x-component of the gradient with respect to center $A_\mu$ is obtained as

$$\frac{\partial}{\partial A_{\mu, x}} S_{\mu \nu \rho \sigma} =$$

$$\frac{\partial}{\partial A_{\mu, x}} \int \phi_{\mu}(\hat{\alpha}, \vec{r} - \vec{A}_\mu - \vec{g}_1, \tilde{n}, \tilde{l}, \tilde{m})\phi_{\nu}(\alpha, \vec{r} - \vec{A}_\nu - \vec{g}_2, n, l, m) d^3r =$$

$$\frac{\partial}{\partial A_{\mu, x}} \sum_{t, u, v} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^3r =$$
\[
\int \sum_{t,u,v} G_{x}^{\alpha \nu}(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r =
\]

\[
G_{x}^{\alpha \nu}(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 0) \left( \frac{\pi}{\gamma} \right)^{\frac{3}{2}}
\]

(14)

Equation (14) thus defines the coefficients \(G_{x}^{\alpha \mu}\); similarly the coefficients \(G_{y}^{\alpha \mu}, G_{z}^{\alpha \nu}, G_{y}^{\alpha \nu}, G_{z}^{\alpha \nu}\) can be defined.

In the following, we use the identity

\[
S_{\mu \tilde{\nu}, \nu \tilde{\nu}} = S_{\mu \tilde{\nu}(\tilde{\gamma} - \tilde{\gamma})} = S_{\mu \tilde{\nu} \tilde{\nu}}
\]

2. Kinetic energy integrals

In equation (15), the expression for the kinetic energy integrals for the case of spherical Gaussian type functions is reiterated.

\[
T_{\mu \tilde{\nu} \tilde{\nu}} =
\]

\[
\int \phi_{\mu}(\tilde{\alpha}, \tilde{r} - \tilde{A}_{\mu}, \tilde{n}, \tilde{l}, \tilde{m}) \left( -\frac{1}{2} \Delta r \right) \phi_{\nu}(\alpha, \vec{r} - \vec{A}_{\nu} - \tilde{g}, n, l, m) d^{3}r =
\]

\[
-n(2n + 2l + 1) \int \phi_{\mu}(\tilde{\alpha}, \tilde{r} - \tilde{A}_{\mu}, \tilde{n}, \tilde{l}, \tilde{m}) \phi_{\nu}(\alpha, \vec{r} - \vec{A}_{\nu} - \tilde{g}, n - 1, l, m) d^{3}r +
\]

\[
\alpha(4n + 2l + 3) \int \phi_{\mu}(\tilde{\alpha}, \tilde{r} - \tilde{A}_{\mu}, \tilde{n}, \tilde{l}, \tilde{m}) \phi_{\nu}(\alpha, \vec{r} - \vec{A}_{\nu} - \tilde{g}, n, l, m) d^{3}r -
\]

\[
2\alpha^{2} \int \phi_{\mu}(\tilde{\alpha}, \tilde{r} - \tilde{A}_{\mu}, \tilde{n}, \tilde{l}, \tilde{m}) \phi_{\nu}(\alpha, \vec{r} - \vec{A}_{\nu} - \tilde{g}, n + 1, l, m) d^{3}r =
\]

\[
-n(2n + 2l + 1) \sum_{t,u,v} E(\tilde{n}, \tilde{l}, \tilde{m}, n - 1, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r +
\]

\[
\alpha(4n + 2l + 3) \sum_{t,u,v} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r -
\]

\[
2\alpha^{2} \sum_{t,u,v} E(\tilde{n}, \tilde{l}, \tilde{m}, n + 1, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r
\]

(15)

The x-component of the gradient is therefore:

\[
\frac{\partial}{\partial A_{\mu,x}} T_{\mu \tilde{\nu} \tilde{\nu}} =
\]

\[
-n(2n + 2l + 1) \sum_{t,u,v} G_{x}^{\alpha \nu}(\tilde{n}, \tilde{l}, \tilde{m}, n - 1, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r +
\]

\[
\alpha(4n + 2l + 3) \sum_{t,u,v} G_{x}^{\alpha \nu}(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r -
\]

\[
2\alpha^{2} \sum_{t,u,v} G_{x}^{\alpha \nu}(\tilde{n}, \tilde{l}, \tilde{m}, n + 1, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^{3}r
\]
\[
\begin{align*}
\alpha(4n + 2l + 3) & \int \sum_{t,u,v} G^A_{x}\mu(n, \tilde{\ell}, \tilde{\ell}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^3r - \\
2\alpha^2 & \int \sum_{t,u,v} G^A_{x}\mu(n, \tilde{\ell}, \tilde{\ell}, n + 1, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) d^3r
\end{align*}
\]  

(16)

As CRYSTAL uses spherical Gaussian type functions with \( n = 0 \), this reduces to

\[
\frac{\partial}{\partial A_{\mu,x}} T_{\mu\nu\tilde{g}} = 
\begin{align*}
\left( \frac{\pi}{\gamma} \right)^{\frac{3}{2}} & \alpha(4n + 2l + 3)G_{x}\mu(0, \tilde{\ell}, \tilde{\ell}, 0, l, m, 0, 0, 0) - \\
2 \left( \frac{\pi}{\gamma} \right)^{\frac{3}{2}} & \alpha^2 G_{x}\mu(0, \tilde{\ell}, \tilde{\ell}, 1, l, m, 0, 0, 0)
\end{align*}
\]  

(17)

Explicit differentiation with respect to the other center \( \tilde{A}_{\nu} \) is more difficult because the kinetic energy operator applies to that center. However, the differentiation can easily be avoided by applying translational invariance:

\[
\frac{\partial}{\partial A_{\mu,x}} T_{\mu\nu\tilde{g}} = - \frac{\partial}{\partial A_{\nu,x}} T_{\mu\nu\tilde{g}}
\]  

(18)

3. Nuclear attraction integrals

The nuclear attraction integrals are defined as

\[
N_{\mu\nu\tilde{g}} = - \sum_{a} Z_{a} \int \phi_{\mu}(\tilde{\alpha}, \vec{r} - \tilde{A}_{\mu}, \tilde{n}, \tilde{\ell}, \tilde{\ell}) A(\vec{r} - \tilde{A}_{a}) \phi_{\nu}(\alpha, \vec{r} - \tilde{A}_{\nu} - \vec{g}, n, l, m) d^3r = \\
- \sum_{a} Z_{a} \int \sum_{t,u,v} E(\tilde{n}, \tilde{\ell}, \tilde{\ell}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) A(\vec{r} - \tilde{A}_{a}) d^3r
\]  

(19)

where \( A \) is the Coulomb potential function in the molecular case, the Euler-MacLaurin potential function for systems periodic in one dimension\[^{2}\], Parry’s potential function\[^{3}\] for systems periodic in two dimensions, and the Ewald potential function for systems periodic in three dimensions\[^{4,32,24}\]. The summation with respect to \( a \) runs over all nuclei of the primitive unit cell.

The x-component of the partial derivative with respect to the center \( A_{\mu,x} \) is obtained as:
\[ \frac{\partial}{\partial A_{\mu,x}} N_{\mu \nu \bar{g}} = \]
\[ - \sum_a Z_a \int \sum_{t,u,v} G_A^A(\bar{n}, \bar{l}, \bar{m}, n, l, m, t, u, v) \Lambda(\gamma, \bar{r} - \bar{P}, t, u, v) A(\bar{r} - \bar{A}_a) d^3r \]  
(20)

In the same way, the partial derivative with respect to \( A_{\nu,x} \) is obtained. The partial derivative with respect to the set of third centers \( \bar{A}_a \) is obtained by translational invariance:

for each center \( \bar{A}_a \), there is a derivative with value

\[ - \frac{\partial}{\partial \bar{A}_\mu} - \frac{\partial}{\partial \bar{A}_\nu} . \]

4. Multipolar integrals

The electronic charge density is expressed with a lattice basis as:

\[ \rho(\vec{r}) = - \sum_{g,\mu,\nu} P_{\nu g}^\mu \phi_\mu(\bar{\alpha}, \vec{r} - \bar{A}_\mu, \bar{n}, \bar{l}, \bar{m}) \phi_\nu(\alpha, \vec{r} - \bar{A}_\nu - \bar{g}, n, l, m) \]  
(21)

Then, the Ewald potential due to this charge density is given by:

\[ \Phi_{\text{ew}}(\rho; \vec{r}) = \int A(\vec{r} - \vec{r}') \rho(\vec{r}') d^3r' \]  
(22)

The Ewald energy of the electrons (i.e. the Ewald energy of the electrons in the primitive unit cell with all the electrons) is obtained as

\[ E = \frac{1}{2} \int \int \rho(\vec{r}) A(\vec{r} - \vec{r}') \rho(\vec{r}') d^3r d^3r' \]  
(23)

For efficiency reasons, the calculation of the Ewald potential is done approximatively. A multipolar expansion up to an order \( L \) is performed for the charge distribution in the long range. Therefore, the electrons do not feel the Ewald potential created by the correct charge distribution, but the Ewald potential created by the multipolar moments. It is thus necessary to compute the multipolar moments of the charge distribution which are defined as

\[ \eta^m(\rho_c; \bar{A}_c) = \int \rho_c(\vec{r}) X^m_l(\vec{r} - \bar{A}_c) d^3r \]  
(24)

with \( X^m_l \) being regular solid harmonics and the charge \( \rho_c(\vec{r}) \) defined as

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\[ \rho_c(\vec{r}) = - \sum_{\vec{g}, \mu \in c, \nu} P_{\nu \vec{g} \mu} \phi_{\mu}(\vec{\alpha}, \vec{r} - \vec{A}_\mu, \vec{n}, \vec{l}, \vec{m}) \phi_{\nu}(\vec{\alpha}, \vec{r} - \vec{A}_\nu - \vec{g}, n, l, m) = \]

\[ - \sum_{\vec{g}, \mu \in c, \nu} P_{\nu \vec{g} \mu} \sum_{t, u, v} E(\vec{n}, \vec{l}, \vec{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) \]

\[ (25) \]

c is an index for the shell. The total electronic charge \( \rho(\vec{r}) \) is thus obtained by summing over all shells \( c \):

\[ \rho(\vec{r}) = \sum_c \rho_c(\vec{r}) \]

\[ (26) \]

In CRYSTAL, the multipole is located at center \( \vec{A}_\mu \) and therefore it is convenient to take the derivative with respect to center \( \vec{A}_\nu \) and obtain the derivative with respect to \( \vec{A}_\mu \) by translational invariance. The expression computed for the gradients is thus

\[ - \sum_{\vec{g}, \mu \in c, \nu} P_{\nu \vec{g} \mu} \int \frac{\partial}{\partial A_{\nu,x}} \left( \phi_{\mu}(\vec{\alpha}, \vec{r} - \vec{A}_\mu, \vec{n}, \vec{l}, \vec{m}) \phi_{\nu}(\vec{\alpha}, \vec{r} - \vec{A}_\nu - \vec{g}, n, l, m) X^m_l(\vec{r} - \vec{A}_\mu) \right) d^3r = \]

\[ - \sum_{\vec{g}, \mu \in c, \nu} P_{\nu \vec{g} \mu} \int \sum_{t, u, v} G^{A_{\nu}}(\vec{n}, \vec{l}, \vec{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) X^m_l(\vec{r} - \vec{A}_\mu) d^3r \]

\[ (27) \]

5. Field integrals

If the electronic charge distribution is approximated with an expansion up to the maximum quantum number \( L \), the Ewald potential of this model charge distribution is obtained as

\[ \Phi^{ew}(\rho^{model}; \vec{r}) = \sum_c \Phi^{ew}(\rho^{model}_c; \vec{r}) = \sum_c \sum_{l=0}^{L} \sum_{m=-l}^{l} \eta^m_l(\rho_c; \vec{A}_c) Z^m_l(\vec{A}_c) A(\vec{r} - \vec{A}_c) \]

\[ (28) \]

with \( Z^m_l(\vec{A}_c) \) being the spherical gradient operator in a renormalized form. The model charge distribution is expressed as

\[ \rho^{model}_c(\vec{r}) = \sum_{l=0}^{L} \sum_{m=-l}^{l} \eta^m_l(\rho_c; \vec{A}_c) \delta^m_l(\vec{A}_c, \vec{r}) \]

\[ (29) \]

and

\[ \delta^m_l(\vec{A}_c, \vec{r}) = \lim_{\alpha \to \infty} Z^m_l(\vec{A}_c) \Lambda(\alpha, \vec{r} - \vec{A}_c, 0, 0, 0) \]

\[ (30) \]
The integral of the electronic charge distribution and the Ewald potential function is required which gives rise to the field integrals which are defined as follows:

\[
M_{\mu\nu\tilde{c}}^{m} = Z_{l}^{m}(\tilde{A}_{c}) \int \phi_{\mu}(\alpha, \vec{r} - \tilde{A}_{\mu}, \vec{n}, \vec{I}, \vec{m}) \phi_{\nu}(\alpha, \vec{r} - \tilde{A}_{\nu} - \vec{g}, n, l, m) \left[ A(\vec{r} - \tilde{A}_{c}) - \sum_{n} \frac{1}{|\vec{r} - \tilde{A}_{c} - \vec{n}|} \right] d^{3}r = 
\]

\[
Z_{l}^{m}(\tilde{A}_{c}) \int \sum_{t,u,v} E(\vec{n}, \vec{l}, \vec{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) \left[ A(\vec{r} - \tilde{A}_{c}) - \sum_{n} \frac{1}{|\vec{r} - \tilde{A}_{c} - \vec{n}|} \right] d^{3}r (31)
\]

The term \( A(\vec{r} - \tilde{A}_{c}) - \sum_{n} \frac{1}{|\vec{r} - \tilde{A}_{c} - \vec{n}|} \) instead of \( A(\vec{r} - \tilde{A}_{c}) \) appears because the multipolar approximation is only done for the charge distribution in the long range. The penetration depth \( pen \) is a certain threshold for which the integrals are evaluated exactly.\(^{26}\)

For the gradients, the derivative with respect to all the centers is needed. The partial derivative with respect to \( A_{\mu,x} \) is obtained as

\[
\partial_{A_{\mu,x}} M_{\mu\nu\tilde{c}}^{m} = 
\]

\[
Z_{l}^{m}(\tilde{A}_{c}) \int \sum_{t,u,v} G_{x}^{\alpha_{\mu}}(\vec{n}, \vec{l}, \vec{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) \left[ A(\vec{r} - \tilde{A}_{c}) - \sum_{n} \frac{1}{|\vec{r} - \tilde{A}_{c} - \vec{n}|} \right] d^{3}r (32)
\]

In similar way, the partial derivative with respect to center \( \tilde{A}_{\nu} \) is computed. Finally, the partial derivatives with respect to the centers \( \tilde{A}_{c} \) are obtained from translational invariance.

6. Spheropole

This term arises because the charge distribution is approximated by a model charge distribution in the long range.\(^{26}\)

\[
\Phi^{ew}(\rho_{c}; \vec{r}) = \Phi^{ew}(\rho_{c}^{model}; \vec{r}) + \Phi^{ew}(\rho_{c} - \rho_{c}^{model}; \vec{r}) = \Phi^{ew}(\rho_{c}^{model}; \vec{r}) + \Phi^{coul}(\rho_{c} - \rho_{c}^{model}; \vec{r}) + Q_{c} (33)
\]

The calculation of the Coulomb potential \( \Phi^{coul}(\rho_{c} - \rho_{c}^{model}; \vec{r}) \) is restricted to contributions from those charges inside the penetration depth \( pen \). The use of the Coulomb potential \( \Phi^{coul}(\rho_{c} - \rho_{c}^{model}; \vec{r}) \) instead of the Ewald potential \( \Phi^{ew}(\rho_{c} - \rho_{c}^{model}; \vec{r}) \) is correct, if \( \rho_{c} - \rho_{c}^{model} \) is of zero charge, dipole, quadrupole and spherical second moment.\(^{25}\) However, this condition
leads to a correction in the three-dimensional case: although the difference \( \rho_c - \rho_c^{\text{model}} \) has zero charge, dipole and quadrupole moment, it has in general a non-zero spherical second moment \( Q_c \). Therefore, the potential must be shifted by \( Q \) defined as:

\[
Q = \sum_c Q_c = \sum_c \frac{2\pi}{3V} \int (\rho_c(\vec{r}) - \rho_c^{\text{model}}(\vec{r}))|\vec{r}|^2 d^3r
\] (34)

Three types of contributions are obtained: zero, first and second order HGTFs. They have to be combined with the corresponding \( E \)-coefficient. For the zeroth order, a contribution of

\[
E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 0) \left( \frac{3}{2\gamma} + (\vec{A}_\mu - \vec{P})^2 \right)
\]

is computed. The derivative is therefore

\[
\frac{\partial}{\partial A_{\mu,x}} \left( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 0) \left( \frac{3}{2\gamma} + (\vec{A}_\mu - \vec{P})^2 \right) \right)
\] (35)

To obtain the derivative \( \frac{\partial}{\partial A_{\mu,x}} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 0) \), we use the identity

\[
\frac{\partial}{\partial A_{\mu,x}} \left( \sum_{t,u,v} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) \right) =
\sum_{t,u,v} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \frac{\tilde{\alpha}}{\gamma} \Lambda(\gamma, \vec{r} - \vec{P}, t + 1, u, v) +
\sum_{t,u,v} \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v) \frac{\partial}{\partial A_{\mu,x}} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) =
\sum_{t,u,v} G_{x}^{A_{\mu}}(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) \Lambda(\gamma, \vec{r} - \vec{P}, t, u, v)
\] (36)

which gives

\[
\frac{\partial}{\partial A_{\mu,x}} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) = G_{x}^{A_{\mu}}(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t, u, v) - \frac{\tilde{\alpha}}{\gamma} E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, t - 1, u, v)
\] (37)

A similar operation is necessary for the components with \( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 1, 0, 0) \), \( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 1, 0) \) and \( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 1) \) (first order HGTFs) which are multiplied with prefactors \( 2(P_x - A_{\mu,x}) \), \( 2(P_y - A_{\mu,y}) \) and \( 2(P_z - A_{\mu,z}) \), respectively. Finally, derivatives of the products of \( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 2, 0, 0) \), \( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 2, 0) \) and \( E(\tilde{n}, \tilde{l}, \tilde{m}, n, l, m, 0, 0, 2) \) (second order HGTFs) with 2 are required.
B. Bielectronic integrals

We define a bielectronic integral as

$$B_{\mu\nu\bar{g}\bar{r}\bar{n}\sigma} = \int \phi_{\mu}(\alpha_1, \bar{r} - \bar{A}_{\mu}, n_1, l_1, m_1) \phi_{\nu}(\alpha_2, \bar{r} - \bar{A}_{\nu} - \bar{g}, n_2, l_2, m_2) \frac{1}{|\bar{r} - \bar{r}'|} \phi_{\tau}(\alpha_3, \bar{r}' - \bar{A}_{\tau} - \bar{n}, n_3, l_3, m_3) \phi_{\sigma}(\alpha_4, \bar{r}' - \bar{A}_{\sigma} - \bar{h}, n_4, l_4, m_4) d^3r d^3r' = \sum_{t,u,v} E(n_1, l_1, m_1, n_2, l_2, m_2, t, u, v) \sum_{t',u',v'} E(n_3, l_3, m_3, n_4, l_4, m_4, t', u', v') [t, u, v] \left[ \frac{1}{|\bar{r} - \bar{r}'|} \right] [t', u', v'] \quad (38)$$

The expression $[t, u, v] \left[ \frac{1}{|\bar{r} - \bar{r}'|} \right] [t', u', v']$ is defined as

$$[t, u, v] \left[ \frac{1}{|\bar{r} - \bar{r}'|} \right] [t', u', v'] = \int \int \Lambda(\gamma, \bar{r} - \bar{P}, t, u, v) \frac{1}{|\bar{r} - \bar{r}'|} \Lambda(\gamma', \bar{r}' - \bar{P}', t', u', v') d^3r d^3r' \quad (39)$$

The partial derivative with respect to $A_{\mu,x}$ is obtained as

$$\frac{\partial}{\partial A_{\mu,x}} B_{\mu\nu\bar{g}\bar{r}\bar{n}\sigma} = \sum_{t,u,v} G_{x}^{A_{\mu}}(n_1, l_1, n_2, l_2, m_2, t, u, v) \sum_{t',u',v'} E(n_3, l_3, n_4, l_4, m_4, t', u', v') [t, u, v] \left[ \frac{1}{|\bar{r} - \bar{r}'|} \right] [t', u', v'] \quad (40)$$

Similarly, gradients with respect to the other centers are obtained. One of the gradients can be obtained by translational invariance if the other three gradients have been computed.

In the context of periodic systems, it is necessary to perform summations over the lattice vectors $\bar{g}, \bar{h}, \bar{n}$. We define a Coulomb integral as follows

$$C_{\mu\nu\bar{g}\bar{r}\bar{n}\sigma} = \sum_{\bar{n}} B_{\mu\nu\bar{g}\bar{r}\bar{n}\sigma} + \bar{h} \quad (41)$$

Similarly, we define an exchange integral as follows:

$$X_{\mu\nu\bar{g}\bar{r}\bar{n}\sigma} = \sum_{\bar{n}} B_{\mu\bar{r}\bar{n}\nu\bar{g}\sigma} + \bar{h} \quad (42)$$
V. TOTAL ENERGY AND GRADIENT

A. Total energy

The correct summation of the Coulomb energy is the most severe problem of the total energy calculation. The individual contributions to the Coulomb energy, such as for example the nuclear-nuclear interaction, are divergent for periodic systems. Thus, a scheme based on the Ewald method is used to sum the individual contributions. The total energy is then expressed as the sum of kinetic energy $E_{\text{kin}}$, the Ewald energies of the nuclear-nuclear repulsion $E_{\text{NN}}$, nuclear-electron attraction $E_{\text{coul-nuc}}$, electron-electron repulsion $E_{\text{coul-el}}$, and finally the exchange energy $E_{\text{exch-el}}$.

$$E_{\text{total}} = E_{\text{kin}} + E_{\text{NN}} + E_{\text{coul-nuc}} + E_{\text{coul-el}} + E_{\text{exch-el}} =$$

$$= \sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}} T_{\mu\vec{g}} + E_{\text{NN}}$$

$$- \sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}} \sum_a Z_a \int \phi_\mu(\vec{\alpha}, \vec{r} - \vec{A}_\mu, \vec{n}, \vec{m}) \phi_\nu(\alpha, \vec{r} - \vec{A}_\nu - \vec{g}, n, l, m) A(\vec{r} - \vec{A}_a) d^3r$$

$$+ \frac{1}{2} \sum_{\vec{g},\mu,\nu} \left( - QS_{\mu\vec{g}\nu} + \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}} C_{\mu\vec{g}\tau0\sigma\vec{h}} - \sum_{c} \sum_{l=0}^{L} \sum_{m=-l}^{l} \eta_{\mu\nu}(\rho_c; \vec{A}_c) M_{\mu\nu}^{m} \right)$$

$$- \frac{1}{2} \sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}} X_{\mu\vec{g}\tau0\sigma\vec{h}} - \frac{1}{2} \sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}} \sum_{\vec{h},\tau,\sigma} P_{\sigma\vec{h}} X_{\mu\vec{g}\tau0\sigma\vec{h}} \tag{43}$$

B. Gradient of the total energy

The force with respect to the position of the nuclei can be calculated similarly to the molecular case. The derivatives of all the integrals are necessary, and the derivative of the density matrix is expressed with the help of the energy-weighted density matrix. The full force is obtained as:

$$\vec{F}_{\vec{A}_i} = - \frac{\partial E_{\text{total}}}{\partial \vec{A}_i} =$$

$$- \sum_{\vec{g},\mu,\nu} P_{\nu\vec{g}} \frac{\partial T_{\mu\vec{g}}}{\partial \vec{A}_i} - \frac{\partial E_{\text{NN}}}{\partial \vec{A}_i}$$
\begin{align*}
+ \sum_{\vec{g},\mu,\nu} P_{\vec{g} \mu \nu} \sum_a Z_a \frac{\partial}{\partial A_i} \left[ \int \phi_{\mu}(\alpha_2, \vec{r} - \vec{A}_\mu, n_2, l_2, m_2) \phi_{\nu}(\alpha_1, \vec{r} - \vec{A}_\nu - \vec{g}, n_1, l_1, m_1) A(\vec{r} - \vec{A}_\nu) d^3 r \right]
\end{align*}

\begin{align*}
- \frac{1}{2} \sum_{\vec{g},\mu,\nu} P_{\vec{g} \mu \nu} \left\{ - \mathcal{S}_{\mu \nu} \frac{2\pi}{3V} \sum_c \sum_{h,\sigma,\tau \in c} P_{\sigma \tau \vec{g} \vec{h}} \right. \\
\left. \frac{\partial}{\partial A_i} \int \left[ - \phi_{\sigma}(\alpha_2, \vec{r} - \vec{A}_\sigma, n_2, l_2, m_2) \phi_{\tau}(\alpha_1, \vec{r} - \vec{A}_\tau - \vec{h}, n_1, l_1, m_1) 
+ \sum_{l=0}^L \sum_{m=-l}^l \int \phi_{\tau}(\alpha_2, \vec{r} - \vec{A}_\tau, n_2, l_2, m_2) \phi_{\sigma}(\alpha_1, \vec{r} - \vec{A}_\sigma - \vec{h}, n_1, l_1, m_1) X^m_l(\vec{r} - \vec{A}_c) d^3 r \right] r^2 d^3 r \\
+ \sum_{\tau,\sigma} P_{\tau \sigma \vec{h} \vec{g} \vec{h} \vec{g}} \frac{\partial C_{\mu \nu \vec{g} \vec{h} \vec{g} \vec{h} \vec{g}}}{\partial A_i} \\
+ \sum_{c} \sum_{l=0}^L \sum_{m=-l}^l \sum_{h,\tau \in c} \sum_{\sigma,\tau \in c} P_{\sigma \tau \vec{h} \vec{g} \vec{h} \vec{g}} \\
\frac{\partial}{\partial A_i} \left[ \int \phi_{\tau}(\alpha_2, \vec{r} - \vec{A}_\tau, n_2, l_2, m_2) \phi_{\sigma}(\alpha_1, \vec{r} - \vec{A}_\sigma - \vec{h}, n_1, l_1, m_1) X^m_l(\vec{r} - \vec{A}_c) d^3 r \right] \right]\end{align*}

(44)

The last addend is the energy weighted density matrix; the integral is over the first Brillouin zone.

**VI. STRUCTURE OF THE GRADIENT CODE**

The present structure of the gradient code is indicated in figure 1. The first step is to compute the gradient of the Ewald energy of the nuclei in subroutine GRAMAD (the Ewald energy is computed in ENEMAD). The control module TOTGRA then first calls routines to compute the gradient of the bielectronic integrals (labeled with SHELLX \(\nabla\)) as these routines will change their structure. The subroutine SHELLX \(\nabla\) calls subroutines which explicitly compute the derivatives of Coulomb and exchange integrals, and multiplies the gradients a first time with the density matrix. Back in TOTGRA again, the second multiplication with the density matrix is performed. The next step is to compute the derivatives of the multi-
poles (MONIRG) and to compute the energy weighted density matrix (PDIGEW). Then, the gradients of the one-electron integrals are computed (CJAT0G, CJAT1G, CJAT2G or CJAT3G, depending on the dimension). The field integrals and their gradients are now multiplied with the multipolar integrals and their gradients, and a multiplication with the density matrix is performed. This concludes the calculation of the gradients.

The structure has been simplified to focus on the most important parts. In addition, as already mentioned, the code will undergo changes during the optimization process so that a too detailed description seems to be unadvised.
FIGURES

FIG. 1. The present structure of the gradient code. The left column describes the purpose of the routines, the middle column gives the names of the corresponding routines, and the right column gives the name of the routines in the energy code. One arrow indicates that the routine is a subroutine, two arrows indicate that it is a subroutine called from a subroutine.
| Feature                                           | Module 1 | Module 2 |
|--------------------------------------------------|----------|----------|
| Nuclear-nuclear repulsion gradients              | GRAMAD   | ENEMAD   |
| Gradient control module                          | TOTGRA   | TOTENY + MONMAD |
| Gradient of bielectronic integrals, first multiplication with density matrix | SHELLX\(\nabla\) | SHELLX |
| Gradient of Coulomb and exchange integrals       | \(\nabla\) VIC5J\(\nabla\), VIC5K\(\nabla\), VIC5L\(\nabla\) | VIC5J, VIC5K, VIC5L |
| Second multiplication of gradients of bielectronic integrals with density matrix | \(\nabla\) MONIRG | MONIRR+QGAMMA |
| Calculation of multipoles and their gradients, multiplication with density matrix | \(\nabla\) OLIPAG | POLIPA |
| Multipolar gradients                             | \(\nabla\) PDIGEW | derived from PDIG |
| Energy weighted density matrix                   | \(\nabla\) CJAT0G, CJAT1G, CJAT2G, CJAT3G | CJAT0, CJAT1, CJAT2, CJAT3 |
| Multiplication of field integrals and their gradients with multipolar integrals and their gradients, multiplication with density matrix |  |  |
| Printing of forces                               |  |  |
VII. EXAMPLES

In tables I, II and III, we give examples of the accuracy of the gradients. First, in table I, a chain of NiO molecules is considered, with ferromagnetic ordering (all the Ni spins up) and with antiferromagnetic ordering (nearest Ni spins are antiparallel). The oxygen atoms are moved by 0.01 Å from their equilibrium positions which results in a non-vanishing force. The agreement between numerical and analytical gradient is better than 0.0001 \( E_h a_0 \). As we discussed in our first article, the agreement can be improved by using stricter "ITOL"-parameters (these are parameters which control the accuracy of the evaluation of the integrals). Indeed, when increasing these parameters, the agreement further improves up to an error of less than \( 10^{-5} E_h a_0 \).

In table II, a LiF layer with a lattice constant of 5 Å is considered with one atom being displaced from its equilibrium position. The forces agree to \( 2 \times 10^{-5} E_h a_0 \) when default ITOL parameters (6, 6, 6, 6, 12) are used.

Finally, in table III, a three-dimensional, ferromagnetically polarized NiO solid is considered. When displacing the oxygen ions, the forces agree to better than \( 2 \times 10^{-5} E_h a_0 \).

As a whole, the accuracy is certainly very high and can further be improved by applying stricter cutoff (ITOL) parameters.

VIII. CONCLUSION

In this article, we described the implementation of analytical gradients in the code CRYSTAL. In its present form, the code is capable of computing highly accurate Hartree-Fock gradients for systems with 0, 1, 2 and 3-dimensional periodicity. Both closed-shell restricted Hartree-Fock as well as unrestricted Hartree-Fock calculations can be performed.

A first step of improving the efficiency of the code has been completed with the coding of gradients for the bipolar expansion, and a further enhancement of the efficiency will be one of the future directions. Of highest importance is the implementation of symmetry which
will lead to high saving factors. Other targets are the implementation of gradients with respect to the lattice vector, an extension to metallic systems, and the implementation of density functional gradients.

IX. ACKNOWLEDGMENTS

The author would like to thank CCP3 and Prof. N. M. Harrison for their interest and support of this work (EPSRC grant GR/K90661), Mr. V. R. Saunders for many helpful discussions, and Prof. R. Dovesi and the Turin group for helpful discussions and hospitality.
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TABLE I. Ferromagnetic (FM) and antiferromagnetic (AFM) NiO chain (i.e. a chain with alternating nickel and oxygen atoms). The distance between two oxygen atoms is chosen as 5 Å. The force is computed numerically and analytically with the oxygen atoms being displaced. A \( [5s4p2d] \) basis set was used for nickel, and a \([4s3p]\) basis set for oxygen.

| magnetic ordering | ITOL parameter | displacement of oxygen in Å | analytical derivative \( E_h/a_0 \) | numerical derivative \( E_h/a_0 \) |
|------------------|----------------|----------------------------|--------------------------------|----------------------------|
| FM               | 6 6 6 6 12     | 0.01                       | 0.001274                        | 0.001188                   |
| FM               | 8 8 8 8 14     | 0.01                       | 0.001246                        | 0.001249                   |
| AFM              | 6 6 6 6 12     | 0.01                       | 0.001276                        | 0.001191                   |
| AFM              | 8 8 8 8 14     | 0.01                       | 0.001250                        | 0.001252                   |

TABLE II. Forces on the atoms of a LiF layer when one of the atoms is displaced from its equilibrium position. A \([4s3p]\) basis set was used for the fluorine atom and a \([2s1p]\) basis set for the lithium atom. Default ITOL parameters were used.

| atom | analytical derivative \( E_h/a_0 \) | numerical derivative \( E_h/a_0 \) |
|------|--------------------------------|----------------------------|
| F at (0.5 Å, 0 Å, 0 Å) | 0.001379 | 0.001400 |
| Li at (2.5 Å, 0 Å, 0 Å) | -0.020731 | -0.020726 |
| F at (2.5 Å, 2.5 Å, 0 Å) | 0.010384 | 0.010376 |
| Li at (0 Å, 2.5 Å, 0 Å) | 0.008969 | 0.008950 |
TABLE III. Ferromagnetic NiO in an fcc structure at a lattice constant of 4.2654 Å. We compare numerical and analytical derivatives when moving the oxygen ion parallel to the x-direction. Default ITOL parameters were used, the basis sets are the same as in table [1].

| Displacement of Oxygen (Å) | Analytical Derivative ($E_h/a_0$) | Numerical Derivative ($E_h/a_0$) |
|---------------------------|-----------------------------------|---------------------------------|
| 0.01                      | 0.001499                          | 0.001485                        |
| 0.02                      | 0.002939                          | 0.002925                        |
| 0.03                      | 0.004387                          | 0.004378                        |
| 0.04                      | 0.005857                          | 0.005847                        |
| 0.05                      | 0.007352                          | 0.007346                        |