

Energy gradients with respect to atomic positions and cell parameters for the Kohn-Sham density-functional theory at the Γ point

Valéry Weber

Department of Chemistry, University of Fribourg, 1700 Fribourg, Switzerland
and Los Alamos National Laboratory, Theoretical Division, Los Alamos, New Mexico 87545

Christopher J. Tymczak^{a)} and Matt Challacombe

Los Alamos National Laboratory, Theoretical Division, Los Alamos, New Mexico 87545

The application of theoretical methods based on density-functional theory is known to provide atomic and cell parameters in very good agreement with experimental values. Recently, construction of the exact Hartree-Fock exchange gradients with respect to atomic positions and cell parameters within the Γ -point approximation has been introduced [V. Weber *et al.*, J. Chem. Phys. **124**, 214105 (2006)]. In this article, the formalism is extended to the evaluation of analytical Γ -point density-functional atomic and cell gradients. The infinite Coulomb summation is solved with an effective periodic summation of multipole tensors [M. Challacombe *et al.*, J. Chem. Phys. **107**, 9708 (1997)]. While the evaluation of Coulomb and exchange-correlation gradients with respect to atomic positions are similar to those in the gas phase limit, the gradients with respect to cell parameters needs to be treated with some care. The derivative of the periodic multipole interaction tensor needs to be carefully handled in both direct and reciprocal space and the exchange-correlation energy derivative leads to a surface term that has its origin in derivatives of the integration limits that depend on the cell. As an illustration, the analytical gradients have been used in conjunction with the QUICCA algorithm [K. Németh and M. Challacombe, J. Chem. Phys. **121**, 2877 (2004)] to optimize one-dimensional and three-dimensional periodic systems at the density-functional theory and hybrid Hartree-Fock/density-functional theory levels. We also report the full relaxation of forsterite supercells at the B3LYP level of theory.

I. INTRODUCTION

The Kohn-Sham approach to density-functional theory has been proven to be a highly competitive method for a wide range of applications in solid-state physics and chemistry. The hybrid Hartree-Fock/density-functional theory (hybrid-HF/DFT) model chemistries are an important next step in accuracy beyond the generalized gradient approximation.¹⁻⁴

In preceding papers, we have developed linear scaling quantum chemical methods for construction of the periodic Coulomb, exchange-correlation,⁵ and the exact Hartree-Fock exchange⁶ matrices within the Γ -point approximation. In this paper, the implementation of the Coulomb and exchange-correlation energy gradients with respect to atomic positions and cell parameters at the Γ point is presented.

While the Γ -point approximation uses only the $\mathbf{k}=0$ point to sample the Brillouin zone, it does, however, converge to the \mathbf{k} -space integration limit, in the worst case with the inverse unit cell volume (see for example Refs. 7 and 8). Convergence of the Γ -point approximation to the corresponding \mathbf{k} -space limit was recently demonstrated by us for DFT,⁵ HF, and hybrid-HF/DFT (Ref. 6) theories, as well as for the Hartree-Fock atomic and cell gradients.⁹ For one-

dimensional fluoric acid chains (HF)_n, convergence of the Hartree-Fock minimum image convention (HF-MIC) Γ -point energy, atomic, and cell forces to the converged large cell Γ -point approximation with respect to cell length have been explicitly shown to be exponential in the cell size.⁹ A fast convergence of the total energy and geometrical parameters have also been observed for three-dimensional (3D) systems such as MgO and urea.^{5,6,9} In general, the Γ -point approach enables study of very large complex and disordered systems such as liquids, low concentration defects, adsorption of large molecule on surfaces, etc., where conventional methods of sampling the Brillouin zone may become computationally too demanding, and where the Γ -point approximation is well justified.

Finding crystal structures of condensed systems can be formulated as a minimization of the total energy with respect to atomic coordinates and cell vectors. The problem is then minimization of the total energy with L degrees of freedom, where $L=3N_{\text{atm}}+3$; N_{atm} is the number of atoms, $3N_{\text{atm}}-3$ is the number of independent coordinates after the elimination of translation, and the number of independent vector elements after the elimination of cell rotations is 6. This minimization can be achieved with the help of an efficient optimizer¹⁰⁻¹² and knowledge of the gradients with respect to atomic positions and cell parameters.

The analytical cell gradient method of density-functional

^{a)}Electronic mail: tymczak@lanl.gov

theory using Gaussian-type atomic orbital (GTAO) for one-dimensional extended systems was implemented by Hirata and Iwata.¹³ The 3D case has been implemented by Kudin and Scuseria.^{14,15} Their approach for the Coulomb problem is based on the direct space fast multipole method. Recently Doll *et al.*¹⁶ presented an implementation of Hartree-Fock cell gradients¹⁷ in the CRYSTAL03 (Ref. 18) package for 3D systems. Their code is based on GTAO and the summation of the Coulomb energy is performed with the Ewald method,¹⁹ which is a combination of direct and reciprocal cell summations. The strategy to compute the analytic Hartree-Fock gradients for periodic systems, in the frame of the CRYSTAL03 package has been presented by Doll *et al.*^{20,21} Their implementation is based on the Hermite-Gaussian-type functions in the context of the McMurchie-Davidson algorithm.²²

This paper describes the complete implementation of the atomic and lattice gradients within the Kohn-Sham approach to density-functional theory at the Γ point. The infinite Coulomb summation is solved with an effective periodic summation of multipole tensors.^{5,23} We show that, like for the exact HF exchange, the evaluation of the atomic gradients within the Γ -point approximation does not lead to special difficulties. The implementation requires mainly the evaluation of the derivative of the basis function with respect to atomic positions. However, difficulties arise when the derivative of the total energy is taken with respect to lattice parameters. For the periodic far-field Coulomb term, the derivative of the multipole interaction tensor needs to be carefully handled in both direct and reciprocal space. The exchange-correlation energy derivative leads to a surface term, which has its origin in derivatives of the integration limits that depend on the cell. We finally demonstrate the convergence of geometrical parameters and total energy for a few periodic systems within the DFT and hybrid-HF/DFT Γ -point supercell approach. The full relaxation of the geometrical parameters were done with the QUICCA algorithm.^{10,12}

The remainder of this paper is organized as follows: In Sec. II, we introduce the formalism and discuss the implementation of the Coulomb and exchange-correlation gradients with respect to atomic positions and cell parameters at the Γ -point approximation. Then full optimization of several 3D periodic systems are given in Sec. III as an illustration of the formalism. Finally in Sec. IV we summarize our results.

II. FORMALISM

The primitive cell can be represented by the three vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} . Let us define M as the 3×3 matrix composed of the primitive cell vectors,

$$M = (\mathbf{a}, \mathbf{b}, \mathbf{c}).$$

The position of any replicated cell is $\mathbf{R}(\mathbf{n}) = M\mathbf{n}$, with $\mathbf{n} = (n_a, n_b, n_c)$, a vector of integers. The position of atom A in the cell $\mathbf{R}(\mathbf{n})$ is $\mathbf{A} = M(\mathbf{f}_A + \mathbf{n})$, with $\mathbf{f}_A = (f_{Aa}, f_{Ab}, f_{Ac})$, the fractional coordinates of atom A in the central cell.

An unnormalized Cartesian-Gaussian-type function (CGTF) centered on atom A is

$$\phi_a(\mathbf{r}) = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\zeta_a(\mathbf{r} - \mathbf{A})^2},$$

where the triad $a = (a_x, a_y, a_z)$ sets the angular symmetry and the exponent ζ_a is chosen to describe a particular length scale. Gaussian basis functions are often contracted to approximate atomic eigenfunctions.

The total energy within the Γ -point approximation^{5,6} can be expressed as

$$E(\mathbf{f}_A, \mathbf{f}_B, \dots, M) = \sum_{ab} P_{ab} \left(T_{ab} + \frac{1}{2} (J_{ab} + \alpha_1 K_{ab}) \right) + \alpha_2 E^{xc} + h_{\text{nuc}}, \quad (1)$$

where P is the density matrix, T is the kinetic-energy matrix, J is the electron-electron and electron-nuclear Coulomb matrix, E^{xc} is the exchange-correlation energy, K is the exact Hartree-Fock exchange matrix, and h_{nuc} is the nuclear-nuclear and nuclear-electron energy. The factors α_1 and α_2 are mixing coefficients of the exact Hartree-Fock exchange and exchange-correlation energies, respectively.

The derivative of the total energy, Eq. (1), with respect to a general external perturbation λ is

$$\frac{\partial E}{\partial \lambda} = \sum_{ab} P_{ab} \left(\frac{\partial T_{ab}}{\partial \lambda} + \frac{\partial h_{\text{nuc}}}{\partial \lambda} \right) \Big|_P + \frac{1}{2} \sum_{ab} P_{ab} \left(\frac{\partial J_{ab}}{\partial \lambda} \Big|_P + \alpha_1 \frac{\partial K_{ab}}{\partial \lambda} \Big|_P \right) + \alpha_2 \frac{\partial E^{xc}}{\partial \lambda} \Big|_P - \sum_{ab} W_{ab} \frac{\partial S_{ab}}{\partial \lambda},$$

where $|_P$ means that P is held constant, $W = PFP$ is the energy-weighted density matrix, and F the Fockian or Kohn-Sham Hamiltonian. The gradients with respect to fractional coordinates and cell parameters are simply given by $\lambda = f_{Gj}$ and $\lambda = M_{ij}$, respectively. The Hartree-Fock exchange gradients with respect to atomic and cell parameters, i.e., $\partial K_{ab} / \partial \lambda |_P$, have been previously derived.⁹

The energy gradient with respect to the fractional coordinate f_{Gj} can be obtained through the linear transform

$$\frac{\partial E}{\partial f_{Gj}} = \sum_{i=x,y,z} M_{ij} \frac{\partial E}{\partial G_i},$$

where $\partial E / \partial G_i$ is the standard gradient with respect to atomic position. In the following, we describe the implementation of the Coulomb and exchange-correlation gradients with respect to atomic and cell parameters.

A. Coulomb integrals

The periodic quantum Coulomb sum involves the three contributions (for more detail about the formalism see Refs. 5 and 23),

$$J_{ab} = J_{ab}^{\text{In}} + J_{ab}^{\text{PFF}} + J_{ab}^{\text{TF}},$$

where J_{ab}^{In} is the inner cell set sum evaluated by the quantum chemical tree code (QCTC),²⁴ J_{ab}^{PFF} is the periodic far-field term and J_{ab}^{TF} is a surface term which corrects the boundary at infinity.

1. Inner sum

The inner cell set contribution to the Coulomb matrix is

$$J_{ab}^{\text{In}} = \sum_{\mathbf{R} \in \text{In}} \int \int \rho_{ab}(\mathbf{r}) |\mathbf{r} - \mathbf{r}' + \mathbf{R}|^{-1} \rho_{\text{tot}}(\mathbf{r}') dV dV', \quad (2)$$

where

$$\rho_{ab}(\mathbf{r}) = \sum_{\mathbf{R}'} \phi_a(\mathbf{r}) \phi_b(\mathbf{r} + \mathbf{R}'),$$

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{ab} P_{ab} \rho_{ab}(\mathbf{r}) - \sum_A Z_A \delta(\mathbf{r} - \mathbf{A}),$$

the index A runs over the atoms in the cell, Z_A is the charge of atom A , and $\delta(\mathbf{r})$ is the Dirac delta function. The derivatives of Eq. (2) with respect to atomic position G_i and cell parameter M_{ij} are

$$\left. \frac{\partial J_{ab}^{\text{In}}}{\partial G_i} \right|_P = 2 \sum_{\mathbf{R} \in \text{In}} \int \int \frac{\partial \rho_{ab}(\mathbf{r})}{\partial G_i} |\mathbf{r} - \mathbf{r}' + \mathbf{R}|^{-1} \rho_{\text{tot}}(\mathbf{r}') dV dV',$$

and

$$\left. \frac{\partial J_{ab}^{\text{In}}}{\partial M_{ij}} \right|_P = \sum_{\mathbf{R} \in \text{In}} \int \int \left(2 \frac{\partial \rho_{ab}(\mathbf{r})}{\partial M_{ij}} |\mathbf{r} - \mathbf{r}' + \mathbf{R}|^{-1} + \rho_{ab}(\mathbf{r}) \frac{\partial |\mathbf{r} - \mathbf{r}' + \mathbf{R}|^{-1}}{\partial M_{ij}} \right) \rho_{\text{tot}}(\mathbf{r}') dV dV',$$

where the factors of two arise from the bra/ket symmetry; the derivatives $\partial \rho_{ab} / \partial G_i$, $\partial |\mathbf{r} - \mathbf{r}' + \mathbf{R}|^{-1} / \partial M_{ij}$ and $\partial \rho_{ab} / \partial M_{ij}$ are straightforward and do not need to be addressed in more detail. Note that similar terms arise for h_{nuc} and are treated in an equivalent way as J_{ab}^{In} .

2. Periodic far field

We use a spherical multipole method in order to compute the periodic far field correction to the Coulomb matrix,^{5,23} which is

$$J_{ab}^{\text{PFF}} = \sum_{lm'l'} (-1)^l \rho_{ab}^{lm} \mathcal{M}_{l+l'}^{m+m'} \rho_{\text{tot}}^{l'm'}, \quad (3)$$

where \mathcal{M}_l^m is an effective multipole interaction tensor that accounts for the direct infinite lattice summation. The spherical densities ρ_{ab}^{lm} and ρ_{tot}^{lm} are obtained by projecting $\rho_{ab}(\mathbf{r})$ and $\rho_{\text{tot}}(\mathbf{r})$, respectively, onto the regular spherical harmonics $O_l^m(\mathbf{r})$ as

$$\rho_{ab}^{lm} = \int \rho_{ab}(\mathbf{r}) O_l^m(\mathbf{r}) dV \quad \text{and} \quad \rho_{\text{tot}}^{lm} = \int \rho_{\text{tot}}(\mathbf{r}) O_l^m(\mathbf{r}) dV.$$

The derivatives of Eq. (3) with respect to atomic position G_i and the cell parameter M_{ij} are

$$\left. \frac{\partial J_{ab}^{\text{PFF}}}{\partial G_i} \right|_P = 2 \sum_{lm'l'} (-1)^l \frac{\partial \rho_{ab}^{lm}}{\partial G_i} \mathcal{M}_{l+l'}^{m+m'} \rho_{\text{tot}}^{l'm'},$$

and

$$\left. \frac{\partial J_{ab}^{\text{PFF}}}{\partial M_{ij}} \right|_P = \sum_{lm'l'} (-1)^l \left(2 \frac{\partial \rho_{ab}^{lm}}{\partial M_{ij}} \mathcal{M}_{l+l'}^{m+m'} + \rho_{ab}^{lm} \frac{\partial \mathcal{M}_{l+l'}^{m+m'}}{\partial M_{ij}} \right) \rho_{\text{tot}}^{l'm'},$$

where $\partial \rho_{ab}^{lm} / \partial G_i$ and $\partial \rho_{ab}^{lm} / \partial M_{ij}$ are simple and do not need to be shown here. The calculation of $\partial \mathcal{M}_l^m / \partial M_{ij}$ is shown in the Appendix.

3. Tin foil

The tin-foil correction to the Coulomb matrix is

$$J_{ab}^{\text{TF}} = \frac{2\pi}{3V_{\text{uc}}} (QS_{ab} - 2\mathbf{d}_{ab} \cdot \mathbf{D}), \quad (4)$$

where V_{uc} is the unit cell volume, Q is the trace of the system quadrupole, S_{ab} is an element of the overlap matrix, \mathbf{D} the dipole moment of the system, and \mathbf{d}_{ab} the dipole moment of the distribution ρ_{ab} . The derivatives of Eq. (4) with respect to atomic position G_i and the cell parameter M_{ij} are

$$\left. \frac{\partial J_{ab}^{\text{TF}}}{\partial G_i} \right|_P = \frac{2\pi}{3V_{\text{uc}}} \left(\left. \frac{\partial Q}{\partial G_i} \right|_P S_{ab} + Q \frac{\partial S_{ab}}{\partial G_i} - 2 \frac{\partial \mathbf{d}_{ab}}{\partial G_i} \cdot \mathbf{D} - 2\mathbf{d}_{ab} \cdot \left. \frac{\partial \mathbf{D}}{\partial G_i} \right|_P \right),$$

and

$$\left. \frac{\partial J_{ab}^{\text{TF}}}{\partial M_{ij}} \right|_P = \frac{2\pi}{3V_{\text{uc}}} \left(\left. \frac{\partial Q}{\partial M_{ij}} \right|_P S_{ab} + Q \frac{\partial S_{ab}}{\partial M_{ij}} - 2 \frac{\partial \mathbf{d}_{ab}}{\partial M_{ij}} \cdot \mathbf{D} - 2\mathbf{d}_{ab} \cdot \left. \frac{\partial \mathbf{D}}{\partial M_{ij}} \right|_P - \frac{1}{V_{\text{uc}}} \frac{\partial V_{\text{uc}}}{\partial M_{ij}} (QS_{ab} - 2\mathbf{d}_{ab} \cdot \mathbf{D}) \right),$$

where the derivatives $\partial Q / \partial G_i|_P$, $\partial \mathbf{d}_{ab} / \partial G_i$, $\partial \mathbf{D} / \partial G_i|_P$, $\partial S_{ab} / \partial G_i$, $\partial Q / \partial M_{ij}|_P$, $\partial \mathbf{d}_{ab} / \partial M_{ij}$, and $\partial \mathbf{D} / \partial M_{ij}|_P$ are straightforward; the terms $\partial S_{ab} / \partial M_{ij}$ and $\partial V_{\text{uc}} / \partial M_{ij}$ are given, e.g., in Ref. 16.

B. Exchange-correlation integrals

In Ref. 5, Tymczak and Challacombe showed that the exchange-correlation energy, for a periodic system, can be computed over a cubic region V_{\square} , and is completely equivalent to the integration over the unit cell V_{uc} . The exchange-correlation energy is thus

$$E^{\text{xc}}[\rho] = \int_{V_{\text{uc}}} f(\mathbf{r}) dV \equiv \int_{V_{\square}} f(\mathbf{r}) dV, \quad (5)$$

where $\rho(\mathbf{r}) = \sum_{ab} P_{ab} \rho_{ab}(\mathbf{r} + \mathbf{R})$ is the periodic electronic density. In the following, the subscript \square will always refer to the cuboid cell. This simple integration volume should be contrasted with more conventional methods for computing the exchange-correlation matrix, involving the ‘‘Becke weights,’’²⁵ which requires integration over all space, V_{∞} . While Eq. (5) is written in an abstract form for simplicity, in

TABLE I. Progression of the cell parameter a_0 , bond lengths (C–C and C–F), bond angle (F–C–F), and total energy E for polytetrafluoroethylene (CF₂)_{2n} using the periodic Γ -point PW91/6-31G** level of theory and the TIGHT thresholds. Lengths, angles, and energies are in angstroms, degrees, and atomic units, respectively.

	n	a_0	CC	CF	FCF	E/n
MONDOSCF ^a	1	3.400	1.823	1.339	116.9	−475.261 618
	2	2.701	1.588	1.360	109.9	−475.418 440
	3	2.640	1.571	1.361	109.5	−475.433 042
	4	2.634	1.570	1.361	109.5	−475.435 044
	5	2.633	1.571	1.361	109.5	−475.435 451
	6	2.632	1.570	1.361	109.5	−475.435 536
CRYSTAL03 ^b	1	2.628	1.569	1.360	109.5	−475.430 945

^a Γ point.

^b12 k points.

practice the code relies on the approach of Pople *et al.*²⁶ and Challacombe.²⁷

The derivatives of Eq. (5) with respect to atomic position G_i and cell parameter M_{ij} are given by

$$\left. \frac{\partial E^{xc}}{\partial G_i} \right|_P = \int_{V_\square} \left. \frac{\partial \rho(\mathbf{r})}{\partial G_i} \right|_P v_{xc}[\rho(\mathbf{r})] dV,$$

and

$$\left. \frac{\partial E^{xc}}{\partial M_{ij}} \right|_P = \int_{V_\square} \left. \frac{\partial \rho(\mathbf{r})}{\partial M_{ij}} \right|_P v_{xc}[\rho(\mathbf{r})] dV + \delta_{ij} \int_{S_{j\square}} f(\mathbf{r}) dS, \quad (6)$$

where $S_{j\square}$ is the surface area of the cuboid cell with its normal vector along the j th Cartesian direction. The derivative $\partial \rho(\mathbf{r}) / \partial M_{ij}|_P$ is simple and does not need to be addressed in more detail.

The surface integral [rightmost term in Eq. (6)], which is not present in previous derivations,^{15,28} has its origin in the derivative of the limits of the integral in Eq. (5). The surface integral is approximated by

$$\int_{S_{j\square}} f(\mathbf{r}) dS = \frac{1}{2h} \int_{V_{j\square}} f(\mathbf{r}) dV + \mathcal{O}(h^2),$$

where h is a small number (typically 10^{-4} a.u.) and $V_{j\square} = S_{j\square} \times [-h, h]$ is a thin volume where the integration over the interval $[-h, h]$ is carried out along the normal to the surface $S_{j\square}$ (i.e., along the j th Cartesian direction). This simple domain, i.e., $V_{j\square}$, can be efficiently integrated with the help of the HICU algorithm²⁷ to any desired accuracy.

III. NUMERICAL EXAMPLES

All developments were implemented in the MONDOSCF (Ref. 29) suite of linear scaling quantum chemistry programs. The code was compiled using the HP FORTRAN compiler F95 V5.5A (Ref. 30) and the `-04` option and the Compaq C compiler CC V6.5 (Ref. 31) and the `-01` flag. All calculations were carried out on a cluster of 256 4-CPU HP/Compaq Alphaservert ES45s with the Quadrics QsNet High Speed Interconnect.

The TIGHT level of numerical accuracy has been used throughout this work. Thresholds that define the TIGHT

accuracy level include a matrix threshold $\tau=10^{-6}$, as well as other numerical thresholds detailed in Ref. 5, which deliver at least eight digits of relative accuracy in the total energy and four digits of absolute accuracy in the forces.

In order to demonstrate the capabilities of our implementation of the Kohn-Sham density-functional analytic atomic and cell gradients, we present in this section full optimization studies of one-dimensional (1D) and 3D periodic systems without any cell or atomic positions symmetry constraints. The optimizations were carried out with the QUICCA algorithm.^{10,12}

Our first benchmark case is the optimization of 1D polytetrafluoroethylene (CF₂)_{2n} at the Perdew-Wang³² level of theory. The PW91 functional has been obtained from the Density-Functional Repository.³³ The second benchmark is cubic MgO and was optimized at the Perdew-Burke-Ernzerhof³⁴ (PBE) and Becke 3-parameter Lee-Yang-Parr³⁵ (B3LYP) level of theory. Finally, orthorhombic magnesium orthosilicate (Mg₂SiO₄, forsterite) was optimized at the B3LYP (Refs. 35 and 36) level of theory.

Table I shows the progression of the cell parameters a_0 , bond lengths (C–C and C–F), bond angle (F–C–F), and total energies E computed for polytetrafluoroethylene (CF₂)_{2n} at the Γ -point PW91 with the split-valence 6-31G** basis set. Comparisons are made to cell parameter, bond length, and bond angle values obtained with the CRYSTAL03 (Ref. 18) package and a 12 k -points net at the PW91/6-31G** level of theory. While the atomic and cell parameters for polytetrafluoroethylene agree perfectly between the k -space integration and the Γ -point approximation, the energies do not. The reason for this disagreement can be found in the different basis set used. CRYSTAL03 uses spherical harmonics d shell consisting of five atomic orbitals while MONDOSCF employs pure Cartesian basis functions, i.e., six atomic orbitals per Cartesian d shells. This leads to a slightly lower energy in the MONDOSCF calculations.

Table II shows the progression of the cell parameters, total energies, and fractional coordinates of oxygen computed for various MgO supercells (cubic symmetry) at the Γ -point PBE (Ref. 34) and B3LYP (Ref. 35) level of theories using the 8-61G(Mg)/8-51G(O) basis sets. The basis sets

TABLE II. Progression of the cell parameter a_0 , total energy E , and fractional coordinate of the oxygen f_O in the primitive cell for cubic (MgO) $_n$ using the periodic Γ -point PBE/8-61G(Mg)/8-51G(O) and B3LYP/8-61G(Mg)/8-51G(O) level of theories and the TIGHT thresholds. Cell parameters and energies are in angstroms and atomic units, respectively.

		n	a_0	E/n	f_O
MONDOSCF ^a	PBE	4	4.331	-275.243 165	0.4998
		32	4.213	-275.284 428	0.5000
		108	4.212	-275.284 641	0.5000
CRYSTAL03 ^b	PBE	1	4.212	-275.284 731	1/2
MONDOSCF ^a	B3LYP	4	4.328	-275.389 093	0.4972
		32	4.204	-275.431 167	0.5000
		108	4.204	-275.431 343	0.5000
CRYSTAL03 ^b	B3LYP	1	4.204	-275.431 235	1/2
Expt. ^c		1	4.20		

^a Γ point.

^b $8 \times 8 \times 8$ \mathbf{k} points.

^cExperimental value (Ref. 40).

were specially optimized at the HF level for MgO by Causà *et al.*³⁷ and were obtained from Ref. 38. The primitive cubic cell coordinates used for this system are given in Ref. 39. For comparison, we report the optimized cell parameter of cubic MgO obtained with the CRYSTAL03 code and an $8 \times 8 \times 8$ \mathbf{k} -points integration grid as well as the experimental cell parameter.⁴⁰ For both PBE and B3LYP, the smallest system (MgO) $_4$ shows a large discrepancy of the cell parameter, energy, and fractional coordinate of the oxygen with respect to its \mathbf{k} -space integration counterpart. The larger systems give cell parameter and fractional coordinate of the oxygen in very good agreement with the CRYSTAL03 results, and the energies systematical converge while the system grows.

In Table III, we present the optimization of forsterite (orthorhombic symmetry) at the B3LYP/8-61G*(Mg)/88-31G*(Si)/8-51G*(O) Γ -point approximation. The basis sets were obtained from Ref. 38. For comparison, we report the optimized cell parameters of forsterite obtained by Jochym *et al.*⁴¹ at the PW91 level of theory and a $3 \times 3 \times 3$ \mathbf{k} -points integration grid with the VASP (Refs. 42 and 43) package. We also report the experimental cell parameters

TABLE III. Progression of the cell parameters a_0 , b_0 , c_0 , and total energy E for orthorhombic (Mg $_2$ SiO $_4$) $_n$ using the periodic Γ -point B3LYP/8-31G*(Mg)/88-31G*(Si)/8-51G*(O) level of theory and the TIGHT thresholds. The number $n=4, 8, 16, 24$ correspond to the (super) cells $1 \times 1 \times 1$, $2 \times 1 \times 1$, $2 \times 1 \times 2$, and $3 \times 1 \times 2$, respectively. Cell parameters and energies are in angstroms and atomic units, respectively.

	n	a_0	b_0	c_0	E/n
MONDOSCF ^a	4	4.726	10.181	6.119	-991.264 858
	8	4.762	10.184	6.119	-991.260 767
	16	4.787	10.258	5.996	-991.271 696
	24	4.787	10.257	5.995	-991.271 841
VASP ^b	4	4.800	10.306	6.041	
Expt. ^c	4	4.756	10.195	5.981	

^a Γ point.

^b $3 \times 3 \times 3$ \mathbf{k} points and PW91 (Ref. 41).

^cExperimental values (Ref. 40).

measured by Yoder and Sahama.⁴⁴ As for the MgO case, the smallest system (Mg $_2$ SiO $_4$) $_4$ shows a large discrepancy for the cell parameters with respect to the VASP and experimental values. The larger systems, i.e., the $2 \times 1 \times 2$ and $3 \times 1 \times 2$ supercells, give cell parameters in very good agreement with the experimental data, and the energies systematically converge while the system grows. The cell parameters obtained from the Γ -point B3LYP/8-61G*(Mg)/88-31G*(Si)/8-51G*(O) level of theory deviate less than 1% with respect to the experimental values.

IV. CONCLUSIONS

In a previous paper, construction of the analytical exact Hartree-Fock exchange gradients with respect to atomic and cell parameters within the Γ -point approximation has been introduced. In this article, the formalism for evaluation of the density-functional analytic gradients in Γ -point approximation for Cartesian-Gaussian-type basis functions was presented and implemented in the MONDOSCF package. We show that, like for the exact HF exchange, the evaluation of the atomic gradients within the Γ -point approximation does not lead to difficulties. The implementation requires mainly the evaluation of the derivative of the basis function with respect to atomic positions. However, complications arise when derivatives of the total energy are taken with respect to lattice parameters. For the periodic far-field Coulomb term, the derivative of the multipole interaction tensor needs to be carefully handled in both direct and reciprocal space. The exchange-correlation energy derivative leads to a surface term, which has its origin in the derivative of the limits of the integration over the cell.

The analytical atomic and cell gradients have been used in conjunction with the QUICCA algorithm to optimize a few 1D and 3D periodic systems at the DFT and hybrid-HF/DFT level of theory. Convergence of bond lengths, bond angles, and cell parameters within the DFT and hybrid-HF/DFT Γ -point supercell approach and under full relaxation with no symmetry has been demonstrated for 1D and 3D systems to better than three digits. Thus, we could show that a relative accuracy better than three digits can be already achieved with cubic cells of about 600 Å³.

ACKNOWLEDGMENTS

This work has been supported by the Swiss National Science Foundation, the Swiss Office for Education and Science through the European COST Action D14, and the US Department of Energy under Contract No. W-7405-ENG-36 and the ASCI project. The advanced Computing Laboratory of Los Alamos National Laboratory is acknowledged.

APPENDIX: COMPUTATION OF THE DERIVATIVE OF THE \mathcal{M} TENSOR WITH RESPECT TO CELL PARAMETERS

Following the work of Challacombe *et al.*²³ and Tymczak and Challacombe,⁵ the \mathcal{M}_l^m tensor can be written into direct and reciprocal space terms as

$$\begin{aligned}\mathcal{M}_l^m &= \sum_{\mathbf{R} \in \text{PFF}} \tilde{P}_l^m(\cos \theta_{\mathbf{R}}) e^{im\phi_{\mathbf{R}}} \mathcal{G}_l(\beta, R) \\ &- \sum_{\mathbf{R} \in \text{In}} \tilde{P}_l^m(\cos \theta_{\mathbf{R}}) e^{im\phi_{\mathbf{R}}} \mathcal{F}_l(\beta, R) \\ &+ \frac{4\pi^{3/2}(i/2)^l}{V_{\text{uc}}\Gamma(l+1/2)} \sum_{\mathbf{G} \neq \{\emptyset\}} G^{l-2} e^{-\pi^2 G^2/\beta^2} \\ &\times \tilde{P}_l^m(\cos \theta_{\mathbf{G}}) e^{im\phi_{\mathbf{G}}},\end{aligned}$$

where \mathbf{G} is a reciprocal lattice vector, $G=|\mathbf{G}|$, $R=|\mathbf{R}|$, \tilde{P}_l^m is a scaled associated Legendre polynomial, $\beta=\sqrt{\pi}/V_{\text{uc}}^{1/3}$ for convenience,

$$\mathcal{G}_l(\beta, R) = \frac{\gamma(l+1/2, \beta^2 R^2)}{\Gamma(l+1/2)R^{l+1}},$$

and

$$\mathcal{F}_l(\beta, R) = \frac{\Gamma(l+1/2, \beta^2 R^2)}{\Gamma(l+1/2)R^{l+1}},$$

where $\Gamma(a, x) = \int_x^\infty t^{a-1} \exp(-t) dt$ is the gamma function, $\Gamma(a) = \Gamma(a, 0)$, and $\gamma(a, x) = \int_0^x t^{a-1} \exp(-t) dt$ is the incomplete gamma function.⁴⁵ The derivative of \mathcal{M}_l^m with respect to cell parameters M_{ij} is

$$\begin{aligned}\frac{\partial \mathcal{M}_l^m}{\partial M_{ij}} &= \sum_{\mathbf{R} \in \text{PFF}} e^{im\phi_{\mathbf{R}}} \left(\tilde{P}_l^m \frac{\partial \mathcal{G}_l}{\partial M_{ij}} \right)_{\beta} + \left(\frac{\partial \tilde{P}_l^m}{\partial M_{ij}} + im \tilde{P}_l^m \frac{\partial \phi_{\mathbf{R}}}{\partial M_{ij}} \right) \mathcal{G}_l - \sum_{\mathbf{R} \in \text{In}} e^{im\phi_{\mathbf{R}}} \left(\tilde{P}_l^m \frac{\partial \mathcal{F}_l}{\partial M_{ij}} \right)_{\beta} + \left(\frac{\partial \tilde{P}_l^m}{\partial M_{ij}} + im \tilde{P}_l^m \frac{\partial \phi_{\mathbf{R}}}{\partial M_{ij}} \right) \mathcal{F}_l \\ &+ \frac{4\pi^{3/2}(i/2)^l}{V_{\text{uc}}\Gamma(l+1/2)} \sum_{\mathbf{G} \neq \{\emptyset\}} G^{l-3} e^{-\pi^2 G^2/\beta^2} e^{im\phi_{\mathbf{G}}} \times \left(\frac{-1}{V_{\text{uc}}} \frac{\partial V_{\text{uc}}}{\partial M_{ij}} G \tilde{P}_l^m + \left((l-2) - 2 \left(\frac{\pi G}{\beta} \right)^2 \right) \frac{\partial G}{\partial M_{ij}} \tilde{P}_l^m \right. \\ &\left. + G \left(\frac{\partial \tilde{P}_l^m}{\partial M_{ij}} + im \tilde{P}_l^m \frac{\partial \phi_{\mathbf{G}}}{\partial M_{ij}} \right) \right).\end{aligned}$$

Note that because $\mathcal{M}_l^m \neq \mathcal{M}_l^m(\beta)$, it follows that $\partial \mathcal{M}_l^m / \partial \beta = 0$. The derivative of the scaled associated Legendre polynomial $\tilde{P}_l^m(\cos \theta)$ is

$$\frac{\partial \tilde{P}_l^m}{\partial M_{ij}}(\cos \theta) = \frac{l \cos \theta \tilde{P}_l^m - (l+m) \tilde{P}_{l-1}^m}{\sqrt{1 - \cos^2 \theta}} \frac{\partial \theta}{\partial M_{ij}},$$

which holds for both $\theta = \theta_{\mathbf{R}}$ and $\theta = \theta_{\mathbf{G}}$. Derivation of $\mathcal{G}_l(\beta, R)$ and $\mathcal{F}_l(\beta, R)$ are given by

$$\frac{\partial \mathcal{G}_l}{\partial M_{ij}} \Big|_{\beta} = \left(\frac{2(\beta R)^{2l} e^{-\beta^2 R^2}}{\Gamma(l+1/2)R^{l+1}} - \mathcal{G}_l(\beta, R) \frac{(l+1)}{R} \right) \frac{\partial R}{\partial M_{ij}},$$

and

$$\frac{\partial \mathcal{F}_l}{\partial M_{ij}} \Big|_{\beta} = - \left(\frac{2(\beta R)^{2l} e^{-\beta^2 R^2}}{\Gamma(l+1/2)R^{l+1}} + \mathcal{F}_l(\beta, R) \frac{(l+1)}{R} \right) \frac{\partial R}{\partial M_{ij}}.$$

The derivatives $\partial V_{\text{uc}} / \partial M_{ij}$ and $\partial G / \partial M_{ij}$ can be found in Ref. 16 and the remaining derivatives, i.e., $\partial R / \partial M_{ij}$, $\partial \theta_{\mathbf{R}} / \partial M_{ij}$, $\partial \theta_{\mathbf{G}} / \partial M_{ij}$, $\partial \phi_{\mathbf{R}} / \partial M_{ij}$, and $\partial \phi_{\mathbf{G}} / \partial M_{ij}$ are easily computed.

¹ P. M. Gill, B. J. Johnson, J. A. Pople, and M. J. Frisch, *Int. J. Quantum Chem.* **S26**, 319 (1992).

² A. D. Becke, *J. Chem. Phys.* **98**, 1372 (1993).

³ V. Barone, C. Adamo, and F. Mele, *Chem. Phys. Lett.* **249**, 290 (1996).

⁴ C. Adamo, M. Cossi, and V. Barone, *THEOCHEM* **493**, 145 (1999).

⁵ C. J. Tymczak and M. Challacombe, *J. Chem. Phys.* **122**, 134102 (2005).

⁶ C. J. Tymczak, V. Weber, E. Schwegler, and M. Challacombe, *J. Chem. Phys.* **122**, 124105 (2005).

⁷ C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971).

⁸ N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, New York, 1976).

⁹ V. Weber, C. Daul, and M. Challacombe, *J. Chem. Phys.* **124**, 214105 (2006).

¹⁰ K. Németh and M. Challacombe, *J. Chem. Phys.* **121**, 2877 (2004).

¹¹ T. Bučko, J. Hafner, and J. Ángyán, *J. Chem. Phys.* **122**, 124508 (2005).

¹² K. Németh and M. Challacombe, *J. Chem. Phys.* **123**, 194112 (2005).

¹³ S. Hirata and S. Iwata, *J. Phys. Chem. A* **102**, 8426 (1998).

¹⁴ K. N. Kudin and G. E. Scuseria, *Phys. Rev. B* **61**, 5141 (2000).

¹⁵ K. N. Kudin and G. E. Scuseria, *Phys. Rev. B* **61**, 16440 (2000).

¹⁶ K. Doll, R. Dovesi, and R. Orlando, *Theor. Chim. Acta* **112**, 394 (2004).

¹⁷ R. Dovesi, R. Orlando, C. Roetti, C. Pisani, and V. V. R. Saunders, *Phys. Status Solidi B* **217**, 63 (2000).

¹⁸ R. Dovesi, V. R. Saunders, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and E. Apra, computer code CRYSTAL03 (University of Torino, Torino, 2003).

¹⁹ P. P. Ewald, *Ann. Phys.* **64**, 253 (1921).

²⁰ K. Doll, V. R. Saunders, and N. M. Harrison, *Int. J. Quantum Chem.* **82**, 1 (2001).

²¹ K. Doll, *Comput. Phys. Commun.* **137**, 74 (2001).

²² L. E. McMurchie and E. R. Davidson, *J. Comput. Phys.* **26**, 218 (1978).

²³ M. Challacombe, C. White, and M. HeadGordon, *J. Chem. Phys.* **107**, 10131 (1997).

²⁴ M. Challacombe and E. Schwegler, *J. Chem. Phys.* **106**, 5526 (1997).

²⁵ A. D. Becke, *J. Chem. Phys.* **88**, 2547 (1988).

²⁶ J. A. Pople, P. M. W. Gill, and B. G. Johnson, *Chem. Phys. Lett.* **199**, 557 (1992).

²⁷ M. Challacombe, *J. Chem. Phys.* **113**, 10037 (2000).

²⁸ M. Tobita, S. Hirata, and R. J. Bartlett, *J. Chem. Phys.* **118**, 5776 (2003).

²⁹ M. Challacombe, C. Tymczak, K. Németh, V. Weber, C. K. Gan, E. Schwegler, G. Henkelman, and A. Niklasson, computer code MONDOSCF (Los Alamos National Laboratory, Los Alamos, New Mexico, 2001).

³⁰ Computer code Hewlett-Packard Fortran compiler, F95 V5.5A (Compaq

- Computer Corporation, Houston, 2003).
- ³¹ Computer code Compaq C compiler, C V6.5 (Compaq Computer Corporation, Houston, 2002).
- ³² J. Perdew, J. Chevary, S. Vosko, K. Jackson, M. Pederson, D. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- ³³ Functionals were obtained from the Density Functional Repository as developed and distributed by the Quantum Chemistry Group, CCLRC Daresbury Laboratory, Daresbury, Cheshire, WA4 4AD United Kingdom. Contact Huub van Dam (h.j.vandam@dl.ac.uk) or Paul Sherwood for further information (2003).
- ³⁴ J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ³⁵ A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- ³⁶ P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).
- ³⁷ M. Causà, R. Dovesi, C. Pisani, and C. Roetti, Phys. Rev. B **33**, 1308 (1986).
- ³⁸ R. Dovesi, V. Saunders, C. Roetti, M. Causà, N. Harrison, R. Orlando, and C. Zicovich-Wilson, computer code CRYSTAL98 Basis Sets (University of Torino, Torino, 1998).
- ³⁹ Periodic coordinates used in MONDOSCF validation (2004), URL <http://www.t12.lanl.gov/~mchalla/>.
- ⁴⁰ R. W. G. Wyckoff, *Crystal Structure* (Wiley, New York, 1963).
- ⁴¹ P. T. Jochym, K. Parlinski, and P. Krzywiec, Comput. Mat. Sci. **29**, 414418 (2004).
- ⁴² G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- ⁴³ G. Kresse and J. Furthmüller, Comp. Math. Sci. **6**, 15 (1996).
- ⁴⁴ H. S. Yoder and G. Sahama, Am. Mineral. **42**, 475 (1957).
- ⁴⁵ *Handbook of Mathematical Functions* (Dover, New York, 1987).