



All-electron formalism for total energy strain derivatives and stress tensor components for numeric atom-centered orbitals



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ABSTRACT

We derive and implement the strain derivatives of the total energy of solids, i.e., the analytic stress tensor components, in an all-electron, numeric atom-centered orbital based density-functional formalism. We account for contributions that arise in the semi-local approximation (LDA/GGA) as well as in the generalized Kohn–Sham case, in which a fraction of exact exchange (hybrid functionals) is included. In this work, we discuss the details of the implementation including the numerical corrections for sparse integrations grids which allow to produce accurate results. We validate the implementation for a variety of test cases by comparing to strain derivatives performed via finite differences. Additionally, we include the detailed definition of the overlapping atom-centered integration formalism used in this work to obtain total energies and their derivatives.

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1. Introduction

Density-functional theory (DFT) enjoys high popularity as an *ab initio* formalism to compute the ground state electron density and energy of molecules, clusters, and solids. As formalized in the Hellmann–Feynman theorem and generalized in the $2n + 1$ theorem [1], the so-called atomic forces, i.e., the derivatives of the Born–Oppenheimer potential-energy surface with respect to the nuclear coordinates, can be derived as analytical expressions. Care must be taken since correction terms can arise, e.g., Pulay terms [2] if the basis functions move with the atoms. The atomic forces enable efficient DFT-based structure optimization algorithms that allow to determine the local minima of the potential-energy surface associated with the electronic ground state. By these means, one can identify the stable and metastable geometries at zero Kelvin, which in turn provide the founding for further computational investigations, e.g., via first-principles atomistic thermodynamics [3]. To apply such structure optimization methods to materials modeled as periodic solids, one must additionally take into account the lattice degrees of freedom and the respective derivatives of the energy with respect to strain, i.e., the stress.

The strain tensor ε describes the elastic deformation of a crystal relative to a reference state. This corresponds to a transformation

of all real space coordinates and its derived quantities, e.g., the atomic positions \mathbf{R}

$$R_{\alpha}(\varepsilon) = \sum_{\beta} (\delta_{\alpha\beta} + \varepsilon_{\alpha\beta}) R_{\beta}(0) \quad (1)$$

with respect to the zero strain reference $\mathbf{R}(0)$. $\alpha, \beta = 1, 2, 3$ denote the Cartesian components. In general, Greek indices stand for the three Cartesian components throughout this paper. For a unit cell with volume V , the stress tensor σ is defined [4,5] as the first order change in the total (Born–Oppenheimer) energy of the unit cell E_{tot} under a symmetrical, infinitesimal strain deformation ε

$$\sigma_{\lambda\mu} = \frac{1}{V} \left. \frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\lambda\mu}} \right|_{\varepsilon=0}. \quad (2)$$

Given that only symmetric strain deformations are used in the definition of the stress tensor, the stress tensor is symmetric as well and thus consists of six independent entries. Although this definition is unique, a practical implementation of these derivatives depends very much on the numerical details chosen for the DFT formalism, e.g., on the basis set type.

Nielsen and Martin [6,7] first demonstrated that the stress can indeed be efficiently and accurately assessed in a DFT framework. For this purpose, they employed a plane wave basis set expansion (together with norm-conserving pseudopotentials) and the local-density approximation. Later works extended the stress tensor implementation for plane waves to ultra-soft pseudopotentials [8]

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including the contributions of the generalized orthonormality condition. Thonhauser and coworkers [9] as well as Nagasako and coworkers [5] summarized the strain derivatives for the linearized augmented plane wave method. The former derived a surface term due to the discontinuities at the boundaries between muffin tins and interstitial region and the latter presented a correction because the number of plane waves in the interstitial region changes under strain. Kresse and coworkers [10] as well as Torrent and coworkers [11] derived the stress tensor for the projector augmented-wave (PAW) method and discussed the additional terms arising from the compensating charges of the PAW method. Kudin and coworkers [12] discussed the implementation of the stress tensor for Gaussian-type orbitals (GTO) while evaluating the electrostatic contributions entirely in real space using a fast multipole method. Doll and coworkers [13,14] employed GTOs, too, including the strain derivatives for Hartree–Fock calculations. Furthermore, Soler and coworkers [15] presented the strain derivatives for numeric atom-centered orbitals with norm-conserving pseudopotentials calculating the electrostatics by fast Fourier transforms.

In this paper, we derive the strain derivatives, i.e., the analytical stress tensor components, in an all-electron, numeric atom-centered orbital based density-functional formalism. We discuss our implementation of these formulae in the electronic structure theory code FHI-aims [16] including strain derivatives of hybrid functionals and the van der Waals (vdW) correction scheme of Tkatchenko and Scheffler [17]. Hereby, all electrostatic contributions are evaluated in real space using a multipole expansion including Ewald’s method [18] together with corrections. Furthermore, we account for Pulay terms due to our atom-centered basis functions.

The remainder of the paper is organized as follows: In Section 2, the general mathematical formalism of DFT and of the analytical stress tensor are presented. Section 3 gives a detailed derivation of the various contributions that arise in a numeric atom-centered orbital based DFT formalism. Details of the numerical implementation are discussed in Section 4. Finally in Section 5, we investigate the accuracy and the efficiency of our implementation by comparing our analytical stress tensor components to strain derivatives computed via finite differences. We compare these two quantities for a wide range of systems that range from metals via semiconductors and insulators to organic crystals to demonstrate the general validity of our implementation across the periodic table. Furthermore, we also study the behavior of our implementation for different exchange–correlation functionals, basis set sizes, system sizes, and integration grids to investigate the convergence behavior of the analytical stress tensor. The computational performance of our implementation is discussed in Section 5 as well. For the sake of completeness, Section 6 gives an overview on how the stress tensor can be used to optimize the unit cell of a crystal (i.e., finding energy minima) under external pressure.

2. Formalism

2.1. Total energy in DFT

In Kohn–Sham (KS) DFT, the total energy of a system at given nuclear configuration reads [19,20]

$$E_{\text{tot}} = E_{\text{KS}}[n_0] + E_{\text{nuc}} \quad (3)$$

with the ground state electron density n_0 , the nuclear–nuclear energy E_{nuc} , and the Kohn–Sham energy functional

$$E_{\text{KS}}[n] = T_s[n] + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n]. \quad (4)$$

T_s is the kinetic energy functional of non-interacting electrons, E_{ext} the electron–nuclear energy, E_{H} the Hartree energy, and E_{xc}

the exchange–correlation energy functional. For clarity, we avoid an explicitly spin-polarized notation, a formal generalization to collinear (scalar) spin-DFT is straightforward and in fact included in the implementation. Also, it is important to note that the formally correct separation of the electrostatic interactions in E_{nuc} , E_{ext} , and E_{H} is computationally not possible in periodic systems, as discussed in more detail in Section 3.4.

The ground state electron density for fixed nuclear coordinates is obtained by solving the variational equation for the electron density n ,

$$\delta \left[E_{\text{KS}}[n] - \mu \left(\int d\mathbf{r} n(\mathbf{r}) - N_e \right) \right] = 0, \quad (5)$$

with the chemical potential $\mu = \delta E_{\text{KS}} / \delta n$ and the number of electrons N_e . This yields the Kohn–Sham single particle equation [20],

$$\hat{h}_{\text{KS}} |\psi_i\rangle = \epsilon_i |\psi_i\rangle, \quad (6)$$

the solution of which yields the Kohn–Sham orbitals ψ_i and the corresponding eigenvalues ϵ_i . The electron density is

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \quad (7)$$

in which f_i denotes the occupation number of the orbitals. Furthermore,

$$\hat{h}_{\text{KS}} = \hat{t}_s + \hat{v}_{\text{ext}} + \hat{v}_{\text{H}}[n] + \hat{v}_{\text{xc}}[n] \quad (8)$$

is the Kohn–Sham Hamiltonian. \hat{t}_s is the kinetic operator, \hat{v}_{ext} the electron–nuclear potential, \hat{v}_{H} the Hartree potential, and \hat{v}_{xc} the exchange–correlation potential.

In practice, Eq. (6) is solved by expanding the Kohn–Sham orbitals ψ_i in a given basis set

$$\psi_i(\mathbf{r}) = \sum_j c_{ij} \varphi_j(\mathbf{r}) \quad (9)$$

with the expansion coefficients c_{ij} and the basis functions $\varphi_j(\mathbf{r})$, which leads to a generalized eigenvalue problem of the form

$$\sum_j \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle c_{ji} = \epsilon_i \sum_j \langle \varphi_i | \varphi_j \rangle c_{ji}. \quad (10)$$

Here, $\langle \cdot | \cdot \rangle$ denotes the usual bra–ket notation for the inner product in Hilbert space (integral in real space). In the case of FHI-aims, the basis functions are real-valued atom-centered orbitals, i.e., they depend on the position of the atoms, and the basis set expansion takes the following explicit form

$$\psi_i(\mathbf{r}) = \sum_{jJ} c_{ij} \varphi_j(\mathbf{r} - \mathbf{R}_J). \quad (11)$$

The sum runs over all atoms J and basis functions j which are associated with atom J , and \mathbf{R}_J denotes the position of atom J . Accordingly, the density is a function of the expansion coefficients and thus Eq. (5) translates into a minimization of E_{KS} with respect to the expansion coefficients under the constraint of orthonormalized orbitals,

$$E_{\text{KS}}[n_0] = \min_{\{c_{ij}\}} \left[E_{\text{KS}} - \sum_i f_i \epsilon_i (\langle \psi_i | \psi_i \rangle - 1) \right]. \quad (12)$$

2.2. Fundamental formulae for strain derivatives

2.2.1. Properties of strain derivatives

The total energy derivative in Eq. (2) can be written as

$$\left. \frac{\partial E_{\text{tot}}}{\partial \epsilon_{\lambda\mu}} \right|_{\epsilon=0} = \sum_i \left. \frac{\partial E_{\text{tot}}(u_i)}{\partial u_i} \frac{\partial u_i}{\partial \epsilon_{\lambda\mu}} \right|_{\epsilon=0}, \quad (13)$$

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