Computer Physics Communications 215 (2017) 26–46

Contents lists available at ScienceDirect

Computer Physics Communications

journal homepage: www.elsevier.com/locate/cpc

Lattice dynamics calculations based on density-functional perturbation theory in real space

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ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form
1 February 2017
Accepted 3 February 2017
Available online 11 February 2017

Keywords:
Lattice dynamics
Density-function theory
Density-functional perturbation theory
Atom-centered basis functions

ABSTRACT

A real-space formalism for density-functional perturbation theory (DFPT) is derived and applied for the computation of harmonic vibrational properties in molecules and solids. The practical implementation using numeric atom-centered orbitals as basis functions is demonstrated exemplarily for the all-electron Fritz Haber Institute *ab initio* molecular simulations (*FHI-aims*) package. The convergence of the calculations with respect to numerical parameters is carefully investigated and a systematic comparison with finite-difference approaches is performed both for finite (molecules) and extended (periodic) systems. Finally, the scaling tests and scalability tests on massively parallel computer systems demonstrate the computational efficiency.

1. Introduction

Density-functional theory (DFT) [1,2] is to date the most widely applied method to compute the ground-state electronic structure and total energy for polyatomic systems in chemistry, physics, and material science. Via the Hellmann–Feynman [3,4] theorem the DFT ground state density also provides access to the first derivatives of the total energy, i.e., the forces acting on the nuclei and the stresses acting on the lattice degrees of freedom. The forces and stress in turn can be used to determine equilibrium geometries with optimization algorithms [5], to traverse thermodynamic phase space with *ab initio* molecular dynamics [6], and even to search for transition states of chemical reactions or structural transitions [7]. Second and higher order derivatives, however, cannot be calculated on the basis of the ground state density alone, but also require knowledge of its response to the corresponding perturbation: The $2n+1$ theorem [8] proves that the nth order derivative of the density/wavefunction is required to determine the $2n+1$th derivative of the total energy. For example, for the calculation of vibrational frequencies and phonon band-structures (second order derivative) the response of the electronic structure to a nuclear displacement (first order derivative) is needed. These derivatives can be calculated in the framework of density-functional perturbation theory (DFPT) [9–11] viz. the coupled perturbed self-consistent field (CPSCF) method [12–17].[1] DFPT and CPSCF then provide access to many fundamental physical phenomena, such as superconductivity [18,19], phonon-limited carrier lifetimes [20–22] in electron transport and hot electron relaxation [23,24], Peierls instabilities [25], the renormalization of the electronic structure due to nuclear motion [26–35], Born effective charges [36], phonon-assisted transitions in spectroscopy [37–39], infrared [40] as well as Raman spectra [41], and much more [42].

In the literature, implementations of DFPT using a *reciprocal-space* formalism have been mainly reported for plane-wave (PW) basis sets for norm-conserving pseudopotentials [9,10,36], for ultrasoft pseudopotentials [43], and for the projector augmented wave method [44]. These techniques were also used for all-electron, full-potential implementations with linear muffin tin orbitals [45] and linearized augmented plane-waves [46,47]. For codes using localized atomic orbitals, DFPT has been mainly implemented to treat finite, isolated systems [12–17], but only a few literature reports exist for the treatment of periodic boundary conditions with such basis sets [48–50]. In all these cases, which only considered perturbations commensurate with the unit cell (Γ-point perturbations), the exact same *reciprocal-space* formalism has been used as in the case of plane-waves.

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[1] Formally, DFPT and CPSCF are essentially equivalent, but the term DFPT is more widely used in the physics community, whereas CPSCF is better known in quantum chemistry.

http://dx.doi.org/10.1016/j.cpc.2017.02.001

Sun and Bartlett [51] have analytically generalized the formalism to account for non-commensurate perturbations (corresponding to non-Γ periodicity in reciprocal-space), but no practical implementation has been reported.

In the aforementioned reciprocal-space implementations, each perturbation characterized by its reciprocal-space vector $\mathbf{q}$ requires an individual DFPT calculation. Accordingly, this formalism can become computationally expensive quite rapidly, whenever the response to the perturbations is required to be known on a very tight $\mathbf{q}$ grid. To overcome this computational bottleneck, various interpolation techniques have been proposed in literature: For instance, Giustino et al. [52] suggested to Fourier-transform the reciprocal-space electron–phonon coupling elements to real-space. The spatial localization of the perturbation in real-space (see Fig. 1) allows an accurate interpolation by using Wannier functions as a compact, intermediate representation. In turn, this then enables a back-transformation onto a dense $\mathbf{q}$ grid in reciprocal-space.

To our knowledge, however, no *real-space* DFPT formalism that **directly** exploits the spatial localization of the perturbations under periodic boundary conditions has been reported in the literature, yet. This is particularly surprising, since real-space formalisms have attracted considerable interest for standard ground-state DFT calculations [53–59] in the last decades due to their favorable scaling with respect to the number of atoms and their potential for massively parallel implementations. Formally, one would expect a real-space DFPT formalism to exhibit similar beneficial features and thus to facilitate calculations of larger systems with less computational expense on modern multi-core architectures.

We here derive, implement, and validate a real-space formalism for DFPT. The inspiration for this approach comes from the work of Giustino et al. [52], who demonstrated that Wannierization [60] can be used to map reciprocal-space DFPT results to real-space, which in turn enables numerically efficient interpolation strategies [61]. In contrast to these previous approaches, however, our DFPT implementation is formulated directly in real space and utilizes the exact same localized, atom-centered basis set as the underlying ground-state DFT calculations. This allows us to exploit the inherent locality of the basis set to describe the spatially localized perturbations and thus to take advantage of the numerically favorable scaling of such a localized basis set. In addition, all parts of the calculation consistently rely on the same real-space basis set. Accordingly, all computed response properties are known in an accurate real-space representation from the start and no potentially error-prone interpolation (re-expansion) is required. However, this reformulation of DFPT also gives rise to many non-trivial terms that are discussed in this paper. For instance, the fact that we utilize atom-centered orbitals require accounting for various Pulay-type terms [62]. Furthermore, the treatment of spatially localized perturbations that are not translationally invariant with respect to the lattice vectors requires specific adaptions of the algorithms used in ground-state DFT to compute electrostatic interactions, electronic densities, etc. We also note that the proposed approach facilitates the treatment of isolated molecules, clusters, and periodic systems on the same footing. Accordingly, we demonstrate the validity and reliability of our approach by using the proposed real-space DFPT formalism to compute the electronic response to a displacement of nuclei and harmonic vibrations in molecules and phonons in solids.

The remainder of the paper is organized as follows. In Section 2 we succinctly summarize the fundamental theoretical framework used in DFT, in DFPT, and in the evaluation of harmonic force constants. Starting from the established real-space formalism for ground-state DFT calculations, we derive the fundamental relations required to perform DFPT and lattice dynamics calculations in Section 3. The practical and computational implications of these equations are then discussed in Section 4 using our own implementation in the all-electron, full-potential, numerical atomic orbitals based code *FHI-aims* [55,63,64] as an example. In Section 5 we validate our method and implementation for both molecules and extended systems by comparing vibrational and phonon frequencies computed with DFPT to the ones computed via finite-differences. Furthermore, we exhaustively investigate the convergence behavior with respect to the numerical parameters of the implementation (basis set, system sizes, integration grids, etc.) and we discuss the performance and scaling with system size. Eventually, Section 6 summarizes the main ideas and findings of this work and highlights possible future research directions, for which the developed formalism seems particularly promising.

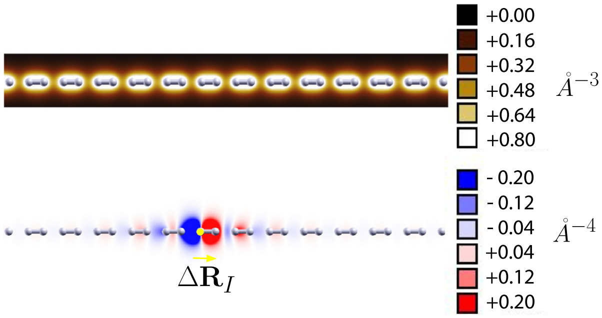

Fig. 1. Periodic electronic density $n(\mathbf{r})$ and spatially localized response of the electron density $dn(\mathbf{R})/d\mathbf{R}_I$ to a perturbation viz. displacement of atom $\Delta\mathbf{R}_I$ shown exemplarily for an infinite line of H_2 molecules.

2. Fundamental theoretical framework

2.1. Density-functional theory

In DFT, the total energy is uniquely determined by the electron density $n(\mathbf{r})$

$$E_{KS} = T_s[n] + E_{ext}[n] + E_H[n] + E_{xc}[n] + E_{ion--ion}, \tag{1}$$

in which T_s is the kinetic energy of non-interacting electrons, E_{ext} the electron-nuclear, E_H the Hartree, E_{xc} the exchange–correlation, and $E_{ion--ion}$ the ion–ion repulsion energy. All energies are functionals of the electron density. Here we avoid an explicitly spin-polarized notation, a formal generalization to collinear (scalar) spin-DFT is straightforward.

The ground state electron density $n_0(\mathbf{r})$ (and the associated ground state total energy) is obtained by variationally minimizing Eq. (1)

$$\frac{\delta}{\delta n}\left[E_{KS} - \mu\left(\int n(\mathbf{r})\,d\mathbf{r} - N_e\right)\right] = 0, \tag{2}$$

whereby the chemical potential $\mu = \delta E_{KS}/\delta n$ ensures that the number of electrons N_e is conserved. This yields the Kohn–Sham single particle equations

$$\hat{h}_{KS}\psi_i = \left[\hat{t}_s + \hat{v}_{ext}(r) + \hat{v}_H + \hat{v}_{xc}\right]\psi_i = \epsilon_i\psi_i, \tag{3}$$

for the Kohn–Sham Hamiltonian $\hat{h}_{KS}$. In Eq. (3) $\hat{t}_s$ is the single particle kinetic operator, $\hat{v}_{ext}$ the (external) electron-nuclear potential, $\hat{v}_H$ the Hartree potential, and $\hat{v}_{xc}$ the exchange–correlation potential. Solving Eq. (3) yields the Kohn–Sham single particle states ψ_i and their eigenenergies ϵ_i. The single particle states determine the electron density via

$$n(\mathbf{r}) = \sum_i f(\epsilon_i)|\psi_i(r)|^2, \tag{4}$$

in which $f(\epsilon_i)$ denotes the Fermi–Dirac distribution function.