Sensitivity analysis of total energy in electronic structure calculations

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A variation of the total energy of a system of atoms with respect to a change in atomic positions, i.e., the sensitivity of the total energy, also known as Hellmann-Feynman forces (HFF), is a very important quantity in the physics of materials. Its efficient evaluation has many applications such as finding stable atomic positions or in molecular dynamics calculations.

The HFF are the gradients of the total energy (including the interaction energy of atomic cores) with respect to the movement of atomic centers. According to the Hellmann-Feynman theorem [3], supposing that a fixed discretization basis is used, the forces can be calculated from the gradient of the Hamiltonian (energy operator) H

$$\vec{f_i} = -\nabla e_{\text{TOT}} = -\nabla \left(\psi^+ H \psi \right) = -\psi^+ \nabla \left(H \right) \psi \,, \tag{1}$$

where the gradient is considered with respect to the shift of atomic centers, $^+$ denotes Hermitian transpose and ψ is the wave function describing a quantum state.

We present several approaches for evaluating the HFF within the density functional theory in combination with nonlocal ab-initio pseudopotentials and the finite-element method, as implemented in our new real space code for electronic structure calculations [6, 2, 1].

The total energy in the density functional theory is given by (see e.g. [4, 5])

$$e_{\text{TOT}} = \sum_{i=1}^{n} w_i \int \psi_i^+ \frac{1}{2} \nabla^2 \psi_i + \int \psi_i^+ V_{\text{EXT}} \psi + \int E_{\text{H}}(\rho) + \int E_{\text{XC}}(\rho) + e_{\text{ION}} \,, \tag{2}$$

where V_{EXT} is the external potential, E_{H} is the electrostatic energy, E_{XC} is the exchange-correlation energy, ρ is the charge density and e_{ION} is the atomic core repulsion energy. In our case V_{EXT} is the sum of pseudopotentials of atomic cores, each of them constituted by a long-range local part and a short-range nonlocal l-dependent part:

$$V_{\text{EXT}} = \sum_a \left(V_{\text{LOC}}^a + \sum_l V_{\text{NL}}^{a,l} P_l^a \right) \,, \tag{3}$$

where P_l^a is a projection operator into a l-subspace, spanned by the spherical harmonics basis $Y_{l,m}$, of the a-th center.

Following from (1), the gradient of the total energy contains only the terms with the explicit dependence on atom positions:

$$\nabla_a e_{\text{TOT}} = \int \nabla V_{\text{LOC}}^a \rho + \sum_{l,i} w_i \int \psi_i^+ \nabla \left(V_{\text{NL}}^{a,l} P_l^a \right) \psi_i + \nabla e_{\text{ION}} \,. \tag{4}$$

The most difficult term of equation (4) is the middle one: the nonlocal part of electron-ion interaction. In the contribution, several approaches to evaluating this term will be analyzed in terms of convergence properties and computing demands using test calculations on simple molecules of nitric oxide, carbon dioxide and tetrafluormethane, see Fig. 1, with interatomic distances scaled by a variable factor.
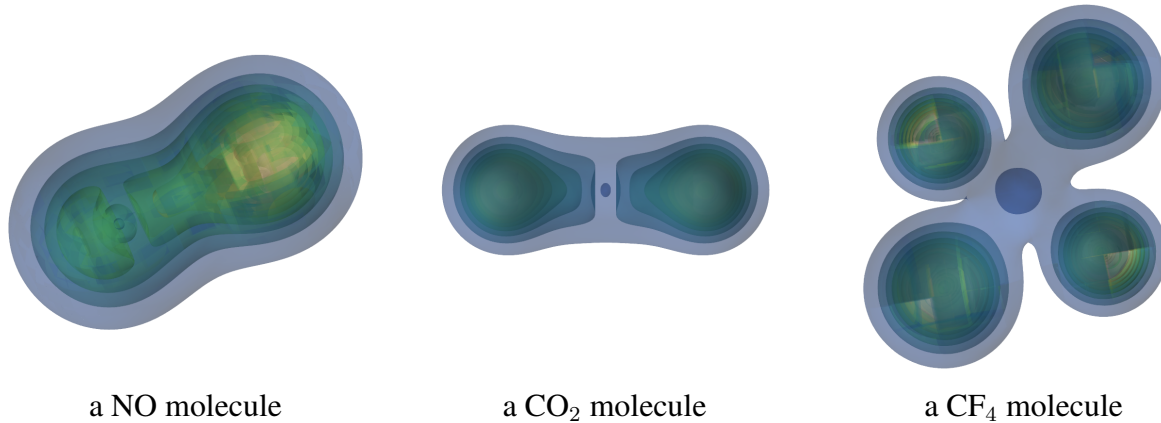

a NO molecule   a CO_2 molecule   a CF_4 molecule

Fig. 1. The self-consistent charge densities ρ of the test molecules

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