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Accelerating the convergence of force calculations in electronic-structure computations

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The Hellmann-Feynman forces in local-density-functional calculations are very sensitive to the self-consistency of the charge or the screening potential. This is due to the omission of a correction term that is frequently ignored. This term can be calculated approximately using a very simple ansatz, which is very easy to code and consumes negligible amounts of computer time, and yet can lead to substantial improvement in the convergence of forces with respect to self-consistency.

In the past decade, the local-density approximation (LDA) to the density-functional formalism¹ has contributed significantly to the understanding of structural and electronic properties in a wide class of materials. The results obtained have in many cases preceded confirming experiments. The calculations do require a substantial amount of computing time and the complexity of the problem scales like the third power of the number of atoms. It is thus not surprising that many authors are in constant pursuit of better and faster algorithms² that can speed up the calculations even though the LDA formulation itself has not changed much over the years. For static structural problems, such as the atomic structure of complex systems (surface relaxation and reconstruction, relaxation around defect sites, and systems with many atoms per unit cell and many degrees of freedoms), and for dynamical calculations such as molecular-dynamics simulations, it is very important to calculate the forces that act on the atoms accurately and efficiently.

The formulation for calculating forces in electronic-structure computations via the Hellmann-Feynman theorem³⁻⁵ has been known for a long time. Nevertheless, calculating forces accurately is still a nontrivial task and calculating forces efficiently is even more difficult. If the basis set employed in the LDA calculations is independent of the atomic positions, such as the plane-wave basis set that is usually used together with pseudopotentials, calculations of forces are relatively straightforward.^{4,5} If the basis set depends on the atomic positions, the force calculations become rather difficult and messy

even within the framework of the pseudopotential approach. A good example is the “mixed-basis” approach where atomiclike orbitals are used together with plane waves and the force expressions become considerably more complicated than the pure plane-wave case.⁶

LDA calculations, as traditionally formulated, need to solve for the charge density self-consistently because the electron screening potential in the Hamiltonian is itself a functional of the charge density. It is well known that the total energy, as a functional of the charge density, converges quadratically with the charge density, i.e., error in the charge density only contributes to error in the total energy in the second order.^{7,8} That is why the total energy, as a variational quantity, is rather forgiving on the degree of self-consistency of the charge or the potential, as long as the energy expression is written carefully in terms of the “output” charge only.^{7,8} In some systems, such as Si and C, excellent results can be obtained via proper superposition of atomic charge densities.⁷ The forces, as calculated via the Hellmann-Feynman theorem, are, on the other hand, much more sensitive to the level of self-consistency. This is unfortunate since, for many applications, especially when we have situations involving dynamical simulations or searching for ground-state configurations, the forces are actually more important than the energy since they tell us the direction in which to move the atoms.

The sensitivity of the forces to the level of self-consistency of the charge or the potential can be seen as follows: Consider the total energy of a system, E_{tot} , as

given by the LDA:

$$E_{\text{tot}} = \sum \epsilon - \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{HXC}}^{\text{input}} + \xi_{\text{HXC}}(\rho) + E_{\text{Ewald}}, \quad (1)$$

where $\sum \epsilon$ is the sum of eigenvalues (implicitly over band and $\mathbf{k}$ indices); $\rho(\mathbf{r})$ is the charge density; ξ_{HXC} is the sum of the Hartree energy and exchange-correlation energy and is a functional of $\rho(\mathbf{r})$; $V_{\text{HXC}}^{\text{input}}$ is the input Hartree and exchange-correlation potential, with the suffix “input” emphasizing that the screening potential is the input that determines the Hamiltonian; and E_{Ewald} is the “Ewald” energy of the ionic cores.

If the atomic positions, as denoted by τ , are given small displacements $\tau \rightarrow \tau + \delta\tau$, the energy change δE_{tot} is

$$\delta E_{\text{tot}} = \delta \sum \epsilon - \int d\mathbf{r} \rho(\mathbf{r}) \delta V_{\text{HXC}}^{\text{input}} + \int d\mathbf{r} \delta \rho(\mathbf{r}) (V_{\text{HXC}} - V_{\text{HXC}}^{\text{input}}) + \delta E_{\text{Ewald}}, \quad (2)$$

where $V_{\text{HXC}} = \delta \xi_{\text{HXC}} / \delta \rho$ is the Hartree and exchange-correlation potential as computed from the output charge density. Force expressions that are usually given for the Hellmann-Feynman force are actually the sum of the first two terms.⁹ In a plane-wave basis set, these two terms reduce to the familiar expression⁴ in Fourier space:

$$F_{\tau} = -\frac{dE}{d\tau} = -i \sum_{\mathbf{G}} \mathbf{G} V_{\tau}(\mathbf{G}) e^{i\mathbf{G} \cdot \tau} \rho(\mathbf{G}), \quad (3)$$

where the $\mathbf{G}$'s are the reciprocal-lattice vectors, the $V_{\tau}(\mathbf{G})$'s here are the Fourier components of the ionic potential due to an atomic core positioned at τ , and the $\rho(\mathbf{G})$'s are the Fourier components of the charge density, and we have suppressed the normalization cell volume. This expression is correct if the charge or the electron screening potential is fully self-consistent. If not, then there should be an extra term

$$\int d\mathbf{r} \delta \rho(\mathbf{r}) (V_{\text{HXC}} - V_{\text{HXC}}^{\text{input}}).$$

The existence of this term has been noted by a few authors.¹⁰ This missing term is the main reason that Hellmann-Feynman forces are so sensitive to the level of self-consistency. It should be noted that due to the variational property of the density functional, the total energies are usually acceptable even if self-consistency is not achieved completely, but the forces computed according to Eq. (3) or similar expressions do not give the correct gradient of the energy surface unless the extra term in Eq. (2) is added.

This “correction” term

$$\mathbf{F}_c = \int d\mathbf{r} (\delta \rho / \delta \tau) (V_{\text{HXC}}^{\text{input}} - V_{\text{HXC}})$$

can in principle be calculated. However, calculating $\delta \rho / \delta \tau$, which is the change of the charge density in response to the displacement of the atomic position, is nontrivial. Using second-order perturbation theory, we may write down an expression for this correction term. In practice, it is worth the effort to consider this term only if it can be coded straightforwardly and can be evaluated quickly. Unfortunately, neither is true. It is thus common practice to ignore this term altogether and iterate the charge to a very high level of self-consistency

where this term will disappear automatically.

We will show that a very simple ansatz, namely, by approximating the charge density ρ by a superposition of atomic charge densities, can lead to a very reasonable approximation for this correction term $\mathbf{F}_c$, which in turn can cut down dramatically on the requirement of self-consistency or the “quality” of charge density in the Hellmann-Feynman force evaluation. By superposition of atomic charge densities, we mean that

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}, j} \bar{\rho}_j(\mathbf{r} - \mathbf{R} - \tau_j), \quad (4)$$

and the Fourier space,

$$\rho(\mathbf{G}) = \sum_j e^{-i\mathbf{G} \cdot \tau_j} \bar{\rho}_j(\mathbf{G}), \quad (5)$$

where j is an index for atomic sites and $\bar{\rho}_j(\mathbf{G})$ is the “atomic” charge density for the atom positioned at τ_j . We will take $\bar{\rho}_j(\mathbf{r})$ to be a spherically symmetric function for simplicity and also because this is already good enough for the present purpose. In principle, even for atoms of the same species in a large and complex unit cell, the “atomic” charge density for inequivalent atoms of the same species need not be the same, but we are going to ignore this for the purpose of calculating $\mathbf{F}_c$. The examples quoted below will all assume the same $\bar{\rho}_j(\mathbf{G})$ for the same species. From Eq. (5),

$$\mathbf{F}_c = i \sum_{\mathbf{G}} \mathbf{G} e^{i\mathbf{G} \cdot \tau_j} \bar{\rho}_j(\mathbf{G}) [V_{\text{HXC}}^{\text{input}}(\mathbf{G}) - V_{\text{HXC}}(\mathbf{G})]. \quad (6)$$

The usefulness of considering the force-correction term due to the lack of self-consistency is illustrated below with an example that concerns a first-principles calculation of the growth mode of Au on Ag(110). This is not an artificial problem that is created solely for the purpose of testing the method. This is a real problem that we have addressed, and the force-correction term has contributed to a substantial saving of computation time and effort. We will just briefly describe the Au-Ag(110) problem and the calculation, and more details about the physics of the problem can be found in Ref. 11 and references therein. The system that will be used for illustration consists of 18 atoms per unit cell, 4 Au and 14 Ag. The atoms are arranged in a repeated slab geometry in a $c(2 \times 2)$ surface unit cell, with seven layers of Ag orientated in the (110) direction and two layers of Au, one layer on each side of the Ag slab, and the repeated slabs are separated by a vacuum equivalent to the thickness of five Ag layers. The calculations were done within the local-density approximation, using the mixed-basis pseudopotential approach. One important aspect of the calculation involves the determination of the ground-state geometry and atomic positions for a few situations involving Au overlayers and Au-Ag surface alloy. The Hellmann-Feynman forces⁶ are calculated and the force matrix is also determined to guide us to the equilibrium positions of the atoms.

Table I lists the forces in the z direction (forces in the plane are zero by symmetry) that act on different atoms for one of the starting configurations that we have considered. The forces that were calculated when the charge

TABLE I. The forces in the “z” direction acting on various atoms. The first two atoms are Au and the other atoms are Ag. The first column is the force when the calculation is fully self-consistent. The second column is the force (correction term included) calculated from the output of the first iteration, with the input charge being a superposition of atomic charge density. The third column is the force calculated from the first iteration if the correction term is omitted. The forces are in Ry/a.u.

Force (final)	Force (first iteration) (with correction term)	Force (first iteration) (without correction term)
−0.0081	−0.0057	1.7456
−0.0100	−0.0177	1.3253
0.0059	0.0021	1.5425
−0.0115	−0.0161	1.3125
0.0194	0.0149	0.8043
0.0190	0.0133	0.7607
−0.0125	−0.0144	0.2846
−0.0165	−0.0197	0.2961

and potential are fully self-consistent are compared with the forces calculated from Eq. (2) with the output charge and potential in the first iteration with and without the force-correction term F_c . In this example, the input electronic potential corresponds to that of a superposition of atomic charge densities [Eq. (5)]. The total energy when the calculation is fully self-consistent is -1318.849 Ry and the total energy from the output charge density of the first iteration is -1318.458 Ry. The input potential is thus reasonable but not very good. From Table I, the forces from the first iteration without the F_c are basically totally useless. Even the sign and the order of magnitude are wrong. However, once the F_c term, as computed by Eq. (7), is included, the forces are reasonably close to their “true” values. The improvement is in fact rather dramatic.

In the second example, we consider a configuration characterized by a set of atomic positions $\{\tau'\}$ in which the atoms are moved by small displacements from a previous configuration $\{\tau\}$ and we already have the self-consistent charge density $\rho(\mathbf{r}, \{\tau\})$ for the atoms at $\{\tau\}$. Such a situation is frequently encountered when we are calculating the force matrix by finite differences, where we compute the change of forces acting on atoms by moving individual atoms in very small displacements. Molecular-dynamics simulations (with ionic and electronic degrees of freedom decoupled)¹² will also encounter similar situations. In this case we predict the new charge $\rho(\mathbf{r}, \{\tau'\})$ by

$$\rho(\mathbf{r}, \{\tau'\}) = \rho(\mathbf{r}, \{\tau\}) + \sum_{\mathbf{R}, j} \bar{\rho}_j(\mathbf{r} - \mathbf{R} - \tau'_j) - \sum_{\mathbf{R}, j} \bar{\rho}_j(\mathbf{r} - \mathbf{R} - \tau_j), \quad (7)$$

where $\mathbf{r}$ are lattice vectors and the index j indicates atomic sites. $\bar{\rho}_j$ indicates atomic charges at site j . We note that similar or more sophisticated charge-wavefunction-potential “predictors” have been employed successfully by other authors.¹² This actually gives a very good prediction of the charge density, much superior to a

FIG. 1. The total absolute error of the forces, as defined in the text, with (solid dots) and without (open circles) the correction term F_c , computed at each iteration step. The forces are in Ry/a.u. The lines serve as guides to the eye only.

FIG. 2. (a) The force acting on atom 1, with (solid dots) and without (open circles) the correction term F_c , computed at each iteration step; (b) the force acting on atom 2, with (solid dots) and without (open circles) the correction term F_c , computed at each iteration step. The forces are in Ry/a.u. The lines serve as guides to the eye only.

simple superposition of atomic charge density. The total energy calculated at the first iteration is already within 1 mRy of the final total energy. We might expect that the forces calculated will also be reasonable, but they are not unless the correction term is taken into account. In Fig. 1 we plot the sum of the absolute errors of the forces as the iteration proceeds, defined as

$$\text{Error}(I) = \sum_j |f_j(I) - f_j(\text{final})|, \quad (8)$$

where $\text{Error}(I)$ is the error in the I th iteration, $f_j(I)$ is the force in the z direction on the atom j in the I th iteration, and $f(\text{final})$ is the final converged value. Figure 1 shows that the correction term reduces the error and improves the force convergence significantly. It is more interesting to look at the forces acting on individual atoms; Figs. 2(a) and 2(b) show the forces acting on the top two atoms as a function of iteration, and it again demonstrates the usefulness of the force-correction term F_c . Note that without F_c , the forces can point in a wrong direction for some atoms in the first few iterations, even though the total energy is already very good. With the correction term, the forces are much more reliable.

The sole purpose of the atomic charge densities is to achieve the fastest convergence when using the charge predictor [Eq. (7)] and the force corrector [Eq. (6)], and there is more than one way of obtaining these atomic charge densities. One obvious way is to perform a Herman-Skillman-type atomic calculation to extract the atomic charges. We can also perform a bulk calculation in which all atoms are equivalent (e.g., Au or Ag in the fcc structure) and extract the atomic charges by inverting the equation (in Fourier space):

$$\rho_{\text{solid}}(\mathbf{G}) = \sum_j e^{-i\mathbf{G} \cdot \mathbf{r}_j} \bar{\rho}(\mathbf{G}). \quad (9)$$

We can only obtain information for a few discrete $|\mathbf{G}|$ in this manner, but we can obtain other values by interpolation. We have adopted the latter approach in our calculations.

In summary, we showed that the high sensitivity of the Hellmann-Feynman forces to the self-consistency of charge and potential is mainly due to the frequent omission of a term F_c in the force expression. This term is nonzero as long as the charge or the potential is not fully self-consistent. While calculating F_c directly and exactly is nontrivial and probably not worth the trouble, it is shown that F_c can be approximated effectively by a very simple ansatz. Coding this term then becomes very simple and computing it takes a negligible amount of effort. The resulting improvement in the accuracy of the forces is, however, rather significant, at least in one series of calculations of metal overlayers on metals that we have recently performed.

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¹See, e.g., *Theory of the Inhomogeneous Electron Gas*, edited by N. H. March and S. Lundqvist (Plenum, New York, 1983); *The Electronic Structure of Complex Systems*, edited by P. Phariseau and W. M. Temmerman (Plenum, New York, 1984); R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).

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