Derivation of force theorems in density-functional theory: Application to the full-potential LMTO method

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A systematic technique for deriving force theorems within density-functional theory is presented. It is based on an arbitrary guess at the response of the electrons to a shift of a nucleus, yielding a valid force theorem for each choice. Application to the full-potential linear-muffin-tin-orbital method gives a workable force expression which is unusually insensitive to deviations from self-consistency.

The local-density approximation (LDA) within density-functional theory (DFT),[1] as a reasonably accurate description of the electron-electron interaction, has proved to be extremely useful in the calculation of the electronic properties of such varied systems as molecules, solids, and surfaces. DFT reduces the intractable problem of the coupled motion of many interacting electrons to the much simpler question of independent electrons in an effective, density-dependent, single-particle potential; the LDA then gives an explicit prescription for constructing the potential in an approximate way. This gives a practical scheme for calculating the total energy of any system consisting of electrons and nuclei as function of the nuclear positions. The forces on the nuclei, as the derivatives of this total energy function, are then well defined. It is of advantage to have these forces available during the course of the calculation, as has been amply demonstrated by applications of the Car-Parrinello method[2] in recent years. First, by moving the atoms along the forces as the calculation proceeds, the equilibrium geometry can be found, opening the door to a meaningful treatment of many-atom systems. Second, true *ab initio* molecular-dynamics calculations can be done. This permits a microscopic simulation of phenomena such as diffusion or melting with the full reliability and accuracy of the LDA.

Up to now, most such calculations have been done using the plane-wave pseudopotential (PW-PP) method,[3] because in this approach the forces are trivial to obtain. While many new and important results have been obtained, a problem is that the straightforward PW-PP approach is only suited to systems with weakly scattering *sp* electrons. It is therefore desirable to obtain force theorems for more sophisticated approaches which can be applied more generally, such as the full-potential linear augmented plane-wave (FLAPW) (Refs. 4 and 5) and the full-potential linear muffin-tin orbital (FP-LMTO) (Ref. 6) methods. Recently, two different force theorems have been presented for the FLAPW method.[4,5] In this paper, we present a systematic technique for deriving force theorems in arbitrary basis sets. We show that a force theorem is associated with any arbitrary ansatz

for the response of the charge density when the nuclei are moved. The freedom in defining the density change can be used to tailor the force theorem to the basis set in question. The technique is then used to obtain a force expression for the FP-LMTO method.

Different force theorems must of course yield the same numerical forces when evaluated for the fully self-consistent system. Formally, the equivalence can be demonstrated by transformations using the self-consistency equations (i.e., the Schrödinger equation and the definitions of the effective potential and the total energy) but this can be extremely tedious in practice. We introduce the freedom to transform between equivalent force expressions at an earlier level by associating different force theorems with different "guesses" as to how the electron density changes when the nuclei are moved. Consider the motion of the nuclei along some paths $\mathbf{R}_\nu(x)$, parametrized by a variable x. For each value of x we denote the self-consistent charge density by $\rho_{\rm sc}(x)$ and the LDA (or Kohn-Sham, KS) total energy by $E_{\rm KS}[\rho_{\rm sc}(x)]$. The aim is to determine the first-order change in the total energy as x varies around a chosen value x_0. This is some linear combination of the forces for the geometry corresponding to $x = x_0$. By choosing the path so that only one atom is moved, separate force components are isolated. An attempt to differentiate the KS energy directly can lead to extremely complicated expressions. To avoid this, we choose any arbitrary trial density $\tilde\rho(x)$ which depends smoothly on x, conserves the electronic charge, and satisfies $\tilde\rho(x_0) = \rho_{\rm sc}(x_0)$. It is then useful to consider the following energy expression:

$$\tilde E(x) = E_H[\tilde\rho(x)], \tag{1}$$

where E_H is the Harris energy functional, defined for any trial density ρ by

$$E_H[\rho] = \sum_{\rm occ} \epsilon_i - \int \rho V_{\rm eff}[\rho]d^3r + U[\rho] + E_{\rm xc}[\rho]. \tag{2}$$

The eigenvalues ϵ_i are calculated in the effective potential made from the density ρ (whereas in the KS energy

the eigenvalues correspond to the potential which generates ρ). The electrostatic and LDA exchange-correlation energies and the effective potential are given by, respectively,

$$U[\rho] = \tfrac{1}{2} \int \rho(\mathbf{r})\phi(\mathbf{r})d^3r + \tfrac{1}{2}\sum_\nu Z_\nu \phi_\nu, \qquad (3)$$

$$E_{\rm xc}[\rho] = \int \rho(\mathbf{r})\epsilon_{\rm xc}[\rho(\mathbf{r})]d^3r, \qquad (4)$$

$$V_{\rm eff}(\mathbf{r}) = \phi(\mathbf{r}) + \mu_{\rm xc}[\rho(\mathbf{r})]. \qquad (5)$$

Here $\phi(\mathbf{r})$ denotes the electrostatic potential of the total (electron plus nuclear) charge density, ϕ_ν is the electrostatic potential felt by the νth nucleus with atomic number Z_ν, and $\epsilon_{\rm xc}$ and $\mu_{\rm xc}$ are the LDA exchange-correlation energy density and potential, respectively. The Harris and KS energies are equal to first order respective to variations around the self-consistent density.[7] Therefore the derivatives $d\tilde{E}/dx$ and $dE_{\rm KS}[\rho_{\rm sc}(x)]/dx$ are equal at x_0. This is because $\tilde{\rho}(x) - \rho_{\rm sc}(x)$ goes to zero smoothly as x approaches x_0 and consequently the leading term of $E_H[\tilde{\rho}(x)] - E_{\rm KS}[\rho_{\rm sc}(x)]$ is proportional to $(x - x_0)^2$. The desired force can therefore be obtained by differentiating $\tilde{E}(x)$ for *any* arbitrary definition of $\tilde{\rho}$ satisfying the three requirements.

There are two major advantages when the force expression is derived by the "detour" over $\tilde{\rho}$ and $\tilde{E}$. First, in the Harris functional the double-counting terms $-\int \rho V_{\rm eff}$, U, and $E_{\rm xc}$ are evaluated for the input trial density and not for the output density constructed from the wave functions, making the differentiation of these terms much easier. Similarly, the change in the eigenvalues is needed for the explicit potential change $\delta V_{\rm eff}(\tilde{\rho})$ and not for $\delta V_{\rm sc}$. Second, the freedom in choosing $\tilde{\rho}$ can be exploited to obtain a force expression which is tailored to a specific basis set. For example, in augmentation methods it is natural to treat the density inside the atomic spheres separately from the interstitial density. Note that the arbitrary choice of $\tilde{\rho}$ is equivalent to a guess at the way in which $\rho_{\rm sc}$ changes as the nuclei move. In fact, the well-known Hellman-Feynman (HF) force expression[8] corresponds to the assumption that the electronic density is frozen. Choosing $\tilde{\rho}(x) = \rho_{\rm sc}(x_0)$ for all values of x, only the contributions due to the shift of the nuclear electrostatic potentials survive in the variations of $V_{\rm eff}$ and in the double-counting terms. If furthermore the Schrödinger equation is solved by means of a geometry-independent or complete basis set, by first-order perturbation theory the variations of the eigenvalue sum and $\int \rho V_{\rm eff}$ cancel in Eq. (2). This leaves only δU as the total energy change, recovering the result that the variation of the total energy can be calculated using only the classical electrostatic forces on the nucleii. The HF force expression is thus associated with the counterintuitive assumption that the electron density does not respond to the nuclear motion.

We next show how the technique can be used to derive a force theorem for the FP-LMTO method. This illustrates how the freedom in defining $\tilde{\rho}$ is used to tailor

the force theorem to a specific basis set. The LMTO basis results from a rather involved construction in which atom-centered Hankel-function envelopes are augmented smoothly by numerical solutions of the radial Schrödinger equation within muffin-tin spheres.[9] A major advantage is that convergence can be attained with a small basis. The disadvantage is that the change in the total energy for a shift of a nucleus is not given simply by the electrostatic force on the nucleus. If one defines $\tilde{\rho}(x) = \rho_{\rm sc}(x_0)$ as above, then $\delta \sum \epsilon_i - \delta \int \rho V_{\rm eff}$ is not automatically zero. The term which is left arises because the basis functions change when an atom is moved; expressing this using the derivatives of the basis functions respective to the atomic positions gives the so-called Pulay force.[10] The LMTO Pulay force arises because the envelopes centered on the moving atom are shifted and, additionally, because the augmentation sphere for all basis functions is moved. Considering the complexity of the problem, it is not surprising that an explicit expression for the Pulay correction in the LMTO basis has not been obtained to date.

Instead of attempting to evaluate the Pulay force, we choose a definition of $\tilde{\rho}(x)$ which is better suited to the LMTO basis. Intuitively, a natural choice would be to move the density within each atomic sphere rigidly along with its atom. As a refinement in the same spirit, we decompose the self-consistent density at the reference geometry $x = x_0$ into a sum of nonspherical atom-centered contributions as

$$\rho_{\rm sc}(\mathbf{r}) = \sum_\nu \rho_\nu(\mathbf{r} - \mathbf{R}_\nu). \qquad (6)$$

This decomposition is easy to obtain when the interstitial density is given using an atom-centered basis set. Each ρ_ν is given as a numerical spheric-harmonic expansion inside the corresponding atomic sphere and as a linear combination of Hankel functions outside it. We define $\tilde{\rho}$ at another geometry by reoverlapping the ρ_ν at the shifted positions. In other words, the ansatz is that each atom drags its partial density along with it. Clearly this is a more realistic assumption than the one underlying the HF theorem, and we argue below that the associated force theorem is therefore less sensitive to errors in the density. In the present context, the important feature is that this definition leads to tractable terms when $\tilde{E}$ is differentiated.

To derive the force theorem, we write down the first-order change $\delta \tilde{E}$ as the variation of Eq. (2) and use perturbation theory to cancel various contributions of $\delta \sum \epsilon_i$ against terms from the double-counting integrals. For brevity, we defer the details to a future publication[11] and sketch the main points. In the interstitial region (IR), the variation of the trial density is nonzero. It has the special form of a rigid shift for each partial density ρ_ν. Therefore the coefficients R_m are fixed in the expansion of the interstitial density as $\rho_{\rm sc} = \sum_m R_m \chi_m$. Hereby the set $\{\chi_m\}$ denotes the atom-centered Hankel functions used to expand the ρ_ν outside the atomic spheres. All relevant information about the interstitial potential is contained in the integrals $V_m = \int_{\rm IR} \chi_m V_{\rm eff}$. By first-order perturbation theory, the changes in the V_m lead to a contribu-

tion of $\sum_m R_m \delta V_m$ to $\delta \sum \epsilon_i$. Because of our choice of a rigid shift (i.e., $\delta R_m = 0$), this term cancels the variation $\delta \int_{IR} \rho V_{eff} = \delta \sum R_m V_m = \sum R_m \delta V_m$. The first simplification therefore is to simultaneously leave away the changes in the interstitial potential and $\int_{IR} \rho V_{eff}$. An analogous situation arises for the density inside an atomic sphere. This density changes by the decompose-and-reoverlap process, since the "tails" of the densities centered on other sites shift relative to the selected sphere. Consequently the "potential parameters" which describe the sphere potential are also modified. However, this change of the parameters does not have to be calculated. First-order pertubation theory and the self-consistency of the reference density can be invoked to show that the corresponding contribution to the eigenvalue change cancels against the sphere contribution to $\delta \int \rho V_{eff}$. The final expression thus involves the eigenvalue changes for a *rigid shift* of the sphere potentials. For the sphere densities, cancellation is not complete: terms are left which involve the multipole moments of the sphere charge density and the electrostatic potential on the sphere surface. For angular momentum zero, these are simply the changes in the total sphere charge and Madelung potential, respectively. The final force expression is

$$\delta E = \delta^{(R)} \sum_{occ} \epsilon_i + \tfrac{1}{2} \delta^{(R)} \int_{IR} \rho\phi + \delta^{(R)} \int_{IR} \rho\epsilon_{xc}$$
$$+ \tfrac{1}{2} \sum_{\nu L} \frac{1}{S_\nu^l} (\phi_{\nu L} \delta^{(R)} Q_{\nu L} - Q_{\nu L} \delta^{(R)} \phi_{\nu L}), \qquad (7)$$

where $\delta^{(R)}$ denotes the variation associated with the rigid-shift-and-reoverlap procedure. For the eigenvalue sum, we define this as the change when the sphere potentials are shifted rigidly and the interstitial potential integrals are kept frozen. For the interstitial integrals, $\delta^{(R)}$ includes the change in the integrand as well as of the integration domain. The νth atomic sphere has the radius S_ν, density multipole moments $Q_{\nu L}$, and the surface electrostatic potential $\sum_L \phi_{\nu L} Y_L$. Most terms can be calculated using gradients of the structure constants (used to expand the charge-density basis functions χ_m around the different sites). The change in the eigenvalue sum is evaluated using matrix pertubation theory for the Hamiltonian and overlap matrices.

The force theorem of Eq. (7) is not in the form of the Hellman-Feynman force plus a Pulay correction, and it is far from obvious how to bring it into such a form by direct manipulations. The HF force essentially consists of the change in the eigenvalue sum when only the external potential is varied while the interaction parts of the potential are kept frozen. Our FP-LMTO force theorem involves the change in the eigenvalue sum when the sphere potentials are shifted rigidly and the interstitial potential integrals are frozen. This is in some sense analogous to, but in practice distinct from the situation for the HF force expression.

We note some further features of the LMTO force expression. First, core states do not contribute, as a consequence of the ansatz that each nucleus drags its partial density (including its core) along with it. Second, the expression shows some similarity to the local force
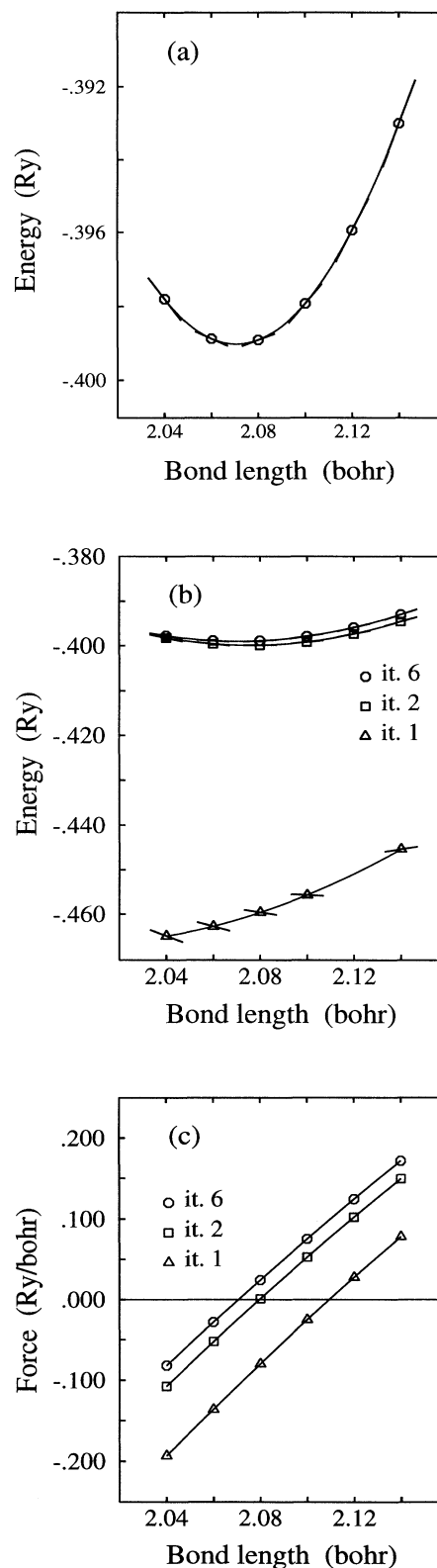

FIG. 1. The Harris total energy and the force for the N_2 dimer as function of the bond length at self-consistency (a), and the convergence of both quantities with iteration number (b),(c). The total energy of the dimer at equilibrium is -217.399 Ry.

theorem derived by Andersen within the atomic-sphere approximation.[9] Third, a different LMTO force theorem could be derived by choosing the interstitial density as fixed and shifting the sphere densities rigidly. We have not pursued this, but in that case there would be no interstitial contributions but additional surface integral terms would arise.

To test the force theorem of Eq. (7), we have implemented it in a full-potential LMTO method designed for molecules and clusters, to be presented in detail elsewhere.[11] In brief, as discussed for an earlier FP-LMTO method,[6] the main problem is to obtain an accurate representation, valid in the interstitial region, of the product of two Hankel functions centered at the same or at different sites. That is, we require an expansion of the form

$$\phi_{\nu L \alpha} \phi_{\nu' L' \alpha'} = \sum_{\nu'' L'' \alpha''} C_{\nu'' L'' \alpha''}^{\nu L \alpha \nu' L' \alpha'} \chi_{\nu'' L'' \alpha''}, \qquad (8)$$

where $\phi_{\nu L \alpha}$ is a Hankel function centered at site ν with angular momentum L and the $\chi_{\nu'' L'' \alpha''}$ are functions of the charge-density Hankel-function set. The index α runs over different localizations (i.e., kinetic energies). Using Eq. (8), the three-center integrals for the interstitial potential matrix elements can be reduced to two-center integrals and the wave function can be squared to calculate the output density. In the previous method, the expansion was obtained by adjusting the coefficients until the two sides of Eq. (8) match smoothly on all spheres simultaneously, a procedure which is adequate for close-packed spheres but not suited to molecules. In the new cluster method, the expansion is first calculated for two atoms arranged along the z axis and the coefficients are tabulated as function of the interatomic distance. For a general position of the atoms, the expansion is obtained by rotating the tabulated fit using the rotation matrices for the spherical harmonics. The tabulated fit is made by direct numerical integration and can be made as accurate as desired. For the exchange-correlation integrals over the interstitial region, direct numerical integration on a mesh was used. In other respects the method resembles the previous FP-LMTO approach, including the correct treatment of higher angular momenta inside the atomic spheres. In sum, one obtains a cluster full-potential LMTO method which has an accuracy that can be systematically improved, has no need for "empty spheres," and supplies the forces on the nuclei.

Table I presents calculated binding energies, bond lengths, and vibrational frequencies for some typical

TABLE I. Calculated bond lengths (bohr), binding energies (eV), and vibrational frequencies (cm^{-1}) for typical dimers as compared to experimental data; results obtained using energies and forces are given separately.

	d_E	d_F	d_{exp}	E_B	$E_{B,exp}$	ν_E	ν_F	ν_{exp}
BF	2.411	2.412	2.385	9.00	7.85	1410	1389	1401
N$_2$	2.079	2.076	2.067	11.29	9.76	2461	2454	2358
C$_2$	2.363	2.356	2.348	7.11	6.24	1895	1905	1855
CO	2.142	2.139	2.132	12.87	11.09	2176	2181	2169

dimers, showing good agreement to experiment[12] except for the well-known effect of overbinding which is due to the LDA.[13] Our main interest here is to test the force theorem. The upper curve of Fig. 1 shows the converged binding energy for the N$_2$ dimer as function of the bond length and the calculated forces as lines of the corresponding slope, demonstrating that the force expression accurately reproduces the derivative of the total energy. This is confirmed by the agreement between the bond lengths and frequencies calculated using the total energy and the forces in Table I. Figure 1 also shows the convergence of the total energy and forces for the first few iterations. As expected, the force does not agree with the derivative of the energy before self-consistency is reached. A surprising feature is that, at least for the cases considered here, the force is *less* sensitive to errors in the density than the total energy. (Energies converge from below because we have evaluated and plotted the Harris functional energy.) The forces for the first iteration already give a reasonable bond length and vibrational frequency whereas the total energy gives an unacceptable result. To our knowledge, this behavior is different from that seen in calculations based on the straightforward Hellman-Feynman theorem in the PW-PP method, but is similar to that seen for a FP-LAPW force theorem.[4] We attribute the insensitivity of the force to deviations from self-consistency to the fact that a more realistic assumption for the electron response to the nuclear motion was "built in" by our definition of $\tilde{\rho}$.

In conclusion, we have shown that different force theorems can be associated with different "guesses" at the electronic response to the nuclear motion. By defining the density response in a suitable way, the force theorem can be tailored to a specific method, as was demonstrated by deriving a force theorem for the FP-LMTO method. The chosen ansatz for this case, namely, that each atom drags its partial density along with it, leads to a force expression which seems to be less sensitive to deviations from self-consistency than the standard Hellman-Feynman force.

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