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All-electron and pseudopotential force calculations using the linearized-augmented-plane-wave method

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All-electron and pseudopotential formulations for atomic forces in the linear-augmented-plane-wave (LAPW) method within the local-density approximation are presented. Due to the fact that the basis functions in the LAPW method (and in other linear muffin-tin-orbitals-based methods) have discontinuous second derivatives across the muffin-tin sphere boundaries, a large surface contribution to the incomplete-basis-set corrections to the Hellmann-Feynman force is shown to exist. The formulations are applied to frozen-phonon calculations in semiconductor, transition-metal, and noble-metal systems. The results are in excellent agreement with total-energy calculations and experiment.

I. INTRODUCTION

Density-functional theory and specifically the local-density approximation[1] (LDA) has been used with considerable success to investigate the properties of solids, surfaces, and molecules.[2] A basic application of the theory is the determination of the equilibrium atomic configuration of a given solid-state system. The problem is essentially one of finding the geometry with the lowest total energy. This can be accomplished by directly calculating the total energy for different atomic geometries and finding the equilibrium geometry using some fitting procedure. While this is certainly a valid approach, it is not an efficient one, especially for large and complex systems. A better approach is to calculate the atomic forces rather than the total energy since the former provides much more information.

Both pseudopotential and all-electron methods have been used to solve the Kohn-Sham equations, and there is generally very good agreement between these approaches when they are applied to the same system. Many all-electron methods such as the linear-augmented-plane-wave (LAPW) (Refs. 3 and 4) and linear muffin-tin-orbitals methods (LMTO) (Ref. 5) use dual representations for all the relevant quantities in the calculation. Space is partitioned into two regions, nonoverlapping so-called muffin-tin (MT) spheres centered on each atom, and the remaining interstitial region. Within the spheres the basis functions, charge density, and potential are expanded in terms of numerical radial functions multiplied by spherical harmonics. In the interstitial region these quantities are all expanded in plane waves (as in the LAPW method) or in spherical partial waves (as in the LMTO method). While this dual representation results in the efficient and accurate treatment of transition elements and first-row elements, which are difficult to treat using plane-wave basis sets, as are often employed in pseudopotential calculations,[6] it complicates the determination of atomic forces. Indeed, virtually no realistic force calculations using the LAPW or LMTO methods have appeared in the literature.[7]

The force on an atom is equal to the electrostatic force on its nucleus, according to the Hellmann-Feynman (HF) theorem.[8] However, the forces so obtained in any *ab initio* electronic-structure calculation can be grossly inaccurate. This is because the calculated charge density and thus the electric field are necessarily approximate. On the other hand, the change in total energy due to the shift of the atoms, and thus the force, can be computed accurately in an electronic-structure calculation. In particular, methodologies based on the density-functional theory using the LDA (Ref. 1) have provided good total-energy results. As shown by Pulay,[9] the HF force (the electrostatic force on the nuclei) should in general be supplemented with a contribution due to the use of an incomplete basis-function set (IBS) in practical calculations. This contribution vanishes if the basis functions are independent of atomic positions (floating basis set). It is thus unnecessary to evaluate the relatively complex IBS correction in the plane-wave pseudopotential method,[10] for example. Unfortunately, it is impractical to use only plane-wave basis sets for systems with localized orbitals.

In this paper, we present all-electron and pseudopotential formulations for the calculation of atomic forces within the LAPW method. We find that the IBS correction to the HF force has a contribution due to the discontinuity in the second derivative of the wave functions (and thus the kinetic-energy density) across the MT sphere boundaries, in addition to the contributions that are present in other methods that employ localized basis functions.[11,12] In addition, there is a correction from the core states in the all-electron formalism. We have tested the all-electron formalism by performing frozen-phonon calculations. We find that the core correction can be large and may cancel most of the HF force. In spite of this, the results of force calculations are in good agreement with total-energy calculations and experiment. As an alternative to dealing with the core electron states, the use of pseudopotentials within the LAPW method[13,14] for total-energy and force calculations is also discussed.

The rest of the paper is organized as follows. The equations for all-electron atomic forces are derived in Sec. II. The pseudopotential formalism for electronic structure and/or total energy as well as force calculations is described in Sec. III. In Sec. IV, we present the results of frozen-phonon calculations for Si, Mo, and Ag. The results are summarized in Sec. V.

II. ALL-ELECTRON FORCE

We shall first find the general atomic force within the density-functional formalism. We will assume that the charge density and potentials are self-consistent. The total energy in the LDA is given by (in atomic units)

$$E=\sum_i n_i\varepsilon_i-\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}'-\int\rho(\mathbf{r})\mu_{\mathrm{xc}}(\mathbf{r})d^3\mathbf{r}+\int\rho(\mathbf{r})\varepsilon_{xc}(\mathbf{r})d^3\mathbf{r}+\tfrac{1}{2}\sum_{\alpha,\beta}{}'\sum_{\mathbf{R}}\frac{Z_\alpha Z_\beta}{|\tau_\alpha-\tau_\beta+\mathbf{R}|}\ , \tag{1}$$

with

$$\rho(\mathbf{r}=\sum_i n_i|\psi_i(\mathbf{r})|^2\ , \tag{2}$$

where z_α and τ_α are the atomic number and position of atom α within a particular unit cell, $\mathbf{R}$ is the lattice vector, n_i is the occupation number of the state i at the k point $\mathbf{k}_i$ times the weight of the k point, $\rho(\mathbf{r})$ is the electronic charge density, and ε_i and ψ_i are eigenvalues and eigenfunctions, respectively, and are determined for the core and valence states with respective approximations (see below) from the Kohn-Sham equations

$$H\psi_i=[\hat{T}+V_{\mathrm{eff}}(\mathbf{r})]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})\ , \tag{3}$$

where $\hat{T}$ is the single-particle kinetic-energy operator and

$$V_{\mathrm{eff}}(\mathbf{r})=-\sum_\alpha\sum_{\mathbf{R}}\frac{Z_\alpha}{|\mathbf{r}-\tau_\alpha+\mathbf{R}|}+\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'+\mu_{\mathrm{xc}}(\mathbf{r}) \tag{4}$$

is the effective potential, consisting of nuclear, Hartree, and exchange-correlation potentials. To find the force on atom α, we displace the atom by a small amount $\delta\tau_\alpha$ and calculate the change in the total energy from Eq. (1). Using Eq. (4) and the general relationship between the exchange-correlation potential and energy density,

$$\mu_{\mathrm{xc}}(\mathbf{r})=\frac{\delta}{\delta\rho(\mathbf{r})}\{\rho\varepsilon_{\mathrm{xc}}[\rho]\}\ , \tag{5}$$

the change in the total energy can be shown to be

$$\delta E=\sum_i\varepsilon_i\delta n_i+\sum_i n_i\delta\varepsilon_i-\int\rho(\mathbf{r})\delta V_{\mathrm{eff}}(\mathbf{r})d^3\mathbf{r}-\mathbf{F}^{\alpha}_{\mathrm{HF}}\cdot\delta\tau_\alpha\ , \tag{6}$$

where

$$\mathbf{F}^{\alpha}_{\mathrm{HF}}=Z_\alpha\frac{d}{d\tau_\alpha}\left[-\sum_\beta{}'\sum_{\mathbf{R}}\frac{Z_\beta}{|\tau_\alpha-\tau_\beta+\mathbf{R}|}+\int\frac{\rho(\mathbf{r})}{|\tau_\alpha-\mathbf{r}|}d^3\mathbf{r}\right] \tag{7}$$

is the HF force, and is equal to the electrostatic force on the nucleus. The first term in Eq. (6) ideally vanishes to first order in $\delta\tau_\alpha$ as a result of electron-number conservation.[15] The atomic force on atom α is thus given by

$$\mathbf{F}^\alpha=-\frac{\delta E}{\delta\tau_\alpha}=\mathbf{F}^{\alpha}_{\mathrm{HF}}-\frac{1}{\delta\tau_\alpha}\left[\sum_i n_i\delta\varepsilon_i-\int\rho(\mathbf{r})\delta V_{\mathrm{eff}}(\mathbf{r})d^3\mathbf{r}\right]\ . \tag{8}$$

The second term represents a correction to the HF force, whose existence was first shown explicitly by Pulay[9] for the Hartree-Fock method. The above equation is still completely general within the LDA.

We now must evaluate the variation in the eigenvalues, which depends on the method of solution of the Kohn-Sham equation. In the all-electron LAPW method, the orbitals are divided into core and valence states, which are treated using different approximations. The core states, being low lying in energy and localized around the nucleus, should be fairly well described by neglecting the nonspherical potential:

$$H_{\mathrm{MT}}\psi_i(\mathbf{r})=[\hat{T}+V^S_{\mathrm{eff}}(\mathbf{r})]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})\ , \tag{9}$$

where V^S_{eff} is the spherical part of the effective potential. In this spherical-potential approximation, the eigenfunctions become the spherical harmonics times radial functions, which are obtained through numerical integration. The first-order change in the eigenvalue sum for the core states of atom α is given by

$$\sum_i n_i\delta\varepsilon_i=\int\rho^\alpha_c(\mathbf{r})[\delta V_{\mathrm{eff}}+\nabla V_{\mathrm{eff}}(\mathbf{r})\cdot\delta\tau_\alpha]d^3\mathbf{r}\ , \tag{10}$$

where ρ^α_c is the core charge density of atom α and we have taken advantage of the fact that the core charge density is spherical. The core correlation to the HF force is thus

$$\mathbf{F}^{\alpha}_{\mathrm{core}}=-\frac{1}{\delta\tau_\alpha}\left[\sum_i n_i\delta\varepsilon_i-\int\rho^\alpha_c(\mathbf{r})\delta V_{\mathrm{eff}}(\mathbf{r})d^3\mathbf{r}\right]=-\int\rho^\alpha_c(\mathbf{r})\nabla V_{\mathrm{eff}}(\mathbf{r})d^3\mathbf{r}\ . \tag{11}$$

This result agrees with the LAPW total-energy calculation if the core charge density is localized within the MT sphere. Because the spherical potential in Eq. (9) outside the MT sphere is extrapolated from the potential inside it, the correction of those core states that have a substantial portion of its charge density outside the MT sphere may not be the same as numerically calculated from the total energy. This can be avoided by treating such core states variationally (i.e., like the valence states).

The valence-state wave functions are expanded in terms of a set of LAPW basis functions $\Phi_{\mathbf{G}}$ (for brevity, we omit the labeling of $\mathbf{k}_i$),

$$\psi_i(\mathbf{r})=\sum_{\mathbf{G}} C_i(\mathbf{G})\phi_{\mathbf{G}}(\mathbf{r}) \ . \tag{12}$$

With these variational wave functions, the Kohn-Sham equation becomes the following secular equations:

$$\sum_{\mathbf{G}'}(H_{\mathbf{G}\mathbf{G}'}-\varepsilon_i O_{\mathbf{G}\mathbf{G}'})C_i(\mathbf{G}')=0 \ , \tag{13}$$

where

$$H_{\mathbf{G}\mathbf{G}'}=\langle \phi_{\mathbf{G}}|H|\phi_{\mathbf{G}'}\rangle \tag{14a}$$

and

$$O_{\mathbf{G}\mathbf{G}'}=\langle \phi_{\mathbf{G}}|\phi_{\mathbf{G}'}\rangle \tag{14b}$$

are, respectively, the Hamiltonian and overlap matrices. Since the augmentation to the plane waves is position dependent, the Hamiltonian and overlap matrices change as atom α is moved. The resulting change in the eigenvalue ε_i can be obtained from Eq. (13) and is given by

$$\delta\varepsilon_i=\sum_{\mathbf{G},\mathbf{G}'} C_i^*(\mathbf{G})(\delta H_{\mathbf{G}\mathbf{G}'}-\varepsilon_i\delta O_{\mathbf{G}\mathbf{G}'})C_i(\mathbf{G}') \ . \tag{15}$$

In view of Eq. (14), this can be rewritten in a more compact form,

$$\delta\varepsilon_i=\delta\langle \psi_i|(H-\varepsilon_i)|\psi_i\rangle \tag{16}$$

if we let

$$\delta\psi_i(\mathbf{r})=\sum_{\mathbf{G}} C_i(\mathbf{G})\delta\phi_{\mathbf{G}}(\mathbf{r}) \ . \tag{17}$$

With this definition, the change in the norm of the wave functions is given by

$$\delta\langle \psi_i|\psi_i\rangle=\langle \delta\psi_i|\psi_i\rangle+\langle \psi_i|\delta\psi_i\rangle \ . \tag{18}$$

Similarly, the change in the potential energy is

$$\delta\langle \psi_i|V_{\text{eff}}|\psi_i\rangle=\langle \delta\psi_i|V_{\text{eff}}|\psi_i\rangle+\langle \psi_i|V_{\text{eff}}|\delta\psi_i\rangle +\langle \psi_i|\delta V_{\text{eff}}|\psi_i\rangle \ . \tag{19}$$

It should be pointed out that the continuity of the wave functions and the potential is taken into account implicitly in writing down Eqs. (18) and (19). The continuity is important as we are dealing with the movement of a MT sphere with a sharp boundary, and an additional term results if there is a discontinuity at the boundary. This is exactly the case with the kinetic energy in the LAPW method, because the second derivative of the basis functions (and thus of the wave functions) is in general discontinuous. As the α atom shifts to a new position, its MT sphere and the interstitial region around it are redefined, and there is a finite change in the kinetic energy in the nonoverlapping regions of the old and new MT spheres of atom α:

$$\delta T_i^{(1)}=\mathbf{D}_i\cdot\delta\boldsymbol{\tau}_\alpha \tag{20a}$$

with

$$\mathbf{D}_i=\oint[\psi_i^*(\mathbf{r})\hat{T}\psi_i(\mathbf{r})|_{\text{MT}}-\psi_i^*(\mathbf{r})\hat{T}\psi_i(\mathbf{r})|_I]d\mathbf{S}_\alpha \ , \tag{20b}$$

where MT and I indicate that the kinetic energy is to be evaluated using the MT and interstitial wave functions, respectively. The change in the wave function again gives rise to a volume contribution:

$$\delta T_i^{(2)}=\langle \delta\psi_i|\hat{T}|\psi_i\rangle+\langle \psi_i|\hat{T}|\delta\psi_i\rangle \ . \tag{21}$$

Substituting Eqs. (18)–(21) in Eq. (16), we arrive at

$$\delta\varepsilon_i=\langle \delta\psi_i|(H-\varepsilon_i)|\psi_i\rangle+\langle \psi_i|(H-\varepsilon_i)|\delta\psi_i\rangle +\mathbf{D}_i\cdot\delta\boldsymbol{\tau}_\alpha+\int \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\delta V_{\text{eff}}(\mathbf{r})d^3\mathbf{r} \ . \tag{22}$$

The IBS correction to the HF force from the valence electrons is thus

$$\begin{aligned}\mathbf{F}_{\text{IBS}}^\alpha&=-\frac{1}{\delta\boldsymbol{\tau}_\alpha}\left[\sum_i n_i\delta\varepsilon-\int \rho_v(\mathbf{r})\delta V_{\text{eff}}(\mathbf{r})d^3\mathbf{r}\right]\\ &=-\sum_i n_i\left[\left\langle\frac{\delta\psi_i}{\delta\boldsymbol{\tau}_\alpha}\right|(H-\varepsilon_i)\left|\psi_i\right\rangle+\left\langle\psi_i\right|(H-\varepsilon_i)\left|\frac{\delta\psi_i}{\delta\boldsymbol{\tau}_\alpha}\right\rangle+\mathbf{D}_i\right] \ ,\end{aligned} \tag{23}$$

where the index i goes over all occupied valence states. As mentioned earlier, the above expression differs from that given previously for localized basis-function methods[11,12] by the MT surface contribution, as defined by Eq. (20b). The sum of the HF force and the core and IBS corrections, given respectively by Eqs. (7), (11), and (23), provide the total atomic force on atom α.

We now proceed to find the IBS correction in terms of the basis functions, which are defined piecewise in the interstitial and MT regions,

$$\phi_{\mathbf{G}}(\mathbf{r})=\begin{cases}\Omega^{-1/2}e^{i(\mathbf{k}_i+\mathbf{G})\cdot\mathbf{r}} \ , & r\in I\\ \sum_{l,m}[a_{lm}^\alpha(\mathbf{G})u_l(r_\alpha)+b_{lm}^\alpha(\mathbf{G})\dot{u}_l(r_\alpha)]Y_{lm}(\hat{r}_\alpha) \ , & |\mathbf{r}-\boldsymbol{\tau}_\alpha|\le R_\alpha \ ,\end{cases} \tag{24}$$

where Ω is the unit cell volume, R_α is the MT radius of atom α, and $\mathbf{r}_\alpha=\mathbf{r}-\boldsymbol{\tau}_\alpha$. The coefficients $a_{lm}^{\alpha}(\mathbf{G})$ and $b_{lm}^{\alpha}(\mathbf{G})$ are determined by matching the basis function and its radial derivative on the MT sphere and thus depend on $\boldsymbol{\tau}_\alpha$ through the phase factor $\exp[i(\mathbf{k}_i+\mathbf{G})\cdot\boldsymbol{\tau}_\alpha]$. The change in the basis functions from moving atom α is nonvanishing only inside its MT sphere and is given by

$$\frac{\delta\phi_{\mathbf{G}}}{\delta\boldsymbol{\tau}_\alpha}=i(\mathbf{k}_i+\mathbf{G})\phi_{\mathbf{G}}-\nabla\phi_{\mathbf{G}} , \tag{25}$$

where the variations in u_l and $\dot{u}_l$ are neglected (discussed below). Substituting Eqs. (12) and (25) into Eq. (23), we finally have

$$\mathbf{F}_{\mathrm{IBS}}^{\alpha}=-\sum_i n_i \left[i\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C_i^*(\mathbf{G})C_i(\mathbf{G}')\langle\phi_{\mathbf{G}}|(H-\varepsilon_i)|\phi_{\mathbf{G}'}\rangle_{\mathrm{MT}} -\langle\nabla\psi_i|(H-\varepsilon_i)|\psi_i\rangle_{\mathrm{MT}}-\langle\psi_i|(H-\varepsilon_i)|\nabla\psi_i\rangle_{\mathrm{MT}}+\mathbf{D}_i \right] , \tag{26}$$

where the subscript MT means the integrations are over the MT sphere of atom α only. Detailed expressions that we use in our calculations are given in the Appendix.

The above IBS correction corresponds to total-energy calculations where the radial augmentation functions are frozen. This is different from the usual LAPW calculations, in which the radial functions are determined by the following equations:

$$H_{\mathrm{MT}}u_l Y_{lm}=\varepsilon_l u_l Y_{lm} , \tag{27a}$$

$$H_{\mathrm{MT}}\dot{u}_l Y_{lm}=(\varepsilon_l\dot{u}_l+u_l)Y_{lm} , \tag{27b}$$

where $H_{\mathrm{MT}}=\hat{T}+V_{\mathrm{eff}}^{S}(r)$ with V_{eff}^{S} being the spherical part of the effective potential. The ε_l's are energy parameters and are chosen to lie within the valence bands with the corresponding angular momentum. Equation (27) ensures that the basis functions as given by Eq. (24) are orthogonal to core states[3,4] that are localized within the MT sphere, but it also makes them dependent upon (the spherical part of) the effective potential. As a result, $\delta\phi_{\mathbf{G}}|\delta\boldsymbol{\tau}$ should have additional contributions from the changes in u_l and $\dot{u}_l$ and from the accompanying changes in $a_{lm}^{\alpha}(\mathbf{G})$ and $b_{lm}^{\alpha}(\mathbf{G})$. However, it is impractical to calculate these contributions because δV_{eff} is not readily obtainable (one could, for instance, use the linear-response theory to estimate δV_{eff}, but the effort could parallel or even exceed that of the force calculations described here). For a given system and a given set of energy parameters, the size of the term can be determined by performing total-energy calculations using relaxed and frozen augmentation functions. Thus, if the change in the total energy from moving the α atom by $\delta\boldsymbol{\tau}_\alpha$ is δE in the usual LAPW calculations and is δE_{FA} when using the same set of augmentation functions for both configurations, the force due to the variation of u_l and $\dot{u}_l$ is given by

$$\mathbf{F}_{\mathrm{FAC}}=\frac{\delta E_{\mathrm{FA}}-\delta E}{\delta\boldsymbol{\tau}_\alpha} , \tag{28}$$

which we shall call the frozen augmentation correction (FAC). Another way of calculating the FAC is suggested by the foregoing line of derivation, which relates it to the change in the sum of valence eigenvalues arising from merely changing u_l and $\dot{u}_l$ (with the position of the atoms and the potential left unchanged). Denoting the eigenvalue sum by S, we have

$$\mathbf{F}_{\mathrm{FAC}}=\frac{S[\{u_l,\dot{u}_l\};V_{\mathrm{eff}}]-S[\{u_l',\dot{u}_l'\};V_{\mathrm{eff}}]}{\delta\boldsymbol{\tau}_\alpha} , \tag{29}$$

where the primed quantities refer to the final atomic configuration (where the α atom is moved by $\delta\boldsymbol{\tau}_\alpha$). We have calculated the FAC for the test cases presented in Sec. IV using both Eqs. (28) and (29). It is found that the FAC is quite small if the energy parameters are appropriately chosen.

III. PSEUDOPOTENTIAL FORMALISM

Pseudopotentials have been used in conjunction with the LAPW formalism[14] in a comparative study of pseudopotentials and all-electron calculations for Si. Here we present a general formulation[13] that includes the effects of nonlocal potentials, which may not be neglected in general. Expressions for the atomic force are also given here.

The nonlocal part of the pseudopotentials would significantly complicate the evaluation of the Hamiltonian matrices if it were to leak into the interstitial region and other MT spheres. It is therefore desirable to have the nonlocality confined within the MT sphere of the atom for which the pseudopotential is generated. This condition is satisfied by the potentials generated using the Kerker scheme.[16] In this scheme, a pseudo-wave-function is obtained by matching a well-behaved analytical function onto the all-electron wave function at the chosen core radius. The resulting pseudopotentials for different angular momentum l thus match exactly (at the corresponding core radii) onto the all-electron potential minus the core screening. The pseudopotential is then local beyond the largest of the core radii for all angular momentum l. The restrained nonlocality requirement is satisfied by using core radii which are smaller than the MT radius. We find it possible to generate smooth pseudopotentials for the study of bulk systems using this procedure. Of course "hard" pseudopotentials present no difficulty in the LAPW method.

In order to facilitate the treatment of the electron-ion and ion-ion interaction in the LAPW formalism,[17] we separate the pseudopotential of atom α into two parts: (i) a point charge (ionic charge) potential, $-Z_{\rm ion}^{\alpha}/r$, which replaces the potential of its nucleus in the all-electron formalism, and (ii) a pseudopotential that is taken to be[10] (we use lower case for the potential of individual atoms and upper case for the total crystalline pseudpotential)

$$\hat{v}\,_{\rm ps}^{\alpha}(\mathbf{r})=v_L^{\alpha}(r)+\hat{v}\,_{\rm NL}^{\alpha}(\mathbf{r})=v_L^{\alpha}(r)+\sum_{l=0}^{l_{\rm max}} v_l^{\alpha}(r)\hat{P}_l \ , \tag{30}$$

where $\hat{P}_l$ is an operator that projects out the component of a wave function with the angular momentum l. The local part $v_L^{\alpha}(r)$ is obtained by subtracting the point-charge potential in (i) from the atomic pseudopotential for some chosen l. The latter is subtracted from the atomic pseudopotential for all l (up to $l_{\rm max}$) to give the nonlocal potentials, $v_l^{\alpha}(r)$. As mentioned, the nonlocal part vanishes for $r>R_{\alpha}$. Since the atomic pseudopotential for any l approaches $-Z_{\rm ion}^{\alpha}/r$ at large r, the local part is short ranged. Nevertheless, it does extend beyond its own MT sphere. It is thus necessary to convert the local part into the plane-wave representation in the interstitial region and lattice harmonics representation in the MT spheres. To do this, we first carry out the following decomposition:

$$v_L^{\alpha}(r)=w_{\alpha}(r)+\tilde{v}_{\alpha}(r) \ , \tag{31}$$

where the two components are given by

$$w_{\alpha}(r)=\begin{cases} v_L^{\alpha}(r)-(A_{\alpha}+B_{\alpha}r^2) \ , & r\le R_{\alpha} \\ 0 \ , & r\ge R_{\alpha} \ , \end{cases} \tag{32a}$$

and

$$\tilde{v}_{\alpha}(r)=\begin{cases} A_{\alpha}+B_{\alpha}r^2 \ , & r\le R_{\alpha} \\ v_L^{\alpha}(r) \ , & r\ge R_{\alpha} \ , \end{cases} \tag{32b}$$

where A_{α} and B_{α} are determined such that $\tilde{v}_{\alpha}(r)$ and its derivative are continuous at $r=R_{\alpha}$. The function $\tilde{v}_{\alpha}$ is now a smooth and slow-varying function. It is thus possible to expand

$$\tilde{V}(\mathbf{r})=\sum_{\alpha}\sum_{\mathbf{R}}\tilde{v}_{\alpha}(|\mathbf{r}-\tau_{\alpha}-\mathbf{R}|) \tag{33}$$

in plane waves, which is subsequently evaluated in the MT spheres and projected onto lattice harmonics.[3,4] The total pseudopotential of the crystal is given by

$$\hat{V}_{\rm ps}(\mathbf{r})=\sum_{\alpha}\sum_{\mathbf{R}}\left[w_{\alpha}(|\mathbf{r}-\tau_{\alpha}-\mathbf{R}|)+\sum_{l}v_l^{\alpha}(|\mathbf{r}-\tau_{\alpha}-\mathbf{R}|)\hat{P}_l\right] +\tilde{V}(\mathbf{r}) \ . \tag{34}$$

The Kohn-Sham equation, Eq. (3), must now be solved with the new Hamiltonian

$$H=\hat{T}+\hat{V}_{\rm ps}(\mathbf{r})+V_{\rm eff}(\mathbf{r}) \ , \tag{35}$$

where $V_{\rm eff}$ is given by Eq. (4) in which the nuclear charge Z_{α} is now replaced by the ionic charge $Z_{\rm ion}^{\alpha}$. The muffin-tin part of the Hamiltonian, which is used to determine u_l and $\dot{u}_l$, is now

$$H_{\rm MT}^{\alpha}=\hat{T}+w_{\alpha}(r)+\sum_{l}v_l^{\alpha}(r)\hat{P}_l+\tilde{V}^{S}(r)+V_{\rm eff}^{S}(r) \ , \tag{36}$$

where $\tilde{V}^{S}$ and $V_{\rm eff}^{S}$ are, respectively, the spherical part of $\tilde{V}$ and $V_{\rm eff}$. The Hamiltonian matrix elements can be evaluated in exactly the same manner as in the all-electron method.[3,4] The total energy is given by Eq. (1) since the pseudopotentials are treated as classical (external) potentials.

The IBS correction to the atomic force can be separated into pseudopotential and nonpseudopotential contributions. The nonpseudopotential terms are again given by Eq. (26) (with $H=\hat{T}+V_{\rm eff}$). The pseudopotential contribution to the force is given by

$$\mathbf{F}_{\rm ps}^{\alpha}=-\frac{\delta}{\delta\tau_{\alpha}}\langle\psi|\hat{V}_{\rm ps}|\psi_i\rangle \ . \tag{37}$$

The contribution of the atom-centered pseudopotentials [first term in Eq. (34)] comes from the change in $a_{lm}^{\alpha}(\mathbf{G})$ and $b_{lm}^{\alpha}(\mathbf{G})$ only, while that of $\tilde{V}$ is similar to Eq. (19). Recalling Eq. (25), one obtains

$$\mathbf{F}_{\rm ps}^{\alpha}=-\sum_{i}n_i\left[i\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C_i^{*}(\mathbf{G})C_i(\mathbf{G}')\langle\phi_{\mathbf{G}}|\hat{V}_{\rm ps}|\phi_{\mathbf{G}'}\rangle_{\rm MT}-\langle\nabla\psi_i|\tilde{V}|\psi_i\rangle_{\rm MT}-\langle\psi_i|\tilde{V}|\nabla\psi_i\rangle_{\rm MT}+\left\langle\psi_i\left|\frac{\delta\tilde{V}}{\delta\tau_{\alpha}}\right|\psi_i\right\rangle\right] \ . \tag{38}$$

Adding on the nonpseudopotential contributions, we have

$$\mathbf{F}_{\rm IBS}^{\alpha}=-\sum_{i}n_i\left[i\sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C_i^{*}(\mathbf{G})C_i(\mathbf{G}')\langle\phi_{\mathbf{G}}|(H-\varepsilon_i)|\phi_{\mathbf{G}'}\rangle_{\rm MT} -\langle\nabla\psi_i|(H'-\varepsilon_i)|\psi_i\rangle_{\rm MT}-\langle\psi_i|(H'-\varepsilon_i)|\nabla\psi_i\rangle_{\rm MT}+\mathbf{D}_i+\left\langle\psi_i\left|\frac{\delta\tilde{V}}{\delta\tau_{\alpha}}\right|\psi_i\right\rangle\right] \ , \tag{39}$$

TABLE I. Calculated all-electron total energy (referenced to the equilibrium energy) per atom and the x component of the HF force, the core correction, the IBS correction, and the total force on the Si atom for small displacements associated with the Γ-point phonon in Si.

x	ΔE (mRy)	F_{HF} (Ry/a_B)	F_{core} (Ry/a_B)	F_{IBS} (Ry/a_B)	F (Ry/a_B)
−0.005	2.422	0.036 53	−0.000 76	−0.002 72	0.033 04
0.005	1.988	−0.030 08	0.003 62	0.001 89	−0.024 57

where

$$H'=\hat{T}+V_{\text{eff}}(\mathbf{r})+\tilde{V}(\mathbf{r}) \ . \tag{40}$$

Equation (39) is very similar to the all-electron formula, Eq. (26), and can be evaluated in the same manner (see the Appendix). The last term of Eq. (39), which is absent from the all-electron formula, is simply

$$-\int \rho_v \frac{\delta\tilde{V}}{\delta\tau_\alpha} d^3\mathbf{r} \ ,$$

which can be conveniently integrated after symmetrizing $\delta\tilde{V}$.

IV. FROZEN-PHONON CALCULATIONS

In this section, we present frozen-phonon calculations for Si, Mo, and Ag as tests of the all-electron and pseudopotential formulations of atomic forces. Two comments on the calculations are in order. The first concerns the use of the radial mesh. To accurately calculate the electric field at the nucleus, it is necessary to use a mesh with the innermost points lying very close to the nucleus in an all-electron calculation. For instance, we used 340 points with a logarithmic step size of 0.03 for Ag. In pseudopotential calculations, a fewer number (150 for Ag) of radial mesh points is sufficient because of the smoothness of the wave functions. Second, because the wave function, charge density, and potential are expanded in plane waves in the interstitial and in spherical harmonics (lattice harmonics) in the MT spheres, there exist discontinuities in these quantities on the MT spheres. Although we truncate the summation over l at $l_{\max}=8$, the rms discontinuities seem to be appreciable (a fraction of a percent). Increasing $l_{\max}$ to 12 reduces the discontinuities by about one order of magnitude. However, the agreement between total-energy and force results is not significantly improved. Thus $l_{\max}=8$ seems to be sufficient and is used in all calculations.

Total energies and forces are computed for Γ-point frozen optic-phonon configurations in Si using the all-electron formalism. The LO and TO modes of diamond structure at the Γ point are degenerate. The two atoms move in opposite directions along the bond. Let the atoms be in the positions $\pm(\frac{1}{8}+x)a(1,1,1)$, where $a=5.43$ Å is the lattice constant. Five special k points[18] are used for Brillouin-zone (BZ) integration, which should be quite accurate for insulators (this is equivalent to two special k points in the irreducible BZ for the undistorted lattice). The MT radius was chosen to be $R=2.1$ a.u. LAPW basis functions with $|\mathbf{k}+\mathbf{G}|\le K_{\max}=7.5/R$ are included. This yields a basis set of about 200 LAPW's. The valence states are treated semirelativistically and the core states fully relativistically. The Wigner interpolation formula[19] is used for the exchange-correlation potential. The calculated total energy and force for two atomic displacements are given in Table I. As the mode is not symmetric with respect to the sign of x, the energy and force are fitted to the following functions (Ref. 20):

TABLE II. Comparisons of k, $k_{\max}$, and the frequency of the Γ-point optical phonon in Si calculated from total energy and atomic force, results of a plane-wave pseudopotential calculation (Ref. 20), and experiment.

	k (Ry/a_B^2)	k_{xyz} (Ry/a_B^3)	f (THz)
Present work			
Total energy	0.5586	0.4026	15.37
Force	0.5613	0.4030	15.40
Percentage difference	0.5	0.1	0.2
Pseudopotential[b]			
Total energy	0.5436[a]	0.357	15.16
Force	0.5422[a]	0.355	15.14
Percentage difference	0.3	0.6	0.1
Experiment	0.5704[a]	0.382[b]	15.53[c]

[a] Determined from the corresponding frequency.
[b] Reference 20.
[c] Reference 21.

$$\Delta E=\frac{k}{2}u^2+4k_{xyz}\left[\frac{u}{\sqrt{3}}\right]^3 ,$$
$$F=ku+\frac{4}{\sqrt{3}}k_{xyz}u^2 , \qquad (41)$$

where $u=\sqrt{3}xa$ is the atomic displacement. The two coefficients k and k_{xyz} are determined from the calculated total energies and from the calculated forces, and the phonon frequency is then determined from the k values. The results are compared in Table II, together with that of the pseudopotential calculation of Yin and Cohen[20] and the experimental values.[20,21] The agreement between the k and k_{xyz} calculated from the total energies and from the forces in the present work is excellent, as the discrepancy is less than 0.5%, and is comparable to the plane-wave pseudopoential calculation.[20] Results of both the present all-electron calculation and the pseudopotential calculation[20] are in good agreement with experiment.

The separate contributions to the total forces are also given in Table I. In the present case, the core and IBS corrections are one to two orders of magnitude smaller than the HF force. As we mentioned earlier, the force calculation assumes the frozen augmentation approximation. However, the FAC's are found to be very small. By using the augmentations generated in the self-consistent calculation for the equilibrium configuration, the total energy for $x=\pm0.005$ is recalculated and found to be lower by approximately 5 μRy, or only 0.2% of the total-energy differences. This is in the opposite direction of the discrepancy between the total-energy and force results. There is thus a numerical error of 0.7%.

Next, we perform all-electron and pseudopotential tests regarding the H-point phonon of Mo. The frequency of this mode was first calculated using a pseudopotential approach[22] but the result was 9% smaller than the experimental value. However, a recent paper[23] placed the local-density theoretical prediction at a much closer 2.7% below the experimental value, using a superlinearized augmented-plane-wave method. A large number of k points are also necessary to obtain a well-converged phonon frequency.[23] For our test purposes, we have therefore chosen to compare the calculated force with the total-energy result only. For this purpose, we use a set of six special k points[18] and no artificial temperature broadening. Because of the extended nature of the p semicore states, we treat the semicore states variationally in a separate window in our all-electron calculations. Although the semicore states are strictly not orthogonal to the valence states, this procedure has often been adopted in the LAPW study for such systems. The use of this procedure for the $4p$ states enables us to avoid the core correction problem mentioned earlier for extended core states.

The following parameters are used in the all-electron calculations. The lattice constant is taken to be $a=3.11$ Å and the MT radius of Mo chosen to be 2.45 a.u. All LAPW's up to $K_{\max}=9/R$ are included in the basis functions. The energy parameters are placed close to the Fermi energy, except for the $l=1$ energy parameter in the valence state window, which is set to 1.0 Ry (the Fermi level is about 0.8 Ry) to avoid the possible appearance of the so-called "ghost" bands. The core states are treated relativistically and the valence states (including the semicore states) semirelativistically. The Hedin-Lundqvist exchange-correlation potential[24] is employed. Because of the anharmonicity of this mode,[23] we calculated the total energy and force for four values of δ, the displacement of Mo in units of a. The results are listed in Table III. To compare the total energy with the calculated force, the total energies are fitted to a sixth-order polynomial (only the even-powered terms are present due to symmetry):

$$E=e_0+e_2\delta^2+e_4\delta^4+e_6\delta^6 . \qquad (42)$$

The rms error of the fit is less than 10^{-6} Ry. From Eq. (42), one can numerically determine the force on the atoms (this shall be referred to as the total-energy force). These are also given in Table III. Comparison of the total-energy force and calculated force shows a discrepancy of about 3%. Part of the discrepancy is due to the frozen augmentation used in the force calculations. The phonon frequency is lowered if the augmentation functions from the equilibrium geometry are used. The resulting FAC, as shown in the last row of Table III, is about 1.7% of the total-energy force. The numerical error in the force calculations is thus 1–2 %.

For the pseudopotential calculations, we construct the pseudopotential using the Kerker scheme[16] in the

TABLE III. Comparison of total-energy and force results of all-electron calculation on the H-point phonon of Mo: Total energy (referenced to the equilibrium energy), total-energy force ($F_{\rm TE}$), HF force, core and IBS corrections, total calculated force ($F_{\rm tot}$) and its difference from the total-energy force, and FAC as a percentage of the total-energy force for small atomic displacements.

δ	0.005	0.010	0.015	0.020
ΔE (mRy)	0.1424	0.5751	1.3124	2.3719
$F_{\rm TE}$ (Ry/a_B)	0.009 72	0.019 80	0.030 46	0.041 70
$F_{\rm HF}$ (Ry/a_B)	0.047 35	0.094 37	0.142 18	0.188 30
$F_{\rm core}$ (Ry/a_B)	−0.047 33	−0.094 05	−0.141 04	−0.186 04
$F_{\rm IBS}$ (Ry/a_B)	0.009 36	0.018 84	0.028 50	0.038 33
$F_{\rm tot}$ (Ry/a_B)	0.009 39	0.019 15	0.029 64	0.040 58
$(F_{\rm TE}-F_{\rm tot})/F_{\rm TE}$	3.4%	3.3%	2.8%	2.7%
$F_{\rm FAC}/F_{\rm TE}$	1.7%	1.7%	1.7%	1.7%

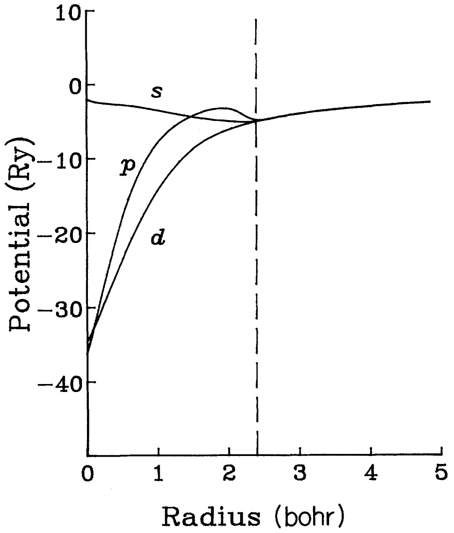

FIG. 1. *Ab initio* pseudopotential of Mo generated using the Kerker scheme. Vertical dashed line indicates the muffin-tin radius used in bulk calculations.

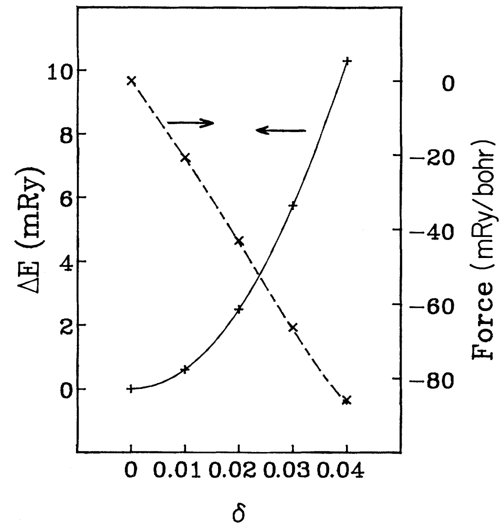

FIG. 2. Calculated pseudopotential total energies (relative to its equilibrium value) (+, left scale) and force on Mo atoms (crosses, right scale) as a function of atomic displacement in units of lattice constant. The solid line is a polynomial fit to the calculated total energies and the dashed line is the negative of its derivative with respect to the atomic displacement.

configuration (Mo)$4d^6 5s^{0.7} 5p^{0.3}$. The pseudopotential generated is shown in Fig. 1. The core radii used are 2.37 (s and p) and 1.34 (d) in atomic units. In the bulk calculations, the MT radius of Mo is chosen to be $R=2.4$ a.u. The $l=0$ potential is used here as the local pseudopotential. The equilibrium lattice constant is found to be 3.11 Å, using 40 special k points in the irreducible BZ. The calculated energy and force are given in Table IV. Again, the total-energy forces are obtained by fitting the calculated energies to Eq. (42). The total-energy forces are seen to be greater than the calculated forces by about 1%. The discrepancies agree surprisingly well with the FAC. A visual comparison of the results is shown in Fig. 2.

As a further example, let us consider all-electron and pseudopotential calculations concerning the H-point phonon in bcc Ag. We take the lattice constant to be 6.1 a.u., such that the atomic volume is approximately equal to its equilibrium value of the fcc structure. We use six special k points and a fictitious temperature of 4 mRy for smoothing the occupation near the Fermi level. According to our tests, this mode has negligible anharmonicity. We thus calculate the total energy and force at the small displacement $\delta=0.01$ and compare the results by assuming quadratic variation of the energy with the displacement. The results are given in Table V. The agreement between the total-energy and force results is excellent in both the all-electron and pseudopotential calculations.

We have also tabulated the contribution of the individual terms to the atomic force in Tables III–V. As is known, the core corrections in an all-electron calculation can be large. In fact, the core corrections in Tables III and V are almost the same size as the HF force. The total forces are smaller by as much as one order of magnitude. Despite this, the results show that the total force can be computed accurately.

An important factor that constrains the accuracy of the calculated force is the FAC. In the above examples, the FAC's are all less than 2% of the forces. This quanti-

TABLE IV. Comparison of total-energy and force results of pseudopotential calculations on the H-point phonon of Mo: Total energy (referenced to the equilibrium energy), total-energy force (F_{TE}), HF force, IBS corrections, total calculated force (F_{tot}) and its difference from the total-energy force, and FAC as a percentage of the total-energy force for small atomic displacements.

δ	0.01	0.02	0.03	0.04
ΔE (mRy)	0.6104	2.4958	5.7462	10.2988
F_{TE} (Ry/a_B)	0.020 96	0.043 50	0.067 03	0.086 49
F_{HF} (Ry/a_B)	−0.069 77	−0.137 55	−0.202 73	−0.264 79
F_{IBS} (Ry/a_B)	0.090 48	0.180 61	0.269 07	0.350 62
F_{tot} (Ry/a_B)	0.020 70	0.043 05	0.066 34	0.085 83
$(F_{\mathrm{TE}}-F_{\mathrm{tot}})/F_{\mathrm{TE}}$	1.2%	1.0%	1.0%	0.8%
$F_{\mathrm{FAC}}/F_{\mathrm{TE}}$	1.2%	1.1%	1.0%	0.9%

TABLE V. Total-energy and force results of all-electron and pseudopotential calculations on the H-point phonon of Ag: Total energy (referenced to the equilibrium energy), total-energy force, HF force, IBS correction, total calculated force and its difference from the total-energy force, and FAC as a percentage of the total-energy force for $\delta=0.01$.

	All electron	Pseudopotential
ΔE (mRy)	0.7837	0.7462
F_{TE} (Ry/a_B)	0.012 85	0.012 23
F_{HF} (Ry/a_B)	$-0.088\,41$	$-0.027\,01$
F_{core} (Ry/a_B)	0.093 14	0.0
F_{IBS} (Ry/a_B)	0.008 25	0.039 25
F_{tot} (Ry/a_B)	0.012 99	0.012 24
$(F_{\mathrm{TE}}-F_{\mathrm{tot}})/F_{\mathrm{TE}}$	-1.1%	-0.1%
$F_{\mathrm{FAC}}/F_{\mathrm{TE}}$	1.2%	1.3%

ty is, however, dependent on the choice of the energy parameters. As in LAPW total-energy calculations, the energy parameters should be placed within or at the "center" of the bands with the corresponding angular momentum character in order to minimize the FAC. In the above all-electron calculations for bcc Ag, the $l=2$ parameter is set to 0.2 Ry. If we choose it instead to be 0.3 Ry (near the top edge of the *d* band), the FAC increases from 1.2% to 4.2%. How the FAC depends on the energy parameters is of course system dependent. In the two-window calculations for Mo, the FAC changes very little when the $l=2$ parameter is moved from 0.7 to 0.5 Ry.

As we have mentioned, the basic difference between the present formulation of the atomic force and those for localized basis methods lies in the contribution from the discontinuity in the kinetic-energy density to the IBS correction. In our calculation of the atomic force, this term is combined with others in the IBS correction (see the Appendix). To see how important it is, we have recalculated the all-electron forces for the three systems studied above, without including this contribution. The results are compared in Table VI with the total-energy force and the force calculated with the surface discontinuity contribution. It is clear that inclusion of the contribution due to the kinetic-energy discontinuity is essential in obtaining the correct atomic force.

The present force calculations are carried out by using input potentials and output eigenvalues, wave functions, and charge densities, and we find that the calculated force converges at least as fast as the total energy. The force calculation is also fairly efficient; the increase in the computer time is at most 50% of that used in corresponding total-energy calculations. Optimization of the algorithm can be expected to further reduce the computational cost.

V. CONCLUSIONS

We have presented formulations for the calculation of atomic forces in the LAPW method. A muffin-tin surface contribution to the IBS correction is shown to exist. Such a term is also present in other muffin-tin-based methods (such as the LMTO method). We have also discussed a pseudopotential approach that utilizes the LAPW basis functions for total-energy and force calculations. The results presented here show that the calculated force is accurate enough to be of practical use.

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TABLE VI. Comparison of the all-electron total-energy force and the total forces (in units of Ry/a_B) calculated with and without the contribution from the kinetic-energy discontinuity. The values for Si are the *x* component.

Displacement	F_{TE}	F_{tot} (with discontinuity)	F_{tot} (without discontinuity)
Si			
$x=-0.005$	0.032 90	0.033 04	0.049 91
$x=0.005$	$-0.024\,42$	$-0.024\,57$	$-0.034\,94$
Mo			
$\delta=0.01$	0.019 80	0.019 15	0.029 93
$\delta=0.02$	0.041 70	0.040 58	0.062 24
Ag			
$\delta=0.01$	0.012 85	0.012 99	0.024 10

were done at the Cornell National Supercomputer Facility. It is a pleasure to acknowledge helpful conversations with W. E. Pickett and M. R. Pederson.

APPENDIX: DETAILS OF FORCE CALCULATIONS

The HF force is readily obtained from the $l=1$ components of the electrostatic potential around the atom α. Let the potential around the atom be

$$V_{\mathrm{es}}(\mathbf{r}_\alpha)=\sum_{l,m} V_{lm}^{\mathrm{es}}(r_\alpha)Y_{lm}(\hat{r}_\alpha)\ . \tag{A1}$$

The HF force is given by

$$\begin{aligned}\mathbf{F}_{\mathrm{HF}}^{\alpha}&=Z_\alpha\nabla_\alpha V_{\mathrm{es}}(\mathbf{r}_\alpha)|_{\mathbf{r}_\alpha=0}\\&=Z_\alpha\sum_{m=-1}^{1}\lim_{r_\alpha\to 0}\frac{V_{1m}^{\mathrm{es}}(r_\alpha)}{r_\alpha}\nabla_\alpha[r_\alpha Y_{1m}(\hat{r}_\alpha)]\ .\end{aligned} \tag{A2}$$

Alternatively, it can be calculated directly from the electrostatic potential on and the charge density in the MT sphere, using the analytical formula[17] for the electrostatic potential within the MT sphere,

$$\mathbf{F}_{\mathrm{HF}}^{\alpha}=Z_\alpha\sum_{m=-1}^{1}\left\{\frac{4\pi}{3}\int_0^{R_\alpha}\rho_{1m}(r)\left[1-\left[\frac{r}{R_\alpha}\right]^3\right]dr+\frac{V_{1m}^{\mathrm{es}}(R_\alpha)}{R_\alpha}\right\}\nabla[rY_{1m}(\hat{r})]\ , \tag{A3}$$

where ρ_{1m} are the $l=1$ components of the charge density in the spherical harmonics expansion. It is clear from Eq. (A3) that the HF force is sensitive to the charge density near the nuclei. Thus, an accurate charge-density profile near the nuclei is necessary. Because the core charge density is spherical, the core correction, Eq. (11), is similarly given by

$$\mathbf{F}_{\mathrm{core}}^{\alpha}=-\sum_{m=-1}^{1}\int\rho_c^\alpha(r_\alpha)\nabla[V_{1m}^{\mathrm{eff}}(r_\alpha)Y_{1m}(\hat{r}_\alpha)]d^3\mathbf{r}_\alpha\ . \tag{A4}$$

The integrals in (A4) are special cases of the integral

$$\mathbf{I}=\int\nabla[f(r)Y_{lm}^{*}(\hat{r})]g(r)Y_{l'm'}(\hat{r})d^3\mathbf{r}\ , \tag{A5}$$

which can be evaluated by applying the Wigner-Eckart theorem and is nonvanishing only if $l-l'=\pm1$ and $|m-m'|\leq 1$. We now simplify Eq. (26) for the IBS correction. First consider the two terms involving the gradient of the wave functions. Using the nonrelativistic Hamiltonian, we find

$$\begin{aligned}\langle\nabla\psi_i|(H-\varepsilon_i)|\psi_i\rangle_{\mathrm{MT}}+\langle\psi_i|(H-\varepsilon_i)|\nabla\psi_i\rangle_{\mathrm{MT}}&=\int_{\mathrm{MT}}\nabla[\psi_i^{*}(-\tfrac{1}{2}\nabla^2-\varepsilon_i)\psi_i]d^3\mathbf{r}+\int_{\mathrm{MT}}V_{\mathrm{eff}}\nabla(\psi_i^{*}\psi_i)d^3\mathbf{r}\\&=\oint\psi_i^{*}(-\tfrac{1}{2}\nabla^2-\varepsilon_i)\psi_i|_{\mathrm{MT}}d\mathbf{S}_\alpha+\int_{\mathrm{MT}}V_{\mathrm{eff}}\nabla(\psi_i^{*}\psi_i)d^3\mathbf{r}\ .\end{aligned} \tag{A6}$$

Combining (A6) with the kinetic-energy discontinuity term $\mathbf{D}_i$ [Eq. (20b)] yields

$$\langle\nabla\psi_i|H|\psi_i\rangle_{\mathrm{MT}}+\langle\psi_i|H|\nabla\psi_i\rangle_{\mathrm{MT}}-\mathbf{D}_i=\oint\psi_i^{*}(-\tfrac{1}{2}\nabla^2-\varepsilon_i)\psi_i|_I d\mathbf{S}_\alpha+\int_{\mathrm{MT}}V_{\mathrm{eff}}\nabla(\psi_i^{*}\psi_i)d^3\mathbf{r}\ . \tag{A7}$$

The second term in (A7), after summing over all occupied valence states i, is simply

$$\sum_i n_i\int_{\mathrm{MT}}V_{\mathrm{eff}}\nabla(\psi_i^{*}\psi_i)d^3\mathbf{r}=\int_{\mathrm{MT}}V_{\mathrm{eff}}\nabla\rho_v d^3\mathbf{r}\ , \tag{A8}$$

which is an integral of the type (A5) if the charge density and potential are expressed in terms of spherical harmonics. Using the plane-wave expansion of the wave functions in the intersitial, the surface integral in (A7) becomes

$$\oint\psi_i^{*}(-\tfrac{1}{2}\nabla^2-\varepsilon_i)\psi_i|_I d\mathbf{S}_\alpha=\sum_{\mathbf{G}'}\sum_{\mathbf{G}}C_i^{*}(\mathbf{G}')C_i(\mathbf{G})[\tfrac{1}{2}(\mathbf{G}+\mathbf{k}_i)^2-\varepsilon_i]\oint\phi_{\mathbf{G}'}^{*}\phi_{\mathbf{G}}d\mathbf{S}_\alpha\ . \tag{A9}$$

By substituting the MT representation for the basis functions, we can decouple **G** and G' in Eq. (9). With the definitions

$$A_{lm}^{i}=\sum_{\mathbf{G}}C_i(\mathbf{G})a_{lm}^{\alpha}(\mathbf{G}),\quad B_{lm}^{i}=\sum_{\mathbf{G}}C_i(\mathbf{G})b_{lm}^{\alpha}(\mathbf{G}) \tag{A10}$$

and

$$\begin{aligned}E_{i,lm}^{(1)}&=\sum_{\mathbf{G}}[\tfrac{1}{2}(\mathbf{G}+\mathbf{k}_i)^2-\varepsilon_i]C_i(\mathbf{G})a_{lm}^{\alpha}(\mathbf{G})\ ,\\E_{i,lm}^{(2)}&=\sum_{\mathbf{G}}[\tfrac{1}{2}(\mathbf{G}+\mathbf{k}_i)^2-\varepsilon_i]C_i(\mathbf{G})b_{lm}^{\alpha}(\mathbf{G})\ ,\end{aligned} \tag{A11}$$

the surface integral reads

$$\oint\psi_i^{*}(-\tfrac{1}{2}\nabla^2-\varepsilon_i)\psi_i|_I d\mathbf{S}_\alpha=\sum_{l',m'}[A_{l'm'}^{i}u_{l'}(R_\alpha)+B_{l'm'}^{i}\dot{u}_{l'}(R_\alpha)]^{*}\sum_{l,m}[E_{i,lm}^{(1)}u_l(R_\alpha)+E_{i,lm}^{(2)}\dot{u}_l(R_\alpha)]\oint Y_{l'm'}^{*}Y_{lm}d\mathbf{S}_\alpha\ . \tag{A12}$$

The last integral is evaluated in a way similar to (A5). The summation over lm and $l'm'$ is simplified by the selection rules mentioned above. Finally, to evaluate the first term in Eq. (26), we separate the Hamiltonian into MT and non-

MT (nonspherical potential) terms,

$$H=H_{\mathrm{MT}}+V_{\mathrm{eff}}^{\mathrm{NS}} . \tag{A13}$$

Using Eqs. (24) and (27), we find

$$\langle \phi_{\mathbf{G}}|(H_{\mathrm{MT}}-\varepsilon_i)|\phi_{\mathbf{G}'}\rangle=\sum_{l,m}\{a_{lm}^{\alpha *}(\mathbf{G})[a_{lm}^{\alpha}(\mathbf{G}')(\varepsilon_l-\varepsilon_i)+b_{lm}(\mathbf{G}')]+b_{lm}^{\alpha *}(\mathbf{G})b_{lm}^{\alpha}(\mathbf{G}')(\varepsilon_l-\varepsilon_i)N_l\} , \tag{A14}$$

where we have used the orthogonality relation

$$\int_0^{R_\alpha} u_l \dot{u}_l r^2 dr \equiv 0 \tag{A15}$$

and

$$N_l=\int_0^{R_\alpha} \dot{u}_l^2 r^2 dr . \tag{A16}$$

The force due to the MT Hamiltonian in the first term of Eq. (26) is therefore

$$-i\sum_i n_i \sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C_i^*(\mathbf{G})C_i(\mathbf{G}')\langle \phi_{\mathbf{G}}|(H_{\mathrm{MT}}-\varepsilon_i)|\phi_{\mathbf{G}'}\rangle_{\mathrm{MT}}$$

$$=\sum_i n_i \sum_{l,m}\mathrm{Im}\{\,\mathbf{A}_{lm}^i[2A_{lm}^i(\varepsilon_l-\varepsilon_i)+B_{lm}^i]^*+\mathbf{B}_{lm}^i[2B_{lm}^i(\varepsilon_l-\varepsilon_i)N_l+A_{lm}^i]^*\} , \tag{A17}$$

where Im means taking the imaginary part and

$$\mathbf{A}_{lm}^i=\sum_{\mathbf{G}}\mathbf{G}C_i(\mathbf{G})a_{lm}^{\alpha}(\mathbf{G}) , \quad \mathbf{B}_{lm}^i=\sum_{\mathbf{G}}\mathbf{G}C_i(\mathbf{G})b_{lm}^{\alpha}(\mathbf{G}) . \tag{A18}$$

As the nonspherical potential is in the form

$$V_{\mathrm{eff}}^{\mathrm{NS}}(\mathbf{r})=\sum_\nu V_\nu(r)\sum_M C_{L_\nu M}^{\nu}Y_{L_\nu M}(\hat{r}) , \tag{A19}$$

its contribution to the first term in Eq. (26) is calculated as follows:

$$-i\sum_l n_i \sum_{\mathbf{G},\mathbf{G}'}(\mathbf{G}'-\mathbf{G})C_i(\mathbf{G})^*C_i(\mathbf{G}')\langle \phi_{\mathbf{G}}|V_{\mathrm{eff}}^{\mathrm{NS}}|\phi_{\mathbf{G}'}\rangle_{\mathrm{MT}}$$

$$=2\sum_i n_i \sum_{l,m}\sum_{l',m'}\sum_{\nu,M}\mathrm{Im}\left[C_{L_\nu M}^{\nu}\int Y_{l'm'}^{*}Y_{L_\nu M}Y_{lm}\,d\Omega\int(A_{l'm'}^i u_{l'}+B_{l'm'}^i\dot{u}_{l'})^*V_\nu(\mathbf{A}_{lm}^i u_l+\mathbf{B}_{lm}^i\dot{u}_l)r^2dr\right] , \tag{A20}$$

where the angular integral (Gaunt integral) vanishes unless $|l'-l|\le L\le l'+l$ and $m'=M+m$.

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