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Real-space implementation of nonlocal pseudopotentials for first-principles total-energy calculations

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We present a real-space method for performing the operations that involve the nonlocal parts of the Kohn-Sham Hamiltonian in a first-principles plane-wave total-energy calculation. In contrast to the conventional reciprocal-space formulation, where the number of operations required to compute the nonlocal contributions to the energies, forces, and stresses scales as the cube of the system size, the numerical work to compute these quantities with our real-space algorithm scales as the square of the number of atoms in the unit cell. The scheme, which can be applied to any potential expressible as a sum of separable terms, uses an approximate method to project the nonlocal potential on the core region of each atom. Errors introduced in the projection step are extremely well controlled and will not be a cause of problems in practical calculations. We have implemented the method in a conjugate-gradient total-energy program and, for illustrative purposes, demonstrate that the method produces excellent results on a two-atom cell of silicon.

Since its introduction in 1985 by Car and Parrinello[1] the first-principles molecular-dynamics method has established itself as the method of choice for performing plane-wave pseudopotential calculations on large systems. One of the novel features of the approach is that self-consistent solutions to the Kohn-Sham Hamiltonian are obtained by direct minimization of the Kohn-Sham functional. The minimization process can be accomplished either by introducing fictitious dynamics to evolve the wave functions to their ground state,[1] or by use of steepest-descent and conjugate-gradient methods.[2]

An important part of the efficiency of the Car-Parrinello method stems from the use of fast Fourier transform (FFT) methods. Terms in the Kohn-Sham Hamiltonian arising from the local potential and kinetic energy are diagonal in real and reciprocal space, respectively, and FFT techniques allow many parts of the molecular-dynamics algorithm to be performed in $O(MN \ln N)$ operations, where M is the number of occupied bands and N is the number of plane waves used to expand each Kohn-Sham wave function. Indeed in the case where the pseudopotential is purely local the only sections of the Car-Parrinello algorithm which scale less favorably than $O(MN \ln N)$ are associated with band orthogonalization steps which require $O(M^2N)$ operations. In the more general case where the pseudopotential has nonlocal components, there is a second part of the molecular-dynamics method which scales as the cube of the system size, concerned with evaluating nonlocal contributions to the total energy, forces, and stresses. Conventionally these quantities are evaluated in reciprocal space and require $O(mMN)$ operations where m is the number of atoms in the unit cell.

The molecular-dynamics approach is being used to investigate even larger systems and the stage has already been reached where nonlocal and orthogonalization operations have become the dominant parts of the calculation. In general the prefactor associated with the nonlocal operations is larger than that for the orthogonalization steps, especially for finite-temperature simulations in which the forces are computed on every time step. It is therefore of great interest to devise a method which improves the performance of the nonlocal parts of the program. Recently there has been a move to generalize separable potentials to include multiple nonlocal projectors per l value[3,4] which can both improve the transferability of the potential and reduce the number of plane waves per atom required to converge the calculation. This development increases the proportion of time spent performing nonlocal projections and provides further motivation for developing an improved algorithm for computing the nonlocal contributions to the energy.

In this paper we present a novel real-space approach for performing the nonlocal operations in a Car-Parrinello calculation. The method allows the nonlocal parts of the calculation to be performed in $O(mMP)$ operations where P is the number of operations required to perform a real-space projection of the potential, and is independent of system size. Our scheme is both accurate and efficient and promises to greatly reduce the overhead

for performing nonlocal operations in large molecular-dynamics calculations.

Nonlocal pseudopotentials are usually implemented in molecular-dynamics programs using a separable form generated, for example, using the procedure suggested by Kleinman and Bylander.[5] Following the notation of Gonze, Kräckell, and Scheffler[6] the real-space form of separable pseudopotential may be written as

$$v(\mathbf{r},\mathbf{r}')=\sum_l \sum_{m=-l}^{+l} E_l Y_{lm}^*(\theta_{\mathbf{r}},\phi_{\mathbf{r}})\zeta_l(r)\zeta_l(r') \times Y_{lm}(\theta_{\mathbf{r}'},\phi_{\mathbf{r}'}) , \quad (1)$$

where l and m are orbital and azimuthal angular momentum quantum numbers, respectively, Y_{lm} are spherical harmonics, $\zeta_l(r)$ are radial projection functions which vanish beyond some critical core radius r_c, and E_l is an angular momentum-dependent energy. In order to compute the contribution to the nonlocal energy for the ith atom from band n in the conventional reciprocal-space formulation we would write

$$\varepsilon_{\mathbf{k},n}^i=\sum_l \sum_{m=-l}^{+l} E_l Z_{lm}^* Z_{lm} , \quad (2a)$$

where

$$Z_{lm}=\sum_{\mathbf{G}} \lambda_{lm}(\mathbf{G}+\mathbf{k})c_{\mathbf{G}+\mathbf{k},n} , \quad (2b)$$

with

$$\lambda_{lm}(\mathbf{G}+\mathbf{k})=\frac{4\pi i^l}{\sqrt{\Omega_{\text{cell}}}}\zeta_l(|\mathbf{G}+\mathbf{k}|)Y_{lm}(\theta_{\mathbf{G}+\mathbf{k}},\phi_{\mathbf{G}+\mathbf{k}}) \times e^{i(\mathbf{G}+\mathbf{k})\cdot\tau_i} , \quad (2c)$$

and

$$\zeta_l(q)=\int_0^\infty r^2\zeta_l(r)j_l(qr)dr , \quad (2d)$$

where τ_i is the position vector of atom i, $c_{\mathbf{G}+\mathbf{k},n}$ are the plane-wave coefficients, j_l is a Bessel function of order l, and where the sum over $\mathbf{G}$ runs over all $|\mathbf{G}+\mathbf{k}|<G_{\max}$, where $G_{\max}$ is the plane-wave cutoff. For each value of l and m construction of the quantity Z_{lm} requires order N operations per atom per band. Thus the total nonlocal energy of the system can be obtained in $O(mMN)$ operations where m is the number of atoms in the cell. The magnitude of the prefactor is directly proportional to the number of l and m values for which Z_{lm} must be computed. The Hellmann-Fenyman forces on all the atoms can also be computed in $O(mMN)$ operations but compared with the energy the prefactor is about three times as large, reflecting the fact that there are three components to the force for each atom.

It has been understood for some time that there are advantages in performing the nonlocal operations in real space instead of reciprocal space.[7,8] In a real-space formulation we would write for the quantity Z_{lm} in Eq. (2b)

$$Z_{lm}=\int_{|\mathbf{r}-\tau_i|<r_c}\zeta_l(\mathbf{r}-\tau_i)Y_{lm}(\theta_{\mathbf{r}-\tau_i},\phi_{\mathbf{r}-\tau_i}) \times\Psi_{\mathbf{k},n}(\mathbf{r})d\mathbf{r} . \quad (3)$$

The fact that $\zeta_l(r)$ is zero for $|\mathbf{r}|>r_c$ ensures that Z_{lm} can be computed in real space via Eq. (3), in a time which is independent of the system size. Thus it ought to be possible to compute the total energy and its derivatives in real space in $O(mMP)$ operations where P is the number of operations required to perform the integration in Eq. (3). However, in practice it is not obvious how Eq. (3) should be used to compute Z_{lm}. The essential difficulty is that for practical purposes $\Psi_{\mathbf{k},n}(\mathbf{r})$ is only known at a discrete set of points, $\Psi_{\mathbf{k},n}(\boldsymbol{l})$, where $\boldsymbol{l}$ corresponds to the mesh vectors of the real-space FFT grid.

It is instructive to examine the difference between Z_{lm} and a quantity U_{lm} which is the simplest possible estimate for Z_{lm} given the constraints of the discrete Fourier mesh. We write

$$U_{lm}=\Omega_{\text{mesh}}\sum_{\boldsymbol{l}}\zeta_l(|\boldsymbol{l}-\tau_i|)Y_{lm}(\theta_{\boldsymbol{l}-\tau_i},\phi_{\boldsymbol{l}-\tau_i}) \times\Psi_{\mathbf{k},n}(\boldsymbol{l}) , \quad (4)$$

where Ω_{mesh} is the volume associated with each mesh point and the sum runs over all $\boldsymbol{l}$ for which $|\boldsymbol{l}-\tau_i|<\mathbf{r}_c$. The right-hand side of Eq. (4) can be recast to read

$$U_{lm}=\sum_{\mathbf{G}}\sum_{\Gamma}\lambda_{lm}(\Gamma+\mathbf{G}+\mathbf{k})c_{\mathbf{G}+\mathbf{k},n} , \quad (5)$$

where $\{\Gamma\}$ are the set of lattice vectors which are reciprocal to the real-space Fourier transform mesh vectors $\{\boldsymbol{l}\}$ and where the sum over $\mathbf{G}$ includes all vectors for which $|\mathbf{G}+\mathbf{k}|<G_{\max}$. Let us define the smallest nonzero value of $|\Gamma|$ to be Γ_1. If wrap around error is to be avoided when operating with the local potential on the wave function in the Car-Parrinello method, the Fourier transform grid should strictly be chosen so that $\Gamma_1>4G_{\max}$.[9] Comparing Eqs. (2) and (5) we see that the real-space estimate of Z_{lm} suggested by Eq. (4) has a type of wrap around error caused by the sum over the nonzero values of Γ in the second sum in Eq. (5). This error can in general be quite substantial because there is no reason to expect $\zeta_l(q)$ and hence $\lambda_{lm}(q)$ to be small for wave vectors of order $4G_{\max}$. A further conclusion of significance which may be drawn from Eqs. (4) and (5) is that the value of U_{lm} is independent of the value of $\zeta_l(q)$ for wave vectors in the range $G_{\max}<q<\gamma$ where $\gamma=\Gamma_1-G_{\max}$.

Our strategy for estimating Z_{lm} is based upon the idea of replacing $\zeta_l(r)$ in Eq. (4) with a new radial projection operator $\chi_l(r)$ which eliminates the wrap around error which is evident in Eq. (5) by ensuring $\chi_l(q)$ is zero for large values of wave vector. The price to pay for this truncation of $\chi_l(q)$ is that $\chi_l(r)$ is now no longer zero outside the core region. However, we can amply compensate for this difficulty, by slightly increasing the volume of the Fourier grid which is summed over, and by exploiting the complete freedom which is available in defining $\chi_l(q)$ for q in the range $G_{\max}<q<\gamma$ to maximize the weight of the real-space projector in the core region of the atom. We have found that generating $\chi_l(r)$ following the four-step process outlined below produces an excellent scheme for computing nonlocal energies and forces in real space.

(1) Select the plane-wave cutoff $G_{\max}$ which is to be

used in the solid-state calculation.

(2) Set $\chi_l(q)=\zeta_l(q)$ for $0<q<G_{\max}$ and $\chi_l(q)=0$ for $q>\gamma$.

(3) Select a real-space cutoff radius R_0, generally about 1.5–2.0 r_c.

(4) Variationally select $\chi_l(q)$ for $G_{\max}<q<\gamma$ by minimizing

$$I=\int_{R_0}^{\infty}[r\chi_l(r)]^2dr \ . \tag{6}$$

As a consequence of the fact that the new potential is zero by construction for $q>\gamma$ we now have the identity

$$Z_{lm}=\Omega_{\text{mesh}}\sum_{l}\chi_l(|l-\tau_i|)Y_{lm}(\theta_{l-\tau_i},\phi_{l-\tau_i}) \times\Psi_{\mathbf{k},n}(l) \ , \tag{7}$$

where the sum over l runs over all space. In practice Z_{lm} is estimated by including only those terms where l lies in the sphere defined by $|l-\tau_i|<R_0$. The error in our estimate, Δ, is associated with all the FFT mesh points which lie outside the sphere of radius R_0 and can be approximately written as

$$\Delta=\int_{|\mathbf{r}-\tau_i|>R_0}\chi_l(\mathbf{r}-\tau_i)Y_{lm}(\theta_{\mathbf{r}-\tau_i},\phi_{\mathbf{r}-\tau_i}) \times\Psi_{\mathbf{k},n}(\mathbf{r})d\mathbf{r} \tag{7a}$$

or

$$\Delta=\frac{4\pi i^l}{\sqrt{\Omega_{\text{cell}}}}\sum_{\mathbf{G}}W_l(\mathbf{G}+\mathbf{k})Y_{lm}(\theta_{\mathbf{G}+\mathbf{k}},\phi_{\mathbf{G}+\mathbf{k}}) \times e^{i(\mathbf{G}+\mathbf{k})\cdot\tau_i}c_{\mathbf{G}+\mathbf{k},n} \ , \tag{7b}$$

where

$$W_l(\mathbf{G}+\mathbf{k})=\int_{R_0}^{\infty}r^2\chi_l(r)j_l(|\mathbf{G}+\mathbf{k}|r)dr \ . \tag{7c}$$

For large r the spherical Bessel functions are oscillatory and decay like $1/r$. The object of step (4) is to variationally select χ_l to minimize W_l and hence minimize the error Δ. Numerical tests indicate that $W_l(q)$ can be made to be totally negligible for very modest choices of R_0 over the entire range of wave vectors $0<q<G_{\max}$. The variational optimization in step (4) of the generation process is the key to accurate and efficient calculation of nonlocal energies in real space. The prefactor for performing the summation in Eq. (7) is such that the real-space projection technique will offer a performance advantage over the conventional approach when there are more than about 10 atoms in the unit cell.

As it stands Eq. (6) is not a practical form for computation of χ_l. However, it is straightforward to recast the variational step as an integral equation for χ_l of the form

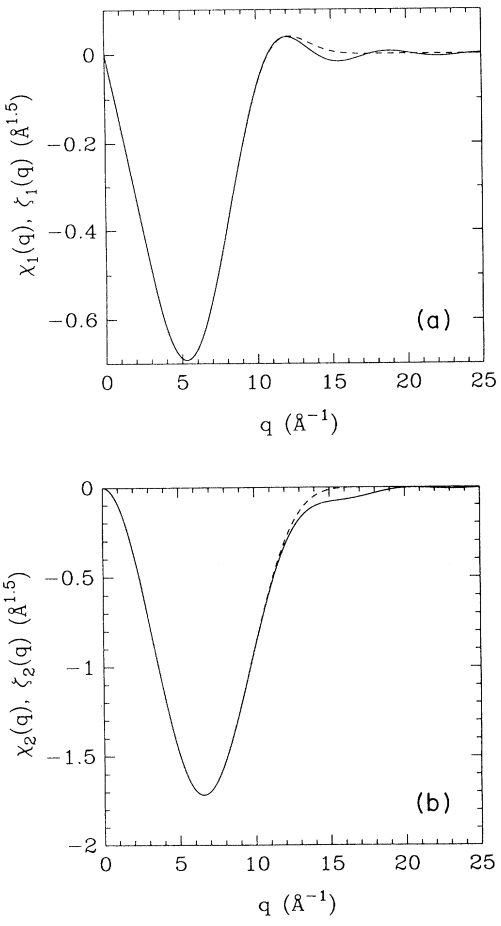

FIG. 1. (a) and (b) depict the reciprocal-space form of the $l=1$ and $l=2$ components, respectively, of the projector functions for the separable silicon potential. The solid lines show the original projectors $\zeta_l(q)$ while the dashed curves show the form of $\chi_l(q)$ derived following the prescription set out in the text.

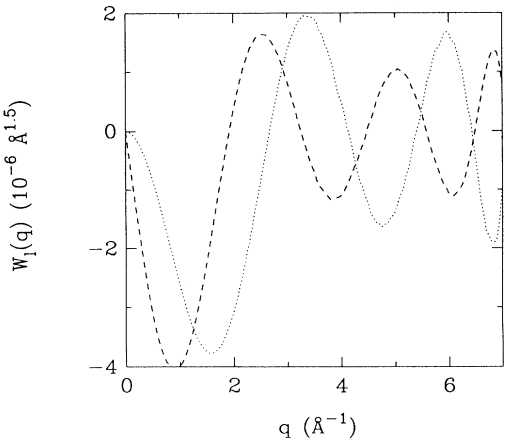

FIG. 2. Reciprocal-space form for error estimate function $W_l(q)$ defined in Eq. (7c). The dashed and dotted curves correspond to the $l=1$ and $l=2$ cases, respectively.

TABLE I. Comparison of nonlocal energies and forces for a two-atom cell of silicon calculated in real and reciprocal space using a conjugate-gradient total-energy program.

	Reciprocal space	Real space
Energy (eV)	−10.685 519 7	−10.685 513 9
Forces (eV/Å) atom no. 1		
x	1.290 944	1.290 895
y	1.290 942	1.290 892
z	1.290 944	1.290 894
Forces (eV/Å) atom no. 2		
x	−1.290 992	−1.291 024
y	−1.290 990	−1.291 022
z	−1.290 991	−1.291 024

$$\int_0^{G_{\max}} A(q,q')\chi_l(q')dq' = \frac{\pi}{2}q^2\chi_l(q) - \int_{G_{\max}}^{\gamma} A(q,q')\chi_l(q')dq' , \quad (8)$$

where q is in the range $G_{\max} < q < \gamma$ and where

$$A(q,q') = q^2q'^2\int_0^{R_0} j_l(qr)r^2 j_l(q'r)dr . \quad (8a)$$

The left-hand side of Eq. (8) is a known quantity and $\chi_l(q)$ is readily obtained for q between $G_{\max}$ and γ by discretizing q and q' and treating Eq. (8) as a matrix equation.

Figures 1(a) and 1(b) depict the form of $\zeta_l(q)$ and $\chi_l(q)$ for a silicon pseudopotential with nonlocal p and d components generated using a variation of Kleinman and Bylander's scheme.[5] The potential had a cutoff radius $r_c = 0.95$ Å and $\chi_l(q)$ was generated using $R_0 = 1.8$ Å, $G_{\max} = 7.24$ Å^{-1}, and $\gamma = 17.85$ Å^{-1}. The corresponding error estimate functions $W_l(q)$ are shown in Fig. 2. The high quality of the real-space projection technique is assured by the fact that the maximum value of $W_l(q)$ is five or six orders of magnitude smaller than maximum value of $\zeta_l(q)$.

We have implemented the real-space nonlocal potential scheme in a conjugate-gradient total-energy code. As a further illustration of the method we have performed two calculations of energies and forces for a two-atom cell of silicon using the Kleinman-Bylander potential discussed above. In the first calculation nonlocal operations were performed in reciprocal space while in the second nonlocal projections were evaluated entirely in real space. The cell we considered had an optic phonon displacement and used atomic positions $\tau_l = (0.1, 0.1, 0.1)a_0$ and $\tau_2 = (-0.1, -0.1, -0.1)a_0$, where $a_0 = 5.427$ Å is the equilibrium lattice constant of silicon. Table I summarizes the results. It is evident that results from the real and reciprocal-space calculation are in excellent agreement. Nonlocal contributions to the total energies computed by the two methods agree to 6 μeV per cell, while nonlocal contributions to the forces agree to about 50 μeV/Å. It should be emphasized that there is nothing special about the two-atom cell considered here and that the real-space method is equally applicable to cells of arbitrary shape and size.

In conclusion, we have presented a practical scheme for performing the nonlocal projections in a total-energy calculation in real space. The method will substantially reduce the computational cost of Car-Parrinello calculations on large systems.

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