

SEPARABLE PSEUDOPOTENTIALS THROUGH DOUBLE-EXPONENTIAL INTEGRATION

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Iterative diagonalization algorithms within the first-principles plane-wave pseudopotential framework require the repeated calculation of matrix times vector products. We show that using the double-exponential formula for numerical integration the nonlocal pseudopotentials are transformed into a separable form with projector functions independent of species of atoms. Since the separable form proposed here is compatible with the fast Fourier transformation technique, the number of operations for the nonlocal part of the Hamiltonian expressed in plane waves is reduced from $O(NN_{\text{at}}N_{\text{el}})$ to $O(N \log N N_{\text{el}})$, where N , N_{at} , and N_{el} are the numbers of plane waves, atoms, and electrons, respectively.

1 INTRODUCTION

First-principles total-energy calculations based on density-functional theory[1] have greatly contributed to our understanding of condensed-matter systems. In particular, pseudopotential calculations using a plane-wave basis[2] have become major theoretical tools to solve large-scale problems arising in condensed-matter physics and materials science. In such calculations eigensolutions are obtained by applying a Hamiltonian operator to a trial wave function repeatedly[3]. Since most pseudopotentials[4, 5] are dependent on angular-momenta of the wave function, the Hamiltonian operator contains a nonlocal part, which would naively make the operation time-consuming. A separable form proposed by Kleinman and Bylander[6] (KB) achieves a substantial reduction of computer resources needed by the operation[7]. Unfortunately, however, unphysical results are sometimes obtained with the separable form constructed carelessly[8]. In the present study we describe how to convert the nonlocal part of pseudopotentials into another separable form which is both numerically accurate and compatible with an efficient scheme recently proposed by Goedecker[9].

2 PSEUDOPOTENTIALS MADE SEPARABLE

In the present study we assume that the nonlocal part is associated with a single l without loss of generality. The nonlocal part of the pseudopotential Hamiltonian within the plane-wave formulation[2] is of the form

$$\delta V_{l\vec{k}\vec{G}\vec{G}'} = \sum_a \exp\{i(\vec{G} - \vec{G}') \cdot \vec{R}_a\} \sum_{m=-l}^l Y_{lm}(\widehat{\vec{k} + \vec{G}}) Y_{lm}^*(\widehat{\vec{k} + \vec{G}'}) U_{al}(|\vec{k} + \vec{G}|, |\vec{k} + \vec{G}'|), \quad (1)$$

with

$$U_{al}(q, q') = \int_0^\infty r^2 j_l(qr) j_l(q'r) \delta V_{al}(r) dr, \quad (2)$$

where j_l is a spherical Bessel function and \vec{R}_a and $\delta V_{al}(r)$ are the position and nonlocal correction potential for the a 'th atom, respectively. Applying the nonlocal operator defined as Eq.(1) to the trial wave function requires explicit matrix-vector multiplication, which is reduced to componentwise multiplication of vectors within a separable approximation proposed by KB[6]. In the KB scheme the nonlocal part is written as

$$\delta V_{l\vec{k}\vec{G}\vec{G}'}^{\text{KB}} = \sum_a \frac{1}{\xi_{al}} \sum_{m=-l}^l \xi_{alm}(\vec{k} + \vec{G}) \xi_{alm}^*(\vec{k} + \vec{G}'), \quad (3)$$

with

$$\xi_{alm}(\vec{q}) = \exp(i\vec{q} \cdot \vec{R}_a) Y_{lm}(\vec{q}) \int_0^\infty r^2 j_l(|\vec{q}|r) \phi_{al}(r) \delta V_{al}(r) dr, \quad (4)$$

and

$$\xi_{al} = \int_0^\infty |r \phi_{al}(r)|^2 \delta V_{al}(r) dr, \quad (5)$$

where $\phi_l(r)$ is an atomic reference pseudo-wave function, which is supposed to mimic the trial function in the vicinity of the pseudoatom. Though the KB scheme is widely accepted as an essential constituent technique of the large-scale pseudopotential calculations, as mentioned above, however, its careless application may yield unphysical results[8]. In addition, the application of the nonlocal operator within the KB scheme still requires $O(NN_{\text{at}}N_{\text{el}})$ operations for the whole system, where N , N_{at} , and N_{el} are the numbers of plane waves, atoms, and electrons, respectively.

To derive another separable form which is more numerically stable and suitable for the large-scale calculations, we adopt a double-exponential (DE) transformation formula for numerical integration[10]. In the present separable form Eq.(2) is replaced by

$$U_{al}^{\text{DE}}(q, q') = \sum_{i=-\infty}^{\infty} r_i^2 j_l(qr_i) j_l(q'r_i) \delta V_{al}(r_i) w_i, \quad (6)$$

where sampling points r_i and weights w_i are given by

$$r_i \equiv \eta(ih + h_o) = \exp \left\{ \frac{ih + h_o}{2} - \exp(-ih - h_o) \right\}, \quad (7)$$

and

$$w_i = h\eta'(ih + h_o), \quad (8)$$

respectively. Since in the numerical integration with the DE formula the selection of the sampling points and weights (and thus $ih + h_o$) is not tightly bound to the integrand[10], we can use a single set of them for the whole calculations. The nonlocal part within the present scheme is written as

$$\delta V_{ik\vec{G}\vec{G}'}^{\text{DE}} = \sum_a \exp\{i(\vec{G} - \vec{G}') \cdot \vec{R}_a\} \sum_{i=-\infty}^{\infty} \sum_{m=-l}^l Z_{ilm}(\vec{k} + \vec{G}) Z_{ilm}^*(\vec{k} + \vec{G}') \delta V_{al}(r_i), \quad (9)$$

where

$$Z_{ilm}(\vec{q}) = Y_{lm}(\vec{q}) r_i j_l(qr_i) \sqrt{w_i}. \quad (10)$$

We define a quantity incorporating the structure factor and nonlocal correction potentials as,

$$\delta V_{il}(\vec{q}) = \sum_a \exp(i\vec{q} \cdot \vec{R}_a) \delta V_{al}(r_i). \quad (11)$$

Using Eq.(11), we rewrite Eq.(9) as a convolution form,

$$\delta V_{ik\vec{G}\vec{G}'}^{\text{DE}} = \sum_{i=-\infty}^{\infty} \sum_{m=-l}^l Z_{ilm}(\vec{k} + \vec{G}) Z_{ilm}^*(\vec{k} + \vec{G}') \delta V_{il}(\vec{G} - \vec{G}'). \quad (12)$$

The remarkable asset of the present separable form defined as Eq.(12) is that since neither the positions nor the species of atoms affect the projectors $Z_{ilm}(\vec{q})$, its application to the trial wave function can be performed in the efficient way recently proposed by Goedecker[9] as follows:

- form a vector $W(\vec{G}') = Z_{ilm}^*(\vec{k} + \vec{G}') \psi_{\vec{k}}(\vec{G}')$,
- transform $W(\vec{G}')$ into real space, multiply it with a factor which is a real-space representation of $\delta V_{il}(\vec{q})$, and then transform the product vector back to reciprocal space,
- and multiply the obtained vector with $Z_{ilm}(\vec{k} + \vec{G})$ in a componentwise way.

The most time-consuming steps of this procedure is the forward and inverse transformations, which can be done by the fast Fourier transformation (FFT) method[11]. Evaluation and transformation of Eq.(11) must be performed only once beforehand. Thus the number of operations required is reduced from $O(NN_{\text{at}}N_{\text{el}})$ to $O(N \log N N_{\text{el}})$.

3 TEST CALCULATIONS

The test calculations are performed for diamond at a plane-wave cut-off energy of 108Ry using the Ceperlay-Alder[12] exchange-correlation as parametrized by Perdew and Zunger[13] and the pseudopotentials which Bachelet *et al.*[4] proposed. The \bar{k} -space sampling is done via a set of ten special points[14] in the irreducible wedge of the Brillouin zone. The nonlocal part, which consists of the p and d components, is treated analytically [Eqs.(1) and (2)] and using the present scheme [Eqs.(7), (8), (10)-(12)] with ten, twenty and thirty integration points over an interval for $ih + h_o$ in Eqs.(7) and (8) of $[-3, 4]$ in practice. Total energies[2] and pressures[15] are obtained as a function of (fictitious) lattice constant ranging from 0.95 to $1.02a_{\text{expt}}$, where $a_{\text{expt}} = 3.567 \times 10^{-10}\text{m}$ [16].

Figure 1 shows the total-energy curves. Though the present approach with ten integration points broke down, that with twenty points yielded the results different from those for the analytical scheme only by 10^{-21}J/atom , which was a small constant shift. This indicates that the present approach is comparable to the KB scheme[17] in accuracy. When thirty points were employed, the results for the present and analytical approaches agreed to the accuracy of 10^{-24}J/atom , which fell within rounding error. This accuracy of the present scheme is further confirmed by the results of the pressures shown in Fig.2. Except for the case of ten integration points, the results obtained by the present and analytical approaches agreed within 10^6Pa and the constant shift appeared in the total energies canceled out. It should be emphasized that there is nothing special about diamond considered here. We believe that the present separable form is equally applicable to a wide class of materials if the integration interval and points are carefully chosen.

4 CONCLUSION

In the present study we show that the nonlocal part of the pseudopotential Hamiltonian operator is transformed into a separable form using the DE transformation formula for numerical integration. Since the projector functions are independent of the type of atoms, the present separable form is compatible with Goedecker's scheme which exploits the FFT technique. We also show that describing static structural properties of diamond requires twenty to thirty integration points, which indicates that the present approach is practical.

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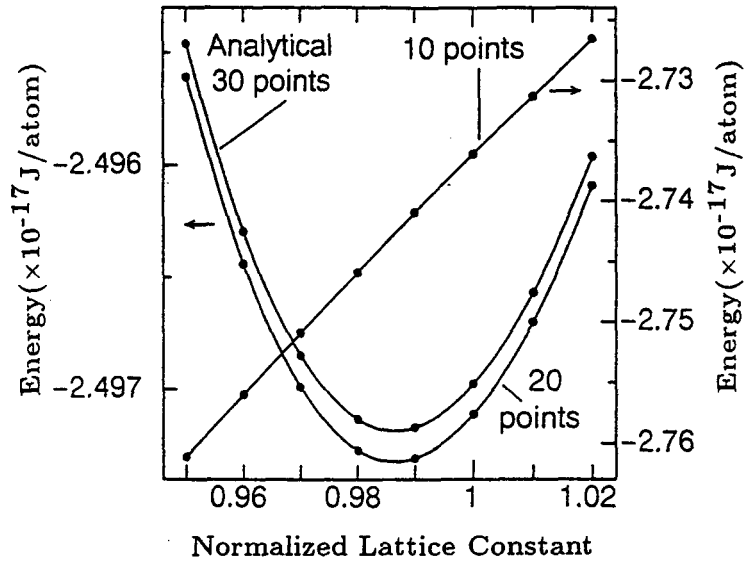


Figure 1: Total energy versus normalized lattice constant calculated with the analytical and present approaches. The curves for the analytical approach and the present one with thirty integration points are not resolved.

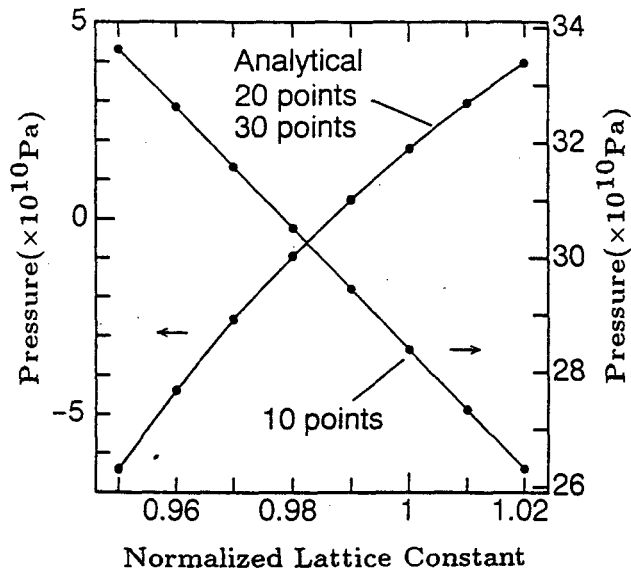


Figure 2: Pressure versus normalized lattice constant calculated with the analytical and present approaches. The curves except for the present approach with ten integration points are not resolved.