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Projector-basis technique and Car-Parrinello scaling in mixed-basis, linearized-augmented-plane-wave, and extended linearized-augmented-plane-wave electronic-structure methods

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It is shown that by exploiting auxiliary or projector-basis functions as a local representation of plane waves, highly efficient implementations of several band-structure techniques can be obtained. Examples are nonlocal pseudopotential methods with (1) plane-wave and (2) mixed (plane waves plus local orbitals) basis sets, and the all-electron (3) linearized-augmented-plane-wave and (4) extended linearized-augmented-plane-wave methods. The computation in all of the proposed techniques scales as $N^2\ln(N)$, where N is the number of atoms in the unit cell. Early calculations are presented for the plane-wave and mixed-basis approaches.

INTRODUCTION

Local-density-approximation electronic-structure calculations have made very substantial contributions to the understanding of many problems in condensed-matter physics. The range of problems that can be treated directly using these techniques is, however, limited by the fact that the computational requirements increase rapidly with the number of atoms in the unit cell. With the exception of the Car-Parrinello (CP) (Ref. 1) and related techniques (discussed below), the computing time for these calculations scales as $O(N^3)$, where N is the number of atoms in the unit cell. The CP method, which uses fast-Fourier-transform (FTT) techniques to achieve an improved scaling of $O(N^2/\ln N)$, has permitted calculations for larger and more complex unit cells than could be treated using conventional algorithms. Unfortunately, because the CP method requires the use of a pure plane-wave basis set, its application to systems containing transition-metal and rare-earth atoms is restricted. Moreover, in most implementations, if a nonlocal pseudopotential is used, the scaling reverts to $O(N^3)$. Here we present a method that permits mixed-basis and linearized-augmented-plane-wave (LAPW) calculations to be performed with a computational effort comparable to plane-wave-only CP calculations with a similarly sized basis. Since mixed and LAPW basis functions are normally more efficient than plane wave (meaning that a smaller basis set may be used), this represents a substantial improvement.

As discussed by Soler and Williams,[2] the generic advantage of the CP approach lies in the fact that optimizations are performed simultaneously rather than hierarchically. In performing a geometry optimization using conventional methods, three optimizations are being performed in a hierarchical fashion. These are (1) the optimization of the geometry, which uses calculated forces and energies from self-consistent electronic-structure calculations along the path to the minimum, (2) the iteration to self-consistency which involves exact diagonalizations of the secular equation at each step, and (3) the individual diagonalizations, which may be regarded as optimizations of the eigenvectors. In conventional electronic-structure calculations at a fixed atomic geometry, two optimizations (self-consistency and diagonalizations) are performed hierarchically. On the other hand, the CP method exploits the fact that in the early stages of a geometry optimization, approximate forces and energies would be sufficient and that in the iteration to self-consistency, approximate eigenvectors would be sufficient in the initial iterations. In particular, each step of the CP iteration consists of a refinement of approximate eigenvectors using an iterative method, a refinement of the charge density using the refine eigenvectors, and a refinement of the geometry using approximate forces calculated from the non-self-consistent charge density. Thus, as the calculation proceeds, the three optimizations are performed simultaneously.

These ideas have been exploited to some extent in calculations using augmented-plane-wave and LAPW basis sets that are appropriate for transition-metal systems.[2-4] However, the resulting reductions in computing time, while significant, have been much less dramatic than the speed-up of the CP method compared to conventional plane-wave-based methods for *sp*-bonded materials. This can be understood in terms of the computational requirements of refining the eigenvectors in an iterative diagonalization. Several such schemes are available. Since they have been reviewed elsewhere,[5] only the salient features are discussed here. The key component of an iterative diagonalization is a calculation of the operation of the Hamiltonian on approximate eigenvectors x. This is required, for example, in the calculation of the residual vectors $R(x)$,

$$R(x)=(H-\epsilon O)x \ , \tag{1}$$

where H is the Hamiltonian, O is the overlap, and ϵ is the eigenvalue (usually approximated by the expectation value of H on x). In a plane-wave basis set, O is diagonal and may be neglected. With a local potential the operation of H on a single eigenvector can be computed in $O(N \ln N)$ time as follows. The operation of the kinetic energy T on a wave function ψ is performed in reciprocal space (where it is diagonal) in $O(N)$ time and the operation of the potential V is performed in real space also in $O(N)$ time. The limiting step is the transformation of the wave functions to real space (where the operation of the potential is applied) and the subsequent back-transformation of $V\psi$. This is done using fast-Fourier transforms (FFT's), which take $O(N \ln N)$ time. [Note that in most iterative diagonalization procedures there is an orthogonalization of the eigenvectors, which takes $O(N^3)$ time; for practical system sizes this is not the limiting step.] With other basis sets, FFT's have not been exploited in this way, and, as a result, in general, calculating the operation of H on a wave function requires $O(N^2)$ computation and thus a total-effort scaling as MN^2, where M is the number of bands. Since M scales with the size of the system, these are N^3 methods; this explains the relatively small gains in efficiency when iterative diagonalization schemes are used with non-plane-wave basis sets.

Here we describe real-space techniques that use an auxiliary or projector-basis set for obtaining $O[N^2\ln(N)]$ scaling for plane-wave and mixed-basis calculations with nonlocal angular-momentum-dependent pseudopotentials and for the all-electron LAPW (Ref. 6) and extended LAPW methods.[7] The key idea is to construct a local representation of the plane-wave sectors of the basis sets, in which matrix elements can be rapidly and accurately evaluated. We emphasize that although the use of the projector basis bears some relationship to the technique that Kleinman and Bylander used to construct separable pseudopotentials,[8] the present plane-wave technique does not require a separable form for the pseudopotential.

PLANE-WAVE BASIS WITH NONLOCAL PSEUDOPTENTIAL

In order to perform the operation of the nonlocal pseudopotential in real space, we note that the nonlocality may be confined with a cutoff radius r_c and explicit methods for constructing such pseudopotentials are well known.[9,10] Thus, the operation of the nonlocal part of the pseudopotential in the real space only depends on the wave function inside r_c. In order to exploit this fact, we define a set of local projection-basis functions f_j around each atom, where j labels the function and the atom index has been suppressed. The explicit form of the projector basis is not particularly important, except that it must be sufficiently flexible to represent the wave functions inside r_c accurately. In our implementation, we use an angular momentum representation of polynomials up to some cutoff power $l_{\max}$,

$$\begin{gathered} f_j(\mathbf{r})=r^p Y_{LM}(r), \quad L=0,\ldots,l_{\max} \ , \\ p=L,\ldots,l_{\max}, \quad M=-L,\ldots,L \ , \end{gathered} \tag{2}$$

where the real spherical harmonics Y_{LM} are used to avoid complex arithmetic. This is a flexible basis provided that the number of functions is comparable to the number of Fourier-transform mesh points, needed to represent the wave function, that lie inside or close to r_c.

We define a local matrix $A_{j,k}$ for each atom, which maps from the Fourier-transform mesh points (index k) within and near r_c to coefficients of the projector basis functions (index j). This matrix is constructed using the standard least-squares method if the number of functions is smaller than the number of mesh points, or using an interpolation with a smoothness criterion[11] if the number of projector functions is larger than the number of mesh points. Note that the size of the matrix A and the cost of constructing it depends on the number of projector functions and the density of the Fourier-transform mesh. Neither of these quantities depends on the system size.

Next, we construct the matrix elements, $V_{j,j'}$, of the projector basis functions with the nonlocal pseudopotential. Note that with the choice of $f_j(\mathbf{r})$ above, these require a small number of simple one-dimensional integrals for a conventional l-dependent pseudopotential V^{NL} (where NL denotes nonlocal). Finally, we construct the matrix T defined by

$$T=A^T V A \ . \tag{3}$$

This is a square matrix of dimension equal to the number of mesh points in the sphere n_k and moreover, to the extent that the projector-basis functions are flexible enough to mimic the plane waves inside r_c,

$$\langle \Psi_i | V^{\mathrm{NL}} | \Psi_j \rangle = \psi_i^* T \psi_j \ , \tag{4}$$

where the Ψ's are the wave functions, and on the right-hand side of the equation the ψ's are the real-space representations, i.e., vectors of length n_k containing the values of the Ψ's on the local mesh points. The operation of T in the calculation of Eq. (4) may be understood as follows. The A matrix on the right-hand side operates on the ket, yielding a representation as a linear combination of projector functions. Similarly, the A^T on the left-hand side operates on the bra, transforming it to the same representation. Then V operates in this space. Further, we note that this requires a mesh that can represent a single wave function and map it (via A) onto the projector basis so, for the operation of the nonlocal pseudopotential, we may use a mesh that is less dense (by a factor of $2^3=8$) than the mesh used for the local potential, which needs to be capable of representing products of wave functions. Such a sparser mesh can be used for the operation of V^{NL} even though V^{NL} may have high-Fourier components, because its operation is performed in the space of projector basis functions to arbitrary precision; V^{NL} is never represented in plane waves or on an FFT mesh, nor is $V^{\mathrm{NL}}\Psi$ (which would also require a denser mesh). Rather, as discussed above, the calculation implied by Eq. (4), with the T matrix is equivalent [by the associative property of matrix multiplication, $(\psi_i^* A^T)V(A\psi_j) = \psi_i^*(A^TVA)\psi_j$] to the following sequence of operations: (1) transform Ψ_j to a linear combination of projector functions using the matrix A; (2) transform Ψ_i^* to a linear combination of projector-basis functions using the matrix A^T; and (3) operate V^{NL} in this space using the matrix V.

Thus the plane-wave method proceeds as follows. The matrices T (one for each atom) are precalculated. The kinetic energy is diagonal in momentum space and so it is applied there. Next a real-space representation of the wave functions is obtained using FFT's. The local part of the potential, V^L, is then applied in this real-space representation as in the Car-Parrinello approach, and V^{NL} is applied by gathering the elements of the vectors ψ (and multiplying by a phase factor for calculations at general points in the Brillouin zone), operating on them with the matrices T (one for each atom), and then scattering (and removing the phase if necessary) the vectors $T\psi$. In order to obtain the momentum-space representation of the operation of the Hamiltonian on Ψ, we apply FFT's to the real-space representations of $V^L\Psi$ and $V^{\mathrm{NL}}\Psi$ and add the kinetic-energy term, which is already in momentum space. For this step, two FFT's are required, one on the usual mesh and one on the sparser mesh, which is used for the operation of V^{NL}. Note, however, that the FFT on the sparse mesh is approximately an order of magnitude faster than that on the denser mesh, so that this is not a real disadvantage.

Since the size of the matrices T is independent of N, the computation required to operate V^{NL} on a single wave function in real space scales as N (there are N matrices T). The computation required for the FFT's, however, scales as $N\ln(N)$. Thus, the method scales as $MN\ln(N)$. Since the number of bands M scales with the number of atoms, this is $N^2\ln(N)$ scaling. We have implemented this technique; numerical results are presented below. Finally, we remark that the functions f_j are internal to the construction of the matrices T and do not appear elsewhere; hence, the term projector basis.

MIXED-BASIS TECHNIQUE

In this section we show how the projector basis may be used to produce a mixed-basis nonlocal pseudopotential technique that also has $N^2\ln(N)$ scaling. It is expected that this approach and the LAPW approach described below will be useful for systems with hard pseudopotentials such as first-row and transition-metal materials.

The basis we adopt consists of plane waves and strictly localized basis functions (described below). These localized functions are similar in spirit to the functions used by Kang *et al.*,[12] but we propose an alternate construction. The approach described below is, however, completely general and could be applied to any mixed-basis technique using plane waves and strictly localized orbitals.

By strictly localized, we mean confined within some radius r_c. The use of strictly localized basis functions ensures that matrix elements involving local orbitals associated with different atoms are zero. Here we propose modified muffin-tin orbitals, since it is known that the muffin-tin orbitals $u_L(r)Y_{LM}(\mathbf{r})$ provide an efficient basis. The muffin-tin orbitals are defined by

$$[T^s + \langle V^L(\mathbf{r})\rangle_{\mathrm{ang}} + V_L^{\mathrm{NL}}(r)]u_L(r) = E_L u_L(r) , \qquad (5)$$

where T^s is the kinetic-energy operator (including the centrifugal term), V^L is the local part of the potential, V_L^{NL} is the nonlocal pseudopotential, $\langle\ \rangle_{\mathrm{ang}}$ denotes an angular average, and the E_L are energy parameters chosen in the valence-band region as in, for example, the LAPW method. The modification consists of the subtraction of a tail function to bring the local basis functions smoothly to zero at r_c. In order to avoid degrading the basis through this subtraction, the tail functions must be smooth, i.e., they must be representable in terms of the plane-wave sector of the basis. In the present approach, we subtract a constant and two smooth Gaussians from the muffin-tin orbitals in order to make the value and the first two derivatives zero at the sphere boundary.

We now show how to construct an $N^2\ln(N)$ method from this basis using projector functions. First, separate the potential into two components, a soft local potential, and a possibly hard, nonlocal component which is confined within r_c. Here the "nonlocal component" includes not only the nonlocal pseudopotential, but also contains the hard parts of the Hartree and exchange-correlation potentials and of the local pseudopotential. The potential-generation step must, therefore, be constructed to handle hard potentials. The techniques used in the dual-space representation of the LAPW method can be adapted to this purpose.[13]

Next we construct matrices T, as in the plane-wave method above, that provide the operation of the hard part of the potential on the real-space representation of the plane-wave sector of the wave functions. In operating the Hamiltonian, however, we will construct extended representations of the wave functions inside the spheres consisting of the ψ vectors described above, augmented by the coefficients of the local orbitals within the atom in question. We denote these extended vectors ψ'. We thus need an extended matrix T' that will operator in the ψ' space. The upper diagonal block, which operates in the plane waves, is the T matrix. The lower diagonal block operates in the local orbitals and is just the matrix elements of the hard part of the potential in this space. The off-diagonal blocks B and B^T (because both the local orbitals and projector functions are real, T' will be real) are constructed using the projector functions as follows:

$$B = QA , \qquad (6)$$

where A is the matrix that transforms the real-space representation of the plane waves into the projector basis as above and elements of Q are the matrix elements between the projector-basis functions and the local orbitals. In practice, we modify Q and the lower diagonal block of T' to include the soft part of the potential as well, since these terms need to be included.

Unlike the pure plane-wave case, the basis functions are not orthogonal with a mixed basis. Thus, it is necessary to construct the (initially, identity) overlap matrix. This can be done using the same procedure. We construct an O' matrix that operates on the vectors ψ'. The upper diagonal block is the identity matrix, the lower diagonal block is the overlap matrix for the local orbital sector of the basis, and the off-diagonal blocks are constructed identically to B and B^T, except that the overlap between projector functions and local orbitals is substituted for the Q matrix.

Thus, the method proceeds exactly like the plane-wave method described above, except that instead of gathering the vectors ψ for each atom and operating with T, we gather extended vectors ψ' that include the local orbital coefficients for the atom in question and operate with T' and O'. Thus, this is also an efficient method with $N^2\ln(N)$ scaling. Finally, we remark that the additional (compared to the pure plane-wave method) back-Fourier transform arising from the presence of an overlap matrix is on the sparse mesh. Moreover, this additional cost is expected to be more than compensated by the reduction in the number of plane waves and, thus, the sizes of the Fourier-transform meshes and local matrices in this method and the ones that follow. Numerical results addressing the efficiency of the mixed basis and the accuracy of using the projector basis to couple the local orbital and plane-wave sectors are presented below.

THE LAPW METHOD

In view of the relationship between the LAPW method and nonlocal pseudopotential methods, which has been elucidated by Goedecker and Maschke,[4] it is perhaps not surprising that the projector-function technique is useful in the LAPW method as well. The LAPW method, however, is an all-electron technique. In the following, we show how the LAPW method can be transformed into an $N^2\ln(N)$ technique using projector-basis functions. We expect that this method will be useful for systems where the frozen-core approximation and, hence, the use of pseudopotentials, is not adequate, and for calculations of properties such as electric-field gradients that depend on an accurate treatment of the wave functions near the nuclei.

In the LAPW method, space is divided into nonoverlapping atom-centered spheres of radius r_c, and a dual representation of the potential and wave functions is used. For simplicity, we consider a single atom. The potential V is given by

$$V(\mathbf{r})=V^I(\mathbf{r})[1-\theta(r-r_c)]+V_c(\mathbf{r})\theta(r-r_c) , \tag{7}$$

where $\theta(x)$ is one for negative arguments and zero for positive arguments, V^I is the interstitial representation of the potential (which is expanded in plane waves), and V_c is the sphere representation of the potential (represented in terms of lattice harmonic coefficients tabulated on a radial mesh). As mentioned, a dual representation is also used for the wave functions Ψ,

$$\Psi(\mathbf{r})=\Psi^I(\mathbf{r})[1-\theta(r-r_c)]+\Psi_c(\mathbf{r})\theta(r-r_c) , \tag{8}$$

where the interstitial representation is plane waves

$$\Psi^I(\mathbf{r})=\sum_{\mathbf{g}} c_{\mathbf{g}} e^{i(\mathbf{k}+\mathbf{g})\mathbf{r}} \tag{9}$$

and the sphere representation is given by

$$\Psi_c(\mathbf{r})=\sum_{LM}[A_{LM}u_L(r)+B_{LM}u_L'(r)]Y_{LM}(\mathbf{r}) , \tag{10}$$

where $u_L(r)$ is defined by Eq. (5) but with a local, all-electron potential, $u_L'(r)$ is the derivative of $u_L(r)$ with respect to E_L, and again we use real-spherical harmonics to avoid complex arithmetic. The coefficients $c_{\mathbf{g}}$ are the coefficients of the LAPW basis functions and the A_{LM} and B_{LM} coefficients depend on them through the constraints that the value and first derivative of the wave function be continuous at r_c. In the following, the projector-basis functions are used as a local representation of the plane waves, from which the matching coefficients are constructed.

In order to construct an $N^2\ln(N)$ method using this basis, we will take $V^I(\mathbf{r})$ as the local potential analogous to that in the plane-wave method described above and construct two local matrices T^{LAPW} and O^{LAPW}, which operate on the ψ vector (see below) to reproduce the remaining terms in the Hamiltonian and overlap. Thus, we begin with a plane-wave basis extending over all space and with the smooth (plane-wave) interstitial Hamiltonian. We then construct local matrices $T^{(1)}$ and $O^{(1)}$, which remove the contributions to the plane-wave Hamiltonian and overlap from the interiors of the spheres. Finally, we construct local matrices $T^{(2)}$ and $O^{(2)}$, which add the effect of the Hamiltonian and overlap inside the spheres acting on the LAPW wave functions.

First we consider the terms that are subtracted to account for the fact that the plane waves are prevented from extending into the sphere by the action of the step function on Ψ^I. We denote the resulting matrices (operating on ψ) as $T^{(1)}$ for the Hamiltonian and $O^{(1)}$ for the overlap,

$$T^{(1)}=A^TH^IA \tag{11}$$

and

$$O^{(1)}+A^TRA , \tag{12}$$

where H^I and R are the matrix elements among the projector functions of the interstitial Hamiltonian (kinetic energy plus V^I) and overlap matrix, respectively. As mentioned, $T^{(1)}$ and $O^{(1)}$ are used to account for the fact that in the LAPW method, the plane-wave sector of the basis does not extend into the sphere and, accordingly, the integrations for the matrix elements are restricted to $r<r_c$.

In order to calculate the matrices $T^{(2)}$ and $O^{(2)}$ that arise from the augmentation, it is convenient to construct a matrix U that maps from the space of projector functions f_j to the space of A_{LM} and B_{LM} coefficients. Thus, the first dimension of U is the number of A and B

coefficients $[2(l_{\max}+1)^2]$ and the second dimension is the number of projector functions. This matrix can be readily computed from the value and derivative of each projector function at r_c, and the LAPW matching conditions. Having done this, it is straightforward to construct these matrices:

$$T^{(2)}=A^TU^TH^{(2)}UA \tag{13}$$

and

$$O^{(2)}=A^TU^TD^{(2)}UA\ , \tag{14}$$

where $H^{(2)}$ is the Hamiltonian matrix in the space of muffin-tin orbitals and $D^{(2)}$ is the corresponding overlap matrix. The overlap in the muffin-tin-orbital space, denoted $D^{(2)}$, is diagonal if, as in most implementations of the LAPW method, the u' functions are orthogonalized to the u functions.

Thus, we have

$$T^{\mathrm{LAPW}}=T^{(2)}-T^{(1)} \tag{15}$$

and

$$O^{\mathrm{LAPW}}=O^{(2)}-O^{(1)}\ . \tag{16}$$

These matrices then may be applied in the same way as in the mixed-basis method above except that, since there are no localized orbitals, they operate in the ψ space rather than the ψ' space.

We remark that at no point was the strong-sphere Hamiltonian H_c applied to anything except the muffin-tin orbitals. The projector functions are used only as a local representation of the plane-wave sector extended into the spheres. We also note that the result of our transformation of the LAPW method has some similarities to the result of the transformation of Goedecker and Maschke,[4] except that our transformation is to the $N^2\ln(N)$ plane-wave method described above, but with an overlap, and theirs is to a form analogous to a conventional separable pseudopotential, again with an overlap component. The advantage of our approach is that we achieve $N^2\ln(N)$ computational complexity. We speculate that this improved scaling, together with the capability of calculating atomic forces in the LAPW method (see Ref. 2 and Yu, Singh, and Krakauer, Ref. 13), may lead to practical dynamical simulations for open-shell transition-metal systems.

EXTENDED LAPW METHOD

There are some situations in which all-electron calculations are needed and in which the linearization of the LAPW method is undesirable. Examples are systems with extended core states and materials with very narrow (e.g., $4f$) bands. It has been shown that an extension of the LAPW method,[7] in which specially constructed, strictly localized orbitals are added to the basis, can be quite useful.[14] In the present section we combine the ideas of the preceding two sections to obtain $N^2\ln(N)$ behavior for this approach, as well. We do this by constructing two matrices T^E and O^E analogous to the T' and O' matrices of the mixed-basis method. They will operate on vectors ψ' consisting of the mesh representation of the plane-wave sector of the LAPW basis augmented by the coefficients of the local orbitals on the atom in question. The upper diagonal blocks are the T^{LAPW} and O^{LAPW} matrices of the preceding section and the lower diagonal blocks are the matrix elements among the local orbitals. In order to construct the off-diagonal blocks, we first transform to the projector basis, then to the A_{LM} and B_{LM} coefficients, and then use matrix elements between the muffin-tin orbitals and local orbitals. Thus,

$$B^E=Q^EUA\ , \tag{17}$$

where B^E and Q^E are analogous to B and Q, and U and A are as in the preceding section.

ACCURACY AND COMPUTATIONAL EFFICIENCY: NUMERICAL RESULTS

Of course, it is not sufficient to show that a method has a desirable scaling. It is also necessary that the proposed approach be sufficiently accurate for the intended purpose and that the prefactor that governs the relationship between the computational scaling and the actual cost of calculations be sufficiently small. So far, we have only completed the implementation of the pure plane-wave technique and, as a result, we can only present self-consistent numerical results for that method. (Non-self-consistent calculations testing the mixed-basis approach are also presented.) We note that the only additional approximation in the other three methods as compared to the corresponding conventional techniques (which are well established) is the use of projector functions as a local representation of the plane-wave sector of the basis sets. This approximation is the same in all four methods, and so its adequacy for the plane-wave method is a strong indication that it will be adequate for the other three methods as well, and non-self-consistent mixed-basis calculations that support this are presented below.

In order to test the adequacy of the projector-function representation, we present early calculations for diamond. This material was chosen as a a test because of its hard nonlocal pseudopotential (in contrast with the soft, nearly local silicon pseudopotential). We also present non-self-consistent calculations for diamond using the mixed-basis method. In order to demonstrate the computational efficiency of our approach, we present timings for a well-converged calculation on K_3C_{60}.

For diamond, we generated a nonlocal pseudopotential using the Troullier-Martins[12] scheme, the Hedin-Lundqvist exchange-correlation functional,[15] and a core radius of 1.15 a.u. For the construction of the matrices we include all mesh points within $1.1r_c$, and chose the $l=2$ component to be the local pseudopotential. The A matrix for these calculations, which are presented in Table I, was determined using least squares with $l_{\max}=7$. This yields 204 projector-basis functions. The choice of r_c yields 459 FFT mesh points in each sphere at the experimental structure, although this number varies with both the lattice parameter and the frozen-phonon amplitude. The fact that the physically important $l=0$ and 1

TABLE I. Calculated properties of diamond. The band gap and width are at the experimental lattice parameter of 3.567 Å. The lattice parameter is calculated by total-energy minimization. LAPW denotes the previous all-electron calculations of band energies in Ref. 17. The LAPW lattice parameter and optical-phonon frequency (ω_{TO}) are from additional calculations.

Property	This study	LAPW
Direct band gap	5.54 eV	5.51 eV
Γ-X_1 band gap	4.71 eV	4.68 eV
Valence-band width	21.31 eV	21.06 eV
Lattice parameter	3.52 Å	3.53 Å
ω_{TO} (10^{12} Hz)	39.8	38.6

components are not taken as the local potential means that any errors in the handling of the nonlocal part of the pseudopotentials will have large effects on the band structure. The calculations were performed using an energy cutoff of 72 Ry, which yields a basis of approximately 800 plane waves and is well converged for this pseudopotential. Self-consistently was obtained with Brillouin-zone samplings consisting of ten special points in the irreducible wedge for the band structure and five special points for the frozen-phonon calculation.[16] As may be seen from Table I, the calculated band energies are in quite satisfactory agreement with LAPW calculations (agreement with experiment is not expected for local-density-functional calculations).

The optic-phonon frequency ω_{TO} was calculated at the experimental lattice parameter (3.567 Å) using the frozen-phonon approach. Total energies were calculated for nine distortions, with a maximum displacement of 0.058 a.u., corresponding to a maximum energy difference of approximately 6 mRy, and fit to a cubic polynomial. The resulting frequency is in good agreement with LAPW calculations and the experimental frequency[18] of 3.99×10^{13} Hz. The lattice parameter, obtained by total-energy minimization, is also in very satisfactory agreement with standard LAPW calculations and experiment. The agreement of the ω_{TO} with standard calculations is particularly significant because of the small energy differences involved and the fact that FFT mesh points enter and leave the spheres used to operate V^{NL} during this calculation (the number of points varied between 459 and 489 for the range of distortions used). This is an indication of the stability of the procedure. As a further test, we performed parallel calculations of the band structure of diamond, varying the number of mesh points used in the operation of V^{NL} and the number of projector-basis functions. The results were found to be very stable, as is illustrated in Table II. In the table, results of self-consistent calculations (using two special **k** points) are shown. In the first calculation, 459 points were used to fit 204 projector-basis functions as in the calculations discussed above. In the second, 650 projector-basis functions ($l_{max}=11$) were used to interpolate 429 points (all points up to $1.05r_c$). The largest difference is 2.5 meV in the valence-band width. The calculated total energies agree to better than 0.2 mRy. These results show that our approach is very stable.

TABLE II. Calculated band energies of diamond with (I) 459 mesh points and 204 projector-basis functions, and (II) with 429 points and 650 projector-basis functions.

Property	(I)	(II)	Difference
Direct band gap	5.5328 eV	5.5319 eV	−0.0008 eV
Γ-X_1 band gap	4.6995 eV	4.7015 eV	0.0020 eV
Valence-band width	21.3177 eV	21.3153 eV	0.0025 eV

In order to test the mixed-basis approach, we have performed non-self-consistent calculations for the band structure of diamond using a charge density obtained from a conventional LAPW pseudopotential calculation[13] with a Kerker pseudopotential. We used a sphere radius of 1.45 a.u. (this defines the extent of the local orbital sector of the basis; the pseudopotential core radius is 1.15 a.u.). The calculations were performed using the iterative diagonalization, discussed above, with a plane-wave cutoff of 23.3 Ry (corresponding to 137 plane waves at the Γ point and 150 at X) and a minimal set of local orbitals consisting of one s and three p functions per atom, for a total of eight local orbitals per cell. The least-squares algorithm was used to couple the plane-wave and local sectors, with $l_{max}=8$, yielding 285 projector-basis functions. Band energies at Γ and X are given in Table III along with results using only the plane-wave sector of the basis. For comparison, well-converged LAPW eigenvalues are given for the same potential. As expected, the pure plane-wave calculation is far from convergence with a 23.3-Ry cutoff. The results show, however, that the mixed-basis sector adds sufficient variational freedom to bring the eigenvalues quite close to their converged values. The agreement between the mixed-basis and LAPW calculations demonstrates that the projector-basis technique is sufficiently accurate to couple the local orbital and plane-wave sectors in our approach.

As mentioned, K_3C_{60} is used to investigate the efficiency. We use the same pseudopotential with a plane-wave energy cutoff of 64 Ry and a $120\times120\times120$-FFT mesh. This yields approximately 42 000 plane-wave basis functions and vectors ψ with approximately 350 elements. The timings were obtained on a single processor

TABLE III. Band eigenvalues (in eV) for diamond using a pure plane-wave basis and a mixed basis (see text) with a cutoff of 23.3 Ry. LAPW denotes converged LAPW eigenvalues with the same potential. The energy zero has been adjusted to the valence-band maximum obtained in the LAPW calculation.

State	Plane wave	Mixed basis	LAPW
Γ_1	−21.32	−21.52	−21.54
$\Gamma_{25'}$	2.03	0.02	0.00
Γ_{15}	7.26	5.48	5.48
X_1	−12.27	−12.74	−12.76
X_4	−5.17	−6.42	−6.43
X_1	4.97	4.56	4.55

of an IBM 3090 computer.[19] Using two iterations of the iterative scheme of Ref. 3, and computing 180 bands, we use approximately 6500 sec of processor time per **k** point. Of this, approximately 4700 sec was spent on the FFT's and 270 sec on the multiplications with the T matrices. This is quite encouraging, particularly in view of the fact that our codes are not yet well optimized.

SUMMARY AND CONCLUSIONS

The key problem in efficiently performing electronic-structure calculations with techniques that use plane waves and local quantities (nonlocal pseudopotentials, local sectors of the basis or augmentations of the plane waves, for example) is finding efficient ways of coupling the plane waves to the local quantities. This has been recognized for some time, and in the case of the pure plane-wave basis with nonlocal pseudopotentials, there has been some recent progress.[20–22] Troullier and Martins[21] suggested using a local real-space representation of the pseudopotential, but did not provide a scheme for constructing such a representation. King-Smith, Payne, and Lin[22] implemented a scheme for performing real-space projections of separable pseudopotentials and have presented encouraging results for silicon. The advantages of real-space techniques and mesh-based representations have also been exploited in non-plane-wave contexts.[23] Further, there has been significant recent progress in generalizing separable pseudopotentials to reduce the number of plane waves needed to represent the wave functions and, thus, computational requirements of standard Car-Parrinello codes.[24,25]

The approach presented here differs from previous work in that (1) we have presented explicit prescriptions for the construction of the required operators and (2) the projector-basis technique is generally applicable to problems involving coupling between plane waves and local functions and, as a result, can be applied to plane-wave calculations with conventional l-dependent pseudopotentials, as well as a variety of methods using other basis sets.

We have shown how four electronic-structure techniques can be implemented in a computationally efficient way using projector functions. We have implemented the plane-wave method and obtained early numerical results using it. We are in the process of implementing the remaining three methods, and expect them to be among the fastest electronic-structure techniques for large systems.

Note added in proof. The functions defined in (2) include irregular functions in addition to polynomials. Improved fits are obtained if these are removed by restricting p and L to be both even or both odd.

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