Finite-Difference-Pseudopotential Method: Electronic Structure Calculations without a Basis

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We present a method for performing electronic structure calculations without the explicit use of a basis. We combine a finite difference approach with *ab initio* pseudopotentials. In contrast to methods which use a plane wave basis, our calculations are performed completely in "real space." No artifacts such as supercell geometries need be introduced for localized systems. Although this approach is easier to implement than one with a plane wave basis, no loss of accuracy occurs. The electronic structure of several diatomic molecules, Si_2, C_2, O_2, and CO, are calculated to illustrate the utility of this method.

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One of the most successful methods for calculating the electronic structure of condensed matter systems is based on combining pseudopotentials with a plane wave basis [1]. Only valence electrons need be considered in this method. Since the resulting pseudopotential is weak compared to the all-electron potential, plane waves often are a reasonable basis. However, for localized systems such as clusters [2,3], disordered systems such as liquids or glasses [4,5], or semiperiodic systems such as surfaces [6,7], the direct application of a plane wave basis is nontrivial. One procedure to enable the use of plane waves is the supercell approach. The "forced" periodicity allows standard "band structure" codes to be used for nonperiodic systems. However, the disadvantages of this plane-wave–supercell approach are notable. The plane wave basis is required to replicate not only the electronic states of the system of interest, but also "vacuum" regions imposed by the supercell geometry. Replicating the vacuum in the supercell for a localized system can be almost as costly as replicating the "real" part of the wave function. In a recent calculation for a complex surface, the 7×7 reconstruction of the (111) silicon surface, 700 atoms were effectively treated: approximately 400 real atoms in the supercell and a vacuum contribution effectively corresponding to another 300 atoms [6,7]. The supercell approach also presents problems for charged systems. If one considers a charged defect within a supercell configuration, each cell is charged. The total electronic energy diverges. A simple "fix" to this problem is to insert a uniform compensating charge in each supercell, but determining the effect of this uniform background in terms of a total energy, or binding energy, is highly nontrivial [8,9]. One additional complication that arises with the use of plane waves concerns the use of fast Fourier transforms (FFT) for handling the convolutions. While FFT's are a great advantage in expediting the calculation, these transforms present computational communication obstacles when one attempts to implement such codes on parallel computer architectures.

Here we present a new approach which eliminates these problems. Our approach is *much simpler* to implement than the plane wave basis without any loss of accuracy. The approach is based on utilizing the *finite difference method* [10]. The "basis" in this approach is a real space grid. It might be suspected that a grid approach would not be competitive with plane waves. A fine grid may result in so many points as to result in an unworkable scheme. As we shall demonstrate, it need not be the case for most electronic structure problems involving localized systems such as clusters or molecular systems. Plane wave expansions and finite difference descriptions are intimately related. If the wave function is slowly varying, then it should be easy to expand the function in a plane basis. Concurrently, for a slowly varying function, the wave function can be expanded in a Taylor series, and a finite difference method using relatively few discretization points will work well. One clear limitation of the finite difference approach and the plane wave basis is that neither will be very effective in describing an all-electron potential.

A key aspect of our work is the availability of *higher order* expansions for the kinetic energy operator, i.e., expansions of the Laplacian. If we impose a simple, uniform grid on our system where the points are described in a finite domain by (x_i, y_j, z_k), we may write

$$\frac{\partial^2\psi}{\partial x^2} = \sum_{n=-N}^{N} C_n \psi(x_i + nh, y_j, z_k) + O(h^{2N+2}), \qquad (1)$$

where h is the grid spacing. The approximation is accurate to $O(h^{2N+2})$ upon the assumption that ψ can be approximated accurately by a power series in h. Algorithms are available to compute the coefficients C_n for arbitrary order in h [11]. If the kinetic energy operator can be expanded as in Eq. (1), then we can set up a one-electron Schrödinger equation over the grid. We will

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employ the local density approximation (LDA). We assume a uniform grid over the three dimensions, but this is not a necessary assumption. Over these grid points we must solve

$$-\frac{\hbar^2}{2m}\left[\sum_{n_1=-N}^{N} C_{n_1}\psi(x_i+n_1h,y_j,z_k)+\sum_{n_2=-N}^{N} C_{n_2}\psi(x_i,y_j+n_2h,z_k)+\sum_{n_3=-N}^{N} C_{n_3}\psi(x_i,y_j,z_k+n_3h)\right]$$

$$+[\,V_{\rm ion}(x_i,y_j,z_k)+\,V_H(x_i,y_j,z_k)+V_{\rm xc}(x_i,y_j,z_k)]\psi(x_i,y_j,z_k)=E\;\psi(x_i,y_j,z_k). \tag{2}$$

If there are M grid points, the size of the full matrix resulting from the above eigenvalue problem is $M \times M$. Here $V_{\rm ion}$ is the nonlocal ionic pseudopotential, V_H is the Hartree potential, and $V_{\rm xc}$ is the local density expression for the exchange and correlation potential. The two fixed grid parameters used in setting up the matrix are the grid spacing h and the order N.

There are several issues which must be addressed to solve Eq. (2). The first concerns the procedure by which the self-consistent field is constructed [12]. The exchange-correlation potential $V_{\rm xc}$ is trivial once the charge density has been constructed over the grid. The Hartree potential can be determined by setting up a matrix equation and solving with direct or iterative methods, or as we have done for the isolated systems by solving for V_H by direct numerical integration.

Another issue concerns the nonlocality of the ionic pseudopotential, i.e., the angular momentum dependence of this potential. These pseudopotentials are constructed as for any LDA electronic structure calculation [13]. We employ the Kleinman-Bylander [14] form in real space [15]:

$$V_{\rm ion}(x,y,z)\;\psi(x,y,z)=V_{\rm loc}(x,y,z)\;\psi(x,y,z)+\sum_{lm}G_{lm}\;u_{lm}(x,y,z)\Delta V_l(x,y,z), \tag{3}$$

where

$$G_{lm}=\frac{\int u_{lm}(x,y,z)\;\Delta V_l(x,y,z)\;\psi(x,y,z)\;dx\,dy\,dz}{\int u_{lm}(x,y,z)\;\Delta V_l(x,y,z)\;u_{lm}(x,y,z)\;dx\,dy\,dz}. \tag{4}$$

$V_{\rm loc}$ is the local ionic pseudopotential; $\Delta V_l = V_{\rm loc} - V_l$ is the difference between other l components of the ionic and the local ionic potential. The functions u_{lm} are solutions to the atomic pseudopotential for the valence states of interest. Usually, one component is taken as the local component, e.g., $V_l = V_s$ where V_s is the s component. The range of ΔV_l is usually much less than a bond length. The nonlocality in $V_{\rm ion}$ is reflected by the occurrence of $\psi(x,y,z)$ in G_{lm}. The integral involving $\psi(x,y,z)$ is performed over the grid, i.e., $\int u_{lm}(x,y,z)\;\Delta V_l(x,y,z)\;\psi(x,y,z)dx\,dy\,dz = \sum_{ijk} u_{lm}(x_i,y_j,z_k)\Delta V_l(x_i,y_j,z_k)\psi(x_i,y_j,z_k)h^3$.

The full matrix for these isolated systems is real, symmetric, and sparse. These attributes can be utilized in expediting the diagonalization procedure. The sparsity of the matrix is a function of the order N to which the kinetic energy is expanded. We have employed an iterative diagonalization procedure which can take advantage of the sparsity to solve for the eigenvalues and vectors. An alternate approach to using the sparsity in performing the matrix vector products is to leave the matrix in operator format. Using this procedure, there is no need to store the matrix in any sparse form since the coefficients $C_{n_i}, i = 1,2,3$ and $n = -N,...,N$ in Eq. (2) are constant and as a result, the matrix-by-vector kinetic operations required by the diagonalization routine can be performed in "stencil" form. The nonlocal operations are accomplished by performing them as vector-by-vector operations. This strategy not only saves storage, it leads to an efficient implementation on most high-performance vector and parallel computers.

To illustrate the utility of the finite-difference-pseudopotential (FDP) method, we will calculate the electronic structure of several simple diatomic molecules. We have chosen to examine Si_2, C_2, O_2, and CO. We have calculated the electronic structure of these molecules with a finite difference approach and with a plane wave basis.

Three items need to be addressed: the domain to contain the atoms, the order N, and the grid spacing h. Given the pseudoatom wave functions, we chose a radius $R_{\rm max}$ beyond which we expect the atomic states to vanish. Typically this radius encompasses at least 99% of the valence charge. We chose $R_{\rm max}$ to be 6.8 a.u. for Si and 5.6 a.u. for C and O (1 a.u. = 0.529 Å). The domain is constructed by requiring all atoms of interest to reside at least $R_{\rm max}$ from a surface. In the standard finite difference method, the order N is fixed (at $N = 1$) and the mesh size h is varied to obtain a desired accuracy. Typically to determine the accuracy the results of the two meshes are compared (h and $h/2$), and an estimate of the error is then determined. A more appropriate mesh spacing h can then be derived if necessary. However, since we have knowledge of the eigenvalues and the pseudo wave functions as determined by a direct integration of the atomic pseudopotentials, we can use this information to compare with the results obtained by the finite difference method. With our approach we have two parameters, N and h, to obtain the desired accuracy. We start with a large grid spacing and continuously reduce h until the eigenvalues and wave functions are replicated. We do this for several orders of N in Eq. (1). We have experimented

TABLE I. Atomic energy levels (in Ry) from pseudopotentials by direct integration (DI) and from finite difference calculations (FD). Also, the lowest excitation (in eV) as calculated from finite difference pseudopotentials and as measured from atomic spectra [16].

	Silicon	Carbon	Oxygen
E_s (FD)	−0.78	−0.99	−1.74
E_s (DI)	−0.80	−1.00	−1.74
E_p (FD)	−0.29	−0.38	−0.68
E_p (DI)	−0.31	−0.40	−0.68
$^3P \rightarrow {}^1D$ (FD)	0.77	1.31	1.87
$^3P \rightarrow {}^1D$ (Expt.)	0.78	1.26	1.84

with $N = 4$, 6, and 9. We find that for most applications orders higher than $N = 6$ do not provide significant improvement. For example, if N is increased from 6 to 9, the total electronic energy of the oxygen atom changes by less than ~0.01 Ry for $h = 0.4$ a.u. All the calculations reported here are done with $N = 6$. The grid spacing was taken to be $h = 0.75$ a.u. for silicon, and $h = 0.4$ for carbon and oxygen. The matrix size obtained from this procedure is comparable with that obtained using plane waves, but no costly FFT's or packing or unpacking of vectors needs to be performed.

TABLE II. Properties of diatomic molecules. The experimental data are from [19]. The theoretical results are from a finite-difference-pseudopotential (FDP) calculation, and from other methods using similar forms for the local density approximation.

	Si_2	C_2	O_2	CO
	Cohesive Energy (eV)			
Experiment	3.0	6.32	5.21	11.24
FDP	4.2	7.3	7.5	11.1
Other theory	4.18[a]	7.24[b]	7.53[b]	9.6 [c]
	Bond length (Å)			
Experiment	2.24	1.24	1.21	1.13
FDP	2.25	1.21	1.21	1.13
Other theory	2.25[a]	1.25[b]	1.21[b]	1.17[c]
	Vibrational mode (cm^{-1})			
Experiment	511	1855	1580	2170
FDP	520	1909	1630	2000
Other theory	486[a]	1903[b]	1606[b]	2100[c]

[a] From Ref. [17].
[b] From Ref. [20].
[c] From Ref. [21].

In Table I, we list the pseudopotential eigenvalues from the direct integration of the atomic Schrödinger equation and as calculated using the finite difference method as outlined above. The largest error in the eigenvalues is on the order of ~0.01 Ry. This is the type of error which one would introduce using a plane wave basis. We expect error cancellation to occur for the diatomic molecules and the relative energy difference should be converged to better than this tolerance. As a test of the atomic wave functions from our finite difference method, we have calculated the lowest excitations for the atomic species of interest, a $^3P \rightarrow {}^1D$ transition. Using perturbation theory to include spin polarization, we compare the calculated transition to measured atomic spectra [17]. In Fig. 1, we illustrate the wave function from finite difference calculations and compare the wave functions from direct integration.

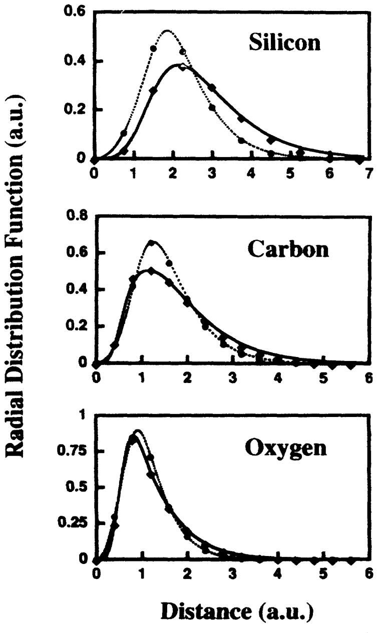

FIG. 1. Radial pseudo-wave-function distributions for silicon, carbon, and oxygen for the s state (dashed line) and p state (solid line). The solid points correspond to a finite difference description for the s state (●) and the p state (♦).

The diatomic molecules were computed following the same prescription as for the atomic species. By determining the electronic energy change as a function of bond length, we can find the cohesive energy, the equilibrium bond length, and the vibrational modes. The cohesive energy from local density calculations is not very reliable without including gradient corrections [18]. Our motivation here is not to improve on this formalism, but to test the accuracy of the finite difference method. We have determined the cohesive energy by subtracting the energy of the constituent atoms from the molecular energy without gradient corrections. Typically, we find an overbinding by ~1–2 eV compared to experiment. This overbinding is reassuring in that incomplete or poorly converged bases often yield cohesive energies which are underbound compared to experiment. In our cohesive calculations, we have included spin polarization via perturbation theory for both the atom and the molecule [17]. Bond lengths are accurately reproduced by our calculations as are the vibrational modes. The vibrational modes were determined by fitting a cubic polynomial to the energy versus bond length curve. The vibrational modes are accurate to within a few percent on the basis of this fitting. Our results are summarized in Table

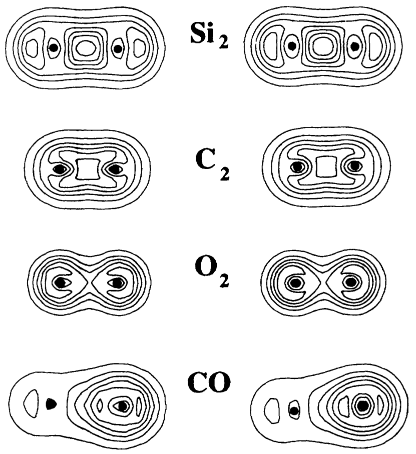

FIG. 2. Pseudocharge densities for Si_2, C_2, O_2, and CO molecules. The left hand side corresponds to finite-difference-pseudopotential calculations; the right hand side corresponds to pseudopotential plane wave calculations. The densities are in atomic units. The contour spacings are 0.0125 for Si_2, 0.05 for C_2, and 0.15 for O_2 and CO.

II. In Fig. 2, we compare the charge density of the diatomic molecules as calculated from the finite difference method to plane wave calculations using the same pseudopotential in a supercell geometry. (The total energies, bond lengths, and vibrational frequencies agree to within computational accuracy.) The charge densities are nearly identical; the chief difference is a finer grid used for the plane wave basis.

It is very gratifying to note that the finite difference wave functions reproduce the dipole moment of the CO molecule. The dipole in CO is extraordinarily sensitive to the bond length and even changes sign with changing bond length [21]. At large distances the dipole corresponds to C^+O^-. At smaller distance the sign reverses, and at equilibrium, the dipole corresponds to C^-O^+. The dipole we calculate is $-0.1D$, as compared to the experimental value of $-0.122D$ [22].

In summary, we have presented a method for performing electronic structure calculations without the explicit use of a basis. We have combined the finite difference approach with *ab initio* pseudopotentials. In contrast to methods which use a plane wave basis, our calculations are performed completely in "real space." No artifacts such as supercell geometries need be introduced for localized systems. The method is applicable to charged systems. Moreover, it is much easier to implement than are plane waves, and it is amenable to parallel machine architectures.

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