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Optimized pseudopotentials

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A plane-wave basis has great advantages for many calculations in the physics of solids. To apply this basis to a wider class of materials, the atomic characteristic of a pseudopotential is identified which leads to rapid convergence in the solid, and a new method for generating pseudopotentials optimized according to this criterion is shown. As a test case, an *ab initio* plane-wave basis determination of the structural properties of fcc copper is performed. The results indicate that these optimized pseudopotentials will facilitate study of transition metals and first-row nonmetals.

Theoretical studies based on *ab initio* electronic structure calculations are useful for elucidating many materials problems in the physics of solids. Specialized basis sets (i.e., other than plane waves) have proven to be effective for calculations of total energies and band structures of solids.[1] The use of such a set is vital if the behavior of the core electrons of the solid is to be considered explicitly. However, the behavior of the core electrons frequently has a minimal effect on properties of interest in the solid, and the implicit inclusion of the core states into a pseudopotential opens up the possibility of using a plane-wave basis for electronic structure calculations. This choice of basis has many advantages for a wide range of calculations, including studies of forces on ions,[2] phonon frequencies, corrections to quasiparticle self-energies,[3] and dielectric matrices.[4] The plane-wave basis provides controlled convergence and high numerical accuracy. In addition, using this basis for the single-particle states allows for a convenient and unbiased representation of the charge density. Furthermore, when a plane-wave basis is used, the equation-of-motion method of Car and Parrinello[5] can be implemented to increase calculational efficiency tremendously. The method is especially efficient when used with the excellent fast Fourier-transform algorithms which are currently available.

The main drawback to using plane waves as a basis is that real materials require many basis functions for their description. The problem of convergence becomes critical for materials which have sharply peaked valence states. In describing these substances, a prohibitive number of plane waves would be required, making the use of the conventional plane-wave approach impossible. As a result, almost all *ab initio* calculations involving transition metals and first-row nonmetals have been performed with specialized basis sets.[1]

Optimizing the convergence with basis size of quantities of interest, including total energy, would allow the benefits of the plane-wave basis to be derived in as wide a class of systems as possible. As a result, several approaches have been proposed to achieve this goal. Most of these[6–8] focus on improving the norm-conserving pseudopotentials[9] which have been very widely used in the literature to address problems in the theory of solids. Each of these approaches was either designed for a specific case[6] or did not significantly affect convergence of total energies.[7,8] The purpose of this paper is to isolate those features of a pseudopotential which are responsible for the convergence of the total energy in a plane-wave basis. Having done that, we then formulate a criterion which can be used to create a pseudopotential with optimal convergence and which should be applicable to any element.

We have found that the convergence of the total energy of solids with plane-wave basis size mirrors the convergence of the total energies of the isolated pseudoatoms which comprise the solid. In physical terms, we can understand this correspondence by dividing materials into four classes from the point of view of convergence. In the first class, valence states in the atom and solid are very similar. For this class, which includes noble gas solids and ionic solids, correspondence between atomic and solid convergence should be excellent. The second class contains solids in which the valence electrons are distributed nearly uniformly throughout the solid, such as free-electron metals. For these materials, the solid valence states will require many fewer plane waves for convergence than the atomic states. Consequently, they do not present a convergence problem, and their convergence does not need to be optimized. The third class contains materials such as transition metals which combine characteristics of the first two classes. In this class, some valence states in the solid are free-electron-like and do not present a convergence problem, and others are highly peaked around each atomic site and resemble the corresponding atomic eigenstates strongly. Because the latter states control convergence and because they are similar in the atom and solid, materials in the third class have convergence properties which correspond closely to those of the constituent atoms. In the fourth class are the systems which exhibit covalent bonding. Here, no direct relationship between atom and solid exists, since the states in the solid do not resemble the atomic states. However, the bonding states in the solid are confined in interatomic regions of approximately the same volume as the atomic states. Therefore, we expect convergence of atomic and solid total energies to be similar for covalent systems as well.

We have checked these claims and found close correspondence between the convergence of the atomic and solid total energies for a number of elements which are particularly problematic to treat with standard plane-wave approaches because of slow convergence. Specifically, we examined ionic, transition metal, and covalent systems including oxygen, copper, and carbon. All the results are qualitatively very similar. Below we discuss in detail and exhibit results for copper, which is about as difficult a case as exists for the plane-wave method.

The fact that atomic and solid total energies do converge similarly for all solids for which convergence is a problem presents a general criterion for the generation of optimally convergent pseudopotentials: To make the total energies of solids converge optimally, it is sufficient in principle to create pseudopotentials which give optimal total-energy convergence for the constituent atoms. In practice, we implement this criterion with two approximations; we require the potential to be continuous, and we optimize only the atomic kinetic-energy convergence. It can be proven[10] using scaling arguments that total-energy convergence and kinetic-energy convergence are very similar in the limit of large cutoff energies. By requiring pseudopotential to be continuous, we lower the cutoff energy above which this is ture. In fact, we have found kinetic-energy convergence to mirror total-energy convergence for all continuous pseudopotentials which we have examined, for all cutoff energies of interest. One or both of these approximations may be eliminated to obtain marginally better results. The method we have chosen has the merits of straightforwardness of implementation and numerical stability.

Our goal is to create an atomic pseudo wave function which has a continuous pseudopotential and kinetic-energy convergence to a certain level of tolerance in as small a basis as possible. A pseudo wave function gives rapid kinetic-energy convergence when the high Fourier components of the pseudo wave function contain very little kinetic energy. If one simply minimizes the kinetic energy of the pseudo wave function, as proposed by Cohen and Heine,[11] no control is exercised over the *distribution* of the remaining kinetic energy among the Fourier components of the pseudo wave function. To achieve optimal convergence, the kinetic energy in the high Fourier components of the pseudo wave function must be minimized directly. To accomplish this, it is sufficient to minimize the portion of the kinetic energy in the atomic pseudo wave function above some cutoff q_c in Fourier space while ensuring that the pseudo wave function has two continuous derivatives. We can begin with any pseudo wave function $F(r)$ which matches the atomic eigenfunction smoothly at $r=r_c$. To it we add a correction function $C(r)$, which optimizes the convergence of the original wave function. The result is Ψ, the optimized wave function, which equals $F+C$ for $r \le r_c$ and which equals the all-electron wave function for $r > r_c$. We find it efficient and convenient to have an analytic form for F. In practice, we write F as a sum of four Bessel functions whose wave vectors q_i' are chosen so that their logarithmic derivatives match that of the all-electron wave function, $\phi_1(r)$, at r_c:

$$F(r)=\sum_{i=1}^{4} \alpha_i j_l(q_i' r); \quad \frac{j_l'(q_i' r_c)}{j_l(q_i' r_c)}=\frac{\phi_l'(r_c)}{\phi_l(r_c)} .$$

The coefficients of these four functions are chosen to normalize the wave function and to make it continuous with two continuous derivatives at r_c. Because normalization is a quadratic constraint on the α_i's, a sum of three Bessel functions cannot always be found which satisfies these constraints. Accordingly, a fourth Bessel function is included whose coefficient is chosen arbitrarily within the range of values which permits the constraints to be met. To the expression F, we add $C(r)$, which we expand in Bessel functions whose wave vectors q_i are chosen so that the functions have a node at r_c:

$$C(r)=\sum_{i=1}^{N} \beta_i j_l(q_i r); \quad j_l(q_i r_c)=0 .$$

Lagrange multipliers enforce the constraints of normalization and continuity of two derivatives at r_c, and the coefficients β_i of these Bessel functions are chosen to minimize the kinetic energy beyond the cutoff q_c, which is expressed as follows:

$$-\int_0^\infty d^3r\, \Psi_l^*(r)\nabla^2\Psi_l(r) - \int_0^{q_c} d^3q\, q^2 |\Psi_l(q)|^2 .$$

The pseudopotential is calculated by directly inverting the Schrödinger equation.

This scheme for generating pseudopotentials has two parameters which may be chosen differently depending upon the application. The parameter r_c may be varied to insure transferability of the pseudopotentials. For any given r_c, our method provides the wave function which converges most rapidly. The other parameter q_c is determined iteratively. A q_c is chosen and the amount of kinetic energy beyond q_c is minimized. Then q_c is varied until exactly the tolerated quantity of kinetic energy is found beyond q_c after minimization.

We now illustrate this approach for the case of copper. We begin with an all-electron calculation of an atom of Cu^{1+} $(3d^9 4s^{0.75} 4p^{0.25})$. We pick the cutoff radius $r_c=1.97a_0$ to be smaller than half the interatomic spacing. We optimize convergence for a tolerance of 1 mRy, and this leads to $q_c=7.14$. In the expression for F, α_4 is fixed equal to 0.5. Five Bessel functions are included in the correction function C for the potential we present. (Extending the set of Bessel functions in C up to twenty gave only marginal improvement of convergence.) The coefficients and wave vectors for F and C are contained in Table I.

As a test of the improvement achieved, we compare the convergence of our optimized potential to a pseudopotential created by the standard method of Hamann, Schluter, and Chiang (HSC).[9] We optimized only the d pseudopotential, because the d electrons clearly govern convergence, even after optimization. The s and p wave functions have r_c's of $2.6a_0$. We chose the HSC d wave function so that the HSC and new wave functions match the all-electron wave function exactly for the same range of radius, $r_c = 1.97a_0$. The d wave functions of these two potentials and their Fourier transforms are compared in Fig. 1. Notice that although the two pseudo wave functions are quite similar in real space, the new wave function has a Fourier transform which converges much more rapidly. The ionic pseudopotentials which give rise to these wave functions are compared in Fig. 2. The new potential is deeper and somewhat less convergent in Fourier space than the HSC potential. If potential well depth or potential Fourier-transform convergence were used as criteria,[7] the HSC potential would be considered preferable to the optimized potential. However, the criterion of atomic total-energy convergence indicates that the optimized potential is far superior. In Fig. 3, we show by solid lines the atomic total energy as a function of wave vector for both pseudopotentials. This calculation predicts that the total energy of solid copper will converge to within 1 mRy at a plane-wave cutoff energy of 50 Ry (500 plane waves for fcc copper) with the new pseudopotential, whereas the same level of convergence for the HSC case requires a cutoff of 115 Ry (1700 plane waves for fcc copper).

In order to verify the predictions of the atomic calculations, these pseudopotentials were then used to calculate the total energy of fcc copper at the experimental lattice constant. For these calculations we used 256 **k** points in Brillouin zone (10 in the irreducible sector).[12] The results are plotted as dots in Fig. 3. The close correlation between atomic and solid total-energy curves both for the standard HSC potential and for our new potential shows that the criterion of atomic total-energy convergence does indeed have great predictive power in general. In addition, the fact that a potential which was created to optimize atomic total-energy convergence also exhibits a large improvement in convergence of the solid total energy,

TABLE I. Expansion of the optimized d pseudo wave function for $r < r_c$. Coefficients and wave vectors of the spherical Bessel functions of angular momentum 2 are provided in atomic units for functions F and C, which are defined in the text.

Function F			Function C		
i	α_i	q_i'	i	β_i	q_i
1	1.619452	2.278679	1	0.203543	2.926964
2	2.436893	3.921348	2	−0.448616	4.618887
3	1.744898	5.536289	3	−0.827052	6.258186
4	0.500000	7.142447	4	−0.169339	7.879067
			5	0.016011	9.491198

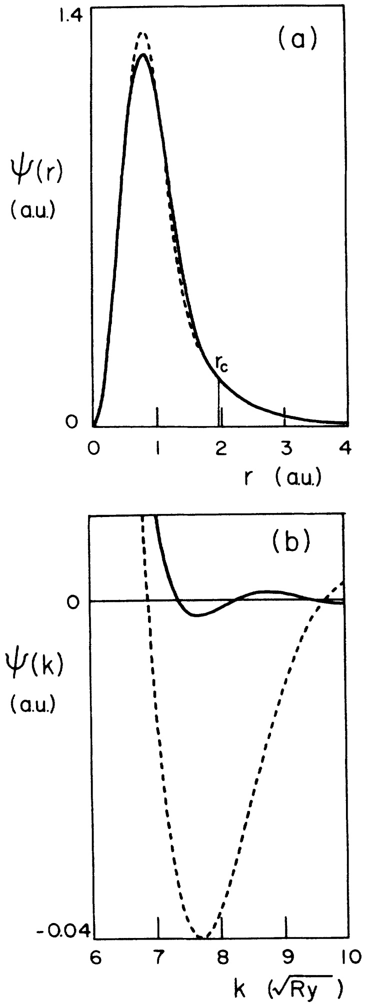

FIG. 1. Pseudo wave functions (a) in real space and (b) in Fourier space, for the copper 3d eigenstate, generated by the HSC method (dashed line) and by the present approach (solid line). The pseudo wave functions are normalized to unity.

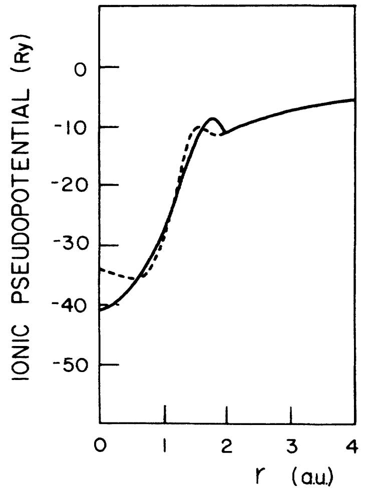

FIG. 2. Pseudopotentials for the copper 3d eigenstate using the HSC method (dashed line) and the present approach (solid line).

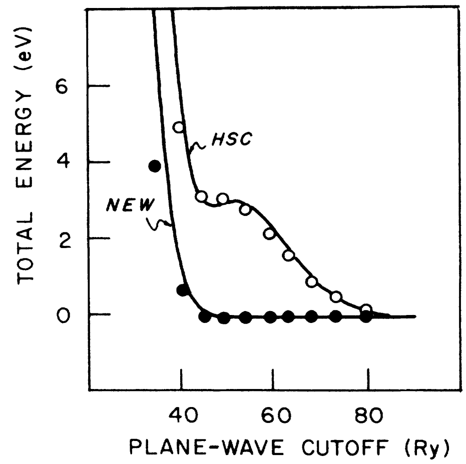

FIG. 3. Atomic (solid lines) and fcc solid (dots) total energies as a function of cutoff energy for copper in the HSC and present approaches. The zero of atomic total energy for each pseudopotential was chosen to be the total atomic energy at a cutoff energy of 324 Ry. The zero of solid total energy was chosen for each pseudopotential so that the atomic and solid total energies coincide at a cutoff energy of 80 Ry.

shows that we have gone beyond identifying a valid criterion and have produced and exhibited a potential which possesses markedly improved convergence.

Using this new pseudopotential, we performed the first *ab initio* plane-wave basis determination of the structural properties of a noble metal. We computed the total energy of fcc copper at 15 atomic volumes ranging from a 27% compression to a 34% expansion relative to the calculated equilibrium volume. For these calculations, we used 1372 **k** points in the Brillouin zone (44 in the irreducible sector) and a cutoff energy of 50 Ry, the value predicted by the atomic calculation. The enlarged **k** point set was essential to describe the shape of the Fermi surface realistically. Using 50 Ry as a cutoff energy insures that all total energies are converged to within 1 mRy. This tolerance is an upper bound to the convergence of all energy differences, and energy differences between similar structures will probably be converged to a much more stringent tolerance. Accordingly, a much smaller cutoff energy may be used for many applications. The equilibrium lattice constant, cohesive energy, and bulk modulus of fcc copper which result from these calculations agree very well with experiment. Experimental and calculated bulk properties of fcc copper are compared in Table II.

TABLE II. Comparison of the bulk properties of fcc copper as obtained by the present method of calculation to experimental values.

	Experiment	Present	% Difference
Lattice constant (a.u.)	6.81	7.03	+3.2
Cohesive energy (Ry/atom)	0.257	0.287	+11.7
Bulk modulus (Mbar)	1.42	1.48	+4.2

In conclusion, we have addressed the problem of improving convergence in a plane-wave basis. We identify the essential features of a pseudopotential which determine its convergence properties. From this, we develop a criterion which we use to create optimally convergent pseudopotentials. Using this principle, it should be possible to optimize the convergence characteristics for any atom, without sacrificing accuracy. This makes it possible to scrutinize solids containing transition metals and first-row nonmetals with the plane-wave pseudopotential formalism. As a result of this work, we envision that the simplicity and versatility of calculations using a plane-wave basis can now be extended to a wide range of ionic, covalent, and transition metal systems.

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[1] For example, see L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986); C. T. Chan, D. Vanderbilt, S. G. Louie, and J. R. Chelikowsky, *ibid.* **33**, 7941 (1986); M. H. Kang, R. C. Tatar, E. J. Mele, and Paul Soven, *ibid.* **35**, 5457 (1987); O. K. Andersen, *ibid.* **12**, 3060 (1975), and references therein.

[2] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[3] R. W. Godby, M. Schluter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[4] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **37**, 2733 (1988).

[5] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[6] For example, see Y. Bar-Yam, S. T. Pantelides, and J. D. Joannopoulos, Phys. Rev. B **39**, 3396 (1989).

[7] For example, see D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985), and references therein.

[8] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[9] D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[10] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos (unpublished).

[11] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[12] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).