

THE DESIGN OF CONVERGENT AND TRANSFERABLE *AB INITIO* PSEUDOPOTENTIALS

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ABSTRACT. This paper exhibits a criterion for creating pseudopotentials which possess rapid convergence in a plane-wave basis set. We demonstrate the applicability of this criterion in conjunction with many prescriptions for insuring transferability. These pseudopotentials are more efficient than other standard pseudopotentials, and this makes *ab initio* electronic structure investigations of larger systems and systems containing "problem" elements feasible. Atomic and structural results for the cases of copper, carbon, nitrogen, and oxygen are provided as examples.

1. Introduction

The sharply-peaked atomic wavefunctions of the first-row nonmetals and transition metals are very difficult to describe in a plane-wave basis set. For this reason, specialized basis sets have been the method of choice for most *ab initio* descriptions of materials containing these elements. Because the plane-wave pseudopotential method has many positive features, there is great interest in developing pseudopotentials which have sufficiently good convergence and transferability characteristics to allow the study of these "problem" elements.

Our work¹ has demonstrated that a key element in the creation of tractable pseudopotentials is the control of the convergence of the total energy of the free atom described by a pseudopotential, i.e. the pseudoatom. This is because the convergence of a pseudoatom's total energy and that of solids containing the pseudoatom are remarkably similar in a wide range of materials. Furthermore, our work shows that the convergence of the kinetic energy of the pseudoatom is an excellent predictor of the convergence of the total energy of the pseudoatom, and therefore of the total energy of solids containing that pseudoatom as well.

The convergence of the kinetic energy of the pseudowavefunction is a powerful predictor of the convergence characteristics of the pseudopotential in solid-state environments because its validity is independent of the method chosen for insuring transferability. To illustrate this fact, we demonstrate the use of this atomic criterion to generate high-quality pseudopotentials within three different pseudopotential formalisms. In Section 2, the use of the criterion with simple norm conservation is illustrated for the case of copper. In Section 3, the criterion is used in conjunction with a transferability criterion involving explicit optimization of logarithmic derivatives at several energies. In Section 4, the use of the criterion within the nonlocal generalized eigenvalue formalism of Vanderbilt² is discussed.

2. Optimization of Kinetic Energy with Norm Conservation

2.1 RATIONALE

Because the convergence of the kinetic energy of the pseudowavefunction mirrors the convergence characteristics of the pseudopotential, it is desirable to create a pseudowavefunction with rapid kinetic-energy convergence. In this section, we demonstrate a particularly simple way to achieve this goal. We create a pseudowavefunction whose Fourier transform possesses a minimal amount of kinetic energy beyond a cutoff q_c . This will provide good convergence using a plane-wave cutoff energy equal to $(q_c)^2$, using Rydberg energy units. This wavefunction also matches the

all-electron wavefunction outside a real-space cutoff radius r_c , conserves norm, and has the same eigenvalue as the all-electron reference state.

2.2 COMPUTATIONAL DETAILS

The wavefunction is constructed as follows. Inside r_c , the wavefunction ψ_1 is expanded in a complete set of spherical Bessel functions of the proper angular momentum whose logarithmic derivatives at r_c match that of the reference wavefunction ϕ_1 .

$$\psi_1(r) = \theta(r_c - r) \sum_{i=1}^N \alpha_i j_l(q_i r) + \theta(r - r_c) \phi_1(r)$$

where $N \sim 10$ and the q_i are wavevectors chosen to match

$$\frac{j_l'(q_i r_c)}{j_l(q_i r_c)} = \frac{\phi_1'(r_c)}{\phi_1(r_c)}$$

The kinetic energy $KE_{q>q_c}$ of the wavefunction beyond q_c is conveniently expressed as the difference between the kinetic energy in real space and the kinetic energy from 0 to q_c in Fourier space.

$$KE_{q>q_c} = - \int_0^\infty d^3 r \psi_1^*(r) \nabla^2 \psi_1(r) - \int_0^{q_c} d^3 q q^2 |\psi_1(q)|^2$$

This is the quantity we wish to minimize. All of the integrals remain the same throughout the calculation and can therefore be tabulated. Defining the following integrals,

$$A_i = \int_0^{r_c} dr r^2 [j_l(q_i r)]^2$$

$$B_i(q) = \sqrt{\frac{2}{\pi}} \int_0^{r_c} dr r^2 j_l(q_i r) j_l(q r)$$

$$C(q) = \sqrt{\frac{2}{\pi}} \int_{r_c}^{\infty} dr r^2 j_l(qr) \phi_l(r)$$

$$D_{ij} = \int_0^{q_c} dq q^4 B_i(q) B_j(q)$$

$$E_i = \int_0^{q_c} dq q^4 B_i(q) C(q)$$

$$F = \int_{r_c}^{\infty} dr r^2 \phi_l(r) \nabla^2 \phi_l(r)$$

$$G = \int_0^{q_c} dq q^4 [C(q)]^2$$

the expression for $KE_{q>q_c}$ may be rewritten

$$KE_{q>q_c} = \left[\left(\sum_{i=1}^N \alpha_i^2 q_i^2 A_i \right) - F \right] - \left[\left(\sum_{i=1}^N \sum_{j=1}^N \alpha_i \alpha_j D_{ij} \right) + \sum_{i=1}^N \alpha_i E_i + G \right]$$

We now wish to minimize $KE_{q>q_c}$ subject to the constraints of norm conservation and wavefunction smoothness at r_c . This minimization can be performed rapidly by various scientific computer library minimization subroutines. The calculation takes us about five CPU seconds on a Cray-2.

2.3 RESULTS

As may be seen in Figure 1, the application of this procedure to copper greatly improves the convergence properties of the total energy for both a single copper pseudoatom and for copper FCC solid relative to the same calculations performed using a standard

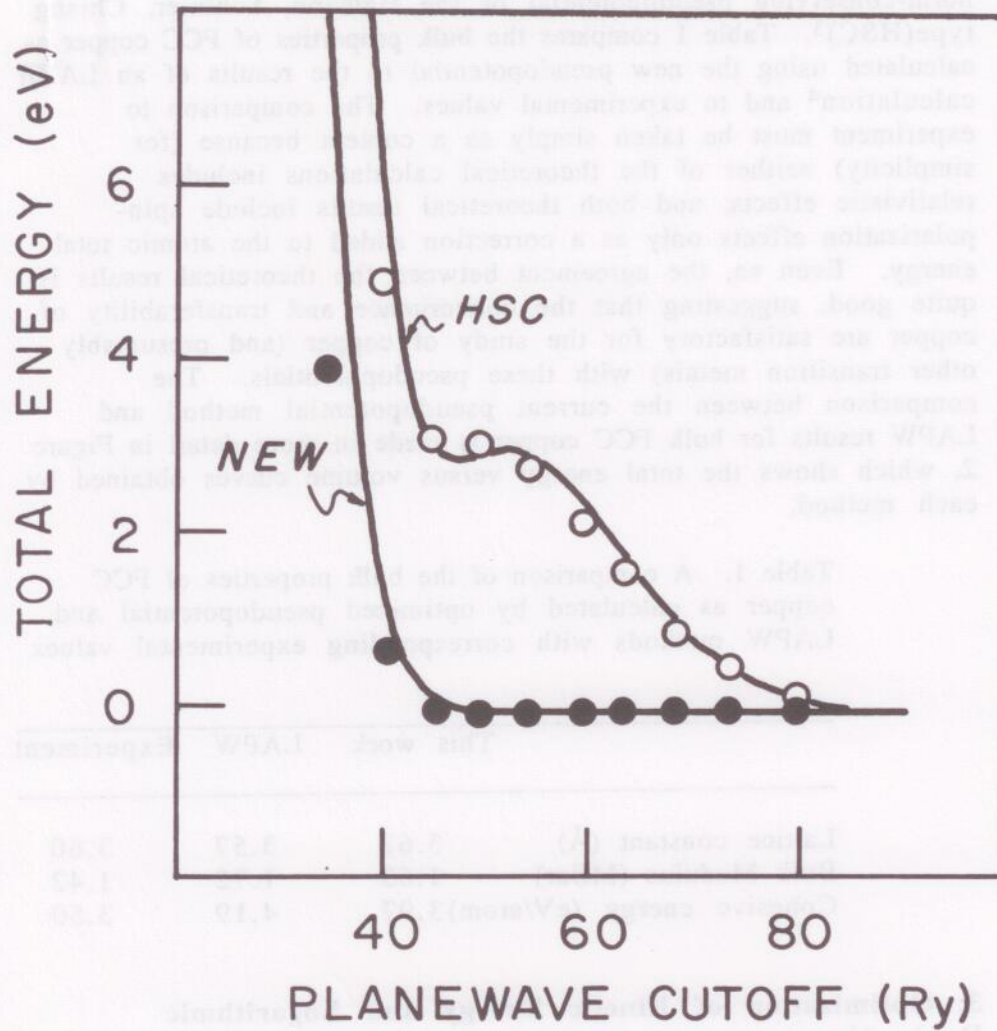


Figure 1. Convergence of the total energy of copper as a free pseudoatom and in FCC copper using HSC and optimized norm-conserving pseudopotentials.

norm-conserving pseudopotential of the Hamann, Schluter, Chiang type(HSC)³. Table 1 compares the bulk properties of FCC copper as calculated using the new pseudopotential to the results of an LAPW calculation⁴ and to experimental values. The comparison to experiment must be taken simply as a context because (for simplicity) neither of the theoretical calculations includes relativistic effects, and both theoretical results include spin-polarization effects only as a correction added to the atomic total energy. Even so, the agreement between the theoretical results is quite good, suggesting that the convergence and transferability of copper are satisfactory for the study of copper (and presumably other transition metals) with these pseudopotentials. The comparison between the current pseudopotential method and LAPW results for bulk FCC copper is made in more detail in Figure 2, which shows the total energy versus volume curves obtained by each method.

Table 1. A comparison of the bulk properties of FCC copper as calculated by optimized pseudopotential and LAPW methods with corresponding experimental values

	This work	LAPW	Experiment
Lattice constant (Å)	3.62	3.57	3.60
Bulk Modulus (MBar)	1.63	1.72	1.42
Cohesive energy (eV/atom)	3.97	4.19	3.50

3. Optimization of Kinetic Energy and Logarithmic Derivatives

3.1 RATIONALE

The aforementioned procedure is most effective when the transferability needs of the material are modest. In the particular example of copper, we obtained good agreement with theory and

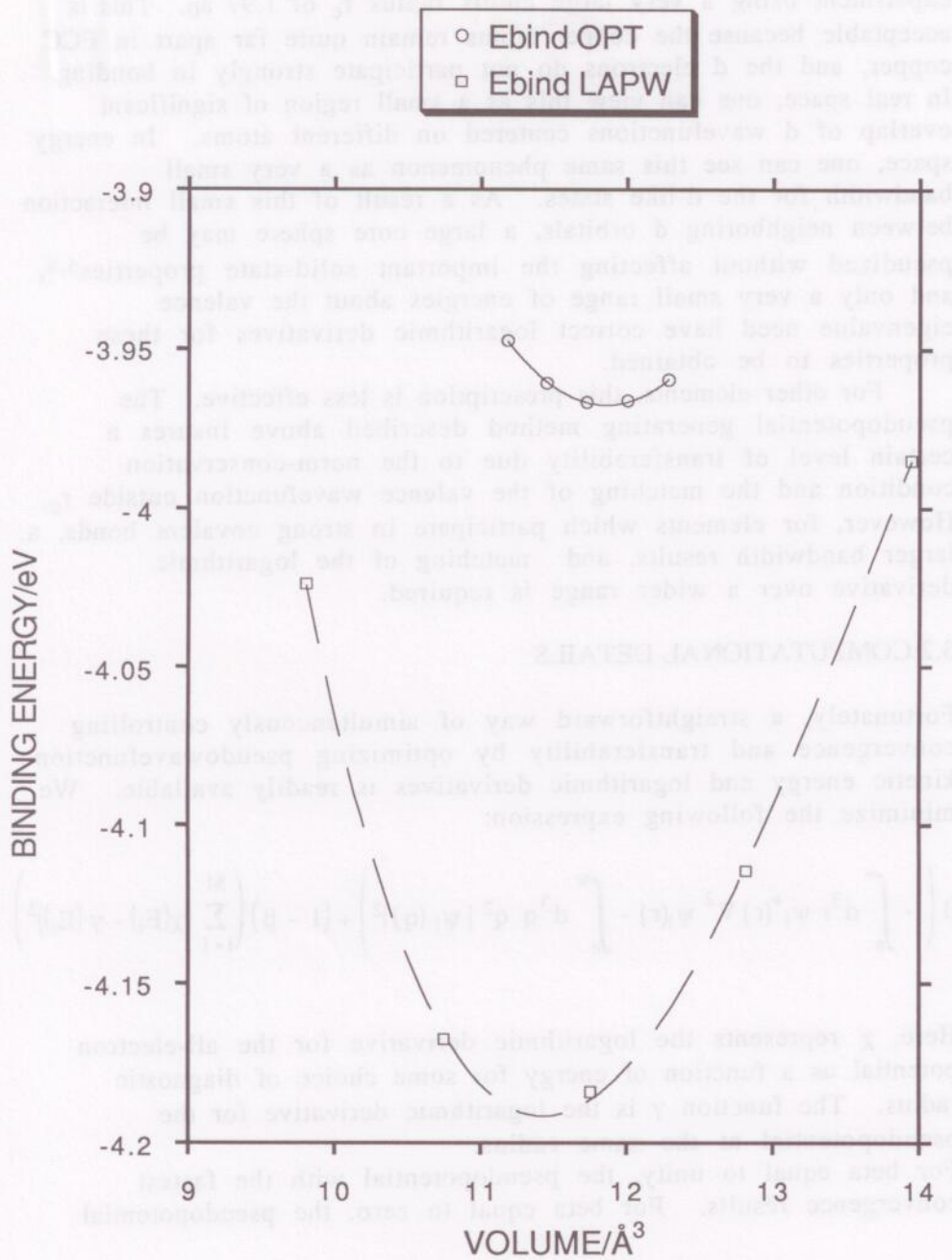


Figure 2. Graph of energy versus volume for FCC copper as calculated by the pseudopotential method with an optimized pseudopotential and by the LAPW method.

experiment using a very large cutoff radius r_c of $1.97 a_0$. This is acceptable because the copper atoms remain quite far apart in FCC copper, and the d electrons do not participate strongly in bonding. In real space, one can view this as a small region of significant overlap of d wavefunctions centered on different atoms. In energy space, one can see this same phenomenon as a very small bandwidth for the d-like states. As a result of this small interaction between neighboring d orbitals, a large core sphere may be pseudized without affecting the important solid-state properties^{5,6}, and only a very small range of energies about the valence eigenvalue need have correct logarithmic derivatives for these properties to be obtained.

For other elements, this prescription is less effective. The pseudopotential generating method described above insures a certain level of transferability due to the norm-conservation condition and the matching of the valence wavefunction outside r_c . However, for elements which participate in strong covalent bonds, a larger bandwidth results, and matching of the logarithmic derivative over a wider range is required.

3.2 COMPUTATIONAL DETAILS

Fortunately, a straightforward way of simultaneously controlling convergence and transferability by optimizing pseudowavefunction kinetic energy and logarithmic derivatives is readily available. We minimize the following expression:

$$\beta \left(- \int_0^{\infty} d^3r \psi_1^*(r) \nabla^2 \psi_1(r) - \int_0^{r_c} d^3q q^2 |\psi_1(q)|^2 \right) + (1 - \beta) \left(\sum_{i=1}^M (\chi(E_i) - \gamma(E_i))^2 \right)$$

Here, χ represents the logarithmic derivative for the all-electron potential as a function of energy for some choice of diagnostic radius. The function γ is the logarithmic derivative for the pseudopotential at the same radius.

For beta equal to unity, the pseudopotential with the fastest convergence results. For beta equal to zero, the pseudopotential

which best fits the all-electron logarithmic derivative at a series of chosen energies is found. For beta between zero and one, potentials with improved transferability *and* convergence are generated. The value of beta phenomenologically represents the relative difficulties caused by convergence and transferability error in a particular element.

3.3 RESULTS

The energies which were used for fitting the logarithmic derivative for the p potential in carbon are shown in Figure 3. The pseudopotential logarithmic derivative curve at the cutoff radius of $1.4 a_0$ agrees well with the all-electron curve throughout the bandwidth of the diamond. It agrees with the all-electron result better than the HSC potential used for comparison does. Figure 4 shows the superior convergence properties of the new carbon pseudopotential relative to the HSC potential. In addition, the excellent agreement between atom and solid gives further support to the validity of the atomic convergence criterion in covalent materials. Thus, the enhanced prescription for pseudopotential generation achieves improvement of convergence and transferability for a difficult test case. Note that there is a marked similarity between this procedure for beta equal zero and the procedure of Teter and Allan⁷. They make no explicit provision for the control of convergence characteristics, but the method for the control of transferability is quite similar.

4. Optimization of Kinetic Energy with Non-norm-conserving Pseudopotentials

The prescription of Section 3 has the advantage that it creates a single potential for each angular momentum which has nearly the best overall characteristics of convergence and transferability possible. For many elements, this allows in-depth analysis of materials which is not possible or much more difficult using standard norm-conserving pseudopotentials. We believe that little improvement over the current approach is possible within the

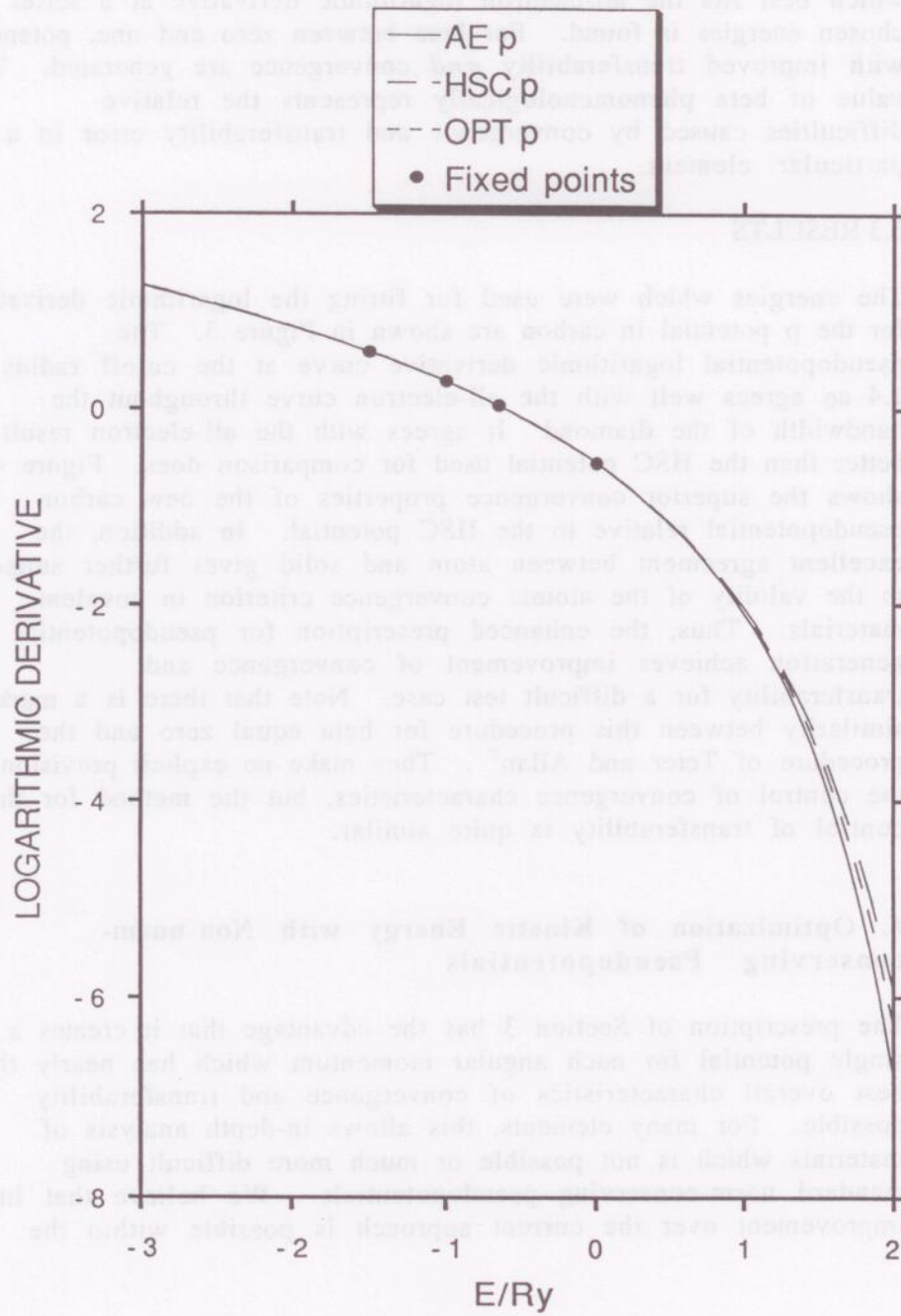


Figure 3. Logarithmic derivatives of carbon all-electron potential and HSC and optimized pseudopotentials at $r_{\log} = 1.4a_0$.

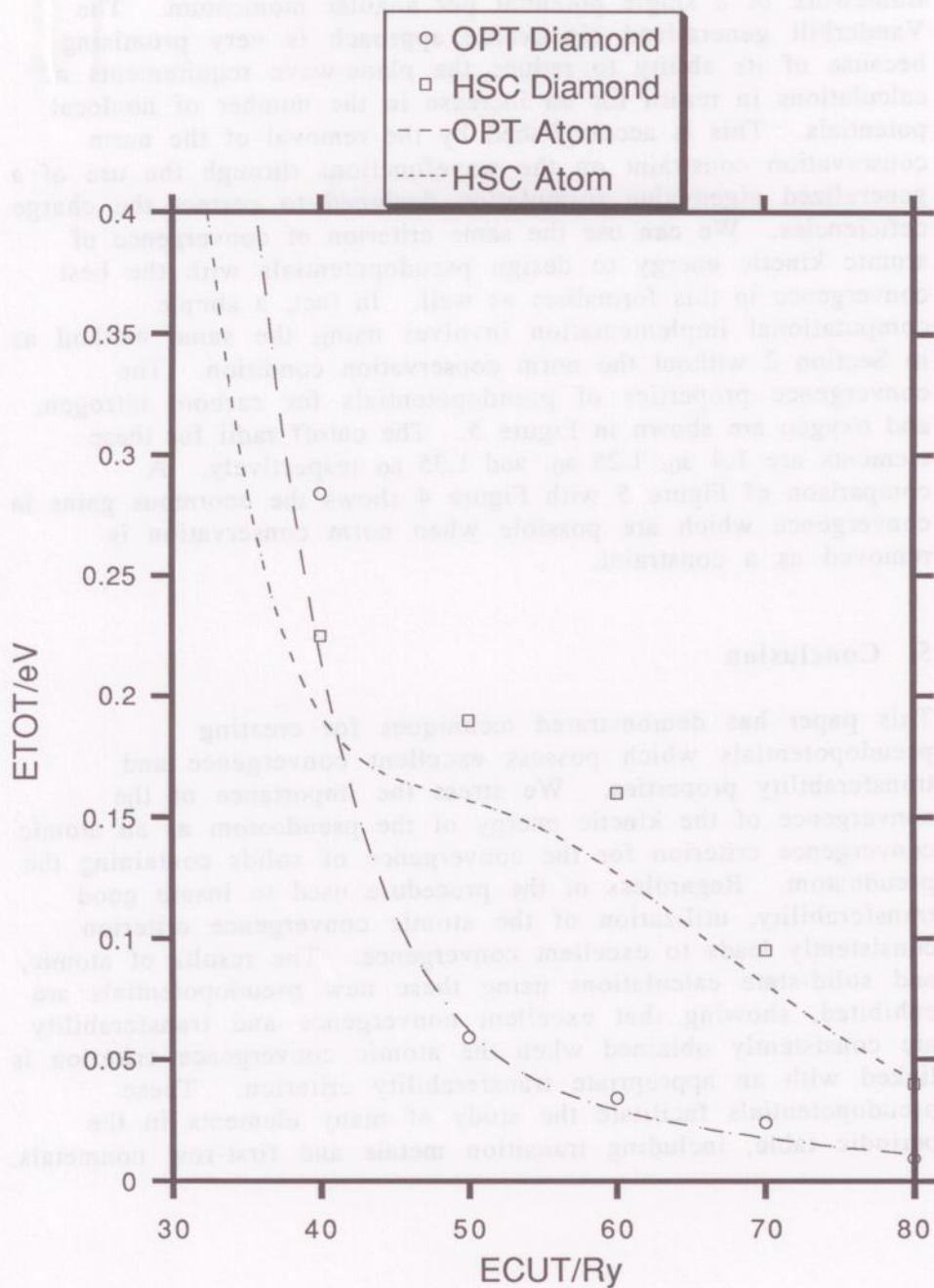


Figure 4. Convergence of the total energy of carbon as a free pseudoatom and in diamond using HSC and optimized norm-conserving pseudopotentials.

framework of a single potential per angular momentum. The Vanderbilt generalized eigenvalue approach is very promising because of its ability to reduce the plane-wave requirements of calculations in return for an increase in the number of nonlocal potentials. This is accomplished by the removal of the norm conservation constraint on the wavefunctions through the use of a generalized eigenvalue formulation designed to correct the charge deficiencies. We can use the same criterion of convergence of atomic kinetic energy to design pseudopotentials with the best convergence in this formalism as well. In fact, a simple computational implementation involves using the same method as in Section 2 without the norm conservation condition. The convergence properties of pseudopotentials for carbon, nitrogen, and oxygen are shown in Figure 5. The cutoff radii for these elements are $1.4 a_0$, $1.25 a_0$, and $1.35 a_0$ respectively. A comparison of Figure 5 with Figure 4 shows the enormous gains in convergence which are possible when norm conservation is removed as a constraint.

5. Conclusion

This paper has demonstrated techniques for creating pseudopotentials which possess excellent convergence and transferability properties. We stress the importance of the convergence of the kinetic energy of the pseudoatom as an atomic convergence criterion for the convergence of solids containing the pseudoatom. Regardless of the procedure used to insure good transferability, utilization of the atomic convergence criterion consistently leads to excellent convergence. The results of atomic, and solid-state calculations using these new pseudopotentials are exhibited, showing that excellent convergence and transferability are consistently obtained when the atomic convergence criterion is linked with an appropriate transferability criterion. These pseudopotentials facilitate the study of many elements in the periodic table, including transition metals and first-row nonmetals.

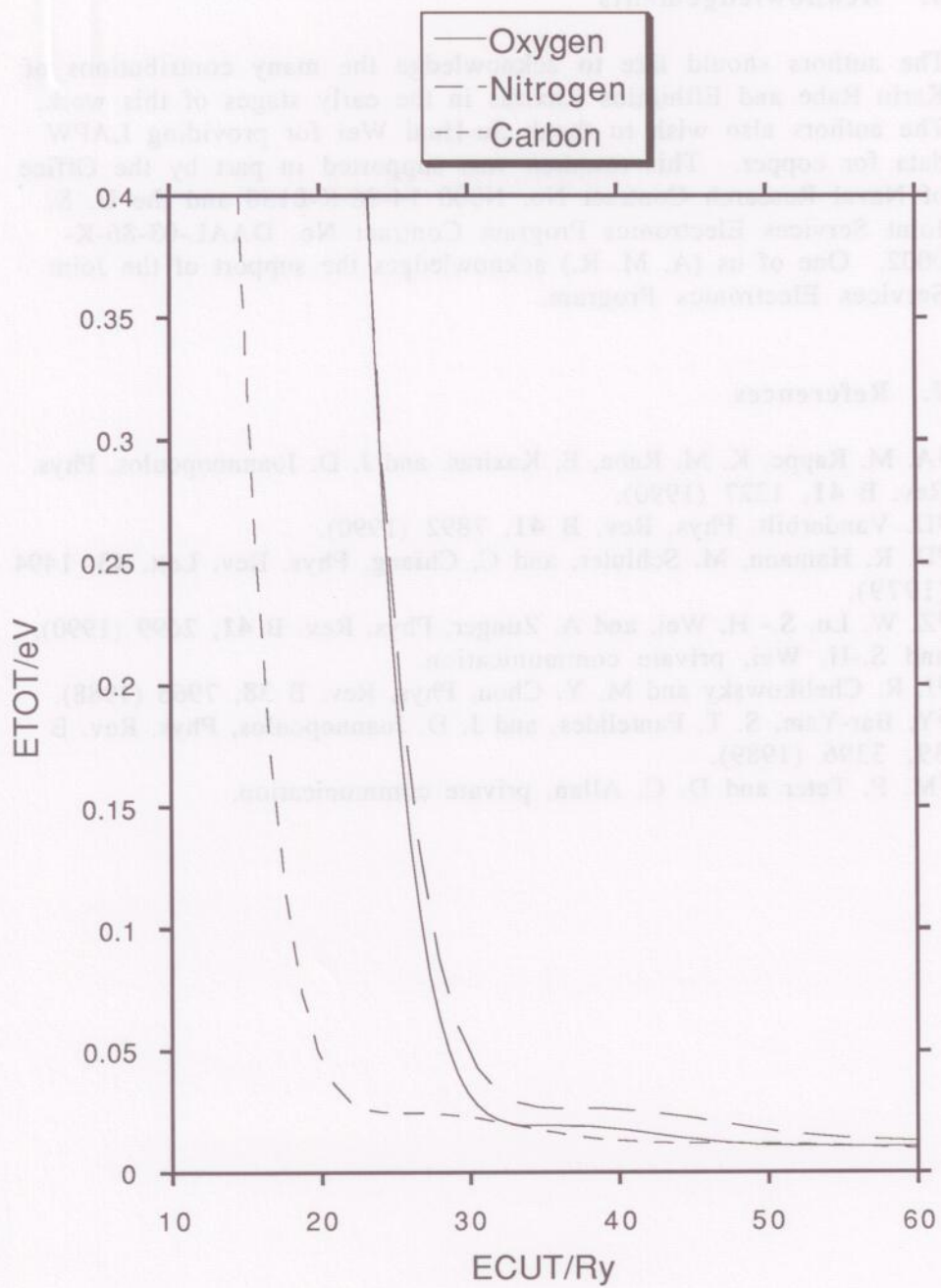


Figure 5. Convergence of the total energies of pseudoatoms of first-row nonmetals in non-norm-conserving formalism.

6. Acknowledgements

The authors should like to acknowledge the many contributions of Karin Rabe and Efthimios Kaxiras in the early stages of this work. The authors also wish to thank Su-Huai Wei for providing LAPW data for copper. This research was supported in part by the Office of Naval Research Contract No. N000 14-86-K-0158 and the U. S. Joint Services Electronics Program Contract No. DAAL-03-86-K-0002. One of us (A. M. R.) acknowledges the support of the Joint Services Electronics Program.

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