Truncated pseudopotentials for alloy calculations

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In first-principles plane-wave pseudopotential calculations, there is a subtle interplay between the convergence of the wave function and the pseudopotential expansions. Changing the cutoff of the plane-wave expansion often causes a change in the calculated physical quantities. We discuss the origin of this problem and how to ameliorate it by introducing a simple truncation of the pseudopotential in the reciprocal space. By exploiting the arbitrariness inherent in pseudopotentials, the method also provides an extra handle to ''tune'' the pseudopotentials to yield the best possible agreement with the all-electron results for bulk systems. We demonstrate the benefits of this truncation using Pd as an example and illustrate the results by calculations for some Pd-Al alloys. [S0163-1829(99)00836-X]

I. INTRODUCTION

Electronic (band) structure theory plays an important role in elucidating the properties of materials and in the interpretation of experimental data. Throughout its long history, many different approaches and techniques have been developed. Ranging from (semi-)empirical methods for modeling optical properties to first-principles calculations of the structural and dynamical properties of (dis)ordered systems, each approach has its own set of advantages and disadvantages. First-principles methods, although by now quite powerful and popular, are not appropriate for all problems; the choice of method should be dictated by the physical insight that can be obtained.

Pseudopotentials[1,2] have been applied within the whole spectrum of electronic structure theory, from simple models to semiempirical and first-principles calculations. The use of pseudopotentials in modern first-principles electronic structure calculations of solids[2] is by now widespread. This popularity is based in large part on the compatibility between pseudopotentials and the use of plane waves as a convenient basis set for expanding the electronic states; the elimination of the core electrons and the short wavelength structure in the valence wave functions allow Fourier expansions to converge reasonably rapidly. This rapid convergence in reciprocal space has been used to great effect[1] in semiempirical calculations: the bands of semiconductors and simple metals often can be described by only a few Fourier components. For first-principles calculations, pseudopotentials and a plane-wave basis are computationally simpler than the more accurate all-electron approaches, and can be extended more easily to make use of modern techniques such as iterative diagonalization to treat large systems.

A prominent feature (and advantage) of pseudopotentials is their inherent arbitrariness, that can be utilized in constructing better pseudopotentials. This arbitrariness has led to many different ways of constructing first-principles pseudopotentials[3,4] that differ considerably from each other, yet produce physically meaningful, but not identical, results.

It is important to keep in mind that these pseudopotentials are *approximations* to the underlying all-electron results. As such, the quality of a first-principles pseudopotential should be judged by comparing the calculated results with all-electron, *not* experimental, results.[5] In what follows, we restrict our attention to the generation and use of first-principles pseudopotentials; since the applications of empirical and semiempirical pseudopotentials are different, the criteria for judging their quality are also different.

In any electronic structure calculation, both all-electron and pseudopotential, there are convergence issues. In order to compare the properties of different systems, it is necessary that each system is separately converged. As evident from many works,[6] physical properties may change as a function of the basis set even though the total energy is apparently reasonably converged. In a recent study[7] of Zr-Al alloys, we briefly noted that this problem could be partially overcome for pseudopotentials and plane-wave basis sets by introducing a truncation of the pseudopotential in reciprocal space. This procedure also yields an extra way to ''tune'' the pseudopotential, which in the case of Zr, allowed us to obtain the correct sign of the bcc-fcc energy difference. In what follows, we demonstrate these points in more detail using Pd as an example. These Pd pseudopotentials are then used to calculate the structural properties and heats of formation of some representative Pd-Al alloys.

II. APPROACH AND EXAMPLES

The typical construction of a pseudopotential starts from an all-electron calculation of the free atom[3,4] or an atomic site in the solid state.[8] (For pseudopotentials that are updated during the calculation, see Ref. 9.) This construction is generally done in real space. For real space methods,[10,11] this pseudopotential can be used directly, albeit with care.

In plane-wave methods, the pseudopotential is transformed into reciprocal space, either explicitly or implicitly in the determination of matrix elements. Typically, the size of the plane-wave basis set is defined by the maximum kinetic

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energy E_{cut} of the plane waves, which in turn determines the maximum Fourier component of the pseudopotential needed. (In what follows, we define all of the maximum Fourier components in terms of the equivalent plane wave basis cutoff E_{cut} with the understanding that individual terms may include plane waves with kinetic energy $4E_{cut}$.) The convergence with E_{cut} is determined by the structure in (i) the (pseudo-)wave functions and (ii) the potential. These two aspects are related, but our experience (as shown below) has been that it is the potential that limits the convergence.

If E_{cut} is changed, as often must be done when using the pseudopotential in different (alloy) environments or in different compounds, the expansion of the pseudopotential changes accordingly. Similarly, if the lattice constant is changed at constant E_{cut}, the number of terms (plane waves) in the expansion of the pseudopotential will change. If the pseudopotential and wave functions are well converged in reciprocal space for this E_{cut}, the changes in the calculated properties will be small. If, however, the Fourier components around E_{cut} are still sizable, this can lead to undesired results such as changes in structural properties with E_{cut}.

Our recipe for improving the stability of the pseudopotentials is simple: we truncate the pseudopotential in reciprocal space at an effective plane wave basis cutoff energy E_{ps} and let this truncation *define* the pseudopotential. (The long-range Coulomb part, however, is not truncated but taken fully into account.) For $E_{cut} \lesssim E_{ps}$, there is no difference compared to the conventional approach. The truncation (expressed below as an effective cutoff energy, consistently with the cutoff of the plane-wave expansion) is arbitrary and can be chosen to give the best possible agreement with all-electron results. An obvious advantage of this approach is that the pseudopotential is constant for $E_{cut} > E_{ps}$, and hence the convergence will be dominated by the structure in the wave functions. On the other hand, the pseudopotential Fourier transformed to real space could have additional small wavelength structure ($\lambda < 2\pi\hbar/\sqrt{2mE_{ps}}$) not in the original one; this problem is also implicit in the conventional choice $E_{cut} = E_{ps}$. The Fourier filtering method used in the context of the real-space methods for calculating the electronic structure[10] is related in spirit to our approach.

As a starting point we use the normconserving pseudopotentials of Troullier and Martins,[4] transformed into the fully separable nonlocal Kleinman–Bylander form.[12] For the bulk and alloy calculations we use a plane-wave pseudopotential method[13] and a full-potential all-electron method,[14] both described in more detail elsewhere. As our example, we have chosen the transition metal Pd. Several different electronic configurations and cutoff radii were tested in order to find the ones that best reproduce the all-electron results *for bulk systems*. We ended up using the configuration $4d^{9.5}5s^{0.25}5p^{0.25}$ and pseudopotential cutoff radii $r_c^s = 3.0$, $r_c^p = 3.5$, and $r_c^d = 2.0$. Using smaller cutoff radii for the s and p channels yields somewhat larger lattice constants, in better agreement with experiments, but in worse agreement with the all-electron results.

The convergence of the total energy of bulk fcc Pd as a function of both E_{cut} and E_{ps} is shown in Fig. 1. The curve labeled for $E_{ps} = E_{cut}$ (filled circles) shows that to converge the total energy E_{tot} requires $E_{cut} > 60$ Ry. As discussed

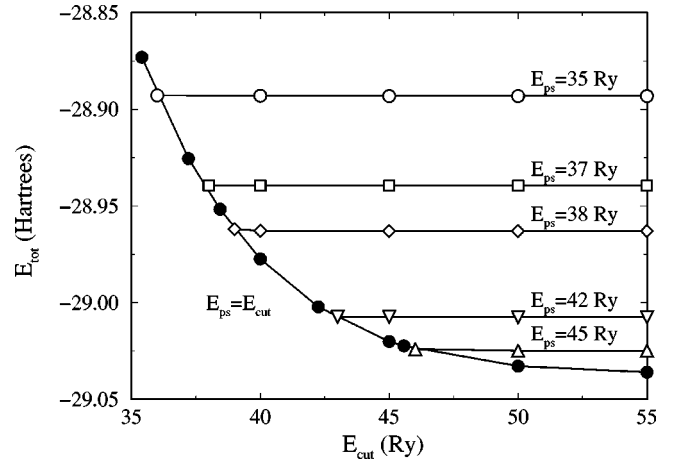FIG. 1. Total energy vs. plane-wave cutoff energy, E_{cut}, for different pseudopotential truncations, E_{ps}, for fcc Pd at $a = 7.28$ a.u.

above, one might expect that in this case the physical properties could vary significantly with E_{cut}; this expectation is borne out by the calculated lattice constants and bulk moduli shown in Fig. 2. (The lattice constants and bulk moduli were determined from simple fits of the total energy versus volume; both the pseudopotential and all-electron calculations used identical sets of lattice constants in the fit.) Not only are there large variation with E_{cut}, but the behavior is not monotonic; in fact, if additional E_{cut} are included, these curves are even more jagged.
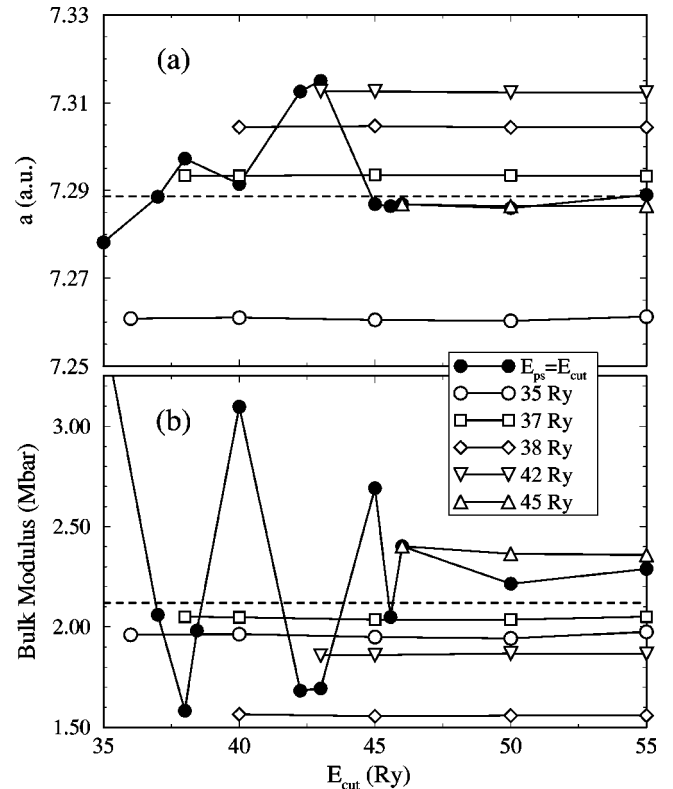

FIG. 2. Calculated (a) lattice constants and (b) bulk moduli for fcc Pd as a function of plane-wave cutoff E_{cut} for the conventional choice of $E_{ps} = E_{cut}$ and for different pseudopotential truncations (with $E_{cut} > E_{ps}$; see text). The dashed lines indicate the all-electron results.

TABLE I. Lattice constants a (a.u.) and bulk moduli B (Mbar) for fcc and bcc Pd, and the fcc-bcc energy difference ($\Delta E_{\text{bcc-fcc}}$, eV/atom) obtained using pseudopotentials (PP) truncated at 37 Ry ($E_{\text{cut}}=40$ Ry) and 45 Ry ($E_{\text{cut}}=50$ Ry) and the all-electron (AE) method.

	a_{fcc}	B_{fcc}	a_{bcc}	B_{bcc}	$\Delta E_{\text{bcc-fcc}}$
PP (37 Ry)	7.293	2.05	5.799	2.42	0.055
PP (45 Ry)	7.286	2.36	5.808	2.23	0.053
AE	7.289	2.12	5.802	2.16	0.059

Also shown in Fig. 1 are the total energies as a function of E_{cut} for different pseudopotential truncations E_{ps}. For a given truncation and $E_{\text{cut}}>E_{\text{ps}}$, there is an almost horizontal line branching off the ''conventional'' curve. (In Figs. 1 and 2, E_{cut} for the truncated pseudopotentials is always chosen greater than E_{ps}, the same as is done in practice.) The fact that there is such little variation in total energy with E_{cut}, even for $E_{\text{ps}}=35$ Ry, demonstrates that a plane-wave cutoff of $E_{\text{cut}}\sim 38$ Ry is already sufficient for converging the structure in the wave functions. Clearly the truncation greatly affects the value of the total energy. However, there is no variational principle arguing that any particular choice is better; the different branches and total energies correspond to *different* pseudopotentials. Thus, if one is interested in the properties of the free atom, for example in order to get the cohesive energy, it is necessary to transform the truncated pseudopotential back to real space, rather than using the original one.

That the pseudopotentials for different truncations are in fact different can be seen in Fig. 2. For all truncations, the calculated lattice constants and bulk moduli are stable with respect to E_{cut} for $E_{\text{cut}}>E_{\text{ps}}$. (As $E_{\text{cut}}\rightarrow E_{\text{ps}}$, these curves join the $E_{\text{cut}}=E_{\text{ps}}$ curve, and thus, for $E_{\text{cut}}\approx E_{\text{ps}}$, there can be significant variations in the calculated properties. For this reason, we typically pick $E_{\text{cut}}-E_{\text{ps}}\gtrsim 1$ Ry in actual calculations.) As can be seen from the curves, calculated values of these properties vary with the truncation used. There seems to be an optimum value (in comparison with the all-electron results) for the truncation, although the same truncation might not necessarily produce both the best possible lattice constant and bulk modulus. One must, therefore, experiment with the truncation—and perhaps change the electronic configuration and/or cutoff radii—in order to obtain structural properties in good agreement with the all-electron calculations. Since the bulk modulus is more sensitive to the procedure used for fitting the equation of state, we use the lattice constant and the energy difference between structures as the primary quantities to compare with the all-electron results. In Table I, calculated pseudopotential and all-electron properties of fcc and bcc Pd are compared, and demonstrate that the truncated pseudopotential with $E_{\text{ps}}=37$ Ry reproduces the all-electron results quite well. In addition, a practical consideration is that one prefers a plane-wave cutoff E_{cut} as small as possible. One should not, however, try to use the truncation as a way of pushing the cutoff in the plane-wave expansion unrealistically low; the convergence must always be checked before introducing any truncation.

As an illustration of the transferability of these pseudopotentials, we calculated the heats of formation of Pd-Al alloys
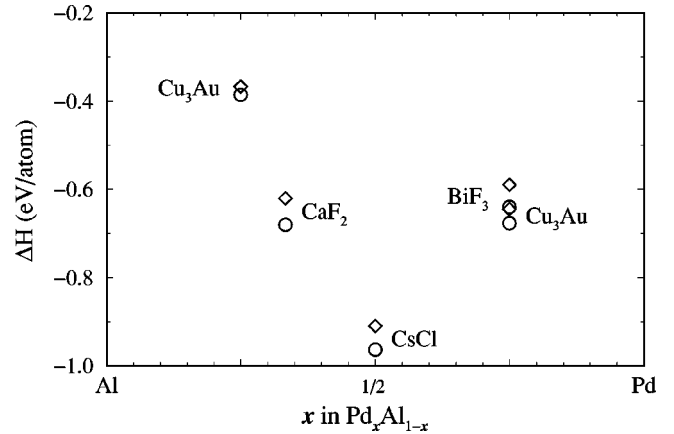

FIG. 3. Heats of formation of representative Pd-Al alloys in various structures obtained with all-electron (diamonds) and pseudopotential (circles) methods ($E_{\text{cut}}=37$ Ry, $E_{\text{ps}}=40$ Ry).

in some simple structures. We chose Al as the other component of the alloy because the plane wave expansion in the case of Al is fully converged (to better than 1 μHartree/atom) at the cutoff values used for Pd, meaning there should be no problems arising from the Al part. Again, we stress that in alloy calculations, e.g., predicting features of the phase diagrams by calculating the heats of formation,[7] the consistency of the set of calculations is often more essential than the exact agreement of the numbers obtained with the experiment in each case, especially since the uncertainties in the experimental heats are often of the same (or larger) scale.

In Fig. 3 we show the heats of formation for some Pd-Al alloys calculated using a plane wave cutoff of 40 Ry and the pseudopotential truncation at 37 Ry, compared with the all-electron result. Consistent with the results shown in Fig. 1, these heats were within 0.0002 eV/atom of the results for $E_{\text{cut}}=55$ Ry. The heats of formation given by the pseudopotential calculation are close to those obtained with the all-electron method. Moreover, the difference between the two methods for the heats of the same alloy always have the same sign and are of the same order which is important in the interpretation of the phase diagrams. The lattice constants for the different structures, given in Table II, also show good agreement between the two methods. It is interesting to note that a pseudopotential that gives a very good agreement with *experiment* for fcc Pd yields lattice constants for the alloys that scatter much more in comparison with the all-electron values than the ones obtained with the pseudopotential described above.

III. SUMMARY

In conclusion, we have shown that in standard first-principles plane-wave pseudopotential approaches the effec-

TABLE II. Lattice constants a (a.u.) for some Pd-Al alloys obtained for a Pd pseudopotential truncated at 37 Ry ($E_{\text{cut}}=40$ Ry) compared to the all-electron (AE) results.

Compound structure	Pd_3Al Cu_3Au	Pd_3Al BiF_3	$PdAl$ $CsCl$	$PdAl_2$ CaF_2	$PdAl_3$ Cu_3Au
PP	7.238	11.491	5.728	11.017	7.326
AE	7.230	11.496	5.706	11.037	7.350

tive real-space pseudopotential varies with the plane-wave basis cutoff E_{cut}. This behavior can result in calculated properties that depend strongly on plane-wave cutoff. By introducing a simple truncation of the pseudopotential in reciprocal space—and using this Fourier representation to define the pseudopotential—the stability of the plane-wave pseudopotential calculations can be improved. This scheme can be trivially used in the context of any standard first-principles pseudopotential generation method, with the added benefit that the convergence of the wave functions and the pseudopotential can be monitored separately. By exploiting the arbitrariness inherent in the representation of the pseudopotentials, one can tune them in order to improve agreement with the all-electron results for *bulk* systems. For compounds with several different atomic species, each may have a different truncation associated with it, and E_{cut} is chosen greater than the largest E_{ps}. This scheme, while simple, adds the level of stability in the properties of the pseudopotential essential for making meaningful first-principles comparisions among different alloys systems, including relative heats of formation.

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