First-principles local pseudopotentials for group-IV elements

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(Received 9 December 2002; revised manuscript received 1 August 2003; published 4 November 2003)

A simple scheme is proposed for generating first-principles local pseudopotentials, and applied to group-IV elements. The scheme is based on solving Kohn-Sham equations inversely, using the density from a nonlocal pseudopotential calculation. The generated local pseudopotentials have been applied in the calculations of dimers and solids including diamond and fcc structures of Si, Ge, and Sn. Fairly good results are obtained for bond lengths and lattice constants, while the results for energies and energy eigenvalues (e.g., excitation energies of atoms and band structures of solids) compare less well with those given by the corresponding nonlocal pseudopotentials. However, our work indicates the important features required by a good local pseudopotential of a group-IV element.

I. INTRODUCTION

The remarkable success of first-principles nonlocal pseudopotentials has diminished interest in local pseudopotentials. Compared with nonlocal pseudopotentials, the local counterparts are, in general, less competitive in their transferability since it is difficult to find a single smooth potential which leads to good norm-conserving valence orbitals for the different angular momenta involved in the valence states. However, local pseudopotentials have their advantages. Besides their simplicity, there are some cases where the use of nonlocal pseudopotentials can be problematic. In particular, we are interested in orbital-free calculations,[1] where an approximate electron kinetic energy is used so that the electron density is the only variable. Such calculations are much more efficient than those using Kohn-Sham (KS) orbitals;[2] however, orbital dependent nonlocal pseudopotentials cannot be applied in a straightforward way. Evidently, local pseudopotentials with good transferability can be very useful.

Early orbital-free calculations[3] used empirical local pseudopotentials.[4] In more recent work,[5,6] first-principles local pseudopotentials have been applied. These pseudopotentials are generated by inverting an electron density, through either KS (Ref. 2) or orbital-free[1] calculations, so that they reproduce a given density.[6,7] However, the densities used in this procedure are taken from the bulk or simulate a bulk environment. The pseudopotentials generated in this way were designed specifically for studying an extended system and the degree to which they are transferable to a finite system such as a cluster or molecule is uncertain. Here we present a simple and straightforward scheme for generating local pseudopotentials which is also based on an inversion procedure. In this scheme, the local bare ion pseudopotential is constructed from a local KS potential, which is obtained from a given density by solving KS equations inversely. The densities used are the free pseudoatom densities yielded by a popular nonlocal pseudopotential, and the resulting potentials may be regarded as the local equivalents of the nonlocal pseudopotentials. The method is applied to group-IV elements. The local pseudopotentials give fairly good results on bond lengths of dimers and lattice constants of solids. However, the calculated band structures for diamond structures

and the energy differences between fcc and diamond structures are less accurate when compared with those obtained from the corresponding nonlocal pseudopotentials. We analyze the features leading to these successes and failures, and point out how further improvements can be made.

Generating a local KS potential from a given density was originally motivated by a fundamental problem in density-functional theory,[2,8] i.e., the v representability of an electron density.[9] Chen and Stott showed that for a small number of spin-unpolarized electrons any reasonable spherically symmetric density is the nondegenerate ground-state density or a linear combination of degenerate ground-state densities for some local potential.[10] In the case of a two- or three-level system, the effective potential can be constructed from a given density by solving KS equations inversely. The inversion procedure is based on the reduction of N one-body Schrödinger equations to a set of $N-1$ nonlinear differential equations, which involve the given density directly.[11] This approach has been used to deduce the effective potential of Be, Ne, and C atoms from the corresponding all-electron densities.[12] We follow the same inversion procedure[10,11] and generate the local KS potential for group-IV atoms. Instead of all-electron densities used in the earlier calculations, we have used the pseudoatom densities from nonlocal pseudopotential calculations since only the valence electrons influence the physical properties of interest. From the resulting local KS potentials, local bare ion pseudopotentials are constructed in the usual manner by unscreening and subtracting the exchange and correlation potentials. Consequently, the local pseudopotential and the nonlocal one give the same free atom electron density.

In the following section, we outline the method used for generating the local pseudopotentials of group-IV elements. The pseudopotentials are described in Sec. III. The results of applying these pseudopotentials in calculations of dimers and solids are presented and discussed in Sec. IV, and conclusions are drawn in Sec. V.

II. METHOD

To generate a local KS potential from a given density, we follow the scheme of Chen and Stott.[10] The valence configu-

ration of group-IV atoms is s^2p^2. The electron density from a nonlocal pseudopotential calculation has spherical symmetry and is normalized to four. Given this density, the KS equations for s and p states are solved inversely, using the transformation introduced by Dawson and March.[11] The potential $V(r)$ is determined within a constant. It has the same ground-state density as the corresponding nonlocal pseudopotential. The KS potential generated in this way is the exact functional derivative of the kinetic energy, and as such has been used in developing approximate kinetic functionals.[13] A local ionic pseudopotential $V_{ps}(r)$ is constructed by subtracting the Hartree and exchange-correlation potentials from the generated local KS potential $V(r)$. For the exchange-correlation potential, we use the local-density approximation[2] with the Perdew-Zunger parametrization[14] of the results of Ceperley and Alder for a uniform electron gas.[15] The resulting local pseudopotential has the same ground-state density as the corresponding nonlocal pseudopotential. Since the local KS potential is generated within a constant, the local pseudopotential is shifted so that at large r (>18 a.u.) it coincides with the corresponding nonlocal pseudopotential.

One difficulty with the local pseudopotential $V_{ps}(r)$ is that it differs from $-4/r$ outside the core by a small oscillatory tail with roughly the range of the valence orbitals so that rV_{ps} oscillates about (-4). For C, the maximum amplitude of the tail is about 0.2, while for Si, Ge, and Sn, the amplitudes are 0.03, 0.01, and 0.03, respectively. The reason for the small deviations from $-4/r$ outside the core is that a single local pseudopotential cannot reproduce both s and p orbitals of the corresponding nonlocal pseudopotential (see below) and a compromise between the two is made outside the core. It is interesting to note that similar long-range tails have been also seen in the more sophisticated local pseudopotentials including the nearly exact exchange potential.[16,17] The small deviations from $-4/r$ caused numerical problems in the treatment of a diamond or fcc structure. As pointed out by Bylander and Kleinman,[16] there should be no long overlapping tails for ionic pseudopotentials to be transferable from atoms to solids. We therefore modify the local pseudopotential by truncating the tail at a point where V_{ps} crosses over $-4/r$. For Ge and Sn, this can be done at two points, and we found that truncating at larger r (8.35 a.u. for Ge and 5.09 a.u. for Sn) gives better results in the calculations of dimers and solids. For C and Si, the truncation is made at $r=3.19$ and 4.20 a.u., respectively. The modifications of the potentials are very small and invisible on a plot of the local pseudopotential.

III. LOCAL PSEUDOPOTENTIALS OF GROUP-IV ELEMENTS

The computer code FHI98PP developed by Fuch and Scheffler[18] was used to generate nonlocal norm-conserving, spin-averaged scalar relativistic pseudopotentials of the generalized Bachelet-Hamann-Schlüter (BHS) type[19] for group-IV elements. The electron density for the neutral pseudoatom obtained from the nonlocal pseudopotential cal-
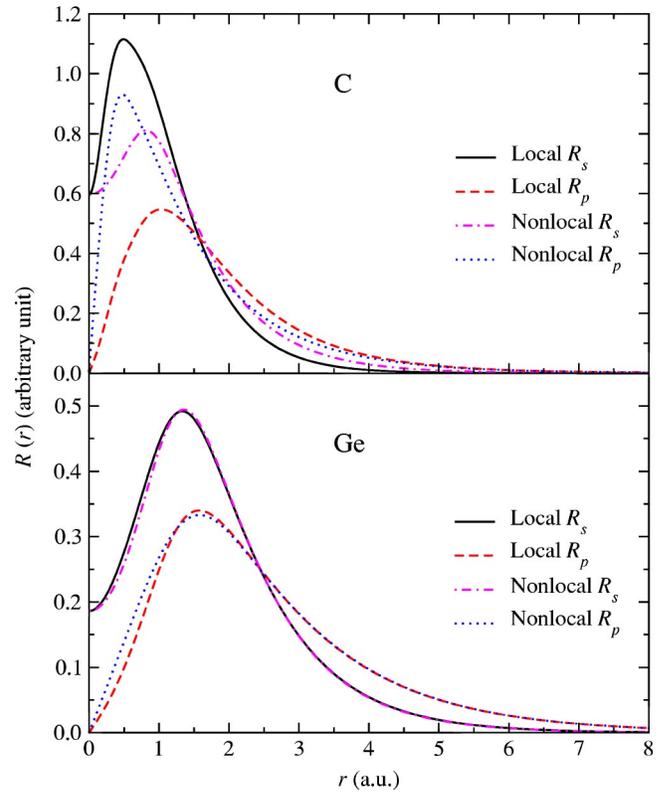

FIG. 1. The radial s and p wave functions, $R_s(r)$ and $R_p(r)$, from local and nonlocal pseudopotential calculations of C and Ge atoms.

culation is then inverted to a local pseudopotential as described above.

By construction, the generated local pseudopotential gives the same ground-state density as the corresponding nonlocal pseudopotential, so that the sum of the squares of the orbitals is the same for both sets. However, the wave functions do not coincide exactly with the nonlocal pseudo-wave-functions. As shown in Fig. 1, the most extreme case is the C atom for which there is the largest degree of nonlocality. The wave functions for the Ge atom for which very good agreement is achieved are also shown in Fig. 1. The agreement is fairly good for the wave functions of Si and Sn. Of particular interest for the group-IV elements is the degree to which a local pseudopotential can give energetically favored diamond structures which will depend on the s-p splitting. In this light a key parameter is the energy difference between the lowest s and p states, $\varepsilon = E_p - E_s$, obtained from the local KS potential. The results are given in Table I along with corre-

TABLE I. The energy difference between s and p states, i.e., $\varepsilon = E_p - E_s$ (in eV), obtained from local pseudopotential calculations compared with the results from nonlocal pseudopotential calculations.

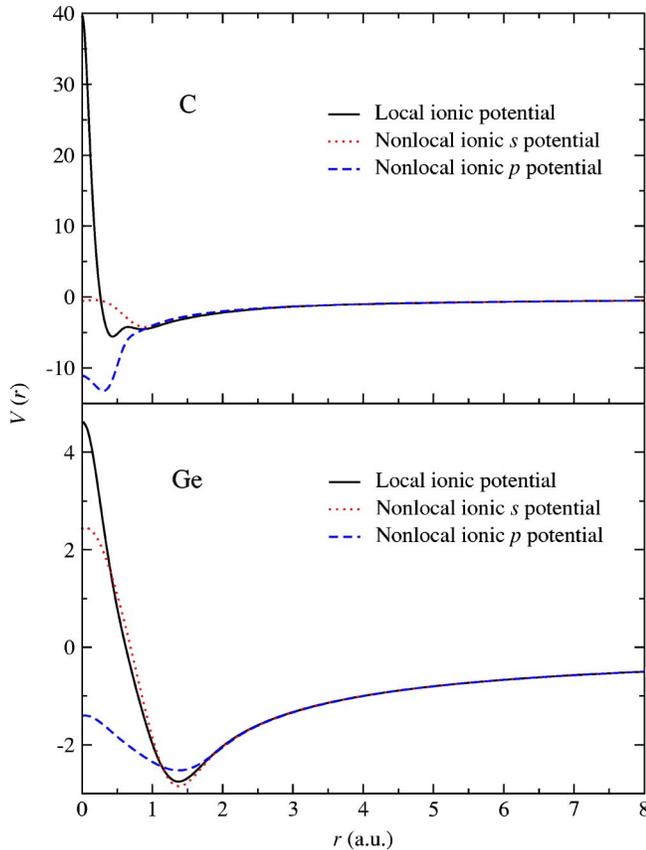|	C	Si	Ge	Sn
Local	20.009	7.692	7.589	5.671
Nonlocal	8.223	6.716	7.899	6.943

FIG. 2. The local and nonlocal ionic pseudopotentials of C and Ge.

sponding values for the nonlocal potentials, which are the same as those from all-electron calculations. The agreement is very good for Ge, and worst for C where the local results for ε is too much large.

The local pseudoion potentials for C and Ge are shown in Fig. 2 along with the corresponding nonlocal pseudopotentials. For Ge, the local pseudopotential is closest to the nonlocal s pseudopotential, and similarly for Si and Sn, although there are differences so that the local potential strikes a compromise between the s and p nonlocal potentials which yields the correct density. However, the local pseudopotential for C is rather strange. There is a large spike at the origin, and the most striking feature is the double minima at $r \approx 0.4$ and 0.9 a.u. This originates from the minima of the nonlocal s and p pseudopotentials. This double shell feature appears in the local pseudopotential of C but not Ge because for the former the minima of the nonlocal s and p pseudopotentials are well separated from each other. Compared with other group-IV atoms, a C atom has a smaller core and no p states in the core, both of which are the factors forcing small cutoff radii in generating a nonlocal pseudopotential. The cutoff radii used for C are 0.72 and 0.46 a.u. for s and p states, respectively, while the corresponding radii for Ge are 1.07 and 1.27 a.u.

Using different cutoff radii for generating the nonlocal pseudopotential has a marginal effect on the corresponding local pseudopotential. For Si, the change in ε for the local potential is less than 0.2 eV when the cutoff radii for nonlo-

cal s and p pseudopotentials vary from about 0.80 to 1.30 a.u. The cutoff radii were selected that gave the local value of ε closest to that for the nonlocal pseudopotential. For Si, a local pseudopotential was also generated from the Troullier-Martins-type nonlocal pseudopotential.[20] Again, the local value of ε does not differ much from the value obtained from the BHS-type nonlocal pseudopotential, and the generated local pseudopotential gives about the same results in the calculations of dimer and solids.

The transferability of the local pseudopotentials was first tested by calculating atomic excitation and ionization energies for a number of occupied configurations different from the reference configuration for which the local pseudopotential was generated. The errors in these energies and energy eigenvalues with respect to all-electron calculations range from a few millielectron volt to a few hundreds millielectron volt, while the corresponding errors given by nonlocal pseudopotentials and frozen-core all-electron calculations are no more than a few tens millielectron volt. Again the results for Ge are the most satisfactory, the errors in the energy eigenvalues being comparable to those given by the nonlocal pseudopotential.

IV. APPLICATION

The transferability of the local pseudopotentials generated for Si, Ge, and Sn was further tested by applying them in calculations of dimers and solids including diamond and fcc structures for each of the three elements. Instead of using our local pseudopotentials in orbital-free calculations where the results will be affected by the choice of kinetic-energy functionals, we have used a Kohn-Sham plane-wave method so that a direct comparison can be made with the results for the corresponding nonlocal pseudopotential. The results are presented and discussed in this section.

A. Computational details

The computer code ABINIT (version 3.2.3) developed by Xavier Gonze and his abinit group[21] was used in the calculations. For the diamond structure a fcc supercell was used with two symmetrically placed nonequivalent atoms per cell. The lattice constant was optimized. For the dimer, a simple cubic supercell was used with the lattice constant of 30 a.u., a single (Γ) **k** point, and a plane-wave energy cutoff $E_{cut} = 12$ a.u. In the calculation of diamond and fcc structures $E_{cut} = 24$ a.u. and $8 \times 8 \times 8 = 516$ **k** points were used. These values are more than necessary for convergence of the diamond structure, but were required for the fcc structure which is metallic. In the calculation of fcc structures, the cold smearing scheme[22] was used with the smearing factor equal to 0.06 Hartree. The convergence of the total energy and lattice constant with respect to the energy cutoff, the number of **k** points and the smearing factor in the calculations of the diamond and fcc structures was checked for Si using both local and nonlocal pseudopotentials. The convergence with the local pseudopotential is comparable to, and in some cases better than that with the nonlocal pseudopotential.

TABLE II. Results for Si, Ge, and Sn calculated using local and nonlocal pseudopotentials. Listed are: the bond length of a dimer, d_{dimer} (Å), the lattice constant of a diamond structure, a_{dia} (Å), the lattice constant of a fcc structure, a_{fcc} (Å), the ratio in the volume per atom of fcc to diamond structures, v_{fcc}/v_{dia}, and the energy difference between a fcc and a diamond structure, $\Delta E = E_{fcc} - E_{diamond}$ (eV/atom). Numbers in parentheses are the percentage errors with respect to experimental results.

	d_{dimer}	a_{dia}	a_{fcc}	v_{fcc}/v_{dia}	ΔE
Si					
Local	2.183(−2.8%)	5.301(−2.4%)	3.611	0.632	−0.17
Nonlocal	2.184(−2.8%)	5.384(−0.8%)	3.824	0.717	0.50
Experiment	2.246 [a]	5.430 [b]			
Ge					
Local	2.245	5.482(−3.1%)	4.151	0.869	0.56
Nonlocal	2.275	5.568(−1.6%)	4.189	0.851	0.43
Experiment		5.658 [b]			
Sn					
Local	2.604(−5.2%)	6.416(−1.1%)	4.960	0.924	0.46
Nonlocal	2.673(−2.7%)	6.468(−0.3%)	4.757	0.796	0.10
Experiment	2.746 [c]	6.49 [b]			

[a]Reference 23.
[b]Reference 24.
[c]Reference 25.

B. Results and discussion

The calculated bond lengths of dimers and lattice constants of diamond and fcc structures are listed in Table II for Si, Ge, and Sn, along with the corresponding values from nonlocal pseudopotential calculations. The results given by local pseudopotentials are in good agreement with both the results of nonlocal pseudopotentials and available experimental results. The discrepancies with respect to experimental values are within the typical error due to the local-density approximation. For fcc structures, our results for nonlocal pseudopotentials agree with earlier calculations for Si and Ge (Ref. 26) and the very recent calculation of Sn.[27] Figure 3 shows the total energy as a function of lattice constant for diamond and fcc structures. In all cases, the shape of the curve obtained with the local pseudopotential is very similar to the corresponding one for the nonlocal pseudopotential. The ratios of the volume per atom of fcc to diamond structures obtained by local and nonlocal pseudopotentials, given in Table II, agree fairly well with each other. However, except for Ge, the energy difference between fcc and diamond structures calculated with local pseudopotentials do not agree well with the results of nonlocal pseudopotentials; indeed for Si, the local pseudopotential wrongly gives the energy of fcc slightly lower than that of diamond.

The calculated band structures for a diamond structure at the optimized lattice constant given in Table II are shown in Figs. 4–6 for Si, Ge, and Sn, respectively. For Si, the band structure given by our nonlocal pseudopotential is in very good agreement with the published result obtained from similar calculations at the experimental lattice constant.[26] The band structure from our local pseudopotential agrees reasonably well with the one from the nonlocal pseudopotential, although there are differences in the band widths and

gaps. The agreement is best for Ge, except for the lowest unoccupied band; the local pseudopotential gives a larger gap. The nonlocal pseudopotential includes the scalar relativistic effect, which, as shown in Ref. 28, is responsible for the reduced gap in Ge. This relativistic effect, however, is not transferred to the local potential when it is inverted from the pseudoatom density. The local pseudopotential for Sn gives a poor band structure as shown in Fig. 6. Although the shape of each band is similar to that of the nonlocal pseudopotential, the band gaps are wrong. In particular, the gap between the highest occupied and lowest unoccupied bands at the Γ point is too large.

In general, our local pseudopotentials give fairly good results for bond lengths of dimers and lattice constants of solids. The results for diamond structures are better than might be expected for a local pseudopotential because of the sp hybridization involved in the formation of covalent tetrahedral bonds. However, except for Ge, the band structures of diamonds and energy differences between fcc and diamond structures do not agree well with the results given by the nonlocal pseudopotentials. It is therefore worthwhile to revisit the properties of the local pseudopotentials described in the preceding section and identify the features that lead to the results presented in this section.

The good transferability of the nonlocal pseudopotential is due to the norm conservation, i.e., it reproduces all-electron energy eigenvalues, and generates pseudo-wave-functions that are properly normalized and coincide with the corresponding all-electron wave functions outside the core. By construction, our local pseudopotential has the same ground-state density as the corresponding nonlocal pseudopotential, so that the occupied s and p local pseudo-wave-functions together, as a pair, are correctly normalized, but not
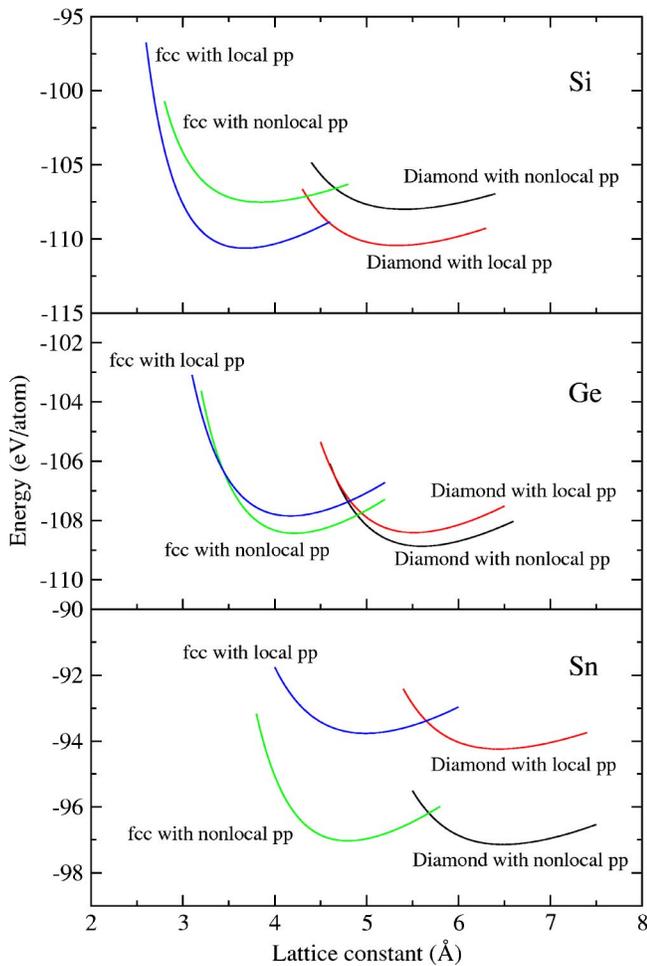
FIG. 3. The total energies of a diamond and a fcc structure as functions of the lattice constant obtained by local and nonlocal pseudopotential (pp) calculations on Si, Ge, and Sn.
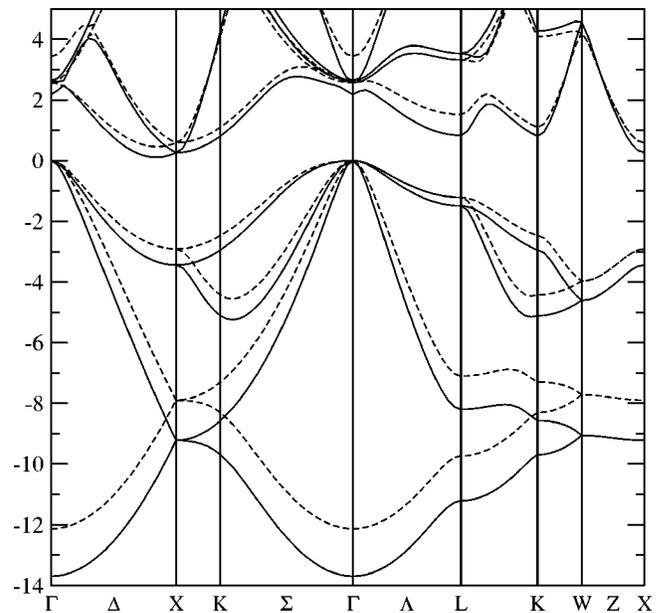

FIG. 4. The band structure of a Si diamond given by local (solid curves) and nonlocal (dashed curves) pseudopotentials. Energies are measured from the highest-occupied state.

differences and energy eigenvalues such as excitation and ionization energies and band structures.

The local bare ion pseudopotentials that we have obtained deviate slightly from $-4/r$ outside the core, and this causes numerical problems which affect the equilibrium crystal structures. We removed this tail in a rather arbitrary fashion. A systematic method for obtaining bare ion potentials which have the correct form outside the core could be based on the variational principle for the Kohn-Sham potential with the bare ion potential fixed at $-4/r$ outside the core and varying inside the core only.

individually. Consequently, the energy dependence of the s- and p-wave scattering at valence energies is incorrect. However, except for C, the local pseudo-wave-functions agree fairly well with the corresponding nonlocal pseudo-wave-functions, as seen in Fig. 1.

We also treated the dimer and the diamond structure of C using the local pseudopotential. The nonlocal pseudopotential gives fairly good results for the dimer bond length 1.29 Å and lattice constant 3.525 Å compared with the experimental value 1.24 Å[23] and 3.567 Å,[24] respectively. But, the local pseudopotential gave a -10% error in the dimer bond length and converged results for the diamond structure could not be obtained, probably because of the poor convergence of the Fourier components of the pseudopotential due to the large spike in the local pseudoion potential as $r \rightarrow 0$ (cf. Fig. 2).

As shown in Table I, the local pseudopotentials do not reproduce well the energy differences between s and p states, except for Ge. The reasonable results for bond lengths and lattice constants suggest that correct energy eigenvalues of the pseudoatom may not be critical for these properties. However, they are crucial for properties involving energy
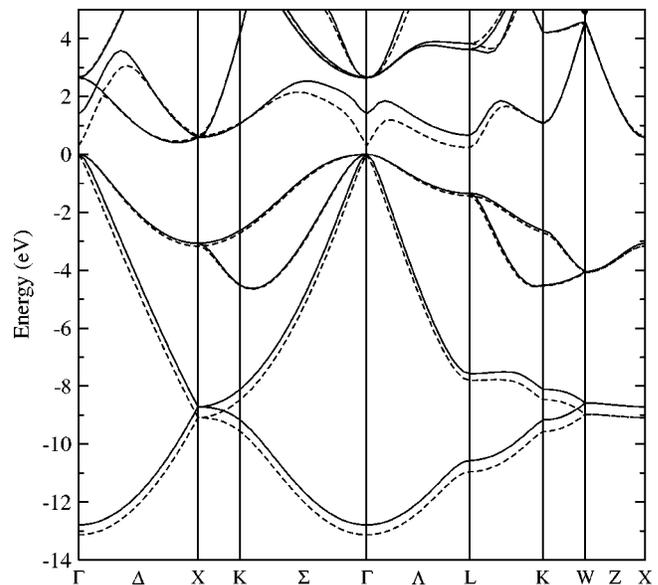

FIG. 5. The band structure of a Ge diamond given by local (solid curves) and nonlocal (dashed curves) pseudopotentials. Energies are measured from the highest-occupied state.
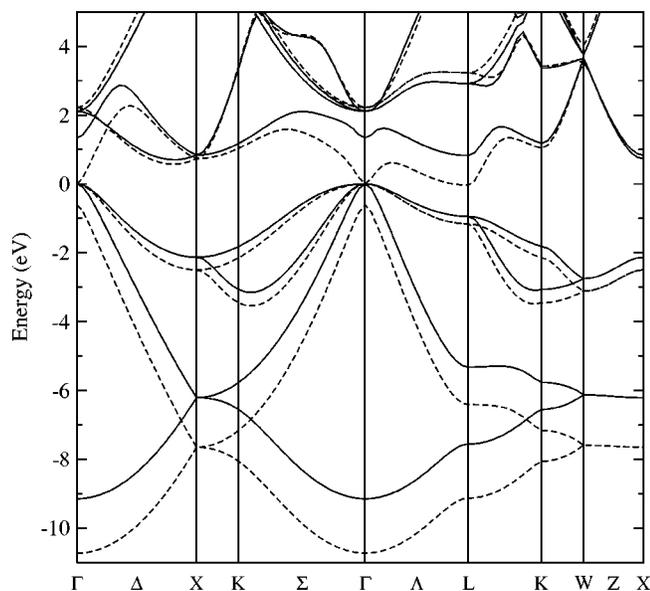
FIG. 6. The band structure of a Sn diamond given by local (solid curves) and nonlocal (dashed curves) pseudopotentials. Energies are measured from the highest-occupied state.

V. CONCLUSIONS

We have presented a simple scheme for generating first-principles local pseudopotentials of group-IV elements. The local pseudopotential is constructed from a local KS potential, which is obtained by solving KS equations inversely, using the density from a nonlocal pseudopotential calculation. The scheme for inverting an electron density to a local KS potential is applied here to group-IV elements but is not limited to these, as shown in earlier work.[10,12,13] The potential generated in this way is the local equivalent of the full nonlocal pseudopotential. The local pseudopotentials give fairly good results on bond lengths of dimers and lattice constants of solids for Si, Ge, and Sn. The results related to energies and energy eigenvalues (e.g., atomic excitation energies and band structures of solids) do not agree so well with those given by nonlocal pseudopotentials. Nevertheless, our work indicates the important features required by a good local pseudopotential for a group-IV element, namely, the properly normalized and reasonably accurate pseudo-wave-functions, the correct long-range Coulomb tail, and accurate s-p splitting. In addition, we believe the local pseudopotential for Ge presented in this work can be usefully applied in efficient orbital-free calculations, which are currently restricted to the use of local pseudopotentials, and orbital-free simulations of liquid Ge are in progress. We are also investigating the degree to which the local pseudopotential can be optimized by employing the flexibility in the nonlocal pseudopotential in the core region.

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