

## All-electron pseudopotentials

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We present an *ab initio* procedure for the construction of pseudopotentials accommodated to a crystal environment under study, which takes into account the response of the core charge density to the valence electrons of an atom in a bond. Within pseudopotential methodology, core electrons are treated differently from valence electrons; however, the core electrons are considered as “frozen” in space and independent of the atom’s valence electrons after they were relaxed and adapted to a crystal-valence charge density. In this way the frozen-core approximation is removed despite the fact that the frozen-core technique is still used and no all-electron solid-state calculation is required. Since the all-electron core-valence response is taken into account properly, the treatment of nonlinear properties of exchange-correlation functionals is naturally included and corrections using model core charges for nonlinear functionals are eliminated. Contrary to standard pseudopotentials based on the atomic charge density of a free atom, the new all-electron pseudopotentials are functionals of the crystal charge density. Consequently, the intuitive *ad hoc* choice of occupation numbers, which is necessary for the construction of pseudopotentials by existing methods, is avoided and energy windows for pseudopotentials are put at optimum positions. In this paper, core-level shifts were calculated within the pseudopotential framework. The results of test calculations for diamond, silicon, nonmagnetic fcc  $\beta$ -Co, cubic TiC, and hexagonal TiS<sub>2</sub> are presented. [S0163-1829(98)05743-9]

### I. INTRODUCTION

The density-functional scheme in the local-density approximation (LDA) coupled with a pseudopotential technique is now a standard approach successfully describing the electronic and structural properties of solid systems. Using pseudopotentials the tremendous simplification of computational effort is achieved by treating core electrons differently from valence electrons. Deep core electrons are considered as “frozen” in space and independent of the atom’s valence environment (the frozen-core approximation).

In standard techniques the frozen core and the corresponding pseudopotential are derived from the atomic calculation performed for a “suitable” occupation of atomic valence states. In this way the core and the valence states anticipating crystal environment are constructed, and by application of some pseudopotential-generating methods<sup>1–6</sup> more or less transferable pseudopotentials are generated. Additionally, particularly for magnetic materials, model core charges<sup>7,8</sup> were introduced to improve transferability from an atom to a solid by representing “unscreening” and “rescreening” processes in the derivation and in the application of pseudopotentials more accurately. At present the standard application of pseudopotentials neglects core-relaxation effects by definition.

In this paper we present a pseudopotential-generation technique that takes into account all electron (core and valence) interactions of an atom in a bond and generates an “all-electron” pseudopotential (AEPP) with the relaxed core. Within pseudopotential methodology, core electrons are treated differently from valence electrons; however, the valence states are constructed under boundary conditions reflecting the surroundings of the atom in the crystal environment and the core states are rectified to them. Therefore, both the core and valence states are self-consistently adapted to

the chemical bond. Contrary to standard pseudopotentials based on the atomic charge density, the new AEPP’s are functionals of the crystal charge density and, therefore, do not correspond to any choice of occupation numbers of any atomic configuration.

We have tested the AEPP approach for carbon, silicon, SiC, and transition metals, namely, for Co in its nonmagnetic fcc  $\beta$  phase, and for TiS<sub>2</sub> and TiC. Core-level shifts were calculated within the pseudopotential framework.

The main ideas of the AEPP method are explained in the next section. In Sec. III, the atomlike calculation (in the core region) based on the input quantities obtained from self-consistent crystal pseudo-wave-functions is described. The construction of new pseudopotentials is explained in Sec. IV. Numerical tests and applications are shown in Sec. V. In Secs. VI and VII, relations to other existing methods are discussed and main features of the present approach are summarized.

### II. ALL-ELECTRON PSEUDOPOTENTIAL METHOD

Standard procedures for constructing pseudopotentials rely on potentials and radial wave functions derived from all-electron calculations of *free* atoms. For given reference energies (which are usually equal to the eigenvalues of free-atom valence states) it is required that pseudo-wave-functions match exactly the corresponding all-electron wave functions outside a certain cutoff radius. Then, the pseudopotential is exact for the reference energies, for which it was generated. In some neighborhood of the reference energies, the pseudopotential is correct within a reasonable accuracy. Resulting pseudopotential is unscreened with nonlinear LDA exchange and correlation terms related to the valence charge density of the isolated atom.

The AEPP method is based on an iterative procedure

starting with the standard free-atom-based pseudopotential described above. The AEPP pseudopotential is adapted to the crystal environment by iterative steps. As a matter of fact, the construction of the AEPP pseudopotential needs one or two iterations and convergence is reached even in the case of the “unsuitably” chosen input pseudopotential. Computationally, this iterative procedure needs only few additional iterations usual in standard self-consistent calculations.

At the beginning, we suppose to have an all-electron potential of a free atom, in any “reasonable” configuration. “Unreasonable” input only increases the number of iterations and does not affect the final AEPP. Then, the following steps are performed: First, the pseudopotential is derived from the all-electron potential to satisfy the standard conditions, i.e., matching the value and the derivatives of both the potential and the wave functions at the cutoff radius  $R_C$  and fulfilling the normconserving condition. Any of the standard pseudopotential techniques can be used here. Second, this pseudopotential is used for the self-consistent calculation of crystal wave functions. These first two points do not differ from the usual self-consistent calculations of the charge density in a crystal. Third, radial partial charge densities, referred to as the atom of interest, are derived from the crystal wave functions. Fourth, these charge densities, outside a sphere of the pseudopotential cutoff radius  $R_C$ , are employed as boundary conditions for valence wave functions in the next all-electron atomiclike calculation. In this calculation, the boundary conditions derived from the crystal charge density replace the boundary conditions of the free atom. By that, a succeeding all-electron potential is obtained in the region  $0 < r < R_C$ , i.e., core states are recalculated and relaxed to the crystal charge density. The succeeding all-electron potential obtained by the fourth step is then used for deriving a succeeding AEPP pseudopotential along the first step. The novel feature, with respect to the standard self-consistent iterative scheme, is the additional outer iterative loop updating the pseudopotentials according to the self-consistent crystal charge densities.

For practical purposes, one to three passes through the outer iterative loop are sufficient. One should realize that the valence charge density is self-consistent at the end of the inner (i.e., standard self-consistent) loop for the first pseudopotential, and the new AEPP entering the inner loop again is new mainly for the core region. Consequently, we do not need many iterations in the inner loop during the next passes through the outer loop. Two or three runs through the outer loop totally adds 5–7 iterations through the standard inner loop to achieve self-consistency between the charge density and the pseudopotential. Therefore, the generation of the AEPP only slightly increases the number of standard valence charge iterations. The outer loop is computationally fast and can be appended to any standard pseudopotential code.

The essential feature of our approach is that the AEPP pseudopotentials are functionals of the self-consistent crystal charge density. In consequence of iterations in the outer loop, the core is self-consistent with the crystal charge density, relaxed and accommodated to the chemical environment of an atom in a solid and then frozen in the usual sense of pseudopotential methods. This frozen core does not correspond to any configuration of a free atom and cannot be derived from a free atom in principle.

As a result of the all-electron self-consistency, the refer-

ence energies of the AEPP are located in the range of solid-state eigenvalues in a natural way, and reasonable pseudopotentials for angular momentum components are provided also for the angular momentum channels that are not occupied or even do not exist as bound states in the case of free atoms. Additionally, the exchange and correlation nonlinear potential terms are taken into account properly without the necessity of the model core charge for nonlinear core-valence corrections.<sup>7</sup>

In complicated crystalline configurations where atoms of the same type at different positions have different nearest neighborhoods, the AEPP's are supposed to be generated for each nonequivalent position separately, as if the atoms were of a different type.

For simplicity of the presentation of the AEPP technique we describe the construction of generalized normconserving  $l$ -dependent semilocal AEPP's that are transformed into a separable form, subsequently. The present scheme may also be exploited differently, namely for the construction of pseudopotential waves according to the projector augmented-wave method by Blöchl,<sup>9</sup> or for the derivation of ultrasoft pseudopotentials according to Vanderbilt,<sup>10</sup> supposing that the augmentation charges are taken into account properly.

### III. ATOMICLIKE CALCULATION

In this section, we describe a procedure for the reconstruction of all-electron atomiclike quantities, related to a given atomic site, from the results of the previous pseudopotential solid-state calculation. It makes it possible to include the proper node structure of originally nodeless valence pseudo-wave-functions together with core states in a fully consistent way and to gain all-electron information from pseudopotential quantities. This procedure is analogous to that originally intended for evaluating the radiative matrix elements of Ref. 11 where some more general aspects of using the procedures of this type have been discussed.

The method is based on the following: If the pseudopotential is generated for the cutoff radius  $R_C$ , then the pseudopotential quantities match the corresponding all-electron quantities outside a sphere of radius  $R_C$  surrounding an atom, and they can be used as boundary conditions to calculate the corresponding atomiclike quantities inside the sphere. Moreover, if the pseudopotential is normconserving, then the amount of pseudocharge inside the sphere is correct, which yields a simple normalization condition for reconstructing the valence wave functions with the proper node structure.

The proper aim of doing this procedure is to derive a new pseudopotential. The pseudopotential simulates the total effect of an atomic nucleus and its core charge density upon the valence states. Because the charge density and the potential of both are spherically symmetric, all the input quantities for the pseudopotential construction are required to depend only on the distance from the nucleus. Therefore, the input quantities for the atomiclike calculation are considered to be spherically averaged, which does not introduce additional approximation. In fact, it is an approximation to the same extent as considering the effect of core electrons (described by the pseudopotential) to be spherical. This is not absolutely exact in a solid but standard in all-electron methods.

First, we construct the radial partial-valence pseudo-

charge-density by summing over all occupied states,

$$\rho_l^{\text{sps}}(r) = \sum_{k,n} \sum_{m=-l}^l \frac{1}{4\pi r^2} \int_{SPH} d\Omega d\Omega' \psi_{k,n}^*(r\hat{\mathbf{n}}) \times Y_{lm}(\hat{\mathbf{n}}) Y_{lm}^*(\hat{\mathbf{n}}') \psi_{k,n}(r\hat{\mathbf{n}}'), \quad (1)$$

where  $\psi_{k,n}$  denotes the crystal pseudo-wave-function with  $\vec{k}$  as the vector of the first Brillouin zone and a band index  $n$ . Throughout this paper, the superscript sps will be used for the spherically averaged quantities taken from a self-consistent pseudopotential calculation in a solid.

The total valence-radial pseudo-charge-density  $\rho^{\text{sps}}(r)$  is defined by the spherical average of the crystal pseudo-charge-density with respect to the chosen atomic site,

$$\rho^{\text{sps}}(r) = \frac{1}{4\pi r^2} \int_{SPH} d\Omega \rho^{\text{crystal,ps}}(r\hat{\mathbf{n}}). \quad (2)$$

Obviously,  $\rho^{\text{sps}}$  is related to  $\rho_l^{\text{sps}}$  of Eq. (1) by

$$\rho^{\text{sps}}(r) = \sum_l \rho_l^{\text{sps}}(r). \quad (3)$$

Second, another necessary input quantity that must be derived from the pseudopotential solid-state calculation is the spherical average of the electrostatic potential

$$V_{\text{es}}^{\text{sps}}(r) = \frac{1}{4\pi r^2} \int_{SPH} d\Omega V_{\text{es}}[\rho^{\text{crystal,ps}}](r\hat{\mathbf{n}}). \quad (4)$$

The angular momentum  $l$  components of the charge density  $\rho_l^{\text{sps}}(r)$  are needed up to the cutoff radius  $R_C$  so that the logarithmic derivative and the partial charge inside the sphere may be determined at  $r = R_C$ . The total radial-valence charge-density  $\rho^{\text{sps}}(r)$  and the electrostatic-potential  $V_{\text{es}}^{\text{sps}}(r)$  are relevant, for the present scheme, throughout the range  $R_C \leq r \leq R_{\text{core}}$ , where  $R_{\text{core}}$  is the “core” radius chosen so that the core charge density vanish beyond  $R_{\text{core}}$ . Now, let us describe how these solid-state quantities are used in atomic-like calculation.

In a standard LDA calculation of electronic states of an atom, one-electron radial wave functions and corresponding eigenvalues are determined in such a way that the wave functions have the proper number of nodes, they are normalizable throughout the infinite range, and normalized to given occupation numbers. From the wave functions, the charge density is evaluated. Then, the exchange and correlation potentials and, by solving the Poisson's equation, the electrostatic potential are computed, the total all-electron potential is formed, and the whole procedure starts again until stable results are reached. The present procedure differs from the standard scheme in three points: (i) the boundary conditions for the valence wave functions, (ii) the evaluation of the valence charge density, and (iii) solving the Poisson's equation.

For the present scheme, the atomic all-electron potential can be used at the starting point for the initial step. Then, the radial wave functions  $R_{E,l}(r)$  and the corresponding eigenvalues are calculated (a) for the core states in a standard way, and (b) for the valence states throughout the range  $0 \leq r$

$\leq R_C$  in such a way that the radial wave functions have the proper number of nodes within this interval and at  $r = R_C$  they satisfy the boundary condition

$$\frac{d}{dr} \ln[r R_{E,l}^{\text{val,at}}(r)] = \frac{1}{2} \frac{d}{dr} \ln[r^2 \rho_l^{\text{sps}}(r)], \quad (5)$$

which replaces the standard condition for the wave functions to be normalizable and determines the eigenvalue  $E_l$ . The normalization condition for the valence atomiclike radial wave functions is

$$\int_0^{R_C} |R_{E,l}^{\text{val,at}}(r)|^2 r^2 dr = \int_0^{R_C} \rho_l^{\text{sps}}(r) r^2 dr. \quad (6)$$

Now, let us consider the calculation of the charge density. For the core states,

$$\rho^{\text{core}}(r) = \sum n_i |R_i^{\text{core}}|^2, \quad (7)$$

as in the standard atomic calculation. However, this cannot be used for the valence states, since—owing to the boundary condition of Eq. (5)—the radial wave functions, if calculated beyond  $R_C$ , are generally divergent. Nevertheless, the charge density must be well defined with respect to determining the exchange-correlation potential for calculating the core states, although the effect of the particular shape of the charge density in the outer region upon the core functions is very slight. We define

$$\rho^{\text{val,at}}(r) = \begin{cases} \sum_l |R_{E,l}^{\text{val,at}}(r)|^2 & \text{for } r \leq R_C \\ \rho^{\text{sps}}(r) & \text{for } R_C < r \leq R_{\text{core}} \\ \rho^{\text{val,at}}(R_{\text{core}}) & \text{for } r > R_{\text{core}}. \end{cases} \quad (8)$$

The constant value of the charge density beyond  $R_{\text{core}}$  does not affect any relevant quantity except for the exchange-correlation potential for the calculation of the core wave functions that are vanishing in this region. Therefore, changing this term results in an additive shift of eigenvalues, which is not relevant to the results of further calculations.

After evaluating the total charge density  $\rho^{\text{val,at}} + \rho^{\text{core}}$ , the potential is to be calculated. The last question that should be discussed here is the calculation of the electrostatic potential  $V_{\text{es}}$ . In the present scheme, there is no boundary condition for solving the Poisson's equation in the usual way. Therefore, we make use of the linearity of this equation and split it into the core and the valence parts, solving the Poisson's equation for each part separately with different boundary conditions. We calculate the “core Hartree” potential  $V_{\text{es}}^{\text{core}}$  as a solution of the Poisson's equation with  $\rho^{\text{core}}$ , satisfying the boundary condition

$$V_{\text{es}}^{\text{core}}[\rho^{\text{core}}](r) = Q_{\text{core}}/r \quad \text{for } r > R_{\text{core}}, \quad (9)$$

denoting the core charge by  $Q_{\text{core}}$ , and the “valence Hartree” potential  $V_{\text{es}}^{\text{val}}$  as a solution with  $\rho^{\text{val,at}}$  inside the sphere of radius  $R_C$  matching the average electrostatic potential in a solid at the surface of the sphere  $V_{\text{es}}^{\text{sps}}$  defined by Eq. (4). The boundary condition for the solution inside  $R_C$  is, therefore,

$$V_{\text{es}}^{\text{val}}(R_C) = V_{\text{es}}^{\text{sps}}(R_C), \quad (10)$$

and we define, consistently with Eq. (8)

$$V_{\text{es}}^{\text{val}}(r) = \begin{cases} V_{\text{es}}^{\text{sps}}(r) & \text{for } R_C < r \leq R_{\text{core}} \\ V_{\text{es}}^{\text{val}}(R_{\text{core}}) & \text{for } r > R_{\text{core}}. \end{cases} \quad (11)$$

Finally, we evaluate the total potential

$$V^{\text{at}}(r) = -\frac{Z_N}{r} + V_{\text{es}}^{\text{core}}[\rho^{\text{core}}](r) + V_{\text{es}}^{\text{val}}[\rho^{\text{val,at}}](r) + V_{\text{xc}}[\rho^{\text{core}} + \rho^{\text{val,at}}](r), \quad (12)$$

and the next run of the iterative loop of the atomiclike calculation can start. A stable, self-consistent all-electron potential  $V^{\text{at}}$  is supposed to be reached before constructing the pseudopotential by the procedure described in the next section.

At this point, it should be noted that the boundary condition for the valence electronic states of Eq. (5) cannot be simulated by a particular choice of atomic-valence configuration, since the shape of the valence wave functions for  $r > R_C$  has no meaning in the present scheme. Therefore, the resulting all-electron potential  $V^{\text{at}}(r)$  does not correspond to any particular set of atomic valence occupation numbers generally.

#### IV. CONSTRUCTION OF THE PSEUDOPOTENTIAL

Using the self-consistent results of the previous atomiclike calculation, the procedure that generates pseudopotential is performed. In particular, for a given cutoff radius  $R_C$ , each component  $V_l^{\text{scr}}(r)$  of the screened pseudopotential and each corresponding pseudo-wave-function are generated in such a way that the following three conditions are fulfilled.

(i) At  $r = R_C$  the potential  $V_l^{\text{scr}}(r)$  matches the all-electron potential up to the second derivative,

$$\frac{d^{(i)}}{dr^{(i)}} V_l^{\text{scr}}(r) = \lim_{r \rightarrow R_C^-} \frac{d^{(i)}}{dr^{(i)}} V^{\text{at}}(r) \quad \text{for } i=0,1,2. \quad (13)$$

(ii) At  $r = R_C$  radial pseudo-wave-functions  $R_{E_l,l}^{\text{ps}}(r)$  match the corresponding atomiclike radial functions by their values and first derivatives,

$$\frac{d^{(i)}}{dr^{(i)}} R_{E_l,l}^{\text{ps}}(r) = \lim_{r \rightarrow R_C^-} \frac{d^{(i)}}{dr^{(i)}} R_{E_l,l}^{\text{val,at}}(r) \quad \text{for } i=0,1. \quad (14)$$

(iii) The correct energy derivative of the pseudo-wave-function is ensured by the norm-conserving condition,

$$\int_0^{R_C} |R_{E_l,l}^{\text{ps}}(r)|^2 r^2 dr = \int_0^{R_C} |R_{E_l,l}^{\text{val,at}}(r)|^2 r^2 dr. \quad (15)$$

Equations (6) and (15) imply the same normalization of subsequent pseudopotentials in the iterative loop. We define the pseudo-charge-density for  $r \leq R_C$ ,

$$\rho^{\text{ps}} = \sum_l |R_{E_l,l}^{\text{ps}}(r)|^2. \quad (16)$$

It should be noted that the continuity of the potential and its derivatives up to the second order implies the continuity of the higher derivatives of the radial pseudo-wave-function, too. The reference energies  $E_l$  of the pseudo-wave-function (i.e., its eigenvalue with respect to the corresponding potential) are identical with the eigenvalues of the previous atomiclike calculation. From Eqs. (14), (16), and (8) it follows that

$$\rho^{\text{ps}}(R_C) = \rho^{\text{val,at}}(R_C). \quad (17)$$

The complete ionic pseudopotential, like in standard approaches, is derived by subtracting the electrostatic and the exchange-correlation potentials related to the valence pseudo-charge-density from the screened pseudopotential. We treat this procedure in two cases separately.

For  $r \leq R_C$ , the ionic pseudopotential is determined by

$$V_l^{\text{ion}}(r) = V_l^{\text{scr}}(r) - V_{\text{es}}[\rho^{\text{ps}}](r) - V_{\text{xc}}[\rho^{\text{ps}}](r). \quad (18)$$

The Poisson equation for  $V_{\text{es}}$  is solved inside the sphere of the radius  $R_C$  with the boundary condition analogous to Eq. (10),

$$V_{\text{es}}[\rho^{\text{ps}}](R_C) = V_{\text{es}}^{\text{sps}}(R_C). \quad (19)$$

Outside the sphere of the radius  $R_C$ , the local ionic potential  $V_{\text{loc}}^{\text{ion}}$  is constructed directly, supposing that all the pseudoquantities match the all-electron atomiclike corresponding quantities beyond  $R_C$ . By this procedure, boundary-condition problems of Poisson's equation are avoided. For  $r > R_C$  we define

$$V_{\text{loc}}^{\text{ion}}(r) = V_{\text{es}}^{\text{core}}[\rho^{\text{core}}](r) - \frac{Z_N}{r} + V_{\text{xc}}[\rho^{\text{core}} + \rho^{\text{val,at}}](r) - V_{\text{xc}}[\rho^{\text{val,at}}](r). \quad (20)$$

Beyond  $R_{\text{core}}$ , since the boundary condition for the first term is determined by Eq. (9), and  $\rho^{\text{core}}$  vanish, the asymptotic behavior is

$$V_{\text{loc}}^{\text{ion}}(r) = (-Z_N + Q_{\text{core}})/r. \quad (21)$$

Equations (13), (12), (10), (19), and (17) imply the continuity of the ionic pseudopotential at  $R_C$ , namely,

$$V_l^{\text{ion}}(R_C) = \lim_{r \rightarrow R_C^+} V_{\text{loc}}^{\text{ion}}(r) \quad (22)$$

for each  $l$ . The final  $l$ -dependent semilocal pseudopotential

$$V_l(r) = \begin{cases} V_l^{\text{ion}}(r) & \text{for } r \leq R_C \\ V_{\text{loc}}^{\text{ion}}(r) & \text{for } r > R_C \end{cases} \quad (23)$$

is applicable in the standard manner. For the efficient evaluation of the Hamilton matrix elements, a separable form is derived by the method of Kleinman and Bylander,<sup>12</sup> or by Blöchl's method,<sup>13</sup> which is more reliable concerning ghost states. Alternatively, pseudopotentials can be described by a linear combination of error functions and Gaussian functions,<sup>2</sup> which allows an analytic calculation of the non-local pseudopotential components.

TABLE I. Comparison of the AEPP and FPA eigenvalues. For each element and structure (specified in the first column), the AEPP is constructed and applied to the pseudoatom with a test configuration of valence occupation numbers (the second column). In remaining columns the differences between AEPP and FPA eigenvalues (in brackets relative differences in %) are given. For tests and comparison with ground-state configurations we used also ionic configurations used by other authors.

Atom—structure	Test configuration	$\Delta\varepsilon = \text{AEPP pseudoatom} - \text{full-potential atom (eV)}$					
		2s		2p		3d	
C — diamond	$s^2p^2d^0$	-0.100	(-0.7%)	0.087	(1.6%)	-0.005	(-0.5%)
	$s^{1.75}p^2d^{0.25}$	-0.113	(-0.7%)	0.101	(1.3%)	-0.001	(-0.6%)
C — SiC	$s^2p^2d^0$	-0.133	(-1.0%)	0.098	(1.8%)	-0.006	(-0.6%)
	$s^{1.75}p^2d^{0.25}$	-0.153	(-1.0%)	0.115	(1.5%)	-0.001	(-0.8%)
C — TiC	$s^2p^2d^0$	0.021	(0.2%)	-0.036	(-0.7%)	0.002	(0.2%)
	$s^{1.75}p^2d^{0.25}$	-0.001	(-0.0%)	-0.044	(-0.6%)	0.000	(0.2%)
		3s		3p		3d	
Si — diamond	$s^2p^2d^0$	0.037	(0.3%)	0.051	(1.2%)	-0.005	(-0.7%)
	$s^1p^{1.5}d^{0.5\text{ a}}$	-0.073	(-0.3%)	0.052	(0.4%)	0.055	(1.2%)
Si — SiC	$s^2p^2d^0$	0.038	(0.3%)	0.044	(1.1%)	-0.005	(-0.6%)
	$s^1p^{1.5}d^{0.5\text{ a}}$	-0.005	(-0.0%)	0.057	(0.4%)	0.044	(0.9%)
Si — CoSi <sub>2</sub>	$s^2p^2d^0$	0.043	(0.4%)	0.051	(1.2%)	-0.005	(-0.7%)
	$s^1p^{1.5}d^{0.5\text{ a}}$	-0.086	(-0.4%)	0.038	(0.3%)	0.066	(1.4%)
		3d		4s		4p	
Co — fcc $\beta$ -Co	$d^7s^2p^0$	-0.316	(-3.5%)	-0.031	(-0.6%)	0.007	(0.5%)
	$d^7s^1p^{0.25\text{ b}}$	-0.407	(-2.6%)	-0.080	(-0.7%)	-0.031	(-0.5%)
Co — CoSi <sub>2</sub>	$d^7s^2p^0$	-0.423	(-4.7%)	-0.037	(-0.7%)	-0.004	(-0.3%)
	$d^7s^1p^{0.25\text{ b}}$	-0.487	(-3.1%)	-0.078	(-0.7%)	-0.050	(-0.8%)
		3d		4s		4p	
Ti — TiC	$d^2s^2p^0$	0.101	(2.1%)	-0.006	(-0.1%)	-0.032	(-2.0%)
	$d^2s^1p^{0.25}$	0.166	(1.6%)	0.022	(0.2%)	-0.050	(-0.9%)
Ti — TiS <sub>2</sub>	$d^2s^2p^0$	0.099	(2.1%)	-0.024	(-0.5%)	-0.038	(-2.4%)
	$d^2s^1p^{0.25}$	0.140	(1.4%)	-0.015	(-0.2%)	-0.082	(-1.5%)

<sup>a</sup>See Ref. 25.

<sup>b</sup>See Ref. 16.

## V. NUMERICAL TESTS AND APPLICATIONS

Since the primary objective of test calculations is to verify the AEPP method, a considerable effort has been made to produce the results that are rid of uncertainties due to basis set and numerical precision, and special care has been taken to achieve fully convergent results. For the construction of the radial atomiclike wave functions and the pseudopotentials satisfying the conditions of Eqs. (13)–(15), the phase-shift technique<sup>6</sup> has been applied. The Ceperley-Alder term has been used for exchange and correlation potentials.

### A. Transferability tests

The resulting AEPP derived from crystal charge densities do not correspond to any atomic configuration, therefore, we at first tested the AEPP in free-pseudoatom calculations. We derived AEPP for different crystals and applied them to the calculations of eigenvalues of the pseudoatoms having various atomic valence configurations. For the same valence configurations we performed standard full-potential atomic (FPA) calculations. The differences between the AEPP and the FPA eigenvalues are shown in Table I.

In this table, the positive energy differences indicate the lower binding energies of the AEPP compared to the FPA. In

the tetrahedrally bonded diamond the differences are negative for 2s and positive for 2p electrons as expected for the  $sp^3$  bond. We observe the same for silicon. Moreover, the better the agreement between the AEPP and the ionic FPA justifies the ionic configuration for generating the standard pseudopotential of Si. The ionic configuration is better also for cobalt and titanium atoms, especially for 3d electrons.

The results show that for “simple” carbon and silicon atoms the differences are small for any physically reasonable valence configuration. On the other hand, we see that the “problematic” d states in transition-metal atoms exhibit the biggest differences between the AEPP and the FPA results.

To summarize the results presented in this section, we conclude that the AEPP's, derived from crystal charge densities and optimized for use in a solid, have reproduced the eigenvalues of free atoms with a reasonable accuracy. This fact illustrates that the standard transferability of pseudopotentials from an atom to a crystal can be reversed, i.e., our AEPP's are transferable from a crystal to free atoms.

### B. Total-energy tests

According to the scheme described in previous sections, we generated AEPP's for C, Si, and Co atoms from diamond,

TABLE II. Lattice constants and bulk moduli calculated with pseudopotentials derived from the ground-state atomic configuration, calculated with the AEPP's, and taken from an experiment.

	Lattice constant (Å)			Bulk modulus (GPa)		
	ground <sup>a</sup>	present	experiment	ground <sup>a</sup>	present	experiment
silicon	5.37	5.41	5.43	101	95.7	98
diamond	3.48	3.52	3.57	445	440	440
fcc $\beta$ -Co	3.49	3.41	3.38 <sup>b</sup>	313	308	310 <sup>b</sup>
TiC	4.18	4.29	4.32	515	239	242

<sup>a</sup>As ground-state configurations,  $(3s^2, 3p^2)$ ,  $(2s^2, 2p^2)$ ,  $(4s^2, 4p^0, 3d^7)$ , and  $(4s^2, 4p^0, 3d^2)$  were used for Si, C, Co, and Ti, respectively.

<sup>b</sup>For fcc  $\beta$ -Co, values calculated by means of the FLAPW method (Ref. 15) are given instead of the experimental values. Results of the pseudopotential calculation by Milman *et al.* (Ref. 16), using the pseudopotential derived from a free atom in the ionic configuration  $(s^1 p^{0.25} d^7)$ , are 3.45 Å and 296 GPa, respectively.

silicon, and fcc-Co crystals, and for Ti and C atoms from TiC crystal. Using these AEPP's we performed standard total-energy calculations<sup>14</sup> for various lattice constants and calculated the structural properties of crystals by fitting the Murnaghan-Birch equation of state to the calculated points. Resulting lattice constants and bulk moduli are presented in Table II. For comparison, corresponding values calculated from standard pseudopotentials derived from free atoms in the ground-state configurations and experimental values are given.

The fact that AEPP's are derived from the previous calculation of electronic states in a crystal that presumes the choice of a lattice constant (the experimental value in this case) could cast doubt on the *ab initio* quality of the results presented here. In Sec. V D, the sensitivity of AEPP's with respect to the choice of the lattice constant is tested.

The results in Table II show that even for simple materials, e.g., for diamond and silicon, where  $d$  states are not significant (however, included in all calculations), the agreement with an experiment is better than for the pseudopotentials derived from the ground-state configuration of free atoms. In the case of the fcc  $\beta$ -Co, the AEPP results are in better agreement with full-potential linearized augmented plane wave (FLAPW) calculations<sup>15</sup> than with the pseudopotential calculations based on the *ad hoc* atomic configuration by Milman *et al.*<sup>16</sup> The results for TiC show that the bulk modulus provided by "ground-state" pseudopotentials is more than 100% off the experiment. It is quite understandable since the ground-state configuration of the Ti atom does not contain  $p$  electrons, the accurate description of which is necessary for the slightly ionic Ti-C bonds along  $x$ ,  $y$ , and  $z$  directions in the cubic (NaCl) structure of TiC. On the other hand, in the close-packed fcc structure of cobalt  $p$ -like states do not play an important role, which explains the reasonable results of the atomic ground-state configuration in this case.

### C. Core relaxation effects: Core-level shifts in SiC

In the silicon crystal, all silicon atoms are tetrahedrally bonded to four Si atoms, and this chemical environment determines the energy positions of the core levels of the silicon atom. The situation is identical for carbon atoms in diamond. However, in the SiC crystal, silicon atoms are tetrahedrally bonded to four carbon atoms and vice versa. The electronic

valence charges of the Si and also the C atoms are different than in Si and C crystals due to the charge transfer from the silicon atom to the carbon atom in SiC. The decrease in the atomic charge in the Si atom yields to an increase in the binding energy of the core levels in the silicon atom. The increase in the case of the carbon atom yields to a decrease in the binding energy of the core  $1s$  level of the carbon atom. Consequently, the core levels of Si and C atoms in SiC are shifted with respect to the same levels in pure silicon and diamond crystals (core-level shifts).

The essential feature of the AEPP's is that core states are relaxed and accommodated to the chemical environment of an atom in a solid. Therefore, two AEPP's of silicon, one derived from the silicon crystal and the second from the SiC crystal, have two different cores with different core levels. The differences between corresponding core-level energies determine the core-level shifts of Si. The same holds for two AEPP's of carbon, one derived from diamond, the second from the SiC crystal.

The core-levels and the valence-band spectra of amorphous tetrahedrally bonded  $\text{Si}_{1-x}\text{C}_x$  ( $0 \leq x \leq 1$ ) were measured by Fang and Ley.<sup>17</sup> From the photoemission measurement, the authors derived the values  $-1.43 \pm 0.07$  eV and  $1.20 \pm 0.07$  eV for the core shifts of the C  $1s$  and Si  $2p$  levels, respectively. Our calculations described above yield values  $-1.49$  eV for C  $1s$  and  $1.63$  eV for Si  $2p$ .

Standard pseudopotential calculations neglect core-relaxation effects by definition. By this example, we demonstrate that this restriction is removed by the AEPP's and that the relaxation of cores can be quantitatively treated within the pseudopotential approach.

### D. Sensitivity of the AEPP's to the input data

The resulting AEPP's are determined by the structure, the lattice constant, and the cutoff radius  $R_C$ . The cutoff radius  $R_C$  is a fairly insensitive parameter within a wide range of reasonable values. In our calculations, as an optimum convenient choice leading to reasonably soft pseudopotentials, the cutoff radius has been determined by the condition that total pseudocharge inside the sphere of radius  $R_C$  is equal to the valence charge (number of valence electrons) of the pseudopotential. For C, Si, and Co, and for Ti and C in TiC, the resulting  $R_C = 1.81, 2.76, 2.53, 2.7$ , and  $2.1$  a.u., respectively. For the

first iterative step, the superposition of atomic-valence charge densities can be used instead of the crystal pseudopotential. But, in our tests, changing the condition for the valence charge inside  $R_C$  from 100% to 70% had no meaningful influence on fully converged results (except for the size of the basis set that can be affected). There is no restriction for  $R_C$  with respect to the atom's own core states that are treated properly for  $R_C$  inside the core region as well as for large  $R_C$  in the region where the core charge density has vanished. The spheres of radii  $R_C$  of neighboring atoms can slightly overlap (what inevitably happens if  $R_C$  is determined by 100% of the valence charge) on the condition that no sphere is interfering deeply in core regions of neighboring atoms. Possible inaccuracy can arise only if the pseudowave-functions differ from the all-electron wave functions in the region of the overlap. In the presented test calculations it is not the case since the pseudopotential generating technique that we use ensures the continuity of wave functions up to the fourth derivative at  $R_C$ , which decreases the real "effective cutoff radius" for which the difference between pseudoquantities and the corresponding all-electron quantities is negligible.

The experimental value of the lattice constant and the crystal structure has been used for the construction of the AEPP's in the tests described previously in Secs. V A, V B, and V C. The natural question is, how sensitive is the AEPP with respect to the value of the lattice constant and to the corresponding crystal charge density that is used for constructing the AEPP via boundary conditions at  $R_C$ .

To answer this question, we performed the iterative calculations described as follows: At first the charge density in a crystal, using a lattice constant  $a^0$  and pseudopotentials derived from free atoms, has been calculated. Employing this charge density, the AEPP  $V[a^0]$  has been derived. Then, using standard total-energy calculations, the minimum energy (equilibrium) lattice constant  $a_{eq,0}^1$  has been determined. The notation indicates that  $a_{eq,0}^1$  is based on the  $V[a^0]$  pseudopotential. In the next iterative step, i.e., for deriving the new AEPP, the charge-density distributions related to this equilibrium lattice constant  $a_{eq,0}^1$  have been used. With the new pseudopotential  $V[a_{eq,0}^1]$ , the new equilibrium lattice constant  $a_{eq,1}^2$  has been found. Employing the new charge distribution related to  $a_{eq,1}^2$ , the new pseudopotential  $V[a_{eq,1}^2]$  has been derived and used for the new total-energy calculation. In this way, the series of equilibrium lattice constants  $\{a_{eq,i-1}^i\}$  and of pseudopotentials  $V[a_{eq,i-1}^i]$  has been found. The purpose of these calculations was (i) to study the sensitivity of the pseudopotentials to the lattice constants used in the preceding steps, and (ii) to verify whether the iterative scheme described above creating the series of "self-constructing" pseudopotentials  $V[a_{eq,i-1}^i]$  converges to a meaningful lattice constant and bulk modulus.

The numerical tests show that starting from the experimental  $a^0$  the only relevant change, if any, between subsequent terms in the series of pseudopotentials  $V[a_{eq,i-1}^i]$  was detected during the first iterative step, i.e., from  $V[a^0]$  to  $V[a_{eq,0}^1]$ . Even this change is small compared to the difference between the  $V[a^0]$  and the atomic ground-state-based pseudopotential.

All the tests show that the sensitivity of pseudopotential  $V[a^i]$  with respect to lattice constant  $a^i$  is negligible on condition that the lattice constant  $a^i$  is not far (a few percent) from the equilibrium value  $a_{eq,i-1}^i$ . Since the LDA equilibrium value  $a_{eq,i-1}^i$  is different from the experimental value only by a few percent, a value near the experimental lattice constant is a quite satisfactory input for the construction of the AEPP's.

By enlarging the starting lattice constant,  $V[a^0]$  approaches the standard free-atom based pseudopotential, since it corresponds to the AEPP generated for an infinite lattice constant (i.e., for noninteracting atoms). Even if the starting lattice constant is significantly larger than the equilibrium value (or infinite, which is equivalent to deriving  $V[a^0]$  from a free atom), the convergency is usually very fast since the free-atom based pseudopotentials do not lead to completely wrong lattice constant  $a_{eq,0}^1$  in most cases.

The laborious test calculations via "self-constructing" AEPP's (SCAEPP's) described above confirm that the series of SCAEPP's  $\{V[a_{eq,i-1}^i]\}$  (and, therefore, the series of the lattice constants  $\{a_{eq,i-1}^i\}$ ) converges. The limit values of the converged lattice constants and bulk moduli are the same as the values presented in Table II within the accuracy of the presented digits. Also, the tests confirm that the iterative calculation of the limit of SCAEPP's is not needed for the practical use.

The last input parameter in the present scheme for constructing pseudopotentials is a crystal structure. In order to study the "geometry effect" we applied our scheme for the determination of titanium pseudopotential from two different compounds: TiC and TiS<sub>2</sub>. These compounds differ in the structure (cubic vs hexagonal, respectively), interatomic distance (2.16 vs 2.42 Å), and the symmetry of the charge distribution around titanium atoms (0.133, 0.216, and 0.528 vs 0.106, 0.150, and 1.504 electrons for *s*, *p*, and *d* *l*-projected partial charges within the sphere of radius 2.16 Å, respectively). At the end of TiC and TiS<sub>2</sub> calculations we obtained two AEPP's for Ti. Both reproduce correct eigenvalues used for the free-pseudoatom calculation (see Table I). However, the amounts of the *s*, *p*, and *d* partial charges are different in these pseudoatoms. It corresponds to the fact that the local symmetry of the valence charge in the TiC and TiS<sub>2</sub> differs. This indicates that the "geometry effect" is not negligible for the AEPP of Ti. The AEPP technique reflects the changes in the angular momentum character of electron states of the Ti atom in the bond and accommodates them for the required nonspherical application. This accommodation is important particularly for transition-metal elements, and as a consequence, the "most suitable" atomic configurations for creating Ti pseudopotentials by means of standard free-atom-based techniques should be different for pseudopotentials dedicated for Ti in TiC and for Ti in TiS<sub>2</sub>.

In the case of TiS<sub>2</sub> we have studied occupied and unoccupied states by means of a polarized x-ray absorption. For calculating the spectra, the accuracy in the angular momentum character of the electronic states is crucial, particularly for *p* states, since the *p* states of titanium are created by the sulfur-titanium bond, and the dipole transition rule selects these states in the case of the Ti *K* spectra. The test calculation was done using three types of pseudopotentials: the

pseudopotentials derived from ground-state configurations of free atoms, the standard pseudopotentials<sup>2</sup> that are based on ionic configurations, and the AEPP's. In the first case, the resulting density of states for occupied electronic states was in good agreement with other calculations, but the Ti *K* absorption spectrum was in disagreement with the experiment. In the second case, the BHS pseudopotentials led to results similar to LMTO band-structure calculations of Wu *et al.*<sup>18</sup> that are also in poor accordance with the experiment. On the other hand, the calculations based on the AEPP's of Ti and S give practically the same results as the FLAPW calculations,<sup>19</sup> and a good agreement between the calculated Ti *K* absorption spectrum and the experiment in the energy range up to 25 eV above Fermi level (x-ray absorption near-edge structure region). In detail, these results have been described in Ref. 20.

## VI. RELATIONS TO EXISTING METHODS

The present approach described in Secs. III and IV is not bound to a particular pseudopotential-generating technique. Besides the phase-shift technique, other techniques—such as those of Refs. 4 and 5—could be used as well, as long as the conditions of Eqs. (13)–(15) are ensured. Also, the ultrasoft pseudopotential scheme<sup>10</sup> can be used in combination with the present approach. Relaxation of the generalized norm-conserving constraint  $Q_{i,j}=0$  does not cause any change in the procedure described above, except for Eqs. (2) and (6), where the augmentation charges  $Q_{i,j}$  must be taken into account.

Relations to other approaches closing the gap between pseudopotential and all-electron methods should be mentioned. In this respect, we consider (i) the methods using solid-state all-electron calculations to construct pseudopotentials,<sup>21–23</sup> and (ii) Blöchl's projector augmented-wave method (PAW).<sup>9</sup>

Contrary to the methods in (i), the present approach does not require a preceding all-electron calculation. This could save computational expenses, if the self-consistent pseudopotential iterative loop of the present scheme is performed in combination with relaxing the structure or other calculations. Additionally, the present scheme is not affected by restrictions and/or difficulties of any particular all-electron method, e.g., those related to orthogonality of eigenvectors or large energy differences between core and valence states (see, e.g., Ref. 24).

Parallel features can be found between the PAW method and the present approach. However, the following essential differences should be mentioned: (a) In the present approach, the whole solid-state calculation is performed using a simple plane-wave basis set; no partial waves derived from an isolated atom are needed. (b) Frozen core is relaxed and accom-

modated to the system under study; however, the technical advantages of the frozen-core approximation are retained. (c) The relation between the pseudo- and the all-electron quantities is more complicated in the present approach than in the PAW method, where the parallel basis sets for all electron and pseudo-Hilbert spaces have been introduced. In the present approach, the transformation between the all-electron quantities and the corresponding pseudopotential quantities is dependent on the particular pseudopotential-generating scheme and the reconstruction scheme.

## VII. SUMMARY

The present pseudopotentials are self-consistently derived from radial partial charge densities referred to the atom of interest that interacts with other atoms in a solid. Different from the standard procedures that construct pseudopotentials and pseudo-wave-functions satisfying boundary conditions of a *free* atom, we use boundary conditions determined by the self-consistent solid-state calculation of the electronic structure. By a completely *ab initio* procedure, within a pseudopotential framework, (1) the intuitive *ad hoc* choice of valence occupation numbers, which is necessary for the construction of pseudopotentials by existing methods, is avoided; (2) the all-electron core response is taken into account properly, i.e., the frozen-core approximation is avoided; (3) the nonlinear core-valence exchange-correlation term is treated correctly since the ionic pseudopotential is unscreened with the correct valence charge density, and, therefore, any other (e.g., a model core charge) approximations of it are avoided; and (4) optimum locations for the energy windows, i.e., the energy transferability ranges for pseudopotentials, are found in a natural way.

The applications of the AEPP's, e.g., for calculating total energies, forces, and stress tensors, are not affected and are the same as in the case of standard pseudopotentials. The procedures for reconstructing the all-electron wave functions in the core region and for generating AEPP's are not computationally expensive and can be used in standard pseudopotential packages.

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