PHYSICAL REVIEW B VOLUME 22, NUMBER 2 15 JULY 1980

Spin-dependent correlated atomic pseudopotentials

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(Received 26 November 1979)

The previously developed first-principles density-functional (nonlocal) atomic pseudopotentials are extended to include explicit spin effects as well as electronic correlation effects beyond the local-spin-density (LSD) formalism. Such angular-momentum–and spin-dependent pseudopotentials enable the extension of pseudopotential applications to study magnetic problems (e.g., transition-metal and other open-shell impurities in solids, ferromagnetic surfaces, etc.). As the spurious electronic self-interaction terms characterizing the LSD energy functional are self-consistently removed, these pseudopotentials can also be used to calculate reliably localized electronic states (e.g., deep defect levels, surface and interface states, narrow-band states in solids, etc.). Applications to atoms show that this pseudopotential method removes many of the anomalies of the LSD approach, including the systematically high total energy, the failure to predict the stability of negative ions, the lack of correlation between orbital energies and observed ionization potentials, and the erroneous ordering of *s* and *d* levels of the 3*d* transition elements Sc to Fe in their $d^{n-1}s^1$ configuration.

I. INTRODUCTION

In this paper, I show how the recently developed density-functional first-principles atomic pseudopotentials can be generalized to include spin-polarization and self-interaction cancellation effects. Such generalized potentials permit the extension of the pseudopotential techniques to treat magnetic problems as well as localized electronic states.

Although pseudopotentials have been very successful in describing the electronic properties of systems as diverse as bulk semiconductors, surfaces and interfaces of metals and semiconductors,[1] and cohesive properties of solids,[2] practically all applications have been restricted to nonmagnetic phenomena. The development of a pseudopotential approach to magnetism holds the potential of attacking problems such as surface properties of ferromagnetic materials, transition-metal and general open-shell impurities and defects in semiconductors, spin-density waves and magnetic phase transitions in compounds, calculation of spin densities in solids, and many others.

Pseudopotential and all-electron methods that use, in one form or another, the local-density-functional (LDF) approach[3] to describe electronic screening tend grossly to misrepresent localized electronic states: Relative to experiment, the one-electron energies of these states are too high;[4,5] they produce exchange energies that are too low[5] (10%–15%) and correlation energies that are too high[5] (100%–200%). Recently,[6-8] a simple generalization of the spin-density formalism has been suggested that overcomes these problems systematically by self-consistently removing the spurious self-interaction terms from the LDF energy functional. I show here how these self-interaction corrections can be incorporated into atomic pseudopotentials. This will enable the extension of pseudopotential applications to systems where itinerant and localized states coexist in similar energy regions, such as deep impurities in solids, localized surface and interface states, Mott insulators, etc.

In Sec. II, I discuss the scope of the present approach in the context of the existing pseudopotential methods: the empirical, semiempirical, and first-principles pseudopotential approaches. In Sec. III, the method of obtaining spin-dependent pseudopotentials (III A) and self-interaction–corrected pseudopotentials (III B) is outlined. Sections IV A and IV B describe, respectively, applications for these two classes of pseudopotentials.

II. PSEUDOPOTENTIALS AND THE SCOPE OF THE PRESENT STUDY

Consider a many-electron system with an electronic density matrix $\rho(\vec{r},\vec{r}\,')$, interacting with an external potential $V_{\text{ext}}(\vec{r})$. The conventional *all-electron* (ae) approach, treating both core (c) and valence (v) states on the same footing, represents the effective one-body-like potential for the system as a sum of the external potential and the interelectronic response ("screening")

$$V_{\text{eff}}^{\text{ae}} = V_{\text{ext}}(\vec{r}) + V_{\text{scr}}^{\text{c,v}}(\rho(\vec{r},\vec{r}\,')) . \tag{1}$$

Here $V_{\text{scr}}^{\text{c,v}}(\rho(\vec{r},\vec{r}))$ is a functional of the total core plus valence electronic density $\rho = \rho^{\text{c}} + \rho^{\text{v}}$ and includes the interelectronic Coulomb repulsion $V_{\text{ee}}^{\text{c,v}}(\rho(r))$ as well as exchange $V_x^{\text{c,v}}(\rho(\vec{r},\vec{r}\,'))$ (e.g., the Hartree-Fock approximation) and possibly correlation $V_c^{\text{c,v}}(\rho(\vec{r},\vec{r}\,'))$ terms (e.g., the density-functional approximation[3]). The external potential

$V_{\text{ext}}(\vec{r})$ may be identified with the electron-nuclear $-(Z_c+Z_v)/r$ potential for atoms, the internuclear repulsion in polyatomic systems, etc. The eigenstates $\{\psi_j(\vec{r})\}$ of the all-electron Hamiltonian $-\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\text{ae}}$ have a nodal structure resulting from the mutual orthogonality constraint. These eigenfunctions form the basis for constructing the self-consistent all-electron charge density $\rho(\vec{r},\vec{r}\,')$.

The pseudopotential (ps) representation replaces (1) by

$$V_{\text{eff}}^{\text{ps}} = [V_{\text{ext}}^{\text{v}}(\vec{r}) + W_R(\vec{r},\vec{r}\,')] + V_{\text{scr}}^{\text{v}}(n(\vec{r},\vec{r}\,')), \qquad (2)$$

where $V_{\text{ext}}^{\text{v}}(\vec{r})$ is the valence-projected external potential (e.g., $-Z_v/r$ for an atom of valency Z_v), $W_R(\vec{r},\vec{r}\,')$ is the repulsive part of the pseudopotential, and $V_{\text{scr}}^{\text{v}}(n(\vec{r},\vec{r}\,'))$ is the same as $V_{\text{scr}}^{\text{c,v}}(\rho(\vec{r},\vec{r}\,'))$ in Eq. (1) except that it is a functional of the valence pseudodensity $n(\vec{r},\vec{r}\,')$ rather than the all-electron "true" density $\rho(\vec{r},\vec{r}\,')=\rho^c+\rho^v$. Frequently, the first two terms in (2) are referred to as the bare pseudopotential, and the spatial nonlocality in $W_R(\vec{r},\vec{r}\,')$ is replaced by an angular momentum dependence with a projection operator $\hat{P}_l$:

$$V_{\text{eff}}^{\text{ps}} = \sum_l V_l(\vec{r})\hat{P}_l + V_{\text{scr}}^{\text{v}}(n(\vec{r},\vec{r}\,')). \qquad (3)$$

The eigenstates $\{\chi_j(\vec{r})\}$ of the pseudo-Hamiltonian $-\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\text{ps}}$ span only the valence subspace and form the basis for the self-consistent pseudodensity $n(\vec{r},\vec{r}\,')$.

To the extent that the construction of the pseudopotentials $V_l(\vec{r})$ can be made simple, the study of valence-related properties of solids through the solution of the pseudopotential single-particle problem is both computationally and conceptually simpler than that study via the solution of the all-electron problem. This relative simplicity stems not only from the fact that the pseudopotential approach treats a smaller number of ("reactive") electrons and permits nodeless and spatially smooth ground-state wave functions, but it is also due to the fact that to within a good approximation, the first term in (3) can be constructed once and for all from simple prototype systems (e.g., atoms) and then used to replace the core electrons in complex systems. These nearly system-invariant transferable quantities are the atomic pseudopotentials $v_l(r)$ that form the total pseudopotential $V_l(\vec{r})$ through a linear superposition over sites at:

$$V_l(\vec{r}) = \sum_\alpha v_l^{(\alpha)}(\vec{r}-\vec{\tau}_\alpha)\hat{P}_{l,\alpha} \qquad (4)$$

where $\hat{P}_{l,\alpha}$ is an angular momentum projection operator with origin at $\vec{\tau}_\alpha$. Note that unlike the pseudopotential, the screening potential in a solid $V_{\text{scr}}^{\text{v}}(n)$ is generally nonlinear with respect to decomposition into atomic sites, and hence it is strongly system dependent.

Using the decomposition of the effective potential underlying Eqs. (3) and (4), one can broadly divide the pseudopotential approaches that have been used for practical electronic structure calculations into three groups: the empirical, semiempirical, and first-principles pseudopotential methods.

The *empirical pseudopotential method*[9,10] does not express the pseudopotential V_l or the screening $V_{\text{scr}}^{\text{v}}$ in terms of microscopically specified interactions (e.g., charge-density-dependent Coulomb, exchange and correlation potentials, and the orthogonality-hole and the core structure, etc.), but rather represents $V_{\text{eff}}^{\text{ps}}$ by an arbitrary analytical or numerical form with parameters adjusted to fit a selected set of experimental data (e.g., energy levels of ions,[11] interband transitions in semiconductors,[9,10] Fermi surface in metals,[12] etc.) through a pseudopotential calculation. Both the pseudopotential and the screening are then assumed to be transferable from one crystal to another containing the same atoms. No self-consistency in the treatment can be defined, as $V_{\text{eff}}^{\text{ps}}$ in this form is independent of the variational charge density $n(\vec{r})$. No meaningful comparison can be made between these calculations and *nonempirical* all-electron band structure calculations (using imperfectly known exchange and correlation screening), as the former approach attempts to reduce to zero the many-body corrections to the band energies by fitting to experiment. The empirical pseudopotential method has produced for semiconductors the most accurate band structures known today.[9,13]

The *semiempirical pseudopotential method*[14,15] calculates the screening $V_{\text{scr}}^{\text{v}}(n(\vec{r}))$ from the density $n(\vec{r})$ using a well-defined microscopic model (e.g., the density-functional approximation). It then represents the pseudopotential $v_l(r)$ by an arbitrary empirical form with parameters adjusted to obtain a fit to selected experimental data (ionic structure,[15] band structure[14]) through a pseudopotential calculation with $V_{\text{eff}}^{\text{ps}}$. Here only the atomic pseudopotentials are assumed to be transferable, and a self-consistency in the treatment is possible. Only local approximations to the pseudopotential [e.g., retaining only a single l component in Eq. (3)] have been utilized in this apporach. As some correlation effects are introduced via empirically adjusting the pseudopotential, again no meaningful comparison can be made with all-electron calculations on the same system, even if an identical description is used for screening. Hence, semiempirical $X\alpha$-type *pseudopotential* band structures for Si, diamond, Ge, etc., do not compare well with *all-electron* calculations using the same $X\alpha$ approach for $V_{\rm scr}^{\rm v}$. As only the energy eigenvalues of the pseudopotential equations and not the detailed wave function or charge density are constrained to fit experiment, the semiempirical pseudopotential method has often yielded charge densities which differ from those obtained from experiments or from first principles calculations.[16,17] The semiempirical pseudopotential method has been successfully used to study a large variety of surface and chemisorption problems.[18]

The *first-principles pseudopotential method*[6,19,20] calculates both the pseudopotential $V_l(\vec{r})$ and the screening $V_{\rm scr}^{\rm v}(n(\vec{r}))$ from the same (chosen) microscopic model for electronic interactions. As such, it establishes a one-to-one correspondence between the pseudopotential and the all-electron approaches using the same screening theory. It permits the analysis of both the success and the failure of a certain pseudopotential model in terms of the underlying method used to describe the exchange and correlation effects (e.g., Hartree-Fock, correlated Hartree-Fock, LSD). At the limit where the basic pseudopotential frozen core approximation becomes exact, the pseudopotential and the all-electron band structures match (e.g., for bulk Si, the pseudopotential and all-electron band structures agree to within an average deviation of 0.06 eV/state over a range of 20 eV).[21] Its major limitation is that no perfect agreement can be obtained at present with experiment: As our present knowledge of electronic correlation potentials is limited, so is the agreement between the pseudopotential calculation of certain properties and experiment. Some of these discrepancies are discussed in Sec. III B. The basic advantage of the first-principles pseudopotential method lies in its physical transparency and the possibility it offers to improve *systematically* upon the results as our understanding of many-electron effects improves.

In this paper I show how two recent elaborations on the theory of the interacting electron system within the density-functional formalism—the spin-polarization[22] and self-interaction cancellation effects[8]—can be simply incorporated in the first-principles pseudopotential method. Empirical as well as semiempirical pseudopotentials are difficult to generalize to include a spin dependency, as the pertinent experimental data needed for the fit is inherently limited. Most spin-polarized atoms form solids that are nonmagnetic, and hence their observed interband spectra cannot be used to pin the atomic pseudopotential spin dependency; for the magnetic solids, only a small subset of the transition observed in spin-polarized photoemission is associated with a clearly interpretable spin splitting. Similarly in ions or atoms, many of the weak transitions associated with a spin reversal are not known. Still, spin-dependent pseudopotentials are needed for problems, such as pseudopotential studies of surfaces of magnetic transition metals, transition-metal and other open-shell impurities and defects in semiconductors, spin-density waves, general magnetic phase transitions in compounds, as well as the calculation of spin densities of solids that have now become experimentally accessible.

The inclusion of self-interaction corrections in the local spin-density formalism permits a generalization of this theory to describe not only itinerant electronic states but also localized configurations. Such a generalization is impossible in the empirical pseudopotential method (as the potential is independent of charge and orbital densities). Self-interaction effects are important whenever there is a coexistence of itinerant and localized electronic states, e.g., surface and interface states of semiconductors and metals, deep impurities, Mott insulators, and Anderson localized states, etc.

III. METHOD

The problem of obtaining accurate first-principles atomic pseudopotentials from a given all-electron model has been solved by Goddard, Kahn, Melius, and others[20] for the Hartree-Fock and correlated Hartree-Fock models, and by Zunger *et al.*[6,19] for the density-functional model. The Hartree-Fock first-principles pseudopotentials have been used to calculate the electronic properties of a large number of molecules and clusters.[20] The first-principles density-functional pseudopotentials of Zunger *et al.* have been used to calculate the electronic properties of some semiconductors [Si (Refs. 21 and 23), Ge (Ref. 23), GaAs (Ref. 24)], bulk transition metals [Mo (Refs. 25 and 26), W (Ref. 26)], diatomic molecules [Si_2 (Ref. 17), O_2 (Ref. 27)], the relaxed GaAs (110) surface,[24] the cohesive properties of bulk Si (Ref. 28), Mo and W (Ref. 26), and to develop an orbital radii scheme that successfully predicts the crystal structure of as many as 495 binary compounds.[29] Using this latter approach, the extension to spin-polarized density-functional pseudopotentials is straightforward, as will be discussed in the next section.

A. Spin-polarized atomic pseudopotentials

The local spin-density[22] (LSD) single-particle description of the electronic states of an atom (or ion) with Z_c core (c) and Z_v valence (v) electrons, and electron charge density of $\rho(\vec{r}) = \rho_\downarrow(\vec{r}) + \rho_\uparrow(\vec{r})$ and spin-polarization $\xi(\vec{r}) = (\rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r}))/\rho(\vec{r})$ is given in the central field approximation by

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{ext}}(r) + V_{\text{scr}}^{c,v}(\rho(r),\xi(r))]\psi_{nl\sigma}(r) = \epsilon_{nl\sigma}\psi_{nl\sigma}(r)\,, \tag{5}$$

where the external potential is

$$V_{\text{ext}}(r) = -(Z_c + Z_v)/r \tag{6}$$

and the spin (with index σ) dependent screening is

$$V_{\text{scr}}^{c,v}(\rho(r),\xi(r)) = V_{\text{ee}}(\rho(r)) + V_{\text{xc}}^{\sigma}(\rho(r),\xi(r))\,. \tag{7}$$

Here, $V_{\text{ee}}(\rho(r))$ is the interelectronic Coulomb repulsion due to $\rho(r)$, and the exchange-correlation potential $V_{\text{xc}}^{\sigma}(\rho(r),\xi(r))$ is the functional derivative of the total exchange and correlation energy $E_{\text{xc}}^{\text{LSD}}$ with respect to the spin-density $\rho_\sigma(r)$. $E_{\text{xc}}^{\text{LSD}}$ is usually replaced in the local approximation by[3]

$$E_{\text{xc}}^{\text{LSD}} = \int \rho(r)\epsilon_{\text{xc}}(\rho(r),\xi(r))dr\,, \tag{8}$$

where $\epsilon_{\text{xc}}(\rho,\xi)$ is the exchange-correlation energy per particle of a uniform spin-polarized electron liquid. The total energy of this system is given by

$$E_{\text{ae}}^{\text{LSD}} = T(\rho,\xi) + E_{\text{ext}}(\rho) + \tfrac{1}{2}E_{\text{ee}}(\rho) + E_{\text{xc}}^{\text{LSD}}(\rho,\xi)\,, \tag{9}$$

where $T(\rho,\xi)$ is the noninteracting kinetic energy, $E_{\text{ext}}(\rho)$ is the interaction energy of $\rho(r)$ with the $V_{\text{ext}}(r)$ and $E_{\text{ee}}(\rho)$ is the interaction of $\rho(r)$ with the Coulomb potential $V_{\text{ee}}(\rho(r))$. The variational density is determined via

$$\rho(r) = \sum_{nl\sigma} \rho_{nl\sigma}(r) \tag{10}$$

from the spin-orbital densities $\rho_{nl\sigma}(r) = N_{nl\sigma}^{c,v}|\psi_{nl\sigma}^2(r)|$ (where $N_{nl\sigma}^{c,v}$ is the occupation numbers of both core and valence states), given by the self-consistent orthogonal solutions $\{\psi_{nl\sigma}(r)\}$ of Eq. (5).

In the pseudopotential representation, one considers a fictitious atom having only Z_v (valence) electrons with density $n(r)$. The electrons interact via an interelectronic repulsive potential $V_{\text{ee}}(n(r))$ and an exchange-correlation potential $V_{\text{xc}}^{\sigma}(n,\xi)$ as well as with a (yet unspecified) external potential:

$$V_{\text{ext}}^{v} = V_{\text{ps}} = -Z_v/r + W_R\,. \tag{11}$$

The corresponding total energy is

$$E_{\text{ps}}^{\text{LSD}} = T(n,\xi) + E_{\text{ps}}(n) + \tfrac{1}{2}E_{\text{ee}}(n) + E_{\text{xc}}^{\text{LSD}}(n,\xi)\,, \tag{12}$$

where the interaction energy with the external potential is

$$E_{\text{ps}}(n) = \int n(r)V_{\text{ps}}(r)dr\,. \tag{13}$$

The variational single-particle equation is

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{ps}} + V_{\text{scr}}^{v}(n(r),\xi(r))]\chi_{nl\sigma}(r) = \lambda_{nl\sigma}\chi_{nl\sigma}(r)\,, \tag{14}$$

with the pseudo-(valence) screening

$$V_{\text{scr}}^{v}(n(r),\xi(r)) = V_{\text{ee}}(n(r)) + V_{\text{xc}}^{\sigma}(n(r),\xi(r))\,. \tag{15}$$

The variational density is given by the spin-orbital pseudodensities $n_{nl\sigma}(r)$ and the valence occupation $N_{nl\sigma}^{v}$ numbers as:

$$\begin{aligned} n(r) &= \sum_{nl\sigma} n_{nl\sigma}(r)\,, \\ n_{nl\sigma}(r) &= N_{nl\sigma}^{v}|\chi_{nl\sigma}^2(r)|\,. \end{aligned} \tag{16}$$

We now look for the external potential V_{ps} that will produce certain desired relations between the solutions $\{\lambda_{nl\sigma}, \chi_{nl\sigma}(r)\}$ of the pseudopotential single-particle equation (14) and those $\{\epsilon_{nl\sigma}, \psi_{nl\sigma}(r)\}$ of the full all-electron equation (5). Following our previous work on the nonpolarized pseudopotentials,[6,19] we require that: (i) the energy eigenvalue spectra $\{\lambda_{nl\sigma}\}$ of the pseudoatom be equal to the valence spectra $\{\epsilon_{nl\sigma}\}$ of the "true" atom in the ground electronic state; (ii) the wave functions $\{\chi_{nl\sigma}(n)\}$ of the pseudoatom be normalized, monotonic, and nodeless for each of the lowest spatial symmetries; and (iii) the pseudo-wave-functions $\{\chi_{nl\sigma}(n)\}$ match the "true" wave functions $\{\psi_{nl\sigma}^{v}(n)\}$ of the valence states asymptotically from $r = +\infty$ to the innermost point possible under constraint (ii). We require that this "maximum similarity constraint" be achieved in a particular manner that will permit: (a) a simple unitary relation between the "true" wave functions and the pseudo-wave-functions and (b) that the pseudopotential V_{ps} derived from these pseudo-wave-functions be approximately energy independent, i.e., transferable from one system to the other, and hence useful for calculations on arbitrary systems.

The motivations for choosing these constraints are the following: Constraint (i) ensures that the spectral properties derived from the pseudopotential single-particle equation match those of the valence electrons of the all-electron problem. Hence, one-electron excitation energies or differences in total energies (corresponding to different electronic configurations) can be reliably reproduced. Constraint (ii) ensures that the solutions of the pseudopotential equation are legitimate ground-state orbitals (that is, normalized and nodeless). This also permits their expansion in simple and spatially smooth basis functions (as χ is monotonic and nodeless for the lowest states). Constraint (iii) ensures that the chemical information included in the "tail" part of the "true" valence wave functions is contained in the pseudo-wave-functions and that this continue to be so, to within a good approximation, even if the atomic pseudopotential is used in chemical environments different from that used for its construction (i.e., atoms).[30]

We proceed by first constructing pseudo-wave-functions that satisfy (ii) and (iii) and then use them and condition (i) to derive the pseudopotential V_{ps}. To satisfy these conditions, the initial step is to construct the pseudo-wave-functions as a linear combination of the known core and valence all-electron wave functions for each spin [condition (iii)(a)]:

$$\chi_{nl\sigma}^{(0)}(r)=\sum_{n'} C_{n,n'}^{(l,\sigma)}\psi_{n'l\sigma}^{c,v}(r)\,. \tag{17}$$

As the exchange-correlation potential in Eq. (5) is spin-dependent, the spatial form of the all-electron as well as pseudo-wave-functions is different for different spins. The expansion coefficients $\{C_{n,n'}^{(l,\sigma)}\}$ are to be determined such that $\chi_{nl\sigma}^{(0)}$ be normalized, monotonic, and nodeless [condition (ii)] and have the maximum possible similarity to the "true" valence orbital. The expression (17) amounts to a rotation of the core and valence wave functions of the full Hamiltonian to form a pseudo-wave-function $\chi_{nl\sigma}^{(0)}$ with desired properties. At the limit where the exchange takes its simple Hartree-Fock form, such a rotation (amounting to an interchange of columns in the determinental description of the total wave function), leaves the total energy expression invariant. To this limit, the variational properties of the total energy expression in the frozen-core approximation remain intact.

In the simple case of a first-row atom (i.e., 1*s* core), this yields

$$\begin{aligned}\chi_{2s,\sigma}^{(0)}(r)&=C_{1s,2s}^{(0,\sigma)}\psi_{1s,\sigma}(r)+C_{2s,2s}^{(0,\sigma)}\psi_{2s,\sigma}(r)\,,\\ \chi_{2p,\sigma}^{(0)}(r)&=\psi_{2p,\sigma}(r)\,,\end{aligned} \tag{18}$$

where the pseudo-2*p* orbital equals the real 2*p* orbital, since the latter is already nodeless. One has to mix sufficient $\psi_{1s,\sigma}$ into $\psi_{2s,\sigma}$ to eliminate the node in the latter and obtain at the same time a pseudo-orbital $\chi_{2s,\sigma}^{(0)}$ with a maximum similarity to $\psi_{2s,\sigma}$ outside the core. Such a maximum similarity is achieved by including the *minimum* amount of $\psi_{1s,\sigma}$ necessary to eliminate the node in $\chi_{2s,\sigma}^{(0)}$. The minimal amount of mixing is hence achieved when $\chi_{2s,\sigma}^{(0)}(0)=0$. Together with the normalization condition on the pseudo-orbital, this determines the expansion coefficients from

$$\begin{aligned}&\chi_{2s,\sigma}^{(0)}(0)=C_{1s,2s}^{(0,\sigma)}\psi_{1s,\sigma}(0)+C_{2s,2s}^{(0,\sigma)}\psi_{2s,\sigma}(0)=0\,,\\ &|C_{1s,2s}^{(0,\sigma)}|^2+|C_{2s,2s}^{(0,\sigma)}|^2=1\,,\end{aligned} \tag{19}$$

from which one can solve for $C_{1s,2s}^{(0,\sigma)}$ and $C_{2s,2s}^{(0,\sigma)}$ given the known amplitudes of the all-electron orbitals at the origin.

In the general case of an arbitrary number of core orbitals, the coefficients are determined by minimizing the core projection $\langle\chi_{nl\sigma}^{(0)}|\hat{P}_c|\chi_{nl\sigma}^{(0)}\rangle$, seeking a normalized, monotonic, and nodeless orbital with minimum core amplitude $\chi_{nl\sigma}^{(0)}(0)=\chi_{nl\sigma}^{\prime(0)}(0)=\chi_{nl\sigma}^{\prime\prime(0)}=0$. This is accomplished by an iterative core-minimization procedure subject to the above constraints. Note that if one relaxes the condition that the monotonic $\chi_{nl\sigma}^{(0)}$ be zero at the origin, then the region of space where $\chi_{nl\sigma}^{(0)}$ and $\psi_{nl\sigma}$ are close is reduced. A similar procedure for determining $\chi_{nl\sigma}$ has been used in the Hartree-Fock pseudopotentials.[20]

Since the all-electron orbitals $\{\psi_{nl\sigma}(r)\}$ form an orthogonal set, the choice (17) will produce a (small) constant deviation between $\chi_{nl\sigma}^{(0)}$ and the "true" valence orbital $\psi_{nl\sigma}$ at large distances from the origin. This results from the fact that $\lim_{r\to\infty}\chi_{nl\sigma}^{(0)}(r)=C_{n,n}^{(l,\sigma)}\psi_{nl\sigma}$ and $|C_{n,n}^{(l,\sigma)}|^2<1$ due to orthogonality. To correct for this constant deviation, we construct in the second step from (17) the final pseudo-wave-function in which we introduce a wave-function component that lies outside the atomic LSD orthogonal space[19]:

$$\chi_{nl\sigma}^{(1)}(r)=\frac{1}{M_{nl\sigma}}\left[\sum_{n'\neq n}\left(\frac{C_{n,n'}^{(l,\sigma)}}{C_{n,n}^{(l,\sigma)}}\right)\psi_{n'l\sigma}(r)+f_{nl\sigma}(r)\right]+\psi_{nl\sigma}(r)\,, \tag{20}$$

where $M_{nl\sigma}$ is a constant that normalizes $\chi_{nl\sigma}^{(1)}$, and $f_{nl\sigma}(r)$ is an arbitrary function that overlaps with $\{\psi_{n'l\sigma}(r)\}$ and decays rapidly at large distance. We chose for $f_{nl\sigma}(r)$ the simple function:

$$f_{nl\sigma}(r)=-A_{nl\sigma}r^{l+2}e^{-\alpha_{l\sigma}r}\,. \tag{21}$$

Since $\chi_{nl\sigma}^{(0)}$ is already very close to the true wave function $\psi_{nl\sigma}$ outside the core region, the correction $f_{nl\sigma}$ is usually very small and is used to improve the agreement between the pseudo-wave-function moments $\langle\chi_i|r^p|\chi_i\rangle$ and the moments of the true wave functions $\langle\psi_i|r^p|\psi_i\rangle$ for $p>1$. The agreement[19] is normally to within 3% using $\chi_{nl\sigma}^{(0)}$ and better than 1% using $\chi_{nl\sigma}^{(1)}$. The normalization requirement on $\chi_{nl\sigma}^{(1)}$ produces a second-order algebraic equation for $A_{nl\sigma}$ as a function of $\alpha_{l\sigma}$. We then determine $\alpha_{l\sigma}$ by requiring that the charge-accumulation function for the pseudo-orbital,

$$Q_{nl\sigma}^{\text{ps}}(R)=\int_0^R|\chi_{nl\sigma}^{(1)}|^2dr\,, \tag{22}$$

will match the all-electron charge-accumulation function

$$Q_{nl\sigma}^{\text{ae}}(R)=\int_0^R|\psi_{nl\sigma}(r)|^2dr \tag{23}$$

starting from $R=\infty$ to the smallest $R=R_c$ possible under our constraints.[19]

The resulting final pseudo-wave-function is nodeless, normalized, monotonic, has a minimum core projection, and is numerically identical to the true wave function from $r=\infty$ [as from Eq. (20) one gets $\lim_{r\to\infty}\chi^{(1)}_{nl\sigma}(r)=\psi_{nl\sigma}(r)$] to a point $r=R_c$ that normally falls inwards to the last orbital maxima in $\psi_{nl\sigma}(r)$. Since the orbital charge-accumulation functions in Eqs. (22) and (23) are equal, $Q^{\text{ps}}_{nl\sigma}(R)=Q^{\text{ae}}_{nl\sigma}(R)$ for $r\geq R_c$, the electrostatic potential set by any pseudo-orbital density $V_{\text{ee}}(\chi^2_{nl\sigma})$ is identical to that set by the "true" orbital density $V_{\text{ee}}(\psi^2_{nl\sigma})$ for $r\geq R_c$. As pointed out by Hamann *et al.*,[31] the identity proved by Shaw and Harrison guarantees that if $Q^{\text{ps}}_{nl\sigma}(R)=Q^{\text{ae}}_{nl\sigma}(R)$ for $R\geq R_c$, then the logarithmic spatial and energy derivatives of $\chi_{nl\sigma}(r)$ and $\psi_{nl\sigma}(r)$ are also identical for $r\geq R_c$. This means that the corresponding pseudopotential has a low energy dependence [condition (iii) (b)] in that it produces pseudo-wave-functions that continue to simulate the all-electron wave functions even in a changed chemical environment where the energy spectrum is modified. The fact that we have chosen to construct our pseudo-wave-functions with a minimum core amplitude adds a new aspect to this; not only the $r\geq R_c$ behavior produces a low energy dependence, but also the anchoring of the pseudo-wave-functions to the origin $\chi_{nl\sigma}(0)=\chi'_{nl\sigma}(0)=\chi''_{nl\sigma}(0)=0$ makes it energy costly for bonding forces to modify the wave function in the core (and hence, by normalization, throughout the valence region) away from the form for which a maximum similarity to the "true" wave function has been established. Extensive tests on atomic pseudopotentials derived from such pseudo-wave-functions have indeed indicated a very low energy dependence.[6,19]

We also note that one can simply recover, to within a good approximation, the "true" valence function $\psi_j(r)$ of arbitrary systems from the calculated pseudo-wave-function $\chi_j(r)$ using the known core orbitals and the assumed function $f(r)$, e.g.,

$$\psi_j(r)=\chi_j^{(1)}(r)-\sum_{\text{core}}\left(\langle\chi_j^{(1)}|\psi^{\text{core}}\rangle-M_j\langle f|\psi^{\text{core}}\rangle\right)\psi^{\text{core}}-Mf(r)\,. \qquad (24)$$

This permits the assessment of the accuracy of a pseudopotential calculation once it has been completed. The simplicity of this core orthogonalization hinges on the choice of the *linear* form of Eqs. (17) and (20).

Having obtained the desired set of pseudo-spin-orbitals $\{\chi^{(1)}_{nl\sigma}\}$, we now find the pseudopotential in Eq. (14) that will produce these orbitals in a self-consistent calculation, subject to the constraint (i) that the ground-state energy spectrum $\{\lambda_{nl\sigma}\}$ match the spectrum $\{\epsilon_{nl\sigma}\}$ of the all-electron equation (5). Note that this approach is distinctly different from that underlying both the empirical and the semi-empirical pseudopotential methods (cf. Sec. II) in which one starts from a postulated parametrized form for the potential and allows the fitting of the energy eigenvalues (and possibly the peak of the wave function) to also implicitly determine the shape of the wave functions.

From (14), the form (20) of the spin orbitals, and $\lambda_{nl\sigma}=\epsilon_{nl\sigma}$, one obtains an angular-momentum- (l) and spin- (σ) dependent nonlocal pseudopotential:

$$V^{(l,\sigma)}_{\text{ps}}(r)=\epsilon_{nl\sigma}+\frac{1}{2}\,\frac{\nabla^2\chi^{(1)}_{nl\sigma}(r)}{\chi^{(1)}_{nl\sigma}(r)}-V^{\text{v}}_{\text{scr}}(n(r),\xi(r)). \qquad (25\text{a})$$

As the all-electron orbitals entering (20) are solutions to Eq. (5), one can use

$$\epsilon_{nl\sigma}+\frac{1}{2}\,\frac{\nabla^2\chi^{(0)}_{nl\sigma}(r)}{\chi^{(0)}_{nl\sigma}(r)}=\frac{\sum_{n'}C^{(l,\sigma)}_{n,n'}(\epsilon_{nl\sigma}-\epsilon_{n'l\sigma})\psi_{n'l\sigma}(r)}{\sum_{n'}C^{(l,\sigma)}_{n,n'}\psi_{n'l\sigma}(r)}+V^{\text{c,v}}_{\text{scr}}(\rho(r))\,. \qquad (25\text{b})$$

The extra function $f_{nl\sigma}(r)$ that enters $\chi^{(1)}_{nl\sigma}(r)$ in Eq. (20) contributes additional terms to $\nabla^2\chi^{(1)}_{nl\sigma}/\chi^{(1)}_{nl\sigma}$ that can be evaluated analytically.

The final spin-dependent nonlocal pseudopotential is hence determined by $\{C^{(l,\sigma)}_{n,n'}\}$ in Eq. (17), $\{A_{nl\sigma},\alpha_{l\sigma}\}$ in Eq. (20), and the known all-electron results $\{\psi_{nl\sigma}(r),\epsilon_{nl\sigma}\}$. Given the first two sets, the pseudopotential can be easily constructed from Eq. (25a) by standard programs. We have obtained $V^{(l,\sigma)}_{\text{ps}}(r)$ for a number of atoms in numerical form. We find that it can be conveniently fitted to the analytical form[32]:

$$V^{(l,\sigma)}_{\text{ps}}(r)=\frac{C^{(l,\sigma)}_1}{r^2}e^{-C^{(l,\sigma)}_2 r}-\frac{Z_{\text{c}}}{r}e^{-C_3 r}-\frac{Z_{\text{v}}}{r}. \qquad (26)$$

The physical significance of this form is discussed elsewhere.[32]

In Sec. IV A applications of the spin-dependent nonlocal pseudopotential to the calculation of the interconfigurational energies of transition-metal atoms are presented.

B. Self-interaction-corrected atomic pseudopotentials

The spin-density functional expression for the total energy, both in its all-electron [Eq. (9)] and pseudopotential [Eq. (12)] form, contains spurious electron self-interaction terms: the self-Coulomb $\frac{1}{2}E_{\text{ee}}(\rho_{nl\sigma})$ and the self-exchange-correlation $E^{\text{LSD}}_{\text{xc}}(\rho_{nl\sigma},1)$ terms [with the corresponding contributions $\frac{1}{2}E_{\text{ee}}(n_{nl\sigma})$ and $E^{\text{LSD}}_{\text{xc}}(n_{nl\sigma},1)$ in the pseudopotential expression]. The corresponding terms in the screening potential are $V_{\mathrm{ee}}(\rho_{nl\sigma})$ and $V_{\mathrm{xc}}^{\sigma}(\rho_{nl\sigma}, 1)$.

In the extreme limit of a single-electron system (e.g., H, He$^+$, or all alkali atoms in a pseudopotential representation) the total energy does not equal $T(\rho,\xi)+E_{\mathrm{ext}}(\rho)$ as it should, since $\frac{1}{2}E_{\mathrm{ee}}+E_{\mathrm{xc}}(\rho,1)\neq 0$, leading to very substantial errors.[23] Clearly, this defect stems from the attempt underlying the LSD theory to describe the imperfectly known exchange and correlation energies in terms of local potentials. Whereas the electron self-Coulomb potential is positive, the self-exchange-correlation potential is negative. The partial success of LSD in describing localized states rests on the fact that often most of the self-Coulomb term is canceled by the self-exchange-correlation term. For extended states, both are individually small. While retention of these self-interaction terms makes the screening potential $V_{\mathrm{scr}}^{\mathrm{c,v}}(\rho,\xi)$ conveniently *local* (i.e., state independent) it also results in some systematic errors in the predictions of the LSD theory.

Recently, Zunger, Perdew, and Oliver[8] have shown that a self-consistent compensation of the self-interaction terms results in a systematic improvement in a number of properties calculated by LSD. These include the following:

(1) The exchange energies E_x^{LSD} of atoms are systematically *underestimated* by 10%–15% in LSD (Ref. 5) compared with the exact Hartree-Fock results, whereas in the self-interaction–corrected (SIC) approach the errors are reduced by a factor of 5.

(2) The correlation energies E_c^{LSD} of atoms are *overestimated* by as much as 100%–200% in LSD (Ref. 5) compared with experiment, whereas a similar reduction of about a factor of 5 in the error is accomplished in the SIC-LSD approach.

(3) The experimentally stable negative ions (e.g., H$^-$, O$^-$, F$^-$, etc.) are predicted by LSD to be unstable,[33] whereas in SIC LSD their stability is confirmed and the calculated electron affinities are in very good agreement with experiment.

(4) The large-r electrostatic limit $-(Q+1)/r$ of the potential of an ion of charge Q is realized by the SIC-LSD approach, whereas LSD erroneously predicts a $-Q/r$ limit.

(5) Whereas the absolute value of the LSD total energy of a metal surface is *too low* when compared with the exact value,[34] the LSD energy for atoms is *too high*.[5] Furthermore, the lowest-order correction to the LSD exchange and correlation energy predicted by many-body theory (i.e., the density-gradient correction[35]) is positive and so can only worsen the agreement of the calculated atomic energies and experiment. When the SIC is applied, the atomic total energies become very close to the experimental values and are systematically *lower*, in line with the results for a metal surface (which has no self-interaction corrections). Gradient corrections can now improve the agreement with experiment.

(6) Whereas self-consistent density-functional band-structure calculations for insulators (e.g., rare-gas solids[36]) tend to underestimate the one-electron band gap by as much as 40%, simple models for the self-interaction corrections to the band gap account for almost 100% of these errors.

The self-interaction-corrected LSD total energy expression proposed by Zunger and Cohen,[6] Perdew,[7] and Zunger, Perdew, and Oliver[8] is

$$E_{\mathrm{ae}}^{\mathrm{LSD\,SIC}} = E_{\mathrm{ae}}^{\mathrm{LSD}} - \sum_{nl\sigma} N_{nl\sigma}^{\mathrm{c,v}}\delta_{nl\sigma}\,, \tag{28}$$

where $E_{\mathrm{ae}}^{\mathrm{LSD}}$ is given by Eq. (9) and $N_{nl\sigma}^{\mathrm{c,v}}$ denotes the occupation numbers. The orbital-dependent correction is

$$\delta_{nl\sigma} = \tfrac{1}{2}E_{\mathrm{ee}}(\hat{\rho}_{nl\sigma}) + E_{\mathrm{xc}}^{\mathrm{LSD}}(\hat{\rho}_{nl\sigma}, 1)\,. \tag{29}$$

The corresponding variational effective potential is:

$$V_{\mathrm{eff}}^{\mathrm{LSD\,SIC}} = V_{\mathrm{ext}}(r) + V_{\mathrm{scr}}^{\mathrm{c,v}}(\hat{\rho}(r), \hat{\xi}(r)) - V_{\mathrm{ee}}(\hat{\rho}_{nl\sigma}(r)) - V_{\mathrm{xc}}^{\uparrow}(\hat{\rho}_{nl\sigma}, 1)\,, \tag{30}$$

where $\hat{\rho}(r)$ and $\hat{\xi}(r)$ indicate the charge density and spin polarization, respectively, calculated with orbitals that are self-consistent with $V_{\mathrm{eff}}^{\mathrm{LSD\,SIC}}(r)$ rather than with the LSD potential [Eqs. (5)–(7)]. Since the SIC effective potential in Eq. (30) is state dependent, its solutions $\{\hat{\psi}_{nl\sigma}(r)\}$ do not form an orthogonal set. This can be overcome by including off-diagonal Lagrange multipliers and transforming the problem into a canonical form. One can evaluate the effects of this nonorthogonality by arbitrarily performing a Schmidt orthogonalization of $\{\hat{\psi}_{nl\sigma}(r)\}$ at each interaction step in solving the SIC equation with the potential (30). The effect in atoms is very small[8] (e.g., 10^{-4} hartree in the total energy of Ne) and is neglected here.

The application of the self-interaction-corrected LSD approach to pseudopotentials is straightforward. One first solves the all-electron atomic single-particle equation with the self-interaction–corrected potential in Eq. (30). From the resulting orthogonalized orbitals $\{\hat{\psi}_{nl\sigma}(r)\}$ one constructs the pseudo-wave-functions $\{\hat{\chi}_{nl\sigma}^{(1)}(r)\}$ as in Eq. (20). This yields the corrected pseudo-charge-density $\hat{n}(r)$ and the spin-orbital densities as in (16). The SIC pseudopotential equation is then

$$\left[-\tfrac{1}{2}\nabla^2 + \hat{V}_{\mathrm{ps}}^{(l,\sigma)}(r) + V_{\mathrm{scr}}^{\mathrm{v}}(\hat{n}(r), \hat{\xi}(r)) - V_{\mathrm{ee}}(\hat{n}_{nl\sigma}(r)) - V_{\mathrm{xc}}^{\uparrow}(\hat{n}_{nl\sigma}(r), 1)\right]\hat{\chi}_{nl\sigma}^{(1)}(r) = \hat{\epsilon}_{nl\sigma}^{\mathrm{SIC}}\hat{\chi}_{nl\sigma}^{(1)}(r) \tag{31}$$

from which we calculate the SIC pseudopotential $\hat{V}_{\rm ps}^{(l,\sigma)}(r)$ using $\{\chi_{nl\sigma}^{(1)}(r), \hat{\epsilon}_{nl\sigma}^{\rm SIC}\}$. The SIC pseudopotentials differ from the LSD pseudopotentials in Eq. (25) both due to the difference between $\hat{\chi}_{nl\sigma}^{(1)}$ and $\chi_{nl\sigma}^{(1)}$ and due to the explicit existence of the $[-\frac{1}{2}V_{\rm ee}(\hat{n}_{nl\sigma}) - V_{\rm xc}^{\dagger}(\hat{n}_{nl\sigma}, 1)]$ terms in Eq. (31). Both the LSD and the SIC-LSD pseudopotentials exhibit the same type of nonlocal form (i.e., are different for different angular momenta l and spins σ). At the limit of no spin polarization ($n_{nl+}=n_{nl-}$), we obtain the usual unpolarized pseudopotential. The LSD-SIC atomic pseudopotentials for a number of atoms have been calculated and the results are presented in Sec. IV B.

IV. RESULTS

A. Spin-polarized atomic pseudopotentials

The spin-polarized atomic pseudopotentials $V_{\rm ps}^{(l,\sigma)}(r)$ of Eq. (25) have been calculated for the $3d$ series Ca to Cu. The potentials were generated from the $d^{n-1}s^1$ high-spin configuration, and hence reproduce by definition [constraint (i) in Sec. III] the all-electron energy eigenvalues $\epsilon_{3d,\sigma}$, $\epsilon_{4s,\sigma}$, and $\epsilon_{4p,\sigma}$ for this configuration. To test their energy dependence, the energy eigenvalues obtained by applying these pseudopotentials to the $d^{n-2}s^2$ configuration have been compared with the energy eigenvalues of the all-electron problem in the same $d^{n-2}s^2$ configuration. We use the unpolarized potential for systems with zero net spin (e.g., Ni $3d^{10}4s^0$). Using the spin-polarized pseudopotentials for systems with a net spin, we reproduce accurately all the spin splittings, as core spin polarization is included in the pseudopotential: There is agreement to within better than 0.002 a.u., indicating a good transferability of the pseudopotentials.

As a further application, the interconfigurational energy (ic),

$$\Delta E_{\rm ic}^{\rm ps} = E_{\rm ps}^{\rm LSD}(d^{n-2}s^2) - E_{\rm ps}^{\rm LSD}(d^{n-1}s^1)\,, \tag{32}$$

has been calculated using the energy expression (12). It has been compared to the all-electron result:

$$\Delta E_{\rm ic}^{\rm ae} = E_{\rm ae}^{\rm LSD}(d^{n-2}s^2) - E_{\rm ae}^{\rm LSD}(d^{n-1}s^1) \tag{33}$$

using the energy expression (9). We use the exchange-correlation functional of Ceperley[37] to represent $V_{\rm xc}^{\sigma}(n,\xi)$. Although $E_{\rm ps}^{\rm LSD}$ is much smaller in absolute magnitude than the core + valence energy $E_{\rm ae}^{\rm LSD}$ (e.g., for Sc in the d^1s^2 configuration $E_{\rm ps}^{\rm LSD}/E_{\rm ae}^{\rm LSD} = 0.002$), the *differences* in the pseudopotential total energies should follow the differences in the all-electron total energies. Figure 1 shows a plot of $\Delta E_{\rm ic}^{\rm ps}$ and $\Delta E_{\rm ic}^{\rm ae}$ indicating that this expectation is indeed met.

Figure 2 shows a plot of the all-electron and pseudopotential radial $4s$ wave functions for Cr in the s^1d^5 configurations. It is seen that the two sets of wave functions $\{\chi_{4s,+}^{(1)}; \chi_{4s,-}^{(1)}\}$ and $\{\psi_{4s,+}; \psi_{4s,-}\}$ agree from $r=\infty$ to about $r=2.8$ a.u. and that the spin dependence of the all-electron orbitals is faithfully reproduced by the pseudo-orbitals. We conclude that the spin-dependent pseudopotentials can be reliably used to replace the all-electron potentials for calculations of valence properties.

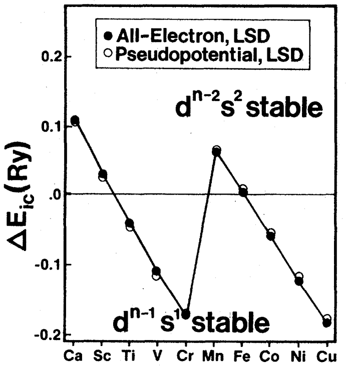

FIG. 1. The interconfigurational energies of the $3d$ elements calculated with the all-electron LSD energy expression [Eq. (33)] and the pseudopotential LSD expression [Eq. (32)].

B. Self-interaction-corrected pseudopotentials

The SIC pseudopotentials $\hat{V}_{\rm ps}^{(l,\sigma)}(r)$ have been calculated for Si and the $3d$ transition elements. Figure 3 shows $\hat{V}_{\rm ps}^{(l,\sigma)}(r)$ for $l=0,1$ in the unpolarized $3s^23p^2$ ground state of Si together with the SIC screening,

$$\hat{V}_{\rm scr}^{(l,\sigma)} = V_{\rm scr}^{\rm v}(\hat{n}(r), \hat{\xi}(r)) - V_{\rm ee}(\hat{n}_{nl\sigma}(r)) - V_{\rm xc}^{\dagger}(\hat{n}_{nl\sigma}(r), 1) \tag{34}$$

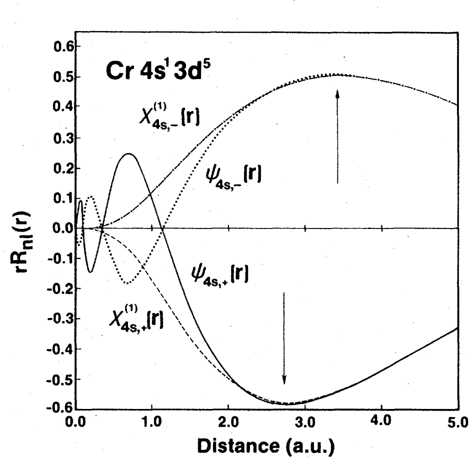

FIG. 2. All-electron and pseudo-$4s$ wave functions for Cr in the $s^1\,d^5$ configuration.

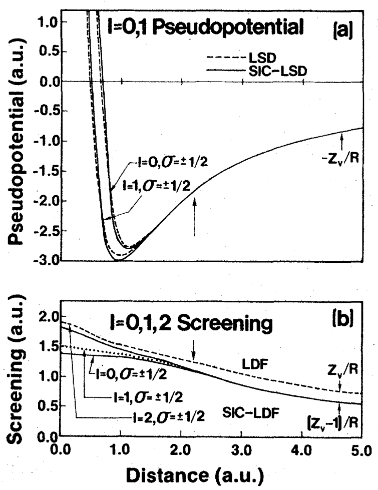

FIG. 3. (a) LSD (---) and SIC-LSD (—) pseudopotentials for Si ($3s^2 3p^2$). (b) The local LDF screening [---, Eq. (15)] and the state-dependent nonlocal SIC screening [full and dotted lines, (Eq. 34)]. The vertical arrows indicate the position of the bond center in bulk silicon. Arrows point to the limiting form of the pseudopotential and screening.

of Eq. (31), where $V_{\text{scr}}^{\text{v}}(\hat{n},\xi)$ is given by expression (15) but with the density $\hat{n}(r)$ calculated self-consistently with SIC. It is seen that self-interaction effects tend to somewhat deepen the pseudopotential near its minima but have a negligible effect on the crossing point $\hat{V}_{\text{ps}}^{(l,\sigma)}(r_{l\sigma})=0$ and on the potential outside the core region. At distances that correspond to the bond center in the bulk solid (vertical arrows in Fig. 3), the SIC pseudopotential is numerically identical with the LSD potential.

The effects of SIC on the screening [Eq. (34)] are more pronounced: Whereas the LSD screening $V_{\text{scr}}^{\text{v}}(n(r),\xi(r))$ [dashed line in Fig. 3(b)] is state independent and behaves asymptotically for the neutral atom at large-r as Z_{v}/r, the SIC screening is state dependent and has a corrected larger-r limit of $(Z_{\text{v}}-1)/r$. The *screened* atomic pseudopotential in the LSD approach hence decays very rapidly at large distances from the atomic origin as the interelectronic repulsion $V_{\text{ee}}(n(r))$ cancels the core attraction $-Z_{\text{v}}/r$ and only the exponentially decaying ($\sim e^{\beta r}$) exchange-correlation part $V_{\text{xc}}(n(r),\xi(r))$ is left. On the other hand, the SIC-screened pseudopotential approaches at large distances the correct electrostatic limit of $-1/r$ [or $-(Q+1)/r$ for a Q-charged ion] as the Coulomb and exchange-correlation self-interactions are eliminated. We note that in recent calculations of the vacancy in bulk Si, and LSD-type pseudo-potential was used.[38,39] This leads to the asymptotic behavior of $\sim(1/\epsilon)e^{-\beta r}$ for the screened defect potential of a neutral vacancy V^0 and $-1/r\epsilon$ and $-2/r\epsilon$ for the singly- and doubly-ionized vacancy (V^+ and V^{++}, respectively), while the electrostatically correct limits are $-1/\epsilon r$, $-2/\epsilon r$, and $-3/\epsilon r$ for V^0, V^+, and V^{++}, respectively, where ϵ represents dielectric screening. The use of properly self-interaction–corrected pseudopotentials might have a significant effect on the relative stabilities of V^0, V^+, and V^{++} relative to the LSD calculation of Ref. 39.

Figure 3(b) indicates that SIC affects not only the large-r behavior of the screening: At distances smaller than the bond center in the solid, the d screening (calculated here from the $3s^2 3p^1 3d^1$ configuration and spin average for clarity of display) is close to the local LSD screening as the d orbital density in Si is very diffused, while the more localized $3s$ and $3p$ orbitals give rise to significantly lower screening potentials. The nonlocality of the SIC screening in Si extends to a distance comparable to the bond center in the solid and hence can affect the band structure. The behavior of the screening in Fig. 3(b) indicates that Latter's suggestion[40] to remedy the self-interaction problem in the LSD formalism by matching a $-1/r$ tail to the potential starting from an outer point R_L (where $-Z/R+V_{\text{scr}}(R)=-1/R_L$) is insufficient, as SIC has important effects even for $r<R_L$. We find, indeed, that SIC atomic total energies are much closer to experiment than those obtained with a Latter tail correction.[40]

Figures 4 and 5 show respectively, the SIC pseudopotential $\hat{V}_{\text{ps}}^{(l,\sigma)}(r)$ and screening $\hat{V}_{\text{scr}}^{(l,\sigma)}(r)$ [Eq. (34)] of the spin-polarized Fe atom in the $(4s^1 4p^0 3d^5)_+(4s^1 4p^0 3d^1)_-$ configuration. Whereas SIC effects on the pseudopotentials are relatively small [cf. Fig. 3(a)], spin effects are pronounced and prevail at distances beyond the potential's minimum. The minority spin ($\sigma=-\frac{1}{2}$) pseudopotential is consistently deeper than the majority spin ($\sigma=\frac{1}{2}$) pseudopotential. The opposite is true of the screening potentials as the majority spin wave functions are more localized than the minority spin wave functions. Whereas spin effects reduce the magnitude of the crossing points of the *bare pseudopotential* $\hat{V}_{\text{ps}}^{(l,\sigma)}(r_{l\sigma}^0)=0$ for spin down ($r_{l-}^0<r_{l+}^0$), the crossing points of the total *screened pseudopotential* $\hat{V}_{\text{ps}}^{(l,\sigma)}(r_{l\sigma})+\hat{V}_{\text{scr}}^{(l,\sigma)}(r_{l\sigma})+l(l+1)/2r_{l\sigma}^2=0.0$ show $r_{l-}>r_{l+}$ with a reduced difference (i.e., $2|r_{l+}-r_{l-}|/|r_{l+}+r_{l-}|=2\%-4\%$).

In a previous study,[29] the crossing points $\{r_l\}$ of the *unpolarized* screened pseudopotential were shown to constitute a sensitive intrinsic l-dependent length scale for atoms. As r_l^{-1} is a measure of the scattering power of a screened atomic core for electrons of angular momentum l, it can also be used as an anisotropic electronegativity scale.

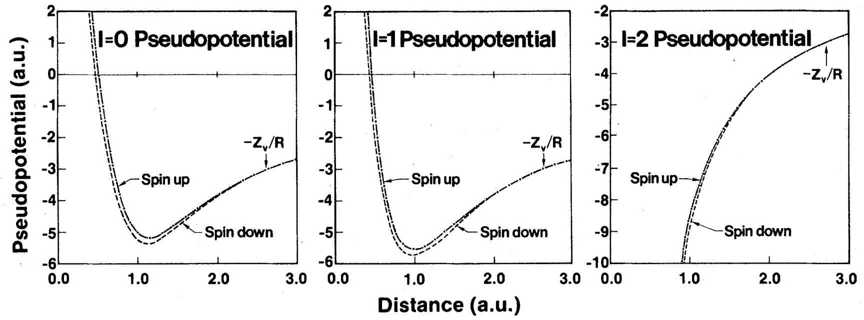

FIG. 4. The orbital and spin-dependent self-interaction-corrected pseudopotential for Fe. The $(4s^1 4p^0 3d^5)_{\rm up}(4s^1 4p^0 3d^1)_{\rm down}$ configuration was used.

We found that the $\{r_l\}$ values of atoms scale linearly with the average node position of the all-electron valence orbital $\psi_{nl}(r)$ of the same l (length scale) and that $\{r_l^{-1}\}$ scales linearly with the multiplet averaged experimental ionization energy of the valence electron with the same l (energy scale). This has lead to a successful attempt to use the orbital radii $\{r_l\}$ as structural indices in predicting the stable crystal structures of the binary AB compounds. The scheme has been applied to 495 binary compounds, including transition elements as well as simple elements, and has produced a remarkable topological separation between more than 20 different structures.[29] The present generalization of the density-functional pseudopotentials of Ref. 6 to include SIC as well as spin effects offers the possibility of establishing spin-sensitive orbital radii. Although the difference between the crossing points for spin up and spin down found here are not large, these differences may be of importance for the structural coordinates of *magnetic* binary compounds.

The introduction of self-interaction corrections to the effective potential [Eq. (31)] affects the energy eigenvalues significantly. Using the form (31) of the SIC effective potential and the form (14) for the LSD effective potential, one obtains the following for the corresponding orbital energies:

$$\begin{aligned}\hat\epsilon^{\rm SIC}_{nl\sigma} = {} & \langle\hat\chi_{nl\sigma}|-\tfrac12\nabla^2|\hat\chi_{nl\sigma}\rangle + \langle\hat\chi_{nl\sigma}|\hat V^{(l,\sigma)}_{\rm ps}|\hat\chi_{nl\sigma}\rangle \\ & + \langle\hat\chi_{nl\sigma}|V^{\rm v}_{\rm scr}(\hat n,\hat\xi)|\hat\chi_{nl\sigma}\rangle + \langle\hat\chi_{nl\sigma}|-V_{\rm ee}(\hat n_{nl\sigma})|\hat\chi_{nl\sigma}\rangle \\ & + \langle\hat\chi_{nl\sigma}|-V_x^{\uparrow}(\hat n_{nl\sigma},1)|\hat\chi_{nl\sigma}\rangle \\ & + \langle\hat\chi_{nl\sigma}|-V_c^{\uparrow}(\hat n_{nl\sigma},1)|\hat\chi_{nl\sigma}\rangle\,. \end{aligned} \tag{35}$$

The contributions appearing here are kinetic, pseudopotential, local screening, self-Coulomb, self-exchange, and self-correlation, respectively, and the hat symbol indicates that the orbitals are calculated self-consistently from the SIC effective potential. The corresponding expression for the uncorrected LSD orbital energy is

$$\begin{aligned}\epsilon^{\rm LSD}_{nl\sigma} = {} & \langle\chi_{nl\sigma}|-\tfrac12\nabla^2|\chi_{nl\sigma}\rangle + \langle\chi_{nl\sigma}|V^{(l,\sigma)}_{\rm ps}|\chi_{nl\sigma}\rangle \\ & + \langle\chi_{nl\sigma}|V^{\rm v}_{\rm scr}(n,\xi)|\chi_{nl\sigma}\rangle\,. \end{aligned} \tag{36}$$

Table I depicts the individual contributions to the orbital energies for Si $3d^2 3p^2$ and Zn $4s^2 3d^{10}$. The main conclusions are:

(1) Self-interaction corrections lower the orbital energies significantly (30%–50%). The lowering is strongly orbital dependent and hence one-electron gaps are modified as well (e.g., the s-d gap in Zn changed from 4.4 to 11.1 eV). Localized orbitals (e.g., Zn $3d$) show a much larger energy lowering than relatively diffused orbitals (Zn $4s$).

(2) The differences in orbital kinetic energies and local screening energy (with and without SIC) reflect only the self-consistent modification of the wave functions due to SIC effects (e.g., $\hat\chi$ vs χ). These are small for all nontransition elements but significant for the $3d$ elements. Hence, self-consistent LSD orbitals cannot be reliably used to estimate SIC effects in these systems.

(3) The SIC effects on the pseudopotential energy is small relative to the effect on the total screening energy for s,p orbitals (viz., Fig. 3 which compares the SIC and LSD pseudopotentials and screening for Si), whereas for d orbitals the change in the pseudopotential energy is significant

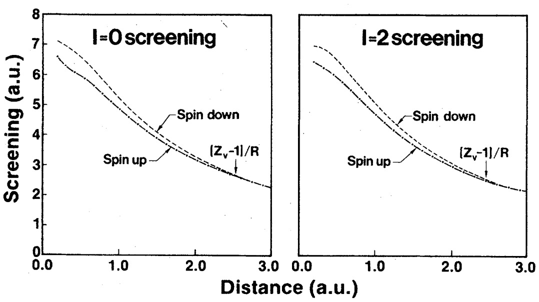

FIG. 5. The orbital and spin-dependent self-interaction-corrected screening for Fe in the $(4s^1 4p^0 3d^5)_{\rm up}(4s^1 4p^0 3d^1)_{\rm down}$ configuration. Arrows point to the limiting form of the screening.

TABLE I. Components of the orbital energies of Si $3s^2 3p^2$ and Zn $4s^2 3d^{10}$ as obtained in LSD [Eq. (36)] and the SIC-LSD [Eq. (35)]. Energies are in eV and the orbital moment $\langle \chi_{nl\sigma} | r | \chi_{nl\sigma} \rangle$ is given in Bohr radii. DIFF indicates the difference, in eV, between the LSD and self-interaction corrected results.

		Si 3*s*			Si 3*p*			Zn 4*s*			Zn 3*d*	
	SIC	LSD	DIFF	SIC	LSD	DIFF	SIC	LSD	DIFF	SIC	LSD	DIFF
Kinetic	7.92	7.88	0.04	10.18	10.10	0.08	4.64	4.81	−0.17	306.80	302.26	4.54
Pseudopotential	6.21	6.19	0.02	2.56	2.55	0.01	5.76	5.41	0.35	−97.74	−95.90	−1.84
Local screening	−23.62	−23.84	0.22	−15.75	−15.85	0.10	−15.10	−15.26	0.16	−216.67	−215.83	−0.84
Self-Coulomb	−11.25	0.0	−11.25	−8.68	0.0	−8.68	−9.04	0.0	−9.04	−28.78	0.0	−28.78
Self-exchange	6.55	0.0	6.55	4.99	0.0	4.99	5.21	0.0	5.21	16.48	0.0	16.48
Self-correlation	0.52	0.0	0.52	0.43	0.0	0.43	0.47	0.0	0.47	0.79	0.0	0.79
Orbital energy	−13.67	−9.77	−3.90	−6.27	−3.20	−3.07	−8.06	−5.04	−3.02	−19.12	−9.47	−9.65
Orbital moment	2.18	2.19	−0.5%	2.86	2.89	−1.0%	2.74	2.73	0.4%	0.89	0.91	−2.2%

relative to the change in the screening energy (e.g., 14% in Zn 3*d*). Hence, LSD pseudopotentials cannot be used with a SIC screening to correctly describe localized *d* orbitals.

(4) Self-Coulomb corrections always dominate the positive self-exchange and correlation corrections, the latter being about 60% of the former. Self-interaction correction hence tends always to *lower* the orbital energy.

(5) Equations (28) and (29) describe the effects of SIC on the total energy. In the pseudopotential case one obtains

$$E_{\mathrm{ps}}^{\mathrm{SIC\ LSD}} = E_{\mathrm{ps}}^{\mathrm{LSD}} - \sum_{nl\sigma} N_{nl\sigma}^{\mathrm{v}} \delta_{nl\sigma} \tag{37}$$

with

$$\delta_{nl\sigma} = \tfrac{1}{2} \langle \hat{\chi}_{nl\sigma} | V_{\mathrm{ee}}(\hat{n}_{nl\sigma}) | \hat{\chi}_{nl\sigma} \rangle + \langle \hat{\chi}_{nl\sigma} | \epsilon_{\mathrm{xc}}(\hat{n}_{nl\sigma_1} 1) | \hat{\chi}_{nl\sigma} \rangle , \tag{38}$$

where ϵ_{xc} is the spin-polarized exchange and correlation energy per particle. We find for Si, $\delta_{3s} = -0.70$ eV and $\delta_{3p} = -0.59$ eV; for Zn, $\delta_{4s} = -0.60$ eV and $\delta_{3d} = -2.03$ eV. Using $N_{3s} = 2$ and $N_{3p} = 2$ for Si and $N_{4s} = 2$ and $N_{3d} = 10$ for Zn, the corresponding direct corrections to the total energy are −2.6 eV for Si (2.6%) and −21.5 eV for Zn (1.2%). Hence the SIC lowering of the total energy of atoms brings it into much better agreement with experiment than the LSD energy, which is systematically too high.

Figure 6 shows the difference $\epsilon_{3d} - \epsilon_{4s}$ in orbital energies obtained with the standard LSD approximation and with the SIC-LSD approximation for the 3*d* transition elements. For reference, we give the same quantity as obtained in the Hartree-Fock (HF) approximation.[41] We note that for the $d^{n-1}s^1$ configuration LSD predicts erroneously that the *d* orbital is above the *s* orbital from Sc to Fe (in the $d^{n-2}s^2$ configuration this is true only for Sc). The SIC-LSD approximation produces *d*-*s* one-electron gaps that are consistently negative, as obtained in HF and experiment. The erroneous ordering of *d* and *s* levels for Sc-Fe in LSD may have significant effects on the band structure of the corresponding elemental solids and on the ordering of the transition metal impurity levels in semiconductors calculated previously with the LSD.[42]

We have applied the SIC pseudopotentials of F, O, and Cl to calculate the negative ions O^-, F^-, and Cl^-, which are predicted to be unstable by the conventional LSD approach.[33] We have reproduced our results on these ions obtained with the all-electron SIC approach. Owing to the correct large-*r* limiting form of the SIC-screened pseudopotential, these ions are predicted to be stable. The electron affinities (calculated as a difference in total energies of the negatively charged ion and atom) are 1.5 eV for O^- (observed: 1.5 eV), 3.4 eV for F^- (observed: 3.6 eV), and 3.6 eV for Cl^-

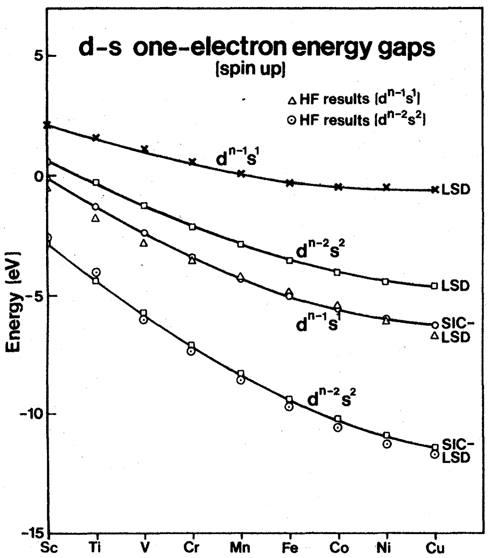

FIG. 6. The one-electron *d* to *s* energy gap in transition elements as obtained in LSD, SIC-LSD, and Hartree-Fock (HF).

(observed: 3.8 eV). As this approach includes a realistic description of correlation effects, the results are much better than those obtained by the Hartree-Fock approach[41]: −0.5 eV (negative!), 1.4 eV, and 2.6 eV for O^-, F^-, and Cl^-, respectively.

Finally, we compare the SIC-LSD atomic orbital energies with the LSD orbital energies and with the observed ionization energies of the outermost electron in the atom (Table II). We have used the improved correlation functional of Ceperley,[37] which constitutes an improvement over the von Barth–Hedin form.[43] The long-known nonapplicability of Koopmans theorem to the LSD formalism arises not only from orbital relaxation effects (which are relatively small for outer orbitals) but also from the existence of the spurious self-interaction terms in the potential.[4] Hence, the difference in the unrelaxed LSD total energies for the atom and the ion with one hole in the $nl\sigma$ orbital is to lowest order

$$\Delta E^{\mathrm{LSD}}_{nl\sigma} \cong -\epsilon^{\mathrm{LSD}}_{nl\sigma} + \tfrac{1}{2}\langle \chi_{nl\sigma} | V_{ee}(n_{nl\sigma}) | \chi_{nl\sigma}\rangle . \qquad (39)$$

As the self-Coulomb term is typically of the same order as $-\epsilon^{\mathrm{LSD}}_{nl\sigma}$, the latter constitutes a poor approximation to $\Delta E^{\mathrm{LSD}}_{nl\sigma}$ (Table II). While Slater's transition-state procedure[4] eliminates this term, it does not provide a physical description of the ground state potential in the atom. The SIC-LSD approach eliminates this difficulty by constructing self-consistently self-interaction–compensated orbitals and potentials. Indeed, Table II shows that the SIC-LSD approach yields orbital energies that compare very well with experiment. The remaining discrepancies are due to orbital relaxation effects.

TABLE II. The negative of the pseudopotential SIC LSD and LSD orbital energies for the outermost electron in the ground atomic state is compared to the observed first ionization potential (IP) (in eV). Ceperley's (Ref. 37) correlation is used for both LSD and the SIC-LSD calculations.

Atom	$\mathrm{IP}_{\mathrm{expt}}$	$-\hat{\epsilon}^{\,\mathrm{SIC}}$	$-\epsilon^{\mathrm{LSD}}$
Li	5.4	5.4	3.2
B	8.3	8.3	4.05
C	11.3	11.5	6.1
N	14.6	14.9	8.3
F	17.4	18.6	10.4
Mg	7.6	7.4	4.8
Al	6.0	5.6	3.0
P	11.0	10.1	6.25
Ar	15.75	15.3	9.3
Ca	6.11	5.9	3.8
Cr	6.8	6.7	4.0
Kr	14.0	14.0	9.4

We have previously indicated that the lowering in the orbital energies of occupied localized states due to the self-consistent removal of self-interaction terms provides the necessary explanation for the anomalously small energy gaps calculated for insulators in LSD. Although the empirical scaling of the LSD exchange coefficient $\alpha = \frac{2}{3}$ or the lack of self-consistency in band structure calculations often have the effect of increasing the calculated band gap towards its experimental value, when such devices are avoided, the band gaps predicted by band theory are anomalously small (11.2 eV in Ne [Ref. 36(a)] relative to the observed value of 21.4 eV,[44] 8.3 eV in Ar [Ref. 36(a)] relative to the observed value of 14.2 eV,[44] or 6.8 eV in Kr [Ref. 36(b)] relative to 11.6 eV (Ref. 44)).

Calculating the differences in the $2p$, $3p$, and $4p$ orbital energies for Ne, Ar, and Kr, respectively, with and without SIC (i.e., $\Delta_{nl\sigma} \equiv \hat{\epsilon}^{\mathrm{SIC}}_{nl\sigma} - \epsilon^{\mathrm{LSD}}_{nl\sigma}$), we find that the discrepancy between the experimental- and LSD-calculated band gaps closely matches $\Delta_{nl\sigma}$. This confirms the suggestion that self-interaction effects are the dominant correction to the anomalously small band gaps obtained in LSD calculations for insulators.[8] Since the SIC pseudopotential mimics very accurately the all-electron SIC orbital energies, the success of the latter approach in explaining quantitatively the systematically low LSD band gaps is shared by this pseudopotential approach. Detailed self-consistent band structure calculations on insulators with the SIC pseudopotentials developed here may provide a practical way to improve significantly the predicted band structure of such systems.

V. SUMMARY AND CONCLUSIONS

Whereas the empirical and semiempirical pseudopotential methods can be made to fit certain experimental quantities through adjustment of parameters, the first-principles pseudopotential approach involves the use of the imperfectly known exchange and correlation interactions but provides the possibility for *systematic* improvements and establishes a firm connection to the all-electron descriptions of the electronic structure. In this paper, the previously developed density-functional nonlocal atomic pseudopotential method[6,19] is extended to include spin-dependent effects as well as an accurate description of correlation effects that go beyond the local spin-density formalism.

We derive spin- and angular-momentum-dependent pseudopotentials $V^{(l,\sigma)}_{\mathrm{ps}}(r)$ from the known LSD atomic structure. These atomic pseudopotentials produce pseudo-wave-functions that are normalized, monotonic, and nodeless for the ground state, have a "maximum similarity" to the "true" all-electron valence orbitals outside the core, and produce the same orbital charge accumulation functions from $r=\infty$ to some point $r=R_C$ inward of the last maxima of the "true" orbital. In addition, these pseudo-wave-functions are given as a simple rotation in the orthogonal space of the "true" core and valence atomic orbital and include an additional simple analytic component that lies outside this orbital space. This simple linear form allows one to conveniently recover the "true" wave functions from the pseudo-wave-functions. For atoms, the energy spectrum of the screened pseudpotential is identical to the valence spectrum of the all-electron Hamiltonian for the ground electronic state and continues to mimic the latter to within 0.005 Ry for excited states over an energy range of 1 to 1.5 Ry.

The calculated spin-dependent LSD atomic pseudopotential $V_{\text{ps}}^{(l,\sigma)}(r)$ is shown to accurately reproduce the all-electron interconfigurational energies $E(d^{n-2}s^2)-E(d^{n-1}s^1)$ of all 3*d* transition elements. These spin-polarized pseudopotentials can hence be used to establish for the first time a pseudopotential theory of magnetism, including pseudopotential calculations of magnetic impurities, magnetic surfaces, and phase transitions.

The spin-dependent pseudopotential $\hat{V}_{\text{ps}}^{(l,\sigma)}(r)$, corrected for self-interaction effects, cures many of the discrepancies previously encountered in the local spin-density formalism when applied to localized states. These include the anomalously high atomic total energies, the erroneous order of *s* and *d* levels of the 3*d* transition elements Sc to Fe in the $d^{n-1}s^1$ configuration, the failure to predict the experimentally established stability of the negative ions, and the large discrepancies between the LSD energy eigenvalues and the observed ionization energies. The calculation of such self-interaction–corrected atomic pseudopotentials can establish the basis for reliable pseudopotential applications to localized states such as deep impurity states, surface and interface states, and narrow-band materials.

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[30] While in the all-electron representation [Eq. (5)] all of the core and valence (orthogonal) eigenstates are treated on the same footing with a common external potential [Eq. (6)] for all quantum states, in the pseudopotential representation one needs a different external potential W_R [Eq. (11)] for the different states. This phenomena (referred to loosely as pseudopotential nonlocality) is a direct consequence of eliminating the core subspace from explicit consideration, requiring at the same time that the valence energy spectrum of the pseudopotential system match that of the all-electron system (condition ii). This feature is common to all nonlocal pseudopotential approaches. We note, how-

ever, that the Hohenberg and Kohn density-functional theorem applies in its original form to local external potentials. One cannot simply prove that the pseudopotential energy functional Eq. (12) has a minimum at the correct density. The more general proof of Gilbert [Phys. Rev. B 12, 2111 (1975)] for nonlocal external potentials holds here. In the present approach, the pseudo-charge-density is constructed to be identical to the true valence charge density over a large region of space, minimizing thereby the deviations of the variational total energy from the pseudopotential total energy.

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