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Relativistic norm-conserving pseudopotentials

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The simple procedure to extract pseudopotentials from *ab initio* atomic calculations introduced by Hamann, Schlüter, and Chiang is extended to handle the case of heavy atoms. The solutions of the full core Dirac equation are used as references, following a recent suggestion by Kleinman. As an example, results for the atoms of group IV (C, Si, Ge, Sn, Pb) are presented.

I. INTRODUCTION

Work involving the theory of pseudopotentials, which has had many different justifications at different times during its development,[1,2] has recently been concentrated on nonlocal one-electron effective potentials derived from all-electron atomic calculations.[3–5] The crucial point of such potentials is their transferability from the reference (atomic) system, which they reproduce by construction, to different chemical environments.[2] Within this new family, those pseudopotentials which, besides the atomic valence eigenvalues, reproduce exactly the atomic all-electron wave functions beyond a chosen radius under the constraint of strict norm conservation[5] seem to guarantee optimum transferability, as has been shown by several different tests.[6,7] This property has recently encouraged different groups[7,8] to adopt these pseudopotentials in the study of the structural properties of crystals.

Kleinman[9] observed that the procedure of Ref. 5 to construct these pseudopotentials can be easily extended to include relativistic effects up to but not including order α^2 once a solution of the atomic all-electron Dirac equation is available; i.e., that it is possible to construct a pseudopotential for the wave function of each relativistic one-electron state in the valence shell such that, when compared to the corresponding all-electron wave function, the pseudo-wave-function shares, to order α^2, the same property of norm conservation as specified in Ref. 5, and therefore, presumably, the same transferability. An error of α^2 is the minimum price to be paid for having the true relativistic wave function represented by a single radial wave function obeying an effective Schrödinger equation. In constrast to this, perturbation expansions which include relativistic effects without actually solving the Dirac equation start with a single-spinor Pauli equation and end up with results which are correct to order $Z^2\alpha^2$ only.[10] More sophisticated scalar relativistic equations can do better,[11] but they are unable to provide spin-orbit splitting energies.

Although valence electrons are significantly affected by relativistic effects in heavy atoms, which explains the need for relativistic pseudopotentials,[12] a Schrödinger pseudo-wave-function can be associated with each valence wave function of the original Dirac atom. For small binding energies (valence electrons) the major component of each wave function is essentially decoupled from the minor component outside the core region, and thus for the all-electron Dirac atom the major component of the valence wave functions obeys, *outside* the core region, a Schrödinger-type equation.[9] On the other hand, *inside* the core region, any *pseudo*-wave-function differs from its corresponding all-electron wave function. As a result, the prescription for obtaining pseudopotentials from the inversion of the Schrödinger equation[5] need to be applied only to the major component of a valence all-electron Dirac wave function in order to produce a pseudopotential which automatically absorbs not only the core-electron orthogonality effects, but also all relativistic effects to order α^2. We shall go through the previous statements more carefully and describe the techniques used for the actual implementation of this idea as suggested by Kleinman.[9] Then we will present illustrative results group-IV atoms.

II. FORMALISM AND METHOD

For a central potential $V(r)$ the Dirac equation reduces to two coupled radial equations.[13,14] Following Kleinman[9] we use atomic units ($c=\alpha^{-1}=137.037$) and the symbols G and F for the radial part of the major and minor components of the Dirac wave functions in the standard representation[13]; κ is the relativistic quantum number, equal to l for $j=l-\frac{1}{2}$ and to $-(l+1)$ for $j=l+\frac{1}{2}$, and the Dirac equations read

$$\frac{dF}{dr}-\frac{\kappa}{r}F+[\epsilon-V(r)]\alpha G=0\ , \tag{1}$$

$$\frac{dG}{dr}+\frac{\kappa}{r}G-\left[\frac{2}{\alpha^2}+\epsilon-V(r)\right]\alpha F=0\ . \tag{2}$$

We consider an atomic system and repeat Kleinman's argument. Equation (2) for valence electrons (small ϵ) outside the core region [small $V(r)$] becomes

$$F=\frac{\alpha}{2}\left[\frac{dG}{dr}+\frac{\kappa}{r}G\right]\ , \tag{2'}$$

which, substituted into (1), gives

$$-\frac{1}{2}\left[\frac{d^2G}{dr^2}-\frac{\kappa(\kappa+1)}{r^2}G\right]+[V(r)-\epsilon]G=0\ . \tag{1'}$$

Equation (1') is correct up to but not including terms of order α^2. Let us assume we have solved the self-consistent one-electron Dirac problem, i.e., Eqs. (1) and (2), for an atom. This implies the choice of some suitable scheme for the description of the many-electron interactions.[15] We shall discuss this point further below. Our output is a set of one-electron eigenvalues and (two-component) radial wave functions, plus one self-consistent potential

$$\{\ \psi_{nlj}(r),E_{nlj}\ \}\ \ V(r)\ . \tag{3}$$

One can formally apply to the relativistic all-electron results (3) the procedure of Ref. 5, with only two differences: first, l and j, rather than l alone, will label valence states and thus pseudopotentials; second, the reduction of the all-electron *Dirac* equation, obeyed by valence electrons, to an effective *Schrödinger* equation needs some careful considerations in view of the presence of the minor component. For the Dirac atom the normalization of the radial wave function reads

$$\int_0^\infty [\,|G(r)|^2+|F(r)|^2]dr=1\ , \tag{4}$$

so that the condition on the major component alone is

$$\int_0^\infty |G(r)|^2dr=1-\int_0^\infty |F(r)|^2dr\ . \tag{5}$$

Therefore, if one were to use the relativistic pseudopotentials to obtain and deal with both major and minor components of the atomic pseudo-wave-functions, i.e., if one were to solve *Dirac's* equation for molecular or solid-state systems, it would be necessary to define the norm conservation using Eq. (5), i.e., considering the function $R_{lj}^{(2)}$ as a major component and then introducing a minor component of the pseudo-wave-function. The resulting pseudopotentials would be fully analogous to Ref. 5 correct to order α^2. This choice would obviously produce a pseudo-wave-function whose major component $R_{lj}(r)$ has a norm

$$\int_0^\infty |R_{lj}(r)|^2dr=1-\int_0^\infty |F_{lj}(r)|^2dr \simeq 1-\alpha^2\ , \tag{6}$$

due to the charge contribution of the minor component.

However, since the approximation equation (2') already introduced an error α^2, we accept an additional error of order α^2 by imposing the normalization condition

$$\int_0^\infty |R_{lj}|^2dr=1\ . \tag{7}$$

This tiny error ($\alpha^2=5.3\times10^{-5}$) affects the pseudo-wave-function only for $r<r_c$ as is evident from Fig. 1, but it guarantees that the correct

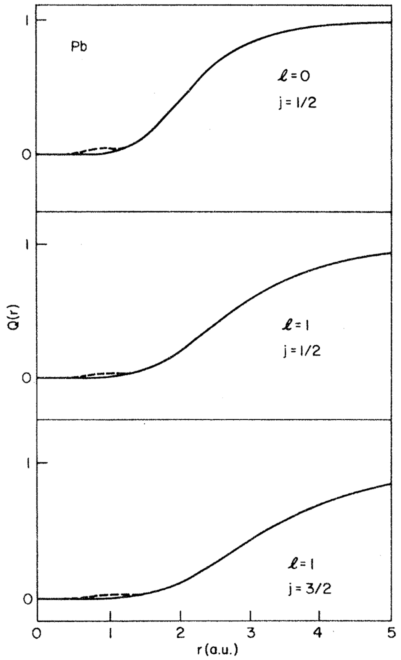

FIG. 1. Integrated all-electron (dash) and pseudo-(solid) valence charge density of the relativistic Pb atom.

amount of charge, *with no error,* be associated to pseudo-wave-functions when minor components are not taken into account. It is apparent from all the results displayed for Pb (Figs. 2–5) that the errors of order α^2 introduced by both the approximation equation (2′) and the normalization equation (7) are negligible for all practical purposes.

The identity that relates the properties of norm conservation and logarithmic derivatives of the wave functions[5,16] has its counterpart in the case of the all-electron *Dirac* equation where major and minor components are both retained.[14] After some manipulations, the identity can be expressed (in atomic units) as

$$-2\pi\left[r^2\Xi^2\frac{\partial}{\partial\epsilon}\left(\frac{2c\xi}{\Xi}\right)\right]_R=4\pi\int_0^R(\Xi^2+\xi^2)r^2dr\ , \tag{8}$$

where $\xi=F/r$ and $\Xi=G/r$. We see that for the all-electron Dirac atom the quantity $2c\xi/\Xi$ in Eq. (8) plays the same role as the quantity ϕ'/ϕ in Eq. (1) of Ref. 5. Another way to see this is to note that, *for valence electrons outside the core,* we can rewrite Eq. (2′) as

$$\frac{\Xi'}{\Xi}=\frac{2c\xi}{\Xi}-\frac{\kappa+1}{r}\ , \tag{9}$$

where $\kappa+1/r$ does not depend on the energy ϵ. For all lj values present in the valence shell we compare the right-hand side of Eq. (9), obtained by integration of the all-electron Dirac equation, with the quantity ϕ'/ϕ, obtained from integrating Schrödinger's equation with the appropriate relativistic pseudopotential V_{lj}. A comparison of the logarithmic derivatives for Pb is given in Fig. 2.

In the following illustrating cases the occupation of the states, with $j=l\pm\frac{1}{2}$ for partially filled shells, was chosen according to the degeneracy of the all-electron Dirac solutions. We note that this particular weighting does not correspond to the configuration which minimizes the total energy of the atom in the local-density functional approximation. It is furthermore convenient to define the average pseudopotential $\bar{V}_l$ in a different way than done in Ref. 9. We define

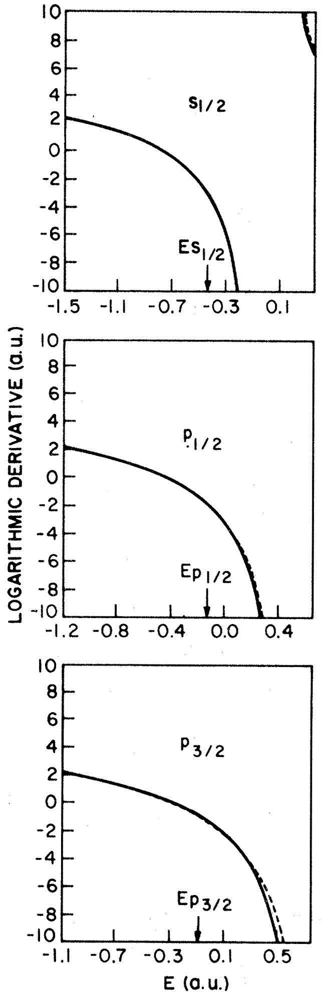

FIG. 2. Logarithmic derivatives of the Pb relativistic wave functions at the covalent radius for lead (i.e., $r=2.78$ a.u.) (full line stands for the pseudoatom, dashed line stands for the all-electron atom). Arrows indicate the position of eigenvalues. The identity relating norm conservation and logarithmic derivatives for Schrödinger atoms has its counterpart in the case of Dirac atoms (see text).

$$\bar{V}_l^{\text{ion}}(r)=\frac{1}{2l+1}[lV_{l,l-1/2}^{\text{ion}}(r)+(l+1)V_{l,l+1/2}^{\text{ion}}]\ , \tag{10}$$

i.e., an average potential weighted by the different j degeneracies of the $l\pm\frac{1}{2}$ states. The total ionic pseudopotential

$$V_{\text{ps}}^{\text{ion}}(r)=\sum_{l,m}[\,|\,l+\tfrac{1}{2},m+\tfrac{1}{2}\rangle V_{l,l+1/2}^{\text{ion}}(r)\langle l+\tfrac{1}{2},m+\tfrac{1}{2}\,|+|\,l-\tfrac{1}{2},m-\tfrac{1}{2}\rangle V_{l,l-1/2}^{\text{ion}}\langle l-\tfrac{1}{2},m-\tfrac{1}{2}\,|\,]\ , \tag{11}$$

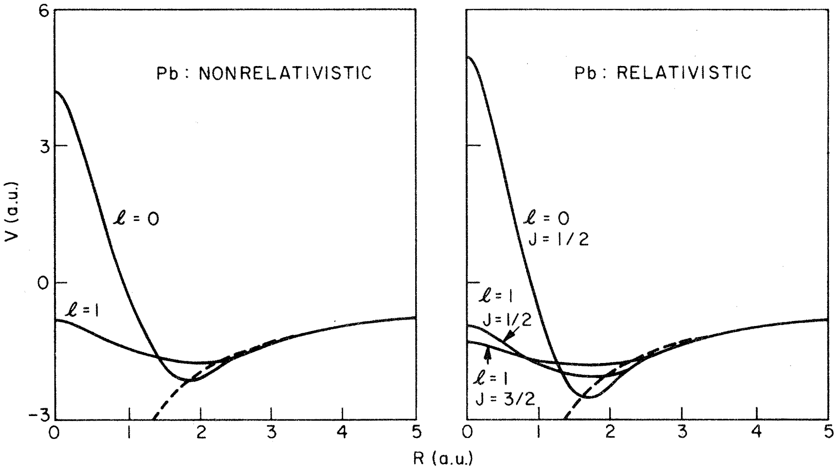

FIG. 3. Nonrelativistic (Schrödinger) and relativistic (Dirac) ionic pseudopotentials for lead. Note the big shift of the s potential and the appearance of two different $p_{1/2}$ and $p_{3/2}$ potentials in the relativistic case. Dashed curve is $-Z_v/r$.

can then be rewritten as

$$V_{\mathrm{ps}}^{\mathrm{ion}}(r)=\sum_{l}|l\rangle[\bar{V}_l^{\mathrm{ion}}(r)+V_l^{\mathrm{so}}(r)\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}]\langle l| \ , \tag{12}$$

where

$$V_l^{\mathrm{so}}(r)=\frac{2}{2l+1}[V_{l,l+1/2}^{\mathrm{ion}}(r)-V_{l,l-1/2}^{\mathrm{ion}}(r)] \ . \tag{13}$$

This definition of $\bar{V}_l$ contains all scalar parts of the relativistic pseudopotential.

The program we used to solve the all-electron Dirac equation is an improved version of the scheme first proposed by Liberman, Waber, and Cromer[17] and incorporates the Wigner[18] interpolation scheme for the exchange and correlation potential. Relativistic corrections to local-density exchange functionals have recently been discussed by Rajagopal[19] and by MacDonald and Vosko.[20] For test purposes we have incorporated the functional correction of MacDonald and Vosko into our calculations. These corrections tend to weaken the attractive exchange interaction for very high densities, but rapidly tend towards zero for lower electron densities. Test results for Pb show a reduction of the total atom binding energy (about 21 000 a.u.) by 44.4 a.u. which amounts to 0.2%. This reduction results almost entirely from the 1s level.

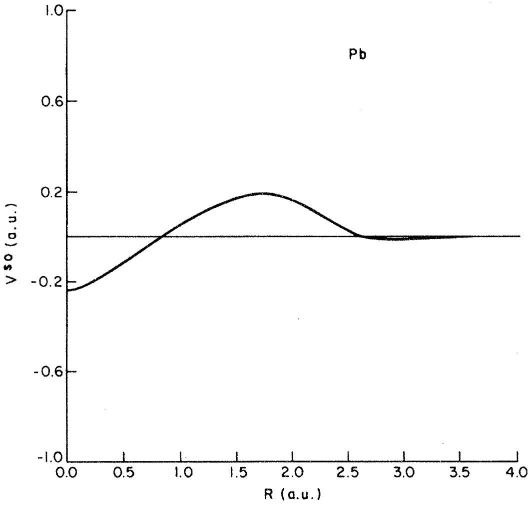

FIG. 4. Pb spin-orbit pseudopotential for p states as defined by Eq. (16) in the text.

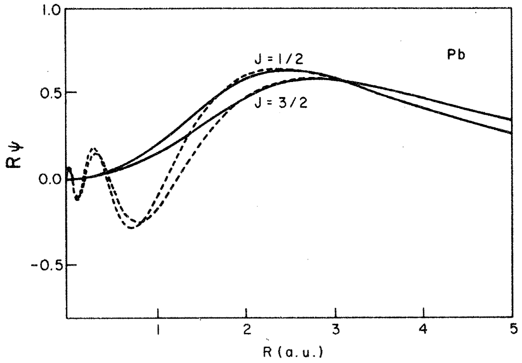

FIG. 5. Relativistic all-electron (dash) and pseudo- (solid) wave functions for $p_{1/2}$ and $p_{3/2}$ states of Pb. For the relativisitic all-electron atom the major component of the wave function is shown.

The influence of the relativistic correction of exchange on the 6*s* and 6*p* valence electrons is in the range of 10^{-3} to 10^{-4} a.u. and can thus be safely neglected in the construction of pseudopotentials. Similar results have recently been reported by MacDonald *et al.*[21] for band-structure calculations on Pd and Pt.

III. ILLUSTRATIVE RESULTS

We show some characteristics of the pseudopotentials resulting from the procedure previously described. In Fig. 3 we display the bare-ion relativistic pseudopotentials obtained for the Pb atom, and compare them to the nonrelativistic potentials. We see that the $l=0$ potential is deeper for the relativistic ion. The $l=1$ potential splits into two potentials $j=l\pm\frac{1}{2}$, whose j-weighted average is also deeper than the nonrelativistic $l=1$ potential. The spin-orbit pseudopotential [as defined by Eq. (13)] is shown in Fig. 4. It appears as a weak potential which extends as far as all of the pseudopotentials differ from the $-Z_v/r$ Coulomb tail. The wave functions and pseudo-wave-functions of Pb $p_{1/2}$ and $p_{3/2}$ are shown in Fig. 5. The dotted lines correspond to the major component of the all-electron relativistic solution while solid lines indicate pseudo-wave-functions. By construction[5,9] the pseudo- and real wave functions agree up to α^2 beyond a chosen "core radius" r_c. The integrals of the real and pseudo-charge-densities[3] from 0 to r agree exactly for $r>r_c$ (Fig. 1), given the choice of the normalization condition equation (7), since the contribution of charge density due to the minor component is also mostly located within $r<r_c$.

In Table I we compare the eigenvalues of the all-electron Dirac and Schrödinger equations for C, Si, Ge, Sn, and Pb. The spin-orbit splitting of the valence p electrons increases from 9 mV for C to 1.5 eV for Pb, approximately following a quadratic law $\Delta E_{\text{so}}\propto Z^2$ which can be predicted from simple Thomas-Fermi arguments.[22] The center of mass of the doublets (defined as a j-weighted average) also changes with respect to the nonrelativistic case and we see that the s valence electrons, deeper in energy and more localized near the nuclei, are affected by relativistic effects more strongly than the p valence electrons. For Ge, Sn, and Pb, the effects are sizable and should be included in high-precision crystal calculations.

TABLE I. Valence s and p levels of the Schrödinger and Dirac atoms. The Wigner exchange-correlation approximation was adopted for both. The average p level is obtained for relativistic doublets weighting the $p_{1/2}$ and $p_{3/2}$ by their degeneracies and is displayed to the right of the doublets. Energies in a.u.

		Schrödinger	Dirac	
C	s	-0.4994	-0.5000	
	p	-0.1989	-0.1992	
			-0.1989	-0.1990
Si	s	-0.3988	-0.4006	
	p	-0.1559	-0.1565	
			-0.1553	-0.1561
Ge	s	-0.4266	-0.4390	
	p	-0.1525	-0.1562	
			-0.1492	-0.1515
Sn	s	-0.3701	-0.3975	
	p	-0.1476	-0.1569	
			-0.1402	-0.1458
Pb	s	-0.3580	-0.4505	
	p	-0.1451	-0.1795	
			-0.1255	-0.1435

IV. CONCLUSION

We have extended the simple pseudopotential prescription of Hamann, Schlüter, and Chiang[5] to the full relativistic all-electron Dirac atom according to a suggestion of Kleinman.[9] The resulting pseudopotentials meet the transferability tests of Ref. 5 for heavy atoms, thus providing effective potentials for elements strongly affected by relativistic effects.

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