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Spin-orbit splitting in semiconductors and insulators from the *ab initio* pseudopotential

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In this Brief Report, we give the expressions required for using the vector (spin-orbit) part of the *ab initio* pseudopotential in a crystalline calculation. Inclusion of the spin-orbit interaction using the vector part of the pseudopotential in first order reproduces the measured spin-orbit splittings in Ge as well as the rare-gas solids and agrees with all-electron calculations.

The *ab initio* pseudopotential method for solid-state calculations has been extensively developed.[1] In particular, relativistic effects for heavy atoms can be included up to order α^2 in the pseudopotentials.[2] (Here α is the fine-structure constant.) The result is most conveniently split into two terms:

$$\hat{V}_{\mathrm{ps}}^{\mathrm{ion}}(\mathbf{r}) = \sum_{l} |l\rangle [\hat{V}_l^{\mathrm{ion}}(r) + \hat{V}_l^{\mathrm{SO}}(r)\mathbf{L}\cdot\mathbf{S}] \langle l| \,. \qquad (1)$$

The scalar part (first term) includes the effect of the mass shift and the Darwin term. This has been shown to have an important effect on the eigenvalues in the density functional treatment of Ge and GaAs.[3] However, up to this point, the vector (spin-orbit) part of the ionic pseudopotential (the second term) has not been explicitly included in solid-state calculations. In this Brief Report, we give the relevant expressions for evaluating the spin-orbit part of the potential in a plane-wave basis. We show that the *ab initio* pseudopotential method accurately gives spin-orbit splittings in solids, properly accounting for the varying enhancement over atomic splittings from covalent Ge to the rare-gas solids.

The spin-orbit part of the Hamiltonain is the second term in Eq. (1):

$$H^{\mathrm{SO}} = \sum_{l(\neq 0)} |l\rangle \hat{V}_l^{\mathrm{SO}}(r)\mathbf{L}\cdot\mathbf{S}\langle l| \,. \qquad (2)$$

There is no $l=0$ contribution to the spin-orbit coupling. We expand the wave functions of the zeroth-order Hamiltonian [given by the first term of Eq. (1) together with the usual kinetic energy and screening terms from the density functional approach[4]] in plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} \psi_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \qquad (3)$$

where Ω is the crystal volume. With each $|n\mathbf{k}\rangle$ is associated a spinor which can be up or down relative to the z axis. In first order, the matrix required is then just

$$H_{sn\mathbf{k},s'n'\mathbf{k}}^{\mathrm{SO}} = \sum_{\mathbf{G},\mathbf{G}'} \psi_{n\mathbf{k}}^{*}(\mathbf{G}) H_{s,\mathbf{k}+\mathbf{G};s',\mathbf{k}+\mathbf{G}'}^{\mathrm{SO}} \psi_{n'\mathbf{k}}(\mathbf{G}'), \qquad (4)$$

where s denotes the spin. The problem thus reduces to formulating the spinor plane-wave matrix elements of Eq. (2). Once this is done, evaluation and diagonalization of Eq. (4) proceeds in the same way as in the empirical pseudopotential method (EPM).[5]

For the case of one type of atom, the matrix elements of Eq. (2) are

$$H_{s\mathbf{K},s'\mathbf{K}'}^{\mathrm{SO}} = \langle s|\mathbf{S}|s'\rangle \cdot \sum_{l(\neq 0)} \sum_{i,j} \int \frac{d\mathbf{r}}{\Omega} e^{-i\mathbf{K}\cdot\mathbf{r}} \mathbf{L} V_l^{\mathrm{SO}}(|\mathbf{r}-\mathbf{R}_j-\boldsymbol{\tau}_i|) \hat{P}_l e^{i\mathbf{K}'\cdot\mathbf{r}}. \qquad (5)$$

Generalization to more than one atomic type is straightforward. A compressed notation has been adopted with $\mathbf{K}=\mathbf{k}+\mathbf{G}$. The angular momentum projection operator $\hat{P}_l$ is written in for $|l\rangle\langle l|$ and is understood to project around the site centered at $\mathbf{R}_j+\boldsymbol{\tau}_i$. Here the sites are denoted by lattice vector $\mathbf{R}_j$ and basis vector $\boldsymbol{\tau}_i$. The sum over sites reduces to a structure factor. The remaining difficulty is the angular part of the integration. This may be done along the lines described in Ref. 6. After some algebra, and specializing to the cases of $l=1$ and $l=2$ only, one obtains

$$H_{s\mathbf{K},s'\mathbf{K}'}^{\mathrm{SO}} = -i\langle s|\mathbf{S}|s'\rangle \cdot \left[12\pi \frac{\mathbf{K}\times\mathbf{K}'}{KK'} V_{l=1}^{\mathrm{SO}}(K,K') + 60\pi \frac{\mathbf{K}\times\mathbf{K}'}{KK'} \frac{\mathbf{K}\cdot\mathbf{K}'}{KK'} V_{l=2}^{\mathrm{SO}}(K,K') \right] S(\mathbf{K}'-\mathbf{K}), \qquad (6)$$

where

$$V_l^{\mathrm{SO}}(K,K') = \frac{1}{\Omega_c} \int_0^\infty r^2 dr\, j_l(Kr) V_l^{\mathrm{SO}}(r) j_l(K'r), \qquad (7)$$

with Ω_c being the cell volume and j_l being a spherical Bessel function. The structure factor is defined as

$$S(\mathbf{G}) = \sum_{i} e^{i\mathbf{G}\cdot\boldsymbol{\tau}_i}. \qquad (8)$$

These expressions can be implemented straightforwardly to supplement a standard *ab initio* pseudopotential band-structure calculation. The matrix in Eq. (4) is augmented by the zeroth-order eigenvalues on the diagonal forming a standard eigenvalue problem, the solution of which yields the spin-orbit-split spectrum in first order.

This approach has been applied to the case of Ge with

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TABLE I. Comparison of present calculation of spin-orbit splitting of band states for Ge to empirical pseudopotential (EPM) results and experiment. Energies are in eV.

Ge	Present	EPM (Ref. 5)	Expt (Ref. 7)
$\Gamma_{7v} \rightarrow \Gamma_{8v}$ (Δ_0)	0.30	0.29	0.297
$\Gamma_{6c} \rightarrow \Gamma_{8c}$ (Δ_0')	0.22	0.21	0.200
$L_{6v} \rightarrow L_{4,5v}$ (Δ_1)	0.19	0.20	0.184
$L_{6c} \rightarrow L_{4,5c}$	0.10	0.09	...

TABLE II. Comparison of the spin-orbit splitting of the highest occupied p states in the atom to the crystal and experiment. Energies are in eV.

	Atom	Solid	Expt.
Ge	0.19	0.30	0.296[a]
Ar	0.18	0.20	0.2[b]
Kr	0.65	0.72	0.64[b]
Xe	1.26	1.40	1.3[b]

[a]Reference 6. [b]Reference 7.

the results summarized in Table I. For comparison, the results of the EPM calculation of Ref. 5 are shown as well as the electroreflectance data from Ref. 7. In the EPM calculation, the spin-orbit coupling is modeled with one adjustable parameter which is scaled to reproduce the measured spin-orbit splitting at the valence-band edge. Agreement of the *ab initio* pseudopotential calculation with the EPM approach and experiment is excellent. We have assigned the measured Δ_1 splitting to the spin-orbit splitting of the valence bands near the L point in the Brillouin zone. The calculated spin-orbit splitting of the valence band along Λ is nearly constant away from Γ. The Δ_1' and Δ_1'' splittings associated with the E_1' feature in the electroreflectance spectrum do not seem to be simply related to the spin-orbit splittings of the valence and conduction bands near the L point.[7] To our knowledge, there is no published fully relativistic band-structure calculation for Ge at this time, so comparison of the present relativistic pseudopotential calculation to all-electron-type calculations is not possible. We do note that Bachelet and Christensen report a fully relativistic calculation for GaAs[3] based on the linear-muffin-tin-orbital (LMTO) method. They obtain spin-orbit splittings in good agreement with experiment and which scale from our Ge results in a reasonable way.

The present approach has also been used for the case of rare-gas solids. The resulting spin-orbit splitting of the valence-band edge is shown in Table II for Ar, Kr, and Xe in comparison to experiment[8] as well as the corresponding splitting of the atomic p levels. The results agree well with the photoemission experiments. They also agree with the all-electron calculations of Rössler[9] who finds splittings of 0.18, 0.70, and 1.37 eV for Ar, Kr, and Xe, respectively. We also note the case of Ge in comparison to the spin-orbit splitting of the atomic levels.[10] For Ge the enhancement of the spin-orbit splitting in the crystal in comparison to the atom is about 1.5 as generally observed.[11] In a covalent material such as Ge, the bonding leads to compression of the valence orbitals. That is, the p-type wave functions at the valence-band edge exhibit a broad plateau in the bonding region which leads to more weight in the region where the vector part of the pseudopotential is nonzero (extending for a radius of approximately 1.8 a.u. around the atomic sites). This enhances the spin-orbit splitting in the crystal. However, in the rare-gas solids there is very little enhancement because of the weak bonding. The wave functions at the valence-band edge in this case are essentially unchanged from the atomic wave functions.

It may at first be surprising that calculations based on the local density approximation (LDA) (Ref. 4) should give good results for the spin-orbit splittings in the crystal. The minimum gap is generally underestimated for semiconductors and insulators when calculated using the LDA. In fact, for Ge the gap is calculated to be zero; the valence bands and conduction bands overlap at $k = 0$ when the spin-orbit splitting is included.[3] In semiconductors and insulators it has been shown that a direct calculation of the quasiparticle energies is required to obtain the correct gaps.[12] We suggest two reasons for the success of the LDA band-structure calculation for the spin-orbit splittings. First, the spin-orbit interaction derives primarily from the core region where screening is unimportant. Therefore, use of the LDA for the exchange-correlation part of the screening potential has a small influence on the spin-orbit interaction which is, in the present case, frozen into the vector part of the ionic pseudopotential in Eq. (1). Second, the quasiparticle wave function has been shown to be very closely approximated by the wave function in the LDA calculation.[12] Taken together these suggest that the matrix elements of the spin-orbit part of the Hamiltonian calculated using a LDA band structure can be quite reasonable.

In summary, we have implemented the vector part of the *ab initio* pseudopotential, the spin-orbit term, and demonstrated that the pseudopotential approach yields good spin-orbit splittings in solid-state calculations.

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