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Orthogonalized linear combinations of atomic orbitals. IV. Inclusion of relativistic corrections

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The relativistic corrections to the band-structure calculation have been implemented in the orthogonalized linear combinations of atomic orbitals method. A two-step process is suggested such that the scalar-relativistic effects due to the spin-independent mass-velocity and Darwin terms are treated first. Spin-orbit interaction is then included on the basis of the spin-polarized band structures. All other higher-order corrections are ignored. Test calculations on scalar-relativistic corrections are demonstrated in the elemental methods Ni, Nb, and Ce with increasing atomic mass numbers. The results are in very good agreement with the established results using other band methods. The full relativistic band structure is calculated for ferromagnetic Fe. It is shown that the effect of spin-orbit interaction in Fe is of considerable importance compared with the scalar-relativistic correction.

I. INTRODUCTION

The linear combination of atomic orbitals (LCAO) method has been a popular method to study the band structure of solids since its use in the first realistic calculation with Li in 1966.[1] Over the years, the method has been systematically refined and improved, and has been applied to a variety of condensed-matter systems for their electronic structures.[2–5] In 1975, an orthogonalized version of the method, or the orthogonalized linear combinations of atomic orbitals (OLCAO) method,[6] was introduced such that the core states in the basis expansion were completely eliminated from the final secular equation, resulting in a much reduced matrix dimension. The method is particularly appearing for complicated systems with a large number of atoms in the unit cell or with heavy atoms with large cores. The OLCAO method has been successfully applied to complex crystals[7] and amorphous solids.[8] In recent years, introduction of efficient self-consistent schemes.[9] extension to f-electron systems,[10] implementation of spin-polarized version,[7,11,12] development of first-principles total-energy calculations,[13] and timely application to high-temperature superconductors[14,15] have made the OLCAO method one of the premier methods in the modern band theory of solids. However, in many systems with complex crystal structures and with heavy atoms in which the OLCAO method is supposed to be most competitive, relativistic effects become very important and cannot be totally ignored. While corrections to the relativistic effects in other methods of band-structure calculation such as the Korringa-Kohn-Rostoker (KKR),[16] APW,[17] linear augmented-plane-wave (LAPW),[18] linear muffin-tin orbitals (LMTO),[19–21] etc. method are quite standard, at least at the scalar-relativistic (SR) level, such corrections have not been fully explored with the OLCAO method. Relativistic molecular calculations with LCAO method using numerical basis have been developed quite some time ago.[22] Wang and Callaway have studied the spin-orbit interaction in ferromagnetic Ni and Fe using the linear combination of Gaussian-type orbitals (LCGO) method,[11,12] but not with the full relativistic corrections. It is therefore desirable to add the full relativistic corrections to the OLCAO method which is sufficiently efficient to be applicable to complex systems with heavy elements such as the high-temperature superconducting oxides[14] or the rare-earth–iron–boron permanent magnets.[7]

In this paper, we describe an implementation of relativistic corrections to the OLCAO method and present test results on the well-studied bench mark systems to assess the accuracy of the relativistic OLCAO method. We follow the usual approach of separating the SR effects from the spin-orbit coupling. The SR effect is treated as additional corrective terms to the potential, while the spin-orbit coupling matrix elements are added to the spin-polarized Hamiltonian matrix before diagonalization in a manner similar to the work of Koelling and Harmon.[23]

The organization of this paper is as follows. The formalism for SR correction is outlined in Sec. II. This SR correction is then applied to three elemental metals, Ni, Nb, and Ce, with increasing atomic mass numbers and correspondingly increasing relativistic effects. The results are discussed in Sec. III. In Sec. IV, addition of spin-orbit coupling with application to ferromagnetic Fe is described. A brief conclusion is presented in the last section.

II. FORMALISM ON SCALAR-RELATIVISTIC CORRECTION

We start with the Dirac equation for a relativistic electron in a solid and split the electronic wave function into the "large" and "small" components:[24]

$$c\sigma * \mathbf{p}\psi_v + (mc^2 - E - e\phi)\psi_u = 0 \ , \tag{1a}$$

$$c\sigma * \mathbf{p}\psi_u - (mc^2 + E + e\phi)\psi_v = 0 \ . \tag{1b}$$

In the equations above, σ stands for Pauli spin matrices, $\mathbf{p}$ the momentum operator, and ϕ is the scalar potential experienced by the electron. We assume that there is no external magnetic field applied. The ratio of "large" component ψ_u to the "small" component ψ_v can be estimated to be $2c/v$, where v is the velocity of the electron. Since the velocity of light c is much larger than v, one needs to only concentrate on the "large" component involving two component spinors with up spin α and down spin β.

If we define the energy $E'=E-mc^2$ with the rest energy taken out, Eq. (1a) takes the form

$$(E'+e\phi)\psi_n=\frac{1}{2m}-(\sigma\cdot\mathbf{P})K(\sigma\cdot\mathbf{P})\psi_n \tag{2}$$

and by taking the approximation

$$K=\frac{1}{1+[(E'+e\phi)/2mc^2]}\simeq 1-\frac{E'+e\phi}{2mc^2} ,$$

the Dirac equation can be simplified to the form

$$(E'+e\phi)\psi=\left[\frac{1}{2m}\mathbf{p}^2-\frac{\mathbf{p}^4}{8m^3c^2}-\frac{e\hbar^2}{8m^2c^2}\nabla*\nabla\phi \right. \\ \left. -\frac{e\hbar}{4m^2c^2}\sigma*\nabla\phi\times\mathbf{p}\right]\psi , \tag{3}$$

where we have dropped the subscript u for the "large" component of the wave function for convenience. In comparison with the nonrelativistic Schrödinger equation, there are three additional terms to the Hamiltonian on the right-hand side of (3) which are called the mass-velocity, Darwin, and spin-orbit coupling terms, respectively. Note that the Pauli matrices σ are involved only in the spin-orbit interaction term. This means that the first two corrective terms have no off-diagonal matrix elements between the two components of the spinor. They do not mix the spin components and thus behave like a scalar. The term "scalar-relativistic correction" is used if we take into account only the first two terms and leave the spin-orbit coupling for further treatment. This separation of spin-dependent and spin-independent parts of relativistic corrections is extremely convenient in terms of real calculations. In the SR framework, the symmetry of the Hamiltonian is not changed and the effect of both mass-velocity and Darwin terms can be absorbed as corrections to the one-electron potential of the Schrödinger equation. This change in the effective crystal potential is the same for both spin components so the SR correction can be applied to the paramagnetic bands as well as the spin-polarized bands. In general, the spin-orbit coupling parameters are smaller than the SR shifts by typically an order of magnitude and the effect is important only in small regions of **k** space where certain band degeneracy exists.[25] In the ordinary band-structure calculations, it is customary to consider only the SR effect and ignore the spin-orbit interactions unless specifically desired.

In the OLCAO method, it is quite straightforward to calculate the matrix elements of the mass-velocity and Darwin terms. For the mass-velocity term, we may write

$$\mathbf{p}^4=(p_x^2+p_y^2+p_z^2)\cdot(p_x^2+p_y^2+p_z^2) \tag{4}$$

where p_x, p_y, and p_z are substituted by the corresponding differentiation operators. It is easy to carry out the differentiation operation between Bloch sums:

$$\Phi_{\mathbf{k},\alpha i}=\frac{1}{\sqrt{N}}\sum_n(-i\mathbf{k}\cdot\mathbf{R}_n)\phi_i(\mathbf{r}-\mathbf{R}_n-\tau_\alpha) \tag{5}$$

where the atomic wave functions ϕ are expanded in terms of Gaussian-type orbitals which, in general, take the form

$$x^n y^l z^m \exp(-\alpha r^2) . \tag{6}$$

In this case, it is convenient to use a generalized formula for the overlap integral between two Gaussian orbitals as shown by Lafon:[26]

$$S_{n1l1m1,n2l2m2}(\alpha_1,\alpha_2,\mathbf{A},\mathbf{B})=\int x_A^{n1}y_A^{l1}Z_A^{m1}\exp(-\alpha_1\mathbf{A})x_B^{n2}y_B^{l2}z_B^{m2}\exp(-\alpha_2\mathbf{B})d\tau \\ =S_{n1,n2}(\alpha_1,\alpha_2,A_x,B_x)S_{l1,l2}(\alpha_1,\alpha_2,A_y,B_y)S_{m1,m2}(\alpha_1,\alpha_2,A_z,B_z) \tag{7}$$

where

$$S_{n1,n2}(\alpha_1,\alpha_2,A_x,B_x)=\exp(-h\overline{AB}_x)\sum_{r1}\begin{bmatrix}n_1\\r_1\end{bmatrix}\overline{AD}_x^{\,n1-r1}\sum_{r2}\begin{bmatrix}n_2\\r_2\end{bmatrix}\overline{BD}_x^{\,n2-r2}E_{r1+r2}(\beta) \tag{8}$$

and

$$\beta=\alpha_1+\alpha_2,\quad h=\alpha_1\alpha_2/\beta ,$$

$$\mathbf{D}=(\alpha_1\mathbf{A}+\alpha_2\mathbf{B})/\beta,\quad AB_x=B_x-A_x , \tag{9}$$

$$E_n(\beta)=N_n\beta^{-(n+1)/2} ,$$

$$N_n=\pi^{1/2}\begin{cases}1 & \text{if } n=0\\ 0 & \text{if } n \text{ is odd}\\ (n-1)!!/2^{n/2} & \text{if } n \text{ is even} .\end{cases} \tag{10}$$

Using these formulas, differentiations with respect to the Cartesian coordinates x, y and z can be easily carried out and the contribution to the matrix element from the mass-velocity term between atomic orbitals can be evaluated in terms of generalized overlap integrals.

For the Darwin term, we need the second derivatives of the crystal potential. In the direct-space OLCAO formalism,[6] the crystal potential is generally expressed as a superposition of the atomiclike potentials which are cast into some linear combinations of Gaussian functions:

$$V(r)=\sum_\mu V_A(r-R_\mu) , \tag{11}$$

$$V_A(r)=-\frac{Z_A}{r}\exp(-\alpha r^2)+\sum_i C_i\exp(-\beta_i r^2) . \tag{12}$$

The second derivative of the V_A obviously also consists of linear combination of Gaussian-type functions, but of higher order. With the help of a generalized formula for the three-center integrals of Gaussian functions,[26] there is no difficulty in calculating the contribution from the Darwin term analytically. However, a more convenient numerical procedure may be adopted. One simply calculates the Darwin correction as a function of r and linearly fit to a set of Gaussian functions with the same exponentials as in the crystal potential itself. The correction then appears as a modification of the coefficients C_l in (12).

Sometimes a problem arises when the accuracy of the numerical potential is not satisfactory, especially in the region near the nuclei. Repeated differentiation of V_A in the Darwin term may magnify the numerical inaccuracy. In this case, one may separate the total one-electron potential into Coulomb and exchange parts:

$$V_A(r) = -\frac{Z}{r} + V_{\text{Coul}}(r) + V_{\text{exch}}(r) \ . \tag{13}$$

The second-order derivative of the Coulomb part is equal to the electron charge density according to Poisson's equation:

$$\nabla^2 V_{\text{Coul}}(r) = -4\pi\rho(r) \ . \tag{14}$$

In the local density theory, the exchange part is also a function of charge density ρ. We may use charge density function instead of the potential function in the evaluation of the Darwin term. The Darwin correction due to $V_{\text{exch}}(r)$ is generally less than that of $V_{\text{Coul}}(r)$. The site-decomposed charge density function is available from the self-consistent scheme; it can also be calculated directly from the Bloch functions; or it may also be approximated by the atomic charge density since in the core region, the charge density of a free atom and that in a solid are the same. In the core region where the relativistic effect is the most important, the nuclei Coulomb part of (13) dominates. The contribution to the Darwin term from the nuclear charge Z is a δ function of the form

$$-\nabla\cdot\nabla\left[-\frac{Z}{r}\right] = 4\pi Z\delta(r) \ . \tag{15}$$

At the nucleus, only s electrons experience this interaction which has a positive sign. This means that for s electrons, the effect of Darwin correction results in an increase in energy and therefore leads to a direct competition with the mass-velocity term which is always negative.

III. APPLICATION OF SCALAR-RELATIVISTIC CORRECTION

At the present stage, calculation of relativistic effects in metals is generally limited to the SR level. We have calculated the SR energy bands of elemental metals Ni, Nb, and Ce as a test for our method. The selection of these three metals as prototypes is quite obvious. $3d$, $4d$, and $4f$ electronic orbitals are, respectively, involved in these three crystals with an increasing atomic mass number. Since the diagonal Hamiltonian matrix elements of the central-cell atom in the OLCAO method are good estimates to the energy levels of the corresponding atomic orbitals, a preliminary estimate for the relativistic effects in an individual atom can be obtained by inspecting the diagonal Hamiltonian matrix elements. There are two general trends in the shifting of the energy levels in atoms due to relativistic effect. First, the shift is much larger for atoms of larger Z; second, within the same atom, the differences between relativistic and nonrelativistic energy levels are usually getting less and less from inner shells to the outmost ones and then become larger and larger for higher excited states as the energy is increased. These features in atoms had been discussed by Koelling and McDonald[27] with typical results tabulated. Our calculation shows that not only are both of these tendencies well kept, but also the magnitudes of these shifts are in close agreement with the estimates of Ref. 27 for the corresponding neutral atoms.

The band structures of Ni and Nb are calculated self-consistently using the OLCAO method. For Ce, the previously published band[10] in which the OLCAO method was extended to the f-electron system is used. SR corrections according to the above-outlined steps are calculated and applied to respective band structures. In Figs. 1–3,

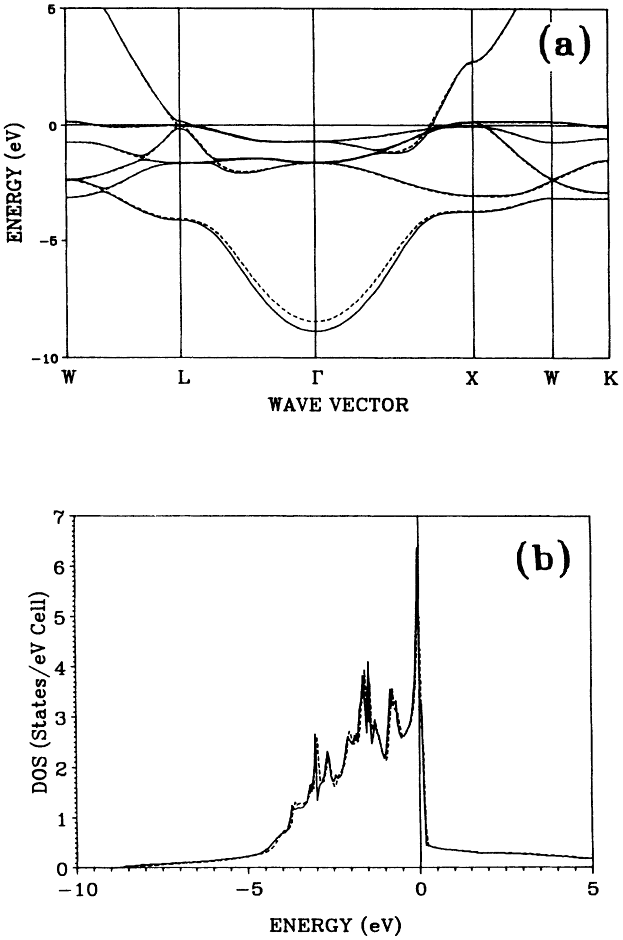

FIG. 1. Band structure (a) and DOS (b) of fcc Ni. Dashed line, nonrelativistic result; solid line, with scalar-relativistic correction.

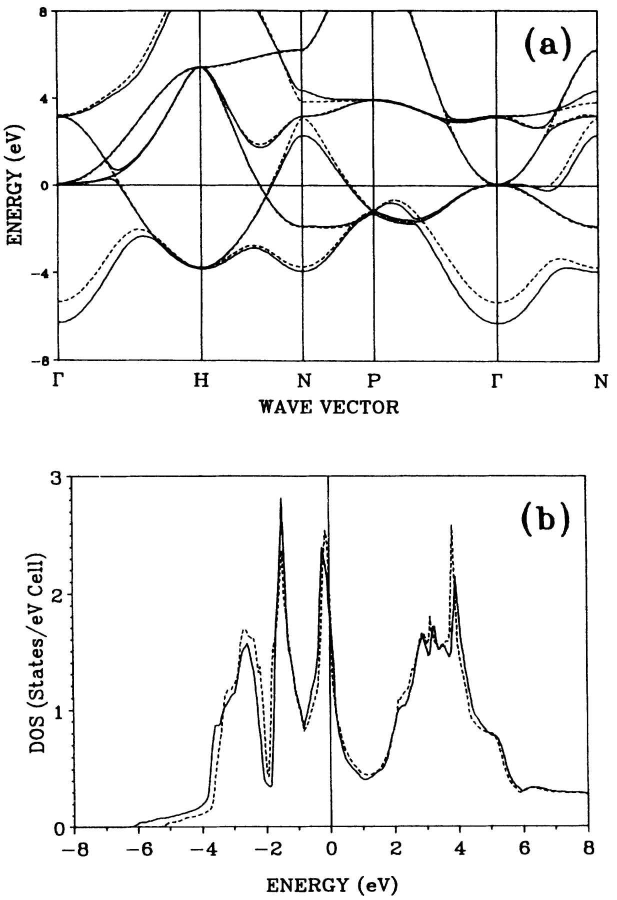

FIG. 2. Band structure (a) and DOS (b) of bcc Nb. Dashed line, nonrelativistic result; solid line, with scalar-relativistic correction.

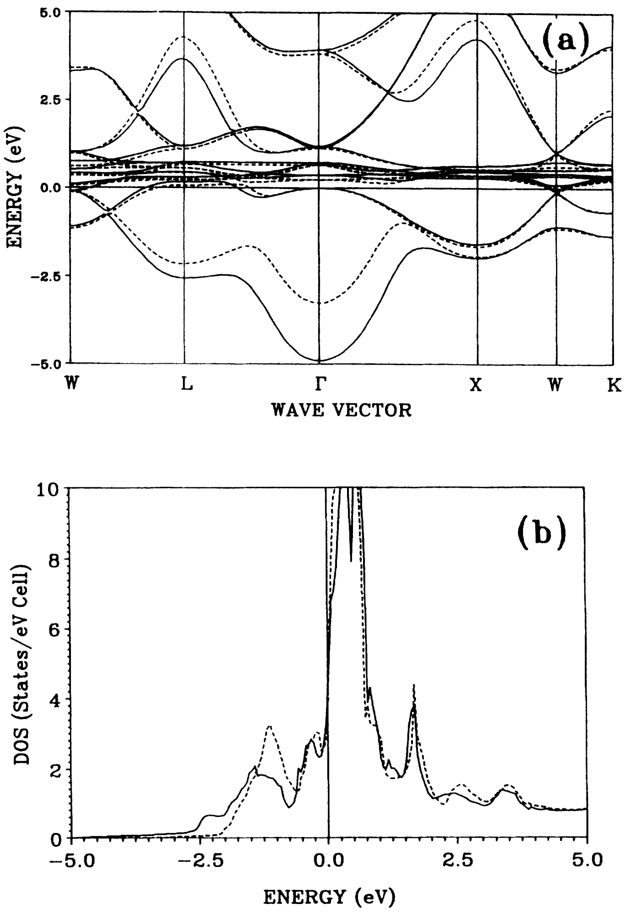

FIG. 3. Band structure (a) and DOS (b) of fcc Ce. Dashed line, nonrelativistic result; solid line, with scalar-relativistic correction.

we display the band structures and the densities of states (DOS) of paramagnetic fcc Ni, bcc Nb, and fcc γ-Ce, respectively. The dotted lines are for the nonrelativistic results and the solid lines are for the SR results. In all three cases, the energy shifts are due to the combined effects of the mass-velocity and Darwin terms. It is clear that the general tendencies of the energy shifts in a free atom are retained, although the shifts vary in the different regions of the Brillouin zone (BZ). At the Γ point, the center of the BZ, the relativistic shift in energy for the lowest s band is the largest, the downward shift in energy due to SR correction is about 0.43 eV for Ni, 0.94 eV for Nb, and 1.63 eV for Ce, and so the Z dependence of the relativistic shift is well established.

The above results should be compared with existing relativistic band-structure calculations using other methods. Kim, Harmon, and Lynch, in studying the optical properties of Nb, have presented the nonrelativistic and SR band structures of Nb using the KKR method.[28] Their results are almost identical to ours for both cases for bands throughout the entire BZ. The entire separation between Γ_1 and $\Gamma_{25'}$ is 5.3 eV for the nonrelativistic case and 6.3 eV for the SR case. The latter number is in excellent agreement with the value of 6.4 eV obtained by Elyashar and Koelling[29] using the self-consistent relativistic APW method. For Ni, our nonrelativistic band structure is in very good agreement with that of Moruzzi *et al.*[30] using the self-consistent augmented-spherical-wave (ASW) method. However, our relativistic energy band for Ni is in much better agreement with the recent angle-resolved UV photoelectron spectroscopic measurement.[31] For example, experimental estimation for the energies from $\Gamma_1 \rightarrow \Gamma_{25'}$ and $\Gamma_1 \rightarrow \Gamma_{12}$ are 7.5 and 8.3 eV, respectively. Our scalar-relativistic band gives 7.2 and 8.2 eV for these two energy differences. The nonrelativistic calculation of Moruzzi *et al.* gave 6.8 and 7.8 eV for the same energy separations. In the case of Ce, the scalar-relativistic band is in good agreement with that of Pickett, Freeman, and Koelling.[32]

The DOS's for the three metals are shown in part (b) of Figs. 1–3. As is evident, the relativistic effect in Ni is almost negligible since the biggest shift in energy is at the bottom of the s band at Γ where the state has a very low DOS. The difference between relativistic and nonrelativistic DOS becomes appreciable in the case of Nb, especially in the range of higher binding energy. In the case of Ce, the difference becomes very large. For example, the peak at -1.2 eV has been shifted to -1.9 eV and becomes much more broadened. An extra peak at -2.3 eV has appeared which was not present in the nonrelativistic calculation. Since electrons near the Fermi surface move at relatively low speeds, the relativistic effects are expected to be less appreciable near Fermi energy. This can be clearly seen from the energy band and DOS diagrams for Ni and Nb. For Ce, there is a considerable shift of $4f$ bands near the Fermi level.

IV. FULL RELATIVISTIC CORRECTION AND APPLICATION TO FERROMAGNETIC Fe

To consider the full relativistic correction, the spin-orbit coupling term in Eq. (3) must be considered. Although the correction due to spin-orbit coupling is in general smaller than the SR corrections, it may play an important role in certain cases. A prime example is the anisotropy in magnetization in permanent magnets. Only through spin-orbit coupling can the local spin moments be related to the orbital moments in determining the magnetic anisotropy energy. Magneto-optical Kerr effect is another example which can be understood only if the electronic structures with both spin-orbit interaction and exchange splitting are explicitly considered.

There are different approaches to treat spin-orbit coupling, depending on the system under study and the physical process involved. For optical processes in cubic semiconductors, one tends to concentrate on the states at the band edges of the spectrum. A calculation at high symmetrical points of the BZ using perturbation theory for the degenerate case usually serves the purpose. However, we would like to have a general and yet convenient scheme to treat the problem of spin-orbit coupling in the framework of the OLCAO method. The general approach is similar to that adapted by other methods,[23] namely, a spin-polarized band structure is established first, and the spin-orbit interaction is added on as a correction to the spin-polarized Hamiltonian. This approach is more general and can be equally well suited for the systems with strong or weak exchange splittings.

The spin-polarized band-structure calculation provides two Hamiltonian matrices, one for spin-up band (minority spin band), the other for spin-down band (majority spin band). In the absence of spin-orbit interaction, these two matrices are diagonalized separately to yield spin-up and spin-down bands. When the spin-orbit coupling term is included in the Hamiltonian, not only are the original up and down matrices modified, they are also coupled together such that the matrix size is doubled. The procedure can be represented schematically as follows:

$$\begin{bmatrix} \underline{U} & \underline{O} \\ \underline{O} & \underline{D} \end{bmatrix} \rightarrow \begin{bmatrix} \underline{U}' & \underline{\Delta} \\ \underline{\Delta}^{\dagger} & \underline{D}' \end{bmatrix} , \tag{16}$$

where $\underline{U}$ ($\underline{U}'$) and $\underline{D}$ ($\underline{D}'$) are the original (corrected) Hamiltonian matrices for spin-up and spin-down states, respectively, $\underline{O}$ is a zero matrix, and $\underline{\Delta}$ is the coupling matrix. We shall assume that SR corrections have already been included in $\underline{U}$ and $\underline{D}$ as described in Sec. II. A similar idea was employed by Misemer in a cluster-type approach.[33]

To obtain explicit expressions for $\underline{\Delta}$ and to make corrections for $\underline{U}$ and $\underline{D}$, we need to evaluate the matrix elements of the spin-orbit coupling term between spin-polarized Bloch bases. If we follow a first-principles type of approach, as was done by Wang and Callaway[11,12] in their study of ferromagnetic Ni and Fe, a large number of integrals involving the derivative of the crystal potential and the Gaussian-like orbitals in the basis expansion must be evaluated. Such an approach appears to be not very practical for complex systems such as the $Nd_2Fe_{14}B$ hard magnet which we eventually will be interested in. Hence we follow a simpler approach in which the strength of this coupling is treated as a parameter. These parameters are obtained either from experiments, or from atomic calculations. In fact, the spin-orbit interaction is rather short ranged and to a good approximation, can be considered to confine within the central-cell atom. Under this assumption, the matrix elements between Bloch bases are reduced to the matrix elements between atomic orbitals and the calculation is essentially reduced to a calculation at the atomic level.

In the parametrization form, we write the spin-orbit coupling term as

$$\xi \mathbf{l}\cdot\mathbf{s} = \xi(\mathbf{j}^2 - \mathbf{l}^2 - \mathbf{s}^2)/2 \tag{17}$$

where ξ is the spin-orbit coupling parameter. $\mathbf{j}$, $\mathbf{l}$, and $\mathbf{s}$ are the total, orbital, and spin quantum numbers for the atom. ξ is given by the expression

$$\xi = \frac{\hbar^2}{2m^2c^2} \int |\phi_{nl}(\mathbf{r})|^2 \frac{1}{r} \frac{dV(r)}{dr} d\mathbf{r} \tag{18}$$

where V is the atomic potential and $\phi_{nl}(r)$ are the atomic orbitals. The parameters ξ can be obtained from the atomic self-consistent field calculations such as those by Herman and Skillman[34] and utilized in our band-structure calculation. The matrix elements of (17) between atomic wave functions are quite simple. Due to the spin polarization, the atomic wave functions are direct products $|\alpha,l,m\rangle\,|s,m_s\rangle$ where $|\alpha,l,m\rangle$ denotes the spatial parts and $|s,m_s\rangle$ and spin part of the wave function (with $m_s = \pm\frac{1}{2}$). The angular quantum numbers l,m are explicitly written out while all other indices are absorbed in the collective index α. These direct product wave functions can be transformed into coupling wave functions:

$$|l,m\rangle\,|s,m_s\rangle = \sum_{j,m_j} \langle l,s,j,m_j|l,m,s,m_s\rangle\,|l,s,j,m_j\rangle \tag{19}$$

where the transformation coefficients $\langle l,s,j,m_j|l,m,s,m_s\rangle$ are obtained from the inverse transformation of the well-known Clebsch-Gordan coefficients for two angular momenta coupling.[35] The matrix elements of (17) between the coupling wave functions then become trivial, because the coupling wave functions are simultaneous eigenfunction of total, orbital, and spin angular momentum operators and we have

$$\xi\langle \mathbf{l}\cdot\mathbf{s}\rangle = \xi[j(j+1) - l(l+1) - \tfrac{3}{4}]/2 . \tag{20}$$

Equation (20) provides us with all that is needed for the matrix elements of (16). Diagonalization of (16) together with the overlap matrix which is not changed for both up and down spin leads to the new Bloch functions including spin-orbit coupling. There is no difficulty in classifying the new Bloch states by their symmetric properties if needed.

We have applied the above procedure to the case of band structure of ferromagnetic Fe. In Fig. 4, we present the self-consistent spin-polarized band structure and the total DOS of bcc Fe in which only the SR correction has been included. We have obtained a spin moment of $2.15\mu_B$ per Fe site which is in good agreement with experiment.[36] Like fcc Ni discussed in Sec. III, the effect of SR correction is quite small. This can be seen more clearly from the spin projected DOS shown in Fig. 5. The SR result (solid line) and the nonrelativistic result (dashed line) are almost identical. The full relativistic band including spin-orbit interaction is shown in Fig. 6(a). In this calculation, we have used the value of 0.037 eV for the parameter ξ for the Fe $3d$ electrons, same as from the atomic self-consistent field calculation.[34] Our result is very similar to that of Wang and Callaway using a first-principles approach for the spin-orbit interaction parameter, although they did not include the SR effects in their calculation. Note also that some of the accidental degeneracies in the Fe band have been removed by the spin-orbit interaction. In Fig. 6(b), we compare the total DOS of Fe

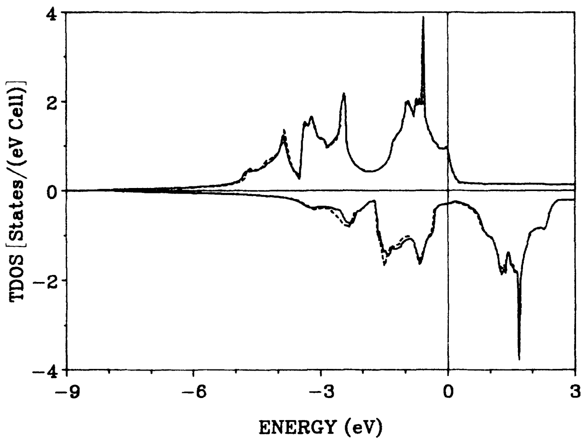

FIG. 5. Spin-projected total DOS of Fe. Upper panel, majority spin; lower panel, minority spin. Dashed line corresponds to the nonrelativistic calculation.

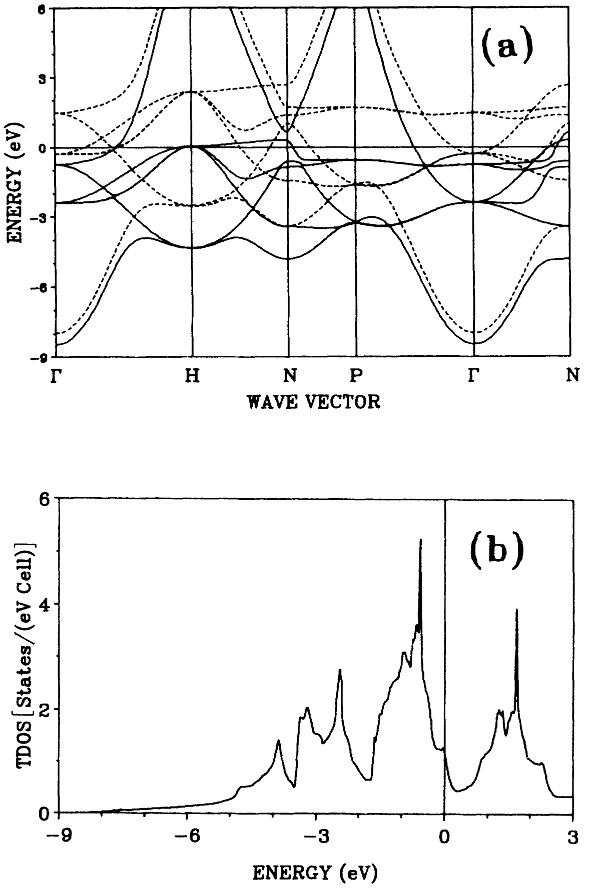

FIG. 4. (a) Spin-polarized band structure for bcc Fe with scalar-relativistic correction. Solid line, majority spin; dashed line, minority spin. (b) Total DOS for bcc Fe with scalar-relativistic correction.

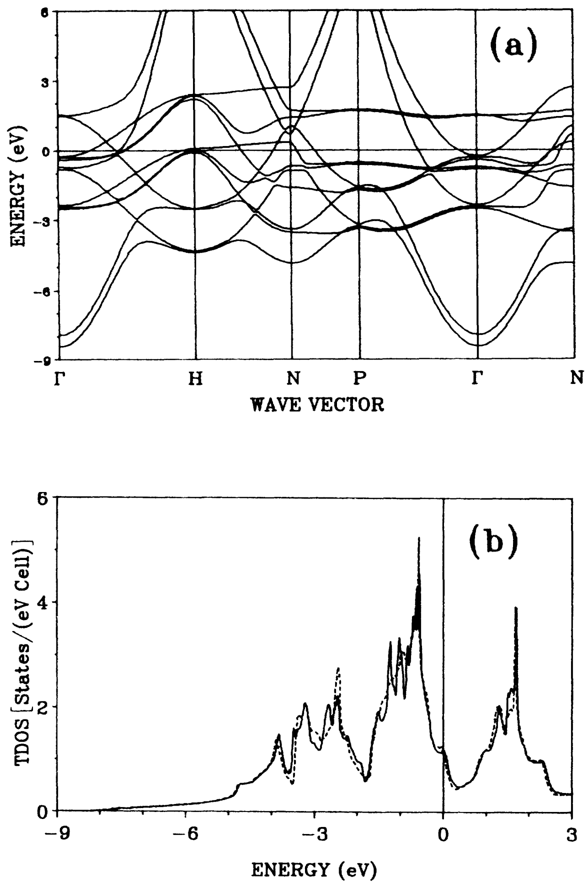

FIG. 6. (a) Full relativistic band structure of Fe including spin-orbit coupling; (b) Total DOS of Fe. Solid line, full relativistic result; dashed line, scalar-relativistic result.

with the without spin-orbital coupling. Although the difference cannot be considered to be substantial, it is actually larger than the difference between the nonrelativistic and the SR correction alone. We note that additional structures have appears at -1.0, -1.2, -1.6, and -2.7 eV. Such structures may be too small to be detected experimentally. Hence, at least in the $3d$ metals, the spin-orbit interaction is probably of equal importance to the scalar-relativistic effect. The same may not be true for crystals involving heavier elements.

The method for spin-orbit coupling correction has also been applied to a much more complicated system $Nd_2Fe_{14}B$ to estimate the local orbital moments in this crystal.[37] Although the SR effect was not considered in that study because the spin-polarized band structure was not calculated self-consistently,[7] the results are quite satisfactory and are reported elsewhere.[37]

V. CONCLUSION

We have successfully implemented the relativistic corrections in the OLCAO method, and as such, have advanced the method to a more sophisticated and competitive level. Test calculations on Ni, Nb, Ce, and ferromagnetic Fe show that our relativistic results are very satisfactory and in good agreement with similar calculations using other methods. The correction procedure is quite simple and is divided into two steps. The SR correction is carried out first and then the spin-orbit coupling is introduced in a general form on the basis of spin-polarized band structure. The additional computation required for the relativistic correction, either in the SR case (mass-velocity term and Darwin term) or with the spin-orbit coupling, is not unduly excessive or cumbersome. Therefore this method can be easily extended to other more complicated systems where other methods may not be as convenient. It is hoped that our method will lead to a serious calculation on the magnetic anisotropy energy in high performance magnet[38] and to the study of magneto-optical properties of magnetic materials with large Kerr rotation angles.[39].

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[1] E. E. Lafon and Chun C. Lin, Phys. Rev. **152**, 579 (1966).

[2] R. C. Chaney, Chun C. Lin, and E. E. Lafon, Phys. Rev. B **3**, 459 (1971).

[3] J. E. Simmons, Chun C. Lin, D. F. Fouguet, E. E. Lafon, and R. C. Chaney, J. Phys. C **8**, 1549 (1975).

[4] See, for example, W. Y. Ching and J. Callaway, Phys. Rev. B **9**, 5115 (1974); **11**, 1324 (1975).

[5] C. S. Wang and J. Callaway, Comput. Phys. Commun. **14**, 327 (1978), and references cited therein.

[6] W. Y. Ching and Chun C. Lin. Phys. Rev. B **12**, 5536 (1975); (paper I), **16**, 2989 (1977), (paper II).

[7] See, for example, Z.-Q. Gu and W. Y. Ching, Phys. Rev. B **36**, 8530 (1987), and references cited therein.

[8] See, for example, W. Y. Ching, Phys. Rev. B **34**, 2080 (1986), and references cited therein.

[9] P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B **20**, 1433 (1979).

[10] Y. P. Li, Z.-Q. Gu, and W. Y. Ching, Phys. Rev. B **32**, 8377 (1985) (paper III).

[11] C. S. Wang and J. Callaway, Phys. Rev. B **9**, 4897 (1974).

[12] M. Singh, C. S. Wang, and J. Callaway, Phys. Rev. B **11**, 287 (1977).

[13] B. N. Harmon, W. Weber, and D. R. Hamann, Phys. Rev. B **25**, 1109 (1982); W. Y. Ching and B. N. Harmon, *ibid.* **34**, 5305 (1986).

[14] W. Y. Ching, Y.-N. Xu, G. L. Zhao, K. W. Wong, and F. Zandiehnadem, Phys. Rev. Lett. **59**, 1333 (1987); W. Y. Ching, G. L. Zhao, Y. N. Xu, and K. W. Wong, in *Progress in High Temperature Superconductivity*, edited by B. E. Baaquie, C. K. Chew, C. H. Lai, C. H. Oh, and K. K. Phua (World Scientific, Singapore, 1989), Vol. 12, p. 58.

[15] T. C. Leang, X. W. Wang, and B. N. Harmon, Phys. Rev. B **37**, 384 (1988).

[16] Y. Onodera and M. Okazaki, J. Phys. Soc. Jpn. **21**, 1273 (1966).

[17] L. F. Mathesis, Phys. Rev. **151**, 450 (1966); D. D. Koelling, Phys. Rev. **188**, 1049 (1969).

[18] A. H. McDonald, W. E. Pickett, and D. D. Koelling, J. Phys. C **13**, 2675 (1980).

[19] N. E. Christensen, J. Phys. F **8**, L51 (1978).

[20] C. Godreche, J. Magn. Magn. Mater. **29**, 262 (1982).

[21] H. Ebert, P. Strange, and B. L. Gyorffy, J. Appl. Phys. **63**, 3052 (1988).

[22] See, for example, D. E. Ellis and A. Rosen, Z. Phys. A **283**, 3 (1977); A. Rosen and D. E. Ellis, J. Chem. Phys. **62**, 3039 (1975).

[23] D. D. Koelling and B. N. Harmon, J. Phys. C **10**, 3107 (1977).

[24] M. Weissbluth, *Atoms and Molecules* (Academic, New York, 1978), p. 315.

[25] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[26] E. E. Lafon, J. Comput. Phys. **83**, 185 (1989).

[27] D. D. Koelling and A. H. McDonald, in *Relativistic Effects in Atoms, Molecules and Solids*, edited by G. L. Malli (Plenum, New York, 1981), pp. 227–304.

[28] Bong-Soo Kim, B. N. Harmon, and D. W. Lynch, Phys. Rev. B **39**, 13 146 (1989).

[29] N. Elyashar and D. D. Koelling, Phys. Rev. B **15**, 3620 (1977).

[30] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New YOrk, 1978).

[31] H. Mårtensson and P. O. Nilsson, Phys. Rev. B **30**, 3047 (1984).

[32] W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B **23**, 1266 (1981).

[33] D. K. Misemer, J. Magn. Magn. Mater. **72**, 267 (1988).

[34] F. Herman and S. Skillman, *Atomic Structure Calculation* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

[35] See, for example, D. M. Brink and G. R. Satchler, *Atomic Momentum* (Clarendon, Oxford, 1968).

[36] W. Y. Ching, Y.-N. Xu, B. N. Harmon, and J. Ye (unpublished).

[37] Xue-Fu Zhong and W. Y. Ching, J. Appl. Phys. (to be published).

[38] Xue-Fu Zhong and W. Y. Ching, Phys. Rev. B **40**, 5292 (1989).

[39] See, for example, H. Ebert, P. Strange, and B. L. Gyorffy, J. Phys. (Paris) Colloq. **49**, C8-31 (1988).