Journal of Computational Physics **172,** 387–391 (2001)
doi:10.1006/jcph.2001.6830, available online at http://www.idealibrary.com on IDEAL®

Analytic Spin-Orbit Coupling Matrix Element Formulae in FLAPW Calculations

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Received February 16, 2001

The full-potential, linearized augmented, plane wave (FLAPW) method is used widely for accurate electronic structure calculations. For the electronic structure of solids with heavy elements, it is necessary to include spin-orbit coupling interactions. We present simple analytic formulae for calculating FLAPW spin-orbit matrix elements. These will serve to simplify the calculations and save computational time.

Key Words: electronic structure; FLAPW; spin-orbit interaction.

The highly precise, full-potential, linearized augmented, plane wave (FLAPW) method [1] is widely used for local density first principles electronic structure calculations of solids. In usual calculations, relativistic effects are included at the scalar relativistic level where only the Darwin and mass–velocity terms are included. Sometimes, it is necessary to include spin-orbit interaction for more accurate electronic structure calculations of heavy element solids. While algorithms for including spin-orbit interactions in the FLAPW method are well known [2, 3], simple formulae for their matrix element calculations have not been given yet. In this paper, we present simple analytic formulae that can be used easily for spin-orbit matix element calculations.

It is a good approximation to include spin-orbit effects near the nuclei and to include only the spherical part of the potential since relativistic effects are important near the nucleus where the kinetic energy is large. In this approximation the spin-orbit Hamiltonian can be written as

$$H^{so} = \frac{1}{(2Mc)^2 r}\frac{dV_{MT}(r)}{dr}\sigma \cdot L, \tag{1}$$

where

$$M \equiv m + \frac{1}{2c^2}[\epsilon - V_{MT}(r)] \tag{2}$$

and $V_{MT}(r)$ is the spherical or muffin-tin part of the potential. The augmented plane wave

0021-9991/01 $35.00

(APW) basis in FLAPW calculations is

$$\phi(\mathbf{k}_n;\mathbf{r}) = \begin{cases} \Omega^{-1/2}\exp(i\mathbf{k}_n\cdot\mathbf{r}) & \text{interstitial region} \\ \sum_{lm}[A_{lm}(\mathbf{k}_n)u_l(E_l;r) + B_{lm}(\mathbf{k}_n)\dot{u}_l(E_l;r)]Y_{lm}(\hat{r}) & \text{inside the muffin-tin,} \end{cases} \tag{3}$$

where

$$\mathbf{k}_n \equiv \mathbf{k} + \mathbf{K}_n. \tag{4}$$

Here $\mathbf{K}_n$ is a reciprocal lattice vector and Ω is the volume of real space unit cell and $\mathbf{k}$ is a vector in the irreducible Brillouin zone. We will delete the n index in $\mathbf{k}_n$ later on for simplicity, unless otherwise required. $u_l(E_l;r)$ and $\dot{u}_l(E_l;r)$ are the radial solution and its energy derivative inside the atomic muffin-tin. The expansion coefficients, A_{lm} and B_{lm}, are determined by matching the wavefunction continuously at the muffin-tin radius [4].

$$A_{lm}(\mathbf{k}) = \frac{4\pi R^2}{\Omega^{1/2}} i^l a_l(k) Y^*_{lm}(\hat{k}), \quad a_l(k) = (j_l'(k)\dot{u}_l - j_l(k)\dot{u}_l') \tag{5}$$

$$B_{lm}(\mathbf{k}) = \frac{4\pi R^2}{\Omega^{1/2}} i^l b_l(k) Y^*_{lm}(\hat{k}), \quad b_l(k) = (j_l(k)u_l' - j_l'(k)u_l). \tag{6}$$

The spin-orbit matrix element between $\phi(\mathbf{k};\mathbf{r})$ and $\phi(\mathbf{k}';\mathbf{r})$ can be written as

$$\langle\phi^s(\mathbf{k})|H^{so}|\phi^{s'}(\mathbf{k}')\rangle \tag{7}$$

$$= \left\langle \phi^s(\mathbf{k}) \middle| \frac{1}{(2Mc)^2 r}\frac{dV_{MT}(r)}{dr}\sigma\cdot L \middle| \phi^{s'}(\mathbf{k}') \right\rangle \tag{8}$$

$$= \sum_l R^l_{ksk's'} \sum_{mm'} Y_{lm}(\hat{k})\langle lms|\sigma\cdot L|lm's'\rangle Y^*_{lm'}(\hat{k}'), \tag{9}$$

where s and s' are added to represent spin directions and the radial part can be written as

$$R^l_{ksk's'} = \frac{(4\pi R^2)^2}{\Omega}\big\{a_l^s(k)a_l^{s'}(k')\xi_l^{ss'} + a_l^s(k)b_l^{s'}(k')\dot{\xi}_l^{ss'} + b_l^s(k)a_l^{s'}(k')\dot{\xi}_l^{s's} + b_l^s(k)b_l^{s'}(k')\ddot{\xi}_l^{ss'}\big\}, \tag{10}$$

where

$$\xi_l^{ss'} = \left\langle u_l^s \middle| \frac{1}{(2Mc)^2 r}\frac{dV_{MT}(r)}{dr} \middle| u_l^{s'} \right\rangle \tag{11}$$

$$\dot{\xi}_l^{ss'} = \left\langle \dot{u}_l^s \middle| \frac{1}{(2Mc)^2 r}\frac{dV_{MT}(r)}{dr} \middle| u_l^{s'} \right\rangle \tag{12}$$

$$\ddot{\xi}_l^{ss'} = \left\langle \dot{u}_l^s \middle| \frac{1}{(2Mc)^2 r}\frac{dV_{MT}(r)}{dr} \middle| \dot{u}_l^{s'} \right\rangle. \tag{13}$$

Equation (9) is a usual expression used for the spin-orbit matrix element calculations. It contains a summation over magnetic quantum numbers, m and m'. In addition, it requires

calculations of the spherical harmonics $Y_{lm}(\hat{k})$ for each APWs. We show that the matrix element calculation in Eq. (9) can be simplified by performing analytic summation as will be shown in Eq. (28).

The scalar product between spin and orbital angular momenta can be written as

$$\sigma \cdot L = \frac{1}{2}(\sigma_+ L_- + \sigma_- L_+) + \sigma_z L_z \tag{14}$$

in terms of the raising (+) or lowering (−) operator of the angular momentum; e.g.,

$$L_+ = L_x + iL_y, \quad L_- = L_x - iL_y. \tag{15}$$

The summation over the magnetic quantum number m, m' in Eq. (9) can be performed analytically by using raising or lowering property of L_+ or L_- as shown in the Appendix. The results are

$$\langle k|L_-|k'\rangle_l = -\frac{2l+1}{4\pi} P_l'(\cos\gamma) \frac{k_x' - ik_y'}{kk'} \left(-k_z + k_z' \frac{k_x k_x' + k_y k_y'}{k_x'^2 + k_y'^2} + ik_z' \frac{k_x k_y' - k_y k_x'}{k_x'^2 + k_y'^2} \right) \tag{16}$$

$$\langle k|L_+|k'\rangle_l = \frac{2l+1}{4\pi} P_l'(\cos\gamma) \frac{k_x' + ik_y'}{kk'} \left(-k_z + k_z' \frac{k_x k_x' + k_y k_y'}{k_x'^2 + k_y'^2} - ik_z' \frac{k_x k_y' - k_y k_x'}{k_x'^2 + k_y'^2} \right) \tag{17}$$

$$\langle k|L_z|k'\rangle_l = i\frac{2l+1}{4\pi} P_l'(\cos\gamma) \frac{k_x k_y' - k' k_y}{kk'} = i\frac{2l+1}{4\pi} P_l'(\cos\gamma) \frac{[\mathbf{k}\times\mathbf{k}']_z}{kk'}, \tag{18}$$

where

$$\langle k|L_-|k'\rangle_l \equiv \sum_m Y_{lm}^*(\hat{k}) L_- Y_{lm}(\hat{k}'), \tag{19}$$

$$\langle k|L_z|k'\rangle_l \equiv \sum_m Y_{lm}^*(\hat{k}) L_z Y_{lm}(\hat{k}'), \tag{20}$$

$$\langle k|L_+|k'\rangle_l \equiv \sum_m Y_{lm}^*(\hat{k}) L_+ Y_{lm}(\hat{k}'), \tag{21}$$

$P_l(x)$ and $P_l'(x)$ represent the Legendre polynomials of order l and their derivatives with respect to x and γ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. From the above equations, we can see that the complex conjugate of a spin-orbit coupling (SOC) matrix element has the property

$$\langle k'|L_-|k\rangle_l^* = -\langle k'|L_+|k\rangle_l. \tag{22}$$

If we interchange the order of application of the basis for $\mathbf{k}$ and $\mathbf{k}'$, the summations change sign; for example,

$$\langle k'|L_-|k\rangle_l = -\langle k|L_-|k'\rangle_l. \tag{23}$$

Spin-angular integration in Eq. (9) can be written

$$\sum_l R^l_{kk'} \sum_{mm'} Y_{lm}(\hat{k}) \langle lms|\sigma \cdot L|lm's'\rangle Y^*_{lm'}(\hat{k}') \tag{24}$$

$$= \sum_l R^l_{kk'} \left(\frac{1}{2}\langle s|\sigma_+|s'\rangle \langle k'|L_-|k\rangle_l + \frac{1}{2}\langle s|\sigma_-|s'\rangle \langle k'|L_+|k\rangle_l + \langle s|\sigma_z|s'\rangle \langle k'|L_z|k\rangle_l \right). \tag{25}$$

If we use the relation Eq. (15), $\langle k|L_x|k'\rangle_l$ and $\langle k|L_y|k'\rangle_l$ can be calculated

$$\langle k|L_x|k'\rangle_l = i \frac{2l+1}{4\pi} P'_l(\cos\gamma) \frac{[\mathbf{k}\times\mathbf{k}']_x}{kk'} \tag{26}$$

$$\langle k|L_y|k'\rangle_l = i \frac{2l+1}{4\pi} P'_l(\cos\gamma) \frac{[\mathbf{k}\times\mathbf{k}']_y}{kk'}. \tag{27}$$

We can see that the summations for L_x, L_y, and L_z are purely imaginary from the above equations and Eq. (18). From Eqs. (18), (26), and (27), the SOC matrix element in Eq. (9) can be written simply by using the vector product of two $\mathbf{k}$ vectors of the APWs as

$$\langle \phi^s(\mathbf{k})|H^{so}|\phi^{s'}(\mathbf{k}')\rangle = i \frac{\sigma \cdot (\mathbf{k}\times\mathbf{k}')}{kk'} \sum_l \frac{2l+1}{4\pi} R^l_{ksk's'} P'_l(\cos\gamma), \tag{28}$$

where

$$\sigma \cdot (\mathbf{k}\times\mathbf{k}') = \langle s|\sigma_x|s'\rangle [\mathbf{k}\times\mathbf{k}']_x + \langle s|\sigma_y|s'\rangle [\mathbf{k}\times\mathbf{k}']_y + \langle s|\sigma_z|s'\rangle [\mathbf{k}\times\mathbf{k}']_z. \tag{29}$$

We can see the property of Eq. (23) follows from the property of the vector product in Eq. (28). While the SOC matrix elements in Eq. (28) become purely imaginary if s and s' indicate the same spin directions, they are complex numbers since the spin parts are complex numbers. While a similar form to Eq. (28) appears in a planewave pseudopotential formulation [5], that formulation cannot be applied directly to the FLAPW method.

Several points are appropriate for discussion at this point. First, the spin part of the matrix element in Eqs. (24) and (29) can be calculated by applying eigen-spinors of $\sigma \cdot \mathbf{B}$ to both sides of the spin matrices, where B is an infinitesimal magnetic field. Second, if the magnitude of $\mathbf{k}$ or $\mathbf{k}'$ vanishes, the summation formulas cannot be used. In this case, the spin-orbital matrix element is zero since $\mathbf{k} = 0$ in the interstitial region gives a vanishing orbital momentum in the muffin-tin region. Third, we removed the summation over the magnetic quantum numbers m and m' of the spherical harmonics in Eq. (9) in the matrix element calculation which simplifies the calculation.

To conclude, we derived a simple analytic formula that can be used for the calculation of spin-orbit matrix elements in the FLAPW method. This formula can save computational time and simplify the calculation.

APPENDIX

$$\langle k|L_-|k'\rangle = \sum_m Y^*_{lm}(\hat{k}) L_- Y_{lm}(\hat{k}') \tag{A.1}$$

$$= L'_- \sum_m Y^*_{lm}(\hat{k}) Y_{lm}(\hat{k}') \tag{A.2}$$

$$= L'_- \frac{2l+1}{4\pi} P_l(\cos\gamma) \tag{A.3}$$

$$= -\frac{2l+1}{4\pi} P_l'(\cos\gamma)\exp(-i\phi')\{-\cos\theta\sin\theta' + \sin\theta\cos\theta'\cos(\phi-\phi') - i\cot\theta'\sin\theta\sin\theta'\sin(\phi-\phi')\} \tag{A.4}$$

$$= -\frac{2l+1}{4\pi} P_l'(\cos\gamma)\frac{k_y - ik'_y}{kk'}\left(-k_z + k'_z\frac{k_xk_y + k_yk'_y}{{k'_x}^2 + {k'_y}^2} + ik'_z\frac{k_xk'_y - k_yk_y}{{k'_y}^2 + {k'_y}^2}\right). \tag{A.5}$$

L'_- means L'_- operator acts on the coordinate of $\mathbf{k}'$. In the above calculation, use was made of the angular representation of the lowering and raising operator.

$$L_- = L_x - iL_y = -\exp(-i\phi)\left\{\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right\} \tag{A.6}$$

$$L_+ = L_x + iL_y = \exp(i\phi)\left\{\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right\}. \tag{A.7}$$

The angle γ between $\mathbf{k}$ and $\mathbf{k}'$ is given by

$$\cos\gamma = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi-\phi'). \tag{A.8}$$

In a similar way,

$$\langle k|L_+|k'\rangle = \sum_m Y^*_{lm}(\hat{k})L_+Y_{lm}(\hat{k}') \tag{A.9}$$

$$= \frac{2l+1}{4\pi} P_l'(\cos\gamma)\frac{k_y + ik'_y}{kk'}\left(-k_z + k'_z\frac{k_xk_y + k_yk'_y}{{k'_y}^2 + {k'_y}^2} - ik'_z\frac{k_xk'_y - k_yk_y}{{k'_y}^2 + {k'_y}^2}\right) \tag{A.10}$$

$$\langle k|L_z|k'\rangle = \sum_m Y^*_{lm}(\hat{k})L_zY_{lm}(\hat{k}') \tag{A.11}$$

$$= i\frac{2l+1}{4\pi} P_l'(\cos\gamma)\frac{k_xk'_y - k_yk_y}{kk'}. \tag{A.12}$$

ACKNOWLEDGMENT

This work was supported by DARPA (DAAG55-97-0130).

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