Spin-orbit coupling in all-electron mixed basis approach

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Abstract

In the evaluation of the spin-orbit coupling (SOC), the use of the $\mathbf{L} \cdot \mathbf{S}$ formula is invalid in the interatomic region where the effective potential is not spherically symmetric. This problem occurs in the LCAO, LMTO, and APW methods, while the plane-wave pseudopotential and PAW methods cannot treat the spin-orbit splitting (SOS) of core orbitals. To avoid these problems, we adopt the all-electron mixed basis approach, which uses both plane waves (PWs) and atomic orbitals (AOs) as a basis set. In this method, the general form $\mathbf{S} \cdot \nabla V \times \mathbf{p}$ can be used for PWs, while the standard form $\mathbf{L} \cdot \mathbf{S}$ can be used for AOs, which are well localized inside the non-overlapping atomic sphere in the spherical potential region and composed of the numerical radial function on a logarithmic radial mesh and analytic cubic harmonics. We present the explicit formula of the AO-AO, PW-AO and PW-PW matrix elements of the SOC for spin-polarized systems. In particular, the AO-AO matrices are explicitly derived for p , d , and f orbitals. The method is applied to the SOS of core and valence levels in X-ray photoelectron spectra (XPS). The results are in excellent agreement with the available experimental data, which suggests the validity of the present method.

I. INTRODUCTION

Reliable first-principles determination of fine splitting of electronic levels due to the spin-orbit coupling (SOC) is often required to compare with precise experimental data such as X-ray photoelectron spectra (XPS)¹⁻³. The SOC is also very important in Rashba effect⁴, Dzyaloshinskii-Moriya interaction⁵, quantum qubit such as NV⁻ center⁶, spintronics⁷, topological insulators⁸, and so on. There is a timely importance in the SOC also because the current induced magnetization switching spintronic devices recently invented by using the spin-orbit torques originate from the SOC⁹⁻¹². However, in the calculation of the SOC and the spin-orbit splitting (SOS), the use of the $\mathbf{L} \cdot \mathbf{S}$ form is invalid in the interatomic region, where the effective potential is not spherically symmetric. This problem occurs in the methods such as the linear combination of atomic orbitals (LCAO), the linear muffin-tin orbitals (LMTO), and the augmented plane waves (APW), although not being discussed a lot in the literatures¹³⁻¹⁶. On the other hand, the plane wave (PW) expansion method using pseudopotentials or projector augmented waves (PAW) cannot treat the SOS of the core orbitals. Not only for these problems, there are several other deficiencies in the existing methods. For example, the LCAO method has a problem of an incomplete basis set¹⁷ and a basis set superposition error (BSSE)¹⁸, the PW expansion cannot describe all electrons and needs to exclude core orbitals from the Fock space¹⁹. The method using muffin-tin orbitals cannot simply be applied to isolated systems or systems with surfaces without using a complete full-potential approach²⁰.

In order to avoid these problems, we have developed the all-electron mixed basis approach^{21,22}, which uses both PWs and atomic orbitals (AOs) as a basis set. Although this method has a new problem called the overcompleteness problem²³, it can be reduced by confining the AOs inside the non-overlapping atomic spheres. Then, the complicated calculations of the AO-AO overlap matrices can be avoided simultaneously. In our TOMBO code, AOs are constructed by a product of the numerical radial function in a logarithmic mesh and the analytic cubic harmonics. In particular for the valence AOs, the radial function is confined inside the non-overlapping atomic sphere by subtracting a smooth quadratic function with the same amplitude and derivative at the atomic sphere²⁴. This quadratic function inside the sphere smoothly connects to the tail of the true AO outside the sphere. Sum of this smoothly connected part and the truncated part is equal to the true AO. Then, the former can be well described by a linear combination of PWs, and the latter is used as AO in the program. Most importantly, since the core and valence AOs are both well localized in

the non-overlapping atomic sphere, the use of the the $\mathbf{L} \cdot \mathbf{S}$ form of the SOC in this region, where the potential is spherically symmetric, is justified. On the other hand, the extended part of the orbitals can be well described by PWs, for which the general form $\mathbf{S} \cdot \nabla V \times \mathbf{p}$ of the SOC can be used without any approximation. This method can be used in determining the SOS in core orbitals without problem.

In this paper, we newly implemented the SOC in our all-electron mixed basis code, TOMBO²⁴, although the mass-velocity and Darwin terms, the so-called semi-relativistic terms, were already included²¹. Here we show the explicit formula of the AO-AO, PW-AO and PW-PW matrix elements of the SOC using the cubic harmonics. The AO-AO matrices constitute of the on-site integral inside the non-overlapping atomic sphere, which involves the standard form of the spin-orbit coupling: $\mathbf{S} \cdot \mathbf{L}$. Below, the AO-AO matrices are explicitly derived for p , d , and f orbitals in terms of the cubic harmonics. The PW-AO matrices can be calculated in a similar way when PWs are expanded in spherical waves. On the other hand, the PW-PW matrices can be accurately treated in Fourier space without using the $\mathbf{S} \cdot \mathbf{L}$ form. We also show the explicit form to treat the SOC for the spin polarized systems. Another important merit of using the all-electron mixed basis approach is that the required cut-off energy for PWs is significantly smaller than that for the usual PW expansion approach accompanied with the pseudopotential or APW method. To demonstrate the validity of the present method, we will show the results of the spin-orbit splitting of several atoms, molecules and silicon crystal.

II. FORMULATION

The spin-orbit interaction in the one-electron Hamiltonian is expressed as

$$H_{\text{SO}} = -\frac{1}{4c^2} \boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}) = \frac{1}{2c^2} \mathbf{S} \cdot (\nabla V \times \mathbf{p}), \quad (1)$$

where $\boldsymbol{\sigma}$ is Pauli's spin matrix, $\mathbf{S} = \boldsymbol{\sigma}/2$, $\mathbf{E} = -\nabla V$ is the electric field, $\mathbf{p} = -i\nabla$ is the momentum operator, and $c = 137.036$ is the light velocity in Hartree atomic unit ($m = e = \hbar = 1$). In the all-electron mixed basis approach, AOs are well localized inside the non-overlapping atomic sphere, where the potential around the j th atom can be regarded as spherically symmetric, $V_j(r_j)$, as a very good approximation. Then, the electric field can be expressed as $\mathbf{E} = -\nabla V_j = -(\mathbf{r}_j/r_j) dV_j/dr_j$, where $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$ denotes the electron coordinate around the nuclear position $\mathbf{R}_j$. Therefore, using

the angular momentum $\mathbf{L} = \mathbf{r}_j \times \mathbf{p}$, we can rewrite (1) as

$$H_{\text{SO}} = \frac{1}{2c^2} \frac{1}{r_j} \frac{dV_j}{dr_j} \mathbf{S} \cdot \mathbf{L}. \quad (2)$$

For simplicity, we assume the Γ -point ($\mathbf{k} = 0$) calculation only, although the generalization to the $\mathbf{k} \neq 0$ calculation is straightforward. In the all-electron mixed basis approach, the KS wave function of the λ th level is expressed as

$$\varphi_\lambda(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\mathbf{G}}^\lambda e^{i\mathbf{G} \cdot \mathbf{r}} + \sum_{jnlm} c_{jnlm}^\lambda \sum_{nlm} R_{nl}(r_j) K_{lm}(\hat{\mathbf{r}}_j) = \sum_{\mathbf{G}} c_{\mathbf{G}}(\mathbf{r} | \mathbf{G}) + \sum_{jnlm} c_{jnlm}(\mathbf{r} | jnlm), \quad (3)$$

where Ω is the volume of the unit cell, $c_{\mathbf{G}}^\lambda$ and c_{jnlm}^λ are the expansion coefficients, $\mathbf{G}$ is the reciprocal lattice vector, and $R_{nl}(r_j)$ and $K_{lm}(\hat{\mathbf{r}}_j)$ represent, respectively, the numerical radial function in logarithmic mesh and the (angular part) cubic harmonics constituting the AO.

A. Spin Polarized Systems

The SOC Hamiltonian for PWs in spin polarized systems reads

$$\begin{aligned} H_{\text{SO}} &= \frac{1}{4c^2} \mathbf{S} \cdot \left\{ \nabla(V_\uparrow + V_\downarrow) \times \mathbf{p} \right\} + \frac{1}{8c^2} (\sigma_z \mathbf{S} + \mathbf{S} \sigma_z) \cdot \left\{ \nabla(V_\uparrow - V_\downarrow) \times \mathbf{p} \right\} \\ &= \frac{1}{4c^2} \mathbf{S} \cdot \left\{ \nabla(V_\uparrow + V_\downarrow) \times \mathbf{p} \right\} \\ &\quad + \frac{1}{8c^2} \left(|\uparrow\rangle\langle\uparrow| \mathbf{S} - |\downarrow\rangle\langle\downarrow| \mathbf{S} + \mathbf{S} |\uparrow\rangle\langle\uparrow| - \mathbf{S} |\downarrow\rangle\langle\downarrow| \right) \cdot \left\{ \nabla(V_\uparrow - V_\downarrow) \times \mathbf{p} \right\}. \end{aligned} \quad (4)$$

Thus we have

$$\langle \uparrow | H_{\text{SO}} | \uparrow \rangle = \frac{1}{2c^2} \langle \uparrow | \mathbf{S} | \uparrow \rangle \cdot \left\{ \nabla V_\uparrow \times \mathbf{p} \right\}, \quad (5a)$$

$$\langle \uparrow | H_{\text{SO}} | \downarrow \rangle = \frac{1}{4c^2} \langle \uparrow | \mathbf{S} | \downarrow \rangle \cdot \left\{ \nabla(V_\uparrow + V_\downarrow) \times \mathbf{p} \right\}, \quad (5b)$$

$$\langle \downarrow | H_{\text{SO}} | \uparrow \rangle = \frac{1}{4c^2} \langle \downarrow | \mathbf{S} | \uparrow \rangle \cdot \left\{ \nabla(V_\uparrow + V_\downarrow) \times \mathbf{p} \right\}, \quad (5c)$$

$$\langle \downarrow | H_{\text{SO}} | \downarrow \rangle = \frac{1}{2c^2} \langle \downarrow | \mathbf{S} | \downarrow \rangle \cdot \left\{ \nabla V_\downarrow \times \mathbf{p} \right\}. \quad (5d)$$

For spherical potential for AOs defined inside the non-overlapping sphere, $\nabla V_\sigma \times \mathbf{p}$ can be replaced by $(1/r)(dV_\sigma/dr)\mathbf{L}$, and Eqs. (5a)-(5d) become

$$\langle \uparrow | H_{\text{SO}} | \uparrow \rangle = \frac{1}{2c^2} \langle \uparrow | \mathbf{S} | \uparrow \rangle \cdot \mathbf{L} \frac{1}{r} \frac{dV_\uparrow}{dr}, \quad (6a)$$

$$\langle \uparrow | H_{\text{SO}} | \downarrow \rangle = \frac{1}{4c^2} \langle \uparrow | \mathbf{S} | \downarrow \rangle \cdot \mathbf{L} \frac{1}{r} \frac{d}{dr} (V_\uparrow + V_\downarrow), \quad (6b)$$

$$\langle \downarrow | H_{\text{SO}} | \uparrow \rangle = \frac{1}{4c^2} \langle \downarrow | \mathbf{S} | \uparrow \rangle \cdot \mathbf{L} \frac{1}{r} \frac{d}{dr} (V_\uparrow + V_\downarrow), \quad (6c)$$

$$\langle \downarrow | H_{\text{SO}} | \downarrow \rangle = \frac{1}{2c^2} \langle \downarrow | \mathbf{S} | \downarrow \rangle \cdot \mathbf{L} \frac{1}{r} \frac{dV_\downarrow}{dr}. \quad (6d)$$

B. Matrix Elements

There are three kinds of matrix elements, PW-PW, PW-AO and AO-AO, to be calculated. Since the potential is expanded in Fourier space as

$$V(\mathbf{r}) = \sum_{\mathbf{G}''} \tilde{V}_{\mathbf{G}''} e^{i\mathbf{G}'' \cdot \mathbf{r}}, \quad (7)$$

the PW-PW matrix elements can be identified to be

$$\begin{aligned} \langle \mathbf{G} s_z | H_{\text{SO}} | \mathbf{G}' s'_z \rangle &= -\frac{i}{2c^2 \Omega} \int e^{-i\mathbf{G} \cdot \mathbf{r}} \langle s_z | \mathbf{S} | s'_z \rangle \cdot (\nabla V \times \nabla) e^{i\mathbf{G}' \cdot \mathbf{r}} d\mathbf{r} \\ &= \frac{i}{2c^2} \tilde{V}_{\mathbf{G}-\mathbf{G}'} \langle s_z | \mathbf{S} | s'_z \rangle \cdot \mathbf{G} \times \mathbf{G}' \end{aligned} \quad (8)$$

from (1), where $|\mathbf{G} s_z\rangle$ denotes the direct product of the PW $|\mathbf{G}\rangle$ and the spin function $|s_z\rangle$ with the spin eigenvalue $s_z = \frac{1}{2}$ or $-\frac{1}{2}$. (Here we assumed the spin unpolarized systems but the generalization to spin polarized systems is straightforward.) In the calculation of the AO-AO and PW-AO matrix elements, the identity

$$\mathbf{S} \cdot \mathbf{L} = \frac{1}{2} (S_+ L_- + S_- L_+) + S_z L_z \quad (9)$$

can be used for the spherical harmonics because AOs are well confined in the non-overlapping atomic sphere. Here $S_\pm = S_x \pm iS_y$ and $L_\pm = L_x \pm iL_y$ are the ladder operators. From this expression, it is obvious that different l, l' pairs do not contribute, and it is only necessary to consider the matrix elements sandwiched with the same angular momentum quantum number l . The cubic harmonics are defined as (here and hereafter we omit the suffix j) $K_{0,1} = 1$, $K_{1,1} = x$, $K_{1,2} = y$, $K_{1,3} = z$, $K_{2,1} = xy$, $K_{2,2} = yz$, $K_{2,3} = zx$, $K_{2,4} = (3z^2 - r^2)/\sqrt{6}$, $K_{2,5} = (x^2 - y^2)/2$,

$K_{3,1} = x(5x^2 - 3r^2)/2\sqrt{15}$, $K_{3,2} = y(5y^2 - 3r^2)/2\sqrt{15}$, $K_{3,3} = z(5z^2 - 3r^2)/2\sqrt{15}$, $K_{3,4} = x(y^2 - z^2)/2$, $K_{3,5} = y(z^2 - x^2)/2$, $K_{3,6} = z(x^2 - y^2)/2$, and $K_{3,7} = xyz$ apart from the prefactor $\sqrt{(2l+1)!!}/\sqrt{4\pi}r^l$.

There is a orthonormalization relation between two cubic harmonics,

$$\int K_{l,m}(\hat{\mathbf{r}})K_{l',m'}(\hat{\mathbf{r}})d\hat{\mathbf{r}} = \delta_{ll'}\delta_{mm'}, \quad (10)$$

where $\hat{\mathbf{r}}$ denotes $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$. For the AO-AO matrix elements, we have

$$\langle jnlms_z | H_{\text{SO}} | jnlm's'_z \rangle = -\frac{1}{2c^2} \langle lms_z | \mathbf{S} \cdot \mathbf{L} | lm's'_z \rangle \int_0^\infty R_{nl}^2(r) \frac{dV_j(r)}{dr} r dr, \quad (11)$$

where $|lms_z\rangle$ denotes the direct product of the cubic harmonics $K_{l,m}$ and the spin function $|s_z\rangle$ with the spin eigenvalue $s_z = \frac{1}{2}$ or $-\frac{1}{2}$. For the s orbitals ($l = 0$), obviously

$$\langle 00s_z | \mathbf{S} \cdot \mathbf{L} | 00s'_z \rangle = 0, \quad (12)$$

where $s, s'_z = \frac{1}{2}, -\frac{1}{2}$. For the p orbitals ($l = 1$), we have

$$\langle 1ms_z | \mathbf{S} \cdot \mathbf{L} | 1m's'_z \rangle = \begin{pmatrix} 0 & \frac{i}{2} & 0 & 0 & 0 & \frac{1}{2} \\ -\frac{i}{2} & 0 & 0 & 0 & 0 & \frac{i}{2} \\ 0 & 0 & 0 & -\frac{1}{2} & -\frac{i}{2} & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & -\frac{i}{2} & 0 \\ 0 & 0 & \frac{i}{2} & \frac{i}{2} & 0 & 0 \\ \frac{1}{2} & -\frac{i}{2} & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (13a)$$

where the order of the element ms_z is $1 \uparrow, 2 \uparrow, 3 \uparrow, 1 \downarrow, 2 \downarrow$, and $3 \downarrow$. For the d orbitals ($l = 2$), we have

$$\langle 2ms_z | \mathbf{S} \cdot \mathbf{L} | 2m's'_z \rangle = \begin{pmatrix} 0 & 0 & 0 & 0 & -i & 0 & \frac{1}{2} & \frac{i}{2} & 0 & 0 \\ 0 & 0 & -\frac{i}{2} & 0 & 0 & -\frac{1}{2} & 0 & 0 & \frac{\sqrt{3}i}{2} & \frac{i}{2} \\ 0 & \frac{i}{2} & 0 & 0 & 0 & -\frac{i}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ i & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}i}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{2} & \frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{i}{2} & 0 & 0 & 0 & 0 & 0 & 0 & i \\ \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}i}{2} & \frac{i}{2} & 0 & 0 & \frac{i}{2} & 0 & 0 \\ -\frac{i}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & -\frac{i}{2} & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{3}i}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{i}{2} & -\frac{1}{2} & 0 & 0 & -i & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (13b)$$

where the order of the element ms_z is $1 \uparrow, 2 \uparrow, 3 \uparrow, 4 \uparrow, 5 \uparrow, 1 \downarrow, 2 \downarrow, 3 \downarrow, 4 \downarrow$, and $5 \downarrow$. For the f orbitals ($l = 3$), we have

$$\langle 3ms_z | \mathbf{S} \cdot \mathbf{L} | 3m's'_z \rangle$$

$$= \begin{pmatrix} 0 & -\frac{3i}{4} & 0 & 0 & -\frac{\sqrt{15}i}{4} & 0 & 0 & 0 & 0 & -\frac{3}{4} & 0 & 0 & \frac{\sqrt{15}}{4} & 0 \\ \frac{3i}{4} & 0 & 0 & -\frac{\sqrt{15}i}{4} & 0 & 0 & 0 & 0 & 0 & -\frac{3i}{4} & 0 & 0 & -\frac{\sqrt{15}}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{4} & \frac{3i}{4} & 0 & \frac{\sqrt{15}}{4} & -\frac{\sqrt{15}i}{4} & 0 & 0 \\ 0 & \frac{\sqrt{15}i}{4} & 0 & 0 & \frac{i}{4} & 0 & 0 & 0 & 0 & -\frac{\sqrt{15}}{4} & 0 & 0 & \frac{1}{4} & i \\ \frac{\sqrt{15}i}{4} & 0 & 0 & -\frac{i}{4} & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{15}i}{4} & 0 & 0 & \frac{i}{4} & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & i & -\frac{\sqrt{15}}{4} & -\frac{\sqrt{15}i}{4} & 0 & -\frac{1}{4} & -\frac{i}{4} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 & -i & 1 & 0 & 0 \\ 0 & 0 & \frac{3}{4} & 0 & 0 & -\frac{\sqrt{15}}{4} & 0 & 0 & \frac{\sqrt{3}i}{4} & 0 & 0 & -\frac{\sqrt{15}i}{4} & 0 & 0 \\ 0 & 0 & -\frac{3i}{4} & 0 & 0 & -\frac{\sqrt{15}i}{4} & 0 & -\frac{\sqrt{3}i}{4} & 0 & 0 & -\frac{\sqrt{15}i}{4} & 0 & 0 & 0 \\ -\frac{3}{4} & \frac{3i}{4} & 0 & -\frac{\sqrt{15}}{4} & -\frac{\sqrt{15}i}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\sqrt{15}}{4} & 0 & 0 & -\frac{1}{4} & i & 0 & -\frac{\sqrt{15}i}{4} & 0 & 0 & -\frac{i}{4} & 0 & 0 \\ 0 & 0 & \frac{\sqrt{15}i}{4} & 0 & 0 & \frac{i}{4} & 1 & -\frac{\sqrt{15}i}{4} & 0 & 0 & \frac{i}{4} & 0 & 0 & 0 \\ \frac{\sqrt{15}}{4} & \frac{\sqrt{15}i}{4} & 0 & \frac{1}{4} & -\frac{i}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i \\ 0 & 0 & 0 & -i & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 \end{pmatrix}, \quad (13c)$$

where the order of the element ms_z is $1 \uparrow, 2 \uparrow, 3 \uparrow, 4 \uparrow, 5 \uparrow, 6 \uparrow, 7 \uparrow, 1 \downarrow, 2 \downarrow, 3 \downarrow, 4 \downarrow, 5 \downarrow, 6 \downarrow$, and $7 \downarrow$. All these matrices have zero diagonal elements only, because the cubic harmonics is expressed in either symmetric or antisymmetric combination of spherical harmonics with respect to the L_z eigenvalue, *i.e.*, the magnetic quantum number m , the expectation value of L_z sandwiched with the same cubic harmonics is always zero. (Note that the second index of the spherical harmonics is the magnetic quantum number m but the second index of the cubic harmonics is not the magnetic quantum number.)

For the PW-AO matrix elements, PWs are first expanded in terms of the cubic harmonics as

$$e^{i\mathbf{G} \cdot \mathbf{r}} = e^{i\mathbf{G} \cdot \mathbf{R}_j} \left[4\pi \sum_l i^l j_l(Gr_j) \sum_{m=1}^{2l+1} K_{lm}(\hat{\mathbf{G}}) K_{lm}(\hat{\mathbf{r}}_j) \right], \quad (14)$$

where $j_l(x)$ is the spherical Bessel function, $\hat{\mathbf{G}} = \mathbf{G}/|\mathbf{G}|$, $\hat{\mathbf{r}}_j = \mathbf{r}_j/|\mathbf{r}_j|$. Therefore, the PW-AO matrix

elements are obtained as

$$\langle \mathbf{G} s_z | H_{\text{SO}} | j n l m' s'_z \rangle = \frac{(-i)^l}{2c^2} e^{-i\mathbf{G} \cdot \mathbf{R}_j} \sum_{m=1}^{2l+1} \langle l m s_z | \mathbf{S} \cdot \mathbf{L} | l m' s'_z \rangle K_{lm}(\hat{\mathbf{G}}) \int_0^\infty j_l(Gr) \frac{dV_j}{dr} R_{nl}(r) r dr. \quad (15)$$

C. Diagonalization

There are two approaches to treat the spin-orbit interaction. One is to use perturbation theory and the other is to diagonalize the full Hamiltonian. In the former approach we construct the matrix elements sandwiched by the eigenfunctions of the unperturbed Hamiltonian, *i.e.*, the Hamiltonian without the spin-orbit interaction, as

$$\begin{aligned} \langle \lambda s_z | H_{\text{SO}} | \lambda' s'_z \rangle &= \sum_{\mathbf{G}} c_{\mathbf{G}}^{\lambda*} \sum_{\mathbf{G}'} c_{\mathbf{G}'}^{\lambda'} \langle \mathbf{G} s_z | H_{\text{SO}} | \mathbf{G}' s'_z \rangle \\ &+ \left(\sum_{\mathbf{G}} c_{\mathbf{G}}^{\lambda*} \sum_{j n l m} c_{j n l m}^{\lambda} \langle \mathbf{G} s_z | H_{\text{SO}} | j n l m s'_z \rangle + c.c. \right) \\ &+ \sum_{j n l m} c_{j n l m}^{\lambda*} \sum_{m'} c_{j n l m'}^{\lambda} \langle j n l m s_z | H_{\text{SO}} | j n l m' s'_z \rangle, \end{aligned} \quad (16)$$

where c.c. means the complex conjugate. As an approximation, one may solve the secular equation

$$\begin{vmatrix} \langle \lambda \frac{1}{2} | H_{\text{SO}} | \lambda' \frac{1}{2} \rangle + (\varepsilon_\lambda - \varepsilon) \delta_{\lambda\lambda'} & \langle \lambda \frac{1}{2} | H_{\text{SO}} | \lambda' - \frac{1}{2} \rangle \\ \langle \lambda - \frac{1}{2} | H_{\text{SO}} | \lambda' \frac{1}{2} \rangle & \langle \lambda - \frac{1}{2} | H_{\text{SO}} | \lambda' - \frac{1}{2} \rangle + (\varepsilon_\lambda - \varepsilon) \delta_{\lambda\lambda'} \end{vmatrix} = 0. \quad (17)$$

in the degenerate complex of the states, $|\lambda s_z\rangle$ and $|\lambda' s'_z\rangle$, where the Kohn–Sham energies ε_λ and $\varepsilon_{\lambda'}$ are all the same. One can apply such an approach, for example, to the atomic spectra or to the calculation of the core electron binding energy (CEBE) of molecules or defects/surfaces/interfaces in X-ray photoelectron spectroscopy (XPS). A more accurate treatment is to solve Eq. (17) beyond the degenerate complex of the states, $|\lambda s_z\rangle$ and $|\lambda' s'_z\rangle$, where ε_λ and $\varepsilon_{\lambda'}$ can be different. This becomes equivalent to perform the full matrix diagonalization of $H + H_{\text{SO}}$.

III. RESULTS AND DISCUSSION

For an isolated hydrogen-like atom, we can see the eigenvalues defined by resultant orbital angular momentum quantum number $j = l + s_z$ are split as

$$|\epsilon_{nlj=l+1/2} - \epsilon_{nl}^0| : |\epsilon_{nlj=l-1/2} - \epsilon_{nl}^0| = l : l + 1, \quad (18)$$

so this result is used in checking the result of isolated atoms having a closed shell.

Table I shows the results calculated for the levels at the 1S_0 ground state of isolated rare gas atoms, Ne, Ar, and Kr. $E_{\text{SOC}}^{\text{calc}}$ and $E_{\text{SOC}}^{\text{calc}}(+\text{SR})$ are the first-principles results obtained by diagonalizing the full $H + H_{\text{SO}}$ without and with the scalar relativistic correction (SR), respectively. The last column lists available experimental data^{25–30} for comparison. The resulting spin-orbit splitting $E_{\text{SOC}}^{\text{calc}}(+\text{SR})$ for Ne, Ar, and Kr shows excellent agreement with the experimental data. These SOS values are observed in XPS experiments. It is known that the XPS results for one particular material could be diverse between different research and measurements; so if there are differences, those values are written on the lower right. From these results, we can see that our program works quite well. Figures 1(a)-(e) show the energy diagram of the Kohn–Sham (KS) energy eigenvalues

TABLE I: Spin-orbit splitting in units of eV calculated for rare gas atoms by using the full eigenvalue problem $\Delta E_{\text{SOC}}^{\text{calc}}$ and $\Delta E_{\text{SOC}}^{\text{calc}}(+\text{SR})$, where (+SR) means the scalar relativistic correction. The available experimental values are also listed in the last column for comparison.

Atom	Level	$\Delta E_{\text{SOC}}^{\text{calc}}$	$\Delta E_{\text{SOC}}^{\text{calc}}(+\text{SR})$	Experiment
^{10}Ne	1S_0 $2p$	0.103	0.103	0.097 ^a
^{18}Ar	1S_0 $2p$	2.209	2.211	2.68 ^b _{± 0.95}
	$3p$	0.176	0.177	0.177 ^c
^{36}Kr	1S_0 $2p$	51.677	51.853	
	$3p$	7.482	7.387	
	$3d$	1.306	1.304	
	$4p$	0.615	0.597	0.666 ^d
^{54}Xe	1S_0 $3d$	12.91	12.92	12.6 ^e
	$4p$	10.38	9.82	
	$4d$	2.59	2.58	
	$5p$	0.76	0.77	

^a Ref.²⁵.

^b Ref.^{26, 27}.

^c Ref.²⁸.

^d Ref.²⁹.

^e Ref.³⁰.

for some levels of the rare gas atoms. The fully diagonalized absolute energy levels (right side of each figure) are also quite reasonable. In fact, the p orbitals for $l = 1$ are split into two states,

$j = \frac{3}{2}$ and $j = \frac{1}{2}$, and the energy shifts from ϵ_{nl}^0 without considering SOC are analytically evaluated as $\frac{1}{2}\zeta_{n1}$ ($j = \frac{3}{2}$) and ζ_{n1} ($j = \frac{1}{2}$), *i.e.*, $\Delta\epsilon_{np\frac{3}{2}-np} : \Delta\epsilon_{np\frac{1}{2}-np} = 1 : 2$. Similarly for the d orbitals corresponding to $l = 2$, the energy shifts are analytically evaluated as ζ_{n2} ($j = \frac{5}{2}$) and $\frac{3}{2}\zeta_{n2}$ ($j = \frac{3}{2}$), *i.e.*, $\Delta\epsilon_{nd\frac{5}{2}-nd} : \Delta\epsilon_{nd\frac{3}{2}-nd} = 2 : 3$. We can confirm that these analytical relationships are satisfied in all Figs. 1(a)-(e). This clearly indicates the validity of the present method.

FIG. 1: Energy diagram of rare gas atoms: (a) Ne (2p), (b) Ar (2p), (c) Ar (3p), (d) Kr (2p), (e) Kr (3d), (f) Kr (2p), and (g) Kr (4p)

In Table II, we show the calculated SOS of several open shell atoms Na, Mg, Al, Si, P, S and Cl, which have nonzero spin magnetic moment. The error bars are the width of the slightly split levels due to the spin polarization of these systems. We also list experimental data^{31–38} for comparison. The results are fairly good for all atoms, indicating again the validity of the present method.

TABLE II: SOS of the open shell atoms in units of eV.

Experimental values are listed for comparison.

Atom		Level	$\Delta E_{\text{SOC}}^{\text{calc}}$	Experiment
^{11}Na	$^2\text{S}_{\frac{1}{2}}$	$2p$	$0.182_{\pm 0.040}$	0.14^{f}
^{12}Mg	$^1\text{S}_0$	$2p$	0.286	0.28^{g}
^{13}Al	$^2\text{P}_{\frac{1}{2}}$	$2p$	$0.441_{\pm 0.05}$	$0.415_{\pm 0.015}^{\text{h}}$
^{14}Si	$^3\text{P}_0$	$2p$	$0.660_{\pm 0.154}$	$0.615_{\pm 0.015}^{\text{i}}$
^{15}P	$^4\text{S}_{\frac{3}{2}}$	$2p$	$0.941_{\pm 0.279}$	0.87^{j}
^{16}S	$^3\text{P}_0$	$2p$	$1.274_{\pm 0.274}$	1.13^{k}
^{17}Cl	$^2\text{P}_{\frac{3}{2}}$	$2p$	$1.68_{\pm 0.16}$	1.6^{k}

^f Ref.³¹

^g Ref.³²

^h Ref.^{33,34}

ⁱ Ref.^{35,36}

^j Ref.³⁷

^k Ref.³⁸

TABLE III: SOS in units of eV calculated for several molecules using full eigenvalue problem of $H + H_{\text{SO}}$ without and with the scalar relativistic correction. For comparison, experimental data are listed together.

Molecule		MO	$\Delta E_{\text{SOC}}^{\text{calc}}$	$\Delta E_{\text{SOC}}^{\text{calc}}(+\text{SR})$	Experiment
HBr	$^1\Sigma$	π	0.290	0.282	0.33^{l}
BrCN	$^1\Sigma$	2π	0.169	0.168	0.18^{l}
		1π	0.061	0.081	$(0.09)^{\text{l}}$
HCl	$^1\Sigma$	π	0.083	0.083	0.08^{l}
HI	$^1\Sigma$	π	0.558	0.523	0.67^{l}
I_2	$^1\Sigma_g$	π_g	0.603	0.563	0.63^{m}
		π_u	0.592	0.547	0.79^{m}
		$4d$	$1.942_{\pm 0.651}$	$1.875_{\pm 0.696}$	1.76^{n}

^l Ref.⁴⁰.

^m Ref.⁴¹.

ⁿ Ref.⁴².

Next, we calculated the SOS for several molecules, HBr, BrCN, HCl, HI, and I₂. For the bond length, we used the following values: H-Br=1.414 Å, Br-C=1.159 Å, C-N=1.159 Å, H-Cl=1.274 Å, H-I=1.609 Å, and I-I=2.666 Å.³⁹ Table III shows the results of the SOS calculated for these molecules together with colored the previous experiments^{40,42}. From this table, we see that $\Delta E_{\text{SOC}}^{\text{calc}}(+\text{SR})$ calculated by the full $H + H_{\text{SO}}$ diagonalization with the scalar relativistic correction shows good agreement with the experimental values. Figures.2(a)-(e) show the energy diagram for each molecular orbital. From these figures, we can identify how the molecular orbital levels split. In the case of molecules, the split is not simply 1:2 or 2:3 as in the rare gas atoms. This is of course because the complicated nature of the molecular orbitals.

FIG. 2: Energy diagram of some molecules: (a) HBr (π), (b) BrCN (2π), (c) BrCN (π), (d) HCl (π), (e) HI (π), (f) I₂ (π_g), (g) I₂ (π_u), and (h) I₂ ($4d$)

In order to see how much PWs contribute to the SOS, we estimated the SOS with and without

PWs in the calculation. As shown in Table IV, the AOs only results slightly overestimate the results using both AOs and PWs. The PW contribution is about 0.1-0.4%. Thus we can conclude that PW-PW and PW-AO parts can be safely neglected thus saving the effort for computation of large blocks of the H_{SO} matrix. In this case, the calculation using only the AO-AO block becomes similar to the atomic mean-field integral (AMFI) approximation by Hess et al.⁴³

TABLE IV: PW contribution to the SOS in units of eV

Molecule		MO	AOs only	AOs and PWs
HBr	$^1\Sigma$	π	0.2833	0.2828
BrCN	$^1\Sigma$	2π	0.1679	0.1676
		1π	0.0812	0.0809
HCl	$^1\Sigma$	π	0.0834	0.0832
HI	$^1\Sigma$	π	0.5240	0.5237
I ₂	$^1\Sigma_g$	π_g	0.565	0.563
		π_u	0.548	0.547
		$4d$	1.876	1.875

Finally, we calculated Si2*p* core level of silicon crystal at the Γ point. We used a simple cubic unit cell including 64 Si atoms. The calculated spin-orbit splitting $\Delta E_{SOC}^{calc} = 0.62 \pm 0.1$ eV, and the shifts from the original KS eigenvalue without SOC are $\Delta\epsilon_{2p_{3/2}-2p} = 0.205 \pm 0.05$ eV and $\Delta\epsilon_{2p_{1/2}-2p} = -0.415 \pm 0.05$ eV. Experimentally we know that the splitting value is 0.615 ± 0.15 eV^{35,36}. Our result shows excellent agreement with the experimental value.

FIG. 3: Energy diagram of the core 2*p* level of silicon crystal

Table V lists the size of the assumed cubic unit cell, the PW cut-off energy, and the number of basis functions, and the number of Kohn–Sham levels used for the SOS calculation. It should be emphasized that the PW cut-off energy is relatively small (typically $\sim 50 - 170$ eV) compared to the usual PW expansion method accompanied with pseudopotential or APW method (typically $\sim 300 - 500$ eV). As demonstrated above, this is a distinct merit of using the all-electron mixed basis approach. The number of KS levels used in the diagonalization of $H + H_{\text{SO}}$ is typically 100-300 except for silicon crystal. We confirmed the result does not change even if we increase these numbers.

For the calculations of molecules, non-overlapping atomic spheres are selected so that they do not overlap each other and the total energy becomes smaller with a sufficient cutoff energy

TABLE V: Cell size and cut-off energy for each systems

System	Unit cell [$\text{\AA}$]	$E_{\text{cut-off}}$ (PWs) [eV]	basis (AOs + PWs)	levels used for SOS
Ne	12.0	104.4	4174 (5+4169)	108
Ar	14.0	129.6	9180 (9+9171)	116
Kr	14.0	76.7	4187 (18+4169)	134
Xe	18.0	46.4	4196 (27+4169)	152
HBr	14.0	172.6	14166 (19+14147)	234
BrCN	14.0	129.7	9196 (25+9171)	246
HCl	14.0	76.7	4179 (10+4169)	216
HI	12.0	176.5	9199 (28+9171)	252
I ₂	18.0	150.4	24459 (54+24405)	304
Si ₆₄ (crystal)	10.86	81.6	2429 (320+2109)	914
Na	18	46.4	4175 (6+4169)	114
Mg	16	58.7	4169 (6+4175)	110
Al	16	58.7	4178 (9+4169)	116
Si	16	58.7	4178 (9+4169)	118
P	16	71.0	5584 (9+5575)	122
S	16	84.6	7162 (9+7153)	120
Cl	18	46.4	7162 (9+7153)	120

for PWs (given in Table V). In each atomic sphere, the effective potential in the Kohn–Sham equation is assumed spherically symmetric. So, using large atomic spheres probability gives an error. Concrete values for the radius of the atomic sphere used in this study are listed in Table VI.

TABLE VI: Radius of non-overlapping atomic sphere

Molecule	Atom	Radius of Atomic Sphere [$\text{\AA}$]
HBr	H	0.260
	Br	1.139
BrCN	Br	1.000
	C	0.780
	N	0.318
HCl	H	0.200
	Cl	0.999
H	H	0.369
	I	0.900
I ₂	I	0.800

IV. CONCLUDING REMARKS

In this paper, we have implemented the spin-orbit coupling (SOC) in the all-electron mixed basis code, TOMBO. For this purpose, we have presented the explicit matrix form of SOC Hamiltonian using the cubic harmonics, which is useful in any kind of first-principles calculations. There is a distinct merit of using the all-electron mixed basis approach in the evaluation of the SOC, because AOs are well confined in the non-overlapping atomic sphere, where the potential is spherically symmetric and the standard $\mathbf{S} \cdot \mathbf{L}$ form can be used. The AO-AO matrices were explicitly derived for p , d , and f orbitals in the cubic harmonics representation. The PW-AO matrices can be calculated in a similar way when PWs are expanded in spherical waves. On the other hand, the PW-PW matrices can be accurately treated in Fourier space without using the $\mathbf{S} \cdot \mathbf{L}$ form. We showed several results for the spin-orbit splitting of atoms and molecules as well as silicon crystal. All the results are in good agreement with available experimental data, suggesting the validity

of the present method. The present method is applicable to transition elements and rare earth elements also and even solid compounds as well. Such calculations will be planned as a future study.

Here, we discussed the spin-orbit splitting, *i.e.* the relative energies, only, but it is also very important to determine the absolute energy values in XPS. For such a purpose, we have to go beyond DFT and adopt GW approximation⁴⁴. Moreover, although the present method allows us to calculate the SOC interaction between core electrons and valence electrons, we have not focused the spin-orbit splitting of the conduction levels at all. In order to see how the present method works on the conduction levels, further investigations are necessary. All these studies are left for our future subjects.

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