PHYSICAL REVIEW B **78**, 245107 (2008)

$\mathbf{k}\cdot\mathbf{p}$ formula for use with linearized augmented plane waves

Tatsuya Shishidou and Tamio Oguchi
ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

(Received 16 September 2008; revised manuscript received 5 November 2008; published 5 December 2008)

We provide $\mathbf{k}\cdot\mathbf{p}$ formalism within the full-potential linearized augmented plane-wave (LAPW) method. Unlike the pure plane waves, the LAPW functions do not behave trivially in moving from $\mathbf{k}$ to $\mathbf{k}+\mathbf{q}$ and their incompleteness as a basis set should be taken into account. Derivatives of the sphere matching coefficients play the key role, for which we find a simple formula. Concrete formula for the $\mathbf{k}\cdot\mathbf{p}$ matrix elements is derived and numerically tested. Generalized second-order perturbation theory allowing for a degenerate case is presented and the literally exact electronic band gradients and curvatures are accessible.

DOI: 10.1103/PhysRevB.78.245107 PACS number(s): 71.15.Ap, 71.15.Dx

I. INTRODUCTION

$\mathbf{k}\cdot\mathbf{p}$ method[1] was founded a long time ago to examine the properties of electronic energy bands of a periodic solid. It had been widely used as an aid to parametrize the energy-band structure from the experimental observables such as effective masses and energy-band gaps.[2] Now it is receiving revived interests from the society of modern first-principles electronic structure calculations.[3–12] Let us recapitulate the $\mathbf{k}\cdot\mathbf{p}$ method to see its advantage and usefulness and at the same time to point out a hindered problem in applying it to the first-principles calculations. From the Bloch theorem, the wave functions at $\mathbf{k}+\mathbf{q}$ can be put in the form of

$$\psi_{\mathbf{k}+\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}}\chi_{\mathbf{k}}(\mathbf{r}), \tag{1}$$

where $\chi_{\mathbf{k}}$ carries the crystal momentum $\mathbf{k}$. The $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian H, which determines $\chi_{\mathbf{k}}$ and the eigenvalues $E(\mathbf{k}+\mathbf{q})$, is defined in terms of the original Hamiltonian $\mathcal{H}$ as

$$H = e^{-i\mathbf{q}\cdot\mathbf{r}}\mathcal{H}e^{i\mathbf{q}\cdot\mathbf{r}} = \mathcal{H} + \mathbf{q}\cdot\mathbf{v} + q^2/2m, \tag{2a}$$

$$\mathbf{v} = -i[\mathbf{r},\mathcal{H}]. \tag{2b}$$

The last equality in Eq. (2a) is valid for Schrödinger and Pauli-type $\mathcal{H}$ with the effective potential being in a local form. The function $\chi_{\mathbf{k}}$ is expandable in terms of a *complete* set of Bloch waves at $\mathbf{k}$. In the conventional derivation of textbook $\mathbf{k}\cdot\mathbf{p}$ formula,[1] χ is expanded by the wave functions at $\mathbf{k}$ as

$$\chi_{\mathbf{k}} = \sum_i \psi_{i\mathbf{k}}C_i. \tag{3}$$

Admitting Eq. (3), the secular equation $\Sigma_j H_{ij}C_j = E(\mathbf{k}+\mathbf{q})C_i$ comes with very simple matrix elements

$$H_{ij} = E_i(\mathbf{k})\delta_{ij} + \mathbf{q}\cdot\mathbf{v}_{ij} + \frac{q^2}{2m}\delta_{ij}, \tag{4a}$$

$$\mathbf{v}_{ij} = \langle\psi_{i\mathbf{k}}|\mathbf{v}|\psi_{j\mathbf{k}}\rangle. \tag{4b}$$

Hence by tabulating the matrix elements of $\mathbf{v}$ in terms of the wave functions at the reference point $\mathbf{k}$, one can immediately discuss arbitrary $\mathbf{k}+\mathbf{q}$ points. This is the great advantage of the $\mathbf{k}\cdot\mathbf{p}$ method over the usual non-$\mathbf{k}\cdot\mathbf{p}$ calculations,[5–7] in which one has to repeat the cumbersome procedure of setting up the Hamiltonian and overlap matrices for each $\mathbf{k}$ point. Furthermore, since $\mathbf{q}$ can be any like a complex vector, the $\mathbf{k}\cdot\mathbf{p}$ method can be applied to the complex band-structure problem.[8–10] In discussing the close vicinity of a given $\mathbf{k}$, one can regard the $\mathbf{q}$-dependent terms in Eq. (4a) as a *perturbation* acting on the eigenstates at $\mathbf{k}$ $[E_n(\mathbf{k}),\psi_{n\mathbf{k}}]$. The first- and second-order perturbation theories provide the expressions of Taylor-expansion coefficients of $E_n(\mathbf{k}+\mathbf{q})$ to second order in $\mathbf{q}$. The electronic band energy gradient (or the group velocity) and the curvature (or the inverse effective-mass tensor), both of which are important quantities in discussing the transport properties, are obtained without relying on any numerical procedure of fitting the energy bands.[11] The analytical expression of $E_n(\mathbf{k}+\mathbf{q})$ from the $\mathbf{k}\cdot\mathbf{p}$ perturbation may enable one to construct an efficient Brillouin-zone (BZ) integration scheme.[3] Our specific motivation for the $\mathbf{k}\cdot\mathbf{p}$ method comes from the following origin. We are currently extending our band-structure calculation code, which is based on the full-potential linearized augmented plane-wave (APW) (LAPW) (FLAPW) (Refs. 13–16) method, to realize GW-approximation[17] calculations. To get the GW self-energy, we ought to evaluate the $\mathbf{q}\rightarrow 0$ limit of

$$\langle\psi_{n\mathbf{k}}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\psi_{m,\mathbf{k}+\mathbf{q}}\rangle\langle\psi_{m,\mathbf{k}+\mathbf{q}}|e^{i\mathbf{q}\cdot\mathbf{r}}|\psi_{n'\mathbf{k}}\rangle/q^2. \tag{5}$$

In other words, an expression for quadratic q expansion of a function $\chi = e^{-i\mathbf{q}\cdot\mathbf{r}}\psi_{\mathbf{k}+\mathbf{q}}$ is needed. This may be achieved by applying the second-order $\mathbf{k}\cdot\mathbf{p}$ perturbation theory. In what follows, we refer to Eqs. (3) and (4) as the "standard" $\mathbf{k}\cdot\mathbf{p}$ formula.

To incorporate the $\mathbf{k}\cdot\mathbf{p}$ approach in the first-principles calculations, one needs to be aware of the problem arising from the use of an incomplete basis-function set (IBS). If ψ's are true wave functions of $\mathcal{H}$, the ansatz (3) exactly holds. In practical calculations, however, we obtain $\psi_{i\mathbf{k}}$ variationally. It is expanded in terms of a certain incomplete basis set $\{\phi_\zeta(\mathbf{k},\mathbf{r})\}$ and hence $\{\psi_{i\mathbf{k}}\}$ would never be a complete set at $\mathbf{k}$. Instead of Eq. (3), we must consider the adequate Hilbert space for the function $\chi_{\mathbf{k}}$. It should, from the variational space for $\psi_{\mathbf{k}+\mathbf{q}}$, be spanned by the following functions:

$$\Phi_\zeta(\mathbf{k},\mathbf{q},\mathbf{r}) \equiv e^{-i\mathbf{q}\cdot\mathbf{r}}\phi_\zeta(\mathbf{k}+\mathbf{q},\mathbf{r}). \tag{6}$$

If plane waves are used as the basis functions (the subscript ζ is then a reciprocal-lattice vector $\mathbf{G}$), ansatz (3) exceptionally stands. A function $\Phi_{\mathbf{G}}(\mathbf{k},\mathbf{q},\mathbf{r})$ turns out to be a basis function at $\mathbf{k}$, $\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r})$. Thus the space $\{\phi_{\mathbf{G}}(\mathbf{k})\}$ or the equivalent space $\{\psi_{i\mathbf{k}}\}$ provides necessary and sufficient space for $\chi_{\mathbf{k}}$ even with a practical truncation of $|\mathbf{k}+\mathbf{G}| \leq G_{\max}$.

For those IBS, which do not have the property of

$$\{\Phi_{\zeta}(\mathbf{k},\mathbf{q},\mathbf{r})\} = \{\phi_{\zeta}(\mathbf{k},\mathbf{r})\}, \tag{7}$$

one should consider Eq. (6) as the basis function for χ. By rotating it with the eigenvectors at $\mathbf{k}$, $Z_{\zeta i}(\mathbf{k})$, we have

$$\tilde{\psi}_{i\mathbf{k}}(\mathbf{q},\mathbf{r}) = \sum_{\zeta} \Phi_{\zeta}(\mathbf{k},\mathbf{q},\mathbf{r}) Z_{\zeta i}(\mathbf{k}), \tag{8}$$

which is labeled by the eigenstates at $\mathbf{k}$ and is to be substituted for $\psi_{i\mathbf{k}}$ in Eq. (3). As a result, the matrix elements of Eq. (4) will undergo some modifications, which we shall call IBS corrections. In practice, $\tilde{\psi}$'s or the matrix elements of H are to be expanded in power series of q and truncated at some order, which we designate as N_{kp}. By tabulating in advance the Taylor-expansion coefficients of the matrix elements at the reference $\mathbf{k}$, we can perform $\mathbf{k}\cdot\mathbf{p}$-like calculations. This type of solution to the IBS problem was first proposed by the community of the empirical tight-binding method.[18,19] It is to start from the usual secular equation at $\mathbf{k}+\mathbf{q}$ and Taylor expand the Hamiltonian matrix elements $\mathcal{H}_{\zeta\zeta'}(\mathbf{k}+\mathbf{q})$, from which they find effective $\mathbf{k}\cdot\mathbf{p}$ corrections to the energies. Our discussion above might be regarded as a reformulation of their method by clarifying the basis set for χ.

The aim of this paper is to derive an LAPW $\mathbf{k}\cdot\mathbf{p}$ formula that explicitly contains the IBS corrections and enables efficient $\mathbf{k}\cdot\mathbf{p}$ calculations within the FLAPW methodology. We examine the property of LAPW functions $\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r})$ when $\mathbf{k}$ is moved to $\mathbf{k}+\mathbf{q}$. The key factor is the $\mathbf{k}$ dependency of the augmentation functions, from which the IBS corrections are introduced. It is found that this $\mathbf{k}$ dependency can be described by a simple transformation matrix U. We formulate the IBS corrections in terms of U, which are easy to calculate in a manner similar to the usual FLAPW procedure. Details of the FLAPW method in the muffin-tin (MT) sphere region, such as the use of the scalar-relativistic theory of Koelling and Harmon[20] and the inclusion of spin-orbit coupling, are to be reflected automatically in our LAPW $\mathbf{k}\cdot\mathbf{p}$ formula. The overall accuracy is controlled by the truncation order N_{kp} of the q expansion.

Related to the present topic, we should mention two major previous works. One is by Krasovskii and Schattke,[5–10] which has close connection to the present method. They have been working to bring in the $\mathbf{k}\cdot\mathbf{p}$ approach into the FLAPW scheme. They noticed that the LAPW basis set does not have the property (7). Rather than deriving the IBS corrections, they increased variational degrees of freedom by adding localized functions inside the MT sphere region and constructed the extended LAPW (ELAPW) basis set. This enables $\mathbf{k}\cdot\mathbf{p}$ calculations with the standard $\mathbf{k}\cdot\mathbf{p}$ formula to the satisfactory accuracy at the expense of increased computational efforts due to the enlarged size of the basis set. They modified the treatment of relativity[7] since the scalar-relativistic theory by Koelling and Harmon,[20] which is widely used in FLAPW method, does not fit to their method. This method has been successfully used for a wide variety of applications. The other was done by Pickard and Payne.[4] They have derived a second-order $\mathbf{k}\cdot\mathbf{p}$ expression to be used for Vanderbilt's ultrasoft pseudopotentials. In this case, the IBS problem does not take place since the basis functions are plane waves while the use of a nonlocal potential and an overlap operator in the Kohn-Sham equation brought the complexity to their formula.

It should also be noted that the standard $\mathbf{k}\cdot\mathbf{p}$ formula has been used in the APW (Refs. 21–23) and LAPW calculations[12] by overlooking the IBS problem and without adding the extra variational degrees of freedom. This yields catastrophic results if applied to localized states as will be shown in Sec. III.

The rest of this paper is organized as follows. We introduce the formalism in Sec. II, test it by actual numerical calculations in Sec. III, and present our conclusions in Sec. IV. A discussion on the Hermiticity of Hamiltonian matrix and a derivation of the generalized perturbation theory are given in Appendixes A and B.

II. FORMALISM

A. Property of LAPW functions

The LAPW basis-function set $\{\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r})\}$ is one of the best suited basis sets to represent all-electron nodal wave functions. It is optimized to a given nucleus geometry through its atomic-position-dependent augmentation. It is also optimized to a given $\mathbf{k}$, at which we are to solve the single-electron problem, with the augmentation function depending on $\mathbf{k}$ in a nontrivial way. The former dependency is well known to yield the IBS corrections in the atomic force formula.[24] The latter gives rise to an LAPW-specific $\mathbf{k}\cdot\mathbf{p}$ formula.

In the LAPW approach, the space is partitioned into the nonoverlapping MT sphere region and the interstitial (I) region. In the I region, the LAPW function is just a plane-wave, $\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r})=\Omega^{-1/2}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$, where Ω is the unit-cell volume. Inside the tth MT sphere, it may be expressed by

$$\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{t}}\sum_{L} Y_L(\hat{\mathbf{r}}_t)[a_{tL}(\mathbf{k}+\mathbf{G})u_{tl}(r_t) + b_{tL}(\mathbf{k}+\mathbf{G})\dot{u}_{tl}(r_t)], \quad r_t \leq S_t,$$

where S_t and $\mathbf{t}$ are the MT radius and position of atom t, respectively, $\mathbf{r}_t=\mathbf{r}-\mathbf{t}$, and L is a combined index $L=(lm)$. The radial function u_l and its energy derivative $\dot{u}_l$ satisfy the equations $\mathcal{H}_{\mathrm{MT}}u_lY_L=\varepsilon_l u_l Y_L$ and $\mathcal{H}_{\mathrm{MT}}\dot{u}_lY_L=(u_l+\varepsilon_l\dot{u}_l)Y_L$ with $\mathcal{H}_{\mathrm{MT}}$ being the spherical part of $\mathcal{H}$. To simplify the notation we shall omit the atom index t of a, b, u, and $\dot{u}$ unless it brings ambiguity. Further, to have brief formulas, we introduce an index $\kappa(=1,2)$, and let (a_κ,u_κ) represent (a,u) and $(b,\dot{u})$, for $\kappa=1$ and $\kappa=2$, respectively. The LAPW function inside the tth sphere is rewritten as

$$\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{t}}\sum_{L\kappa} a_{L\kappa}(\mathbf{k}+\mathbf{G})\varphi_{L\kappa}(\mathbf{r}_t), \tag{9}$$

$$\varphi_{L\kappa}(\mathbf{r}) = u_{l\kappa}(r) Y_L(\hat{\mathbf{r}}). \tag{10}$$

Although the conventional definition of the matching coefficients $a_{L\kappa}$ includes the atomic Bloch phase factor $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{t}}$, we have separated it out for ease in analyzing the property of LAPW functions. These $a_{L\kappa}$'s are determined by imposing the continuity with the I expression on the MT sphere up to the first derivative in terms of $\mathbf{r}_t$. Rayleigh expansion of the I expression about the atom t reads

$$\phi_{\mathbf{G}}(\mathbf{k},\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{t}} \sum_L J_L(\mathbf{k}+\mathbf{G}, r_t) Y_L(\hat{\mathbf{r}}_t), \tag{11}$$

$$J_L(\mathbf{K},r) = 4\pi\Omega^{-1/2} i^l j_l(Kr) Y_L^*(\hat{\mathbf{K}}), \tag{12}$$

where j_l stands for the spherical Bessel function. Matching of the I and MT expressions is given by their radial parts of each L. This leads to at arbitrary $\mathbf{K}$

$$J_L(\mathbf{K},S) = \sum_\kappa a_{L\kappa}(\mathbf{K}) u_{l\kappa}(S), \tag{13a}$$

$$J_L'(\mathbf{K},S) = \sum_\kappa a_{L\kappa}(\mathbf{K}) u_{l\kappa}'(S), \tag{13b}$$

and the coefficients are found as

$$a_{L\kappa}(\mathbf{K}) = \frac{(-)^{\kappa+1}}{[\dot{u}_l, u_l]_S} [u_{l\bar{\kappa}}(r), J_L(\mathbf{K},r)]_S, \tag{14}$$

where the square brackets denote the Wronskian

$$[f(r), g(r)]_S = f(S) g'(S) - f'(S) g(S)$$

and we introduced an auxiliary index $\bar{\kappa}(=2,1)$, which represents the counterpart of $\kappa(=1,2)$.

Having the definition of LAPW function, we think about the basis functions for χ defined by Eq. (6). The property (7) is seen only in the I region. Therefore

$$\begin{aligned}\Phi_{\mathbf{G}}(\mathbf{k},\mathbf{q},\mathbf{r}) &= e^{-i\mathbf{q}\cdot\mathbf{r}} \phi_{\mathbf{G}}(\mathbf{k}+\mathbf{q},\mathbf{r}) \\ &= \begin{cases} \Omega^{-1/2} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ e^{-i\mathbf{q}\cdot\mathbf{r}_t} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{t}} \sum_{L\kappa} a_{L\kappa}(\mathbf{k}+\mathbf{q}+\mathbf{G}) \varphi_{L\kappa}(\mathbf{r}_t), & r_t \le S_t \end{cases}\end{aligned} \tag{15}$$

Note in the sphere expression that the atomic phase factor returns to that at $\mathbf{k}$. However, there is no way that $e^{-i\mathbf{q}\cdot\mathbf{r}_t} a_{L\kappa}(\mathbf{k}+\mathbf{q}+\mathbf{G})$ returns to $a_{L\kappa}(\mathbf{k}+\mathbf{G})$. Among the q-dependent factors $e^{-i\mathbf{q}\cdot\mathbf{r}_t}$ and $a_{L\kappa}$, we shall leave the former and Taylor expand only the latter in terms of q that needs the knowledge of $\mathbf{K}$ derivatives of $a_{L\kappa}(\mathbf{K})$. From Eq. (14), this can be attained once the $\mathbf{K}$ derivatives of $J_L(\mathbf{K},S)$ and $J_L'(\mathbf{K},S)$ are found. Consider an identity $e^{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot\mathbf{r}} e^{i\mathbf{K}\cdot\mathbf{r}}$, Rayleigh expand each plane wave except $e^{i\mathbf{q}\cdot\mathbf{r}}$, multiply Y_L^* from the left, and perform the angular integration. Then we have

$$J_L(\mathbf{q}+\mathbf{K},r) = \sum_{L'} J_{L'}(\mathbf{K},r) \int Y_L^*(\hat{\mathbf{r}}) e^{i\mathbf{q}\cdot\mathbf{r}} Y_{L'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}}.$$

By Taylor expanding $J(\mathbf{q}+\mathbf{K})$ and $e^{i\mathbf{q}\cdot\mathbf{r}}$, we equate each coefficient of first-order q moments. This yields a formula for the $\mathbf{K}$ derivative of J. With $\alpha = \{x, y, z\}$,

$$J_L^{(\alpha)}(\mathbf{K},r) \equiv \frac{\partial J_L(\mathbf{K},r)}{\partial K_\alpha} = ir \sum_{L'} \langle Y_L | \hat{\alpha} | Y_{L'} \rangle J_{L'}(\mathbf{K},r), \tag{16}$$

where the symbol $\hat{\alpha}$ on the right-hand side denotes $\hat{\mathbf{r}}_\alpha$. The point is that the procedure of taking $\mathbf{K}$ derivative of $J(\mathbf{K})$, which would be cumbersome, is now replaced by the procedure of summing up J's that have the same $\mathbf{K}$ argument, which is much easier to pursue. By combining Eqs. (14) and (16) and further by using Eq. (13), we have, for the $\mathbf{K}$ derivative of $a_{L\kappa}$,

$$a_{L\kappa}^{(\alpha)}(\mathbf{K}) \equiv \frac{\partial a_{L\kappa}(\mathbf{K})}{\partial K_\alpha} = \sum_{L'\kappa'} U_{L\kappa,L'\kappa'}^{(\alpha)} a_{L'\kappa'}(\mathbf{K}) \tag{17a}$$

with

$$U_{L\kappa,L'\kappa'}^{(\alpha)} = i \langle Y_L | \hat{\alpha} | Y_{L'} \rangle W_{l\kappa,l'\kappa'} \tag{17b}$$

and

$$\begin{aligned} W_{l\kappa,l'\kappa'} &= \frac{(-)^{\kappa+1}}{[\dot{u}_l, u_l]_S} [u_{l\bar{\kappa}}, r u_{l'\kappa'}]_S \\ &= \frac{1}{[\dot{u}_l, u_l]_S} \begin{pmatrix} [\dot{u}_l, r u_{l'}]_S & [\dot{u}_l, r \dot{u}_{l'}]_S \\ -[u_l, r u_{l'}]_S & -[u_l, r \dot{u}_{l'}]_S \end{pmatrix}. \end{aligned} \tag{17c}$$

It states that the $\mathbf{K}$ derivative of $a_{L\kappa}(\mathbf{K})$ is expressible by a linear combination of $a_{L'\kappa'}(\mathbf{K})$'s with $l' = l \pm 1$. It is notable that the coefficients for this linear combination, $U^{(\alpha)}$, do not depend on $\mathbf{K}$. They are determined solely from Gaunt's coefficients $\langle Y_L | \hat{\alpha} | Y_{L'} \rangle$ and the matrix W, whose elements are made of the values of the radial functions at $r = S$. In the definition of W [Eq. (17c)] its κ dependence is presented in matrix form. For instance, the element with $\kappa = \kappa' = 1$ is calculated as

$$[\dot{u}_l, r u_{l'}]_S = \dot{u}_l(S) u_{l'}(S) + S [\dot{u}_l, u_{l'}]_S.$$

Using Eq. (17), we can express the Taylor expansion of $a(\mathbf{q}+\mathbf{K})$ as

$$\begin{aligned} a_\xi(\mathbf{q}+\mathbf{K}) &= \left[1 + \mathbf{q}\cdot\nabla_{\mathbf{K}} + \frac{1}{2}(\mathbf{q}\cdot\nabla_{\mathbf{K}})^2 + \cdots \right] a_\xi(\mathbf{K}) \\ &= \sum_{\xi'} \left[\mathbf{1} + \mathbf{q}\cdot\mathbf{U} + \frac{1}{2}(\mathbf{q}\cdot\mathbf{U})^2 + \cdots \right]_{\xi\xi'} a_{\xi'}(\mathbf{K}) \\ &= \sum_{\xi'} [e^{\mathbf{q}\cdot\mathbf{U}}]_{\xi\xi'} a_{\xi'}(\mathbf{K}), \end{aligned} \tag{18}$$

where ξ is a combined index $\xi = (L\kappa)$, $\mathbf{1}$ is a unit matrix, and $\mathbf{q}\cdot\mathbf{U}$ is an abbreviation of $\Sigma_\alpha q_\alpha U^{(\alpha)}$. Provided that the augmentation inside the MT sphere is truncated at $l_{\max}$ and that we like to have the q expansion of $a_{L\kappa}$ to the order of N_{kp}, the Gaunt coefficient in U indicates that we may need to prepare

$a_{L\kappa}$ up to $l_{\max}+N_{kp}$ for the right-hand side of Eq. (18). The extra $a_{L\kappa}$'s ($l>l_{\max}$), which do not exist in usual calculations, are taking a role of storing the necessary $J_L(S)$ and $J_L'(S)$. In the present realization of the method, to ensure the full accuracy in the first- and second-order coefficients of the q expansion, we generate J_L and J_L' up to $l_{\max}+2$ and make the extra $a_{L\kappa}$'s from Eq. (14) with the values of $u_{l\kappa}(S)$ and $u_{l\kappa}'(S)$, which are arbitrary, set up as those at $l_{\max}$. Thus we construct $U^{(\alpha)}$ in the l space of $(l_{\max}+2,\ l_{\max}+2)$.

We return to Eq. (15) and convert it into the form of Eq. (8). Utilizing Eq. (18) and redefining the zeroth-order matching coefficients, which now include the atomic phase factor

$$A_\xi(\mathbf{k}+\mathbf{G}) \equiv e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{t}} a_\xi(\mathbf{k}+\mathbf{G}),$$

$$A_{\xi i}(\mathbf{k}) = \sum_{\mathbf{G}} A_\xi(\mathbf{k}+\mathbf{G}) Z_{\mathbf{G}i}(\mathbf{k}),$$

we have

$$\begin{aligned}\tilde{\psi}_{i\mathbf{k}}(\mathbf{q},\mathbf{r}) &= \sum_{\mathbf{G}} \Phi_{\mathbf{G}}(\mathbf{k},\mathbf{q},\mathbf{r}) Z_{\mathbf{G}i}(\mathbf{k}) \\ &= \begin{cases} \psi_{i\mathbf{k}}, & \mathbf{r} \in I \\ e^{-i\mathbf{q}\cdot\mathbf{r}_t}\sum_{\xi\xi'}\varphi_\xi(\mathbf{r}_t)[e^{\mathbf{q}\cdot\mathbf{U}}]_{\xi\xi'}A_{\xi' i}(\mathbf{k}), & r_t \le S_t. \end{cases}\end{aligned} \tag{19}$$

This $\tilde{\psi}_{i\mathbf{k}}$ forms the basis set of the present LAPW $\mathbf{k}\cdot\mathbf{p}$ method. It possesses $\mathbf{q}$ dependency in the MT region through the head factor $e^{-i\mathbf{q}\cdot\mathbf{r}_t}$ and the decomposition of the matching coefficients. At zeroth order in $\mathbf{q}$, $\tilde{\psi}_{i\mathbf{k}}$ coincides with $\psi_{i\mathbf{k}}$ throughout the entire space. At higher orders, $\tilde{\psi}_{i\mathbf{k}}$ is finite only in the MT region and it has zero value and zero slope on the MT sphere. For practical purpose, Eq. (19) may be approximated here by Taylor expanding the sphere expression in terms of $\mathbf{q}$. Rather than doing so, we proceed with the following strategy: for any operator $\hat{O}$ we first derive its rigorous matrix representation in terms of the exact $\tilde{\psi}$, $O_{ij}(\mathbf{q})=\langle\tilde{\psi}_{i\mathbf{k}}(\mathbf{q})|\hat{O}|\tilde{\psi}_{j\mathbf{k}}(\mathbf{q})\rangle$, and then we expand $O_{ij}(\mathbf{q})$ up to a given truncation order N_{kp}. In Sec. II B, we will deal with the most important operator: the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian H.

B. k·p Hamiltonian and its representation

We give here the explicit form of the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian $H=e^{-i\mathbf{q}\cdot\mathbf{r}}\mathcal{H}e^{i\mathbf{q}\cdot\mathbf{r}}$ and provide its matrix representation in terms of the basis functions $\tilde{\psi}_{i\mathbf{k}}$. In the I region, kinematics is usually treated nonrelativistically. Unless the effective potential is in nonlocal form, H in the I region is given by Eq. (2) with the nonrelativistic velocity operator

$$\mathbf{v} = -i\nabla/m. \tag{20}$$

In tth MT region, H is written as

$$H = e^{-i\mathbf{q}\cdot(\mathbf{r}_t+\mathbf{t})}\mathcal{H}e^{i\mathbf{q}\cdot(\mathbf{r}_t+\mathbf{t})} = e^{-i\mathbf{q}\cdot\mathbf{r}_t}\mathcal{H}e^{i\mathbf{q}\cdot\mathbf{r}_t}, \quad r_t \le S_t. \tag{21}$$

We cannot proceed further from the above if the scalar-relativistic theory of Koelling and Harmon is employed in $\mathcal{H}$. Their kinetic-energy operator $\hat{T}_\mathrm{S}$ does not have an explicit form except in acting on u or $\dot{u}$. We cannot valuate $e^{-i\mathbf{q}\cdot\mathbf{r}_t}\hat{T}_\mathrm{S}e^{i\mathbf{q}\cdot\mathbf{r}_t}$ nor the commutator $[\mathbf{r}_t,\hat{T}_\mathrm{S}]$ as was discussed by Krasovskii and Schattke and this is the reason why they had to give up the use of $\hat{T}_\mathrm{S}$. In the present method, however, this is not problematic at all. In constructing secular equation for χ, the factors on both sides of $\mathcal{H}$ are canceled out with the head factor $e^{-i\mathbf{q}\cdot\mathbf{r}_t}$ in our basis function $\tilde{\psi}$. Thus we leave Eq. (21) as it is.

By inserting $\chi=\Sigma_j\tilde{\psi}_{j\mathbf{k}}C_j$ into the equation $H\chi=E\chi$, we have a secular equation $\Sigma_j[H_{ij}-E(\mathbf{k}+\mathbf{q})S_{ij}]C_j=0$. Although the zeroth-order wave functions $\{\psi_{i\mathbf{k}}\}$ are orthonormalized, $\{\tilde{\psi}_{i\mathbf{k}}\}$ are not due to the $\mathbf{q}$-dependent terms in the MT region. The eigenvalue problem is generalized. The contribution from the I region to H_{ij} and S_{ij} is

$$\begin{aligned}\langle\tilde{\psi}_{i\mathbf{k}}|H|\tilde{\psi}_{j\mathbf{k}}\rangle_I = {}& E_i(\mathbf{k})\delta_{ij} + \mathbf{q}\cdot\mathbf{v}_{Iij} - \langle\psi_{i\mathbf{k}}|\mathcal{H}|\psi_{j\mathbf{k}}\rangle_{\mathrm{MT}} \\ &+ \frac{q^2}{2m}(\delta_{ij} - \langle\psi_{i\mathbf{k}}|\psi_{j\mathbf{k}}\rangle_{\mathrm{MT}}),\end{aligned}$$

$$\langle\tilde{\psi}_{i\mathbf{k}}|\tilde{\psi}_{j\mathbf{k}}\rangle_I = \delta_{ij} - \langle\psi_{i\mathbf{k}}|\psi_{j\mathbf{k}}\rangle_{\mathrm{MT}}$$

with

$$\mathbf{v}_{Iij} = \langle\psi_{i\mathbf{k}}|\mathbf{v}|\psi_{j\mathbf{k}}\rangle_I. \tag{22}$$

The matrix element (22) is easy to calculate by taking analytical derivative of the plane-wave representation of $\psi_{i\mathbf{k}}$ and by using the step function and fast Fourier transforms (FFT). The sphere subtraction terms are calculated by the usual FLAPW procedure. Construct $h^{(0)}$ and $o^{(0)}$ for each atom, which is an eigenstate-independent small matrix of $\mathcal{H}$ and overlap matrix in terms of the atomic basis φ_ξ, respectively, as

$$h^{(0)}_{L\kappa,L'\kappa'} = \langle L\kappa|\mathcal{H}|L'\kappa'\rangle_t, \tag{23a}$$

$$o^{(0)}_{L\kappa,L'\kappa'} = \langle L\kappa|L'\kappa'\rangle_t = \delta_{LL'}\delta_{\kappa\kappa'}\langle u_{l\kappa}|u_{l\kappa}\rangle. \tag{23b}$$

This $o^{(0)}$ in the $(L\kappa)$ space is a diagonal matrix since $\langle u_l|\dot{u}_l\rangle=0$. Refer to Appendix A to have the actual formulas of Eq. (22) and the $\mathcal{H}_{\mathrm{MT}}$ part in Eq. (23a), in which the LAPW Hermiticity problem is circumvented. Having $h^{(0)}$ and $o^{(0)}$, we calculate

$$\langle\psi_{i\mathbf{k}}|\mathcal{H}|\psi_{j\mathbf{k}}\rangle_{\mathrm{MT}} = \sum_t\sum_{\xi\xi'} A^*_{\xi i}(\mathbf{k})h^{(0)}_{\xi\xi'}A_{\xi' j}(\mathbf{k}),$$

$$\langle\psi_{i\mathbf{k}}|\psi_{j\mathbf{k}}\rangle_{\mathrm{MT}} = \sum_t\sum_{\xi} A^*_{\xi i}(\mathbf{k})o^{(0)}_{\xi}A_{\xi j}(\mathbf{k}).$$

From Eqs. (19) and (21), the MT contribution to H_{ij} and S_{ij} is expressed similarly but with $h^{(0)}$ and $o^{(0)}$ being transformed as follows:

$$\langle\tilde{\psi}_{i\mathbf{k}}|H|\tilde{\psi}_{j\mathbf{k}}\rangle_{\mathrm{MT}} = \sum_t\sum_{\xi\xi'} A^*_{\xi i}(\mathbf{k})[h(\mathbf{q})]_{\xi\xi'}A_{\xi' j}(\mathbf{k}),$$

$$\langle \widetilde{\psi}_{i\mathbf{k}} | \widetilde{\psi}_{j\mathbf{k}} \rangle_{\mathrm{MT}} = \sum_t \sum_{\xi\xi'} A^*_{\xi i}(\mathbf{k})[o(\mathbf{q})]_{\xi\xi'} A_{\xi' j}(\mathbf{k})$$

with

$$h(\mathbf{q}) = (e^{\mathbf{q}\cdot\mathbf{U}})^\dagger h^{(0)} e^{\mathbf{q}\cdot\mathbf{U}}, \tag{24}$$

$$o(\mathbf{q}) = (e^{\mathbf{q}\cdot\mathbf{U}})^\dagger o^{(0)} e^{\mathbf{q}\cdot\mathbf{U}}. \tag{25}$$

Putting together the I and MT contributions, we obtain the rigorous expression for the $\mathbf{k}\cdot\mathbf{p}$ matrices H and S as follows:

$$\begin{aligned} H_{ij} = {} & E_i(\mathbf{k})\delta_{ij} + \mathbf{q}\cdot\mathbf{v}_{Iij} + \frac{q^2}{2m}(\delta_{ij} - \langle \psi_{i\mathbf{k}} | \psi_{j\mathbf{k}} \rangle_{\mathrm{MT}}) \\ & + \sum_t \sum_{\xi\xi'} A^*_{\xi i}(\mathbf{k})[h(\mathbf{q}) - h^{(0)}]_{\xi\xi'} A_{\xi' j}(\mathbf{k}), \end{aligned} \tag{26}$$

$$S_{ij} = \delta_{ij} + \sum_t \sum_{\xi\xi'} A^*_{\xi i}(\mathbf{k})[o(\mathbf{q}) - o^{(0)}]_{\xi\xi'} A_{\xi' j}(\mathbf{k}). \tag{27}$$

By Taylor expanding $h(\mathbf{q})$ and $o(\mathbf{q})$, we can have a useful expression for practical calculations, in which the $\mathbf{q}$ dependency is fully extracted out. If we write

$$h(\mathbf{q}) = h^{(0)} + \sum_\alpha q_\alpha h^{(\alpha)} + \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta h^{(\alpha\beta)} + \cdots,$$

the Taylor-expanded components are found as

$$h^{(\alpha)} = (U^{(\alpha)})^\dagger h^{(0)} + h^{(0)} U^{(\alpha)}, \tag{28a}$$

$$h^{(\alpha\beta)} = (U^{(\alpha)})^\dagger h^{(\beta)} + h^{(\beta)} U^{(\alpha)}, \tag{28b}$$

$$h^{(\alpha\beta\gamma)} = (U^{(\alpha)})^\dagger h^{(\beta\gamma)} + h^{(\beta\gamma)} U^{(\alpha)}. \tag{28c}$$

Namely, they can be constructed sequentially from the lowest order by multiplying $U^{(\alpha)}$ by the Taylor components of the preceding order. Now we rearrange H and S in the form of

$$H_{ij} = H_{ij}^{(0)} + \sum_\alpha q_\alpha H_{ij}^{(\alpha)} + \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta H_{ij}^{(\alpha\beta)} + \cdots, \tag{29}$$

$$S_{ij} = S_{ij}^{(0)} + \sum_\alpha q_\alpha S_{ij}^{(\alpha)} + \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta S_{ij}^{(\alpha\beta)} + \cdots. \tag{30}$$

Then for H we have

$$H_{ij}^{(0)} = E_i(\mathbf{k})\delta_{ij}, \tag{31a}$$

$$H_{ij}^{(\alpha)} = h_{ij}^{(\alpha)} + v_{Iij,\alpha}, \tag{31b}$$

$$H_{ij}^{(\alpha\beta)} = h_{ij}^{(\alpha\beta)} + \delta_{\alpha\beta}(\delta_{ij} - o_{ij}^{(0)})/m, \tag{31c}$$

$$H_{ij}^{(\alpha\beta\gamma)} = h_{ij}^{(\alpha\beta\gamma)} \tag{31d}$$

with a trivial definition of

$$h_{ij}^{(g)} = \sum_t \sum_{\xi\xi'} A^*_{\xi i}(\mathbf{k}) h^{(g)}_{\xi\xi'} A_{\xi' j}(\mathbf{k}), \quad g = \{0, \alpha, \alpha\beta, \alpha\beta\gamma, \ldots\}.$$

In $H^{(g)}$ higher than second order, only the MT contribution $h^{(g)}$ exists. The overlap components $S^{(g)}$ are all expressed by the MT term except for $g=0$. Defining the MT overlap matrix $o_{ij}^{(g)}$ in the same way as for $h_{ij}^{(g)}$, we have

$$S_{ij}^{(g)} = \begin{cases} \delta_{ij}, & g = 0, \\ o_{ij}^{(g)}, & g \neq 0. \end{cases} \tag{32}$$

The explicit formulas of our basis functions [Eq. (19)] and the $\mathbf{k}\cdot\mathbf{p}$ matrices (26) and (27) and their Taylor-expanded expressions [Eqs. (31) and (32)] constitute the central result of the present work. We refer to them as the LAPW $\mathbf{k}\cdot\mathbf{p}$ formula or simply the present $\mathbf{k}\cdot\mathbf{p}$ formula.

Actual procedures of the present LAPW $\mathbf{k}\cdot\mathbf{p}$ calculations are as follows. From Eq. (28), we preprocess the matrices $h^{(g)}$ and $o^{(g)}$ in the atomic $(L\kappa)$ basis up to the truncation order N_{kp}. Computational efforts for it can be reduced by making use of the sparseness of U. At a reference $\mathbf{k}$, we calculate and store the $\mathbf{k}\cdot\mathbf{p}$ matrices $H_{ij}^{(g)}$ and $S_{ij}^{(g)}$. We can use them for variational $\mathbf{k}\cdot\mathbf{p}$ calculations at arbitrary $\mathbf{k}+\mathbf{q}$ that involve the numerical diagonalization procedure. For very small q or for getting the electronic band gradients and curvatures, we can rely on the perturbation theory, whose prescription will be given in Sec. II C.

C. Second-order $\mathbf{k}\cdot\mathbf{p}$ perturbation

In dealing with the close vicinity of a given $\mathbf{k}$, we may rely on the second-order perturbation theory. We shall write the first- and second-order terms of H and S in the following way:

$$H^{[1]} = \sum_\alpha q_\alpha H^{(\alpha)}, \quad H^{[2]} = \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta H^{(\alpha\beta)},$$

$$S^{[1]} = \sum_\alpha q_\alpha S^{(\alpha)}, \quad S^{[2]} = \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta S^{(\alpha\beta)},$$

and consider them as a perturbation acting on the eigenstates at $\mathbf{k}$ and derive the first- and second-order changes in energy. One may suppose that this is an elementary task. However, we have the overlap matrix and the perturbation theory for the generalized eigenvalue problem is not widely discussed. Thus some explanation seems to be needed here.

Pickard and Payne[4] derived the generalized second-order perturbation formulas restricted to a nondegenerate band. According to that a state n at $\mathbf{k}$ would have the following energy shift:

$$E_n^{[1]} = H_{nn}^{[1]} - E_n^{(0)} S_{nn}^{[1]}, \tag{33a}$$

$$\begin{aligned} E_n^{[2]} = {} & H_{nn}^{[2]} - E_n^{(0)} S_{nn}^{[2]} - E_n^{[1]} S_{nn}^{[1]} \\ & + \sum_{j(\neq n)} \frac{(H_{nj}^{[1]} - E_n^{(0)} S_{nj}^{[1]})(H_{jn}^{[1]} - E_n^{(0)} S_{jn}^{[1]})}{E_n^{(0)} - E_j^{(0)}}, \end{aligned} \tag{33b}$$

where $E_n^{(0)}$ stands for $E_n(\mathbf{k})$.

We consider here a general case that the state $\psi_{n\mathbf{k}}$ falls in M-fold degenerate states with the same eigenvalue $E_M^{(0)}$. The eigenfunctions within the subspace M have arbitrariness since any unitary transformation within M is allowed. Among such infinite possibilities we have to find out one set, in which each state is continuously connected to one of the perturbed wave functions under the adiabatic switching on of the perturbation and thus can be named the "zeroth-order wave function." We shall write this transformation from the original "naive" eigenfunctions $\{\psi_{\mu\mathbf{k}}\}$ into the physically relevant zeroth-order wave functions as

$$\psi_{n\mathbf{k}} = \sum_{\mu \in M} \psi_{\mu\mathbf{k}} C^{(0)}_{\mu n}. \tag{34}$$

This $C^{(0)}$ may be deduced by the projection-operator technique with the compatibility relation of $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$.[1] It is noted that for a given $\mathbf{k}$, the $\mathbf{q}$ dependency of $C^{(0)}$ is only through its cosine $\hat{\mathbf{q}}$. $C^{(0)}$ can also be found by dealing numerically with the energy matrices given below. Refer to Appendix B for the detailed derivation.

At $\mathbf{k}$ we consider the following energy matrices within the subspace M, which can be regarded as a simple extension of Eq. (33):

$$\varepsilon^{[1]}_{\mu\mu'} = H^{[1]}_{\mu\mu'} - E^{(0)}_M S^{[1]}_{\mu\mu'} = \sum_\alpha q_\alpha \varepsilon^{(\alpha)}_{\mu\mu'}, \tag{35a}$$

$$\begin{aligned} \varepsilon^{[2]}_{\mu\mu'} &= H^{[2]}_{\mu\mu'} - E^{(0)}_M S^{[2]}_{\mu\mu'} - \sum_{\mu'' \in M} (S^{[1]}_{\mu\mu''}\varepsilon^{[1]}_{\mu''\mu'} + \varepsilon^{[1]}_{\mu\mu''}S^{[1]}_{\mu''\mu'})/2 \\ &\quad + \sum_{j \notin M} \frac{(H^{[1]}_{\mu j} - E^{(0)}_M S^{[1]}_{\mu j})(H^{[1]}_{j\mu'} - E^{(0)}_M S^{[1]}_{j\mu'})}{E^{(0)}_M - E^{(0)}_j} \\ &= \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta \varepsilon^{(\alpha\beta)}_{\mu\mu'} \end{aligned} \tag{35b}$$

and we calculate and store their Taylor coefficients $\varepsilon^{(\alpha)}_{\mu\mu'}$ and $\varepsilon^{(\alpha\beta)}_{\mu\mu'}$. Note that the bases of these matrices are labeled by the original eigenfunction μ and we need not know $C^{(0)}$ at this stage.

When $\mathbf{q}$ is specified, we construct $\varepsilon^{[1]}$ and $\varepsilon^{[2]}$ and proceed with the exact analogy with the usual degenerate perturbation theory.[19] We first diagonalize $\varepsilon^{[1]}$ and obtain the eigenvectors. If the degeneracy is fully lifted, these eigenvectors provide $C^{(0)}$. If not, we have to continue to the second-order process: we transform $\varepsilon^{[2]}$ via the eigenvectors of $\varepsilon^{[1]}$, pick up each submatrix where the degeneracy remains, and diagonalize it to have the final eigenvectors. By mapping these two processes onto a single $\mu \rightarrow n$ transformation, we obtain $C^{(0)}$. The first- and second-order changes in energy for the state n are expressed by

$$E^{[1]}_n = [C^{(0)\dagger}\varepsilon^{[1]}C^{(0)}]_{nn}, \tag{36a}$$

$$E^{[2]}_n = [C^{(0)\dagger}\varepsilon^{[2]}C^{(0)}]_{nn}. \tag{36b}$$

The electronic band energy gradient and curvature are defined for this split-off band and they are given by

$$\partial_\alpha E_n(\mathbf{k}) = [C^{(0)\dagger}\varepsilon^{(\alpha)}C^{(0)}]_{nn}, \tag{37a}$$

$$\partial_\alpha\partial_\beta E_n(\mathbf{k}) = [C^{(0)\dagger}(\varepsilon^{(\alpha\beta)} + \varepsilon^{(\beta\alpha)})C^{(0)}]_{nn}/2. \tag{37b}$$

D. Wave function

We shortly bring up the $\mathbf{k}\cdot\mathbf{p}$ wave function χ with envisioning its practical use. It is written as

$$\chi_m = \sum_i \widetilde{\psi}_{i\mathbf{k}}(\mathbf{q},\mathbf{r}) C_{im}(\mathbf{q}). \tag{38}$$

If we use the second-order $\mathbf{k}\cdot\mathbf{p}$ perturbation theory, C is obtained in the form

$$C_{im} = C^{(0)}_{im} + \sum_\alpha q_\alpha C^{(\alpha)}_{im} + \frac{1}{2}\sum_{\alpha\beta} q_\alpha q_\beta C^{(\alpha\beta)}_{im}. \tag{39}$$

Actual formulas of $C^{(g)}$ can be found from Appendix B. In addition to C, we ought to exercise care in the q dependency of $\widetilde{\psi}_{i\mathbf{k}}$. As a particular example, we consider the following quantity appeared in Eq. (5):

$$\begin{aligned} I_{nm\mathbf{k}}(\mathbf{q}) &= \langle \psi_{n\mathbf{k}} | e^{-i\mathbf{q}\cdot\mathbf{r}} | \psi_{m,\mathbf{k}+\mathbf{q}} \rangle = \langle \psi_{n\mathbf{k}} | \chi_m \rangle \\ &= \sum_i \langle \psi_{n\mathbf{k}} | \widetilde{\psi}_{i\mathbf{k}}(\mathbf{q}) \rangle C_{im}(\mathbf{q}). \end{aligned} \tag{40}$$

From Eq. (19), we can write

$$\langle \psi_{n\mathbf{k}} | \widetilde{\psi}_{i\mathbf{k}}(\mathbf{q}) \rangle = \delta_{ni} + \sum_t \sum_{\xi\xi'} A^*_{\xi n}(\mathbf{k}) [R(\mathbf{q}) e^{\mathbf{q}\cdot\mathbf{U}} - o^{(0)}]_{\xi\xi'} A_{\xi' i}(\mathbf{k}) \tag{41}$$

with a matrix R defined in the atomic basis

$$R_{L\kappa,L'\kappa'}(\mathbf{q}) = \langle \varphi_{L\kappa} | e^{-i\mathbf{q}\cdot\mathbf{r}_t} | \varphi_{L'\kappa'} \rangle_t. \tag{42}$$

The Taylor-expansion coefficients of $R(\mathbf{q})$ are

$$R^{(0)}_{L\kappa,L'\kappa'} = o^{(0)}_{L\kappa,L'\kappa'} = \delta_{LL'}\delta_{\kappa\kappa'} \langle u_{l\kappa} | u_{l\kappa} \rangle, \tag{43a}$$

$$R^{(\alpha)}_{L\kappa,L'\kappa'} = -i \langle L | \hat{\alpha} | L' \rangle \langle u_{l\kappa} | r | u_{l'\kappa'} \rangle, \tag{43b}$$

$$R^{(\alpha\beta)}_{L\kappa,L'\kappa'} = (-i)^2 \langle L | \hat{\alpha}\hat{\beta} | L' \rangle \langle u_{l\kappa} | r^2 | u_{l'\kappa'} \rangle. \tag{43c}$$

Hence, besides U, it is necessary to calculate $R(\mathbf{q})$ or $R^{(g)}$'s, the matrices of $\mathbf{r}$ moments. Taylor-expansion coefficients of Eq. (40) are to be expressed by those of R, $\exp(\mathbf{q}\cdot\mathbf{U})$, and C.

In calculating valence charge density, where $|\chi|^2$ is relevant, the head factor $e^{-i\mathbf{q}\cdot\mathbf{r}_t}$ in $\widetilde{\psi}_{i\mathbf{k}}$ is canceled and the q dependency of $|\chi|^2$ is determined by U and C.

III. TESTS OF THE LAPW $\mathbf{k}\cdot\mathbf{p}$ FORMULA

To demonstrate how our method works, we present actual calculations for Si and Cu. Usual density-functional self-consistent field (SCF) calculations were performed with scalar-relativistic FLAPW method. For exchange-correlation functional we employed the local density approximation. Energy cutoffs were 20 and 100 Ry for the LAPW basis functions and the star functions of the effective potential, respectively. Inside the MT spheres, the expansion in terms of spherical harmonics was truncated at $l_{\max}=8$ for the wave function, charge density, and effective potential. The MT radii were chosen as 1.15 Å. The BZ integration was per-

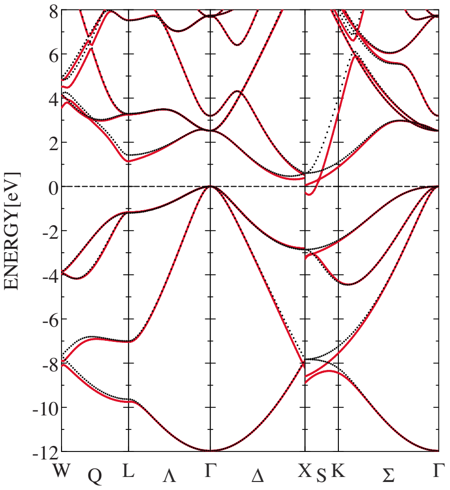

FIG. 1. (Color online) Energy-band dispersion of Si obtained by the variational $\mathbf{k}\cdot\mathbf{p}$ calculation (red lines) with taking the reference point at Γ. The $\mathbf{k}\cdot\mathbf{p}$ matrices were constructed to second order based on the present LAPW $\mathbf{k}\cdot\mathbf{p}$ formula. Black dots are the exact FLAPW bands. Valence-band top is set at 0 eV.

formed by using the improved tetrahedron method[25] with (8,8,8) mesh points for Si and (16,16,16) for Cu.

Under the converged SCF potential, at a particular $\mathbf{k}$ that we chose as a reference point of the $\mathbf{k}\cdot\mathbf{p}$ method, we calculated full eigenspectrum (E_i, ψ_i) and constructed the $\mathbf{k}\cdot\mathbf{p}$ matrices $H_{ij}^{(g)}$ and $S_{ij}^{(g)}$ with their size being equal to the number of LAPW basis functions at this $\mathbf{k}$. One may reduce this size in practical $\mathbf{k}\cdot\mathbf{p}$ calculations. Here, in order to monitor fundamental errors if exist, it was necessary not to deteriorate the degrees of variational freedom of χ.

Figure 1 shows the energy-band structure of Si obtained from the variational $\mathbf{k}\cdot\mathbf{p}$ calculation. There Γ was chosen as the reference point. The $\mathbf{k}\cdot\mathbf{p}$ matrices were constructed to second order based on the present LAPW $\mathbf{k}\cdot\mathbf{p}$ formula and were numerically diagonalized along high-symmetry lines. The agreement with the exact result is quite good except along the S line $(2\pi/a)(\eta,\eta,0)$ with $3/4 \leq \eta \leq 1$, which is located far from Γ. By increasing the truncation order of the IBS corrections, we can systematically improve the agreement. In the next place we fed the $\mathbf{k}\cdot\mathbf{p}$ matrices into the second-order perturbation method described in Sec. II C and Appendix B. Produced band energies along several high-symmetry lines from several reference points were compared with the exact ones and we calculated the root-mean-square error $|\Delta E|$. In Fig. 2 we plot $|\Delta E|/q^3$ as a function of q. If the band gradients or curvatures from the present $\mathbf{k}\cdot\mathbf{p}$ formula have a margin of error, $|\Delta E|/q^3$ would diverge in $q \to 0$. Such behavior is not seen in Fig. 2 and we conclude that our formula is valid. It might be interesting to see the consequence of using the standard $\mathbf{k}\cdot\mathbf{p}$ formula [Eq. (4)]. We constructed the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian matrix based on Eq. (4) at several reference points and performed the second-order perturbative calculations. The resultant error was analyzed in Fig. 3. Note that we plot $|\Delta E|/q^2$ instead of $|\Delta E|/q^3$. The red and blue solid lines diverge in $\mathbf{q} \to 0$, which means that the gradients at X along Δ and the gradients at K along Σ contain some errors. Other plots reach nonzero values in $q \to 0$, indicating that the curvatures are neither accurate. In Tables I and II we list the values of the band gradients and curvatures at X obtained by the first- and second-order $\mathbf{k}\cdot\mathbf{p}$ perturbations and make a comparison between the present and standard $\mathbf{k}\cdot\mathbf{p}$ results. The error of the standard $\mathbf{k}\cdot\mathbf{p}$ results in the band gradient is very small and might be attributed to the inconsistency in the treatment of relativity. The exact FLAPW eigenvalues are generated scalar relativistically while the standard $\mathbf{k}\cdot\mathbf{p}$ formula assumes the nonrelativistic

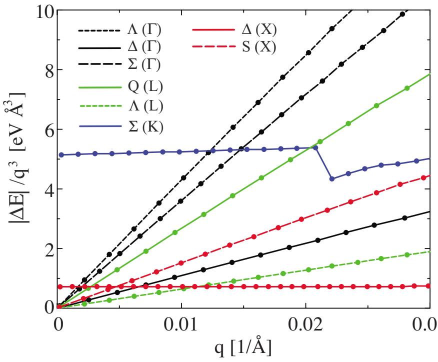

FIG. 2. (Color online) Analyzing the error in the band energies of Si calculated by the second-order perturbation theory with the $\mathbf{k}\cdot\mathbf{p}$ matrices constructed from the present LAPW $\mathbf{k}\cdot\mathbf{p}$ formula. The root-mean-square error of the band energies $|\Delta E|$ divided by q^3, where q is the distance in k space from the $\mathbf{k}\cdot\mathbf{p}$ reference point, is plotted as a function of q. Analysis is done for several high-symmetry lines and for several $\mathbf{k}\cdot\mathbf{p}$ reference points. $|\Delta E|$ is measured for the lowest seven bands when the reference point is taken at Γ or L while the lowest six bands at K and X.

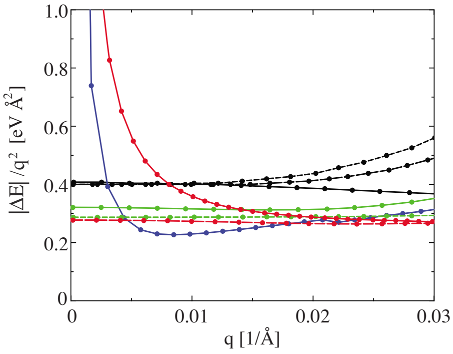

FIG. 3. (Color online) Same as Fig. 2 but with the $\mathbf{k}\cdot\mathbf{p}$ matrix constructed from the standard $\mathbf{k}\cdot\mathbf{p}$ formula given by Eq. (4). $|\Delta E|$ divided by q^2 instead of q^3 is plotted.

TABLE I. Electronic band gradients of Si X_1 bands along the Δ line obtained by the first-order $\mathbf{k}\cdot\mathbf{p}$ perturbation. Values from the present LAPW $\mathbf{k}\cdot\mathbf{p}$ formula, which are proved to be accurate from the analysis given in Fig. 2, are compared with those from the standard $\mathbf{k}\cdot\mathbf{p}$ formula of Eq. (3). Units are in eV Å.

Band	Valence X_1	Conduction X_1
Present $\mathbf{k}\cdot\mathbf{p}$	±6.6836	±1.5328
Standard $\mathbf{k}\cdot\mathbf{p}$	±6.6859	±1.5365

TABLE II. Longitudinal band curvatures of Si at X normalized to that of a free-electron band $1/m$(=3.81 eV Å^2) obtained by the second-order **k**·**p** perturbation. The curvatures by the present LAPW **k**·**p** formula, which are proved to be accurate from Fig. 2, are compared with those by the standard **k**·**p** formula.

Band	Valence X_1	X_4	Conduction X_1
Present **k**·**p**	0.50842	0.77433	1.1699
Standard **k**·**p**	0.57253	0.87291	1.1746

kinematics. However, the discrepancy in the curvatures is so large, more than 10% for the valence bands, and is attributed to the IBS problem.[19]

We carried out the same type of test calculation on Cu. It is known that the **k**·**p** method has difficulty in dealing with localized states such as semicore states d and f bands.[7,23] Results by the second-order perturbation calculation with the reference point Γ are shown in Fig. 4 and Table III. The results with the standard **k**·**p** formula completely collapse for the 3d bands as revealed in Fig. 4 in the middle and upper panels on the right-hand side. It even misses the sign of curvature for the Λ_3 band departing from Γ_{12} and that for the Δ_2' band (see also Table III). In sharp contrast to this, the present scheme produces excellent results (the left-hand side of Fig. 4). The error analysis given in Fig. 5 shows that the band curvatures from the present formula are free from errors. Among the reference points and dispersion lines tested in Fig. 5, only Σ bands departing from K have finite band gradients. Their values are listed in Table IV. Like in the case of Si, the standard **k**·**p** formula produces reasonable band gradients. The reason for this manifests itself in the perturbative formula [Eq. (33)]. The band gradient (or the first-order energy shift) can be obtained from the information of the relevant state only. The band curvature (or the second-order energy shift) needs the information of the complete wave functions of $\mathcal{H}$ and is apparently subjected to the IBS problem.[19]

For 3d bands, both the perturbative and variational calculations with the second-order **k**·**p** matrices are reasonably good only in the close vicinity of the reference point (typically within 0.3 Å^{-1}). Higher-order $H^{(g)}$ and $S^{(g)}$ are necessary to make the applicable range wider. By taking N_{kp}=16, it covers the entire BZ as shown in Fig. 6.

For the test purposes, we have used full-band **k**·**p** matrices. In practical use of the present method, one may like to reduce the size of the **k**·**p** matrices, N, while maintaining some desired accuracy. In order to have a rough idea on how much we can reduce, we calculated the Si curvatures at the valence-band top, Γ_{25}', with the second-order perturbation theory by changing N. The calculated values showed quick convergence. At N=15, where the unoccupied bands within the energy separation of 15 eV from the valence-band top were taken into account in addition to the occupied bands, the error of the calculated curvatures was already reduced to 1%. Although such convergence behavior should be different for each material and each band and thus one has to monitor it, including bands within the energy interval of about 20 eV from the band marked would provide reasonable results. In performing variational **k**·**p** calculations with single reference point, it seems that one needs to include more states. In the calculation of Fig. 6, we cut N down to one third of the full size. The band dispersion generated was not in good quality. To have a good description for the occupied bands throughout the BZ, we had to increase N to half of the full size.

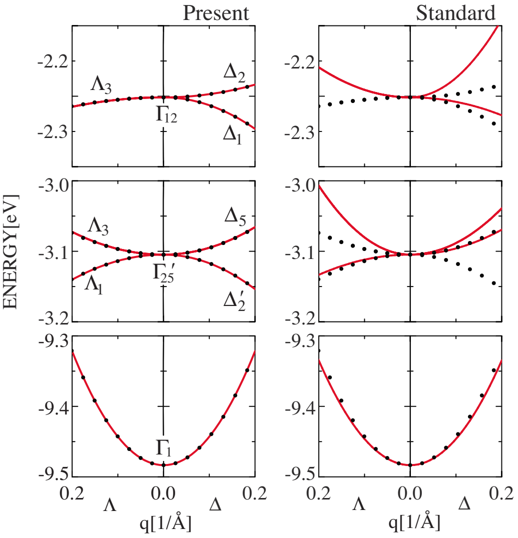

FIG. 4. (Color online) Energy-band dispersion of Cu by the second-order **k**·**p** perturbation (red lines) with taking the reference point at Γ. Plot is done along Λ and Δ lines in the vicinity of Γ and compared with the exact FLAPW bands (black dots). Energy is measured from the Fermi level. Left panel: using the **k**·**p** matrices constructed from the present LAPW **k**·**p** formula. Right panel: standard formula.

TABLE III. Longitudinal electronic band curvatures of Cu evaluated at Γ for bands appeared in Fig. 4. The curvatures are deduced by the second-order **k**·**p** perturbation and are normalized to that of a free-electron band $1/m$. The values by the present LAPW **k**·**p** formula, which are considered to be exact, are compared with those by the standard **k**·**p** formula.

		Γ_{25}'				Γ_{12}		
Band	Γ_1	Λ_1	Λ_3	Δ_2'	Δ_5	Λ_3	Δ_1	Δ_2
Present **k**·**p**	1.0597	−0.2332	0.2120	−0.3213	0.2560	−0.0875	−0.2933	0.1183
Standard **k**·**p**	0.9741	−0.1881	0.6406	0.2318	0.4306	0.2793	−0.1667	0.7254

TABLE IV. Electronic band gradients of Cu evaluated at K for the lowest five bands. Values obtained by the first-order perturbation with the present LAPW **k** · **p** formula are compared to those with the standard **k** · **p** formula. Units are in eV Å. Band numbering is in ascending order of energy.

Band	1	2	3	4	5
Present **k** · **p**	−1.4516	−0.9337	2.2431	1.0661	0.6387
Standard **k** · **p**	−1.4569	−0.9326	2.2436	1.0699	0.6400

IV. CONCLUSIONS

We derived the formula for the **k** derivatives of the sphere matching coefficients, from which we constructed the LAPW **k** · **p** formalism. The IBS corrections are shown to exist inside the MT region and are easily calculated by transforming the usual sphere matrices. The explicit derivation of the IBS correction terms allows us to perform efficient **k** · **p** calculations without adding extra variational degrees of freedom to the basis-function set. We demonstrated that our formula delivers the exact electronic band gradients and curvatures. Variational **k** · **p** calculations with a single reference point are in principle possible by taking the q-truncation order sufficiently high. We are going to employ the present scheme to evaluate the long-wavelength limit of the ingredients in the GW self-energy.

ACKNOWLEDGMENTS

The authors thank C. Friedrich, A. Schindlmayr, and S. Blügel, who motivated us to incorporate the **k** · **p** method in the FLAPW-GW calculations. This work has been supported in part by a Grant-in-Aid for Scientific Research in Priority Area "Development of New Quantum Simulators and Quantum Design" and a Grant-in-Aid for Young Scientists of the Ministry of Education, Culture, Sports, Science and Technology, Japan. The computation in this work has been partly performed using the facilities of the Supercomputer Center, Institute for Solid State Physics, University of Tokyo and Information Media Center, Hiroshima University.

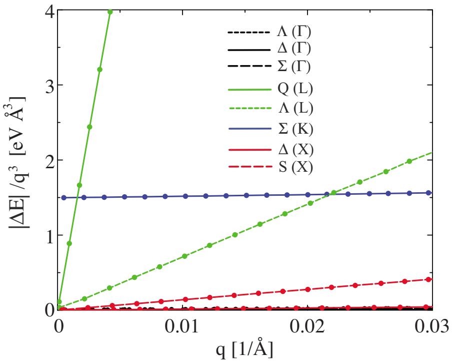

FIG. 5. (Color online) Analyzing the error in the band energies of Cu calculated by the second-order perturbation with using the **k** · **p** matrices constructed from the present **k** · **p** formula. The root-mean-square error of the band energies $|\Delta E|$ divided by q^3 is plotted. $|\Delta E|$ is measured for the lowest six bands around Γ and L while the lowest five bands around K and X.

APPENDIX A: HERMITICITY OF THE k · p MATRIX

In the LAPW method, it is known that the formula of the Hamiltonian matrix elements is not explicitly Hermitian if it is derived straightforwardly. This is due to the kinetic-energy part T and the finite l truncation in the sphere augmentation function. Popular solutions to this would be (i) to use the expression given by Koelling and Arbman,[26] which is made explicitly Hermitian by applying the technique of spherical Bessel function summation,[27] or (ii) to simply enforce the Hermiticity[28] by taking the Hermite conjugate of the straightforward expressions: $T_{ij} \Leftarrow (T_{ij} + T_{ji}^*)/2$.

Corresponding to this issue in the ordinary LAPW calculations, our first-order **k** · **p** Hamiltonian matrix $H^{(\alpha)}$ reveals the same problem and is subjected to the following modifications. If one uses the solution (i), the matrix element of the spherical part of the Hamiltonian in terms of the atomic basis should be

$$\langle L\kappa|\mathcal{H}_{\mathrm{MT}}|L'\kappa'\rangle = \delta_{LL'}\begin{pmatrix} \varepsilon_l + \varpi_l u_l u_l' & \varpi_l \dot{u}_l u_l' \\ \varpi_l \dot{u}_l u_l' & \varepsilon_l N_l + \varpi_l \dot{u}_l \dot{u}_l' \end{pmatrix}, \tag{A1}$$

which is Hermite in κ space. Here N_l is the norm of $\dot{u}_l$ and $\varpi_l = 1/[\dot{u}_l, u_l]_S$. For the solution (ii),

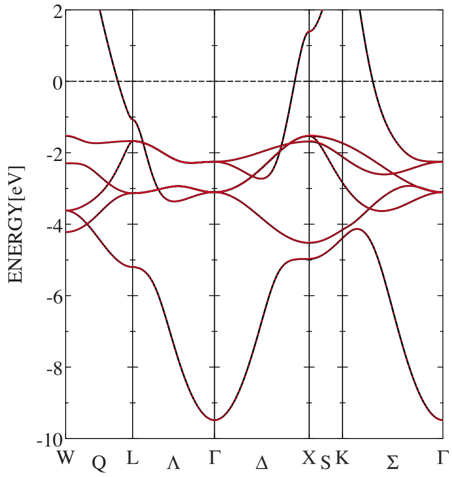

FIG. 6. (Color online) Energy-band dispersion of Cu obtained by the variational **k** · **p** calculation (red lines). The **k** · **p** matrices were constructed based on the present LAPW **k** · **p** formula with $N_{kp} = 16$. The reference point was set at Γ. Black dots are the exact FLAPW bands.

$$\langle L\kappa|\mathcal{H}_{\mathrm{MT}}|L'\kappa'\rangle = \delta_{LL'}\begin{pmatrix} \varepsilon_l & 1/2 \\ 1/2 & \varepsilon_l N_l \end{pmatrix}. \tag{A2}$$

In either case, the matrix of the interstitial velocity operator should be calculated by

$$\mathbf{v}_{Iij} = \frac{1}{2}\left(\left\langle \psi_i \left| \frac{-i\nabla}{m} \right| \psi_j \right\rangle_I + \mathrm{H.c.}\right). \tag{A3}$$

APPENDIX B: GENERALIZED PERTURBATION THEORY

We discuss a generalized perturbation theory and derive formulas for perturbed wave functions and eigenenergies to second order in the perturbation strength. Notations are independent from those of the text. Suppose that we have solved the eigenproblem for an unperturbed system $H^{(0)}$ variationally,

$$\Phi_i^{(0)} = \sum_l \phi_l^{(0)} Z_{li}, \tag{B1}$$

$$\langle \Phi_i^{(0)}|H^{(0)}|\Phi_j^{(0)}\rangle \equiv H_{ij}^{(0)} = E_i^{(0)}\delta_{ij}, \tag{B2}$$

$$\langle \Phi_i^{(0)}|\Phi_j^{(0)}\rangle \equiv S_{ij}^{(0)} = \delta_{ij}. \tag{B3}$$

Usually, the perturbed wave functions are expressed by means of a liner combination of $\Phi^{(0)}$. Such an approach implicitly assumes that the variational basis-function set $\{\phi^{(0)}\}$ remains unchanged against the applied perturbation. We consider a general case that the basis functions do change their form by the perturbation, while we assume that we know their dependency in an explicit given form. We define the following to be used as an expansion basis set for the perturbed wave functions:

$$\begin{aligned}\Phi_i &= \sum_l (\phi_l^{(0)} + \lambda\phi_l^{(1)} + \lambda^2\phi_l^{(2)} + \cdots)Z_{li} \\ &= \Phi_i^{(0)} + \lambda\Phi_i^{(1)} + \lambda^2\Phi_i^{(2)} + \cdots .\end{aligned} \tag{B4}$$

λ is a real parameter and its power represents the perturbation order. This $\{\Phi\}$ is no longer orthonormal to each other,

$$\begin{aligned}S_{ij} \equiv \langle \Phi_i|\Phi_j\rangle &= \delta_{ij} + \lambda(\langle \Phi_i^{(1)}|\Phi_j^{(0)}\rangle + \langle \Phi_i^{(0)}|\Phi_j^{(1)}\rangle) \\ &\quad + \lambda^2(\langle \Phi_i^{(2)}|\Phi_j^{(0)}\rangle + \langle \Phi_i^{(1)}|\Phi_j^{(1)}\rangle + \langle \Phi_i^{(0)}|\Phi_j^{(2)}\rangle) \\ &= S_{ij}^{(0)} + \lambda S_{ij}^{(1)} + \lambda^2 S_{ij}^{(2)} + \cdots .\end{aligned} \tag{B5}$$

Evaluation of the Hamiltonian matrix element would be more complicated since we have both the change in the Hamiltonian itself and the change in the basis $\{\Phi\}$. Nevertheless we can write it in the form

$$H_{ij} \equiv \langle \Phi_i|H|\Phi_j\rangle = H_{ij}^{(0)} + \lambda H_{ij}^{(1)} + \lambda^2 H_{ij}^{(2)} + \cdots . \tag{B6}$$

In order to comprehend general cases, we are going to deal with M-fold degenerate states in the unperturbed system with the eigenvalue $E_M^{(0)}$. There exists an indeterminacy in the unperturbed eigenfunctions $\{\Phi_\mu^{(0)}\}$ $(\mu \in M)$ in the sense that any unitary transformation within the subspace M can be taken. The important task is, with the exact analogy to the usual degenerate perturbation theory with $S_{ij} = \delta_{ij}$, to find a unitary matrix $C_{\mu m}^{(0)}$, which transforms the original naive eigenfunctions $\{\Phi_\mu^{(0)}\}$ into the zeroth-order wave functions $\{\Phi_m^{(0)}\}$ that bear physical relevance to the perturbed wave functions $\{\Psi_m\}$ in the way that each $\Phi_m^{(0)}$ is continuously connected to Ψ_m in the limit of $\lambda \to 0$. We write

$$\Phi_m^{(0)} = \sum_{\mu \in M} \Phi_\mu^{(0)} C_{\mu m}^{(0)}. \tag{B7}$$

Since the derivation of formulas goes at length, we think that it is better to write the final results here in order to provide in which direction we will go. The first- and second-order changes in energy for a state m are given by

$$E_m^{(1)} = [C^{(0)\dagger}\varepsilon^{(1)}C^{(0)}]_{mm}, \quad E_m^{(2)} = [C^{(0)\dagger}\varepsilon^{(2)}C^{(0)}]_{mm} \tag{B8}$$

with

$$\varepsilon_{\mu\mu'}^{(1)} = H_{\mu\mu'}^{(1)} - E_M^{(0)} S_{\mu\mu'}^{(1)}, \tag{B9}$$

$$\begin{aligned}\varepsilon_{\mu\mu'}^{(2)} &= H_{\mu\mu'}^{(2)} - E_M^{(0)} S_{\mu\mu'}^{(2)} - \sum_{\mu'' \in M} (S_{\mu\mu''}^{(1)}\varepsilon_{\mu''\mu'}^{(1)} + \varepsilon_{\mu\mu''}^{(1)} S_{\mu''\mu'}^{(1)})/2 \\ &\quad + \sum_{j \notin M} \frac{(H_{\mu j}^{(1)} - E_M^{(0)} S_{\mu j}^{(1)})(H_{j\mu'}^{(1)} - E_M^{(0)} S_{j\mu'}^{(1)})}{E_M^{(0)} - E_j^{(0)}}.\end{aligned} \tag{B10}$$

These matrices $\varepsilon^{(1)}$ and $\varepsilon^{(2)}$ are defined in the subspace M with the original states μ and thus can be calculated in advance without knowing $C^{(0)}$. The perturbed wave function can also be written by separating out $C^{(0)}$ in the following way:

$$\Psi_m = \sum_{\mu \in M}\left[\sum_i^{\mathrm{all}} \Phi_i(\delta_{i\mu} + \lambda c_{i\mu}^{(1)} + \lambda^2 c_{i\mu}^{(2)} + \cdots)\right] C_{\mu m}^{(0)}. \tag{B11}$$

In the square brackets all are labeled by the original states. When the summation i runs over the degenerate block M in concern, we must use the original μ representation of Φ. For $i \in M$, the coefficients $c^{(1)}$ and $c^{(2)}$ are given by

$$c_{i\mu}^{(1)} = -\frac{1}{2} S_{i\mu}^{(1)}, \tag{B12}$$

$$\begin{aligned}c_{i\mu}^{(2)} &= -\frac{1}{2} S_{i\mu}^{(2)} + \frac{3}{8}\sum_{\mu' \in M} S_{i\mu'}^{(1)} S_{\mu'\mu}^{(1)} - \frac{1}{2}\sum_{k \notin M} \frac{V_{ikM}^{(1)} V_{k\mu M}^{(1)}}{(\Delta_{Mk})^2} \\ &\quad - \frac{1}{2}\sum_{k \notin M} \frac{S_{ik}^{(1)} V_{k\mu M}^{(1)} + V_{ikM}^{(1)} S_{k\mu}^{(1)}}{\Delta_{Mk}}.\end{aligned} \tag{B13}$$

For $i \notin M$,

$$c_{i\mu}^{(1)} = \frac{V_{i\mu M}^{(1)}}{\Delta_{Mi}}, \tag{B14}$$

$$c_{i\mu}^{(2)} = \frac{V_{i\mu M}^{(2)}}{\Delta_{Mi}} - \sum_{\mu' \in M} \left[\frac{V_{i\mu' i}^{(1)} V_{\mu' \mu M}^{(1)}}{(\Delta_{Mi})^2} + \frac{V_{i\mu' M}^{(1)} S_{\mu' \mu}^{(1)}}{2\Delta_{Mi}} \right]. \tag{B15}$$

We have introduced the following abbreviations:

$$\Delta_{ij} = E_i^{(0)} - E_j^{(0)}, \tag{B16}$$

$$V_{ijn}^{(1)} = H_{ij}^{(1)} - E_n^{(0)} S_{ij}^{(1)}, \tag{B17}$$

$$V_{ijM}^{(2)} = H_{ij}^{(2)} - E_M^{(0)} S_{ij}^{(2)} + \sum_{k(\notin M)} V_{ikM}^{(1)} V_{kjM}^{(1)} / \Delta_{Mk}. \tag{B18}$$

We are going to derive the above formulas for $\varepsilon^{(1)}$, $\varepsilon^{(2)}$, $c^{(1)}$, and $c^{(2)}$, and also we will give the prescription for how to determine $C^{(0)}$. In this derivation it is convenient to write the perturbed wave function Ψ_m by separating the expansion sums inside and outside the subspace M as

$$\Psi_m = \sum_{\mu \in M} \Phi_\mu C_{\mu m} + \sum_{j \notin M} \Phi_j A_{jm}. \tag{B19}$$

Here $C^{(0)}$ is not separated out yet since at this point it is not clear whether such separation is possible. At the end we will see that Eq. (B19) can be transformed into the form of Eq. (B11). The equation $H\Psi_m = E_m \Psi_m$ becomes

$$\sum_\mu (H - E_m) \Phi_\mu C_{\mu m} + \sum_j (H - E_m) \Phi_j A_{jm} = 0. \tag{B20}$$

By multiplying Φ_i^* $(i \notin M)$ from the left, expanding each component in terms of power series of λ, and equating the coefficients of λ and λ^2, we obtain

$$A_{im}^{(1)} = \frac{1}{\Delta_{Mi}} \sum_\mu V_{i\mu M}^{(1)} C_{\mu m}^{(0)}, \tag{B21}$$

$$A_{im}^{(2)} = \frac{\sum_\mu (V_{i\mu M}^{(2)} - E_m^{(1)} V_{i\mu i}^{(1)} / \Delta_{Mi}) C_{\mu m}^{(0)} + \sum_\mu V_{i\mu M}^{(1)} C_{\mu m}^{(1)}}{\Delta_{Mi}} \tag{B22}$$

Next we pay attention to C's. Analogous to the usual perturbation theory, $C^{(1)}$ and $C^{(2)}$ are indeterminable but constrained by the orthonormality condition

$$\langle \Psi_m | \Psi_{m'} \rangle = \delta_{mm'}. \tag{B23}$$

At zeroth order this leads to $\Sigma_\mu C_{\mu m}^{(0)*} C_{\mu m'}^{(0)} = \delta_{mm'}$. Equating the coefficients of λ in Eq. (B23), we have

$$\sum_\mu (C_{\mu m}^{(1)*} C_{\mu m'}^{(0)} + C_{\mu m}^{(0)*} C_{\mu m'}^{(1)}) = -\sum_{\mu\mu'} C_{\mu m}^{(0)*} S_{\mu\mu'}^{(1)} C_{\mu' m'}^{(0)}.$$

Based on the convention, we shall take $\Sigma_\mu C_{\mu m}^{(0)*} C_{\mu m'}^{(1)}$ as a half of the right-hand side. This yields

$$C_{\mu m}^{(1)} = -\frac{1}{2} \sum_{\mu'} S_{\mu\mu'}^{(1)} C_{\mu' m}^{(0)}.$$

Equating the coefficients of λ^2 in Eq. (B23), we get

$$\sum_\mu (C_{\mu m}^{(2)*} C_{\mu m'}^{(0)} + C_{\mu m}^{(0)*} C_{\mu m'}^{(2)}) = 2 \sum_{\mu\mu'} C_{\mu m}^{(0)*} Q_M^{\mu\mu'} C_{\mu' m'}^{(0)}$$

with

$$Q_M^{\mu\mu'} = -\frac{1}{2} S_{\mu\mu'}^{(2)} + \frac{3}{8} \sum_{\mu''} S_{\mu\mu''}^{(1)} S_{\mu''\mu'}^{(1)} - \frac{1}{2} \sum_{k \notin M} \frac{V_{\mu k M}^{(1)} V_{k\mu' M}^{(1)}}{(\Delta_{Mk})^2} - \frac{1}{2} \sum_{k \notin M} \frac{S_{\mu k}^{(1)} V_{k\mu' M}^{(1)} + V_{\mu k M}^{(1)} S_{k\mu'}^{(1)}}{\Delta_{Mk}}.$$

With the same choice as for $C^{(1)}$, we set

$$C_{\mu m}^{(2)} = \sum_{\mu'} Q_M^{\mu\mu'} C_{\mu' m}^{(0)}.$$

One may recognize that $C^{(1)}$ and $C^{(2)}$ have been obtained in the form

$$C_{\mu m}^{(g)} = \sum_{\mu'} c_{\mu\mu'}^{(g)} C_{\mu' m}^{(0)}, \quad g = 1,2$$

with $c^{(1)}$ and $c^{(2)}$ defined by Eqs. (B14) and (B15), respectively.

In Eq. (B20), multiplying Φ_μ^* from the left, we obtain

$$O(\lambda): \sum_{\mu'} (\varepsilon_{\mu\mu'}^{(1)} - E_m^{(1)} \delta_{\mu\mu'}) C_{\mu' m}^{(0)} = 0, \tag{B24}$$

$$O(\lambda^2): \sum_{\mu'} (F_{\mu\mu' m} - E_m^{(2)} \delta_{\mu\mu'}) C_{\mu' m}^{(0)} = 0 \tag{B25}$$

with $\varepsilon^{(1)}$ defined by Eq. (B9) and

$$F_{\mu\mu' m} = V_{\mu\mu' M}^{(2)} - \left(S_{\mu\mu'}^{(1)} E_m^{(1)} + \sum_{\mu''} \varepsilon_{\mu\mu''}^{(1)} S_{\mu''\mu'}^{(1)} \right) / 2. \tag{B26}$$

The first-order equation (B24), which is a standard $M \times M$ secular equation, should be solved first. By diagonalizing the matrix $\varepsilon^{(1)}$, we can get the first-order change in energy,

$$E^{(1)} = U^\dagger \varepsilon^{(1)} U \tag{B27}$$

where U represents the eigenvectors of $\varepsilon^{(1)}$. If all the degeneracy is lifted by this process, we can set $C^{(0)} = U$ and Eq. (B25) is interpreted as an equation just to determine the second-order energy $E_m^{(2)} = (U^\dagger F_m U)_{mm}$. If the degeneracy remains, Eq. (B25) must be used to determine not only $E^{(2)}$ but also $C^{(0)}$ by further rotating U within each of the block where $E^{(1)}$'s are the same. This can be done automatically based on the following procedure. Calculate the matrix $\varepsilon^{(2)}$ defined by Eq. (B10) and transform it via U,

$$G_{mm'} = [U^{\dagger}\varepsilon^{(2)}U]_{mm'} \tag{B28}$$

One can prove that this G is connected to $F_{\mu\mu' m}$ given in Eq. (B26) by the relation $G_{mm'}=\Sigma U^{*}_{\mu m}F_{\mu\mu' m'}U_{\mu' m'}$ since $\varepsilon^{(1)}$ is diagonal in the m space. Modify this G so that its off-diagonal elements vanish unless they are within the same degenerate block

$$G'_{mm'} = \delta_{mm'}E^{(1)}_{m} + \begin{cases} G_{mm'}, & E^{(1)}_{m} = E^{(1)}_{m'} \\ 0, & E^{(1)}_{m} \neq E^{(1)}_{m'} \end{cases} \tag{B29}$$

The first term is added just to maintain the ordering of the eigenstates m determined by the first-order perturbation. By back transforming G', we make $G''_{\mu\mu'}=[UG'U^{\dagger}]_{\mu\mu'}$. By diagonalizing G'', we can have $C^{(0)}$ and $E^{(2)}$,

$$E^{(1)} + E^{(2)} = C^{(0)\dagger}G''C^{(0)}. \tag{B30}$$

This procedure is valid also for the case that the degeneracy is fully removed at the first-order perturbation.

In this way, $C^{(0)}$ can be deduced numerically by handling the matrices $\varepsilon^{(1)}$ and $\varepsilon^{(2)}$. The first- and second-order changes in energy for the state m can be written in terms of these matrices and $C^{(0)}$,

$$E^{(g)}_{m} = [C^{(0)\dagger}\varepsilon^{(g)}C^{(0)}]_{mm}, \quad g = 1,2$$

By construction $C^{(0)}$ always diagonalizes $\varepsilon^{(1)}$ but not $\varepsilon^{(2)}$. However, its off-diagonal elements if exist are negligible compared to the energy intervals in $E^{(1)}$'s. By using the expressions obtained for $E^{(1)}$ and $C^{(1)}$, we can rewrite the expansion coefficients (B21) and (B22) in the form of

$$A^{(g)}_{im} = \sum_{\mu} a^{(g)}_{i\mu}C^{(0)}_{\mu m}, \quad g = 1,2$$

with

$$a^{(1)}_{i\mu} = \frac{1}{\Delta_{Mi}}V^{(1)}_{i\mu M},$$

$$a^{(2)}_{i\mu} = \frac{V^{(2)}_{i\mu M}}{\Delta_{Mi}} - \sum_{\mu'}\left[\frac{V^{(1)}_{i\mu' i}V^{(1)}_{\mu'\mu M}}{(\Delta_{Mi})^{2}} + \frac{V^{(1)}_{i\mu' M}S^{(1)}_{\mu'\mu}}{2\Delta_{Mi}}\right].$$

One should recognize that we have proved all the formulas given at the beginning [Eqs. (B8)–(B15)].

We shall rewrite the perturbed wave function of Eq. (B11) by calling the function within the square brackets as Ψ_{μ},

$$\Psi_{m} = \sum_{\mu\in M}\Psi_{\mu}C^{(0)}_{\mu m}, \tag{B31}$$

$$\Psi_{\mu} = \sum_{i}^{\text{all}}\Phi_{i}[\delta_{i\mu} + c^{(1)}_{i\mu} + c^{(2)}_{i\mu} + O(\lambda^{3})]. \tag{B32}$$

There are some quantities for which the knowledge of $C^{(0)}$ is not required. As an example of such cases, we discuss the following density matrix:

$$\mathcal{D} = \sum_{n}\theta(E_F - E_n)|\Psi_n\rangle\langle\Psi_n|, \tag{B33}$$

where E_F is the Fermi level and $\theta(E_F-E_n)$ gives the occupancy of the perturbed state n. We assume that E_F is not changed by the applied perturbation.[29] This $\mathcal{D}$ has a contribution from the states discussed above that show M-fold degeneracy in the unperturbed system,

$$\mathcal{D}_M \equiv \sum_{m\in M}\theta(E_F - E_m)|\Psi_m\rangle\langle\Psi_m|. \tag{B34}$$

We want to have a formula of $\mathcal{D}_M$, in which the rotation matrix $C^{(0)}$ is not contained. The discussion in what follows can straightforwardly be applied to the calculation of charge density $\Sigma_n\theta(E_F-E_n)\Psi^{*}_{n}\Psi_{n}$.

For metallic systems, the occupation is subjected to change by the perturbation. Taylor expanding it, we have

$$\theta(E_F - E_m) = \theta_M - \theta'_M E^{(1)}_{m} - \theta'_M E^{(2)}_{m} + \frac{1}{2}\theta''_M[E^{(1)}_{m}]^{2} + O(\lambda^{3}) \tag{B35}$$

with the abbreviations defined by

$$\theta_M = \theta(E_F - E^{(0)}_{M}), \tag{B36a}$$

$$\theta'_M = \left.\frac{\partial\theta(x)}{\partial x}\right|_{x=E_F-E^{(0)}_{M}}, \tag{B36b}$$

$$\theta''_M = \left.\frac{\partial^{2}\theta(x)}{\partial x^{2}}\right|_{x=E_F-E^{(0)}_{M}}, \tag{B36c}$$

which are all zeroth-order quantities. The actual formulas of θ' and θ'' depend on the method to calculate θ and should be found easily. To demonstrate how Eq. (B34) is transformed into the original $\{\mu\}$ representation, it will be enough to show how we convert the term containing $[E^{(1)}_{m}]^{2}$. Making use of Eq. (B8) and the fact that $C^{(0)\dagger}\varepsilon^{(1)}C^{(0)}$ is diagonal,

$$\begin{aligned}\sum_{m}[E^{(1)}_{m}]^{2}|\Psi_m\rangle\langle\Psi_m| &= \sum_{mm'm''}[C^{(0)\dagger}\varepsilon^{(1)}C^{(0)}]_{mm''}[C^{(0)\dagger}\varepsilon^{(1)}C^{(0)}]_{m''m'}|\Psi_m\rangle\langle\Psi_{m'}| \\ &= \sum_{\mu\mu'\mu''}\varepsilon^{(1)}_{\mu\mu''}\varepsilon^{(1)}_{\mu''\mu'}|\Psi_{\mu}\rangle\langle\Psi_{\mu'}|.\end{aligned}$$

Note that the density matrix is no more diagonal in the μ space. Substituting Eq. (B32) for Ψ_{μ}, $\mathcal{D}_M$ is written in the form of $\mathcal{D}_M=\Sigma_{ij}|\Phi_i\rangle\langle\Phi_j|\mathcal{D}_M(ij)$. The coefficients are given by

$$\mathcal{D}^{(0)}_{M}(ij) = \theta_M\delta(\Delta_{Mi})\delta_{ij}, \tag{B37a}$$

$$\begin{aligned}\mathcal{D}^{(1)}_{M}(ij) = {}& \theta_M[\delta(\Delta_{Mj})c^{(1)}_{ij} + \delta(\Delta_{Mi})c^{(1)*}_{ji}] \\ & - \theta'_M\delta(\Delta_{Mi})\delta(\Delta_{Mj})\varepsilon^{(1)}_{ij},\end{aligned} \tag{B37b}$$

$$\mathcal{D}_M^{(2)}(ij) = \theta_M\left[\delta(\Delta_{Mj})c_{ij}^{(2)} + \delta(\Delta_{Mi})c_{ji}^{(2)*} + \sum_k \delta(\Delta_{Mk})c_{ik}^{(1)}c_{jk}^{(1)*}\right] + \frac{1}{2}\theta_M''\delta(\Delta_{Mi})\delta(\Delta_{Mj})\sum_k \delta(\Delta_{ik})\varepsilon_{ik}^{(1)}\varepsilon_{kj}^{(1)} - \theta_M'\left[\delta(\Delta_{Mj})\sum_k \delta(\Delta_{jk})c_{ik}^{(1)}\varepsilon_{kj}^{(1)} + \delta(\Delta_{Mi})\sum_k \delta(\Delta_{ik})\varepsilon_{ik}^{(1)}c_{jk}^{(1)*} + \delta(\Delta_{Mi})\delta(\Delta_{Mj})\varepsilon_{ij}^{(2)}\right]. \tag{B37c}$$

Summing up $\mathcal{D}_M$'s, the density matrix is found in the form of $\mathcal{D}=\Sigma|\Phi_i\rangle\langle\Phi_j|\mathcal{D}(ij)$ and

$$\mathcal{D}^{(0)}(ij) = \theta_i\delta_{ij}, \tag{B38a}$$

$$\mathcal{D}^{(1)}(ij) = \theta_j c_{ij}^{(1)} + \theta_i c_{ji}^{(1)*} - \theta_i'\delta(\Delta_{ij})\varepsilon_{ij}^{(1)}, \tag{B38b}$$

$$\mathcal{D}^{(2)}(ij) = \theta_j c_{ij}^{(2)} + \theta_i c_{ji}^{(2)*} + \sum_k \theta_k c_{ik}^{(1)}c_{jk}^{(1)*} - \theta_i'\delta(\Delta_{ij})\varepsilon_{ij}^{(2)} + \frac{1}{2}\theta_i''\delta(\Delta_{ij})\sum_k \delta(\Delta_{ik})\varepsilon_{ik}^{(1)}\varepsilon_{kj}^{(1)} - \theta_j'\sum_k \delta(\Delta_{jk})c_{ik}^{(1)}\varepsilon_{kj}^{(1)} - \theta_i'\sum_k \delta(\Delta_{ik})\varepsilon_{ik}^{(1)}c_{jk}^{(1)*}. \tag{B38c}$$

These coefficient matrices, $\mathcal{D}_M(ij)$ and $\mathcal{D}(ij)$, are Hermite. For insulating cases, we can set $\theta'=\theta''=0$.

---

[1] M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Dover, New York, 2001).

[2] M. Cardona and F. H. Pollak, Phys. Rev. **142**, 530 (1966).

[3] C. J. Pickard and M. C. Payne, Phys. Rev. B **59**, 4685 (1999).

[4] C. J. Pickard and M. C. Payne, Phys. Rev. B **62**, 4383 (2000).

[5] E. E. Krasovskii, A. N. Yaresko, and V. N. Antonov, J. Electron Spectrosc. Relat. Phenom. **68**, 157 (1994).

[6] E. E. Krasovskii and W. Schattke, Phys. Rev. B **60**, R16251 (1999).

[7] E. E. Krasovskii and W. Schattke, Phys. Rev. B **63**, 235112 (2001).

[8] E. E. Krasovskii and W. Schattke, Solid State Commun. **93**, 775 (1995).

[9] E. E. Krasovskii and W. Schattke, Phys. Rev. B **56**, 12874 (1997).

[10] E. E. Krasovskii and W. Schattke, Phys. Rev. Lett. **93**, 027601 (2004).

[11] N. Hamada, T. Imai, and H. Funashima, J. Phys.: Condens. Matter **19**, 365221 (2007).

[12] C. Persson and C. Ambrosch-Draxl, Comput. Phys. Commun. **177**, 280 (2007).

[13] M. Weinert, J. Math. Phys. **22**, 2433 (1981).

[14] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[15] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B **26**, 4571 (1982).

[16] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984).

[17] F. Aryasetiawan, in *Strong Coulomb Correlations in Electronic Structure Calculations, Beyond the Local Density Approximation*, edited by V. I. Anisimov (Gordon and Breach, New York, 2000).

[18] M. Graf and P. Vogl, Phys. Rev. B **51**, 4940 (1995).

[19] T. B. Boykin, Phys. Rev. B **52**, 16317 (1995).

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

[21] N. J. Parada and G. W. Pratt, Jr., Phys. Rev. Lett. **22**, 180 (1969).

[22] D. D. Buss and N. J. Parada, Phys. Rev. B **1**, 2692 (1970).

[23] T. J. Kuebbing, K. Schwarz, S. B. Trickey, and J. B. Conklin, Jr., Phys. Rev. Lett. **26**, 1251 (1971).

[24] R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).

[25] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).

[26] D. D. Koelling and G. O. Arbman, J. Phys. F: Met. Phys. **5**, 2041 (1975).

[27] T. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967).

[28] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994).

[29] In the case of using **k**·**p** perturbation theory, this is not an assumption and E_F stays the same.