Orbital Magnetism of Bloch Electrons I. General Formula

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We derive an exact formula of orbital susceptibility expressed in terms of Bloch wave functions, starting from the exact one-line formula by Fukuyama in terms of Green’s functions. The obtained formula contains four contributions: (1) Landau-Peierls susceptibility, (2) interband contribution, (3) Fermi surface contribution, and (4) contribution from occupied states. Except for the Landau-Peierls susceptibility, the other three contributions involve the crystal-momentum derivatives of Bloch wave functions. Physical meaning of each term is clarified. The present formula is simplified compared with those obtained previously by Hebborn et al. Based on the formula, it is seen first of all that diamagnetism from core electrons and Van Vleck susceptibility are the only contributions in the atomic limit. The band effects are then studied in terms of linear combination of atomic orbital treating overlap integrals between atomic orbitals as a perturbation and the itinerant feature of Bloch electrons in solids are clarified systematically for the first time.

1. Introduction

The effect of a magnetic field on electrons in crystals is fascinating and one of the basic problems of solid state physics. Although the fundamental principles are simple, our understanding of this problem has been far from complete due to the complicated matrix elements between different Bloch bands, called as the interband effects of a magnetic field. One of the typical problems of this interband effect is the orbital magnetism.

After the pioneering work of orbital magnetism by Landau for free electrons, the effect of periodic potential was considered by Peierls who obtained the Landau-Peierls formula for the orbital susceptibility,

\[ \chi_{LP} = \frac{e^2}{\hbar c^2} \sum_{\ell, k} \left\{ \frac{\partial^2 \epsilon_i}{\partial k_{2\ell}} \frac{\partial^2 \epsilon_i}{\partial k_{2\ell}} - \left( \frac{\partial^2 \epsilon_i}{\partial k_{\ell} \partial k_{\ell}} \right)^2 \right\} \frac{\partial f(\epsilon_i)}{\partial \epsilon}, \tag{1.1} \]

where \( f(\epsilon) \) is the Fermi distribution function and \( \epsilon_i(k) \) is the Bloch band energy. This Landau-Peierls formula is obtained by considering the effect of a magnetic field by a phase factor

\[ \exp\left( \frac{ie}{\hbar} \int_{r_i}^{r_f} A \cdot d\ell \right), \tag{1.2} \]

the so-called Peierls phase in the hopping integral of the single-band tight-binding model. Here \( A \) is a vector potential and \( e < 0 \) is the electron charge. Attaching the Peierls phase to the hopping integral corresponds to the modification of the energy dispersion, \( \epsilon_i(k) \rightarrow \epsilon_i(k - e A / \hbar) \), in the presence of a magnetic field.

Apparently \( \chi_{LP} \) does not include the deformation of the wave function resulting from the interband matrix elements of the magnetic field. Therefore it is believed that \( \chi_{LP} \) includes only the intraband effects. (It is not so simple as we show later in the present paper.) Furthermore, \( \chi_{LP} \) vanishes for insulators since it is proportional to \( \partial f(\epsilon_i)/\partial \epsilon \). On the other hand, in bismuth and its alloys, it has been known experimentally that the diamagnetism takes its maximum when the chemical potential is located in the band gap, i.e., in the insulating state. Apparently the Landau-Peierls formula fails to explain the large diamagnetism in bismuth and its alloys, which had been a mystery for a long time.

Stimulated by this experimental fact, there were various efforts to clarify the interband effects of magnetic field on orbital susceptibility. For example, several theoretical studies showed that the difference between the total susceptibility and \( \chi_{LP} \) is in the same order of the difference between \( \chi_{LP} \) and Landau susceptibility, even in the nearly-free electron cases. The large diamagnetism of bismuth was finally understood by Fukuyama and Kubo who calculated the magnetic susceptibility based on the Wigner representation. It was clarified that the interband effect of a magnetic field and the strong spin-orbit interaction are essential.

After these theoretical efforts, one of the present authors (hereafter referred as I) discovered an exact but very simple formula of orbital susceptibility as

\[ \chi = \frac{e^2}{\hbar^2 c^2} k_B T \sum_{\ell, n} \text{Tr} \gamma_{ii} \mathcal{G}(k, \epsilon_n), \tag{1.3} \]

where \( \mathcal{G} \) is the thermal Green’s function \( \mathcal{G}(k, \epsilon_n) \) in a matrix form whose \((ij)\) component is the matrix element between the \(i\)- and \(j\)-th band. \( \epsilon_n \) is Matsubara frequency and \( \gamma_{ii} \) represents the current operator in the \( \mu \)-direction divided by \( e/\hbar \). The spin multiplicity of 2 has been taken into account and...
Tr is to take trace over the band indices. Originally this formula is derived based on the Luttinger-Kohn representation.22 However, as discussed in I, this formula is valid in the usual Bloch representation because the two representations are related by a unitary transformation and the trace is invariant under the unitary transformation. This exact one-line formula (1.3) has been applied to practical models such as Weyl equation realized in graphene and an organic conductor \( \alpha \)-(BEDT-TTF)\(_2\)I\(_3\).23-25 and Dirac equation in bismuth.26-29 expressed in the Luttinger-Kohn-type Hamiltonians.

For the Bloch representation, the exact formula written in terms of Bloch wave functions had been derived by Heborn et al.11-13 (especially in Ref.13 which will be called as HLSS in the following) before the exact one-line formula (1.3) was derived. It was proved in I with the help of the formulation by Ichimaru17 that (1.3) is equivalent to the results by HLSS. However HLSS’s result is very complicated for the practical use. Because of this difficulty, orbital susceptibility for Bloch electrons in general has not been explored in detail. In particular, quantitative estimation of various contributions and their physical meaning have not been clarified.

In the single-band tight-binding model, there is a fundamental problem. When one restricts the band indices of the Green’s functions in (1.3) to a single band, one obtains a susceptibility defined as \( \chi_1 \) which is different from \( \chi_{\text{LP}} \).21,30-32 On the other hand, in the two-dimensional honeycomb lattice (or graphene)30-35 which is a typical two-band tight-binding model, it was shown that the orbital susceptibility based on the Peierls phase (eq. (1.2)) is not equal to either \( \chi_1 \) or \( \chi_{\text{LP}} \).30-32 From these results, it was claimed that the formula (1.3) cannot be applied to the tight-binding models on one hand,32 and that there are some “correction terms” to the exact formula (1.3) on the other hand,30,31 both of which are of course unjustified. As shown in the present paper, these confusions come from the misusage of the exact formula (1.3).

In this paper, starting from the exact one-line formula (1.3) and rewriting it in terms of Bloch wave functions, we derive a new and exact formula of the orbital susceptibility in a different way from those of HLSS. As shown later explicitly, the new formula is equivalent to the previous results. However, it is simpler than the previous results and contains only four contributions: (1) Landau-Peierls susceptibility, \( \chi_{\text{LP}} \), (2) interband contribution, \( \chi_{\text{inter}} \), (3) Fermi surface contribution, \( \chi_{\text{FS}} \), and (4) contribution from occupied states, \( \chi_{\text{occ}} \). Except for \( \chi_{\text{LP}} \), the other three contributions involve the crystal-momentum derivatives of Bloch wave functions. The physical meaning of each term is discussed. In the atomic limit, \( \chi_{\text{inter}} \) is equal to the Van Vleck susceptibility and \( \chi_{\text{occ}} \) is equal to the atomic diamagnetism (or contributions from core-level electrons). \( \chi_{\text{FS}} \) is a newly found contribution proportional to \( f'(\varepsilon_i) \). Then, we apply the present formula to the model of linear combination of atomic orbitals. We will show that the orbital susceptibility can be calculated systematically by studying the effects of overlap integrals between atomic orbitals as a perturbation from the atomic limit. In this method, itinerant features of Bloch electrons in solids are clarified for the first time. In most of researches, the atomic diamagnetism and Van Vleck contributions are treated separately from \( \chi_{\text{LP}} \). However, the present exact formula contains all the contributions on the same basis. Furthermore we find that \( \chi_{\text{occ}} \) contains the contributions not only from the core-level electrons (known as atomic diamagnetism), but also from the occupied states in the partially-filled band. This contribution has not been recognized before.

As mentioned above, when we restrict the band indices of the Green’s functions in (1.3) to a single band, we do not obtain \( \chi_{\text{LP}} \). In this paper, we show that the total of several contributions in (1.3) gives \( \chi_{\text{LP}} \). In these contributions, the \( f \)-sum rule which involves the summation over the other bands plays important roles. This means that the band indices of the Green’s functions in (1.3) should not be restricted to a single band when one consider a single-band tight-binding model.

While preparing this paper, we notice that Gao et al.36 studied orbital magnetism in terms of Berry phase using the wave-packet approximation. Their main interest is in the case with broken time-reversal symmetry37-40 which is not the subject of the present paper. However we can compare our results with theirs in the case where the time-reversal symmetry is not broken. We find that their results are almost equivalent with ours except for a term which has a different prefactor, possibly due to the wave-packet approximation they used.

In section 2 we derive a new formula for orbital susceptibility in Bloch representation. Our main results are summarized in eqs. (2.28)-(2.32) where four contributions are identified. In section 3 we apply the obtained formula to the model of linear combination of atomic orbitals. Section 4 is devoted to discussions and future problems.

2. Orbital susceptibility in terms of Bloch wave functions

2.1 Bloch wave functions and current operator

In order to explore the implications of eq. (1.3) in the Bloch representation, some essential ingredients are introduced. Thermal Green’s function for the \( \ell \)-th band in (1.3) is simply given by

\[
\gamma_\ell = \frac{1}{i\varepsilon_n - \varepsilon_\ell(k)},
\]

where \( \varepsilon_n \) is Matsubara frequency and \( \varepsilon_\ell(k) \) is the Bloch band energy. \( \ell \) denotes the band index and the wave vector \( k \) is within the first Brillouin zone. In order to obtain the explicit form of the current operator \( \gamma_\ell \) in (1.3), it is necessary to have information of Bloch wave functions in a periodic potential \( V(r) \). From the Bloch’s theorem, the eigenfunctions of the
Hamiltonian are given by
\[ e^{ik} u_{ik}(r), \] (2.2)
where \( u_{ik}(r) \) is a periodic function with the same period as \( V(r) \) and satisfies the equation
\[ H_k u_{ik}(r) = \varepsilon_k(k) u_{ik}(r), \] (2.3)
with
\[ H_k = \frac{\hbar^2 k^2}{2m} - \frac{ie^2}{m} k \cdot \nabla - \frac{\hbar^2}{2m} \nabla^2 + V(r). \] (2.4)
Here \( k \cdot \nabla \) indicates the inner product between \( k \) and \( \nabla \). For simplicity, we assume a centrosymmetric potential, \( V(-r) = V(r) \). In this case we can choose \( \bar{u}_{ik}(r) = u_{ik}(-r) \)\(^{13} \) where \( u_{ik}^{\dagger}(r) \) is the complex conjugate of \( u_{ik}(r) \).

For \( \gamma_{\mu} \), we calculate the current operator
\[ j(r) = -\frac{i e \hbar}{2m} \sum_{\alpha, \alpha} \left[ \bar{\psi}_{\alpha}(r) \nabla \psi_{\alpha}(r) - \nabla \bar{\psi}_{\alpha}(r) \psi_{\alpha}(r) \right]. \] (2.5)

Substituting the expansion
\[ \psi_{\alpha}(r) = \sum_{\ell, k} \bar{c}_{\ell \alpha} e^{\frac{i}{\hbar} k \cdot r} u_{ik}(r), \] (2.6)
into eq. (2.5) and making the Fourier transform, we obtain
\[ j_q = \frac{e}{\hbar} \sum_{\ell, \ell'} \left[ \int u_{ik}^{\dagger}(k - i \mathbf{v}) u_{ik} \, dr \right] \bar{c}_{\ell \alpha} \bar{c}_{\ell' \alpha}, \] (2.7)
where the definition of \( H_k \) in (2.4) has been used. Since \( \gamma_{\mu} \) in (1.3) is defined as a current operator divided by \( e/\hbar \), the matrix element of \( \gamma_{\mu} \) is given by (see Appendix A)
\[ \left[ \gamma_{\mu} \right]_{\ell \ell'} = \int u_{ik}^{\dagger} \frac{\partial H_k}{\partial k_{\mu}} u_{ik} \, dr = \frac{\partial \varepsilon_k(k)}{\partial k_{\mu}} \delta_{\ell \ell'} + p_{\ell \ell' \mu}, \] (2.8)
with \( p_{\ell \ell' \mu} \) being the off-diagonal matrix elements\(^{21,41} \)
\[ p_{\ell \ell' \mu} = (\varepsilon_{\ell'}(k) - \varepsilon_{\ell}(k)) \int u_{ik}^{\dagger} \frac{\partial u_{ik}}{\partial k_{\mu}} \, dr. \] (2.9)

Although the integral in (2.9) is sometimes called (interband) “Berry connection”, this kind of terms has been familiar for a long time in the literature.\(^{12,41,42} \) Note that the intraband “Berry connection” vanishes in the present Hamiltonian with \( V(r) = V(-r) \), as shown in (A-8).

Here we have used the Fourier integral theorem\(^^{22} \) for functions with the lattice periodicity. Originally, the range of the real-space integral on the right-hand side of eqs. (2.7) or (2.9) is within a unit cell,\(^^{22} \) i.e., \( \int_{V} \cdots \, dr \), where \( V \) and \( \Omega \) are the volumes of the whole system and of the unit cell, respectively. However, the range of integral can be extended to the whole system size \( V \) by using the periodicity of \( u_{ik}(r) \), i.e., \( \int_{\Omega} \cdots \, dr = \int_{V} \cdots \, dr \). In the following, the real-space integrals are defined in this way.

2.2 New formula for orbital susceptibility

Using the above matrix elements for \( \gamma_{\mu} \) and thermal Green’s functions, we calculate the formula (1.3) in the Bloch representation. Due to the existence of two terms in each \( \left[ \gamma_{\mu} \right]_{\ell \ell'} \), there appear sixteen terms. Classifying by the band indices of four Green’s functions in (1.3), we obtain
\[ \chi = \sum_{\alpha} \chi_{\alpha}, \] (2.10)
with
\[ \chi_1 = \frac{e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa'} \left( \frac{\partial \varepsilon_{\ell}(k)}{\partial k_{x}} \right)^2 \left( \frac{\partial \varepsilon_{\ell'}(k)}{\partial k_{y}} \right)^2 G_{\ell}^4, \] (2.11)
\[ \chi_2 = \frac{2 e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa', \ell, \ell'} \frac{\partial \varepsilon_{\ell}(k)}{\partial k_{x}} \frac{\partial \varepsilon_{\ell'}(k)}{\partial k_{y}} p_{\ell \ell' \ell' \ell} G_{\ell}^2 G_{\ell'}^2 G_{\ell'}^2 G_{\ell}, \] (2.12)
\[ \chi_3 = \frac{2 e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa', \ell, \ell'} \frac{\partial \varepsilon_{\ell}(k)}{\partial k_{x}} \frac{\partial \varepsilon_{\ell'}(k)}{\partial k_{y}} p_{\ell \ell' \ell' \ell} G_{\ell}^2 G_{\ell'}^2 G_{\ell'}^2 G_{\ell} + (x \leftrightarrow y), \] (2.13)
\[ \chi_4 = \frac{2 e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa', \ell, \ell'} \frac{\partial \varepsilon_{\ell}(k)}{\partial k_{x}} \frac{\partial \varepsilon_{\ell'}(k)}{\partial k_{y}} p_{\ell \ell' \ell' \ell} G_{\ell}^2 G_{\ell'}^2 G_{\ell'}^2 G_{\ell} + (x \leftrightarrow y), \] (2.14)
\[ \chi_5 = \frac{2 e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa', \ell, \ell'} \frac{\partial \varepsilon_{\ell}(k)}{\partial k_{x}} \frac{\partial \varepsilon_{\ell'}(k)}{\partial k_{y}} p_{\ell \ell' \ell' \ell} G_{\ell}^2 G_{\ell'}^2 G_{\ell'}^2 G_{\ell}, \] (2.15)
\[ \chi_6 = \frac{e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa', \ell, \ell'} p_{\ell \ell' \ell' \ell} G_{\ell}^2 G_{\ell'}^2 G_{\ell'}^2 G_{\ell} + (x \leftrightarrow y), \] (2.16)
\[ \chi_7 = \frac{e^2}{\hbar^2 c^2} k_B T \sum_{\kappa, \kappa', \ell, \ell'} p_{\ell \ell' \ell' \ell} G_{\ell}^2 G_{\ell'}^2 G_{\ell}^2 G_{\ell'}^2 G_{\ell}^2 G_{\ell}, \] (2.17)
where \( (x \leftrightarrow y) \) means a term obtained by replacing \( (x,y) \) to \( (y,x) \). Schematic representation of the contributions to \( \chi_1 \sim \chi_7 \) are shown in Fig. 1. The summation with prime \( \Sigma' \) means that all the band indices \( (\ell, \ell', \ell'' \text{ or } \ell, \ell', \ell'', \ell'''') \) are different with each other. In the following we write \( \varepsilon_{\ell} \) for \( \varepsilon_{\ell}(k) \) as far as it is not confusing.

The first contribution \( \chi_1 \) will be purely intraband since only the intraband matrix elements of \( \gamma_{\mu} \)’s are involved. After taking the summation over Matsubara frequency \( n \) and making
where \( f(\epsilon_l) \) is the Fermi distribution function. This \( \chi_1 \) is similar to the Landau-Peierls susceptibility \( \chi_{LP} \) in (1.1), but there are two differences. The numerical prefactor of the second term of \( \chi_1 \) is different from \( \chi_{LP} \) and the last term of \( \chi_1 \) does not appear in \( \chi_{LP} \). We will show shortly that \( \chi_{LP} \) is obtained by adding some other contributions from \( \chi_2, \chi_5 \) and \( \chi_6 \). As discussed in Section 1, this means that one should not pick up only \( \chi_1 \) in discussing the orbital susceptibility in a single-band model.

Next let us consider \( \chi_2 \). The summation over \( n \) in \( \chi_2 \) gives

\[
\chi_2 = \frac{2e^2}{\hbar^2 c^2} \sum_{\ell \neq \ell'} \sum_{k \ell' k'} \frac{\partial \epsilon_{\ell'} \partial \epsilon_{\ell}}{\partial k_x \partial k_y} \langle p_{\ell' x} p_{\ell y} \rangle
\]

\[
= \chi_{2;1} + \chi_{2;2} + \chi_{2;3},
\]

(2.19)

where the \( j \)-th term in \( \chi_n \) is denoted as \( \chi_{n;j} \). For \( \chi_{2;1} \), the summation over \( \ell' \) can be carried out and we obtain

\[
\chi_{2;1} = \frac{e^2}{2\hbar^2 c^2} \sum_{\ell \neq \ell'} f'(\epsilon_{\ell'}) \left\{ \frac{\partial^2 \epsilon_{\ell'}^2}{\partial k_x^2 \partial k_y^2} + \frac{\partial \epsilon_{\ell'} \partial^3 \epsilon_{\ell'}}{\partial k_x \partial k_y \partial k^2} \right\}
\]

\[+ (x \leftrightarrow y), \]

(2.20)

where we have used the \( f \)-sum rule\(^8,21\)

\[
\sum_{\ell' \neq \ell} \frac{P_{\ell' \mu} P_{\ell' \nu}}{\epsilon_{\ell'} - \epsilon_{\ell}} = 1 \left( \frac{\partial^2 \epsilon_{\ell}}{\partial k_x \partial k_y} - \frac{\hbar^2}{m} \delta_{\mu \nu} \right),
\]

(2.21)

with \( \mu = x, \nu = y \) and the integration by parts. This \( \ell' \)-summation is schematically shown in Fig. 1(b), in which the red square indicates the part of the diagram representing the \( f \)-sum rule.

The \( f \)-sum rule in eq. (2.21) results from the completeness property of \( u_{\ell k} \) [see eq. (A-13) in Appendix A]. (Various formulas used in the present paper are listed in Appendix A.) One may call the left-hand side of (2.21) as “interband” since it contains the off-diagonal matrix elements of the current operator \( P_{\ell' \mu} \). On the other hand, the right-hand side of (2.21) is expressed by a single-band property, \( \epsilon_{\ell'} \), and as a result, \( \chi_{2;1} \) looks like an “intraband” contribution. This indicates that the naive classification of “intraband” and “interband” does not apply.

For \( \chi_{2;2} \), the summation over \( \ell' \) can also be carried out, and we obtain

\[
\chi_{2;2} = \frac{-2e^2}{\hbar^2 c^2} \sum_{\ell \neq \ell'} f'(\epsilon_{\ell'}) \frac{\partial \epsilon_{\ell'} \partial \epsilon_{\ell}}{\partial k_x \partial k_y} \int \frac{\partial u_{\ell k}^*}{\partial k_x} \frac{\partial u_{\ell k}}{\partial k_y} d\mathbf{r} + (x \leftrightarrow y),
\]

(2.22)
where we have used

\[ \sum_{\ell' \neq \ell} \frac{P_{\ell' \ell} P_{\ell' \ell'}}{(\varepsilon_{\ell'} - \varepsilon_{\ell'})^2} = \int \frac{\partial u^\dagger_{\ell' k}}{\partial k_x} \frac{\partial u_{\ell k}}{\partial k_y} \, dr. \]  

(2.23)

(See (A-15).)

The last term of \( \chi' \) is given by

\[ \chi_{23} = -\frac{2e^2}{\hbar^2 c^2} \sum_{\ell \neq \ell', k} \frac{\partial \varepsilon_{\ell}}{\partial k_x} \frac{\partial \varepsilon_{\ell'}}{\partial k_y} \int \frac{\partial u^\dagger_{\ell' k}}{\partial k_x} \frac{\partial u_{\ell k}}{\partial k_y} \, dr \times \left( \int u^\dagger_{\ell' k} \frac{\partial u_{\ell k}}{\partial k_x} \, dr \right) + (x \leftrightarrow y). \]  

(2.24)

Here the \( \ell' \)-summation can not be carried out due to the presence of the denominator, \( 1 /(\varepsilon_{\ell} - \varepsilon_{\ell'}) \). This denominator is the same as what appears in the second-order perturbation of the interband process.

Features similar to \( \chi' \) are present in \( \chi_5 \) and \( \chi_6 \), as seen in Fig.1, where the excluded terms of \( \ell = \ell' \) in \( \chi_6 \) are supplemented by \( \chi_5 \), leading to the independent summations over \( \ell' \) and \( \ell'' \). As a result, using the \( f \)-sum rule, we obtain

\[ \chi_{51} + \chi_{61} = \frac{e^2}{6\hbar^2 c^2} \sum_{\ell, k} f'(\varepsilon_{\ell}) \left( \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x^2} \frac{\partial^2 \varepsilon_{\ell}}{\partial k_y^2} - \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x^{\dagger} \partial k_y^{\dagger}} \right)^2 + (x \leftrightarrow y). \]  

(2.25)

Detailed calculations are shown in Appendix B. [For the definitions of \( \chi_{51} \) and \( \chi_{61} \), see (B-10) and (B-11).]

Now, we can see that sum of \( \chi_1, \chi_{21} \) and \( \chi_{51} + \chi_{61} \) becomes

\[ \frac{e^2}{6\hbar^2 c^2} \sum_{\ell, k} f'(\varepsilon_{\ell}) \left\{ \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x^2} \frac{\partial^2 \varepsilon_{\ell}}{\partial k_y^2} - \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x^{\dagger} \partial k_y^{\dagger}} \right\}^2 - \frac{3}{2} \left\{ \frac{\partial \varepsilon_{\ell}}{\partial k_x} \frac{\partial^3 \varepsilon_{\ell}}{\partial k_x^2 \partial k_y} + \frac{\partial \varepsilon_{\ell}}{\partial k_y} \frac{\partial^3 \varepsilon_{\ell}}{\partial k_x \partial k_y^2} \right\}. \]  

(2.26)

It is seen that the first two terms give \( \chi_{LP} \), while the last term can be combined with other contributions after the transformation

\[ \frac{\partial^3 \varepsilon_{\ell}}{\partial k_x^2 \partial k_y} = 2 \int \frac{\partial u^\dagger_{\ell' k}}{\partial k_x} \frac{\partial H_{\ell' k}}{\partial k_x} \frac{\partial u_{\ell k}}{\partial k_y} \, dr \]  

\[ + 4 \int \frac{\partial u^\dagger_{\ell' k}}{\partial k_x} \left( \frac{\partial H_{\ell' k}}{\partial k_y} \frac{\partial u_{\ell k}}{\partial k_x} - \frac{\partial H_{\ell' k}}{\partial k_x} \frac{\partial u_{\ell k}}{\partial k_y} \right) \, dr, \]  

(2.27)

which is obtained by putting \( \mu \nu \tau \) as \( xy \) in eq. (A-18) in Appendix A.

Other terms in \( \chi_3, \chi_7 \) are calculated similarly, whose details are shown in Appendix B. We obtain the total susceptibility \( \chi \) as follows, which is exact as eq. (1.3).

\[ \chi = \chi_{LP} + \chi_{\text{inter}} + \chi_{FS} + \chi_{\text{occ}}. \]  

(2.28)
than
\[ \sum_{\ell \neq \ell', k} \frac{f(\varepsilon_i)}{\Delta E} \int \frac{\partial \mu}{\partial k_x} \left( \frac{\partial H_{k}}{\partial k_x} + \frac{\partial \varepsilon_i}{\partial k_x} \right) u_{\ell'k}^* dr \]
\[ - \int \frac{\partial \mu}{\partial k_y} \left( \frac{\partial H_{k}}{\partial k_y} + \frac{\partial \varepsilon_i}{\partial k_y} \right) u_{\ell'k}^* dr \right|^2. \] (2.33)

Then the \( \ell' \) summation can be carried out using the completeness property of \( u_{\ell'k}^* \). For example, a typical term can be written as
\[ \sum_{\ell, k} \frac{f(\varepsilon_i)}{\Delta E} \int \frac{\partial \mu}{\partial k_x} \left( \frac{\partial H_{k}}{\partial k_x} + \frac{\partial \varepsilon_i}{\partial k_x} \right) \frac{\partial \mu}{\partial k_x} u_{\ell'k}^* dr, \] (2.34)

which is arbitrarily small when \( \Delta E \) is large. This is in a sharp contrast with the \( f \)-sum rule (2.21) in which the right-hand side is finite when \( \Delta E \) is large.

We call the third contribution in (2.28) as \( \chi_{\text{FS}} \) (FS stands for “Fermi surface”), since it is proportional to \( f'(\varepsilon_i) \). This is a newly found contribution, but its physical meaning is not clear at present. However, the factor
\[ \frac{\partial H_{k}}{\partial k_k} + \frac{\partial \varepsilon_i}{\partial k_k}, \] in the integral in \( \chi_{\text{FS}} \) is common with \( \chi_{\text{inter}} \), indicating some close relationship between \( \chi_{\text{FS}} \) and \( \chi_{\text{inter}} \).

The fourth contribution, \( \chi_{\text{occ}} \), has contributions from the occupied states (“occ” stands for occupied states). As shown in the next section, \( \chi_{\text{occ}} \) is equal to the atomic diamagnetism in the atomic limit. Furthermore, we show that \( \chi_{\text{occ}} \) contains the contributions not only from the core-level electrons, but also from the occupied states in the partially-filled band. (See the right-hand side of Fig. 2.) This contribution has not been recognized before.

2.4 Comparison with the result by HLSS

For the orbital susceptibility in (2.28), we have only four contributions which are simpler than those obtained previously by HLSS, i.e., eqs. (4.3)-(4.6) in Ref.13 In Appendix C, we prove the equivalence between the present result and HLSS. Here we summarize the differences between the two.

(1) The result by HLSS is not symmetric with respect to the exchange of \( x \) and \( y \). This is because they used Landau gauge, \( A = (-Hy, 0, 0) \). On the other hand, the present formula is symmetric with respect to \( x \) and \( y \) because we have used the gauge-invariant formalism (1.3). In order to prove the equivalence between our result and that by HLSS, we have to symmetrize the HLSS’s result. (See details in Appendix C.)

(2) Among the four contributions in the present formula, \( \chi_{\text{LP}} \) is determined solely from the energy dispersion \( \varepsilon_i(k) \). The other three contributions involve the \( k \)-derivatives of wave functions. In contrast, HLSS’s result contains a term
\[ \frac{e^2}{2 \hbar c^2} \sum_{\ell, k} f'(\varepsilon_i) \int \frac{\partial u_{k}^*}{\partial k_x} \frac{\partial u_{k}^*}{\partial k_y} dr. \] (2.36)
(See eq. (C.1).) As shown above in eq. (2.27), this term can be rewritten in terms of \( u_{k}^* \) and has been included in \( \chi_{\text{FS}} \) in our formalism. It is important to use (2.27) in order to simplify the final expression. Note that, in contrast to (2.36), \( \chi_{\text{LP}} \) cannot be rewritten in terms of \( u_{k}^* \).

(3) The result by HLSS contains several terms which have a common denominator of \( 1/(\varepsilon_i - \varepsilon_F) \). In our formula, these contributions are summed up into a single term as \( \chi_{\text{inter}} \). The method how we can sum up the several terms in HLSS into a single term is explained in Appendix C.

(4) As explained above, each contribution in the present formula has a rather clear meaning compared with the previous ones. For example, \( \chi_{\text{inter}} \) and \( \chi_{\text{occ}} \) are contributions naturally connected to the Van Vleck susceptibility and atomic diamagnetism, respectively. Note that, in the HLSS’s formula, the contribution of the atomic diamagnetism is expressed as the first term of \( \chi_{\text{d}}(\text{HLSS}) \) in eq. (C.1), i.e.,
\[ -\frac{2e^2}{\hbar c^2} \sum_{\ell, k} \frac{\hbar^2}{m} f'(\varepsilon_i) \int \frac{\partial u_{k}^*}{\partial k_x} \frac{\partial u_{k}^*}{\partial k_y} dr. \] (2.37)

However, the numerical prefactor is different from that of the present result. (See the term proportional to \( \hbar^2/m \) in \( \chi_{\text{occ}} \).) As shown in the next section, this term reproduces the orbital susceptibility from the core-electrons in the atomic limit. \( \chi_{\text{occ}} \) in the present formula gives a correct prefactor, while eq. (2.37) by HLSS does not. As shown in Appendix C, we find that
the correct term is obtained in the HLSS’s formula when we rewrite the interband contributions into a single term as $\chi_{\text{inter.}}$ [For details, see eq. (C.4).]

2.5 Comparison with the results by Gao et al.

Let us discuss here the recent work by Gao et al. who studied orbital magnetism in terms of Berry phase. They are interested in the case with broken time-reversal symmetry in which spontaneous orbital magnetization appears. In this case, there are several terms involving the Berry curvature denoted as $\Omega$. In the present notation, its $z$-component is given by

$$\Omega_z = i \int \left( \frac{\partial u_{ik}^\dagger}{\partial k_x} \frac{\partial u_{ik}}{\partial k_y} - \frac{\partial u_{ik}^\dagger}{\partial k_y} \frac{\partial u_{ik}}{\partial k_x} \right) dr. \quad (2.38)$$

However, in our case with a centrosymmetric potential, $\Omega_z$ vanishes since there is a relation $u_{ik}^\dagger(-r) = u_{ik}(r)$. As a result, we do not have the contributions coming from the Berry curvature. However, we can compare our results with theirs in the case where the time-reversal symmetry is not broken.

Details of calculations are shown in Appendix D. By using the completeness property of $u_{ik}$, we can show that their results are almost equivalent with our results except for the coefficient of $\chi_{\text{FS}}$. We think that this difference is due to the wave-packet approximation used in their formalism. Nevertheless, their formula for the orbital susceptibility based on the wave-packet approximation is fairly accurate.

3. Band effect from atomic limit

The obtained formula in eqs. (2.29)-(2.32) is exact. However, in order to calculate each contribution explicitly, it is necessary to specify the functional form of $u_{ik}(r)$. For example, $u_{ik}(r)$ can be obtained in general from the first-principle band calculation. In this paper, however, we will study each contribution from the atomic limit to see possible band effects based on the linear combination of atomic orbitals (LCAO). In the atomic limit, it is found that diamagnetic susceptibility from core electrons and Van Vleck susceptibility are the only contributions to $\chi$. Then, $\chi$ is estimated by treating the overlap integrals between atomic orbitals as a perturbation. We will show that there appear several contributions to $\chi$ in addition to $\chi_{\text{LP}}$. In this perturbative method, the itinerant feature of Bloch electrons in solids are clarified systematically. Schematic picture is shown in Fig. 2.

3.1 Atomic limit

In order to study the atomic limit in the present formula, it is appropriate to use LCAO. Let us consider a situation in which the periodic potential $V(r)$ is written as

$$V(r) = \sum_{R_i} V_0(r - R_i), \quad (3.1)$$

where $R_i$ represent lattice sites and $V_0(r)$ is a potential of a single atom. We use atomic orbitals $\phi_n(r)$ which satisfy

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_0(r) \right) \phi_n(r) = E_n \phi_n(r). \quad (3.2)$$

Using these atomic orbitals, we consider the LCAO wave function

$$\varphi_{ik}(r) = \frac{1}{\sqrt{N}} \sum_{R_i} e^{-ik(r-R_i)} \phi_n(r-R_i), \quad (3.3)$$

which is used as a basis set for $u_{ik}(r)$. Here $N$ is the total number of unit cells. It is easily shown that $\varphi_{ik}(r)$ are periodic functions with the same period with $V(r)$.

In the atomic limit, $V_0(r - R_i)$ and $\phi_n(r - R_i)$ are confined in a unit cell and there is no overlap between nearest-neighbor $V_0(r - R_i)$ or nearest-neighbor $\phi_n(r - R_i)$. In this case, it is easily shown that the LCAO wave function, $\varphi_{ik}(r)$, in (3.3) satisfies the equation (2.3) with energy $\varepsilon_i = E_i$ that is independent on $k$. Therefore, $u_{ik}$ is just given by

$$u_{ik}(r) = \varphi_{ik}(r) = \frac{1}{\sqrt{N}} \sum_{R_i} e^{-ik(r-R_i)} \phi_n(r-R_i). \quad (3.4)$$

By substituting eq. (3.4) and $\varepsilon_i = E_i$ into eqs. (2.29)-(2.32), we obtain $\chi_{\text{LP}}, \chi_{\text{inter}}, \chi_{\text{FS}}$ and $\chi_{\text{occ.}}$. Since $E_i$ is $k$-independent, $\chi_{\text{LP}} = \chi_{\text{FS}} = 0$. For $\chi_{\text{inter}}$, we obtain

$$\chi_{\text{inter}} = -\frac{e^2}{\hbar c^2} \sum_{\ell \neq l', k} \frac{f(E_i)}{E_i - E_{l'}} \left[ \frac{1}{N} \sum_{R_i \neq R_j} \right] \int \langle x - R_{i\ell} \rangle e^{i(k(r-R_i) + k'(r-R_j))} \nabla y \phi_{l'}(r-R_i) dr$$

$$- \int \langle y - R_{j\ell} \rangle e^{i(k(r-R_j) - k'(r-R_i))} \nabla x \phi_{l'}(r-R_i) dr \right|^2. \quad (3.5)$$

Since there is no overlap between atomic orbitals, only the terms with $R_i = R_j$ survives. Thus $\chi_{\text{inter}}$ is simplified as

$$\chi_{\text{inter}} = -\frac{e^2}{\hbar c^2} \sum_{\ell \neq l', k} \frac{f(E_i)}{E_i - E_{l'}} \left[ \frac{1}{N} \sum_{R_i \neq R_j} \right] \int \phi_{l'}^*(r) (x \nabla_y - y \nabla_x) \phi_{l'}(r) dr \right|^2, \quad (3.6)$$

where the $r$-integral is shifted to the center of the atomic orbital, $R_i$. The right-hand side of (3.6) is nothing but the Van Vleck susceptibility which we denote as $\chi_{\text{Van Vleck}}$.

Similarly, by substituting (3.4) and $\varepsilon_i = E_i$ into (2.32), we
obtain
\[
\chi_{\text{occ}} = -\frac{e^2}{2\hbar c^2} \sum_{\ell,k} f(E_k) \int \frac{\partial \phi_{\ell}^*}{\partial k_x} \frac{\partial \phi_k}{\partial k_x} dr + (x \leftrightarrow y)
\]
\[
= -\frac{e^2}{2\hbar c^2} \sum_{\ell,k} f(E_k) \int (x^2 + y^2)|\phi_\ell(r)|^2 dr.
\]
(3.7)

This is just the atomic diamagnetism coming from the core electrons which we denote as \(\chi^{(\text{atomic dia.)}}\). Therefore, in the atomic limit, we have \(\chi = \chi^{(\text{Van Vleck})} + \chi^{(\text{atomic dia.)}}\). (See the left-hand side of Fig. 2.)

### 3.2 Perturbation with respect to the overlap integrals

Next we consider the case in which there are overlap integrals between the nearest-neighbor atomic orbitals. In this case, using \(\phi_{\ell k}(r)\) in eq. (3.3), we expand \(u_{\ell k}\) as
\[
u_{\ell k}(r) = \sum_n c_{\ell,n}(k)\phi_{nk}(r)
\]
\[
= \frac{1}{\sqrt{N}} \sum_n \sum_{R_i} c_{\ell,n}(k)e^{-ik(r-R_i)}\phi_n(r-R_i).
\]
(3.8)

(Note that \(c_{\ell,n}(k) = \delta_{\ell,n}\) in the atomic limit.) The coefficients \(c_{\ell,n}(k)\) should be determined in order for \(u_{\ell k}\) to satisfy the equation (2.3). This can be achieved by solving the eigenvalue problem
\[
\sum_m h_{nm}(k)c_{\ell,m}(k) = \epsilon_{\ell}(k)\sum_m s_{nm}(k)c_{\ell,m}(k),
\]
where the Hamiltonian matrix elements are
\[
h_{nm}(k) = \int \phi_{mk}^*(r)H_{\ell k}\phi_{nk}(r) dr,
\]
and \(s_{nm}(k)\) represents the integral
\[
s_{nm}(k) = \int \phi_{mk}^*(r)\phi_{nk}(r) dr.
\]
(3.9)
(3.10)
(3.11)

\(h_{nm}(k)\) and \(s_{nm}(k)\) can be calculated perturbatively with respect to the overlap integral
\[
\int \phi_{mk}^*(r-R_j)\phi_{nk}(r-R_i) dr,
\]
(3.12)
with \(\phi\) being an operator and \(R_j \neq R_i\). For example, the first-order term of \(h_{nm}(k)\) contains the hopping integral used in the tight-binding model.

By substituting eq. (3.8) and \(\epsilon_{\ell}(k)\) into eqs. (2.29)-(2.32), we can show that each of four contributions, \(\chi_{\text{LP}}, \chi_{\text{inter}}, \chi_{\text{FS}}\), and \(\chi_{\text{occ}}\), is calculated perturbatively with respect to the overlap integrals. In contrast to the atomic limit, there are two new features: (1) \(\epsilon_{\ell}(k)\) has band dispersion due to the hopping integrals, and (2) \(u_{\ell k}(r)\) has an additional \(k\)-dependence through \(c_{\ell,n}(k)\) in eq. (3.8). The latter gives several contributions to the orbital susceptibility originating from the \(k\)-derivatives of \(u_{\ell k}(r)\). One may expect that \(\chi_{\text{LP}}\) is dominant in the first-order perturbation. However, we find that the situation is not so simple even in the single-band case. Each of \(\chi_{\text{LP}}, \chi_{\text{inter}}, \chi_{\text{FS}}\) and \(\chi_{\text{occ}}\) depends on the location of the chemical potential as well as on the details of the model. In the forthcoming paper, we will discuss several explicit models such as single-band and two-band tight-binding models.

### 4. Discussions

Based on the exact formula, we have shown rigorously that the orbital susceptibility for Bloch electrons can be described in terms of four contributions, \(\chi = \chi_{\text{LP}} + \chi_{\text{inter}} + \chi_{\text{FS}} + \chi_{\text{occ}}\). Except for the Landau-PEierls susceptibility, \(\chi_{\text{LP}}\), the other three contributions involve the crystal-momentum derivatives of \(\chi_{\ell k}\)'s. These contributions represent the effects of the deformation of the wave function due to the magnetic field. We find that \(\chi_{\text{occ}}\) contains the contributions from the occupied states in the partially-filled band, which has not been recognized before. We applied the present formula to the model of LCAO. In the atomic limit where there are no overlap integrals, \(\chi_{\text{inter}}\) becomes \(\chi^{(\text{Van Vleck})}\) and \(\chi_{\text{occ}}\) becomes \(\chi^{(\text{atomic dia.)}}\). These two are the only contributions to \(\chi\) in the atomic limit. When the overlap integrals are finite, we have discussed that \(\chi\) can be calculated by treating the overlap integrals as a perturbation. In this method, itinerant features of Bloch electrons in solids can be clarified systematically for the first time.

The present formalism can be used as a starting point for various extensions. Several future problems are as follows:

(1) It is very interesting to apply the present formula to the multi-band tight-binding models. A typical example is the honeycomb lattice which is a model for graphene.\(^{30-35}\) In this case, we have A- and B-sublattice in a unit cell, and as a result, we have massless Dirac electrons (or more precisely, Weyl electrons) which is a typical two-band model. The orbital susceptibility has been calculated by several groups\(^{30-32}\) based on the Peierls phase. In contrast, in the present formula, all the contributions from Bloch bands are included rigorously. Application of the present formula to graphene will be discussed in the forthcoming paper.

(2) In the present Hamiltonian, the spin-orbit interaction is not included. It is also a very interesting problem to study the orbital susceptibility in the presence of spin-orbit interaction. As discussed recently by Gao et al.,\(^{36}\) the orbital susceptibility in the Hamiltonian with broken time-reversal symmetry\(^{37-40}\) is another interesting problem. This will be also studied in the forthcoming paper. As suggested\(^{36}\) there appear several terms which is written in terms of Berry curvatures.

(3) We have confined ourselves in the orbital susceptibility in this paper. The transport coefficients are of course interesting quantities.\(^{43}\) Hall conductivity in the Weyl equation realized in graphene and an organic conductor \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\)\(^{23-25}\) as well as in bismuth\(^{26,29}\) has been discussed. The similar method used in this paper can be applied to the Hall conductivity in the Bloch representation.
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Appendix A: Various formulas for matrix elements of Bloch wave functions

In this appendix, we derive various useful formulas which are quite often used in the derivations. First, we make \( k \) derivative of the equation for \( u_{\ell k} \) in eq. (2.3)

\[
\frac{\partial H_k}{\partial k} u_{\ell k} + H_k \frac{\partial u_{\ell k}}{\partial k} = \frac{\partial \varepsilon_{\ell}^j}{\partial k} u_{\ell k} + \varepsilon_{\ell} \frac{\partial u_{\ell k}}{\partial k}
\]

(A.1)

In the following, we write \( \varepsilon_{\ell}^j \) for \( \varepsilon_{\ell}(k) \). When we multiply \( u_{\ell k}^\dagger \) and make the real-space integral, we obtain

\[
\int u_{\ell k}^\dagger \frac{\partial H_k}{\partial k} u_{\ell k} dr = \int u_{\ell k}^\dagger \frac{\partial \varepsilon_{\ell}^j}{\partial k} \delta_{\ell'\ell} + (\varepsilon_{\ell} - \varepsilon_{\ell'}) \int u_{\ell k}^\dagger \frac{\partial u_{\ell k}}{\partial k} dr.
\]

(A.2)

Exchange of \( \ell \leftrightarrow \ell' \) gives eq. (2.8).

Next, the \( k_\mu \) and \( k_\nu \) derivative of eq. (2.3) gives

\[
\left( \frac{\hbar^2}{m} \delta_{\mu\nu} - \frac{\partial^2 \varepsilon_{\ell}}{\partial k_\mu \partial k_\nu} \right) u_{\ell k} + \left( \frac{\partial H_k}{\partial k_\mu} - \frac{\partial \varepsilon_{\ell}}{\partial k_\mu} \right) \frac{\partial u_{\ell k}}{\partial k_\nu} + \left( \frac{\partial H_k}{\partial k_\nu} - \frac{\partial \varepsilon_{\ell}}{\partial k_\nu} \right) \frac{\partial u_{\ell k}}{\partial k_\mu} + (H_k - \varepsilon_{\ell}) \frac{\partial^2 u_{\ell k}}{\partial k_\mu \partial k_\nu} = 0.
\]

(A.3)

When we multiply \( u_{\ell k}^\dagger \) and make the real-space integral, we obtain

\[
\left( \frac{\hbar^2}{m} \delta_{\mu\nu} - \frac{\partial^2 \varepsilon_{\ell}}{\partial k_\mu \partial k_\nu} \right) \delta_{\ell'\ell} + \int u_{\ell k}^\dagger \left( \frac{\partial H_k}{\partial k_\mu} - \frac{\partial \varepsilon_{\ell}}{\partial k_\mu} \right) \frac{\partial u_{\ell k}}{\partial k_\nu} dr + \int u_{\ell k}^\dagger \left( \frac{\partial H_k}{\partial k_\nu} - \frac{\partial \varepsilon_{\ell}}{\partial k_\nu} \right) \frac{\partial u_{\ell k}}{\partial k_\mu} dr + (\varepsilon_{\ell} - \varepsilon_{\ell'}) \int u_{\ell k}^\dagger \frac{\partial^2 u_{\ell k}}{\partial k_\mu \partial k_\nu} dr = 0.
\]

(A.4)

Similarly, when we multiply \( \frac{\partial^2 u_{\ell k}}{\partial k_\nu \partial k_\sigma} \) and make the real-space integral, then we obtain

\[
\int \frac{\partial^2 u_{\ell k}^\dagger}{\partial k_\sigma \partial k_\nu} (\varepsilon_{\ell} - H_k) \frac{\partial^2 u_{\ell k}}{\partial k_\mu \partial k_\nu} dr = \int \frac{\partial^2 u_{\ell k}^\dagger}{\partial k_\mu \partial k_\nu} \left( \frac{\partial H_k}{\partial k_\sigma} - \frac{\partial \varepsilon_{\ell}}{\partial k_\sigma} \right) \frac{\partial u_{\ell k}}{\partial k_\nu} dr + \int \frac{\partial^2 u_{\ell k}^\dagger}{\partial k_\nu \partial k_\sigma} \left( \frac{\partial H_k}{\partial k_\mu} - \frac{\partial \varepsilon_{\ell}}{\partial k_\mu} \right) \frac{\partial u_{\ell k}}{\partial k_\sigma} dr
\]

\[
+ \left( \frac{\hbar^2}{m} \delta_{\mu\nu} - \frac{\partial^2 \varepsilon_{\ell}}{\partial k_\mu \partial k_\nu} \right) \int \frac{\partial^2 u_{\ell k}^\dagger}{\partial k_\sigma \partial k_\nu} u_{\ell k} dr.
\]

(A.5)

We can obtain other series of formulas by making \( k \)-derivative of the orthonormal condition, \( \int u_{\ell k}^\dagger u_{\ell' k} dr = \delta_{\ell'\ell} \). First we obtain

\[
\int u_{\ell k}^\dagger \frac{\partial u_{\ell k}}{\partial k_\mu} dr = -\int \frac{\partial u_{\ell k}^\dagger}{\partial k_\mu} u_{\ell k} dr.
\]

(A.6)

Furthermore if the system is centrosymmetric, i.e., if \( V(-r) = V(r) \) holds, we can choose \( u_{\ell k}^\dagger (-r) = u_{\ell k}(r) \). In this case, we can make further convenient formulas. Firstly, using the change of variable \( r \to -r \), we obtain

\[
\int u_{\ell k}^\dagger \frac{\partial u_{\ell k}}{\partial k_\mu} dr = \int \frac{\partial u_{\ell k}^\dagger}{\partial k_\mu} u_{\ell k} dr.
\]

(A.7)

Combining this relation with (A.6) with \( \ell = \ell' \), we obtain

\[
\int u_{\ell k}^\dagger \frac{\partial u_{\ell k}}{\partial k_\mu} dr = \int \frac{\partial u_{\ell k}^\dagger}{\partial k_\mu} u_{\ell k} dr = 0.
\]

(A.8)

(This integral is the so-called intraband “Berry connection”.) This formula is used quite often. Further \( k \)-derivatives give

\[
\int u_{\ell k}^\dagger \frac{\partial^2 u_{\ell k}}{\partial k_\mu \partial k_\nu} dr = -\int \frac{\partial u_{\ell k}^\dagger}{\partial k_\nu} \frac{\partial u_{\ell k}}{\partial k_\mu} dr.
\]

(A.9)

Using the relation \( u_{\ell k}(-r) = u_{\ell k}(r) \), we can also show that \( p_{\ell'\mu} \) in (2.9) is real and

\[
\int \frac{\partial^2 u_{\ell k}^\dagger}{\partial k_\sigma \partial k_\nu} \frac{\partial H_k}{\partial k_\mu} \frac{\partial u_{\ell k}}{\partial k_\nu} dr = \int \frac{\partial u_{\ell k}^\dagger}{\partial k_\nu} \frac{\partial H_k}{\partial k_\mu} \frac{\partial^2 u_{\ell k}}{\partial k_\sigma \partial k_\nu} dr.
\]

(A.10)
Furthermore, from the $k_v$ derivative of eq. (A.2) with $\ell = \ell'$, we obtain

$$\int u_{ik}^\dagger \frac{\partial H_k}{\partial k_{\mu}} \frac{\partial u_{ik}}{\partial k_v} \, dr = \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} \frac{\partial H_k}{\partial k_v} u_{ik} \, dr = \frac{1}{2} \left( \frac{\partial^2 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v} - \frac{\hbar^2}{m} \delta_{\mu \nu} \right).$$  

(A-11)

Note that $\mu$ and $v$ can be exchanged ($\mu \leftrightarrow v$) in (A-11). Finally, using (A-11) and (A-1), we have

$$\int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} (\varepsilon_{\ell} - H_k) \frac{\partial u_{ik}}{\partial k_v} \, dr = \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} \left( \frac{\partial H_k}{\partial k_v} - \frac{\partial \varepsilon_{\ell}}{\partial k_v} \right) u_{ik} \, dr = \frac{1}{2} \left( \frac{\partial^2 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v} - \frac{\hbar^2}{m} \delta_{\mu \nu} \right).$$  

(A-12)

By using $p_{\ell'\nu, \mu}$ in (2.9), we obtain the $f$-sum rule$^{8,21}$ as follows:

$$\sum_{\ell' \neq \ell} \frac{p_{\ell'\mu} p_{\ell'\nu}}{(\varepsilon_{\ell} - \varepsilon_{\ell'}) \varepsilon_{\ell} - \varepsilon_{\ell'}} \int u_{ik}^\dagger \frac{\partial u_{ik}}{\partial k_{\mu}} \, dr \int u_{ik}^\dagger \frac{\partial u_{ik}}{\partial k_{\nu}} \, dr = \sum_{\ell' \neq \ell} \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} (\varepsilon_{\ell} - H_k) u_{i'k} \, dr \int u_{i'k}^\dagger \frac{\partial u_{ik}}{\partial k_{\nu}} \, dr$$

$$= \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} (\varepsilon_{\ell} - H_k) \frac{\partial u_{ik}}{\partial k_{\nu}} \, dr = \frac{1}{2} \left( \frac{\partial^2 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v} - \frac{\hbar^2}{m} \delta_{\mu \nu} \right),$$  

(A-13)

where we have added the $\ell' = \ell$ term which is equal to zero due to the factor $(\varepsilon_{\ell} - \varepsilon_{\ell'})$. We have also used the relations (A-1) and (A-6), and the completeness property, $\sum_{\ell'} u_{i\ell k}(r) u_{i'k}(r') = \delta(r - r')$. Similarly we obtain

$$\sum_{\ell' \neq \ell, \ell'} \frac{p_{\ell'\mu} p_{\ell'\nu}}{(\varepsilon_{\ell} - \varepsilon_{\ell'}) \varepsilon_{\ell} - \varepsilon_{\ell'}} \int u_{ik}^\dagger \frac{\partial u_{ik}}{\partial k_{\mu}} \, dr \int u_{ik}^\dagger \frac{\partial u_{ik}}{\partial k_{\nu}} \, dr = \sum_{\ell' \neq \ell} \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} (\varepsilon_{\ell} - H_k) u_{v'k} \, dr \int u_{v'k}^\dagger \frac{\partial u_{ik}}{\partial k_{\nu}} \, dr$$

$$= \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} (\varepsilon_{\ell} - H_k) \frac{\partial u_{ik}}{\partial k_{\nu}} \, dr = \frac{1}{2} \left( \frac{\partial^2 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v} - \frac{\hbar^2}{m} \delta_{\mu \nu} \right),$$  

(A-14)

where we have added the $\ell'' = \ell$ term in (A-14) and $\ell' = \ell$ term in (A-15) which are equal to zero since $\int u_{ik}^\dagger (\partial u_{ik}/\partial k_{\mu}) \, dr = 0$ (eq. (A-8)).

When we multiply $u_{ik}^\dagger$ to the $k_{\nu}, k_v, k_\tau$ derivative of eq. (2.3) and make the real-space integral, we obtain

$$\frac{\partial^3 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v \partial k_\tau} = \int u_{ik}^\dagger \left( \frac{\partial H_k}{\partial k_{\mu}} - \frac{\partial \varepsilon_{\ell}}{\partial k_{\mu}} \right) \frac{\partial^2 u_{ik}}{\partial k_v \partial k_\tau} \, dr + \int u_{ik}^\dagger \left( \frac{\partial H_k}{\partial k_v} - \frac{\partial \varepsilon_{\ell}}{\partial k_v} \right) \frac{\partial^2 u_{ik}}{\partial k_\tau \partial k_{\mu}} \, dr + \int u_{ik}^\dagger \left( \frac{\partial H_k}{\partial k_\tau} - \frac{\partial \varepsilon_{\ell}}{\partial k_\tau} \right) \frac{\partial^2 u_{ik}}{\partial k_{\mu} \partial k_v} \, dr,$$

(A-16)

where we have used (A-8). On the other hand, $k_{\tau}$ derivative of (A-11) gives

$$\int u_{ik}^\dagger \frac{\partial H_k}{\partial k_\tau} \frac{\partial^2 u_{ik}}{\partial k_\tau \partial k_{\mu}} \, dr = - \int \frac{\partial u_{ik}^\dagger}{\partial k_\tau} \frac{\partial H_k}{\partial k_{\mu}} u_{ik} \, dr + \frac{1}{2} \frac{\partial^2 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v \partial k_\tau}.$$  

(A-17)

Substituting this relation into the right-hand side of (A-16) and using (A-9), we can show

$$\frac{1}{2} \frac{\partial^3 \varepsilon_{\ell}}{\partial k_{\mu} \partial k_v \partial k_\tau} = \int \frac{\partial u_{ik}^\dagger}{\partial k_{\mu}} \left( \frac{\partial H_k}{\partial k_{\nu}} - \frac{\partial \varepsilon_{\ell}}{\partial k_{\nu}} \right) \frac{\partial u_{ik}}{\partial k_v} \, dr + \int \frac{\partial u_{ik}^\dagger}{\partial k_{\nu}} \left( \frac{\partial H_k}{\partial k_{\tau}} - \frac{\partial \varepsilon_{\ell}}{\partial k_{\tau}} \right) \frac{\partial u_{ik}}{\partial k_\tau} \, dr + \int \frac{\partial u_{ik}^\dagger}{\partial k_{\tau}} \left( \frac{\partial H_k}{\partial k_{\mu}} - \frac{\partial \varepsilon_{\ell}}{\partial k_{\mu}} \right) \frac{\partial u_{ik}}{\partial k_v} \, dr.$$  

(A-18)

**Appendix B:** Calculations of $\chi_3 \ast \chi_7$

First, we calculate $\chi_3$, and $\chi_7$. The summation over $n$ gives

$$\chi_3 = \frac{e^2}{\hbar c^2} \sum_{\ell \neq \ell'} \frac{\partial \varepsilon_{\ell}}{\partial k_\kappa} \frac{\partial \varepsilon_{\ell'}}{\partial k_\kappa} \int p_{\ell'\nu} p_{\ell'\mu} \left\{ \frac{f'(\varepsilon_{\ell}) + f'(\varepsilon_{\ell'})}{(\varepsilon_{\ell} - \varepsilon_{\ell'})^2} - 2 \frac{f(\varepsilon_{\ell}) - f(\varepsilon_{\ell'})}{(\varepsilon_{\ell} - \varepsilon_{\ell'})^2} \right\} \, dx \, dy$$

$$= \frac{2e^2}{\hbar c^2} \sum_{n \neq n'} \frac{\partial \varepsilon_{\ell}}{\partial k_\kappa} \frac{\partial \varepsilon_{\ell'}}{\partial k_\kappa} \int p_{\ell'\nu} p_{\ell'\mu} \left\{ \frac{f'(\varepsilon_{\ell})}{(\varepsilon_{\ell} - \varepsilon_{\ell'})^2} - 2 \frac{f(\varepsilon_{\ell})}{(\varepsilon_{\ell} - \varepsilon_{\ell'})^2} \right\} \, dx \, dy.$$  

(B-1)
and carried out by using the formula (A-14) and its complex conjugate. As a result, we obtain

\[
\chi_{4,1} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f'(\epsilon_t)}{(\epsilon_{t'} - \epsilon_t)^2(\epsilon_{t'} - \epsilon_{t'})} - \frac{f'(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2(\epsilon_{t'} - \epsilon_{t''})} \right\} + \left( x \leftrightarrow y \right), \tag{B-2}
\]

Next, we calculate

\[
\chi_{4,2} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f'(\epsilon_t)}{(\epsilon_{t'} - \epsilon_t)^2} - \frac{f'(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2} \right\} \left( x \leftrightarrow y \right), \tag{B-3}
\]

and

\[
\chi_{4,3} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2} \right\} u_{t'k} dr + (x \leftrightarrow y). \tag{B-4}
\]

In the following, we denote the \( j \)-th term in the parentheses of \( \chi_n \) as \( \chi_{n,j} \). The summation over \( \ell'' \) in \( \chi_{4,1} \), \( \chi_{4,2} \), \( \chi_{4,3} \) can be carried out by using the formula (A-14) and its complex conjugate. As a result, we obtain

\[
\chi_{4,1} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f'(\epsilon_t)}{(\epsilon_{t'} - \epsilon_t)^2(\epsilon_{t'} - \epsilon_{t'})} - \frac{f'(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2(\epsilon_{t'} - \epsilon_{t''})} \right\} + \left( x \leftrightarrow y \right), \tag{B-2}
\]

\[
\chi_{4,2} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f'(\epsilon_t)}{(\epsilon_{t'} - \epsilon_t)^2} - \frac{f'(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2} \right\} \left( x \leftrightarrow y \right), \tag{B-3}
\]

and

\[
\chi_{4,3} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2} \right\} u_{t'k} dr + (x \leftrightarrow y). \tag{B-4}
\]

In the same way, the summation over \( \ell' \) in \( \chi_{4,4} \) and \( \chi_{4,5} \) are carried out and we obtain

\[
\chi_{4,4} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2} \right\} u_{t'k} dr + (x \leftrightarrow y), \tag{B-5}
\]

\[
\chi_{4,5} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} p_{t'\ell'}(\epsilon_{t'} - \epsilon_{t'}) \left\{ \frac{f(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^2} \right\} u_{t'k} dr + (x \leftrightarrow y). \tag{B-6}
\]

We find that the second term in \( \chi_{4,1} \) cancels with \( \chi_{3,1} \). For the first term in \( \chi_{4,1} \), we can carry out the \( \ell' \) summation by using the explicit form of \( p_{t'\ell'} \) and the completeness property of \( u_{t'k} \). As a result, we obtain

\[
\chi_{3,1} + \chi_{4,1} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} f'(\epsilon_t) \int \frac{d \epsilon_{t''}}{d k_x} \left( \frac{\partial H_{t''}}{\partial k_x} \frac{\partial u_{t''k}}{\partial k_y} - \frac{\partial \epsilon_{t''}}{\partial k_x} \right) u_{t'k} dr + (x \leftrightarrow y). \tag{B-8}
\]

We also find that the second terms in \( \chi_{4,2} \) and \( \chi_{4,4} \) cancel with \( \chi_{3,2} \). Then, rewriting \( \chi_{4,4} \) and \( \chi_{4,5} \) by \( x \leftrightarrow y \), and making the change of variables \( \epsilon_{t'} \leftrightarrow \epsilon_t \) etc., we obtain

\[
\chi_{3,2} + \chi_{4,2} + \chi_{4,3} + \chi_{4,4} + \chi_{4,5} = \frac{2e^2}{\hbar^2c^2} \sum_{t' \ell' k} \frac{\partial \epsilon_{t'}}{\partial k_z} f'(\epsilon_t) \int \frac{d \epsilon_{t''}}{d k_x} \left( \frac{\partial H_{t''}}{\partial k_x} \frac{\partial u_{t''k}}{\partial k_y} - \frac{\partial \epsilon_{t''}}{\partial k_x} \right) u_{t'k} dr + (x \leftrightarrow y), \tag{B-9}
\]

Next, we calculate \( \chi_5, \chi_6, \) and \( \chi_7 \). The summation over \( n \) gives

\[
\chi_5 = \frac{e^2}{\hbar^2c^2} \sum_{t \ell k} p_{t\ell x} p_{t\ell y} \left\{ \frac{f'(\epsilon_t)}{(\epsilon_{t'} - \epsilon_t)^3} - \frac{2f(\epsilon_t)}{(\epsilon_{t'} - \epsilon_t)^3} \right\} + (x \leftrightarrow y), \tag{B-10}
\]

\[
\chi_6 = \frac{e^2}{\hbar^2c^2} \sum_{t' \ell k} p_{t'\ell x} p_{t'\ell y} \left\{ \frac{f'(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^3(\epsilon_{t'} - \epsilon_{t''})} - \frac{2f(\epsilon_t)}{(\epsilon_{t'} - \epsilon_{t''})^3(\epsilon_{t'} - \epsilon_{t''})} + \frac{2f(\epsilon_{t''})}{(\epsilon_{t'} - \epsilon_{t''})^3(\epsilon_{t'} - \epsilon_{t''})} \right\} + (x \leftrightarrow y), \tag{B-11}
\]

\[
\chi_7 = \frac{e^2}{\hbar^2c^2} \sum_{t' \ell k} p_{t'\ell x} p_{t'\ell y} \left\{ \frac{f(\epsilon_t)}{(\epsilon_{t'} - \epsilon_{t'})(\epsilon_{t'} - \epsilon_{t'})} \right\} + (x \leftrightarrow y), \tag{B-12}
\]
where we have arranged the terms by using change of variables, \( \ell \leftrightarrow \ell' \), etc. We can see that the excluded terms of \( \ell' = \ell'' \) in \( \chi_{5.1} \) and \( \chi_{6.2} \) are exactly supplemented by \( \chi_{5.1} \) and \( \chi_{5.2} \), respectively. Therefore the \( \ell' \)- and \( \ell'' \)-summations in \( \chi_{5.1} + \chi_{6.1} \) and \( \chi_{5.2} + \chi_{6.2} \) are independent to each other, and we can use the \( f \)-sum rule (A-13) and (A-15). As a result, we obtain

\[
\chi_{5.1} + \chi_{6.1} = \frac{e^2}{\hbar^2 c^2} \sum_{\ell, k} f' (\varepsilon_\ell) \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x \partial k_y} \int \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_x} \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_y} d\ell + (x \leftrightarrow y),
\]

which is shown in (2.25), and

\[
\chi_{5.2} + \chi_{6.2} = \frac{e^2}{\hbar^2 c^2} \sum_{\ell, k} f (\varepsilon_\ell) \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x \partial k_y} \int \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_x} \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_y} d\ell + (x \leftrightarrow y).
\]

Similarly, we can see that the excluded terms of \( \ell' = \ell'' \) in \( \chi_{6.3} \) (eq. (B-12)) are exactly supplemented by \( \chi_{6.3} \) in (B-11) by changing \( \ell \leftrightarrow \ell' \) and \( x \leftrightarrow y \) in \( \chi_{6.3} \). As a result, applying (A-14) and its complex conjugates to \( \ell' \)- and \( \ell'' \)-summations, we obtain

\[
\chi_{6.3} + \chi_1 = \frac{2e^2}{\hbar^2 c^2} \sum_{\ell, k} f (\varepsilon_\ell) \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x \partial k_y} \int \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_x} \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_y} u_{\ell_{\ell_{\ell}} k} d\ell + (x \leftrightarrow y).
\]

Now all the contributions are arranged into the forms which have either \( f (\varepsilon_\ell) \), \( f' (\varepsilon_\ell) \), or \( f (\varepsilon_\ell) / (\varepsilon_\ell - \varepsilon_\ell') \). The contributions with \( f (\varepsilon_\ell) / (\varepsilon_\ell - \varepsilon_\ell') \) are \( \chi_{2.3} \) in (2.24), \( \chi_{3.2} + \chi_{4.2} + \chi_{5.3} + \chi_{5.4} + \chi_{5.5} \) in (B-9) and \( \chi_{6.3} + \chi_1 \) in (B-15). Comparing each term and using the \( x \leftrightarrow y \) terms, we can see that the several terms cancel with each other and the remaining terms can be rewritten in a compact form as

\[
\chi_{2.3} + \chi_{3.2} + \chi_{4.3} + \chi_{4.4} + \chi_{4.5} + \chi_{5.3} + \chi_{5.4} + \chi_{5.5} + \chi_1
\]

\[
\frac{2e^2}{\hbar^2 c^2} \sum_{\ell, k} f (\varepsilon_\ell) \frac{\partial^2 \varepsilon_{\ell}}{\partial k_x \partial k_y} \int \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_x} \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_y} u_{\ell_{\ell_{\ell}} k} d\ell + (x \leftrightarrow y).
\]

We find it more convenient to rewrite (B-16) as follows: First from eq. (A-4), we obtain for \( \ell \neq \ell' \)

\[
\int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial H_k}{\partial k_x} u_{\ell_{\ell_{\ell}} k} d\ell - \int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial \varepsilon_{\ell}}{\partial k_x} u_{\ell_{\ell_{\ell}} k} d\ell = - \int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial H_k}{\partial k_x} u_{\ell_{\ell_{\ell}} k} d\ell + \int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial \varepsilon_{\ell}}{\partial k_x} u_{\ell_{\ell_{\ell}} k} d\ell + (\varepsilon_\ell - \varepsilon_\ell') \int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial^2 u_{\ell_{\ell_{\ell}} k}}{\partial k_x \partial k_y} d\ell.
\]

Using this relation, we can show

\[
\int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial H_k}{\partial k_x} u_{\ell_{\ell_{\ell}} k} d\ell - \int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial \varepsilon_{\ell}}{\partial k_x} u_{\ell_{\ell_{\ell}} k} d\ell = \frac{1}{2} \left\{ \int u^*_{\ell_{\ell_{\ell}} k} \left( \frac{\partial H_k}{\partial k_x} + \frac{\partial \varepsilon_{\ell}}{\partial k_x} \right) u_{\ell_{\ell_{\ell}} k} d\ell - \int u^*_{\ell_{\ell_{\ell}} k} \left( \frac{\partial H_k}{\partial k_x} + \frac{\partial \varepsilon_{\ell}}{\partial k_x} \right) u_{\ell_{\ell_{\ell}} k} d\ell \right\}
\]

\[
+ (\varepsilon_\ell - \varepsilon_\ell') \int u^*_{\ell_{\ell_{\ell}} k} \frac{\partial^2 u_{\ell_{\ell_{\ell}} k}}{\partial k_x \partial k_y} d\ell.
\]

With use of this formula, (B-16) can be rewritten as

\[
\frac{e^2}{\hbar^2 c^2} \sum_{\ell, k} f (\varepsilon_\ell) \left\{ \int \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_x} \left( \frac{\partial H_k}{\partial k_x} + \frac{\partial \varepsilon_{\ell}}{\partial k_x} \right) u_{\ell_{\ell_{\ell}} k} d\ell - \int \frac{d\varepsilon_{\ell_{\ell_{\ell}}}}{\partial k_x} \left( \frac{\partial H_k}{\partial k_x} + \frac{\partial \varepsilon_{\ell}}{\partial k_x} \right) u_{\ell_{\ell_{\ell}} k} d\ell + (\varepsilon_\ell - \varepsilon_\ell') \int \frac{\partial^2 u_{\ell_{\ell_{\ell}} k}}{\partial k_x \partial k_y} u_{\ell_{\ell_{\ell}} k} d\ell \right\}
\]

\[
\times \left\{ \int u^*_{\ell_{\ell_{\ell}} k} \left( \frac{\partial H_k}{\partial k_x} + \frac{\partial \varepsilon_{\ell}}{\partial k_x} \right) u_{\ell_{\ell_{\ell}} k} d\ell - \int u^*_{\ell_{\ell_{\ell}} k} \left( \frac{\partial H_k}{\partial k_x} + \frac{\partial \varepsilon_{\ell}}{\partial k_x} \right) u_{\ell_{\ell_{\ell}} k} d\ell \right\} + (x \leftrightarrow y)
\]

\[
= \frac{e^2}{\hbar^2 c^2} \sum_{\ell, k} f (\varepsilon_\ell) (\varepsilon_\ell - \varepsilon_\ell') \frac{\partial^2 u_{\ell_{\ell_{\ell}} k}}{\partial k_x \partial k_y} u_{\ell_{\ell_{\ell}} k} d\ell + (x \leftrightarrow y).
\]

where the cross terms vanish. We can rewrite the second summation in (B-19) by using the completeness property of \( u_{\ell_{\ell_{\ell}} k} \)
the complex conjugate of eq. (A5) as
\[ \frac{\epsilon^2}{2\hbar^2 c^2} \sum_{\ell, k} f(\epsilon_i) \left\{ \frac{2}{\hbar^2} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{\partial^2 \epsilon_i}{\partial \bar{x} \partial y} \right) \frac{\partial^2 u_{1k}}{d\epsilon_i} d\epsilon_i \right\} + (x \leftrightarrow y), \] (B20)
where we have used the relation (A9).

Here we collect all the contributions as follows:
\[ \chi_{1} + \chi_{22} + \chi_{51} + \chi_{61} = \frac{\epsilon^2}{6\hbar^2 c^2} \sum_{\ell, k} f'(\epsilon_i) \left\{ \frac{\partial^2 \epsilon_i}{\partial \bar{x} \partial y} \right\} \left( \frac{\partial^2 \epsilon_i}{\partial \bar{x} \partial y} \right) \] (B21)
\[ = -\frac{\epsilon^2}{\hbar^2 c^2} \sum_{\ell, k} f(\epsilon_i) \left\{ \frac{2}{\hbar^2} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{\partial H_{k}}{\partial \bar{x}} \right) \frac{\partial u_{1k}}{d\epsilon_i} d\epsilon_i \right\} \] (B22)
\[ + \frac{\epsilon^2}{2\hbar^2 c^2} \sum_{\ell, k} f(\epsilon_i) \left\{ \frac{2}{\hbar^2} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{\partial H_{k}}{\partial \bar{x}} - \frac{\partial H_{k}}{\partial \bar{y}} \right) \frac{\partial u_{1k}}{d\epsilon_i} d\epsilon_i \right\} + (x \leftrightarrow y), \] (B23)
Here the first two terms in (B21) are just equal to the Landau-Peierls susceptibility, \( \chi_{LP} \). The first summation in (B23) involving two bands (\( \ell \) and \( \ell' \)) is denoted as \( \chi_{inter} \). In the following, we rewrite the remaining terms a little further.

As discussed in Section 2, the last term in (B21) can be rewritten by using the formula in eq. (2.27). As a result, sum of (B21) and (B22) becomes
\[ \chi_{LP} + \frac{\epsilon^2}{\hbar^2 c^2} \sum_{\ell, k} f'(\epsilon_i) \left\{ \frac{\partial \epsilon_i}{\partial \bar{x}} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{3}{2} \frac{\partial \epsilon_i}{\partial \bar{x}} + \frac{1}{2} \frac{\partial \epsilon_i}{\partial \bar{y}} \right) \frac{\partial u_{1k}}{d\epsilon_i} d\epsilon_i \right\} \] (B24)
Furthermore, we notice it is convenient to rewrite the first term of the second summation in (B23) as
\[ \frac{\epsilon^2}{\hbar^2 c^2} \sum_{\ell, k} f(\epsilon_i) \left\{ \frac{\partial \epsilon_i}{\partial \bar{x}} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{\partial H_{k}}{\partial \bar{x}} \right) \frac{\partial u_{1k}}{d\epsilon_i} d\epsilon_i \right\} \] (B25)
\[ = \frac{\epsilon^2}{\hbar^2 c^2} \sum_{\ell, k} f(\epsilon_i) \left\{ \frac{\partial \epsilon_i}{\partial \bar{x}} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{\partial H_{k}}{\partial \bar{x}} - \frac{\partial H_{k}}{\partial \bar{y}} \right) \frac{\partial u_{1k}}{d\epsilon_i} d\epsilon_i \right\} \] (B26)
\[ = \frac{\epsilon^2}{\hbar^2 c^2} \sum_{\ell, k} f'(\epsilon_i) \frac{\partial \epsilon_i}{\partial \bar{x}} \int \frac{d^2 u^{\dagger}_{1k}}{d\epsilon_i} \left( \frac{\partial H_{k}}{\partial \bar{x}} \right) \frac{\partial u_{1k}}{d\epsilon_i} d\epsilon_i \] (B27)
where we have used the relation (A10). It is now apparent that the summation in (B24) and (B25) should be added. Using these expressions, we finally obtain \( \chi = \chi_{LP} + \chi_{inter} + \chi_{FS} + \chi_{occ} \) as shown in (2.28).
Appendix C: Proof of equivalence of the present result with that obtained by HLSS

In this Appendix, we prove the equivalence of the present result with HLSS’s result; eqs. (4.3)-(4.6) in Ref.\(^{13}\) (or equivalently eqs. (53)-(56) in Ref.\(^{12}\)). In the notation of the present paper, their result is given by

\[
\chi_{(HLSS)} = \chi_{1}^{(HLSS)} + \chi_{2}^{(HLSS)} + \chi_{3}^{(HLSS)} + \chi_{4}^{(HLSS)},
\]

where

\[
\chi_{1}^{(HLSS)} = \frac{e^2}{\hbar c^2} \sum_{\ell, k} f'(e_\ell) \left\{ \frac{\partial^2 \epsilon_\ell}{\partial k^2} \frac{\partial \epsilon_\ell}{\partial k} - \left( \frac{\partial^2 \epsilon_\ell}{\partial k, \partial k} \right)^2 + \frac{3}{2} \left( \frac{\partial \epsilon_\ell}{\partial k, \partial k, \partial k} + \frac{\partial \epsilon_\ell}{\partial k, \partial k} \right) \right\},
\]

\[
\chi_{2}^{(HLSS)} = \frac{2e^2}{\hbar c^2} \sum_{\ell, k} f'(e_\ell) \frac{\partial \epsilon_\ell}{\partial k} \left\{ \frac{\partial u^+_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr - \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} dr - \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} dr \right\},
\]

\[
\chi_{3}^{(HLSS)} = \frac{4e^2}{\hbar c^2} \sum_{\ell, k} f'(e_\ell) \left\{ \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} u_{ik} dr - \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} u_{ik} dr + \frac{\partial u^+_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\}^2.
\]

\[
\chi_{4}^{(HLSS)} = \frac{2e^2}{\hbar c^2} \sum_{\ell, k} \frac{\hbar^2}{m} f'(e_\ell) \left\{ \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} u_{ik} dr - \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} u_{ik} dr + \frac{\partial u^+_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\}^2.
\]

First, using the complex conjugate of (B-17), we rewrite the last term of \(\chi_{4}^{(HLSS)}\) as

\[
-\frac{e^2}{\hbar c^2} \sum_{\ell \neq \ell', k} f'(e_\ell - e_{\ell'}) \left\{ \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} u_{ik} dr - \frac{\partial u^+_{ik}}{\partial k} \frac{\partial H_k}{\partial k_\ell} u_{ik} dr + \frac{\partial u^+_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\}^2.
\]

Then combining with \(\chi_{3}^{(HLSS)}\), we obtain

\[
\chi_{3}^{(HLSS)} + \text{last term of } \chi_{4}^{(HLSS)} = -\frac{e^2}{\hbar c^2} \sum_{\ell \neq \ell', k} \frac{f'(e_\ell)}{(e_\ell - e_{\ell'})} \left\{ \frac{\partial u^+_{ik}}{\partial k} \left( \frac{\partial H_k}{\partial k_\ell} + \frac{\partial \epsilon_\ell}{\partial k} \right) u_{ik} dr - \frac{\partial u^+_{ik}}{\partial k} \left( \frac{\partial H_k}{\partial k_\ell} + \frac{\partial \epsilon_\ell}{\partial k} \right) u_{ik} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\}^2
\]

\[
+2(e_\ell - e_{\ell'}) \text{Re} \left\{ \frac{\partial u^+_{ik}}{\partial k} \left( \frac{\partial H_k}{\partial k_\ell} + \frac{\partial \epsilon_\ell}{\partial k} \right) u_{ik} dr - \frac{\partial u^+_{ik}}{\partial k} \left( \frac{\partial H_k}{\partial k_\ell} + \frac{\partial \epsilon_\ell}{\partial k} \right) u_{ik} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\}^2
\]

\[
-\frac{e^2}{\hbar c^2} \sum_{\ell \neq \ell', k} \frac{f'(e_\ell)}{(e_\ell - e_{\ell'})} \left\{ \frac{\partial u^+_{ik}}{\partial k} \left( \frac{\partial H_k}{\partial k_\ell} + \frac{\partial \epsilon_\ell}{\partial k} \right) u_{ik} dr - \frac{\partial u^+_{ik}}{\partial k} \left( \frac{\partial H_k}{\partial k_\ell} - \frac{\partial \epsilon_\ell}{\partial k} \right) u_{ik} dr \right\} \frac{\partial u_{ik}}{\partial k} \frac{\partial \epsilon_\ell}{\partial k_\ell} \frac{\partial u_{ik}}{\partial k} \frac{\partial u_{ik}}{\partial k} dr \right\} + \frac{\partial ^2 \epsilon_{ik}}{\partial k_\ell \partial k_\ell} (e_\ell - H_k) \frac{\partial ^2 u_{ik}}{\partial k_\ell \partial k_\ell} dr \right\}.
\]

where we have used the completeness property of \(u_{\ell k}\). Now the first term on the right-hand side is the same as \(\chi_{\text{inter}}\) of
eq. (2.30). The second summation can be rewritten by using the complex conjugate of eq. (A-5) as

\[- \frac{e^2}{\hbar^2 c^2} \sum_{i,k} f(e_i) \left\{ \int \frac{\partial u_{ik}^*}{\partial k_y} \left( 3 \frac{\partial H_k}{\partial k_x} + \frac{\partial^2 u_{ik}}{\partial k_x^2} \right) dr - \int \frac{\partial u_{ik}^*}{\partial k_x} \left( \frac{\partial H_k}{\partial k_y} + \frac{\partial^2 u_{ik}}{\partial k_x \partial k_y^2} \right) dr \right\} \]

\[= - \frac{e^2}{\hbar^2 c^2} \sum_{i,k} f(e_i) \left\{ \frac{1}{2} \frac{\partial}{\partial k_x} \left[ \int \frac{\partial u_{ik}^*}{\partial k_y} \left( 3 \frac{\partial H_k}{\partial k_x} + \frac{\partial^2 u_{ik}}{\partial k_x^2} \right) dr \right] - \frac{1}{2} \frac{\partial}{\partial k_y} \left[ \int \frac{\partial u_{ik}^*}{\partial k_x} \left( \frac{\partial H_k}{\partial k_y} + \frac{\partial^2 u_{ik}}{\partial k_x \partial k_y^2} \right) dr \right] \right\} \]

\[- \left( \frac{3 \hbar^2}{2 m} + \frac{1}{2} \frac{\partial^2 e_i}{\partial k_y^2} \right) \int \frac{\partial u_{ik}^*}{\partial k_y} \frac{\partial u_{ik}}{\partial k_x} dr + \left( \frac{\hbar^2}{2 m} - \frac{1}{2} \frac{\partial^2 e_i}{\partial k_x^2} \right) \int \frac{\partial u_{ik}^*}{\partial k_x} \frac{\partial u_{ik}}{\partial k_y} dr + \frac{\partial^2 e_i}{\partial k_x \partial k_y} \int \frac{\partial u_{ik}^*}{\partial k_x} \frac{\partial u_{ik}}{\partial k_y} dr \right\}. \tag{C.4} \]

where we have used (A-9) and (A-10). We find that the last three terms plus the first term of \( \chi^{(HLS)} \) are equal to \( \chi^\text{occ} \) in (2.32).

Using these relations and integration by parts, we can now write

\[\chi^{(HLS)} = \chi_{LP} + \chi_{\text{inter}} + \chi^\text{occ} + \frac{e^2}{\hbar^2 c^2} \sum_{i,k} f'(e_i) \left\{ \frac{\partial e_i}{\partial k_x} \frac{\partial^2 e_i}{\partial k_x^2} + \frac{\partial e_i}{\partial k_y} \frac{\partial^2 e_i}{\partial k_y^2} \right\} \]

\[+ \frac{e^2}{\hbar^2 c^2} \sum_{i,k} f'(e_i) \left\{ \frac{\partial e_i}{\partial k_x} \left[ \frac{3}{2} \frac{\partial H_k}{\partial k_x} + \frac{1}{2} \frac{\partial^2 u_{ik}}{\partial k_x \partial k_y^2} \right] \frac{\partial u_{ik}}{\partial k_y} dr - \frac{\partial e_i}{\partial k_y} \left[ \frac{3}{2} \frac{\partial H_k}{\partial k_y} + \frac{1}{2} \frac{\partial^2 u_{ik}}{\partial k_x \partial k_y^2} \right] \frac{\partial u_{ik}}{\partial k_x} dr \right\} \tag{C.5} \]

The fourth term can be rewritten in terms of \( u_{ik} \) as carried out in eq. (2.27). Then collecting all the terms, we obtain

\[\chi^{(HLS)} = \chi_{LP} + \chi_{\text{inter}} + \chi^\text{occ} + \frac{e^2}{\hbar^2 c^2} \sum_{i,k} f'(e_i) \left\{ 2 \frac{\partial e_i}{\partial k_x} \int \frac{\partial u_{ik}^*}{\partial k_y} \frac{\partial H_k}{\partial k_x} + \frac{\partial e_i}{\partial k_y} \frac{\partial^2 u_{ik}}{\partial k_x \partial k_y^2} dr \right\} \]

\[+ \frac{\partial e_i}{\partial k_y} \int \frac{\partial u_{ik}^*}{\partial k_x} \frac{\partial u_{ik}}{\partial k_y} dr - \frac{\partial e_i}{\partial k_x} \int \frac{\partial u_{ik}^*}{\partial k_y} \frac{\partial u_{ik}}{\partial k_x} dr \right\} \tag{C.6} \]

Apparently (C.6) is not symmetric with respect to the exchange of \( x \) and \( y \). This is because HLS used the Landau gauge \( A = (-yH, 0, 0) \). As mentioned by Heiborn and Sondheimer if the other gauge \( A = (0, xH, 0) \) is chosen, a result in which \( x \) and \( y \) interchanged will be obtained. Thus by taking the average of this expression and the original one, we can have a result that is symmetric with respect to \( x \) and \( y \). After this symmetrization, we can see that (C.6) is equal to \( \chi = \chi_{LP} + \chi_{\text{inter}} + \chi_{\text{FS}} + \chi^\text{occ} \).

**Appendix D: Comparison of the present result with that obtained by Gao et al**

In this Appendix, we compare our results with those obtained by Gao et al\(^{36}\) in the case where the time-reversal symmetry is not broken and the Berry curvature \( \Omega_2 \) is equal to zero. In this case, the thermodynamic potential per spin in the second order of \( B \) becomes (see eq. (6) in Ref.\(^{36}\))

\[\frac{\hbar^2 c^2}{2e^2} \Omega^{(2)} = g_L - \sum_{i,k} \frac{f'(e_i)}{4} v_0 \cdot P_E + \sum_{i \neq k} \frac{f'(e_i)}{4} G_{E \ell} G_{E \ell}^* + \sum_{i,k} \frac{f'(e_i)}{8m} \left( B^2 g_{ii} - B_i g_{ij} B_j - \sum_{i,k} \frac{f'(e_i)}{8} e_{i k l} e_{j k l} B_i B_j g_{i j} \alpha_{i j} \right), \tag{D.1} \]

where \( g_L \) represents the Landau-Peierls term and the repeated indices \( i, j, k \) etc. on the right-hand side are summed over. Various quantities are defined as follows:\(^{36}\)

\[P_E = \frac{1}{4} \left[ \int (B \times \hat{D}) u_{ik}^* (\hat{V} + v_0) \cdot (B \times \hat{D}) u_{ik} dr + \text{c.c.} \right], \]

\[G_{E \ell} = -B \cdot M_{E \ell}, \quad M_{E \ell} = \frac{1}{2} \sum_{\ell' \neq \ell} \sum_{i \neq k} V_{E \ell, \ell'} A_{E \ell, \ell'} + v_0 \cdot A_{E \ell, \ell}, \tag{D.2} \]

\[g_{ii} = \int \frac{\partial u_{ik}^*}{\partial k_i} \frac{\partial u_{ik}}{\partial k_j} dr, \quad \alpha_{ij} = \frac{\partial^2 e_i}{\partial k_i \partial k_j}, \]

\[=16\]
where \( \hat{V} = -\frac{i}{\hbar} [\hat{r}, \hat{H}] \), \( v_0 = \int u_{i k}^\dagger \hat{V} u_{\ell k} dr \), \( V_{\ell \ell'} = \int u_{i k}^\dagger \hat{V} u_{\ell k} dr \), and \( \hat{D} = \frac{\partial}{\partial k} + i a_0 \). The quantities, \( a_0 \) and \( A_{\ell \ell'} \), are intraband and interband Berry connection, respectively, defined as

\[
a_0 = i \int u_{i k}^\dagger \frac{\partial u_{i k}}{\partial k} dr, \quad A_{\ell \ell'} = i \int u_{i k}^\dagger \frac{\partial u_{i k}}{\partial k} dr. \tag{D-3}
\]

In our Hamiltonian with \( V(-r) = V(r) \) and with time-reversal symmetry, \( a_0 \) is equal to zero as shown in (A-8). \( A_{\ell \ell'} \) is a well-known quantity in the literatures,\(^{12, 41, 42} \), and it appears in \( p_{\ell \ell'} \) (eq. (2.9)) in the present formalism. Gao et al defined \( \hat{H}_0 \) as the Hamiltonian without external field.\(^{36} \) In the present notation, it should be \( H_k \). Then, the velocity operator \( \hat{V} \) is just \( \partial H_k / \partial k \). Therefore, their \( v_0 \) should be simply equal to \( \partial \epsilon_\ell / \partial k \), as shown in (2.8). Then, the \( \mu \) component of \( P_E \) can be rewritten as

\[
P_{E,\mu} = \frac{1}{4} \left[ \epsilon_{\mu \nu \tau} \epsilon_{\mu' \nu' \tau'} B_{\nu' \tau'} \int \frac{\partial u_{i k}^\dagger}{\partial k} \left( \frac{\partial H_k}{\partial k_{\mu'}} + \frac{\partial \epsilon_\ell}{\partial k_{\mu'}} \right) \frac{\partial u_{i k}}{\partial k} dr + c.c. \right]. \tag{D-5}
\]

By putting \( B = (0, 0, B) \), we can show that the second term in (D-1) corresponds to \( \chi_{\text{FS}} \), but its coefficient is half of our result.

Next, let us study \( M_{\ell \ell'} \). We can rewrite the \( \mu \) component of \( M_{\ell \ell'} \) as

\[
M_{\ell \ell'} = \frac{i}{2} \epsilon_{\mu \nu \tau} \left( \sum_{\ell' \neq \ell} \int u_{i k}^\dagger \frac{\partial H_k}{\partial k_{\nu'}} u_{\ell' k}^\dagger \int u_{i k}^\dagger \frac{\partial u_{i k}}{\partial k_{\tau}} dr + \frac{\partial \epsilon_\ell}{\partial k_{\nu'}} \int u_{i k}^\dagger \frac{\partial u_{i k}}{\partial k_{\tau}} dr \right). \tag{D-6}
\]

By using the completeness property of \( u_{i k}^\dagger \), we can show that \( M_{\ell \ell'} \) is rewritten as

\[
M_{\ell \ell'} = \frac{i}{2} \epsilon_{\mu \nu \tau} \int u_{i k}^\dagger \left( \frac{\partial H_k}{\partial k_{\nu'}} + \frac{\partial \epsilon_\ell}{\partial k_{\nu'}} \right) \frac{\partial u_{i k}}{\partial k_{\tau}} dr. \tag{D-7}
\]

in our case. Therefore, the third term in (D-1) turns out to be exactly equal to \( \chi_{\text{inter}} \).

Similarly, the total of fourth and fifth terms in (D-1) is equal to \( \chi_{\text{occ}} \) in our results. Thus we can show that Gao et al’s results (D-1) are almost equivalent to our result except for the coefficient of \( \chi_{\text{FS}} \).
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