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# Rigorous theory for chemical shifts in crystal: Application to graphite

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A rigorous theory for chemical shifts in crystal is developed. In this formalism, it is clearly seen that the shielding tensor is divided into a demagnetizing term and a microscopic term. The former is caused by the demagnetizing field and is proportional to the bulk susceptibility. The latter is caused by a periodic current, which is, in the atomic limit, reduced to the ordinary expression for the shielding tensor by Ramsey. A new expression for the shielding tensor for the on-site approximation is derived based on the rigorous theory. The present theory is applied to graphite, and it is shown that the temperature-dependent part of the observed shift is due to the demagnetizing term.

## I. INTRODUCTION

The magnetic interactions between a nucleus and electrons bring about a deviation of the magnetic field experienced by the nucleus from an external field. This phenomenon is observed in the slight shift of the resonance frequency in an NMR measurement. There are two kinds of such shifts: the Knight shift and the chemical shift. The Knight shift is caused by dipole-dipole interactions between the nuclear spin and the electron spin. It is seen in metals and provides information on density of states. The chemical shift is caused by the electrons' orbital motion. Because of the significant dependence on the local electronic structure near the nucleus, the chemical shift is used as a powerful probe of the bonding structure of molecules.

Theoretically, the chemical shift has been studied for a long time. The general theory of the chemical shift was given by Ramsey.[1] By second-order perturbation theory, he derived the expression of a shielding tensor consisting of paramagnetic and diamagnetic terms. Ramsey's expression is general and applicable to any system in principle. In the case of large systems, however, it causes a serious problem. Namely, the long-range parts of the paramagnetic and the diamagnetic terms are divergently large and cancel each other. To remove this difficulty, several refinements have been made,[2,3] but they are effective only for molecules which are finite systems, so cannot be applied to crystals.

The chemical shift of periodic lattice was discussed by Stephen[4] and Hebborn.[5] With the devices used in the calculation of orbital susceptibility, they succeeded in removing the difficulty of large cancellation. In their theory, however, the demagnetizing term which depends on the shape of the specimen was discussed with using the macroscopic theory of classical electrodynamics, so was not derived microscopically. Furthermore, they showed only the general expression of shielding tensor which is too complicated to calculate numerically. This might be the reason why the importance of their works has not been recognized and the expression derived by them has not been used in the actual calculations.

The expressions[6] used in the actual calculations for crystals are based on the Ramsey's expression. The problem of these expressions is that they are derived with questionable approximations that ignore the difficulty of the large cancellation. Such expressions are also dissatisfactory in the point that they can not include the long-range part. Vaughan *et al.*[7] proposed a formalism in which the long-range part is included as a bulk correction using the local-field theory. However, usual local-field theory is valid only for the point magnetic dipole moment, so cannot be applied to such cases that the magnetization is induced by free electrons. Therefore, the formalism by Vaughan *et al.* is not general.

One of the reasons the long-range part has not yet been discussed seriously is its smallness in most materials. Usually, the orbital susceptibility is so small that the bulk correction is not needed. However, high-resolution measurement of NMR shift in graphite was recently performed and the shift largely related to the susceptibility was reported.[8] To explain the observed fact, a rigorous chemical shift formalism for crystal is needed.

In the present paper, we derive a general chemical shift expression for crystals. For this purpose, we calculate the shielding tensor in a different way from the formalisms proposed so far. Before we see method's details, in Sec. II we clarify the difficulties in the ordinary chemical shift formalisms applied to crystal. In Sec. III, the new method of calculation of the shielding tensor is described, where the current density is shown to be divided into magnetizing terms and microscopic terms. In Secs. IV and V, the magnetizing term and the microscopic terms are discussed in detail, respectively. In Sec. VI, the present formalism is applied to explain the observed NMR shift in graphite. In the present paper, we use the unit $\hbar = 1$.

## II. DIFFICULTIES IN RAMSEY'S THEORY OF CHEMICAL SHIFT APPLIED TO CRYSTAL

Resonance shift in NMR is defined in terms of the change of the interaction energy between a nuclear magnetic moment $\boldsymbol{\mu}$ and external magnetic field $\mathbf{B}^0$ as

$$E_0 + \Delta E = -\boldsymbol{\mu} \cdot (1 - \sigma) \cdot \mathbf{B}^0 , \tag{2.1}$$

where $\sigma$ is called shielding tensor. In the case of chemical shift, this interaction energy is expressed as[9]

$$\Delta E=-\boldsymbol{\mu}\cdot\frac{1}{c}\int\frac{\mathbf{r}\times\mathbf{J}}{r^3}d^3r\ , \tag{2.2}$$

where $\mathbf{J}$ is current density defined as

$$\mathbf{J}=\frac{e}{2mi}(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*)-\frac{e^2}{mc}\mathbf{A}\,|\Psi|^2\ . \tag{2.3}$$

If we take Landau gauge

$$\mathbf{A}=\tfrac{1}{2}\mathbf{B}^0\times\mathbf{r} \tag{2.4}$$

for vector potential and calculate the first-order term of the current density in the external magnetic field, Ramsey's expression

$$\begin{aligned}\sigma&=\sigma^{(p)}+\sigma^{(d)}\ ,\\ \sigma^{(p)}&=-\frac{e^2}{m^2c}\sum_{i\cdot j}\frac{\langle i\,|\,\mathbf{L}/r^3\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,i\rangle}{\varepsilon_j-\varepsilon_i}\ ,\\ \sigma^{(d)}&=\frac{e^2}{2mc^2}\sum_i\left\langle i\left|\frac{r^2I-\mathbf{rr}}{r^3}\right|i\right\rangle\ ,\end{aligned} \tag{2.5}$$

is obtained. This is not convenient for crystals, since it is not explicitly seen that the shielding tensor is independent of the gauge of the vector potential. In spite of this inconvenience, Ramsey's expression has been used for the calculation of crystals. As is the wave function of the system, the Bloch orbital is adopted and expressed as a linear combination of atomic orbitals:

$$\psi_{l\mathbf{k}}=\frac{1}{\sqrt{N}}\sum_{\mu,\mathbf{R}}A_{l\mu}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}}\phi_\mu(\mathbf{r}-\mathbf{R})\ . \tag{2.6}$$

Substituting it into (2.5) and neglecting the terms except for $\mathbf{R}=0$, which we call on-site approximation, hereafter, the expressions

$$\sigma^{(p)}=-\frac{e^2}{2m^2c^2}\sum_{l,l',\mathbf{k},\mathbf{k}'}\ \sum_{\mu,\nu,\lambda,\zeta}\frac{A^*_{l'\lambda}(\mathbf{k}')A_{l'\mu}(\mathbf{k}')A^*_{l\nu}(\mathbf{k})A_{l\zeta}(\mathbf{k})}{\varepsilon_{l'}(\mathbf{k}')-\varepsilon_l(\mathbf{k})}\times\left[\left\langle\phi_\nu\left|\frac{\mathbf{L}}{r^3}\right|\phi_\mu\right\rangle\langle\phi_\lambda\,|\,\mathbf{L}\,|\,\phi_\zeta\rangle+\left\langle\phi_\lambda\left|\frac{\mathbf{L}}{r^3}\right|\phi_\zeta\right\rangle\langle\phi_\nu\,|\,\mathbf{L}\,|\,\phi_\mu\rangle\right]\ , \tag{2.7}$$

$$\sigma^{(d)}=\frac{e^2}{2mc^2}\sum_{l,\mathbf{k}}\sum_{\mu,\nu}A^*_{l\mu}(\mathbf{k})A_{l\nu}(\mathbf{k})\left\langle\phi_\mu\left|\frac{r^2I-\mathbf{rr}}{r^3}\right|\phi_\nu\right\rangle\ , \tag{2.8}$$

are obtained. These are the expressions which have been used for calculating the crystal shielding tensor. However, there are two problems. One is that there is no validity in the on-site approximation. In Ramsey's expression (2.5), the matrix elements of angular momentum between the eigenstates are needed. The matrix elements, however, are not definite for the extended eigenfunctions as are Bloch orbitals. Therefore, one cannot assure any validity in replacing the matrix element $\langle i\,|\,\mathbf{L}\,|\,j\rangle$ by the angular momentum of atomic orbital.

The other problem is that since long-range contribution is not included, the shift that is proportional to the bulk susceptibility cannot been explained. In the formalism by Vaughan *et al.*,[7] the long-range contribution is taken into account using the ordinary local field theory. In this formalism, the bulk correction is the sum of the demagnetizing and the Lorentz term:

$$\mathbf{H}=-D\mathbf{M}+\tfrac{4}{3}\pi\mathbf{M}\ . \tag{2.9}$$

Here, $D$ is the demagnetizing factor. However, this formalism is valid only when the current is so localized near the atoms that the magnetic moment is reasonably approximated by point dipole. On the other hand, in the case of free electron, the bulk correction is different from Eq. (2.9). Kubo[10] discussed the Landau diamagnetization with the use of Wigner representation and showed that the current density of free electrons in a given potential field $V(\mathbf{r})$ is written as

$$\mathbf{J}=\tfrac{1}{3}c\beta\mu_B^2\mathbf{B}^0\times\nabla n(\mathbf{r})\ , \tag{2.10}$$

where $n$ is the electron density given by

$$n(\mathbf{r})=Ne^{-\beta v(\mathbf{r})}\Big/\int e^{-\beta v}d^3r\ , \tag{2.11}$$

where $N$ is the total electron number. The magnetic field induced by the current (2.10) can be calculated as

$$\mathbf{B}=\int\left[\frac{3\mathbf{rr}-r^2}{r^3}+\frac{8\pi}{3}\delta(\mathbf{r})\right]\mathbf{M}d^3r\ , \tag{2.12}$$

with

$$\mathbf{M}=\chi\mathbf{B}^0\ , \tag{2.13}$$

where $\chi$ is

$$\chi=-\tfrac{1}{3}\beta\mu_B^2n\ , \tag{2.14}$$

which is the free electrons susceptibility. The expression (2.12) is the same as the magnetic field induced by the magnetization $\mathbf{M}$. Therefore, the bulk correction of free electrons is only the demagnetizing term:

$$\mathbf{H}=-D\mathbf{M}\ . \tag{2.15}$$

So, the usual local field theory is not general and the formalism which connects these limiting cases is needed.

## III. CALCULATION OF CURRENT DENSITY

As seen in Sec. II, the theories of chemical shift for crystals which are commonly used are not general and have some difficulties. To remove the difficulties and deal with general cases, a rigorous chemical shift formalism for crystals is needed. For this aim, we calculate the current density in this section.

From Eq. (2.2), we see that the first-order term of the current density in external magnetic field is needed to calculate the shielding tensor. In the calculation of current density for crystals, the Landau gauge is not convenient, since it is not periodic and causes the unphysically large cancellation of the paramagnetic term and the diamagnetic term. A similar situation occurs in the calculation of magnetic susceptibility. To remove the difficulty of the large cancellation, the following technique has been successfully used.[11–13] Namely, the vector potential is introduced in the form of

$$\mathbf{A}(\mathbf{r})=\frac{\mathbf{A}_{\mathbf{q}}}{i}(e^{i\mathbf{q}\cdot\mathbf{r}}-e^{-i\mathbf{q}\cdot\mathbf{r}}) \equiv \mathbf{A}^{(+)}(\mathbf{r})+\mathbf{A}^{(-)}(\mathbf{r}) , \tag{3.1}$$

and the limit $\mathbf{q}\rightarrow 0$ was taken in the final expression. In the calculation of the current density, we also use the same device.

The Hamiltonian of electrons in the magnetic field is written as

$$\begin{aligned}\mathcal{H}&=\frac{1}{2m}\left[\mathbf{p}-\frac{e}{c}\mathbf{A}\right]^2+V(\mathbf{r})\\ &=\left[\frac{\mathbf{p}^2}{2m}+\mathbf{v}(\mathbf{r})\right]-\frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}+\mathbf{p})+\frac{e^2}{2mc^2}\mathbf{A}^2\\ &\equiv\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2 ,\end{aligned} \tag{3.2}$$

where $\mathcal{H}_n$ is the $n$th-order term in the magnetic field. For the basis function, we adopt the Luttinger-Kohn (LK) function[14] defined as

$$\chi_{l\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}\mathcal{U}_{l0} , \tag{3.3}$$

where $u_{l\mathbf{k}}$ is the periodic part of Bloch function

$$\psi_{l\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}\mathcal{U}_{l\mathbf{k}} . \tag{3.4}$$

As will be seen later, we need only terms $\mathcal{H}_0,\mathcal{H}_1$ in the calculation of current density, so we omit the term $\mathcal{H}_2$ hereafter. To express the Hamiltonian in LK representation, we expand the field operator in terms of LK functions:

$$\Psi=\sum_l\int d^3k\,\chi_{l\mathbf{k}}A_{l\mathbf{k}} . \tag{3.5}$$

Then, the Hamiltonian can be expressed as

$$\mathcal{H}_0=\sum_{l,l'}\int d^3k\,E_{ll'}(\mathbf{k})A^\dagger_{l\mathbf{k}}A_{l'\mathbf{k}} , \tag{3.6}$$

$$\mathcal{H}_1=-\frac{e}{mci}\mathbf{A}_{\mathbf{q}}\cdot(\mathbf{j}_{\mathbf{q}}-\mathbf{j}_{-\mathbf{q}}) , \tag{3.7}$$

where

$$E_{ll'}(\mathbf{k})=\left[\frac{k^2}{2m}+\varepsilon_l(0)\right]\delta_{ll'}+\frac{\mathbf{k}\cdot\mathbf{P}_{ll'}}{m} , \tag{3.8}$$

$$\mathbf{P}_{ll'}=\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}\mathcal{U}^*_{l0}\frac{1}{i}\nabla\mathcal{U}_{l'0}d^3r , \tag{3.9}$$

$\Omega$ is the volume of a unit cell,

$$\mathbf{j}_{\mathbf{q}}=\sum_{ll'}\int d^3k\,\gamma\,A^\dagger_{l\mathbf{k}^+}A_{l'\mathbf{k}^-} , \tag{3.10}$$

$$\gamma(\mathbf{k})_{ll'}=\mathbf{k}\delta_{ll'}+\mathbf{P}_{ll'} , \tag{3.11}$$

$$\mathbf{k}^{\pm}=\mathbf{k}\pm\frac{\mathbf{q}}{2} , \tag{3.12}$$

and $\varepsilon_l(0)$ is the energy of $l$th band at $\mathbf{k}=0$. The current-density operator is also written in this representation as

$$\mathbf{J}=\mathbf{J}^{(p)}+\mathbf{J}^{(d)} , \tag{3.13}$$

$$\mathbf{J}^{(p)}=\frac{e}{2mi}\sum_{l,l'}\int d^3k\int d^3k'(\chi^*_{l\mathbf{k}}\nabla\chi_{l'\mathbf{k}'}-\chi_{l'\mathbf{k}'}\nabla\chi^*_{l\mathbf{k}})A^\dagger_{l\mathbf{k}}A_{l'\mathbf{k}'} , \tag{3.14}$$

$$\mathbf{J}^{(d)}=-\frac{e^2}{mc}\mathbf{A}\sum_{l,l'}\int d^3k\int d^3k'\,\chi^*_{l\mathbf{k}}\chi_{l'\mathbf{k}'}A^\dagger_{l\mathbf{k}}A_{l'\mathbf{k}'} . \tag{3.15}$$

To calculate the linear term in the magnetic field, we expand the density matrix in powers of the magnetic field:

$$\rho=\rho_0+\rho_1+\cdots , \tag{3.16}$$

where

$$\rho_0=\frac{1}{Z_0}e^{-\beta\mathcal{H}_0} , \tag{3.17}$$

$$\rho_1=-\frac{1}{Z_0}\int_0^\beta d\lambda\,e^{-(\beta-\lambda)\mathcal{H}_0}\mathcal{H}_1e^{-\lambda\mathcal{H}_0} , \tag{3.18}$$

with

$$Z_0=\text{Tr}(e^{-\beta\mathcal{H}_0}) . \tag{3.19}$$

By taking the thermal average, we have the current density term which is linear in the magnetic field.

$$\begin{aligned}\langle \mathbf{J} \rangle &= \mathrm{Tr}(\mathbf{J}^{(p)}\rho_1)+\mathrm{Tr}(\mathbf{J}^{(d)}\rho_0)\\ &\equiv \langle \mathbf{J}^{(p)} \rangle + \langle \mathbf{J}^{(d)} \rangle \ ,\end{aligned} \tag{3.20}$$

$$\begin{aligned}\langle \mathbf{J}^{(p)} \rangle = -\frac{e^2}{2m^2 c\beta i} \sum_{l,l',n} \int d^3k (\chi^*_{l\mathbf{k}} \nabla \chi_{l'\mathbf{k}} - \chi_{l'\mathbf{k}} \nabla \chi^*_{l\mathbf{k}})\\ \times [\mathcal{G}(\mathbf{k}^+)(\mathbf{A}^{(+)}\cdot\gamma)\mathcal{G}(\mathbf{k}^-)+\mathcal{G}(\mathbf{k}^-)(\mathbf{A}^{(-)}\cdot\gamma)\mathcal{G}(\mathbf{k}^+)]_{l'l} \ ,\end{aligned} \tag{3.21}$$

$$\langle \mathbf{J}^{(d)} \rangle = -\frac{e^2}{mc\beta} \mathbf{A} \sum_{l,l',n} \int d^3k \, \chi^*_{l\mathbf{k}} \chi_{l'\mathbf{k}} \mathcal{G}_{l'l}(\mathbf{k}) \ . \tag{3.22}$$

In the above expression, $\mathcal{G}$ is the thermal Green's function defined as

$$\begin{aligned}\mathcal{G}_{ll'}(\mathbf{k};i\varepsilon_n) &= \int_0^\beta d\lambda \, e^{i\varepsilon_n \lambda} G_{ll'}(\mathbf{k};\lambda)\\ &= [i\varepsilon_n + \mu - E(\mathbf{k})]^{-1}_{ll'} \ ,\end{aligned} \tag{3.23}$$

where

$$-\langle TA_{l\mathbf{k}}(\lambda) A^\dagger_{l'\mathbf{k}'}(\lambda') \rangle_0 = \delta(\mathbf{k}-\mathbf{k}') G_{ll'}(\mathbf{k};\lambda-\lambda') \ , \tag{3.24}$$

$$A_{l\mathbf{k}}(\lambda) = e^{\lambda \mathcal{H}_0} A_{l\mathbf{k}} e^{-\lambda \mathcal{H}_0} \ , \tag{3.25}$$

$$\varepsilon_n = \frac{2n+1}{\beta}\pi \ , \tag{3.26}$$

and we define

$$\langle \cdots \rangle \equiv \mathrm{Tr}(\cdots \rho_0) \ . \tag{3.27}$$

Expanding the Green's function of the paramagnetic current in powers of **q** as

$$\langle \mathbf{J}^{(P)} \rangle = \langle \mathbf{J}^{(P)} \rangle_0 + \langle \mathbf{J}^{(P)} \rangle_1 + \langle \mathbf{J}^{(P)} \rangle_2 + \cdots \ , \tag{3.28}$$

and using the identity

$$\mathcal{G}\gamma\mathcal{G} = m\frac{\partial \mathcal{G}}{\partial \mathbf{k}} \ , \tag{3.29}$$

it can be shown that the zeroth-order term of the paramagnetic current cancels the diamagnetic current

$$\langle \mathbf{J}^{(P)} \rangle_0 + \langle \mathbf{J}^{(d)} \rangle = 0 \ , \tag{3.30}$$

and the first-order term can be written in the limit **q**→0 as follows:

$$\begin{aligned}\langle \mathbf{J}^{(P)} \rangle_1 = -\frac{ie^2}{4m^3 c\beta} \sum_{l,l'n} \int d^3k (\chi^*_{l\mathbf{k}} \nabla \chi_{l'\mathbf{k}} - \chi_{l'\mathbf{k}} \nabla \chi^*_{l\mathbf{k}})\\ \times (\mathcal{G}\gamma_\mu \mathcal{G}\gamma_\nu \mathcal{G})_{l'l} \epsilon_{\mu\nu\lambda} B^0_\lambda\\ \equiv \mathbf{J}^{\mathrm{mic}} \ .\end{aligned} \tag{3.31}$$

This current has the lattice periodicity and is, on average, zero in a unit cell. So, hereafter we call this the microscopic current. The magnetic field induced by this current is expressed as

$$\begin{aligned}\mathbf{B}^{\mathrm{mic}} &\equiv \frac{1}{c}\int \frac{\mathbf{r}\times\mathbf{J}^{\mathrm{mic}}}{r^3} d^3r\\ &= -\frac{ie^2}{2m^3 c\beta} \sum_n \int d^3k \, \mathrm{Tr}(l\mathcal{G}\gamma_\mu \mathcal{G}\gamma_\nu \mathcal{G}) \epsilon_{\mu\nu\lambda} B^0_\lambda \ ,\end{aligned} \tag{3.32}$$

where $l$ is defined with the angular momentum **L** as

$$l_{ll'} = \int \chi^*_{l\mathbf{k}} \frac{\mathbf{L}}{r^3} \chi_{l'\mathbf{k}} d^3r \ . \tag{3.33}$$

Though the terms higher than this goes to zero as **q**→0, we cannot neglect the second-order term,

$$\begin{aligned}\langle \mathbf{J}^{(P)} \rangle_2 = -\frac{e^2}{2m^2 c\beta} \sum_{l,l',n} \int d^3k \left[ \chi^*_l \frac{\nabla}{i} \chi_{l'} - \chi_{l'} \frac{\nabla}{i} \chi^*_l \right] A^\sigma(\mathbf{r}) \frac{q_\alpha q_\beta}{8}\\ \times (\mathcal{G}\gamma^\sigma \partial_\alpha \partial_\beta \mathcal{G} + \partial_\alpha \partial_\beta \mathcal{G}\gamma^\sigma \mathcal{G} - \partial_\alpha \mathcal{G}\gamma^\sigma \partial_\beta \mathcal{G} - \partial_\beta \mathcal{G}\gamma^\sigma \partial_\alpha \mathcal{G})_{ll'}\\ \equiv \mathbf{J}^{\mathrm{mag}} \ .\end{aligned} \tag{3.34}$$

This is because $\mathbf{J}^{\mathrm{mag}}$ is the current which induces the bulk magnetic moment, as will be discussed in the next section.

## IV. MAGNETIZING CURRENT

In this section, we look into the physical implication of the current density $\mathbf{J}^{\mathrm{mag}}$ defined in (3.4). As mentioned in Sec. III, the total magnetic moment is induced only by this current. To see this, we calculate the total magnetic moment:

$$\mathbf{M} = \frac{1}{2c}\int \mathbf{r}\times\mathbf{J}^{\mathrm{mag}} d^3r \ . \tag{4.1}$$

The integral of the above is mainly contributed by the region with large **r**, where the oscillation with lattice periodicity can be neglected. So, the following term in $\mathbf{J}^{\mathrm{mag}}$ [see Eq. (3.34)] can be approximated by the average value in unit cell.

$$\frac{1}{i}(\chi_{l\mathbf{k}}^{*}\nabla\chi_{l'\mathbf{k}}-\chi_{l'\mathbf{k}}\nabla\chi_{l\mathbf{k}}^{*})\simeq\frac{1}{\Omega}\int_{\text{cell}}\frac{1}{i}(\chi_{l\mathbf{k}}^{*}\nabla\chi_{l'\mathbf{k}}-\chi_{l'\mathbf{k}}\nabla\chi_{l\mathbf{k}}^{*})d^{3}r=\frac{2}{(2\pi)^{3}}\gamma_{ll'}\ . \tag{4.2}$$

With this approximation, the magnetic moment can be expressed as (see Appendix A)

$$M_{Z}=\int m_{Z}(\mathbf{r})d^{3}r\ , \tag{4.3}$$

$$m_{Z}(\mathbf{r})=\frac{4\mu_{B}^{2}}{m^{2}\beta}\sum_{n}\frac{1}{(2\pi)^{3}}\int d^{3}r\,\mathrm{Tr}(\gamma_{x}\mathcal{G}\gamma_{y}\mathcal{G}\gamma_{x}\mathcal{G}\gamma_{y}\mathcal{G})B_{z}^{0}(\mathbf{r}). \tag{4.4}$$

Here, we assumed that the direction of the magnetic field is parallel to the $z$ axis and the spin factor of 2 is included. Therefore, we have the magnetic susceptibility expression,

$$\chi=\frac{4\mu_{B}^{2}}{m^{2}\beta}\sum_{n}\frac{1}{(2\pi)^{3}}\int d^{3}k\,\mathrm{Tr}(\gamma_{x}\mathcal{G}\gamma_{y}\mathcal{G}\gamma_{x}\mathcal{G}\gamma_{y}\mathcal{G})\ . \tag{4.5}$$

This is just the same as the exact formula for magnetic susceptibility given by Fukuyama.[13] It should be noted that Fukuyama derived this formula by the use of free energy, while we have derived it here by calculating current density. The magnetic field induced by the current

$$\mathbf{B}^{\text{mag}}\equiv\frac{1}{c}\int\frac{\mathbf{r}\times\mathbf{J}^{\text{mag}}}{r^{3}}d^{3}r\ , \tag{4.6}$$

can be calculated similarly as

$$B_{z}^{\text{mag}}=\int\left[\frac{3z^{2}-r^{2}}{r^{5}}+\frac{8\pi}{3}\delta(\mathbf{r})\right]m_{Z}(\mathbf{r})d^{3}r\ . \tag{4.7}$$

To get this expression, the singularity at $\mathbf{r}=0$ should be dealt with carefully. This is the same form as the magnetic field induced by the magnetization $\mathbf{m}$ and the magnetic field $\mathbf{H}$ can be expressed as

$$\mathbf{H}=\mathbf{H}_{0}-D\mathbf{m} \tag{4.8}$$

[see Eq. (2.14)]. So, the magnetic field induced by the current $\mathbf{J}^{\text{mag}}$ is written as

$$\mathbf{B}^{\text{mag}}=(4\pi-D)\chi\mathbf{B}^{0}\ . \tag{4.9}$$

The total magnetic field induced by electron orbital motion is the sum of $\mathbf{B}^{\text{mic}}$ in (3.33) and $\mathbf{B}^{\text{mag}}$ in (4.9). Therefore, we obtain shielding tensor expression:

$$\sigma_{ij}=-[(4\pi-D)\chi]_{ij}+\frac{ie^{2}}{m^{3}c\beta}\sum_{n}\int d^{3}k\,\mathrm{Tr}(l_{i}\mathcal{G}\gamma_{\mu}\mathcal{G}\gamma_{\nu}\mathcal{G})\epsilon_{\mu\nu j}\ . \tag{4.10}$$

In the above, the spin factor of 2 is included. This is the chemical shift expression for crystal which we propose in this paper. The first term in (4.10) is the demagnetizing field contribution and the second term comes from the microscopic current which has the lattice periodicity and is free from the ambiguity which occurs in applying Ramsey's expression to crystal. As will be seen in the next section, this expression is equivalent to those by Stephen[4] and Hebborn.[5] In their works, however, the demagnetizing term which depends on the specimen shape was introduced by macroscopic arguments. While in the present paper, the magnetizing term is derived microscopically.

## V. MICROSCOPIC CURRENT

In this section, we discuss the microscopic current defined in Eq. (3.32) in detail. In (3.32), the microscopic current is expressed in terms of LK basis function and thermodynamic Green's function. In spite of its simplicity, this expression is neither convenient for seeing the physical implication of this current, nor for calculating numerically. So, we transform it into a Bloch representation, in which the thermodynamic Green's function is diagonalized and, after the summation over $n$, is written in terms of a Fermi distribution function. Since the calculation is rather lengthy, the details are shown in Appendix B. The result is as follows:

$$\mathbf{J}^{\text{mic}}=\mathbf{J}^{1}+\mathbf{J}^{2}+\mathbf{J}^{3}+\mathbf{J}^{4}+\mathbf{J}^{5}\ , \tag{5.1}$$

$$J_{\alpha}^{1}=-\frac{e^{2}}{2mc}\int d^{3}k\sum_{l}f_{l}i\left[\mathcal{U}_{l}^{*}\frac{\partial\mathcal{U}_{l}}{\partial k_{\mu}}-\frac{\partial\mathcal{U}_{l}^{*}}{\partial k_{\mu}}\mathcal{U}_{l}\right]\epsilon_{\mu\alpha\lambda}B_{\lambda}^{0}\ , \tag{5.2}$$

$$J_{\alpha}^{2}=\frac{e^{2}}{4mc}\int d^{3}k\sum_{l}f_{l}\left[2ik_{\alpha}\frac{\partial\mathcal{U}_{l}^{*}}{\partial k_{\mu}}\frac{\partial\mathcal{U}_{l}}{\partial k_{\nu}}+\cdots\right]\epsilon_{\mu\nu\lambda}B_{\lambda}^{0}\ , \tag{5.3}$$

$$J_{\alpha}^{3}=\frac{e^{2}}{4m^{2}c}\int d^{3}k\sum_{l}\frac{\partial f}{\partial\varepsilon_{l}}\frac{1}{\Omega'}\left[i\int_{\text{cell}}\frac{\partial\mathcal{U}_{l}^{*}}{\partial x_{\mu}}\frac{\partial\mathcal{U}_{l}}{\partial k\nu}d^{3}r+k_{\mu}\int_{\text{cell}}\mathcal{U}_{l}^{*}\frac{\partial\mathcal{U}_{l}}{\partial k\nu}d^{3}r+m\frac{\partial\varepsilon_{l}}{\partial k_{\mu}}\int_{\text{cell}}\mathcal{U}_{l}^{*}\frac{\partial\mathcal{U}_{l}}{\partial k_{\nu}}d^{3}r\right](2ik_{\alpha}\mathcal{U}_{l}^{*}\mathcal{U}_{l}+\cdots)\epsilon_{\mu\nu\lambda}B_{\lambda}^{0}\ , \tag{5.4}$$

$$J_\alpha^4=\frac{e^2}{4m^2c}\int d^3k\sum_{l\neq l'}\frac{f_l-f_{l'}}{\varepsilon_l-\varepsilon_{l'}}\frac{1}{\Omega}\left[i\int_{\text{cell}}\frac{\partial\mathcal{U}_{l'}^*}{\partial x_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r+k_\mu\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\right.$$
$$\left.+m\frac{\partial\varepsilon_l}{\partial k_\mu}\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\right](2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\epsilon_{\mu\nu\lambda}B_\lambda^0\ , \tag{5.5}$$

$$J_\alpha^5=\frac{e^2}{4mc}\int d^3k\sum_{l,l'}f_l\frac{1}{\Omega}\int\frac{\partial\mathcal{U}_{l'}^*}{\partial k_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\epsilon_{\mu\nu\lambda}B_\lambda^0\ , \tag{5.6}$$

with

$$(2ik_\alpha AB+\cdots)\equiv 2ik_\alpha AB+A\frac{\partial B}{\partial x_\alpha}-\frac{\partial A}{\partial x_\alpha}B\ , \tag{5.7}$$

and

$$\Omega'=\frac{\Omega}{(2\pi)^3}\ . \tag{5.8}$$

Here we mention that this expression is equivalent to the volume terms of Stephen[4] and Hebborn.[5] Next, we investigate several limiting cases.

### A. Free electron

For free electrons, the periodic part of the Bloch orbital is constant. Therefore, all the terms vanish due to the derivative with respect to the wave vector. In this case, Eq. (4.10), the chemical shift consists only of the demagnetizing term:

$$\sigma=-(4\pi-D)\chi\ . \tag{5.9}$$

The above is consistent with Eq. (2.14). The order of the chemical shift given by Eq. (5.9) is $10^{-6}$. This is much smaller than the order of the Knight shift ($\sim 10^{-3}$) for usual metals.

### B. Nearly free electron

We consider only the single-band case and assume that Fermi level is near the bottom of the band. In this case, the Bloch function can be approximated within the first order of periodic potential as

$$\psi_{\mathbf{k}}=\frac{1}{(2\pi)^{3/2}}e^{i\mathbf{k}\cdot\mathbf{r}}\left[1-\frac{2m}{\hbar^2}\sum_{\mathbf{g}}\frac{V_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{r}}}{\mathcal{G}^2+2\mathbf{k}\cdot\mathbf{g}}\right]\ , \tag{5.10}$$

where $\mathbf{g}$ are reciprocal lattice vectors and $V_{\mathbf{g}}$ are Fourier components of periodic potential.[15] If we neglect all the $V_{\mathbf{g}}$ except for the smallest value of $\mathbf{g}$, we have the shielding tensor due to the microscopic current for cubic lattice (see Appendix C):

$$\sigma=\frac{1}{\pi}\left[\frac{e^2}{\hbar c}\right]^2\frac{|V_{\mathbf{g}_0}|}{me^2/2\hbar^2}\frac{a}{a_B}\times\left[\ln\left[\frac{1+2\tilde{k}_F}{1-2\tilde{k}_F}\right]-4\tilde{k}_F\right]\ . \tag{5.11}$$

Here, $a$ is the lattice constant and $\tilde{k}_F$ is defined as

$$\tilde{k}_F\equiv\frac{ak_F}{2\pi}\ . \tag{5.12}$$

By taking $\tilde{k}_F \ll 1$, we have

$$\sigma=\frac{16}{3\pi}\left[\frac{e^2}{\hbar c}\right]^2\frac{|V_{\mathbf{g}_0}|}{me/2\hbar^2}\frac{a}{a_B}\tilde{k}_F^3$$
$$=\frac{4}{\pi^2}\left[\frac{e^2}{\hbar c}\right]^2\frac{|V_{\mathbf{g}_0}|}{me^4/2\hbar^2}\frac{a}{a_B}n\ , \tag{5.13}$$

where $n$ is the number of electrons per unit cell. If we take the values $|V_{\mathbf{g}0}|/(me^4/2\hbar^2)\sim 0.01$, $a/a_B\sim 1$, $\tilde{k}_F\sim\frac{1}{4}$ to estimate the order of the shift, we have

$$\sigma\sim 1\times 10^{-8}\ . \tag{5.14}$$

This is negligibly small as compared to the magnetizing term (5.9). Therefore, the bulk correction by nearly free conduction electrons is only the demagnetizing term and the Lorentz term vanishes. For quantitative shielding tensor calculations in real metals, it must be remarked that the conduction electrons have rapidly oscillating core parts in the wave function, the contribution of which is not included in the estimation of Eq. (5.14). Moreover, the contribution by core electrons must be added to the chemical shift by the conduction electrons.

### C. Atomic limit

For investigating the atomic limit, tight-binding approximation is useful.

$$\psi_{l\mathbf{k}}=\sqrt{\Omega'}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}}\phi_l(\mathbf{r}-\mathbf{R})\ , \tag{5.15}$$

where $\phi_l$ is atomic orbital. If we neglect the overlap of wave functions between atoms and the energy dispersion, the remaining terms are

$$\mathbf{J}^{\text{mic}}=\mathbf{J}^{(P)}+\mathbf{J}^{(d)}\ , \tag{5.16}$$

$$\mathbf{J}^{(P)}=\frac{e^2}{4m^2c}\sum_{l\neq l}\frac{f_{l'}-f_l}{\varepsilon_l-\varepsilon_{l'}}\langle\phi_l\,|\,\mathbf{B}^0\cdot\mathbf{L}\,|\,\phi_{l'}\rangle$$
$$\times\sum_{\mathbf{R}}\left[\phi_{l'}(\mathbf{r}-\mathbf{R})\frac{1}{i}\nabla\phi_l(\mathbf{r}-\mathbf{R})-\phi_l(\mathbf{r}-\mathbf{R})\frac{1}{i}\nabla\phi_{l'}(\mathbf{r}-\mathbf{R})\right]\ , \tag{5.17}$$

$$\mathbf{J}^{(d)}=-\frac{e^2}{2mc}\sum_l f_l\sum_{\mathbf{R}}\mathbf{B}^0\times(\mathbf{r}-\mathbf{R})\,|\,\phi_l(\mathbf{r}-\mathbf{R})\,|^2\ . \tag{5.18}$$

The term $\mathbf{R}=0$ is just the same as the expression given by Ramsey. Furthermore, when the distance between atoms is large comparing with the extent of atomic orbital, the contribution from other atoms can be approximated by localized dipole moment. In this case, we can use the Lorentz local field formalism. It should be noted, however, that the current (5.17) and (5.18) are periodic and have no surface. So, we calculate the dipole sum as follows.

$$\sigma^{\mathrm{mic}}=\left[-\frac{4\pi}{3}+4\pi\right]\chi+\sigma^{(\mathrm{atom})} . \qquad (5.19)$$

Therefore, the total chemical shift is written as

$$\sigma=-\left[\frac{4}{3}\pi-D\right]\chi+\sigma^{(\mathrm{atom})} , \qquad (5.20)$$

where $\sigma^{(\mathrm{atom})}$ is the shielding tensor calculated by the term $\mathbf{R}=0$ in (5.17) and (5.18).

## VI. APPLICATION TO THE GRAPHITE AND COMPARISON WITH EXPERIMENT

The electronic and magnetic properties of graphite have been studied extensively for a long time. Because of its quasi-two-dimensionality and semimetallic character, graphite exhibits many unique properties. The large diamagnetic susceptibility is one of these properties. The measurement of the susceptibility of graphite was performed by Ganguli and Krishnan.[16] It was shown that the component parallel to the $c$ axis is about 40 times as large as the one perpendicular to $c$ axis at room temperature and is strongly temperature dependent. The theoretical explanation was given first by McClure.[17] He showed that the interband effect between the bonding $\pi$ and the antibonding $\pi$ band play an important role. After his work, more precise calculations[18,19] were performed and a satisfactory agreement between the theory and the experiment has now been attained.

Recently, a high-resolution $^{13}$C NMR measurement of graphite was performed by Hiroyama and Kume.[8] It was shown that the resonance shift parallel to the $c$ axis is highly temperature dependent and the temperature-dependent part is proportional to the susceptibility.

To explain the observed NMR shift, we apply the formalism developed in previous sections to graphite. First we consider the magnetizing term. In calculating this term, the values of the susceptibility and demagnetizing factors are needed. For susceptibility, we use the experimental value by Ganguli and Krishnan. For the demagnetizing factor, we take the value of the specimen used in the experiment by Hiroyama and Kume. Since it is difficult to get the absolute shift value experimentally, we consider only the anisotropy defined with the parallel $\sigma_{\parallel}$ and the perpendicular $\sigma_{\perp}$ components to the $c$ axis of graphite as

$$\sigma_a=\sigma_{\parallel}-\sigma_{\perp} . \qquad (6.1)$$

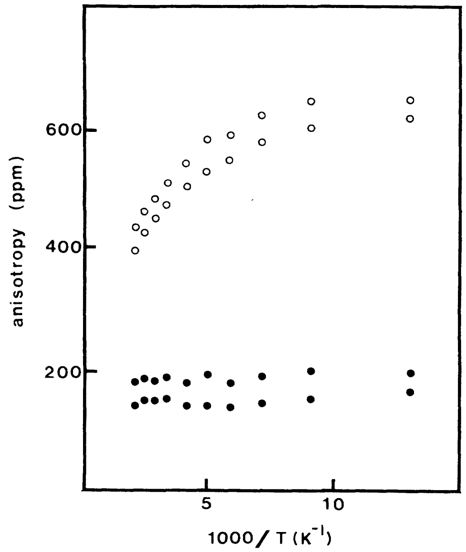

FIG. 1. Anisotropy of NMR shift in graphite. Open circles are the observed values $\sigma_{\mathrm{obs}}$ by Hiroyama and Kume (Ref. 8). Closed circles are the values of $\sigma_{\mathrm{obs}}-\sigma_{\mathrm{mac}}$.

In Fig. 1, the observed anisotropy $\sigma^{\mathrm{obs}}$ and the value $\sigma^{\mathrm{obs}}-\sigma^{\mathrm{mag}}$ are plotted. From this result, we can conclude that the temperature-dependent part of the observed shift is well explained by the term $\sigma^{\mathrm{mag}}$. Therefore, the remaining temperature-independent part must be explained by the term $\sigma^{\mathrm{mic}}$. This is reasonable, because the values of the remaining part are about 140 and 180 ppm for inequivalent carbon atoms, which are close to the experimental values of the NMR shift of atoms in the interior layers of higher stage graphite intercalation compound (GIC).[20,21] Therefore, it might be said that the magnetization of graphite is caused mainly by the extended $\pi$ electron and the contribution of electron localized at atom is small.

Next, we calculate the term $\sigma^{\mathrm{mic}}$. However, it is difficult to evaluate the terms (5.2)–(5.6) precisely. In this paper, we calculate only the on-site terms which are expected to be the largest contributions to $\sigma^{\mathrm{mic}}$. For this purpose, we use the linear combination of atomic orbitals (LCAO) formalism. The Bloch orbital is expressed as the linear combination of the atomic orbital.

$$\psi_{l\mathbf{k}}=\sqrt{\Omega'}\sum_{m,\mathbf{R},\alpha} A_{lm\alpha}(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}+\tau_\alpha)}\phi_m(\mathbf{r}-\mathbf{R}-\tau_\alpha) , \qquad (6.2)$$

where $\alpha$ indicate the inequivalent atoms in a unit cell. We omit the interatomic term and the contribution from other sites. Furthermore, we omit the derivative of both energy and coefficients of atomic orbitals $A_{lm\alpha}(\mathbf{k})$. Then, the shielding tensor is written as follows:

$$\sigma=\sigma^{(P)}+\sigma^{(d)} , \qquad (6.3)$$

where

TABLE I. Calculated results of the NMR shift for graphite within the on-site approximation using Eqs. (6.4) and (6.5).

| Site | Component | Diamagnetic | Paramagnetic | Dipole | Knight | Total |
|---|---|---|---|---|---|---|
| | $\sigma_\perp$ | 63.3 | −451.4 | 3.2 | −0.6 | −385.4 |
| $\alpha$ | $\sigma_\parallel$ | 63.3 | −328.5 | −6.4 | −0.6 | −272.3 |
| | $\sigma_a$ | 0.0 | 122.8 | −9.6 | 0.0 | 113.2 |
| | $\sigma_\perp$ | 63.5 | −446.0 | 7.0 | −1.4 | −377.0 |
| $\beta$ | $\sigma_\parallel$ | 63.2 | −322.9 | −14.0 | −1.4 | −275.1 |
| | $\sigma_a$ | −0.3 | 123.1 | −20.9 | 0.0 | 101.9 |

$$\sigma^{(p)}=-\frac{e^2}{m^2c^2}\sum_{l\neq l'}\frac{\Omega}{(2\pi)^3}\int d^3k\left[-\frac{f(\varepsilon_l(\mathbf{k}))-f(\varepsilon_{l'}(\mathbf{k}))}{\varepsilon_l(\mathbf{k})-\varepsilon_{l'}(\mathbf{k})}\right]\sum_{m_1,m_2,m_3,m_4,\beta}A^*_{lm,\alpha}A_{l'm_2\alpha}A^*_{l'm_3\beta}A_{lm_4\beta}$$

$$\times\left\langle\phi_{m_1}\left|\frac{\mathbf{L}}{r^3}\right|\phi_{m_2}\right\rangle\left\langle\phi_{m_3}\left|\mathbf{L}\right|\phi_{m_4}\right\rangle , \qquad (6.4)$$

$$\sigma^{(d)}=\frac{e^2}{mc^2}\sum_{m,m',l}\frac{\Omega}{(2\pi)^3}\int d^3k\, f_l\, A^*_{lm\alpha}A_{lm'\alpha}\left\langle\phi_m\left|\frac{r^2I-\mathbf{rr}}{r^3}\right|\phi_{m'}\right\rangle . \qquad (6.5)$$

These are similar to the ordinarily used expressions (2.7) and (2.8). The diamagnetic terms are the same. However, there are two differences between the paramagnetic terms. One is the way to average within the Brillouin zone. In the expression (2.7), integrations on wave vectors of occupied states and unoccupied states are performed independently, whereas in (6.4), the integration is done on a single common wave vector. The other occurs when there is more than one atom in a unit cell. In (6.4), the average on the inequivalent atoms is taken as summation over $\beta$, while it is not in (2.7). It should be noted that the expressions (2.7) and (2.8) are derived with a questionable approximation in the calculation of the angular momentum. Whereas, in the present formalism, the validity of approximation is clear and there is no ambiguity. When there is only one atom per unit cell, the paramagnetic part of the microscopic term $\sigma^{(P)}$ given by Eq. (6.4) incidentally agrees with that used by Yamanobe and Ando[22] and Tsang and Resing.[23] However, their derivations of $\sigma^{(P)}$ were not based on valid arguments. Therefore, the magnetizing term cannot be discussed by the theories of these authors. The fact that their expression of $\sigma^{(P)}$ is not the same as the correct one Eq. (6.4) when there is more than one atom in a unit cell might be originated from the inappropriate treatment of the cancellation of the divergent terms.

With the approximated expressions (6.4) and (6.5), we calculate the shielding tensor. To calculate numerically, we use the result of the first-principles band calculation by Saito *et al.*[24] The result is shown in Table I. In this table, the inequivalent atoms which have or do not have the atoms just above and below them in the neighboring graphite layers are denoted by $\alpha$ or $\beta$. The dipole and Knight shifts are calculated by the method of Ref. 21. The calculated anisotropies are 113.2 and 101.9 ppm for the $\alpha$ and $\beta$ sites, respectively, and they are only two-thirds of the observed values 180 and 140 ppm. The reason for the discrepancy between the calculated results and the experimental results might be the on-site approximation adopted in this calculation. Since the overlaps of atoms are anisotropic, the contribution of nearest-neighbor atoms may remove the discrepancy.

## VII. SUMMARY AND CONCLUSION

In this paper, we have derived a rigorous expression for the chemical shift in crystal. For this aim, we have calculated the current density with the use of the sinusoidal vector potential and the LK basis function. In this formalism, the shielding tensor is divided into the magnetizing term and the microscopic term. The magnetizing term corresponds to the demagnetizing term in the ordinary local field theory. It is proportional to the bulk magnetic susceptibility and depends on the shape of the specimen. The microscopic term is induced by the periodic current flowing in the material inner region. It is gauge independent and free from the large cancellation of paramagnetic and diamagnetic terms which is inevitable in Ramsey's expression.

In the case of the free electron, the microscopic term vanishes and only the magnetizing term contributes to the shielding tensor. On the other hand, when the overlap between atoms can be neglected and the localized-dipole approximation is appropriate, the bulk susceptibility is the same as the atomic susceptibility multiplied by density. In this case, the shielding tensor consists of the magnetizing term, Lorentz term, and ordinary chemical shift of the atom.

Generally, the evaluation of shielding tensor is complicated. However, when the bulk susceptibility is small, the magnetizing term can be neglected and the main contribution is the on-site term of microscopic term. The on-site term consists of a paramagnetic component and a diamagnetic component. The diamagnetic component is the same as the commonly used expression of chemical shift in the crystal. However, the paramagnetic component is different from the ordinary one in the way of averaging over the Brillouin zone. The important point is that the ordinary expression is derived with a questionable approximation, while in the present formalism there is no ambiguity.

To explain the observed NMR shift in graphite, the present formalism is applied. The temperature-dependent part of the shift is only well explained by the magnetizing term and the remaining constant part is close to the experimental value of chemical shift in higher stage GIC. This is because the magnetization of graphite is induced mainly by the extended $\pi$ electrons. To explain the constant part of the observed shift, the microscopic term has been calculated within the on-site approximation using the result of the first-principles band calculation. The calculated value is about only two-thirds of the experimental one. This is because the overlap between atoms and the energy dispersion in graphite is not so small as to be neglected. To remove the discrepancy, more precise calculation beyond the on-site approximation is needed.

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## APPENDIX A

With the approximation (4.2), the total magnetic moment (4.1) is written as

$$M_\mu=\frac{1}{2c}\int d^3r\left[-\frac{e^2}{m^2c\beta}\sum_n\frac{1}{(2\pi)^3}\int d^3k\,\epsilon_{\mu\nu\lambda}x_\nu\frac{A^\sigma_{\mathbf{q}}}{i}(e^{i\mathbf{q}\cdot\mathbf{r}}-e^{-\mathbf{q}\cdot\mathbf{r}})\frac{q_\alpha q_\beta}{8}\right.$$
$$\left.\times\mathrm{Tr}(\gamma_\lambda\partial_\alpha\partial_\beta\mathcal{G}\gamma_\sigma\mathcal{G}+\gamma_\lambda\mathcal{G}\gamma_\sigma\partial_\alpha\partial_\beta\mathcal{G}-\gamma_\lambda\partial_\alpha\mathcal{G}\gamma_\sigma\partial_\beta\mathcal{G}-\gamma_\lambda\mathcal{G}\gamma_\sigma\partial_\alpha\mathcal{G})\right]\ . \tag{A1}$$

By integrating partially, we have

$$M_\mu=-\frac{2\mu_\beta^2}{\beta}\sum_n\frac{1}{(2\pi)^3}\int d^3k\frac{A^\sigma_{\mathbf{q}}}{q_\nu}(e^{i\mathbf{q}\cdot\mathbf{r}}+e^{-\mathbf{q}\cdot\mathbf{r}})\frac{q_\alpha q_\beta}{8}\epsilon_{\mu\nu\lambda}$$
$$\times\mathrm{Tr}(\gamma_\lambda\partial_\alpha\partial_\beta\mathcal{G}\gamma_\sigma\mathcal{G}+\gamma_\lambda\mathcal{G}\gamma_\sigma\partial_\alpha\partial_\beta\mathcal{G}-\gamma_\lambda\partial_\alpha\mathcal{G}\gamma_\sigma\partial_\beta\mathcal{G}-\gamma_\lambda\partial_\beta\mathcal{G}\gamma_\sigma\partial_\alpha\mathcal{G})\ . \tag{A2}$$

To get this expression, we neglect the term of the unphysical surface integral. In a real material, current flows inside the material and does not extend infinitely. So, we should think that a damping factor is included in the current expression. Therefore, the surface integral can be neglected.

When the direction of the external magnetic field is parallel to the $z$ axis, we can assume $A_q^Z=0$, $q_Z=0$, we need consider only the terms in which $\nu,\lambda,\sigma,\alpha,\beta$ are $x$ or $y$. After the calculation of all the terms using the identity (3.29), we obtain

$$M_Z=\int d^3r\left[\frac{2\mu_\beta^2}{m^2\beta}\sum_n\frac{1}{(2\pi)^3}\int d^3k\,\mathrm{Tr}(\gamma_x\mathcal{G}\gamma_y\mathcal{G}\gamma_x\mathcal{G}\gamma_y\mathcal{G})(\mathcal{G}_x A_q^y-q_y A_q^x)(e^{i\mathbf{q}\cdot\mathbf{r}}+e^{-\mathbf{q}\cdot\mathbf{r}})\right]\ . \tag{A3}$$

If the spin factor is included, we get Eq. (4.3).

## APPENDIX B

In Bloch representation, the microscopic current is expressed as follows:

$$\langle J_\alpha^{\mathrm{mic}}\rangle=\frac{e^2}{4m^3c\beta}\sum_{l,l'l'',n}\int d^3k\left[2ik_\alpha\mathcal{U}^*_{l\mathbf{k}}\mathcal{U}_{l'\mathbf{k}}+U^*_{l\mathbf{k}}\frac{\partial\mathcal{U}_{l'\mathbf{k}}}{\partial x_\alpha}-\mathcal{U}_{l'\mathbf{k}}\frac{\partial\mathcal{U}^*_{l\mathbf{k}}}{\partial x_\alpha}\right]$$
$$\times\frac{1}{i\varepsilon_n+\mu-\varepsilon_{l'}}j^\mu_{l'l''}\frac{1}{i\varepsilon_n+\mu-\varepsilon_{l''}}j^\nu_{l''l}\frac{1}{i\varepsilon_n+\mu-\varepsilon_l}\epsilon_{\mu\nu\lambda}\beta^0_\lambda\ , \tag{B1}$$

where

$$j^\mu_{ll'}=k^\mu\delta_{ll'}+\frac{(2\pi)^3}{\Omega}\int_{\mathrm{cell}}\mathcal{U}^*_{l\mathbf{k}}\frac{1}{i}\frac{\partial\mathcal{U}_{l'\mathbf{k}}}{\partial x_\mu}d^3r\ . \tag{B2}$$

In taking the summation on $n$, we must consider the following five cases:

(1) $l=l'=l''$;
(2) $l=l'\neq l''$;
(3) $l=l'\neq l''$;
(4) $l'=l''\neq l$;
(5) $l$, $l'$, and $l''$ are different from each other.

Here, we list the equations used in the following calculations:

$$\int_{\text{cell}} \mathcal{U}^*_{l\mathbf{k}} \mathcal{U}_{l'\mathbf{k}} d^3r = \frac{\Omega}{(2\pi)^3}\delta_{ll'} \quad (\text{orthogonality})\ , \tag{B3}$$

$$\sum_l \mathcal{U}^*_{l\mathbf{k}}(\mathbf{r})\mathcal{U}_{l\mathbf{k}}(\mathbf{r}') = \frac{\Omega}{(2\pi)^3}\delta(\mathbf{r}-\mathbf{r}') \quad (\text{completeness})\ , \tag{B4}$$

$$\sum_n \frac{1}{(i\varepsilon_n+\mu-\varepsilon_l)^P} = \frac{\beta}{(P-1)!}\frac{\partial^{P-1}f}{\partial\varepsilon_l^{P-1}}\ , \tag{B5}$$

$$j^{\mu}_{ll'} = \begin{cases} -\dfrac{(2\pi)^3}{\Omega} m(\varepsilon_l-\varepsilon_{l'})\displaystyle\int_{\text{cell}} \mathcal{U}^*_l \frac{\partial \mathcal{U}_{l'}}{\partial k_\mu} d^3r & (l\neq l') \\ m\dfrac{\partial \varepsilon_l}{\partial k_\mu} & (l=l')\ , \end{cases} \tag{B6}$$

$$\int_{\text{cell}} \left[ \frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\frac{\partial \mathcal{U}_l}{\partial x_\mu} + \frac{\partial \mathcal{U}^*_{l'}}{\partial x_\mu}\frac{\partial \mathcal{U}_l}{\partial k_\mu} \right] d^3r = \frac{m}{i}\left[ \frac{\partial \varepsilon_{l'}}{\partial k_\nu}\int_{\text{cell}} \mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\mu} d^3r - \frac{\partial \varepsilon_l}{\partial k_\mu}\int_{\text{cell}} \frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\mathcal{U}_l d^3r \right]$$
$$+ik_\nu \int_{\text{cell}} \mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\mu} d^3r - ik_\mu \int \frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\mathcal{U}_l d^3r + \frac{m}{i}(\varepsilon_{l'}-\varepsilon_l)\int_{\text{cell}} \frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\frac{\partial \mathcal{U}_l}{\partial k_\mu} d^3r\ , \tag{B7}$$

Eqs. (B6) and (B7) are derived in Appendix D. In the following calculation, we do not explicitly write the factor $(e^2/4m^3c)\int d^3k$, $\varepsilon_{\mu\nu\lambda}B^0_\lambda$ for simplicity, but we should conceive these factors to be included.

(1) $l=l'=l''$. In this case, there is no contribution because of the factor $\varepsilon_{\mu\nu\lambda}$

(2) $l=l'\neq l''$. Using Eq. (B3), the current can be calculated as

$$\sum_{l\neq l'',n} \frac{1}{(i\varepsilon_n+\mu-\varepsilon_l)^2(i\varepsilon_n+\mu-\varepsilon_{l''})}\frac{1}{\beta} j^{\mu}_{ll''} j^{\nu}_{l''l}(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots) = \sum_{l\neq l''} \frac{1}{\varepsilon_l-\varepsilon_{l''}}\frac{\partial f}{\partial \varepsilon_l} j^{\mu}_{ll''} j^{\nu}_{l''l}(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots)$$
$$-\sum_{l\neq l'} \frac{f_l-f_{l'}}{\varepsilon_l-\varepsilon_{l'}} j^{\mu}_{ll''} j^{\nu}_{l''l}(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots)\ , \tag{B8}$$

The first term is calculated using the completeness relation (B4) as

$$\sum_{l\neq l''} \frac{m}{\Omega'^2}\frac{\partial f}{\partial \varepsilon_l}\int_{\text{cell}} \mathcal{U}^*_l \frac{1}{i}\frac{\partial \mathcal{U}_{l'}}{\partial x_\mu} d^3r \int_{\text{cell}} \mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\nu} d^3r (2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots)$$
$$= \frac{m}{\Omega'}\sum_l \frac{\partial f}{\partial \varepsilon_l}\int_{\text{cell}} i\frac{\partial \mathcal{U}^*_l}{\partial x_\mu}\frac{\partial \mathcal{U}_l}{\partial k_\nu} d^3r(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots) \tag{B9a}$$
$$-\frac{m^2}{\Omega'}\sum_l \frac{\partial f}{\partial \varepsilon_l}\left[\frac{\partial \varepsilon_l}{\partial k_\mu}-\frac{k_\mu}{m}\right]\int_{\text{cell}} \mathcal{U}^*_l \frac{\partial \mathcal{U}_l}{\partial k_\nu} d^3r(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots)\ , \tag{B9b}$$

and the second term in (B8) is

$$\frac{m^2}{\Omega'}\sum_{l\neq l'} (f_l-f_{l'})\int_{\text{cell}} \mathcal{U}^*_l \frac{\partial \mathcal{U}_{l'}}{\partial k_\mu} d^3r \int_{\text{cell}} \mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\nu} d^3r(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots)$$
$$= -\frac{m^2}{\Omega'}\sum_l f_l \int_{\text{cell}} \frac{\partial \mathcal{U}^*_l}{\partial k_\mu}\frac{\partial \mathcal{U}^*_l}{\partial k_\nu} d^3r(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots) \tag{B10a}$$
$$-\frac{m^2}{\Omega'^2}\sum_{l,l'} f_{l'}\int_{\text{cell}} \mathcal{U}^*_l \frac{\partial \mathcal{U}_{l'}}{\partial k_\mu} d^3r \int_{\text{cell}} \mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\nu} d^3r(2ik_\alpha \mathcal{U}^*_l\mathcal{U}_l+\cdots)\ . \tag{B10b}$$

(3) and (4) $l=l''\neq l'$ and $l'=l''\neq l$. It can be verified that the case (4) is the complex conjugate of the case (3). Similarly to the case (2), we obtain

$$\frac{m^2}{\Omega'}\sum_{l\neq l'}\frac{\partial f}{\partial\varepsilon_l}\frac{\partial\varepsilon_l}{\partial k_\nu}\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}d^2r\,(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'})+\text{c.c.} \tag{B11a}$$

$$-\frac{m^2}{\Omega'}\sum_{l}\frac{\partial f}{\partial\varepsilon_l}\frac{\partial\varepsilon_l}{\partial k_\nu}\left[2ik_\alpha\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]+\text{c.c.} \tag{B11b}$$

$$-\frac{m^2}{\Omega'}\sum_{l\neq l'}\frac{f_l-f_{l'}}{\varepsilon_l-\varepsilon_{l'}}\frac{\partial\varepsilon_l}{\partial k_\nu}\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}d^3r\,(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)+\text{c.c.}\ . \tag{B11c}$$

(5) $l$, $l'$, and $l''$ are different from each other. In this case, the current is divided into three terms as

$$\begin{aligned}&\sum_{l\neq l'\neq l''}\frac{f_l}{(\varepsilon_l-\varepsilon_{l'})(\varepsilon_l-\varepsilon_{l''})}j^{\mu}_{l'l''}j^{\nu}_{l''l}(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ ,\\ &+\sum_{l\neq l'\neq l''}\frac{f_{l'}}{(\varepsilon_{l'}-\varepsilon_{l''})(\varepsilon_{l'}-\varepsilon_{l})}j^{\mu}_{l'l''}j^{\nu}_{l''l}(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ ,\\ &+\sum_{l\neq l'\neq l''}\frac{f_{l''}}{(\varepsilon_{l''}-\varepsilon_{l})(\varepsilon_{l''}-\varepsilon_{l'})}j^{\mu}_{l'l''}j^{\nu}_{l''l}(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ .\end{aligned} \tag{B12}$$

Since the second term is the complex conjugate of the first term, these two terms are calculated as

$$\sum_{l\neq l'}\frac{m}{\Omega'}\frac{f_l}{\varepsilon_l-\varepsilon_{l'}}\int_{\text{cell}}i\frac{\partial\mathcal{U}_{l'}^*}{\partial x_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)+\text{c.c.}\ , \tag{B13a}$$

$$-\frac{m^2}{\Omega'^2}\sum_{l\neq l'}\frac{f_l}{\varepsilon_l-\varepsilon_{l'}}\left[\frac{\partial\varepsilon_{l'}}{\partial k_\mu}-\frac{k_\mu}{m}\right]\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\,(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)+\text{c.c.}\ , \tag{B13b}$$

$$-\frac{m^2}{\Omega'}\sum_{l}f_l\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\left[2ik_\alpha\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]+\text{c.c.} \tag{B13c}$$

The third term in (B12) is calculated as

$$m^2\sum_{l}f_l\left[2ik_\alpha\frac{\partial\mathcal{U}_l^*}{\partial k_\nu}\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]\ , \tag{B14a}$$

$$+\frac{m^2}{\Omega'}\sum_{l}f_l\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\left[2ik_\alpha\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]\ , \tag{B14b}$$

$$-\frac{m^2}{\Omega'}\sum_{l}f_l\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}d^3r\left[2ik_\alpha\frac{\partial\mathcal{U}_l^*}{\partial k_\nu}\mathcal{U}_l+\cdots\right]\ , \tag{B14c}$$

$$+\frac{m^2}{\Omega'^2}\sum_{l,l'}f_{l'}\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_{l'}}{\partial k_\mu}d^3r\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\,(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_l+\cdots)\ . \tag{B14d}$$

By summing up the all terms (B9)–(B11), (B13), and (B14), we obtain

$$\frac{m}{\Omega'}\sum_{l}\frac{\partial f}{\partial\varepsilon_l}\left[i\int_{\text{cell}}\frac{\partial\mathcal{U}_l^*}{\partial x_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r+k_\mu\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r+m\frac{\partial\varepsilon_l}{\partial k_\mu}\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\right](2ik_\alpha\mathcal{U}_l^*\mathcal{U}_l+\cdots)\ , \tag{B15a}$$

$$-\frac{m^2}{\Omega'}\sum_{l}f_l\int_{\text{cell}}\frac{\partial\mathcal{U}_l^*}{\partial k_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r\,(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_l+\cdots)\ , \tag{B15b}$$

$$+m^2\sum_{l}\frac{\partial f}{\partial\varepsilon_l}\frac{\partial\varepsilon_l}{\partial k_\nu}\left[2ik_\alpha\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]+\text{c.c.}\ , \tag{B15c}$$

$$+m^2\sum_{l}f_l\left[2ik_\alpha\frac{\partial\mathcal{U}_l^*}{\partial k_\nu}\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]\ , \tag{B15d}$$

$$-\frac{m^2}{\Omega'}\sum_{l\neq l'}\frac{f_l-f_{l'}}{\varepsilon_l-\varepsilon_{l'}}\frac{\partial\varepsilon_l}{\partial k_\nu}\int_{\text{cell}}\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)+\text{c.c.}\ , \tag{B15e}$$

$$+\frac{m}{\Omega'}\sum_{l\neq l'}\frac{f_l}{\varepsilon_l-\varepsilon_{l'}}i\int\frac{\partial\mathcal{U}_{l'}}{\partial\chi_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)+\text{c.c.}\ , \tag{B15f}$$

$$-\frac{m}{\Omega'}\sum_{l\neq l'}\frac{f_l}{\varepsilon_l-\varepsilon_{l'}}\left[\frac{\partial\varepsilon_{l'}}{\partial k_\mu}-\frac{k_\mu}{m}\right]\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)+\text{c.c.} \tag{B15g}$$

Furthermore, using the Eq. (B7), the term (B15f) can be calculated as

$$\begin{aligned}&\frac{m}{\Omega'}\sum_{l\neq l'}\frac{f_l-f_{l'}}{\varepsilon_l-\varepsilon_{l'}}i\int_{\text{cell}}\frac{\partial\mathcal{U}_l^*}{\partial x_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ ,\\&+\frac{m}{\Omega'}\sum_{l\neq l'}\frac{f_{l'}}{\varepsilon_l-\varepsilon_{l'}}\left[\frac{\partial\varepsilon_l}{\partial k_\mu}\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r-\frac{\partial\varepsilon_l}{\partial k_\nu}\int_{\text{cell}}\frac{\partial\mathcal{U}_{l'}^*}{\partial k_\mu}\mathcal{U}_l d^3r\right](2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ ,\\&-\frac{m}{\Omega'}\sum_{l\neq l'}\frac{f_{l'}}{\varepsilon_l-\varepsilon_{l'}}\left[k_\mu\int_{\text{cell}}\mathcal{U}_{l'}^*\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r-k_\mu\int_{\text{cell}}\frac{\partial\mathcal{U}_{l'}^*}{\partial k_\mu}\mathcal{U}_l d^3r\right](2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ ,\\&-\frac{m^2}{\Omega'}\sum_{l\neq l'}f_{l'}\int_{\text{cell}}\frac{\partial\mathcal{U}_{l'}^*}{\partial k_\mu}\frac{\partial\mathcal{U}_l}{\partial k_\nu}d^3r(2ik_\alpha\mathcal{U}_l^*\mathcal{U}_{l'}+\cdots)\ .\end{aligned} \tag{B16}$$

And the term (B15c) is rewritten by partial integral as

$$\begin{aligned}&-2im^2\sum_l f_l\left[\mathcal{U}_l^*\frac{\partial\mathcal{U}_l}{\partial k_\mu}-\frac{\partial\mathcal{U}_l^*}{\partial k_\mu}\mathcal{U}_l\right]\delta_{\alpha\nu}\ ,\\&-2m^2\sum_l f_l\left[2ik_\alpha\frac{\partial\mathcal{U}_l^*}{\partial k_\nu}\frac{\partial\mathcal{U}_l}{\partial k_\mu}+\cdots\right]\ .\end{aligned} \tag{B17}$$

Therefore, we obtain the final expression (5.2)–(5.5).

## APPENDIX C

If we keep only the first-order term in $V_{\mathbf{g}}$, all the terms except for (5.2) vanish and the microscopic current is written as

$$\mathbf{J}^{\text{mic}}=-\frac{2e^2}{\hbar^2c}\frac{i}{(2\pi)^3}\int d^3k\sum_{\mathbf{g}}\left[\frac{V_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{r}}}{(\mathcal{G}^2+2\mathbf{g}\cdot\mathbf{k})^2}-\frac{V_{\mathbf{g}}^*e^{-i\mathbf{g}\cdot\mathbf{r}}}{(\mathcal{G}^2+2\mathbf{g}\cdot\mathbf{k})^2}\right]\mathbf{B}^a\times\mathbf{g}\ . \tag{C1}$$

From the Maxwell's equation

$$\text{rot}\mathbf{B}=\frac{4\pi}{c}\mathbf{J}\ , \tag{C2}$$

we have the magnetic field induced by the current (C1).

$$\mathbf{B}^{\text{mic}}=-\frac{8\pi e^2}{\hbar^2c^2}\frac{1}{(2\pi)^3}\int d^3k\sum_{\mathbf{g}\neq0}\left[\frac{V_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{k}}}{(\mathcal{G}^2+2\mathbf{g}\cdot\mathbf{k})^2}+\frac{V_{\mathbf{g}}^*e^{-i\mathbf{g}\cdot\mathbf{k}}}{(\mathcal{G}^2+2\mathbf{g}\cdot\mathbf{k})^2}\right]\times\frac{(\mathbf{B}^0\times\mathbf{g})\times\mathbf{g}}{\mathcal{G}^2}\ . \tag{C3}$$

Here, we assume that the position of an atom is at $r=0$ and the phase of periodic potential is taken as $V_{\mathbf{g}}=-|V_{\mathbf{g}}|$. Further, if we neglect the higher-order terms in $\mathbf{g}$ than the terms with

$$\mathbf{g}_0=\frac{2\pi}{a}(\pm1,0,0),\frac{2\pi}{a}(0,\pm1,0),\frac{2\pi}{a}(0,0,\pm1)\ , \tag{C4}$$

for cubic lattice, the shielding tensor is written as

$$\sigma=\frac{16\pi e^2}{\hbar^2c^2}\frac{1}{(2\pi)^3}|V_{\mathbf{g}_0}|\sum_{\pm}\int d^3k\left[\frac{1}{(\mathcal{G}_0^2\pm2k_x\mathcal{G}_0)^2}+\frac{1}{(\mathcal{G}_0^2\pm2k_y\mathcal{G}_0)^2}\right]\ . \tag{C5}$$

By performing the integration, we get the Eq. (5.11).

## APPENDIX D

By differentiating the Schrödinger equation

$$\left[-\frac{1}{2m}\nabla^2+V(\mathbf{r})\right]\psi_{l\mathbf{k}}=\varepsilon_l(\mathbf{k})\psi_{l\mathbf{k}}\ , \tag{D1}$$

with respect to wave vector, we have

$$\left[\frac{1}{2m}\nabla^2-V+\varepsilon_l\right]\left[e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial\mathcal{U}_l}{\partial k_\mu}\right]+\frac{i}{m}\frac{\partial\psi_{l\mathbf{k}}}{\partial x_\mu}+\frac{\partial\varepsilon_l}{\partial k_\mu}\psi_{l\mathbf{k}}=0\ . \tag{D2}$$

If we multiply this by $\psi_{l\mathbf{k}}^*$ and integrate over the unit cell, we obtain the lower equation of (B6) and if we multiply by $\psi^*_{l'\mathbf{k}}$, the upper equation is obtained. Furthermore, if we multiply by

$$e^{-i\mathbf{k}\cdot\mathbf{r}}\frac{\partial \mathcal{U}^*_{l'\mathbf{k}}}{\partial k_\nu}=\frac{\partial \psi^*_{l'\mathbf{k}}}{\partial k_\nu}+ix_\nu\psi^*_{l'\mathbf{k}}\ , \tag{D3}$$

we get

$$\mathcal{M}+\frac{i}{m}\int_{\text{cell}}\frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\frac{\partial \mathcal{U}_l}{\partial x_\mu}d^3r-\frac{k_\mu}{m}\int_{\text{cell}}\frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\mathcal{U}_l d^3r +\frac{\partial \varepsilon_l}{\partial k_\mu}\int_{\text{cell}}\frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\mathcal{U}_l d^3r=0\ , \tag{D4}$$

where $\mathcal{M}$ is calculated as

$$\begin{aligned}
\mathcal{M}&=\int_{\text{cell}}\frac{\partial\psi^*_{l'}}{\partial k_\nu}\left[\frac{1}{2m}\nabla^2-V+\varepsilon_l\right]\left[e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial \mathcal{U}_l}{\partial k_\mu}\right]d^3r+i\int_{\text{cell}}\psi^*_{l'}x_\nu\left[\frac{1}{2m}\nabla^2-V+\varepsilon_l\right]\left[e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial \mathcal{U}_l}{\partial k_\mu}\right]d^3r\\
&=\int_{\text{cell}}\left[-i\varepsilon_{l'}\psi^*_{l'}+\varepsilon_l\frac{\partial\psi^*_{l'}}{\partial k_\nu}\right]e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r+i\int_{\text{cell}}[(-\varepsilon_{l'}\psi^*_{l'})x_V+\psi^*_{l'}x_\nu\varepsilon_l]e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r\\
&\quad+\frac{i}{m}\int_{\text{cell}}\frac{\partial\psi^*_{l'}}{\partial x_\nu}e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r\\
&=-\frac{\partial\varepsilon_{l'}}{\partial k_\nu}\int_{\text{cell}}\mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r-\varepsilon_{l'}\int_{\text{cell}}\frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r+\varepsilon_l\int_{\text{cell}}\frac{\partial \mathcal{U}^*_{l'}}{\partial k_\nu}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r\\
&\quad+\frac{i}{m}\int_{\text{cell}}\frac{\partial \mathcal{U}^*_{l'}}{\partial x_\nu}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r+\frac{k_\nu}{m}\int_{\text{cell}}\mathcal{U}^*_{l'}\frac{\partial \mathcal{U}_l}{\partial k_\mu}d^3r\ .
\end{aligned}$$

Therefore, Eq. (B7) is derived.

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