Orbital Susceptibility of Impurity Systems

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The formulation of orbital susceptibility in the system containing the impurities is studied taking account of the interference between two Green functions. The formulation is very similar to the ordinary Boltzmann-Bloch type theory of electrical conductivity on the basis of two-time Green function. The sum rule for conductivity due to the Edwards' approximation is not satisfied.

§ 1. Introduction

The impurity effect on the orbital diamagnetic susceptibility of free electrons has been discussed by several workers. Peierls[1] has shown that the effect of impurities on the diamagnetic susceptibility is neglected under the condition $\hbar/\tau \ll kT$, where τ denotes the mean free time of the free electron. Kohn and Luming[2] have carried out the calculation for the susceptibility of a simple model of a dilute alloy and have obtained the result that the susceptibility is the same as that of a free electron gas assuming the perturbation to be sufficiently weak.

Recently, Ando[3] has calculated the orbital susceptibility of dilute alloys and has proved that the contribution of impurities to the susceptibility can be neglected under the condition $\hbar/\tau \ll \eta$, where η is a characteristic energy of the order of the Fermi energy. They have calculated the susceptibility by the use of Nakajima's formula[4] and Matsubara and Toyozawa's technique[5] for impurity band conduction, and have estimated it in the lowest order approximation. In this estimate, they have retained only the terms with a δ-singularity[6] in the term $1/(E-H)$ and have neglected the interference between two Green functions in respect of the random average of impurity sites, where H represents the total Hamiltonian of the system. Furthermore, it has been concluded that the effect of interference between two Green functions does not contribute to the result obtained by the lowest order approximation excepting for the change of the expression of a damping constant of electronic states.

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In the succeeding section, after the two-time Green function method for the evaluation of electrical conductivity[7], a calculation of the diamagnetic susceptibility is given to take into account of the interference between two Green functions. This formulation is similar to that of the ordinary Boltzmann-Bloch type theory for the conductivity. In § 3 the evaluation of susceptibility is made. The section 4 will be offered to the calculation of the electrical conductivity by the use of Edwards' approximation for the product of two Green functions[8], however, a sum rule for the conductivity[9] is not satisfied so far as the Edwards' approximation is assumed.

§ 2. Formulation of the problem

We consider an assembly of electrons containing the impurities, whose electrons can be represented by the one-electron model. According to Nakajima[4], the orbital diamagnetic susceptibility has been written as

$$\chi = -\frac{1}{c^2}\frac{S_2(\boldsymbol{q}, -\boldsymbol{q})}{q^2}. \tag{1}$$

Here, $S_2(\boldsymbol{q}, -\boldsymbol{q})$ is obtained by the relations

$$\begin{aligned} S_{\mu\nu}(\boldsymbol{q}, -\boldsymbol{q}') &= \int_0^\beta d\lambda < j_\mu(\boldsymbol{q}, -i\hbar\lambda) j_\nu(-\boldsymbol{q}', 0) > \\ &= S_0(\boldsymbol{q}, -\boldsymbol{q}')\delta_{\mu\nu} + S_2(\boldsymbol{q}, -\boldsymbol{q}')\frac{q'_\mu q'_\nu}{q'^2}, \end{aligned} \tag{2}$$

$$\mu, \nu = \{x, y, z\} \qquad \beta = \frac{1}{kT},$$

$$\boldsymbol{i}(\boldsymbol{r}, t) = \sum_{\boldsymbol{q}} \boldsymbol{i}(\boldsymbol{q}, t) \exp(-i\boldsymbol{q}\boldsymbol{r})$$

and the spatial Fourier transform of current density operator $\boldsymbol{i}(\boldsymbol{r}, t)$, in the representation of the second quantization,

$$\boldsymbol{i}(\boldsymbol{q}, 0) = \frac{e\hbar}{m}\sum_{\boldsymbol{k}} (\boldsymbol{k} - \frac{1}{2}\boldsymbol{q}) a^+_{\boldsymbol{k}-\boldsymbol{q}} a_{\boldsymbol{k}} \tag{3}$$

where $a^+_{\boldsymbol{k}}$ and $a_{\boldsymbol{k}}$ stand for the creation and annihilation operators of a free electron, respectively, whose eigenstates are denoted by a wave vector $\boldsymbol{k}$ as the basis of one electron state. Furthermore, $<\Omega>$ means the expectation value of Ω for the canonical ensemble, that is,

$$<\Omega> = \frac{\mathrm{Tr}\{\Omega \exp(-\beta H)\}}{\mathrm{Tr}\{\exp(-\beta H)\}}.$$

Let us consider the non-uniform system whose volume Ω_0 is unity. The total Hamiltonian of the field-free system

$$H = \sum_{k} \varepsilon_k a^+_k a_k + \sum_{k}\sum_{q} \rho(q)\, V(q) a^+_{k-q} a_k \tag{4}$$

where ε_k is the free electron energy with wave vector k,

$$\rho(q) = \sum_{i} \exp(iqr_i),$$

$$V(q) = \int_{\Omega_0} \exp(-iqr) V(r) dr$$

and i denotes the site of an impurity and $V(r)$ the interaction between an impurity and an electron.

By making use of the Buckingham's identity[10] for non-uniform system

$$S_0(q, \ -q') + S_2(q, \ -q') = \frac{e}{m} <n(q-q')>$$

where $n(q)$ being the Fourier transform of the charge density operator, and of the relation of equation (2), one may easily leads to the expression of $S_2(q, -q')$ as

$$S_2(q, \ -q') = \frac{3e}{2m} <n(q-q')> - \frac{1}{2}\sum_{\mu} S_{\mu\mu}(q, \ -q'). \tag{5}$$

In order to rewrite (5), it is convenient to introduce the Green function defined by

$$G(k, k'; E) = \mathrm{Im} < 0 \left| \ a_k \frac{1}{E - i\epsilon - H} a^+_{k'} \right| 0 > \quad (\epsilon \to +0) \tag{6}$$

where $|0>$ represents the vacuum state in which no electron exists and Im means the imaginary part, and to diagonalize the total Hamiltonian H by a unitary transformation[5]. Let $q' = q$, (5) now reduces to

$$S_2(q, \ -q) = \frac{3e}{2m} <n(0)> - \frac{1}{2}\left(\frac{eh}{\pi m}\right)^2 \sum_{k}\sum_{k'} \int dE \int dE' \left(k - \frac{1}{2}q\right) \cdot \left(k' + \frac{1}{2}q\right)$$

$$\times \frac{f(E') - f(E)}{E - E'} G(k', \ k - q; E) G(k, \ k' + q; \ E') \tag{7}$$

with $f(E)$ the Fermi distribution function.

In order to proceed to the calculation taking account of the interference

between two Green functions in respect of the random average of impurity sites, we utilize the approximation method obtained by Edwards[8]. The two-particle Green function $<G(\boldsymbol{k}', \boldsymbol{k}-\boldsymbol{q}; E)\,G(\boldsymbol{k}, \boldsymbol{k}'+\boldsymbol{q}; E')>_r$ has been written as

$$<G(\boldsymbol{k}', \boldsymbol{k}-\boldsymbol{q}; E)G(\boldsymbol{k}, \boldsymbol{k}'+\boldsymbol{q}; E')>_r = \delta_{\boldsymbol{k},\boldsymbol{k}'+\boldsymbol{q}}G^0(\boldsymbol{k}'; E)G^0(\boldsymbol{k}'+\boldsymbol{q}; E')$$
$$+ n\sum_{\boldsymbol{q}'}G^0(\boldsymbol{k}'; E)G^0(\boldsymbol{k}'+\boldsymbol{q}; E')|V(\boldsymbol{q}')|^2<G(\boldsymbol{k}'+\boldsymbol{q}', \boldsymbol{k}-\boldsymbol{q}; E)$$
$$\times G(\boldsymbol{k}, \boldsymbol{k}'+\boldsymbol{q}+\boldsymbol{q}'; E')>_r \qquad (8)$$

where

$$G^0(\boldsymbol{k}; E) = \frac{\Gamma(\boldsymbol{k}, E)}{(E-\varepsilon_{\boldsymbol{k}})^2+\Gamma^2(\boldsymbol{k}, E)},$$

n denotes the total number of impurities, $\Gamma(\boldsymbol{k}, E)$ a damping constant of electronic state and $<\cdots\cdots>_r$ means an average over the sites of random impurities between two Green functions. Since we need $S_2(\boldsymbol{q}, -\boldsymbol{q})$ in the limit $q\to 0$ as will be shown later, we may consider the value of q quite small for the time, and so, we can do a replacement of some terms in the integrands of (7). Let θ being the wave vector $\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)$ and $\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right)$, θ' between $\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)$ and $\left(\boldsymbol{q}'+\frac{1}{2}\boldsymbol{q}\right)$, and θ'' between $\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right)$ and $\left(\boldsymbol{q}'+\frac{1}{2}\boldsymbol{q}\right)$, we can write the scalar product $\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right)$ as

$$\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right) = \left|\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right|\left|\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right|\cos\theta$$
$$\approx\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{q}'+\frac{1}{2}\boldsymbol{q}\right)\cos\theta''+\left|\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right|\left|\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right|\sin\theta'\sin\theta''\cos(\varphi'-\varphi'') \qquad (9)$$

where we have made use of the consideration that the predominant terms in the second term on the right-hand side of (7) are the terms which have the wave vector $\boldsymbol{k}'$ nearly equal to $\boldsymbol{q}'$. By averaging over the azimuthal coordinate $(\varphi'-\varphi'')$, the second term containing an azimuthal coordinate in (9) vanishes owing to the symmetry of the system. Using the approximation mentioned above, we may get the equation for two-partile Green function corresponding to the Boltzmann-Bloch equation[7] from (8).

Multiplying (8) by $\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right)$ and summing over $\boldsymbol{k}$ and $\boldsymbol{k}'$, we

find the following equation

$$\sum_{\boldsymbol{k}}\sum_{\boldsymbol{k}'}\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right)<G(\boldsymbol{k}',\ \boldsymbol{k}-\boldsymbol{q};\ E)G(\boldsymbol{k},\ \boldsymbol{k}'+\boldsymbol{q};E')>_r$$
$$=\sum_{\boldsymbol{k}}\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)^2 G^0(\boldsymbol{k}-\boldsymbol{q};\ E)G^0(\boldsymbol{k},;E')$$
$$+\sum_{\boldsymbol{k}'}G^0(\boldsymbol{k}';E)G^0(\boldsymbol{k}'+\boldsymbol{q};E')\sum_{\boldsymbol{k}}\sum_{\boldsymbol{q}'}n|V(\boldsymbol{q}'-\boldsymbol{k}')|^2\cos\theta''$$
$$\times\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{q}'+\frac{1}{2}\boldsymbol{q}\right)<G(\boldsymbol{q}',\boldsymbol{k}-\boldsymbol{q};E)G(\boldsymbol{k},\boldsymbol{q}'+\boldsymbol{q};E')>_r. \tag{10}$$

It seems to us that a certain constant vector $\bar{\boldsymbol{k}}_f$ being of the order of the Fermi momentum exists[7], so that the summation term over $\boldsymbol{k}$ and $\boldsymbol{q}'$ in the second term on the right-hand side of (10) is approximately given by

$$n|V(\bar{\boldsymbol{k}}_f-\boldsymbol{k}')|^2\cos\theta_{\bar{\boldsymbol{k}}_f\boldsymbol{k}'}\sum_{\boldsymbol{k}}\sum_{\boldsymbol{q}'}\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{q}'+\frac{1}{2}\boldsymbol{q}\right)$$
$$\times<G(\boldsymbol{q}',\ \boldsymbol{k}-\boldsymbol{q};E)G(\boldsymbol{k},\ \boldsymbol{q}'+\boldsymbol{q};E')>_r \tag{11}$$

where $\cos\theta_{\bar{\boldsymbol{k}}_f\boldsymbol{k}'}$ is a constant independent of $\boldsymbol{q}'$. Then, the solution of (10) can be written down at once

$$\sum_{\boldsymbol{k}}\sum_{\boldsymbol{k}'}\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)\cdot\left(\boldsymbol{k}'+\frac{1}{2}\boldsymbol{q}\right)<G(\boldsymbol{k}',\ \boldsymbol{k}-\boldsymbol{q};\ E)G(\boldsymbol{k},\ \boldsymbol{k}'+\boldsymbol{q};E')>_r$$
$$=\frac{I(\boldsymbol{q},E,E')}{1-\gamma(\boldsymbol{q},\ E,\ E')} \tag{12}$$

where

$$I(\boldsymbol{q},E,E')=\sum_{\boldsymbol{k}}\left(\boldsymbol{k}-\frac{1}{2}\boldsymbol{q}\right)^2 G^0(\boldsymbol{k}-\boldsymbol{q};E)G^0(\boldsymbol{k};E')$$

and

$$\gamma(\boldsymbol{q},E,E')=\sum_{\boldsymbol{k}'}n|\ V(\bar{\boldsymbol{k}}_f-\boldsymbol{k}')|^2\cos\theta_{\bar{\boldsymbol{k}}_f\boldsymbol{k}'}\,G^0(\boldsymbol{k}';\ E)G^0(\boldsymbol{k}'+\boldsymbol{q};E').$$

§ 3. Evaluation of the orbital susceptibility

A damping constant $\Gamma(\boldsymbol{k},E)$ in $G^0(\boldsymbol{k};E)$ can be replaced by $\Gamma(\boldsymbol{k}_f,\varepsilon_f)$ under the conditions $|E-\varepsilon_f|\leq(\hbar^2/2m)\,(2k_fk_p-k_p^2)$ and $|\varepsilon_k-\varepsilon_f|\leq(\hbar^2/2m)\,(2k_fk_p-k_p^2)$ with k_f being the wave number of the Fermi level and k_p the inverse of the range of force due to impurity[3]. Let $G_2(\boldsymbol{q},E,E')$ be $I(\boldsymbol{q},\ E,\ E')/\{1-\gamma(\boldsymbol{q},E,E')\}$,

then we expand $G_2(\boldsymbol{q}, E, E')$ as series in q. By substituting (12) into (7), the term from the constant term in respect of q in $G_2(\boldsymbol{q}, E, E')$ vanishes with the first term on the right-hand side of (7), and the linear term of q disappears because of symmetry. The term containing q^n $(n \geq 3)$ on the right-hand side of (7) does not contribute to the orbital susceptibility, as it has been shown by (1), for the reason of limit $q \to 0$.

The problem now is to find the quadratic terms of q on right-hand side of (12), let $G_2^{(2)}$ be the coefficient of these terms,

$$G_2^{(2)} = \frac{\sum_{\boldsymbol{k}}\left\{\frac{1}{4}G^0(\boldsymbol{k}E)G^0(\boldsymbol{k}E') - \frac{5}{3}\varepsilon_{\boldsymbol{k}}\frac{\partial G^0(\boldsymbol{k}E)}{\partial E}G^0(\boldsymbol{k}E') + \frac{2}{3}\varepsilon_{\boldsymbol{k}}^2\frac{\partial^2 G^0(\boldsymbol{k}E)}{\partial E^2}G^0(\boldsymbol{k}E')\right\}}{1 - \sum_{\boldsymbol{k}'}P(\boldsymbol{k}')G^0(\boldsymbol{k}'E)G^0(\boldsymbol{k}'E')}$$

$$+ \frac{\sum_{\boldsymbol{k}}\varepsilon_{\boldsymbol{k}}G^0(\boldsymbol{k}E)G^0(\boldsymbol{k}E')\sum_{\boldsymbol{k}'}P(\boldsymbol{k}')G^0(\boldsymbol{k}'E)\left\{\frac{2}{3}\varepsilon_{\boldsymbol{k}'}\frac{\partial^2 G^0(\boldsymbol{k}'E')}{\partial E'^2} - \frac{\partial G^0(\boldsymbol{k}'E')}{\partial E'}\right\}}{\left\{1 - \sum_{\boldsymbol{k}'}P(\boldsymbol{k}')G^0(\boldsymbol{k}'E)G^0(\boldsymbol{k}'E')\right\}^2} \tag{13}$$

where

$$P(\boldsymbol{k}) = n\left|V(\overline{\boldsymbol{k}_f} - \boldsymbol{k})\right|^2\cos\theta_{\overline{\boldsymbol{k}}_f\boldsymbol{k}}.$$

The summation over $\boldsymbol{k}$ can be replaced by integration per unit volume, namely $\sum_{\boldsymbol{k}} \to A\int_0^\infty d\varepsilon_{\boldsymbol{k}}\varepsilon_{\boldsymbol{k}}^{1/2}$ $(A = (2\pi^2)^{-1}(2m/\hbar^2)^{3/2})$. By the similar calculation has been made by Ando[3], $G_2^{(2)}$ reduces to

$$G_2^{(2)} = A\pi\left\{\frac{\frac{\Gamma}{4}(E^{1/2} + E'^{1/2}) + \frac{10}{3}(E' - E)(E^{3/2} - E'^{3/2})L + \frac{4}{3\Gamma}(E^{5/2} + E'^{5/2})\{3(E' - E)^2 - 4\Gamma\}^2L^2}{(E' - E)^2 + 4\Gamma_1^2}\right\}$$

$$+ P(A\pi)^2\left\{\frac{2\Gamma(E' - E)(E^{1/2} - E'^{1/2})(E^{3/2} + E'^{3/2}L) + \frac{4}{3}\left\{3(E' - E)^2 - 4\Gamma^2\right\}(E^{3/2} + E'^{3/2})^2L^2}{\{(E' - E)^2 + 4\Gamma_1^2\}^2}\right\} \tag{14}$$

with

$$L = \frac{\Gamma}{(E' - E)^2 + 4\Gamma^2}$$

and

$$2\Gamma_1^2 = \Gamma(2\Gamma - PA\pi\varepsilon_f^{1/2}),$$

where we have made use of the constant value of P in respect of its argument.

Then, we reach the final formula for orbital susceptibility, i.e.,

$$\chi = \frac{2\mu_B^2}{\pi^2}\int dE \int dE' \frac{f(E') - f(E)}{E - E'} G_2^{(2)} \tag{15}$$

where μ_B denotes the Bohr magneton. In the limit $P \to 0$, namely in the case of no impurities, χ reduces to

$$\chi_0 = -\frac{A}{3}\mu_B^2\,\varepsilon_f^{1/2} = -\frac{N\mu_B^2}{2\varepsilon_f} \tag{16}$$

with N the number of electrons in the unit volume of the system. It is not so easy to find the order estimation for impurity effect owing to the slight intricacy of formula (14), however, it seems that the orbital susceptibility of electrons with a small consentration of impurities is quite equal to that of the free electrons so far as both Γ and kT are negligibly small compared with ε_f, as it has already been shown by Ando[3].

§ 4. Sum rule for electrical conductivity

Let us, now, consider the sum rule for electrical conductivity, then we do the calculation of the conductivity using the Edwards' formula (8). Taking the direction of $\boldsymbol{q}$ as the z-axis, we expand $<G(\boldsymbol{k}', \boldsymbol{k} - \boldsymbol{q}; E)G(\boldsymbol{k}, \boldsymbol{k}' + \boldsymbol{q}; E')>_r$ as series in q_z, namely,

$$<G(\boldsymbol{k}',\ \boldsymbol{k} - \boldsymbol{q}; E)G(\boldsymbol{k},\ \boldsymbol{k}' + \boldsymbol{q}; E')>_r = \sum_{n=0}^{\infty} q_z^n g_n(k',\ k;\ k,\ k';\ E,\ E') \tag{17}$$

and also

$$G^0(\boldsymbol{k}' + \boldsymbol{q}; E) = \sum_{n=0}^{\infty} q_z^n G_n^0(k';\ E) \tag{18}$$

with putting $G^0(\boldsymbol{k}; E)$ as $G_0^0(\boldsymbol{k}; E)$. Inserting these equations into (8), we obtain the equations in respect of q^0, q, q^2, q^3 and so on. Since the formula of con-

ductivity is given from the equation of zero-th order in respect of q, using the similar approximation to the second section and defining $\varphi(E,\ E')$ by

$$\varphi(E,\ E') = \sum_{k}\sum_{k'} \boldsymbol{k}\cdot\boldsymbol{k}' g_0(k,\ k';\ k',\ k;\ E,\ E'), \tag{19}$$

we have to find the expression of $\varphi(E,\ E')$. Then, $\varphi(E, E')$ becomes

$$\varphi(E,\ E') = \frac{\sum_{k} k^2 G_0^0(k;\ E) G_0^0(k;\ E')}{1 - \dfrac{\Gamma'}{A\pi\varepsilon_f^{1/2}} \sum_{k} G_0^0(k;\ E) G_0^0(k;\ E')} \tag{20}$$

where

$$\Gamma' = \frac{\pi n \varepsilon_f^{1/2}}{2} \int |\ V(\bar{k}_f^2(1 - \cos\theta))\ |^2 \cos\theta d(\cos\theta).$$

In effect, we may replace the summation over $\boldsymbol{k}$ by integral, as we have made the same procedure in the previous section, and we then have

$$\varphi(E,\ E') = A\frac{2m}{\hbar^2}\left(\frac{\Gamma}{\Gamma - \Gamma'}\right)^{1/2} \frac{(E^{3/2} + E'^{3/2})\{\Gamma(\Gamma - \Gamma')\}^{1/2}}{(E - E')^2 + 2\Gamma(\Gamma - \Gamma')}. \tag{21}$$

Finally, we reach the conductivity proportional to

$$\int dE \int dE' \frac{f(E') - f(E)}{E - E'} \varphi(E,\ E'), \tag{22}$$

that is, the electrical conductivity is proportional to $\{\Gamma/(\Gamma - \Gamma')\}^{1/2}$ which is of the order of unity. It seems to us that the sum rule[9] for the electrical conductivity obtained by using the Edwards' approximation does not satisfied. Therefore, the approximation represented by the so-called "ladder diagrams" seems to have been a good approximation for conductivity, however, it implies the existence of a problem in the Edwards' approximation.

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