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Derivation of the Magnetic Susceptibilities of the Free Electrons by the Linear Response Theory

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The isothermal and adiabatic magnetic susceptibilities are calculated by the method of the linear response theory. The result for the former is the same as the Pauli paramagnetic susceptibility.

First we summarize the linear response theory of irreversible process derived by Kubo.[1] The theory developed a general scheme for the calculation of admittance to the external force statistical-mechanically.

Let us consider an isolated system, the natural motion of which is governed by the Hamiltonian $\mathscr{H}$. We suppose that an external force $F(t)$ is applied to it from the infinite past, $t=-\infty$, when it was at thermal equilibrium, the effect is represented by the perturbation energy

$$\mathscr{H}'=-AF(t) \tag{1}$$

The motion of the system is perturbed by this force, but the perturbation is small if the force is weak. We confine ourselves to weak perturbation and ask for the response of the system in the linear approximation. The response of the system to the force is now observed through the change $\Delta B(t)$ of a certain physical quantity B. The problem is now to express $\Delta B(t)$ in terms of the natural motion of the system. In quantum-statistical mechanics the initial unperturbed state of the system is specified by the density matrix ρ. Under the perturbation (1) the state is represented by $\rho'(t)$, with the condition $\rho'(-\infty)=\rho$. We expand $\rho'(t)$ as

$$\rho'(t)=\rho+\Delta\rho(t)$$

The response ΔB of the quantity B is statistically

$$\begin{aligned}\Delta B&=\mathrm{Tr}\,\Delta\rho(t)B\\&=\frac{i}{\hbar}\int_{-\infty}^{t}Tr\{[A,\rho]B(t-t')\}F(t')dt'\end{aligned} \tag{2}$$

Where $B(t)$ is the Heisenberg representation of B,

$$B(t)=\exp(i\mathscr{H}t/\hbar)B\exp(-i\mathscr{H}t/\hbar)$$

and

$$[A,\ B(t)]=\frac{1}{i\hbar}\{A(0)B(t)-B(t)A(0)\}\ .$$

The response function or delayed effect function is now

$$\phi_{BA}(t)=\frac{i}{\hbar}\mathrm{Tr}[A,\ \rho]B(t) \tag{3}$$

which may also be written using the cyclic properties of trace as

$$\phi_{BA}(t)=\frac{1}{i\hbar}\mathrm{Tr}\rho\,[A,\ B(t)]=<[A,\ B(t)]> \tag{4}$$

which are sometimes more convenient.

Eq. (2) is written as

$$\Delta B(t)=\int_{-\infty}^{t}\phi_{BA}(t-t')F(t')dt' \tag{5}$$

which express the response ΔB as linear in the external force F as superposition of the delayed effects. For the complex admittance we have by the Fourier-Laplace transform

$$\chi_{BA}(\omega)=\int_{0}^{\infty}\phi_{BA}(t)e^{-i\omega t}dt \tag{6}$$

The expression of $\phi_{BA}(t)$ may be written in the convenient form by using the identity

$$\begin{aligned}&[A,\ \exp(-\beta\mathscr{H})]\\&=\exp(-\beta\mathscr{H})\int_{0}^{\beta}\exp(\lambda\mathscr{H})[\mathscr{H},\ A]\exp(-\lambda\mathscr{H})d\lambda\\&=\frac{\hbar}{i}\exp(-\beta\mathscr{H})\int_{0}^{\beta}\exp(\lambda\mathscr{H})\dot{A}\exp(-\lambda\mathscr{H})\,d\lambda\\&=\frac{\hbar}{i}\exp(-\beta\mathscr{H})\int_{0}^{\beta}\dot{A}(-i\hbar\lambda)d\lambda\end{aligned} \tag{7}$$

or

$$[\rho,\ A]=i\hbar\int_{0}^{\beta}\rho\dot{A}(-i\hbar\lambda)d\lambda \tag{8}$$

which is easily seen by writing the expression in matrix form in the representation diagonalizing $\mathscr{H}$.

Let us now assume that the system we observe is statistically represented by the canonical matrix

$$\rho=\exp\{-\beta(\mathscr{H}-\Psi)\}, \qquad \beta=1/kT$$
$$\exp(-\beta\Psi)=\mathrm{Tr}(-\beta\mathscr{H}). \tag{9}$$

By Eq. (3) we have

$$\begin{aligned}\phi_{BA}(t)&=\frac{1}{i\hbar}\mathrm{Tr}[\rho, A]B(t)\\ &=\int_0^\beta \mathrm{Tr}\,\rho\dot{A}(-i\hbar\lambda)B(t)d\lambda\\ &=-\int_0^\beta \mathrm{Tr}\,\rho A(-i\hbar\lambda)\dot{B}(t)d\lambda\end{aligned} \tag{10}$$

With the aid of Eq. (10), the relaxation function

$$\Phi_{BA}(t)\equiv\int_t^\infty \phi_{BA}(t')dt' \tag{11}$$

is transformed into

$$\begin{aligned}\Phi_{BA}(t)&=\frac{i}{\hbar}\int_0^\infty \mathrm{Tr}\rho[B(t'), A]dt'\\ &=\int_0^\beta \mathrm{Tr}\,\rho A(-i\hbar\lambda)B(t)d\lambda-B\,\mathrm{Tr}\,\rho A^0B^0\end{aligned} \tag{12}$$

where A^0 and B^0 are the diagonal parts of A and B with respect to $\mathscr{H}$.

There exists a relation between $\chi_{BA}(\omega)$ and $\Phi_{BA}(t)$:

$$\chi_{BA}(\omega)=\Phi_{BA}(0)-i\omega\int_0^\infty \Phi_{BA}(t)e^{-i\omega t}dt \tag{13}$$

For $t=0$, we have from Eq. (12) and Eq. (13)

$$\begin{aligned}\chi_{BA}(0)&=\Phi_{BA}(0)\\ &=\int_0^\beta \mathrm{Tr}\,\rho A(-i\hbar\lambda)\,\mathrm{B}d\lambda-\beta\,\mathrm{Tr}\,\rho A^0B^0\\ &=\int_0^\beta \mathrm{Tr}\,\rho\{A(-i\hbar\lambda)-A^0\}(B-B^0)d\lambda\end{aligned} \tag{14}$$

$\chi_{BA}(0)$ is the static admittance.

The isothermal admittance, χ_{BA}^T, is

$$\chi_{BA}^T=\int_0^\beta \mathrm{Tr}\,\rho\{A(-i\hbar\lambda)-<A>\}(B-<B>)d\lambda \tag{15}$$

where $<A>$ and $<B>$ are the equilibrium expectations of A and B in thermal equilibrium for $F=0$. Eq. (15) is obtained from the expression

$$\Delta B=\frac{\mathrm{Tr}\exp\{-\beta(\mathscr{H}-AF)\}B}{\mathrm{Tr}\exp\{-\beta(\mathscr{H}-AF)\}}-\frac{\mathrm{Tr}\exp(-\beta\mathscr{H})B}{\mathrm{Tr}\exp(-\beta\mathscr{H})}$$

and by using the expansion

$$\exp\{-\beta(\mathscr{H}-AF)\}=\exp(-\beta\mathscr{H})\{1+\int_0^\beta A(-i\hbar\lambda)d\lambda F+\mathrm{O}(F^2)\}$$

χ_{BA}^T is defined by

$$\chi_{BA}^T=\Delta B/F$$

Expressions (14) and (15) are different without special cases.

Now in our case, the uniform magnetic field $\boldsymbol{H}(t)$ is applied to a spin system of free electrons. The perturbation energy due to $\boldsymbol{H}(t)$ is now

$$\mathscr{H}'=-\boldsymbol{M}\boldsymbol{H}(t) \tag{16}$$

where $\boldsymbol{M}$ is the magnetization of the spin system.

The response function $\phi_{\mu\nu}(t)$ for the magnetization in μ-direction when the external field $\boldsymbol{H}(t)$ lies in ν-direction (μ, $\nu=x$, y, z) is by Eq. (10)

$$\begin{aligned}\phi_{\mu\nu}(t)&=\frac{i}{\hbar}<[M_\mu(t),\,M_\nu]>\\&=\int_0^\beta<\dot{M}_\nu(-i\hbar\lambda)M_\mu>d\lambda\end{aligned} \tag{17}$$

The susceptibility (admittance) is derived from the relation

$$\chi_{\mu\nu}(\omega)=\int_0^\infty\phi_{\mu\nu}(t)e^{-i\omega t}dt$$

The static susceptibility, in particular, for the case $\omega=0$, is written

$$\chi_{\mu\nu}(0)=-\int_0^\infty dt\int_0^\beta<M_\nu(-i\hbar\lambda)\dot{M}_\mu(t)>d\lambda \tag{18}$$

Integration with respect to t is easily performed by noticing that

$$\int_0^\infty\dot{M}_\mu(t)dt=M_\mu(t)\Big]_0^\infty=M_\mu(\infty)-M_\mu(0)$$

and $M_\mu(\infty)$ is taken as the diagonal parts of M_μ. The static susceptibility is thus

$$\chi_{\mu\nu}(0)=\int_0^\infty<\{M_\nu(-i\hbar\lambda)-M_\nu^0\}(M_\mu-M_\mu^0)>d\lambda \tag{19}$$

which is the susceptibility for the isolated system and is not necessarily equal to the isothermal susceptibility,

$$\chi_{\mu\nu}^{T}=\int_{0}^{\beta}<M_{\nu}(-i\hbar\lambda)M_{\mu}>d\lambda-\beta<M_{\nu}><M_{\mu}> \tag{20}$$

If we take the magnetic field of magnitude H along z direction, the magnetization operator due to the spin of the electrons may be written in the second quantization formalism as

$$\begin{aligned} M^{+}&=M_{x}+iM_{y}=g\mu_{B}\sum_{k}a_{k\uparrow}^{+}a_{k\downarrow} \\ M^{-}&=M_{x}-iM_{y}=g\mu_{B}\sum_{k}a_{k\downarrow}^{+}a_{k\uparrow} \\ M_{Z}&=g\mu_{B}\frac{1}{2}\sum_{k}k(a_{k\uparrow}^{+}a_{k\uparrow}-a_{k\downarrow}^{+}a_{k\downarrow}) \end{aligned} \tag{21}$$

It may be easily seen that

$$<M_{\mu}>_{0}=0, \qquad <M_{\mu}M_{\nu}>_{0}=<M_{\mu}^{2}>_{0}\delta_{\mu\nu}$$

and then

$$<M_{\mu}>=\int_{0}^{\beta}<M_{z}(-i\hbar\lambda)M_{z}>_{0}H\delta_{\mu z}d\lambda \tag{22}$$

One can write $<M_{z}>=\chi H$ for the susceptibility and obtain

$$\begin{aligned} \chi&=\frac{1}{4}g^{2}\mu_{B}^{2}\beta\sum_{k}\sum_{k'}<(a_{k\uparrow}^{+}a_{k\uparrow}-a_{k\downarrow}^{+}a_{k\downarrow})(a_{k'\uparrow}^{+}a_{k'\uparrow}-a_{k'\downarrow}^{+}a_{k'\downarrow})> \\ &=\frac{1}{4}\beta g^{2}\mu_{B}^{2}\sum_{k}\sum_{k'}2\{<n_{k\uparrow}n_{k'\uparrow}>_{0}-<n_{k\uparrow}n_{k'\downarrow}>_{0}\} \end{aligned} \tag{23}$$

where $n_{k\sigma}=a_{k\sigma}^{+}a_{k\sigma}$ and the symmetry property of the direction of up and down spins.

For free electrons

$$\begin{aligned} <n_{k\uparrow}n_{k'\downarrow}>_{0}&=<n_{k\uparrow}>_{0}<n_{k'\downarrow}>_{0} \\ <n_{k\uparrow}n_{k'\uparrow}>_{0}&=<n_{k\uparrow}>_{0}<n_{k'\uparrow}>_{0}-<a_{k\uparrow}^{+}a_{k'\uparrow}>_{0}<a_{k\uparrow}a_{k\uparrow}^{+}>_{0} \end{aligned} \tag{24}$$

and $<n_{k\sigma}>$ is the Fermi-Dirac distribution function

$$<n_{k\sigma}>=f_{k}(\varepsilon)=\frac{1}{\exp\beta(\varepsilon_{k}-\varepsilon_{F})+1}$$

Thus, Eq. (23) leads to

$$\chi = -\frac{1}{2}\beta g^2 \mu_B^2 \sum_k f_k(1-f_k) \tag{25}$$

where the function

$$f_k(1-f_k) = \frac{1}{\{\exp\beta(\varepsilon_k-\varepsilon_F)+1\}\{1+\exp(-\beta(\varepsilon_k-\varepsilon_F))\}} \tag{26}$$

has a peak for $\varepsilon_k \sim \varepsilon_F$, and tends to the delta-function at low temperatures. Summation in Eq. (25) is carried out by the integral $\int D(\varepsilon)d\varepsilon$, where $D(\varepsilon)$ is the density of states. Thus Eq. (25) gives

$$\chi = \frac{1}{2} g^2 \mu_B^2 D(\varepsilon_F) \tag{27}$$

This is the isothermal susceptibility that correspond to the Pauli paramagnetism of conduction electrons.[2] Eq. (19) differs from Eq. (20). The former is derived by considering only the change of M with the external force and the probability of the state is retained as it before. Thus Eq. (19) represents an adiabatic susceptibility. In Eq. (19) the perturbation term $\mathscr{H}'$ commute with the unperturbed Hamiltonian $\mathscr{H}$. The wave function does not change with time. Thus the adiabatic susceptibility is equal to zero.

References

1) R. KUBO: J. Phys. Soc. Japan **12** (1957) 570.
2) W. PAULI: Z. Physik, **41** (1927) 81.