Theory of magnetic susceptibility of Bloch electrons in the presence of localized magnetic moments

Gouri S. Tripathi
Department of Physics, Berhampur University, Berhampur-760 007, Orissa, India
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We derive a theory of magnetic susceptibility (χ) of Bloch electrons including the effects of periodic potential, spin-orbit interaction, and localized magnetic moments. We use a temperature-dependent Green's-function technique to evaluate the thermodynamic potential which is then used to obtain a general expression for χ. Our formula for χ is expressed as $\chi=\chi_{\rm MK}+P\chi_{\rm CW}$, where $\chi_{\rm MK}$ is the magnetic susceptibility of Bloch electrons obtained by Misra and Kleinman, which includes spin, orbital, and spin-orbit contributions, P is the shift in the electron paramagnetic resonance frequency, and $\chi_{\rm CW}$ is the Curie-Weiss susceptibility. The second term, which is obtained for the first time by us, is due to the interaction of conduction-electron magnetic moment and the localized magnetic moments. Many-body effects, although not included from first principles, are discussed on the final results of χ, in view of their importance. We also discuss the importance of the theory in possible applications. Finally, we believe that the theory presented in this work is the most general and thorough treatment which has yet been made of this problem.

I. INTRODUCTION

The problem of magnetic susceptibility (χ) of Bloch electrons has been studied for many years. This is one of the quantities, which forms an important basis in understanding both the single-particle and many-particle effects in the solids. Although much work has been done since the foundations laid in this area by Landau[1] and Pauli,[2] it is only recently that the basic mechanisms which contribute to the quantity in solids have been reasonably understood.[3-11] A complete expression for the orbital magnetic susceptibility was first derived by Misra and Roth,[5] and the theory was applied to alkali metals, through the use of a pseudopotential technique, with fairly good agreement with experiment in most of the cases. However, the theory was incomplete in the sense that it ignored the effects of spin and spin-orbit interactions on χ. Misra and Kleinman[6] had derived a more complete theory and expressed χ as a sum of three contributions: $\chi=\chi_0+\chi_s+\chi_{\rm s.o.}$, where $\chi_{\rm o}$ is the orbital susceptibility of Misra and Roth (MR),[5] $\chi_{\rm s}$ is the effective Pauli spin susceptibility, and $\chi_{\rm s.o.}$ is a contribution due to the effect of spin-orbit interaction on the orbital motion of Bloch electrons. It may, however, be noted that the effect of spin-orbit interaction on the spin of electrons is incorporated through the effective g factor in $\chi_{\rm s}$. However, many-body effects were not considered by these authors.

It is well known that the one-electron description is inaccurate insofar as it disregards the spatial correlations between electrons, as demonstrated, for instance, by the grossly incorrect results it yields for the spin susceptibility. Misra *et al.*[7] have considered the many-body effects on χ and derived a reasonably complete theory for this quantity. They have discussed the many-body effects on all the three contributions to χ. The results[8] of exchange-enhanced spin susceptibility of alkali metals based on their theory using pseudopoential formalism and degenerate perturbation theory agree fairly well with experiment.

The theories reviewed above have been successfully applied to simple metals[5,8-11] and narrow-band-gap semiconductors[12-14] which do not have unpaired either d or f shells. The presence of unpaired d or f shells is characteristic of transition and rare-earth metals and their compounds and alloys. The interaction of localized magnetic moments associated with these unpaired d of f shells with the magnetic moment of conduction electrons has an important effect on the various properties of these solids. These interactions which are popularly known as s-d or s-f hybridization are mainly responsible for several properties in these solids. Indeed, the hybridization of f electrons with the band electrons in rare-earth and actinide compounds and dilute alloys is known to give rise to many interesting features and new developments in high-energy photon and electron spectroscopy, itinerant versus localized magnetism, valence instability, dense Kondo behavior, anisotropic interactions, or heavy-fermion superconductivity.[15,16]

It is clear, thus, from the foregoing remarks that the magnetic susceptibility of free and interacting Bloch electrons is well understood in the absence of localized magnetic moments. However, as discussed in the preceding paragraph, the effect of localized magnetic moments on the conduction electrons is extremely important to study the magnetic properties in magnetic solids. We derive, therefore, in this paper, a first-principles theory of magnetic susceptibility of Bloch electrons including the effects of periodic potential, spin-orbit interaction and localized magnetic moments, and report some new findings. The final result for χ can be expressed as a sum of two contributions: $\chi=\chi_{\rm MK}+\chi_{\rm loc}$, where $\chi_{\rm MK}$ is the Misra-Kleinman susceptibility[6] and $\chi_{\rm loc}$ is a new contribution which is expressed as a product of the shift in the electron-paramagnetic-resonance (EPR) frequency, P, and the Curie-Weiss susceptibility, χ_{CW}. In the process, we have derived for the first time a complete expression for P which is very much similar to the expression for the Knight shift (K).[17–19] The theory is the outcome of a complete and most thorough treatment of the well-known magnetic interactions in solids. Although we do not include the effects of electron-electron interactions from first principles, we briefly discuss them on the final results of our derivation, in view of their importance in the calculation of χ. The reason for this omission is that details of many-body effects on the various constituent terms of χ have already been published.[7]

We organize the paper in the following way. In Sec. II, we discuss the Hamiltonian of the problem and obtain the equation of motion of the Green's function in the presence of the relevant magnetic interactions in a representation defined by the periodic part of the Bloch function. In Sec. III, we derive a general expression for χ and outline the physical significance of the various contributing terms. Finally, in Sec. IV, we summarize, discuss the importance of the present work in possible applications and conclude our results.

II. EQUATION OF MOTION OF GREEN'S FUNCTION

The one-particle Green's function $G(\mathbf{r},\mathbf{r}',\mathbf{B},\boldsymbol{\mu},\zeta_l)$ in the presence of periodic potential $V(\mathbf{r})$, spin-orbit interaction, applied magnetic field $\mathbf{B}$, and localized magnetic moment $\boldsymbol{\mu}$ satisfies the equation

$$(\zeta_l-H)G(\mathbf{r},\mathbf{r}',\mathbf{B},\boldsymbol{\mu},\zeta_l)=\delta(\mathbf{r}-\mathbf{r}') \ , \tag{2.1}$$

where

$$\zeta_l=\frac{(2l+1)i\pi}{\beta}+\xi, \quad l=0,\pm1,\pm2,\dots \ , \tag{2.2}$$

ξ being the chemical potential and $\beta^{-1}=k_BT$. Further,

$$H=\frac{1}{2m}\left[\mathbf{p}+\frac{e}{c}\mathbf{A}\right]^2+V(\mathbf{r}) +\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\nabla V\times\left[\mathbf{p}+\frac{e}{c}\mathbf{A}\right]+\tfrac{1}{2}g_0\mu_0\mathbf{B}\cdot\boldsymbol{\sigma}+H_I \ , \tag{2.3}$$

where

$$H_i=\sum_j \mu_0\langle\boldsymbol{\mu}_j\rangle\cdot\mathbf{X}_{j\mathbf{B}} \ . \tag{2.4}$$

In Eq. (2.3) the first four terms are the well-known interactions in the presence of magnetic field, where $\mathbf{A}$ is the magnetic vector potential, $\boldsymbol{\sigma}$ are the Pauli spin matrices, g_0 is the free-electron g factor, and μ_0 is the Bohr magneton. In Eq. (2.4), H_I represents the interactions between the localized magnetic moment due to unpaired d or f shells and the conduction electron magnetic moment. Here

$$\langle\boldsymbol{\mu}_j\rangle=-g_j\mu_0\langle\mathbf{J}_j\rangle \tag{2.5}$$

and

$$\mathbf{X}_{j\mathbf{B}}=\left[\frac{8\pi}{3}\boldsymbol{\sigma}\delta(\mathbf{r}_j)+\left[-\frac{\boldsymbol{\sigma}}{r_j^3}+\frac{3(\boldsymbol{\sigma}\cdot\mathbf{r}_j)\mathbf{r}_j}{r_j^5}\right]\right] +2\mathbf{r}_j\times\left[\boldsymbol{\Pi}+\frac{e}{c}\mathbf{A}\right]\Big/\hbar r_j^3\equiv\mathbf{X}_j^0+\mathbf{X}_{j\mathbf{B}}^1 \ . \tag{2.6}$$

In Eqs. (2.5) and (2.6), g_j and $\mathbf{J}_j$ are the Lande g factor and total angular momentum of the jth ion, respectively, $\langle\ \rangle$ denotes the thermal average value, $\mathbf{r}_j=\mathbf{r}-\mathbf{R}_j$, where $\mathbf{R}_j$ is the position vector of the jth site, and $\boldsymbol{\Pi}$ is the electronic momentum operator in the presence of spin-orbit interaction:

$$\boldsymbol{\Pi}=\mathbf{p}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V \ . \tag{2.7}$$

In Eq. (2.6), the terms from left to right on the right-hand side form the parts of contact, dipolar, and orbital interactions of the conduction-electron magnetic moment with the localized magnetic moment at $\mathbf{R}_j$.

G satisfies the lattice translational symmetry in the absence of magnetic field. However, magnetic field $\mathbf{B}$ destroys this symmetry. In order to take care of this lack of lattice periodicity in the presence of magnetic field, we define[7]

$$G(\mathbf{r},\mathbf{r}',\mathbf{B},\boldsymbol{\mu},\zeta_1)=e^{i\mathbf{h}\cdot\mathbf{r}\times\mathbf{r}'}\widetilde{G}(\mathbf{r},\mathbf{r}',\mathbf{B},\boldsymbol{\mu},\zeta_l) \ , \tag{2.8}$$

where the exponential on the right-hand side represents the Peierl's phase factor defined in the symmetric gauge, $\widetilde{G}$ satisfies the crystal translation symmetry, and $\mathbf{h}=e\mathbf{B}/2\hbar c$.

Substituting Eq. (2.8) in Eq. (2.1), and following the techniques outlined in Refs. 7 and 18, we write Eq. (2.1) in a representation defined by the periodic part of the Bloch function $\psi_{n\mathbf{k}\rho}(\mathbf{r})$, where n is the band index, $\mathbf{k}$ is the reduced wave vector, and ρ is the spin index, as

$$[\zeta_l-H(\boldsymbol{\kappa})]\widetilde{G}(\mathbf{k},\zeta_l)=I \ . \tag{2.9}$$

Here

$$H(\boldsymbol{\kappa})=\frac{1}{2m}(\mathbf{p}+\hbar\boldsymbol{\kappa})^2+V+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\nabla V\times(\mathbf{p}+\hbar\boldsymbol{\kappa}) +\tfrac{1}{2}g_0\mu_0B^\mu\sigma^\mu +\sum_j\mu_0\chi_j^{\tau\mu}B^\mu\left[X_j^\tau-2i\epsilon_{\tau\alpha\gamma}h_{\gamma\beta}\frac{r_j^\alpha\nabla_k^\beta}{r_j^3}\right] . \tag{2.10}$$

In Eq. (2.10),

$$\boldsymbol{\kappa}=\mathbf{k}+i\mathbf{h}\times\nabla_k \ , \tag{2.11}$$

and we have used the relation

$$\langle\mu_j^\tau\rangle=\chi_j^{\tau\mu}B^\mu \ , \tag{2.12}$$

where $\chi_j^{\tau\mu}$ is the paramagnetic susceptibility tensor of the jth ion and is of Curie-Weiss type; $\mathbf{X}_j$ is $\mathbf{X}_{j\mathbf{B}}$ with $\mathbf{B}=0$, and $\epsilon_{\tau\alpha\gamma}$ is an antisymmetric tensor of third rank and we follow Einstein summation convention. We can now write $H(\boldsymbol{\kappa})$, separating the field-independent and field-dependent parts, as

$$H(\boldsymbol{\kappa})=H_0(\mathbf{k})+H'(\mathbf{k}) \ , \tag{2.13}$$

where $H_0(\mathbf{k})$ is the field-independent Hamiltonian,

$$H_0(\mathbf{k})=\frac{1}{2m}(\mathbf{p}+\hbar\mathbf{k})^2+V+\frac{\hbar}{4m^2c^2}\sigma\cdot\nabla V\times(\mathbf{p}+\hbar\mathbf{k}) \tag{2.14}$$

and

$$\begin{aligned}H'(\mathbf{k})=&-i\frac{\hbar}{m}h_{\alpha\beta}\Pi^\alpha\nabla_k^\beta+\tfrac{1}{2}g_0\mu_0B^\mu\sigma^\mu\\&-\frac{\hbar^2}{2m}h_{\alpha\beta}h_{\gamma\delta}\delta_{\alpha\gamma}\nabla_k^\beta\nabla_k^\delta\\&+\sum_j\mu_0\chi_j^{\tau\mu}B^\mu\left[X_j^\tau-2i\epsilon_{\tau\alpha\gamma}h_{\gamma\beta}\frac{r_j^\alpha\nabla_k^\beta}{r_j^3}\right].\end{aligned} \tag{2.15}$$

Here

$$h_{\alpha\beta}=\epsilon_{\alpha\beta\gamma}h^\gamma . \tag{2.16}$$

Equation (2.9) can then be solved by a perturbation expansion

$$\widetilde{G}(\mathbf{k},\zeta_l)=\widetilde{G}_0+\widetilde{G}_0H'\widetilde{G}_0+\widetilde{G}_0H'\widetilde{G}_0H'\widetilde{G}_0+\cdots , \tag{2.17}$$

where

$$\widetilde{G}_0^{-1}=[\zeta_l-H_0(\mathbf{k},\zeta_l)] \tag{2.18}$$

and is diagonal in the basis $U_{n\mathbf{k}\rho}$. Furthermore we have[7]

$$\nabla_k^\alpha\widetilde{G}_0=\frac{\hbar}{m}\widetilde{G}_0\Pi^\alpha\widetilde{G}_0 \tag{2.19}$$

and

$$\nabla_k^\alpha\nabla_k^\gamma\widetilde{G}_0=\frac{\hbar^2}{m}\widetilde{G}_0\widetilde{G}_0\delta_{\alpha\gamma}+\frac{\hbar^2}{m^2}(\widetilde{G}_0\Pi^\alpha\widetilde{G}_0\Pi^\gamma\widetilde{G}_0+\widetilde{G}_0\Pi^\gamma\widetilde{G}_0\Pi^\alpha\widetilde{G}_0) . \tag{2.20}$$

Using Eqs. (2.15), (2.19), and (2.20) in Eq. (2.17) and retaining terms up to second order in magnetic field $\mathbf{B}$, we obtain after a little algebra

$$\widetilde{G}=\widetilde{G}_{\text{cond}}+\sum_j\chi_j^{\tau\mu}\widetilde{G}_{\text{loc}}(\zeta_l) , \tag{2.21}$$

where $\widetilde{G}_{\text{cond}}$ is same as $\widetilde{G}$ obtained by Misra *et al*,[7] their Eq. (3.17), in the absence of electron-electron interactions and with the modification that their $\mathbf{\Pi}$'s are $(\hbar/m)$ times our $\mathbf{\Pi}$'s, and

$$\begin{aligned}\widetilde{G}_{\text{loc}}(\zeta_l)=&\mu_0B^\mu\widetilde{G}_0X_j^\tau\widetilde{G}_0-2i\frac{\hbar}{m}\mu_0\epsilon_{\tau\alpha\gamma}h_{\gamma\beta}B^\mu(\widetilde{G}_0O_j^\alpha\widetilde{G}_0\Pi^\beta\widetilde{G}_0-\widetilde{G}_0\Pi^\beta\widetilde{G}_0O_j^\alpha\widetilde{G}_0)\\&-i\frac{\hbar^2}{m^2}\mu_0h_{\alpha\beta}B^\mu(\widetilde{G}_0\Pi^\alpha\widetilde{G}_0\Pi^\beta\widetilde{G}_0X_j^\tau\widetilde{G}_0+\widetilde{G}_0\Pi^\alpha\widetilde{G}_0X_j^\tau\widetilde{G}_0\Pi^\beta\widetilde{G}_0+\widetilde{G}_0\Pi^\alpha\widetilde{G}_0X_j^\tau\widetilde{G}_0\Pi^\beta\widetilde{G}_0)\\&+\tfrac{1}{2}g_0\mu_0^2B^\mu B^\nu(\widetilde{G}_0\sigma^\nu\widetilde{G}_0X_j^\tau\widetilde{G}_0+\widetilde{G}_0X_j^\tau\widetilde{G}_0\sigma^\nu\widetilde{G}_0)+\sum_{j'}\mu_0^2\chi_{j'}^{\tau'\nu}B^\mu B^\nu\widetilde{G}_0X_j^\tau\widetilde{G}_0X_{j'}^{\tau'}\widetilde{G}_0 ,\end{aligned} \tag{2.22}$$

where

$$O_j^\alpha=\frac{r_j^\alpha}{r_j^3} . \tag{2.23}$$

III. DERIVATION OF χ

The magnetic susceptibility χ can be calculated from the formula

$$\chi=-\left.\frac{\partial^2\Omega}{\partial B_\mu\partial B_\nu}\right|_{\mathbf{B}\to 0} , \tag{3.1}$$

where Ω is the thermodynamic potential:[20,21]

$$\Omega=-\frac{1}{\beta}\operatorname{Tr}\ln(-\widetilde{G}_{\zeta_l}) \tag{3.2}$$

$$\equiv-\frac{1}{2\pi i}\operatorname{tr}\oint_c\phi(\zeta)\widetilde{G}(\zeta)d\zeta . \tag{3.3}$$

Here

$$\phi(\zeta)=-\frac{1}{\beta}\ln(1+e^{-\beta(\zeta-\xi)}) . \tag{3.4}$$

While Tr involves summation over imaginary frequencies and one-particle states, tr involves summation over one-particle states only; the contour c encircles the imaginary axis in a counterclockwise direction. Ω can be separated, using Eq. (2.21), as

$$\Omega=\Omega_{\text{cond}}+\Omega_{\text{loc}} , \tag{3.5}$$

where

$$\Omega_{\text{cond}}=-\frac{1}{\beta}\operatorname{tr}\oint_c\phi(\zeta)\widetilde{G}_{\text{cond}}(\zeta)d\zeta \tag{3.6}$$

and

$$\Omega_{\text{loc}}=\sum_j\chi_j^{\nu\mu}\left[-\frac{1}{\beta}\operatorname{tr}\oint_c\phi(\zeta)\widetilde{G}_{\text{loc}}(\zeta)d\zeta\right] , \tag{3.7}$$

so that Eq. (3.1) can be written as

$$\chi=\chi_{\text{cond}}^{\nu\mu}+\chi_{\text{loc}}^{\nu\mu} , \tag{3.8}$$

where $\chi_{\text{cond}}^{\nu\mu}$ is the magnetic susceptibility of Bloch electrons in the absence of localized magnetic moments and

$$\chi_{\text{loc}}^{\nu\mu}=-\left.\frac{\partial^2\Omega_{\text{loc}}}{\partial B_\mu\partial B_\nu}\right|_{\mathbf{B}\to 0} . \tag{3.9}$$

The evaluation of $\chi_{\text{cond}}^{\nu\mu}$ is discussed in detail in Ref. 7.

These results were first obtained, using Roth's function,[5] by Misra and Kleinman.[6] Therefore, we write

$$\chi^{\nu\mu}_{\rm cond}=\chi^{\nu\mu}_{\rm MK}\ , \tag{3.10}$$

where

$$\chi^{\nu\mu}_{\rm MK}=\chi^{\nu\mu}_{\rm o}+\chi^{\nu\mu}_{\rm s}+\chi^{\nu\mu}_{\rm s.o.}\ . \tag{3.11}$$

Here $\chi_{\rm o}$, $\chi_{\rm s}$, and $\chi_{\rm s.o.}$ are the orbital, spin, and spin-orbit contributions to the magnetic susceptibility.

We shall now derive an expression for $\chi^{\nu\mu}_{\rm loc}$. From Eqs. (2.22) and (3.7), we obtain

$$\begin{aligned}\Omega_{\rm loc}=\sum_{j\mathbf{k}}\chi_j^{\tau\mu}\Bigg\{&\mu_0B^\mu X^\tau_{jn\rho,n\rho'}f(E_{n\mathbf{k}})+i\frac{\hbar^2}{m^2}h_{\alpha\beta}\mu_0B^\mu\Bigg[X^\tau_{jn\rho,n\rho'}\Pi^\alpha_{n\rho'm\rho''}\Pi^\beta_{m\rho''n\rho}\left[\frac{f'(E_n)}{E_{mn}}+\frac{3f(E_n)}{E^2_{mn}}+\frac{4\phi(E_n)}{E^3_{mn}}\right]\\
&+\Pi^\alpha_{n\rho,m\rho'}\Pi^\beta_{m\rho',q\rho''}X^\tau_{jq\rho'',n\rho}\left[\frac{f(E_n)}{E_{qn}E_{mn}}+\frac{2\phi(E_n)}{E^2_{mn}E_{qn}}\right]\\
&-\Pi^\alpha_{n\rho,m\rho'}X^\tau_{jm\rho'q\rho''}\Pi^\beta_{q\rho''n\rho}\left[\frac{f(E_n)}{E_{qn}E_{mn}}+\frac{2\phi(E_n)}{E^2_{mn}E_{qn}}+\frac{2\phi(E_n)}{E^2_{qn}E_{mn}}\right]\\
&-X^\tau_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}\left[\frac{f(E_n)}{E_{mn}E_{qn}}+\frac{2\phi(E_n)}{E^3_{mn}}\right]\\
&+\Pi^\alpha_{n\rho,n\rho}\Pi^\beta_{n\rho,m\rho'}X^\tau_{jm\rho',n\rho}\left[\frac{f(E_n)}{E^2_{mn}}+\frac{2\phi(E_n)}{E^3_{mn}}\right]\Bigg]\\
&+2A_j^{\eta\beta}\left[\frac{C^\eta_{jn\rho,m\rho'}\Pi^\beta_{m\rho'n\rho}-\Pi^\beta_{n\rho,m\rho'}C^\eta_{jm\rho'n\rho}}{E^2_{mn}}\right]\phi(E_n)+A_j^{\eta\beta}\left[\frac{C^\eta_{jn\rho,m\rho'}\Pi^\beta_{m\rho'n\rho}-\Pi^\beta_{n\rho,m\rho'}C^\eta_{jm\rho'n\rho}}{E_{mn}}\right]f(E_n)\\
&+\tfrac14 g_0\mu_0^2B^\mu B^\nu(X^\tau_{jn\rho,n\rho'}\sigma^\nu_{n\rho',n\rho}+\sigma^\nu_{n\rho,n\rho'}X^\tau_{jn\rho'n\rho})f'(E_n)\\
&+\tfrac12 g_0\mu_0^2B^\mu B^\nu\left[\frac{X^\tau_{jn\rho,m\rho'}\sigma^\nu_{m\rho'n\rho}+\sigma^\nu_{n\rho,m\rho'}X^\tau_{jm\rho',n\rho}}{E_{mn}}\right]f(E_n)\Bigg\}\\
+\sum_{\mathbf{k},\mathbf{k}'j,j'}&\mu_0^2\chi_j^{\tau\mu}\chi_{j'}^{\tau'\nu}B^\mu B^\nu(X^\tau_{jn\mathbf{k}\rho,n\mathbf{k}'\rho'}X^{\tau'}_{j'n'\mathbf{k}'\rho',n\mathbf{k}\rho}+X^{\tau'}_{j'n\mathbf{k}\rho,n'\mathbf{k}'\rho'}X^\tau_{jn'\mathbf{k}'\rho',n\mathbf{k}\rho})\frac{f(E_{n\mathbf{k}})}{E_{n\mathbf{k}}-E_{n'\mathbf{k}'}}\ ,\end{aligned} \tag{3.12}$$

where

$$A_j^{\eta\beta}C_j^\eta=2i\frac{\hbar}{m}\mu_0B^\mu\epsilon_{\tau\eta\alpha}h_{\alpha\beta}O_j^\eta\ . \tag{3.13}$$

Repeated indices imply summation. In the last term of Eq. (3.12), the matrix elements are taken between Bloch functions, while the other terms are expressed as functions of matrix elements taken between the periodic parts of the Bloch function.

Using the partial integration technique and the periodic nature of the integrand, it can be shown as

$$\begin{aligned}-i\frac{\hbar^2}{m^2}h_{\alpha\beta}\mu_0\chi_j^{\tau\mu}B^\mu\sum_{\mathbf{k}}&\left[\frac{\Pi^\alpha_{n\rho,n\rho}X^\tau_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}}{E^2_{mn}}-\frac{\Pi^\alpha_{n\rho,n\rho}\Pi^\beta_{n\rho,m\rho'}X^\tau_{jm\rho'n\rho}}{E^2_{mn}}\right]f(E_n)\\
=\sum_{\mathbf{k}}\Bigg[&i\frac{\hbar^2}{m^2}h_{\alpha\beta}\mu_0\chi_j^{\tau\mu}B^\mu\Bigg[2\frac{X^\tau_{jn\rho,n\rho'}\Pi^\alpha_{n\rho',m\rho''}\Pi^\beta_{m\rho''n\rho}}{E^3_{mn}}-\frac{\Pi^\alpha_{n\rho,m\rho'}\Pi^\beta_{m\rho',q\rho''}X^\tau_{jq\rho'',n\rho}}{E^2_{mn}E_{qn}}-\frac{X^\tau_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E^2_{qn}E_{mn}}\\
&-\frac{\Pi^\alpha_{n\rho,m\rho'}X^\tau_{jm\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E^2_{qn}E_{mn}}-\frac{\Pi^\alpha_{n\rho,m\rho'}X^\tau_{jm\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E_{qn}E^2_{mn}}\\
&+\frac{\Pi^\alpha_{n\rho,n\rho}X^\tau_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}}{E^3_{mn}}-\frac{\Pi^\alpha_{n\rho,n\rho}\Pi^\beta_{n\rho,m\rho'}X^\tau_{jm\rho'n\rho}}{E^3_{mn}}\Bigg]\\
&+2A_j^{\eta\beta}\chi_j^{\tau\mu}\frac{C^\eta_{jn\rho,m\rho'}\Pi^\beta_{m\rho'n\rho}-\Pi^\beta_{n\rho,m\rho'}C^\eta_{jm\rho'n\rho}}{E^2_{mn}}\Bigg]\phi(E_n)\ .\end{aligned} \tag{3.14}$$

From Eqs. (3.9), (3.12), and (3.14), and Eq. (3.40) of Ref. 18, we obtain

$$\chi_{\rm loc}^{\nu\mu}=P_j^{\nu\tau}\chi_j^{\tau\mu}\ , \tag{3.15}$$

where

$$P_j^{\nu\tau}=P_{js}^{\nu\tau}+P_{jo}^{\nu\tau}+P_{j\rm s.o.}^{\nu\tau}+P_{j\rm RKKY}^{\nu\tau}\ , \tag{3.16}$$

$$P_{js}^{\nu\tau}=-\sum_{\mathbf{k}}\left[\frac{i}{m}\mu_0^2\epsilon_{\alpha\beta\nu}X_{jn\rho,np'}^{\tau}\Pi_{n\rho',m\rho''}^{\alpha}\Pi_{m\rho'',n\rho}^{\beta}\Big/E_{mn}+\tfrac{1}{2}g_0\mu_0^2X_{jn\rho,n\rho'}^{\tau}\sigma_{n\rho',n\rho}^{\tau}\right]f'(E_n)\ , \tag{3.17}$$

$$P_{jo}^{\nu\tau}=-\frac{e^2}{3mc^2}\sum_{\mathbf{k}}\left[\frac{1}{r_j}\right]_{n\rho,n\rho}\delta_{\nu\tau}f(E_n)+\frac{2}{\hbar}\mu_0^2\epsilon_{\alpha\beta\nu}\sum_{\mathbf{k}}\left[(r_j^{\alpha}\Pi^{\beta})_{n\rho,m\rho'}\left[\frac{L_j^{\tau}}{r_j^3}\right]_{m\rho',n\rho}+\left[\frac{L_j^{\tau}}{r_j^3}\right]_{n\rho,m\rho'}(r_j^{\alpha}\Pi^{\beta})_{m\rho',n\rho}\right]\frac{f(E_n)}{E_{mn}}\ , \tag{3.18}$$

$$\begin{aligned}P_{j\rm s.o.}^{\nu\tau}=\sum_{\mathbf{k}}\Bigg[\frac{i\mu_0^2}{m}\epsilon_{\alpha\beta\nu}\Bigg[&-\frac{3X_{jn\rho,n\rho'}^{\tau}\Pi_{n\rho',m\rho''}^{\alpha}\Pi_{m\rho'',n\rho}^{\beta}}{E_{mn}^2}+\frac{\Pi_{n\rho,n\rho}^{\alpha}X_{jn\rho,m\rho'}^{\tau}\Pi_{m\rho',n\rho}^{\beta}}{E_{mn}^2}-\frac{\Pi_{n\rho,n\rho}^{\alpha}\Pi_{n\rho,m\rho'}^{\beta}X_{jm\rho'n\rho}^{\tau}}{E_{mn}^2}\\&+\frac{\Pi_{n\rho,m\rho'}^{\alpha}\Pi_{m\rho',q\rho''}^{\beta}X_{jq\rho'',n\rho}^{0\tau}}{E_{mn}E_{qn}}+\frac{\Pi_{n\rho,m\rho'}^{\alpha}X_{jm\rho'q\rho''}^{0\tau}\Pi_{q\rho''n\rho}^{\beta}}{E_{mn}E_{qn}}+\frac{X_{jn\rho,m\rho'}^{0\tau}\Pi_{m\rho'q\rho''}^{\alpha}\Pi_{q\rho''n\rho}^{\beta}}{E_{mn}E_{qn}}\Bigg]\\&+\tfrac{1}{2}g_0\mu_0^2\frac{X_{jn\rho,m\rho'}^{\tau}\sigma_{m\rho'n\rho}^{\nu}+\sigma_{n\rho,m\rho'}^{\nu}X_{jm\rho'n\rho}^{\tau}}{E_{mn}}\Bigg]f(E_n)\ ,\end{aligned} \tag{3.19}$$

and

$$P_{j\rm RKKY}^{\nu\tau}=\chi_{j'}^{\tau'\nu}A_{jj'}^{\tau\tau'}\ . \tag{3.20}$$

Here

$$A_{jj'}^{\tau\tau'}=\mu_0^2\sum_{\mathbf{k},\mathbf{k}'}(X_{n\mathbf{k}\rho,n'\mathbf{k}'\rho'}^{\tau}X_{n'\mathbf{k}'\rho',n\mathbf{k}\rho}^{\tau'}e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{jj'}}+X_{n\mathbf{k}\rho,n'\mathbf{k}'\rho'}^{\tau'}X_{n\mathbf{k}'\rho',n\mathbf{k}\rho}^{\tau}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{jj'}})\frac{f(E_{n\mathbf{k}})}{E_{n\mathbf{k}}-E_{n'\mathbf{k}'}}\ . \tag{3.21}$$

It may be noted that, as before, repeated indices imply summation. All the matrix elements in Eqs. (3.17)—(3.21), are taken between the periodic parts of the Bloch function. P_j is the EPR shift at the jth site. P_s, P_o, and $P_{\rm s.o.}$ are the spin, orbital, and spin-orbit contributions to the EPR shift. $P_{\rm RKKY}$ is an additional contribution to this shift due to Ruderman-Kittel-Kasuya-Yosida (RKKY) type of interactions,[22–24] defined through the coupling constant $A_{jj'}^{\tau\tau'}$. It may be noted that P is the counterpart in EPR of the Knight shift K in the NMR. It is no surprise that exactly similar mechanisms contribute to both the quantities. If the crystal is homogeneous, as in the case of ordered magnetic systems, P is same at every site and

$$\chi_{\rm loc}=P\chi_{\rm CW} \tag{3.22}$$

and $\chi_{\rm CW}$ is the Curie-Weiss paramagnetic susceptibility of the solid. Therefore, we have from Eqs. (3.8), (3.10), and (3.22),

$$\chi=\chi_{\rm MK}+P\chi_{\rm CW}\ . \tag{3.23}$$

This is a complete expression for the magnetic susceptibility of Bloch electrons. Apart from containing the well-known orbital, spin, and spin-orbit contributions, it also contains the paramagnetic interactions which give rise to the Curie-Weiss susceptibility modified due to the interaction between the conduction electron magnetic moment and localized magnetic moment. Furthermore, $\chi_{\rm loc}$ contains a RKKY type of interaction which could be either ferromagnetic or antiferromagnetic. Thus, all the magnetic interactions in the solid have been adequately considered in the theory.

One of the most important aspects of the magnetic susceptibility calculations is the many-body effects on the various components of χ. These effects have been considered from first principles in earlier works.[7,8,18] However, for the sake of completeness, we briefly discuss them. χ_s, the spin susceptibility, becomes exchange enhanced by electron-electron interactions, as also P_s. The electron-electron interaction effects on the orbital contributions, χ_o and P_o, are normally small and incorporated through effective mass corrections. The many-body effects on $\chi_{\rm s.o.}$ and $P_{\rm s.o.}$ are interesting insofar as that some of the terms in both $\chi_{\rm s.o.}$ and $P_{\rm s.o.}$ become modified like χ_s and P_s, and the rest like χ_o and P_o. Thus these effects on $\chi_{\rm s.o.}$ and $P_{\rm s.o.}$ have a mixed character. However, the many-body effects on these terms are small and may be neglected in a realistic calculation. Further, many-body effects on $P_{j\rm RKKY}$ can be incorporated following the procedure outlined in an earlier publication on the many-body theory of indirect nuclear spin-spin interactions.[25]

IV. SUMMARY AND CONCLUSION

In this work, we have derived a general theory of magnetic susceptibility χ of Bloch electrons including the effects of periodic potential, spin-orbit interaction, and localized magnetic moments. χ is expressed as a sum of a contribution due to conduction electrons and an additional new contribution due to the interaction of conduction-electron magnetic moment and the localized magnetic moment. While the conduction-electron contribution is the familiar Misra-Kleinman susceptibility (χ_{MK}), which satisfactorily accounts for the magnetic susceptibility of simple metals and semiconductors, the additional contribution χ_{loc} would be important for magnetic solids. We discuss below the importance of this theory in possible applications.

Recently, there has been considerable interest in semimagnetic narrow-band-gap semiconductors[26] of the lead salt family. These semiconductors are multiband systems with strong spin-orbit interaction. They show some unusual and possibly unique properties,[27] related to other semiconductors. They are highly diamagnetic in the intrinsic form and this diamagnetism decreases with increase in carrier concentration, as has been shown by us in our earlier work.[13] The temperature dependence of carrier susceptibility shows an interesting characteristic in that it decreases with an increase in temperature, becomes zero at different temperatures for different carrier concentrations, and then becomes negative.[14] This has been shown as due to the fact that with increase in temperature, χ_s and χ_o decrease monotonically, but $\chi_{s.o.}$ which is positive at low temperatures, decreases and changes sign. Furthermore, the magnetic susceptibility measurements[28–32] of these semiconductors, when alloyed with magnetic impurities like Mn, show certain remarkable characteristics. However, these measurements are not unanimous in their findings. Hamasaki[28] indicated that the magnetic susceptibility of $Pb_{1-x}Mn_xTe$ followed a Curie-Weiss law from 77 to 350 K for x from 1.5 at.% to 10 at.%. The Curie temperature was not more than a few K, suggesting quite weak ferromagnetic Mn-Mn interactions. Morris[29] used samples with $x=2$ and 5 at.% and found Curie-Weiss behavior between 1 and 60 K, with a small, possibly zero, Curie temperature. On the other hand, Andrianov *et al*,[30,31] studied samples with x from 0.1 to 6.5 at.% over the temperature range 4.2 to 300 K. Their plots of $1/\chi$ versus T show a marked bend near 100 K. On the assumption that extrapolation of high-temperature segments of these curves yields a valid Curie temperature, they obtain Θ between -50 and -100 K for $x<1.5$ at.%, where the Curie-Weiss law is written in the form $1/\chi \propto (T-\Theta)$. Thus, they conclude that there is a strong antiferromagnetic coupling which, Liu and Bastard[33] suggest, indicates that super exchange (antiferromagnetic) dominates indirect exchange (ferromagnetic). We believe that the present theory, if suitably applied, would be able to shed some light on the origin of these anomolies.

Another interesting class of compounds, to which the theory could suitably be applied, includes the rare-earth monopnictides RX (R may correspond to Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, and X may correspond to N, P, As, Sb, and Bi) which exhibit metallic behavior and their magnetic properties are due primarily to the $4f$ electrons.[34] The theory could also have interesting applications in the intermetallic compounds, namely V_3Si, V_3Ga, Nb_3Sn, and Nb_3Al, possessing $A15$ crystal structure. These compounds are known to be good superconductors. Susceptibility and NMR measurements have revealed a close relationship between the superconducting transition temperature (T_c) and their normal-state properties. Indeed, susceptibility measurements[35] show that the higher the transition temperature, the stronger the temperature dependence of the susceptibility in the normal state.

In summary, the principal result of this work is a first-principles derivation of the magnetic susceptibility of Bloch electrons in the presence of periodic potential, spin-orbit interaction, and localized magnetic moments, which can be applied to a varieties of solids. However, there is still scope for further improvement. Firstly, the averaged localized-magnetic moment approximation [Eq. (2.4)] is not a good one below and in the vicinity of Kondo temperature. Secondly, the effect of electron-phonon interaction which is important in all the temperature-dependent calculations has not been considered. It may be noted that, in realistic calculations, the effect of electron-phonon interaction is normally incorporated through the modification of band structure via the Debye-Waller factor, through the Fermi function and through the effective mass corrections. However, an elucidation of the present work by including from first principles the magnetic field dependence of electron-phonon self-energy might be of interest in this connection.

In conclusion, we believe that apart from the above omissions and as distinguished from earlier works, the theory presented in this work is a thorough and general treatment of important magnetic interactions in solids.

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