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Theory of total magnetic susceptibility of interacting electrons in metals

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Abstract. We derive expressions for the orbital (χ_O), spin (χ_S) and spin-orbit (χ_{SO}) contributions to the total magnetic susceptibility (χ) of electrons in metals, which includes the effects of lattice potential and exchange-correlation, by using a pseudopotential formalism and degenerate perturbation theory. We have calculated χ for alkali metals as well as for Zn and Cd. Our results agree well with the experimental results. The effects of spin-orbit interaction on the magnetic susceptibility have been investigated. The spin-orbit contribution to χ has been found to be very small for alkali metals but gives a significant diamagnetic contribution in the case of Zn and Cd, as predicted earlier.

1. Introduction

The many-body theory of magnetic susceptibility of solids, in which the effects of the lattice potential, electron-electron interactions and electron-phonon interactions are included, is one of the basic problems of solid-state physics that has not yet been satisfactorily resolved. Although the many-body effects on the orbital susceptibility (χ_O) of metals is negligible (Phillipas and McClure 1972), it is well known that the spin susceptibility (χ_S) of metals is very sensitive to exchange-correlation (xc) effects and the influence of electron-phonon interactions on χ_S is small. Further, it had been hitherto assumed that the effects of spin-orbit coupling can be accounted for in the diamagnetic susceptibility (χ_O) through modification of the Bloch functions and in the spin susceptibility (χ_S) by replacing the free-electron g -factor by the effective g -factor. However, it has been shown (Misra and Kleinman 1972) that there is an additional contribution to the magnetic susceptibility from the effects of spin-orbit coupling (χ_{SO}) on the orbital motion of Bloch electrons, whose contribution is of the same order of magnitude as χ_O for metals like Zn and Cd and some semiconductors (Misra *et al* 1984) even in the absence of xc effects.

The comparison of suitable theoretical results with accurate measurements (Knecht 1975) of χ_S of alkali metals using the de Haas-van Alphen effect allows for a stringent test of the role of electron-electron interactions in the properties of metals. In order to explain these measurements, any theory of χ_S must simultaneously incorporate the lattice potential and the xc effects including the core electrons. However, owing to the enormous complexity of the problem, until recently there have been two different approaches in deriving an expression for χ_S . In one method, the Bloch picture of the electron is adopted in which the electron-electron interaction terms are not considered

insofar as they can be approximated to a one-electron band calculation. In the alternative method the many-body effects on χ_S of an electron gas are first derived and the χ_S of electrons in solids is calculated essentially using an effective-mass model. Further, in deriving a many-body theory of χ_S , the orbital component of the Hamiltonian is not usually included, thereby neglecting the effects of spin-orbit interaction. The spin-orbit interaction is subsequently introduced in an *ad hoc* manner by replacing the g -factor by the effective g -factor.

An expression for χ_S using the Bloch picture of electrons was first derived by Abe (1963) in a nearly free-electron approximation. However, his results for χ_S did not include the important contribution due to exchange enhancement. Moreover, its application is limited only to monovalent metals, since his expression for χ_S diverges when the Fermi surface touches the Brillouin zone boundary. Sampson and Seitz (1940) first calculated χ_S including xc effects by assuming that the shift in the ground-state energy from polarization can be obtained from an independent variation of the populations of the up and down spins. Pines and Nozieres (1966) carried out a calculation similar to that of Sampson and Seitz (1940) but their results differ considerably from the results of Sampson and Seitz because of the use of Bohm-Pines theory for the correlation energy. Brueckner and Sawada (1958) have derived an expression for χ_S of an electron gas at high density using the exact theory of Gell-Mann and Brueckner (1957). Silverstein (1963) calculated χ_S by a method similar to that of Brueckner and Sawada (1958) with the addition of a momentum-transfer interpolation procedure designed to obtain relevant information in the region of metallic densities. In this procedure, the band effects can be taken into account by the introduction of the effective mass into the kinetic energy term. There have been several attempts (Lobo *et al* 1969, Singwi *et al* 1970, Singh and Pathak 1972, Hasegawa and Shimuzu 1973, Rajagopal *et al* 1973) to calculate the frequency- and wavevector-dependent spin-density response function, which in the static and long-wavelength limit gives the usual static spin susceptibility. These theories are mostly based on the generalized random-phase approximation and are direct generalizations of theories of the dielectric function. Vashistha and Singwi (1973) have generalized their theory of the dielectric function to include spin fluctuations by treating the electron liquid as a two-component system. Hamann and Overhauser (1966) have calculated the wavevector-dependent spin susceptibility, taking the dynamically screened electron interaction into account. Kasowski (1969) has estimated the temperature-dependent spin susceptibility in a pseudopotential formalism. Dupree and Geldart (1971) have evaluated the spin susceptibility by expanding the propagators in the expression for the dynamic spin susceptibility of an interacting electron gas in terms of the one-electron self-energies and propagators for non-interacting electrons. Pizzimenti *et al* (1971) have calculated the spin susceptibility of metals in the framework of the Landau (1956) theory on the basis of the treatment of electron correlation developed by Singwi *et al* (1970).

Yafet (1973) has calculated the spin susceptibility for a two-band model with δ -function interactions between conduction electrons using a random-phase approximation. Ishihara and Kojima (1975) have evaluated both the orbital and spin susceptibilities of an electron fluid by considering the free electrons, first- and second-order exchange and ring diagrams. It may be noted that most of these theories have considered the metal as a homogeneous electron gas, which represents only a mathematical model. In a real metal the background potential and the electron density are far from uniform. Kohn and Sham (1965) have used the density-functional formalism (Hohenberg and Kohn 1964) to derive an expression for the spin susceptibility valid for slowly

varying density. They have used the fact that all ground-state properties are functionals of the electron density. The Hohenberg–Kohn–Sham theory of an inhomogeneous electron gas has been generalized (Stoddart and March 1971, Von Barth and Hedin 1972, Rajagopal and Callaway 1973) to include the spin-dependent interaction. Vosko and Perdew (1975) have derived a theory of χ_s of metallic electrons based on the variational principle within the density-functional formalism. The variational expression allows one to treat simultaneously the band and exchange–correlation effects among the conduction electrons and also includes the effect of the core electrons on the lattice. Using this theory, Vosko *et al* (1975) have calculated χ_s for alkali metals, and there is good agreement with the experimental results. Using the Vosko–Perdew theory, Janak (1977) calculated χ_s of a number of metals (including the transition metals) to study the enhancement of response that leads to ferromagnetic instability. His results agree with results of Gunnarson (1976) but differ from those of Vosko *et al* (1975) because of the use of a different approximation for the exchange–correlation functional and the use of different lattice parameters. It may be noted that the results of these calculations are sensitive to the approximation for the exchange–correlation functional. Moreover, since only the spin part of the Hamiltonian is considered, the spin–orbit contributions are completely ignored in these theories.

Misra and Kleinman (1971, 1972) have derived an expression for the magnetic susceptibility of Bloch electrons, which can be written in the form

$$\chi = \chi_0 + \chi_s + \chi_{so} \quad (1.1)$$

where χ_0 is the expression for diamagnetic susceptibility derived by Misra and Roth (1969) by considering the orbital motion of Bloch electrons, χ_s is the effective Pauli spin susceptibility, which is obtained by replacing the free-electron g -factor in the spin susceptibility by the effective g -factor (Yafet 1973), and χ_{so} is the additional contribution of the spin–orbit interaction to the susceptibility. However, they have adopted the Bloch picture of electrons in solids and thus have not considered the electron–electron interaction terms except insofar as they can be approximated in a one-band calculation. It has been observed by Misra and Kleinman that, although the additional spin–orbit contribution to the susceptibility may contain contributions of either sign, it should be considered a spin–orbit correction to χ_0 and distinguished from the spin–orbit contribution to the effective g -factor. This is because of the fact that there are two types of contribution to the magnetic energy of a one-electron eigenstate, terms linear in B (the applied magnetic field) that split the spin degeneracy and terms quadratic in B that do not. (Both terms, of course, contribute quadratically to the free energy.) The linear terms are all included in the g -factor and are always paramagnetic, independent of the sign of the g -factor, i.e. independent of the sign of the splitting of the spin degeneracy. The quadratic terms that arise from a perturbation of the electron wavefunctions by the magnetic field are generally diamagnetic and are responsible for both χ_0 and χ_{so} .

Recently one of us has formulated a theory (Misra *et al* 1982) of the total magnetic susceptibility of solids in which the effects of both lattice potential and electron–electron interactions have been included. We have constructed in k -space, using the Bloch representation, the effective one-particle Hamiltonian and equation of motion of the Green function in the presence of a magnetic field. We have used a finite-temperature Green function formulation where the thermodynamic potential Ω is expressed in terms of the exact one-particle propagator G . We have derived general expressions for the orbital (χ_0), spin (χ_s) and spin–orbit (χ_{so}) contributions to the total magnetic susceptibility χ , which includes many-body effects.

In this paper, we derive tractable expressions for χ_O , χ_S (including spin-orbit interactions) and χ_{SO} of metals from the general results of Misra *et al* (1982) through the use of a pseudopotential formalism (Harrison 1966) and doubly degenerate perturbation theory. The justification for the use of the pseudopotential formalism has been given by Misra and Roth (1969) and Phillipas and McClure (1972).

The organization of the paper is as follows. In section 2, we briefly discuss the general expressions for χ_O , χ_S and χ_{SO} derived by Misra *et al* (1982). In section 3, we formulate a pseudopotential theory appropriate for metals to obtain tractable expressions for χ_O , χ_S and χ_{SO} such that calculations can be easily made. In section 4 we calculate χ_O , χ_S and χ_{SO} of the alkali metals and the divalent HCP metals, Zn and Cd. Finally we compare our results with experimental results as well as the results of the spin-density functional formalism.

2. General expressions for χ_O , χ_S and χ_{SO}

Misra *et al* (1982) have derived an expression for the total magnetic susceptibility (χ) of interacting electrons in solids using a finite-temperature Green function formalism where the thermodynamic potential for an interacting electron system in the presence of a periodic potential, spin-orbit interaction and external magnetic field is expressed in terms of an exact one-particle propagator G . We have constructed in k -space, using the Bloch representation, the equation of motion of the Green function in the presence of the magnetic field and evaluated χ . In this theory χ has been separated into three components:

$$\chi = \chi_O + \chi_S + \chi_{SO} \quad (2.1)$$

where χ_O is the orbital susceptibility, χ_S is the spin susceptibility and χ_{SO} is the additional contribution due to spin-orbit interaction. The expressions for χ_O , χ_S and χ_{SO} (equations (3.42), (3.46) and (3.44) of Misra *et al* (1982)) are

$$\begin{aligned} \chi_O^{\mu\nu} = \sum_k (1 + \delta_{\mu\nu}) \left\{ \frac{e^2}{48\hbar^2 c^2} \varepsilon_{\alpha\beta\mu} \varepsilon_{\gamma\delta\nu} \nabla_k^\alpha \nabla_k^\gamma E_n \nabla_k^\beta \nabla_k^\delta E_n f'(E_n) \right. \\ + \left[\frac{e^2}{4\hbar^2 c^2} \varepsilon_{\alpha\beta\mu} \varepsilon_{\gamma\delta\nu} \left(-\frac{2\hbar^2}{m} \frac{\pi_{n\rho m\rho'}^\alpha \pi_{m\rho' n\rho}^\gamma}{E_{mn}^2} \delta_{\beta\delta} \right. \right. \\ + 2 \frac{\pi_{n\rho m\rho'}^\alpha \pi_{m\rho' n\rho}^\gamma \pi_{n\rho' q\rho''}^\beta \pi_{q\rho'' n\rho}^\delta}{E_{mn}^2 E_{qn}} - 2 \frac{\pi_{n\rho m\rho'}^\alpha \pi_{m\rho' q\rho''}^\gamma \pi_{q\rho'' l\rho'''}^\beta \pi_{l\rho''' n\rho}^\delta}{E_{ln} E_{mn} E_{qn}} \\ - \frac{\pi_{n\rho n\rho}^\alpha \pi_{n\rho m\rho'}^\gamma \pi_{m\rho' q\rho''}^\beta \pi_{q\rho'' n\rho}^\delta}{E_{mn} E_{qn}^2} + \frac{\pi_{n\rho n\rho}^\alpha \pi_{n\rho m\rho'}^\beta \pi_{m\rho' q\rho''}^\gamma \pi_{q\rho'' n\rho}^\delta}{E_{mn}^2 E_{qn}} \\ - \frac{\pi_{n\rho m\rho'}^\beta X_{m\rho' q\rho''}^{\alpha\gamma} \pi_{q\rho'' n\rho}^\delta}{E_{mn} E_{qn}} + \frac{\pi_{n\rho m\rho'}^\beta \pi_{m\rho' q\rho''}^\delta X_{q\rho'' n\rho}^{\alpha\gamma}}{E_{mn} E_{qn}} \\ \left. \left. + \frac{X_{n\rho m\rho'}^{\alpha\gamma} \pi_{m\rho' q\rho''}^\beta \pi_{q\rho'' n\rho}^\delta}{E_{mn} E_{qn}} - \frac{X_{n\rho n\rho}^{\alpha\gamma} \pi_{n\rho m\rho'}^\beta \pi_{m\rho' n\rho}^\delta}{E_{mn}^2} \right) \right. \\ \left. + \frac{ie}{4\hbar c} \varepsilon_{\alpha\beta\nu} \left(\frac{\pi_{n\rho m\rho'}^\beta Y_{m\rho' n\rho}^{\alpha\mu}}{E_{mn}} - \frac{Y_{n\rho m\rho'}^{\alpha\mu} \pi_{m\rho' n\rho}^\beta}{E_{mn}} \right) \right] f(E_n) \} \quad (2.2) \end{aligned}$$

$$\chi_{S}^{\mu\nu} = -\frac{1}{3}(1 + \delta_{\mu\nu})\mu_0^2 \sum_k g_{nn}^{\nu}(k) \sigma_{n\rho n\rho}^{\nu} [g_{nn}^{\mu}(k) \sigma_{n\rho' n\rho}^{\mu} + (2/\mu_0) \Sigma_{n\rho' n\rho}^{l,\mu}] f'(E_n) \quad (2.3)$$

and

$$\begin{aligned} \chi_{SO}^{\mu\nu} = \sum_k (1 + \delta_{\mu\nu}) & \left[\frac{e^2 \varepsilon_{\alpha\beta\mu} \varepsilon_{\gamma\delta\nu}}{2\hbar^2 c^2} \frac{\pi_{n\rho m\rho'}^{\alpha} \pi_{m\rho' n\rho}^{\beta} \pi_{n\rho' q\rho}^{\gamma} \pi_{q\rho' n\rho}^{\delta}}{E_{mn}^2 E_{qn}} \right. \\ & + \frac{ie g \mu_0}{4\hbar c} \varepsilon_{\alpha\beta\nu} \left(-3 \frac{J_{n\rho n\rho'}^{\mu} \pi_{n\rho' m\rho}^{\alpha} \pi_{m\rho' n\rho}^{\beta}}{E_{mn}^2} + \frac{\pi_{n\rho m\rho'}^{\alpha} \pi_{m\rho' q\rho}^{\beta} J_{q\rho' n\rho}^{\mu}}{E_{qn} E_{mn}} \right. \\ & + \frac{\pi_{n\rho m\rho'}^{\alpha} J_{m\rho' q\rho}^{\mu} \pi_{q\rho' n\rho}^{\beta}}{E_{qn} E_{mn}} + \frac{J_{n\rho m\rho'}^{\mu} \pi_{m\rho' q\rho}^{\alpha} \pi_{q\rho' n\rho}^{\beta}}{E_{qn} E_{mn}} \\ & \left. + \frac{\pi_{n\rho n\rho'}^{\alpha} J_{n\rho m\rho'}^{\mu} \pi_{m\rho' n\rho}^{\beta}}{E_{mn}^2} - \frac{\pi_{n\rho n\rho'}^{\alpha} \pi_{n\rho m\rho'}^{\beta} J_{m\rho' n\rho}^{\mu}}{E_{mn}^2} \right) \\ & \left. + \frac{1}{3} g^2 \mu_0^2 \left(\frac{\sigma_{n\rho m\rho'}^{\mu} F_{m\rho' n\rho}^{\nu}}{E_{mn}} + \frac{F_{n\rho m\rho'}^{\mu} \sigma_{m\rho' n\rho}^{\nu}}{E_{mn}} \right) \right] f(E_n). \quad (2.4) \end{aligned}$$

Here the g -matrix $g_{nn}^{\nu}(k)$ and the other factors have been defined as follows:

$$g_{nn}^{\nu}(k) \sigma_{n\rho n\rho}^{\nu} = \frac{ie}{\mu_0 \hbar c} \varepsilon_{\alpha\beta\nu} \sum_{\rho'm} \frac{\pi_{n\rho m\rho'}^{\alpha} \pi_{m\rho' n\rho}^{\beta}}{E_{mn}} + g \sigma_{n\rho n\rho}^{\nu} \quad (2.5)$$

$$X^{\alpha\gamma} = \nabla_k^{\alpha} \nabla_k^{\gamma} \Sigma^0(k) \quad (2.6)$$

$$Y^{\mu\nu} = \partial \Sigma^{l,\nu} / \partial k^{\mu} \quad (2.7)$$

$$F^{\nu} = \sigma^{\nu} + (2/g\mu_0) \Sigma^{l,\nu} \quad (2.8)$$

$$J^{\nu} = \sigma^{\nu} + (1/g\mu_0) \Sigma^{l,\nu} \quad (2.9)$$

π/\hbar is the velocity operator

$$\pi(k, \xi_l) = (\hbar/m)(p + \hbar k) + (\hbar^2/4mc) \boldsymbol{\sigma} \times \nabla V + \nabla_k \Sigma^0(k, \xi_l) \quad (2.10)$$

Σ is the exact self-energy operator whose matrix elements are

$$\Sigma_{nkp, mkr'}(k, B, \xi_l) = \int dr dr' \psi_{nkp}^*(r) \Sigma(r, r', B, \xi_l) \psi_{mkr'}(r') \quad (2.11)$$

and the field-dependent self-energy has been expanded as

$$\Sigma(k, B, \xi_l) = \Sigma^0(k, \xi_l) + B^{\mu} \Sigma^{1,\mu}(k, \xi_l) + B^{\mu} B^{\nu} \Sigma^{2,\mu\nu}(k, \xi_l) \quad (2.12)$$

where ξ_l is the complex energy given by

$$\xi_l = (2l + 1)\pi i / \beta + \mu. \quad (2.13)$$

Also, here $\boldsymbol{\sigma}$ is the Pauli spin matrix; μ_0 is the Bohr magneton; μ is the chemical potential; g is the free-electron g -factor; $A_{n\rho m\rho'}$ is the matrix element of A between $\psi_{nkp}(r)$ and $\psi_{mkr'}(r')$, the two-component Bloch functions, which are eigenfunctions of the Hamiltonian in the absence of a magnetic field; n is the band index; k is the reduced

wavevector; ρ is the spin index; $E_{mn} = E_m - E_n$; $\varepsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor of third rank; and $f(E_n)$ is the Fermi function. Expanding $G(\mathbf{k}, \xi_i)$, using equation (2.12) and making an average exchange enhancement *ansatz* we obtain

$$\Sigma_{n\rho n\rho'}^{l,\mu} = \{\alpha_n(\mathbf{k})/2[1 - \alpha_n(\mathbf{k})]\}\mu_0 g_{nn}^\mu \sigma_{n\rho n\rho'}^\mu \quad (2.14)$$

where

$$\alpha_n(\mathbf{k}) = - \sum_{k'm} v_{nm}(\mathbf{k}, \mathbf{k}') f'(E_m(\mathbf{k}')) \quad (2.15)$$

and $v_{nm}(\mathbf{k}, \mathbf{k}')$ is the matrix element of the effective electron-electron potential in the static screening approximation. Substituting equation (2.14) in equation (2.3), we obtain

$$\chi_S^{\mu\mu} = \sum_{nk} \chi_{\text{OS},n}^{\mu\mu}(\mathbf{k})/[1 - \alpha_n(\mathbf{k})] \quad (2.16)$$

where

$$\chi_{\text{OS},n}^{\mu\mu}(\mathbf{k}) = - \frac{1}{4}\mu_0^2 \sum_{\rho\rho'} g_{nn}^\mu(\mathbf{k}) \sigma_{n\rho n\rho'}^\mu g_{nn}^\mu(\mathbf{k}) \sigma_{n\rho' n\rho}^\mu f'(E_n). \quad (2.17)$$

Further, using equations (2.14) and (2.15) in equation (2.4) the expression for χ_{SO} can be simplified and we obtain

$$\begin{aligned} \chi_{\text{SO}}^{\mu\mu} = \sum_{\substack{k,n,m,q \\ n \neq m,q}} \left\{ \frac{e^2}{\hbar^2 c^2} \varepsilon_{\alpha\beta\mu} \varepsilon_{\gamma\delta\mu} \left(1 + \frac{3}{4} \frac{\alpha_n}{1 - \alpha_n} \right) \frac{\pi_{n\rho m\rho'}^\alpha \pi_{m\rho' n\rho}^\beta \pi_{n\rho' q\rho}^\gamma \pi_{q\rho' n\rho}^\delta}{E_{mn}^2 E_{qn}} \right. \\ + \frac{ieg\mu_0}{2\hbar c} \varepsilon_{\alpha\beta\mu} \left[-3 \left(1 + \frac{1}{2} \frac{\alpha_n}{1 - \alpha_n} \right) \frac{\sigma_{n\rho n\rho'}^\mu \pi_{n\rho' m\rho}^\alpha \pi_{m\rho' n\rho}^\beta}{E_{mn}^2} \right. \\ + \frac{\pi_{n\rho m\rho'}^\alpha \pi_{m\rho' q\rho}^\beta \sigma_{q\rho' n\rho}^\mu}{E_{qn} E_{mn}} + \frac{\pi_{n\rho m\rho'}^\alpha \sigma_{m\rho' q\rho}^\mu \pi_{q\rho' n\rho}^\beta}{E_{qn} E_{mn}} \\ + \frac{\sigma_{n\rho m\rho'}^\mu \pi_{m\rho' q\rho}^\beta \pi_{q\rho' n\rho}^\alpha}{E_{qn} E_{mn}} + \frac{\pi_{n\rho n\rho}^\alpha \sigma_{n\rho m\rho'}^\mu \pi_{m\rho' n\rho}^\beta}{E_{mn}^2} - \left. \frac{\pi_{n\rho n\rho}^\alpha \pi_{n\rho m\rho'}^\beta \sigma_{m\rho' n\rho}^\mu}{E_{mn}^2} \right] \\ \left. + \frac{1}{4} g^2 \mu_0^2 \left(\frac{\sigma_{n\rho m\rho'}^\mu \sigma_{m\rho' n\rho}^\mu}{E_{mn}} + \frac{\sigma_{n\rho m\rho'}^\mu \sigma_{m\rho' n\rho}^\mu}{E_{mn}} \right) \right\} f(E_n). \quad (2.18) \end{aligned}$$

We note that the intuitive result of equation (2.16), which gives rise to the well known Stoner enhancement (White 1970), is essentially equivalent to the usual expression for the exchange-enhanced spin susceptibility but with the free-electron g -factor replaced by the effective g -matrix. We further note that in the above derivation the coupling between $\Sigma_{n\rho n\rho'}^{l,\mu}$ for different occupied bands has been neglected.

3. Pseudopotential formulation

In order to calculate χ_{O} , χ_{S} and χ_{SO} for metals, we evaluate the Bloch functions by considering the sum of the lattice potential and the field-independent part of the self-energy as non-local pseudopotential. The justification of the pseudopotential formulation has been given by Misra and Roth (1969) and Phillipas and McClure (1972). We retain the operator nature of $W(\mathbf{r})$, which does not cause any difficulty since we shall be interested in the matrix elements between states that lie on the Fermi surface.

We consider the case of a general point on the Bragg reflection plane, so that the unperturbed eigenvalue is doubly degenerate if we ignore spin. With the inclusion of spin, each level becomes doubly degenerate, so that we consider two doubly degenerate bands at a general point of the Bragg reflection plane. We write the Hamiltonian as

$$H = p^2/2m + W + W_{SO} \quad (3.1)$$

where we have separated the general pseudopotential (Das and Misra 1971) into two parts: W , the spin-independent part, which is the pseudopotential used by Misra and Roth (1969), and W_{SO} , the pseudopotential for spin-orbit interaction. Using standard techniques of degenerate perturbation theory, we obtain the energy values as

$$\begin{aligned} E_1 &= \frac{1}{2}(\varepsilon_1 + \varepsilon_2) - \frac{1}{2}(\varepsilon_2 - \varepsilon_1)X_1X_2 \\ E_2 &= \frac{1}{2}(\varepsilon_1 + \varepsilon_2) + \frac{1}{2}(\varepsilon_2 - \varepsilon_1)X_1X_2 \end{aligned} \quad (3.2)$$

and the eigenfunctions as

$$\begin{aligned} |\psi_{1\uparrow}\rangle &= a|\psi_-\alpha\rangle - b^*Q_z|\psi_+\alpha\rangle - b^*Q_+|\psi_+\beta\rangle \\ |\psi_{1\downarrow}\rangle &= a|\psi_-\beta\rangle - b^*Q_-|\psi_+\alpha\rangle - bQ_z|\psi_+\beta\rangle \\ |\psi_{2\uparrow}\rangle &= a|\psi_+\alpha\rangle + bQ_z|\psi_-\alpha\rangle + bQ_+|\psi_-\beta\rangle \\ |\psi_{2\downarrow}\rangle &= a|\psi_+\beta\rangle + bQ_-|\psi_-\alpha\rangle + b^*Q_z|\psi_-\beta\rangle \end{aligned} \quad (3.3)$$

where

$$\begin{aligned} \psi_+ &= \frac{\sqrt{2}W_G|k\rangle}{(\varepsilon_2 - \varepsilon_1)[X_1(1 + X_1)]^{1/2}} + \left(\frac{1 + X_1}{2X_1}\right)^{1/2} |k + G\rangle \\ \psi_- &= \left(\frac{1 + X_1}{2X_1}\right)^{1/2} |k\rangle + \frac{\sqrt{2}W_G|k + G\rangle}{(\varepsilon_2 - \varepsilon_1)[X_1(1 + X_1)]^{1/2}} \\ \varepsilon_1 &= \hbar^2 k^2/2m \quad \varepsilon_2 = \hbar^2(k + G)^2/2m \quad W_G = \langle k + G|W|k\rangle \\ X_1 &= \left(1 + \frac{4|W_G|^2}{(\varepsilon_2 - \varepsilon_1)^2}\right)^{1/2} \quad X_2 = \left(1 + \frac{4\hbar^2 D^2 |Q|^2}{m^2(\varepsilon_2 - \varepsilon_1)^2 X_1^2}\right)^{1/2} \\ a &= \left(\frac{1 + X_2}{2X_2}\right)^{1/2} \quad b = \frac{i\sqrt{2}\hbar D/m}{(\varepsilon_2 - \varepsilon_1)X_1[X_2(1 + X_2)]^{1/2}} \quad Q = k \times G \\ D &= (\hbar/4mc^2)U(|G|)S(G) - \lambda_p(m/\hbar)S(G) - \lambda_d(m/\hbar)S(G)(k^2 + k \cdot G). \end{aligned} \quad (3.4)$$

Here $S(G)$ is the structure factor, and the spin-orbit parameters λ_p and λ_d are positive constants that account for the contribution of the core p states and d states respectively.

The matrix elements of $\pi_{n\rho m\rho'}$ and $\sigma_{n\rho m\rho'}$ have been evaluated by using Bloch functions obtained by us. However, in order to calculate χ_O , χ_S and χ_{SO} , we have to calculate the chemical potential and the exchange enhancement factor in the pseudopotential formulation. We start with the familiar expression

$$\frac{1}{4\pi^3} \int d^3k f(E) = N \quad (3.5)$$

where E is the exact energy given in equation (3.2), $f(E)$ is the Fermi function and N is

the total number of electrons per unit volume. We use cylindrical coordinates to evaluate equation (3.5). We choose G parallel to the z axis inside the integration and we can write

$$E_1 = \frac{\hbar^2}{2m} (k_p^2 + q_z^2 + G^2/4) \mp \frac{\hbar^2 G}{2m} \left(q_z^2 + \frac{4m^2 |W_G|^2}{\hbar^4 G^2} + \frac{4D^2}{\hbar^2} k_p^2 \right)^{1/2} \quad (3.6)$$

where

$$k_p^2 = k_x^2 + k_y^2 \quad \text{and} \quad q_z = k_z + G/2.$$

Integrating by parts and using the fact that at zero temperature the derivative of the Fermi function, $f'(E) = -\delta(E - \xi)$, we obtain

$$\frac{1}{4\pi^2} \int dq_z \int k_p^2 \delta(E - \xi) dE = N \quad (3.7)$$

where ξ is the chemical potential. The integration over E causes k_p^2 to be replaced by

$$k_p^2 = -q_z^2 + \delta G^2 + (p - 1)G^2/4 + G(\alpha q_z^2 + \beta G^2)^{1/2} \quad (3.8)$$

which is obtained by solving $E - \xi = 0$. We obtain from equations (3.7) and (3.8)

$$\frac{1}{4\pi^2} \int dq_z [-q_z^2 + \delta G^2 + (p - 1)G^2/4 + G(\alpha q_z^2 + \beta G^2)^{1/2}] = N. \quad (3.9)$$

In the above, the dimensionless quantities α , β , δ , t^2 and p are defined by

$$\begin{aligned} \delta &= 2D^2/\hbar^2 & \alpha &= 1 - 2\delta & \beta &= t^2 + \delta^2 + (p - 1)\delta/2 \\ t^2 &= 4m^2 W_G^2/\hbar^4 G^4 & \text{and} & & p &= 8m\xi/\hbar^2 G^2. \end{aligned} \quad (3.10)$$

Introducing the dimensionless variable

$$\gamma = (2/G)q_z \quad (3.11)$$

we can write equation (3.9) as

$$\frac{G^3}{32\pi^2} \int_{\gamma_-}^{\gamma_+} d\gamma [-\gamma^2 + p + 4\delta - 1 + 2(\alpha\gamma^2 + 4\beta)^{1/2}] = N. \quad (3.12)$$

Here γ_+ and γ_- are the upper and lower limits of γ obtained by solving $E = \xi$ for $k_p = 0$. The solutions can be shown to be

$$\gamma_{\pm} = (1 \pm p^{1/2}) \left(1 \pm \frac{2[(p + 4t^2)^{1/2} - p^{1/2}]}{(1 \pm p^{1/2})^2} \right)^{1/2}. \quad (3.13)$$

We now integrate equation (3.12) to obtain (for both $p > 1$ and $p < 1$)

$$\begin{aligned} \frac{G^3}{32\pi^2} \left(-\frac{1}{3}(\gamma_+^3 - \gamma_-^3) + (p + 2\delta - 1)(\gamma_+ - \gamma_-) \right. \\ \left. + (\gamma_+ z_+ - \gamma_- z_-) + \frac{4\beta}{\alpha^{1/2}} \ln \left| \frac{z_+ - 2\delta + \alpha^{1/2} \gamma_+}{z_- - 2\delta + \alpha^{1/2} \gamma_-} \right| \right) = N \end{aligned} \quad (3.14)$$

where

$$z_{\mp} = \gamma_{\mp} (1 + 4t^2/\gamma_{\mp}^2)^{1/2}. \quad (3.15)$$

It is easy to show the free-electron result that

$$N = \frac{1}{3}(G^3/32\pi^2)p_0^{3/2} \quad (3.16)$$

where

$$p_0 = 8m\xi_0/\hbar^2 G^2 \quad (3.17)$$

and ξ_0 is the Fermi energy. We obtain from equations (3.14) and (3.16)

$$p_0 = \left[\frac{3}{4} \left(-\frac{1}{3}(\gamma_+^3 - \gamma_-^3) + (p + 2\delta - 1)(\gamma_+ - \gamma_-) \right. \right. \\ \left. \left. + (\gamma_+ z_+ - |\gamma_-| z_-) + \frac{4\beta}{\alpha^{1/2}} \ln \left| \frac{z_+ - 2\delta + \alpha^{1/2} \gamma_+}{z_- - 2\delta + \alpha^{1/2} \gamma_-} \right| \right) \right]^{2/3}. \quad (3.18)$$

We note that in the absence of spin-orbit interaction, our expression for p_0 in equation (3.18) reduces to the corresponding expression derived by Misra *et al* (1971). We can write the right-hand side of equation (3.18) as $F(p)$ and write it in the form

$$p = p_0 - [F(p) - p]. \quad (3.19)$$

Thus we can calculate p by a reiteration process and hence the chemical potential ξ can be evaluated.

To calculate χ_0 , χ_s and χ_{SO} , we have first evaluated the matrix elements of π^x , π^y , π^z , σ^x , σ^y and σ^z between the Bloch functions $\psi_{1\uparrow}$, $\psi_{1\downarrow}$, $\psi_{2\uparrow}$ and $\psi_{2\downarrow}$. We have used cylindrical coordinates and integrated the resulting expression by using the techniques outlined earlier for the evaluation of the chemical potential. After considerable algebra, we finally obtain

$$\chi_0 = \chi_0^* \left(1 + \sum_G D_G^0 \right) \quad (3.20)$$

$$\chi_s = \chi_s^* + \sum_G D_G^s \quad (3.21)$$

and

$$\chi_{SO} = \sum_G D_G^{SO}. \quad (3.22)$$

In the above χ_0^* is the free-electron Landau diamagnetic susceptibility, χ_s^* is the exchange-enhanced spin susceptibility for free electrons (i.e. in the absence of band effects), and D_G^0 , D_G^s and D_G^{SO} are G -dependent terms in χ_0 , χ_s and χ_{SO} that account for the band effects and spin-orbit coupling. D_G^0 , D_G^s and D_G^{SO} are given by

$$D_G^0 = \int_{\gamma_-}^{\gamma_+} d\gamma \frac{1}{2p_0^{1/2}} \left[1 - \frac{12G^2 t^2}{G^2 Y^{3/2}} \left(\frac{1}{6} - \frac{k_p^2}{G^2 Y^{1/2}} + \frac{k_p^4}{G^4 Y} \right) \right]_{k_p^2=f_G^2} - 1 - \frac{1}{3}(N/N_0 - 1) \quad (3.23)$$

$$\begin{aligned}
D_G^S = & \frac{e^2}{\pi^2 mc^2} \int_{\gamma_-}^{\gamma_+} \frac{d\gamma}{1 - \alpha_G} \left[\frac{g^2}{64} G + \frac{D^4 \gamma^2}{\hbar^4 Y^2} G - \frac{2D^4}{\hbar^4} (G - G_z) \frac{\gamma}{Y^2} \right. \\
& + \frac{1}{GY^2} \left(\frac{D^4}{\hbar^4} (G - G_z)^2 + \frac{D^4}{\hbar^2} G_{\perp}^2 t^2 + \frac{4D^4}{\hbar^4} G_z^2 t^2 \right) - \frac{g^2 D^2 G_z^2 k_p^2}{4\hbar^2 G^3 Y} \\
& - \frac{g^2 D^2 (G - G_z)^2 (\gamma - 1)^2}{16\hbar^2 G Y} + \frac{mg DW_G G_{\perp}^2}{2\hbar^3 G^3 Y} \\
& \left. - \frac{g D^2 G_z (G - G_z) \gamma (\gamma - 1)}{4\hbar^2 G Y^{3/2}} - \frac{g D^2 G_z^2 (\gamma^2 + 4t^2)}{4\hbar^2 G Y^{3/2}} \right]_{k_p^2 = f_G^2} - \chi_p^* \quad (3.24)
\end{aligned}$$

and

$$\begin{aligned}
D_G^{SO} = & \frac{-e^2 G}{\pi^2 c^2 m \hbar^2 G^3} \int_{\gamma_-}^{\gamma_+} d\gamma \int_0^{f_G^2} dk_p^2 \left[1 + \frac{3}{4} \frac{\alpha_G}{1 - \alpha_G} \frac{m DW_G G_{\perp}^2}{\hbar G^2 Y^{3/2}} \right. \\
& + \frac{2D^2 G_z^2}{G^2} k_p^2 \frac{1}{Y^{3/2}} + \frac{1}{2} D^2 G_z (G - G_z) (\gamma - \gamma^2) \frac{1}{Y^{3/2}} \\
& + \left(1 + \frac{3}{8} \frac{\alpha_G}{1 - \alpha_G} \right) \frac{D^2 G_z^2}{Y} + \frac{16D^4}{\hbar^2} \frac{G_z^2}{G^2} k_p^2 \frac{1}{Y^2} \\
& \left. + D^2 G_z (G - G_z) (\gamma - \gamma^2) \frac{1}{Y^2} \right] \\
& - \frac{16e^2}{\pi^2 mc^2 G^3} \int_{\gamma_-}^{\gamma_+} d\gamma \int_0^{f_G^2} dk_p^2 \left[\left(1 + \frac{3}{4} \frac{\alpha_G}{1 - \alpha_G} \right) \left(\frac{D^2 G^2}{4\hbar^2} \gamma^2 \right. \right. \\
& \left. \left. - \frac{D^4}{2\hbar^4} (G - G_z) \gamma + \frac{D^4}{4\hbar^2} (G - G_z)^2 + \frac{D^4}{\hbar^4} G_z^2 t^2 + \frac{D^2}{4\hbar^2} G_{\perp}^2 t^2 \right) \frac{1}{Y^{5/2}} \right] \\
& + \frac{e^2 g^2}{8\pi^2 mc^2 \hbar^2 G^3} \int_{\gamma_-}^{\gamma_+} d\gamma \int_0^{f_G^2} dk_p^2 \left(\frac{1}{4\hbar^2} G_z^2 \frac{1}{Y^{1/2}} - (\gamma^2 + 4t^2) \frac{1}{Y^{3/2}} \right. \\
& \left. + \frac{D^2 (G - G_z)^2 (\gamma - 1)^2}{Y^{3/2}} \right) \quad (3.25)
\end{aligned}$$

where

$$Y = \gamma^2 + 4t^2 + (16D^2/G^2)k_p^2 \quad (3.26)$$

f_G^2 is the value of k_p^2 obtained by solving the equation $E_n - \xi = 0$, i.e.

$$f_G^2 = \frac{1}{4} G^2 [(p - 1) - \gamma^2 + 4\delta + 2(\alpha\gamma^2 + 4\beta)^{1/2}] \quad (3.27)$$

and α_G is the exchange enhancement factor obtained by one of us (Misra and Misra 1982).

We note that in deriving the expression for D_G^O , we have not considered the many-body effects on the orbital susceptibility, as has been shown by Phillipas and McClure (1972) and Misra *et al* (1982) that such effects on χ_O are very small for metals. We further

note that if spin-orbit interaction is also neglected, then our expression for D_G^0 (equation (3.23)) exactly reduces to the corresponding expression obtained by Misra *et al* (1971). The last term in equation (3.23) is a correction term due to the inclusion of many Bragg reflections.

It is easy to see that in the absence of many-body effects ($\alpha_G = 0$) and spin-orbit effects ($D = 0$), our expression for χ_S reduces to

$$\chi_S = \chi_P \left(1 + \frac{1}{4k_f} \sum_G (\gamma_+ - \gamma_-) G - 1 \right) \quad (3.28)$$

where χ_P is the Pauli susceptibility of free electrons.

If we substitute the values of γ_+ and γ_- from equation (3.13), and expand the terms to second order in W_G , which is equivalent to non-degenerate perturbation theory, we obtain

$$\chi_S = \chi_P \left[1 - \sum_G \frac{|W|^2}{8\xi^2} \left(p^{1/2} \tanh^{-1} p^{1/2} - \frac{p}{1-p} \right) \right]. \quad (3.29)$$

We note that Abe (1963) and Glasser (1964) have derived exactly the same expression for the paramagnetic susceptibility in the nearly free-electron approximation. Thus, their result for χ_S is equivalent to our result using non-degenerate perturbation theory and neglecting both spin-orbit and exchange-correlation effects. However, it should be noted that the use of non-degenerate perturbation theory does not yield correct results for the magnetic susceptibility even for simple metals like lithium (Misra and Roth 1969).

4. Method of calculation

The alkali metals crystallize in the BCC structure with two atoms per cubic unit cell. The reciprocal lattice vector G and the structure factor for a BCC lattice are given by

$$G = (2\pi/a)[(h+l)\hat{i} + (h+k)\hat{j} + (k+l)\hat{k}] \quad (4.1)$$

and

$$S(G) = \frac{1}{2}(1 + e^{-i\pi/2(h+k+l)}) \quad (4.2)$$

where \hat{i} , \hat{j} and \hat{k} are unit vectors along x , y and z directions, respectively.

Zn and Cd are divalent HCP metals with the lattice described by a unit cell having edges

$$a_1 = \frac{1}{2}a\hat{i} - \frac{1}{2}\sqrt{3}a\hat{j} \quad a_2 = \frac{1}{2}a\hat{i} + \frac{1}{2}\sqrt{3}a\hat{j} \quad a_3 = c\hat{k}. \quad (4.3)$$

The unit cell contains two atoms, one at the origin and the other at $\frac{1}{2}a\hat{i} + \frac{1}{2}\sqrt{3}a\hat{j} + \frac{1}{2}c\hat{k}$. The reciprocal lattice vector G and the structure factor $S(G)$ are given by

$$G = (2\pi/a)[(h+k)\hat{i} + \frac{1}{2}\sqrt{3}(k-h)\hat{j} + (a/c)l\hat{k}] \quad (4.4)$$

$$S(G) = \cos[\frac{1}{6}\pi(2h+4k+3l)]. \quad (4.5)$$

Making use of the lattice parameters, we have calculated the lattice vectors G and the structure factor $S(G)$ for each G by a computer program. We have used the zero-temperature Fermi-level pseudopotential form factors $\langle k_f + G | w | k_f \rangle$ of Animalu and

Table 1. Orbital (χ_o), spin (χ_s) and spin-orbit (χ_{so}) contributions to magnetic susceptibility (χ) (in 10^{-6} cgs vol units).

Metal	χ_o	χ_s	χ_{so}	$\chi = \chi_o + \chi_s + \chi_{so}$
Li	-0.1023 ^a	1.9849 ^a	-3.5454×10^{-4a}	1.88259 ^a
Na	-0.2072 ^a -0.2091 ^b	1.0364 ^a 1.0275 ^b	-2.8634×10^{-4a} -2.6831×10^{-4b}	0.82891 ^a 0.81813 ^b
K	-0.1753 ^a -0.1714 ^b	0.8227 ^a 0.8629 ^b	-6.1976×10^{-4a} -10.4020×10^{-4b}	0.64678 ^a 0.69046 ^b
Rb	-0.1654 ^a -0.1652 ^b	0.8059 ^a 0.8056 ^b	-5.4211×10^{-4a} -8.0170×10^{-4b}	0.63995 ^a 0.63959 ^b
Cs	-0.1521 ^a -0.1494 ^b	0.8959 ^a 0.9117 ^b	-5.4512×10^{-3a} -4.0713×10^{-3b}	0.73835 ^a 0.75822 ^b
Zn	-0.2094 ^a	1.3568 ^a	-0.5862 ^a	0.5612 ^a
Cd	-0.3268 ^a	1.4090 ^a	-0.6716 ^a	0.4106 ^a

^a Our calculations with Animalu and Heine parameters as tabulated by Harrison (1966).

^b Our calculations with Woo *et al* (1975) parameters.

Heine as tabulated by Harrison (1966) for metals and also of Woo *et al* (1975) for alkali metals.

In order to calculate D_G^O , D_G^S and D_G^{SO} , we need to know the chemical potential ξ . It has been shown earlier that ξ is related to ξ_0 , the chemical potential for free electrons, through a transcendental equation (equation (3.18)), which contains the pseudo-potential matrix elements and hence depends on G . We have calculated ξ for each value of G by a reiteration process. Finally we have calculated D_G^O , D_G^S and D_G^{SO} by using standard procedures of numerical integration. In our calculations we have used values of G with $0 < |G/2k_f| < 4$ to ensure distinct convergence. The values of spin-orbit parameters used in our calculations have been taken from the work of Misra *et al* (1986) and Misra (1987) on Knight shift.

For the divalent HCP metals Zn and Cd, we have evaluated $D_{G\parallel}^O$, $D_{G\parallel}^S$ and $D_{G\parallel}^{SO}$ for magnetic field parallel to the z direction (i.e. parallel to the hexagonal axis) using $G_x^2 + G_y^2$ for G_{\perp}^2 , which is then summed over G to obtain χ_{\parallel}^O , χ_{\parallel}^S and χ_{\parallel}^{SO} . The values of $D_{G\perp}^O$, $D_{G\perp}^S$ and $D_{G\perp}^{SO}$ (for magnetic field perpendicular to the hexagonal axis) have been calculated in a similar manner using the values of $G_y^2 + G_z^2$ or $G_x^2 + G_z^2$ for G_{\perp}^2 and then summed over G . Finally, the average susceptibility has been calculated using the relation

$$\chi = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}). \quad (4.6)$$

Details of these calculations are available in one of our earlier papers (Das *et al* 1988) for Zn and Cd. Finally, we tabulate our results in table 1 for alkali metals as well as Zn and Cd. In table 2 we compare our results with the indirectly obtained experimental results (in the absence of direct experimental data) for HCP metals, with the available experimental results for alkali metals and with the results of the spin-density functional (SDF) formalism. We note that our results agree well with the experimental results. The results of SDF theory χ_s/χ_P (the susceptibility enhancement) also agree equally well. Our results for the spin-orbit contributions (χ_{so}) show that these are very small (of the order

Table 2. Computed electronic contribution to χ compared with experimental value $\chi_E = \chi_T - \chi_i$ (in 10^{-6} cgs vol units).

Metal	Experimental results			Present calculation		Theor. χ_s/χ_P	Expt. χ_s/χ_P
	Total χ_T	Ionic χ_i	Electronic $\chi_E = \chi_T - \chi_i$	$\chi = \chi_O + \chi_s + \chi_{SO}$	χ_s/χ_P		
Li	1.789 ^c	-0.053 ^c	1.842 ^c	1.882 59 ^a	2.5101 ^a	2.66 ^k 2.57 ^l 2.87 ^m	2.50 ± 0.05 ^f 2.64 ± 0.13 ^g 2.84 ± 0.10 ^h
Na	0.583 ^c	-0.291 ^c	0.874 ^c	0.828 91 ^a 0.818 13 ^b	1.5725 ^a 1.5588 ^b	1.62 ^k 1.63 ^l 1.58 ^m	1.65 ± 0.05 ^f 1.58 ± 0.09 ⁱ 1.72 ± 0.008 ^j
K	0.389 ^c	-0.372 ^c	0.761 ^c	0.646 78 ^a 0.690 46 ^b	1.5439 ^a 1.6194 ^b	1.79 ^k 1.79 ^l 1.70 ^m	1.69 ± 0.07 ⁱ 1.701 ± 0.008 ^j
Rb	0.310 ^c	-0.398 ^c	0.708 ^c	0.639 95 ^a 0.639 59 ^b	1.6174 ^a 1.6168 ^b	1.78 ^k 1.75 ^l 1.73 ^m	1.59 ± 0.12 ⁱ 1.724 ± 0.008 ^j
Cs	0.398 ^c	-0.487 ^c	0.885 ^c	0.738 35 ^a 0.758 22 ^b	1.9458 ^a 1.9799 ^b	2.20 ^k 2.10 ^l 1.91 ^m	1.76 ± 0.06 ^j or 2.24 ± 0.06 ^j
Zn	-1.14 ^d	-1.64 ^d	0.50	0.5612 ^a	1.2076 ^a	1.18 ⁿ	
Cd	-2.309 ^d	-2.593 ^c	0.284	0.4106 ^a	1.4063 ^a	1.18 ⁿ	

^a Our results with Animalu-Heine parameters (Harrison 1966).

^b Our results with Woo *et al* (1975) parameters.

^c Experimental results of Collings (1965).

^d Experimental results of Marcus (1949).

^e Experimental results of Knight (1956).

^f Kushida *et al* (1979).

^g Kettler *et al* (1969).

^h Flesner and Schultz (1976).

ⁱ Whiting *et al* (1978).

^j Knecht (1975).

^k Vosko and Perdew (1975).

^l Vosko *et al* (1975).

^m MacDonald and Vosko (1976), MacDonald *et al* (1976).

ⁿ Janak (1977).

of 10^{-9} to 10^{-12}) for alkali metals but are comparable in magnitude with the orbital susceptibility (χ_O), and are important for metals with complicated crystal structures, particularly HCP metals like Zn and Cd, as predicted (Misra and Kleinman 1972). This is because of the fact that the splitting of the electronic levels on the hexagonal faces of the first zone in HCP metals is entirely due to spin-orbit coupling. Since the strength of the spin-orbit coupling increases with atomic number, this splitting is appreciable in the heavy hexagonal metals (Ashcroft and Mermin 1976 p 169). It is to be noted that no such specific calculation has been made before for the spin-orbit contribution in the SDF formalism except for including the spin-orbit effects in the calculation of χ_s .

5. Results and discussion

The principal result of this paper is the derivation of tractable expressions for the orbital (χ_o), spin (χ_s) and spin-orbit (χ_{so}) contributions to the magnetic susceptibility of electrons in metals through the use of a pseudopotential formalism and degenerate perturbation theory. We have included the effects of the lattice potential, electron-electron interaction and spin-orbit interaction. It has been shown that the earlier well known results are obtained as limiting cases of our results.

The necessity for using degenerate perturbation theory in our calculation is in contrast to the case of total energy as calculated by Harrison (1966), who found that second-order perturbation theory sufficed. This is because we are dealing essentially with energy derivatives, so that the second-order perturbation theory result diverges rather strongly (Misra and Roth 1969) and overestimates the departure from free-electron behaviour.

As an example of our theory, we have calculated the various components of susceptibility for alkali metals as well as two divalent HCP metals, Zn and Cd. It is gratifying to note that our results agree well with the experimental results. It may be noted that our expressions for various components of χ are quite general and applicable to metals with complicated crystal structure.

We note that, in the absence of direct experimental data for either the diamagnetic or the spin susceptibility of Zn and Cd in the literature, it has been the usual practice to calculate the value of the electronic contribution to the susceptibility by the relation $\chi_E = \chi_T - \chi_i$, where χ_E , χ_T and χ_i represent the electronic contribution, the bulk susceptibility and the ionic susceptibility. In table 2 we have compared our results for magnetic susceptibility χ with χ_E . It may be noted that our results for alkali metals as well as Zn and Cd agree fairly well with the indirectly obtained experimental results. The discrepancy in the experimental and theoretical results can be attributed to an uncertainty in the subtraction of χ_i to obtain χ_E . In table 2 we also compare the value of χ_s/χ_F obtained by us with the results obtained by the spin-density functional formalism.

We further note that our results agree with earlier well known results in suitable limits. However, there is no easy way to compare our theory with the spin-density functional theory. Although spin-orbit effects have been included in the expression for χ_s in the SDF theory, the spin-orbit contribution to the electronic susceptibility (χ_{so}), which becomes important for metals like Zn and Cd, has not yet been explicitly obtained using SDF theory.

Finally, we note that we have derived the expressions for χ_o , χ_s and χ_{so} at zero temperature, but it is a simple task to extend our formalism to finite temperatures by modifying our integration over the Fermi surface as well as by explicitly considering the temperature dependence of the pseudopotential.

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