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Theory of Diamagnetic Susceptibility of Metals*

PRASANTA K. MISRA†
Tufts University, Medford, Massachusetts 02153

AND

LAURA M. ROTH
General Electric Research and Development Laboratory, Schenectady, New York 12301

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In order to calculate the diamagnetic susceptibility of real metals, we have generalized the pseudopotential method to the case of a metal in a magnetic field. A general equation of motion is obtained, from which we first derive an expression for the core diamagnetism. We then derive an expression for the diamagnetic susceptibility of Bloch electrons in a magnetic field in terms of a pseudopotential. If our pseudopotential is replaced by the actual lattice potential, the result reduces exactly to expressions derived by other authors for the diamagnetic susceptibility of Bloch electrons. However, we believe that our method is the simplest manner in which this result can be derived. By the use of the pseudopotential and degenerate perturbation theory we obtain the result in a form from which computation can be made easily. We have computed the diamagnetic susceptibility of all the alkali metals and of aluminum. From our expression, the diamagnetic susceptibility of any polyvalent metal to which our approximations apply can be easily computed. We have also found a satisfactory explanation of why certain metals have very high diamagnetic susceptibility. We contradict Glasser's conclusion that the diamagnetic susceptibility and the paramagnetic susceptibility are nonadditive, and correct some algebraic errors in the work of Samoilovich and Rabinovich.

I. INTRODUCTION

It is well known that in classical electrodynamics the resultant magnetic susceptibility of a system of electrons is zero. In quantum theory, on the other hand, there is a nonzero diamagnetic effect, as was first shown by Landau.[1] The diamagnetic susceptibility is found, in general, to be small and independent of the temperature. At very low temperatures, in addition to the steady diamagnetism, there are terms which depend strongly and in an oscillatory fashion on the magnetic field, i.e., the well-known de Haas–Van Alphen effect.[2] However, in the present discussion, we shall limit ourselves to the steady diamagnetic susceptibility. We shall not consider the case of the effect of very high magnetic fields,[3,4] and shall neglect all electron-electron interaction terms whose effects have been shown to be small as long as we do not have superconductivity.[5,6]

Landau[1] showed that for free electrons in a magnetic field the diamagnetic susceptibility per unit volume is

$$\chi=-e^2k_0/12\pi^2mc^2\,, \tag{1.1}$$

where k_0 is the wave number at the top of the Fermi surface. For electrons in a periodic lattice, Peierls[7] used wave functions obtained in the tight-binding approximation and derived an expression for the susceptibility consisting of three terms,

$$\chi=\chi_1+\chi_2+\chi_3\,, \tag{1.2}$$

where χ_1 is the susceptibility of an isolated atom mutliplied by the number of atoms per unit volume, χ_2 is a term which has no simple physical inerpretation and whose magnitude and sign are uncertain, and χ_3 reduces for a simple band with the effective mass m^* to the Landau-Peierls expression

$$\chi_{\text{LP}}=-e^2k_0/12\pi^2m^*c^2\,. \tag{1.3}$$

However, for simple metals, the tight-binding approximation is not appropriate.

Wilson[8] treated the diamagnetism of Bloch electrons by studying the density matrix as a function of the magnetic field. Though he was not able to derive a complete formula by this method, Hebborn and Sondheimer[9] calculated a complete expression for χ in a very complicated way. Much of the complication in their method is caused by the lack of periodicity of the magnetic perturbing terms in the Hamiltonian which gives rise to singular matrix elements in the partition function. To simplify this approach, Hebborn, Luttinger, Sondheimer, and Stiles[10] have considered the effect of a slowly varying space-periodic external field, the result for a uniform field being obtained by letting the period tend to infinity at the end of the calculation.

Kjeldass and Kohn[11] have used a generalized effective mass theory by taking into account fourth-order

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† Now at Utkal University, Bhabaneswar, Orissa, India.

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terms in the expansion of $\mathbf{k}-\mathbf{k}_0$. However, this result has only limited usefulness since it takes into account the very special case of electrons confined to the vicinity of the top or bottom of an energy band. They used their result to calculate the diamagnetic susceptibility of Li and Na, but as they themselves have pointed out, in case of Li, the ratio of the second to the first term in the expansion in powers of k_0 is 0.6 so that higher-order terms may well be important.

Essentially equivalent methods of derivation have been given by Roth,[12] Blount,[13] and Wannier and Upadhaya.[14] They have considered the fact that the action of a magnetic field upon a band can be resolved into two effects. One effect gradually transforms the parameters of that band. The other effect consists of the breaking up of the band into a series of discrete states. The bands thereby become renormalized or field-dependent. They have computed these renormalized bands to calculate the zero-field susceptibility.

Thus, the problem of Bloch electrons in a magnetic field has been solved by many authors,[9,12–14] leading to an extremely long and complicated result. But due to the formidable computational obstacles, no attempt was ever made even to obtain an estimate of the order of the different terms in the final result for χ. Numerical estimates could be made[11] only in the special case of a small number of degenerate electrons, contained near a band minimum in a cubic crystal.

Samoilovich and Rabinovich[15] have calculated the diagmagnetic susceptibility of conduction electrons in a nearly-free-electron approximation. Following a similar procedure, Glasser[16] has obtained an expression for the total magnetic susceptibility of metals also using the nearly-free-electron approximation. These results, which will be discussed further below, have a simpler form than the above mentioned calculations, but have the undesirable feature that their expressions blow up when the Fermi surface touches the zone boundary. Furthermore, the appropriateness of the nearly-free-electron approximation has been justified by the pseudopotential method in the absence of magnetic field, but it is not clear that it is valid in the presence of magnetic fields.

It is clear from the foregoing remarks that there remained a need for a theory of diamagnetism which could actually be applied to metals. The present work was carried out as an attempt in this direction and we believe that we have been able to derive a satisfactory theory and the result obtained is of a very simple form. Thus the steady diamagnetic susceptibility of any metal, except the noble metals and the transition metals, can be easily computed from these results. It is not valid for the latter case because the pseudopotential approximation is not appropriate for these metals.

In our theory there is one important physical approximation. It is well known that the actual lattice potential of polyvalent metals is very large, and it is not possible to use perturbation theory. However, with the great success of the pseudopotential method, it is possible, as we shall see, to use perturbation theory. This is the feature in which the approach is different from traditional band calculations and it simplifies considerably the computation of the result.

The pseudopotential method is a logical outgrowth from the orthogonalized plane wave (OPW) method first proposed by Herring,[17] who suggested orthogonalizing each plane wave to all core wave functions, which has the effect of augmenting each plane wave by adding to it a suitable linear combination of core orbitals. A series of developments from Phillips and Kleinman[18] to Harrison[19] has led to the successful calculation of energy bands of polyvalent metals by the pseudopotential method. The advantages of this method are that the psuedopotential is small and approximate solutions amy be found by the use of perturbation theory. In most of the polyvalent metals the band gaps are of the order of one-tenth of the Fermi energy and the perturbation treatment should be justified. There is, of course, no hope of treating the noble metals or transition metals in this manner since the band gaps are comparable to the Fermi energy.

II. GENERAL EQUATION OF MOTION

We consider a metal in which we assume that the wave functions of the core states are known. Let a core function pertaining to state c be designated $\phi_c(\mathbf{r})$, where c stands for the three quantum numbers n, l, m. These functions are assumed to be orthonormal. We now construct the Bloch functions

$$\phi_{c\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{N}}\sum_i \exp(i\mathbf{k}\cdot\mathbf{R}_i)\phi_c(\mathbf{r}-\mathbf{R}_i)\,, \tag{2.1}$$

where $\mathbf{R}_i$ goes over lattice vectors and N is the number of atoms in the metal. We can write this as

$$\phi_{c\mathbf{k}}(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})u_{c\mathbf{k}}(\mathbf{r})\,, \tag{2.2}$$

where

$$u_{c\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{N}}\sum_i \exp[i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{r})]\phi_c(\mathbf{r}-\mathbf{R})\,. \tag{2.3}$$

A plane wave of wave vector $\mathbf{k}$ can be made orthogonal by the Schmidt process to the core functions of an equivalent $\mathbf{k}$. Let such a function be denoted as $\chi_{\mathbf{k}}$, an ortho-

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gonalized plane wave. Then

$$\chi_{\mathbf{k},\mathbf{G}}=\exp[i(k+G)\cdot r]-\sum_c \phi_{ck}\times\langle\phi_{ck}|\exp[i(k+G)r]\rangle, \quad (2.4)$$

where **G** is a reciprocal-lattice vector. Substituting (3.2) in (2.4), we have

$$\chi_{\mathbf{k},\mathbf{G}}=\exp(i\mathbf{k}\cdot\mathbf{r})\left\{\exp(i\mathbf{G}\cdot\mathbf{r})-\sum_c u_{c\mathbf{k}}\int d\mathbf{r}\times\exp(-i\mathbf{k}\cdot\mathbf{r})u_{c\mathbf{k}}^*\exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{ir}]\right\} \quad (2.5)$$

or

$$\chi_{\mathbf{k},\mathbf{G}}=\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{G},\mathbf{k}}(\mathbf{r}), \quad (2.6)$$

where

$$u_{\mathbf{G},\mathbf{k}}(\mathbf{r})=\exp(i\mathbf{G}\cdot\mathbf{r})-\sum_c u_{c\mathbf{k}}\langle u_{c\mathbf{k}}|\exp(i\mathbf{G}\cdot\mathbf{r})\rangle. \quad (2.7)$$

It can be easily shown that

$$u_{\mathbf{G},\mathbf{k}}(\mathbf{r}+\mathbf{R})=u_{\mathbf{G}\mathbf{k}}(\mathbf{r}). \quad (2.8)$$

We shall use a modified Bloch representation for the basis functions of the problem which has been successfully applied by Roth.[12] We now give an outline of this representation. Let $u_{n\mathbf{k}}(\mathbf{r})$ be the peridoic function of **r** of the Bloch function for zero magnetic field. Let

$$\boldsymbol{\kappa}=\mathbf{k}+(e/c)\mathbf{A}(i\nabla_{\mathbf{k}}) \quad (2.9)$$

be the Fourier transform of the usual free-particle kinetic-momentum operator. Here A is the vector potential and we choose

$$\mathbf{A}(\mathbf{r})=\mathbf{r}\cdot\nabla\mathbf{A}, \quad (2.10)$$

where $\nabla\mathbf{A}$ is a constant dyadic.

Then according to the modified Bloch representation, the new basis functions are

$$\phi_{n\mathbf{k}}=u_{n\kappa^*}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}). \quad (2.11)$$

Since the different components of $\boldsymbol{\kappa}$ do not commute with each other, the order of the factors is chosen to be the completely symmetric combination. The wave function of the system then has the form

$$\Psi(\mathbf{r},t)=\sum_{\mathbf{k},n}\phi_{n\mathbf{k}}\psi_{n\mathbf{k}} \quad (2.12)$$

$$=\sum_{\mathbf{k},n}\exp(i\mathbf{k}\cdot\mathbf{r})u_{n\kappa}(\mathbf{r})\psi_n(\mathbf{k},t), \quad (2.13)$$

the latter being obtained by an integration by parts.

We wish to use this representation for our basis functions. We therefore construct $u_{c\kappa}(\mathbf{r})$ from $u_{c\mathbf{k}}(\mathbf{r})$ as defined in (2.3) by replacing **k** by the operator $\boldsymbol{\kappa}$ in a completely symmetric way, i.e., by replacing **k** by $\boldsymbol{\kappa}$ in the exponential. We now construct

$$u_{\mathbf{G}\kappa}(\mathbf{r})=\exp(i\mathbf{G}\cdot\mathbf{r})-\sum_c u_{c\kappa}\langle u_{c\kappa}|\exp(i\mathbf{G}\cdot\mathbf{r})\rangle. \quad (2.14)$$

Then it can be shown that these have the properties

$$\langle u_{c\kappa}(\mathbf{r})|u_{c'\kappa}(\mathbf{r})\rangle=\delta_{cc'}, \quad (2.15)$$

which is due to the neglect of overlap of the core functions. We have also

$$\langle u_{c\kappa}(\mathbf{r})|u_{\mathbf{G}\kappa}(\mathbf{r})\rangle=0, \quad (2.16)$$

but we note that the $u_{\mathbf{G}\kappa}$ are not orthonormal.

Now we consider the case of a metal in a magnetic field. Without the field, the wave function of an eigenstate of the problem is

$$\Psi(\mathbf{r},t)=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})\{\sum_c u_{c\mathbf{k}}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\mathbf{k}}\psi_G(\mathbf{k},t)\}, \quad (2.17)$$

where $\psi_c(\mathbf{k},t)$ and $\psi_{\mathbf{G}}(\mathbf{k},t)$ are the time-dependent coefficients. When the metal is in a magnetic field, we use the modified Bloch representation for the basis vectors and we write

$$\Psi(\mathbf{r},t)=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})\{\sum_c u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\kappa}\psi_G(\mathbf{k},t)\}. \quad (2.18)$$

Here we make the requirement $\psi_{\mathbf{G}'}(\mathbf{k}+\mathbf{G}',t)=\psi_{\mathbf{G}+\mathbf{G}'}\times(\mathbf{k},t)$, so that the summand is periodic in k. The equations are to be taken in the limit of continuous **k** but we keep the summation for convenience.

We now wish to operate on $\Psi(\mathbf{r})$, with the operator $[\mathbf{p}+e\mathbf{A}(\mathbf{r})/c]$. We have for the coordinate

$$\mathbf{r}\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})[\sum_c u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k},t)]$$

$$=\sum_{\mathbf{k}}[(-i\nabla_{\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{r})]\times[\sum_c u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k},t)]. \quad (2.19)$$

When we integrate by parts, the surface term vanishes since the expression is periodic in **k**. Thus we have

$$\mathbf{r}\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})[\sum_c u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k},t)]$$

$$=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})i\nabla_k[\sum_c u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k},t)]. \quad (2.20)$$

So

$$(\mathbf{p}+e\mathbf{A}(\mathbf{r})/c)\Psi(\mathbf{r})=\sum_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})(\mathbf{p}+\boldsymbol{\kappa})\times[\sum_c u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}}u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k},t)]. \quad (2.21)$$

Now we consider the one-electron Hamiltonian

$$H=H(\mathbf{r},\mathbf{p})=P^2/2m+V(r), \quad (2.22)$$

where $V(\mathbf{r})$ is the periodic potential. We do not explicitly include spin-orbit interaction, but it is straightforward to do so[12] and we shall refer to some of its consequences. When the metal is in a magnetic field, $\mathbf{p}$ is replaced by $\mathbf{p}+e\mathbf{A}/c$.

From (2.21) we obtain

$$H(\mathbf{r},\mathbf{p}+e\mathbf{A}/c)\Psi(\mathbf{r},t)=\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})H(\mathbf{r},\mathbf{p}+\boldsymbol{\kappa}) \times\Big[\sum_{c} u_{c\kappa}\psi_c(\mathbf{k},t)+\sum_{\mathbf{G}} u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k},t)\Big]. \quad (2.23)$$

Also

$$H\Psi(\mathbf{r})=E\Psi(\mathbf{r}). \quad (2.24)$$

Thus, we have from (2.23) and (2.24)

$$\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})-E] \times\Big[\sum_{c} u_{c\kappa}\psi_c(\mathbf{k})+\sum_{\mathbf{G}} u_{\mathbf{G}\kappa}\psi_{\mathbf{G}}(\mathbf{k})\Big]=0. \quad (2.25)$$

We can also write (2.25) as

$$\sum_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})-E]\Big[\sum_{c} u_{c\kappa}\psi_c(\mathbf{k}) +\sum_{\mathbf{G}} \Big(\exp(i\mathbf{G}\cdot\mathbf{r})-\sum_{c}|u_{c\kappa}\rangle \times\langle u_{c\kappa}|\exp(i\mathbf{G}\cdot\mathbf{r})\rangle\Big)\Big]\psi_{\mathbf{G}}(\mathbf{k})=0. \quad (2.26)$$

We now define the operator $V_{R\kappa}$ such that

$$V_{R\kappa}\exp(i\mathbf{G}\cdot\mathbf{r})=-\sum_{c}[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})-E] \times|u_{c\kappa}\rangle\langle u_{c\kappa}|\exp(i\mathbf{G}\cdot\mathbf{r})\rangle. \quad (2.27)$$

Also, the repulsive part of the pseudopotential is defined by[18]

$$V_{R\mathbf{k}}\psi=\sum_{c}(E-\mathcal{E}_c)\phi_{c\mathbf{k}}\langle\phi_{c\mathbf{k}}|\psi\rangle \quad (2.28)$$

from which we have

$$V_{R\mathbf{k}}\exp(i\mathbf{G}\cdot\mathbf{r})=-\sum_{c}[H(\mathbf{r},\,\mathbf{p}+\mathbf{k})-E]|u_{c\mathbf{k}}\rangle \times\langle u_{c\mathbf{k}}|\exp(i\mathbf{G}\cdot\mathbf{r})\rangle. \quad (2.29)$$

Comparing (2.27) and (2.29), we find that $V_{R\kappa}$ is obtained from $V_{R\mathbf{k}}$ by replacing $\mathbf{k}$ by $\boldsymbol{\kappa}$ but not in a symmetric way. From (2.26) and (2.27), we now have

$$\sum_{c\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})-E]u_{c\kappa}\psi_c(\mathbf{k}) +\sum_{\mathbf{G}\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})+V_{R\kappa}-E] \times\exp(i\mathbf{G}\cdot\mathbf{r})\psi_{\mathbf{G}}(\mathbf{k})=0. \quad (2.30)$$

Thus, the general equation of motion of a metal in an external magnetic field can be expressed in the alternative forms of (2.25), (2.26), or (2.30).

III. DIAMAGNETIC SUSCEPTIBILITY OF CORE ELECTRONS

We can write (2.25) as

$$\sum_{\mathbf{k}'} \exp(i\mathbf{k}'\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa}')-E]\Big[\sum_{c'} u_{c'\kappa'}\psi_{c'}(\mathbf{k}') +\sum_{\mathbf{G}'} u_{\mathbf{G}'\kappa'}\psi_{\mathbf{G}'}(\mathbf{k}')\Big]=0. \quad (3.1)$$

Multiplying on the left by $u_{c\kappa}{}^{\dagger}\exp(-i\mathbf{k}\cdot\mathbf{r})$ and integrating over the metal, we obtain

$$\sum_{\mathbf{k}'}\int d\mathbf{r}\,u_{c\kappa}{}^{\dagger}\exp(-i\mathbf{k}\cdot\mathbf{r})\exp(i\mathbf{k}'\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa}')-E] \times\Big[\sum_{c'} u_{c'\kappa'}\psi_{c'}(\mathbf{k}')+\sum_{\mathbf{G}'} u_{\mathbf{G}'\kappa'}\psi_{\mathbf{G}'}(\mathbf{k}')\Big]=0. \quad (3.2)$$

Since $u_{c\kappa}$, $u_{\mathbf{G}\kappa}$ and H are periodic in $\mathbf{r}$, we can break the integral into integrals over the unit cell, giving

$$\sum_{\mathbf{k}'}\int_{\text{cell}} d\mathbf{r}\,u_{c\kappa}{}^{\dagger}\exp(-i\mathbf{k}\cdot\mathbf{r})\Big\{\sum_{\mathbf{R}}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}]\Big\} \times\exp(i\mathbf{k}'\cdot\mathbf{r})[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa}')-E]\Big[\sum_{c'} u_{c'\kappa'}\psi_{c'}(\mathbf{k}') +\sum_{\mathbf{G}'} u_{\mathbf{G}'\kappa'}\psi_{\mathbf{G}}{}'(\mathbf{k}')\Big]=0. \quad (3.3)$$

For a finite crystal, the $\mathbf{k}$'s form a discrete set of points in the first zone. So we obtain

$$\sum_{\mathbf{R}}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}]=N\Delta_{\mathbf{k}\mathbf{k}'}, \quad (3.4)$$

where $\Delta_{\mathbf{k}\mathbf{k}'}$ is a crystalline δ function which vanishes unless $\mathbf{k}=\mathbf{k}'+\mathbf{G}$, in which case it is unity. For $\mathbf{k}$ and $\mathbf{k}'$ in the first zone, $\mathbf{G}=0$ and $\Delta_{\mathbf{k}\mathbf{k}'}$ is a Kronecker δ function. Therefore, (3.3) becomes

$$\int d\mathbf{r}\,u_{c\kappa}{}^{\dagger}[H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})-E] \times\Big[\sum_{c'} u_{c'\kappa}\psi_{c'}(\mathbf{k})+\sum_{\mathbf{G}'} u_{\mathbf{G}'\kappa}\psi_{\mathbf{G}'}(\mathbf{k})\Big]=0. \quad (3.5)$$

From (2.7) and (3.5), we have

$$\sum_{c'}[H_{cc'}(\boldsymbol{\kappa})-E\delta_{cc'}]\psi_{c'}(\mathbf{k}) +\sum_{\mathbf{G}'}\int u_{c\kappa}{}^{\dagger}H\exp(i\mathbf{G}'\cdot\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k})-\sum_{\mathbf{G}'c'}H_{cc'}(\boldsymbol{\kappa}) \times\langle u_{c'\kappa}|\exp(i\mathbf{G}'\cdot\mathbf{r})\rangle\psi_{\mathbf{G}'}(\mathbf{k})=0, \quad (3.6)$$

where

$$H_{cc'}(\boldsymbol{\kappa})\equiv\int d\mathbf{r}\,u_{c\kappa}{}^{\dagger}H(\mathbf{r},\,\mathbf{p}+\boldsymbol{\kappa})u_{c'\kappa}. \quad (3.7)$$

Using the multiplication theorem of Roth,[12] it can be shown that to second order in h

$$H_{cc'}(\boldsymbol{\kappa})=\mathcal{E}_c\delta_{cc'}+\sum_{c'}\int d\mathbf{r}\,\phi_c^*(\mathbf{r})\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^\alpha r^\gamma\right]\phi_{c'}(\mathbf{r}),\tag{3.8}$$

where $\mathcal{E}_{c'}$ is the core energy,

$$h_{\alpha\beta}=\epsilon_{\alpha\beta\gamma}h^\gamma,\tag{3.9}$$

and $\epsilon_{\alpha\beta\gamma}$ is the complete antisymmetric tensor of the third rank and we follow the Einstein summation convention. Similarly, we can simplify the other terms in (3.6) to obtain finally

$$\sum_{c'}\Bigg[(\mathcal{E}_{c'}-E)\delta_{cc'}$$

$$+\int d\mathbf{r}\,\phi_c^*(\mathbf{r})\left(\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^\alpha r^\gamma\right)\phi_{c'}(\mathbf{r})\Bigg]\psi_{c'}(\mathbf{k})$$

$$+\sqrt{N}\sum_{\mathbf{G}'}\int d\mathbf{r}\,\phi_c^*(\mathbf{r})\left[\frac{h}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^\alpha r^\gamma\right]$$

$$\times\chi_{\kappa\mathbf{G}}(\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k})=0,\tag{3.10}$$

where

$$\chi_{\kappa\mathbf{G}}=\exp[i(\boldsymbol{\kappa}+\mathbf{G})\cdot\mathbf{r}]-\sum_{c'}\phi_{c'}(\mathbf{r})\int\phi_{c'}^*(\mathbf{r}')$$

$$\times\exp[i\mathbf{r}'\cdot(\boldsymbol{\kappa}+\mathbf{G}')]d\mathbf{r}'\tag{3.11}$$

and $\chi_{\kappa\mathbf{G}}$ is orthogonal to the core states.

In (3.10), the first part gives the core terms. The second term in the first part gives rise to the Zeeman effect. The third term gives the core diamagnetism. As we shall see, the second part, which is a correction to the core terms due to the presence of conduction electrons, gives rise to terms analogous to the van Vleck paramagnetism.

IV. EVALUATION OF THE CONDUCTION-ELECTRON TERMS

In (2.32), if we replace $\mathbf{k}$ by $\mathbf{k}'$, multiply on the left by $\exp[-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}]$, and integrate over the crystal, we have

$$\sum_{c'\mathbf{k}'}\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r})\exp(i\mathbf{k}'\cdot\mathbf{r})[H(\mathbf{r},\mathbf{p}+\boldsymbol{\kappa}')-E]u_{c'\kappa'}\psi_{c'}(\mathbf{k}')+\sum_{\mathbf{G}'\mathbf{k}'}\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})$$

$$\times\exp(-i\mathbf{k}\cdot\mathbf{r})\exp(i\mathbf{k}'\cdot\mathbf{r})[H(\mathbf{r},\mathbf{p}+\boldsymbol{\kappa}')+V_{R\kappa'}-E]\exp(i\mathbf{G}'\cdot\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k}')=0.\tag{4.1}$$

Also, $u_{c\kappa}$, $H(\mathbf{r},\mathbf{p}+\boldsymbol{\kappa},\mathbf{h})$, and $V_{R\kappa}$ are periodic in $\mathbf{r}$, so that we can break the integral over the unit cell and use (3.4) to obtain

$$\sum_{c'}\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})[H(\mathbf{r},\mathbf{p}+\boldsymbol{\kappa})-E]u_{c'\kappa}\psi_{c'}(\mathbf{k})+\sum_{\mathbf{G}'}\int d\mathbf{r}$$

$$\times\exp(-i\mathbf{G}\cdot\mathbf{r})[H(\mathbf{r},\mathbf{p}+\boldsymbol{\kappa})+V_{R\kappa}-E]\exp(i\mathbf{G}'\cdot\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k})=0.\tag{4.2}$$

Using the multiplication theorem[12] and making some simplification, we obtain to second order in h

$$\sum_{c'}(\sqrt{N})\int d\mathbf{r}\exp[-i(\mathbf{G}+\boldsymbol{\kappa})\cdot\mathbf{r}]\left[(\mathcal{E}_{c'}-E)+\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^\alpha r^\gamma\right]\phi_{c'}(\mathbf{r})\psi_{c'}(\mathbf{k})$$

$$+\sum_{\mathbf{G}'}\left[\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})\left\{\frac{1}{2m}(\mathbf{p}+\boldsymbol{\kappa})^2+V+V_{R\kappa}\right\}\exp(i\mathbf{G}'\cdot\mathbf{r})-E\delta_{\mathbf{G}\mathbf{G}'}\right]\psi_{\mathbf{G}'}(\mathbf{k})=0.\tag{4.3}$$

We have also from (3.10)

$$(\mathcal{E}_c-E)\psi_c=-\sum_{c'}\int d\mathbf{r}\,\phi_c^*(\mathbf{r})\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^\alpha r^\gamma\right]\phi_{c'}(\mathbf{r})\psi_{c'}(\mathbf{k})$$

$$-(\sqrt{N})\sum_{\mathbf{G}'}\int d\mathbf{r}\,\phi_c^*(\mathbf{r})\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^\alpha r^\gamma\right]\chi_{\kappa\mathbf{G}'}\psi_{\mathbf{G}'}(k).\tag{4.4}$$

From (4.3) and (4.4), we have

$$\sum_{c'} N^{1/2}\int d\mathbf{r}\, \chi_{\kappa\mathbf{G}}^{\dagger}(r)\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^{\alpha}r^{\gamma}\right]\phi_{c'}(\mathbf{r})\psi_{c'}(\mathbf{k})-N\sum_{G'c'}\int d\mathbf{r}\exp[-i(\mathbf{G}+\boldsymbol{\kappa})\cdot\mathbf{r}]\int d\mathbf{r}'\,\phi_{c'}^{*}(\mathbf{r}')$$
$$\times\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r'^{\alpha}r'^{\gamma}\right]\chi_{\kappa\mathbf{G}'}(\mathbf{r}')\phi_{c'}(\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k})+\sum_{\mathbf{G}'}\left\{\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})\right.$$
$$\left.\times\left[\frac{1}{2m}(\mathbf{p}+\boldsymbol{\kappa})^{2}+V+V_{R\kappa}\right]\exp(i\mathbf{G}'\cdot\mathbf{r})-E\delta_{\mathbf{G}\mathbf{G}'}\right\}\psi_{\mathbf{G}'}(\mathbf{k})=0. \quad (4.5)$$

Equations (4.3) and (4.5) enable us to eliminate either ψ_G for the core electrons or $\psi_{c'}$ for the conduction electrons. Let us first consider the core electron case. If $E\cong\mathcal{E}_c$, then Eq. (4.5) shows that $\psi_{G'}$ is of order h. If we write the last line as $(H_{\mathbf{G}\mathbf{G}'}{}^{0}-E\delta_{\mathbf{G}\mathbf{G}'})\psi_{\mathbf{G}'}$, we have to this order

$$\sum_{\mathbf{G}'}(H_{\mathbf{G}\mathbf{G}'}{}^{0}-E\delta_{\mathbf{G}\mathbf{G}'})\psi_{\mathbf{G}'}\cong-N^{1/2}\sum_{c'}\int d\mathbf{r}\,\chi_{\kappa,\mathbf{G}}(\mathbf{r})\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}\,\phi_{c'}(\mathbf{r})\psi_{c'}(\mathbf{k}). \quad (4.6)$$

From (3.10) and (4.6) we obtain the interaction term in (3.10) and the contribution to the core susceptibility due to the presence of the conduction electrons is

$$\chi_{\mathrm{I}}=2N\sum_{\mathbf{G}'c}\langle\phi_c|\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}|\chi_{\mathbf{k}\mathbf{G}}\rangle(H^{0}-E)^{-1}{}_{\mathbf{G}\mathbf{G}'}\langle\chi_{\mathbf{k}\mathbf{G}'}|\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}|\phi_c\rangle. \quad (4.7)$$

This is a contribution analogous to the well-known van Vleck paramagnetism. This term vanishes in the absence of spin-orbit interaction, since in that case ϕ_c is an eigenfunction of $(\mathbf{h}/m)\cdot\mathbf{r}\times\mathbf{p}$, and the OPW are of course, orthogonal to the core terms.

Looking now at the conduction electron case, we have from (3.10)

$$\psi_c=-\frac{N^{1/2}}{\mathcal{E}_c-E}\sum_{\mathbf{G}'}\int d\mathbf{r}\,\phi_c^{*}(\mathbf{r})\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r^{\alpha}r^{\gamma}\right]\chi_{\kappa\mathbf{G}'}\psi_{\mathbf{G}'}(\mathbf{k}). \quad (4.8)$$

From (4.5) and (4.8), we have finally

$$-N\sum_{c'\mathbf{G}}\frac{1}{(\mathcal{E}_{c'}-E)}\int dr\,\chi_{\kappa\mathbf{G}}{}^{\dagger}\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}\phi_{c'}(\mathbf{r})\int dr'\,\phi_{c'}^{*}(\mathbf{r}')\frac{\mathbf{h}}{m}\cdot\mathbf{r}\times\mathbf{p}\chi_{\kappa\mathbf{G}'}\psi_{\mathbf{G}'}(\mathbf{k})-N\sum_{\mathbf{G}'c'}\int d\mathbf{r}$$
$$\times\exp[-i(\boldsymbol{\kappa}+\mathbf{G})\cdot\mathbf{r}]\int dr'\,\phi_{c'}(r')\left[\frac{\mathbf{h}}{m}\cdot\mathbf{r}'\times\mathbf{p}'+\frac{h_{\alpha\beta}h_{\gamma\beta}}{2m}r'^{\alpha}r'^{\gamma}\right]\chi_{\kappa\mathbf{G}'}(\mathbf{r}')\phi_{c'}(\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k})$$
$$+\sum_{\mathbf{G}'}\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})\left[\frac{(\mathbf{p}+\boldsymbol{\kappa})^{2}}{2m}+V+V_{R\kappa}-E\right]\exp(i\mathbf{G}'\cdot r)\psi_{\mathbf{G}'}(k)=0, \quad (4.9)$$

where we retain terms up to the second order in h. We see that the first term contributes to the susceptibility of the conduction electrons a term which is similar to the van Vleck paramagnetism except that it is a contribution to the susceptibility of Bloch electrons due to the presence of the core.

The second term consists of matrix elements of $(\mathbf{h}/m)\cdot\mathbf{r}\times\mathbf{p}+(2m)^{-1}h_{\alpha\beta}h_{\gamma\beta}/r^{\alpha}r^{\gamma}$ between OPW's and core terms. In the absence of spin-orbit interaction, the matrix elements of $(\mathbf{h}/m)\cdot\mathbf{r}\times\mathbf{p}$ are zero since in that case ϕ_c is an eigenfunction of $(\mathbf{h}/m)\cdot\mathbf{r}\times\mathbf{p}$ and the OPW's are orthogonal to the core terms. Also the average value of (x^2+y^2) between the core and the OPW's is small since the core terms are small. So apart from the van-Vleck–like term which also vanishes in the absence of spin-orbit interaction and the matrix elements of (x^2+y^2) between the core and the OPW terms which we shall neglect, (4.9) can be written as

$$\sum_{\mathbf{G}'}\int d\mathbf{r}\exp(-i\mathbf{G}\cdot\mathbf{r})\left[\frac{1}{2m}(\mathbf{p}+\boldsymbol{\kappa})+V+V_{R\kappa}-E\right]$$
$$\times\exp(i\mathbf{G}'\cdot\mathbf{r})\psi_{\mathbf{G}'}(\mathbf{k})=0. \quad (4.10)$$

This is due to the motion of the Bloch electrons in the magnetic field. We can write this as

$$H(\boldsymbol{\kappa})\psi(\mathbf{k})=E\psi(\mathbf{k}), \tag{4.11}$$

where

$$H(\boldsymbol{\kappa})=(\mathbf{p}+\boldsymbol{\kappa})^2/2m+V+V_{R\kappa}. \tag{4.12}$$

Let

$$W_\kappa(\mathbf{r})=V(\mathbf{r})+V_{R\kappa}(\mathbf{r}), \tag{4.13}$$

where $W_\kappa(\mathbf{r})$ is the modified pseudopotential in a magnetic field, since without the magnetic field, we have

$$W_{\mathbf{k}}(\mathbf{r})=V(\mathbf{r})+V_{R\mathbf{k}}(\mathbf{r}), \tag{4.14}$$

which is the usual pseudopotential. However, we note that $W_\kappa(\mathbf{r})$ is not obtained from $W_{\mathbf{k}}(\mathbf{r})$ by replacing $\mathbf{k}$ by $\boldsymbol{\kappa}$ in a symmetric way.

As it has been repeatedly discussed,[18,19] since $V_{R\mathbf{k}}(\mathbf{r})$ is a repulsive potential, $W_{\mathbf{k}}(\mathbf{r})$ is a much smaller potential than $V(\mathbf{r})$.

V. DIAMAGNETIC SUSCEPTIBILITY OF BLOCH ELECTRONS

A. Method of Evaluation

We shall now derive from first principles an expression for the diamagnetic susceptibility of Bloch electrons. For Bloch electrons, we have obtained the Schrödinger equation

$$\sum_{\mathbf{G}'} H_{\mathbf{G}'\mathbf{G}}(\boldsymbol{\kappa})\psi_{\mathbf{G}'}(\mathbf{k})=E\psi_{\mathbf{G}}(\mathbf{k}), \tag{5.1}$$

where

$$H(\boldsymbol{\kappa})=(\mathbf{p}+\boldsymbol{\kappa})^2/2m+W_\kappa(\mathbf{r}). \tag{5.2}$$

The result which we shall obtain is completely general and is valid for any type of crystal because throughout our derivation, we can either consider $H(\mathbf{k})$ to be the plane-wave Hamiltonian

$$H(\mathbf{k})=(\mathbf{p}+\mathbf{k})^2/2m+V(\mathbf{r}), \tag{5.3}$$

where $V(\mathbf{r})$ is the crystal potential, and which is appropriate for the case of any crystal, or we can consider $H(\mathbf{k})$ to be

$$H(\mathbf{k})=(\mathbf{p}+\mathbf{k})^2/2m+W_{\mathbf{k}}(\mathbf{r}), \tag{5.4}$$

where $H(\mathbf{k})$ is such that $H(\boldsymbol{\kappa})$ is obtained from it by replacing $\mathbf{k}$ by $\boldsymbol{\kappa}$ in a symmetric way and which is suitable for a pseudopotential formalism. We believe that this is the simplest way to derive an expression for the diamagnetic susceptibility of Bloch electrons in a crystal

The magnetic susceptibility is given by

$$\chi=-\partial^2F/\partial H^2, \tag{5.5}$$

where F is the free energy,

$$F=N'-\frac{1}{\beta}\sum_i \ln(1+\exp[-\beta(\epsilon_i-\zeta)]). \tag{5.6}$$

ζ is the chemical potential which can be regarded as a constant to the second order in magnetic field and $\beta=1/kT$, where k is the Boltzman constant and T the temperature. Let

$$F'(\beta)=F-N\zeta \tag{5.7}$$

$$=-\frac{1}{\beta}\sum_i \ln(1+\exp[-\beta(\epsilon_i-\zeta)]). \tag{5.8}$$

$F'(\beta)$ can be related to the classical partition function by the method of Wilson and Sondheimer.[8] We can express this in the form

$$F'(\beta)=\sum_i T_\beta \exp(-\beta\epsilon_i)=T_\beta\, \mathrm{tr}\Phi(\boldsymbol{\kappa}), \tag{5.9}$$

where T_β represents an inverse Laplace transform and

$$\Phi(\boldsymbol{\kappa})=\exp[-\beta H(\boldsymbol{\kappa})]. \tag{5.10}$$

Let $\Phi(\mathbf{k})$ be the operator such that $\Phi(\boldsymbol{\kappa})$ can be formed from it by replacing $\mathbf{k}$ by $\boldsymbol{\kappa}$ in a symmetric manner. We then have

$$\mathrm{tr}\Phi(\boldsymbol{\kappa})=\mathrm{tr}\Phi(\mathbf{k}), \tag{5.11}$$

which follows from the general principle[12] that the trace of a symmetric function of $\boldsymbol{\kappa}$ is the same as the trace of the same function of $\mathbf{k}$. We shall now evaluate $\Phi(\mathbf{k})$.

B. Expansion Theorem

We wish to prove an expansion theorem. We wish to obtain an expansion series for the operators

$$\nabla_{\mathbf{k}}^{\alpha}\exp[-\beta H(\mathbf{k})] \quad\text{and}\quad \nabla_{\mathbf{k}}^{\alpha}\nabla_{\mathbf{k}}^{\gamma}\exp[-\beta H(\mathbf{k})].$$

First, we expand $\exp[-\beta H(\mathbf{k}+\epsilon)]$ in a Taylor series:

$$\exp[-\beta H(\mathbf{k}+\epsilon)]=\exp(-\beta H)+\epsilon^\alpha\nabla_k^{\alpha}\exp(-\beta H) +\tfrac{1}{2}\epsilon^\alpha\epsilon^\gamma\nabla_{\mathbf{k}}^{\alpha}\nabla_{\mathbf{k}}^{\gamma}\exp(-\beta H)+\cdots, \tag{5.12}$$

where α, β, and γ are Cartesian coordinates and we use the Einstein summation convention. Also

$$H(\mathbf{k}+\epsilon)=H(\mathbf{k})+\epsilon^\alpha\nabla_k^{\alpha}H(\mathbf{k})+\tfrac{1}{2}\epsilon^\alpha\epsilon^\gamma \times\nabla_{\mathbf{k}}^{\alpha}\nabla_{\mathbf{k}}^{\gamma}H(\mathbf{k})+\cdots. \tag{5.13}$$

Now we use the well-known operator-expansion formula of Goldberger and Adams[20]:

$$\exp[-\beta(H+\delta)]=\exp(-\beta H)+\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)(-\delta)\exp(-\beta' H)+\exp(-\beta H)\int_0^\beta d\beta' \times\exp(\beta' H)(-\delta)\exp(-\beta' H)\int_0^{\beta} d\beta''\,\exp(\beta'' H)(-\delta)\exp(-\beta'' H), \tag{5.14}$$

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[20] M. L. Goldberger and E. N. Adams, J. Chem. Phys. **20**, 240 (1952).

where δ is such that

$$H(\mathbf{k}+\epsilon)=H(\mathbf{k})+\delta \tag{5.15}$$

or from (5.13)

$$\delta=[\epsilon^\alpha\nabla_\mathbf{k}{}^\alpha+(\tfrac{1}{2}\epsilon^\alpha\epsilon^\gamma)\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma]H(\mathbf{k})+\cdots. \tag{5.16}$$

From (5.14) and (5.16), we obtain

$$\begin{aligned}\exp[-\beta(H+\delta)]=&\exp(-\beta H)+\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)[-\epsilon^\alpha(\nabla_\mathbf{k}{}^\alpha H)]\exp(-\beta' H)+\exp(-\beta H)\int_0^\beta d\beta'\\&\times\exp(\beta' H)[-\tfrac{1}{2}\epsilon^\alpha\epsilon^\gamma(\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma H)]\exp(-\beta' H)+\exp(-\beta H)\bigg\{\int_0^\beta d\beta'\\&\times\exp(\beta' H)[\epsilon^\alpha\nabla_\mathbf{k}{}^\alpha H]\exp(-\beta' H)\int_0^{\beta'} d\beta''\,\exp(\beta'' H)\\&\times[\epsilon^\gamma\nabla_\mathbf{k}{}^\gamma H]\exp(-\beta'' H)\bigg\}+\text{terms of higher order}.\end{aligned} \tag{5.17}$$

So from (5.12) and (5.17), we have the desired expansions

$$\nabla_\mathbf{k}{}^\alpha\exp(-\beta H)=-\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)(\nabla_\mathbf{k}{}^\alpha H)\exp(-\beta' H), \tag{5.18}$$

$$\begin{aligned}\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma\exp(-\beta H)=&-\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)(\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma H)\exp(-\beta' H)\\&+\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)(\nabla_\mathbf{k}{}^\alpha H)\exp(-\beta' H)\int_0^{\beta'} d\beta''\,\exp(\beta'' H)(\nabla_\mathbf{k}{}^\gamma H)\exp(-\beta'' H)\\&+\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)(\nabla_\mathbf{k}{}^\gamma H)\exp(-\beta' H)\int_0^\beta d\beta''\,\exp(\beta'' H)(\nabla_\mathbf{k}{}^\alpha H)\exp(-\beta'' H).\end{aligned} \tag{5.19}$$

C. Evaluation of $\mathbf{\Phi}(\mathbf{k})$

We have from (5.10)

$$d\Phi(\kappa)/d\beta=-H(\kappa)\Phi(\kappa). \tag{5.20}$$

Using the multiplication theorem[12], we have

$$\frac{d\Phi(\mathbf{k})}{d\beta}=-\exp[-\mathbf{h}\cdot\nabla_\mathbf{k}\times\nabla_{\mathbf{k}'}]H(\mathbf{k})\Phi(\mathbf{k}')|_{\mathbf{k}'=\mathbf{k}}. \tag{5.21}$$

Let

$$\Phi(\mathbf{k})=\Phi_0(\mathbf{k})+\Phi_1(\mathbf{k}), \tag{5.22}$$

where

$$\Phi_0(\mathbf{k})=\exp[-\beta H(\mathbf{k})]. \tag{5.23}$$

From (5.21), we have

$$\begin{aligned}\frac{d\Phi_0(\mathbf{k})}{d\beta}+\frac{d\Phi_1(\mathbf{k})}{d\beta}=&-H(\mathbf{k})\Phi_0(\mathbf{k})-H(\mathbf{k})\Phi_1(\mathbf{k})\\&+ih_{\alpha\beta}(\nabla_\mathbf{k}{}^\alpha H)\nabla_\mathbf{k}{}^\beta(\Phi_0+\Phi_1)+\tfrac{1}{2}h_{\alpha\beta}h_{\gamma\delta}\\&\times(\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma H)\nabla_\mathbf{k}{}^\beta\nabla_\mathbf{k}{}^\delta(\Phi_0+\Phi_1)\end{aligned} \tag{5.24}$$

and for Φ_1,

$$\begin{aligned}\frac{d\Phi_1(\mathbf{k})}{d\beta}=&-H\Phi_1+[ih_{\alpha\beta}(\nabla_\mathbf{k}{}^\alpha H)\nabla_\mathbf{k}{}^\beta\\&+\tfrac{1}{2}h_{\alpha\beta}h_{\gamma\beta}(\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma H)\nabla_\mathbf{k}{}^\beta\nabla_\mathbf{k}{}^\delta](\Phi_0+\Phi_1).\end{aligned} \tag{5.25}$$

Treating the second term in the right as an inhomogeneous term, the equation can be solved for Φ_1:

$$\begin{aligned}\Phi_1=&\exp(-\beta H)\int_0^\beta d\beta'\,\exp(\beta' H)[ih_{\alpha\beta}(\nabla_\mathbf{k}{}^\alpha H)\nabla_\mathbf{k}{}^\beta\\&+\tfrac{1}{2}h_{\alpha\beta}h_{\gamma\delta}(\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma H)\nabla_\mathbf{k}{}^\beta\nabla_\mathbf{k}{}^\delta](\Phi_0+\Phi_1).\end{aligned} \tag{5.26}$$

We can now iterate this expression to obtain, up to the second order in the magnetic field,

$$\begin{aligned}\Phi_1\cong&\Phi_0\int_0^\beta d\beta'\,\exp(\beta' H)[ih_{\alpha\beta}(\nabla_\mathbf{k}{}^\alpha H)\nabla_\mathbf{k}{}^\beta\\&+\tfrac{1}{2}h_{\alpha\beta}h_{\gamma\delta}(\nabla_\mathbf{k}{}^\alpha\nabla_\mathbf{k}{}^\gamma H)\nabla_\mathbf{k}{}^\beta\nabla_\mathbf{k}{}^\delta]\exp(-\beta' H)\\&+\Phi_0\int_0^\beta d\beta'\,\exp(\beta' H)ih_{\alpha\beta}(\nabla_\mathbf{k}{}^\alpha H)\nabla_\mathbf{k}{}^\beta\exp(-\beta' H)\\&\times\int_0^\beta d\beta''\,\exp(\beta'' H)ih_{\gamma\delta}(\nabla_\mathbf{k}{}^\gamma H)\nabla_\mathbf{k}{}^\delta\exp(-\beta'' H).\end{aligned} \tag{5.27}$$

which is to be used with (5.18) and (5.19).

D. Evaluation of tr Φ_1 (k)

We now take the trace with the functions $u_{n\mathbf{k}}(\mathbf{r})$ defined by

$$H_{\mathbf{k}}u_{n\mathbf{k}}=\mathcal{E}_n(\mathbf{k})u_{n\mathbf{k}}. \tag{5.28}$$

We now adopt the convention that any running index means that the sum over all the bands shall be taken, except that the diagonal terms have already been separated out. Then it can be easily shown that the first term of tr Φ_1 in (5.27) vanishes from time reversal symmetry. Also we write

$$P_{mn}{}^{\alpha}=\int d^3x\, u_{m,\mathbf{k}}{}^*(\nabla_{\mathbf{k}}{}^{\alpha}H_{\mathbf{k}})u_{n,\mathbf{k}}\,, \tag{5.29}$$

$$\Phi_0(E_m)=\exp(-\beta E_m)\,, \tag{5.30}$$

$$\Phi_0'(E_m)=-\beta\exp(-\beta E_m)\,, \tag{5.31}$$

$$\Phi_0''(E_m)=\beta^2\exp(-\beta E_m)\,. \tag{5.32}$$

Then, after some algebra, it can be shown that

$$\begin{aligned}
\mathrm{tr}\Phi_1(\mathbf{k})=\frac{h_{\alpha\beta}h_{\gamma\delta}}{m^4}\bigg\{&-\frac{m^2}{12}(\nabla_{\mathbf{k}}{}^{\alpha}\nabla_{\mathbf{k}}{}^{\gamma}E_m)(\nabla_{\mathbf{k}}{}^{\beta}\nabla_{\mathbf{k}}{}^{\delta}E_m)\Phi_0''(E_m)+m\delta_{\alpha\gamma}\frac{P_{mn}{}^{\beta}P_{nm}{}^{\delta}}{E_{nm}{}^2}\Phi_0'(E_m)+2m\delta_{\alpha\gamma}\frac{P_{mn}{}^{\beta}P_{nm}{}^{\delta}}{E_{nm}{}^3}\Phi_0(E_m)\\
&-\frac{P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}}{E_{nm}E_{lm}E_{qm}}\Phi_0'(E_m)-\frac{2(P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}-P_{lm}{}^{\beta}P_{mn}{}^{\alpha}P_{nq}{}^{\gamma}P_{ql}{}^{\delta})}{E_{nm}{}^2E_{lm}E_{qm}}\Phi_0(E_m)+(P_{mm}{}^{\beta}P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{mm}{}^{\delta}\\
&-P_{mn}{}^{\beta}P_{nn}{}^{\alpha}P_{nn}{}^{\gamma}P_{nm}{}^{\delta})\left[\frac{2\Phi_0(E_m)}{E_{nm}{}^4}+\frac{\Phi_0'(E_m)}{E_{nm}{}^3}\right]+P_{mn}{}^{\beta}P_{nn}{}^{\alpha}P_{nm}{}^{\gamma}P_{mm}{}^{\delta}\left[\frac{2\Phi_0'(E_m)}{E_{nm}{}^3}+\frac{\Phi_0''(E_m)}{E_{nm}{}^2}\right]\\
&-P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{ml}{}^{\delta}P_{lm}{}^{\beta}\left[\frac{\Phi_0(E_m)}{E_{nm}{}^2E_{lm}{}^2}+\frac{2\Phi_0(E_m)}{E_{nm}{}^3E_{lm}}+\frac{\Phi_0'(E_m)}{E_{nm}{}^2E_{lm}}\right]+P_{mm}{}^{\beta}P_{mq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}\\
&\times\left[\frac{2\Phi_0(E_m)}{E_{lm}{}^3E_{qm}}-\frac{2\Phi_0(E_m)}{E_{qm}{}^3E_{lm}}+\frac{2\Phi_0'(E_m)}{E_{lm}{}^2E_{qm}}+\frac{\Phi_0''(E_m)}{E_{lm}E_{qm}}\right]-\frac{2P_{mn}{}^{\beta}P_{nn}{}^{\alpha}P_{nl}{}^{\gamma}P_{lm}{}^{\delta}}{E_{nm}{}^2E_{lm}}\Phi_0'(E_m)-\frac{P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{qn}{}^{\gamma}P_{nm}{}^{\delta}}{E_{nm}{}^2E_{qm}}\Phi_0'(E_m)\\
&-2(P_{mn}{}^{\beta}P_{nn}{}^{\alpha}P_{nl}{}^{\gamma}P_{lm}{}^{\delta}-P_{lm}{}^{\beta}P_{mn}{}^{\alpha}P_{nn}{}^{\gamma}P_{nl}{}^{\delta})\left[\frac{\Phi_0(E_m)}{E_{nm}{}^3E_{lm}}+\frac{\Phi_0(E_m)}{E_{nm}{}^2E_{lm}{}^2}\right]\\
&-\frac{2(P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{qn}{}^{\gamma}P_{nm}{}^{\delta}-P_{mn}{}^{\alpha}P_{nq}{}^{\gamma}P_{qn}{}^{\delta}P_{nm}{}^{\beta})}{E_{nm}{}^3E_{qm}}\Phi_0(E_m)\bigg\}.
\end{aligned} \tag{5.33}$$

Also, it can be shown by partial integration that

$$\begin{aligned}
\left[\frac{P_{mm}{}^{\beta}P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{mm}{}^{\delta}}{E_{nm}{}^3}+\frac{P_{mn}{}^{\alpha}P_{nn}{}^{\beta}P_{nm}{}^{\gamma}P_{mm}{}^{\delta}}{E_{nm}{}^3}+\frac{P_{mq}{}^{\alpha}P_{ql}{}^{\delta}P_{lm}{}^{\gamma}P_{mm}{}^{\beta}}{E_{qm}{}^2E_{lm}}\right]\Phi_0'(E_m)=\bigg[&-2m\frac{P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}}{E_{nm}{}^3}\delta_{\beta\delta}\\
&+\frac{2(P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}-P_{lm}{}^{\beta}P_{mn}{}^{\alpha}P_{nq}{}^{\gamma}P_{ql}{}^{\delta})}{E_{nm}{}^2E_{lm}E_{qm}}-\frac{2P_{mm}{}^{\beta}P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{mm}{}^{\delta}}{E_{nm}{}^4}+\frac{2P_{mn}{}^{\beta}P_{nn}{}^{\alpha}P_{nn}{}^{\gamma}P_{nm}{}^{\delta}}{E_{nm}{}^4}\\
&+P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{ml}{}^{\delta}P_{lm}{}^{\beta}\left(\frac{1}{E_{nm}{}^2E_{lm}{}^2}+\frac{2}{E_{nm}{}^3E_{lm}}\right)-P_{mm}{}^{\beta}P_{mq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}\left(\frac{2}{E_{lm}{}^3E_{qm}}-\frac{2}{E_{qm}{}^3E_{lm}}\right)\\
&+\frac{2(P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{qn}{}^{\gamma}P_{nm}{}^{\delta}-P_{mn}{}^{\alpha}P_{nq}{}^{\gamma}P_{qn}{}^{\delta}P_{nm}{}^{\beta})}{E_{nm}{}^3E_{qm}}+2(P_{mn}{}^{\beta}P_{nn}{}^{\alpha}P_{nl}{}^{\gamma}P_{lm}{}^{\delta}-P_{lm}{}^{\beta}P_{mn}{}^{\alpha}P_{nn}{}^{\gamma}P_{nl}{}^{\delta})\\
&\times\left(\frac{1}{E_{nm}{}^3E_{lm}}+\frac{1}{E_{nm}{}^2E_{lm}{}^2}\right)\bigg]\Phi_0(E_m).
\end{aligned} \tag{5.34}$$

From (5.34) and (5.35), we have

$$\mathrm{tr}\Phi_1(\mathbf{k})=\frac{h_{\alpha\beta}h_{\gamma\delta}}{m^4}\Bigg[-\frac{m^2}{12}\sum_{m}\nabla_{\mathbf{k}}{}^{\alpha}\nabla_{\mathbf{k}}{}^{\gamma}E_m\nabla_{\mathbf{k}}{}^{\beta}\nabla_{\mathbf{k}}{}^{\delta}E_m\Phi_0''(E_m)+\sum_{\substack{m,q,l\\ m\neq q,l}}\frac{P_{mm}{}^{\beta}P_{mq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}}{E_{lm}E_{qm}}\Phi_0''(E_m)$$

$$+\sum_{\substack{m,n\\ m\neq n}}\frac{mP_{mn}{}^{\beta}P_{nm}{}^{\delta}}{E_{nm}{}^2}\delta_{\alpha\gamma}\Phi_0'(E_m)-\sum_{\substack{m,l,n,q\\ m\neq l,n,q}}\frac{P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}}{E_{nm}E_{lm}E_{qm}}\mathrm{G}\Phi_0'(E_m)-\sum_{\substack{m,n,q\\ m\neq n,q}}\frac{P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{mq}{}^{\delta}P_{qm}{}^{\beta}}{E_{nm}{}^2E_{qm}}\Phi_0'(E_m)$$

$$+\sum_{\substack{m,l,q\\ m\neq l,q}}P_{mm}{}^{\beta}P_{mq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}\left(\frac{2}{E_{lm}{}^2E_{qm}}+\frac{1}{E_{lm}E_{qm}{}^2}\right)\Phi_0'(E_m)\Bigg],\qquad(5.35)$$

where we have returned to the usual convention on indices.

E. General Formula for Diamagnetic Susceptibility

We now substitute (5.36) in (5.8), replacing Φ_0 by the function in (5.7). We note that the energy derivative of this function is the Fermi function $f(E)$. Then from (5.5) we obtain

$$\chi=\frac{2h_{\alpha\beta}h_{\gamma\delta}}{m^4H^2}\Bigg[\frac{m^2}{12}\sum_{m,\mathbf{k}}\nabla_{\mathbf{k}}{}^{\alpha}\nabla_{\mathbf{k}}{}^{\gamma}E_m\nabla_{\mathbf{k}}{}^{\beta}\nabla_{\mathbf{k}}{}^{\delta}E_mf'(E_m)-\sum_{\substack{m,q,l,\mathbf{k}\\ m\neq q,l}}\frac{P_{mm}{}^{\beta}P_{mq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}}{E_{lm}E_{qm}}f'(E_m)-\sum_{\substack{m,n,\mathbf{k}\\ m\neq n}}2m\frac{P_{mn}{}^{\beta}P_{nm}{}^{\delta}}{E_{nm}{}^2}\delta_{\alpha\gamma}f(E_m)$$

$$+\sum_{\substack{m,l,n,q,\mathbf{k}\\ m\neq l,n,q}}\frac{2P_{mn}{}^{\beta}P_{nq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}}{E_{nm}E_{lm}E_{qm}}f(E_m)+\sum_{\substack{m,n,q,\mathbf{k}\\ m\neq n,q}}\frac{2P_{mn}{}^{\alpha}P_{nm}{}^{\gamma}P_{mq}{}^{\delta}P_{qm}{}^{\beta}}{E_{nm}{}^2E_{qm}}f(E_m)$$

$$-\sum_{\substack{m,l,q,\mathbf{k}\\ m\neq l,q}}2P_{mm}{}^{\beta}P_{mq}{}^{\alpha}P_{ql}{}^{\gamma}P_{lm}{}^{\delta}\left(\frac{2}{E_{lm}{}^2E_{qm}}+\frac{1}{E_{lm}E_{qm}{}^2}\right)f(E_m)\Bigg].\qquad(5.36)$$

This gives the diamagnetic susceptibility of Bloch electrons. We note that this is a general theory of Bloch electrons in a magnetic field which has been derived from first principles and is valid for any crystal. We believe that this method of derivation is the simplest way to derive an expression for the diamagnetic susceptibility of Bloch electrons. However, we note that we have neglected $\nabla_{\mathbf{k}}W$ and $\nabla_{\mathbf{k}}\nabla_{\mathbf{k}}W$ terms since they are small. We have also neglected the field-dependent terms of $W_{\mathbf{k}}$.

This expression for the susceptibility can be shown to be equivalent to that of Roth[12] for the case we have treated, i.e., in the absence of the effects of spin. If we evaluate the terms up to the order of k^2, our result reduces to that of Kohn and Kjeldaas.[11]

VI. SIMPLIFICATION FOR METALS

A. Pseudopotential

In order to calculate the diamagnetic susceptibility of metals we have to know accurately the lattice potential in a self-consistent calculation. The actual lattice potential $V(\mathbf{r})$ is very large and so it cannot be realistically treated as a small parameter in a perturbation expansion. On the other hand, the pseudopotential which is the sum of the lattice potential and the repulsive potential is small and therefore we can apply a perturbation expansion.

We shall retain the operator nature of $W(\mathbf{r})$. It can be easily shown that $W(\mathbf{r})$ may be separated into a sum of individual (but overlapping) pseudopotentials centered upon the individual ions. Since each ionic pseudopotential will be spherically symmetric, in the matrix element, only the magnitudes of the right- and left-hand wave numbers and of the difference in wave numbers are required. In the present case, we shall be interested in matrix elements between states which lie on the Fermi surface so that the only dependence of the matrix elements is on the magnitude of the difference.

We also note that the diagonal matrix elements of P are proportional to $\nabla_{\mathbf{k}}E$, while the nondiagonal matrix elements are proportional to $\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle\equiv W_{\mathbf{G}}$. In using perturbation theory, we shall take $W_{\mathbf{G}}$ as a small parameter and we shall retain terms up to the order of $|W_{\mathbf{G}}|^2$.

B. Application of Nondegenerate Perturbation Theory

We shall now use time-independent nondegenerate second-order perturbation theory which is applicable to the case of monovalent metals when the Fermi surface is well within the Brillouin zone. Later, we shall have to use degenerate perturbation theory to treat the general case of polyvalent metals.

We wish to solve the equation

$$[T+W(\mathbf{r})]\psi_{\mathbf{k}}(\mathbf{r})=E\psi_{\mathbf{k}}(\mathbf{r}),\qquad(6.1)$$

where $W(\mathbf{r})$ is of first-order smallness. From standard perturbation theory, we obtain

$$\psi_{\mathbf{k}}=|\mathbf{k}\rangle+\sum_{\mathbf{G}}{}'\frac{2m\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle}{\mathbf{k}^2-|\mathbf{k}+\mathbf{G}|^2}|\mathbf{k}+\mathbf{G}\rangle,\tag{6.2}$$

$$E=\frac{k^2}{2m}+\langle\mathbf{k}|W|\mathbf{k}\rangle+\sum_{\mathbf{G}}{}'\frac{2m\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle\langle\mathbf{k}|W|\mathbf{k}+\mathbf{G}\rangle}{k^2-|\mathbf{k}+\mathbf{G}|^2},\tag{6.3}$$

$$P_{nm}{}^{\alpha}=-\sum_{\mathbf{G}}\frac{2mG^{\alpha}\langle\mathbf{k}_m+\mathbf{G}|W|\mathbf{k}_m\rangle}{G^2+2\mathbf{k}\cdot\mathbf{G}}\delta(\mathbf{k}_m-\mathbf{k}_n+\mathbf{G}),\tag{6.4}$$

$$P_{mm}{}^{\alpha}=k_m{}^{\alpha}+m\nabla_k{}^{\alpha}\langle\mathbf{k}_m|W|\mathbf{k}_m\rangle+\cdots.\tag{6.5}$$

Substituting these in (5.37) and retaining terms up to the second order, we obtain after some simplification

$$\chi=-\frac{h^2}{12\pi^3m^2H^2}\iiint d^3\mathbf{k}\,f'(E)-\frac{8h_{\alpha\beta}h_{\gamma\delta}}{\pi^3H^2}\sum_{\mathbf{G}}G^{\alpha}G^{\gamma}\times\left\{\iiint d^3k\frac{|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2}{(G^2+2\mathbf{k}\cdot\mathbf{G})^3}f'(E)\left[\frac{\delta_{\beta\delta}}{6}-\frac{k^{\beta}k^{\delta}}{G^2+2\mathbf{k}\cdot\mathbf{G}}\right]+m\iiint d^3\mathbf{k}\frac{|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2}{(G^2+2\mathbf{k}\cdot\mathbf{G})^4}f(E)\times\left[\delta_{\beta\delta}+\frac{8k^{\beta}k^{\delta}}{G^2+2\mathbf{k}\cdot\mathbf{G}}\right]\right\},\tag{6.6}$$

where H is along the z direction.

The chemical potential can be evaluated up to the second order from the relations

$$\frac{1}{4\pi^2}\int d^3k\,f(E)=N,\tag{6.7}$$

$$f(E)=f(E_0)+(E-E_0)f'(E_0)+\cdots,\tag{6.8}$$

$$\frac{1}{4\pi^3}\int d^3k\,f_{\zeta}(E_0)=\frac{1}{4\pi^3}\left[\int d^3k\,f_{\zeta_0}(E_0)+\int d^3k(\zeta-\zeta_0)\frac{\partial f}{\partial\zeta}\bigg|_0+\cdots\right],\tag{6.9}$$

and

$$\frac{1}{4\pi^3}\int d^3k\,f_{\zeta_0}(E_0)=N,\tag{6.10}$$

where ζ_0 is the chemical potential for free electrons:

$$\zeta_0=(9\pi N^2)^{1/3}(\pi/2m).\tag{6.11}$$

From these, we have

$$\zeta=\zeta_0+\langle\mathbf{k}_F|W|\mathbf{k}_F\rangle-\frac{|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{4\zeta^{1/2}\zeta_0{}^{1/2}}\times a^{1/2}\tanh^{-1}a^{1/2},\tag{6.12}$$

where

$$a=8m\zeta/G^2.\tag{6.13}$$

We shall now evaluate χ. When the Fermi surface is well within the first Brillouin zone, there is no problem in evaluating the integrals. When the Fermi surface is outside the Brillouin zone, we use Harrison's method[19] of taking the principal values of divergent integrals. In this case, we find that the singularities cancel out to give the same result as before. We obtain in both cases

$$\chi=-\frac{\mu^2N}{2\zeta_0}\left[1-\frac{1}{8\zeta_0{}^{1/2}\zeta^{3/2}}\sum_{\mathbf{G}}|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2\times\left(\left\{\frac{\zeta}{\zeta_0}a^{1/2}\tanh^{-1}a^{1/2}-\frac{a}{1-a}\right\}+2\frac{(G_x{}^2+G_y{}^2)}{G^2}\times\left\{\frac{5a^2-3a^3}{8(1-a)^2}+\tfrac{3}{8}a^{3/2}\tanh^{-1}a^{1/2}\right\}\right)\right],\tag{6.14}$$

where μ is the Bohr magneton.

C. Comparison with Other Results

We now compare the above result with that of others. We write down the result of Samoilovich and Rabinovich,[15] who have obtained an expression for the diamagnetic susceptibility in the nearly-free-electron model by expanding the partition function in powers of V; the result of Glasser,[16] who has obtained an expression for the total magnetic susceptibility in a nearly-free-electron approximation by a similar approach to that of Samoilovich and Rabinovich; and the result of Abe,[21] who has derived an expression for the paramagnetic susceptibility in a nearly-free-electron approach.

Glasser (*Ref. 16*):

$$\chi=\frac{\mu^2N}{\zeta_0}\left[1-\sum_{\mathbf{G}}\frac{V_{\mathbf{G}}{}^2}{8\zeta_0{}^2}\left(\left\{a^{1/2}\tanh^{-1}a^{1/2}-\frac{a}{1-a}\right\}-\frac{(G_x{}^2+G_y{}^2)}{G^2}\left\{\frac{5a^2-3a^2}{8(1-a)^2}+\tfrac{3}{8}a^{3/2}\tanh^{-1}a^{1/2}\right\}\right)\right].\tag{6.15}$$

Abe (*Ref. 21*):

$$\chi=\frac{3\mu^2N}{2\zeta_0}\left[1-\sum_{\mathbf{G}}\frac{V_{\mathbf{G}}{}^2}{8\zeta_0{}^2}\left(a^{1/2}\tanh^{-1}a^{1/2}-\frac{a}{1-a}\right)\right].\tag{6.16}$$

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[21] R. Abe, Progr. Theoret. Phys. (Kyoto) **29**, 23 (1963).

Samoilovich and Rabinovich (Ref. 15):

$$\chi=-\frac{\mu^2N}{2\zeta_0}\left[1-\sum_{\mathbf{G}}\frac{V_{\mathbf{G}}^2}{8\zeta_0^2}\left(\left\{a^{1/2}\tanh^{-1}a^{1/2}-\frac{a}{1-a}\right\}+\frac{(G_x^2+G_y^2)}{G^2}\frac{a}{(1-a)^2}\right)\right]. \qquad (6.17)$$

When we compare our result with the above results, we replace $|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2$ by $V_{\mathbf{G}}^2$. We find that if we add our result (6.14) (replacing ζ by ζ_0), which is an expression for the diagmagnetic susceptibility to that of Abe (6.16), which is an expression for paramagnetic susceptibility, we obtain the result of Glasser (6.15), which is an expression for the total magnetic susceptibility. On the other hand, we note that our result does not agree with that of Samoilovich and Rabinovich (6.16). However, we find that Samoilovich and Rabinovich[15] have committed some algebraic errors in the course of their derivation; in particular, in the last integral of their Eq. (10), the expression $(1-4x^2)$ should be replaced by $\frac{1}{2}(1-4x^2)^2$. We have derived an expression for the diamagnetic susceptibility following their procedure after making the necessary corrections and we find that this result is the same as our result (6.14).

We also note that we disagree with Glasser's conclusion[16] that the paramagnetic susceptibility and the diamagnetic susceptibility are not additive. Glasser's erroneous conclusion is due to the use of the incorrect expression for the diamagnetic susceptibility obtained by Samoilovich and Rabinovich.

Finally, we note that the above expressions derived by us and by others are only valid for the case where the Fermi surface is well within the first Brillouin zone, or, with the use of the principle value as in Harrison's method,[19] well away from the zone faces. To cover the case where the Fermi surface is close to a zone face, we now wish to derive an expression using degenerate perturbation theory.

D. Application of Degenerate Perturbation Theory

We assume that the unperturbed eigenvalue is only doubly degenerate. We now expand

$$\psi=a_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})+a_{\mathbf{k}+\mathbf{G}}\exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}] \qquad (6.18)$$

and ignore the other coefficients. Here $\mathbf{k}$ lies near the zone boundary which bisects the vector $\mathbf{G}$. Using standard methods, we now obtain

$$\psi=\frac{[E-(\mathbf{k}+\mathbf{G})^2/2m]\exp(i\mathbf{k}\cdot\mathbf{r})+\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle\exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}]}{[(E-(\mathbf{k}+\mathbf{G})^2/2m)^2+|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2]^{1/2}}. \qquad (6.19)$$

We now adopt the convention that the suffix (−) indicates the functions pertaining to the lower-energy values and (+) indicates the functions pertaining to the higher-energy values. After some simplification, we finally obtain

$$P_{++}{}^{\alpha}=k^{\alpha}+\tfrac{1}{2}G^{\alpha}-\frac{\frac{1}{4}G^{\alpha}[k^2/2m-(\mathbf{k}+\mathbf{G})^2/2m]}{[\frac{1}{4}(k^2/2m-(\mathbf{k}+\mathbf{G})^2/2m)^2+|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2]^{1/2}}, \qquad (6.20)$$

$$P_{--}{}^{\alpha}=k^{\alpha}+\tfrac{1}{2}G^{\alpha}+\frac{\frac{1}{4}G^{\alpha}[k^2/2m-(\mathbf{k}+\mathbf{G})^2/2m]}{[\frac{1}{4}(k^2/2\mathrm{m}-(\mathbf{k}+\mathbf{G})^2/2m)^2+|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2]^{1/2}}, \qquad (6.21)$$

$$P_{-+}{}^{\alpha}=\frac{G^{\alpha}\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle}{[(k^2/2m-(\mathbf{k}+\mathbf{G})^2/2m)^2+4|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2]^{1/2}}, \qquad (6.22)$$

$$E_{+}=\tfrac{1}{2}\left[\frac{k^2}{2m}+\frac{(\mathbf{k}+\mathbf{G})^2}{2m}\right]+\left[\tfrac{1}{4}\left(\frac{k^2}{2m}-\frac{(\mathbf{k}+\mathbf{G})^2}{2m}\right)^2+|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2\right]^{1/2}, \qquad (6.23)$$

$$E_{-}=\tfrac{1}{2}\left[\frac{k^2}{2m}+\frac{(\mathbf{k}+\mathbf{G})^2}{2m}\right]-\left[\tfrac{1}{4}\left(\frac{k^2}{2m}-\frac{(\mathbf{k}+\mathbf{G})^2}{2m}\right)^2+|\langle\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2\right]^{1/2}. \qquad (6.24)$$

Substituting these in (5.37), we obtain after some simplification the same result as (6.6), except that in the denominators we must make the replacement

$$G^2+2\mathbf{k}\cdot\mathbf{G}\rightarrow[(G^2+2\mathbf{k}\cdot\mathbf{G})^2+16m^2\mathrm{K}\mathbf{k}+\mathbf{G}|W|\mathbf{k}\rangle|^2]^{1/2}. \qquad (6.25)$$

We now evaluate the chemical potential by the method outlined above and obtain

$$\zeta=\zeta_0+\frac{2\zeta^{3/2}}{a\zeta^{1/2}{}_0}\left\{1+\frac{1}{4a^{1/2}}\left[(1-a^{1/2})^2F_1-(1+a^{1/2})^2F_2\right]\right\}+\frac{|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{8\zeta^{1/2}\zeta_0^{1/2}}a^{1/2}\ln\left|\frac{(1-a^{1/2})(1+F_1)}{(1+a^{1/2})(1+F_2)}\right|, \qquad (6.26)$$

where

$$F_1=\left[1+\frac{16m^2|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{G^4(1-a^{1/2})^2}\right]^{1/2}\tag{6.27}$$

and

$$F_2=\left[1+\frac{16m^2|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{G^4(1+a^{1/2})^2}\right]^{1/2}.\tag{6.28}$$

From (6.6), (6.25) and (6.26), we have, after simplification.

$$\begin{aligned}\chi=-\frac{\mu^2N}{2\zeta_0}\left(\frac{\zeta}{\zeta_0}\right)^{1/2}\bigg\{&1-\frac{1}{2a}[2-(1-a^{1/2})F_1-(1+a^{1/2})F_2]+\frac{(G_x^2+G_y^2)}{G^2}\bigg[\frac{1}{2a^{1/2}}\left(\frac{1}{F_1}-\frac{1}{F_2}\right)\\&+\tfrac{3}{4}\left(1-\frac{|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2a^2+4\zeta^2(1-a)}{4\zeta\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle a^{3/2}}\tan^{-1}\frac{4\zeta\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle a^{3/2}}{|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2a^2+4\zeta^2(1-a)}\right)\\&+\frac{a^{3/2}G^8}{128\times64m^4|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2\zeta^2}\bigg[(1-a^{1/2})F_1\bigg[(1-a^{1/2})\bigg((1+a^{1/2})^2-\frac{24m^2|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{G^4}\bigg)\\&+\frac{64m^2|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{G^4}\bigg]-(1+a^{1/2})F_2\bigg[(1+a^{1/2})\bigg((1-a^{1/2})^2-\frac{24m^2|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{G^4}\bigg)\\&+\frac{64m^2|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{G^4}\bigg]\bigg]+\frac{3|\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle|^2}{64\zeta^2}a^{3/2}\ln\left|\frac{(1+F_1)(1-a^{1/2})}{(1+F_2)(1+a^{1/2})}\right|\bigg]\bigg\}.\end{aligned}\tag{6.29}$$

This is the expression for the diamagnetic susceptibility of a metal obtained by using degenerate perturbation theory. Far from the zone boundary this expression can be expanded to second order in $|\langle k_F+G|W|k_F\rangle|$ and it reduces as it should to Eq. (6.14) and so to the corrected version of Samoilovich and Rabinovich. This verifies the use of the principle value for the case of the Fermi surface lying outside the Brillouin zone.

E. Comparison of Results

In order to use these results for actual crystals we must sum $\zeta-\zeta_0$ and $\chi-\chi_0$, from (6.26) and (6.29), over reciprocal-lattice vectors $\mathbf{G}$. We evaluate ζ and the a's, which depend on the G's, by iterating the summed form of (6.26), and using (6.13). We then calculate χ from the summed form of (6.29) which we can write

$$\chi=\chi_0(1+\textstyle\sum_G D_G),\tag{6.30}$$

where χ_0 is the diamagnetic susceptibility of free electrons.

To see the variation of the susceptibility with Fermi level, we have chosen the eight (111) $\mathbf{G}$ vectors which are the nearest-neighbor reciprocal-lattice shell for a face-centered lattice such as aluminum. In evaluating $\sum_{\text{shell}} D_G$, we note that for cubic symmetry we can replace $G_x^2+G_y^2$ by $\frac{2}{3}G^2$ in (6.29). We have made the calculation using the parameters for aluminum. The value of $\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle$ for Al varies with a, but for the purpose of comparison we have chosen the value

$$\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle=0.075\ \text{Ry},\tag{6.31}$$

which is the average value of this quantity for a in the neighborhood of 1, as obtained from the results of Animalu and Heine tabulated by Harrison.[19] The value

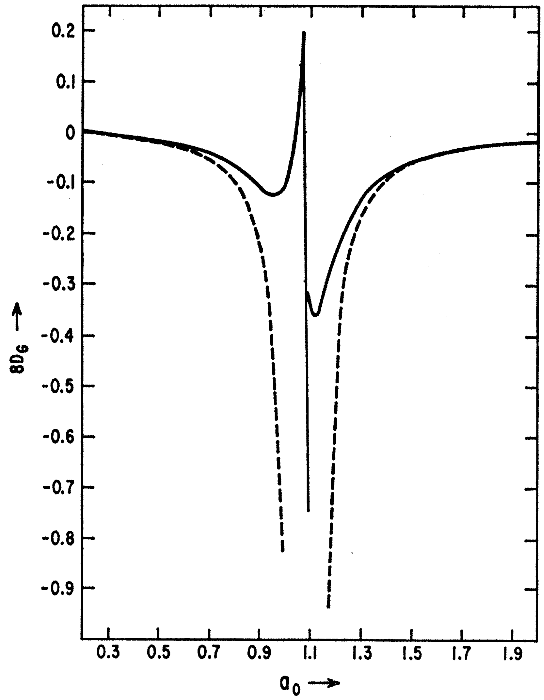

FIG. 1. Plot of $8D_G$, as defined in (6.30), versus $a_0=8m\zeta_0/G^2$, calculated by using for G the eight nearest-neighbor reciprocal-lattice vectors for a face-centered cubic lattice, and parameters appropriate to aluminum. Dashed curve, second-order perturbation theory; solid curve, degenerate perturbation theory.

TABLE I. Some details of susceptibility calculation.

	G shell	a_0	$\langle k_F+G\|W_G\|k_F\rangle$[a]	$\sum_{\text{shell}}D_G$ Nondegenerate	Degenerate
Li	110	0.7698	0.0934	−0.1856	−0.1204
	200	0.3849	0.0626	−0.0038	−0.0037
	211	0.2565	0.0173	−0.0004	−0.0004
Na	110	0.7698	0.0200	−0.0338	−0.0313
	200	0.3849	0.0093	−0.0002	−0.0002
	211	0.2565	0.0036	−0.0000	−0.0000
Al	111	1.694	0.0152	−0.0358	−0.0329
	200	1.271	0.0580	−0.0110	−0.0110
	220	0.635	0.0564	−0.0027	−0.0027

[a] From calculation of Animalu and Heine as tabulated by Harrison, Ref. 19.

of ζ_0 for Al is 0.8596 Ry. However, we wish to vary ζ_0 and a_0, which are related by

$$\epsilon_0=(\hbar^2G^2/8m)a_0=0.5099a_0\text{ Ry},$$

using $G=2.696\times10^8$ cm^{-1} for aluminum.

In Fig. 1 we have plotted the variation of $\sum D_G$ with a_0 for both the second-order nondegenerate perturbation-theory result of (6.14) and the degenerate perturbation-theory result of (6.29). For the nondegenerate case the magnitude of $\sum D_G$ becomes large for a close to 1, and goes to infinity as $a=1$, which occurs for a value of a_0 of about 1.1. The degenerate perturbation theory result however remains finite when a approaches 1.

We have applied the theory to the case of the alkali metals and to Al. The values of $\langle\mathbf{k}_F+\mathbf{G}|W|\mathbf{k}_F\rangle$ used were obtained from the results of Animalu as tabulated by Harrison.[19] The method outlined above was used to evaluate the D_G's and these were summed over neighbor shells until convergence was obtained, using a CDC 6400 computer. In Table I we give some details of the calculation for Li, Na, and Al. In Table II are given the results for the diamagnetic susceptibility for the alkalis and aluminum which we notice do not differ much from the free-electron result. We have compared our result with experiment where possible. However, in only two cases, those of Li and Na, has the diamagnetic susceptibility been measured directly. Direct measurement means that both the total magnetic susceptibility and the spin susceptibility have been measured experimentally so that the diamagnetic susceptibility is measured by computing the difference. For the experimental results, we have used the results of Pugh and Goldman,[22] Bowers,[23] and Schumacher and Slichter.[24]

TABLE II. Diamagnetic susceptibility of alkali metals and Al (10^{-6}cgs vol. units).

Metal	Free-electron χ_0	χ from (6.29)	Experimental χ[a]
Li	−0.266	−0.233	−0.14±0.15
Na	−0.215	−0.208	−0.07±0.13
K	−0.179	−0.176	
Rb	−0.159	−0.158	
Cs	−0.147	−0.145	
Al	−0.138	−0.132	

[a] References 22–24.

There has been no theoretical estimate or "direct" experimental measurement of the diagmagnetic susceptibility of any polyvalent metal. We have calculated the diamagnetic susceptibility of Al as an example, but we can evaluate the diamagnetic susceptibility of any polyvalent metal to which the pseudopotential formalism is applicable.

VII. CONCLUSION

The principal result of this paper is the obtaining of a tractable expression for the diamagnetic susceptibility of simple metals, through the use of a pseudopotential formalism and degenerate perturbation theory. Along the way we have been able to rederive the general result for the susceptibility of Bloch electrons in a reasonably simple fashion.

The necessity for using degenerate perturbation theory in our calculation is in contrast to the case of the total energy as calculated by Harrison,[19] 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, as Fig. 1 shows, and overestimates the departure from free-electron behavior. Our calculation shows that for the cases studied, the departure from the free electron or one OPW result is quite small. The reason for this is that a does not come very close to 1 in any of these materials. In the few cases where experimental results were available, this conclusion was consistent with them, within the rather large errors quoted.

Large deviations from the free-electron results can be obtained if a is close to 1 and if the interaction is sufficiently large. In fact, the deviation can be eigher direction as can be seen in Fig. 1. It would be interesting to see whether this theory can account for the large diamagnetism of some materials such as bismuth.

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[22] W. Pugh and J. E. Goldman, Phys. Rev. **99**, 1633(E) (1955); **99**, 1641(A) (1955).

[23] R. Bowers, Phys. Rev. **99**, 1640(A) (1955).

[24] R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).