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Theory of the Diamagnetism of Bloch Electrons*

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This paper deals with the diamagnetic susceptibility of a degenerate gas of Bloch electrons in a cubic lattice. It is shown that the effective Hamiltonian of such electrons in a magnetic field is rigorously a particular power series in **P** of the form $\tilde{H}=E(\mathbf{P})$, where $\mathbf{P}=(\hbar/i)\nabla-(e/c)\mathbf{A}$ and $E(\hbar\mathbf{k})$ is the energy of the band in question. (Because of the noncommutativity of the components of **P**, $E(\hbar\mathbf{k})$ does *not* determine $E(\mathbf{P})$ uniquely. $E(\mathbf{P})$ is not a symmetrized power series in the components of **P**.) By expanding $E(\mathbf{P})$ in powers of **P**, one is led to a series expansion for the diamagnetic susceptibility of the form

$$\chi=-\frac{e^2k_0}{12\pi^2mc^2}\left(\frac{m}{m^*}+c_2k_0^2+c_4k_0^4+\cdots\right),$$

where $k_0=(3\pi^2n)^{\frac{1}{3}}$ and n is the number of electrons per unit volume. (For a spherical band, k_0 is the wave number on the surface of the Fermi sea.) The first term of this series is the well-known Landau-Peierls expression, the higher terms are corrections to it. In the tight binding approximation the second term becomes dominant and reduces correctly to the atomic diamagnetism. We have calculated the first two terms of this series for Li and Na. For Na the second term was found to be very small; for Li it is more than half as large as the first and of opposite sign. Our numerical results are $\chi_{\mathrm{Li}}=-0.074\times10^{-6}$ and $\chi_{\mathrm{Na}}=-0.26\times10^{-6}$ cgs volume units.

1. INTRODUCTION

THE quantum theory of the diamagnetism of conduction electrons has been discussed from different points of view by a number of authors. Free electrons were treated in a classic paper by Landau[1] who showed that for a degenerate electron gas the diamagnetic susceptibility per unit volume is

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

where k_0 is the wave number at the top of the Fermi surface. The next important advance was made by Peierls[2] who extended Landau's theory to the case of tightly bound Bloch electrons. He obtained an expression for the susceptibility consisting of the following three terms

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

where χ_1 is the susceptibility of an isolated metal atom multiplied by the number of atoms per unit volume; χ_2 is a term which has no simple physical interpretation and whose magnitude and even sign are uncertain; and χ_3 is given by

$$\chi_3=-\frac{e^2}{48\pi^3\hbar^2c^2}\int\!\!\int\left[\frac{\partial^2E}{\partial k_1^2}\frac{\partial^2E}{\partial k_2^2}-\left(\frac{\partial^2E}{\partial k_1\partial k_2}\right)^2\right]\frac{1}{|\nabla_{\mathbf{k}}E|}dS, \tag{1.3}$$

where $E(\mathbf{k})$ is the energy of the band in question and the integration extends over the Fermi surface. This last term is a direct generalization of Landau's result (1.1). For a simple band with the effective mass m^*, it reduces to the Landau-Peierls expression

$$\chi_{\mathrm{LP}}=-\frac{e^2k_0}{12\pi^2m^*c^2}. \tag{1.4}$$

For simple metals the tight-binding approximation and hence the theory of Peierls are not appropriate.

More recently Wilson[3] has treated the diamagnetism of Bloch electrons without recourse to the tight binding approximation by studying the density matrix as a function of the magnetic field. He obtained a number of contributions, among them Peierls' χ_3, Eq. (1.3), a term χ_1' which in the tight binding limit reduces to the atomic diamagnetism (Peierls' χ_1) as well as other terms some of which are not explicitly evaluated. Wilson states that he expects certain of these other terms to be of the same order of magnitude as χ_1'. With some reservations Wilson believed all terms other than χ_3 to be of minor importance. This elegant procedure can lead in principle to an exact evaluation of the diamagnetism of Bloch electrons. However, because of its complexity an application to real metals appears very difficult.

Adams[4] has also independently derived an expression for the diamagnetic susceptibility which, however, like Wilson's is very difficult to evaluate. Adams criticized the usual procedure of taking χ_3 to be the dominant contribution to the diamagnetic susceptibility and showed that in many important cases there are other contributions of comparable magnitude.

Apart from these theoretical considerations new interest in the diamagnetic susceptibility has been aroused by recent experimental developments. During

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* Supported in part by the Office of Naval Research.

[1] L. Landau, Z. Physik **64**, 629 (1930).

[2] R. Peierls, Z. Physik **80**, 763 (1933).

[3] A. H. Wilson, Proc. Cambridge Phil. Soc. **49**, 292 (1953).

[4] E. N. Adams II, Phys. Rev. **89**, 633 (1953).

the past two years Slichter and his co-workers[5] have for the first time succeeded in measuring separately the spin susceptibilities of two metals, Li and Na. As the total susceptibility is generally regarded as a sum of three terms,

$$\chi_{\text{tot}}=\chi_{\text{spin}}{}^{(\text{cond})}+\chi_{\text{dia}}{}^{(\text{cond})}+\chi_{\text{dia}}{}^{(\text{core})} \tag{1.5}$$

(where "cond" refers to conduction electrons), a combination of Slichter's results with measurements of χ_{tot} and estimates of the core diamagnetism, $\chi_{\text{dia}}{}^{(\text{core})}$, yields experimental estimates of the diamagnetism of the conduction electrons.

It will be clear from the foregoing remarks that there remained a need for a theory of diamagnetism which could actually be applied to some simple metals. The present paper represents an attempt in this direction. It is closely related in spirit to the method of Bardeen,[6] extended by Silverman and Kohn,[7] for calculating the cohesive energies of the alkali-metals. These authors expand the energy as a power series in k^α, and from this expansion obtain the total energy, per unit volume, of the conduction electrons in the form

$$E_{\text{total}}=n(E_0+A_2k_0{}^2+A_4k_0{}^4+\cdots); \tag{1.6}$$

here n is the number of conduction electrons per unit volume and

$$k_0{}^3=3\pi^2n. \tag{1.7}$$

(For a spherical band, k_0 is the wave number on the surface of the Fermi sea.) For both Li and Na the first two terms of this series give an excellent approximation. In the present paper we extend this approach to problems involving an external magnetic field by means of the formalism of Luttinger and Kohn[8] which yields a similar series for the diamagnetic susceptibility[9]:

$$\chi=-\frac{e^2k_0}{12\pi^2mc^2}\left(\frac{m}{m^*}+c_2k_0{}^2+c_4k_0{}^4+\cdots\right). \tag{1.8}$$

The first term in this series is just the Landau-Peierls expression, (1.4). The coefficients of the higher order terms can be expressed in two ways: Either in terms of energy differences and momentum matrix elements between the entire set of Bloch waves at $\mathbf{k}=0$; or in terms of simple integrals involving the functions which occur in the power series expansion of the Bloch waves of the band in question, say the mth near $\mathbf{k}=0$:

$$\psi_{m\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}[u_m(\mathbf{r})+k_\alpha u_m{}^\alpha(\mathbf{r})+k_\alpha k_\beta u_m{}^{\alpha\beta}(\mathbf{r})+\cdots]. \tag{1.9}$$

We note at once, from (1.8), that in cases where the band is sufficiently empty ($k_0\rightarrow 0$), the Landau-Peierls expression χ_{LP}, Eq. (1.4), becomes an exact expression for the total diamagnetic susceptibility. This fact does not depend on m^*/m being close to 1. The higher order terms in (1.8) contain, first of all, corrections which come from the more complete Peierls expression (1.3) when not only the quadratic terms of $E(\hbar\mathbf{k})$ are taken into account. But they also contain other contributions which in general are of the same order of magnitude (in Li they are even much larger). Thus the Peierls expression (1.3) gives the correct susceptibility for sufficiently few electrons but in applying it, there is no point to include in $E(\hbar\mathbf{k})$ terms higher than quadratic in $\mathbf{k}$.[10]

In the limit of infinite lattice parameter (tight binding), m/m^* vanishes exponentially while the c_i approach certain finite limiting values. Since $k_0\rightarrow 0$, like the reciprocal of the interatomic spacing, the second term in (1.8) alone survives, and we have shown that it reduces correctly to the ordinary atomic diamagnetism, i.e., to Peierls' χ_1.[11]

We see then that the first two terms of (1.8) give the exact result in the following three limiting cases:

(1) number of conduction electrons→0;
(2) free electrons;
(3) tightly bound electrons.

When one is not near the tight-binding limit (where special cancellations take place due to atomic sum rules) the rapid convergence of (1.8) depends on the following condition:

$$\bar{p}^2(\hbar k_0)^2/m^2(\Delta E)^2\ll 1, \tag{1.10}$$

where $\bar{p}$ is a mean momentum matrix element between Bloch states at $\mathbf{k}=0$ and ΔE is a mean energy denominator between such states. This condition is written down merely to indicate the general circumstances under which (1.8) may be expected to be useful.

We have obtained explicit expressions for the coefficient c_2 in (1.8) and evaluated it for both Li and Na. The results of taking the first two terms in (1.8) are as follows:

$$\begin{aligned}\text{Li: }\chi&=(0.37\chi_{\text{LP}})=-0.074\times10^{-6}\text{ cgs volume units,}\\ \text{Na: }\chi&=(1.02\chi_{\text{LP}})=-0.26\times10^{-6}\text{ cgs volume units.}\end{aligned} \tag{1.11}$$

In the case of Li the ratio of the second to the first term is 0.6 so that higher order terms may well be important. However, our calculation shows clearly that the Landau-Peierls result is too large. In the case

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[5] Schumacher, Carver, and Slichter, Phys. Rev. **95**, 1089 (1954); R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

[6] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

[7] R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950); R. A. Silverman, Phys. Rev. **85**, 227 (1952).

[8] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[9] From here on we shall, for simplicity, talk about a nondegenerate band with minimum at $\mathbf{k}=0$, in a cubic crystal.

[10] This statement holds equally well for ellipsoidal energy surfaces.

[11] However, when evaluated for the actual lattice parameter in Li and Na it is very much smaller than Peierls' χ_1.

of Na, the second term is very small[12] and our result should represent a reliable estimate.[13]

These theoretical results may be compared with the (indirectly obtained) experimental values given in reference 5:

$$\begin{aligned} &\text{Li: } \chi_{\text{exp}}=(-0.14\pm0.15) \\ &\qquad\qquad\times10^{-6}\text{ cgs volume units,} \\ &\text{Na: } \chi_{\text{exp}}=(-0.07\pm0.11) \\ &\qquad\qquad\times10^{-6}\text{ cgs volume units.} \end{aligned} \tag{1.12}$$

(Reference 5 gives $\chi=-0.18$ for Li due to an arithmetic error.) In both cases there are indications of a discrepancy between theory and experiment. More accurate experimental data would be very desirable.

The details of our calculation are described in the following sections.

2. ELIMINATION OF INTERBAND MATRIX ELEMENTS

The Hamiltonian of a Bloch electron in a magnetic field can be represented by a matrix of the form

$$(m\mathbf{k}|H|n\mathbf{k}'), \tag{2.1}$$

where $\mathbf{k}$ is the wave vector running over the first Brillouin zone and m and n are quantum numbers labeling different bands. Our procedure for calculating the susceptibility consists of two steps:

(1) The elimination of interband matrix elements, that is, the diagonalization of (2.1) with respect to the band indices m and n by means of an appropriate unitary transformation:

$$(m\mathbf{k}|e^{-S}He^{S}|n\mathbf{k}')=(\mathbf{k}|\tilde{H}_m|\mathbf{k}')\delta_{mn}. \tag{2.2}$$

(2) With the transformed Hamiltonian $(\mathbf{k}|\tilde{H}_m|\mathbf{k}')$, the susceptibility of the electrons in the mth band can then be calculated using the trace method of Peierls.[2]

This section is concerned with step 1, the next section with step 2. From here on we shall generally use atomic units, that is $e=1$, $m=1$, $\hbar=1$, but in our final results we shall restore these constants.

The Hamiltonian of a Bloch electron in an external magnetic field is given by

$$H=\tfrac{1}{2}P^{\alpha}P^{\alpha}+V(\mathbf{r}), \tag{2.3}$$

where

$$P^{\alpha}=p^{\alpha}-(1/c)A^{\alpha}, \tag{2.4}$$

V is the periodic potential, and p^{α} and A^{α} are the α components of the momentum and vector potential, respectively. The usual summation convention is employed. P^{α} is of course the velocity operator. The operators x^{α} and P^{α} satisfy the following commutation relations

$$[x^{\alpha},P^{\beta}]=i\delta^{\alpha\beta}, \tag{2.5}$$

and if the magnetic field $\mathcal{H}$ is in the x_3 direction

$$[P^1,P^2]=(i/c)\mathcal{H},\quad [P^2,P^3]=[P^1,P^3]=0. \tag{2.6}$$

We express the Hamiltonian (2.3) in the representation of Luttinger and Kohn[8] which is convenient for problems involving Bloch electrons in external electromagnetic fields. The basis functions of this representation are

$$\chi_{m\mathbf{k}}(\mathbf{r})=u_{m0}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.7}$$

where the u_{m0} are the set of all Bloch waves with $\mathbf{k}=0$. The $\chi_{m\mathbf{k}}$ form a complete orthogonal set of functions which are normalized as follows:

$$\int \chi_{m\mathbf{k}}{}^{*}\chi_{n\mathbf{k}'}d\mathbf{r}=\delta_{mn}\delta(\mathbf{k}-\mathbf{k}'), \tag{2.8}$$

where the integration extends over all space. This corresponds to the following normalization of the u_{m0}:

$$\int_{\text{cell}} u_{m0}{}^{*}u_{n0}d\mathbf{r}=\frac{\Omega}{(2\pi)^3}\delta_{mn}, \tag{2.9}$$

where Ω is the volume of one crystal cell.

Before expressing the Hamiltonian in this representation let us briefly discuss the matrix elements of the relevant operators. We first consider x^{α} which enters into the Hamiltonian via the vector potential A^{α}.

$$\begin{aligned} (m\mathbf{k}|x^{\alpha}|n\mathbf{k}') &= \int u_{m0}{}^{*}e^{-i\mathbf{k}\cdot\mathbf{r}}x^{\alpha}u_{n0}e^{i\mathbf{k}'\cdot\mathbf{r}}d\mathbf{r} \\ &= -\frac{1}{i}\frac{\partial}{\partial k_{\alpha}}\int u_{m0}{}^{*}e^{-i\mathbf{k}\cdot\mathbf{r}}u_{n0}e^{i\mathbf{k}'\cdot\mathbf{r}}d\mathbf{r} \\ &= -\frac{1}{i}\frac{\partial}{\partial k_{\alpha}}\delta(\mathbf{k}-\mathbf{k}')\delta_{mn}. \end{aligned} \tag{2.10}$$

We note that the $\mathbf{k}$-dependent part is identical with the matrix element of x^{α} in a plane wave representation. This makes it convenient to introduce the following notation: Let Q be an operator which is a function of p^{α} and x^{α}. We then define

$$(\mathbf{k}|Q|\mathbf{k}')\equiv\frac{1}{(2\pi)^3}\int e^{-i\mathbf{k}\cdot\mathbf{r}}Qe^{i\mathbf{k}'\cdot\mathbf{r}}d\mathbf{r}. \tag{2.11}$$

Equation (2.10) can now be rewritten as

$$(m\mathbf{k}|x^{\alpha}|n\mathbf{k}')=\delta_{mn}(\mathbf{k}|x^{\alpha}|\mathbf{k}'). \tag{2.12}$$

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[12] This is due to the smallness of $\bar{p}$, Eq. (1.10). The Bloch function u_0 in the 3s-band at $\mathbf{k}=0$ is nearly everywhere almost a constant so that $(1/i)\nabla u_0\approx0$. This is also the reason why for Na, $m^*\approx m$.

[13] Here, as elsewhere in this paper, we neglect the effects of electron-electron interaction, which are believed to be small. See D. Pines, in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 424. Also, H. Konezawa, Progr. Theoret. Phys. **15**, 273 (1956).

Similarly the matrix elements of p^α and P^α are

$$\begin{aligned}(m\mathbf{k}|p^\alpha|n\mathbf{k}') &= \delta_{mn}k_\alpha\delta(\mathbf{k}-\mathbf{k}')+p^\alpha{}_{mn}\delta(\mathbf{k}-\mathbf{k}')\\ &= \delta_{mn}(\mathbf{k}|p^\alpha|\mathbf{k}')+p^\alpha{}_{mn}\delta(\mathbf{k}-\mathbf{k}'), \quad (2.13)\end{aligned}$$

and

$$(m\mathbf{k}|P^\alpha|n\mathbf{k}') = \delta_{mn}(\mathbf{k}|P^\alpha|\mathbf{k}')+p^\alpha{}_{mn}\delta(\mathbf{k}-\mathbf{k}'), \quad (2.14)$$

where the $p^\alpha{}_{mn}$ are the matrix elements of the momentum operators between Bloch waves at $\mathbf{k}=0$:

$$p^\alpha{}_{mn} \equiv \frac{(2\pi)^3}{\Omega}\int_{\text{cell}} u_{m0}{}^*\frac{1}{i}\frac{\partial}{\partial x^\alpha}u_{n0}d\mathbf{r}. \quad (2.15)$$

We can now evaluate the kinetic energy, $\frac{1}{2}P^\alpha P^\alpha$, in our representation

$$\begin{aligned}\tfrac{1}{2}(m\mathbf{k}|P^\alpha P^\alpha|n\mathbf{k}') &= \tfrac{1}{2}\textstyle\sum_{i,\,\mathbf{k}''}(m\mathbf{k}|P^\alpha|i\mathbf{k}'')(i\mathbf{k}''|P^\alpha|n\mathbf{k}')\\ &= \tfrac{1}{2}\delta_{mn}(\mathbf{k}|P^\alpha P^\alpha|\mathbf{k}')+p^\alpha{}_{mn}(\mathbf{k}|P^\alpha|\mathbf{k}')\\ &\quad +\tfrac{1}{2}\textstyle\sum_i p^\alpha{}_{mi}p_{in}{}^\alpha\delta(\mathbf{k}-\mathbf{k}'), \quad (2.16)\end{aligned}$$

where the symbol $\sum$ denotes both summation over repeated band indices and integration over repeated wave vectors in the first Brillouin zone. In the last step of (2.16) we have used the fact that

$$\begin{aligned}\sum_{\mathbf{k}''\text{ over zone}}(\mathbf{k}|P^\alpha|\mathbf{k}'')(\mathbf{k}''|P^\alpha|\mathbf{k}') &= \sum_{\text{all }\mathbf{k}''}(\mathbf{k}|P^\alpha|\mathbf{k}'')(\mathbf{k}''|P^\alpha|\mathbf{k}')\\ &= (\mathbf{k}|P^\alpha P^\alpha|\mathbf{k}'). \quad (2.17)\end{aligned}$$

In other words, matrix multiplication in $\mathbf{k}$ space is the same as in the free electron case. For although $\mathbf{k}''$ runs only over the first Brillouin zone, the δ-function character of $(\mathbf{k}|P^\alpha|\mathbf{k}')$ [see Eqs. (2.4), (2.10), and (2.13)] allows one to extend the integration over all k space.

The potential energy has a representation of the form

$$(m\mathbf{k}|V(\mathbf{r})|n\mathbf{k}') = V_{mn}\delta(\mathbf{k}-\mathbf{k}'). \quad (2.18)$$

Combining (2.16) with (2.18), we obtain for the total Hamiltonian:

$$\begin{aligned}(m\mathbf{k}|H|n\mathbf{k}') &= \tfrac{1}{2}\delta_{mn}(\mathbf{k}|P^\alpha P^\alpha|\mathbf{k}')+p^\alpha{}_{mn}(\mathbf{k}|P^\alpha|\mathbf{k}')\\ &\quad +(\tfrac{1}{2}\textstyle\sum_i p^\alpha{}_{mi}p^\alpha{}_{in}+V_{mn})\delta(\mathbf{k}-\mathbf{k}'). \quad (2.19)\end{aligned}$$

Now setting $\mathbf{k}$ and $\mathbf{A}$ equal to zero, we see that

$$\tfrac{1}{2}\textstyle\sum_i p^\alpha{}_{mi}p^\alpha{}_{in}+V_{mn} = \epsilon_m\delta_{mn}, \quad (2.20)$$

where ϵ_m is the energy of the mth band at $\mathbf{k}=0$, so that we have finally

$$\begin{aligned}(m\mathbf{k}|H|n\mathbf{k}') &= \delta_{mn}[\epsilon_m\delta(\mathbf{k}-\mathbf{k}')+\tfrac{1}{2}\delta_{\alpha\beta}(\mathbf{k}|P^\alpha P^\beta|\mathbf{k}')]\\ &\quad +p^\alpha{}_{mn}(\mathbf{k}|P^\alpha|\mathbf{k}'). \quad (2.21)\end{aligned}$$

This expression is valid in any gauge and reduces to Eq. (II.45) of Luttinger and Kohn[8] with their particular choice of gauge.

The Hamiltonian (2.21) has terms which are diagonal in the band indices and terms which are off-diagonal. The procedure of Luttinger and Kohn consists of the elimination of the off-diagonal terms to higher and higher orders of $(\mathbf{k}|P^\alpha|\mathbf{k}')$ by successive unitary transformations.

Let us write

$$H = H_0+H_1+H_2, \quad (2.22)$$

where

$$\begin{aligned}(m\mathbf{k}|H_0|n\mathbf{k}') &= \delta_{mn}\epsilon_m\delta(\mathbf{k}-\mathbf{k}'),\\ (m\mathbf{k}|H_1|n\mathbf{k}') &= p^\alpha{}_{mn}(\mathbf{k}|P^\alpha|\mathbf{k}'), \quad (2.23)\\ (m\mathbf{k}|H_2|n\mathbf{k}') &= \tfrac{1}{2}\delta_{mn}\delta^{\alpha\beta}(\mathbf{k}|P^\alpha P^\beta|\mathbf{k}').\end{aligned}$$

The first transformation is equivalent to that of reference 8. We define

$$H^{(2)} \equiv \exp[-S^{(1)}]H\exp[S^{(1)}], \quad (2.24)$$

and choose $S^{(1)}$ so as to remove the off-diagonal part of H, namely H_1, to first order.[14] Clearly $S^{(1)}$ is determined by the equation

$$[H_0,S^{(1)}]+H_1 = 0, \quad (2.25)$$

which, by (2.23) gives

$$\begin{aligned}(m\mathbf{k}|S^{(1)}|n\mathbf{k}') &= -\frac{p^\alpha{}_{mn}}{\omega_{mn}}(\mathbf{k}|P^\alpha|\mathbf{k}') \quad \text{for} \quad \omega_{mn}\neq 0\\ &= 0 \quad \text{for} \quad \omega_{mn}=0, \quad (2.26)\end{aligned}$$

where $\omega_{mn}\equiv\epsilon_m-\epsilon_n$. The transformed Hamiltonian is now given by

$$\begin{aligned}H^{(2)} &= H_0+\tfrac{1}{2}[[H_0,S^{(1)}],S^{(1)}]\\ &\quad +[H_1,S^{(1)}]+H_2+\cdots, \quad (2.27)\end{aligned}$$

where the omitted terms are of the third and higher orders in P^α. $H^{(2)}$ contains terms diagonal in the band index (intraband) of orders 0, 2, 4, etc., and off-diagonal (interband) terms of orders 2, 3, 4, etc.

The next step is to remove the interband matrix elements of order 2 by a further unitary transformation generated by $S^{(2)}$, given by

$$\begin{aligned}&(m\mathbf{k}|S^{(2)}|n\mathbf{k}')\\ &= -\frac{1}{2\omega_{mn}}\sum_i\left(\frac{1}{\omega_{mi}}-\frac{1}{\omega_{in}}\right)p^\alpha{}_{mi}p^\beta{}_{in}(\mathbf{k}|P^\alpha P^\beta|\mathbf{k}')\\ &\qquad \text{for} \quad \omega_{mn}\neq 0\\ &= 0 \qquad \text{for} \quad \omega_{mn}=0. \quad (2.28)\end{aligned}$$

The diagonal matrix elements of the new Hamiltonian, $H^{(4)}$, are the same as those of $H^{(2)}$ to orders 0 and 2 but different in higher orders. $H^{(4)}$ contains interband elements of orders 3, 4, etc.

This procedure may be continued so that after the nth transformation the intraband part of $H^{(2n)}$, up to order $2n$ inclusive, is not changed by further transformations, and its interband parts are of orders $n+1$ and higher. In this way one obtains a series expansion of

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[14] The superscript (1) on $S^{(1)}$ indicates that it is of first order in P^α; the superscript (2) in $H^{(2)}$ indicates that its diagonal terms coincide with those of the completely diagonalized Hamiltonian up to second order in P^α inclusive.

$\tilde{H}_m$ in even powers of P^α:

$$(\mathbf{k}|\tilde{H}_m|\mathbf{k}')=\epsilon_m\delta(\mathbf{k}-\mathbf{k}')+\sum_{l=2}^{\infty}E_m{}^{\alpha_1\alpha_2\cdots\alpha_l}(\mathbf{k}|P^{\alpha_1}P^{\alpha_2}\cdots P^{\alpha_l}|\mathbf{k}'). \tag{2.29}$$

In the absence of a magnetic field,

$$(\mathbf{k}|P^\alpha|\mathbf{k}')=k_\alpha\delta(\mathbf{k}-\mathbf{k}'), \tag{2.30}$$

so that, by (2.29),

$$(\mathbf{k}|\tilde{H}_m|\mathbf{k}')=\left[\epsilon_m+\sum_{l=2}^{\infty}E_m{}^{\alpha_1\alpha_2\cdots\alpha_l}k_{\alpha_1}k_{\alpha_2}\cdots k_{\alpha_l}\right]\delta(\mathbf{k}-\mathbf{k}'). \tag{2.31}$$

The factor in parentheses must be just the expansion of the energy of the mth band, $E_m(\mathbf{k})$, in powers of $\mathbf{k}$. It should, however, be noted that a knowledge of the power-series expansion of $E_m(\mathbf{k})$ does *not* uniquely determine the coefficients $E_m{}^{\alpha_1\alpha_2\cdots\alpha_l}$ but only certain linear combinations of these. Thus, for example, the coefficient in $E_m(\mathbf{k})$ of $k_1{}^2k_2{}^2$ gives only the combination

$$E_m{}^{1122}+E_m{}^{2211}+E_m{}^{1212}+E_m{}^{2121}+E_m{}^{1221}+E_m{}^{2112}.$$

In the presence of a magnetic field, the Hamiltonian (2.29) can then *in a certain sense* be regarded as

$$(\mathbf{k}|\tilde{H}_m|\mathbf{k}')=(\mathbf{k}|E_m(\mathbf{P})|\mathbf{k}'), \tag{2.32}$$

where $E_m(\mathbf{P})$ corresponds to some particular set of expansion coefficients $E_m{}^{\alpha_1\alpha_2\cdots\alpha_l}$ of some $E_m(\mathbf{k})$. Which set it is cannot be ascertained from a knowledge of $E_m(\mathbf{k})$ alone, and different sets will in general lead to different Hamiltonians because of the noncommutativity of the P^α. The only way we know of determining the correct set is by the successive unitary transformations discussed above or by some other equivalent perturbation procedure. It might be remarked that the correct set is not the completely symmetrical one in which all terms such as $E_m{}^{1122}$, $E_m{}^{1212}$, etc., are equal.

We have used the procedure described in this section to diagonalize the Hamiltonian up to fourth order in P^α, inclusive, with the following results:

$$E_m{}^{\alpha\beta}=\tfrac{1}{2}\delta_{\alpha\beta}+\sum_i\frac{p^\alpha{}_{mi}p^\beta{}_{im}}{\omega_{mi}}, \tag{2.33}$$

$$\begin{aligned}E_m{}^{\alpha\beta\gamma\delta}=&\sum_{j\neq m}\sum_{i,k}\frac{p^\alpha{}_{mi}p^\beta{}_{ij}p^\gamma{}_{jk}p^\delta{}_{km}}{\omega_{mi}\omega_{mj}\omega_{mk}}\\&-\tfrac{1}{2}\sum_i\frac{p^\alpha{}_{mi}p^\beta{}_{im}}{(\omega_{mi})^2}\cdot\sum_k\frac{p^\gamma{}_{mk}p^\delta{}_{km}}{\omega_{mk}}\\&-\tfrac{1}{2}\sum_i\frac{p^\alpha{}_{mi}p^\beta{}_{im}}{\omega_{mi}}\sum_k\frac{p^\gamma{}_{mk}p^\delta{}_{km}}{(\omega_{mk})^2}\\&-\tfrac{1}{4}\sum_i\frac{1}{(\omega_{mi})^2}\cdot(p^\alpha{}_{mi}p^\beta{}_{im}\delta^{\gamma\delta}\\&\qquad-2p^\alpha{}_{mi}p^\delta{}_{im}\delta^{\beta\gamma}+p^\gamma{}_{mi}p^\delta{}_{im}\delta^{\alpha\beta}).\end{aligned} \tag{2.34}$$

The coefficients $E_m{}^{\alpha_1,\alpha_2\cdots\alpha_l}$ can also be expressed in terms of the functions u_m, $u_m{}^\alpha$, $u_m{}^{\alpha\beta}$, $\cdots$ which occur in the expansion of the periodic part of the Bloch-wave $\psi_{m\mathbf{k}}$ in powers of $\mathbf{k}$ [see Eq. (1.9)]. This expansion can be generated by the unitary transformation e^S:

$$\begin{aligned}\psi_{m\mathbf{k}}=e^S\chi_{m\mathbf{k}}&=(\exp S^{(1)}\exp S^{(2)}\cdots)\chi_{m\mathbf{k}}\\&=(1+S^{(1)}+\tfrac{1}{2}(S^{(1)})^2+S^{(2)}+\cdots)\chi_{m\mathbf{k}}.\end{aligned} \tag{2.35}$$

Using the expressions (2.26) and (2.28) for $S^{(1)}$ and $S^{(2)}$ in the absence of a magnetic field, one obtains an expansion of the form (1.9), with

$$\begin{aligned}&u_m=u_{m0},\\&u_m{}^\alpha=\sum_i u_{j0}\frac{p^\alpha{}_{jm}}{\omega_{mj}},\\&u_m{}^{\alpha\beta}=\sum_{n\neq m}\sum_i u_{n0}\frac{p^\alpha{}_{ni}p^\beta{}_{im}}{\omega_{im}\omega_{nm}}-\tfrac{1}{2}u_{m0}\sum_i\frac{p^\alpha{}_{mi}p^\beta{}_{im}}{(\omega_{im})^2}.\end{aligned} \tag{2.36}$$

By means of (2.36), Eqs. (2.33) and (2.34) can be rewritten as follows:

$$E_m{}^{\alpha\beta}=\tfrac{1}{2}\delta_{\alpha\beta}+\left(u_m{}^\alpha,\frac{1}{i}\frac{\partial}{\partial x^\beta}u_m\right), \tag{2.33$'$}$$

$$\begin{aligned}E_m{}^{\alpha\beta\gamma\delta}=&\left(u_m{}^{\beta\alpha},\frac{1}{i}\frac{\partial}{\partial x^\gamma}u_m{}^\delta\right)\\&-\tfrac{1}{2}\left(u_m,\frac{1}{i}\frac{\partial}{\partial x^\alpha}u_m{}^\beta\right)(u_m{}^\gamma,u_m{}^\delta)\\&-\tfrac{1}{4}[(u_m{}^\alpha,u_m{}^\beta)\delta^{\gamma\delta}-2(u_m{}^\alpha,u_m{}^\delta)\delta^{\beta\gamma}\\&\qquad+(u_m{}^\delta,u_m{}^\gamma)\delta^{\alpha\beta}].\end{aligned} \tag{2.34$'$}$$

One advantage of this reformulation is the following. In the spherical approximation,[15] the functions u_m, $u_m{}^\alpha$, $u_m{}^{\alpha\beta}$, $\cdots$ are obtained as solutions of differential equations so that by using (2.33′) and (2.34′) one circumvents the infinite sums over other bands.†

3. DIAMAGNETIC SUSCEPTIBILITY

To evaluate the diamagnetic susceptibility it is convenient to write the Hamiltonian as a sum of two terms, a completely symmetrized Hamiltonian and a remainder. (To simplify our notation we shall for the rest of this section suppress the common band index m

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[15] That is the familiar Wigner-Seitz approximation in which the polyhedral cell is approximated by a sphere.

† *Note added in proof.*—The $u_m{}^{\alpha\beta}$ needed in (2.34′) is defined in (2.36). In general it consists of a part symmetric in α and β, as well as a small antisymmetric part involving high-order spherical harmonics ($l\geqslant 4$). A knowledge of the Bloch wave (1.10) evidently yields only the symmetric part. However, in the spherical approximation, which is used in Sec. 4, $u_m{}^{\alpha\beta}$ is entirely symmetrical ($l=0, 2$) and hence can be completely determined from the wave function (1.10). We are indebted to Dr. C. Herring for drawing out attention to this matter.

and take our zero of energy at the bottom of the mth band.)

$$(\mathbf{k}|\tilde{H}|\mathbf{k}')=\sum_{l=2}^{\infty}\mathcal{E}^{\alpha_1\alpha_2\cdots\alpha_l}(\mathbf{k}|P^{\alpha_1}P^{\alpha_2}\cdots P^{\alpha_l}|\mathbf{k}')+(\mathbf{k}|R|\mathbf{k}'). \quad (3.1)$$

Here $\mathcal{E}^{\alpha_1\alpha_2\cdots\alpha_l}$ is the average of all $E^{\alpha_1\alpha_2\cdots\alpha_l}$ with a given set of superscripts; for example

$$\mathcal{E}^{1122}=\mathcal{E}^{1212}=\cdots=\tfrac{1}{6}(E^{1122}+E^{2211}+E^{1212}+E^{2121}+E^{1221}+E^{2112}), \quad (3.2)$$

$$\mathcal{E}^{1111}=E^{1111}.$$

The $\mathcal{E}$'s are completely determined by the expansion of the energy $E(\mathbf{k})$ in powers of k_α. [See the discussion following Eq. (2.31).]

Starting from Eqs. (2.31) and (2.34), and using the commutation relations (2.6) for the P^α, we find that to fourth order in P^α the remainder is given by

$$(\mathbf{k}|R|\mathbf{k}')=(1/c^2)[E^{1221}-E^{1122}]\delta(\mathbf{k}-\mathbf{k}')\mathcal{H}^2. \quad (3.3)$$

To this order, then, the remainder term produces a uniform shift of all energy levels proportional to the square of the field. Since it is of the form of a constant times $\delta(\mathbf{k}-\mathbf{k}')$ it has no effect on the wave functions. Its contribution to the susceptibility is simply the coefficient of $-\frac{1}{2}\mathcal{H}^2\delta(\mathbf{k}-\mathbf{k}')$ in (3.3) multiplied by n, the number of electrons per unit volume,

$$\chi_R=-n\frac{2}{c^2}(E^{1221}-E^{1122})$$

$$=-\frac{2}{3\pi^2c^2}(E^{1221}-E^{1122})k_0^3. \quad (3.4)$$

The symmetrized part of the Hamiltonian (3.1) is identical to the Fourier expansion

$$\tilde{H}_{\text{symm}}=\textstyle\sum_s A_s e^{i\mathbf{P}\cdot\mathbf{r}_s}, \quad (3.5)$$

where the $\mathbf{r}_s$ are the translation vectors of the lattice and the A_s are coefficients, independent of $\mathcal{H}$, chosen to give the correct dependence of E on $\mathbf{k}$ in the absence of the field. This identity can be verified by expanding (3.5) in powers of P^α. The susceptibility due to (3.5) has been evaluated by Peierls[2] and gives the result χ_3, Eq. (1.3). In the spirit of the present paper, we substitute in (1.3) a power series expansion of the energy

$$E(\mathbf{k})=\mathcal{E}^{11}k^2+[(3/5)\mathcal{E}^{1111}+(6/5)\mathcal{E}^{1122}]k^4+[-(2/5)\mathcal{E}^{1111}+(6/5)\mathcal{E}^{1122}]\times[5(k_1^2k_2^2+k_2^2k_3^2+k_3^2k_1^2)-k^4]+\cdots, \quad (3.6)$$

where the omitted terms are of order k^6 and higher. This gives

$$\chi_3=-\frac{\mathcal{E}^{11}}{6\pi^2c^2}k_0-\frac{7}{9\pi^2c^2}\left(\frac{3}{5}\mathcal{E}^{1111}+\frac{6}{5}\mathcal{E}^{1122}\right)k_0^3. \quad (3.7)$$

The total diamagnetic susceptibility per unit volume is obtained by combining (3.4) and (3.7). Recalling that $\mathcal{E}^{11}=1/(2m^*)$ and writing

$$\mathcal{E}^{(4)}\equiv(3/5)\mathcal{E}^{1111}+(6/5)\mathcal{E}^{1122}, \quad (3.8)$$

for the coefficient of the first fourth-order term in $E(\mathbf{k})$, Eq. (3.6), we obtain

$$\chi=-\frac{k_0}{12\pi^2c^2}\left[\frac{1}{m^*}+\left(\frac{28}{3}\mathcal{E}^{(4)}+8(E^{1221}-E^{1122})\right)k_0^2+\cdots\right] \quad (3.9)$$

in atomic units. In arbitrary units, this becomes

$$\chi=-\frac{e^2k_0}{12\pi^2mc^2}\left[\frac{m}{m^*}+\left(\frac{28}{3}\mathcal{E}^{(4)}+8(E^{1221}-E^{1122})\right)a_0^2k_0^2+\cdots\right] \quad (3.10)$$

where a_0 is the Bohr radius and $\mathcal{E}^{(4)}$, E^{1221}, E^{1122} are evaluated in atomic units. This expression is of the required form (1.8). Further canonical transformations yield terms of higher order in k_0.

We shall now show that our expression (3.9) for χ reduces correctly to the atomic diamagnetism in the limit where the lattice parameter, a, becomes infinite (tight binding). In this limit the band $E(\mathbf{k})$ becomes infinitely narrow and the Peierls term χ_3 tends to zero exponentially with a. Therefore only χ_R survives; and since k_0 approaches zero as a^{-1}, while all the $E^{\alpha_1\alpha_2\cdots\alpha_l}$ approach finite (or vanishing) limits, we need to keep only the term of lowest order in k_0. Thus, by (3.4) we have

$$\chi\rightarrow-n(2/c^2)(E^{1221}-E^{1122}). \quad (3.11)$$

We must now evaluate $E^{1221}-E^{1122}$ in the tight-binding limit. By (2.34),

$$E^{1221}-E^{1122}=\sum_{j\neq m}\sum_{i,k}\frac{p^1{}_{mi}p^2{}_{ij}p^2{}_{jk}p^1{}_{km}}{\omega_{mi}\omega_{mj}\omega_{mk}}-\sum_{j\neq m}\sum_{i,k}\frac{p^1{}_{mi}p^1{}_{ij}p^2{}_{jk}p^2{}_{km}}{\omega_{mi}\omega_{mj}\omega_{mk}}+\sum_i\frac{p^1{}_{mi}p^1{}_{im}}{(\omega_{im})^2}\left(1+\sum_k\frac{p^1{}_{mk}p^1{}_{km}}{\omega_{mk}}\right). \quad (3.12)$$

In the present limit the u_{n0} become superpositions of atomic functions, so that the $p^\alpha{}_{ij}$ are simply momentum matrix elements between atomic functions. We can therefore use the following relationships, which are a consequence of the commutation relations of x^α and $x^\alpha x^\beta$ with the total Hamiltonian:

$$x_{mn}{}^\alpha\omega_{mn}=-ip^\alpha{}_{mn},$$
$$(x^\alpha x^\beta)_{mn}\omega_{mn}=-i(x^\alpha p^\beta+p^\alpha x^\beta)_{mn}. \quad (3.13)$$

With their help it is shown in the Appendix that in the tight-binding limit

$$E^{1221}-E^{1122}\rightarrow\tfrac{1}{12}(r^2)_{mm},\tag{3.14}$$

where m is taken to be an s-state. Substitution into (3.11) gives

$$\chi\rightarrow -n(1/6c^2)(r^2)_{mm},\tag{3.15}$$

which is just the well-known expression for atomic diamagnetism (in atomic units).

4. APPLICATION TO METALLIC Li AND Na

The theory which we have developed in the preceding sections was applied to the metals Li and Na for two reasons. They are the two simplest metals, whose theory has been studied in considerable detail in the past; and they are the only metals for which there exists at present an (indirect) experimental value of the diamagnetic susceptibility (see reference 5). The object of the theoretical calculation is the evaluation of the effective mass m^* and the coefficients $E^{\alpha\beta\gamma\delta}$ with which χ can be evaluated by Eq. (3.10).[16] As the algebraic and numerical work is rather extensive, we have, in the case of Li, calculated these parameters by both methods described in the preceding section; that is, by summation over intermediate states [Eqs. (2.33) and (2.34)] and by using the Bardeen expansion functions u_m, $u_m{}^{\alpha}$, $u_m{}^{\alpha\beta}$ [Eqs. (2.33′) and (2.34′)]. Both methods should give the same results and in fact agreed quite closely.

Summation over Intermediate States

We shall first describe the summation over intermediate states. The band of interest, m, is an s-band. That is, u_{m0} belongs to the identity representation A_1 of the cubic group. Since the momentum operator $(1/i)\partial/\partial x^{\alpha}$ transforms like T_1, the intermediate states u_{i0} and u_{k0} occurring in the matrix-elements in (2.33) and (2.34) also transform like T_1, while the intermediate states u_{j0} transform like A_1, E, or T_1. Thus a typical state of the first group has the form

$$u_{i0}=(x/r)f_i(\mathbf{r})\quad(\text{“}p\text{-like”}),\tag{4.1}$$

where $f(\mathbf{r})$ has cubic symmetry and vanishes on the cell boundary, while the states of the second group are of three types:

$$\begin{aligned}u_{j0}&=g_j(\mathbf{r}), &&(\text{“}s\text{-like”})\\ \text{or}\quad &\frac{x^2-y^2}{r^2}h_j{}^{(1)}(\mathbf{r}), &&(\text{“}d\text{-like”})\\ \text{or}\quad &\frac{xy}{r^2}h_j{}^{(2)}(\mathbf{r}), &&(\text{“}d\text{-like”})\end{aligned}\tag{4.2}$$

where g, $h^{(1)}$, $h^{(2)}$ have cubic symmetry and vanishing derivatives on the cell-boundary.

It can hardly cause a substantial error in either the matrix-elements or the energy denominators if we impose the boundary conditions not on the actual cell boundary but rather on the surface of the Wigner-Seitz sphere. In that case $h^{(1)}$ and $h^{(2)}$ become identical and the functions f, g, and h are spherically symmetrical. The f_i, for example, are determined by the following equations:

$$\begin{gathered}\left[\frac{1}{2}\left(-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}+\frac{2}{r^2}\right)+V(r)-E_i\right]f_i=0,\\ f_i(r_s)=0,\end{gathered}\tag{4.3}$$

where r_s is the radius of the Wigner-Seitz sphere and $V(r)$ is the ionic potential.

A series of s, p, and d functions was calculated by numerical methods and the matrix-elements calculated. These were then substituted in (2.33) and (2.34).

Lithium

The summations (2.33) and (2.34) were carried out using four s-like, three p-like, and three d-like functions. (These numbers do not include the 3- and 5-fold degeneracies of the p- and d-functions.) The potential was the semiempirical potential constructed by Seitz to fit the optical spectrum of atomic Li,[17] and $r_s=3.21$.

$$\begin{aligned}\mathcal{E}^{11}&=1/2m^*=0.363,\\ \mathcal{E}^{(4)}&=-0.02,\\ E^{1221}-E^{1122}&=-0.16.\end{aligned}\tag{4.4}$$

The surprisingly small value of $\mathcal{E}^{(4)}$, which has been noted before (see reference 7) is the result of an apparently fortuitous near-cancellation of contributions coming from intermediate s- and d-like states. The band is therefore very nearly parabolic, although its effective mass is substantially different from 1 ($m^*=1.34$). In the term $E^{1221}-E^{1122}$, however, there is no major cancellation so that the fourth order (in P^{α}) contribution to χ is quite substantial.

Sodium

Four s-like, four p-like, and two d-like functions were used. The potential was the Prokofjew potential,[18] and $r_s=4.069$.

$$\begin{aligned}\mathcal{E}^{11}&=0.480,\\ \mathcal{E}^{(4)}&=-0.01,\\ E^{1221}-E^{1122}&=0.02.\end{aligned}\tag{4.5}$$

These numbers show that the diamagnetic behavior of the conduction electrons of Na is very similar to that of free electrons, for which the corresponding numbers

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[16] $\mathcal{E}^{(4)}$ is obtained from the $E^{\alpha\beta\gamma\delta}$ by (3.8) and (3.2).

[17] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[18] W. Prokofjew, Z. Physik **58**, 255 (1929).

are 0.5, 0, and 0, respectively. The susceptibility, calculated by Eq. (3.10), is given in Eq. (1.11).

Use of Bardeen Expansion Functions

To evaluate $E^{\alpha\beta}$ and $E^{\alpha\beta\gamma\delta}$ from (2.33′) and (2.34′), we have to construct the functions occurring in the Bardeen expansion (1.9) of the Bloch waves. These functions are discussed in reference 7. The results were as follows:

Lithium

$$\begin{aligned} \mathcal{E}^{11} &= 1/(2m^*) = 0.363, \\ \mathcal{E}^{(4)} &= -0.01, \\ E^{1221}-E^{1122} &= -0.15. \end{aligned} \tag{4.4′}$$

The rather close agreement with (4.4) constitutes a check on the calculations. We believe that the results (4.4′) are slightly more accurate and have used them to calculate χ according to Eq. (3.10). The result was given earlier in Eq. (1.11).

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APPENDIX: TIGHT-BINDING LIMIT

With the help of (3.13) the expression (3.12), required for the calculation of χ, can be reduced to an expectation value of r^2 in the atomic state m which we take to be an s state. Let us begin with the first term, which we shall call T_1:

$$\begin{aligned} T_1 &\equiv \sum_{j\neq m}\sum_{i,k} \frac{p^1{}_{mi}p^2{}_{ij}p^2{}_{jk}p^1{}_{km}}{\omega_{mi}\omega_{mj}\omega_{mk}} \\ &= \sum_{j\neq m}\sum_{i,k} \frac{x^1{}_{mi}p^2{}_{ij}p^2{}_{jk}x^1{}_{km}}{\omega_{mj}} \\ &= \sum_{j\neq m} \frac{(x^{(1)}p^{(2)})_{mj}(p^{(2)}x^{(1)})_{jm}}{\omega_{mj}}. \end{aligned} \tag{A.1}$$

Since "m" is an s state

$$(x^{(1)}p^{(2)}-x^{(2)}p^{(1)})_{mj}=0, \tag{A.2}$$

so that, by (3.13),

$$\begin{aligned} \frac{(x^{(1)}p^{(2)})_{mj}}{\omega_{mj}} &= \frac{1}{2}\frac{(x^{(1)}p^{(2)}+x^{(2)}p^{(1)})_{mj}}{\omega_{mj}} \\ &= \tfrac{1}{2}i(x^{(1)}x^{(2)})_{mj}. \end{aligned} \tag{A.3}$$

Substituting into (A.1) gives

$$T_1=\tfrac{1}{2}i(x^{(1)}x^{(2)}p^{(2)}x^{(1)})_{mm}. \tag{A.4}$$

The next term in (3.12) can be transformed as follows:

$$\begin{aligned} T_2 &\equiv -\sum_{j\neq m}\sum_{i,k} \frac{p^1{}_{mi}p^1{}_{ij}p^2{}_{jk}p^2{}_{km}}{\omega_{mi}\omega_{mj}\omega_{mk}} \\ &= -\sum_{j\neq m} \frac{(x^{(1)}p^{(1)})_{mj}(p^{(2)}x^{(2)})_{jm}}{\omega_{mj}} \\ &= -\tfrac{1}{2}i\sum_{j\neq m} ((x^{(1)})^2)_{mj}(p^{(2)}x^{(2)})_{jm} \\ &= -\tfrac{1}{2}i((x^{(1)})^2p^{(2)}x^{(2)})_{mm} \\ &\qquad +\tfrac{1}{2}i((x^{(1)})^2)_{mm}(p^{(2)}x^{(2)})_{mm}. \end{aligned} \tag{A.5}$$

Combining with (A.4), we find

$$\begin{aligned} T_1+T_2 &= +\tfrac{1}{2}i(x^{(1)})^2{}_{mm}(p^{(2)}x^{(2)})_{mm} \\ &\qquad +\tfrac{1}{2}i[(x^{(1)})^2(x^{(2)}p^{(2)}-p^{(2)}x^{(2)})]_{mm} \\ &= -\tfrac{1}{12}(r^2)_{mm}, \end{aligned} \tag{A.6}$$

where we have used the fact that

$$(p^{(2)}x^{(2)})_{mm}=-\tfrac{1}{2}i, \tag{A.7}$$

which follows from (3.13) and the commutation relation of x and p.

Finally, we take the last term in (3.12) which we call T_3. By (3.13),

$$\begin{aligned} \sum_i \frac{p^1{}_{mi}p^1{}_{im}}{(\omega_{mi})^2} &= \sum_i (ix^{(1)}{}_{mi})(-ix^{(1)}{}_{im}) \\ &= [(x^{(1)})^2]_{mm}=\tfrac{1}{3}(r^2)_{mm}. \end{aligned} \tag{A.8}$$

The other sum in this term gives

$$\begin{aligned} \sum_k \frac{p^1{}_{mk}p^1{}_{km}}{\omega_{mk}} &= \sum_k p^1{}_{mk}(-ix^1{}_{km}) = -i(p^{(1)}x^{(1)})_{mm} \\ &= -\tfrac{1}{2}, \end{aligned} \tag{A.9}$$

by Eq. (A.7). (This is a well-known atomic sum rule.) By combining (A.8) and (A.9), we obtain

$$T_3=\tfrac{1}{6}(r^2)_{mm}. \tag{A.10}$$

Thus we find, in the tight-binding limit,

$$E^{1221}-E^{1122}=T_1+T_2+T_3=\tfrac{1}{12}(r^2)_{mm}. \tag{A.11}$$

When this is substituted into (3.11), one obtains the well-known atomic diamagnetic susceptibility (3.15).