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Theory of the Magnetic Susceptibility of Crystals

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Zusammenfassung. Es wird ein Ausdruck für die feldunabhängige magnetische Suszeptibilität von Elektronen in einem periodischen Potential nach einer neuen Methode abgeleitet. Vergleichsweise werden die in der Literatur existierenden Methoden kurz besprochen. Das Resultat lässt sich leicht für die beiden Näherungen fast freier und stark gebundener Elektronen spezialisieren, in welchen eine einfache Interpretation möglich ist.

1. Introduction

At the Varenna summer school 1956 a new method for treating the problem of the field independant magnetic susceptibility of electrons in a periodic potential was briefly reported[1]. The present paper contains a detailed evaluation of this method. Simultaneously the same problem has been treated again by HEBBORN and SONDHEIMER[2]*). Since we feel that our method gives some insight into the problem not shared by the earlier treatments of PEIERLS[3], ADAMS[4], WILSON[5] and also of ref. 2 we decided to publish this work.

As was mentioned in ref. 1 the motivation for this investigation was to understand the rather anomalous temperature dependence of the susceptibility experimentally found for many semiconductors. We will not, however, enter into this question here since a separate paper is devoted to the problem of the temperature dependence of the susceptibility[6].

In order to compare our method with those already existing in the literature[3–5] we shall discuss some of the main points of the earlier treatments.

An important feature in PEIERLS fundamental paper[3] is the use of an effective Hamiltonian E_{op} related to the true one-electron Hamiltonian by an equivalence theorem. Peierls worked out this theorem in tight

*) This autor is indepted to Dr. SONDHEIMER for sending him a preprint.

binding approximation only. But its validity is not restricted to this approximation. The effective Hamiltonian is of the form

$$E_{op} = E(\boldsymbol{k}_{op}) \tag{1.1}$$

where $E(\boldsymbol{k})$ is the energy of an eigenstate with wave vector $\boldsymbol{k}$ of the true Hamiltonian including the perturbation by the magnetic field H (assumed in the z-direction) and $\boldsymbol{k}_{op}$ is a rather complicated operator obeying the commutation relation

$$\hbar^2 [k_{op,\,x}, k_{op,\,y}] = -\frac{\hbar}{i} \frac{e}{c} H\,. \tag{1.2}$$

For vanishing magnetic field $E(\boldsymbol{k})$ is a single energy band of the crystal, while for $H \neq 0$ it includes contributions from the other bands. Apart from these contributions in $E(\boldsymbol{k})$ however, Peierls' E_{op} is essentially a one band model and the equivalence theorem therefore only approximate. Some implications of interband effects in a magnetic field have been discussed by HARPER[7]).

Another equivalence theorem well known in solid state theory is the effective mass theory which was originally developed for electrostatic perturbations[8]) and extended to the magnetostatic case by LUTTINGER[9]). Luttinger's version for a constant magnetic field is again of the form (1·1,2) but now $E(\boldsymbol{k})$ represents an unperturbed energy band $E_n(\boldsymbol{k})$ and $\boldsymbol{k}_{op}$ the kinetic momentum $\boldsymbol{p} - e/c\, \boldsymbol{A}$. If one replaces in Peierls' paper his effective Hamiltonian by that of Luttinger a closer examination shows that one obtains the familiar Landau-Peierls term χ_3 while the other two terms χ_1 and χ_2 are missing.

In a more recent paper KJELDAAS and KOHN[10]) have applied a generalization of LUTTINGER and KOHN's version of the effective mass theory[8]) to the problem of the magnetic susceptibility. In this version the effective mass approximation consists in neglecting terms of higher than second order in a power series expansion in $\boldsymbol{k} - \boldsymbol{k}_0$ where $\boldsymbol{k}_0$ is the wave vector at the minimum of the energy band in consideration. In the case of a magnetic perturbation this leads to Luttingers effective Hamiltonian $E_n(\boldsymbol{p} - e/c\, A)$ in second order, as shown in ref. 8. The generalization of KJELDAAS and KOHN consists in taking into account fourth order terms in the expansion in $\boldsymbol{k} - \boldsymbol{k}_0$ (they put $\boldsymbol{k}_0 = 0$) which leads to an effective Hamiltonian of the form

$$E_{op} = E_n\left(\boldsymbol{p} - \frac{e}{c} \boldsymbol{A}\right) + R\left(\boldsymbol{p} - \frac{e}{c} \boldsymbol{A}\right) \tag{1.3}$$

taken in fourth order in $\boldsymbol{k}$. As stated above, the first term of (1.3) gives rise (to any order in $\boldsymbol{k}$) to Peierls' χ_3. The contribution of the remainder R is shown by the authors to coincide, in tight binding approximation, with the atomic diamagnetism χ_1 of Peierls. This shows that Kjeldaas and Kohn's effective Hamiltonian (1.3), although useful in certain applications, gives no improvement over Peierls' original theory.

Such an improvement in the spirit of an equivalence theorem has been achieved by ADAMS[4]), making use of his multiband formulation of the effective mass theory[11]) which is rigorous in principle. As result Adams gets, in addition to the Landau-Peierls term, two new terms of exceedingly complicated structure, containing interband effects not present in Peierls' χ_1 and χ_2. The basic quantities in Adams' multiband formulation of the effective mass theory turn out, after closer inspection[12]), to be the matrix elements between Bloch states of the operator $\boldsymbol{p}$ and of a certain part of $\boldsymbol{x}$ having the periodicity of the lattice (see appendix A). This suggests quite generally that a straightforward use of the Bloch representation would eliminate the extra complications inherent in any equivalence theorem. Our method is guided by this observation.

Another method which follows this mode of approach by Bloch functions instead of using an equivalent Hamiltonian is the density matrix formalism of WILSON[5]). This formalism is very powerful in the case of free electrons because it does not make use of perturbation theory in the field H (and therefore accounts for the de Haas-van Alphen effect). For electrons in a periodic potential however, perturbation theory is indispensable and Wilson's method is less direct. A complete formula for the field independent susceptibility although obtainable in principle with this method has not been given by Wilson because of its considerable complexity. This has been achieved only recently by HEBBORN and SONDHEIMER[2]). Much of the complications in Wilson's method are due to the explicit use of the Bloch wave functions which also make the result rather difficult to interpret.

In our method a general formula expressing the susceptibility in terms of matrix elements in Bloch representation is derived in section 2 (see also ref. 1). In order that these matrix elements have good mathematical properties the choice of an infinite normalisation volume is of importance. Some care is necessary however with the definition of the diagonal sum (trace) when the wave vector $\boldsymbol{k}$ varies continuously. At this point an approximation is introduced which consist in treating certain almost diagonal operators as if they were rigorously diagonal. (This point was not clearly realized in ref. 1). Furthermore the well known difficulty of having a constant magnetic field in infinite space needs some discussion. This difficulty is shown however, to be of harmless nature so far as the susceptibility is concerned. In fact, no singularities occur other than δ-functions in $\boldsymbol{k}$ and derivatives thereof. In appendix A it is shown that these singular functions are easily 'regularized' by going over to a magnetized region of finite extension. No use of this regularisation is made however since, starting from the general susceptibility formula, it is an easy task to eliminate the singularities by partial integrations over $\boldsymbol{k}$. This is done in section 3. Finally with the help of relations between matrix elements derived in appendix A some further simplifications are made in section 4 and the result is written as a sum of six terms. The most important contributions are the Landau-Peierls diamagnetism χ_P (Peierls' χ_3), the atomic diamagnetism χ_a (Peierls' χ_1), a Langevin-Debye type paramagnetism χ_L and a van Vleck type term χ_V. The identification of the last three terms is easily obtained by passing to the limit of tightly bound electrons where all other contributions disappear. In the limit of nearly free electrons, on the other hand, the susceptibility is given by χ_P alone.

Apart from χ_P which is determined entirely by the energy band structure, all other terms additionally depend upon the matrix elements of $\boldsymbol{p}$ and of the periodic part of $\boldsymbol{x}$ mentioned above. Clearly, the relations existing between these matrix elements are not sufficient to eliminate all matrix elements in favour of the energy band structure. These matrix elements are identical with the basic quantities in Adams' result and also with the integrals over Bloch functions used by Wilson and by Hebborn and Sondheimer (we use the same notation as these authors so far as possible).

As usual this paper is based upon the one-electron picture and electron spin is neglected (which means that spin-orbit coupling is neglected, see ref. 1). No symmetries other than those already existing in this framework – namely the lattice periodicity and the time reversal symmetry – are assumed. The implications of some symmetries (e. g. existence of an inversion centre in the crystal) are studied in appendix B.

2. Outline of the Formalism

In a small magnetic field H the free energy Φ and thermodynamic potential Ω of crystal electrons are, per unit volume,

$$\Phi - N\zeta = \Omega = \Omega_0 - M_0 H - \frac{1}{2}\chi \cdot H^2 + \cdots \tag{2.1}$$

where χ is the field independent magnetic susceptibility and M_0 the permanent magnetic moment, which is zero except for ferromagnetic substances. N is the number of electrons per unit volume and ζ the Fermi energy. The thermodynamic potential $V.\ \Omega$ for a crystal of volume V may be written in the usual way as a trace

$$\Omega = \frac{2}{V} \cdot \text{Trace } F(\mathfrak{H}) \tag{2.2}$$

where $\mathfrak{H}$ is the Hamiltonian of an electron moving in a periodic potential $V(\boldsymbol{x})$ and in a magnetic field $\boldsymbol{H} = \text{rot } \boldsymbol{A}$ ($\text{div } \boldsymbol{A} = 0$)

$$\mathfrak{H} = \frac{1}{2\,m}(\boldsymbol{p} - e\,\boldsymbol{A})^2 + V = \mathfrak{H}_0 + \mathfrak{H}'; \; \mathfrak{H}_0 = \frac{p^2}{2\,m} + V \tag{2.3}$$

$$\mathfrak{H}' = -\frac{e}{m}\,\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2}{2\,m}\,\boldsymbol{A}^2. \tag{2.3$'$}$$

(We put $\hbar = c = 1$ in this paper.) The factor 2 in eq. (2.2) accounts for the degeneracy of the electron spin which is neglected in $\mathfrak{H}$. F is the function

$$F(E) \equiv -kT\log\left[1 + \exp\left(-\frac{E-\zeta}{kT}\right)\right] \tag{2.4}$$

characteristic of Fermi-Dirac statistics.

Eq. (2.2) is evidently independent of the choice of the representation, which implies immediately the gauge invariance of Ω. Indeed, with the gauge transformation

$$\tilde{\psi}(\boldsymbol{x}) = e^{ie\Lambda(\boldsymbol{x})}\,\psi(\boldsymbol{x})\;;\; \tilde{\boldsymbol{A}}(\boldsymbol{x}) = \boldsymbol{A}(\boldsymbol{x}) + \frac{\partial\Lambda}{\partial\boldsymbol{x}}$$

ψ being any wave function, it follows that

$$\tilde{\psi}^*(\boldsymbol{x})\cdot\tilde{\mathfrak{H}}\,\tilde{\psi}(\boldsymbol{x}) = \psi^*(\boldsymbol{x})\cdot\mathfrak{H}\,\psi(\boldsymbol{x})$$

where $\tilde{\mathfrak{H}}$ is the Hamiltonian (2.3) with $\boldsymbol{A}$ replaced by $\tilde{\boldsymbol{A}}$.

Since $F(z)$ is a regular function in the neighbourhood of the real axis and vanishes exponentially for large positive z we may apply Cauchy's formula as indicated in ref. 1,

$$\Omega = \frac{1}{2\pi i}\oint dz\,F(z)\cdot\frac{2}{V}\,\text{Trace}\,(z - \mathfrak{H})^{-1} \tag{2.5}$$

where the contour encloses all eigenvalues of $\mathfrak{H}$. $(z - \mathfrak{H})^{-1}$ is then written as a formal expansion in the perturbation $\mathfrak{H}'$.

$$\left.\begin{aligned}
(z - \mathfrak{H})^{-1} &= (z - \mathfrak{H}_0)^{-1} + (z - \mathfrak{H}_0)^{-1}\,\mathfrak{H}'\,(z - \mathfrak{H}_0)^{-1} + \\
&\quad + (z - \mathfrak{H}_0)^{-1}\,\mathfrak{H}'(z - \mathfrak{H}_0)^{-1}\,\mathfrak{H}'(z - \mathfrak{H}_0)^{-1} + \cdots = \\
&= (z - \mathfrak{H}_0)^{-1} - \frac{e}{m}(z - \mathfrak{H}_0)^{-1}\,\boldsymbol{A}\cdot\boldsymbol{p}\,(z - \mathfrak{H}_0)^{-1} + \\
&\quad + \frac{e^2}{2\,m}(z - \mathfrak{H}_0)^{-1}\,\boldsymbol{A}^2\,(z - \mathfrak{H}_0)^{-1} + \\
&\quad + \frac{m^2}{e^2}(z - \mathfrak{H}_0)^{-1}\,\boldsymbol{A}\cdot\boldsymbol{p}\,(z - \mathfrak{H}_0)^{-1}\,\boldsymbol{A}\cdot\boldsymbol{p}\,(z - \mathfrak{H}_0)^{-1} + \cdots
\end{aligned}\right\} \tag{2.6}$$

It is now natural to choose the Bloch representation defined by $\mathfrak{H}_0$,

$$\mathfrak{H}_0\,|\,n\,\boldsymbol{k}) = E_n(\boldsymbol{k})\cdot|\,n\,\boldsymbol{k}) \tag{2.7}$$

where the energy bands labelled by n may still be degenerate. For the moment we assume a finite normalization volume V and periodic boundary conditions so that

$$(n\,\boldsymbol{k} \mid n'\,\boldsymbol{k}') = \delta_{n\,n'}\,\delta_{\boldsymbol{k}\boldsymbol{k}'}$$

and the $\boldsymbol{k}$ form a discrete set of points extending over the reduced Brillouin zone.

The reason for making the assumption of a finite V is to give a precise meaning to the trace in eq. (2.2), which now assumes the simple form

$$\Omega = \frac{2}{V} \sum_n \sum_{\boldsymbol{k}} (n\,\boldsymbol{k} \mid F(\mathfrak{H}) \mid n\,\boldsymbol{k})$$

There is however a difficulty with this assumption in the case of a homogenous field, $\boldsymbol{H} = (0,0,H)$, say, or in an appropriate gauge,

$$\boldsymbol{A} = \frac{H}{2} \cdot (-\,x_2, x_1, 0) \tag{2.8}$$

Indeed, the coordinates x_j do not exist, strictly speaking, as operators in a finite system with periodic boundary conditions. We may therefore assume for a moment that $\boldsymbol{H}$ is constant only in the interior of a region U situated within V, but that $\boldsymbol{A}$ goes to zero at the boundary of U. To eliminate the boundary effects thereby introduced we shall afterwards go to the double limit $V \to \infty$ and $U \to \infty$, which from the formal point of view is the appropriate situation.

The first limit, $V \to \infty$, is obtained by the usual replacements

$$\sqrt{V/(2\,\pi)^3} \cdot \mid n\,\boldsymbol{k}) \to \mid n\,\boldsymbol{k})$$
$$(V/(2\,\pi)^3) \cdot \delta_{\boldsymbol{k}\boldsymbol{k}'} \to \delta\,(\boldsymbol{k} - \boldsymbol{k}')$$
$$((2\,\pi)^3/V) \cdot \sum_{\boldsymbol{k}} \to \int d^3 k\,.$$

In the last line integration is to extend over the reduced Brillouin zone. The new normalization is

$$(n\,\boldsymbol{k} \mid n'\,\boldsymbol{k}') = \delta_{n\,n'}\,\delta\,(\boldsymbol{k} - \boldsymbol{k}') \tag{2.9}$$

It then follows that for any function $f(\boldsymbol{k})$

$$\sum_{\boldsymbol{k}} \mid n\,\boldsymbol{k})\, f(\boldsymbol{k})\,(n\,\boldsymbol{k} \mid \to \int d^3 k \mid n\,\boldsymbol{k})\, f(\boldsymbol{k})\,(n\,\boldsymbol{k} \mid \tag{2.10}$$

and for any diagonal operator O

$$\left.\begin{aligned} &\frac{2}{V}\,\mathrm{Trace}\ O = \frac{2}{V} \sum_n \sum_{\boldsymbol{k}} (n\,\boldsymbol{k} \mid O \mid n\,\boldsymbol{k}) = \\ &= \frac{2}{V} \sum_n \sum_{\boldsymbol{k}} \sum_{\boldsymbol{k}',\,|\boldsymbol{k}'-\boldsymbol{k}|<\varepsilon} (n\,\boldsymbol{k} \mid O \mid n\,\boldsymbol{k}') \to \frac{1}{4\pi^3} \sum_n \int d^3 k \int_{|k'-k|<\varepsilon} d^3 k' (n\,\boldsymbol{k} \mid O \mid n\,\boldsymbol{k}') \end{aligned}\right\} \tag{2.11}$$

where ε is arbitrarily small. The approximation introduced in this paper is to apply (2.11) for operators which ar not rigorously diagonal in $\boldsymbol{k}$ but contain first or second derivatives of $\delta(\boldsymbol{k} - \boldsymbol{k}')$*).

We have now to make a few remarks concerning the second limit, $U \to \infty$, since, as is seen from (2.8) and from (3.2) below, the perturbation $\mathfrak{H}'$ is unbounded in $\boldsymbol{x}$ and the matrix elements of x_j contain a singularity $\partial/\partial k'_j \; \delta(\boldsymbol{k} - \boldsymbol{k}')$. Although such singular expressions are easily treated by partial integration and lead to a finite result for each term in the trace of the expansion (2.6) a justification of this procedure may be desirable. It is easily obtained with the device of a finite magnetized region U introduced above. In fact, it is shown in appendix A that the δ-function contained in the matrix elements of x_j can be considered as the following limit (see eq. (A. 16))

$$\delta_{n n'} \; \delta(\boldsymbol{k} - \boldsymbol{k}') = \lim_{U \to \infty} \Delta_{n n'}(\boldsymbol{k}, \boldsymbol{k}') \tag{2.12}$$

where $\Delta_{nn'}$ is a regular function in $\boldsymbol{k}$ and $\boldsymbol{k}'$ with a steep maximum at $\boldsymbol{k} = \boldsymbol{k}'$.

We would like to add a remark about the question of convergence of the perturbation theory, although in the present paper we are interested only in the first few coefficients of the perturbation expansion (2.6). It is clear from the properties of $\mathfrak{H}'$ in the limit $U \to \infty$ that perturbation theory ceases to be convergent in this limit. In fact, as is well known, the switching on of a homogenous magnetic field changes the character of the electronic states entirely in that closed orbits and discontinuities in the spectrum occur (see PEIERLS[13]), p. 151). On the other hand, for a finite extension U of the field there always exists a finite upper limit H_m of the field strength such that no closed orbits and no discontinuities in the spectrum exist and perturbation theory is therefore applicable. This means that in the case of a finite U a finite convergence radius proportional to H_m exists which goes to zero in the limit $U \to \infty$. The existence of each term in the trace of (2.6) in this limit indicates however that Ω may be obtained as an asymptotic series in H.

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*) The rigorous procedure would be to keep the region U finite troughout the calculation, replacing $\boldsymbol{A}$ by $\varphi_U \cdot \boldsymbol{A}$ (φ_U is defined in appendix A). $\mathfrak{H}'$ then contains only bounded operators and

$$\Omega - \Omega_0 = (2/U) \sum_n \int d^3k \; (n\boldsymbol{k} \,|\, F(\mathfrak{H}) - F(\mathfrak{H}_0) \,|\, n\boldsymbol{k})$$

is a rigorous definition. A closer examination of this formula shows that the corrections to the result of this paper are terms containing first and second derivatives of the quantity $\Delta_{nn'}$ defined in (A.16), which remain finite as U goes to infinity.

We are now in a position to work in the double limit indicated above. Using (2·5, 7, 8) and the rules (2·10, 11), eq. (2.5) can be written as

$$\left.\begin{aligned} \Omega = \Omega_0 + \frac{1}{2\pi i} \oint dz\, F(z) \frac{1}{4\pi^3} \Big\{ - \frac{eH}{2m} \cdot \mu(z) + \\ + \left(\frac{eH}{2m}\right)^2 (\Delta(z) + \pi(z)) \Big\} \end{aligned}\right\} \tag{2.13}$$

with

$$\Omega_0 = \frac{1}{4\pi^3} \sum_n \int d^3k\, F\big(E_n(\boldsymbol{k})\big)$$

and

$$\left.\begin{aligned} \mu(z) &= \sum_n \int d^3k \int_\varepsilon d^3k' (z - E_n(\boldsymbol{k}))^{-1} (n\boldsymbol{k} \,|\, l_3 \,|\, n\boldsymbol{k}') \cdot (z - E_n(\boldsymbol{k}'))^{-1} \\ \Delta(z) &= \sum_n \int d^3k \int_\varepsilon d^3k' (z - E_n(\boldsymbol{k}))^{-1} \cdot \\ &\quad \cdot \left(n\boldsymbol{k} \left| \frac{m}{2} (x_1^2 + x_2^2) \right| n\boldsymbol{k}'\right) (z - E_n(\boldsymbol{k}'))^{-1} \\ \pi(z) &= \sum_n \sum_{n''} \int d^3k \int_\varepsilon d^3k' \int d^3k'' (z - E_n(\boldsymbol{k}))^{-1} \cdot \\ &(n\boldsymbol{k} \,|\, l_3 \,|\, n''\boldsymbol{k}'') (z - E_{n''}(\boldsymbol{k}''))^{-1} (n''\boldsymbol{k}'' \,|\, l_3 \,|\, n\boldsymbol{k}') \cdot (z - E_n(\boldsymbol{k}'))^{-1}. \end{aligned}\right\} \tag{2.14}$$

Here l_3 is the 3-compoment of angular momentum,

$$\boldsymbol{l} = \boldsymbol{x} \times \boldsymbol{p}$$

and an abbreviated notation for the integration over the small sphere $|\boldsymbol{k} - \boldsymbol{k}'| < \varepsilon$ has been introduced. Comparing with (2.1) we have

$$\left.\begin{aligned} M_0 &= + \frac{1}{2\pi i} \oint dz\, F(z) \frac{1}{4\pi^3} \cdot \frac{e}{2m} \mu(z) \\ \chi &= - \frac{1}{2\pi i} \oint dz\, F(z) \frac{1}{2\pi^3} \left(\frac{e}{2m}\right)^2 (\Delta(z) + \pi(z)) \end{aligned}\right\} \tag{2.15}$$

Apart from notation and the neglect of spin the formula for χ is the same as in ref. 1. The proof that M_0 vanishes will be given in the next section.

3. Evaluation of M_0 and χ

With the help of the expressions for the matrix elements of p_j, x_j ($j = 1, 2, 3$) and l_3 which follow from appendix A,

$$(n\boldsymbol{k} \,|\, p_j \,|\, n'\boldsymbol{k}') = P_{j,nn'}(\boldsymbol{k}) \cdot \delta(\boldsymbol{k} - \boldsymbol{k}') \tag{3.1}$$

$$(n\boldsymbol{k} \,|\, x_j \,|\, n'\boldsymbol{k}') = \delta_{nn'} \frac{1}{i} \frac{\partial}{\partial k_j'} \delta(\boldsymbol{k} - \boldsymbol{k}') + X_{j,nn'}(\boldsymbol{k}) \cdot \delta(\boldsymbol{k} - \boldsymbol{k}') \tag{3.2}$$

$$\left.\begin{aligned}(n\,\boldsymbol{k}\mid l_3\mid n'\,\boldsymbol{k}') &= P_{2,nn'}(\boldsymbol{k}')\cdot\frac{1}{i}\frac{\partial}{\partial k_1'}\,\delta(\boldsymbol{k}-\boldsymbol{k}')-\\ &-P_{1,nn'}(\boldsymbol{k}')\cdot\frac{1}{i}\frac{\partial}{\partial k_2'}\,\delta(\boldsymbol{k}-\boldsymbol{k}')+L_{3,nn'}(\boldsymbol{k})\cdot\delta(\boldsymbol{k}-\boldsymbol{k}')\end{aligned}\right\}\tag{3.3}$$

$P_{j,nn'}$, $X_{j,nn'}$, $L_{3,nn'}$ being regular function of $\boldsymbol{k}$, the evaluation of (2.14) is straightforward. It is useful to introduce a matrix notation in the band index, calling $E(\boldsymbol{k})$ the diagonal matrix with elements $E_n(\boldsymbol{k})$ and using the symbol «tr» to designate trace formation with respect to n. Then with the help of (3.3) the quantity $\mu(z)$ defined in (2.14) assumes the form

$$\left.\begin{aligned}\mu(z) &= \int_\varepsilon d^3k\int d^3k'\,tr\Big[(z-E(\boldsymbol{k}))^{-1}\Big\{P_2(\boldsymbol{k}')\frac{1}{i}\Big(\frac{\partial}{\partial k'_1}\,\delta(\boldsymbol{k}-\boldsymbol{k}')\Big)-\\ &-P_1(\boldsymbol{k}')\frac{1}{i}\Big(\frac{\partial}{\partial k_2'}\,\delta(\boldsymbol{k}-\boldsymbol{k}')\Big)+L_3(\boldsymbol{k})\cdot\delta(\boldsymbol{k}-\boldsymbol{k}')\Big\}(z-E(\boldsymbol{k}'))^{-1}\Big].\end{aligned}\right\}\tag{3.4}$$

In the expression for $\Delta(z)$ we first write, with the help of (A. 13)

$$(n\,\boldsymbol{k}\mid x_1^2+x_2^2\mid n'\,\boldsymbol{k}')=\sum_{n''}\int d^3k''\sum_{j=1,2}(n\boldsymbol{k}\mid x_j\mid n''\boldsymbol{k}'')\,(n''\boldsymbol{k}''\mid x_j\mid n'\boldsymbol{k}')\,.$$

Making use of (3.2) we obtain

$$\left.\begin{aligned}\Delta(z) &= \int_\varepsilon d^3k\int d^3k'\int d^3k''\sum_{j=1,2}\frac{m}{2}\,tr\Big[(z-E(\boldsymbol{k}))^{-1}\cdot\\ &\cdot\Big\{\frac{1}{i}\Big(\frac{\partial}{\partial k_j''}\,\delta(\boldsymbol{k}-\boldsymbol{k}'')\Big)+X_j(\boldsymbol{k})\cdot\delta(\boldsymbol{k}-\boldsymbol{k}'')\Big\}\cdot\\ &\cdot\Big\{\frac{1}{i}\Big(\frac{\partial}{\partial k_j'}\,\delta(\boldsymbol{k}''-\boldsymbol{k}')\Big)+X_j(\boldsymbol{k}'')\cdot\delta(\boldsymbol{k}''-\boldsymbol{k}')\Big\}(z-E(\boldsymbol{k}'))^{-1}\Big]\end{aligned}\right\}\tag{3.5}$$

Similarly we get for $\pi(z)$

$$\left.\begin{aligned}\pi(z) &= \int_\varepsilon d^3k\int d^3k'\int d^3k''\,tr\Big[(z-E(\boldsymbol{k}))^{-1}\cdot\\ &\cdot\Big\{P_2(\boldsymbol{k}'')\frac{1}{i}\Big(\frac{\partial}{\partial k_1''}\,\delta(\boldsymbol{k}-\boldsymbol{k}'')\Big)-P_1(\boldsymbol{k}'')\frac{1}{i}\Big(\frac{\partial}{\partial k_2''}\,\delta(\boldsymbol{k}-\boldsymbol{k}'')\Big)+\\ &+L_3(\boldsymbol{k})\cdot\delta(\boldsymbol{k}-\boldsymbol{k}'')\Big\}(z-E(\boldsymbol{k}''))^{-1}\Big\{P_2(\boldsymbol{k}')\frac{1}{i}\Big(\frac{\partial}{\partial k_1'}\,\delta(\boldsymbol{k}''-\boldsymbol{k}')\Big)-\\ &-P_1(\boldsymbol{k}')\frac{1}{i}\Big(\frac{\partial}{\partial k_2'}\,\delta(\boldsymbol{k}''-\boldsymbol{k}')\Big)+L_3(\boldsymbol{k}'')\,\delta(\boldsymbol{k}''-\boldsymbol{k}')\Big\}(z-E(\boldsymbol{k}'))^{-1}\Big].\end{aligned}\right\}\tag{3.6}$$

The further procedure entails partial integrations to eliminate the derivatives of the δ-functions. It is important that all surface integrals thereby introduced vanish. Indeed, these surface integrals always contain a $\delta(\boldsymbol{k}-\boldsymbol{k}')$ where the wave vector $\boldsymbol{k}$ is an inner point of the domain of integration (which is either the reduced zone or the sphere ε) whereas $\boldsymbol{k}'$ moves about the boundary surface. (This argument may be put on firmer ground with the help of the 'regularized' δ-function, $\Delta_{nn'}(\boldsymbol{k},\boldsymbol{k}')$ of eq. (2.12), using standard procedures. We shall not enter into these details however.)

We begin with the evaluation of $\mu(z)$. Partial integration with respect to $\boldsymbol{k}'$ yields

$$\mu(z) = \int d^3 k \int_{\varepsilon} d^3 k' \, tr \Big[(z - E(\boldsymbol{k}))^{-1} \Big\{ -\frac{1}{i} \frac{\partial}{\partial k_1'} \big(P_2(\boldsymbol{k}') \, (z - E(\boldsymbol{k}'))^{-1} \big) + \\ + \frac{1}{i} \frac{\partial}{\partial k_2'} \big(P_1(\boldsymbol{k}') \, (z - E(\boldsymbol{k}'))^{-1} \big) + L_3(\boldsymbol{k}) \Big\} \Big] \, \delta(\boldsymbol{k} - \boldsymbol{k}') \, .$$

Introducing the abbreviation

$$\frac{\partial}{\partial k_j} f(\boldsymbol{k}) \equiv f_{|j}$$

and using the matrix formula

$$\frac{\partial}{\partial k_j} (z - E(\boldsymbol{k}))^{-1} = (z - E)^{-1} E_{|j} (z - E)^{-1} \tag{3.7}$$

we get, after a cyclic permutation of factors in the trace,

$$\left. \begin{aligned} \mu(z) = \int d^3 k \, tr \Big[(z - E)^{-2} \Big\{ - \frac{1}{i} P_{2/1} + \frac{1}{i} P_{1/2} - \\ - \frac{1}{i} P_2 \cdot (z - E)^{-1} E_{|1} + \frac{1}{i} P_1 \cdot (z - E)^{-1} E_{|2} + L_3 \Big\} \Big] \, . \end{aligned} \right\} \tag{3.8}$$

Now since $E(\boldsymbol{k})$ is a diagonal matrix, $E|_j$ commutes with $(z-E)^{-1}$. Therefore the third and fourth term of the curled bracket of (3.8) are proportional to $(-1/i)$ $(P_2 E|_1 - P_1 E|_2)$ which according to (A. 8) is the hermitian conjugate of the matrix

$$A \equiv \frac{1}{i} (E_{|1} \cdot P_2 - E_{|2} \cdot P_1) \, . \tag{3.9}$$

In the trace of eq. (3.8) only the diagonal elements of this matrix occur, which, however, vanish according to eq. (A.19'),

$$A_{nn} = 0 \, , \quad \text{all } n \tag{3.9'}$$

For the first two terms of the curled bracket in (3.8) we use the formula

$$-\frac{1}{i} (P_{2/1} - P_{1/2}) = L_3^+ - L_3 \tag{3.10}$$

which follows from eq. (A. 20) and the definitions (A. 15, 15'). ($^+$denotes hermitian conjugation.) Then eq. (3.8) reduces to

$$\mu(z) = \int d^3 k \, tr \, [(z - E)^{-2} \, L_3^+] = \sum_n \int d^3 k \left(\frac{\partial}{\partial E_n} (z - E_n)^{-1} \right) \cdot L_{3,nn}^+ \, .$$

Going back to the expression (2.15) for M_0 and making use of the property

$$L_{3,nn}^+ = L_{3,nn} \tag{3.10'}$$

which follows from (3.10) with the help of (A. 19') we can write

$$M_0 = \frac{e}{2m} \cdot \sum_n \mu_n \tag{3.11}$$

with
$$\mu_n = \frac{1}{4\pi^3} \int d^3 k\, F'(E_n(\boldsymbol{k})) \cdot L_{3,nn}(\boldsymbol{k}) \tag{3.11'}$$

μ_n is the permanent magnetic moment contributed by the n^{th} band in units of the Bohr magneton $e/2\,m$.

To show that all contributions μ_n vanish, the time reversal symmetry (T-invariance) of $\mathfrak{H}_0$ is essential. Indeed, with the help of (B.6) and (B. 9), eq. (3.11') can also be written as

$$\mu_n = -\frac{1}{4\pi^3} \int d^3 k\, F'(E_n(-\boldsymbol{k})) \cdot L^*_{3,nn}(-\boldsymbol{k})\,.$$

Since the reduced Brillouin zone is invariant under the reflexion $\boldsymbol{k} \to -\boldsymbol{k}$ and because of (3.10') it follows that

$$\mu_n = -\mu_n = 0; \quad \text{all } n\,. \tag{3.12}$$

It can be proven that exactly the same reasoning holds if the electron spin is included (i.e. spin-orbit coupling not neglected)*). Thus in a one-electron picture T-invariance (which for an electron with spin is expressed by $\mathfrak{H}_0 = \omega\, \mathfrak{H}_0^*\, \omega^{-1}$ with $\omega = -i\sigma_2$) quite generally implies the vanishing of a permanent magnetic moment so that the latter is always due to the simultaneous presence of more than one electron (exchange effects).

We turn now to the evaluation of $\Delta(z)$ and $\pi(z)$. Since in these expressions derivation of a δ-function occurs in two of the factors we want to make use of the identity

$$\frac{\partial}{\partial k_j''}\, \delta(\boldsymbol{k} - \boldsymbol{k}'') = -\frac{\partial}{\partial k_j}\, \delta(\boldsymbol{k} - \boldsymbol{k}'') \tag{3.13}$$

in order not to introduce new derivatives of δ-functions by partial integration. (Note that according to (2.12) this rule may be considered as the limit $U \to \infty$ of the equality of (A. 17) and (A. 17'). All formal manipulations are therefore entirely justified.) Then a first partial integration of (3.5) yields

$$\begin{aligned}\Delta(z) = \int_\varepsilon d^3 k \int d^3 k' \int d^3 k''\, \frac{m}{2} \sum_{j=1,2} tr \Big[(z - E(\boldsymbol{k}))^{-1} \cdot \\ \cdot \Big\{ -\frac{1}{i} \Big(\frac{\partial}{\partial k_j}\, \delta(\boldsymbol{k} - \boldsymbol{k}'') \Big) + X_j(\boldsymbol{k})\, \delta(\boldsymbol{k} - \boldsymbol{k}'') \Big\} \cdot \\ \cdot \Big\{ -\frac{1}{i} \Big(\frac{\partial}{\partial k_j'} (z - E(\boldsymbol{k}'))^{-1} \Big) + X_j(\boldsymbol{k}'')\, (z - E(\boldsymbol{k}'))^{-1} \Big\} \Big]\, \delta(\boldsymbol{k}'' - \boldsymbol{k}')\,.\end{aligned}$$

A further partial integration with respect to k_j leads to

$$\begin{aligned}\Delta(z) = \frac{m}{2} \int d^3 k \sum_{j=1,2} tr \Big[\Big\{ + \frac{1}{i} \frac{\partial}{\partial k_j} (z - E(\boldsymbol{k}))^{-1} + \\ + (z - E(\boldsymbol{k}))^{-1} X_j(\boldsymbol{k}) \Big\} \Big\{ -\frac{1}{i} \cdot \frac{\partial}{\partial k_j} (z - E(\boldsymbol{k}))^{-1} + \\ + X_j(\boldsymbol{k})\, (z - E(\boldsymbol{k}))^{-1} \Big\} \Big]\end{aligned}$$

*) This is also true if (2.11) is replaced by the rigorous definition.

or, with use of (3.7) and after a cyclic permutation of factors in the trace, to

$$\Delta(z) = \frac{m}{2} \int d^3 k \sum_{j=1,2} tr \left[(z - E)^{-2} \left\{ \frac{1}{i} E_{|j} (z - E)^{-1} + X_j \right\} \cdot \right.$$
$$\left. \cdot \left\{ - \frac{1}{i} (z - E)^{-1} E_{|j} + X_j \right\} \right] .$$

Recalling that $E(\boldsymbol{k})$ is a diagonal matrix and that therefore the diagonal elements of $E|_j X_j - X_j E|_j$ vanish we get

$$\Delta(z) = \frac{m}{2} \int d^3 k \sum_{j=1,2} tr \left[(z - E)^{-4} (E_{|j})^2 + (z - E)^{-2} (X_j)^2 \right]$$

and with use of the identity

$$(z - E_n)^{-s-1} = \frac{1}{s!} \cdot \frac{\partial^s}{\partial E_n{}^s} (z - E_n)^{-1} \tag{3.14}$$

$$\Delta(z) = \frac{m}{2} \int d^3 k \sum_{j=1,2} \sum_n \left[\frac{1}{3!} \left(\frac{\partial^3}{\partial E_n{}^3} (z - E_n)^{-1} \right) \cdot (E_{n/j})^2 + \right.$$
$$\left. + \left(\frac{\partial}{\partial E_n} (z - E_n)^{-1} \right) \cdot (X_j^2)_{nn} \right] . \tag{3.15}$$

Similarly a first partial integration of $\pi(z)$, eq. (3.6), yields

$$\pi(z) = \int d^3 k \int_{\varepsilon} d^3 k' \int d^3 k'' \, tr \Big[\big(z - E(\boldsymbol{k}) \big)^{-1} \cdot$$
$$\cdot \left\{ - P_2(\boldsymbol{k}'') \frac{1}{i} \left(\frac{\partial}{\partial k_1} \delta (\boldsymbol{k} - \boldsymbol{k}'') \right) + P_1(\boldsymbol{k}'') \frac{1}{i} \left(\frac{\partial}{\partial k_2} \delta (\boldsymbol{k} - \boldsymbol{k}'') \right) + \right.$$
$$+ L_3(\boldsymbol{k}) \, d \, (\boldsymbol{k} - \boldsymbol{k}'') \Big\} \big(z - E(\boldsymbol{k}'') \big)^{-1} \left\{ - \frac{1}{i} \frac{\partial}{\partial k'_1} \left(P_2(\boldsymbol{k}') \big(z - E(\boldsymbol{k}') \big)^{-1} \right) + \right.$$
$$+ \frac{1}{i} \frac{\partial}{\partial k'_2} \left(P_1(\boldsymbol{k}') \big(z - E(\boldsymbol{k}') \big)^{-1} \right) + L_3 (\boldsymbol{k}'') \big(z - E (\boldsymbol{k}') \big)^{-1} \Big\} \Big] \, \delta(\boldsymbol{k}'' - \boldsymbol{k}')$$

where we have made the replacement (3.13) in the first curled bracket. After a partial integration with respect to k_1 and k_2 we get

$$\pi(z) = \int d^3 k \, tr \left[\left\{ + \frac{1}{i} \left(\frac{\partial}{\partial k_1} \big(z - E(\boldsymbol{k}) \big)^{-1} \right) \cdot P_2(\boldsymbol{k}) - \right. \right.$$
$$\left. - \frac{1}{i} \left(\frac{\partial}{\partial k_2} \big(z - E(\boldsymbol{k}) \big)^{-1} \right) \cdot P_1(\boldsymbol{k}) + \big(z - E(\boldsymbol{k}) \big)^{-1} \cdot L_3(\boldsymbol{k}) \right\} \cdot$$
$$\cdot \big(z - E(\boldsymbol{k}) \big)^{-1} \left\{ - \frac{1}{i} \cdot \frac{\partial}{\partial k_1} \left(P_2(\boldsymbol{k}) \big(z - E(\boldsymbol{k}) \big)^{-1} \right) + \right.$$
$$\left. \left. + \frac{1}{i} \cdot \frac{\partial}{\partial k_2} \left(P_1(\boldsymbol{k}) \big(z - E(\boldsymbol{k}) \big)^{-1} \right) + L_3(\boldsymbol{k}) \big(z - E(\boldsymbol{k}) \big)^{-1} \right\} \right] .$$

Making use of (3.7) this expression becomes, after a cyclic permutation of factors in the trace,

$$\pi(z) = \int d^3 k\, tr \Big[(z-E)^{-2} \Big\{ \frac{1}{i} E_{|1} (z-E)^{-1} P_2 - - \frac{1}{i} E_{|2} (z-E)^{-1} P_1 + L_3 \Big\} (z-E)^{-1} \Big\{ -\frac{1}{i} P_{2|1} + \frac{1}{i} P_{1/2} - - \frac{1}{i} P_2 (z-E)^{-1} E_{|1} + \frac{1}{i} P_1 (z-E)^{-1} E_{|2} + L_3 \Big\} \Big] .$$

Commuting $E_{|j}$ with $(z-E)^{-1}$ we can make use of the definition (3.9) and the relation (3.10) to write

$$\pi(z) = \int d^3 k\, tr \left[(z-E)^{-2} \{ (z-E)^{-1} A + L_3 \} \cdot \cdot (z-E)^{-1} \{ A^+ (z-E)^{-1} + L_3^+ \} \right]$$

or, making another cyclic permutation in the trace,

$$\pi(z) = \int d^3 k\, tr \big[(z-E)^{-4} A (z-E)^{-1} A^+ + + (z-E)^{-3} \{ A (z-E)^{-1} L_3^+ + L_3 (z-E)^{-1} A^+ \} + + (z-E)^{-2} L_3 (z-E)^{-1} L_3^+ \big] .$$

The trace, which consists in a double sum over n and n', will now be divided into the parts with $n = n'$ and $n \neq n'$. Using (3.9') and (3.14) we get

$$\left. \begin{aligned} \pi(z) = {} & \int d^3 k \sum_n \frac{1}{2!} \left(\frac{\partial^2}{\delta E_n^2} (z - E_n)^{-1} \right) \cdot | L_{3,nn} |^2 + \\ & + \int d^3 k \sum_n \sum_{n}{}' \Big[\frac{1}{3!} \left(\frac{\partial^3}{\partial E_n^3} (z - E_n)^{-1} \right) \cdot | A_{nn'} |^2 + \\ & + \frac{1}{2!} \left(\frac{\partial^2}{\partial E_n^2} (z - E_n)^{-1} \right) \cdot \left\{ A_{nn'} L^*_{3,nn'} + L_{3,nn'} A^*_{nn'} \right\} + \\ & + \left(\frac{\partial}{\partial E_n} (z - E_n)^{-1} \right) \cdot | L_{3,nn'} |^2 \Big] \cdot (z - E_{n'})^{-1} \end{aligned} \right\} \quad (3.16)$$

where $\sum_{n'}{}'$ means summation over $n' \neq n$.

With these results (3.15, 16) the susceptibility formula (2.15) may be written in the form of eq. (7) of ref. 1,

$$\chi = - \left(\frac{e}{2\, m} \right)^2 \cdot \pi^{-3} \sum_n (D_n + P_n) \quad (3.17)$$

where D_n and P_n, as obtained from $\Delta(z)$ and $\pi(z)$ respectively, are given by

$$D_n = + \frac{m}{4} \int d^3k \sum_{j=1,2} \left[\frac{1}{3!} (E_{n|j})^2 \cdot F'''(E_n) + (X_j^2)_{nn} \cdot F'(E_n) \right] \quad (3.17')$$

$$\left.\begin{aligned} P_n = {} & \frac{1}{2} \int d^3 k \frac{1}{2!} \mid L_{3,nn} \mid^2 \cdot F''(E_n) + \\ & + \frac{1}{2} \int d^3 k \sum_{n'}{}' \left[\frac{1}{3!} \mid A_{nn'} \mid^2 \cdot \frac{\partial^3}{\delta E_n{}^3} G(E_n, E_{n'}) + \right. \\ & + \frac{1}{2!} (A_{nn'} L_{3,nn'}^* + L_{3,nn'} A_{nn'}^*) \frac{\partial^2}{\partial E_n{}^2} G(E_n, E_{n'}) + \\ & \left. + \mid L_{3,nn'} \mid^2 \frac{\partial}{\partial E_n} G(E_n, E_{n'}) \right] . \end{aligned}\right\} \quad (3.17'')$$

In the last expression use has been made of Cauchy's formula

$$\frac{1}{2\pi i} \oint dz \frac{F(z)}{(z-E)\,(z-E')} = \frac{F(E)-F(E')}{E-E'} \equiv G(E, E') \ . \quad (3.18)$$

4. Final Result and Discussion

The main task of the last section was to eliminate the singularities $\partial/\partial k_j' \, \delta\,(\boldsymbol{k} - \boldsymbol{k}')$. In eqs. (3.17', 17'') we arrived at well defined integrals extending over the reduced Brillouin zone. The expressions permit still some important simplifications. First we want to replace in P_n the derivatives of the function $G(E_n, E_{n'})$ defined in (3.18) by derivatives of the simpler function $F(E_n)$. This is done with the help of the reduction formula

$$(E-E') \frac{\partial^s}{\partial E^s} G(E, E') = F^{(s)}(E) - s \cdot \frac{\partial^{s-1}}{\partial E^{s-1}} G(E, E'); \ s \geqslant 1.$$

Introducing the Fermi distribution function

$$f(E) = F'(E) = (1 + e^{(E-\zeta)/kT})^{-1} \quad (4.1)$$

and using the abbreviation

$$B_{nn'} \equiv L_{3,nn'} - \frac{A_{nn'}}{E_n - E_{n'}} \ ; \ n \neq n' \quad (4.2)$$

eq. (3.17'') may be written as

$$P_n = P_n^{(1)} + P_n^{(2)} + P_n^{(3)} + P_n^{(4)} + P_n^{(5)} \quad (4.3)$$

with
$$\left.\begin{aligned}
P_n^{(1)} &= \frac{1}{12}\int d^3 k \sum_{n'}{}' \frac{|A_{nn'}|^2}{E_n - E_{n'}} f''(E_n)\\
P_n^{(2)} &= \frac{1}{4}\int d^3 k \; |L_{3,nn}|^2 \cdot f'(E_n)\\
P_n^{(3)} &= \frac{1}{4}\int d^3 k \sum_{n'}{}' \left[|L_{3,nn'}|^2 - |B_{nn'}|^2\right] \cdot f'(E_n)\\
P_n^{(4)} &= \frac{1}{2}\int d^3 k \sum_{n'}{}' \frac{|B_{nn'}|^2}{E_n - E_{n'}} \cdot f(E_n)\\
P_n^{(5)} &= -\frac{1}{2}\int d^3 k \sum_{n'}{}' \frac{|B_{nn'}|^2}{E_n - E_n} \cdot G(E_n, E_{n'})
\end{aligned}\right\} \qquad (4.3')$$

Similarly we write eq. (3.17′) as
$$D_n = D_n^{(1)} + D_n^{(2)} \qquad (4.4)$$

with
$$\left.\begin{aligned}
D_n^{(1)} &= \frac{m}{24}\int d^3 k \left[(E_{n|1})^2 + (E_{n|2})^2\right] \cdot f''(E_n)\\
D_n^{(2)} &= \frac{m}{4}\int d^3 k \left[(X_1^2)_{nn} + (X_2^2)_{nn}\right] \cdot f(E_n)
\end{aligned}\right\} \qquad (4.4')$$

An important simplification is possible for $P_n^{(1)}$. From the definition (3.7) it follows that
$$\sum_{n'}{}' \frac{|A_{nn'}|^2}{E_n - E_{n'}} = (E_{n|1})^2 \sum_{n'}{}' \frac{P_{2,nn'} P_{2,nn'}^*}{E_n - E_{n'}} + $$
$$+ (E_{n|2})^2 \sum_{n'}{}' \frac{P_{1,nn'} P_{1,nn'}^*}{E_n - E_{n'}} - E_{n|1} E_{n|2} \sum_{n'}{}' \frac{P_{2,nn'} P_{1,nn'}^* + P_{1,nn'} P_{2,nn'}^*}{E_n - E_{n'}}$$

which according to (A. 8) and the sum rule (A. 21) may be expressed entirely in terms of the energy band structure,
$$\left.\begin{aligned}
\frac{1}{m^2}\sum_{n'}{}' \frac{|A_{nn'}|^2}{E_n - E_{n'}} &= \frac{1}{2}\left(E_{n|11} - \frac{1}{m}\right)(E_{n|2})^2 + \\
&+ \frac{1}{2}\left(E_{n|22} - \frac{1}{m}\right)(E_{n|1})^2 - E_{n|12} E_{n|1} E_{n|2}
\end{aligned}\right\} \qquad (4.5)$$

Now, the sum of $P_n^{(1)}$ and $D_n^{(1)}$ reduces to
$$\left.\begin{aligned}
P_n^{(1)} + D_n^{(1)} &= \frac{m^2}{24}\int d^3 k \left[E_{n|11} (E_{n|2})^2 + \right.\\
&\left. + E_{n|22} (E_{n|1})^2 - 2 E_{n|12} E_{n|1} E_{n|2}\right] \cdot f''(E_n)
\end{aligned}\right\} \qquad (4.6)$$

Because of the relation
$$E_{n|j} \cdot f''(E_n) = \frac{\partial}{\partial k_j} f'(E_n)$$

we may perform a partial integration

$$\int d^3 k\, E_{n|jj'}\, E_{n|l}\, E_{n|l'}\, f''(E_n) = \oint d\sigma \cdot n_l\, E_{n|jj'}\, E_{n|l'}\, f'(E_n)$$
$$- \int d^3 k\, (E_{n|jj'}\, E_{n|l'})_{|l} \cdot f'(E_n)$$

where the surface integral extends over the boundary of the reduced zone and n is the outside normal. This boundary is a polyhedron, each face of which goes over into the opposite face by a translation through a vector $\boldsymbol{K}_\alpha$ of the reciprocal lattice. Because of the symmetry (B. 19) and since the normal $\boldsymbol{n}$ has opposite sign for opposite faces, the surface integral is zero. Therefore partial integration of (4.6) yields

$$D_n^{(1)} + P_n^{(1)} = -\frac{m^2}{12} \int d^3 k \left[E_{n|11}\, E_{n|22} - (E_{n|12})^2\right] \cdot f'(E_n) \tag{4.7}$$

This is just the contribution of the n^{th} band to the Landau-Peierls diamagnetism χ_P which according to (3.17) is

$$\left.\begin{aligned} \chi_P &= -\left(\frac{e}{2\,m}\right)^2 \pi^{-3} \sum_n \left(D_n^{(1)} + P_n^{(1)}\right) = \\ &= +\frac{e^2}{6} (2\,\pi)^{-3} \sum_n \int d^3 k \left[E_{n|11}\, E_{n|22} - (E_{n|12})^2\right] f'(E_n) \end{aligned}\right\} \tag{4.8}$$

The other terms in (4.5′, 6′) yield

$$\left.\begin{aligned} \chi_a &= -\left(\frac{e}{2\,m}\right)^2 \pi^{-3} \sum_n D_n^{(2)} = \\ &= -\frac{e^2}{2\,m} (2\,\pi)^{-3} \sum_n \int d^3 k \left[(X_1^2)_{nn} + (X_2^2)_{nn}\right] f(E_n) \end{aligned}\right\} \tag{4.9}$$

$$\left.\begin{aligned} \chi_L &= -\left(\frac{e}{2\,m}\right)^2 \pi^{-3} \sum_n P_n^{(2)} = \\ &= -\frac{e^2}{2\,m^2} (2\,\pi)^{-3} \sum_n \int d^3 k\, |\, L_{3,nn}\,|^2\, f'(E_n) \end{aligned}\right\} \tag{4.10}$$

$$\left.\begin{aligned} \chi' &= -\left(\frac{e}{2\,m}\right)^2 \pi^{-3} \sum_n P_n^{(3)} = \\ &= -\frac{e^2}{2\,m^2} (2\,\pi)^{-3} \sum_n \int d^3 k \sum_{n'}{}' \left[|\, L_{3,nn'}\,|^2 - |\, B_{nn'}\,|^2\right] f'(E_n) \end{aligned}\right\} \tag{4.11}$$

$$\left.\begin{aligned} \chi_V &= -\left(\frac{e}{2\,m}\right)^2 \pi^{-3} \sum_n P_n^{(4)} = \\ &= -\frac{e^2}{m^2} (2\,\pi)^{-3} \sum_n \int d^3 k \sum_{n'}{}' \frac{|\, B_{nn'}\,|^2}{E_n - E_{n'}}\, f(E_n) \end{aligned}\right\} \tag{4.12}$$

$$\left.\begin{aligned} \chi'' &= -\left(\frac{e}{2\,m}\right)^2 \pi^{-3} \sum_n P_n^{(5)} = \\ &= +\frac{e^2}{m^2} (2\,\pi)^{-3} \sum_n \int d^3 k \sum_{n'}{}' \frac{|\, B_{nn'}\,|^2}{E_n - E_{n'}}\, G(E_n, E_{n'}) \end{aligned}\right\} \tag{4.13}$$

The total susceptibility is, apart from the Pauli spin paramagnetism,

$$\chi = \chi_P + \chi_a + \chi_L + \chi_V + \chi' + \chi'' \tag{4.14}$$

χ_a is purely diamagnetic (note that according to (A. 11) the X_j are hermitian matrices) and χ_L is paramagnetic, while χ_V, χ' and χ'' have no unique sign. Moreover the electrons of all filled bands (core electrons) contributs to χ_a, χ_V and χ'' (factor $f(E_n)$ or $G(E_n, E_n'))$ while in χ_P, χ_L and χ' only the electrons (and holes) in the neighbourhood of the Fermi energy ζ (conduction electrons) are of importance (factor $f'(E_n)$).

In our calculation χ_P is the only term which depends on the energy band structure $E_n(\boldsymbol{k})$ alone and not on other matrix elements. Some authors[14]) also quote a term which contains $E_n|_{1122}$ only. It can be shown however that this term is gauge dependent and vanishes in our gauge (2.8). To be more precise, with the one-parameter gauge group introduced in ref. 1

$$\boldsymbol{A}' = -H \cdot \left(\lambda x_2, (\lambda - 1)\, x_1, o\right) = \boldsymbol{A} + \text{grad}\left[H\left(\frac{1}{2} - \lambda\right) x_1 x_2\right]$$

$\boldsymbol{A}$ being given by (2.8), this term is found to be

$$\chi_\lambda = -(2\lambda - 1)^2 \cdot \frac{e^2}{2} (2\pi)^{-3} \sum_n \int d^3 k\, E_{n|1122} \cdot f(E_n)$$

On the other hand it can be shown that χ_P is independent of the gauge parameter λ.

A term of a peculiar nature is χ'' since it contains a factor $G(E_n, E_{n'})$ which cannot be reduced to the Fermi function $f(E_n)$. Since by symmetrisation with respect to n and n'

$$\left.\begin{aligned} &\sum_n \sum_{n'}{}' \frac{|B_{nn'}|^2}{E_n - E_{n'}} G(E_n, E_{n'}) = \\ &= \frac{1}{2} \sum_n \sum_{n'}{}' \frac{|B_{nn'}|^2 - |B_{n'n}|^2}{E_n - E_{n'}} G(E_n, E_{n'}) \end{aligned}\right\} \tag{4.15}$$

χ'' is due to the anti-symmetric part of $|B_{nn'}|$. According to (3.9) and (A. 19″) the $B_{nn'}$ as defined in (4.2) may be considered as the non-diagonal elements of the matrix

$$B = L_3 - m\,(E_{|1} X_2 - E_{|2} X_1)$$

which can be shown to be non-hermitian in general so that $|B_{nn'}| \neq |B^+_{nn'}| = |B_{n'n}|$ is possible*).

In deriving the result (4.8 – 13) no explicit use has been made of symmetry properties of $\mathfrak{H}_0$ other than the lattice periodicity. It can be seen that T-invariance of $\mathfrak{H}_0$ does not induce any further simplification

*) The occurence of $G(E_n, E_{n'})$ in X'' is probably due to our approximation (2.11). This is suggested by the result of ref. 2 which is entirely expressible in terms of $f(E_n)$.

of the result. For instance it does not imply the vanishing of χ_L. This is only the case if in addition invariance of $\mathfrak{H}_0$ with respect to the inversion $\boldsymbol{x} \rightarrow - \boldsymbol{x}$ (P-invariance) is assumed. Indeed, as follows from appendix B, T- and P-invariance together imply

$$L_{3,nn}(\boldsymbol{k}) = 0; \quad \text{all } n \tag{4.16}$$

(Strictly speaking (4.16) implies the vanishing of χ_L for nondegenerate energy bands only because otherwise $L_{3,nn}$ contains a trace over the index labelling this degeneracy).

It is instructive to write down the result (4.14) for the limiting cases of nearly free and of tightly-bound electrons.

In the case of nearly free electrons where the periodic potential is considered as a small perturbation, it follows from (C. 1) and the definitions (A. 15), (3.9), (4.2) that χ_P is the only term of importance,

$$\chi \cong \chi_P \quad \text{(nearly free electrons)} \tag{4.17}$$

In tight binding approximation, on the other hand, the energy bands of interest are all very narrow, so that one may put (see (C. 3))

$$E_{n|j} \cong 0$$

at least for the occupied bands ($E_n \lesssim \zeta$). Then according to (3.9), (4.2)

$$B_{nn'} \cong L_{3,nn'}; \quad n \neq n' \tag{4.18}$$

so that χ' vanishes in this limit. According to (4.13, 15, 18) the hermiticity of L_3, which is shown in appendix C to be valid in this approximation, implies $\chi'' \cong 0$ so that

$$\chi \cong \chi_a + \chi_L + \chi_V \quad \text{(tightly-bound electrons)} \tag{4.19}$$

Since in this approximation the $\boldsymbol{k}$ dependence disappears, $\boldsymbol{k}$-integration simply yields the volume of the reduced Brillouin zone,

$$\int d^3 k = (2\pi)^3/v \tag{4.20}$$

v being the volume of the unit cell of the crystal (which in the case of a Bravais lattice is also the volume per atom). Since there is no preferred axis with atomic states we may finally write eqs. (4.9, 10, 12) in the form

$$\chi_a \cong -\frac{e^2}{3\,mv} \cdot \sum_n \langle n \,|\, r^2 \,|\, n\rangle\, f(E_n) \tag{4.21}$$

$$\chi_V \cong -\frac{4}{3\,v}\left(\frac{e}{2\,m}\right)^2 \sum_n \sum_{n'}{}' \frac{|\langle n \,|\, \boldsymbol{l} \,|\, n'\rangle|^2}{E_n - E_{n'}}\, f(E_n) \tag{4.22}$$

$$\chi_L \cong -\frac{2}{3\,v}\left(\frac{e}{2\,m}\right)^2 \sum_n |\langle n \,|\, \boldsymbol{l} \,|\, n\rangle|^2\, f'(E_n) \tag{4.23}$$

These expressions are well known for atomic systems where f is the Maxwell distribution[15]): χ_a is a Langevin-Pauli diamagnetism, χ_V a van Vleck paramagnetism and χ_L a Langevin-Debye paramagnetism $\mu^2/3kT$. (Note the factor 2 for spin degeneracy.) Since P-invariance holds in atomic systems χ_L is non-zero only for completely or nearly degenerate states $|n\rangle$, $|\langle n|\boldsymbol{l}|n\rangle|^2$ being a sum over nondiagonal 'low frequency elements'[15]). It is interesting to note also that (4.21) and (4.22) are identical with PEIERLS's χ_1 and χ_2 respectively.

Appendix A: Matrix elements

We write the Bloch states defined by (2.7) and (2.9) as

$$|n\,\boldsymbol{k}) = e^{i\boldsymbol{k}\boldsymbol{x}}\, u_{n\boldsymbol{k}}(\boldsymbol{x}) \tag{A.1}$$

where $u_{n\boldsymbol{k}}$ is invariant under translations through a lattice vector $\boldsymbol{R}_\alpha$,

$$u_{n\boldsymbol{k}}(\boldsymbol{x} + \boldsymbol{R}_\alpha) = u_{n\boldsymbol{k}}(\boldsymbol{x}) \tag{A.2}$$

Consider now an operator O with this same symmetry (periodic O). Reducing the unit cell Ω_α at $\boldsymbol{R}_\alpha$ to the cell Ω_0 at the origin by

$$\boldsymbol{x} = \boldsymbol{x}' + \boldsymbol{R}_\alpha \tag{A.3}$$

and making use of (A. 2) the matrix element of O may be written as

$$(n\boldsymbol{k}\,|\,O\,|\,n'\boldsymbol{k}') = \sum_\alpha e^{i(\boldsymbol{k}'-\boldsymbol{k})\,\boldsymbol{R}_\alpha} \cdot$$

$$\cdot \int_{\Omega_0} d^3x'\, e^{-i\boldsymbol{k}\boldsymbol{x}'}\, u^*_{n\boldsymbol{k}}(\boldsymbol{x}')\, O\, e^{i\boldsymbol{k}'\boldsymbol{x}'}\, u^{n'\boldsymbol{k}'}(\boldsymbol{x}')$$

where summation over α extends over the infinite crystal. One proves in the usual way, starting from a finite normalization volume V, that in the limit $V \to \infty$

$$\sum_\alpha e^{i\boldsymbol{k}\boldsymbol{R}_\alpha} = \frac{(2\pi)^3}{v} \cdot \delta(\boldsymbol{k}) \tag{A.4}$$

where v is the volume of the unit cell. Thus

$$(n\boldsymbol{k}\,|\,O\,|\,n'\boldsymbol{k}') = O_{nn'}(\boldsymbol{k}) \cdot \delta(\boldsymbol{k} - \boldsymbol{k}') \quad \text{(periodic } O) \tag{A.5}$$

where

$$O_{nn'}(\boldsymbol{k}) = \frac{(2\pi)^3}{v} \int_{\Omega_0} d^3x\, e^{-i\boldsymbol{k}\boldsymbol{x}}\, u^*_{n\boldsymbol{k}}\, O\, e^{i\boldsymbol{k}\boldsymbol{x}}\, u_{n'\boldsymbol{k}} \tag{A.5'}$$

With $O = 1$ the normalization

$$\frac{(2\pi)^3}{v} \int_{\Omega_0} u^*_{n\boldsymbol{k}}\, u_{n'\boldsymbol{k}}\, d^3x = \delta_{nn'}; \quad \text{all } \boldsymbol{k} \tag{A.6}$$

follows from (2.9). Taking $O = p_j = 1/i\ \partial/\partial x_j$ we get the matrix element (3.1) with

$$P_{j,nn'}(\boldsymbol{k}) = \frac{(2\pi)^3}{v} \int_{\Omega_0} u^*_{n\boldsymbol{k}} \left(\frac{1}{i}\frac{\partial}{\partial x_j} + k_j\right) u_{n'\boldsymbol{k}}\, d^3x \tag{A.7}$$

Since partial integration of (A. 7) yields a vanishing surface integral because of the periodicity (A. 2), it follows that the P_j are hermitian matrices in the band index n,

$$P_j^+(\boldsymbol{k}) = P_j(\boldsymbol{k}) \tag{A.8}$$

The matrix element of the coordinate x_j, for which the rule (A. 4) does not apply, may be writtens as

$$(n\boldsymbol{k} \mid x_j \mid n'\boldsymbol{k}') = \int d^3 x\, u^*_{n\boldsymbol{k}}\, u_{n'\boldsymbol{k}'} \frac{1}{i} \frac{\partial}{\partial k'_j} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}}$$

or

$$\left.\begin{aligned} (n\boldsymbol{k} \mid x_j \mid n'\boldsymbol{k}') = \frac{1}{i} \frac{\partial}{\partial k'_j} \int u^*_{n\boldsymbol{k}}\, u_{n'\boldsymbol{k}'}\, e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}}\, d^3 x\, - \\ - \int u^*_{n\boldsymbol{k}} \frac{1}{i} \frac{\partial u_{n'\boldsymbol{k}'}}{\partial k'_j} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}}\, d^3 x \end{aligned}\right\} \tag{A.9}$$

In the second integral the differentiation $1/i\, \partial/\partial k'_j$, behaves like a periodic operator, so that we can apply (A. 5,5′) and get

$$- \int u^*_{n\boldsymbol{k}} \frac{1}{i} \frac{\partial u_{n'\boldsymbol{k}'}}{\partial k'_j} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}}\, d^3 x = X_{j,nn'}(\boldsymbol{k}) \cdot \delta(\boldsymbol{k}-\boldsymbol{k}') \tag{A.10}$$

with

$$X_{j,nn'}(\boldsymbol{k}) = \frac{(2\pi)^3}{v} \cdot \int\limits_{\Omega_0} u^*_{n\boldsymbol{k}}\, i \frac{\partial}{\partial k_j} u_{n'\boldsymbol{k}}\, d^3 x \tag{A.10′}$$

With (A. 1) and the normalization (2.9), eq. (3.2) follows immediately from (A. 8). Eq. (A. 9) suggests the interpretation that the operator x_j be split into a periodic and a non-periodic part which somewhat resemble (without being identical to) a saw tooth function and a stepped function respectively. Application of $i\, \partial/\partial k_j$ to eq. (A. 6) immediately proves the hermitian property of the matrix (A. 10′),

$$X_j^+(\boldsymbol{k}) = X_j(\boldsymbol{k}) \tag{A.11}$$

The basic assumption underlying the Bloch representation is that the functions $u_{n\boldsymbol{k}}$ for any $\boldsymbol{k}$ in the reduced zone form a complete set within the domain Ω_0. Taking into account the normalization (A. 5) the completeness relation is

$$\sum_n u_{n\boldsymbol{k}}(\boldsymbol{x})\, u^*_{n\boldsymbol{k}}(\boldsymbol{x}') = \frac{v}{(2\pi)^3} \delta(\boldsymbol{x}-\boldsymbol{x}'); \quad \text{all } \boldsymbol{k} \tag{A.12}$$

The completeness of the Bloch states (A. 1) is then a consequence of (A. 12). With the value (4.20) for the volume of the reduced zone it can be expressed as

$$\sum_n \int d^3 k\, | n\boldsymbol{k})\, (n\boldsymbol{k} | = \mathbf{1} \tag{A.13}$$

Then it follows for any periodic operator O, making use of (A. 5) and (3.2), that

$$\left.\begin{aligned}(n\boldsymbol{k} \mid x_j\, O \mid n'\boldsymbol{k}') &= \sum_{n''} \int d^3 k'' \,(n\boldsymbol{k} \mid x_j \mid n''\boldsymbol{k}'')\,(n''\boldsymbol{k}'' \mid O \mid n'\boldsymbol{k}') = \\ &= O_{nn'}(\boldsymbol{k}') \frac{1}{i} \cdot \frac{\partial}{\partial k'_j} \delta(\boldsymbol{k}-\boldsymbol{k}') + \left(X_j(\boldsymbol{k})\, O(\boldsymbol{k})\right)_{nn'} \cdot \delta(\boldsymbol{k}-\boldsymbol{k}')\end{aligned}\right\} \quad (A.14)$$

and

$$\left.\begin{aligned}(n\boldsymbol{k} \mid O x_j \mid n'\boldsymbol{k}') &= O_{nn'}(\boldsymbol{k}) \frac{1}{i} \frac{\partial}{\partial k'_j} \delta(\boldsymbol{k}-\boldsymbol{k}') + \\ &+ \left(O(\boldsymbol{k})\, X_j(\boldsymbol{k})\right)_{nn'} \cdot \delta(\boldsymbol{k}-\boldsymbol{k}')\end{aligned}\right\} \quad (A.14')$$

If we put $O = p_l$ in (A. 14) we obtain eq. (3.3) with

$$L_3 = X_1\, P_2 - X_2\, P_1 \quad (A.15)$$

The hermitian conjugate is by (A. 8,11)

$$L_3^+ = P_2\, X_1 - P_1\, X_2 \quad (A.15')$$

Comparison of (A. 14) and (A.14') shows that although l_3 is a hermitian operator, $L_3(\boldsymbol{k})$ is in general not a hermitian matrix.

The matrix element of a function

$$\varphi_U(\boldsymbol{x}) = \begin{cases} 1 \text{ inside a region } U \\ \text{o outside } U \end{cases}$$

may be written with the help of (A. 2, 3, 6) as

$$\left.\begin{aligned}\Delta_{nn'}(\boldsymbol{k}, \boldsymbol{k}') \equiv (n\boldsymbol{k} \mid \varphi_U(\boldsymbol{x}) \mid n'\boldsymbol{k}') &= \sum_{\alpha} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{R}_\alpha} \cdot \\ \cdot \int_{\Omega_0} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}'}\, u^*_{n\boldsymbol{k}}(\boldsymbol{x}')\, u_{n'\boldsymbol{k}'}(\boldsymbol{x}') &\cdot \varphi_u(\boldsymbol{x}' + \boldsymbol{R}_\alpha)\, d^3 x'\end{aligned}\right\} \quad (A.16)$$

or

$$\Delta_{nn'}(\boldsymbol{k}, \boldsymbol{k}') \cong \frac{v}{(2\pi)^3}\, \delta_{nn'} \cdot \sum_{\boldsymbol{R}_\alpha \text{ in } U} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{R}_\alpha} \quad (A.16')$$

The inaccuracy of the last formula caused by the cells Ω_α that are cut by the boundary of U vanishes in the limit $U \to \infty$. Thus eq. (2.12) follows from (A. 16', 4).

For the discussion in section 2 we are interested in the matrix elements of $\varphi_U(\boldsymbol{x}) \cdot x_j$ which represents the vector potential for a magnetic field with the same behaviour as φ_U except at the boundary of U (to avoid complications φ_U may be assumed to be continous at this boundary). In analogy to eq. (A. 9) we can write

$$\begin{aligned}(n\boldsymbol{k} \mid \varphi_U(\boldsymbol{x}) \cdot x_j \mid n'\boldsymbol{k}') &= \frac{1}{i} \cdot \frac{\partial}{\partial k'_j} \int d^3 x\, u^*_{n\boldsymbol{k}}\, u_{n'\boldsymbol{k}'}\, \varphi_U(\boldsymbol{x})\, e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}} - \\ &- \int d^3 x\, u^*_{n\boldsymbol{k}} \frac{1}{i} \cdot \frac{\partial u_{n'\boldsymbol{k}'}}{\partial k'_j}\, \varphi_U\, e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{x}}\end{aligned}$$

Using (A. 13) the second integral may be expressed as

$$\sum_{n''} \int d^3 k'' \, (n\,\boldsymbol{k} \mid \varphi_U \mid n''\,\boldsymbol{k}'') \cdot \int d^3 x \, u^*_{n''\boldsymbol{k}''} \; \frac{1}{i} \frac{\partial u_{n'\boldsymbol{k}'}}{\partial k'_j} e^{i(\boldsymbol{k}'-\boldsymbol{k}'')\boldsymbol{x}}$$

With the help of (A. 10, 16) we get

$$\left.\begin{aligned} (u\boldsymbol{k} \mid \varphi_U(\boldsymbol{x}) \cdot x_j \mid n'\boldsymbol{k}') &= \frac{1}{i} \frac{\partial}{\partial k'_j} \Delta_{nn'}(\boldsymbol{k}, \boldsymbol{k}') + \\ &+ \Big(\Delta(\boldsymbol{k}, \boldsymbol{k}') \cdot X_j(\boldsymbol{k}')\Big)_{nn'} \end{aligned}\right\} \qquad \text{(A.17)}$$

An alternative form may be obtained in expressing x_j by the derivative $-1/i\,\partial/\partial k_j$ instead of $+1/i\,\partial/\partial k'_j$ applied to $\exp i(\boldsymbol{k}'-\boldsymbol{k})\,\boldsymbol{x}$. It is

$$\left.\begin{aligned} (n\,\boldsymbol{k} \mid \varphi_U(\boldsymbol{x}) \cdot x_j \mid n'\,\boldsymbol{k}') &= -\frac{1}{i} \cdot \frac{\partial}{\partial k_j} \Delta_{nn'}(\boldsymbol{k}, \boldsymbol{k}') + \\ &+ \Big(X_j(\boldsymbol{k}) \cdot \Delta(\boldsymbol{k}, \boldsymbol{k}')\Big)_{nn'} \end{aligned}\right\} \qquad \text{(A.17')}$$

From (A.14,14') it follows after a partial integration

$$\left.\begin{aligned} &\int_\varepsilon d^3 k' \, (n\,\boldsymbol{k} \mid i\,[O, x_j] \mid n'\,\boldsymbol{k}') = \\ &= \frac{\partial}{\partial k_j} O_{nn'}(\boldsymbol{k}) + i[O(\boldsymbol{k}), X_j(\boldsymbol{k})]_{nn'} \end{aligned}\right\} \qquad \text{(A.18)}$$

By applying this formula to $O = \mathfrak{H}_0$ and making use of the commutation relation

$$i[\mathfrak{H}_0, x_j] = \frac{1}{m} p_j$$

we obtain the formula

$$\frac{1}{m} P_j(\boldsymbol{k}) = E_{|j} + i[E(\boldsymbol{k}), X_j(\boldsymbol{k})] \qquad \text{(A.19)}$$

or in components

$$P_{j,nn}(\boldsymbol{k}) = m\,E_{n|j} \qquad \text{(A.19')}$$

$$P_{j,nn'}(\boldsymbol{k}) = i\,m\,\Big(E_n(\boldsymbol{k}) - E_{n'}(\boldsymbol{k})\Big) \cdot X_{j,nn'}(\boldsymbol{k});\; n \neq n' \qquad \text{(A.19'')}$$

A second relation is obtained with $O = p_l$ and the commutator

$$i[p_l, x_j] = \delta_{lj}$$

In this case (A. 17) yields the sum rule

$$\delta_{lj} = P_{l|j} + i[P_l(\boldsymbol{k}), X_j(\boldsymbol{k})] \qquad \text{(A.20)}$$

Recalling the definitions (A. 15, 15') one sees that eq. (3.10) is an immediate consequence of (A. 20). The diagonal part of (A. 20) together with (A.19',19'') yields

$$E_{n|jl} = \frac{1}{m}\,\delta_{lj} + \frac{1}{m^2} \sum_{n'}{}' \frac{P_{l,nn'}\,P_{j,n'n} + P_{j,nn'}\,P_{l,n'n}}{E_n - E_{n'}} \qquad \text{(A.21)}$$

Appendix B: Symmetries

The basis for the symmetry relations to be derived in this appendix is a representation in terms of the periodic part of the Bloch states (A. 1). As is seem from (2.3, 7) it satisfies the Schrödinger equation

$$\mathfrak{H}_{\boldsymbol{k}}\, u_{n\boldsymbol{k}} = E_n(\boldsymbol{k})\, u_{n\boldsymbol{k}}; \quad \text{all } \boldsymbol{k} \tag{B.1}$$

with

$$\mathfrak{H}_{\boldsymbol{k}} = \frac{1}{2\,m}\left(\frac{1}{i}\cdot\frac{\partial}{\partial \boldsymbol{x}} + \boldsymbol{k}\right)^2 + V(\boldsymbol{x}) \tag{B.1'}$$

T-invariance: According to Wigner's definition of time reversal[16]) any wave function $\psi(\boldsymbol{x}, t)$ is transformed into $\psi^*\,(\boldsymbol{x}, -t)$. This transformation leaves the Schrödinger equation

$$\mathfrak{H}_0\,\psi = i\,\frac{\partial\psi}{\delta t} \tag{B.2}$$

invariant if $\mathfrak{H}_0$ is real,

$$\mathfrak{H}_0 = \mathfrak{H}_0^* \qquad (T\text{-invariance}) \tag{B.3}$$

T-invariance is thus verified for the $\mathfrak{H}_0$ in (2.3). The corresponding invariance of $\mathfrak{H}_{\boldsymbol{k}}$ is, according to (B. 1')

$$\mathfrak{H}_{\boldsymbol{k}} = \mathfrak{H}_{-\boldsymbol{k}}^* \tag{B.3'}$$

Thus time reversal of $u_{n\boldsymbol{k}}$ has to be defined as

$$u_{n\boldsymbol{k}} \to u_{n\boldsymbol{k}}{}' = u_{n,-\boldsymbol{k}}^* \tag{B.4}$$

According to (B. 1,3') the new $u_{n\boldsymbol{k}}{}'$ satisfy the equation

$$\mathfrak{H}_{\boldsymbol{k}}\, u_{n\boldsymbol{k}}{}' = E_n(-\boldsymbol{k})\, u_{n\boldsymbol{k}}{}' \tag{B.5}$$

and may be normalized according to (A. 6). By virtue of their completeness the $u_{n\boldsymbol{k}}$ may be taken as basis for an expansion of $u_{n\boldsymbol{k}}{}'$,

$$u_{n\boldsymbol{k}}{}' = \sum_{n''} u_{n''\boldsymbol{k}}\; S_{n''n}\,(\boldsymbol{k}) \tag{B.6}$$

Eq. (B. 5) together with (B. 1) yields, after multiplication with $u_{n\boldsymbol{k}}^*$ and integration, using (A. 6),

$$\left(E_{n'}\,(\boldsymbol{k}) - E_n(-\boldsymbol{k})\right)\cdot S_{n'n}\,(\boldsymbol{k}) = 0$$

If $\boldsymbol{k}$ is not a point of degeneracy (note that $\boldsymbol{k}$-independent degeneracies have been admitted but not explicitly labelled in this paper) this equation implies

$$E_n\,(-\boldsymbol{k}) = E_n(\boldsymbol{k}) \tag{B.6}$$

and also that $S(\boldsymbol{k})$ is diagonal in n. By an appropriate choice of phases of the $u_{n\boldsymbol{k}}$ it is therefore always possible to have

$$S_{n'n}(\boldsymbol{k}) = \delta_{n'n}$$

and thus
$$u^*_{n,-\boldsymbol{k}} = u_{n\boldsymbol{k}} \tag{B.7}$$

The implication of this equality is, according to (A. 7) and (A. 10′),
$$P_j{}^*(-\boldsymbol{k}) = -\,P_j(\boldsymbol{k});\ X_j{}^*(-\boldsymbol{k}) = +\,X_j(\boldsymbol{k}) \tag{B.8}$$

from which, in view of the definition (A. 15), it follows that
$$L_3^*\,(-\boldsymbol{k}) = -\,L_3(\boldsymbol{k}) \tag{B.9}$$

P-invariance: Spatial inversion transforms a general $\psi\,(\boldsymbol{x}, t)$ into $\psi\,(-\,\boldsymbol{x}, t)$ and the Schrödinger equation (B. 2) is invariant if $\mathfrak{H}_0$ conserves the parity,
$$\mathfrak{H}_0(\boldsymbol{x}) = \mathfrak{H}_0\,(-\boldsymbol{x})\ \ (P\text{-invariance}) \tag{B.10}$$

The corresponding invariance of $\mathfrak{H}_{\boldsymbol{k}}$ is according to (B. 1′)
$$\mathfrak{H}_{\boldsymbol{k}}(\boldsymbol{x}) = \mathfrak{H}_{-\boldsymbol{k}}\,(-\boldsymbol{x}) \tag{B.10′}$$

Thus space inversion of $u_{n\boldsymbol{k}}$ has to be defined as
$$u_{n\boldsymbol{k}} \to u_{n\boldsymbol{k}}{}''(\boldsymbol{x}) = u_{n,-\boldsymbol{k}}\,(-\boldsymbol{x}) \tag{B.11}$$

From here onwards, the same reasoning again leads to (B. 6) and to
$$u_{n,-\boldsymbol{k}}\,(-\boldsymbol{x}) = u_{n\boldsymbol{k}}(\boldsymbol{x}) \tag{B.12}$$

Applied to (A. 7) and (A. 10′) this relation yields
$$P_j\,(-\boldsymbol{k}) = -\,P_j(\boldsymbol{k});\ X_j\,(-\boldsymbol{k}) = -\,X_j(\boldsymbol{k}) \tag{B.13}$$

and, according to (A.15),
$$L_3\,(-\boldsymbol{k}) = L_3(\boldsymbol{k}) \tag{B.14}$$

Combination of T- and P-invariance, (B.8,13), and use of the hermiticity (A.8,11) leads to
$$P_{j,n'n}(\boldsymbol{k}) = P_{j,nn'}(\boldsymbol{k});\ X_{j,n'n}(\boldsymbol{k}) = -X_{j,nn'}(\boldsymbol{k}) \tag{B.15}$$

Similarly (B.9,14) together with (3.8) yields
$$L_{3,nn'} + L_{3,n'n} = \frac{1}{i}\,(P_{2,nn'|1} - P_{1,nn'|2}) \tag{B.16}$$

For n $= n'$ this equation goes over into (4.16) in view of (A. 19′).

A quite different type of symmetry occurs if one tries to extend eq. (B.1,1′) to $\boldsymbol{k}$-points outside of the reduced zone. This is obviously possible formally since $\boldsymbol{k}$ plays the role of a parameter, the restriction to the reduced zone originating from the completeness hypothesis. If $\boldsymbol{K}_\alpha$ is a vector of the reciprocal lattice so that
$$e^{i\boldsymbol{K}_\alpha \boldsymbol{R}_\beta} = 1;\ \text{all}\ \beta$$

the function

$$v_{nk} \equiv e^{i\boldsymbol{K}_\alpha \boldsymbol{x}}\, u_{n,\boldsymbol{k}+\boldsymbol{K}_\alpha} \tag{B.17}$$

obviously has again the periodicity (A.2) and, furthermore, satisfies the equation

$$\mathfrak{H}_{\boldsymbol{k}}\, v_{n\boldsymbol{k}} = E_n\,(\boldsymbol{k} + \boldsymbol{K}_\alpha)\, v_{n\boldsymbol{k}} \tag{B.18}$$

Again the reasoning is the same as between (B.5) and (B.7), the result being

$$E_n\,(\boldsymbol{k} + \boldsymbol{K}_\alpha) = E_n(\boldsymbol{k}) \tag{B.19}$$

and

$$e^{i\boldsymbol{K}_\alpha \boldsymbol{x}}\, u_{n,\boldsymbol{k}+\boldsymbol{K}_\alpha} = u_{n\boldsymbol{k}} \tag{B.20}$$

or according to (A.1)

$$|\, n, \boldsymbol{k} + \boldsymbol{K}_\alpha) = |\, n\, \boldsymbol{k}) \tag{B.20'}$$

Appendix C: Nearly Free and Tightly-Bound Electrons

The modifications for nearly free electrons are most easily obtained from the relation

$$i[\boldsymbol{p}, \mathfrak{H}_0] = \frac{\partial V}{\partial \boldsymbol{x}}$$

the right hand side of which is a small periodic function. Using (A.5) for $O = \boldsymbol{p}$ and $\partial V/\partial \boldsymbol{x}$ we have

$$i\Big(E_{n'}(\boldsymbol{k}) - E_n(\boldsymbol{k})\Big) \cdot P_{j,nn'}(\boldsymbol{k}) = \varepsilon_{j,nn'}(\boldsymbol{k}) \equiv \frac{(2\pi)^3}{v} \int_{\Omega_0} u^*_{u\boldsymbol{k}}\, u_{n'\boldsymbol{k}} \frac{\partial V}{\partial x_j}\, d^3x$$

Thus according to (A. 19″) the non-diagonal elements of X_j are of order ε as are those of P_j. On the other hand P-invariance holds in zeroth order in $\partial V/\partial \boldsymbol{x}$ so that according to (B.15) the diagonal elements of X_j are at least of first order in ε. Therefore, with (A.19′),

$$X_j = O(\varepsilon);\; P_j = m\, E_{|j} + O(\varepsilon) \tag{C.1}$$

We only mention that the energy band structure follows by integration of eq. (A.21) taking into account the symmetries (B.6,19) and is, in an appropriate labelling,

$$E_{n\alpha}(\boldsymbol{k}) = \frac{1}{2\,m}\,(\boldsymbol{k} + \boldsymbol{K}_\alpha)^2 + O(\varepsilon^2)$$

(It is of the form of fig. 11, p. 86, of PEIERLS[13])).

The tight binding approximation, as is well known (see e. g. PEIERLS[13]), p. 79ff) starts from the assumption that the periodic potential may be written as

$$V(\boldsymbol{x}) = \sum_\alpha U\,(\boldsymbol{x} - \boldsymbol{R}_\alpha)$$

where $U(\boldsymbol{x})$ is an atomic potential. (We restrict the discussion to Bravais lattices. For lattices with more than one atom per unit cell the tight binding approximation is more complicated). In this approximation the

Bloch states can be built up from the atomic wave functions $\varphi_n(\boldsymbol{x})$ which satisfy the Schrödinger equation

$$\left(\frac{1}{2m} p^2 + U\right) \varphi_n = e_n \varphi_n$$

Indeed, if $U(\boldsymbol{x})$ and $\varphi_n(\boldsymbol{x})$ do not overlap appreciably for neighbouring atoms in the crystal then

$$u_{n\boldsymbol{k}}(\boldsymbol{x}) = \sqrt{\frac{v}{(2\pi)^3}} \sum_\alpha e^{i\boldsymbol{k}(\boldsymbol{R}_\alpha - \boldsymbol{x})} \varphi_n(\boldsymbol{x} - \boldsymbol{R}_\alpha) \tag{C.2}$$

(which has the correct periodicity (A.2)), approximately satisfies the Schrödinger equation (B.1) with

$$E_n(\boldsymbol{k}) = e_n \tag{C.3}$$

If the φ_n are normalized to one and form a complete set then also (A.6) and (A.12) are approximately fulfilled. With (C.2) it follows from (A.7) and (A. 10′) that

$$P_{j,nn'}(\boldsymbol{k}) \cong \int d^3x\, \varphi_n^* \frac{1}{i} \cdot \frac{\partial}{\partial x_j} \varphi_{n'} \equiv < n \mid p_j \mid n' > \tag{C.4}$$

and

$$\chi_{j,nn'}(\boldsymbol{k}) \cong \int d^3x\, \varphi_n^* x_j \varphi_{n'} \equiv < n \mid x_j \mid n' > \tag{C.5}$$

(C. 4) shows that $P_j(\boldsymbol{k})$ does not appreciably depend on $\boldsymbol{k}$ so that according to (3.10) L_3 becomes a hermitian matrix in this limit,

$$L_3^+ - L_3 \cong 0 \tag{C.6}$$

and, with the help of the completeness of the atomic states $\mid n >$, is approximately given by

$$L_{3,nn'}(\boldsymbol{k}) \cong < n \mid l_3 \mid n' > \tag{C.7}$$

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