PHYSICAL REVIEW VOLUME 180, NUMBER 3 15 APRIL 1969

Theory of the g Shift of Conduction Electrons

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(Received 18 October 1968)

A simple derivation of the conduction-electron g factor in a crystal having inversion symmetry is presented. The result obtained for the g shift is unambiguous for each state (of wave vector $\mathbf{k}$), and reduces to the correct isolated-atom g shift in the tight-binding limit. Previous work has failed to satisfy these requirements. Two formulas suitable for computation of $\delta g(\mathbf{k})$ are derived.

I. INTRODUCTION AND CONCLUSION

In a crystal having inversion symmetry, the (nominally) spin-up and spin-down Bloch states for each wave vector $\mathbf{k}$ are degenerate,[1] even though spin-orbit coupling does not allow energy levels that are eigenfunctions of spin. A magnetic field splits this degeneracy by an energy $g\mu_B H$. ($\mu_B \equiv$ Bohr magneton.) A shift $\delta g(\mathbf{k})$ of the g factor from its free-electron value arises from spin-orbit interaction with the periodic potential of the crystal. The theory of this shift was developed by Yafet,[2] Roth,[3] and Blount,[4] and has been applied to several semiconductors and to the alkali metals.[5] A review of this work was completed by Yafet.[6]

The theoretical treatments of $\delta g(\mathbf{k})$ suffer from three deficiencies: The derivations seem (to us) extremely complicated. Secondly, the final expression for $\delta g(\mathbf{k})$ is ambiguous, since it depends on the relative phase (as a function of $\mathbf{k}$) with which Bloch functions are defined. Finally, δg does not reduce to the correct isolated-atom g shift in the tight-binding limit.

The $\mathbf{k}$ dependence of $g(\mathbf{k})$ can cause broadening of a conduction-electron spin resonance. Usually the resonance width is less than that caused by the spread in $g(\mathbf{k})$ because an electron scatters through many $\mathbf{k}$ states at the Fermi surface during a spin-lattice relaxation time. The observed g is then a time-averaged value, equal to the density-of-states average of $g(\mathbf{k})$ over the Fermi surface. It has been shown that the cyclotron orbit average of $g(\mathbf{k})$ is phase-invariant, even if $g(\mathbf{k})$ itself is not.[7] This suggests the inference that $g(\mathbf{k})$ is not physically significant, and therefore need not be phase-invariant. We disagree. Conduction-electron spin resonance can be observed even if the electron mean free path is smaller than a cyclotron orbit size. A motionally narrowed linewidth contribution would then be $1/T_2 = (\delta\omega)^2\tau_c$,[8] where in this case $\delta\omega$ is proportional to the spread in $g(\mathbf{k})$, and τ_c is the electron-scattering time. Consequently, the g factors of specific Bloch states are physically relevant; and a correct theoretical treatment must yield a $g(\mathbf{k})$ that is phase invariant.

In the derivation that follows an additional term appears in the expression for $\delta g(\mathbf{k})$ which renders it phase-invariant. We are able to show that the Fermi-surface average of this extra term is zero; thus calculations of the average g based on previous expressions for $g(\mathbf{k})$ need not be revised on this account. Insofar as this last result might not have been foreseen, the demonstration given here is essential.

The failure of prior theory to reduce to the correct isolated-atom g shift was noted recently.[9] A relativistic contribution to δg,

$$(\delta g)'' = -(m^2c^2)^{-1}\int \psi^\dagger p^2 \psi d^3r\,, \tag{1}$$

previously omitted, was shown to be the remedy. This term is comparatively small in all metals except lithium. In this case, however, it accounts for approximately two thirds of the observed g shift.

The simplicity of the derivation presented below depends on the fact that the splitting $g\mu_B H$ is linear in H. Accordingly, first-order perturbation theory suffices. We need merely evaluate the difference in expectation value of the perturbation for (unperturbed) spin-up and spin-down wave packets.[10] Interband and intraband mixing, caused by the magnetic field H, contribute only in higher order and can be ignored. Only two critical questions arise during the derivation: the relationship between the spin-up and spin-down wave packets (Sec. II), and the correct choice of gauge associated with the magnetic field (Sec. III). The theory is valid to all orders in spin-orbit coupling.

II. WAVE FUNCTIONS IN THE BLOCH REPRESENTATION

The Hamiltonian of an electron in a potential energy field $V(\mathbf{r})$ is

$$\mathcal{H}_0 = p^2/2m + V(\mathbf{r}) + (\hbar/4m^2c^2)[\boldsymbol{\sigma}\times(\nabla V)]\cdot\mathbf{p}\,. \tag{2}$$

The last term is the spin-orbit coupling energy. $\{\sigma_i\}$

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[7] See Ref. 3; and Ref. 6, Appendix C.

[8] D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

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[10] We assume throughout this paper that we are calculating $g(\mathbf{k})$ for a Bloch state $\mathbf{k}$ that is not degenerate (except for spin). Extensions of the theory to encompass added degeneracy would follow well-known procedures, e.g., Sec. 7 of Ref. 6.

are the Pauli matrices. The spatial periodicity of $V(\mathbf{r})$ allows the eigenfunctions of $\mathcal{H}_0$ to have the Bloch form

$$\varphi_{n\mathbf{k}s}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}s}(\mathbf{r})\,, \tag{3}$$

where $u_{n\mathbf{k}s}(\mathbf{r})$ is periodic in $\mathbf{r}$ and is a two-component spinor. n is the band index and s the spin direction, $\uparrow$ or $\downarrow$. We will define

$$u_{n\mathbf{k}\uparrow}(\mathbf{r})\equiv\begin{pmatrix}\mu_{n\mathbf{k}}(\mathbf{r})\\ \lambda_{n\mathbf{k}}(\mathbf{r})\end{pmatrix}. \tag{4}$$

$\mu_{n\mathbf{k}}(\mathbf{r})$ is the large component and $\lambda_{n\mathbf{k}}(\mathbf{r})$ the small, which in the absence of spin-orbit coupling would be zero. Throughout this paper, $\mathbf{k}$ is just a wave-vector label (a c number, not an operator).

The spin-down counterpart of (4) can be obtained by applying the operator[1] C to (4), where

$$C\equiv -i\sigma_y K_0 J\,. \tag{5}$$

K_0 denotes complex conjugation and J is the inversion operator ($\mathbf{r}\rightarrow -\mathbf{r}$). The center of inversion of the crystalline unit cell must be taken to be $\mathbf{r}=0$. Accordingly, we have

$$u_{n\mathbf{k}\downarrow}(\mathbf{r})=\begin{pmatrix}-\lambda_{n\mathbf{k}}^{*}(-\mathbf{r})\\ \mu_{n\mathbf{k}}^{*}(-\mathbf{r})\end{pmatrix}. \tag{6}$$

This equation also specifies the relative phases of up- and down-spin Bloch functions.

Mathematical difficulties arise when dealing with the coordinate operator $\mathbf{r}$ together with wave functions that are not square-integrable over infinite space. To avoid these problems, we use the Bloch representation.[11] If a general wave function ψ is

$$\psi(\mathbf{r})\equiv\sum_{ns}\int d^3k\, f_{ns}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}s}(\mathbf{r})\,, \tag{7}$$

in the coordinate representation, then ψ is

$$\psi(\mathbf{k})=[f_{0\uparrow}(\mathbf{k})\quad f_{0\downarrow}(\mathbf{k})\quad f_{1\uparrow}(\mathbf{k})\quad f_{1\downarrow}(\mathbf{k})\quad\cdots]\,, \tag{8}$$

in the Bloch representation. $\psi(\mathbf{k})$ is an (infinite) *column* vector. In this representation the x component of $\mathbf{r}$, for example, is[12]

$$x=iI\partial/\partial k_x+X_{nsn's'}(\mathbf{k})\,, \tag{9}$$

where I is an (infinite) unit matrix, and

$$X_{nsn's'}(\mathbf{k})\equiv i\int d^3r u_{n\mathbf{k}s}^{\dagger}(\mathbf{r})\partial[u_{n'\mathbf{k}s'}(\mathbf{r})]/\partial k_x\,. \tag{10}$$

The Hamiltonian (2) is, of course, a diagonal matrix in this representation. The diagonal elements

$$\mathcal{H}_{nsns}(\mathbf{k})\equiv E_n(\mathbf{k}) \tag{11}$$

are just the energy bands, and are independent of s.

An up-spin wave packet in the band $E_0(\mathbf{k})$ has a wave function, say,

$$\psi_{\uparrow}(\mathbf{k})=[f(\mathbf{k})\quad 0\quad 0\quad 0\quad\cdots]\,. \tag{12}$$

We will assume $f(\mathbf{k})$ to be nonzero only in a small ($\mathbf{k}$-space) neighborhood of $\mathbf{k}_0$, the point where we wish to compute $g(\mathbf{k})$. The corresponding down-spin wave packet is not obtained merely by interchanging the two top entries of the *column* vector (12). The reason is that spin is flipped by a physical interaction involving, say, the operator $\mathcal{H}_x$, the interaction of an electron with an x-directed magnetic field. The matrix element of $\mathcal{H}_{xp}$ (the periodic part of $\mathcal{H}_x$) will have an amplitude M and phase $e^{i\alpha(\mathbf{k})}$ defined by

$$Me^{i\alpha(\mathbf{k})}\equiv\int\varphi_{0\mathbf{k}\downarrow}^{\dagger}\mathcal{H}_{xp}\varphi_{0\mathbf{k}\uparrow}d^3r\,. \tag{13}$$

We assume, of course, that $\varphi_{0\mathbf{k}\uparrow}$ and $\varphi_{0\mathbf{k}\downarrow}$ are the spin-eigenstates associated with a z-directed magnetic field, i.e.,

$$\int\varphi_{0\mathbf{k}\downarrow}^{\dagger}\mathcal{H}_{zp}\varphi_{0\mathbf{k}\uparrow}d^3r=0\,. \tag{14}$$

Each $\mathbf{k}$ component of a spin-down packet $\psi_{\downarrow}(\mathbf{k})$ generated from $\psi_{\uparrow}(\mathbf{k})$ by the action of $\mathcal{H}_x$, will be created with the relative phase $e^{i\alpha(\mathbf{k})}$. Consequently the appropriate down-spin wave packet is the *column* vector,

$$\psi_{\downarrow}(\mathbf{k})=[0\quad f(\mathbf{k})e^{i\alpha(\mathbf{k})}\quad 0\quad 0\quad\cdots]\,. \tag{15}$$

This conclusion, together with the evaluation of (13), is discussed at length in Appendix C. Equations (12) and (15) are the two wave functions whose energy difference in a magnetic field will give the g factor directly.

It will be of interest to know the difference $\Delta\mathbf{S}$ between the centers of mass $\mathbf{S}_{\uparrow}$ and $\mathbf{S}_{\downarrow}$ of (12) and (15). The x component of $\mathbf{S}_{\uparrow}$ is, for example,

$$S_{\uparrow x}=\int d^3k\psi_{\uparrow}^{\dagger}(\mathbf{k})x\psi_{\uparrow}(\mathbf{k})\,. \tag{16}$$

By employing (9) and the assumed localization of ψ in $\mathbf{k}$ space, we obtain

$$\Delta S_x\equiv(\mathbf{S}_{\uparrow}-\mathbf{S}_{\downarrow})_x=X_{0\uparrow0\uparrow}(\mathbf{k})-X_{0\downarrow0\downarrow}(\mathbf{k})+\partial\alpha(\mathbf{k})/\partial k_x\,. \tag{17}$$

It follows from (4), (6), (10), and the normalization integral of (4), that the first and second terms of (17) are equal but opposite in sign. Accordingly, each component of $\Delta\mathbf{S}$ is similar to

$$\Delta S_x=2(X_{0\uparrow0\uparrow}+\tfrac{1}{2}\partial\alpha/\partial k_x)\,. \tag{18}$$

This shift in c.m. (during a spin flip from $\downarrow$ to $\uparrow$) would not occur in the absence of spin-orbit coupling. $\Delta\mathbf{S}$ is independent of the relative phase (as a function of $\mathbf{k}$)

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[11] This is sometimes called the crystal momentum representation; e.g., E. N. Adams, II, J. Chem. Phys. **21**, 2013 (1953).

[12] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1953), 2nd ed., p. 48, Eq. (2.82.3).

with which Bloch functions are defined, even though the two terms in (18) individually are not. This is proved in Appendix A.

III. ENERGY SPLITTING IN A MAGNETIC FIELD

The energy splitting $g\mu_BH$ between the two opposite-spin wave packets (12) and (15) will define $g(\mathbf{k})$, except for the small additive correction $(\delta g)''$ given by Eq. (1). However, extreme care must be exercised in the choice of gauge describing $\mathbf{H}$. The reason is that the physical significance of a wave function depends on the particular vector potential $\mathbf{A}(\mathbf{r})$ that is used. Consider the velocity operator $\mathbf{v}$. In the absence of spin-orbit coupling, it is just $\mathbf{p}/m$. With spin-orbit coupling (and no magnetic field) it is

$$\mathbf{v}=\boldsymbol{\pi}/m=\mathbf{p}/m+(\hbar/4m^2c^2)\boldsymbol{\sigma}\times(\boldsymbol{\nabla}V). \qquad (19)$$

This is just the commutator $(\mathbf{r}\mathcal{H}_0-\mathcal{H}_0\mathbf{r})/i\hbar$. The customary notation $\boldsymbol{\pi}=(\pi^x,\pi^y,\pi^z)$ is introduced for later convenience. In a magnetic field, $\mathbf{p}$ is replaced by $\mathbf{p}+(e/c)\mathbf{A}$ in (2), so the velocity operator becomes

$$\mathbf{v}=\boldsymbol{\pi}/m+(e/mc)\mathbf{A}(\mathbf{r}). \qquad (20)$$

The second term arises from the commutator of $\mathbf{r}$ with $\mathbf{A}\cdot\mathbf{p}$.

Consider again the wave packet (12). If we include its time dependence, the nonzero component is

$$f(\mathbf{k})e^{-iE_0(\mathbf{k})t/\hbar}. \qquad (21)$$

The group velocity $\mathbf{v}_G$ of this packet is

$$\mathbf{v}_G=\boldsymbol{\nabla}_kE_0(\mathbf{k})/\hbar, \qquad (22)$$

and is independent of time. When we turn on a magnetic field, we want our (approximate) wave function to retain this physical property. Otherwise the question we hope to answer by perturbation theory would not be relevant to the physically characterized electron we had in mind.[13] The velocity (22) will continue to be the expectation value of the $\boldsymbol{\pi}/m$ term of (20). Consequently, we must demand that the $\mathbf{A}$ term of (20) have zero expectation value for the wave function (21). This means that we must pick a gauge such that the null point of $\mathbf{A}(\mathbf{r})$ travels with the center of the wave packet. This is just the Jones and Zener gauge[14]

$$\begin{aligned}\mathbf{A}&=\tfrac{1}{2}\mathbf{H}\times(\mathbf{r}-\mathbf{v}_Gt),\\ \varphi&=(1/2c)(\mathbf{H}\times\mathbf{v}_G)\cdot\mathbf{r}.\end{aligned} \qquad (23)$$

The scalar potential φ is required so that the electric field $-\boldsymbol{\nabla}\varphi-c^{-1}\partial\mathbf{A}/\partial t$ is zero. We have assumed, without loss of generality, that $f(\mathbf{k})$ is chosen so that the c.m. $\mathbf{S}_\uparrow=0$ at $t=0$.

The Hamiltonian $\mathcal{H}$ with the field on is explicitly time-dependent. If we choose $\mathbf{H}$ in the z direction, then[15] for $t=0$

$$\mathcal{H}=\mathcal{H}_0+\mu_eH\sigma_z-e\varphi(\mathbf{r})+(eH/2mc)(x\pi^y-y\pi^x)+e^2A^2/2mc^2. \qquad (24)$$

The second term is the interaction of $\mathbf{H}$ with the free-electron intrinsic moment μ_e. The third is the scalar potential term from (23). The fourth and fifth terms are derived from (2) after substitution of $\mathbf{p}+e\mathbf{A}/c$ for $\mathbf{p}$, and use of (19). We may neglect the fifth term because it is proportional to H^2.

The energy difference associated with $[\delta g(\mathbf{k})-(\delta g)'']\mu_BH$ is the difference in expectation values of the third and fourth terms of (24) for $\psi_\uparrow$, Eq. (12), and $\psi_\downarrow$, Eq. (15). Employing (9) and its y counterpart, we obtain

$$\begin{aligned}\delta g(\mathbf{k})=(\delta g)''+(\delta g)'''&\\ +2\hbar^{-1}\sum_{s,n\neq0}&(X_{0\uparrow ns}\pi_{ns0\uparrow}{}^y-Y_{0\uparrow ns}\pi_{ns0\uparrow}{}^x)\\ +4\hbar^{-1}[&(X_{0\uparrow0\uparrow}+\tfrac{1}{2}\partial\alpha/\partial k_x)\pi_{0\uparrow0\uparrow}{}^y\\ &-(Y_{0\uparrow0\uparrow}+\tfrac{1}{2}\partial\alpha/\partial k_y)\pi_{0\uparrow0\uparrow}{}^x],\end{aligned} \qquad (25)$$

where $(\delta g)'''\equiv(2\mu_e/\mu_B)[(\sigma_z)_{0\uparrow0\uparrow}-1]$. Half of the last term comes from the scalar potential. To obtain the form shown, we have made use of the relation

$$m\mathbf{v}_G=\boldsymbol{\pi}_{0\uparrow0\uparrow}=\boldsymbol{\pi}_{0\downarrow0\downarrow}, \qquad (26)$$

as well as, $X_{0\uparrow0\uparrow}=-X_{0\downarrow0\downarrow}$, employed previously in deriving Eq. (18). In order to obtain the term involving the summation, one must employ

$$\sum_s X_{0\uparrow ns}\pi_{ns0\uparrow}{}^y=-\sum_s X_{0\downarrow ns}\pi_{ns0\downarrow}{}^y, \qquad (27)$$

and its $Y\pi^x$ counterpart. These may be derived from the definitions (4) and (6), and from interband orthogonality relations.

The contributions to (25) have simple physical interpretations. The first term, $(\delta g)''$, is the relativistic effect,[9] Eq. (1). The second, $(\delta g)'''$, corresponds to the average tilt of the intrinsic electron moment. The third

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[13] This need for caution may seem unusual at first sight. But it is demonstrated by the following simple example: Consider the effect of a small perturbation on the Bloch function $\varphi_\mathbf{k}$, having $E=E_0(\mathbf{k})$, and suppose the perturbation is just the vector potential $\mathbf{A}=\boldsymbol{\kappa}$, a constant vector. This will cause corrections to the wave function and energy to all orders. One can show that the latter will converge to $E=E_0(\mathbf{k}+e\boldsymbol{\kappa}/\hbar c)$. But curl $\mathbf{A}=0$; so the perturbation represents no physical effect at all. Therefore, the gauge $\mathbf{A}=\boldsymbol{\kappa}$, describing zero magnetic field, has caused the function $\varphi_\mathbf{k}$ to represent in zeroth order the ordinary electronic state $\varphi_{\mathbf{k}+e\boldsymbol{\kappa}/\hbar c}$. The fact that only a restricted class of gauges can suitably be associated with a given zeroth-order wave function does not mean the theory is not gauge-invariant. One can always transform to arbitrary gauge provided one transforms the (zeroth-order) wave function also.

[14] H. Jones and C. Zener, Proc. Roy. Soc. (London) **A144**, 101 (1934); see also Ref. 12, p. 51. It is sometimes forgotten that the equation $d\mathbf{k}/dt=(-e/\hbar c)\mathbf{v}_G\times\mathbf{H}$, for the motion of Bloch electrons in a magnetic field, is valid only in a Jones and Zener gauge.

[15] No loss in generality results from selecting $t=0$. Identical results are obtained by taking expectation values of $\mathcal{H}(t)$ with time-dependent wave packets, e.g., (21).

is the g shift associated with the intrinsic orbital magnetic moment of a wave packet,[16] $\langle(\mathbf{r}-\mathbf{S}_\uparrow)\times m\mathbf{v}\rangle$, $\mathbf{S}_\uparrow$ being the c.m. of the packet. The fourth arises from the c.m. shift $\Delta\mathbf{S}$ of the wave packet during spin flip. With the help of (18), this term is just $2\hbar^{-1}(\Delta\mathbf{S}\times m\mathbf{v}_G)_z$. Half of this represents an additional magnetic moment associated with the displacement of $\mathbf{S}_\uparrow$ from the mean position $\frac{1}{2}(\mathbf{S}_\uparrow+\mathbf{S}_\downarrow)$. The other half arises from the energy of the displaced electric charge in the scalar potential φ.

The physical interpretation of the $\Delta\mathbf{S}$ term depends on the choice of gauge. In Appendix B we show that if a gauge is chosen such that the null point of $\mathbf{A}(\mathbf{r})$ is forced to remain precisely at the c.m. of the wave packet at all times, even as the spin is flipped from $\downarrow$ to $\uparrow$, then the Lorentz-force contribution of $d(\Delta\mathbf{S})/dt$ causes an increment $\Delta\mathbf{k}$ in the wave vector. This produces a shift in band energy from $E_0(\mathbf{k})$ to $E_0(\mathbf{k}+\Delta\mathbf{k})$, a change which is just the energy difference associated with the last term of Eq. (25).

Prior theoretical work had failed to obtain the $\alpha(\mathbf{k})$ contributions to $\delta g(\mathbf{k})$. They are necessary in order that $\delta g(\mathbf{k})$ be phase-invariant, and therefore physically meaningful. In Appendix A we show that (a) the last term of (25) is phase-invariant, (b) the cyclotron orbit average of the $\alpha(\mathbf{k})$ terms alone are phase-invariant, and (c) the latter averages are identically zero.

IV. CALCULABLE FORMS FOR THE g SHIFT

Equation (25) is not suitable for numerical calculation of $\delta g(\mathbf{k})$ on account of the infinite sum required by the second term. In this section, we present two alternative expressions for the g shift. They depend only on wave functions in the energy band of interest. From the definition of $\boldsymbol{\pi}$ [Eq. (19)]

$$\boldsymbol{\pi}_{ns0\uparrow}=\hbar\mathbf{k}\delta_{n,0}\delta_{s,\uparrow}+\int u_{n\mathbf{k}s}{}^{\dagger}\boldsymbol{\pi}u_{0\mathbf{k}\uparrow}d^3r\,, \tag{28}$$

where $\delta_{n,0}$ and $\delta_{s,\uparrow}$ are Kronecker δ's. From (10) and the orthogonality relations of $\{u_{n\mathbf{k}s}\}$ we have, for example,

$$X_{0\uparrow ns}=-i\int\left(\frac{\partial u_{0\mathbf{k}\uparrow}(\mathbf{r})^{\dagger}}{\partial k_x}\right)u_{n\mathbf{k}s}(\mathbf{r})d^3r\,. \tag{29}$$

With the help of (28), (29), and the completeness of $\{u_{n\mathbf{k}s}(\mathbf{r})\}$, we find that (25) can be written

$$\begin{aligned}\delta g(\mathbf{k})=&\frac{2}{i\hbar}\int\left[\left(\frac{\partial u_{0\mathbf{k}\uparrow}{}^{\dagger}}{\partial k_x}\right)\pi^y u_{0\mathbf{k}\uparrow}-\left(\frac{\partial u_{0\mathbf{k}\uparrow}{}^{\dagger}}{\partial k_y}\right)\pi^x u_{0\mathbf{k}\uparrow}\right]d^3r\\&+\frac{2}{\hbar}\left[\left(X_{0\uparrow0\uparrow}+\frac{\partial\alpha}{\partial k_x}\right)\pi_{0\uparrow0\uparrow}{}^y-\left(Y_{0\uparrow0\uparrow}+\frac{\partial\alpha}{\partial k_y}\right)\pi_{0\uparrow0\uparrow}{}^x\right]\\&+2(X_{0\uparrow0\uparrow}k_y-Y_{0\uparrow0\uparrow}k_x)+(\delta g)''+(\delta g)'''.\end{aligned} \tag{30}$$

The $n=0$ terms needed to complete the sum over n, so closure could be used, were obtained from the last term of (25).

It is of interest to evaluate Eq. (30) in the tight-binding limit. For the case of an S band, the periodic part of the Bloch function in a unit cell Ω is [Eq. (4)] $\mu_{\mathbf{k}}(\mathbf{r})=\varphi_S(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}$, $\lambda_{\mathbf{k}}(\mathbf{r})=0$ (in the limit of large lattice constant). $\varphi_S(\mathbf{r})$ is a free-atom S-state wave function. The first term of (30) reduces to

$$(\delta g)'=(2mc^2)^{-1}\int_\Omega\left(x\frac{\partial V}{\partial x}+y\frac{\partial V}{\partial y}\right)\varphi^{\dagger}\varphi d^3r\,. \tag{31}$$

This contribution arises from the $\boldsymbol{\sigma}\times(\boldsymbol{\nabla}V)$ term of $\boldsymbol{\pi}$, Eq. (19). The second and third terms of (30) are zero because the diagonal elements of X and Y are zero, and $\nabla_{\mathbf{k}}\alpha=0$. Consequently,

$$\delta g=(\delta g)'+(\delta g)''. \tag{32}$$

In the tight-binding limit $(\delta g)''=-3(\delta g)'$.[9] Since $(\delta g)'$ is positive, δg is negative. It was shown in a previous paper[9] that Eq. (32) is the correct free-atom g shift.[17]

It is sometimes useful to convert as much of (25) as possible into surface integrals over the cellular polyhedron.[5] The algebraic steps needed to accomplish this have already been indicated,[2] so we omit the derivation here. The final result is

$$\begin{aligned}\delta g(\mathbf{k})=&\frac{2}{\hbar}\int_\Omega\varphi^{\dagger}(x\pi^y-y\pi^x)\varphi d^3r+(\delta g)''\\&+(\delta g)'''+\frac{2}{\hbar}\left[\left(\frac{\partial\alpha}{\partial k_x}\right)\pi_{0\uparrow0\uparrow}{}^y-\left(\frac{\partial\alpha}{\partial k_y}\right)\pi_{0\uparrow0\uparrow}{}^x\right]\\&-\frac{i}{\hbar}\int\left[\varphi^{\dagger}\pi^{\nu}\left(xe^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial u}{\partial k_y}\right)+(\pi^{\nu}\varphi)^{\dagger}\left(xe^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial u}{\partial k_y}\right)\right]dS\\&+\frac{i}{\hbar}\int\left[\varphi^{\dagger}\pi^{\nu}\left(ye^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial u}{\partial k_x}\right)+(\pi^{\nu}\varphi)^{\dagger}\left(ye^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial u}{\partial k_x}\right)\right]dS\\&-\frac{\pi_{0\uparrow0\uparrow}{}^y}{2\hbar(\partial E_0/\partial k_x)}\int\left[\frac{\partial\varphi^{\dagger}}{\partial k_x}\pi^{\nu}\frac{\partial\varphi}{\partial k_x}+\left(\pi^{\nu}\frac{\partial\varphi}{\partial k_x}\right)^{\dagger}\frac{\partial\varphi}{\partial k_x}\right]dS\\&+\frac{\pi_{0\uparrow0\uparrow}{}^x}{2\hbar(\partial E_0/\partial k_y)}\int\left[\frac{\partial\varphi^{\dagger}}{\partial k_y}\pi^{\nu}\frac{\partial\varphi}{\partial k_y}+\left(\pi^{\nu}\frac{\partial\varphi}{\partial k_y}\right)^{\dagger}\frac{\partial\varphi}{\partial k_y}\right]dS\,.\end{aligned} \tag{33}$$

π^{ν} is the component of $\boldsymbol{\pi}$ in the direction of the outward normal of the surface element dS (of the cellular polyhedron). The subscripts $0\mathbf{k}\uparrow$ have been omitted from all $\boldsymbol{\sigma}$'s and u's.

ACKNOWLEDGMENT

It is a pleasure to thank A. D. Brailsford for helpful comments on the presentation of this material.

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[16] C. Herring, Ref. 6, Appendix B.

[17] The only prior discussion of this point is Ref. 2, p. 683, where it is alleged that $(\delta g)'$ alone is the correct free-atom g shift.

APPENDIX A: PROPERTIES OF $\alpha(k)$

The phase invariance of $\Delta\mathbf{S}$ is established from the definitions of the two terms appearing in (18). Suppose we replace our original set of Bloch functions $\{\varphi_{0\mathbf{k}s}\}$ by the set

$$\varphi_{0\mathbf{k}s}' \equiv e^{iw(\mathbf{k})}\varphi_{0\mathbf{k}s}\,, \tag{A1}$$

where $w(\mathbf{k})$ is any real, continuous function of $\mathbf{k}$. It follows from Eq. (10) that

$$X_{0\uparrow0\uparrow}' = X_{0\uparrow0\uparrow} - \partial w/\partial k_x\,. \tag{A2}$$

Consequently, the diagonal elements of X are phase-dependent. Now, from Eqs. (13) and (A1),

$$e^{i\alpha'(\mathbf{k})} = e^{i\alpha(\mathbf{k})+2iw(\mathbf{k})}\,. \tag{A3}$$

Therefore,

$$\partial\alpha'/\partial k_x = \partial\alpha/\partial k_x + 2\partial w/\partial k_x\,. \tag{A4}$$

Eqs. (A2) and (A4) imply the invariance of $\Delta\mathbf{S}$, Eq. (18).

We also wish to prove that the cyclotron orbit average of the α terms in (25) are phase invariant. If we define a two-dimensional vector $\mathbf{F}$

$$F_x = -\partial\alpha/\partial k_y\,,\quad F_y = \partial\alpha/\partial k_x\,, \tag{A5}$$

and use (26), we must show that the cyclotron orbit average of $F_x v_{Gx} + F_y v_{Gy}$ is phase-invariant. The cyclotron orbit average is not the integral with respect to dl around the orbit, but the integral with respect to $dl/(v_{Gx}^2+v_{Gy}^2)^{1/2}$. The reason is that the line element dl (in k space) must receive a weight proportional to the amount of time an orbiting electron spends in that line element. Consequently, from the Jones-Zener equation[14] for $d\mathbf{k}/dt$, we must divide dl by the magnitude of $\mathbf{v}_G$ in the xy plane. Accordingly, the appropriate average is

$$\int \mathbf{F}\cdot\mathbf{n}dl = \int\int \operatorname{div}\mathbf{F}dk_x dk_y\,, \tag{A6}$$

where $\mathbf{n}$ is the unit vector $(v_{Gx},v_{Gy})/(v_{Gx}^2+v_{Gy}^2)^{1/2}$. Gauss' theorem applies since, from Eq. (22), $\mathbf{n}$ is perpendicular to the orbit. But $\operatorname{div}\mathbf{F}\equiv 0$, from (A5). Therefore, the cyclotron orbit average of the α terms in Eq. (25) is not only phase-invariant, but identically zero.

The density-of-states average over the Fermi surface of the α terms is also zero. This follows as a corollary of the foregoing result, since the operator $\int dS/|\mathbf{v}_G|$ over Fermi-surface area elements dS is equivalent to the operator $\int dk_z \int dl/(v_{Gx}^2+v_{Gy}^2)^{1/2}$.

APPENDIX B: ΔS CONTRIBUTIONS TO $\delta g(k)$

In Sec. III, $\delta g(\mathbf{k})$ was derived by calculating the energy difference between $\psi_\uparrow$ and $\psi_\downarrow$ with the Hamiltonian (24). The last term of Eq. (25) arose from the c.m. shift $\Delta\mathbf{S}\equiv\mathbf{S}_\uparrow-\mathbf{S}_\downarrow$. It is of interest to reinterpret the energy difference associated with this shift by considering a gauge $\mathbf{A}(\mathbf{r},t)$, $\varphi(\mathbf{r},t)$ that has its null point always at the c.m. of the wave packet, even as the spin is being flipped. There will be an additional contribution to $d\mathbf{k}/dt$, from the Jones-Zener equation,[14] caused by the extra velocity $d(\Delta\mathbf{S})/dt$. Accordingly,

$$\Delta\mathbf{k} = \int_0^\tau \frac{-e}{\hbar c}\left(\frac{d(\Delta\mathbf{S})}{dt}\right)\times\mathbf{H}dt\,, \tag{B1}$$

where τ is the time during which the spin is flipped from ↓ to ↑, i.e., $\Delta\mathbf{S}=\int_0^\tau d(\Delta\mathbf{S})$. It follows that

$$\Delta\mathbf{k} = (-e/\hbar c)\Delta\mathbf{S}\times\mathbf{H}\,. \tag{B2}$$

The energy difference ΔE_0 associated with $\Delta\mathbf{k}$ is just $E_0(\mathbf{k}+\Delta\mathbf{k})-E_0(\mathbf{k})$,

$$\Delta E_0 \cong \nabla_{\mathbf{k}}E_0\cdot\Delta\mathbf{k} = \hbar\mathbf{v}_G\cdot\Delta\mathbf{k}\,. \tag{B3}$$

On combining (B2) and (B3), we obtain

$$\Delta E_0 = (e/c)(\Delta\mathbf{S}\times\mathbf{v}_G)\cdot\mathbf{H}\,. \tag{B4}$$

This equals the energy difference that led to the last term of Eq. (25). In this gauge it is a change in band energy, whereas in the former gauge it was a change in (vector and scalar) potential energy.

APPENDIX C: PHASE RELATIONS BETWEEN $\psi_\uparrow$ AND $\psi_\downarrow$

In Sec. II, we chose an arbitrary envelope function $f(\mathbf{k})$ for $\psi_\uparrow$, subject only to the requirement that it be nonzero in a small k-space neighborhood. In order to determine the appropriate envelope function $f'(\mathbf{k})$ for $\psi_\downarrow$, we must examine the perturbation $\epsilon\mathcal{H}_x$, caused by a small x-directed magnetic field of magnitude ϵ, which can flip a spin from ↑ to ↓. As in Sec. III, we must employ a Jones-Zener gauge (23). Accordingly, if the ϵ^2 term is neglected,

$$\mathcal{H}_x = \mu_e\sigma_x + (e/2mc)[y(\boldsymbol{\pi}+m\mathbf{v}_G)_z - z(\boldsymbol{\pi}+m\mathbf{v}_G)_y]\,. \tag{C1}$$

In the Bloch representation the coordinates y and z are operators analogous to (9). Since $\boldsymbol{\pi}_{0\downarrow0\uparrow}=0$, the $iI\partial/\partial k$ terms of (C1) cannot flip spin. (They affect only the cyclotron motion of the wave packet.) The remaining terms are

$$\mathcal{H}_{xp} \equiv \mu_e\sigma_x + (e/2mc)[Y(\boldsymbol{\pi}+m\mathbf{v}_G)_z - Z(\boldsymbol{\pi}+m\mathbf{v}_G)_y]\,, \tag{C2}$$

where $Y(\mathbf{k})$ and $Z(\mathbf{k})$ are matrices like X in (9). The operator $\mathcal{H}_{xp}$ has the periodicity of the crystal. Consequently, the envelope function $f'(\mathbf{k})$ for $\psi_\downarrow$ will satisfy $|f'(\mathbf{k})|=|f(\mathbf{k})|$. (Each wave-vector component is conserved.) There are, however, an infinite variety of wave packets satisfying this relation. For example, if we wish to translate a given wave packet a distance $\mathbf{R}$, we merely multiply its envelope function by the phase function $e^{-i\mathbf{k}\cdot\mathbf{R}}$. Since the Hamiltonian (with $\mathbf{H}\neq 0$) has an $\mathbf{r}$-dependent vector potential, the energy of a wave packet depends on its location. Clearly, the phase variation of $f'(\mathbf{k})$ is critical. We must choose for $\psi_\downarrow$ the envelope function obtained from $\psi_\uparrow$ by an operation that corresponds to spin rotation in a real experiment, e.g., $\mathcal{H}_{xp}$.

An intuitive way to correctly specify $\psi_\downarrow(\mathbf{k})$, Eq. (15), is to recall the time-dependent Schrödinger equation $i\hbar\dot{a}_m=\sum_n \mathcal{H}'_{mn}a_n e^{i\omega_{mn}t}$, for a perturbation $\mathcal{H}'$. The phase with which an amplitude a_m develops includes multiplicatively the phase factor of the matrix element $\mathcal{H}_{mn}'$.

Evaluation of the phase $\alpha(\mathbf{k})$, defined by Eq. (13), requires several steps similar to those used in obtaining (30) from (25). The object is to obtain an expression for α involving only the Bloch functions $\varphi_{0\mathbf{k}s}$. We find

$$Me^{i\alpha}=\mu_e\int u_{0\mathbf{k}\downarrow}{}^{\dagger}\sigma_x u_{0\mathbf{k}\uparrow}d^3r$$
$$-\frac{ie}{2mc}\int\left(\frac{\partial u_{0\mathbf{k}\downarrow}{}^{\dagger}}{\partial k_y}\right)(\hbar k_z+mv_{Gz}+\pi_z)u_{0\mathbf{k}\uparrow}d^3r$$
$$+\frac{ie}{2mc}\int\left(\frac{\partial u_{0\mathbf{k}\downarrow}{}^{\dagger}}{\partial k_z}\right)(\hbar k_y+mv_{Gy}+\pi_y)u_{0\mathbf{k}\uparrow}d^3r. \quad \text{(C3)}$$

PHYSICAL REVIEW VOLUME 180, NUMBER 3 15 APRIL 1969

Quantum Oscillations in the Peltier Effect of Zinc*†

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(Received 15 November 1968)

Peltier measurements have been employed to study quantum oscillations in the thermoelectric power of zinc single crystals. The three lowest frequencies, due to the α, β, and γ orbits, were observed at temperatures ranging from 1.2 to 4.5°K and in fields to 22 kG. The amplitudes found were between 0.01 and 1 μV/K°. An attempt has been made to correlate these measurements with an expression derived by Horton. As his calculation is valid only for the case of a free-electron sphere, his results have been heuristically extended to include metals with complex Fermi surfaces. The theory and measurements agree only in the form of the temperature dependence; neither the absolute amplitudes nor the field dependence is correctly predicted by the theory. It is suggested that the disagreement may arise from the assumption of independent bands in the extension of Horton's single-band calculation. In particular, the oscillating density of states gives rise to a strongly energy-dependent relaxation time, which may significantly affect the thermoelectric power. An approximate calculation of the oscillation amplitude to be expected from this mechanism is presented. Although the agreement with the data is again not perfect, there are some qualitative indications that favor this model. Experiments in a longitudinal configuration should shed further light on the problem, and such experiments are now in progress.

I. INTRODUCTION

QUANTUM oscillations in zinc were first observed by Marcus in the diamagnetic susceptibility[1] [de Haas–van Alphen (dHvA) effect]. Subsequent work has revealed the Fermi surface of zinc in great detail[2–8] and contributed substantially to our present understanding of quantum oscillations in general and magnetic breakdown in particular. In view of this extensive and intensive study one may well question the value of yet further measurements of quantum oscillations in this particular metal.

Whereas the theory of the dHvA effect is now firmly established and understood, the theory of quantum oscillations of the transport coefficients is still in a very imperfect state. The principal difference between these two is that the susceptibility is an equilibrium property of the electron gas and can therefore be deduced from the free energy, while transport properties cannot, of course, be treated correctly from a thermodynamic approach; indeed, a satisfactory quantum theory of transport which leads to explicit results in a form permitting comparison with experiment is not as yet at hand. It is of interest, therefore, to study transport phenomena in some detail, with particular attention to their temperature and field dependences, so that the successes as well as the limitations of existing theories

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* This work was supported by a research grant from the National Science Foundation.

† Based on a thesis submitted by H. J. Trodahl in partial fulfillment of the requirements for a Ph.D. degree in the Department of Physics, Michigan State University.

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