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Magnetic susceptibility of dilute nonmagnetic alloys

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A simple and transparent formula is given for the magnetic susceptibility of nonmagnetic alloys, valid for general Bloch bands and to all orders in the impurity potential. In the free-electron-band model the expression for $\Delta\chi$ per solute atom gives a firm theoretical foundation to the formula used by Henry and Rogers, which accounts quite well for their experimental results. The derivation makes use of the Weyl-Wigner formalism of the quantum theory of solids.

I. INTRODUCTION

The magnetic susceptibility of solids containing magnetic and nonmagnetic impurities has been a subject of continuing and vigorous interest among theoretical and experimental physicists. Although a large amount of experimental data[1] has been accumulated for the past two decades on the magnetic susceptibility of nonmagnetic solids with nonmagnetic impurities, very little understanding, if any, exists in this particular field.[2] Perhaps this situation is not surprising since it is quite well known that even for pure nonmagnetic crystals the magnetic susceptibility is not yet fully understood.[3] In most cases, it is in situations where the band-structure effects dominate that efforts to quantitatively understand the experimental data become a formidable task even for the pure-crystal case.

A general expression for the magnetic susceptibility χ of Bloch electrons was first obtained by Hebborn and Sondheimer[4] and was later rederived in simpler and more elegant fashion by other authors.[5,6] Efforts toward giving a corresponding general χ for solids with nonmagnetic impurities were initiated by Kohn and Luming[7] by considering an idealized model of a free-electron band. Until now other attempts to give an expression of χ for general Bloch bands[8] can at best proceed only as a power-series expansion in the strength of the impurity potential. Recent experimental data[2] clearly indicate the urgent need for a better understanding and a more complete theory, that explicitly incorporates the band-structure effects of the host lattice, of the magnetic susceptibility of dilute nonmagnetic alloys.

The present work approaches the problem by the use of the Weyl-Wigner formalism of quantum theory, not very widely known in solid-state physics, although its embryonic and disguised form is already apparent in the operator method of Roth and Blount[5] and in the formalism of the dynamics of band electrons by Wannier.[9] The result for χ is given to order $\hbar^2$ valid for general nondegenerate Bloch bands and to all orders in the impurity potential. The effect of Bloch-electron interaction can, in principle, be incorporated by the use of a screened impurity potential. The expression for χ reduces to all well-known limiting cases. It is applied to the free-electron-band model of dilute alloys of copper and gives a firm theoretical foundation to the theory of Henry and Rogers,[7] which accounts quite well for their experimental results.

The outline of the paper is as follows. Section II describes the Weyl-Wigner formulation of the quantum mechanics of Bloch electrons and generalizes the method used by Wannier and Upadhyaya[6] for calculating the free energy to order $\hbar^2$. The result is valid even for cases where spatial inhomogeneity or defects exist in the pure-crystal host. Section III derives an expression for χ to order $\hbar^2$ valid for general nondegenerate Bloch bands and to all orders in the impurity potential. In Sec. IV it is shown how the formula used by Henry and Rogers follows from a general expression given for χ.

II. WEYL-WIGNER FORMULATION OF THE DYNAMICS OF BLOCH ELECTRONS. GENERALIZATION OF THE METHOD OF CALCULATING THE FREE ENERGY TO ORDER $\hbar^2$

The Weyl-Wigner formalism is an alternative formulation of quantum mechanics expressed in terms of the Weyl transform instead of quantum operators and Wigner functions instead of state vectors.[10] The power of this quite rigorous formalism in discussing multiband quantum dynamics and particles of higher spin is not very well appreciated in solid-state physics although equivalent but less rigorous methods exist in the literature.[5,11] Quite recently the author[12] has rigorously shown that an alternative formulation of the quantum mechanics of Bloch electrons in solids is possible using a complete set of functions $w_\lambda(\vec{r}, \vec{q})$, labeled by the band index λ and lattice point $\vec{q}$, and a complete set of functions $b_\lambda(\vec{r}, \vec{p})$, labeled by band index λ and crystal momentum $\vec{p}$, the two complete sets being related by a unitary Fourier transformation.

Examples of these complete sets are the Wannier function and Bloch function, both with and without a magnetic field.[9] The Weyl-Wigner formalism of the quantum mechanics of solids unifies the Roth, Blount, and Wannier formalisms which often appear heuristic and unrelated in the literature.

Let $w_\lambda(\vec{r},\vec{q})$ be any localized state labeled by a band index λ and lattice point $\vec{q}$. Let $b_\lambda(\vec{r},\vec{p})$ be its "lattice Fourier transform." Thus we write

$$b_\lambda(\vec{r},\vec{p}) = (N\hbar^3)^{-1/2}\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}} w_\lambda(\vec{r},\vec{q}) , \quad (1)$$

$$w_\lambda(\vec{r},\vec{q}) = (N\hbar^3)^{-1/2}\sum_{\vec{p}} e^{-(i/\hbar)\vec{p}\cdot\vec{q}} b_\lambda(\vec{r},\vec{p}) , \quad (2)$$

$$\sum_{\vec{q}} e^{(i/\hbar)(\vec{p}-\vec{p}\,')\cdot\vec{q}} = N\hbar^3\delta_{\vec{p},\vec{p}\,'} , \quad (3)$$

$$\sum_{\vec{p}} e^{(i/\hbar)(\vec{q}-\vec{q}\,')\cdot\vec{p}} = N\hbar^3\delta_{\vec{q},\vec{q}\,'} , \quad (4)$$

where N is the total number of lattice points. For convenience, we introduce the Dirac ket and bra notation:

$$b_\lambda(\vec{r},\vec{p}) = |\vec{p},\lambda\rangle = |p\rangle , \quad (5)$$

$$w_\lambda(\vec{r},\vec{q}) = |\vec{q},\lambda\rangle = |q\rangle , \quad (6)$$

$$\langle\vec{p},\lambda'|\vec{q},\lambda\rangle = (N\hbar^3)^{-1/2} e^{-(i/\hbar)\vec{p}\cdot\vec{q}}\delta_{\lambda'\lambda} , \quad (7)$$

$$\langle\vec{p},\lambda|\vec{p}\,',\lambda'\rangle = \delta_{\lambda\lambda'}\delta_{\vec{p}\vec{p}\,'} , \quad (8)$$

$$\langle\vec{q},\lambda|\vec{q}\,',\lambda'\rangle = \delta_{\lambda\lambda'}\delta_{\vec{q}\vec{q}\,'} , \quad (9)$$

$$\sum_p |p\rangle\langle p| = 1 , \quad (10)$$

$$\sum_q |q\rangle\langle q| = 1 . \quad (11)$$

By using the closure relation, Eqs. (10) and (11), the following identity holds for an arbitrary operator A:

$$A = \sum_{p',p'',q',q''} |p''\rangle\langle p''|q''\rangle\langle q''|A|q'\rangle\langle q'|p'\rangle\langle p'| . \quad (12)$$

Introducing the notation

$$\vec{p}\,' = \vec{p}+\vec{u} , \quad \vec{q}\,' = \vec{q}+\vec{v} ,$$

$$\vec{p}\,'' = \vec{p}-\vec{u} , \quad \vec{q}\,'' = \vec{q}-\vec{v} ,$$

and using Eq. (7), we obtain

$$A = (N\hbar^3)^{-1}\sum_{\vec{p},\vec{q},\lambda,\lambda'} A_{\lambda\lambda'}(\vec{p},\vec{q})\Delta_{\lambda\lambda'}(\vec{p},\vec{q}) , \quad (13)$$

where

$$A_{\lambda\lambda'}(\vec{p},\vec{q}) = \sum_{\vec{v}} e^{(2i/\hbar)\vec{p}\cdot\vec{v}}\langle\vec{q}-\vec{v},\lambda|A|\vec{q}+\vec{v},\lambda'\rangle, \quad (14)$$

$$\Delta_{\lambda\lambda'}(\vec{p},\vec{q}) = \sum_{\vec{u}} e^{(2i/\hbar)\vec{q}\cdot\vec{u}}|\vec{p}-\vec{u},\lambda\rangle\langle\vec{p}+\vec{u},\lambda'| . \quad (15)$$

By applying Eqs. (1) and (2) it is easy to obtain the following equivalent expressions for $A_{\lambda\lambda'}(\vec{p},\vec{q})$ and $\Delta_{\lambda\lambda'}(\vec{p},\vec{q})$:

$$A_{\lambda\lambda'}(\vec{p},\vec{q}) = \sum_u e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\langle\vec{p}+\vec{u},\lambda|A|\vec{p}-\vec{u},\lambda'\rangle, \quad (16)$$

$$\Delta_{\lambda\lambda'}(\vec{p},\vec{q}) = \sum_v e^{(2i/\hbar)\vec{p}\cdot\vec{v}}|\vec{q}+\vec{v},\lambda\rangle\langle\vec{q}-\vec{v},\lambda'| . \quad (17)$$

In Eq. (13) the operator nature of A is transferred to $\Delta_{\lambda\lambda'}(\vec{p},\vec{q})$. The reader who is familiar with the alternative formulation of quantum mechanics in terms of the Weyl transform and the Wigner function[10] will recognize $A_{\lambda\lambda'}(\vec{p},\vec{q})$ and $\Delta_{\lambda\lambda'}(\vec{p},\vec{q})$ as corresponding to the Weyl transform of the operator A and to the Δ function, respectively, in that formalism. We will refer to $A_{\lambda\lambda'}(\vec{p},\vec{q})$ as the lattice Weyl transform of the operator A. [Our definition of $A_{\lambda\lambda'}(\vec{p},\vec{q})$ differs from that of the continuous $(\vec{p},\vec{q})$ formalism by a factor of 2 in the exponential and the absence of $\frac{1}{2}$ inside the ket and bra, and, of course, by the replacement of the integral with a summation.] Thus an alternative formulation of the quantum mechanics of solids is possible using the two complete sets of functions $w_\lambda(\vec{r},\vec{q})$ and $b_\lambda(\vec{r},\vec{p})$. Examples of these complete sets are the Wannier functions and Bloch functions, both with and without a magnetic field.[9] Blount's "mixed representation"[11] and Wannier's formulation[9] of the dynamics of Bloch electrons in a solid are both an embryonic form of a discrete $(\vec{p},\vec{q})$ version of the statistical formulation of quantum mechanics when considered in terms of the Weyl transform instead of operators and the Wigner function instead of state vectors.[10] The power of this method of doing quantum mechanics in solid-state theory is demonstrated by the author[13] in calculating the magnetic susceptibility of bismuth, and more recently[14] in giving a rigorous quantum-mechanical basis of the distribution-function method in impurity screening, the Thomas-Fermi in the absence of a magnetic field, and the quasiclassical approximation for nonzero magnetic field, applicable for nondegenerate Bloch bands and quasiparticles of higher spin.

The virtue of the Weyl-Wigner formulation is that it enables us to generalize[12] the method of Wannier and Upadhyaya (WU) for calculating the free energy to order $\hbar^2$, from which the magnetic susceptibility χ can be calculated. The magnetic susceptibility is calculated from the free energy by the following relation[5]:

$$\chi = \lim_{B\to 0}\left(-\frac{1}{V}\frac{\partial^2 F}{\partial B^2}\right). \quad (18)$$

V is the volume of the system, B is the magnetic field strength, F is given by

$$F = N\mu + \mathrm{Tr}\,F(\mathcal{H}), \quad (19)$$

$$F(\mathcal{H}) = -k_B T\ln\{1+\exp[(\mu-\mathcal{H})/k_B T]\} , \quad (20)$$

and by the use of the Laplace transform of $F(\mathcal{H})$, we write

$$F(\mathcal{H})=\int_{c-i\infty}^{c+i\infty}\phi(s)e^{s\mathcal{H}}\,ds\ , \tag{21}$$

$$e^{s\mathcal{H}}=\sum_n\frac{s^n}{n!}\mathcal{H}^n\ . \tag{22}$$

The author[12] has recently generalized the method used in WU for calculating $\mathrm{Tr}\mathcal{H}^n$, using the technique of the Weyl transform[13] applied to solid-state theory, as described above, which is valid even in cases where spatial inhomogeneity or defects exist in the pure crystal host. We have[12,13] (Appendix C)

$$\mathrm{Tr}\mathcal{H}^n=\frac{\tilde{\mathrm{T}}\mathrm{r}}{N\hbar^3}\sum_{\vec{p},\vec{q}}\left\{[H(\vec{p},\vec{q})]^n-\frac{1}{2!}\left(\frac{\hbar}{2}\right)^2\frac{n(n-1)}{6}[H(\vec{p},\vec{q})]^{n-2}\left(\left[\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]-\left[\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{p}}\right]\right)\right\}+O(\hbar^4), \tag{23}$$

and from Eq. (21)

$$\mathrm{Tr}F(\mathcal{H})=\frac{\tilde{\mathrm{T}}\mathrm{r}}{N\hbar^3}\sum_{\vec{p}\,\vec{q}}\left\{F(H(\vec{p},\vec{q}))-\frac{1}{2!}\left(\frac{\hbar}{2}\right)^2\tfrac{1}{6}F''(H(\vec{p},\vec{q}))\left(\left[\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]-\left[\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{p}}\right]\right)\right\}+O(\hbar^4), \tag{24}$$

where [;] is a symmetrized tensor contraction, i.e.,

$$\left[\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]=\frac{\partial^2H(\vec{p},\vec{q})}{\partial p_i\partial p_j}\frac{\partial^2H(\vec{p},\vec{q})}{\partial q_i\partial q_j}+\frac{\partial^2H(\vec{p},\vec{q})}{\partial q_i\partial q_j}\frac{\partial^2H(p,q)}{\partial p_i\partial p_j}\ ;$$

moreover, the p's as well as the q's must never have identical indices where repeated indices are summed over. N is the total number of lattice points, $\tilde{\mathrm{T}}\mathrm{r}$ refers to taking the trace over band indices, $\vec{q}$ and $\vec{p}$ refer to lattice coordinates and crystal momentum $\hbar\vec{k}$ (limited to the first Brillouin zone), respectively. $H(\vec{p},\vec{q})$ is a matrix given by the formula (Appendix B)

$$H(\vec{p},\vec{q})_{\lambda\lambda'}=\sum_{\vec{v}}e^{(2i/\hbar)\vec{p}\cdot\vec{v}}\langle A_\lambda(\vec{x},\vec{q}-\vec{v})\mathcal{H}A_{\lambda'}(\vec{x},\vec{q}+\vec{v})\rangle, \tag{25}$$

or by the equivalent expression

$$H(\vec{p},\vec{q})_{\lambda\lambda'}=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\langle B_\lambda(\vec{x},\vec{p}+\vec{u})\mathcal{H}B_{\lambda'}(\vec{x},\vec{p}-\vec{u})\rangle\ . \tag{26}$$

The eigenstates $A_\lambda(\vec{r},\vec{q})$ and $B_\lambda(\vec{r},\vec{p})$ are the magnetic Wannier function and magnetic Bloch function, respectively, where λ labels the energy band. We thus have[6]

$$H(\vec{p},\vec{q})_{\lambda\lambda'}=W_\lambda(\vec{p}-(e/c)\vec{A}(\vec{q});B)\delta_{\lambda\lambda'}+V(\vec{p},\vec{q};B)_{\lambda\lambda'}\ , \tag{27}$$

where the dependence of W_λ on B beyond the vector potential can, in principle, be obtained as a series expansion[6] in powers of B:

$$\begin{aligned}W_\lambda(\vec{p}-(e/c)\vec{A}(\vec{q});B)&=W_\lambda^0(\vec{p}-(e/c)\vec{A}(\vec{q}))+BW_\lambda^{(1)}(\vec{p}-(e/c)\vec{A}(\vec{q}))\\&\quad+B^2W_\lambda^{(2)}(\vec{p}-(e/c)\vec{A}(\vec{q}))+\dots\ .\end{aligned} \tag{28}$$

$W_\lambda^0(\vec{p})$ is the energy-band function of a pure crystal in the absence of B, $W_\lambda(\vec{p};B)$ is given in WU for spinless Bloch electrons and by Roth[5,15] for Bloch electrons in the presence of spin-orbit coupling. $W_\lambda(\vec{p};B)$ is often referred to as a renormalized energy-band function.[6] $V(\vec{p},\vec{q})_{\lambda\lambda'}$ is given by Eqs. (25) and (26) with $\mathcal{H}$ replaced by $V_I(\vec{r})$ and can be explicitly written as (Appendix B)

$$V(\vec{p},\vec{q};B)_{\lambda\lambda'}=V^0(\vec{p},\vec{q})_{\lambda\lambda'}+BV^{(1)}(\vec{p},\vec{q})_{\lambda\lambda'}+B^2V^{(2)}(\vec{p},\vec{q})_{\lambda\lambda'}+\dots\ , \tag{29}$$

where

$$V^0(\vec{p},\vec{q})_{\lambda\lambda'}=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\phi^0_{\lambda\lambda'}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})\ , \tag{30}$$

$$V^{(1)}(p,q)_{\lambda\lambda'}=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\left(\Theta^{(1)}_{\lambda\lambda'}(\vec{p},\vec{u})+\sum_\gamma\beta^{(1)}_{\lambda'\gamma}(\vec{p}-\vec{u})\phi^0_{\lambda\gamma}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})+\sum_\gamma\beta^{(1)*}_{\lambda\gamma}(\vec{p}+\vec{u})\phi^0_{\gamma\lambda'}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})\right), \tag{31}$$

$$\begin{aligned}V^{(2)}(\vec{p},\vec{q})_{\lambda\lambda'}=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\Bigg(&\Theta^{(2)}_{\lambda\lambda'}(\vec{p},\vec{u})+\sum_\gamma\beta^{(2)}_{\lambda'\gamma}(\vec{p}-\vec{u})\phi^0_{\lambda\gamma}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})+\sum_\gamma\beta^{(2)*}_{\lambda\gamma}(\vec{p}+\vec{u})\phi^0_{\gamma\lambda'}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})\\&+\sum_{\gamma\gamma'}\beta^{(1)*}_{\lambda\gamma}(\vec{p}+\vec{u})\beta^{(1)}_{\lambda'\gamma'}(\vec{p}-\vec{u})\phi^0_{\gamma\gamma'}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})\Bigg)\ ,\end{aligned} \tag{32}$$

$$\phi^0_{\alpha\beta}(\vec{p}+\vec{u},\vec{p}-\vec{u};2\vec{u})=\int e^{-(2i/\hbar)\vec{u}\cdot\vec{r}}u^{0*}_\alpha(\vec{r},\vec{p}+\vec{u})V_I(\vec{r})u^0_\beta(\vec{r},\vec{p}-\vec{u})\,d^3r\ . \tag{33}$$

$u_\alpha^0(\vec{r}, \vec{p})$ is the periodic part of a Bloch function. $\Theta_{\lambda\lambda'}^{(1)}(\vec{p}, \vec{u})$ and $\Theta_{\lambda\lambda'}^{(1)}(\vec{p}, \vec{u})$ are defined by Eqs. (B18) and (B19). The coefficients $\beta^{(1)}$ and $\beta^{(2)}$ come from the expansion of the modified Bloch function in powers of the magnetic field strength B (Appendix A)

$$b_\lambda(\vec{r}, \vec{p}) = b_\lambda^0(\vec{r}, \vec{p}) + B \sum_\gamma \beta_{\lambda\gamma}^{(1)} b_\lambda^0(\vec{r}, \vec{p}) + B^2 \sum_\gamma \beta_{\lambda\gamma}^{(2)} b_\gamma^0(\vec{r}, \vec{p}) + \dots , \tag{34}$$

and can easily be obtained from the work in WU. $V^0(\vec{p}, \vec{q})_{\lambda\lambda'}$ can also be written as

$$V^0(\vec{p}, \vec{q})_{\lambda\lambda'} = \sum_{\vec{v}} e^{(2i/\hbar)\vec{p}\cdot\vec{v}} \langle a_\lambda^0(\vec{r} - (\vec{q} - \vec{v})) V_I(\vec{r}) a_{\lambda'}^0(\vec{r} - (\vec{q} + \vec{v})) \rangle , \tag{35}$$

where $a_\lambda^0(\vec{r} - \vec{q})$ is the Wannier function in the absence of the magnetic field. Note that for a free-electron-band model $V^0(\vec{p}, \vec{q})_{\lambda\lambda'} = V_I(\vec{q})$. All summations over lattice points $\vec{q}, \vec{v}$ and crystal momentum $\vec{p}, \vec{u}$ (limited to the first Brillouin zone) may be replaced by appropriate integrals.

III. EXPRESSION FOR χ TO ORDER $\hbar^2$ VALID FOR GENERAL NONDEGENERATE BLOCH BANDS AND ARBITRARY STRENGTH OF THE IMPURITY POTENTIAL

The calculation of χ using Eqs. (18) and (24) is straightforward and is based on the assumption that $H(\vec{p}, \vec{q})$ is nearly diagonal in bands (Appendix C) and the final result for $\Delta\chi$, the change of the magnetic susceptibility of the crystalline solid due to the presence of impurity centers, may be written

$$\Delta\chi = N_I(\chi - \chi_0) , \tag{36}$$

where N_I is the number of impurity centers, χ_0 is the magnetic susceptibility of the pure crystal host, and χ is given by the following formula:

$$\begin{aligned}\chi = -\frac{\tilde{\mathrm{T}}\mathrm{r}}{V}\left(\frac{1}{h}\right)^3 \int d^3p\, d^3q \Bigg(&\frac{\partial f(\Sigma^0)}{\partial \Sigma^0}(\Sigma^{(1)})^2 + f(\Sigma^0)\Sigma^{(2)} - \frac{\hbar^2}{48}\Bigg\{ \frac{\partial f(\Sigma^0)}{\partial \Sigma^0}\Bigg(\left[\frac{\partial^2 \Sigma^{(2)}}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{q}}\right] + 2\left[\frac{\partial^2 \Sigma^{(1)}}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 V^{(1)}}{\partial\vec{q}\partial\vec{q}}\right] \\ &+ \left[\frac{\partial^2 \Sigma^0}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 \Sigma^{(2)}}{\partial\vec{q}\partial\vec{q}}\right] - \left[\frac{\partial^2 \Sigma^{(2)}}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{p}}\right] - 2\left[\frac{\partial^2 \Sigma^{(1)}}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 \Sigma^{(1)}}{\partial\vec{q}\partial\vec{p}}\right] - \left[\frac{\partial^2 V^0}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 \Sigma^{(2)}}{\partial\vec{q}\partial\vec{p}}\right]\Bigg) \\ &+ \Sigma^{(2)}\frac{\partial^2 f(\Sigma^0)}{\partial(\Sigma^0)^2}\left(\left[\frac{\partial^2 \Sigma^0}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{q}}\right] - \left[\frac{\partial^2 V^0}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{p}}\right]\right) + (\Sigma^{(1)})^2 \frac{\partial^3 f(\Sigma^0)}{\partial(\Sigma^0)^3}\left(\left[\frac{\partial^2 \Sigma^0}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{q}}\right] - \left[\frac{\partial^2 V^0}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{p}}\right]\right) \\ &+ 2\Sigma^{(1)}\frac{\partial^2 f(\Sigma^0)}{\partial(\Sigma^0)^2}\left(\left[\frac{\partial^2 \Sigma^{(1)}}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{q}}\right] + \left[\frac{\partial^2 \Sigma^0}{\partial\vec{p}\partial\vec{p}}; \frac{\partial^2 V^{(1)}}{\partial\vec{q}\partial\vec{q}}\right] - \left[\frac{\partial^2 \Sigma^{(1)}}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 V^0}{\partial\vec{q}\partial\vec{p}}\right] - \left[\frac{\partial^2 V^0}{\partial\vec{p}\partial\vec{q}}; \frac{\partial^2 \Sigma^{(1)}}{\partial\vec{q}\partial\vec{p}}\right]\right)\Bigg\}\Bigg) .\end{aligned} \tag{37}$$

The various quantities entering in the above expression are defined as follows (for magnetic field in the z direction using a symmetric gauge): $f(x)$ is the Fermi-Dirac distribution function,

$$\Sigma^0 = W^0(\vec{p}) + V^0(\vec{p}, \vec{q}) , \tag{38}$$

$$\Sigma^{(1)} = (e/2c)(\vec{q} \times \nabla_p)_z W^0(\vec{p}) + W^{(1)}(\vec{p}) + V^{(1)}(\vec{p}, \vec{q}) , \tag{39}$$

$$\Sigma^{(2)} = (e/2c)^2(\vec{q} \times \nabla_p)_z(\vec{q} \times \nabla_p)_z W^0(\vec{p}) + (e/c)(\vec{q} \times \nabla_p)_z W^{(1)}(\vec{p}) + 2W^{(2)}(\vec{p}) + 2V^{(2)}(\vec{p}, \vec{q}) . \tag{40}$$

For simplicity[16] one may take $V^0(\vec{p},\vec{q})_{\lambda\lambda'} = V_\lambda^0(\vec{p},\vec{q})\delta_{\lambda\lambda'}$, making Σ^0 diagonal in bands.

Various well-known limiting cases can be obtained from Eq. (37). Thus for the case $V_I(\vec{r}) \to 0$ one can easily derive from Eq. (37) the result in WU and that of Roth[5] for Bloch electrons without and with spin-orbit coupling, respectively. Other limiting cases discussed by Hebborn and Scannes[8] can also easily be obtained from Eq. (37). For the general Bloch bands and arbitrary strength of the impurity potential, there are corrections to Eq. (37) that arise from the fourth- and higher-order (even) Poisson brackets[11] multiplied by $\hbar^4$ and $(\hbar^2)^l$, respectively, in the expansion for $\mathrm{Tr}\mathcal{H}^n$ in powers of $\hbar^2$. Equation (37) should provide a very reasonable approximation in most cases; it has the novel features of being transparent and of being valid to all orders in the impurity potential for general nondegenerate Bloch bands. Section IV discusses an immediate success of the present theory as applied to dilute alloys of copper.

IV. APPLICATION TO A FREE-ELECTRON-BAND MODEL OF DILUTE ALLOYS OF COPPER

For the case of the free-electron-band model and arbitrary strength of the impurity potential, Eq. (37) yields a result which is exact up to the second-order derivative of $V_I(\vec{q})$, the corrections just mentioned above being of order $\hbar^4$ multiplied by an integral involving $(\nabla^2/m)(\nabla^2/m)V_I(\vec{q})$. We will show that in the free-electron-band model Eq. (37) gives a firm theoretical foundation of the theory of Henry and Rogers[1,7] which accounts quite well for their experimental results for various solutes in copper. This is in marked contrast to the theory of Kohn and Luming[7] which fails to justify the formula for $\Delta\chi$ per solute atom used by Henry and Rogers.

For free electrons, we have (see Appendix B)

$$\Sigma^0 = p^2/2m + V_I(\vec{q}) , \quad (41)$$

$$\Sigma^{(1)} = (e/2mc)(\vec{q}\times\vec{p})_z + \mu_B\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} , \quad (42)$$

$$\Sigma^{(2)} = (e/2c)^2(1/m)(q_x^2+q_y^2) , \quad (43)$$

and Eq. (37) reduces to

$$\chi = \chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 , \quad (44)$$

where

$$\chi_1 = \frac{-2h^{-3}}{V}\int d^3p\, d^3q\, f'(\Sigma^0)\left[\left(\frac{e}{2mc}L_z\right)^2 + \mu_B^2\right] , \quad (45)$$

$$\chi_2 = \frac{-2h^{-3}}{V}\int d^3p\, d^3q \frac{e^2}{4mc^2}(q_x^2+q_y^2) f(\Sigma^0) , \quad (46)$$

$$\chi_3 = \frac{2h^{-3}}{V}\int d^3p\, d^3q\, \tfrac{1}{3} f'(\Sigma^0)\mu_B^2 , \quad (47)$$

$$\chi_4 = \frac{2h^{-3}}{24V}\int d^3p\, d^3q\, f'''(\Sigma^0)\frac{\hbar^2\nabla^2}{m}V_I(\vec{q}) \times\left[\left(\frac{e}{2mc}L_z\right)^2 + \mu_B^2\right] , \quad (48)$$

$$\chi_5 = \frac{2h^{-3}}{24V}\int d^3p\, d^3q\, f''(\Sigma^0)\frac{\hbar^2\nabla^2}{m}V_I(\vec{q})\frac{e^2}{4mc^2}(q_x^2+q_y^2) , \quad (49)$$

where factors of 2 in front of integrals account for the ± spin band. We note that for $V_I(\vec{q}) = 0$, we have $\chi = \chi_0 = \chi_{spin}(0) + \chi_{orb}(0)$ where

$$\chi_{orb}(0) = \frac{2}{3}\frac{h^{-3}}{V}\int d^3p\, d^3q\, f'\left(\frac{p^2}{2m}\right)\mu_B^2 , \quad (50)$$

$$\chi_{spin}(0) = \frac{-2h^{-3}}{V}\int d^3p\, d^3q\, f'\left(\frac{p^2}{2m}\right)\mu_B^2 . \quad (51)$$

In view of Eqs. (45), (47), and (48), and Eqs. (50) and (51), we can write for an arbitrary strength of $V_I(\vec{q})$

$$\Delta\chi_{orb} = \chi_{orb}(0)\Delta g_1/g , \quad (52)$$

$$\Delta\chi_{spin} = \chi_{spin}(0)\Delta g_2/g , \quad (53)$$

where

$$g = \frac{2h^{-3}}{V}\int d^3p\, d^3q\, f'\left(\frac{p^2}{2m}\right) , \quad (54)$$

$$\Delta g_1 = \frac{2h^{-3}}{V}\int d^3p\, d^3q\left[f'(\Sigma^0) - f'\left(\frac{p^2}{2m}\right)\right] , \quad (55)$$

$$\Delta g_2 = \Delta g_1 + \frac{2}{24}\frac{h^{-3}}{V}\int d^3p\, d^3q\, f'''(\Sigma^0)\frac{\hbar^2\nabla^2}{m}V_I(\vec{q}) . \quad (56)$$

By writing $(L_z) = (\vec{q}\times\vec{p})_z^2 = q_x^2p_y^2 - 2q_xq_yp_xp_y + q_y^2p_x^2$ and integrating with respect to $\vec{p}$, the first terms of χ_1 and χ_4 can be combined with χ_2 and χ_5, resulting in the expression for $\Delta\chi$ per solute atom as

$$\Delta\chi = -\frac{e^2}{6mc^2}\int d^3q\,\Delta\rho(\vec{q})|\vec{q}|^2 + \chi_{orb}(0)\Delta g_1/g + \chi_{spin}(0)\Delta g_2/g , \quad (57)$$

where

$$\Delta\rho(\vec{q}) = \frac{2h^{-3}}{V}\int d^3p\left\{\left[f(\Sigma^0) + \tfrac{1}{24}f''(\Sigma^0)\frac{\hbar^2\nabla^2}{m}V_I(\vec{q}) - f\left(\frac{p^2}{2m}\right)\right] + \left[f'(\Sigma^0) + \tfrac{1}{24}f'''(\Sigma^0)\frac{\hbar^2\nabla^2}{m}V_I(\vec{q}) - f'\left(\frac{p^2}{2m}\right)\right]\frac{p^2}{3m}\right\} . \quad (58)$$

Equation (57), with $\Delta g_1 = \Delta g_2$ and a similar consistent approximation for $\Delta\rho(\vec{q})$, is exactly the expression used by Henry and Rogers,[1] as pointed out by Kohn and Luming,[7] in analyzing their data on dilute alloys of Zn, Ga, Ge, and As with Cu which accounts quite well for their experimental results.

Thus the use of Eq. (57) by Henry and Rogers, as pointed out by Kohn and Luming,[7] is given a firm theoretical foundation. Here lies the essential discrepancy between Eq. (57) and the theory of Kohn and Luming.[7] We believe that the copper conduction electron can be approximately described by a free-electron-band model and Eq. (37) should provide a good approximation for copper as used by Henry and Rogers. On the other hand, the theory presented by Kohn and Luming[7] does not contain the entire expression for $\Delta\chi$ per solute atom used by Henry and Rogers.

V. DISCUSSION

We would like to summarize the approximation used in deriving Eq. (37). The final expression for χ rests on the assumption that $H(\vec{p},\vec{q})$ is a matrix which is nearly diagonal in bands and the noncommutivity of $H(\vec{p},\vec{q})$ with its derivatives gives correction of higher order than $\hbar^2$ in Eq. (24). However, all the results are exact if a diagonal $H(\vec{p},\vec{q})$ is used, which in principle can always be found by the method of successive unitary transformations in the manner used by Blount[11,17] and Suttorp and de Groot.[18] The nondiagonality of $H(\vec{p},\vec{q})$ as used here occurs only in the Weyl transform of the impurity potential $V_{\lambda\lambda'}(\vec{p},\vec{q})$ since the basis states used are the magnetic Wannier function and magnetic Bloch function. Their use allows us to express all features of the theory in terms of the field-free quantities in a fairly straightforward manner. The result based on the approximate diagonality of $V_{\lambda\lambda'}(\vec{p},\vec{q})$ is a reasonable approximation in most cases; for example, in the absence of the magnetic field the assumption that matrix elements of the impurity potential between two Wannier functions are diagonal in band is not uncommon.[16] For a one-electron-band model such as discussed in Sec. IV, this approximation is irrelevant.

We conclude that the present theory has all the important elements of an exact theory, and higher-order corrections can possibly be handled by parametrization in actual calculation for χ. It would be very interesting to see if the Weyl-Wigner formulation as used here can be employed to unify the treatment of the magnetic susceptibility of magnetic and nonmagnetic alloys. No work has been started in this direction.

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APPENDIX A: MAGNETIC WANNIER FUNCTION AND MAGNETIC BLOCH FUNCTION

In this Appendix we will give the derivation of the Wannier function and Bloch function in a uniform magnetic field as a series expansion in powers of the magnetic field strength B. The result is given up to second order in B. This allows us to express all the features of the theory in terms of field-free quantities and could serve as a basis for a real and detailed calculation of the magnetic susceptibility of dilute alloys. We choose the symmetric gauge for the vector potential, $\vec{A}=\frac{1}{2}\vec{B}\times\vec{r}$.

We will consider nondegenerate bands, as spin degeneracy with and without spin-orbit coupling does not present any new difficulties since these problems can be treated formally, exactly as in the spinless case.[11] Following Wannier[9] the periodic part $u_\lambda(\vec{r},\vec{p})$ of the modified Bloch function $b_\lambda(\vec{r},\vec{p})$ [we reserve the name magnetic Bloch function for $B_\lambda(\vec{r},\vec{p})$ defined below] satisfies the following equation:

$$[\mathcal{H}+V(\vec{r})]u_\lambda(\vec{r},\vec{p})=\sum_{\vec{q}'} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda(\vec{q})\times u_\lambda(\vec{r},\vec{p}+(e/2c)\vec{B}\times\vec{q}) , \quad \text{(A1)}$$

where

$$\mathcal{H}=\frac{1}{2m}\left(\frac{\hbar}{i}\vec{\nabla}+\hbar\vec{k}-\frac{1}{2}\frac{e}{c}\vec{B}\times i\frac{\partial}{\partial\vec{k}}\right)^2 .$$

The magnetic Bloch function $B_\lambda(\vec{r},\vec{p})$ is then related to the modified Bloch function $b_\lambda(\vec{r},\vec{p})$ by the relation

$$B_\lambda(\vec{r},\vec{p})=e^{i\vec{k}\cdot\vec{r}}u_\lambda(\vec{r},\vec{p}-\tfrac{1}{2}(e/c)\vec{B}\times\vec{r}) . \quad \text{(A2)}$$

Indeed, for $B=0$, Eq. (A1) is the equation for the periodic part of a Bloch function. From Eq. (A1) a power-series expansion in B for $u_\lambda(\vec{r},\vec{p})$ and $W_\lambda(\vec{q})$ can be obtained. Writing

$$\mathcal{H}=\mathcal{H}^0+B\mathcal{H}^{(1)}+B^2\mathcal{H}^2 , \quad \text{(A3)}$$

$$u_\lambda(\vec{r},\vec{p})=u_\lambda^0(\vec{r},\vec{p})+Bu_\lambda^{(1)}(\vec{r},\vec{p})+B^2u_\lambda^{(2)}(\vec{r},\vec{p})+\ldots , \quad \text{(A4)}$$

$$W_\lambda(\vec{q})=W_\lambda^0(\vec{q})+BW^{(1)}(\vec{q})+B^2W^{(2)}(\vec{q})+\ldots , \quad \text{(A5)}$$

$$u_\lambda(\vec{r},\vec{p}+(e/2c)\vec{B}\times\vec{q})=\exp\left(\frac{e}{2\hbar c}\vec{B}\times\vec{q}\cdot\frac{\partial}{\partial\vec{k}}\right)u_\lambda(\vec{r},\vec{p}) , \quad \text{(A6)}$$

substituting in Eq. (A1) and equating coefficient of powers of B on both sides, we obtain the following equation:

$$\mathcal{H}^0u_\lambda^0(\vec{r},\vec{p})=\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda(\vec{q})u_\lambda^0(\vec{r},\vec{p}) , \quad \text{(A7)}$$

$$\left(\mathcal{H}^0-\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^0(\vec{q})\right)u_\lambda^{(1)}(\vec{r},\vec{p})=-\mathcal{H}^{(1)}u_\lambda^0(\vec{r},\vec{p})+\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^0(\vec{q})\left(\frac{e}{2\hbar c}\hat{z}\times\vec{q}\cdot\frac{\partial}{\partial\vec{k}}u_\lambda^0(\vec{r},\vec{p})\right)+\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^{(1)}(\vec{q})u_\lambda^0(\vec{r},\vec{p}) , \quad \text{(A8)}$$

$$\left(\mathcal{H}^0-\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^0(\vec{q})\right)u_\lambda^{(2)}(\vec{r},\vec{p})=-\mathcal{H}^{(1)}u_\lambda^{(1)}(\vec{r},\vec{p})-\mathcal{H}^{(2)}u_\lambda^0(\vec{r},\vec{p})+\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^0(\vec{q})\left[\frac{e}{2\hbar c}\hat{z}\times\vec{q}\cdot\frac{\partial}{\partial\vec{k}}u_\lambda^{(1)}(\vec{r},\vec{p})+\frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\left(\hat{z}\times\vec{q}\cdot\frac{\partial}{\partial\vec{k}}\right)^2u_\lambda^0(\vec{r},\vec{p})\right]+\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^{(1)}(\vec{q})\left[u_\lambda^{(1)}(\vec{r},\vec{p})+\left(\frac{e}{2\hbar c}\right)\hat{z}\times\vec{q}\cdot\frac{\partial}{\partial\vec{k}}u_\lambda^0(\vec{r},\vec{p})\right]+\sum_{\vec{q}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}W_\lambda^{(2)}(\vec{q})u_\lambda^0(\vec{r},\vec{p}) . \quad \text{(A9)}$$

We are here only interested in $u_\lambda^{(1)}(\vec{r},\vec{p})$ and $u_\lambda^{(2)}(\vec{r},\vec{p})$. $W_\lambda^{(1)}(\vec{p})$ and $W_\lambda^{(2)}(\vec{p})$ have been given in WU. We have for $\delta\neq\lambda$

$$\langle u_\delta^{0*}|u_\lambda^{(1)}\rangle=-\frac{1}{W_\delta^0-W_\lambda^0}\langle u_\delta^{0*}W_{op}^{(1)}u_\lambda^0\rangle , \quad \text{(A10)}$$

$$\langle u_\delta^{0*}|u_\lambda^{(2)}\rangle = -\frac{1}{W_\delta^0 - W_\lambda^0}\left[\langle u_\delta^{0*}W_{\rm op}^{(1)}u_\lambda^{(1)}\rangle + \frac{e^2}{8mc^2}\left\langle u_\delta^{0*}\left(1-\frac{m}{\hbar^2}\frac{\partial^2 W_\lambda^0}{\partial k_x^2}\right)\eta^2 + \left(1-\frac{m}{\hbar^2}\frac{\partial^2 W_\lambda^0}{\partial k_y^2}\right)\xi^2 + 2\frac{m}{\hbar^2}\frac{\partial W_\lambda^0}{\partial k_x \partial k_y}\eta\xi u_\lambda^0\right\rangle\right.$$
$$\left. - W^{(1)}(\vec{p})\langle u_\delta^{0*}|u_\lambda^{(1)}\rangle + \frac{e}{2\hbar c}\hat{z}\cdot\frac{\partial}{\partial\vec{k}}W^{(1)}(\vec{p})\times\left\langle u_\delta^{0*} i\frac{\partial}{\partial\vec{k}}u_\lambda^0\right\rangle\right], \tag{A11}$$

where

$$W_{\rm op}^{(1)} = \hat{z}\cdot\left(\frac{\hbar}{i}\vec{\nabla} + \hbar\vec{k} + \frac{m}{\hbar}\frac{\partial W_\lambda^0}{\partial\vec{k}}\right)\times i\frac{\partial}{\partial\vec{k}},$$

$$\eta = i\frac{\partial}{\partial k_y}, \quad \xi = i\frac{\partial}{\partial k_x},$$

$$W_\lambda^{(1)}(\vec{p}) = \langle u_\lambda^0 W_{\rm op}^{(1)} u_\lambda^0\rangle .$$

For $\delta=\lambda$, $\langle u_\lambda^{0*}|u_\lambda^{(1)}\rangle$ and $\langle u_\lambda^{0*}|u_\lambda^{(2)}\rangle$ are determined by the requirement that the magnetic Wannier function $A_\lambda(\vec{r},\vec{q})$ be orthonormal. We write explicitly

$$A_\lambda(\vec{r},\vec{q}) = \exp[-\tfrac{1}{2}(ie/\hbar c)\vec{B}\cdot\vec{r}\times\vec{q}]a_\lambda(\vec{r}-\vec{q}), \tag{A12}$$

$$a_\lambda(\vec{r}-\vec{q}) = (N\hbar^3)^{-1}\sum_{\vec{p}} e^{(i/\hbar)\vec{p}\cdot\vec{q}}b_\lambda(\vec{r},\vec{p}), \tag{A13}$$

$$b_\lambda(\vec{r},\vec{p}) = e^{i\vec{k}\cdot\vec{r}}u_\lambda(\vec{r},\vec{p}). \tag{A14}$$

The orthonormality condition is expressed by

$$\int \exp\left(\frac{1}{2}\frac{ie}{\hbar c}\vec{B}\times\vec{r}\cdot(\vec{q}'-\vec{q})\right)a_\lambda^*(\vec{r}-\vec{q}')a_\lambda(\vec{r}-\vec{q})\,d^3r = \delta_{\vec{q}\vec{q}'}. \tag{A15}$$

Expanding all quantities in powers of B, we obtain the following relation:

$$\langle a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle = \delta_{\vec{q}\vec{q}'}, \tag{A16}$$

$$\langle a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^{(1)}(\vec{r}-\vec{q}) + a_\lambda^{(1)*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle + \tfrac{1}{2}(ie/\hbar c)\langle(\hat{z}\times\vec{r})\cdot(\vec{q}'-\vec{q})a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle = 0, \tag{A17}$$

$$\langle a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^{(2)}(\vec{r}-\vec{q}) + a_\lambda^{(1)*}(\vec{r}-\vec{q}')a_\lambda^{(1)}(\vec{r}-\vec{q}) + a_\lambda^{(2)*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle + \tfrac{1}{2}(ie/\hbar c)\langle\hat{z}\times\vec{r}\cdot(\vec{q}'-\vec{q})$$
$$\times[a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^{(1)}(\vec{r}-\vec{q}) + a_\lambda^{(1)*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})]\rangle - (1/2!)(e/2\hbar c)^2\langle[\hat{z}\times\vec{r}\cdot(\vec{q}'-\vec{q})]^2 a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle = 0. \tag{A18}$$

$\langle u_\lambda^{0*}|u_\lambda^{(1)}\rangle$ is determined from Eq. (A17) and this was already obtained in WU. Their result is

$$\langle u_\lambda^{0*}|u_\lambda^{(1)}\rangle = \frac{1}{4}\frac{e}{\hbar c}\left(\frac{\partial X_\lambda}{\partial k_y} - \frac{\partial Y_\lambda}{\partial k_x}\right), \tag{A19}$$

where X_λ and Y_λ are the diagonal elements of the Adams operator. We will show here in more detail the derivation of $\langle u_\lambda^{0*}|u_\lambda^{(2)}\rangle$.

We multiply Eq. (A18) by $e^{(i/\hbar)\vec{p}\cdot(\vec{q}-\vec{q}')}$ and sum over $\vec{q}$ and $\vec{q}'$. We obtain

$$\langle b_\lambda^{0*}b_\lambda^{(2)} + b_\lambda^{(1)*}b_\lambda^{(1)} + b_\lambda^{(2)*}b_\lambda^0\rangle + \frac{1}{2}\frac{ie}{\hbar c}\sum_{\vec{q}\vec{q}'} e^{(i/\hbar)\vec{p}\cdot(\vec{q}-\vec{q}')}\langle\hat{z}\times\vec{r}\cdot(\vec{q}'-\vec{q})[a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^{(1)}(\vec{r}-\vec{q}) + a_\lambda^{(1)*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})]\rangle$$
$$-\frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\sum_{\vec{q}\vec{q}'} e^{(i/\hbar)\vec{p}\cdot(\vec{q}-\vec{q}')}\langle[\hat{z}\times\vec{r}\cdot(\vec{q}'-\vec{q})]^2 a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle = 0. \tag{A20}$$

Writing $\hat{z}\times\vec{r}\cdot(\vec{q}'-\vec{q}) = \hat{z}\cdot[(\vec{r}-\vec{q}')\times(\vec{r}-\vec{q}) - \vec{q}'\times\vec{q}]$ and using Eqs. (A16) and (A17), the last two terms in Eq. (A20) can be combined to give

$$\langle b_\lambda^{0*}b_\lambda^{(2)} + b_\lambda^{(2)*}b_\lambda^0\rangle = -\langle b_\lambda^{(1)*}b_\lambda^{(1)}\rangle - \frac{1}{2}\frac{ie}{\hbar c}\sum_{\vec{q}\vec{q}'} e^{(i/\hbar)\vec{p}\cdot(\vec{q}-\vec{q}')}\langle\hat{z}\cdot(\vec{r}-\vec{q}')\times(\vec{r}-\vec{q})[a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^{(1)}(\vec{r}-\vec{q}) + a_\lambda^{(1)*}(\vec{r}-\vec{q}')$$
$$\times a_\lambda^0(\vec{r}-\vec{q})]\rangle + \frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\sum_{\vec{q}\vec{q}'} e^{(i/\hbar)\vec{p}\cdot(\vec{q}-\vec{q}')}\langle[\hat{z}\cdot(\vec{r}-\vec{q}')\times(\vec{r}-\vec{q})]^2 a_\lambda^{0*}(\vec{r}-\vec{q}')a_\lambda^0(\vec{r}-\vec{q})\rangle. \tag{A21}$$

Changing the multiplier operators $\vec{r}-\vec{q}'$ and $\vec{r}-\vec{q}$ to the Adams operators $\vec{r}-i(\partial/\partial\vec{k})$ and $\vec{r}+i(\partial/\partial\vec{k})$, respectively, carrying the summation over $\vec{q}$ and $\vec{q}'$, and using the relation $\vec{r}+i(\partial/\partial\vec{k})e^{i\vec{k}\cdot\vec{r}}u_\lambda(\vec{r},\vec{p}) = e^{i\vec{k}\cdot\vec{r}}i(\partial/\partial\vec{k})u_\lambda(\vec{r},\vec{p})$, we obtain the following:

$$\langle u_\lambda^{0*}u_\lambda^{(2)} + u_\lambda^{(2)*}u_\lambda^0\rangle = -\langle u_\lambda^{(1)*}u_\lambda^{(1)}\rangle - \frac{1}{2}\left(\frac{ie}{\hbar c}\right)\left(\left\langle -i\frac{\partial}{\partial k_x}u_\lambda^{0*}\middle| i\frac{\partial}{\partial k_y}u_\lambda^{(1)}\right\rangle - \left\langle -i\frac{\partial}{\partial k_y}u_\lambda^{0*}\middle| i\frac{\partial}{\partial k_x}u_\lambda^0\right\rangle + \left\langle -i\frac{\partial}{\partial k_x}u_\lambda^{(1)*}\middle| i\frac{\partial}{\partial k_y}u_\lambda^0\right\rangle\right.$$
$$\left. - \left\langle -i\frac{\partial}{\partial k_y}u_\lambda^{(1)*}\middle| i\frac{\partial}{\partial k_x}u_\lambda^0\right\rangle\right) + \frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\left(\left\langle\frac{\partial^2}{\partial k_x^2}u_\lambda^{0*}\middle|\frac{\partial^2}{\partial k_y^2}u_\lambda^0\right\rangle\right.$$
$$\left. + \left\langle\frac{\partial^2}{\partial k_y^2}u_\lambda^{0*}\middle|\frac{\partial^2}{\partial k_x^2}u_\lambda^0\right\rangle - 2\left\langle\frac{\partial^2}{\partial k_x\partial k_y}u_\lambda^{0*}\middle|\frac{\partial^2}{\partial k_x\partial k_y}u_\lambda^0\right\rangle\right). \tag{A22}$$

The left-hand side can easily be cast into an obviously real expression, and Eq. (A22) can be written as

$$\langle u_\lambda^{0*}u_\lambda^{(2)}+u_\lambda^{(2)*}u_\lambda^0\rangle=-\langle u_\lambda^{(1)*}u_\lambda^{(1)}\rangle-\left(\frac{e}{2\hbar c}\right)\frac{\partial}{\partial k_x}\left(\left\langle -i\frac{\partial}{\partial k_y}u_\lambda^{0*}\middle|u_\lambda^{(1)}\right\rangle+\left\langle u_\lambda^{(1)*}\middle|i\frac{\partial}{\partial k_y}u_\lambda^0\right\rangle\right)+\left(\frac{e}{2\hbar c}\right)\frac{\partial}{\partial k_y}\left(\left\langle -i\frac{\partial}{\partial k_x}u_\lambda^{0*}\middle|u_\lambda^{(1)}\right\rangle\right.$$
$$\left.+\left\langle u_\lambda^{(1)*}\middle|i\frac{\partial}{\partial k_x}u_\lambda^0\right\rangle\right)+\frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\left[\frac{\partial^2}{\partial k_x\partial k_y}\left(\left\langle -i\frac{\partial}{\partial k_x}u_\lambda^{0*}\middle|i\frac{\partial}{\partial k_y}u_\lambda^0\right\rangle+\left\langle -i\frac{\partial}{\partial k_y}u_\lambda^{0*}\middle|i\frac{\partial}{\partial k_x}u_\lambda^0\right\rangle\right)\right.$$
$$\left.-\frac{\partial^2}{\partial k_x^2}\left\langle -i\frac{\partial}{\partial k_y}u_\lambda^{0*}\middle|i\frac{\partial}{\partial k_y}u_\lambda^0\right\rangle-\frac{\partial^2}{\partial k_y^2}\left\langle -i\frac{\partial}{\partial k_x}u_\lambda^{0*}\middle|i\frac{\partial}{\partial k_x}u_\lambda^0\right\rangle\right] \quad . \tag{A23}$$

Denoting $\beta_{\lambda\delta}^{(1)}=\langle u_\lambda^{0*}\,|\,u_\delta^{(1)}\rangle$ and $\beta_{\lambda\delta}^{(2)}=\langle u_\lambda^{0*}\,|\,u_\lambda^{(2)}\rangle$ and substituting the expression for $u_\lambda^{(1)}$ in Eq. (A23),

$$u_\lambda^{(1)}=\sum_\delta \beta_{\delta\lambda}^{(1)}u_\delta^0\ , \tag{A24}$$

we finally obtain the expression for $u_\lambda^{(2)}$ in terms of field-free quantities

$$u_\lambda^{(2)}=\sum_\delta \beta_{\delta\lambda}^{(2)}u_\delta^0\ , \tag{A25}$$

where for $\delta\neq\lambda$, $\beta_{\delta\lambda}^{(2)}$ is given by Eq. (A11) and

$$\beta_{\lambda\lambda}^{(2)}=\frac{1}{2}\left[-\sum_\delta|\beta_{\delta\lambda}|^2-\frac{e}{2\hbar c}\frac{\partial}{\partial k_x}\left(\sum_\delta\beta_{\lambda\delta}^{(1)}\langle\lambda|Y|\delta\rangle+\beta_{\lambda\delta}^{(1)*}\langle\delta|Y|\lambda\rangle\right)+\frac{e}{2\hbar c}\frac{\partial}{\partial k_y}\left(\sum_\delta\beta_{\lambda\delta}^{(1)}\langle\lambda|X|\delta\rangle+\beta_{\lambda\delta}^{(1)*}\langle\delta|X|\lambda\rangle\right)\right.$$
$$\left.+\frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\left(\frac{\partial^2}{\partial k_x\partial k_y}\langle\lambda X|Y\lambda\rangle-\frac{\partial^2}{\partial k_x^2}\langle\lambda Y|Y\lambda\rangle-\frac{\partial^2}{\partial k_y^2}\langle\lambda X|X\lambda\rangle\right)\right]\ , \tag{A26}$$

where X and Y are the Adams coordinate operator.

APPENDIX B: WEYL TRANSFORM OF THE HAMILTONIAN FOR BLOCH ELECTRONS AND IMPURITY POTENTIAL IN A UNIFORM MAGNETIC FIELD

Let us write the total Hamiltonian as

$$\mathcal{H}=\mathcal{H}_M+V_I(\vec{r})\ , \tag{B1}$$

where

$$\mathcal{H}_M=\frac{1}{2m}\left(\frac{\hbar}{i}\vec\nabla-\frac{e}{c}\vec{A}(\vec r)\right)^2+V_p(\vec r)\ .$$

$V_p(\vec r)$ is the periodic crystal potential and $V_I(\vec r)$ is the impurity potential. Using the magnetic Wannier function $A_\lambda(\vec r,\vec q)$ the following relation holds for $\mathcal{H}_M$[9]:

$$\mathcal{H}_MA_\lambda(\vec r,\vec q)=\sum_{\vec q'}\exp\left(\frac{1}{2}\frac{ie}{\hbar c}\vec B\times\vec q\cdot\vec q'\right)W_\lambda(\vec q-\vec q')A_\lambda(\vec r,\vec q')\ . \tag{B2}$$

The Weyl transform of $\mathcal{H}_M$ is

$$H_M(\vec p,\vec q)_{\lambda\lambda'}=\sum_{\vec v}e^{(2i/\hbar)\vec p\cdot\vec v}\langle A_\lambda^*(\vec r,\vec q-\vec v)\mathcal{H}_MA_{\lambda'}(\vec r,\vec q+\vec v)\rangle\ . \tag{B3}$$

Using Eq. (B2) and by virtue of the relation $(\vec q+\vec v)\times(\vec q-\vec v)=-2\vec q\times\vec v$, we obtain

$$H_M(\vec p,\vec q)_{\lambda\lambda'}=\sum_{\vec v}\exp\left[\frac{i}{\hbar}\left(\vec p-\frac{e}{2c}\vec B\times\vec q\right)\cdot2\vec v\right]W_{\lambda'}(2\vec v)\delta_{\lambda\lambda'}\ . \tag{B4}$$

Using the relation

$$W_{\lambda'}(2\vec v)=\frac{1}{N\hbar^3}\sum_{\vec p'}W_{\lambda'}(\vec p')e^{-(i/\hbar)\vec p'\cdot2\vec v}\ , \tag{B5}$$

we end up with

$$H_M(\vec p,\vec q)_{\lambda\lambda'}=\sum_{\vec v,\vec p'}\exp\left\{\frac{i}{\hbar}\left[\left(\vec p-\frac{e}{c}\vec A(\vec q)\right)-\vec p'\right]\cdot2\vec v\right\}\times\frac{1}{N\hbar^3}W_{\lambda'}(\vec p')\delta_{\lambda\lambda'}$$
$$=W_\lambda\left(\vec p-\frac{e}{c}\vec A(\vec q)\right)\delta_{\lambda\lambda'}\ . \tag{B6}$$

$W_{\lambda'}(K)$ is referred to as the renormalized energy-band function by Wannier. In the presence of spin-orbit coupling $W_{\lambda'}(K)$ is a 2×2 matrix and it is given by Roth.

We are left with the Weyl transform of the impurity potential $V_I(\vec r)$. Denoting this by $V_{\lambda\lambda'}(\vec p,\vec q)$, we have

$$V_{\lambda\lambda'}(\vec p,\vec q)=\sum_{\vec v}e^{(2i/\hbar)\vec p\cdot\vec v}\langle A_\lambda^*(\vec r,\vec q-\vec v)V_I(\vec r)A_{\lambda'}(\vec r,\vec q+\vec v)\rangle\ . \tag{B7}$$

It is convenient to derive the expression for $V_{\lambda\lambda'}(\vec p,\vec q)$ using magnetic Bloch function $B_\lambda(\vec r,\vec p)$

$$V_{\lambda\lambda'}(\vec p,\vec q)=\sum_{\vec u}e^{(2i/\hbar)\vec q\cdot\vec u}\langle B_\lambda^*(\vec r,\vec p+\vec u)V_I(\vec r)B_{\lambda'}(\vec r,\vec p-\vec u)\rangle\ . \tag{B8}$$

Using the relation (A2) we obtain

$$V_{\lambda\lambda'}(\vec p,\vec q)=\sum_{\vec u}e^{(2i/\hbar)\vec q\cdot\vec u}\phi_{\lambda\lambda'}(\vec p,\vec u,B)\ , \tag{B9}$$

where

$$\phi_{\lambda\lambda'}(\vec p,\vec u,B)=\langle e^{-(2i/\hbar)\vec u\cdot\vec r}\phi_{\lambda\lambda'}(\vec K+\vec u,\vec K-\vec u,\vec r)\rangle\ , \tag{B10}$$

$$\phi_{\lambda\lambda'}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})=u^*_\lambda(\vec{r},\vec{K}+\vec{u})V_I(\vec{r})u_{\lambda'}(\vec{r},\vec{K}-\vec{u})\,, \tag{B11}$$

$$\vec{K}=\vec{p}-(e/c)\vec{A}(\vec{r})\,. \tag{B12}$$

Substituting the expression for $u_\lambda(\vec{r},\vec{p})$ given by Eq. (A24) in Eq. (B11), we have

$$\begin{aligned}\phi_{\lambda\lambda'}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})={}&\phi^0_{\lambda\lambda'}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})+B\Big(\sum_\delta\beta^{(1)}_{\lambda'\delta}(\vec{K}-\vec{u})\phi^0_{\lambda\delta}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})+\sum_\delta\beta^{(1)*}_{\lambda\delta}(\vec{K}+\vec{u})\phi^0_{\delta\lambda'}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})\Big)\\&+B^2\Big(\sum_\delta\beta^{(2)}_{\lambda'\delta}(\vec{K}-\vec{u})\phi^0_{\lambda\delta}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})+\sum_\delta\beta^{(2)*}_{\lambda\delta}(\vec{K}+\vec{u})\phi_{\delta\lambda'}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})\\&+\sum_{\delta,\gamma}\beta^{(1)*}_{\lambda\delta}(\vec{K}+\vec{u})\beta^{(1)}_{\lambda'\gamma}(\vec{K}-\vec{u})\phi^0_{\delta\gamma}(\vec{K}+\vec{u},\vec{K}-\vec{u},\vec{r})\Big)+O(B^3)\,.\end{aligned} \tag{B13}$$

Expanding all quantities in powers of B up to second order and denoting $V_{\lambda\lambda'}(\vec{p},\vec{q})$ by

$$V_{\lambda\lambda'}(\vec{p},\vec{q})=V^0_{\lambda\lambda'}(\vec{p},\vec{q})+BV^{(1)}_{\lambda\lambda'}(\vec{p},\vec{q})+B^2V^{(2)}_{\lambda\lambda'}(\vec{p},\vec{q})+\dots\,, \tag{B14}$$

we have from Eq. (B9)

$$V^0_{\lambda\lambda'}(\vec{p},\vec{q})=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\phi^0_{\lambda\lambda'}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})\,, \tag{B15}$$

$$V^{(1)}_{\lambda\lambda'}(\vec{p},\vec{q})=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\Big(\Theta^{(1)}_{\lambda\lambda'}(\vec{p},\vec{u})+\sum_\delta\beta^{(1)}_{\lambda'\delta}(\vec{p}-\vec{u})\phi_{\lambda\delta}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})+\sum_\delta\beta^{(1)*}_{\lambda\delta}(\vec{p}+\vec{u})\phi^0_{\delta\lambda'}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})\Big)\,, \tag{B16}$$

$$\begin{aligned}V^{(2)}_{\lambda\lambda'}(\vec{p},\vec{q})=\sum_{\vec{u}}e^{(2i/\hbar)\vec{q}\cdot\vec{u}}\Big(&\Theta^{(2)}_{\lambda\lambda'}(\vec{p},\vec{u})+\sum_\delta\beta^{(2)}_{\lambda'\delta}(\vec{p}-\vec{u})\phi^0_{\lambda\delta}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})+\sum_\delta\beta^{(2)*}_{\lambda\delta}(\vec{p}+\vec{u})\phi^0_{\delta\lambda'}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})\\&+\sum_{\delta,\gamma}\beta^{(1)*}_{\lambda\delta}(\vec{p}+\vec{u})\beta^{(1)}_{\lambda'\gamma}(\vec{p}-\vec{u})\phi^0_{\delta\gamma}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})\Big)\,,\end{aligned} \tag{B17}$$

where

$$\Theta^{(1)}_{\lambda\lambda'}(\vec{p},\vec{u})=\int e^{-(2i/\hbar)\vec{u}\cdot\vec{r}}\Theta^{(1)}_{\lambda\lambda'}(\vec{p},\vec{u},\vec{r})\,d^3r\,, \tag{B18}$$

$$\Theta^{(2)}_{\lambda\lambda'}(\vec{p},\vec{u})=\int e^{-(2i/\hbar)\vec{u}\cdot\vec{r}}\Theta^{(2)}_{\lambda\lambda'}(\vec{p},\vec{u},\vec{r})\,d^3r\,, \tag{B19}$$

$$\phi^0_{\alpha\beta}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,2\vec{u})=\int e^{-(2i/\hbar)\vec{u}\cdot\vec{r}}\phi^0_{\alpha\beta}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,\vec{r})\,d^3r\,, \tag{B20}$$

$$\phi^0_{\alpha\beta}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,\vec{r})=u^{0*}_\alpha(\vec{r},\vec{p})V_I(\vec{r})u^0_\beta(\vec{r},\vec{p})\,, \tag{B21}$$

$$\Theta^{(1)}_{\lambda\lambda'}(\vec{p},\vec{u},\vec{r})=\lim_{\vec{p}'\to\vec{p}}\left(\frac{e}{2c}\right)\left[\left(\frac{\partial}{\partial p_x}+\frac{\partial}{\partial p'_x}\right)r_y-\left(\frac{\partial}{\partial p_y}+\frac{\partial}{\partial p'_y}\right)r_x\right]\phi^0_{\lambda\lambda'}(\vec{p}+\vec{u},\,\vec{p}'-\vec{u},\,\vec{r})\,, \tag{B22}$$

$$\begin{aligned}\Theta^{(2)}_{\lambda\lambda'}(\vec{p},\vec{u},\vec{r})={}&\lim_{\vec{p}'\to\vec{p}}\frac{1}{2!}\left(\frac{e}{2\hbar c}\right)^2\Bigg[\left(\frac{\partial^2}{\partial p_y^2}+2\frac{\partial^2}{\partial p_y\partial p'_y}+\frac{\partial^2}{\partial p'^2_y}\right)r_x^2-2\left(\frac{\partial^2}{\partial p_x\partial p_y}+\frac{\partial^2}{\partial p_x\partial p'_y}+\frac{\partial^2}{\partial p_y\partial p'_x}+\frac{\partial^2}{\partial p'_x\partial p'_y}\right)r_xr_y\\&+\left(\frac{\partial^2}{\partial p_x^2}+2\frac{\partial^2}{\partial p_x\partial p'_x}+\frac{\partial^2}{\partial p'^2_x}\right)r_y^2\Bigg]\phi^0_{\lambda\lambda'}(\vec{p}+\vec{u},\,\vec{p}'-\vec{u},\,\vec{r})+\sum_\delta\Gamma^{(-)}_{\lambda'\delta}(\vec{p},\vec{r})\phi^0_{\lambda\delta}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,\vec{r})\\&+\sum_\delta\beta^{(1)}_{\lambda'\delta}(\vec{p}-\vec{u})\Theta^{(1)}_{\lambda\delta}(\vec{p},\vec{u},\vec{r})+\sum_\delta\Gamma^{(+)*}_{\lambda\delta}(\vec{p},\vec{r})\phi^0_{\delta\lambda'}(\vec{p}+\vec{u},\,\vec{p}-\vec{u},\,\vec{r})+\sum_\delta\beta^{(1)*}_{\lambda\delta}(\vec{p}+\vec{u})\Theta^{(1)}_{\delta\lambda'}(\vec{p},\vec{u},\vec{r})\,,\end{aligned} \tag{B23}$$

$$\Gamma^{(\pm)}_{\alpha\gamma}(\vec{p},\vec{r})=\frac{e}{2c}\left(\frac{\partial}{\partial p_x}r_y-\frac{\partial}{\partial p_y}r_x\right)\beta^{(1)}_{\alpha\gamma}(\vec{p}\pm\vec{u})\,. \tag{B24}$$

For the one-electron-band model

$$V^0_{\lambda\lambda'}(\vec{p},\vec{q})=V_I(\vec{q})\delta_{\lambda\lambda'}\,, \tag{B25}$$

$$V^{(1)}_{\lambda\lambda'}(\vec{p},\vec{q})=0\,, \tag{B26}$$

$$V^{(2)}_{\lambda\lambda'}(\vec{p},\vec{q})=0\,. \tag{B27}$$

Equation (B25) can easily be seen by writing

$$V^0_{\lambda\lambda'}(\vec{p},\vec{q})=\sum_{\vec{v}}e^{(2i/\hbar)\vec{p}\cdot\vec{v}}\langle a^{0*}_\lambda(\vec{r}-(\vec{q}-\vec{v}))V_I(\vec{r})a^0_{\lambda'}(\vec{r}-(\vec{q}+\vec{v}))\rangle\,, \tag{B28}$$

and noting that for the free-electron case $a^0_\lambda(\vec{r}-\vec{q})$ is essentially a Dirac δ function.

APPENDIX C: DERIVATION OF THE SUSCEPTIBILITY χ

The expression for $\mathrm{Tr}\mathcal{H}^n$ given in Eq. (23) was obtained from an exact expression recently derived by the author which reads[12]

$$\mathrm{Tr}\mathcal{H}^n=(N\hbar^3)^{-1}\tilde{\mathrm{T}}\mathrm{r}\sum_{\vec{p},\vec{q}}\cos\left[\frac{\hbar}{2}\sum_{\substack{j,k=1\\ j<k}}^{n-1}\left(\frac{\partial^{(j)}}{\partial\vec{p}}\cdot\frac{\partial^{(k)}}{\partial\vec{q}}-\frac{\partial^{(j)}}{\partial\vec{q}}\cdot\frac{\partial^{(k)}}{\partial\vec{p}}\right)\right]$$
$$\times\tfrac{1}{2}[H^{(1)}(\vec{p},\vec{q})H^{(2)}(\vec{p},\vec{q})\cdots H^{(n)}(\vec{p},\vec{q})+H^{(n)}(\vec{p},\vec{q})H^{(n-1)}(\vec{p},\vec{q})\cdots H^{(1)}(\vec{p},\vec{q})]\ . \qquad (C1)$$

The combinatorics employed in evaluating $\mathrm{Tr}\mathcal{H}^n$ to order $\hbar^2$ is very similar to the one used in Ref. 13. This procedure almost wholly neglects the noncommutivity of the $H(\vec{p},\vec{q})$ matrix (whose elements are labeled by band indices) with its derivatives; however in the present formalism using the magnetic Wannier function and the magnetic Bloch function, $H(\vec{p},\vec{q})$ is nearly diagonal in bands for most purposes, the nondiagonality occurring only in the Weyl transform of $V_I(\vec{r})$ which is $V_{\lambda\lambda'}(\vec{p},\vec{q})$. The noncommutivity is estimated to give small corrections to the final results. This has been discussed in Sec. V. The final results are Eqs. (23) and (24) for $\mathrm{Tr}\mathcal{H}^n$ and $\mathrm{Tr}F(\mathcal{H})$, respectively. The magnetic susceptibility χ is obtained from Eq. (18), again neglecting the noncommutivity of $H(\vec{p},\vec{q})$ and $\partial H(\vec{p},\vec{q})/\partial B$ for the same reason mentioned above, and the result is

$$\chi=\lim_{B\to 0}-\frac{1}{V}\frac{\tilde{\mathrm{T}}\mathrm{r}}{N\hbar^3}\sum_{\vec{p},\vec{q}}\Bigg\{f'(H(\vec{p},\vec{q}))(\Omega^{(1)})^2+f(H(\vec{p},\vec{q}))\Omega^{(2)}-\frac{1}{2!}\left(\frac{\hbar}{2}\right)^2\frac{1}{6}\Bigg[f'(H(\vec{p},\vec{q}))\Bigg(\left[\frac{\partial^2\Omega^{(2)}}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]$$
$$+2\left[\frac{\partial^2\Omega^{(1)}}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2\Omega^{(1)}}{\partial\vec{q}\partial\vec{q}}\right]+\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2\Omega^{(2)}}{\partial\vec{q}\partial\vec{q}}\right]-\left[\frac{\partial^2\Omega^{(2)}}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{p}}\right]-2\left[\frac{\partial\Omega^{(1)}}{\partial\vec{p}\partial\vec{q}};\frac{\partial\Omega^{(1)}}{\partial\vec{q}\partial\vec{p}}\right]-\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2\Omega^{(2)}}{\partial\vec{q}\partial\vec{p}}\right]\Bigg)$$
$$+\Omega^{(2)}f''(H(\vec{p},\vec{q}))\Bigg(\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]-\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{p}}\right]\Bigg)+(\Omega^{(1)})^2 f'''(H(\vec{p},\vec{q}))\Bigg(\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]$$
$$-\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{p}}\right]\Bigg)+2\Omega^{(1)}f''(H(\vec{p},\vec{q}))\Bigg(\left[\frac{\partial\Omega^{(1)}}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{q}}\right]+\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{p}};\frac{\partial^2\Omega^{(1)}}{\partial\vec{q}\partial\vec{q}}\right]$$
$$-\left[\frac{\partial^2\Omega^{(1)}}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{q}\partial\vec{p}}\right]-\left[\frac{\partial^2 H(\vec{p},\vec{q})}{\partial\vec{p}\partial\vec{q}};\frac{\partial^2\Omega^{(1)}}{\partial\vec{q}\partial\vec{p}}\right]\Bigg)\Bigg]\Bigg\}\ , \qquad (C2)$$

where

$$\Omega^{(1)}=\frac{dH(\vec{p},\vec{q})}{dB}=\frac{e}{2c}\frac{\partial W}{\partial K_\alpha}e_{\alpha zj}q_j+W^{(1)}+2BW^{(2)}+V^{(1)}+2BV^{(2)}\ , \qquad (C3)$$

$$\Omega^{(2)}=\left(\frac{e}{2c}\right)^2\frac{\partial^2 W}{\partial K_\alpha\partial K_\beta}e_{\beta zi}q_i e_{\alpha zj}q_j+2\frac{\partial}{\partial K_\alpha}(W^{(1)}+2BW^{(2)}+\cdots)\frac{\partial K_\alpha}{\partial B}+2W^{(2)}+2V^{(2)}+O(B^3)\ , \qquad (C4)$$

$$\vec{K}=\vec{p}-(e/c)\vec{A}(\vec{q})\ . \qquad (C5)$$

Taking the indicated limit $B\to 0$ gives Eq. (37) for the zero-field susceptibility χ.

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