Diamagnetism and Paramagnetism

CHAPTER OUTLINE

12.1 **INTRODUCTION**

The magnetization density of a quantum-mechanical system is defined as

$$M^v = -\frac{1}{V}\frac{\partial \Omega}{\partial B^v}, \tag{12.1}$$

where Ω is the thermodynamic potential, V is the volume of the solid, and B^v is the vth component of the magnetic induction **B**, the microscopic field perceived by the nuclei or the electrons due to an external magnetic field **H**. The magnetic susceptibility is defined as

$$\chi^{\mu v} = \lim_{B \to 0}\frac{\partial M^v}{\partial B^\mu} = -\frac{1}{V}\lim_{B \to 0}\frac{\partial^2 \Omega}{\partial B^\mu \partial B^v}. \tag{12.2}$$

It may be noted that the magnetic susceptibility is a tensor, whereas the magnetization is a vector. If a system has positive magnetic susceptibility, it is known as paramagnetic, and if it has negative magnetic susceptibility, it is known as diamagnetic. In a linear medium, $\mathbf{B} = \mu\mathbf{H}$, where μ is known as the magnetic permeability. Because an alternate definition of susceptibility is $\chi^{\mu v} = \lim_{H \to 0}\frac{\partial M^v}{\partial H^\mu}$, a linear system is paramagnetic if $\mu > 1$ and diamagnetic if $\mu < 1$.

There exists a lot of confusion in the literature as to when to use **H** and when to use **B**. **H** is the external applied magnetic field usually produced by external currents. Therefore, experiments that control external currents control **H** more directly than **B**, and hence, it is appropriate to consider **H** as the experimentally applied field. However, when this external magnetic field is applied to the system through external currents, the microscopic field perceived by the nuclei or the electrons is the magnetic induction **B**. Thus, the microscopic Hamiltonian should be written in terms of **B**, whereas the experimental results should be expressed in terms of **H**.

In this chapter, we will first calculate by using approximate methods, the atomic susceptibility, the susceptibility of insulators with filled shells that leads to Larmor diamagnetism, and the susceptibility of a collection of magnetic ions with partially filled shells that leads to paramagnetism. Then we will calculate the magnetic susceptibility of free electrons in metals that leads to Pauli paramagnetism and Landau diamagnetism, as well as the de Haas–van Alphen effect. Finally, we will outline the many-body theory of magnetic susceptibility of Bloch electrons in a magnetic field. We will express the total magnetic susceptibility as a sum of the contributions of the orbital (χ_o), spin (χ_s), and spin-orbit interactions (χ_{so}), and discuss the effects of exchange and correlation on each of these terms. Here, the spin susceptibility χ_s includes the effect of spin-orbit interaction on the spin, whereas χ_{so} is the contribution to magnetic susceptibility from the effect of spin-orbit coupling on the orbital motion of Bloch electrons. In the usual derivations of many-body theories of magnetic susceptibility, attention is focused either on the orbital part or on the spin part of the Hamiltonian, and the effects of spin-orbit coupling are accounted for in χ_o through the modifications of the Bloch functions and in χ_s by replacing the free electron g factor by the effective g factor. In this process, χ_{so}, which is of the same order as χ_s for solids with large effective g factors, has been neglected.

12.2 ATOMIC (OR IONIC) MAGNETIC SUSCEPTIBILITIES

12.2.1 General Formulation

It can be easily shown that the classical Hamiltonian for an electron in a magnetic field $\mathbf{B}$ is given by

$$H = \frac{1}{2m}\left(\mathbf{p} + \frac{e\mathbf{A}(\mathbf{r})}{c}\right)^2, \tag{12.3}$$

where $\mathbf{p}$ is the classical momentum, and $\mathbf{A}(\mathbf{r})$ is the vector potential obtained from the relation $\mathbf{B} = \nabla \times \mathbf{A}$ and $\nabla \cdot \mathbf{A} = 0$. In quantum mechanics, the vector $\mathbf{p}$ is replaced by the operator $-i\hbar\nabla$. Thus, the Hamiltonian for a free electron with spin operator $\hat{\mathbf{s}}$ in a magnetic field $\mathbf{B}$ is given by

$$\hat{H} = \frac{1}{2m}\left(-i\hbar\nabla + \frac{e\mathbf{A}(\mathbf{r})}{c}\right)^2 + g_0\mu_B\mathbf{B}\cdot\hat{\mathbf{s}} = \frac{1}{2m}\left(\hat{\mathbf{p}} + \frac{e\mathbf{A}(\mathbf{r})}{c}\right)^2 + g_0\mu_B\mathbf{B}\cdot\hat{\mathbf{s}}, \tag{12.4}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{s}}$ are the momentum and spin operators. The Hamiltonian of an atom (or ion) in a uniform magnetic field $\mathbf{B}$ (in the z direction) can be written as

$$\hat{H} = \frac{1}{2m}\sum_i\left(\hat{\mathbf{p}}_i + \frac{e\mathbf{A}(\mathbf{r}_i)}{c}\right)^2 + g_0\mu_B B\sum_i\hat{s}_z^i, \tag{12.5}$$

where $\mathbf{r}_i, \mathbf{p}_i$, and $\hat{\mathbf{s}}_i$ are the position, momentum, and spin operator of each electron in the atom (or ion), and $\mathbf{A}(\mathbf{r}_i)$ is the vector potential such that

$$\mathbf{B} = \nabla \times \mathbf{A} \text{ and } \nabla \cdot \mathbf{A} = 0. \tag{12.6}$$

Here, $g_0 \approx 2.0023$ and $\mu_B = e\hbar/2mc$. The first term in the Hamiltonian in Eq. (12.5), in which the sum is taken over all the electrons in the atom, is due to $\hat{T}$, the kinetic energy operator of the electrons, which includes the interaction of the orbital magnetic momentum with the magnetic induction. This interaction is accounted for by including the vector potential $\mathbf{A}(\mathbf{r}_i)$ in the momentum operator $\mathbf{p}_i$ of the electron at $\mathbf{r}_i$. The second term in Eq. (12.5) is due to the interaction of $\mathbf{B}$ with the electron spin and is a consequence of Dirac's relativistic theory. We will assume that

$$\mathbf{A} = -\frac{1}{2}\mathbf{r}\times\mathbf{B}, \tag{12.7}$$

which satisfies both conditions in Eq. (12.6). Thus, the kinetic energy operator, $\hat{T}$, in Eq. (12.5) can be written as

$$\hat{T} = \frac{1}{2m}\sum_i\hat{\mathbf{p}}_i^2 + \mu_B\hat{\mathbf{L}}\cdot\mathbf{B} + \frac{e^2}{8mc^2}B^2\sum_i(x_i^2 + y_i^2), \tag{12.8}$$

where $\hat{\mathbf{L}}$ is the total electronic orbital angular momentum operator,

$$\hat{\mathbf{L}} = \frac{1}{\hbar}\sum_i\mathbf{r}_i\times\hat{\mathbf{p}}_i. \tag{12.9}$$

From Eqs. (12.5), (12.8), and (12.9), we obtain (Problem 12.1)

$$\hat{H} = \frac{1}{2m}\sum_i \hat{\mathbf{p}}_i^2 + \mu_B(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} + \frac{e^2}{8mc^2}B^2\sum_i(x_i^2 + y_i^2), \tag{12.10}$$

where we have approximated $g_0 \approx 2$, and

$$\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i. \tag{12.11}$$

We can rewrite Eq. (12.10) in the alternate form

$$\hat{H} = \hat{H}_0 + \Delta\hat{H}, \tag{12.12}$$

where $\hat{H}_0$ is the Hamiltonian in the absence of the magnetic field, and $\Delta\hat{H}$ is the perturbation due to the magnetic field,

$$\Delta\hat{H} = \mu_B(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} + \frac{e^2 B^2}{8mc^2}\sum_i(x_i^2 + y_i^2). \tag{12.13}$$

If the states $|n>$ are the orbital states of the electrons in the absence of the magnetic field, we obtain, by using second-order perturbation theory,

$$E_n = E_n^0 + \Delta E_n, \tag{12.14}$$

where

$$E_n^0 = <n|H_0|n> \tag{12.15}$$

and

$$\Delta E_n = <n|\Delta\hat{H}|n> + \sum_{n'\neq n}\frac{|<n|\Delta\hat{H}|n'|^2>}{E_n - E_{n'}}. \tag{12.16}$$

From Eqs. (12.13) and (12.16), retaining terms through those quadratic in **B**, we obtain

$$\Delta E_n = \mu_B\mathbf{B} \cdot <n|\hat{\mathbf{L}} + 2\hat{\mathbf{S}}|n> + \sum_{n'\neq n}\frac{|<n|\mu_B\mathbf{B}\cdot(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|n'>|^2}{E_n - E_{n'}} + \frac{e^2 B^2}{8mc^2}<n|\sum_i(x_i^2 + y_i^2)|n>. \tag{12.17}$$

The magnetic susceptibility of atoms, ions, and molecules is obtained from Eq. (12.17). Usually, the first term on the right side of the equation is the dominant term unless it vanishes. As we will see, the first term will be zero for either closed shells or shells with one electron short of being half filled ($J = 0$). However, for magnetic ions, the first term is much larger than the second and third terms, which can be neglected. The collection of ions becomes paramagnetic in such cases.

12.2.2 Larmor Diamagnetism

If a solid has atoms or ions where all the electronic shells are filled, each atom has zero orbital and spin angular momentum in its ground state. Therefore,

$$\hat{\mathbf{J}}|0> = \hat{\mathbf{L}}|0> = \hat{\mathbf{S}}|0> = 0. \tag{12.18}$$

In the ground state, the third term in Eq. (12.17) is the only term that contributes to the magnetic susceptibility,

$$\Delta E_0 = \frac{e^2 B^2}{8mc^2} <0|\sum_i (x_i^2 + y_i^2)|0> = \frac{e^2 B^2}{12mc^2} <0|\sum_i r_i^2|0>, \tag{12.19}$$

which follows from the spherical symmetry of the atom or ion. Assuming that the free energy is equal to the ground-state energy (which is true if and only if $J = 0$), the magnetic susceptibility of the solid of N such ions in a volume V (in a semiclassical approximation) is given by

$$\chi \approx -\frac{\partial^2 \Delta E_0}{\partial B^2} = -\frac{N}{V} <0|\sum_i r_i^2|0>. \tag{12.20}$$

Eq. (12.20) is known as Larmor diamagnetic susceptibility or sometimes as Langevin susceptibility. It is valid only for solids composed of atoms or ions of filled shells.

We will now discuss Hund's rules, which are needed to discuss atoms or ions with partially filled shells.

12.2.3 Hund's Rules

Hund's rules, which are valid for atoms or ions with partially filled shells, were obtained from the analysis of atomic spectra as well as by rigorous theoretical calculations. They are valid for incomplete shells of which the one-electron levels are characterized by orbital angular momentum l. The shell would have $2(2l + 1)$ one-electron levels (including spin). If n is the number of electrons in the shell,

$$0 < n < 2(2l + 1). \tag{12.21}$$

The degeneracy of these levels is lifted by electron–electron interaction as well as by the spin-orbit interaction.

We will first discuss Russsell–Saunders coupling, which states that the Hamiltonian of the atom or ion (with partially filled shells) commutes with the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ and with the total electronic orbital and spin angular momentum $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ (provided the spin-orbit coupling is not too large such that it can be considered as a small perturbation). Thus, the partially filled shells can be indexed by the quantum numbers J, J_z, L, L_z, S, and S_z. This indexing is based on the fact that the eigenvalues of the operators $\hat{\mathbf{J}}^2$, $\hat{\mathbf{J}}_z$, $\hat{\mathbf{L}}^2$, $\hat{\mathbf{L}}_z$, $\hat{\mathbf{S}}^2$, and $\hat{\mathbf{S}}_z$ are $J(J+1)$, J_z, $L(L+1)$, L_z, $S(S+1)$, and S_z.

Hund's rules are as follows:

1. In an incomplete shell, the electrons that lie lowest in energy have the largest total spin S, which is consistent with the exclusion principle. The largest value S can have is equal to the largest magnitude that S_z can have. When $n \leq 2l + 1$, each electron can have parallel spin without multiple occupation of any one-electron level in the shell, provided each electron has a different value of l_z. Thus, when $n \leq 2l + 1$, $S = \frac{1}{2} n$. The exclusion principle requires that when $n > 2l + 1$, the spin of each additional electron has spin opposite to the first $2l + 1$ electrons. Therefore, S is reduced by half a unit from its maximum vale of $l + \frac{1}{2}$ for each electron after the first $2l + 1$ electrons.

2. Once S has been determined, as per Hund's first rule, the total angular momentum L of the electrons of the lowest-lying states has the largest value. For example, the first electron in the shell is in the level $|l_z| = l$, which is its maximum value. The second electron is in the level $|l_z| = l - 1$. When the electrons are half filled, $L = l + (l-1) + \dots [L - (n-1)] = 0$. The spin of the electrons that fill the second half of the shell are opposite to those in the first half, and using the same arguments, $L = 0$.

3. The values of L and S or the states of lowest energy are obtained from the first two rules. However, there are $(2L+1)(2S+1)$ possible states that are degenerate. The degeneracy of these states is lifted by spin-orbit coupling, which is of the form $\lambda(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})$. The total angular momentum J can take on all integral values between $|L - S|$ and $L + S$. Spin-orbit coupling favors minimum J if λ is positive (for shells that are less than half filled) and maximum J if λ is negative (for shells that are more than half filled). Thus, in the ground state,

$$J = |L - S|, \quad n \leq (2l + 1),$$
$$J = L + S, \quad n \geq (2l + 1) \cdot \tag{12.22}$$

We note that when the shell is half full, $L = 0$ and there is no jump in J because $J = S$.

We further note that Hund's rules apply to partially filled d and f shells but not to partially filled p shells, which contain valence electrons and broaden into bands in the solid.

12.2.4 Van Vleck Paramagnetism

We consider the susceptibility of insulators containing ions with a partially filled shell. First, we consider the case where $J = 0$ (shells that are one electron short of being half filled). The first term in Eq. (12.17) still vanishes, as in the case of a filled shell. However, the second and third terms contribute to the shift in the ground-state energy, and we obtain

$$\Delta E_0 = -\sum_n \frac{|<0|\mu_B \mathbf{B} \cdot (\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|n>|^2}{E_n - E_0} + \frac{e^2 B^2}{8mc^2} \sum_i <0|(x_i^2 + y_i^2)|0>. \tag{12.23}$$

Because $J = 0$, assuming as before that the free energy is equal to the ground-state energy, the magnetic susceptibility is given by

$$\chi \approx -\frac{N}{V} \frac{\partial^2 E_0}{\partial B^2}$$
$$\approx -\frac{N}{V}\left[-2\mu_B^2 \sum_n \frac{|<0|\hat{L}_z + 2\hat{S}_z|n>|^2}{E_n - E_0} + \frac{e^2}{4mc^2} <0|\sum_i (x_i^2 + y_i^2)|0> \right]. \tag{12.24}$$

The first term in Eq. (12.24), which is positive, is known as Van Vleck paramagnetism, and the second term is the Larmor diamagnetism derived for ions of filled shells. Thus, the magnetic susceptibility of ions with a shell one electron short of being half filled is obtained by the sum of the two terms. The Van Vleck paramagnetism also exists in molecules that have a more complex structure than single atoms or ions.

It may be noted that the basic assumption made in these derivations is that the ground state is occupied with appreciable probability in thermal equilibrium, and hence, the free energy is equal to

the ground-state energy. However, if the next state is close to the $J = 0$ ground state, the free energy is not just the ground-state energy, and the derivation of the formula for magnetic susceptibility is much more complicated.

12.2.5 Landé g Factor

If $J \neq 0$ for the shell, the first term for the shift in energy in Eq. (12.17) becomes the dominant term compared to the other two terms, which yield the Larmor diamagnetism and Van Vleck paramagnetism. If we ignore the last two terms in Eq. (12.17), we have to consider the matrix elements' dominant term

$$\Delta E_n \approx \mu_B B <n|\hat{L}_z + 2\hat{S}_z|n> . \tag{12.25}$$

Here, we have assumed that $\mathbf{B} = B\hat{\mathbf{z}}$. The ground state $|n>$ is $(2J + 1)$-fold degenerate in the absence of the magnetic field. The matrix elements can be evaluated by diagonalizing and evaluating the matrix elements of the $(2J + 1)$-dimensional square matrix

$$<JLSJ_z|\hat{L}_z + 2\hat{S}_z|JLSJ_z'> , \tag{12.26}$$

where

$$J_z, J_z' = -J, \, ..., \, J. \tag{12.27}$$

To evaluate these matrix elements, we use the Wigner–Eckart theorem according to which the matrix elements of any vector operator $\hat{\mathbf{A}}$ in the $(2J + 1)$-dimensional space of eigenstates of $\mathbf{J}^2$ and $\mathbf{J}_z$ with a given value of J are proportional to the matrix elements of $\hat{\mathbf{J}}$ itself:

$$<JLSJ_z|\hat{\mathbf{A}}|JLSJ_z'> = g(JLS) <JLSJ_z|\hat{\mathbf{J}}|JLSJ_z'> . \tag{12.28}$$

The proportionality constant $g(JLS)$ depends on $\hat{\mathbf{A}}$ but does not depend on the values of J_z and J_z'. Applying the Wigner–Eckart theorem to magnetism,

$$<JLSJ_z|\hat{L}_z + 2\hat{S}_z|JLSJ_z'> = g(JLS) <JLSJ_z|\hat{J}_z|JLSJ_z'> = g(JLS)J_z\delta_{J_zJ_z'}. \tag{12.29}$$

Here, $g(JLS)$ is known as the Landé g factor. The matrix is diagonal in the states of definite J_z, and the ground state $|n>$, which is $(2J + 1)$-fold degenerate, is split into states with definite values of J_z. From Eqs. (12.25) and (12.29), we obtain

$$\Delta E_{J_z} \approx g(JLS) \mu_B B J_z \delta_{J_z J_z'}. \tag{12.30}$$

The energies are uniformly split by $g(JLS)\mu_B B$. The Landé g factor can be evaluated by writing, in analogy with Eq. (12.28),

$$<JLSJ_z|(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|JLSJ_z'> = g(JLS) <JLSJ_z|\hat{\mathbf{J}}|JLSJ_z'> . \tag{12.31}$$

We can also rewrite Eq. (12.31) in the alternate form (Problem 12.2)

$$<JLSJ_z|\hat{\mathbf{L}} + 2\hat{\mathbf{S}}|J'L'S'J_z'> = g(JLS) <JLSJ_z|\hat{\mathbf{J}}|J'L'S'J_z'> , \tag{12.32}$$

because both matrix elements vanish unless $J = J'$, $L = L'$, and $S = S'$. By using the completeness relation,

$$\sum_{J''L''S''J''} |J''L''S''J_z''> <J''L''S''J_z''| = 1, \tag{12.33}$$

we can rewrite Eq. (12.32) in the alternate form

$$\begin{aligned}
&\sum_{J''L''S''J_z''} <JLSJ_z|(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|J''L''S''J_z''> \cdot <J''L''S''J_z''|\hat{\mathbf{J}}|J'L'S'J_z'> \\
&= g(JLS) \sum_{J''L''S''J_z''} <JLSJ_z|\hat{\mathbf{J}}|J''L''S''J_z''> \cdot <J''L''S''J_z''|\hat{\mathbf{J}}|J'L'S'J_z'> \cdot
\end{aligned} \tag{12.34}$$

Because the sum over Eq. (12.34) is taken over a complete set, from Eqs. (12.31), (12.32), and (12.34), we obtain (Problem 12.3)

$$<JLSJ_z|(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \hat{\mathbf{J}}|JLSJ_z'> = g(JLS) <JLSJ_z|\hat{\mathbf{J}}^2|JLSJ_z'> . \tag{12.35}$$

We have, from the relation (Problem 12.4),

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}, \tag{12.36}$$

$$(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}}) = \hat{\mathbf{L}}^2 + 2\hat{\mathbf{S}}^2 + \hat{\mathbf{L}} \cdot \hat{\mathbf{J}} + 2\hat{\mathbf{S}} \cdot \hat{\mathbf{J}} = \frac{1}{2}[3\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2]. \tag{12.37}$$

From Eqs. (12.35) through (12.37), we obtain

$$g(JLS) = \frac{[3J(J+1) - L(L+1) + S(S+1)]}{2J(J+1)}. \tag{12.38}$$

We note that for the $(2J + 1)$-dimensional set of states that make up the degenerate atomic ground state in the zero field, Eq. (12.32) can often be rewritten without the state vectors as

$$\hat{\mathbf{L}} + 2\hat{\mathbf{S}} = g(JLS)\,\mathbf{J}, \tag{12.39}$$

as long as the matrix elements are diagonal in J, L, and S. If the splitting between the zero-field atomic ground-state multiplet and the first excited multiplet is large compared with $k_B T$, then the $(2J + 1)$ states in the ground-state multiplet will contribute significantly to the free energy. In this case, we can rewrite the first term of Eq. (12.32) by using Eq. (12.39), as the interaction $(-\overrightarrow{\mu} \cdot \mathbf{B})$ of the field $\mathbf{B}$ with a magnetic moment,

$$\overrightarrow{\mu} = -g(JLS)\mu_B\mathbf{J}. \tag{12.40}$$

The magnetic susceptibility has to be obtained from the free energy because the free energy cannot be equated with the ground-state energy in this case. When $\mathbf{B} \to 0$, the splitting of the $(2J + 1)$ lowest-lying states would be small compared with $k_B T$. As we will see, the magnetic susceptibility of a collection of magnetic ions is paramagnetic and leads to Curie's law.

12.2.6 Curie's Law

To calculate the Helmholtz free energy F, we assume that only the lowest-lying spin multiplet contributes to the statistical mechanical sums. Thus, only the lowest $2J + 1$ states are thermally excited with appreciable probability. The Helmholtz free energy F, for a single ion in magnetic field **B**, is given by

$$e^{-\beta F} = \sum_{J_z=-J}^{J} e^{-\beta g(JLS)\mu_B B J_z} = \sum_{J_z=-J}^{J} e^{-\beta \gamma B J_z}, \tag{12.41}$$

where

$$\gamma = g(JLS)\mu_B. \tag{12.42}$$

By summing over the geometric series, we obtain

$$e^{-\beta F} = \frac{e^{\beta \gamma B(J+\frac{1}{2})} - e^{-\beta \gamma B(J+\frac{1}{2})}}{e^{\beta \gamma B/2} - e^{-\beta \gamma B/2}}. \tag{12.43}$$

The magnetization of N ions in a volume V is defined as

$$M = -\frac{N}{V} \frac{\partial F}{\partial B}. \tag{12.44}$$

From Eqs. (12.43) and (12.44), we obtain (Problem 12.5)

$$M = \frac{N}{V} \gamma J B_J(\beta \gamma J B), \tag{12.45}$$

where the Brillouin function $B_J(x)$ is defined as

$$B_J(x) = \frac{(2J+1)}{2J} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} x\right). \tag{12.46}$$

If $\beta \gamma B \ll 1$, $x \ll 1$, and

$$\coth x \approx \frac{1}{x} + \frac{1}{3}x + O(x^3), \tag{12.47}$$

from Eqs. (12.46) and (12.47), we obtain

$$B_J(x) \approx \frac{J+1}{3J} x \approx \frac{J+1}{3} \beta \gamma B \approx \frac{J+1}{3} g(JLS)\beta \mu_B B. \tag{12.48}$$

From Eqs. (12.45) and (12.48), we obtain

$$M = \frac{N}{V} \frac{\beta g^2 \mu_B^2}{3} B J(J+1). \tag{12.49}$$

The magnetic susceptibility is

$$\chi = \frac{\partial M}{\partial B} = \frac{N}{V} \frac{(g\mu_B)^2}{3} \frac{J(J+1)}{k_B T}. \tag{12.50}$$

This is known as Curie's law and characterizes paramagnetic systems with "permanent moments" of which the alignment is opposed by thermal disorder but favored by the magnetic field. We note that Curie's law, as derived here, is valid as long as the system of magnetic ions is considered as noninteracting.

We can rewrite Curie's law in the alternate form

$$\chi = \frac{1}{3} \frac{N}{V} \frac{\mu_B^2 p^2}{k_B T}, \tag{12.51}$$

where the "effective Bohr magneton number" p is given by

$$p = g(JLS)\sqrt{J(J+1)}. \tag{12.52}$$

12.3 MAGNETIC SUSCEPTIBILITY OF FREE ELECTRONS IN METALS
12.3.1 General Formulation

The diamagnetic and paramagnetic susceptibilities of free electrons in a metal were calculated by Landau[4] and Pauli, respectively. The diamagnetic susceptibility arises out of the orbital motion of the electrons, and the paramagnetic susceptibility arises out of the realignment of spins in a magnetic field. It can be shown that Pauli paramagnetism is three times the value of Landau diamagnetism with the signs reversed. In addition, there is an oscillatory contribution to the magnetic susceptibility, which is known as the de Haas–van Alphen effect[5]. The de Haas–van Alphen effect is an effective tool to measure the contours of the Fermi surface of a metal.

The spin-orbit interaction is not included in the following derivation for magnetic susceptibility of free electrons. We will first calculate the magnetic susceptibility of a free electron gas confined in a box.

For a free electron gas, one can write the magnetization density M as

$$M = -\frac{1}{V} \frac{\partial F}{\partial B}, \tag{12.53}$$

where F is the free energy

$$F = N\mu - \frac{1}{\beta} \sum_{\mathbf{k}} \ln Z_{\mathbf{k}}, \tag{12.54}$$

$\beta = 1/k_B T$, N is the total number of electrons, μ is the chemical potential, and the partition function is

$$Z_{\mathbf{k}} = 1 + e^{-\beta(E(\mathbf{k})-\mu)}. \tag{12.55}$$

The Schrodinger equation for free electrons in a magnetic field **B** (neglecting spin) is given by

$$H\psi(\mathbf{r}) = \frac{1}{2m}\left(-i\hbar\nabla + \frac{e\mathbf{A}}{c}\right)^2 \psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{12.56}$$

We assume that the magnetic field is along the z direction, $\mathbf{B} = B\hat{z}$, in which case $\mathbf{A} = Bx\hat{y}$ (from $\mathbf{B} = \nabla \times \mathbf{A}$). This is also known as the Landau gauge. In the Landau gauge, we can write

$$H = \frac{1}{2m}[p_x^2 + p_z^2 + (p_y + m\omega_c x)^2], \tag{12.57}$$

where the cyclotron frequency

$$\omega_c = eB/2mc. \tag{12.58}$$

If we make the substitution

$$p_y = \hbar k_y, \ p_z = \hbar k_z, \ \text{and} \ x = -\frac{\hbar}{m\omega_c}k_y + q = x_0 + q, \tag{12.59}$$

Eq. (12.57) can be rewritten in the alternate form

$$H = \frac{1}{2m}(p_x^2 + m^2\omega_c^2 q^2) + \frac{\hbar^2}{2m}k_z^2. \tag{12.60}$$

We consider the electrons to be confined in a rectangular parallelepiped of sides L_x, L_y, and L_z with the Born–von Karman periodic boundary conditions. The solution of Eq. (12.56), which is a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ when $\mathbf{A} = 0$, is modified (by using Eq. 12.60) as

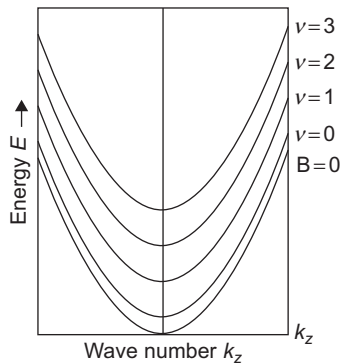$$\psi(\mathbf{r}) = e^{i(k_y y + k_z z)}\phi(x). \tag{12.61}$$

Substituting Eqs. (12.60) and (12.61) in (12.56), we obtain

$$-\frac{\hbar^2}{2m}\phi''(x) + \frac{m\omega_c^2}{2}(x - x_0)^2\phi(x) = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\phi(x), \tag{12.62}$$

FIGURE 12.1

Sketch of the one-dimensional energy sub-bands in the free electron model.

where Eq. (12.62) is the Schrodinger equation of the one-dimensional oscillator centered at x_0. The eigenvalues are

$$E_v = \frac{\hbar^2 k_z^2}{2m} + \left(v + \frac{1}{2}\right)\hbar\omega_c, \quad v = 0, 1, 2, ... \tag{12.63}$$

Thus, the energy of the electron is the sum of the kinetic energy of its undisturbed motion along the z direction, and the quantized energy of the oscillatory motion in the plane orthogonal to the field direction. This part of the energy is the contribution due to the orbital motion. The energy of the one-dimensional sub-bands is plotted as a function of the wave number k_z in Figure 12.1. The wave function in Eq. (12.61) depends on k_y and k_z directly and on k_z and v indirectly through $\phi(x)$.

Because one can choose any k_y for a particular value of k_z and v, the state k_y is degenerate. Further, x_0 lies in the range

$$-L_x/2 < x_0 < L_x/2. \qquad (12.64)$$

If we neglect spin, the states occur on the k_y axis in the intervals of $2\pi/L_y$. One can write

$$-\frac{1}{2\hbar}m\omega_c L_y < k_y < \frac{1}{2\hbar}m\omega_c L_x. \qquad (12.65)$$

FIGURE 12.2

Sketch of the density of states for **B** = 0 and **B** ≠ 0.

Thus, k_y can have $(L_y/2\pi)(m\omega_c L_x/\hbar)$ different values. Furthermore, in the range dk_z, the z-component of k will have $(L_z/2\pi)dk_z$ different values. The density of states is obtained by multiplying by a factor of 2 for spin and dividing by the volume of the cube $(L_x L_y L_z)$,

$$g(v, k_z)dk_z = \frac{2}{(2\pi)^2}\frac{m\omega_c}{\hbar}dk_z. \qquad (12.66)$$

From Eqs. (12.63) and (12.66), we obtain (Problem 12.6)

$$g(E,v)\,dE = \frac{2}{(2\pi)^2}\frac{\hbar\omega_c}{2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E - \left(v + \frac{1}{2}\right)\hbar\omega_c\right)^{-1/2}dE. \qquad (12.67)$$

The total density of states is obtained by summation over all bands that lie "below" the energy E,

$$g(E)\,dE = \sum_{v=0}^{v'} g(E,v)\,dE. \qquad (12.68)$$

It can be easily shown (Problem 12.7) that Eq. (12.68) has the same density of states as the zero-field case. The average density of states is unaffected by a magnetic field. The states are redistributed due to the magnetic field **B**, which pulls together a large number of states into a single level (see Figure 12.2).

The contribution due to spin is $\pm(g/2)\mu_B B$, depending on its direction, where the Bohr magneton $\mu_B = e\hbar/2mc$ and the g factor for free electrons is $g = 2$. If we include the contribution of spin, the energy E is modified as

$$E_\pm = \frac{\hbar^2 k_z^2}{2m} + (2v+1)\mu_B B \pm \frac{g}{2}\mu_B B = E \pm \mu_B B. \qquad (12.69)$$

12.3.2 Landau Diamagnetism and Pauli Paramagnetism

From Eqs. (12.53) through (12.55) and (12.69), we obtain the expression for magnetization per unit volume (Problem 12.8),

$$M = -\frac{d}{dB}\left\{n\mu - \frac{1}{\beta}\int_0^\infty g(E_+)\,\ln\,[e^{\beta(\mu-E)}+1]\,dE_+ - \frac{1}{\beta}\int_0^\infty g(E_-)\,\ln\,[e^{\beta(\mu-E)}+1]\,dE_-\right\}. \qquad (12.70)$$
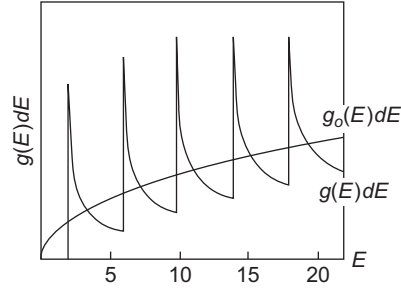
In Eq. (12.70), the summation over the energy states is replaced by an integration because the energy levels are very close together. Here, n is the electron concentration, and μ is the chemical potential. We have

$$n = \int_0^\infty n(E)dE = \int_0^\infty f(E)g(E)dE, \tag{12.71}$$

where $f(E)$ is the Fermi function,

$$f(E) = [1 + e^{\beta(E(\mathbf{k}) - \mu)}]^{-1}. \tag{12.72}$$

The density of states in $\mathbf{k}$ space is given by

$$g(E)dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\, dE. \tag{12.73}$$

From Eqs. (12.71) through (12.73), we obtain

$$n = 2\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \frac{2}{\sqrt{\pi}}\, F(\beta\mu), \tag{12.74}$$

where the Fermi integral $F(x)$ is given by

$$F(x) = \int_0^\infty \frac{y^{1/2}}{1 + e^{(y-x)}}\, dy. \tag{12.75}$$

It can be shown (Problem 12.9) that

$$F(x) \approx \frac{\sqrt{\pi}}{2} e^x, \quad \text{for} \quad x < 0$$

and

$$F(x) \approx \frac{2}{3} x^{3/2,} \quad \text{for} \quad x > 0. \tag{12.76}$$

Using a similar expansion for Eq. (12.70) and for low temperatures, in which the first term is retained, one can show that (Problem 12.10)

$$M = \frac{3n\mu_B^2 B}{2E_F}\left[1 - \frac{1}{3} + \frac{\pi k_B T}{\mu_B B}\left(\frac{E_F}{\mu_B B}\right)^{1/2} \sum_{v=1}^\infty \frac{(-1)^v}{\sqrt{v}}\ \cos\ (\pi v)\ \frac{\sin\left(\frac{\pi}{4} - \frac{\pi v E_F}{\mu_B B}\right)}{\sinh\frac{\pi^2 v k_B T}{\mu_B B}}\right]. \tag{12.77}$$

Here, E_F is the Fermi energy (value of μ at $T = 0$). The magnetic susceptibility is obtained from the expression

$$\chi = \frac{\partial M}{\partial B}. \tag{12.78}$$

For most cases, M is linear in B for attainable field strengths, and the definition reduces to

$$\chi \approx \frac{M}{B}. \tag{12.79}$$

From Eqs. (12.77) and (12.79), we obtain (retaining only the first term in the series expansion),

$$\chi = \chi_P + \chi_L + \chi_{dH-vA}, \tag{12.80}$$

where χ_P is the Pauli spin paramagnetism,

$$\chi_P = \frac{3n\mu_B^2}{2E_F}, \tag{12.81}$$

χ_L is the Landau diamagnetism,

$$\chi_L = -\frac{n\mu_B^2}{2E_F}, \tag{12.82}$$

and χ_{dH-vA} is the de Haas–van Alphen effect, which is oscillatory with a period $\frac{2\mu_B}{E_F}$. This is an additional diamagnetic term given by

$$\chi_{dH-vA} \approx \frac{3n\pi}{2\beta} \left(\frac{\mu_B}{E_F B}\right)^{1/2} \left(\frac{\sin\left(\frac{\pi}{4} - \frac{\pi E_F}{\mu_B B}\right)}{\sinh\left(\frac{\pi^2}{\mu_B \beta B}\right)}\right). \tag{12.83}$$

We note from Eq. (12.83) that because the sin term is oscillatory,

$$\sin\left(\frac{\pi}{4} - \frac{\pi E_F}{\mu_B B}\right) = \sin\left(\frac{\pi}{4} - \frac{\pi E_F}{\mu_B B} + 2n\pi\right), \tag{12.84}$$

χ_{dH-vA} is oscillatory whenever

$$\frac{\pi E_F}{\mu_B B} = \frac{\pi E_F}{\mu_B B} + 2n\pi \tag{12.85}$$

or

$$\frac{1}{B} = \frac{1}{B} + \frac{2n\mu_B}{E_F}. \tag{12.86}$$

χ_{dH-vA} is periodic in $1/B$ with a temperature-independent period $2\mu_B/E_F$. However, these oscillations can be observed only at low temperatures and high magnetic fields. It will be shown that the condition for such oscillations is

$$\hbar\omega_c = 2\mu_B B \gg \frac{1}{\beta}. \tag{12.87}$$

Otherwise, the distribution of electrons in the region of E_F is widely spread, and the oscillations are spread out.
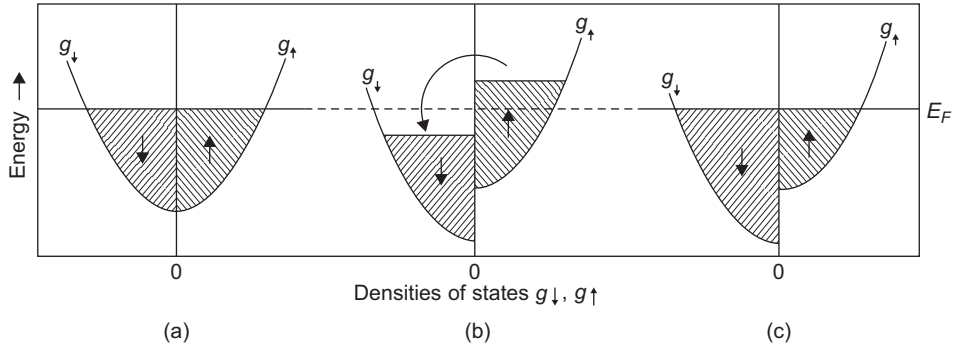
FIGURE 12.3

Sketch of densities of states $g_\downarrow$ and $g_\uparrow$ as a function of energy.

The origin of each of the previous three contributions to the magnetic susceptibility of a free electron gas can be explained in simple manner. The origin of the Pauli spin paramagnetism is the additional contribution $\pm\mu_B B$ to the kinetic energy of the electrons due to the magnetic field, depending on their spin directions. This is shown in Figure 12.3.

In Figure 12.3a, the occupied states for both spins are the same in the absence of a magnetic field. The highest occupied states for each spin have the energy equal to the Fermi energy E_F. In Figure 12.3b, the states of opposite spins are shifted in a magnetic field B. However, the "occupied" states above E_F with spin "up" flow to the "unoccupied" states with spin "down" until the states are filled. The imbalance of the density of states in a magnetic field between the two spin states contributes to the positive Pauli paramagnetism.

The Landau diamagnetic term represents the orbital quantization of the electrons in a magnetic field. It is one-third the contribution of the Pauli paramagnetism and is of the opposite (negative) sign. The theory of diamagnetic susceptibility of metals was derived by Misra and Roth (Ref. 12). The theory of magnetic susceptibility of Bloch electrons was derived by Misra and Kleinman (Ref. 13).

12.3.3 De Haas–van Alphen Effect

The de Haas–van Alphen effect[5], which has been used extensively to investigate the Fermi surfaces of metals, can be explained by first assuming that the Fermi level is approximately constant as B is varied. The validity of this assumption can be seen in Figure 12.4. We note $G(E) \sim G_0(E)$ as the energy increases. Here, $G(E)$ and $G_0(E)$ are the number of states below the energy E in the presence and absence of the magnetic field. Because the number of states below the Fermi level E_F is half of the number of electrons at $T = 0$ (each state can have two electrons), E_F is approximately constant as B is varied.
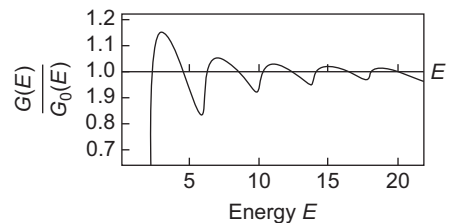
FIGURE 12.4

The ratio of the number of states $G(E)$ below E in a magnetic field to the number $G_0(E)$ in the absence of a magnetic field.

If we consider the case at $T = 0$, all states are filled up to the Fermi level E_F, and all states above it are empty. If we consider a plane slab in **k** space of thickness δk_z at k_z, the number of allowed values of k_z in the range δk_z is $(L_z/2\pi)\,\delta k_z$. The total degeneracy of the state v (neglecting spin) per unit volume in the slice δk_z is (from Eq. 12.66)

$$\frac{m\omega_c}{4\pi^2\hbar}\delta k_z = \xi B. \tag{12.88}$$

Thus, the degeneracy parameter (apart from spin), which is defined as the degeneracy per unit magnetic field per unit volume, is

$$\xi = \frac{e\delta k_z}{4\pi^2\hbar c}. \tag{12.89}$$

We consider the de Haas–van Alphen effect for a free electron gas at absolute zero. Figure 12.5 shows the spectrum of the Landau levels when the energy E is plotted versus B.

At $T = 0$, all levels in the slice δk_z will be filled (Figure 12.5) for which

$$(v + \frac{1}{2})\hbar\omega_c + \frac{\hbar^2 k_z^2}{2m} \leq E_F, \tag{12.90}$$

which can be rewritten in the alternate form,

$$(v + \frac{1}{2})\hbar\omega_c \leq \varepsilon_F', \tag{12.91}$$

where

$$\varepsilon_F' = E_F - \frac{\hbar^2 k_z^2}{2m}. \tag{12.92}$$

At $T = 0$, if v' is the highest filled level, n, the number of electron states in the slice of thickness δk_z is (from Eq. 12.89 and the fact that $v = 0$ is a filled level)

$$n = (v' + 1)\xi B. \tag{12.93}$$

When B is increased, n increases linearly with B until v' coincides with ε_F'. As B is further increased, all the electrons in v' will have energy greater than ε_F', and hence, they will empty out into the orbits in other slices with different values of k_z and ε_F'. This oscillatory evacuation occurs when

$$(v' + \frac{1}{2}) = \frac{\varepsilon_F'}{\hbar\omega_c} = \frac{mc\varepsilon_F'}{e\hbar}\frac{1}{B}. \tag{12.94}$$
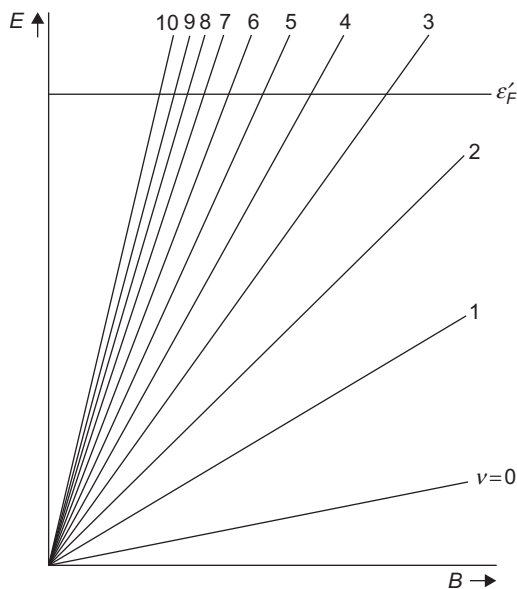

FIGURE 12.5

Sketch of the spectrum of Landau levels versus B.

Hence, the population δn is approximately a periodic function of $1/B$, with period $\frac{e\hbar}{mc\varepsilon_F'}$. The energy of the electrons in the slice δk_z in a magnetic field B such that the population n_0 is

$$E_0 = \hbar\xi B\omega_c \sum_{}^{v'} \left(v+\frac{1}{2}\right) + n_0\frac{\hbar^2 k_z^2}{2m} = \frac{1}{2}\hbar\xi B\omega_c(v'+1)^2 + n_0\frac{\hbar^2 k_z^2}{2m}. \tag{12.95}$$

From Eqs. (12.89) and (12.95), we obtain

$$E_0 = \frac{1}{2}\frac{\hbar\omega_c}{\xi B}n_0^2 + n_0\frac{\hbar^2 k_z^2}{2m}, \tag{12.96}$$

where $n_0 = (v'+1)\xi B$ from Eq. (12.89) for this value of B. For a nearby B that has the same value of v' for the highest filled state,

$$E = \frac{1}{2}\frac{\hbar\omega_c}{\xi B}n^2 + n\frac{\hbar^2 k_z^2}{2m} + (n_0 - n)\varepsilon_F, \tag{12.97}$$

where $(n_0 - n)\varepsilon_F$ is the change in energy arising out of the transfer of $n - n_0$ electrons at the Fermi level while the first two terms are the energy of the electrons in the slice δk_z. From Eqs. (12.92), (12.96), and (12.97), we obtain

$$\delta E = E - E_0 = \frac{\mu}{\xi}(n^2 - n_0^2) + (n_0 - n)\varepsilon_F', \tag{12.98}$$

where

$$\mu = \frac{e\hbar}{2mc}. \tag{12.99}$$

Further, from Eq. (12.94),

$$\varepsilon_F' \approx (n_0/\xi B)\hbar\omega_c = 2\mu n_0/\xi. \tag{12.100}$$

From Eqs. (12.98) and (12.100), we obtain

$$\delta E = \left(\frac{\mu}{\xi}\right)(n - n_0)^2. \tag{12.101}$$

From Eq. (12.101), δM, the magnetization of the slice at $T = 0$,

$$\delta M = -\frac{\partial E}{\partial B} = -\frac{2\mu}{\xi}(n - n_0)\frac{dn}{dB}. \tag{12.102}$$

From Eqs. (12.93), (12.94), and (12.100), we have

$$\frac{dn}{dB} \approx \varepsilon_F'\left(\frac{\xi}{2\mu B}\right). \tag{12.103}$$

From Eqs. (12.102) and (12.103), we obtain

$$\delta M \approx -\frac{\varepsilon_F'}{B}(n - n_0). \tag{12.104}$$

As B is increased, $n - n_0$ oscillates with extrema $\pm \frac{1}{2} \xi B$ because the population of the level v' varies between ξB and 0. Thus, the magnetization varies between $\mp \frac{1}{2} \xi \varepsilon_F$. This oscillation of the magnetization as a periodic function of B is known as the de Haas–van Alphen effect, a more rigorous analysis of which was presented earlier in this section. The de Haas–van Alphen oscillations are sensitive probes of the geometrical property of the Fermi surface. The areas of the extremals of the electron orbits can be determined from the period of oscillation.

Because the de Haas–van Alphen effect is an important tool and is widely used to experimentally measure the contours of the Fermi surface of crystalline solids, we will present the sequence of events that occur when a magnetic field is applied to a free electron gas in a rectangular parallelepiped, the Fermi surface of which is a sphere prior to the application of a magnetic field.

Figure 12.6 shows a plane section in the **k** space. The electron states are uniformly distributed in the (k_x, k_y) plane. The magnetic field **B** is directed normally into the plane section. The **k** states are subjected to a Lorenz force, and all the **k** states rotate with the cyclotron frequency about an axis through the origin and parallel to the field direction.

The magnetic field causes a redistribution of the **k** states that lie on rings that correspond to the energies

$$E_v = (v + \tfrac{1}{2}) \hbar \omega_c = \frac{\hbar^2 k_v^2}{2m}. \tag{12.105}$$

These rings are shown in Figure 12.7. Because the magnetic field **B** is in the z direction, k_z is not affected by it. Thus, in the **k** space, the representative points lie on cylinders (Landau cylinders) of which the cross-sections are the Landau rings.

At $T = 0$, the **k** states are within the Fermi sphere of radius k_F. Thus, the Landau cylinders, shown in Figure 12.8, are either partially occupied or fully empty.

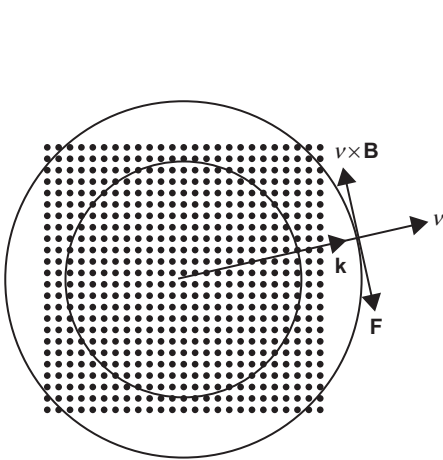

FIGURE 12.6

A magnetic field **B** is directed normally into the plane section of **k** space.
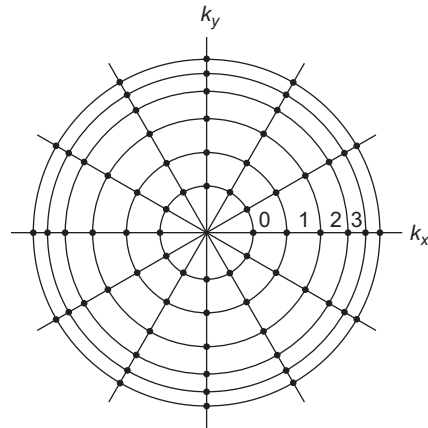
FIGURE 12.7

The Landau levels have a concentric circular form in the (k_x, k_y) plane but have cylindrical surfaces in the **k** space.
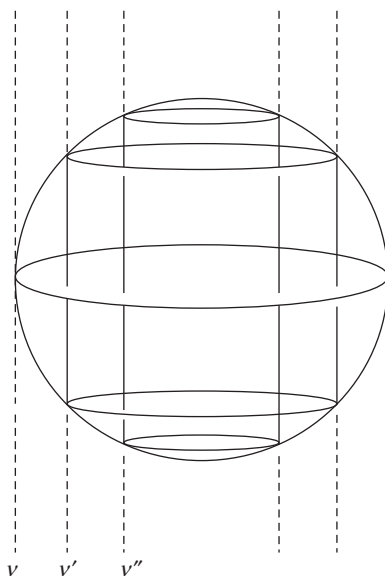
FIGURE 12.8

Landau cylinders. As the magnetic field **B** is increased, the cylinders expand until they become empty when they cross the Fermi sphere.
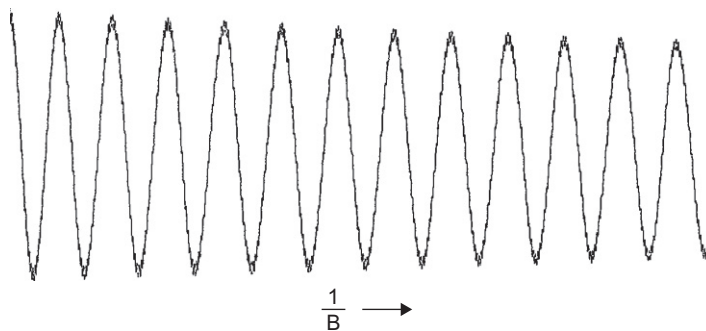
FIGURE 12.9

The de Haas–van Alphen oscillations for a metal with complex structure with decreasing magnetic field.

Figure 12.9 shows the de Haas–van Alphen oscillations for metals with complicated crystal structures as **B** is decreased. Usually, the Fermi surface of such metals has a thin neck and a thick belly. The large-scale oscillations, of which the amplitude decreases with decreasing **B**, are due to the extremal orbits around the thin neck, whereas the barely resolved small-scale oscillations are due to the extremal orbits of the thick belly.

12.4 MANY-BODY THEORY OF MAGNETIC SUSCEPTIBILITY OF BLOCH ELECTRONS IN SOLIDS

12.4.1 Introduction

Misra et al. (Ref. 14) derived an expression for the total magnetic susceptibility (χ) of Bloch electrons in solids (including spin-orbit interaction) that includes both many-body and interband effects.[14] They used a finite-temperature Green's function formalism to express the thermodynamic potential $\Omega(T, V, \mu, \mathbf{B})$ for an interacting electron system in the presence of a periodic potential V (**r**), spin-orbit interaction, and external magnetic field **B** in terms of the exact one-particle propagator G. They showed that the total magnetic susceptibility of a nonferromagnetic solid can be expressed as the sum of three terms,

$$\chi = \chi_o + \chi_s + \chi_{so}, \tag{12.106}$$

where χ_o is the orbital contribution, χ_s is the spin contribution, and χ_{so} is the contribution of the spin-orbit coupling on the orbital motion of the Bloch electrons. An important aspect of their derivation is the analysis of exchange and correlation effects on each of these terms that have been explicitly calculated.

Misra et al. (Ref. 14) have shown that if they make a simple approximation for the self-energy, their expression for χ_o is reduced to the earlier results. If they make drastic assumptions while solving the matrix integral equations for the field-dependent part of the self-energy, their expression for χ_s is equivalent to the earlier results for the exchange-enhanced χ_s but with the g factor replaced by the effective g factor, a result that has been intuitively used but not yet rigorously derived. An important aspect of their derivation is the analysis of exchange and correlation effects on χ_{so} that are more subtle and cannot be included in an intuitive way.

12.4.2 Equation of Motion in the Bloch Representation

The exact one-particle propagator G satisfies the equation

$$(\xi_l - \hat{H})G(\mathbf{r}, \mathbf{r}', \xi_l) + \int d\mathbf{r}'' \hat{\Sigma}(\mathbf{r}, \mathbf{r}'', \xi_l)G(\mathbf{r}'', \mathbf{r}', \xi_l) = \delta(\mathbf{r} - \mathbf{r}'), \tag{12.107}$$

where $\hat{\Sigma}$ is the exact proper self-energy operator, ξ_l is the complex energy,

$$\xi_l = \frac{(2l+1)\pi i}{\beta} + \mu, \quad l = 0, \pm 1, \pm 2, ..., \tag{12.108}$$

and $\hat{H}$ is the Hamiltonian of the Bloch electron in a magnetic field,

$$\hat{H} = \frac{1}{2m}\left(\mathbf{p} + \frac{e\mathbf{A}}{c}\right)^2 + \frac{\hbar^2}{4m^2c^2}\overrightarrow{\sigma} \cdot \overrightarrow{\nabla}V \times \left(\mathbf{p} + \frac{e\mathbf{A}}{c}\right) + V(\mathbf{r}) + \frac{\hbar^2}{8m^2c^2}\nabla^2 V + \frac{1}{2}g\mu_B\mathbf{B} \cdot \overrightarrow{\sigma}. \tag{12.109}$$

In the absence of the magnetic field, both G and $\hat{\Sigma}$ have the symmetry

$$G(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}, \xi_l) = G(\mathbf{r}, \mathbf{r}', \xi_l) \tag{12.110}$$

and

$$\hat{\Sigma}(\mathbf{r}+\mathbf{R},\,\mathbf{r}'+\mathbf{R},\,\xi_l) = \hat{\Sigma}(\mathbf{r},\,\mathbf{r}',\,\xi_l). \tag{12.111}$$

The vector potential in the Hamiltonian destroys this symmetry. It can be shown that in a symmetric gauge $(\mathbf{A} = \frac{1}{2}\,\mathbf{B}\times\mathbf{r})$, both $\hat{G}$ and $\hat{\Sigma}$ can be written as the product of a Peierls phase factor and a part that has the preceding symmetry,

$$G(\mathbf{r},\,\mathbf{r}',\,\xi_l,\,\mathbf{h}) = e^{i\mathbf{h}\cdot\mathbf{r}\times\mathbf{r}'}\,\widetilde{G}(\mathbf{r},\,\mathbf{r}',\,\xi_l,\,\mathbf{h}) \tag{12.112}$$

and

$$\hat{\Sigma}(\mathbf{r},\,\mathbf{r}',\,\xi_l,\,\mathbf{h}) = e^{i\mathbf{h}\cdot\mathbf{r}\times\mathbf{r}'}\,\widetilde{\Sigma}(\mathbf{r},\,\mathbf{r}',\,\xi_l,\,\mathbf{h}), \tag{12.113}$$

where

$$\mathbf{h} = \frac{e\mathbf{B}}{2\hbar c}. \tag{12.114}$$

Substituting Eqs. (12.112) and (12.113) in Eq. (12.108), commuting the differential operator through the Peierls phase factor, and then multiplying the left side by $e^{-i\mathbf{h}\cdot\mathbf{r}\times\mathbf{r}'}$, we obtain (Problem 12.11)

$$
\begin{aligned}
&(\xi_l - \frac{1}{2m}[\mathbf{p}+\hbar\mathbf{h}\times(\mathbf{r}-\mathbf{r}')]^2 - \frac{\hbar}{4m^2c^2}\overrightarrow{\sigma}\cdot\overrightarrow{\nabla}V\times[\mathbf{p}+\hbar\mathbf{h}\times(\mathbf{r}-\mathbf{r}')] - V(\mathbf{r}) - \frac{\hbar^2}{8m^2c^2}\nabla^2 V \\
&-\frac{1}{2}g\mu_B\mathbf{B}\cdot\overrightarrow{\sigma})\widetilde{G}(\mathbf{r},\mathbf{r}',\xi_l,\mathbf{h}) - \int d\mathbf{r}''e^{i\mathbf{h}\cdot(\mathbf{r}'\times\mathbf{r}+\mathbf{r}\times\mathbf{r}''+\mathbf{r}''\times\mathbf{r}')}\widetilde{\Sigma}(\mathbf{r},\mathbf{r}'',\xi_l,\mathbf{h})\widetilde{G}(\mathbf{r}'',\mathbf{r}',\xi_l,\mathbf{h}) = \delta(\mathbf{r}-\mathbf{r}')\cdot
\end{aligned}
\tag{12.115}
$$

One can write the equation of motion in the Bloch representation, i.e., in terms of the basis functions,

$$\psi_{n\mathbf{k}\rho}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}U_{n\mathbf{k}\rho}(\mathbf{r}), \tag{12.116}$$

where $U_{n\mathbf{k}\rho}(\mathbf{r})$ is a periodic two-component function, n is the band index, $\mathbf{k}$ is the reduced wave vector, and ρ is the spin index. Using the Bloch representation, one can show that Eq. (12.115) can be rewritten as (Problem 12.12)

$$[\xi_l - \hat{H}(\overrightarrow{\kappa},\xi_l)]\widetilde{G}(\mathbf{k},\xi_l) = I, \tag{12.117}$$

where

$$\hat{H}(\overrightarrow{\kappa},\xi_l) = \frac{1}{2m}(\mathbf{p}+\hbar\overrightarrow{\kappa})^2 + V(\mathbf{r}) + \frac{\hbar}{4m^2c^2}\overrightarrow{\sigma}\cdot\overrightarrow{\nabla}V\times(\mathbf{p}+\hbar\overrightarrow{\kappa}) + \frac{\hbar^2}{8m^2c^2}\nabla^2 V + \frac{1}{2}g\mu_B\mathbf{B}\cdot\overrightarrow{\sigma} + \Sigma(\overrightarrow{\kappa},\xi_l) \tag{12.118}$$

and

$$\overrightarrow{\kappa} = \mathbf{k} + i\mathbf{h}\times\nabla_{\mathbf{k}}. \tag{12.119}$$

12.4.3 Thermodynamic Potential

The grand partition function of a system is defined as

$$Z_G = Tr\{e^{-\beta(\hat{H}-\mu\hat{N})}\}, \tag{12.120}$$

where μ is the chemical potential, and $\hat{N}$ is the operator giving the number of particles. If we write Z_G in the form

$$Z_G = e^{-\beta\Omega(T,V,\mu,\mathbf{B})}, \tag{12.121}$$

all the thermodynamic properties may be derived from $\Omega(T,V,\mu,\mathbf{B})$, which is called the thermodynamic potential. It can be easily shown that the mean energy E is given by

$$\Omega = E - \mu\overline{N} - TS, \tag{12.122}$$

where $\overline{N}$ is the mean number of particles, and S is the entropy. Because $S \to 0$ when $T \to 0$, the last term in Eq. (12.122) is neglected.

It can be shown that the thermodynamic potential for an interacting system is given by

$$\Omega = \frac{1}{\beta}Tr\,\ln(-\widetilde{G}_{\xi_l}) + \frac{1}{\beta}[-Tr\widetilde{\Sigma}_{\xi_l}\widetilde{G}_{\xi_l} + \phi(\widetilde{G}_{\xi_l})] \equiv \Omega_{qp} + \Omega_{corr}. \tag{12.123}$$

Here, $\widetilde{G}_{\xi_l} \equiv \widetilde{G}(\xi_l)$ and $\widetilde{\Sigma}_{\xi_l} \equiv \widetilde{\Sigma}(G_{\xi_l})$ are the one-particle Green's function and the proper self-energy, respectively. ξ_l stands for the imaginary frequencies, Ω_{qp} is the contribution from quasiparticles, and Ω_{corr} describes the corrections from electron correlations. The functional

$$\phi(\widetilde{G}_{\xi_l}) = \lim_{\lambda \to 1} Tr\sum_n \frac{\lambda^n}{2n} \widetilde{\Sigma}^{(n)}(\widetilde{G}_{\xi_l})\widetilde{G}_{\xi_l}, \tag{12.124}$$

where Tr involves summation over both the imaginary frequencies and one-particle states, and $\Sigma^{(n)}(\widetilde{G}_{\xi_l})$ is the nth-order self-energy part, where only the interaction parameter λ occurring explicitly in Eq. (12.123) is used to determine the order. In fact, $\phi(\widetilde{G}_{\xi_l})$ is defined through the decomposition of $\Sigma^{(n)}(\widetilde{G}_{\xi_l})$ into skeleton diagrams. There are $2n$ $\widetilde{G}_{\xi_l}$ lines for the nth-order diagrams in $\phi(\widetilde{G}_{\xi_l})$. Differentiating $\phi(\widetilde{G}_{\xi_l})$ with respect to $\widetilde{G}_{\xi_l}$ has the effect of "opening" any of the $2n$ lines of the nth-order diagram, and each will give the same contribution when Tr is taken.

12.4.4 General Formula for χ

The magnetic susceptibility is calculated from the expression

$$\chi^{\mu\nu} = -\frac{1}{V}\lim_{\mathbf{B}\to 0} \frac{\partial^2\Omega}{\partial B^\mu \partial B^\nu}. \tag{12.125}$$

From Eqs. (12.121) through (12.123), it can be shown that[14]

$$\chi^{\mu\nu} = \frac{1}{V\beta}\left[-\frac{\partial^2}{\partial B^\mu \partial B^\nu}Tr\,\ln(-\widetilde{G}_{\xi_l}) + Tr\frac{\partial^2\widetilde{\Sigma}_{\xi_l}}{\partial B^\mu \partial B^\nu}\widetilde{G}_{\xi_l} + Tr\frac{\partial\widetilde{\Sigma}_{\xi_l}}{\partial B^\mu}\frac{\partial\widetilde{G}_{\xi_l}}{\partial B^\nu}\right]_{B\to 0}. \tag{12.126}$$

We can expand

$$\widetilde{\Sigma}(\overrightarrow{\kappa}, \mathbf{B}, \xi_l) = \widetilde{\Sigma}(\mathbf{k}, \mathbf{B}, \xi_l) - ih_{\alpha\beta}\frac{\partial\widetilde{\Sigma}(\mathbf{k}, \mathbf{B}, \xi_l)}{\partial k^\alpha}\nabla_\mathbf{k}^\beta - \frac{1}{2}h_{\alpha\beta}h_{\gamma\delta}\frac{\partial^2\widetilde{\Sigma}}{\partial k^\alpha\partial k^\gamma}\nabla_\mathbf{k}^\beta\nabla_\mathbf{k}^\delta + ... \quad (12.127)$$

and

$$\widetilde{\Sigma}(\mathbf{k}, \mathbf{B}, \xi_l) = \Sigma^0(\mathbf{k}, \xi_l) + B^\mu\Sigma^{1,\mu}(\mathbf{k}, \xi_l) + B^\mu B^\nu\Sigma^{2,\mu\nu}(\mathbf{k}, \xi_l) + ..., \quad (12.128)$$

where

$$h_{\alpha\beta} = \in_{\alpha\beta\gamma} h^\gamma, \quad (12.129)$$

$\in_{\alpha\beta\gamma}$ is the antisymmetric tensor of the third rank, and we follow the Einstein summation convention. From Eqs. (12.118), (12.119), (12.127), and (12.128) (Problem 12.13), we obtain

$$\hat{H}(\overrightarrow{\kappa}, \xi_l) = \hat{H}_0(\mathbf{k}, \xi_l) + \hat{H}'(\mathbf{k}, \xi_l), \quad (12.130)$$

where

$$\hat{H}_0(\mathbf{k}, \xi_l) = \frac{1}{2m}(\mathbf{p} + \hbar\mathbf{k})^2 + V(\mathbf{r}) + \Sigma^0(\mathbf{k}, \xi_l) + \frac{\hbar^2}{8mc^2}\nabla^2 V + \frac{\hbar}{4m^2c^2}\overrightarrow{\sigma}\cdot\overrightarrow{\nabla}V\times(\mathbf{p} + \hbar\mathbf{k}) \quad (12.131)$$

and

$$\begin{aligned}\hat{H}'(\mathbf{k}, \xi_l) = &-ih_{\alpha\beta}\prod{}^\alpha\nabla_\mathbf{k}^\beta + \frac{1}{2}g\mu_B B^\mu\sigma^\mu + B^\mu\Sigma^{1,\mu}(\mathbf{k}, \xi_l) - ih_{\alpha\beta}B^\mu\frac{\partial\Sigma^{1,\mu}}{\partial k^\alpha}\nabla_\mathbf{k}^\beta \\ &-\frac{1}{2}h_{\alpha\beta}h_{\gamma\delta}\left[\frac{\hbar^2}{m}\delta_{\alpha\gamma} + \frac{\partial^2\Sigma^0}{\partial k^\alpha\partial k^\gamma}\right]\nabla_\mathbf{k}^\beta\nabla_\mathbf{k}^\delta + B^\mu B^\nu\Sigma^{2,\mu\nu}(\mathbf{k}, \xi_l),\end{aligned} \quad (12.132)$$

where the terms up to the second order in the magnetic field are retained, and $\overrightarrow{\prod}/\hbar$ is the velocity operator,

$$\overrightarrow{\prod} = \frac{\hbar}{m}(\overrightarrow{p} + \hbar\mathbf{k}) + \frac{\hbar^2}{4m^2c^2}\overrightarrow{\sigma}\times\overrightarrow{\nabla}V + \nabla_\mathbf{k}\Sigma^0(\mathbf{k}, \xi_l). \quad (12.133)$$

We can make a perturbation expansion

$$\widetilde{G}(\mathbf{k}, \xi_l) = G_0(\mathbf{k}, \xi_l) + G_0(\mathbf{k}, \xi_l)H'G_0(\mathbf{k}, \xi_l) + G_0(\mathbf{k}, \xi_l)H'G_0(\mathbf{k}, \xi_l)H'G_0(\mathbf{k}, \xi_l) + ..., \quad (12.134)$$

where

$$G_0(\mathbf{k}, \xi_l) = \frac{1}{\xi_l - H_0(\mathbf{k}, \xi_l)}, \quad (12.135)$$

and only terms up to the second order in the magnetic field are retained. It can be shown that (Problem 12.14)

$$\nabla_\mathbf{k}^\alpha G_0(\mathbf{k}, \xi_l) = G_0(\mathbf{k}, \xi_l)\prod{}^\alpha G_0(\mathbf{k}, \xi_l) \quad (12.136)$$

and

$$\nabla_{\mathbf{k}}^{\alpha}\nabla_{\mathbf{k}}^{\gamma}G_0(\mathbf{k},\,\xi_l) = G_0\left[\frac{\hbar^2}{m}\delta_{\alpha\gamma} + \mathrm{X}^{\alpha\gamma}\right]G_0 + G_0\prod^{\alpha}G_0\prod^{\gamma}G_0 + G_0\prod^{\gamma}G_0\prod^{\alpha}G_0, \tag{12.137}$$

where

$$\mathrm{X}^{\alpha\gamma} = \nabla_{\mathbf{k}}^{\alpha}\left[\frac{\hbar^2}{4m^2c^2}(\overrightarrow{\sigma}\times\overrightarrow{\nabla}V)^{\gamma} + \nabla_{\mathbf{k}}^{\gamma}\sum^0(\mathbf{k},\,\xi_l)\right]. \tag{12.138}$$

After considerable algebra (for details, see Misra et al.[14]), the general expression for the total magnetic susceptibility of nonferromagnetic solids (including exchange and correlation effects) is obtained as

$$\chi^{\mu\nu} = \chi_0^{\mu\nu} + \chi_s^{\mu\nu} + \chi_{so}^{\mu\nu}, \tag{12.139}$$

where

$$\begin{aligned}
\chi_0^{\mu\nu} = \sum_{\mathbf{k}}(1+\delta_{\mu\nu})&\left\{\frac{e^2\in_{\alpha\beta\mu}\in_{\gamma\delta\nu}}{48\hbar^2c^2}\nabla_{\mathbf{k}}^{\alpha}\nabla_{\mathbf{k}}^{\gamma}E_n\,\nabla_{\mathbf{k}}^{\beta}\nabla_{\mathbf{k}}^{\delta}E_nf'(E_n)\right.\\
&+\left[\frac{e^2\in_{\alpha\beta\mu}\in_{\gamma\delta\nu}}{4\hbar^2c^2}(-\frac{2\hbar^2}{m}\frac{\prod_{n\rho,m\rho'}^{\alpha}\prod_{m\rho',n\rho}^{\gamma}}{E_{mn}^2}\delta_{\beta\delta} + 2\frac{\prod_{n\rho,m\rho'}^{\alpha}\prod_{m\rho',n\rho''}^{\gamma}\prod_{n\rho'',q\rho''}^{\beta}\prod_{q\rho'',n\rho}^{\delta}}{E_{mn}^2E_{qn}}\right.\\
&-2\frac{\prod_{n\rho,m\rho'}^{\alpha}\prod_{m\rho',q\rho''}^{\gamma}\prod_{q\rho'',l\rho''}^{\beta}\prod_{l\rho'',n\rho}^{\delta}}{E_{\ln}E_{qn}E_{mn}} - \frac{\prod_{n\rho,n\rho}^{\alpha}\prod_{n\rho,m\rho'}^{\gamma}\prod_{m\rho',q\rho''}^{\delta}\prod_{q\rho'',n\rho}^{\beta}}{E_{mn}E_{qn}^2}\\
&+\frac{\prod_{n\rho,n\rho}^{\alpha}\prod_{n\rho,m\rho'}^{\beta}\prod_{m\rho',q\rho''}^{\gamma}\prod_{q\rho'',n\rho}^{\delta}}{E_{mn}^2E_{qn}} - \frac{\prod_{n\rho,m\rho'}^{\beta}\mathrm{X}_{m\rho',q\rho''}^{\alpha\gamma}\prod_{q\rho'',n\rho}^{\delta}}{E_{mn}E_{qn}}\\
&+\frac{\prod_{n\rho,m\rho'}^{\beta}\prod_{m\rho',q\rho''}^{\delta}\mathrm{X}_{q\rho'',n\rho}^{\alpha\gamma}}{E_{mn}E_{qn}} + \frac{\mathrm{X}_{n\rho,m\rho'}^{\alpha\gamma}\prod_{m\rho',q\rho''}^{\beta}\prod_{q\rho'',n\rho}^{\delta}}{E_{mn}E_{qn}} - \frac{\mathrm{X}_{n\rho,n\rho}^{\alpha\gamma}\prod_{n\rho,m\rho'}^{\beta}\prod_{m\rho',n\rho}^{\delta}}{E_{mn}^2}\right]\\
&+\left.\frac{ie}{4\hbar c}\in_{\alpha\beta\nu}\left[\frac{\prod_{n\rho,m\rho'}^{\beta}Y_{m\rho',n\rho}^{\alpha\mu}}{E_{mn}} - \frac{Y_{n\rho,m\rho'}^{\alpha\mu}\prod_{m\rho',n\rho}^{\beta}}{E_{mn}}\right]f(E_n)\right\},
\end{aligned} \tag{12.140}$$

where

$$E_{mn} \equiv E_m - E_n, \tag{12.141}$$

and repeated indices means summation over band and spin. Similarly, one can show[14] that the effective Pauli spin susceptibility, including the exchange and correlation effects is,

$$\chi_s^{\mu\nu} = -\frac{1}{8}\,(1+\delta_{\mu\nu})\mu_B^2\sum_{n,\mathbf{k},\rho,\rho'}g_{nn}^{\nu}(\mathbf{k})\sigma_{n\rho,n\rho'}^{\nu}\left(g_{nn}^{\mu}(\mathbf{k})\sigma_{n\rho',n\rho}^{\mu} + \frac{2}{\mu_B}\Sigma_{n\rho',n\rho}^{1,\mu}\right)f'(E_n), \tag{12.142}$$

where the effective g matrix is defined as

$$g_{nn}^{\nu}(\mathbf{k})\sigma_{n\rho,n\rho'}^{\nu} = \frac{ie}{\mu_B\hbar c}\in_{\alpha\beta\nu}\sum_{m,\rho''}\frac{\prod_{n\rho,m\rho''}^{\alpha}\prod_{m\rho'',n\rho'}^{\beta}}{E_{mn}} + g\sigma_{n\rho,n\rho'}^{\nu}. \tag{12.143}$$

The additional spin-orbit contribution to the magnetic susceptibility is[14]

$$
\begin{aligned}
\chi_{so}^{\mu\nu} = \sum_{\mathbf{k}} (1 + \delta_{\mu\nu}) \Bigg[& \frac{e^2 \in_{\alpha\beta\mu} \in_{\gamma\delta\nu}}{2\hbar^2 c^2} \frac{\Pi_{n\rho,m\rho'}^{\alpha} \Pi_{m\rho',n\rho''}^{\beta} \Pi_{n\rho'',q\rho'''}^{\gamma} \Pi_{q\rho''',n\rho}^{\delta}}{E_{mn}^2 E_{qn}} \\
& + \frac{ieg\mu_B}{4\hbar c} \in_{\alpha\beta\nu} \Bigg\{ -3 \frac{J_{n\rho,n\rho'}^{\mu} \Pi_{n\rho',m\rho''}^{\alpha} \Pi_{m\rho'',n\rho}^{\beta}}{E_{mn}^2} + \frac{\Pi_{n\rho,m\rho'}^{\alpha} \Pi_{m\rho',q\rho''}^{\beta} J_{q\rho'',n\rho}^{\mu}}{E_{qn} E_{mn}} \\
& + \frac{\Pi_{n\rho,m\rho'}^{\alpha} J_{m\rho',q\rho''}^{\mu} \Pi_{q\rho'',n\rho}^{\beta}}{E_{qn} E_{mn}} + \frac{J_{n\rho,m\rho'}^{\mu} \Pi_{m\rho',q\rho''}^{\alpha} \Pi_{q\rho'',n\rho}^{\beta}}{E_{qn} E_{mn}} + \frac{\Pi_{n\rho,n\rho}^{\alpha} J_{n\rho,m\rho'}^{\mu} \Pi_{m\rho'',n\rho}^{\beta}}{E_{mn}^2} \\
& - \frac{\Pi_{n\rho,n\rho}^{\alpha} \Pi_{n\rho,m\rho'}^{\beta} J_{m\rho',n\rho}^{\mu}}{E_{mn}^2} \Bigg\} + \frac{1}{8} g^2 \mu_B^2 \Bigg\{ \frac{\sigma_{n\rho,m\rho'}^{\mu} F_{m\rho',n\rho}^{\nu}}{E_{mn}} + \frac{F_{n\rho,m\rho'}^{\mu} \sigma_{m\rho',n\rho}^{\nu}}{E_{mn}} \Bigg\} \Bigg] f(E_n),
\end{aligned}
\tag{12.144}
$$

where

$$
\overrightarrow{J} = \overrightarrow{\sigma} + \frac{1}{g\mu_B} \Sigma^1,
\tag{12.145}
$$

$$
Y^{\mu\nu} = \frac{\partial \Sigma^{1,\nu}}{\partial \mathbf{k}^{\mu}},
\tag{12.146}
$$

and

$$
F^{\nu} = \sigma^{\nu} + \frac{2}{g\mu_B} \Sigma^{1,\nu}.
\tag{12.147}
$$

12.4.5 Exchange Self-Energy in the Band Model

The exchange contribution to the self-energy is local in $\mathbf{r}$ space. In the simple static screening approximation, the self-energy is independent of ξ_l. Neglecting the field dependence of screening as well as that of $v_{eff}(\mathbf{r}, \mathbf{r}')$,

$$
\widetilde{\Sigma}(\mathbf{r}, \mathbf{r}') = -\frac{1}{\beta} \sum_{\xi_l} v_{eff}(\mathbf{r}, \mathbf{r}') \widetilde{G}(\mathbf{r}, \mathbf{r}', \xi_l),
\tag{12.148}
$$

$\widetilde{\Sigma}$ and $\widetilde{G}$ can be expanded in terms of Bloch states as follows:

$$
\widetilde{\Sigma}(\mathbf{r}, \mathbf{r}') = \sum_{n,m,\mathbf{k},\rho,\rho'} \widetilde{\Sigma}_{n\rho,m\rho'}(\mathbf{k}) \psi_{n\mathbf{k}\rho}(\mathbf{r}) \psi_{m\mathbf{k}\rho'}^{*}(\mathbf{r}')
\tag{12.149}
$$

and

$$
\widetilde{G}(\mathbf{r}, \mathbf{r}') = \sum_{n,m,\mathbf{k},\rho,\rho'} \widetilde{G}_{n\rho,m\rho'}(\mathbf{k}) \psi_{n\mathbf{k}\rho}(\mathbf{r}) \psi_{mk\rho'}^{*}(\mathbf{r}') \cdot
\tag{12.150}
$$

Substituting Eqs. (12.149) and (12.150) in (12.148), we obtain

$$\sum_{n,m,\rho,\rho'} \widetilde{\Sigma}_{n\rho,m\rho'}(\mathbf{k}) \psi_{n\mathbf{k}\rho}(\mathbf{r}) \psi^*_{m\mathbf{k}\rho'}(\mathbf{r}')$$
$$= -\frac{1}{\beta} \sum_{\xi_l,p,q,\mathbf{k}',\overline{\rho},\overline{\rho}'} v_{eff}(\mathbf{r}, \mathbf{r}') \widetilde{G}_{p\overline{\rho},q\overline{\rho}'}(\mathbf{k}', \xi_l) \psi_{p\mathbf{k}'\overline{\rho}}(\mathbf{r}) \psi^*_{q\mathbf{k}'\overline{\rho}'}(\mathbf{r}') . \tag{12.151}$$

If the effective electron–electron interaction is spin independent, then $\rho = \overline{\rho}$, $\rho' = \overline{\rho}'$, and we obtain

$$\overline{\Sigma}_{n\rho,m\rho'}(\mathbf{k}) = -\frac{1}{\beta} \sum_{\mathbf{k}',\xi_l,p,q} <nm|v_{eff}(\mathbf{k}, \mathbf{k}')|pq>_{\rho\rho'} \widetilde{G}_{p\rho,q\rho'}(\mathbf{k}', \xi_l), \tag{12.152}$$

where (Problem 12.15)

$$<nm|v_{eff}(\mathbf{k}, \mathbf{k}')|pq>_{\rho\rho'} = \int \psi^*_{n\mathbf{k}\rho}(\mathbf{r}) \psi_{m\mathbf{k}\rho'}(\mathbf{r}') v_{eff}(\mathbf{r}, \mathbf{r}') \psi_{p\mathbf{k}'\rho}(\mathbf{r}) \psi^*_{q\mathbf{k}'\rho'}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \tag{12.153}$$

Eq. (12.153) is the exchange self-energy in the band model. One can obtain Σ^0, Σ^1, Σ^2, and so on (defined in Eq. 12.128), by expanding $\widetilde{G}$. We make the further approximation

$$<nn|v_{eff}(\mathbf{k}, \mathbf{k}')|pq>_{\rho\rho'} \approx <nn|v_{eff}(\mathbf{k}, \mathbf{k}'|pp>\delta_{pq} = v_{np}(\mathbf{k}, \mathbf{k}')\delta_{pq}. \tag{12.154}$$

From Eqs. (12.152) and (12.154),

$$\widetilde{\Sigma}_{n\rho,n\rho'}(\mathbf{k}) = -\frac{1}{\beta} \sum_{\mathbf{k}',\xi_l,\rho} v_{np}(\mathbf{k}, \mathbf{k}') \widetilde{G}_{p\rho,p\rho'}(\mathbf{k}', \xi_l) . \tag{12.155}$$

Substituting only the value of the first-order terms of **B** occurring in $\widetilde{G}$ from Eq. (12.134) on the right side of Eq. (12.155), and neglecting the terms proportional to f, we obtain (Problem 12.16)

$$\Sigma^{1,\mu}_{n\rho,n\rho'}(\mathbf{k}) \simeq -\sum_{m\mathbf{k}'} v_{nm}(\mathbf{k}, \mathbf{k}')\Sigma^{1,\mu}_{m\rho,m\rho'}(\mathbf{k}')f'_m(\mathbf{k}') - \frac{1}{2}\mu_B \sum_{m\mathbf{k}'} v_{nm}(\mathbf{k}, \mathbf{k}')g^\mu_{mm}(\mathbf{k}')\sigma^\mu_{m\rho,m\rho'}f'_m(\mathbf{k}'). \tag{12.156}$$

Similarly, to calculate $\Sigma^1_{n\rho,m\rho'}(\mathbf{k})$, we assume

$$<nm|v_{eff}(\mathbf{k}, \mathbf{k}')|pq>_{\rho\rho'} = \overline{v}_{nm}(\mathbf{k}, \mathbf{k}')\delta_{np}\delta_{mq}. \tag{12.157}$$

From Eqs. (12.152) and (12.157), we obtain

$$\widetilde{\Sigma}_{n\rho,m\rho'}(\mathbf{k}) = -\frac{1}{\beta} \sum_{\mathbf{k}',\xi_l} \overline{v}_{nm}(\mathbf{k}, \mathbf{k}') \widetilde{G}_{n\rho,m\rho'}(\mathbf{k}', \xi_l) . \tag{12.158}$$

12.4.6 Exchange Enhancement of χ_s

We will first discuss how $\chi^{\mu\mu}_s$ gets exchange enhanced. One can rewrite Eq. (12.142) in the alternate form

$$\chi^{\mu\mu}_s = \chi^{\mu\mu}_{0,s} + \chi^{\mu\mu}_{1\cdot s}, \tag{12.159}$$

where

$$\chi_{0,s}^{\mu\mu} = -\frac{1}{4}\mu_B^2 \sum_{n,\mathbf{k},\rho,\rho'} g_{nn}^\mu \sigma_{n\rho,n\rho'}^\mu g_{nn}^\mu \sigma_{n\rho',n\rho}^\mu f'(E_n) \tag{12.160}$$

is the effective Pauli spin susceptibility for noninteracting Bloch electrons, and

$$\chi_{1,s}^{\mu\mu} = -\frac{1}{2}\mu_B \sum_{n,\mathbf{k},\rho,\rho'} g_{nn}^\mu \Sigma_{n\rho,n\rho'}^{1,\mu} \sigma_{n\rho',n\rho}^\mu f'(E_n) \tag{12.161}$$

is the contribution due to exchange and correlation. If we consider the individual band enhancement and neglect interband interactions in the expression for $\Sigma_{n\rho,n\rho'}^{1,\mu}$ in Eq. (12.156), make an average exchange enhancement ansatz, and assume $v_{nm} \simeq v_{nn}\delta_{nm}$, which is equivalent to the assumption that $\Sigma^{1,\mu}$ is independent of $\mathbf{k}$, we obtain

$$\Sigma_{n\rho,n\rho'}^{1,\mu} = \frac{1}{2}\frac{\alpha_n}{1-\alpha_n}\mu_B g_{nn}^\mu \sigma_{n\rho,n\rho'}^\mu, \tag{12.162}$$

where

$$\alpha_n = -\sum_{\mathbf{k}',m} v_{nm}(\mathbf{k},\,\mathbf{k}')f'(E_m(\mathbf{k}')). \tag{12.163}$$

From Eqs. (12.159) through (12.162), we obtain

$$\chi_s^{\mu\mu} = \sum_n \frac{\chi_{0s,n}^\mu}{(1-\alpha_n)}, \tag{12.164}$$

where $\chi_{0s\cdot n}^{\mu\mu}$ is the contribution to effective Pauli susceptibility for each band. Eq. (12.164) is known as the Stoner enhancement, which was obtained by making drastic assumptions while solving the matrix integral equations for $\Sigma_{n\rho,n\rho'}^{1,\mu}$. However, the neglect of coupling of interband terms, i.e., coupling between $\Sigma_{n\rho,n\rho'}^{1,\mu}$, might be too drastic for systems such as Be, Cd, and so on. It can be easily shown[14] that even in a simple two-band model, the exchange enhancement of χ_s is quite different from the simple form obtained from Eq. (12.164).

12.4.7 Exchange and Correlation Effects on χ_o

The exchange and correlation effects on χ_o are very complicated. We consider only the first term of Eq. (12.140),

$$\chi_0^{\mu\nu} \approx \chi_{LP}^{qp} = \sum_{\mathbf{k}}(1+\delta_{\mu\nu})\frac{e^2 \in_{\alpha\beta\mu}\in_{\gamma\delta\nu}}{48\,\hbar^2 c^2} \nabla_{\mathbf{k}}^\alpha \nabla_{\mathbf{k}}^\gamma E_n \,\nabla_{\mathbf{k}}^\beta \nabla_{\mathbf{k}}^\delta E_n f'(E_n), \tag{12.165}$$

which is the familiar Landau–Peierls susceptibility for quasiparticles (χ_{LP}^{qp}), because the energy in the Landau–Peierls term is the quasiparticle energy. This is the well-known Sampson–Seitz prescription that had been stated without proof. If we include the effects of electron–electron interaction through an effective mass and ignore the band effects, we obtain the well-known results for χ_o,[21]

$$\chi_{LP}^{qp} = \frac{\chi_{LP}}{1+A_1/3}, \tag{12.166}$$

where A_1 is the Fermi-liquid parameter. The second through fifth terms in Eq. (12.140) are corrections to the Landau–Peierls term, which are zero for free electrons, but are of the same order as χ_{LP} for band electrons even in the absence of electron–electron interactions.[12] Therefore, while one considers many-body effects on χ_o, it is wrong to consider only χ_{LP}^{qp} as was done in earlier calculations.

12.4.8 Exchange and Correlation Effects on χ_{so}

The effect of electron–electron interactions is different on the various terms in χ_{so} in Eq. (12.144). A discussion of these effects is beyond the scope of this book except to note that even in the absence of exchange and correlation effects, the contributions of χ_{so} are of the same order as χ_s for some metals and semiconductors.
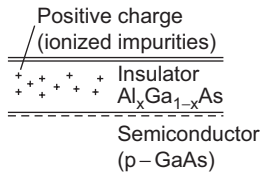
12.5 QUANTUM HALL EFFECT

12.5.1 Introduction

von Klitzing et al.[20] first observed the integer quantum Hall effect (QHE) in a two-dimensional electron gas formed by an inversion layer at an Si/SiO_2 interface (discussed in Chapter 11). We note that a two-dimensional electron gas can be formed at the semiconductor surface if the electrons are fixed close to the surface by an external electric field in either Silicon MOSFETS or GaAs-$Al_xGa_{1-x}As$ heterostructures (Chapter 11). In fact, a two-dimensional electron gas is essential for the observation of the quantum Hall effect. In addition to the quantum phenomena connected with the confinement of electrons within a two-dimensional layer, the Landau quantization of the electron motion in a strong magnetic field is necessary for the interpretation of the quantum Hall effect. We will discuss the integer quantum Hall effect in detail and briefly mention the fractional quantum Hall effect, discovered soon after, because a detailed discussion involving many-body theory is beyond the scope of this book.

12.5.2 Two-Dimensional Electron Gas

The energy of mobile electrons in semiconductors can be written as

$$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2). \qquad (12.167)$$

When the energy for the motion in the z direction is fixed by using a triangular potential with an infinite barrier at the surface ($z = 0$) and with a constant electric field F_s for $z \geq 0$ (z is positive downward), one obtains a quasi-two-dimensional electron gas (as shown in Figure 12.10).

The electrons are confined close to the surface due the electrostatic field F_s normal to the interface originating from the positive charges, which causes a drop in the electron potential toward the surface.
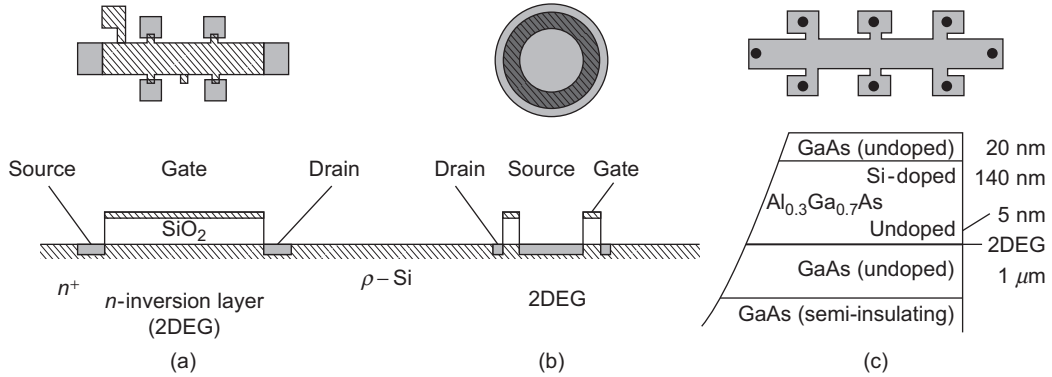

FIGURE 12.10

Two-dimensional electron gas formed close to the semiconductor surface of GaAs-$Al_xGa_{1-x}As$ heterostructures by an external electric field along the z direction.

FIGURE 12.11

Typical geometries and cross-sections of devices used in the quantum Hall experiments. From left to right: (a) Long silicon device (Hall geometry) with potential probes (for R_x measurements) and Hall probes (for R_H measurements): typical length: 0.5 mm. (b) Circular MOS device for σ_{xy} measurements. (c) Cross-section and top view of a GaAs–Al$_{0.3}$Ga$_{0.7}$As heterostructure with Hall geometry.

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The energy of the carriers is grouped into electric sub-bands corresponding to the quantized levels for the motion in the z direction provided the potential well is small compared to the de Broglie wavelength of the electrons. At very low temperatures (T < 4° K), if the carrier densities of the two-dimensional electron gas are small such that only the lowest electric sub-band E_0 is occupied with electrons (the electric quantum limit that occurs when the Fermi energy E_F is small compared with the sub-band separation $E_1 - E_0$), the energy spectrum can be written as

$$E = E_0 + \frac{\hbar^2 k_\parallel^2}{2m^*}, \tag{12.168}$$

where $k_\parallel$ is a wave vector within the plane of the electron gas.

The experimental arrangement for QHE measurements is shown in Figure 12.11. For measurement of current, heavily doped n^+ contacts are used as current contacts and potential probes at the semiconductor surface.

The resistivity component ρ_{xx} is directly proportional to $\sigma_{xx} = \sigma_{yy}$, $\sigma_{xy} = -\sigma_{yx}$. Hence, $\rho_{xx} = \sigma_{xx}/(\sigma_{xx}^2 + \sigma_{yy}^2)$. This means that the condition $\sigma_{xx} = 0$ (fully occupied Landau levels) leads to $\rho_{xx} = 0$. Thus, a correct value for the quantized Hall resistance is $R_H = h/e^2 n$, which is expected only under the condition $\rho_{xx} = 0$.

12.5.3 Quantum Transport of a Two-Dimensional Electron Gas in a Strong Magnetic Field

When a strong magnetic field **B** is applied such that B_z is normal to the interface, the two-dimensional electrons move in cyclotron orbits parallel to the surface. The energy levels can be expressed as

$$E_n = E_0 + \left(n + \frac{1}{2}\right)\hbar\omega_c + gs\mu_B B, \tag{12.169}$$

where ω_c is the cyclotron frequency $(\omega_c = -eB/m^*)$, and s is the spin quantum number, $s = \pm\frac{1}{2}$. Laughlin (Ref. 8) derived an expression of a 2DEG in a strong magnetic field by considering the isotropic effective-mass Hamiltonian

$$\hat{H} = \frac{1}{2m^*}\left[\mathbf{p} + \frac{e}{c}\mathbf{A}\right]^2 - eE_0y, \qquad (12.170)$$

where the y coordinate is related to the vector potential (in the Landau gauge),

$$\mathbf{A} = By\hat{x}. \qquad (12.171)$$

From Eqs. (12.170) and (12.171), the wave functions are given by

$$\psi_{k,n} = e^{ikx}\phi_n(y - y_0), \qquad (12.172)$$

where ϕ_n is the solution of the harmonic-oscillator equations

$$\frac{1}{2m^*}\left[p_y^2 + (\frac{e}{c}B)^2y^2\right]\phi_n = (n + \frac{1}{2})\hbar\omega_c\phi_n \qquad (12.173)$$

and

$$y_0 = \frac{1}{\omega_c}\left[\frac{\hbar k}{m^*} - \frac{cE_0}{B}\right]. \qquad (12.174)$$

The energy of the state is

$$E_{n,k} = (n + \frac{1}{2})\hbar\omega_c - eE_0y_0 + \frac{1}{2}m^*(cE_0B)^2. \qquad (12.175)$$

The y_0 are changed by a vector potential increment $\Delta A\hat{x}$ only through the location of their centers,

$$y_0 \rightarrow y_0 - \Delta A/B. \qquad (12.176)$$

It is obvious from Eqs. (12.175) and (12.176) that the energy changes linearly with ΔA.

From Eq. (12.174), one can obtain the degeneracy factor for each Landau level that is given by the number of center coordinates y_0 (note that $y - y_0$ is a good quantum number) in the sample. For a two-dimensional electron gas confined in a device of dimensions L_x, L_y,

$$\Delta y_0 = \frac{1}{\omega_c}\frac{\hbar\Delta k}{m^*c} = \frac{-\hbar}{eB}\Delta k = \frac{-\hbar}{eB}\frac{2\pi}{L_x} = \frac{-h}{eBL_x}. \qquad (12.177)$$

The degeneracy factor is given by

$$N_0 = \frac{L_y}{\Delta y_0} = \frac{-L_xL_yeB}{h}, \qquad (12.178)$$

(note that e is negative) which is the same as the number of the flux quanta in the sample. The degeneracy factor per unit area (from Eq. 12.178) is

$$N = \frac{N_0}{L_xL_y} = \frac{-eB}{h}. \qquad (12.179)$$

Thus, the degeneracy factor for each Landau level is independent of the effective mass and other semiconductor parameters.

It can be shown that the Hall voltage U_H of a two 2DEG with a surface carrier density n_s ($n_s = nN$, when n energy levels are fully occupied) is

$$U_H = -\frac{B}{n_s e}I, \tag{12.180}$$

where I is the current in the sample. From Eqs. (12.179) and (12.180), the Hall resistance

$$R_H = \frac{U_H}{I} = -\frac{B}{n_s e} = -\frac{B}{nNe} = \frac{h}{ne^2}, \tag{12.181}$$

where $n = 1, 2, 3, \ldots$. Thus, whenever

$$n = -\frac{n_s h}{eB} \tag{12.182}$$

is an integer (by adjusting the magnetic field B and the density of states n_s), the Hall resistance is quantized. When the condition outlined in Eq. (12.182) is satisfied, there is no current flow in the direction of the electric field, and hence, the conductivity $\sigma_{xx} = 0$. The electrons move like free particles perpendicular to the electric field. The quantized plateaus in the Hall resistance are shown in Figure 12.12.
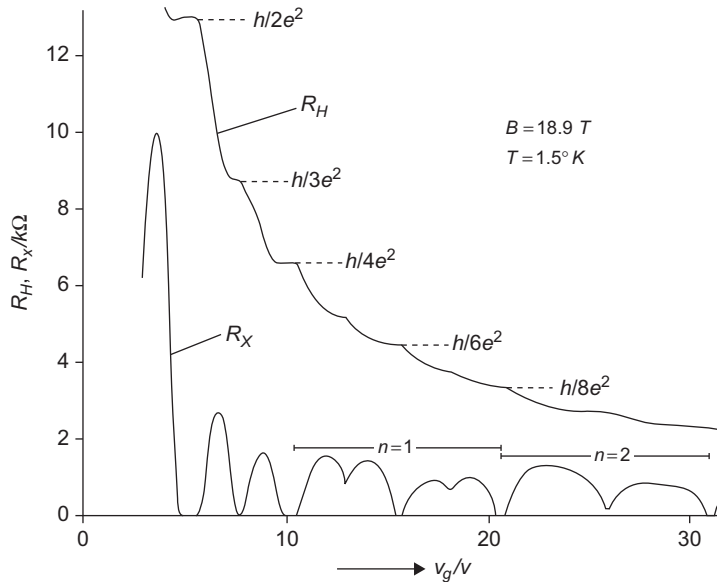
FIGURE 12.12

Gate voltage dependence of the Hall resistance R_H and resistivity R_x at $B = 18.9\ T$ for a long silicon MOS device at $B = 18.9\ T$ and $T = 1.5°\ K$.

12.5.4 Quantum Hall Effect from Gauge Invariance

Laughlin (Refs. 7-9) considered a two-dimensional metallic loop (see Figure 12.13) pierced by a magnetic field B normal to its surface. A voltage U_H is applied between the two edges of the ring. When $\sigma_{xx} = 0$, the energy is conserved and Faraday's law of induction can be written as

$$I = c\frac{\partial E}{\partial \phi}, \qquad (12.183)$$

where E is the total energy of the system, and ϕ is the magnetic flux threading the loop. If $\phi \rightarrow \phi + \Delta\phi$, where $\Delta\phi \equiv \phi_0 = -hc/e$ is a flux quantum, the wave function enclosing the flux changes by a factor 2π, which implies $k \rightarrow k + (2\pi)/L$, where L is the circumference of the ring.

FIGURE 12.13

Quantized Hall resistance for a model two-dimensional metallic loop.

The change in energy ΔE when the states are transported from one edge to the other is

$$\Delta E = -neU_H, \qquad (12.184)$$

where n corresponds to the filled Landau levels. From Eqs. (12.183) and (12.184), we obtain an expression for the dissipationless Hall current and the Hall voltage,

$$I = c\frac{\partial E}{\partial \phi} = c\frac{\Delta E}{\Delta \phi} = -\frac{cneU_H}{\phi_0} = \frac{ne^2 U_H}{h}. \qquad (12.185)$$

The quantized Hall resistance is obtained from the expression

$$R_H = \frac{U_H}{I} = \frac{h}{ne^2}. \qquad (12.186)$$

12.6 FRACTIONAL QUANTUM HALL EFFECT

There have been numerous papers on the fractional quantum Hall effect. It is generally interpreted on the elementary excitations of quasiparticles with a charge $e/3$, $e/5$, $e/7$, and so on. A typical experimental result is shown in Figure 12.14.
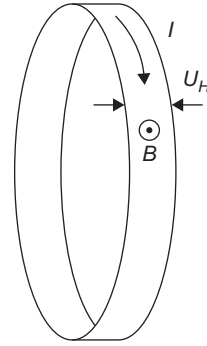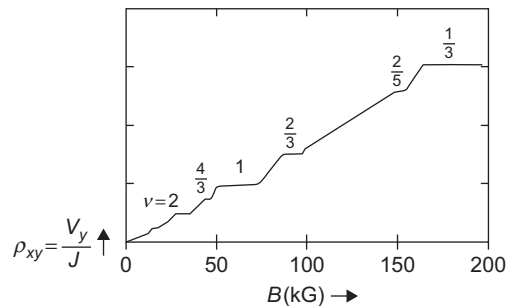

FIGURE 12.14

Schematic diagram of fractional quantum Hall effect in GaAs/Ga$_{1-x}$Al$_x$As heterostructure.

PROBLEMS

12.1. The Hamiltonian of an atom (or ion) in a uniform magnetic field **B** (in the z direction) can be written as

$$H = \frac{1}{2m}\sum_i \left(\mathbf{p}_i + \frac{e\mathbf{A}(\mathbf{r}_i)}{c}\right)^2 + g_0\mu_B B\sum_i \hat{s}_z^i. \tag{1}$$

If

$$\mathbf{A}(\mathbf{r}_i) = -\frac{1}{2}\,\mathbf{r}\times\mathbf{B}, \tag{2}$$

show that Eq. (1) can be rewritten in the alternate form

$$\hat{H} = \frac{1}{2m}\sum_i \hat{\mathbf{p}}_i^2 + \mu_B(\hat{\mathbf{L}} + g_0\hat{\mathbf{S}})\cdot\mathbf{B} + \frac{e^2}{8mc^2}B^2\sum_i(x_i^2 + y_i^2). \tag{3}$$

12.2. We have derived

$$<JLSJ_z|(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|JLSJ_z'> = g(JLS)<JLSJ_z|\hat{\mathbf{J}}|JLSJ_z'>. \tag{1}$$

Show that Eq. (1) can be rewritten in the alternate form

$$<JLSJ_z|\hat{\mathbf{L}} + 2\hat{\mathbf{S}}|J'L'S'J_z'> = g(JLS)<JLSJ_z|\hat{\mathbf{J}}|J'L'S'J_z'>. \tag{2}$$

12.3. We have proved that

$$\sum_{J''L''S''J_z''} <JLSJ_z|(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|J''L''S''J_z''>\cdot<J''L''S''J_z''|\hat{\mathbf{J}}|J'L'S'J_z'>$$
$$= g(JLS)\sum_{J''L''S''J_z''} <JLSJ_z|\hat{\mathbf{J}}|J''L''S''J_z''>\cdot<J''L''S''J_z''|\hat{\mathbf{J}}|J'L'S'J_z'>. \tag{1}$$

Because the sum over Eq. (1) is taken over a complete set, using Eqs. (12.31) and (12.32), show that Eq. (1) can be rewritten in the alternate form

$$<JLSJ_z|(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})\cdot\hat{\mathbf{J}}|JLSJ_z'> = g(JLS)<JLSJ_z|\hat{\mathbf{J}}^2|JLSJ_z'>. \tag{2}$$

12.4. Using the standard relation for the total angular momentum of an electron in an atom,

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}, \tag{1}$$

show that

$$(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})\cdot(\hat{\mathbf{L}} + \hat{\mathbf{S}}) = \hat{\mathbf{L}}^2 + 2\hat{\mathbf{S}}^2 + \hat{\mathbf{L}}\cdot\hat{\mathbf{J}} + 2\hat{\mathbf{S}}\cdot\hat{\mathbf{J}} = \frac{1}{2}[3\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2]. \tag{2}$$

12.5. The Helmholtz free energy is obtained from

$$e^{-\beta F} = \frac{e^{\beta\gamma B\left(J+\frac{1}{2}\right)} - e^{-\beta\gamma B\left(J+\frac{1}{2}\right)}}{e^{\beta\gamma B/2} - e^{-\beta\gamma B/2}}. \tag{1}$$

The magnetization of N ions in a volume V is defined as

$$M = -\frac{N}{V}\frac{\partial F}{\partial B}. \tag{2}$$

From Eqs. (1) and (2), show that

$$M = \frac{N}{V}\gamma J B_J(\beta\gamma JB), \tag{3}$$

where the Brillouin function $B_J(x)$ is defined by

$$B_J(x) = \frac{(2J+1)}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right). \tag{4}$$

12.6. From the equations

$$E_v = \frac{\hbar^2 k_z^2}{2m} + \left(v+\frac{1}{2}\right)\hbar\omega_c, \quad v = 0, 1, 2, \dots \tag{1}$$

and

$$g(v, k_z)\, dk_z = \frac{2}{(2\pi)^2}\frac{m\omega_c}{\hbar}\, dk_z, \tag{2}$$

show that

$$g(E, v)\, dE = \frac{2}{(2\pi)^2}\frac{\hbar\omega_c}{2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E-\left(v+\frac{1}{2}\right)\hbar\omega_c\right)^{-1/2} dE. \tag{3}$$

12.7. In the limiting case, $B \to 0$, the summation

$$g(E)dE = \sum_0^{v'} g(E, v)\, dE \tag{1}$$

can be replaced by an integration because the sub-bands of different quantum numbers move very close to each other. By carrying out this integration (using Eq. 3 from Problem 12.6), and substituting $B = 0$, show that

$$g(E)dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} dE, \tag{2}$$

which is the density of states of free electrons.

12.8. Show from Eqs. (12.53) through (12.55) and (12.69) that the expression for magnetization per unit volume can be written as

$$M = -\frac{d}{dB}\left\{n\mu - \frac{1}{\beta}\int_0^\infty g(E_+) \, \ln[e^{\beta(\mu-E)} + 1] \, dE_+ - \frac{1}{\beta}\int_0^\infty g(E_-) \, \ln[e^{\beta(\mu-E)} + 1] \, dE_-\right\}. \quad (1)$$

12.9. The Fermi integral $F(x)$ is given by

$$F(x) = \int_0^\infty \frac{y^{1/2}}{1 + e^{(y-x)}} \, dy. \quad (1)$$

Show that

$$F(x) \approx \frac{\sqrt{\pi}}{2} e^x, \quad \text{for } x < 0$$

and

$$F(x) \approx \frac{2}{3} x^{3/2}, \quad \text{for } x > 0. \quad (2)$$

12.10. The magnetization per unit volume is given by (Problem 12.8)

$$M = -\frac{d}{dB}\left\{n\mu - \frac{1}{\beta}\int_0^\infty g(E_+) \, \ln[e^{\beta(\mu-E)} + 1] \, dE_+ - \frac{1}{\beta}\int_0^\infty g(E_-) \, \ln[e^{\beta(\mu-E)} + 1] \, dE_-\right\}. \quad (1)$$

By retaining the first term in the expansion similar to the one outlined in the text, show that at very low temperatures

$$M = \frac{3n\mu_B^2 B}{2E_F}\left[1 - \frac{1}{3} + \frac{\pi k_B T}{\mu_B B}\left(\frac{E_F}{\mu_B B}\right)^{1/2} \sum_{v=1}^\infty \frac{(-1)^v}{\sqrt{v}} \, \cos(\pi v) \, \frac{\sin\left(\frac{\pi}{4} - \frac{\pi v E_F}{\mu_B B}\right)}{\sinh\dfrac{\pi^2 v k_B T}{\mu_B B}}\right], \quad (2)$$

where E_F is the Fermi energy (the value of μ at T = 0).

12.11. Substituting Eqs. (12.112) and (12.113) in Eq. (12.108), commuting the differential operator through the Peierls phase factor, and then multiplying the left side of the equation by $e^{-i\mathbf{h}\cdot\mathbf{r}\times\mathbf{r}'}$, show that

$$(\xi_l - \frac{1}{2m}[\mathbf{p} + \hbar\mathbf{h}\times(\mathbf{r}-\mathbf{r}')]^2 - \frac{\hbar}{4m^2c^2}\overrightarrow{\sigma}\cdot\overrightarrow{\nabla}\,V\times[\mathbf{p} + \hbar\mathbf{h}\times(\mathbf{r}-\mathbf{r}')] - V(\mathbf{r}) - \frac{\hbar^2}{8m^2c^2}\nabla^2 V$$
$$- \frac{1}{2}\,g\mu_B\mathbf{B}\cdot\overrightarrow{\sigma})\widetilde{G}(\mathbf{r},\,\mathbf{r}',\,\xi_l,\,\mathbf{h}) - \int d\mathbf{r}''\, e^{i\mathbf{h}\cdot(\mathbf{r}'\times\mathbf{r}+\mathbf{r}\times\mathbf{r}''+\mathbf{r}''\times\mathbf{r}')}\widetilde{\Sigma}(\mathbf{r},\,\mathbf{r}'',\,\xi_l,\,\mathbf{h})\widetilde{G}(\mathbf{r}'',\,\mathbf{r}',\,\xi_l,\,\mathbf{h}) \quad (1)$$
$$= \delta(\mathbf{r}-\mathbf{r}').$$

12.12. Using the Bloch representation, $\psi_{n\mathbf{k}\rho}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}U_{n\mathbf{k}\rho}(\mathbf{r})$, show that Eq. (1) in Problem 12.11 can be rewritten as

$$
\sum_{n'',\rho'',\mathbf{k}',\mathbf{k}''} \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}'' e^{-i\mathbf{k}\cdot\mathbf{r}} U_{n\mathbf{k}\rho}^*(\mathbf{r})
\left(
\begin{matrix}
\xi_l - \dfrac{1}{2m}[\mathbf{p} + \hbar\mathbf{h}\times(\mathbf{r}-\mathbf{r}')]^2 - \dfrac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times[\mathbf{p}+\hbar\mathbf{h}\times(\mathbf{r}-\mathbf{r}')] \\[2mm]
-V(\mathbf{r}) - \dfrac{\hbar^2}{8m^2c^2}\nabla^2 V - \dfrac{1}{2}g\mu_B\mathbf{B}\cdot\vec{\sigma}
\end{matrix}
\right)
$$

$$
\times e^{-\mathbf{k}''\cdot(\mathbf{r}-\mathbf{r}'')} U_{n''\mathbf{k}''\rho''}(\mathbf{r})U_{n''\mathbf{k}''\rho''}^*(\mathbf{r}'')\widetilde{G}(\mathbf{r}'',\mathbf{r}',\xi_l,\mathbf{h})U_{n'\mathbf{k}'\rho'}(\mathbf{r}')e^{i\mathbf{k}'\cdot\mathbf{r}'}
$$

$$
+ \sum_{n'',\rho'',\mathbf{k}',\mathbf{k}''} \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''d\mathbf{r}''' e^{-i\mathbf{k}\cdot\mathbf{r}} U_{n\mathbf{k}\rho}^*(\mathbf{r})e^{i\mathbf{h}\cdot(\mathbf{r}'\times\mathbf{r}+\mathbf{r}\times\mathbf{r}''+\mathbf{r}''\times\mathbf{r}')}\widetilde{\Sigma}(\mathbf{r},\mathbf{r}'')e^{i\mathbf{k}''\cdot(\mathbf{r}''-\mathbf{r}''')}
$$

$$
U_{n''\mathbf{k}''\rho''}(\mathbf{r}'')U_{n''\mathbf{k}''\rho''}^*(\mathbf{r}''')\times\widetilde{G}(\mathbf{r}''',\mathbf{r}',\xi_l,\mathbf{h})U_{n'\mathbf{k}'\rho'}(\mathbf{r}')e^{i\mathbf{k}'\cdot\mathbf{r}'} = \delta_{nn'}\delta_{\rho\rho'}. \tag{1}
$$

By introducing a change of variables $\mathbf{R}_1 = \mathbf{r}'' - \mathbf{r}'$, and $\mathbf{R}_2 = \frac{1}{2}(\mathbf{r}'+\mathbf{r}'')$ in the first term, $\mathbf{R}_1 = \mathbf{r} - \mathbf{r}''$, $\mathbf{R}_2 = \frac{1}{2}(\mathbf{r}+\mathbf{r}'')$, $\mathbf{R}_3 = \mathbf{r}''' - \mathbf{r}'$, and $\mathbf{R}_4 = \frac{1}{2}(\mathbf{r}'+\mathbf{r}''')$ in the second term, and by using partial integration of the type

$$
\sum_{\mathbf{k}''}(\mathbf{r}-\mathbf{r}')e^{i\mathbf{k}''\cdot(\mathbf{r}-\mathbf{r}')}e^{i\mathbf{k}''\cdot(\mathbf{r}'-\mathbf{r}'')}U_{n''\mathbf{k}''\rho''}(\mathbf{r})U_{n''\mathbf{k}''\rho''}^*(\mathbf{r}'')
$$
$$
= \sum_{\mathbf{k}''} e^{i\mathbf{k}''\cdot(\mathbf{r}-\mathbf{r}')}i\nabla_{\mathbf{k}''}e^{i\mathbf{k}''\cdot(\mathbf{r}'-\mathbf{r}'')}U_{n''\mathbf{k}''\rho''}(\mathbf{r})U_{n''\mathbf{k}''\rho''}^*(\mathbf{r}''), \tag{2}
$$

show that Eq. (1) can be rewritten in the form

$$
\sum_{n'',\rho''} [\xi_l - \hat{H}(\vec{\kappa}',\xi_l)]_{n\mathbf{k}\rho,n''\mathbf{k}\rho''}\widetilde{G}_{n''\mathbf{k}\rho'',n'\mathbf{k}'\rho'}(\mathbf{k}',\xi_l)|_{\mathbf{k}'=\mathbf{k}} = \delta_{nn'}\delta_{\rho\rho'}, \tag{3}
$$

where

$$
\vec{\kappa} = \mathbf{k} + i\mathbf{h}\times\nabla_{\mathbf{k}}. \tag{4}
$$

$$
\hat{H}(\vec{\kappa},\xi_l) = \frac{1}{2m}(\mathbf{p}+\hbar\vec{\kappa})^2 + V(\mathbf{r}) + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times(\mathbf{p}+\hbar\vec{\kappa}) + \frac{\hbar^2}{8m^2c^2}\nabla^2 V + \frac{1}{2}g\mu_B\mathbf{B}\cdot\vec{\sigma} + \widetilde{\Sigma}(\vec{\kappa},\xi_l), \tag{5}
$$

$$
\widetilde{\Sigma}_{n\mathbf{k}\rho,n''\mathbf{k}\rho''}(\vec{\kappa}',\xi_l) = \int d\mathbf{r}d\mathbf{r}'\, U_{n''\mathbf{k}\rho''}^*(\mathbf{r})e^{-i\vec{\kappa}'\cdot(\mathbf{r}-\mathbf{r}')}\widetilde{\Sigma}(\mathbf{r},\mathbf{r}',\xi_l)U_{n''\mathbf{k}\rho''}(\mathbf{r}'), \tag{6}
$$

and

$$
\widetilde{G}_{n''\mathbf{k}\rho'',n'\mathbf{k}\rho'}(\mathbf{k}',\xi_l) = \int d\mathbf{r}d\mathbf{r}'\, U_{n''\mathbf{k}\rho''}^*(\mathbf{r})\widetilde{G}(\mathbf{r},\mathbf{r}',\xi_l)e^{-i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')}U_{n'\mathbf{k}\rho'}(\mathbf{r}'). \tag{7}
$$

Hence, show that because the $U_{n\mathbf{k}\rho}'s$ form a complete set of functions, Eq. (3) can be rewritten in the alternate form

$$[\xi_l - \hat{H}(\overrightarrow{\kappa}, \xi_l)]\widetilde{G}(\mathbf{k}, \xi_l) = I. \tag{8}$$

12.13. From Eqs. (12.118), (12.119), (12.127), and (12.128), show that

$$\hat{H}(\overrightarrow{\kappa}, \xi_l) = \hat{H}_0(\mathbf{k}, \xi_l) + \hat{H}'(\mathbf{k}, \xi_l), \tag{1}$$

where

$$\hat{H}_0(\mathbf{k}, \xi_l) = \frac{1}{2m}(\mathbf{p} + \hbar\mathbf{k})^2 + V(\mathbf{r}) + \Sigma^0(\mathbf{k}, \xi_l) + \frac{\hbar^2}{8mc^2}\nabla^2 V + \frac{\hbar}{4m^2c^2}\overrightarrow{\sigma}\cdot\overrightarrow{\nabla}V\times(\mathbf{p} + \hbar\mathbf{k}), \tag{2}$$

and

$$\begin{aligned}
\hat{H}'(\mathbf{k}, \xi_l) = &-ih_{\alpha\beta}\prod{}^{\alpha}\nabla_{\mathbf{k}}^{\beta} + \frac{1}{2}\,g\mu_B B^{\mu}\sigma^{\mu} + B^{\mu}\Sigma^{1,\mu}(\mathbf{k}, \xi_l) - ih_{\alpha\beta}B^{\mu}\frac{\partial\Sigma^{1,\mu}}{\partial k^{\alpha}}\nabla_{\mathbf{k}}^{\beta} \\
&-\frac{1}{2}\,h_{\alpha\beta}h_{\gamma\delta}\left[\frac{\hbar^2}{m}\delta_{\alpha\gamma} + \frac{\partial^2\Sigma^0}{\partial k^{\alpha}\partial k^{\gamma}}\right]\nabla_{\mathbf{k}}^{\beta}\nabla_{\mathbf{k}}^{\delta} + B^{\mu}B^{\nu}\Sigma^{2,\mu\nu}(\mathbf{k}, \xi_l),
\end{aligned} \tag{3}$$

where the terms up to the second order in the magnetic field are retained and $\overrightarrow{\prod}/\hbar$ is the velocity operator,

$$\overrightarrow{\prod} = \frac{\hbar}{m}(\overrightarrow{p} + \hbar\mathbf{k}) + \frac{\hbar^2}{4m^2c^2}\overrightarrow{\sigma}\times\overrightarrow{\nabla}V + \nabla_{\mathbf{k}}\Sigma^0(\mathbf{k}, \xi_l). \tag{4}$$

12.14. The temperature Green's function operator is defined as

$$G_0(\mathbf{k}, \xi_l) = \frac{1}{\xi_l - H_0(\mathbf{k}, \xi_l)}, \tag{1}$$

where $H_0(\mathbf{k}, \xi_l)$ is defined in Eq. (12.131). Show that

$$\nabla_{\mathbf{k}}^{\alpha}G_0(\mathbf{k}, \xi_l) = G_0(\mathbf{k}, \xi_l)\prod{}^{\alpha}G_0(\mathbf{k}, \xi_l) \tag{2}$$

and

$$\nabla_{\mathbf{k}}^{\alpha}\nabla_{\mathbf{k}}^{\gamma}G_0(\mathbf{k}, \xi_l) = G_0\left[\frac{\hbar^2}{m}\delta_{\alpha\gamma} + X^{\alpha\gamma}\right]G_0 + G_0\prod{}^{\alpha}G_0\prod{}^{\gamma}G_0 + G_0\prod{}^{\gamma}G_0\prod{}^{\alpha}G_0, \tag{3}$$

where

$$X^{\alpha\gamma} = \nabla_{\mathbf{k}}^{\alpha}\left[\frac{\hbar^2}{4m^2c^2}(\overrightarrow{\sigma}\times\overrightarrow{\nabla}V)^{\gamma} + \nabla_{\mathbf{k}}^{\gamma}\sum{}^0(\mathbf{k}, \xi_l)\right]. \tag{4}$$

12.15. We have derived

$$\sum_{n,m,\rho,\rho'} \widetilde{\Sigma}_{n\rho,m\rho'}(\mathbf{k})\psi_{n\mathbf{k}\rho}(\mathbf{r})\psi_{m\mathbf{k}\rho'}^*(\mathbf{r}')$$

$$= -\frac{1}{\beta}\sum_{\xi_l,p,q,\mathbf{k}',\overline{\rho},\overline{\rho}'} v_{eff}(\mathbf{r},\mathbf{r}')\widetilde{G}_{p\overline{\rho},q\overline{\rho}'}(\mathbf{k}',\xi_l)\psi_{p\mathbf{k}'\overline{\rho}}(\mathbf{r})\psi_{q\mathbf{k}'\overline{\rho}'}^*(\mathbf{r}') \,. \tag{1}$$

If the effective electron–electron interaction is spin independent, then $\rho = \overline{\rho}$, $\rho' = \overline{\rho}'$. Show that

$$\overline{\Sigma}_{n\rho,m\rho'}(\mathbf{k}) = -\frac{1}{\beta}\sum_{\mathbf{k}',\xi_l,p,q} <nm|v_{eff}(\mathbf{k},\mathbf{k}')|pq>\rho\rho' \,\widetilde{G}_{p\rho,q\rho'}(\mathbf{k}',\xi_l), \tag{2}$$

where

$$<nm|v_{eff}(\mathbf{k},\mathbf{k}')|pq>\rho\rho' = \int \psi_{n\mathbf{k}\rho}^*(\mathbf{r})\psi_{m\mathbf{k}\rho'}(\mathbf{r}')v_{eff}(\mathbf{r},\mathbf{r}')\psi_{p\mathbf{k}'\rho}(\mathbf{r})\psi_{q\mathbf{k}'\rho'}^*(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{3}$$

12.16. From Eqs. (12.152) and (12.154), we have obtained

$$\widetilde{\Sigma}_{n\rho,n\rho'}(\mathbf{k}) = -\frac{1}{\beta}\sum_{\mathbf{k}',\xi_l,\rho} v_{np}(\mathbf{k},\mathbf{k}')\widetilde{G}_{p\rho,p\rho'}(\mathbf{k}',\xi_l) \,. \tag{1}$$

Substituting only the value of the first-order terms of **B** occurring in $\widetilde{G}$ from Eq. (12.134) on the right side of Eq. (1), and neglecting the terms proportional to f, show that

$$\Sigma_{n\rho,n\rho'}^{1,\mu}(\mathbf{k}) \simeq -\sum_{m\mathbf{k}'} v_{nm}(\mathbf{k},\mathbf{k}')\Sigma_{m\rho,m\rho'}^{1,\mu}(\mathbf{k}')f_m'(\mathbf{k}') - \frac{1}{2}\mu_0\sum_{m\mathbf{k}'} v_{nm}(\mathbf{k}')\sigma_{m\rho,m\rho}^{\mu}f_m'(\mathbf{k}). \tag{2}$$

12.17. The isotropic effective-mass Hamiltonian (Eq. 12.170) is given by

$$\hat{H} = \frac{1}{2m^*}\left[\mathbf{p} + \frac{e}{c}\mathbf{A}\right]^2 - eE_0 y, \tag{1}$$

where the y coordinate is related to the vector potential (in the Landau gauge),

$$\mathbf{A} = By\hat{x}. \tag{2}$$

From Eqs. (1) and (2), show that the wave functions are given by

$$\psi_{k,n} = e^{ikx}\phi_n(y - y_0), \tag{3}$$

where ϕ_n is the solution of the harmonic-oscillator equations

$$\frac{1}{2m^*}\left[p_y^2 + (\frac{e}{c}B)^2 y^2\right]\phi_n = (n + \frac{1}{2})\hbar\omega_c\phi_n \tag{4}$$

and

$$y_0 = \frac{1}{\omega_c}\left[\frac{\hbar k}{m^*} - \frac{cE_0}{B}\right]. \tag{5}$$

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