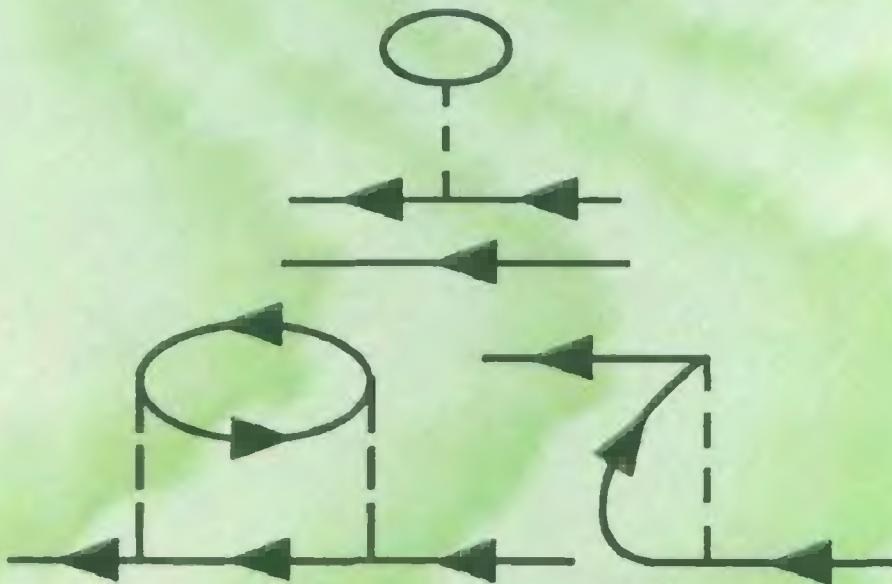


GREEN'S FUNCTIONS FOR SOLID STATE PHYSICISTS

**A REPRINT VOLUME WITH ADDITIONAL MATERIAL ON
THE PHYSICS OF CORRELATED ELECTRON SYSTEMS**



S. DONIACH & E. H. SONDHEIMER

Imperial College Press

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Chapter 4

The Scattering of Fermions by a Localized Perturbation

The effect of impurity atoms on the properties of a metal is of considerable physical interest, both because of the possibility of deliberately introducing impurities so as to study the physics of electron-atom interactions in metals, and because most real materials contain impurities which affect their physical properties.

In this chapter we consider the effect of a single impurity atom on an electron gas. The electron gas is taken to be non-interacting, but is perturbed by the potential due to the impurity atom. (In real metals this will be a screened potential of the Hartree-Fock type.) The problem can immediately be seen to be expressible in terms of the quantum mechanics of scattering of a single electron from the impurity potential. One can imagine that one has solved the Schrödinger equation for the problem and produced a complete set of scattering eigenstates (and bound states if the potential is right). The statistical mechanics of the non-interacting many-electron system then follows by filling up the new set of energy levels according to fermi statistics. Thus in principle we do not need the methods of many-body theory to discuss the effect of impurities in metals, provided the effects of interactions between electrons are neglected. Indeed, historically, this problem was well understood before the techniques of many-body theory were developed.

However, as soon as interactions between electrons are included, we obtain a true many-body problem. It is then no longer possible to treat the statistical mechanics separately from the determination of the energy levels, and we do need to use many-body theory to understand the physics of the situation. It is therefore helpful to formulate the initial problem of a potential acting on a non-interacting fermi gas in terms of Green's functions, so that one is later in a position to generalize to the case of interactions. It turns out that, like the phonon problem, this problem is also a rather nice illustration of many of the properties of

Green's functions which one later requires in the theory of interacting systems.

The end product of the calculation of this chapter will be the effect of the impurity potential on the measurable physical properties of metals. In contrast to the situation in elementary particle problems, where scattering cross-sections can be measured directly as a function of energy and scattering angle, in a metal one has to rely on the effect of the scattering on the bulk thermodynamic properties of the material, such as the low-temperature electronic specific heat and the Pauli susceptibility. We will show, both by the traditional method and by a Green's function calculation, how the effect of impurities on these quantities can be expressed directly in terms of the phase shift of scattering on the impurity potential of the electrons at the fermi level.

4.1. SCATTERING OF A SINGLE ELECTRON

We start by formulating the problem of scattering of a single electron from a potential $U(x)$, in terms of scattering eigenstates $|\Psi\rangle$ satisfying the Schrödinger equation

$$(H_0 + U)|\Psi\rangle = \epsilon|\Psi\rangle \quad (4.1.1)$$

[for a fuller account of scattering theory, see for example Messiah (1961), Chaps. X and XIX]. In order to prescribe the scattering boundary conditions, which we take to be of outgoing wave form, $|\Psi\rangle$ is reexpressed as the solution of the scattering integral equation

$$|\Psi\rangle = |\mathbf{p}\rangle + \frac{1}{\epsilon - H_0 + i\eta} U |\Psi\rangle, \quad (4.1.2)$$

where $|\mathbf{p}\rangle$ is the incident wave. To ensure that $|\Psi\rangle - |\mathbf{p}\rangle$ represents an outgoing scattered wave, η must be chosen real and positive, with $\eta \rightarrow 0+$. The asymptotic behavior of the scattering solutions $|\Psi\rangle$ may be expressed in terms of the transfer or "T" matrix, defined by its matrix elements between states $|\mathbf{p}\rangle$ and $|\mathbf{p}'\rangle$, which are related to the matrix elements of U by means of

$$T(\mathbf{p}', \mathbf{p}) \equiv \langle \mathbf{p}' | T | \mathbf{p} \rangle = \langle \mathbf{p}' | U | \Psi \rangle. \quad (4.1.3)$$

The operator $(\epsilon - H_0 + i\eta)^{-1}$ is diagonal in the p-representation, and its matrix elements form the outgoing wave Green's function of the free

particle Schrödinger equation:

$$\left\langle \mathbf{p} \left| \frac{1}{\epsilon - H_0 + i\eta} \right| \mathbf{p}' \right\rangle = \frac{1}{\epsilon - \epsilon_{\mathbf{p}} + i\eta} \delta_{\mathbf{pp}'} = G^0(\mathbf{p}, \epsilon) \delta_{\mathbf{pp}'} . \quad (4.1.4)$$

In the \mathbf{x} -representation [writing $\langle \mathbf{x} | \Psi \rangle = \Psi(\mathbf{x})$] it is then found that the integral equation (4.1.2) has the well-known form

$$\Psi(\mathbf{x}) = e^{i\mathbf{p} \cdot \mathbf{x}} - \frac{m}{2\pi} \int \frac{e^{i\mathbf{p} \cdot \mathbf{x} - \mathbf{x}'}}{|\mathbf{x} - \mathbf{x}'|} U(\mathbf{x}') \Psi(\mathbf{x}') d^3x' ,$$

which has the required asymptotic behavior. By studying the asymptotic form of $\Psi(\mathbf{x})$, $T(\mathbf{p}', \mathbf{p})$ can be related to the phase shifts in a partial wave analysis of $\Psi(\mathbf{x})$:

$$\Psi(\mathbf{x}) \underset{x \rightarrow \infty}{\simeq} (px)^{-1} \sum_{l=0}^{\infty} (2l+1)i^l e^{i\delta_l} P_l(\cos \theta) \sin(px - \frac{1}{2}l\pi + \delta_l) , \quad (4.1.5)$$

leading to

$$\frac{m}{2\pi} T(\mathbf{p}', \mathbf{p}) = \sum_{l=0}^{\infty} P_l(\cos \theta_{\mathbf{p}' \mathbf{p}}) \frac{e^{2i\delta_l} - 1}{2ip} . \quad (4.1.6)$$

The differential scattering cross-section is given in terms of $T(\mathbf{p}', \mathbf{p})$ by

$$\frac{d\sigma}{d\Omega} = \left| \frac{m}{2\pi} T(\mathbf{p}', \mathbf{p}) \right|^2 .$$

We shall be particularly interested in potentials of very short range. Under conditions such that the wavelength of the incident electron is much greater than the range of the potential (assuming this is not a Coulomb potential), only the s -wave phase shift δ_0 is significant and all the formulas simplify; in particular

$$\frac{m}{2\pi} T = \frac{e^{2i\delta_0} - 1}{2ip} , \quad (4.1.7)$$

from which

$$\frac{d\sigma}{d\Omega} = \frac{\sin^2 \delta_0}{p^2} = \left| \frac{m}{2\pi} T \right|^2 , \quad (4.1.8)$$

and the total cross-section is

$$\sigma = \frac{4\pi \sin^2 \delta_0}{p^2}. \quad (4.1.9)$$

4.2. FORMULATION OF THE MANY-ELECTRON SCATTERING PROBLEM IN TERMS OF FERMION CREATION AND ANNIHILATION OPERATORS

We now consider a set of N electrons, all scattering from the same potential, with hamiltonian

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_i U(\mathbf{x}_i). \quad (4.2.1)$$

The N -electron wave functions for the unperturbed problem ($U = 0$) can be written as Slater determinants of plane wave solutions

$$u_{\mathbf{p}}(\mathbf{x}) = V^{-1/2} e^{i\mathbf{p}\cdot\mathbf{x}}, \quad (4.2.2)$$

which we take to be normalized in a box of volume V , with periodic boundary conditions.

It is now convenient to go over to the formalism of second quantization (see Appendix 1) and to introduce the creation and annihilation operators $a_{\mathbf{p}}^\dagger, a_{\mathbf{p}}$ which for fermions satisfy the anticommutation rules

$$\{a_{\mathbf{p}}, a_{\mathbf{q}}^\dagger\} = \delta_{\mathbf{pq}}, \quad \{a_{\mathbf{p}}, a_{\mathbf{q}}\} = \{a_{\mathbf{p}}^\dagger, a_{\mathbf{q}}^\dagger\} = 0, \quad (4.2.3)$$

where $\{A, B\}$ denotes $AB + BA$.

For present purposes it is not necessary to refer explicitly to the spin states of the particles, but, if required, we can regard the suffix p as referring to both momentum and spin states, and assume that a spin function is included in (4.2.2). The number operator associated with the state \mathbf{p} is

$$n_{\mathbf{p}} = a_{\mathbf{p}}^\dagger a_{\mathbf{p}}; \quad (4.2.4)$$

in accordance with the Pauli principle it has only the two eigenvalues 0 and 1, corresponding to the unoccupied state $|0\rangle$ and the singly occupied state $a_{\mathbf{p}}^\dagger|0\rangle = |\mathbf{p}\rangle$. The many-particle states are of the form

$$|\mathbf{p}_1 \mathbf{p}_2 \dots \mathbf{p}_r\rangle = a_{\mathbf{p}_1}^\dagger a_{\mathbf{p}_2}^\dagger \dots a_{\mathbf{p}_r}^\dagger |0\rangle; \quad (4.2.5)$$

in order to make the sign unique it is necessary, because of the anti-commutation rules (4.2.3), to postulate a definite order for the one-particle states in the state vector.

The hamiltonian (4.2.1) is a sum $\sum_i h_i$ of one-body operators, and its second-quantized form is (see Appendix 1)

$$H = \sum_{\mathbf{p}\mathbf{p}'} \langle \mathbf{p}' | h | \mathbf{p} \rangle a_{\mathbf{p}'}^\dagger a_{\mathbf{p}}, \quad (4.2.6)$$

where $\langle \mathbf{p}' | h | \mathbf{p} \rangle$ is the matrix element

$$\int_V u_{\mathbf{p}}^*(\mathbf{x}) \left(\frac{\mathbf{p}^2}{2m} + U(\mathbf{x}) \right) u_{\mathbf{p}}(\mathbf{x}) d^3x. \quad (4.2.7)$$

With (4.2.2) we obtain at once

$$\langle \mathbf{p}' | h | \mathbf{p} \rangle = \epsilon_{\mathbf{p}} \delta_{\mathbf{p}', \mathbf{p}} + U(\mathbf{p}' - \mathbf{p}), \quad (4.2.8)$$

where $\epsilon_{\mathbf{p}} = \mathbf{p}^2/2m$, and $U(\mathbf{q})$ is the Fourier coefficient

$$U(\mathbf{q}) = \frac{1}{V} \int_V U(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} d^3x \quad (4.2.9)$$

in the Fourier decomposition of the scattering potential

$$U(\mathbf{x}) = \sum_{\mathbf{q}} U(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{x}}. \quad (4.2.10)$$

Since $U(\mathbf{x})$ is real we must have $U(\mathbf{q})^* = U(-\mathbf{q})$.

The hamiltonian is now

$$H = \sum_{\mathbf{p}} \epsilon_{\mathbf{p}} a_{\mathbf{p}}^\dagger a_{\mathbf{p}} + \sum_{\mathbf{q}} U(\mathbf{q}) \sum_{\mathbf{p}} a_{\mathbf{p}+\mathbf{q}}^\dagger a_{\mathbf{p}}. \quad (4.2.11)$$

In order to investigate the effect of the potential on physical properties of the metal we now need to calculate various expectation values of products of the $a_{\mathbf{p}}^\dagger$ and $a_{\mathbf{p}}$ operators with respect either to the perturbed N -particle ground state (at $T = 0$) or to a grand canonical average at finite temperatures.

Examples of such expectation values are the *ground state energy*

$$\begin{aligned} E_G &= \langle \Psi_G | H | \Psi_G \rangle \\ &= \sum_{\mathbf{p}\mathbf{p}'} \{ \delta_{\mathbf{p}\mathbf{p}'} \epsilon_{\mathbf{p}} + U(\mathbf{p} - \mathbf{p}') \} \langle \Psi_G | a_{\mathbf{p}}^\dagger a_{\mathbf{p}'} | \Psi_G \rangle, \end{aligned} \quad (4.2.12)$$

and the *thermodynamic potential* at $T \neq 0$, which may be obtained as in Chap. 2 by inserting a parameter λ in the strength of the potential U and differentiating:

$$\Omega - \Omega_0 = \int_0^1 d\lambda \sum_{\mathbf{pp}'} U(\mathbf{p} - \mathbf{p}') \frac{\text{Tr} \{ e^{-\beta[H(\lambda) - \mu\hat{N}]} a_{\mathbf{p}}^\dagger a_{\mathbf{p}'} \}}{\text{Tr} e^{-\beta[H(\lambda) - \mu\hat{N}]}} \quad (4.2.13)$$

(here we have used a grand canonical average in which the equilibrium electron density is determined by the chemical potential μ). We shall also be interested in the *charge density* in the ground state, given by

$$\langle \rho(\mathbf{x}) \rangle_G = \frac{1}{V} \sum_{\mathbf{pp}'} e^{i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{x}} \langle \Psi_G | a_{\mathbf{p}}^\dagger a_{\mathbf{p}} | \Psi_G \rangle \quad (4.2.14)$$

(with units such that $e = 1$). All these quantities require a knowledge of expectation values of the form $\langle \Psi_G | a_{\mathbf{p}}^\dagger a_{\mathbf{q}} | \Psi_G \rangle$ (or a thermal average at $T \neq 0$), and this leads us again to study a one-particle Green's function for the many-electron system which we define (for $T = 0$) by

$$G^{(N)}(\mathbf{p}, t) = -i \langle \Psi_G^{(N)} | T[\tilde{a}_{\mathbf{p}}(t) \tilde{a}_{\mathbf{p}}^\dagger(0)] | \Psi_G^{(N)} \rangle, \quad (4.2.15)$$

where $|\Psi_G^{(N)}\rangle$ is the exact ground state of the N -electron system and $\tilde{a}_{\mathbf{p}}(t)$ is the Heisenberg operator

$$\tilde{a}_{\mathbf{p}}(t) = e^{iHt} a_{\mathbf{p}} a^{-iHt}. \quad (4.2.16)$$

This definition of G is analogous to Eq. (1.4.6), but for fermions obeying the rules (4.2.3) it is convenient to define the T operator with a change of sign such that

$$\begin{aligned} T[a(t)a^\dagger(t')] &= a(t)a^\dagger(t') & (t > t'), \\ &= -a^\dagger(t')a(t) & (t < t'). \end{aligned} \quad (4.2.17)$$

4.3. SINGLE-ELECTRON GREEN'S FUNCTION

We will show below that, because of the absence of interactions between electrons, the properties defined above in terms of the N -particle states of the system can actually be calculated in terms of a Green's function representing a single electron injected into an *empty* system. This is given by the value of (4.2.15) with N set equal to zero, i.e., by

$$G(\mathbf{p}, t) = -i \langle 0 | T[\tilde{a}_{\mathbf{p}}(t) \tilde{a}_{\mathbf{p}}^\dagger(0)] | 0 \rangle, \quad (4.3.1)$$

where $|0\rangle$ is the vacuum state with no particles present, for which we have $a_p|0\rangle = 0$ for all p . Hence the hamiltonian (4.2.11) is such that $H|0\rangle = 0$. Therefore $e^{iHt}|0\rangle = |0\rangle$, and for $t > 0$ we have

$$\begin{aligned} G(p, t) &= -i\langle 0|e^{iHt}a_p e^{-iHt}a_p^\dagger|0\rangle \\ &= -i\langle 0|a_p e^{-iHt}a_p^\dagger|0\rangle = -i\langle p|e^{-iHt}|p\rangle, \end{aligned} \quad (4.3.2)$$

while, for $t < 0$,

$$\begin{aligned} G(p, t) &= i\langle 0|a_p^\dagger e^{iHt}a_p e^{-iHt}|0\rangle \\ &= i\langle 0|a_p^\dagger e^{iHt}a_p|0\rangle = 0. \end{aligned}$$

Note that, for this particular example, the time-ordered Green's function defined by Eq. (4.3.1) is identical with the *retarded* function

$$G^R(p, t) = -i\theta(t)\langle 0|\{\tilde{a}_p(t), \tilde{a}_p^\dagger(0)\}|0\rangle, \quad (4.3.3)$$

where $\{\cdot, \cdot\}$ denotes an anticommutator.

The quantity which will be used below to express the properties of the N -electron system in terms of those of the one-electron system is the *density of one-electron states*, denoted by $\rho(\epsilon)$. If we confine the system in a box of finite volume V , then the scattering eigenstates of the Schrödinger equation (4.1.1) form a discrete set which we can denote by $|\Psi_m\rangle$ with eigenvalues ϵ_m . $\rho(\epsilon)$ is then defined by

$$\rho(\epsilon) = \sum_m \delta(\epsilon - \epsilon_m). \quad (4.3.4)$$

We now show that $\rho(\epsilon)$ can be obtained from the one-particle Green's function (4.3.1). This follows from the fact that the sum $\sum_p \langle p|e^{-iHt}|p\rangle$ is the trace of the operator e^{-iHt} , and this is invariant under a change of basis from $|p\rangle$ to $|\Psi_m\rangle$. Therefore, for $t > 0$,

$$\begin{aligned} \sum_p G(p, t) &= -i \operatorname{Tr} e^{-iHt} = -i \sum_m \langle \Psi_m|e^{-iHt}|\Psi_m\rangle \\ &= -i \sum_m e^{-i\epsilon_m t}, \end{aligned} \quad (4.3.5)$$

assuming the $|\Psi_m\rangle$ to be normalized; (4.3.5) relates the exact eigenvalues of the problem to the properties of $G(p, t)$. As in Sec. 1.6 we introduce the Fourier transform of $G(p, t)$,

$$G(p, \epsilon) = \int_{-\infty}^{\infty} G(p, t) e^{i\epsilon t} dt. \quad (4.3.6)$$

Since $G(\mathbf{p}, t) = 0$ for $t < 0$ we then obtain, replacing ϵ by $\epsilon + i\eta$ where η is a positive infinitesimal,

$$\begin{aligned} \sum_{\mathbf{p}} G(\mathbf{p}, \epsilon) &= -i \sum_m \int_0^{\infty} e^{i(\epsilon - \epsilon_m + i\eta)t} dt \\ &= \sum_m \frac{1}{\epsilon - \epsilon_m + i\eta}. \end{aligned} \quad (4.3.7)$$

The imaginary part of this is [see Eq. (2.3.11)]

$$-\pi \sum_m \delta(\epsilon - \epsilon_m),$$

and we thus obtain from Eq. (4.3.7) the desired result

$$\rho(\epsilon) = -\frac{1}{\pi} \operatorname{Im} \sum_{\mathbf{p}} G(\mathbf{p}, \epsilon). \quad (4.3.8)$$

To set up an equation of motion from which $G(\mathbf{p}, t)$ can be calculated, we note that $G(\mathbf{p}, t)$ is the diagonal part $F(\mathbf{p}, \mathbf{p}; t)$ of the function

$$F(\mathbf{p}, \mathbf{p}'; t) = -i\langle 0 | T[\tilde{a}_{\mathbf{p}}(t)\tilde{a}_{\mathbf{p}'}^\dagger(0)] | 0 \rangle. \quad (4.3.9)$$

We have

$$\begin{aligned} i \frac{\partial}{\partial t} F(\mathbf{p}, \mathbf{p}'; t) &= i\delta(t)\{F(\mathbf{p}, \mathbf{p}'; 0+) - F(\mathbf{p}, \mathbf{p}'; 0-)\} \\ &\quad - i\langle 0 | T\{[\tilde{a}_{\mathbf{p}}(t), H]\tilde{a}_{\mathbf{p}'}^\dagger(0)] | 0 \rangle, \end{aligned}$$

and, with the form (4.2.11) of H and the anticommutation rules (4.2.3), we easily find that

$$[\tilde{a}_{\mathbf{p}}, H] = \epsilon_{\mathbf{p}}\tilde{a}_{\mathbf{p}} + \sum_{\mathbf{q}} U(\mathbf{q})\tilde{a}_{\mathbf{p}+\mathbf{q}};$$

also

$$F(\mathbf{p}, \mathbf{p}'; 0+) - F(\mathbf{p}, \mathbf{p}'; 0-) = -i(a_{\mathbf{p}}a_{\mathbf{p}'}^\dagger + a_{\mathbf{p}'}^\dagger a_{\mathbf{p}}) = -i\delta_{\mathbf{pp}'}.$$

The equation of motion for $F(\mathbf{p}, \mathbf{p}'; t)$ is thus

$$\left(i \frac{\partial}{\partial t} - \epsilon_{\mathbf{p}}\right) F(\mathbf{p}, \mathbf{p}'; t) = \delta_{\mathbf{pp}'}\delta(t) + \sum_{\mathbf{q}} U(\mathbf{q})F(\mathbf{p} + \mathbf{q}, \mathbf{p}'; t) \quad (4.3.10)$$

[i.e., an inhomogeneous form of the original Schrödinger equation (4.1.1)]. The zero-order approximation is of the diagonal form

$$F^0(\mathbf{p}, \mathbf{p}'; t) = \delta_{\mathbf{pp}'} G^0(\mathbf{p}, t), \quad (4.3.11)$$

and we can again calculate $G^0(\mathbf{p}, t)$ directly: keeping only the first term H_0 in H , we have

$$i \frac{\partial}{\partial t} \tilde{a}_{\mathbf{p}}(t) = [\tilde{a}_{\mathbf{p}}, H_0] = \epsilon_{\mathbf{p}} \tilde{a}_{\mathbf{p}}(t), \quad \text{so that} \quad \tilde{a}_{\mathbf{p}}(t) = a_{\mathbf{p}} e^{-i\epsilon_{\mathbf{p}} t},$$

and, for $t > 0$,

$$\begin{aligned} G^0(\mathbf{p}, t) &= -i e^{-i\epsilon_{\mathbf{p}} t} \langle 0 | a_{\mathbf{p}} a_{\mathbf{p}}^\dagger | 0 \rangle \\ &= -i e^{-i\epsilon_{\mathbf{p}} t} \langle 0 | (1 - a_{\mathbf{p}}^\dagger a_{\mathbf{p}}) | 0 \rangle = -i e^{-i\epsilon_{\mathbf{p}} t}, \end{aligned} \quad (4.3.12)$$

while, for $t < 0$, $G^0(\mathbf{p}, t) = 0$.

As in the phonon problem (Sec. 1.5), the differential equation (4.3.10) and the boundary condition (4.3.11) are together equivalent to an integral equation:

$$\begin{aligned} F(\mathbf{p}, \mathbf{p}'; t) &= \delta_{\mathbf{pp}'} G^0(\mathbf{p}, t) + \int_{-\infty}^{\infty} dt' G^0(\mathbf{p}, t - t') \sum_{\mathbf{q}} U(\mathbf{q}) \\ &\quad \times F(\mathbf{p} + \mathbf{q}, \mathbf{p}'; t'). \end{aligned} \quad (4.3.13)$$

To discuss this equation it is again convenient to work with the Fourier transforms of the time-dependent functions, which are defined as in (4.3.6). The transformed equation is

$$\begin{aligned} F(\mathbf{p}, \mathbf{p}'; \epsilon) &= \delta_{\mathbf{pp}'} G^0(\mathbf{p}, \epsilon) + G^0(\mathbf{p}, \epsilon) \sum_{\mathbf{q}} U(\mathbf{q}) F(\mathbf{p} + \mathbf{q}, \mathbf{p}'; \epsilon) \\ &= \delta_{\mathbf{pp}'} G^0(\mathbf{p}, \epsilon) + G^0(\mathbf{p}, \epsilon) \sum_{\mathbf{q}} U(\mathbf{q} - \mathbf{p}) F(\mathbf{q}, \mathbf{p}'; \epsilon). \end{aligned} \quad (4.3.14)$$

Using the Fourier transform of $G^0(\mathbf{p}, t)$,

$$G^0(\mathbf{p}, \epsilon) = \frac{1}{\epsilon - \epsilon_{\mathbf{p}} + i\eta}, \quad (4.3.15)$$

it may now be seen that Eq. (4.3.14) is equivalent to the original scattering integral equation (4.1.2).

We complete this section by discussing the iterative solution of Eq.

(4.3.14) in powers of U (the Born series). This series solution is defined by

$$F(\mathbf{p}, \mathbf{p}') = \sum_{n=0}^{\infty} F^{(n)}(\mathbf{p}, \mathbf{p}'), \quad F^0(\mathbf{p}, \mathbf{p}') = \delta_{\mathbf{pp}'} G^0(\mathbf{p}),$$

$$F^{(n)}(\mathbf{p}, \mathbf{p}') = G^0(\mathbf{p}) \sum_{\mathbf{q}} U(\mathbf{q} - \mathbf{p}) F^{(n-1)}(\mathbf{q}, \mathbf{p}') \quad (n = 1, 2, 3, \dots),$$

and we obtain for the diagonal part $G(\mathbf{p})$

$$\begin{aligned} G(\mathbf{p}) &= F(\mathbf{p}, \mathbf{p}) = G^0(\mathbf{p}) + G^0(\mathbf{p})U(\mathbf{q} = 0)G^0(\mathbf{p}) \\ &\quad + G^0(\mathbf{p}) \sum_{\mathbf{q}} U(\mathbf{q})G^0(\mathbf{p} + \mathbf{q})U(-\mathbf{q})G^0(\mathbf{p}) \\ &\quad + G^0(\mathbf{p}) \sum_{\mathbf{qq}'} U(\mathbf{q})G^0(\mathbf{p} + \mathbf{q})U(\mathbf{q}')G^0(\mathbf{p} + \mathbf{q} + \mathbf{q}') \\ &\quad \times U(-\mathbf{q} - \mathbf{q}')G^0(\mathbf{p}) + \dots \end{aligned} \quad (4.3.16)$$

The terms in this series can be represented by diagrams, describing multiple scattering processes of successively higher orders, of the form shown in Fig. 4.1. An equivalent expansion may be made of the original equation (4.1.2), and hence of the T matrix: we obtain for the diagonal

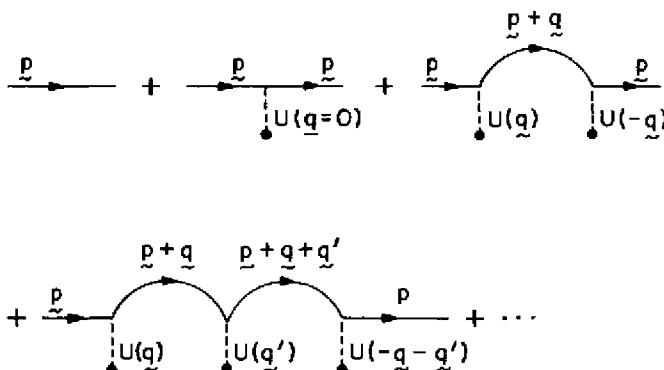


Fig. 4.1. The iteration series for $G(\mathbf{p}, \epsilon)$.

part of this the series

$$\begin{aligned}\langle \mathbf{p}|T|\mathbf{p}\rangle &= \langle \mathbf{p}|U|\mathbf{p}\rangle + \left\langle \mathbf{p}|U \frac{1}{\epsilon - H_0 + i\eta} U|\mathbf{p}\right\rangle \\ &\quad + \left\langle \mathbf{p}|U \frac{1}{\epsilon - H_0 + i\eta} U \frac{1}{\epsilon - H_0 + i\eta} U|\mathbf{p}\right\rangle + \dots\end{aligned}\quad (4.3.17)$$

Writing out these matrix products explicitly, we have

$$\begin{aligned}\langle \mathbf{p}|T|\mathbf{p}\rangle &= U(\mathbf{q} = 0) + \sum_{\mathbf{q}} U(\mathbf{q})G^0(\mathbf{p} + \mathbf{q})U(-\mathbf{q}) \\ &\quad + \sum_{\mathbf{q}\mathbf{q}'} U(\mathbf{q})G^0(\mathbf{p} + \mathbf{q})U(\mathbf{q}')G^0(\mathbf{p} + \mathbf{q} + \mathbf{q}') \\ &\quad \times U(-\mathbf{q} - \mathbf{q}') + \dots\end{aligned}\quad (4.3.18)$$

Comparison with (4.3.16) shows that the series for $G(\mathbf{p}) - G^0(\mathbf{p})$ and $\langle \mathbf{p}|T|\mathbf{p}\rangle$ differ only through extra factors $G^0(\mathbf{p})$ on the left and right of each term in (4.3.16). In fact G and T are connected by the general operator relation

$$G = G^0 + G^0 T G^0 \quad (4.3.19)$$

which can be derived directly in closed form by formal manipulation of the operators [see Messiah (1961), Chap. XIX, Secs. 13, 14].

4.4. CLOSED SOLUTION FOR SHORT-RANGE POTENTIAL

The series for G and T can be summed in closed form for the special case of a potential $U(\mathbf{x})$ of zero range, for which

$$U(\mathbf{x}) = U\delta(\mathbf{x}), \quad U(\mathbf{q}) = U/V = \text{constant}. \quad (4.4.1)$$

This model, although artificial, allows us to derive simple closed expressions for various physical quantities of interest. It has proved very successful in the discussion of qualitative and semiquantitative effects of the short-range potentials due to impurities in real metals where the calculation of the realistic scattering of Bloch electrons by real atomic potentials is quite a difficult task.

When $U(\mathbf{q})$ is independent of \mathbf{q} , the repeated summations over \mathbf{q} in each order of (4.3.16) are independent of each other. For example, the

third-order term gives

$$G^0(\mathbf{p}) \left(\frac{U}{V} \right)^3 \left\{ \sum_{\mathbf{p}} G^0(\mathbf{p}) \right\}^2 G^0(\mathbf{p}) = G^0(\mathbf{p}) \left(\frac{U}{V} \right)^3 \{ V \overline{G^0(\epsilon)} \}^2 G^0(\mathbf{p}), \quad (4.4.2)$$

where

$$\overline{G^0(\epsilon)} = \frac{1}{V} \sum_{\mathbf{p}} G^0(\mathbf{p}, \epsilon). \quad (4.4.3)$$

For free electrons for which $\epsilon_{\mathbf{p}} = \mathbf{p}^2/2m$, this sum diverges. However, in real metals we can treat (4.4.1) as only acting on electrons within a given atomic cell, as defined by Wannier wave functions of the electronic bands in the metal. This leads to a model (the Slater-Koster model) in which the sum over \mathbf{p} -states in (4.4.3) is confined to states lying within a given band, $\epsilon_0 \leq \epsilon_{\mathbf{p}} \leq \epsilon_B$ say, for which the sum converges.

Introducing a density of states function per unit volume for the unperturbed hamiltonian of the metal

$$\rho^0(\epsilon) = \frac{1}{V} \sum_{\mathbf{p} \in \text{band}} \delta(\epsilon - \epsilon_{\mathbf{p}}), \quad (4.4.4)$$

we can separate $\overline{G^0(\epsilon)}$ into its real and imaginary parts, and write

$$\overline{G^0(\epsilon)} = F(\epsilon) - i\pi\rho^0(\epsilon), \quad (4.4.5)$$

where

$$F(\epsilon) = \mathcal{P} \int \frac{\rho^0(\epsilon') d\epsilon'}{\epsilon - \epsilon'}. \quad (4.4.6)$$

In the regions of the band where an effective mass approximation holds, so that $\epsilon_{\mathbf{p}} = \mathbf{p}^2/2m^*$, $\rho^0(\epsilon)$ may be evaluated as

$$\rho^0(\epsilon) = \frac{m^* p(\epsilon)}{2\pi^2}. \quad (4.4.7)$$

The n th-order term in the series for G may now be evaluated explicitly to give

$$G^0(\mathbf{p}) \left(\frac{U}{V} \right)^n \{ V \overline{G^0(\epsilon)} \}^{n-1} G^0(\mathbf{p}) = G^0(\mathbf{p}) \frac{U}{V} (\overline{G^0} U)^{n-1} G^0(\mathbf{p}).$$

Hence the series (4.3.16) for $G(\mathbf{p})$ becomes a geometric series:

$$\begin{aligned} G(\mathbf{p}) &= G^0(\mathbf{p}) + G^0(\mathbf{p}) \frac{U}{V} \left\{ \sum_{n=1}^{\infty} (\bar{G^0} U)^{n-1} \right\} G^0(\mathbf{p}) \\ &= G^0(\mathbf{p}) + G^0(\mathbf{p}) \frac{U/V}{1 - \bar{G^0} U} G^0(\mathbf{p}). \end{aligned} \quad (4.4.8)$$

The T matrix [see Eq. (4.3.19)] is therefore given by

$$T = \frac{U/V}{1 - \bar{G^0}(\epsilon)U}. \quad (4.4.9)$$

This is isotropic, showing that the short-range potential model corresponds to neglecting the higher angular momentum components in the scattering amplitude. Using Eqs. (4.1.7) and (4.4.7) we can express the s-wave phase shift in terms of the real and imaginary parts of $\bar{G^0}(\epsilon)$:

$$e^{2i\delta_0} - 1 = \frac{2\pi i \rho^0(\epsilon)}{F(\epsilon) - \frac{1}{U} - i\pi \rho^0(\epsilon)}, \quad (4.4.10)$$

which gives the simple formula [Friedel (1958), Clogston (1962)]

$$\tan \delta_0 = \frac{\pi \rho^0(\epsilon)}{F(\epsilon) - \frac{1}{U}}. \quad (4.4.11)$$

The cross-section σ is

$$\sigma = \frac{4\pi}{p^2} \frac{\pi^2 (\rho^0)^2}{\left(F - \frac{1}{U} \right)^2 + \pi^2 (\rho^0)^2}. \quad (4.4.12)$$

The dependence of the electron-impurity scattering on electron energy ϵ is thus expressed directly in terms of the density of states $\rho^0(\epsilon)$ of the electron in the original crystal, its *Hilbert transform* $F(\epsilon)$ defined by Eq. (4.4.6), and the potential strength parameter U . In practice $\rho^0(\epsilon)$ is a complicated function of ϵ , but a qualitative idea of the scattering may be obtained by using a model in which $\rho^0(\epsilon)$ is parabolic within a band of width $2\epsilon_0$ and is zero outside. $F(\epsilon)$ is then easily evaluated, and the form of the functions $\rho^0(\epsilon)$ and $F(\epsilon)$ is shown in Fig. 4.2. Suppose that the potential is attractive, so that $U < 0$, and that $|U|$ is so large that the equation $F(\epsilon) - U^{-1} = 0$ has two real roots, ϵ_1 and ϵ_2 , as indicated in

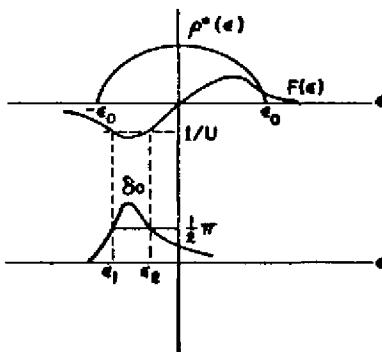


Fig. 4.2. $\rho^*(\epsilon)$, $F(\epsilon)$ and s-wave phase shift for parabolic model. [After Clogston (1962).]

Fig. 4.2. Using (4.4.11) $\delta^0(\epsilon)$ can be evaluated, and its dependence on ϵ is also shown in Fig. 4.2. As may be seen in the figure, δ^0 reaches $\frac{1}{2}\pi$ at the energy ϵ_1 . At this point the cross-section reaches a maximum and the scattering goes through a "resonance." If U is increased further, ϵ_1 moves below the bottom of the band at $-\epsilon_0$. In this region $G^0(\epsilon)$ is real, and the T matrix (4.4.9) now has a *pole* at the energy ϵ_1 . This corresponds to a negative-energy, or bound-state, solution of the Schrödinger equation lying below the bottom of the band.

The closed result (4.4.9) can also be obtained without use of a perturbation expansion, by noting that, when $U(q)$ is constant, the kernel of the integral equation (4.3.14) is "separable." Under these circumstances a solution in closed form can be obtained by elementary methods, and this leads directly to Eq. (4.4.9).

4.5. THE FRIEDEL SUM RULE

In order to apply fermi statistics to the one-particle scattering solutions of the Schrödinger equation discussed in Secs. 4.3 and 4.4, we require some way of calculating how the number of energy levels per unit energy interval is affected by the impurity. This will be evaluated explicitly in Sec. 4.6 using Green's functions. Here we give the more intuitive argument due to Friedel (1952). We consider the impurity to be placed at the center of a large sphere of radius R and confine ourselves to a short-

Chapter 5

Electrons in the Presence of Many Impurities— the Theory of Electrical Resistance in Metals

5.1. THE PHYSICS OF IRREVERSIBLE BEHAVIOR

In the previous chapter we discussed the thermodynamic properties of a non-interacting electron gas in the presence of (essentially) a single impurity. These effects will be proportional to the concentration of impurities at sufficiently low concentrations, so that in real systems we can simply multiply the change of free energy calculated for a single impurity by the concentration of impurities in the system to get the change per unit volume.

However, when we come to consider time-dependent properties of the electron gas, the physics of the effect of impurities differs in an essential way: the response of the system to a single impurity is *no longer* an indication of how the many-impurity system behaves.

To be explicit we will develop, below, the theory of how a particle density disturbance in the electron gas formed at time $t = 0$ spreads out as a function of time t . If there were only one impurity center in the gas, the whole enclosed in a box of side L (periodic boundary conditions), then we could resolve the density disturbance $\rho(\mathbf{x})$ at $t = 0$ in terms of eigenstates of the gas plus impurity. Suppose these eigenstates had wave functions $\varphi_m(\mathbf{x})$, then we could set up a corresponding set of creation operators b_m^\dagger and write [see Appendix 1, Eq. (A.1.12)]

$$\rho(\mathbf{x}) = \sum_{mm'} \langle \varphi_m | \rho(\mathbf{x}) | \varphi_{m'} \rangle b_m^\dagger b_{m'}. \quad (5.1.1)$$

Since the φ_m are exact eigenstates, energy ϵ_m , the resulting time dependence is completely determined:

$$\rho(\mathbf{x}, t) = \sum_{mm'} e^{i(\epsilon_{m'} - \epsilon_m)t} \langle \varphi_m | \rho | \varphi_{m'} \rangle b_m^\dagger b_{m'}. \quad (5.1.2)$$

Now, provided the box is finite, the level spacing between the states ϵ_m

will be finite (apart from accidental degeneracies), so that each term in (5.1.2) is periodic in time. If the numbers ϵ_m are commensurable (i.e., if their ratios are rational numbers), the sum (5.1.2) is also strictly periodic. More generally, it follows from the theory of almost periodic functions that, if the energy levels are discrete, $\rho(\mathbf{x}, t)$ is periodic in the sense that, given any positive δ , a time T exists such that $|\rho(\mathbf{x}, T) - \rho(\mathbf{x}, 0)| < \delta$ [Bocchieri and Loinger (1957), Percival (1961)]. For a large box the level spacing is very small and the cycle time T is correspondingly very long, but nevertheless it is finite. (In classical mechanics this is the so-called Poincaré cycle time.) This means the charge disturbance will always return to its starting value if one waits long enough, and the system is "reversible".

Now let us put in a macroscopic number of impurities placed at random positions in the box. Again we can, in principle, form exact eigenfunctions and for a finite system we will again in principle find a Poincaré time. However, at this point we inject an assertion about the realization of such a measurement in the laboratory. What we assert is that because of the complex and *extensive* nature of the distortion of the wave function by the macroscopic number of impurity scatterers, the "repeat" or Poincaré time is now effectively infinite! We will not try and elucidate further the epistemological problems implied by this assertion [for a review and references see Chester (1963)], but instead we go on to explain how this effect, namely, irreversibility of the response of the system, is built into the mathematics for the particular case of the electron-impurity system.

There are two components to the process of accounting for irreversibility. The most important is the following limiting procedure: in all calculations of the time dependence of the system we will take the limit in which the volume tends to infinity (the particle density remaining constant) *before* considering the asymptotic ($t \rightarrow \infty$) time dependence. The other component in the impurity case is a trick to take care of the randomness of the impurity locations. We will perform an "ensemble" average over the impurity positions. This is not the standard thermodynamic ensemble, but a process whereby we envisage making up a huge number of ingots of our given metal, each with the same impurity concentration, but each with different (random) locations for the impurities. The calculated response will be averaged over members of the ensemble by simply allowing unrestricted averages over the impurity positions. (In the case of liquid metals one would want to include some correlations

between positions of the scattering centers—the metallic ions themselves.) This averaging introduces the phase incoherence of the electronic motion which is a second ingredient of the irreversibility.

The procedure outlined above is sufficient to produce irreversible effects provided the nature of the disturbance in the system (impurities, electron-phonon scattering) extends throughout space. It then transpires that there are two different types of response which can be measured within our model. The theoretically simpler one is the time dependence of the one-electron Green's function. It is hard to think of a measurable physical effect directly related to this Green's function (in fact some tunneling measurements are a way of getting at averages over it), but it is conceptually the easiest to calculate. What comes out is a one-electron lifetime for decay of particle number from a given momentum state p . A *different* response is that of the particle number density perturbation mentioned above. This is the response measured in an electrical conductivity experiment, as will be shown below, and it has a characteristic decay time which is in general different from the one-particle lifetime. The physical reason is that a conservation law is involved. As charge density is scattered out of a given momentum state, other particles are scattered back in. This is the process classically treated by setting up a Boltzmann equation. What we will show below is that these results, in the simple impurity case, can actually be derived in a systematic way from first principles by examining the Green's functions of the electron gas in the presence of the impurities.

5.2. ONE-ELECTRON GREEN'S FUNCTION IN A MANY-IMPURITY SYSTEM

We start by considering the motion of a *single* electron in an array of potentials $U(\mathbf{x} - \mathbf{X}_i)$ located at positions \mathbf{X}_i which are randomly placed. The hamiltonian reads

$$H = \frac{\mathbf{p}^2}{2m} + \sum_i U(\mathbf{x} - \mathbf{X}_i). \quad (5.2.1)$$

It is convenient to rewrite this in second-quantized form in which we allow the possibility of many-electron states. However, it is important to emphasize that the electrons do not interact with each other (except for the constraints on the wave functions imposed by the antisymmetry condition, or Pauli principle). Following the single-impurity problem

we now have

$$H = \sum_{\mathbf{p}} \epsilon_{\mathbf{p}} a_{\mathbf{p}}^\dagger a_{\mathbf{p}} + \sum_{\mathbf{q}} U(\mathbf{q}) \rho_{\mathbf{q}} \sum_{\mathbf{p}} a_{\mathbf{p}+\mathbf{q}}^\dagger a_{\mathbf{p}}. \quad (5.2.2)$$

The only difference between this and the single-impurity hamiltonian (4.2.11) appears in the factor

$$\rho_{\mathbf{q}} = \sum_j e^{-i\mathbf{q} \cdot \mathbf{x}_j}, \quad (5.2.3)$$

which results on making a Fourier representation of the sum over impurity potentials in Eq. (5.2.1). $\rho_{\mathbf{q}}$ is the Fourier transform of the density function $\sum \delta(\mathbf{x} - \mathbf{X}_j)$ for the scattering centers, and $U(\mathbf{q})$ is as before the Fourier transform of the potential function $U(\mathbf{x})$.

Just as in Sec. 4.3 we can study the equation of motion of the single-electron Green's function $G(\mathbf{p}, t)$ by considering the off-diagonal function $F(\mathbf{p}, \mathbf{p}'; t)$, defined as in (4.3.9). The equation of motion now reads

$$\left(i \frac{\partial}{\partial t} - \epsilon_{\mathbf{p}} \right) F(\mathbf{p}, \mathbf{p}'; t) = \delta_{\mathbf{pp}'} \delta(t) + \sum_{\mathbf{q}} U(\mathbf{q}) \rho_{\mathbf{q}} F(\mathbf{p} + \mathbf{q}, \mathbf{p}'; t). \quad (5.2.4)$$

The difference from the earlier equation of motion (4.3.10) is that the potential term appearing on the right-hand side now has a *randomly varying* factor $\rho_{\mathbf{q}}$. There is no longer a scattering solution in closed form as in the single-impurity case, but we can proceed as in Sec. 4.3 by taking the Fourier transform of (5.2.4) and iterating to produce a series solution to the problem:

$$\begin{aligned} F(\mathbf{p}, \mathbf{p}') &= G^0(\mathbf{p}) \delta_{\mathbf{pp}'} + G^0(\mathbf{p}) U(\mathbf{p} - \mathbf{p}') \rho_{\mathbf{p}-\mathbf{p}'} G^0(\mathbf{p}') \\ &\quad + \sum_{\mathbf{q}} G^0(\mathbf{p}) U(\mathbf{q}) \rho_{\mathbf{q}} G^0(\mathbf{p} + \mathbf{q}) U(\mathbf{p} - \mathbf{q} - \mathbf{p}') \\ &\quad \times \rho_{\mathbf{p}-\mathbf{q}-\mathbf{p}'} G^0(\mathbf{p}') + \dots. \end{aligned}$$

The corresponding series for the one-electron Green's function $G(\mathbf{p}) = F(\mathbf{p}, \mathbf{p})$ is

$$\begin{aligned} G(\mathbf{p}) &= G^0(\mathbf{p}) + G^0(\mathbf{p}) [U(\mathbf{q}) \rho_{\mathbf{q}}]_{\mathbf{q}=0} G^0(\mathbf{p}) \\ &\quad + \sum_{\mathbf{q}} G^0(\mathbf{p}) U(\mathbf{q}) \rho_{\mathbf{q}} G^0(\mathbf{p} + \mathbf{q}) U(-\mathbf{q}) \rho_{-\mathbf{q}} G^0(\mathbf{p}) + \dots. \quad (5.2.5) \end{aligned}$$

In order to examine the terms in this series it is convenient to represent a given term by a series of lines representing G^0 connecting at vertices with dashed lines representing $U(\mathbf{q})\rho_{\mathbf{q}}$ (Fig. 5.1):

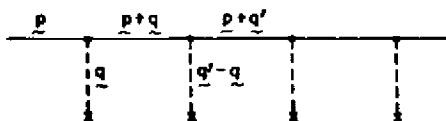


Fig. 5.1. Diagrammatic representation of the Green's function.

At this point we introduce the averaging discussed qualitatively in Sec. 5.1. We assert that the quantity of interest is the *ensemble average* of the Green's function. This is not in itself a very obvious statement—later in this chapter we will show that a measured quantity (the electrical conductivity) can in fact be written as an ensemble average of a response function which is a generalization of the one-particle Green's function. So the present discussion should be taken as introducing a mathematical construct which will be a step in the calculation of a measured quantity (the conductivity).

If there are N impurities in the system at positions $\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_N$, then G is a functional of this set of position vectors

$$G = G[\mathbf{X}_1, \dots, \mathbf{X}_N], \quad (5.2.6)$$

and the ensemble average is defined as

$$\bar{G} = \prod_{i=1}^N \frac{1}{V} \int d^3 X_i G[\mathbf{X}_1, \dots, \mathbf{X}_N]. \quad (5.2.7)$$

(V is the volume of the system.) In this ensemble we assume that each \mathbf{X}_i is uncorrelated with any other. More generally, a distribution function of relative atomic positions could be introduced into the definition to take care of liquids, etc., where correlations between atomic positions have to be taken into account.

This averaging procedure may now be applied, term by term, to the expansion (5.2.5). We then need to consider averages of the form

$\rho_{\mathbf{q}_1} \rho_{\mathbf{q}_2} \cdots \rho_{\mathbf{q}_n}$. On applying (5.2.7) one finds

$$\overline{\rho_{\mathbf{q}}} = \frac{N}{V} \int d^3X e^{-i\mathbf{q} \cdot \mathbf{X}} = N\delta_{\mathbf{q},0}, \quad (5.2.8)$$

where $\delta_{\mathbf{q},0}$ is a Kronecker delta (for the \mathbf{q} -vectors quantized in a large box). For the second-order term we have

$$\overline{\rho_{\mathbf{q}_1} \rho_{\mathbf{q}_2}} = \sum_{ij} e^{-i\mathbf{q}_1 \cdot \mathbf{x}_i} e^{-i\mathbf{q}_2 \cdot \mathbf{x}_j}.$$

There are two contributions to this average – one for $i \neq j$ and the other from the terms in the sum for which $i = j$:

$$\begin{aligned} \overline{\rho_{\mathbf{q}_1} \rho_{\mathbf{q}_2}} &= \sum_{i \neq j} e^{-i\mathbf{q}_1 \cdot \mathbf{x}_i} e^{-i\mathbf{q}_2 \cdot \mathbf{x}_j} + \sum_i e^{-i(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{x}_i} \\ &= N^2 \delta_{\mathbf{q}_1,0} \delta_{\mathbf{q}_2,0} + N \delta_{\mathbf{q}_1 + \mathbf{q}_2,0} \end{aligned} \quad (5.2.9)$$

[we have approximated $N(N-1)$ by N^2 as N is very large].

For the calculation of $G(\mathbf{p})$ we need

$$\overline{\rho_{\mathbf{q}} \rho_{-\mathbf{q}}} = N^2 \delta_{\mathbf{q},0} + N. \quad (5.2.10)$$

It is of crucial importance that this average includes a term, corresponding to a second-order Born scattering from a single atom (see below), which is directly proportional to N and which occurs without restriction on the momentum change \mathbf{q} in the intermediate state.

Let us apply these results to the series (5.2.5). The first-order term may be represented by a diagram (Fig. 5.2) giving a contribution

$$G^0(\mathbf{p}) N U(\mathbf{q} = 0) G^0(\mathbf{p}) \quad (5.2.11)$$

to the expression for $G(\mathbf{p})$.

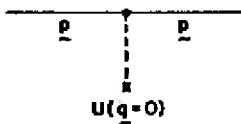


Fig. 5.2. First-order contribution to $G(\mathbf{p})$.

The second-order term may be represented by a pair of diagrams (Fig. 5.3) leading to the terms

$$G^0(\mathbf{p})NU(\mathbf{q} = 0)G^0(\mathbf{p})NU(\mathbf{q} = 0)G^0(\mathbf{p})$$

$$+ G^0(\mathbf{p}) \sum_{\mathbf{q}} NU(\mathbf{q})G^0(\mathbf{p} + \mathbf{q})U(-\mathbf{q})G^0(\mathbf{p}). \quad (5.2.12)$$

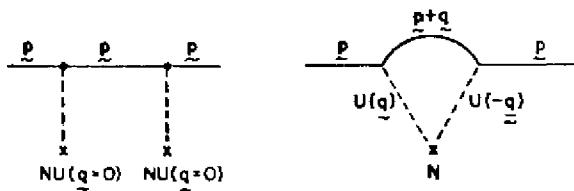


Fig. 5.3. Second-order contribution to $G(\mathbf{p})$.

In these diagrams the single dashed lines each ending in a cross may be thought of as independent scattering (in lowest Born approximation) from two different impurity atoms [i.e., the $i \neq j$ term in Eq. (5.2.9)], while the pair of dashed lines ending in a single cross corresponds to a second Born approximation scattering from the *same* atom [the $i = j$ term in (5.2.9)]. Continuing the same argument, the third-order diagrams are as in Fig. 5.4. These correspond, respectively, to (a) independent first-order Born scatterings from three distinct atoms; (b) a first-order Born scattering from X_i occurring together with a second-order Born

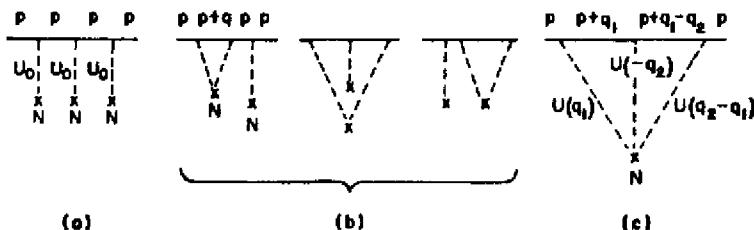


Fig. 5.4. Third-order contribution to $G(\mathbf{p})$.

scattering from a separate atom X_i ; (c) a third-order Born scattering from a single atom.

It is thus seen that the general term in the series is obtained by including all possible repeated scattering events at a single atom. Clearly the general term will involve a very large number of possible diagrams. It is not possible to sum these diagrams in closed form in the general case. However, by introducing the concept of the *irreducible diagram* (Dyson 1949), we can carry out a partial summation, in such a way that there remains only a sum over such irreducible diagrams.

5.3. DYSON'S EQUATION

An irreducible diagram is defined as a diagram which cannot be divided into two sub-diagrams joined only by a single $G^0(p)$ line; all other diagrams are called reducible. For example, in Fig. 5.4 the third and fifth diagrams are irreducible and the others are reducible diagrams. An *irreducible self-energy diagram* is an irreducible diagram which has the $G^0(p)$ lines removed from the two ends. There is a denumerable infinity $\Sigma^{(i)}(p, \epsilon)$ ($i = 0, 1, 2, \dots$) of such diagrams, and the (total) *irreducible self-energy* is defined to be the sum

$$\Sigma(p, \epsilon) = \sum_{i=0}^{\infty} \Sigma^{(i)}(p, \epsilon). \quad (5.3.1)$$

We now rearrange the terms of the perturbation series by collecting together all terms from all orders of the form $G^0(p)\Sigma^{(i)}G^0(p)$, then all terms of the form $G^0(p)\Sigma^{(i)}G^0(p)\Sigma^{(j)}G^0(p)$, and so on. All combinations for all i, j, \dots , occur; hence the sum of all contributions in each group is obtained by replacing each $\Sigma^{(i)}$ by the total self-energy Σ . The complete series may thus be written

$$\begin{aligned} G(p) &= G^0(p) + G^0(p) \sum G^0(p) + G^0(p) \sum G^0(p) \sum G^0(p) + \dots \\ &= G^0(p) + G^0(p) \sum \left\{ G^0(p) + G^0(p) \sum G^0(p) + \dots \right\} \\ &= G^0(p) + G^0(p) \sum G(p). \end{aligned} \quad (5.3.2)$$

This is *Dyson's equation*. Solving for $G(p)$ and remembering the form

(4.3.15) of $G^0(\mathbf{p})$, we have

$$G(\mathbf{p}, \epsilon) = \frac{1}{\{G^0(\mathbf{p})\}^{-1} - \Sigma(\mathbf{p}, \epsilon)} = \frac{1}{\epsilon - \epsilon_{\mathbf{p}} - \Sigma(\mathbf{p}, \epsilon)}. \quad (5.3.3)$$

We thus see that the exact one-electron Green's function is obtained from the unperturbed Green's function by adding the self energy to the unperturbed single-particle energy.

5.4. ONE-ELECTRON GREEN'S FUNCTION IN LOW-DENSITY WEAK SCATTERING APPROXIMATION

To obtain an explicit expression for $\Sigma(\mathbf{p}, \epsilon)$ we have to approximate by selecting a sub-class of irreducible diagrams to be summed. In fact it is easy to classify the diagrams according to their dependence on the concentration $n_{\text{imp.}} = N/V$ of impurities. We note that every scattering cross in a diagram, representing an impurity atom, carries a factor N/V . We therefore obtain a low-density approximation to $\Sigma(\mathbf{p})$ by keeping only the self-energy diagrams with a single cross:

$$\Sigma(\mathbf{p}, \epsilon) = \text{Diagram A} + \text{Diagram B} + \text{Diagram C} + \dots \quad (5.4.1)$$

These diagrams are just the same as those representing the T matrix for scattering from a single impurity [see Fig. 4.1 and Eq. (4.3.19)]; thus, except for a factor N , the sum of the self-energy diagrams (5.4.1) is given by the T matrix for single-center scattering. However, as is indicated by (5.3.3) and as will be discussed further below, in the many-center problem the singularities of $G(\mathbf{p}, \epsilon)$ lie at values of ϵ , in general complex, which differ from the unperturbed energy $\epsilon_{\mathbf{p}}$. Thus we are now really dealing with an analytic continuation in the complex ϵ -plane of the T matrix which was originally defined in Chap. 4 in terms of matrix elements between plane waves corresponding to the unperturbed energy.

We make an additional approximation which is convenient but not necessary. This is to allow the scattering potential from a given atom to be weak, so that only first and second Born scatterings from a given atom [i.e., the first two diagrams of (5.4.1)] need to be taken into account.

The first-order diagram contributes to $\Sigma(\mathbf{p}, \epsilon)$ an amount $NU(\mathbf{q} = 0)$. This simply leads to a shift in the energy of the electron states by the spatial average of the one-center potential:

$$\epsilon_{\mathbf{p}} \rightarrow \epsilon_{\mathbf{p}} + NU(\mathbf{q} = 0) = \epsilon_{\mathbf{p}} + n_{\text{imp.}} \int U(\mathbf{x}) d^3x. \quad (5.4.2)$$

We can take care of this by a suitable redefinition of the energies $\epsilon_{\mathbf{p}}$. This leaves as our final expression for $\Sigma(\mathbf{p}, \epsilon)$, in the low-density weak-potential limit, the contribution of the second-order diagram of (5.4.1):

$$\Sigma(\mathbf{p}, \epsilon) = N \sum_{\mathbf{p}'} U^2(\mathbf{p}' - \mathbf{p}) G^0(\mathbf{p}', \epsilon). \quad (5.4.3)$$

Notice that, in adopting (5.3.3) with (5.4.3) as our approximation to $G(\mathbf{p}, \epsilon)$, we have included diagrams in the series for $G(\mathbf{p})$ of the type of diagram (a) of Fig. 5.5, but have excluded diagrams such as diagram (b).

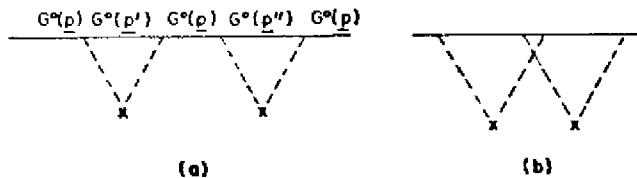


Fig. 5.5. Diagrams (a) contributing, (b) not contributing, to $G(\mathbf{p}, \epsilon)$.

Our low-density approximation thus amounts to neglecting diagrams in which the successive Born scatterings on different atoms “overlap” or interfere with each other. However, by simply shifting the energy states of the unperturbed electron through Eq. (5.4.2), we have automatically included all first-order Born independent scatterings off other atoms (Fig. 5.6). Thus we do not need to worry about these contributions as they are taken care of automatically.

We emphasize that, although $\Sigma(\mathbf{p}, \epsilon)$ is given by a single term in this approximation, we have nevertheless had to consider successive scatterings from many different atoms, i.e., the perturbation series for G had to be summed to *infinite* order to produce (5.3.3). The reason why this

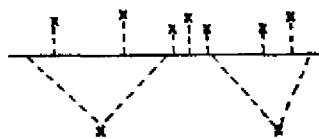


Fig. 5.6. Diagram included in $G(p, \epsilon)$.

is essential may be seen from a simple argument to calculate the propagation of an electron wave through the random medium (Fig. 5.7). In any given slab of the material the wave loses some amplitude by the scattering, provided the centers are random and therefore interfere on average

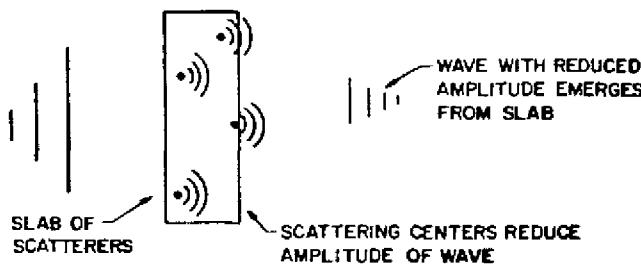


Fig. 5.7. Propagation of electron wave through the random medium.

destructively. Hence the wave will decay exponentially as $e^{-\gamma x}$ as it propagates through a succession of slabs. In quantum-mechanical terms this exponential decay can only be taken into account by summing over an infinite series of scattering events (corresponding to an infinite set of slabs).

How does irreversibility creep into the expression (5.3.3)? Physically what happens can be understood in terms of Fig. 5.7. The electron wave will only lose amplitude in an irreversible manner provided we neglect reflection from the walls of the box of the scattered wavelets in the slab being considered. Mathematically this is done by means of a limiting procedure. If we examine (5.4.3)—neglecting the \mathbf{q} -dependence of $U(\mathbf{q})$ for convenience (this effectively implies the use of a short-range potential)—

then as a function of the complex energy variable ϵ , $\Sigma(\epsilon)$ contains a series of poles at the energy values ϵ_p corresponding to the poles of the one-electron Green's function (4.3.15) at the electron energy levels in the large box enclosing the system. We have

$$\Sigma(p, \epsilon) = N \sum_{p'} \left(\frac{U}{V} \right)^2 \frac{1}{\epsilon - \epsilon_{p'} + i\eta}, \quad (5.4.4)$$

where we have replaced $U(q)$ by U/V , U being an energy parameter.

Substituting back in (5.3.3) it may be seen that as a function of ϵ $G(p, \epsilon)$ now acquires a corresponding spectrum of poles lying near the poles of (5.4.4). The poles of $G(p, \epsilon)$ occur at the values of ϵ satisfying

$$\epsilon - \epsilon_p - \Sigma(p, \epsilon) = 0 \quad (5.4.5)$$

and may be determined graphically as indicated in Fig. 5.8. The spacing between the poles is of order (1/volume) and corresponds to the Poincaré

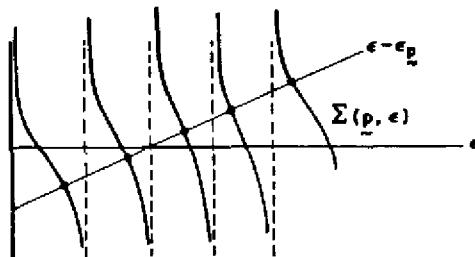


Fig. 5.8. Poles of $G(p, \epsilon)$ for a finite system.

spacing discussed in Sec. 5.1. Irreversibility is now brought in by letting the volume tend to infinity *before* letting the time of observation (corresponding to the precision of taking the Fourier transform in ϵ) become very long. We are in this way ensuring that, if $\Delta\epsilon$ is the spacing between adjacent energy levels and τ is the time of observation, the inequality $\Delta\epsilon \ll \hbar/\tau$ holds. Our limiting procedure thus implies that in a macroscopic system the discrete level structure cannot be resolved and we detect only the *level density*, averaged over an energy interval

\hbar/τ . The sum in (5.4.4) becomes an integral and, since the integrand depends only on ϵ_p , the integral can be written in terms of the density of unperturbed electron states per unit volume

$$\rho(\epsilon) = \frac{1}{V} \sum_p \delta(\epsilon - \epsilon_p), \quad (5.4.6)$$

giving

$$\Sigma(\epsilon) = n_{\text{imp}} U^2 \int_0^\infty \frac{\rho(\epsilon') d\epsilon'}{\epsilon - \epsilon' + i\eta}. \quad (5.4.7)$$

Thus the infinite-volume limit alters the analytic form of the function $\Sigma(\epsilon)$ of the complex variable ϵ : the discrete poles of $\Sigma(p, \epsilon)$ merge to form a *branch cut* along the real axis in the complex ϵ -plane. This results in a finite imaginary contribution to the self-energy for real ϵ : we have

$$\Sigma(\epsilon) = n_{\text{imp}} U^2 [F(\epsilon) - i\pi\rho(\epsilon)], \quad (5.4.8)$$

where $F(\epsilon)$ (as in Sec. 4.4) is the Hilbert transform of $\rho(\epsilon)$. Further, the imaginary part of $\Sigma(\epsilon)$ is negative, and this leads to an *irreversible damping* in the time-dependent Green's function $G(p, t)$. The negative sign comes from the fact that, as discussed in Sec. 4.3, only the retarded ($t > 0$) part of $G(p, t)$ is non-zero for a one-electron system, leading to the prescription used in (5.4.4) and (5.4.7) for going round the poles of $G^0(p', \epsilon)$. To exhibit the damping explicitly we ignore for simplicity the energy dependence of $\Sigma(\epsilon)$ and treat it as a complex constant. Then, writing $\Delta = n_{\text{imp}} U^2 F$, $\Gamma = n_{\text{imp}} U^2 \pi\rho > 0$, we have for $t > 0$

$$\begin{aligned} G(p, t) &= \int_{-\infty}^{\infty} d\epsilon e^{-i\epsilon t} G(p, \epsilon) = \int_{-\infty}^{\infty} d\epsilon \frac{e^{-i\epsilon t}}{\epsilon - \epsilon_p - \Delta + i\Gamma} \\ &= -i e^{-i(\epsilon_p + \Delta)t} e^{-\Gamma t}, \end{aligned} \quad (5.4.9)$$

on closing the contour of integration in the lower half-plane.

To obtain (5.4.9) we needed both the infinite-volume limiting procedure and the random-impurity averaging procedure. For a finite box, the imaginary part of the self-energy (5.4.4) consists of a discrete series of δ -functions which cannot give finite damping of $G(p, t)$. If the scattering is coherent there is also no damping: in particular, if the scattering

centers occupy the lattice points in a periodic lattice, the density function $\rho_{\mathbf{q}}$ is given by

$$\rho_{\mathbf{q}} = N \sum_{\mathbf{K}} \delta_{\mathbf{q}, \mathbf{K}}, \quad (5.4.10)$$

where the sum goes over reciprocal lattice vectors \mathbf{K} . The series for the one-electron Green's function can then be summed to give

$$G(\mathbf{p}, \epsilon) = \frac{1}{\epsilon - \epsilon_{\mathbf{p}}^{(0)} + i\eta}, \quad (5.4.11)$$

where

$$\epsilon_{\mathbf{p}}^{(0)} = \epsilon_{\mathbf{p}} + NU(\mathbf{q} = 0) + N^2 \sum_{\mathbf{K} \neq 0} \frac{|U(\mathbf{K})|^2}{\epsilon_{\mathbf{p}} - \epsilon_{\mathbf{p}+\mathbf{K}}} + \dots \quad (5.4.12)$$

is the one-particle Bloch band energy. The poles of this Green's function lie on the real axis.

Thus in the random impurity case it is seen that the damping of the electron wave as it propagates through the medium results from an infinite sequence of *incoherent* second Born scatterings from successive impurities.

5.5. THEORY OF ELECTRICAL CONDUCTIVITY—LINEAR RESPONSE FORMULATION

Before the development of many-body theory techniques the theory of electrical conduction was based on a Boltzmann equation approach to the time dependence of the semiclassical one-particle distribution function. The essential physical assumption in this theory is the "Stosszahlansatz," or assumption of randomness after successive collision events. The understanding of the mathematical formulation of irreversibility discussed in the last section, however, allows us to dispense with this assumption which had to be imposed arbitrarily. We can now develop the theory starting from the reversible equations of motion and introduce irreversibility essentially as in the one-electron Green's function case. One can in fact proceed in two possible ways. The first is to give a more rigorous derivation, free from the Stosszahlansatz, of kinetic equations such as the Boltzmann equation, which can then be solved to give the transport coefficient of interest. This approach was initiated by van Hove (1955) and has been extensively developed by

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