6.2 Green's Function Method

Let c_j^+ and c_j denote creation and annihilation operators for electrons in state j. The index j stands for any set of quantum numbers that characterizes the electron. For example, it may stand for the momentum vector $\mathbf{p}$ and spin σ, for a site index i and spin σ, or for a MO index, depending on the problem. The time evolution of these operators in the Heisenberg representation is described by $i dc_j^+/dt = [c_j^+, H]_-$ or

$$\begin{aligned} c_j^+(t) &= \mathrm{e}^{\mathrm{i}Ht} c_j^+ \mathrm{e}^{-\mathrm{i}Ht} \\ &= \mathrm{e}^{\mathrm{i}Lt} c_j^+ . \end{aligned} \tag{6.2.1}$$

Here H is the Hamiltonian of the system and L is the Liouville operator associated with H, see (5.1.4). The Green's function $G_{ij}(t-t')$ is defined as

$$G_{ij}(t-t') = -\mathrm{i}\langle \psi_0^N | T(c_i(t)c_j^+(t')) | \psi_0^N \rangle , \tag{6.2.2}$$

where $|\psi_0^N\rangle$ denotes the (exact) ground state of the N-electron system. T is a time-ordering operator; it orders products of time-dependent operators by placing operators with the larger time argument to the left of those with the smaller time argument. The overall sign depends on the number of permutations required to achieve time order. For the operator product in (6.2.2), this implies

$$T(c_i(t)c_j^+(t')) = \begin{cases} c_i(t)c_j^+(t'), & t > t', \\ -c_j^+(t')c_i(t), & t < t'. \end{cases} \tag{6.2.3}$$

One notices that the Green's function is the probability amplitude of finding an electron in state i at time t, when at time t' an electron in state j has been added to the ground state. It describes electron propagation for $t > t'$ and hole propagation for $t < t'$.

A very useful representation of the Green's function appears in the form of spectral densities (Lehmann representation). For that purpose one writes (6.2.2) by means of (6.2.1) in the form

$$G_{ij}(t) = \begin{cases} -\mathrm{i}\sum\limits_n \langle\psi_0^N|c_i e^{-\mathrm{i}Ht}|\psi_n^{N+1}\rangle\langle\psi_n^{N+1}|c_j^+|\psi_0^N\rangle e^{\mathrm{i}E_0^N t} & t > 0\,, \\ \mathrm{i}\sum\limits_m \langle\psi_0^N|c_j^+ e^{\mathrm{i}Ht}|\psi_m^{N-1}\rangle\langle\psi_m^{N-1}|c_i|\psi_0^N\rangle e^{-\mathrm{i}E_0^N t}\,, & t < 0\,. \end{cases} \tag{6.2.4}$$

The $|\psi_n^{N+1}\rangle$ and $|\psi_m^{N-1}\rangle$ denote eigenstate of the $(N+1)$- and $(N-1)$-electron systems, respectively. Their corresponding energies are E_n^{N+1} and E_m^{N-1}, while

E_0^N is the ground-state energy of the N-electron system. If we introduce the electron affinities

$$A_n = E_n^{N+1} - E_0^N \tag{6.2.5a}$$

and the electron ionization potentials

$$I_m = E_m^{N-1} - E_0^N\,, \tag{6.2.5b}$$

one can write (6.2.4) in the form

$$G_{ij}(t) = \begin{cases} -\mathrm{i}\sum\limits_n \langle\psi_0^N|c_i|\psi_n^{N+1}\rangle\langle\psi_n^{N+1}|c_j^+|\psi_0^N\rangle e^{-\mathrm{i}tA_n}, & t > 0\,, \\ \mathrm{i}\sum\limits_m \langle\psi_0^N|c_j^+|\psi_m^{N-1}\rangle\langle\psi_m^{N-1}|c_i|\psi_0^N\rangle e^{\mathrm{i}tI_m}, & t < 0\,. \end{cases} \tag{6.2.6}$$

The Fourier transform of the Green's function is

$$G_{ij}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{\mathrm{i}\omega t} G_{ij}(t) \tag{6.2.7}$$

and if we resort to the form (6.2.6) we obtain the desired spectral representation

$$\begin{aligned} G_{ij}(\omega) &= \sum_n \frac{\alpha_i(n)\alpha_j^*(n)}{\omega - A_n + \mathrm{i}\eta} + \sum_m \frac{\beta_i(m)\beta_j^*(m)}{\omega + I_m - \mathrm{i}\eta} \\ &= \sum f_{ij}^{(n)}(\omega) + \sum g_{ij}^{(m)}(\omega)\,. \end{aligned} \tag{6.2.8}$$

The following notation has been introduced:

$$\alpha_j^*(n) = \langle \psi_n^{N+1} | c_j^+ | \psi_0^N \rangle ,$$
$$\beta_i(m) = \langle \psi_m^{N-1} | c_i | \psi_0^N \rangle . \tag{6.2.9}$$

The positive, infinitesimal number η ensures the correct analytic properties of $G_{ij}(\omega)$. For systems with a large number of electrons N (e.g., solids), it is advantageous to introduce the chemical potential

$$\mu = E_0^{N+1} - E_0^N \simeq E_0^N - E_0^{N-1} . \tag{6.2.10}$$

Here A_n and I_m are written as

$$A_n = \mu + \delta E_n^{N+1}, \quad I_m = -\mu + \delta E_m^{N-1} , \tag{6.2.11}$$

where δE_n^{N+1}, $\delta E_m^{N-1} > 0$ denote the excitation energies of the $(N+1)$- and $(N-1)$-electron systems respectively. For practical purposes we measure the energy ω from μ, from now on.

The spectral representation of $G_{ij}(\omega)$ shows that the Green's function always represents an analytic function in the ω plane except on the real axis. Therefore, it can be constructed from two analytic functions $G_{ij}^{\mathrm{R}}(\omega)$ (retarded Green's function) and $G_{ij}^{\mathrm{A}}(\omega)$ (advanced Green's function), so that it coincides with $G_{ij}^{\mathrm{R}}(\omega)$ in the upper ω half-plane and with $G_{ij}^{\mathrm{A}}(\omega)$ in the lower half-plane. That is

$$G_{ij}(\omega) = \begin{cases} G_{ij}^{\mathrm{R}}(\omega), & \mathrm{Im}\{\omega\} > 0 , \\ G_{ij}^{\mathrm{A}}(\omega), & \mathrm{Im}\{\omega\} < 0 . \end{cases} \tag{6.2.12}$$

The corresponding time-dependent functions $G_{ij}^{\mathrm{R}}(t-t')$ and $G_{ij}^{\mathrm{A}}(t-t')$ are given by

$$G_{ij}^{\mathrm{R}}(t-t') = -\mathrm{i}\theta(t-t') \langle \psi_0^N | [c_i(t), c_j^+(t')]_+ | \psi_0^N \rangle ,$$
$$G_{ij}^{\mathrm{A}}(t-t') = \mathrm{i}\theta(t'-t) \langle \psi_0^N | [c_i(t), c_j^+(t')]_+ | \psi_0^N \rangle , \tag{6.2.13}$$

where $\theta(x)$ is the step function, i.e., $\theta(x) = 1$ for $x > 0$ and zero otherwise. The proof of (6.2.12, 13) can be found in many textbooks (see for example [6.5, 6]) and is not repeated here.

For a determination of the $G^{\mathrm{R(A)}}_{ij}(t-t')$, we have to know their equations of motion:

$$\begin{aligned}\frac{d}{dt}G^{\mathrm{R}}_{ij}(t-t') &= -\mathrm{i}\frac{d}{dt}\{\theta(t-t')\langle\psi^N_0|[c_i(t),c_j^+(t')]_+|\psi^N_0\rangle\}\\ &= -\mathrm{i}\delta(t-t')\langle\psi^N_0|[c_i(t),c_j^+(t)]_+|\psi^N_0\rangle\\ &\quad -\theta(t-t')\langle\psi^N_0|[[c_i(t),H]_-,c_j^+(t')]_+|\psi^N_0\rangle\,. \end{aligned} \tag{6.2.14}$$

A similar equation can be derived for $d[G^{\mathrm{A}}_{ij}(t-t')]/dt$. The two equations can be used to derive an equation of motion for $G_{ij}(\omega)$. Taking the Fourier transforms of $G^{\mathrm{R(A)}}_{ij}(t-t')$ and using (6.2.12), one obtains

$$\begin{aligned}\omega G_{ij}(\omega) &= \omega\langle\!\langle c_i;c_j^+\rangle\!\rangle_\omega\\ &= \langle\psi^N_0|[c_i,c_j^+]_+|\psi^N_0\rangle + \langle\!\langle[c_i,H]_-;c_j^+\rangle\!\rangle_\omega\,. \end{aligned}\tag{6.2.15}$$

This relation can also be directly derived from (6.2.2) by differentiation. The notation $G_{ij}(\omega)=\langle\!\langle c_i;c_j^+\rangle\!\rangle_\omega$ is rather common and will be used repeatedly in the discussion below. The last term on the right-hand side couples the Green's function $G_{ij}(\omega)$ to higher-order Green's functions, something easily demonstrated if we select for H a specific form like

$$H=\sum_{ij\sigma}t_{ij}c^+_{i\sigma}c_{j\sigma}+U\sum_i c^+_{i\uparrow}c_{i\uparrow}c^+_{i\downarrow}c_{i\downarrow} \tag{6.2.16}$$

(Hubbard Hamiltonian). The spin indices are explicitly shown for convenience. One may verify immediately that

$$[c_{i\sigma},H]_-=\sum_j t_{ij}c_{j\sigma}+Uc_{i\sigma}c^+_{i-\sigma}c_{i-\sigma}\,. \tag{6.2.17}$$

Therefore $\langle\!\langle c_{i\sigma};c^+_{j\sigma}\rangle\!\rangle_\omega$ is coupled to $\langle\!\langle c_{i\sigma}c^+_{i-\sigma}c_{i-\sigma};c^+_{j\sigma}\rangle\!\rangle_\omega$. This feature appears again in the derivation of the equation of motion for $\langle\!\langle c_{i\sigma}c^+_{i-\sigma}c_{i-\sigma};c^+_{j\sigma}\rangle\!\rangle_\omega$. Thus, in order to obtain a closed set of equations, one has to terminate the coupling to higher-order Green's functions by a decoupling approximation. We can achieve this by factorizing higher-order Green's functions.

The definitions (6.2.2) and (6.2.13) of the Green's functions G, G^{R}, and G^{A} can be generalized if we replace $c_i(t)$ and $c_j^+(t)$ with any pair of fermion operators $A(t)$ and $B(t)$, thus making all relations (6.2.4–15) hold accordingly. The equation of motion, in particular, will take the form

$$\omega\langle\!\langle A;B\rangle\!\rangle_\omega=\langle\psi^N_0|[A,B]_+|\psi^N_0\rangle+\langle\!\langle[A,H]_-;B\rangle\!\rangle_\omega\,. \tag{6.2.18}$$

For a noninteracting electron gas, the Hamiltonian is

$$H_0 = \sum_{\mathbf{p}\sigma} \left(\frac{p^2}{2m} - \mu \right) c^+_{\mathbf{p}\sigma} c_{\mathbf{p}\sigma} \, . \tag{6.2.19}$$

In order to compute the Green's function, one sets $i = (\mathbf{p}, \sigma)$ and finds

$$[c_i, H_0]_- = [c_{\mathbf{p}\sigma}, H_0]_- = (p^2/2m - \mu) c_{\mathbf{p}\sigma} \, . \tag{6.2.20}$$

From (6.2.15) it follows that

$$\omega G^{(0)}_{\mathbf{p}\sigma,\mathbf{p}'\sigma'}(\omega) = \delta_{\mathbf{p}\mathbf{p}'} \delta_{\sigma\sigma'} + (p^2/2m - \mu) G^{(0)}_{\mathbf{p}\sigma,\mathbf{p}'\sigma'}(\omega) \tag{6.2.21a}$$

Therefore,

$$G^{(0)}_\sigma(\mathbf{p}, \omega) = \frac{1}{\omega - (p^2/2m - \mu) + i\eta \operatorname{sgn} \omega} \, . \tag{6.2.21b}$$

The imaginary part of this function is in accordance with (6.2.8). The poles of $G^{(0)}_\sigma(\mathbf{p}, \omega)$ define the excitation energies of the system. They determine the oscillations of the Fourier transform $G^{(0)}_\sigma(\mathbf{p}, t)$. In the present case the poles are $\omega = p^2/2m - \mu$.

For an infinite system of interacting electrons, the spectral representation of the Green's function (6.2.8) takes the form

$$G(\mathbf{p}, \omega) = \int_0^\infty d\omega' \left(\frac{A(\mathbf{p}, \omega')}{\omega - \omega' + i\eta} + \frac{B(\mathbf{p}, \omega')}{\omega + \omega' - i\eta} \right) \tag{6.2.22}$$

with

$$A(\mathbf{p}, \omega) = \sum_n |\langle \psi^{N+1}_n | c^+_{\mathbf{p}\sigma} | \psi^N_0 \rangle|^2 \delta(\omega - \delta E^{N+1}_n) \, ,$$

$$B(\mathbf{p}, \omega) = \sum_m |\langle \psi^{N-1}_m | c_{\mathbf{p}\sigma} | \psi^N_0 \rangle|^2 \delta(\omega - \delta E^{N-1}_m) \, . \tag{6.2.23}$$

We can also present $G(\mathbf{p}, \omega)$ in terms of a self-energy or mass operator $\Sigma(\mathbf{p}, \omega)$. The following form holds:

$$G(\mathbf{p}, \omega) = \frac{1}{\omega - (p^2/2m - \mu) - \Sigma(\mathbf{p}, \omega)} \, , \tag{6.2.24}$$

which can be understood by starting from (6.2.15). With $H = H_0 + H_1$ and H_0

given by (6.2.19), one obtains

$$\omega G(\mathbf{p}, \omega) = 1 + \left(\frac{p^2}{2m} - \mu\right) G(\mathbf{p}, \omega) + \langle\langle [c_{\mathbf{p}\sigma}, H_1]_- ; c^+_{\mathbf{p}\sigma} \rangle\rangle_\omega \,. \tag{6.2.25}$$

We can define the mass operator $\Sigma(\mathbf{p}, \omega)$ by formally setting

$$\langle\langle [c_{\mathbf{p}\sigma}, H_1]_- ; c^+_{\mathbf{p}\sigma} \rangle\rangle_\omega = \Sigma(\mathbf{p}, \omega) G(\mathbf{p}, \omega) \,. \tag{6.2.26}$$

Equation (6.2.25) can then be written in the form $G = G_0 + G_0 \Sigma G$ with G_0 given by (6.2.21). The formal solution of this equation is (6.2.24).

The excitations of the system are given by

$$\omega = \frac{p^2}{2m} - \mu + \Sigma(\mathbf{p}, \omega) \,. \tag{6.2.27}$$

For "normal" Fermi systems, which excludes for example superconductors, one can expand the self-energy around the energy $\omega = 0$, i.e.,

$$\Sigma(\mathbf{p}, \omega) = \Sigma(\mathbf{p}, 0) + \left.\frac{\partial \Sigma(\mathbf{p}, \omega)}{\partial \omega}\right|_{\omega=0} \omega \,. \tag{6.2.28}$$

For energies close to the Fermi energy, one can write the Green's function in the form

$$G(\mathbf{p}, \omega) = \frac{Z}{\omega - \varepsilon_{\mathbf{p}} - \mathrm{i}\gamma_{\mathbf{p}} \operatorname{sgn} \omega} + G_{\mathrm{inc}}(\mathbf{p}, \omega) \,, \tag{6.2.29}$$

where $G_{\mathrm{inc}}(\mathbf{p}, \omega)$ is the incoherent part. The renormalization constant Z is

$$Z = \frac{1}{1 - \partial \Sigma(\mathbf{p}, \omega)/\partial \omega|_{\omega=0}} \,. \tag{6.2.30}$$

The energies

$$\begin{aligned} \varepsilon_{\mathbf{p}} &= Z(p^2/2m - \mu + \Sigma(\mathbf{p}, 0)) \\ &\simeq v_{\mathrm{F}}^* (p - p_{\mathrm{F}}) \end{aligned} \tag{6.2.31}$$

and

$$\gamma_{\mathbf{p}} \simeq Z \operatorname{Im}\{\Sigma(\mathbf{p}, \varepsilon_{\mathbf{p}})\} \operatorname{sgn} \varepsilon_{\mathbf{p}} \tag{6.2.32}$$

$$\gamma_{\mathbf{p}} \simeq Z \operatorname{Im}\{\Sigma(\mathbf{p}, \varepsilon_{\mathbf{p}})\} \operatorname{sgn} \varepsilon_{\mathbf{p}} \tag{6.2.32}$$

are the real and imaginary parts of the excitation energies of the system. It turns out that for a normal Fermi system $\gamma_{\mathbf{p}} \sim (p - p_{\mathrm{F}})^2$, see Sect. 10.1. As the Fermi energy is approached, the imaginary part of the excitation energy vanishes faster than the real part. Because of the small damping the excitations close to the Fermi energy – called quasiparticles – are well defined. Their velocity v_{F}^* differs from the "bare" Fermi velocity $v_{\mathrm{F}} = p_{\mathrm{F}}/m$ by the renormalization constant Z. The latter defines the residue of the pole of (6.2.29) and describes the weight of the "bare" electron in the quasiparticle. The incoherent part $G_{\mathrm{inc}}(\mathbf{p}, \omega)$ in (6.2.29) is well behaved near the Fermi energy, having branch cuts as a function of ω, but no poles. The concept of quasiparticles, originally introduced by Landau, is discussed in more detail in Sect. 10.1.

The approximate computation of the self-energy $\Sigma(\mathbf{p}, \omega)$ proves to be a central problem in solid-state theory. We can tackle it by applying either perturbation expansions with respect to the electron interaction Hamiltonian H_1 or projection techniques. We can also evaluate $\Sigma(\mathbf{p}, \omega)$ if we start from the equations of motion (6.2.15) and terminate the series of equations, for example by factorization. We will discuss this last method together with the projection technique because they are related methods.

Peter Fulde

Electron Correlations in Molecules and Solids

With 127 Figures

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo
Hong Kong Barcelona
Budapest