# Contents

## Chapter 7

# Introduction to Green's function techniques

The discussion of the scattering formalism in the previous chapter has left two basic questions open: (i) How to calculate the elastic transmission of real systems such as atomic and molecular junctions? and (ii) how to generalize Landauer formula to take into account correlation effects and inelastic mechanisms? Both questions can be answered, at least to a large extent, with the help of Green's function techniques. For this reason, we initiate here a series of three sections devoted to this subject.

### 7.1 Introduction to equilibrium Green's function techniques

In this section, we shall introduce the subject of Green's function techniques by focusing on the case of electronic systems in thermodynamical equilibrium. This chapter is meant to give a first insight into what Green's functions in quantum mechanics are, what kind of physical information they contain and how they can be calculated in some simple situations. Having in mind the first question above, we shall focus on the analysis of single-particle problems.[1] Then, in the next chapter we shall deal with the diagrammatic theory, which provides a systematic perturbative approach to compute the Green's functions of many-body systems where correlations and inelastic mechanisms can play a fundamental role. Finally, since our main goal is the analysis of the transport properties of atomic-scale junctions, we shall present in Section 7.3 the Keldysh formalism that allows us to compute the Green's functions of nonequilibrium systems. In particular,

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[1] A single-particle problem is that in which the particles are either free (they do not interact with anything) or they interact with an external potential (created by an external field or by other particles).

we shall apply this formalism to the calculation of the transmission in some important cases.

The present chapter is organized as follows. First, we shall remind you of the basics of the Schrödinger and Heisenberg representations of quantum mechanics. Then, we shall introduce the retarded and advanced Green's functions in the context of single-particle electron systems and show how they can be computed in some simple examples. We shall then introduce the many-particle Green's functions (valid for any interacting system) and analyze their main analytical properties. Finally, we shall conclude this chapter with a brief discussion of the so-called equation-of-motion method, which provides an interesting strategy for calculating many-particle Green's functions.

One last comment before we get started. We shall make use all the time of the second quantization formalism in our discussion of the Green's functions techniques. So, if you are yet not very familiar with this formalism, we strongly recommend you to read Appendix A.

### 7.1.1 *The Schrödinger and Heisenberg pictures*

Let us start by reviewing the two most standard pictures or representations in quantum mechanics. The usual way to introduce quantum mechanics makes use of the so-called *Schrödinger picture*, which is based on the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi_{\mathrm{S}}(t) = \mathbf{H} \Psi_{\mathrm{S}}(t), \tag{7.1}$$

where $\mathbf{H}$ is the time-independent Hamiltonian of the system and $\Psi_{\mathrm{S}}(t)$ is the time-dependent wave function. Let us stress that in what follows, unless said otherwise, we shall set $\hbar = 1$ to simplify the different formulas and the operators will be written in boldface.

The Schrödinger equation has the formal solution

$$\Psi_{\mathrm{S}}(t) = e^{-i\mathbf{H}(t-t_0)} \Psi_{\mathrm{S}}(t_0), \tag{7.2}$$

where $t_0$ is an arbitrary initial time. Here, the exponential of any operator $\mathbf{A}$ is defined, as usual, by means of its Taylor series

$$\exp(\mathbf{A}) = \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{A}^n. \tag{7.3}$$

From this result, it is obvious that the operator $\exp[-i\mathbf{H}(t - t_0)]$ is the time-evolution operator in the Schrödinger picture, in the sense that by acting on the wave function at a initial time, $t_0$, this operator transforms it into the wave function at the time $t$. If we take $t_0 = 0$, we have

$$\Psi_{\mathrm{S}}(t) = e^{-i\mathbf{H}t}\Psi_{\mathrm{S}}(0). \tag{7.4}$$

For the moment, since we are only interested in equilibrium situations, we shall assume that the operators describing the observables in this representation, $\mathbf{O}_{\mathrm{S}}$, do not have any explicit time dependence.

Another typical representation in quantum mechanics is the so-called *Heisenberg picture*, which can be defined from the Schrödinger one by means of the following unitary transformation

$$\begin{aligned} \Psi_{\mathrm{H}}(t) &= e^{i\mathbf{H}t}\Psi_{\mathrm{S}}(t) = \Psi_{\mathrm{S}}(0) \\ \mathbf{O}_{\mathrm{H}}(t) &= e^{i\mathbf{H}t}\mathbf{O}_{\mathrm{S}}e^{-i\mathbf{H}t}. \end{aligned} \tag{7.5}$$

Thus, in Heisenberg picture the time dependence has been transferred from the wave functions to the operators. The wave function in this representation is stationary and equal to the wave function in Schrödinger picture at time zero, i.e. $\Psi_{\mathrm{H}} = \Psi_{\mathrm{S}}(0)$, whereas the operators, $\mathbf{O}_{\mathrm{H}}(t)$, do depend explictly on time. Their time evolution can be obtained by taking the derivative with respect to time in the previous equation

$$i\frac{\partial}{\partial t}\mathbf{O}_{\mathrm{H}} = [\mathbf{O}_{\mathrm{H}}, \mathbf{H}], \tag{7.6}$$

which is the equation of motion of an operator in this representation.

Both representations are equivalent in the sense that the expectation values in both pictures are the same. This is a simple consequence of the fact that both representations are related by means of a unitary transformation.

### 7.1.2 *Single-particle Green's functions*

As we explained above, we shall introduce the concept of Green's functions in a progressive manner. Here, we shall first focus on the analysis of single-particle electron systems, where many-body interactions play no role. As we shall show, in this case the Green's functions can be introduced in a very intuitive fashion and they are relatively easy to compute.

Green's functions in quantum mechanics were originally introduced in the context of scattering theory. In this theory, one is interested in the evolution of a wave packet representing a particle when this particle approaches a scattering potential. The Huygens' principle in classical wave mechanics provides a convenient way of viewing such a process. If the particle wave function $\psi(\mathbf{r}, t)$ is known at one particular time $t$, it maybe found at any later time $t'$ by considering at time $t$ each point of space $\mathbf{r}$ as a source of spherical waves which propagate outward from $\mathbf{r}$. The strength of the wave amplitude arriving at point $\mathbf{r}'$ at time $t'$ from the point $\mathbf{r}$ will be proportional to the original wave amplitude $\psi(\mathbf{r}, t)$. If we denote the constant of proportionality by $iG(\mathbf{r}', t; \mathbf{r}, t)$, the total wave arriving at the point $\mathbf{r}'$ at time $t'$ will, by Huygens' principle, be

$$\psi(\mathbf{r}', t') = i \int d\mathbf{r}\, G(\mathbf{r}', t'; \mathbf{r}, t)\psi(\mathbf{r}, t) \qquad t' > t. \tag{7.7}$$

$G(\mathbf{r}', t'; \mathbf{r}, t)$ is known as the *Green's function or propagator*, and it describes to us according to Huygens' principle the influence upon $\psi(\mathbf{r}', t')$ of the magnitude of $\psi$ at $\mathbf{r}$ at time $t$. Knowledge of $G$ enables us to construct the physical state which develops in time from any given initial state, and thus is equivalent to a complete solution of the Schrödinger equation.

The next step is to find the equation satisfied by the propagator $G$. For this task, let us first rewrite Eq. (7.7), valid for $t' > t$, in a form valid for all times:

$$\theta(t' - t)\psi(\mathbf{r}', t') = i \int d\mathbf{r}\, G(\mathbf{r}', t'; \mathbf{r}, t)\psi(\mathbf{r}, t), \tag{7.8}$$

where $\theta(t' - t)$ is the step function defined by

$$\theta(t' - t) = \begin{cases} 1 & \text{if } t' > t \\ 0 & \text{if } t' < t \end{cases}. \tag{7.9}$$

Now, let us use the fact that $\psi(\mathbf{r}', t')$ satisfies the Schrödinger equation and apply the operator $[i\partial/\partial t' - \mathbf{H}(\mathbf{r}')]$ to Eq. (7.8):

$$\begin{aligned} \left[i\frac{\partial}{\partial t'} - \mathbf{H}(\mathbf{r}')\right] \theta(t' - t)\psi(\mathbf{r}', t') &= i\delta(t' - t)\psi(\mathbf{r}', t') \qquad (7.10) \\ &= i \int d\mathbf{r} \left[i\frac{\partial}{\partial t'} - \mathbf{H}(\mathbf{r}')\right] G(\mathbf{r}', t'; \mathbf{r}, t)\psi(\mathbf{r}, t), \end{aligned}$$

where we have used the fact that the derivative of a step function is a $\delta$ function. Since this equation is valid for all solutions $\psi$ we can extract from it the Green's function equation:

$$\left[i\frac{\partial}{\partial t'} - \mathbf{H}(\mathbf{r}')\right] G(\mathbf{r}', t'; \mathbf{r}, t) = \delta(\mathbf{r}' - \mathbf{r})\delta(t' - t). \tag{7.11}$$

Together with the boundary condition of a forward propagation in time, that is,

$$G(\mathbf{r}', t'; \mathbf{r}, t) = 0 \qquad \text{for } t' < t, \tag{7.12}$$

Eq. (7.11) defines *the retarded Green's function* and from now on it will be denoted as $G^r$.

As an example, let us compute now the Green's function for a free particle. In this case, the Hamiltonian simply reads: $\mathbf{H}(\mathbf{r}') = -(1/2m)\nabla^2_{\mathbf{r}'}$. Moreover, $G^r(\mathbf{r}', t'; \mathbf{r}, t)$ can depend only upon the difference of the coordinates $(\mathbf{r}', t')$ and $(\mathbf{r}, t)$. We consider its Fourier transform

$$G^r(\mathbf{r}', t'; \mathbf{r}, t) = G^r(\mathbf{r}' - \mathbf{r}; t' - t) = \int \frac{d\mathbf{p}dE}{(2\pi)^4} e^{i\mathbf{p}\cdot(\mathbf{r}'-\mathbf{r}) - iE(t'-t)} G^r(\mathbf{p}, E). \tag{7.13}$$

In terms of $G^r(\mathbf{p}, E)$, Eq. (7.11) is

$$\left[i\frac{\partial}{\partial t'} + \frac{1}{2m}\nabla^2_{\mathbf{r}'}\right] G^r(\mathbf{r}', t'; \mathbf{r}, t) = \tag{7.14}$$

$$\int \frac{d\mathbf{p}dE}{(2\pi)^4}\left[E - \frac{p^2}{2m}\right] G^r(\mathbf{p}, E) e^{i\mathbf{p}\cdot(\mathbf{r}'-\mathbf{r}) - iE(t'-t)} = \int \frac{d\mathbf{p}dE}{(2\pi)^4} e^{i\mathbf{p}\cdot(\mathbf{r}'-\mathbf{r})} e^{-iE(t'-t)}$$

and for $E \neq p^2/2m$

$$G^r(\mathbf{p}, E) = \frac{1}{E - p^2/2m}. \tag{7.15}$$

In order to complete the expression in Eq. (7.15), we need a rule for handling the singularity in the denominator. This is determined by the retarded boundary condition in Eq. (7.12). A way to impose $t' > t$ in the expression of the propagator is to add a positive infinitesimal imaginary part to the denominator and carry out the $E$ integration in Eq. (7.13) first. This integral can now be easily done in the complex plane by using the residue theorem and the result is

$$\begin{aligned} G^r(\mathbf{r}' - \mathbf{r}; t' - t) &= \int \frac{d\mathbf{p}}{(2\pi)^3} e^{i\mathbf{p}\cdot(\mathbf{r}'-\mathbf{r})} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \frac{e^{-iE(t'-t)}}{E - p^2/2m + i\eta} \\ &= -i \int \frac{d\mathbf{p}}{(2\pi)^3} e^{i\mathbf{p}\cdot(\mathbf{r}'-\mathbf{r}) - i\frac{p^2}{2m}(t'-t)} \theta(t' - t). \end{aligned} \tag{7.16}$$

The integral over $\mathbf{p}$ can also be done analytically and we arrive at the final result for the free propagator

$$G^r(\mathbf{r}' - \mathbf{r}; t' - t) = -i\left(\frac{m}{2\pi i(t' - t)}\right)^{3/2} e^{i\frac{m|\mathbf{r}'-\mathbf{r}|^2}{2(t'-t)}} \theta(t' - t). \tag{7.17}$$

Coming back to our general discussion, let us say that it is also convenient to define an alternative Green's function which propagates a solution of the Schrödinger equation backward in time. This function, referred to as *advanced Green's function* and denoted by $G^a$, is defined as

$$\theta(t - t')\psi(\mathbf{r}', t') = -i \int d\mathbf{r}\, G^a(\mathbf{r}', t'; \mathbf{r}, t)\psi(\mathbf{r}, t). \tag{7.18}$$

It is easy to show that it verifies Eq. (7.11) with the boundary condition $G^a(\mathbf{r}', t'; \mathbf{r}, t) = 0$ for $t' > t$. In the case of a free particle, the Fourier transform $G^a(\mathbf{p}, E)$ is also given by Eq. (7.15), but this time the singularity is handled by including a negative infinitesimal imaginary part $(-i\eta)$ in the denominator.

Since in this chapter we will be dealing with equilibrium systems, the Green's functions will depend on the difference of the time arguments. Thus, it is convenient to work with the Fourier transforms of these functions with respect to $t' - t$

$$G^{r,a}(\mathbf{r}', \mathbf{r}; t' - t) = \int_{-\infty}^{\infty} \frac{dE}{2\pi} G^{r,a}(\mathbf{r}', \mathbf{r}; E) e^{-iE(t'-t)}. \tag{7.19}$$

From Eq. (7.11) it is easy to see that the functions $G^{r,a}(\mathbf{r}', \mathbf{r}; E)$ satisfy the following equation

$$\lim_{\eta \to 0^+} \left[ E \pm i\eta - \mathbf{H}(\mathbf{r}') \right] G^{r,a}(\mathbf{r}', \mathbf{r}; E) = \delta(\mathbf{r}' - \mathbf{r}), \tag{7.20}$$

where the infinitesimal imaginary part accompanying the energy argument $E$ ensures that the Green's function (retarded or advanced) satisfies its corresponding boundary condition, as shown in the example of a free particle. Notice that Eq. (7.20) can be also viewed as a relation between the matrix elements of a product of operators in the space representation described by the basis vectors $\{|\mathbf{r}\rangle\}$, i.e. Eq. (7.20) is equivalent to

$$\langle \mathbf{r}' | \lim_{\eta \to 0^+} \left[ (E \pm i\eta)\mathbf{1} - \mathbf{H} \right] \mathbf{G}^{r,a} | \mathbf{r} \rangle = \langle \mathbf{r}' | \mathbf{1} | \mathbf{r} \rangle, \tag{7.21}$$

where $\mathbf{1}$ is the identity operator and the Green's functions have been promoted to operators which act on the basis functions $\{|\mathbf{r}\rangle\}$ spanning the Hilbert space. This relation suggests the following straightforward generalization of the definition of the energy-dependent Green's functions (or operators) which is independent of the representation:[2]

$$\boxed{\mathbf{G}^{r,a}(E) = \lim_{\eta \to 0^+} \left[ (E \pm i\eta)\mathbf{1} - \mathbf{H} \right]^{-1}} \tag{7.22}$$

This expression will be taken as the starting point for our subsequent discussion on the single-particle Green's functions.

Let us start our discussion by saying that Eq. (7.22) can be written in an alternative form in terms of the eigenfunctions and the eigenvalues of the system Hamiltonian $\mathbf{H}$ ($\mathbf{H}|\psi_n\rangle = \epsilon_n|\psi_n\rangle$):

$$\boxed{\mathbf{G}^{r,a}(E) = \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{E - \epsilon_n \pm i\eta}} \tag{7.23}$$

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[2] We will use the term "'Green's function" to refer to both the complex functions defined above and the operators defined in Eq. (7.22). The context will help you to figure out easily whether we refer to a function or to an operator.

where from now on the limit $\lim_{\eta\to 0^+}$ is implicitly assumed in all the expressions in which the parameter $\eta$ appears.

From the previous two equations, one can deduce a number of important properties of the functions $G^{r,a}$. Let us discuss the most useful ones for our purposes:

**Property 1.** The imaginary part of the Green's functions is related to the density of states of the system. To demonstrate this, let us remind that the local density of states in a given position $\mathbf{r}$ can be written in terms of the eigenstates of $\mathbf{H}$ as follows

$$\rho(\mathbf{r},E) = \sum_n |\langle \mathbf{r}|\psi_n\rangle|^2 \delta(E-\epsilon_n). \tag{7.24}$$

From Eq. (7.23) we can write

$$G^{r,a}(\mathbf{r},\mathbf{r},E) = \sum_n \frac{\langle \mathbf{r}|\psi_n\rangle\langle\psi_n|\mathbf{r}\rangle}{E-\epsilon_n \pm i\eta}, \tag{7.25}$$

and comparing these last two equations, one obtains

$$\rho(\mathbf{r},E) = \mp\frac{1}{\pi}\mathrm{Im}\left\{G^{r,a}(\mathbf{r},\mathbf{r},E)\right\}. \tag{7.26}$$

Here, we have used the relation

$$\frac{1}{E\pm i\eta} = \mathcal{P}\left(\frac{1}{E}\right) \mp i\pi\delta(E), \tag{7.27}$$

where $\mathcal{P}$ denotes a Cauchy principal value.[3]

If we use a discrete basis of atomic orbitals, we would have

$$\rho_i(E) = \mp\frac{1}{\pi}\mathrm{Im}\left\{G^{r,a}_{ii}(E)\right\}, \tag{7.28}$$

where $i$ indicates that the density of states has been projected onto the atom (or site) $i$.

**Property 2.** The diagonal Green's functions satisfy in any basis that $\mathrm{Im}\{G^r_{ii}(E)\} \leq 0$ and $\mathrm{Im}\{G^a_{ii}(E)\} \geq 0$. This is obvious from Eq. (7.23).

**Property 3.** The real and imaginary parts of $G^{r,a}$ are related by means of a Hilbert transformation:

$$\mathrm{Re}\left\{\mathbf{G}^{r,a}(E)\right\} = \mp\mathcal{P}\int_{-\infty}^{\infty}\frac{dE'}{\pi}\,\frac{\mathrm{Im}\left\{\mathbf{G}^{r,a}(E')\right\}}{E-E'}. \tag{7.29}$$

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[3] The relation of Eq. (7.27) is only meaningful when $1/(E\pm i\eta)$ appears as the integrand of an energy integral. This relation can be easily proven by considering first $\eta$ as a finite positive real number and then taking the limit $\eta\to 0$.

This is a consequence of the pole structure of Eq. (7.23) and it can be shown with the help of Eq. (7.27). As a result of this relation, $\mathbf{G}^{r,a}(E)$ can be written as

$$\mathbf{G}^{r,a}(E) = \int_{-\infty}^{\infty} dE' \, \frac{\rho(E')}{E - E' \pm i\eta}, \tag{7.30}$$

where we have defined the density operator $\rho(E) \equiv \mp \mathrm{Im}\{\mathbf{G}^{r,a}(E)\}/\pi$. This way of writing the Green's function in terms of the density of states is known as *spectral representation* and, as we shall show below, it is also valid in the case of many-particle interacting systems.

**Property 4.** An important consequence of the spectral representation is the asymptotic form of the diagonal Green's functions for $E \to \infty$. As $\rho_i(E)$ is a bounded function, one has

$$\lim_{E\to\infty} G_{ii}^{r,a}(E) = \frac{1}{E}. \tag{7.31}$$

This is a consequence of the fact that the energy integral of $\rho_i(E)$ is equal to 1, i.e.

$$\int_{-\infty}^{\infty} dE \; \rho_i(E) = \mp \frac{1}{\pi} \int_{-\infty}^{\infty} dE \; \mathrm{Im}\,\{G_{ii}^{r,a}(E)\} = 1. \tag{7.32}$$

**Property 5.** As one can easily see from Eq. (7.22), the following simple relation between $G^r$ and $G^a$ holds:

$$\mathbf{G}^r(E) = [\mathbf{G}^a(E)]^\dagger . \tag{7.33}$$

This means in practice that we only need to compute one of these two types of functions.

**Property 6.** As a last issue, let us consider the case in which the Hamiltonian $\mathbf{H}$ can be written as

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}, \tag{7.34}$$

where $\mathbf{H}_0$ is the Hamiltonian of a problem for which the Green's functions are known, $\mathbf{g}^{r,a}$, and $\mathbf{V}$ is an arbitrary single-particle perturbation. We want to express the Green's functions of the full problem in terms of the unperturbed Green's functions. This can be easily done starting from the definition of Eq. (7.22)

$$\mathbf{G}^{r,a}(E) = \left[(E \pm i\eta)\mathbf{1} - \mathbf{H}_0 - \mathbf{V}\right]^{-1}. \tag{7.35}$$

Taking into account that for the unperturbed problem we have

$$\mathbf{g}^{r,a}(E) = \left[(E \pm i\eta)\mathbf{1} - \mathbf{H}_0\right]^{-1}, \tag{7.36}$$

it is easy to obtain the following relation

$$\mathbf{G}^{r,a}(E) = \mathbf{g}^{r,a}(E) + \mathbf{g}^{r,a}(E)\mathbf{V}\mathbf{G}^{r,a}(E), \tag{7.37}$$

The previous equation is known as *Dyson's equation* and it can also be derived in the many-particle case, as we shall show in the next chapter. However, in the general case the operator $\mathbf{V}$ is replaced by an energy-dependent operator, $\mathbf{\Sigma}(\mathbf{E})$, known as *self-energy.* Dyson's equation is extremely useful to compute the Green's functions in different situations, as we shall illustrate in the next section. We shall also show that it is possible to have a energy-dependent self-energy in single-particle problems when one deals with a subspace of the full Hilbert space of the problem.

### 7.1.3 *Application to tight-binding Hamiltonians*

In this section we shall apply what we have learned so far to the computation of the Green's functions of several simple electronic systems described in terms of tight-binding Hamiltonians.[4] Such Hamiltonians, as we shall see in the next chapters, play a fundamental role in the field of molecular electronics. A generic tight-binding Hamiltonian adopts the following form in the language of second quantization

$$\mathbf{H} = \sum_{i\sigma} \epsilon_i \mathbf{c}^{\dagger}_{i\sigma}\mathbf{c}_{i\sigma} + \sum_{i\neq j;\sigma} t_{ij}\mathbf{c}^{\dagger}_{i\sigma}\mathbf{c}_{j\sigma}. \tag{7.38}$$

Here, the indexes $i$ and $j$ run over the sites (atoms) of the system and $\sigma$ represents the electron spin ($\sigma =\uparrow,\downarrow$). The different operators have the following meaning. For instance, $\mathbf{c}^{\dagger}_{i\sigma}$ is the operator that creates an electron in the site $i$ with spin $\sigma$, while $\mathbf{c}_{i\sigma}$ annihilates such an electron. For the sake of simplicity, we shall assume in this discussion that there is a single relevant orbital per site. The parameters $\epsilon_i$ are the on-site energies, while the *hoppings* $t_{ij}$ describe the coupling between the different sites.

Our goal is the calculation of the different Green's functions $G^{r;a}_{ij}(E)$ in this local basis representation. In principle, we have three methods at our disposal: (i) the definition of Eq. (7.22), (ii) the spectral representation of Eq. (7.23) and (iii) Dyson's equation, see Eq. (7.37). We shall illustrate the use of these different approaches with the analysis of three basic examples that will be frequently used in subsequent chapters.

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[4] The tight-binding approach is explained in all textbooks on solid state theory. Here, we shall use the term tight-binding to refer to models or Hamiltonians where the electronic structure is described in terms a local (atomic-like) basis. We shall not discuss here how the matrix elements of such a Hamiltonian are actually computed, and we shall just use them as parameters.

### 7.1.3.1 *Example 1: A hydrogen molecule*

We describe a hydrogen molecule with the following two-sites tight-binding Hamiltonian (see Fig. 7.1)

$$\mathbf{H} = \epsilon_0 \sum_\sigma (\mathbf{n}_{1\sigma} + \mathbf{n}_{2\sigma}) + t \sum_\sigma (\mathbf{c}^\dagger_{1\sigma}\mathbf{c}_{2\sigma} + \mathbf{c}^\dagger_{2\sigma}\mathbf{c}_{1\sigma}). \tag{7.39}$$

Here, $\mathbf{n}_{i\sigma} = \mathbf{c}^\dagger_{i\sigma}\mathbf{c}_{i\sigma}$, $\epsilon_0$ is the 1$s$-level of the hydrogen atoms and $t$ is the hopping connecting these two levels and it is assumed to be real. Our goal is to compute the retarded/advanced diagonal Green's function of site 1, i.e. $G^{r,a}_{11}(E)$ (since the problem has spin degeneracy, we omit the spin indexes in the Green's functions). For symmetry reasons, this Green's function is equal to $G^{r,a}_{22}(E)$. In order to compute this function, we shall employ the three methods mentioned above:

*Method 1: Direct definition.* According to the definition of Eq. (7.22), the matrix Green's function can be simply calculated by inverting the Hamiltonian of Eq. (7.39). In the basis of the atomic states localized in the hydrogen atoms, $\{|1\rangle, |2\rangle\}$, this Hamiltonian adopts the following matrix form

$$\mathbf{H} = \begin{pmatrix} \epsilon_0 & t \\ t & \epsilon_0 \end{pmatrix}, \tag{7.40}$$

and therefore the matrix Green's function is given by

$$\mathbf{G}^{r,a}(E) = \begin{pmatrix} E^{r,a} - \epsilon_0 & -t \\ -t & E^{r,a} - \epsilon_0 \end{pmatrix}^{-1}, \tag{7.41}$$

where $E^{r,a} \equiv E \pm i\eta$, $\eta$ being the infinitesimal imaginary part of the energy appearing in the definition of Eq. (7.22). Thus, the element $(1,1)$ that we are looking for reads

$$G^{r,a}_{11}(E) = \frac{E^{r,a} - \epsilon_0}{(E^{r,a} - \epsilon_0)^2 - t^2} = \frac{1/2}{E^{r,a} - (\epsilon_0 + t)} + \frac{1/2}{E^{r,a} - (\epsilon_0 - t)}. \tag{7.42}$$

One can show that this expression fulfills the different properties of a Green's function discussed in the previous section. Thus for instance, notice that Eq. (7.42) has precisely the form of the spectral representation of Eq. (7.23). The poles in this case are nothing else but the energies $\epsilon_\pm = \epsilon_0 \pm t$ of the bonding and antibonding orbitals of the hydrogen molecule,[5] see Fig. 7.1. Notice also that the sum of the weights (coefficients appearing in the numerators) is equal to 1.

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[5] The hopping $t$ is indeed a negative quantity and thus $\epsilon_+ = \epsilon_0 + t$ corresponds to the lowest energy level (bonding state).

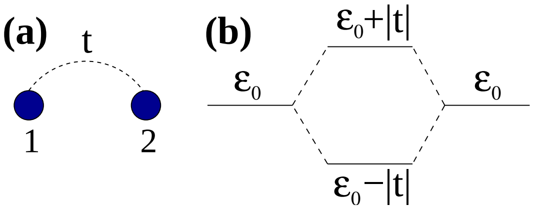

Fig. 7.1 (a) Model for the hydrogen molecule. We consider a single orbital per site (atom) with energy $\epsilon$, and the coupling is described by a hopping $t$. (b) Level scheme of the hydrogen molecule in which the two orbitals hybridize to form the bonding and antibonding states with energies $\epsilon_0 \mp |t|$.

On the other hand, the density of states projected onto the site 1 is given in this case by

$$\rho_1(E) = \mp \frac{1}{\pi} \mathrm{Im}\left\{ G_{11}^{r,a}(E) \right\} = \frac{1}{2}\delta(E - \epsilon_+) + \frac{1}{2}\delta(E - \epsilon_-), \tag{7.43}$$

i.e. it is a sum of delta functions evaluated at the molecular energies. This is a consequence of the fact that we are dealing with a finite system. In a similar way, one could demonstrate that the rest of the properties listed at the end of the previous section are satisfied. In particular, properties 4 and 5 are rather obvious from Eq. (7.42).

*Method 2: Spectral representation.* Let us now use the spectral representation of Eq. (7.23). To evaluate this expression we need both the eigenfunctions and the eigenvalues of the hydrogen molecule. For this purpose we just need to diagonalize the Hamiltonian of Eq. (7.40). The eigenfunctions are simply the bonding ($|\psi_+\rangle$) and antibonding ($|\psi_-\rangle$) states given by: $|\psi_\pm\rangle = (|1\rangle \pm |2\rangle)/\sqrt{2}$ with the corresponding eigenvalues $\epsilon_\pm$. Thus, the function $G_{11}^{r,a}(E)$ is then given by

$$G_{11}^{r,a}(E) = \langle 1|\mathbf{G}|1\rangle = \sum_{n=+,-} \frac{\langle 1|\psi_n\rangle\langle\psi_n|1\rangle}{E^{r,a} - \epsilon_n} = \sum_{n=+,-} \frac{|\langle 1|\psi_n\rangle|^2}{E^{r,a} - \epsilon_n}. \tag{7.44}$$

Using the fact that $\langle 1|\psi_\pm\rangle = 1/\sqrt{2}$, we arrive immediately at the expression of Eq. (7.42). Obviously, this method is not very practical in general since it requires the knowledge of the eigenfunctions of the system, which are typically unknown.

*Method 3: Dyson's equation.* Now, our starting point is Eq. (7.37). The first thing to do is to divide the Hamiltonian of Eq. (7.39) into the unperturbed part $\mathbf{H_0}$ and the perturbation $\mathbf{V}$. The natural choice is that the perturbation be the coupling term between the two atoms (second term in Eq. (7.39)). Thus, these two parts of the Hamiltonian adopt the following matrix form

$$\mathbf{H}_0 = \begin{pmatrix} \epsilon_0 & 0 \\ 0 & \epsilon_0 \end{pmatrix} ; \quad \mathbf{V} = \begin{pmatrix} 0 & t \\ t & 0 \end{pmatrix} . \tag{7.45}$$

To solve Dyson's equation we also need the Green's functions of the unperturbed system, $\mathbf{g}^{r,a}$. These functions are simply given by

$$\mathbf{g}^{r,a} = [E^{r,a}\mathbf{1} - \mathbf{H}_0]^{-1} = \begin{pmatrix} E^{r,a} - \epsilon_0 & 0 \\ 0 & E^{r,a} - \epsilon_0 \end{pmatrix}^{-1} = \frac{1}{E^{r,a} - \epsilon_0}\mathbf{1}. \tag{7.46}$$

Now, we can determine the function $G_{11}^{r,a}(E)$ by taking the element $(1,1)$ in Eq. (7.37), i.e.

$$G_{11}^{r,a}(E) = g_{11}^{r,a}(E) + g_{11}^{r,a}(E) V_{12} G_{21}^{r,a}(E). \tag{7.47}$$

Remember that $\mathbf{g}^{r,a}$ is diagonal, while $\mathbf{V}$ is purely off-diagonal. In order to get a closed equation for $G_{11}^{r,a}$, we still need an equation for $G_{21}^{r,a}$. Taking now the element $(2,1)$ in Eq. (7.37), we get

$$G_{21}^{r,a}(E) = g_{22}^{r,a}(E) V_{21} G_{11}^{r,a}(E). \tag{7.48}$$

Substituting this expression now in Eq. (7.47), we arrive at

$$G_{11}^{r,a}(E) = g_{11}^{r,a}(E) + g_{11}^{r,a}(E) V_{12} g_{22}^{r,a}(E) V_{21} G_{11}^{r,a}(E). \tag{7.49}$$

This equation can now be trivially inverted and using the explicit expression of the unperturbed Green's functions one arrives once more at the result of Eq. (7.42).

We can use the discussion above to illustrate the concept of self-energy, which was briefly mentioned at the end of the last section. In the previous equation, we can identify the following energy-dependent function

$$\Sigma_{11}^{r,a}(E) \equiv V_{12} g_{22}^{r,a}(E) V_{21} = t^2 g_{22}^{r,a}(E). \tag{7.50}$$

This function describes how the properties of the atom 1 are modified via the interaction with the second atom. This can be better seen by rewriting Eq. (7.49) as

$$G_{11}^{r,a}(E) = \frac{1}{E^{r,a} - \epsilon_0 - \Sigma_{11}^{r,a}(E)}, \tag{7.51}$$

where we have used the expressions of the unperturbed Green's functions. In this equation we see that the self-energy renormalizes dynamically (depending on the energy) both the position ($\epsilon_0$) and the lifetime of the energy level in the atom 1 (this latter point will become clearer in the next examples). Notice that the self-energy depends both on the coupling to the second atom and on the electronic structure of this second atom. We shall see in the next examples that, no matter the problem, the concept of self-energy appears naturally and it describes the renormalization of the properties of a finite system due to its interaction with an external system. In particular, we shall show in the next chapter that the concept of self-energy remains valid even in the presence of interactions.

#### 7.1.3.2 *Example 2: Semi-infinite linear chain*

As a first example of an infinite solid, we consider now a semi-infinite linear chain with only nearest-neighbor couplings. This system, which is schematically illustrated in Fig. 7.2(a), will be sometimes used in the next chapters as a model for a metallic electrode. The corresponding tight-binding Hamiltonian of this system reads[6]

$$\mathbf{H} = \epsilon_0 \sum_{i\sigma} \mathbf{n}_{i\sigma} + t \sum_{i\sigma} \left( \mathbf{c}^\dagger_{i\sigma} \mathbf{c}_{i+1\sigma} + \mathbf{c}^\dagger_{i+1\sigma} \mathbf{c}_{i\sigma} \right) , \tag{7.52}$$

where $i = 1, 2, 3, ...$ represents the different sites starting from the surface. We shall carry out here the calculation of the surface Green's function, $G^{r,a}_{11}(E)$. As in the previous example, there are, in principle, three methods avaliable. However, the first two are rather impractical. The first one would require the inversion of an infinite matrix, while the second would need the calculation of the eigenfunctions and eigenvalues of this infinite (non-periodic) system. For these reasons, we shall resort to Dyson's equation. The first step in this method is to choose the unperturbed problem and the corresponding perturbation. One possible choice would be to select the uncoupled atoms as unperturbed system and the coupling between them as the perturbation. Such a legitimate choice would lead us to an infinite algebraic system, which is really difficult to solve (try it, just for fun!). There is an alternative "trick" that does the job in a few steps. The idea goes as follows. Let us consider that the unperturbed system is composed of two uncoupled systems, namely the atom 1 and the rest of the chain. Then, the perturbation is simply the coupling between these two subsystems, i.e.

$$\mathbf{V} = t \sum_{\sigma} \left( \mathbf{c}^\dagger_{1\sigma} \mathbf{c}_{2\sigma} + \mathbf{c}^\dagger_{2\sigma} \mathbf{c}_{1\sigma} \right) . \tag{7.53}$$

This means in practice that the only two non-zero elements of the perturbation are $V_{12} = V_{21} = t$.

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[6] Without loss of generality, we assume here that the hopping element $t$ is real.

Now, we can use Dyson's equation [Eq (7.37)] to obtain the equation for $G^{r,a}_{11}(E)$. Taking the element $(1,1)$ we have

$$G_{11}(E) = g_{11}(E) + g_{11}(E)V_{12}G_{21}(E)$$
$$G_{21}(E) = g_{22}(E)V_{21}G_{11}(E),$$

where the second relation is necessary to obtain a closed equation for $G_{11}(E)$. Here, we have omitted again the spin index $\sigma$ since there is spin degeneracy in this problem and we have also dropped the superindexes $r, a$ because the equations are valid for both retarded and advanced functions. The unperturbed function $g_{11}$ of the site $i = 1$ is simply given by $g_{11}(E) = 1/(E - \epsilon_0)$. On the other hand, the unperturbed function $g_{22}$ is nothing else but the surface Green's function of a semi-infinite chain,[7] which is precisely what we are looking for, i.e. $g_{22} = G_{11}$. This allows us to obtain the following closed equation for $G_{11}(E)$

$$(E - \epsilon_0)G_{11}(E) = 1 + t^2 G^2_{11}(E). \tag{7.54}$$

This is a quadratic equation that possesses two possible solutions. In order to choose the "physical" one, it is necessary to take into account the boundary condition $E \to E^{r,a} = E \pm i\eta$ to distinguish between the retarded and advanced solutions. As a practical advice, remember that the imaginary part of these functions has a well-defined sign. The final solution adopts the following expression

$$G^{r,a}_{11}(E) = \frac{E^{r,a} - \epsilon_0}{2t^2} - \frac{1}{|t|}\sqrt{\left(\frac{E^{r,a} - \epsilon_0}{2t}\right)^2 - 1}. \tag{7.55}$$

The real and imaginary parts of the advanced function are depicted in Fig. 7.2(b). Notice that the imaginary part, and therefore the density of states, is only non-zero in the region $|E - \epsilon_0| < 2|t|$, which defines the energy band of the linear chain. In this region, the Green's function adopts the following form

$$G^{r,a}_{11}(E) = \frac{E - \epsilon_0}{2t^2} \mp \frac{i}{|t|}\sqrt{1 - \left(\frac{E - \epsilon_0}{2t}\right)^2}. \tag{7.56}$$

This expression can be written in a form that is very useful to do algebraic manipulations (see Exercise 6.5) by defining $\cos(\phi) \equiv (E - \epsilon_0)/2|t|$:

$$G^{r,a}_{11}(E) = \frac{1}{|t|}\exp(\mp i\phi) \tag{7.57}$$

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[7] The removal of an atom from the chain does not modify the fact that the remaining chain is again a semi-infinite chain.

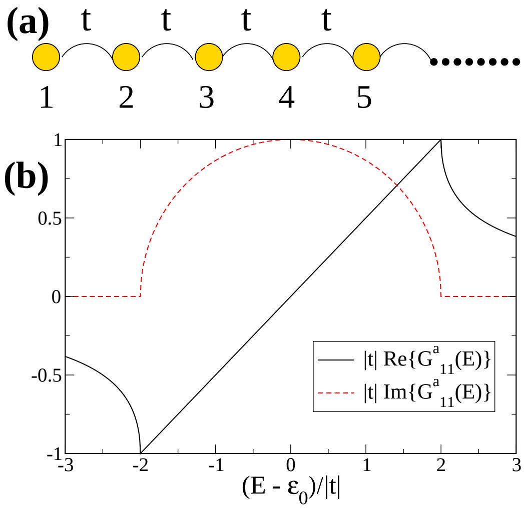

Fig. 7.2 (a) Semi-infinite linear chain with a single orbital per site and only nearest-neighbor couplings. (b) Real and imaginary parts of the advanced surface Green's function, $G^a_{11}$, of the semi-infinite chain as a function of the energy, see Eq. (7.55).

The density of states in the surface atom of the chain can be then expressed as

$$\rho_1(E) = \frac{1}{\pi}\mathrm{Im}\left\{G^a_{11}(E)\right\} = \frac{1}{\pi|t|}\sqrt{1-\left(\frac{E-\epsilon_0}{2t}\right)^2}, \quad |E-\epsilon_0| \leq 2|t|, \tag{7.58}$$

and it can be seen in Fig. 7.2(b). Contrary to the example of the hydrogen molecule, in this case there is an infinite number of states that are grouped in an energy band of width $4|t|$. Notice that we have not specified the actual occupation of this band. If we had an electron per site, the band would be half-filled (with the Fermi energy equal to $\epsilon_0$) and there would be electron-hole symmetry.

It is worth mentioning that in Eq. (7.54) one can identify the self-energy $\Sigma^{r,a}_{11}(E) = t^2 G^{r,a}_{11}(E)$, which plays exactly the same role as in the case of the hydrogen molecule and it has the same functional form.

To conclude this discussion, let us say that one can check that the expression of Eq. (7.55) satisfies the different properties discussed in the previous section. You are encouraged to show, in particular, that

$$\lim_{|E|\to\infty} \mathrm{Re}\left\{G^{r,a}_{11}(E)\right\} = \frac{1}{E}, \tag{7.59}$$

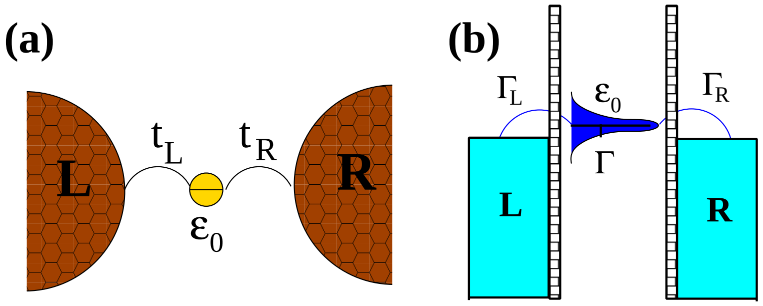

Fig. 7.3 (a) A single level of energy $\epsilon_0$ is coupled to two infinite electrodes via the hoppings $t_L$ and $t_R$. (b) The corresponding energy scheme where one can see the continuum of states in the electrodes filled up to the Fermi energy and the resonant level, which has acquired a half width at half maximum equal to $\Gamma = \Gamma_L + \Gamma_R$ due to the coupling to the reservoirs.

and that the following sum rule is fulfilled

$$\int_{-\infty}^{\infty} dE \; \rho_1(E) = 1. \tag{7.60}$$

### 7.1.3.3 *Example 3: A single level coupled to electrodes*

We consider now the case of single energy level coupled to two infinite electrodes. This is a very important example that will teach us a couple of important lessons for molecular electronics. The system that we are interested in is schematically represented in Fig. 7.3(a), and it is described by the following Hamiltonian

$$\mathbf{H} = \mathbf{H}_L + \mathbf{H}_R + \sum_\sigma \epsilon_0 \mathbf{c}^\dagger_{0\sigma}\mathbf{c}_{0\sigma} + \tag{7.61}$$
$$\sum_\sigma t_L \left(\mathbf{c}^\dagger_{0\sigma}\mathbf{c}_{L\sigma} + \mathbf{c}^\dagger_{L\sigma}\mathbf{c}_{0\sigma}\right) + \sum_\sigma t_R \left(\mathbf{c}^\dagger_{0\sigma}\mathbf{c}_{R\sigma} + \mathbf{c}^\dagger_{R\sigma}\mathbf{c}_{0\sigma}\right).$$

Here, the Hamiltonians $\mathbf{H}_L$ and $\mathbf{H}_R$ describe the left and right electrodes that are coupled to a single energy level. It will not be necessary for the present discussion to specify anything about the shape or concrete electronic structure of these two leads. The subindex 0 refers to the localized level, the energy of which is denoted by $\epsilon_0$. This level is coupled to the electrodes via the hoppings $t_L$ and $t_R$, which are assumed to be real. The subindexes $L$ and $R$ refer here to the outermost sites of the left and right electrodes (we have in mind again that there is a single relevant orbital per site in these leads).

The question that we want to address is: How is this level modified by the coupling to the electrodes? This question is very relevant for many different contexts. We have in mind the problem of a molecule (or atom) coupled to metallic leads, but it is also important for problems like the chemisorption of molecules on surfaces (in this case there would be only one electrode). In order to answer this question, we will compute the local density of states projected onto the level. This requires the calculation of the Green's function $G_{00}(E)$ (no matter whether it is retarded or advanced). For this purpose, we resort to Dyson's equation. Our choice for the unperturbed Hamiltonian $\mathbf{H}_0$ is the sum of the Hamiltonians of the three uncoupled subsystems, i.e. the right hand side of the first line of Eq. (7.61). Thus, the perturbation $\mathbf{V}$ is the term that describes the coupling between the localized level and the electrodes (second line in Eq. (7.61)). Notice that we are assuming that there is no direct coupling between the leads.

With this choice in mind, we take the element $(0,0)$ in Eq. (7.37) to obtain

$$G_{00}(E) = g_{00}(E) + g_{00}(E)V_{0L}G_{L0}(E) + g_{00}(E)V_{0R}G_{R0}(E), \tag{7.62}$$

where $V_{0L} = t_L$ and $V_{0R} = t_R$ and $g_{00}(E) = 1/(E - \epsilon_0)$ is the unperturbed Green's function of the single-level system. As usual, to close this equation, we have to determine the functions $G_{L0}$ and $G_{R0}$. This can be done by taking the corresponding elements in Dyson's equation, i.e.

$$\begin{aligned} G_{L0}(E) &= g_{LL}(E)V_{L0}G_{00}(E) \\ G_{R0}(E) &= g_{RR}(E)V_{R0}G_{00}(E), \end{aligned}$$

where $V_{L/R0} = t_{L/R}$ and $g_{LL}$ and $g_{RR}$ are the Green's functions of the two outermost sites of the left and right electrodes, respectively. Substituting these expressions in Eq. (7.62), we obtain the following closed equation

$$\begin{aligned} G_{00}(E) = g_{00}(E) &+ g_{00}(E)V_{0L}g_{LL}(E)V_{L0}G_{00}(E) \\ &+ g_{00}(E)V_{0R}g_{RR}(E)V_{R0}G_{00}(E). \end{aligned} \tag{7.63}$$

In this expression one can identify, as in the previous examples, the self-energy $\Sigma_{00}(E) = t_L^2 g_{LL}(E) + t_R^2 g_{RR}(E)$, which in this case is the sum of two contributions associated to the two leads. In terms of the self-energy we can express the function $G_{00}(E)$ as

$$G_{00}(E) = \frac{1}{E - \epsilon_0 - \Sigma_{00}(E)}, \tag{7.64}$$

where we have used the expression of $g_{00}(E)$. Here, we see once more that the self-energy describes how the resonant level is modified by the interaction with the leads. In particular, its real part is responsible for the renormalization of the level position, which becomes $\tilde{\epsilon}_0 = \epsilon_0 + \mathrm{Re}\{\Sigma_{00}(E)\}$, while its imaginary part describes the finite energy "width" acquired by the level via the interaction with the leads. This latter point becomes more clear by using the following approximation. Let us assume that the Green's functions of the leads are imaginary for energies in the vicinity of $\epsilon_0$ and that they do not depend significantly on energy in this region.[8] Thus, we can approximate these functions by $g^{r,a}_{LL,RR} \approx \mp i/W_{L,R}$, where $W_{L,R}$ are energy scales related to the density of states of the leads at the energy $\epsilon_0$.[9] For instance, if we modeled the electrodes by the semi-infinite chains like in the previous example, $W_{L,R}$ would then be the magnitude of the bulk hopping element of these chains. Within this approximation, the self-energy becomes $\Sigma^{r,a}_{00} = \mp i\,(\Gamma_L + \Gamma_R)$, where we have defined the scattering rates $\Gamma_{L,R} \equiv t^2_{L,R}/W_{L,R}$. Obviously, with this approximation the level position remains unchanged (see Exercise 6.9). Finally, the function $G_{00}(E)$ adopts in this case the form

$$G^{r,a}_{00}(E) = \frac{1}{E^{r,a} - \epsilon_0 \pm i\,(\Gamma_L + \Gamma_R)}, \tag{7.65}$$

Thus, the local density of states that we wanted to calculate is given by

$$\rho_0(E) = \mp\frac{1}{\pi}\mathrm{Im}\,\{G^{r,a}_{00}(E)\} = \frac{1}{\pi}\frac{\Gamma_L + \Gamma_R}{(E-\epsilon_0)^2 + (\Gamma_L+\Gamma_R)^2}, \tag{7.66}$$

which is a Lorentzian function, where $\Gamma = \Gamma_L + \Gamma_R$ is the half-width at half-maximum (HWHM). This result shows clearly that the resonant level, which originally had zero width (it was an eigenstate of the isolated central system), acquires a finite width $\Gamma$ via the coupling to the leads. This fact is illustrated in Figs. 7.3(b). It is worth stressing that the width depends both on the strength of the coupling to the electrodes (via $t^2_{L,R}$) and on the local electronic structure of the leads (via $W_{L,R}$ or, more generally, via $g_{LL,RR}$). The time scale $\hbar/\Gamma$ can be interpreted as the finite lifetime of the resonant level due to the interaction with the leads, or in other words, as the time that an electron spends in the resonant level.

Thus, the take-home message of this example is that *when an isolated molecule (or an atom) is coupled to a continuum of states, its levels are, in general, shifted and they acquire a width that depends on the strength of the coupling and on the local electronic structure of the leads.*

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[8] This approximation is usually known as *wide-band approximation.*

[9] This energy scales are simply given by $W_{L,R} = 1/[\pi\rho_{L,R}(E=\epsilon_0)]$, where $\rho_{L,R}$ are the local densities of states of the two outermost sites of the leads.

Let us finally say that we hope that you have realized that all the calculations of this section only involve simple algebraic manipulations. Indeed, we shall show in the next chapters that, as long as we deal with systems with only elastic interactions (described by mean-field Hamiltonians), the evaluation of the Green's functions, both in equilibrium and out of equilibrium, reduces to straightforward exercises of linear algebra. So maybe, this Green's function stuff is not so scary after all, don't you think?

For more detailed discussion of Green's functions in the framework of tight-binding models, we recommend the book of Ref. [1].

### 7.1.4 *Many-particle Green's functions*

The goal of this section is to introduce a set of Green functions which are more adequate for describing many-particle systems and they reduce to the ones we have just discussed in the case of single-particle problems. The utility of these many-particle will become apparent in the next chapter when we deal with the perturbation theory. Moreover, it will be clear that we need to introduce a new kind of function known as the causal Green's function.

Let us consider an arbitrary many-electron system that at zero temperature is described by its ground-state many-particle wave function $|\Psi_{\rm H}\rangle$ in the Heisenberg picture. The many-particle retarded Green's function in time domain is defined as follows using the second quantization language and an arbitrary representation (or basis)

$$G^r_{ij}(t,t') = -i\theta(t-t')\langle\Psi_{\rm H}|\left\{\mathbf{c}_{i\sigma}(t), \mathbf{c}^\dagger_{j\sigma}(t')\right\}|\Psi_{\rm H}\rangle, \tag{7.67}$$

where the operators are in Heisenberg picture. We shall only include explicitly the spin index $\sigma$ in $G^r_{ij}$ in those problems where the spin symmetry is broken. In this definition, the step function, $\theta$, ensures that $t > t'$ and the symbol $\{\ ,\ \}$ stands for the anticommutator.

Green's functions are often defined using the basis $\{|\mathbf{r}\rangle\}$ formed by the eigenfunctions of the position operator. The corresponding creation and annihilation operators in this representation are known as *field operators* and they are denoted by $\mathbf{\Psi}^\dagger_\sigma(\mathbf{r})$ and $\mathbf{\Psi}_\sigma(\mathbf{r})$, These operators are simply related to $\mathbf{c}^\dagger_{i\sigma}$ and $\mathbf{c}_{i\sigma}$ by the basis transformation

$$\mathbf{\Psi}_\sigma(\mathbf{r}) = \sum_i \phi_i(\mathbf{r})\mathbf{c}_{i\sigma} \ \text{ and } \ \mathbf{\Psi}^\dagger_\sigma(\mathbf{r}) = \sum_i \phi^*_i(\mathbf{r})\mathbf{c}^\dagger_{i\sigma}, \tag{7.68}$$

where $\phi_i(\mathbf{r})$ are the basis wave functions of the discrete representation.

These field operators satisfy the standard type of anticommutation relations, i.e.

$$\{\mathbf{\Psi}_\sigma(\mathbf{r}), \mathbf{\Psi}^\dagger_{\sigma'}(\mathbf{r}')\} = \delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma,\sigma'}; \;\; \text{etc.} \tag{7.69}$$

In terms of these field operators, the retarded Green's function is defined as

$$G^r(\mathbf{r}t, \mathbf{r}'t') = -i\theta(t-t')\langle\Psi_\mathrm{H}| \left\{\mathbf{\Psi}_\sigma(\mathbf{r},t), \mathbf{\Psi}^\dagger_\sigma(\mathbf{r}',t')\right\} |\Psi_\mathrm{H}\rangle, \tag{7.70}$$

which is a complex function that depends on two spatial arguments and two time arguments.

The advanced Green's function has a similar definition, the only difference being that the propagation takes place backward in time

$$G^a_{ij}(t,t') = i\theta(t'-t)\langle\Psi_\mathrm{H}| \left\{\mathbf{c}_{i\sigma}(t), \mathbf{c}^\dagger_{j\sigma}(t')\right\} |\Psi_\mathrm{H}\rangle. \tag{7.71}$$

Finally, it is convenient to define an additional Green's function, namely the one known as *causal Green's function*, which is defined as follows

$$G^c_{ij}(t,t') = -i\langle\Psi_\mathrm{H}|\mathbf{T}\left[\mathbf{c}_{i\sigma}(t)\mathbf{c}^\dagger_{j\sigma}(t')\right]|\Psi_\mathrm{H}\rangle, \tag{7.72}$$

where $\mathbf{T}$ is the time-ordering operator. It acts on a product of time-dependent operators by ordering them chronologically from right to left. Thus for instance, the previous function has the following explicit form

$$G^c_{ij}(t,t') = \begin{cases} -i\langle\Psi_\mathrm{H}|\mathbf{c}_{i\sigma}(t)\mathbf{c}^\dagger_{j\sigma}(t')|\Psi_\mathrm{H}\rangle & t > t' \\ i\langle\Psi_\mathrm{H}|\mathbf{c}^\dagger_{j\sigma}(t')\mathbf{c}_{i\sigma}(t)|\Psi_\mathrm{H}\rangle & t' > t. \end{cases} \tag{7.73}$$

Notice the sign change for $t' > t$ due to the anticommutation of fermion operators.

So far, our discussion in this section has been a bit technical and there are questions that arise naturally. The first one is: What is the physical meaning of the Green's functions? To answer this question notice that these functions contain factors like $\langle\Psi_\mathrm{H}|\mathbf{c}_{i\sigma}(t)\mathbf{c}^\dagger_{j\sigma}(t')|\Psi_\mathrm{H}\rangle$. Here, $\mathbf{c}^\dagger_{j\sigma}(t')|\Psi_\mathrm{H}\rangle$ describes the creation (or injection) in the ground state of an electron at time $t'$ in the state $j$. Then, the previous expectation value yields the probability amplitude of finding such an electron at a later time $t$ in the state $i$. In other words, the Green's functions simply describe the probability amplitude of the occurrence of certain processes. The type of processes described depends on the arguments of these functions. Thus for instance, they can describe the propagation of electrons in time domain or in energy space, propagation in real space, in momentum space or simply in an atomic lattice.[10]

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[10] In this sense, it is not surprising that the elastic transmission of any real system can be naturally expressed in terms of these functions.

Another natural question is: What is the relation between this definition of the Green's functions and the one put forward in the previous section? At a first glance, it seems that there is no relation at all. However, we shall show below that for single-particle problems the Fourier transform with respect to the time arguments of these new Green's functions fulfill Eqs. (7.22) and (7.23), i.e. these two types of functions are indeed equivalent when there are no many-body interactions.

**Simple example: degenerate electron gas.** To illustrate the previous definitions, we consider now the example of a free electron gas at zero temperature. As we know, the ground state of this noninteracting system is a Fermi sea, where the single-particle states are occupied up to the Fermi energy, $E_{\mathrm{F}}$ (or chemical potential $\mu$). These states, $|\mathbf{k}\sigma\rangle$, are plane waves characterized by an energy $\epsilon_k = k^2/2m$, where $\mathbf{k}$ is the electron momentum. In this case, it is easy to compute both the exact time evolution of the Heisenberg operators and the expectation values over this ground state (Fermi sea). Thus for instance,

$$\langle \Psi_{\mathrm{H}} | \mathbf{c}^{\dagger}_{\mathbf{k}\sigma} \mathbf{c}_{\mathbf{k}'\sigma} | \Psi_{\mathrm{H}} \rangle = \delta_{\mathbf{k},\mathbf{k}'} \theta(k_{\mathrm{F}} - k), \tag{7.74}$$

where $k_{\mathrm{F}}$ is the Fermi momentum.

Bearing these ideas in mind, it is easy to show that the retarded and advanced Green's functions defined in Eqs. (7.67) and (7.71) can be written in the $\mathbf{k}$-basis (momentum space) as

$$\begin{aligned} G^r(\mathbf{k}, t - t') &= -i\theta(t - t') e^{-i\epsilon_k (t-t')} \\ G^a(\mathbf{k}, t - t') &= +i\theta(t' - t) e^{-i\epsilon_k (t-t')}, \end{aligned} \tag{7.75}$$

while the causal function can be written as

$$G^c(\mathbf{k}, t - t') = \begin{cases} -i\theta(k - k_{\mathrm{F}}) e^{-i\epsilon_k (t-t')} & t > t' \\ i\theta(k_{\mathrm{F}} - k) e^{-i\epsilon_k (t-t')} & t < t'. \end{cases} \tag{7.76}$$

Notice first that these functions depend on the difference of the time arguments, which is a general property for equilibrium systems. Notice also that they are diagonal in $k$-space. Having in mind the physical meaning of the Green's functions, it is easy to understand why they have such a simple time dependence. Since we are injecting electrons in a state $|\mathbf{k}\sigma\rangle$, which is an eigenstate of the system, the probability of finding it at a later time in such state must be equal to one. This is precisely what the previous expressions illustrate.

It is instructive to make contact with the results of the previous section. For this purpose we must now Fourier transform the previous functions with respect to the time difference, i.e.

$$G^{r,a,c}(\mathbf{k},E) = \int_{-\infty}^{\infty} d(t-t')\; G^{r,a,c}(\mathbf{k},t) e^{iE(t-t')}. \qquad (7.77)$$

In the course of doing the Fourier transformations, one gets the impression that the time integrals diverge. This can be cured by introducing a small imaginary part in the energy ($E \to E \pm i\eta$).[11] So finally, the retarded and advanced Green's functions in energy space are given by

$$G^{r,a}(\mathbf{k},E) = \frac{1}{E - \epsilon_k \pm i\eta}. \qquad (7.78)$$

This is exactly the result that one would have obtained directly from Eq. (7.22) in this plane wave basis.

On the other hand, the causal function adopts the form

$$G^{c}(\mathbf{k},E) = \frac{\theta(k-k_{\mathrm{F}})}{E-\epsilon_k+i\eta} + \frac{\theta(k_{\mathrm{F}}-k)}{E-\epsilon_k-i\eta} = \frac{1}{E-\epsilon_k+i\mathrm{sgn}(k-k_{\mathrm{F}})\eta}. \qquad (7.79)$$

Therefore, for the free electron gas, the causal Green's function is equal to the retarded one for $E > \mu$ and equal to the advanced one for $E < \mu$. This relation is true in general, as we shall show below.

#### 7.1.4.1 *The Lehmann representation*

The goal is now to get an insight into the energy dependence of the Green's functions introduced above for a general interacting system. For this purpose, we shall derive here the spectral representation of a Green's function, which for the single-particle case reduces to Eq. (7.23). We shall focus our analysis on the causal function defined in Eq. (7.72). In equilibrium, this function depends only on the difference of the time arguments. Choosing $t' = 0$ we have

$$G^{c}_{ij}(t) = -i\langle \Psi_0^N | \mathbf{T}\left[ \mathbf{c}_{i\sigma}(t)\mathbf{c}^{\dagger}_{j\sigma}(0) \right] | \Psi_0^N \rangle, \qquad (7.80)$$

where we have added the superindex $N$ in the ground state wave function, $|\Psi_0^N\rangle = |\Psi_{\mathrm{H}}\rangle$, to indicate the total number of electrons in the system.

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[11] A more rigorous way of solving this problem involves the use of the integral representation of the step function:

$$\theta(t-t') = -\int_{-\infty}^{\infty} \frac{dE}{2\pi i} \frac{e^{-iE(t-t')}}{E+i\eta},$$

where $\eta$ is a positive infinitesimal real number. By the way, are you able to show this result?

Writing explicitly the time-evolution of Heisenberg operators (see Eq. (7.5)) one has

$$\begin{aligned} G^c_{ij}(t) = &-i\theta(t)\langle\Psi^N_0|e^{i\mathbf{H}t}\mathbf{c}_{i\sigma}e^{-i\mathbf{H}t}\mathbf{c}^\dagger_{j\sigma}|\Psi^N_0\rangle \\ &+i\theta(-t)\langle\Psi^N_0|\mathbf{c}^\dagger_{j\sigma}e^{i\mathbf{H}t}\mathbf{c}_{i\sigma}e^{-i\mathbf{H}t}|\Psi^N_0\rangle. \end{aligned} \tag{7.81}$$

We now use the fact that $\mathbf{H}|\Psi^N_0\rangle = E^N_0|\Psi^N_0\rangle$, where $E^N_0$ is the ground state energy of the system with $N$ electrons, to arrive at

$$\begin{aligned} G^c_{ij}(t) = &-i\theta(t)\langle\Psi^N_0|\mathbf{c}_{i\sigma}e^{-i\mathbf{H}t}\mathbf{c}^\dagger_{j\sigma}|\Psi^N_0\rangle e^{iE^N_0 t} \\ &+i\theta(-t)\langle\Psi^N_0|\mathbf{c}^\dagger_{j\sigma}e^{i\mathbf{H}t}\mathbf{c}_{i\sigma}|\Psi^N_0\rangle e^{-iE^N_0 t}. \end{aligned} \tag{7.82}$$

We now insert $\sum_m |\Psi^{N+1}_m\rangle\langle\Psi^{N+1}_m|$ in the part for $t > 0$ and $\sum_m |\Psi^{N-1}_m\rangle\langle\Psi^{N-1}_m|$ in the part for $t < 0$, where $|\Psi^{N+1}_m\rangle$ and $|\Psi^{N-1}_m\rangle$ are the eigenfunctions of the system with one more and one less electrons, respectively. The resulting expression reads

$$\begin{aligned} G^c_{ij}(t) = &-i\theta(t)\sum_m\langle\Psi^N_0|\mathbf{c}_{i\sigma}|\Psi^{N+1}_m\rangle\langle\Psi^{N+1}_m|\mathbf{c}^\dagger_{j\sigma}|\Psi^N_0\rangle e^{-i(E^{N+1}_m-E^N_0)t} \\ &+i\theta(-t)\sum_m\langle\Psi^N_0|\mathbf{c}^\dagger_{j\sigma}|\Psi^{N-1}_m\rangle\langle\Psi^{N-1}_m|\mathbf{c}_{i\sigma}|\Psi^N_0\rangle e^{-i(E^N_0-E^{N-1}_m)t}. \end{aligned}$$

We now Fourier transform with respect to the time argument to obtain the expression of the Green's function in energy space

$$\begin{aligned} G^c_{ij}(E) = &\sum_m \frac{\langle\Psi^N_0|\mathbf{c}_{i\sigma}|\Psi^{N+1}_m\rangle\langle\Psi^{N+1}_m|\mathbf{c}^\dagger_{j\sigma}|\Psi^N_0\rangle}{E-(E^{N+1}_m-E^N_0)+i\eta} \\ &+\sum_m \frac{\langle\Psi^N_0|\mathbf{c}^\dagger_{j\sigma}|\Psi^{N-1}_m\rangle\langle\Psi^{N-1}_m|\mathbf{c}_{i\sigma}|\Psi^N_0\rangle}{E+(E^{N-1}_m-E^N_0)-i\eta}, \end{aligned} \tag{7.83}$$

which in the diagonal case adopts the form

$$G^c_{ii}(E) = \sum_m \frac{|\langle\Psi^{N+1}_m|\mathbf{c}^\dagger_{i\sigma}|\Psi^N_0\rangle|^2}{E-(E^{N+1}_m-E^N_0)+i\eta} + \sum_m \frac{|\langle\Psi^{N-1}_m|\mathbf{c}_{i\sigma}|\Psi^N_0\rangle|^2}{E+(E^{N-1}_m-E^N_0)-i\eta}. \tag{7.84}$$

This expression, referred to as *Lehmann or spectral representation*, shows clearly the pole structure of the Green's functions of a general electron system. The poles appear at the energy of the quasi-particles of the system, that is, at the energies that are necessary to add or remove an electron in the ground state of the system.[12] Before analyzing in more detail the properties of $G^c(E)$, let us see how the spectral representation of the

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[12] Due to the factors $\pm i\eta$, the poles appear slightly shifted with respect to the real axis in the complex plane.

retarded/advanced function looks like. One can repeat the process above to arrive at

$$G^{r,a}_{ij}(E) = \sum_m \frac{\langle \Psi_0^N | \mathbf{c}_{i\sigma} | \Psi_m^{N+1} \rangle \langle \Psi_m^{N+1} | \mathbf{c}^\dagger_{j\sigma} | \Psi_0^N \rangle}{E - (E_m^{N+1} - E_0^N) \pm i\eta} + \sum_m \frac{\langle \Psi_0^N | \mathbf{c}^\dagger_{j\sigma} | \Psi_m^{N-1} \rangle \langle \Psi_m^{N-1} | \mathbf{c}_{i\sigma} | \Psi_0^N \rangle}{E + (E_m^{N-1} - E_0^N) \pm i\eta}. \tag{7.85}$$

The previous expressions of the Green's functions in energy space can be written in a slightly different way in the thermodynamical limit ($N \rightarrow \infty$). Let us focus on the expressions of the denominators. Considering first the part of electrons, we can add and subtract the energy of the ground state with $N+1$ electrons:

$$E - (E_m^{N+1} - E_0^N) = E - (E_0^{N+1} - E_0^N) - (E_m^{N+1} - E_0^{N+1}). \tag{7.86}$$

The energy difference $E_0^{N+1} - E_0^N$ in the limit $N \rightarrow \infty$ is the chemical potential $\mu$ of the system, while $E_m^{N+1} - E_0^{N+1}$ is the energy of the excited state of the system with $N+1$ electrons. Repeating the same operations for the hole part, one can finally write the Green's functions in the thermodynamic limit as (we only consider diagonal elements)

$$G^c_{ii}(E) = \sum_m \frac{|\langle \Psi_m^{N+1} | \mathbf{c}^\dagger_{i\sigma} | \Psi_0^N \rangle|^2}{E - \mu - \epsilon_m^{N+1} + i\eta} + \sum_m \frac{|\langle \Psi_m^{N-1} | \mathbf{c}_{i\sigma} | \Psi_0^N \rangle|^2}{E - \mu + \epsilon_m^{N-1} - i\eta} \tag{7.87}$$

$$G^{r,a}_{ii}(E) = \sum_m \frac{|\langle \Psi_m^{N+1} | \mathbf{c}^\dagger_{i\sigma} | \Psi_0^N \rangle|^2}{E - \mu - \epsilon_m^{N+1} \pm i\eta} + \sum_m \frac{|\langle \Psi_m^{N-1} | \mathbf{c}_{i\sigma} | \Psi_0^N \rangle|^2}{E - \mu + \epsilon_m^{N-1} \pm i\eta}, \tag{7.88}$$

where $\epsilon_m^{N+1} = E_m^{N+1} - E_0^{N+1}$ and $\epsilon_m^{N-1} = E_m^{N-1} - E_0^{N-1}$ are the excitation energies of the system with $N+1$ and $N-1$ electrons, respectively.

From the previous expressions one can show that the spectral representation reduces to Eq. (7.23) in the single-particle case (do it as an exercise). This is one way to establish the connection between the definitions introduced in this section and those of section 7.1.2.

From the general spectral representation, it is possible to derive the following important properties of the exact Green's functions of an arbitrary electronic system, which are practically identical to those of section 7.1.2:

**Property 1.** It is possible to define a spectral density related to the imaginary part of the Green's functions as (we only write the diagonal elements)

$$\rho_i(E) = \sum_m |\langle \Psi_m^{N+1} | \mathbf{c}^\dagger_{i\sigma} | \Psi_0^N \rangle|^2 \delta(E - \mu - \epsilon_m^{N+1}) + \sum_m |\langle \Psi_m^{N-1} | \mathbf{c}_{i\sigma} | \Psi_0^N \rangle|^2 \delta(E - \mu + \epsilon_m^{N-1}). \tag{7.89}$$

In a case in which $i$ stands for a site index in a tight-binding problem, the previous expression represents the quasiparticle density of states of the system projected onto that site. The relation of the previous function to the imaginary part of the Green's functions is obvious. Comparing Eq. (7.89) with Eqs. (7.87) and (7.88), one obtains

$$\rho_i(E) = \mp \frac{1}{\pi} \mathrm{Im}\,\{G^{r;a}_{ii}(E)\} \tag{7.90}$$

$$\rho_i(E) = -\mathrm{sgn}(E-\mu) \frac{1}{\pi} \mathrm{Im}\,\{G^{c}_{ii}(E)\}\,. \tag{7.91}$$

**Property 2.** The diagonal Green's functions satisfy in any basis that $\mathrm{Im}\{G^r_{ii}(E)\} \leq 0$ and $\mathrm{Im}\{G^a_{ii}(E)\} \geq 0$.

**Property 3.** Due to the pole structure of the Green's functions in energy space, their real and imaginary parts are related by means of a Hilbert transformation:

$$\mathrm{Re}\,\{G^{r;a}_{ii}(E)\} = \mp \mathcal{P} \int_{-\infty}^{\infty} \frac{dE'}{\pi} \frac{\mathrm{Im}\,\{G^{r;a}_{ii}(E')\}}{E-E'} \tag{7.92}$$

$$\mathrm{Re}\,\{G^{c}_{ii}(E)\} = -\mathcal{P} \int_{-\infty}^{\infty} \frac{dE'}{\pi} \frac{\mathrm{Im}\,\{G^{c}_{ii}(E')\}\,\mathrm{sgn}(E'-\mu)}{E-E'}. \tag{7.93}$$

As in the single-particle case, it is possible to write the Green's functions in terms of the spectral density as

$$G^{r;a}_{ii}(E) = \int_{-\infty}^{\infty} dE' \, \frac{\rho_i(E')}{E-E' \pm i\eta} \tag{7.94}$$

$$G^{c}_{ii}(E) = \int_{-\infty}^{\infty} dE' \, \frac{\rho_i(E')}{E-E' + \mathrm{sgn}(E'-\mu) i\eta}. \tag{7.95}$$

**Property 4.** The previous expressions imply that

$$\lim_{E\to\infty} G^{r;a}_{ii}(E) = \lim_{E\to\infty} G^{c}_{ii}(E) = \frac{1}{E}, \tag{7.96}$$

where we have used the fact that the spectral density is normalized to 1.

**Property 5.** From the spectral representations, one can easily deduce the following relations

$$G^a_{ij}(E) = \left[G^r_{ji}(E)\right]^* \quad \text{and} \quad G^c_{ij}(E) = \begin{cases} G^r_{ij}(E), \text{ if } \; E > \mu \\ G^a_{ij}(E), \text{ if } \; E < \mu \end{cases}.$$

### 7.1.4.2 *Relation to observables*

So far, we have seen that the Green's functions provide important information such as the density of states of states (or the excitation spectrum).

But the main reason for using Green's functions is that the expectation value of any one-electron operator in the ground state of the system can be expressed in terms of the functions that we have just introduced. Thus for instance, the electronic density $n(\mathbf{r})$ in the ground state is given by

$$n(\mathbf{r}) = \langle \mathbf{n}(\mathbf{r}) \rangle = \sum_{\sigma} \langle \mathbf{\Psi}^{\dagger}_{\sigma}(\mathbf{r}) \mathbf{\Psi}_{\sigma}(\mathbf{r}) \rangle, \tag{7.97}$$

which is directly related to the causal Green's function

$$G^c_{\sigma}(\mathbf{r}t, \mathbf{r}'t') = -i \langle \Psi_{\mathrm{H}} | \mathbf{T} \left[ \mathbf{\Psi}_{\sigma}(\mathbf{r}t) \mathbf{\Psi}^{\dagger}_{\sigma}(\mathbf{r}'t') \right] | \Psi_{\mathrm{H}} \rangle, \tag{7.98}$$

by means of

$$n(\mathbf{r}) = -i \sum_{\sigma} G^c_{\sigma}(\mathbf{r}t, \mathbf{r}t^+), \tag{7.99}$$

where $t^+$ is an abbreviation that means that $t'$ tends $t$ from above.

Analogously, if we use a discrete basis $\{|i\rangle\}$, the occupation of the state $i$ will be given by

$$\langle \mathbf{n}_{i\sigma} \rangle = -i G^c_{ii\sigma}(t, t^+). \tag{7.100}$$

For instance, for the free electron gas, the time-dependent Green's function is given by Eq. (7.76) and thus, the occupation of a state with wave vector $\mathbf{k}$ in the ground state (Fermi sphere) is

$$\langle \mathbf{n}_{\mathbf{k}} \rangle = \theta(k_{\mathrm{F}} - k). \tag{7.101}$$

Let us now demonstrate the general statement made above. One-electron operators can be expressed generically in second quantized form as

$$\mathbf{V} = \sum_{ij\sigma} V_{ij} \mathbf{c}^{\dagger}_{i\sigma} \mathbf{c}_{j\sigma}, \tag{7.102}$$

where $V_{ij} = \langle i | V(\mathbf{r}) | j \rangle$.

Now, we want to compute the expectation value of this operator in the ground state, i.e.

$$\langle \mathbf{V} \rangle = \sum_{i,j,\sigma} V_{ij} \langle \Psi_{\mathrm{H}} | \mathbf{c}^{\dagger}_{i\sigma} \mathbf{c}_{j\sigma} | \Psi_{\mathrm{H}} \rangle. \tag{7.103}$$

The expectation values appearing in the previous expression can be related to the Green's functions. For instance, if we recall the definition of the causal Green's functions in the time representation, we have

$$G^c_{ij}(t) = -i \langle \Psi_{\mathrm{H}} | \mathbf{T}[\mathbf{c}_{i\sigma}(t) \mathbf{c}^{\dagger}_{j\sigma}(0)] | \Psi_{\mathrm{H}} \rangle. \tag{7.104}$$

If we evaluate this function at $t = 0^-$

$$G^c_{ij}(0^-) = -i\langle\Psi_\mathrm{H}|\mathbf{c}^\dagger_{j\sigma}\mathbf{c}_{i\sigma}|\Psi_\mathrm{H}\rangle, \tag{7.105}$$

and therefore

$$\langle\Psi_\mathrm{H}|\mathbf{c}^\dagger_{j\sigma}\mathbf{c}_{i\sigma}|\Psi_\mathrm{H}\rangle = -iG^c_{ij}(0^-). \tag{7.106}$$

On the other hand,

$$G^c_{ij}(0^-) = \int_{-\infty}^{\infty} \frac{dE}{2\pi} G^c_{ij}(E) e^{iE0^+}. \tag{7.107}$$

Making use of the spectral representation for $G^c_{ij}(E)$, we obtain

$$\langle\Psi_\mathrm{H}|\mathbf{c}^\dagger_{j\sigma}\mathbf{c}_{i\sigma}|\Psi_\mathrm{H}\rangle = \frac{1}{2\pi i}\oint dE\, G^c_{ij}(E) = \frac{1}{\pi}\int_{-\infty}^{\mu} dE\, \mathrm{Im}\left\{G^c_{ij}(E)\right\}. \tag{7.108}$$

Similar expressions can also be found in terms of the retarded and advanced functions.

Let us consider as an example the case in which the index $i$ stands for a site in a tight-binding model. The average occupation per spin of this site is

$$\langle\mathbf{n}_{i\sigma}\rangle = \langle\Psi_\mathrm{H}|\mathbf{c}^\dagger_{i\sigma}\mathbf{c}_{i\sigma}|\Psi_\mathrm{H}\rangle = \frac{1}{\pi}\int_{-\infty}^{\mu} dE\, \mathrm{Im}\left\{G^c_{ii}(E)\right\}, \tag{7.109}$$

as it should be, since $\mathrm{Im}\{G^c_{ii}(E)\}/\pi$ is nothing else than the local density of states projected onto the state $i$.

To conclude this subsection, let us say that in general the expectation in the ground state of two-electron operators, i.e. those containing two creation and two annihilation operators, cannot be expressed in terms of the one-particle Green's functions that we have introduced in this chapter. However, a notable exception is the total energy of the system (for a discussion of this issue, see e.g. Ref. [2]).

### 7.1.4.3 *Equation of motion method*

So far we have discussed some of the properties of the "new" Green's functions and we have seen that they contain very important information. Now, let us discuss how they can be computed. In particular, we shall describe in this section a method referred to as *equation of motion*. Let us illustrate it in an example that is already familiar to us, namely in the case of an electron system described by a simple tight-binding Hamiltonian of the form

$$\mathbf{H} = \sum_{ij\sigma} t_{ij}\mathbf{c}^\dagger_{i\sigma}\mathbf{c}_{j\sigma}. \tag{7.110}$$

Here, the diagonal matrix elements $t_{ii}$ correspond to the on-site energies, $\epsilon_i$, in the notation used in previous sections.

Our goal is the calculation of, for instance, the retarded Green's function

$$G^r_{ij,\sigma}(t) = -i\theta(t)\langle \Psi_{\rm H}|\mathbf{c}_{i\sigma}(t)\mathbf{c}^\dagger_{j\sigma}(0) + \mathbf{c}^\dagger_{j\sigma}(0)\mathbf{c}_{i\sigma}(t)|\Psi_{\rm H}\rangle. \tag{7.111}$$

For this purpose, let us calculate its time derivative

$$\begin{aligned}\frac{\partial}{\partial t}G^r_{ij,\sigma}(t) = {} & -i\delta(t)\langle \Psi_{\rm H}|\mathbf{c}_{i\sigma}(t)\mathbf{c}^\dagger_{j\sigma}(0) + \mathbf{c}^\dagger_{j\sigma}(0)\mathbf{c}_{i\sigma}(t)|\Psi_{\rm H}\rangle \\ & -i\theta(t)\langle \Psi_{\rm H}|\frac{\partial}{\partial t}\mathbf{c}_{i\sigma}(t)\mathbf{c}^\dagger_{j\sigma}(0) + \mathbf{c}^\dagger_{j\sigma}(0)\frac{\partial}{\partial t}\mathbf{c}_{i\sigma}(t)|\Psi_{\rm H}\rangle,\end{aligned} \tag{7.112}$$

where we have used the fact that the derivative of the step function is a $\delta$-function.

Now, in order to compute the time derivative of the annihilation operator appearing in the previous equation, we make use of the equation of motion for operators in the Heisenberg picture, see Eq. (7.6). Thus,

$$i\frac{\partial}{\partial t}\mathbf{c}_{i\sigma} = [\mathbf{c}_{i\sigma}, \mathbf{H}] = i\sum_k t_{ik}\mathbf{c}_{k\sigma}, \tag{7.113}$$

where we have used Eq. (7.110) to obtain the last result. Substituting this expression in Eq. (7.112), we arrive at

$$i\frac{\partial}{\partial t}G^r_{ij,\sigma}(t) = \delta(t)\delta_{ij} + \sum_k t_{ik}G^r_{kj,\sigma}(t). \tag{7.114}$$

It is now convenient to Fourier transform to energy space to convert this differential equation into an algebraic one. Thus, introducing

$$G^r_{ij,\sigma}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\; e^{-iEt}G^r_{ij,\sigma}(E)\;;\; \delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\; e^{-iEt} \tag{7.115}$$

in Eq. (7.114), we obtain the following algebraic equation of the Green's function in energy space

$$EG^r_{ij,\sigma}(E) = \delta_{ij} + \sum_k t_{ik}G^r_{kj,\sigma}(E). \tag{7.116}$$

This is nothing else but the element $(i,j)$ of the matrix equation

$$\mathbf{G}^r(E) = \left[E\mathbf{1} - \mathbf{H}\right]^{-1}, \tag{7.117}$$

which is precisely the expression that we used as a definition in section 7.1.2 [see Eq. (7.22)]. Thus, we have shown again the equivalence of the two types of definitions for the case of single-particle systems.

It is important to emphasize that the equation-of-motion method illustrated above is by no means restricted to single-particle systems.

However, if the Hamiltonian contains two-electron terms (with four creation/annihilation operators), there is no straightforward way to get a closed system of equations, as in the previous example. The problem is that the equation of motion for the one-particle Green's function couples this function to higher-order ones containing an increasing number of operators and the resulting algebraic system has, strictly speaking, an infinite dimension. In practice, one has to find an appropriate way of truncating the system, which is not an easy task in general.

In order to illustrate what we meant in the previous paragraph, let us consider the Anderson model that describes the interaction of a single level (including the electron-electron interaction in this level) with a continuum of states. This model can describe, for instance, a magnetic impurity in a metal or a quantum dot (or a molecule) coupled to metallic reservoirs. The Hamiltonian of this model adopts the form

$$\mathbf{H} = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} \mathbf{n}_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\sigma} \left( V_{\mathbf{k}0} \mathbf{c}^{\dagger}_{\mathbf{k}\sigma} \mathbf{c}_{0\sigma} + V_{0\mathbf{k}} \mathbf{c}^{\dagger}_{0\sigma} \mathbf{c}_{\mathbf{k}\sigma} \right) + \sum_{\sigma} \epsilon_0 \mathbf{n}_{0\sigma} + U \mathbf{n}_{0\uparrow} \mathbf{n}_{0\downarrow}, \tag{7.118}$$

where the subindex 0 refers to the correlated level and $\mathbf{k}$ to the metallic states in the reservoirs. Our goal is to compute the (retarded or advanced) Green's function $G_{00,\sigma}(E)$ in the impurity. For this purpose, we proceed as above and determine the time derivative of this function. This calculation requires the evaluation of the time derivative of the operator $\mathbf{c}_{0\sigma}(t)$, which in turn requires the determination of the commutator of this operator with the Hamiltonian. The novel term, as compared with the tight-binding example above, is $U\mathbf{n}_{0\uparrow}\mathbf{n}_{0\downarrow}$ and the corresponding commutator with it is

$$[\mathbf{c}_{0\sigma}, U\mathbf{n}_{0\uparrow}\mathbf{n}_{0\downarrow}] = U\mathbf{c}_{0\sigma}\mathbf{n}_{0\bar{\sigma}}, \tag{7.119}$$

where we have used the notation $\bar{\sigma} = -\sigma$. Inserting this term in the equation of motion, it is straightforward to show that one arrives at (after Fourier transforming to energy space)

$$(E - \epsilon_0) G_{00\sigma}(E) = 1 + \sum_{\mathbf{k}} V_{0\mathbf{k}} G_{\mathbf{k}0}(E) + U G_{\sigma\bar{\sigma}}(E), \tag{7.120}$$

where the $G_{\sigma\bar{\sigma}}$ is a two-particle Green's function defined as $G_{\sigma\bar{\sigma}}(t) = -i\theta(t)\langle \Psi_{\mathrm{H}} | \{ \mathbf{c}_{0\sigma}(t) \mathbf{n}_{0\bar{\sigma}}(t), \mathbf{c}^{\dagger}_{0\sigma}(0) \} | \Psi_{\mathrm{H}} \rangle$, where $\{\ \}$ stands for the anticommutator. Here, the novelty with respect to Eq. (7.116) is the appearance of the function $G_{\sigma\bar{\sigma}}$, which is a expectation value of four operators. To close the equation, we need now an equation for this new expectation value. You can convince yourself that such an equation would contain expectation values of six operators. Then, the equation for these functions would involve terms with eight operators and so on and so forth. So, the only way to solve these equations in practice is to truncate the system with sensible arguments, but in most cases it is not clear how to do it. In the next section we shall discuss a more systematic approach to obtain the Green's functions in interacting problems.

There is one limit in which it is possible to obtain the exact Green's function, namely in the limit where the coupling to the reservoirs tends to zero ($V_{0\mathbf{k}} \to 0$ with $U$ finite). In this case the equation of motion can be truncated and one obtains

$$G_{00\sigma}(E) = \frac{1 - \langle \mathbf{n}_{0\bar{\sigma}} \rangle}{E - \epsilon_0} + \frac{\langle \mathbf{n}_{0\bar{\sigma}} \rangle}{E - \epsilon_0 - U}, \tag{7.121}$$

where $\langle \mathbf{n}_{0\sigma} \rangle$ is the occupation of the level $\epsilon_0$ for spin $\sigma$, which in turn has to be calculated with the full Green's function of Eq. (7.121). Thus, in this limit the Green's functions exhibit poles at energies equal to $\epsilon_0$ and $\epsilon_0 + U$. This tells us in particular that $U$ is the energy that one has to supply to accommodate a second electron in the level. The expression of Eq. (7.121) can be used as an starting point to analyze the so-called Coulomb blockade in quantum dots or molecular transistors.

## 7.2 Green's functions and Feynman diagrams

In the previous section we have seen that the calculation of the zero-temperature Green's functions of a non-interacting system in equilibrium reduces to solving an algebraic linear system, summarized in Dyson's equation. This is practically all we need to tackle the problem of the determination of the elastic transmission of realistic systems. However, if we want to go beyond and treat systems where the electron correlations or inelastic interactions play a major role, we need many-body techniques. For this reason, we present in this section a systematic perturbative approach for the calculation of zero-temperature equilibrium Green's functions.[13] This formalism is valid for any type of system and interaction and it constitutes the most general method for the computation of Green's functions. Moreover, the nonequilibrium formalism introduced in the next section follows closely the perturbative approach that we are about to describe. If you feel familiar with Green's functions, you can skip this section and immediately move on to section 7.3.

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[13] In some sense, this approach is simply a generalization of the perturbation theory for the wave functions that one studies in elementary courses of quantum mechanics.

The perturbative (or diagrammatic) approach is nicely explained in different many-body physics textbooks (see e.g. Refs. [2–4, 6–9]) and for this reason, our description here will be rather brief.[14] This approach is conceptually rather simple, but it contains several technical points that usually make it rather obscure. In the spirit of this course, we shall avoid very formal discussions and we shall provide instead simple plausibility arguments or we shall simply refer to the appropriate literature for more details.

Before the trees do not let us see the forest, let us give a brief overview of what we are about to see. First, we shall learn how to write down a perturbative series for the Green's functions, i.e. how to express systematically the corrections to the Green's function due to a perturbation such as an external potential, electron-electron interaction, etc. Then, we shall discuss how these contributions can be "visualized" with the help of the so-called Feynman diagrams. These diagrams will in turn help us to organize and simplify the perturbative series. Finally, we shall show that this series can be formally resumed and cast in the Dyson's equation, which we have already introduced for case of non-interacting systems. Dyson's equation is expressed in terms of the concept of self-energy. This concept was also introduced in the previous section and in this one its precise meaning will be clarified.

So, it is time to get started. The general problem that we want to tackle in this section is the analysis of an electron system in equilibrium that is described by a Hamiltonian of the following form

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}, \tag{7.122}$$

where $\mathbf{H}_0$ is a single-particle Hamiltonian and $\mathbf{V}$ is a perturbation that may contain an external potential and any type of interaction. Our goal is the compute the Green's functions of the system in terms of the unperturbed Green's functions, i.e. those associated with the Hamiltonian $\mathbf{H}_0$, which are supposed to be known. For this purpose, we shall develop a systematic perturbation theory, but before doing that we shall now introduce a convenient representation of quantum mechanics, known as the *interaction picture*, that will be very useful in what follows.

### 7.2.1 *The interaction picture*

Let us consider a system described by the Hamiltonian of Eq. (7.122). We define the interaction picture starting from the Schrödinger one by means

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[14] This section is mainly based on Chapter 3 of Ref. [2]

of the following unitary transformation[15]

$$\Psi_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t}\Psi_{\mathrm{S}}(t) \;\text{ and }\; \mathbf{O}_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t}\mathbf{O}_{\mathrm{S}}(t)e^{-i\mathbf{H}_0 t}. \tag{7.123}$$

Notice that, contrary to the case of the Schrödinger and Heisenberg pictures, in the interaction picture both wave functions and operators depend explicitly on time.

Let us analyze first the time evolution of the operators. It is obvious from Eq. (7.123) that the operators in this representation are the Heisenberg operators of the unperturbed system. Taking the derivative with respect to time in the definition of an operator in the interaction picture, one obtains

$$i\frac{\partial}{\partial t}\mathbf{O}_{\mathrm{I}} = \left[\mathbf{O}_{\mathrm{I}}, \mathbf{H}_0\right]. \tag{7.124}$$

Therefore, the dynamics of the operators in this representation is governed by $\mathbf{H}_0$ and it is thus known.

Turning to the wave functions, we can make use of the evolution of the wave function in Schrödinger picture to obtain

$$\Psi_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t}\Psi_{\mathrm{S}}(t) = e^{i\mathbf{H}_0 t}e^{-i\mathbf{H}t}\Psi_{\mathrm{S}}(0). \tag{7.125}$$

Let us remind that

$$e^{i\mathbf{H}_0 t}e^{-i\mathbf{H}t} \neq e^{-i\mathbf{V}t},$$

since, in general, $[\mathbf{H}_0, \mathbf{H}] \neq 0$.

In order to find the equation that describes the time evolution of the wave function in this picture, we now take the derivative with respect to time in Eq. (7.123)

$$i\frac{\partial}{\partial t}\Psi_{\mathrm{I}}(t) = -\mathbf{H}_0 e^{i\mathbf{H}_0 t}\Psi_{\mathrm{S}}(t) + ie^{i\mathbf{H}_0 t}\frac{\partial}{\partial t}\Psi_{\mathrm{S}}(t), \tag{7.126}$$

and making use of the Schrödinger equation on the right hand side of the previous expression, one obtains

$$i\frac{\partial}{\partial t}\Psi_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t}(\mathbf{H} - \mathbf{H}_0)\Psi_{\mathrm{S}}(t) = e^{i\mathbf{H}_0 t}\mathbf{V}e^{-i\mathbf{H}_0 t}e^{i\mathbf{H}_0 t}\Psi_{\mathrm{S}}(t), \tag{7.127}$$

which can be simply written as

$$i\frac{\partial}{\partial t}\Psi_{\mathrm{I}}(t) = \mathbf{V}_{\mathrm{I}}(t)\Psi_{\mathrm{I}}(t). \tag{7.128}$$

This equation plays the role of the standard Schrödinger equation in this new picture. Notice that the dynamics of the wave functions is governed by the perturbation. This is very important because it makes possible, by

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[15] In this section we shall also set $\hbar = 1$.

means of an adiabatic hypothesis in which the perturbation is adiabatically switched on, to relate the perturbed and unperturbed ground states of the system by means of the evolution of the wave function in this picture. Due to this fact, the operator that describes the time evolution of the wave functions is of special interest and it will be discussed in detail in the next section.

To end this section, let us discuss now the relation between the Heisenberg picture and the interaction picture. Using the definitions of Eq. (7.123), one can easily show that

$$\begin{aligned} \Psi_{\mathrm{I}}(t) &= e^{i\mathbf{H}_0 t} e^{-i\mathbf{H}t} \Psi_{\mathrm{H}} \\ \mathbf{O}_{\mathrm{I}}(t) &= e^{i\mathbf{H}_0 t} e^{-i\mathbf{H}t} \mathbf{O}_{\mathrm{H}}(t) e^{i\mathbf{H}t} e^{-i\mathbf{H}_0 t}. \end{aligned} \tag{7.129}$$

The inverse transformation is obviously given by

$$\begin{aligned} \Psi_{\mathrm{H}}(t) &= e^{i\mathbf{H}t} e^{-i\mathbf{H}_0 t} \Psi_{\mathrm{I}}(t) \\ \mathbf{O}_{\mathrm{H}}(t) &= e^{i\mathbf{H}t} e^{-i\mathbf{H}_0 t} \mathbf{O}_{\mathrm{I}}(t) e^{i\mathbf{H}_0 t} e^{-i\mathbf{H}t}. \end{aligned} \tag{7.130}$$

### 7.2.2 *The time-evolution operator*

We define the time-evolution operator in the interaction picture as

$$\Psi_{\mathrm{I}}(t) = \mathbf{S}(t, t_0) \Psi_{\mathrm{I}}(t_0). \tag{7.131}$$

It is easy to find a formal expression for the operator $\mathbf{S}$ in terms of the system Hamiltonian. From the definition of the interaction picture one has

$$\Psi_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t} \Psi_{\mathrm{S}}(t). \tag{7.132}$$

Making use of the expression of the time evolution of the wave function in the Schrödinger picture we can write

$$\Psi_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t} e^{-i\mathbf{H}(t-t_0)} \Psi_{\mathrm{S}}(t_0). \tag{7.133}$$

Transforming the wave function $\Psi_{\mathrm{S}}(t_0)$ to the interaction picture, one has finally

$$\Psi_{\mathrm{I}}(t) = e^{i\mathbf{H}_0 t} e^{-i\mathbf{H}(t-t_0)} e^{-i\mathbf{H}_0 t_0} \Psi_{\mathrm{I}}(t_0). \tag{7.134}$$

Comparing this expression with the definition of Eq (7.131), we can identify

$$\mathbf{S}(t, t_0) = e^{i\mathbf{H}_0 t} e^{-i\mathbf{H}(t-t_0)} e^{-i\mathbf{H}_0 t_0}. \tag{7.135}$$

From the definition of the time-evolution operator or from its formal expression, one can easily show the following properties:

- The operator $\mathbf{S}$ is unitary, i.e. $\mathbf{S}^{-1} = \mathbf{S}^{\dagger}$.
- $\mathbf{S}(t,t) = 1$.
- $\mathbf{S}(t,t')\mathbf{S}(t',t'') = \mathbf{S}(t,t'')$.
- $\mathbf{S}(t,t') = \mathbf{S}^{\dagger}(t',t)$ .

The time-evolution operator is also related to the unitary transformation that relates Heisenberg and interaction pictures. From Eq. (7.135) one has

$$\mathbf{S}(0,t) = e^{i\mathbf{H}t} e^{-i\mathbf{H}_0 t}. \tag{7.136}$$

Comparing now with Eq. (7.130), we can write

$$\begin{aligned} \Psi_{\mathrm{H}} &= \mathbf{S}(0,t)\Psi_{\mathrm{I}}(t) \\ \mathbf{O}_{\mathrm{H}}(t) &= \mathbf{S}(0,t)\mathbf{O}_{\mathrm{I}}(t)\mathbf{S}(t,0). \end{aligned} \tag{7.137}$$

The operator $\mathbf{S}$ satisfies its own equation of motion, which is very similar to the equation for the wave functions in this representation. Taking the derivative with respect to time in Eq. (7.135) one has

$$i\frac{\partial}{\partial t}\mathbf{S}(t,t_0) = \mathbf{V}_{\mathrm{I}}(t)\mathbf{S}(t,t_0). \tag{7.138}$$

Finally, the time-evolution operator can be expressed as a perturbative series in the interaction $\mathbf{V}_{\mathrm{I}}(t)$. This can be shown either by solving iteratively the previous equation or by using the equation for the wave function $\Psi_{\mathrm{I}}(t)$. We choose the second option and write Eq. (7.128) as an integral equation

$$\Psi_{\mathrm{I}}(t) = \Psi_{\mathrm{I}}(t_0) - i\int_{t_0}^{t} dt'\; \mathbf{V}_{\mathrm{I}}(t')\Psi_{\mathrm{I}}(t'). \tag{7.139}$$

This equation can now be solved iteratively. To zero order we have

$$\Psi_{\mathrm{I}}(t) = \Psi_{\mathrm{I}}(t_0). \tag{7.140}$$

Substituting this zero-order result in Eq. (7.139) we obtain the first-order result

$$\Psi_{\mathrm{I}}(t) = \left[1 - i\int_{t_0}^{t} dt_1\; \mathbf{V}_{\mathrm{I}}(t_1)\right]\Psi_{\mathrm{I}}(t_0). \tag{7.141}$$

Iterating we can arrive at

$$\begin{aligned} \Psi_{\mathrm{I}}(t) = \Bigg[1 + \sum_n (-i)^n \int_{t_0}^{t} dt_1\; \mathbf{V}_{\mathrm{I}}(t_1)\times \\ \int_{t_0}^{t_1} dt_2\; \mathbf{V}_{\mathrm{I}}(t_2)\cdots\int_{t_0}^{t_{n-1}} dt_n\; \mathbf{V}_{\mathrm{I}}(t_n)\Bigg]\Psi_{\mathrm{I}}(t_0). \end{aligned} \tag{7.142}$$

The expression inside the brackets is just the time-evolution operator $\mathbf{S}(t, t_0)$ expanded as a power series in the operator $\mathbf{V}_{\mathrm{I}}(t)$. This expression is not very inconvenient because the upper limits of the time integrals are different. It is possible to rewrite the previous expression in more adequate manner by noticing that the integration variables fulfill $t > t_1 > t_2 > \cdots > t_n > t_0$. This makes possible to rewrite the time-evolution operator in the interaction picture as

$$\mathbf{S}(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \, \mathbf{T} \left[ \mathbf{V}_{\mathrm{I}}(t_1) \mathbf{V}_{\mathrm{I}}(t_2) \cdots \mathbf{V}_{\mathrm{I}}(t_n) \right], \tag{7.143}$$

where the $n = 0$ term is the unit operator and $\mathbf{T}$ is the time-ordering operator that we introduced in the last section. The demonstration of this last step is left to you as an exercise.

### 7.2.3 *Perturbative expansion of causal Green's functions*

Our goal now is the calculation of a generic causal Green's function, which in a discrete basis is given by

$$iG_{ij}(t, t') = \frac{\langle \Psi_{\mathrm{H}} | \mathbf{T} \left[ \mathbf{c}_{i\sigma}(t) \mathbf{c}^{\dagger}_{j\sigma}(t') \right] | \Psi_{\mathrm{H}} \rangle}{\langle \Psi_{\mathrm{H}} | \Psi_{\mathrm{H}} \rangle}. \tag{7.144}$$

Here, the expectation value is evaluated in the ground state of the system described by the Hamiltonian of Eq. (7.122) and the operators are written in Heisenberg picture. Notice that we omit the superindex $c$ to abbreviate the notation and we introduce the denominator for normalization reasons that will become clear later on.

As explained in the previous section, it is convenient to use the interaction picture. We first transform the operators:

$$iG_{ij}(t, t') = \frac{\langle \Psi_{\mathrm{H}} | \mathbf{T} \left[ \mathbf{S}(0, t) \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{S}(t, t') \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \mathbf{S}(t', 0) \right] | \Psi_{\mathrm{H}} \rangle}{\langle \Psi_{\mathrm{H}} | \Psi_{\mathrm{H}} \rangle}. \tag{7.145}$$

Here, we have used the superindex (0) to emphasize that the operators in the interaction picture correspond to Heisenberg operators of the unperturbed system. We now transform the wave function by using

$$|\Psi_{\mathrm{H}}\rangle = \mathbf{S}(0, t) |\Psi_{\mathrm{I}}(t)\rangle, \tag{7.146}$$

where $t$ is an arbitrary time. Now, we want to relate the state $|\Psi_{\mathrm{I}}(t)\rangle$ with the unperturbed ground state (for $\mathbf{V} = 0$), $|\phi_0\rangle$. This can be done using the so-called adiabatic hypothesis. In this hypothesis, one assumes that if the perturbation is switched on at an initial time, let us say $t = -\infty$, and grows slowly to its actual value at $t = 0$, the physics is not modified. This adiabatic switch on is achieved by replacing the perturbation $\mathbf{V}$ by $\mathbf{V}e^{-\epsilon|t|}$, where $\epsilon$ is an infinitesimally small positive parameter. In this way, at $t = \pm\infty$ the perturbation vanishes and the system tends to the unperturbed ground state

$$|\Psi_{\mathrm{H}}\rangle = \mathbf{S}(0, -\infty)|\phi_0\rangle. \tag{7.147}$$

This procedure is not completely well-defined and one can show that during the evolution of the ground state from $t = -\infty$ to $t = 0$ with the operator $\mathbf{S}$, the wave function acquires a phase that diverges as $\epsilon$ tends to zero. These phase factors are finally canceled by the terms in the denominator of the expectation value. The rigorous statement of this fact is known as the Gell-Mann and Low theorem and for more information we refer you to the book of Fetter and Walecka [2].

We now make use of Eq. (7.147) to write the causal Green's function as follows

$$iG_{ij}(t,t') = \frac{\langle\phi_0|S(\infty,0)\mathbf{T}\left[\mathbf{S}(0,t)\mathbf{c}^{(0)}_{i\sigma}(t)\mathbf{S}(t,t')\mathbf{c}^{(0)\dagger}_{j\sigma}(t')\mathbf{S}(t',0)\right]S(0,-\infty)|\phi_0\rangle}{\langle\phi_0|\mathbf{S}(\infty,-\infty)|\phi_0\rangle}. \tag{7.148}$$

Here, we have used the time symmetry of the problem that implies in particular that the ground state wave function is recovered at $t = +\infty$ (apart from a phase factor). On the other hand, it is obvious that in the previous expression we can introduce the time-evolution operators appearing next to the wave functions inside the time-ordered products. Thus, the expectation value now reads

$$iG_{ij}(t,t') = \frac{\langle\phi_0|\mathbf{T}\left[\mathbf{c}^{(0)}_{i\sigma}(t)\mathbf{c}^{(0)\dagger}_{j\sigma}(t')\mathbf{S}(\infty,-\infty)\right]|\phi_0\rangle}{\langle\phi_0|\mathbf{S}(\infty,-\infty)|\phi_0\rangle}, \tag{7.149}$$

where we have grouped all the pieces of the operator $\mathbf{S}$ since the operator $\mathbf{T}$ ensures the proper ordering. Now, we use the expansion of Eq. (7.143) for the operator $\mathbf{S}$ to write the expectation value as a perturbative expansion

$$\begin{aligned} iG_{ij}(t,t') = \frac{1}{\langle\phi_0|\mathbf{S}(\infty,-\infty)|\phi_0\rangle} & \left[\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{-\infty}^{\infty} dt_1 \ldots\, dt_n \times \right. \\ & \left. \langle\phi_0|\mathbf{T}\left[\mathbf{c}^{(0)}_{i\sigma}(t)\mathbf{c}^{(0)\dagger}_{j\sigma}(t')\mathbf{V}^{(0)}(t_1)\cdots\mathbf{V}^{(0)}(t_n)\right]|\phi_0\rangle\right], \end{aligned} \tag{7.150}$$

where the zero-order term ($n = 0$) corresponds to the unperturbed Green's function, which we shall denote as $G^{(0)}_{ij}(t,t')$. The previous expression is the central result of this section.

The perturbative expansion adopts the same form, irrespectively of the basis used. Thus for instance, if one uses a spatial representation, the previous expression becomes

$$iG(\mathbf{r}t,\mathbf{r}'t') = \frac{1}{\langle\phi_0|\mathbf{S}(\infty,-\infty)|\phi_0\rangle}\left[\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{-\infty}^{\infty}dt_1\cdots\, dt_n\times \right. \tag{7.151}$$
$$\left.\langle\phi_0|\mathbf{T}\left[\mathbf{\Psi}^{(0)}_{\sigma}(\mathbf{r}t)\mathbf{\Psi}^{(0)\dagger}_{\sigma}(\mathbf{r}'t')\mathbf{V}^{(0)}(t_1)\cdots\mathbf{V}^{(0)}(t_n)\right]|\phi_0\rangle\right].$$

### 7.2.4 *Wick's theorem*

With the perturbative formalism that we have developed so far, the problem of calculating a Green's function or any expectation value of an operator in the ground state reduces to the calculation of expectation values in the unperturbed ground state of the following type

$$\langle\phi_0|\mathbf{T}\left[\mathbf{c}^{(0)}_{i\sigma}(t)\mathbf{c}^{(0)\dagger}_{j\sigma}(t')\mathbf{V}^{(0)}(t_1)\cdots\mathbf{V}^{(0)}(t_n)\right]|\phi_0\rangle. \tag{7.152}$$

This is something that we can, in principle, calculate in an exact manner because we know the evolution of the operators in the unperturbed problem. However, in practice, the direct calculation of expectation values like the one in Eq. (7.152) is extremely cumbersome. Fortunately, *Wick's theorem* simplifies enormously this task.

Wick's theorem is the mathematical expression of the fact that the electrons in the unperturbed problem are uncorrelated. Before stating the theorem, let us illustrate it with a simple example. Let us consider the following two-sites tight-binding Hamiltonian

$$\mathbf{H} = \sum_{\sigma}\epsilon_0\left(\mathbf{n}_{1\sigma}+\mathbf{n}_{2\sigma}\right) + t\sum_{\sigma}\left(\mathbf{c}^{\dagger}_{1\sigma}\mathbf{c}_{2\sigma}+\mathbf{c}^{\dagger}_{2\sigma}\mathbf{c}_{1\sigma}\right). \tag{7.153}$$

Let us also assume that we have two electrons in total. If $|\phi_0\rangle$ is the wave function of the noninteracting problem, it seems natural that

$$\langle\phi_0|\mathbf{n}_{1\uparrow}\mathbf{n}_{1\downarrow}|\phi_0\rangle = \langle\phi_0|\mathbf{n}_{1\uparrow}|\phi_0\rangle\langle\phi_0|\mathbf{n}_{1\downarrow}|\phi_0\rangle, \tag{7.154}$$

since in the absence of interactions the probability of finding two electrons simultaneously in $|1\downarrow\rangle$ and in $|1\uparrow\rangle$ must be equal to the product of the probabilities.

Wick's theorem generalizes this result to the expectation value in a noninteracting ground state of a product of an arbitrary number of operators. Without many-body interactions, an average like the one in Eq. (7.152) look like

$$\langle\phi_0|\mathbf{T}\left[\mathbf{c}^{(0)\dagger}_{i\sigma}(t)\mathbf{c}^{(0)\dagger}_{j\sigma}(t')\cdots\mathbf{c}^{(0)\dagger}_{k\sigma}(t_1)\cdots\mathbf{c}^{(0)}_{l\sigma}(t_n)\right]|\phi_0\rangle. \tag{7.155}$$

Wick's theorem establishes that such an expectation value is equal to the sum of all possible factorizations of averages of two operators. Since in our case the operators are fermionic and therefore anticommute, one has to follow the usual criterion, i.e. the factorization that respects the original order does not contain any minus sign, whereas the factorization that differs by an odd number of permutations from the original configuration introduces a minus sign. Thus for instance, the following expectation value of the product of four operators can be decomposed as follows

$$\begin{aligned} &\langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \mathbf{c}^{(0)}_{k\sigma}(t_1) \mathbf{c}^{(0)\dagger}_{l\sigma}(t_2) \right] | \phi_0 \rangle = \qquad (7.156) \\ &\langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \right] | \phi_0 \rangle \langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{k\sigma}(t_1) \mathbf{c}^{(0)\dagger}_{l\sigma}(t_2) \right] | \phi_0 \rangle \\ &- \langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{c}^{(0)\dagger}_{l\sigma}(t_2) \right] | \phi_0 \rangle \langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{k\sigma}(t_1) \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \right] | \phi_0 \rangle . \end{aligned}$$

Notice that in the previous factorization one could have had additional terms containing expectation values like for instance

$$\langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{c}^{(0)}_{k\sigma}(t_1) \right] | \phi_0 \rangle \text{ or } \langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \mathbf{c}^{(0)\dagger}_{l\sigma}(t_2) \right] | \phi_0 \rangle .$$

However, they vanish because these combinations of operators do not conserve the number of electrons.

As a convention, we shall always place the creation operator on the right hand side in the factors resulting from the application of Wick's theorem. The reason is that the basic factor appearing in the decomposition is closely related to a single-particle Green's function of the unperturbed system

$$\langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \right] | \phi_0 \rangle = i G^{(0)}_{ij\sigma}(t,t'). \qquad (7.157)$$

Thus for instance, the expectation value of the previous example can be written as

$$\begin{aligned} &\langle \phi_0 | \mathbf{T} \left[ \mathbf{c}^{(0)}_{i\sigma}(t) \mathbf{c}^{(0)\dagger}_{j\sigma}(t') \mathbf{c}^{(0)}_{k\sigma}(t_1) \mathbf{c}^{(0)\dagger}_{l\sigma}(t_2) \right] | \phi_0 \rangle = \qquad (7.158) \\ &- G^{(0)}_{ij\sigma}(t,t') G^{(0)}_{kl\sigma}(t_1,t_2) + G^{(0)}_{il\sigma}(t,t_2) G^{(0)}_{kj\sigma}(t_1,t'). \end{aligned}$$

### 7.2.5 *Feynman diagrams*

Feynman diagrams are a graphical representation of the different contributions of the perturbative expansion of a Green's function, which result from the application of Wick's theorem. Let us recall that Green's functions can be interpreted as the propagation amplitude of an electron from one state to another. In this sense, the Feynman diagrams turn out to have a simple interpretation in terms of processes that contribute to the total amplitude of propagation of an electron. Moreover, apart from the physical insight that these diagrams provide, they also help in classifying and identifying the contributions resulting from the application of Wick's theorem.

Before describing the Feynman diagrams, we need a "dictionary" that assigns a convenient graphical representation to the different functions that appear in the perturbation theory. Thus for instance, the unperturbed causal Green's functions, which appear in the perturbative expansion through the application of Wick's theorem, will be represented by a solid line. This is shown in Fig. 7.4(a) for the function $G^{(0)}(\mathbf{r}t, \mathbf{r}'t')$ in real space. For this case, the arrow points from the second set of arguments (or event) to the first one (indicating the propagation of an electron from $\mathbf{r}'t'$ to $\mathbf{r}t$). If the problem depends explicitly on the spin, we would have to label the different events with the corresponding spin. If we use a discrete basis, the corresponding line will look like in Fig. 7.4(b).

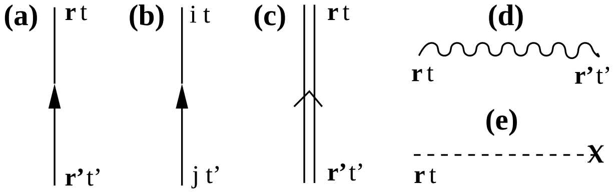

Fig. 7.4 Basic elements of Feynman diagrams. (a) Propagator line between the events $\mathbf{r}'t'$ to $\mathbf{r}t$. (b) Propagator line between the states $j\sigma'$ and $i\sigma$. (c) Full propagator line. (d) Interaction line between the events $\mathbf{r}'t'$ to $\mathbf{r}t$. (e) Interaction line for an external potential.

The full (or dressed) Green's function that corresponds to the total amplitude for the electron propagation will be represented as a double line, as shown in Fig. 7.4(c). On the other hand, the electron-electron interaction between two events will be represented by a wavy line, as in Fig. 7.4(d). Notice that, in general, the interaction is instantaneous and therefore $U(\mathbf{r}t, \mathbf{r}'t') \propto \delta(t - t')$. In the case in which the perturbation is an external potential, $V(\mathbf{r})$, this will then be represented by a dashed line, see Fig. 7.4(e).

The structure of perturbative series and the corresponding Feynman diagrams depends on the type of perturbation under study. In what follows, we shall illustrate the diagrammatic approach with the analysis of two examples where the perturbation is (i) the electron-electron interaction and (ii) an external static potential.

#### 7.2.5.1 *Feynman diagrams for the electron-electron interaction*

Let us analyze the case of an electron system in which the electron-electron interaction is considered to be the perturbation. In this case the Hamiltonian has the following generic form in first quantization

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V} = \sum_{n=1}^{N} h(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N} U(\mathbf{r}_i, \mathbf{r}_j), \tag{7.159}$$

where $h(\mathbf{r})$ is single-electron Hamiltonian and $U(\mathbf{r}, \mathbf{r}')$ is the electron-electron (Coulomb) potential. Using the second quantization language and the basis of the eigenfunctions of the position operator $\{|\mathbf{r}\rangle\}$, the previous Hamiltonian can be expressed in terms of the field operators as follows

$$\begin{aligned} \mathbf{H} = & \sum_{\sigma} \int d\mathbf{r}\ \mathbf{\Psi}^{\dagger}_{\sigma}(\mathbf{r}) h(\mathbf{r}) \mathbf{\Psi}_{\sigma}(\mathbf{r}) & (7.160) \\ & + \frac{1}{2} \sum_{\sigma\sigma'} \int d\mathbf{r} \int d\mathbf{r}'\ \mathbf{\Psi}^{\dagger}_{\sigma}(\mathbf{r}) \mathbf{\Psi}^{\dagger}_{\sigma'}(\mathbf{r}') U(\mathbf{r}, \mathbf{r}') \mathbf{\Psi}_{\sigma'}(\mathbf{r}') \mathbf{\Psi}_{\sigma}(\mathbf{r}). \end{aligned}$$

Thus, the perturbation $\mathbf{V}$ appearing in the perturbative expansion of the causal Green's function of Eqs. (7.151) is given by

$$\mathbf{V}^{(0)}(t) = \frac{1}{2} \sum_{\sigma\sigma'} \int d\mathbf{r} \int d\mathbf{r}'\ \mathbf{\Psi}^{(0)\dagger}_{\sigma}(\mathbf{r}t) \mathbf{\Psi}^{(0)\dagger}_{\sigma'}(\mathbf{r}'t) U(\mathbf{r}, \mathbf{r}') \mathbf{\Psi}^{(0)}_{\sigma'}(\mathbf{r}'t) \mathbf{\Psi}^{(0)}_{\sigma}(\mathbf{r}t). \tag{7.161}$$

Using this expression in Eq. (7.151) and applying Wick's theorem, we arrive at the following expression for the first-order correction for the causal Green's function[16]

$$\begin{aligned} & \delta G^{(1)}(\mathbf{x}, \mathbf{x}') = \frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}'_1\ U(\mathbf{x}_1, \mathbf{x}'_1) \{ & (7.162) \\ & n^{(0)}(\mathbf{r}'_1) G^{(0)}(\mathbf{x}, \mathbf{x}_1) G^{(0)}(\mathbf{x}_1, \mathbf{x}') + i G^{(0)}(\mathbf{x}, \mathbf{x}_1) G^{(0)}(\mathbf{x}_1, \mathbf{x}'_1) G^{(0)}(\mathbf{x}'_1, \mathbf{x}') \\ & + i G^{(0)}(\mathbf{x}, \mathbf{x}'_1) G^{(0)}(\mathbf{x}'_1, \mathbf{x}_1) G^{(0)}(\mathbf{x}_1, \mathbf{x}') + n^{(0)}(\mathbf{r}_1) G^{(0)}(\mathbf{x}, \mathbf{x}'_1) G^{(0)}(\mathbf{x}'_1, \mathbf{x}') \\ & - i G^{(0)}(\mathbf{x}, \mathbf{x}') G^{(0)}(\mathbf{x}'_1, \mathbf{x}_1) G^{(0)}(\mathbf{x}_1, \mathbf{x}'_1) - i n^{(0)}(\mathbf{r}_1) n^{(0)}(\mathbf{r}'_1) G^{(0)}(\mathbf{x}, \mathbf{x}') \Big\}, \end{aligned}$$

where we have used the shorthand $\mathbf{x} \equiv \mathbf{r}t$ to simplify the notation. In Eq. (7.162) it was necessary to write the causal Green's function with equal time arguments, i.e. $G^{(0)}(t, t)$, which has an ambiguous mathematical expression. We have used the following criterion that provides the correct result: $G^{(0)}(t, t^{+})$, i.e. in Eq. (7.162) we have used

$$\begin{aligned} G^{(0)}(\mathbf{x}, \mathbf{x}) &= G^{(0)}(\mathbf{r}t, \mathbf{r}t^{+}) & (7.163) \\ &= i \langle \phi_0 | \mathbf{\Psi}^{(0)\dagger}(\mathbf{r}t) \mathbf{\Psi}^{(0)}(\mathbf{r}t) | \phi_0 \rangle = i n^{(0)}(\mathbf{r}). & (7.164) \end{aligned}$$

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[16] In what follows we shall ignore the spin to simplify the calculation, and we are using the fact that the interaction is instantaneuous to write $U(\mathbf{x}_1, \mathbf{x}'_1) = U(\mathbf{r}_1, \mathbf{r}'_1)\delta(t_1 - t'_1)$.

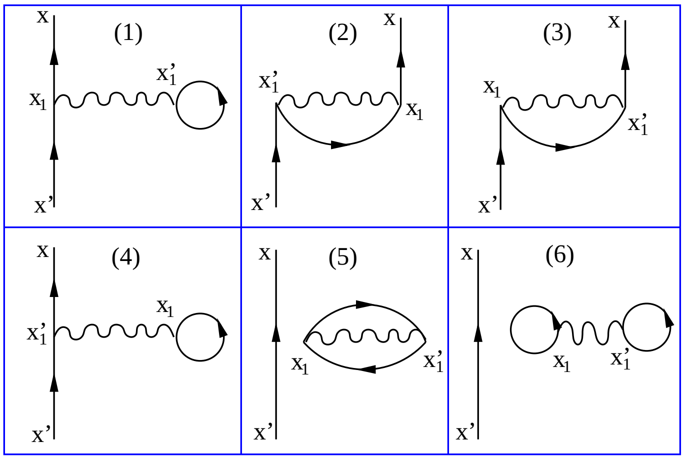

Fig. 7.5 First-order Feynman diagrams for the electron-electron interaction.

Now, we can use the graphical conventions introduced in Fig. 7.4 to represent the six different contributions to the first-order correction of the causal Green's function. This can be seen in Fig. 7.5, where we have numbered the terms from 1 to 6 following the order of Eq. (7.162).

Let us summarize some of the main features of these diagrams, which are also found in higher-order contributions:

- The only thing that matters in the diagrams is their topology, i.e. the way in which the different events are connected.
- The Green's functions with equal time arguments are represented by a closed loop and their value is equal to $in^{(0)}(\mathbf{r})$. If we used a local representation $\{|i\rangle\}$, then we would have
$$G^{(0)}_{ii}(t, t^{+}) = i\langle \mathbf{n}^{(0)}_i \rangle. \tag{7.165}$$
- Notice that all the intermediate events are linked by an interaction line and they have an incoming and an outgoing propagator, which correspond to the scattering process that the electron undergoes due to the electron-electron interaction. These intermediate events are known as vertexes (see Fig. 7.6).
- In Fig. 7.5 there are diagrams that have parts that are not connected to the the rest of the diagram and, in particular, to the initial and final events. Since there is an integration over the intermediate arguments appearing in these disconnected parts, they

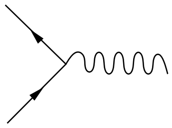

Fig. 7.6 Vertex: point where two propagator lines and an interaction line meet.

simply give a constant that multiplies the contribution of the rest of the diagram. More importantly, one can show that these type of diagrams do not contribute to the final expansion because they are exactly canceled by the denominator of the full Green's functions. For a demonstration of this fact we refer you to the Exercise 7.3.

- As we can see in Fig. 7.5, several diagrams are topologically equivalent (e.g. diagrams 1 and 3 or 2 and 4) and the only difference is the order in which the arguments appear. However, since there are integrations over such intermediate variables, see Eq. (7.162), all these equivalent diagrams give exactly the same contribution. This happens indeed at any order of the perturbative expansion. Thus, at order $n$, any topologically connected diagram appears $2^n n!$ times. The factor $1/2$ in the expression of $V^{(0)}$ together with the factor $1/n!$ in the perturbative expansion (see Eq. (7.151)) cancel exactly this multiplicity. Therefore, we need to consider the topologically connected diagrams only once.

Summarizing, the series of diagrams that contribute to the expansion of the causal Green's function are formed by the topologically distinct connected diagrams. Moreover, the denominator in Eq. (7.151) drops. Therefore, we can finally write the diagrammatic series of Eq. (7.151) as

$$G(\mathbf{r}t,\mathbf{r}'t') = G^{(0)}(\mathbf{r}t,\mathbf{r}'t') + \sum_{n=1}^{\infty}(-i)^{n+1}\int_{-\infty}^{\infty}dt_1\cdots\int_{-\infty}^{\infty}dt_n \times \langle\phi_0|\mathbf{T}\left[\mathbf{\Psi}^{(0)}_{\sigma}(\mathbf{r}t)\mathbf{V}^{(0)}(t_1)\cdots\mathbf{V}^{(0)}(t_n)\mathbf{\Psi}^{(0)\dagger}(\mathbf{r}'t')\right]|\phi_0\rangle_{\text{connected}}, \tag{7.166}$$

where only the contribution of the topologically distinct connected diagrams is considered. Of course, there would be a similar expression for the Green's functions in a discrete representation (or basis).

It is a very useful exercise to find the 10 topologically distinct connected Feynman diagrams that contribute to the second-order correction of the causal Green's function. In Fig. 7.7 we show some of these diagrams.

The Feynman diagrams provide a very intuitive way of evaluating the different contributions to the perturbative expansion of a causal Green's

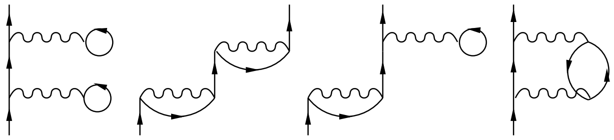

Fig. 7.7 Some of the 10 second-order topologically distinct connected Feynman diagrams for the electron-electron interaction.

function. In this sense, one proceeds sometimes by identifying directly the relevant diagrams rather than calculating the systematic perturbative series. Indeed, one can derive simple rules to quantify the contribution of the different diagrams. For the sake of completeness, we state here these rules for obtaining diagrammatically the contribution at a given order $n$ to the causal Green's function in the case of the electron-electron interaction:

(1) Draw all the topologically distinct connected diagrams containing $n$ interaction lines and $2n+1$ propagator lines between the initial and the final events.
(2) Every event must be labeled with its corresponding space-time coordinate $\mathbf{r}t$ (or $it$, if one works with a discrete basis $|i\rangle$). All the events, apart from the initial and final ones, contain a vertex as the one of Fig. 7.6.
(3) Every propagator line connecting the events $\mathbf{x}_2 = \mathbf{r}_2 t_2$ and $\mathbf{x}_1 = \mathbf{r}_1 t_1$ contributes with a factor $G^{(0)}(\mathbf{x}_1, \mathbf{x}_2)$.
(4) Every interaction line connecting the events $\mathbf{x}_2 = \mathbf{r}_2 t_2$ and $\mathbf{x}_1 = \mathbf{r}_1 t_1$ introduces a factor $U(\mathbf{x}_1, \mathbf{x}_2) = U(\mathbf{r}_1, \mathbf{r}_2)\delta(t_1 - t_2)$. In the case of a discrete basis, this factor would be $U_{ijkl}$ (corresponding matrix element of the Coulomb potential).
(5) One has to include integrals over all intermediate variables.
(6) Every diagram of order $n$ contains a pre-factor $i^n$.
(7) Finally, there is a sign $(-1)^F$, where $F$ is the number of closed loops in the diagram. The closed loop can be formed either by a single propagator or by a combination of several of them. Moreover, a Green's function with equal time variables must be interpreted as $G^{(0)}(\mathbf{x}t, \mathbf{x}'t^+)$.

As an illustration of these rules, let us compute the contribution corresponding to the last diagram in Fig. 7.7. This second-order contribution is equal to

$$-i^2 \int d\mathbf{x}_1 \int d\mathbf{x}'_1 \int d\mathbf{x}_2 \int d\mathbf{x}'_2 \; G^{(0)}(\mathbf{x},\mathbf{x}_1)U(\mathbf{x}_1,\mathbf{x}'_1)G^{(0)}(\mathbf{x}'_1,\mathbf{x}'_2)G^{(0)}(\mathbf{x}'_2,\mathbf{x}'_1)$$
$$G^{(0)}(\mathbf{x}_1,\mathbf{x}_2)U(\mathbf{x}_2,\mathbf{x}'_2)G^{(0)}(\mathbf{x}_2,\mathbf{x}').$$

#### 7.2.5.2 *Feynman diagrams for an external potential*

Now, we assume that the electrons are subjected to an external time-independent perturbation of the form

$$\mathbf{V} = \sum_{i=1}^{N} V(\mathbf{r}_i), \tag{7.167}$$

which in second quantization can be written as (in the interaction picture)

$$\mathbf{V}^{(0)}(t) = \sum_{\sigma} \int d\mathbf{r} \; \mathbf{\Psi}^{(0)\dagger}_{\sigma}(\mathbf{r}t)V(\mathbf{r})\mathbf{\Psi}^{(0)}_{\sigma}(\mathbf{r}t). \tag{7.168}$$

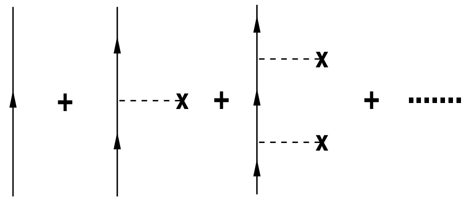

Fig. 7.8 Diagrammatic series for the propagator in the case of an external potential.

For the sake of simplicity, we have assumed that the potential does not depend on the electron spin. In this case, the diagrammatic series is very simple. Applying Wick's theorem to Eq. (7.151), one obtains the diagrammatic series shown in Fig. 7.8. This means that in the propagation of the electron from the initial instance to the final one, one simply has a series of sequential scattering events with the external potential. The rules for computing the contribution to the $n$th-order correction of the causal Green's functions are very simple in this case:

(1) Draw the sequential diagrams like in Fig. 7.8 with $n+1$ propagators and $n$ interaction lines.
(2) Associate the corresponding Green's function to every propagator line.
(3) Assign the corresponding external potential to every interaction line.
(4) Integrate over the intermediate variables.

(5) The prefactor is 1.

Due to the simplicity of the diagrammatic series in this case, it is often possible to sum up all the contributions up infinite order (notice that the diagrammatic expansion leads to a geometrical series). As an illustration of the previous rules, the second-order diagram in Fig. 7.8 gives a contribution equal to

$$\int d\mathbf{x}_1 \int d\mathbf{x}_2 \, G^{(0)}(\mathbf{x},\mathbf{x}_1)V(\mathbf{r}_1)G^{(0)}(\mathbf{x}_1,\mathbf{x}_2)V(\mathbf{r}_2)G^{(0)}(\mathbf{x}_2,\mathbf{x}'). \tag{7.169}$$

### 7.2.6 *Feynman diagrams in energy space*

In spite of all the simplifications that we have introduced in the last section, it is still very difficult to compute the different terms of the perturbative series. This is due to the presence of the integrals over the intermediate arguments. Thus for instance, a diagram of order 1 for the electron-electron interaction contains up to six integrals.

The problem can be simplified by noticing first that in an equilibrium situation the Green's functions depend exclusively on the difference of the time arguments. Thus, we can Fourier transform with respect to time and work in the energy space. The introduction of the Fourier transformation modifies the Feynman diagrams and we now study how this occurs in detail.

On the other hand, if the system is spatially homogeneous, the problem can be simplified even further since then the Green's functions depend only on the difference of the space coordinates. We shall first discuss this case and later on, we shall generalize the results to an arbitrary non-homogeneous system.

As we have just said, if the system is spatially homogeneous and in equilibrium, the Green's functions satisfy

$$G(\mathbf{r}t,\mathbf{r}'t') = G(\mathbf{r}-\mathbf{r}',t-t'), \tag{7.170}$$

or, using the four-dimensional notation ($\mathbf{x} \equiv \mathbf{r}t$), $G(\mathbf{x},\mathbf{x}') = G(\mathbf{x}-\mathbf{x}')$. If we assume that the interaction potential also satisfies $U(\mathbf{x},\mathbf{x}') = U(\mathbf{x}-\mathbf{x}')$, it is convenient to introduce the Fourier transform of the different functions:

$$G(\mathbf{r}t) = \int \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{dE}{2\pi} e^{i(\mathbf{k}\cdot\mathbf{r}-Et)} G(\mathbf{k},t). \tag{7.171}$$

In what follows, we shall use the following simplified notation: $\mathbf{p} \equiv (\mathbf{k},E)$ and $\mathbf{p}\cdot\mathbf{x} = \mathbf{kr} - Et$. With this notation, the different Fourier transforms read

$$G(\mathbf{x}) = \int \frac{d\mathbf{p}}{(2\pi)^4} e^{i\mathbf{px}} G(\mathbf{p});\; U(\mathbf{x}) = \int \frac{d\mathbf{p}}{(2\pi)^4} e^{i\mathbf{px}} U(\mathbf{p}), \tag{7.172}$$

where $d\mathbf{p} \equiv d^3kdE$ is the volume element in $(\mathbf{k}, E)$-space.

In order to illustrate how the diagrams are modified in energy space, we choose a first-order diagram for the electron-electron interaction, namely diagram 2 in Fig. 7.5. The contribution of this diagram, which we shall denote as $D(\mathbf{x}-\mathbf{x}')$, is given by

$$D(\mathbf{x}-\mathbf{x}') = i\int d\mathbf{x}_1 \int d\mathbf{x}_1'\; G^{(0)}(\mathbf{x}-\mathbf{x}_1)U(\mathbf{x}_1-\mathbf{x}_1') \qquad (7.173)$$
$$G^{(0)}(\mathbf{x}_1-\mathbf{x}_1')G^{(0)}(\mathbf{x}_1'-\mathbf{x}').$$

Substituting in the right hand side of this expression the Fourier transform of $G^{(0)}$ and $U$, one has

$$D(\mathbf{x}-\mathbf{x}') = i\int d\mathbf{x}_1 \int d\mathbf{x}_1' \int \frac{d\mathbf{p}}{(2\pi)^4}\int \frac{d\mathbf{q}}{(2\pi)^4}\int \frac{d\mathbf{q}'}{(2\pi)^4}\int \frac{d\mathbf{p}'}{(2\pi)^4} \qquad (7.174)$$
$$G^{(0)}(\mathbf{p})U(\mathbf{q})G^{(0)}(\mathbf{q}')G^{(0)}(\mathbf{p}')e^{i\mathbf{p}(\mathbf{x}-\mathbf{x}_1)}e^{i\mathbf{q}(\mathbf{x}_1-\mathbf{x}_1')}e^{i\mathbf{q}'(\mathbf{x}_1-\mathbf{x}_1')}e^{i\mathbf{p}'(\mathbf{x}_1'-\mathbf{x}')}.$$

This expression can be greatly simplified in the following way. First, we regroup the exponential terms as follows

$$e^{i\mathbf{p}\mathbf{x}}e^{i\mathbf{x}_1(-\mathbf{p}+\mathbf{q}+\mathbf{q}')}e^{i\mathbf{x}_1'(\mathbf{p}'-\mathbf{q}-\mathbf{q}')}e^{-i\mathbf{p}'\mathbf{x}'}. \qquad (7.175)$$

Now, we integrate over the variables $\mathbf{x}_1$ and $\mathbf{x}_1'$:

$$\int d\mathbf{x}_1\; e^{i\mathbf{x}_1(-\mathbf{p}+\mathbf{q}+\mathbf{q}')} = (2\pi)^4\delta(\mathbf{p}-\mathbf{q}-\mathbf{q}') \Rightarrow \mathbf{q}' = \mathbf{p}-\mathbf{q} \qquad (7.176)$$
$$\int d\mathbf{x}_1'\; e^{i\mathbf{x}_1'(\mathbf{p}'-\mathbf{q}-\mathbf{q}')} = (2\pi)^4\delta(\mathbf{p}'-\mathbf{q}-\mathbf{q}') \Rightarrow \mathbf{p}' = \mathbf{q}+\mathbf{q}' = \mathbf{p}.$$

The previous equations simply express the conservation of the four-dimensional moment (momentum and energy) in every vertex, as we illustrate in Fig. 7.9, where the momentum lost by the electron in the scattering process is carried by the interaction line. If we now substitute Eq. (7.176) in Eq. (7.173), we obtain

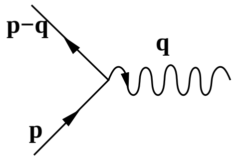

Fig. 7.9 Energy and momentum conservation in a vertex.

$$D(\mathbf{x}-\mathbf{x}') = i\int \frac{d\mathbf{p}}{(2\pi)^4}e^{i\mathbf{p}(\mathbf{x}-\mathbf{x}')}\int \frac{d\mathbf{q}}{(2\pi)^4}G^{(0)}(\mathbf{p})U(\mathbf{q})G^{(0)}(\mathbf{p}-\mathbf{q})G^{(0)}(\mathbf{p}). \qquad (7.177)$$

This implies that the Fourier transform of the diagram can be written as

$$D(\mathbf{p}) = i \int \frac{d\mathbf{q}}{(2\pi)^4} G^{(0)}(\mathbf{p}) U(\mathbf{q}) G^{(0)}(\mathbf{p}-\mathbf{q}) G^{(0)}(\mathbf{p}). \tag{7.178}$$

The previous derivation would be similar for any diagram. The key idea is that the energy and the momentum are conserved in every vertex. Thus, one can view the diagrams as flow diagrams in which the propagator lines and the interaction lines carry momentum and energy. The momentum $\mathbf{k}$ and the energy $E$ carried by the initial propagator are also carried by the final one, due to the conservation of momentum and energy in every vertex of the diagram. This is illustrated in Fig. 7.10 with two first-order diagrams and a second-order one. Notice that, since the interaction lines carry both momentum and energy, one has to assign to them a direction, which is indicated by an arrow in the diagram.

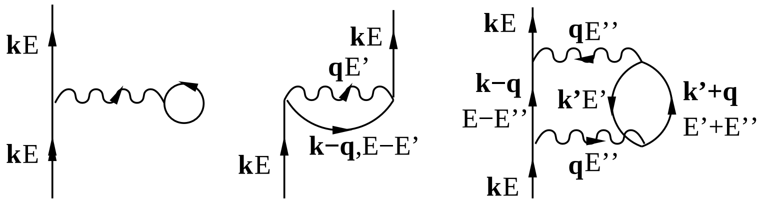

Fig. 7.10 Feynman diagrams in momentum and energy space.

As in the case of real space, it is possible to establish the diagrammatic rules for computing the perturbative expansion of the causal Green's function in energy space. Those rules for the $n$th-order correction now read:

(1) Draw all the topologically distinct connected diagrams with $n$ interaction lines and $2n+1$ propagator lines. These diagrams are the same as in the ones in $(\mathbf{r}, t)$-space.
(2) Assign the flow direction (arrows) of the momentum and energy to every interaction and propagator line.
(3) The momentum and the energy must be conserved in every vertex.
(4) Every propagator with momentum $\mathbf{k}$ and energy $E$ contributes with a factor that is equal to the unperturbed causal Green's function, which for a homogeneous electron gas has the form

$$G^{(0)}(\mathbf{k}, E) = \frac{1}{E - \epsilon_k + i\eta \mathrm{sgn}(k - k_F)}. \tag{7.179}$$

(5) Every interaction line with momentum $\mathbf{k}$ introduces an interaction potential in momentum space. For the homogenous system and for the Coulomb potential, it has the form

$$U(\mathbf{k}) = \frac{4\pi e^2}{k^2}. \tag{7.180}$$

(6) We have to integrate over all intermediate momenta and energies (for a non-homogeneous systems only over the energies).

(7) As a consequence of the previous rule, there is a factor for a diagram of order $n$ equal to $1/(2\pi)^{4n}$ (equal to $1/(2\pi)^n$, if one only needs to integrate over the energies). Moreover, there is a factor $i^n$, as in the case of real space.

(8) As in the case of real space, there is a sign $(-1)^F$, where $F$ is the number of closed loops.

(9) Finally, let us remind that for the diagrams in real space, there was an ambiguity that occurs when the time arguments of the causal Green's function are equal. This problem was solved with the criterion $G^{(0)}(t,t) = G^{(0)}(t,t^+)$. The consequence of this choice when we Fourier transform is the introduction of a convergence factor $\exp(iE\eta)$, which must appear associated to every propagator that forms a closed loop and to those that are connected by an interaction line (if the interaction is instantaneous).

As an example, let us write the contribution of the second-order diagram in Fig. 7.10. The result is

$$\int \frac{d\mathbf{q}}{(2\pi)^3} \int \frac{d\mathbf{k}'}{(2\pi)^3} \int \frac{dE''}{2\pi} \int \frac{dE'}{2\pi} U^2(\mathbf{q}) G^{(0)}(\mathbf{k},E) G^{(0)}(\mathbf{k}-\mathbf{q}, E-E'') \times \\ G^{(0)}(\mathbf{k}',E') G^{(0)}(\mathbf{k}'+\mathbf{q}, E'+E'') G^{(0)}(\mathbf{k},E).$$

To conclude this section, it is convenient to generalize the results obtained so far to the case of non-homogeneous systems. Indeed, this generalization is quite simple. Since the momentum is not a good quantum number, it makes no sense to Fourier transform with respect to the spatial coordinates. However, since the system is in equilibrium, one can still introduce the Fourier transform with respect to the time arguments. This is done exactly in the way explained above for the homogeneous system.

As an example, let us calculate the contribution of second-order diagram of Fig. 7.11 for the Anderson model that we discussed in section 7.1.4.3:

$$U^2 \int \frac{dE''}{2\pi} \int \frac{dE'}{2\pi}\, G^{(0)}_{00\sigma}(E) G^{(0)}_{00\sigma}(E-E'') G^{(0)}_{00\bar{\sigma}}(E') G^{(0)}_{00\bar{\sigma}}(E'+E'') G^{(0)}_{00\sigma}(E).$$

Here, the subindex 0 refers to the impurity level.

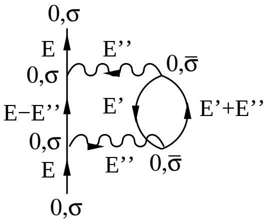

Fig. 7.11 Second-order Feynman diagrams in energy space for the Anderson model.

### 7.2.7 *Electronic self-energy and Dyson's equation*

In the previous sections we have analyzed the structure of the diagrammatic series of an electronic Green's function. In this section we shall show that it is possible to sum formally the diagrams up to infinite order, leading to the Dyson's equation. But before describing this further simplification of the perturbative expansion, let us introduce the concept of self-energy.

In Fig. 7.12 we show again the diagrammatic expansion for the Green's function in the cases in which the perturbation is an external potential and the electron-electron interaction. Notice that in both cases the diagrams have the same type of structure in the following sense. They are formed by an initial and a final Green's function (the same in all diagrams) and by a central part where one can find all the scattering processes. Obviously, this latter part is the interesting one. This structure of the diagrammatic series allows us to define the (improper) electronic self-energy as the sum of the central part of the diagrams to all orders ($\Sigma_I$ in Fig. 7.13). Thus, the diagrammatic series for the self-energy insertion has the form shown in Fig. 7.14 for the cases of an external potential and the electron-electron interaction.

Notice that in the previous discussion we have neither specified the representation nor the space (time/energy). In this sense, the result discussed in the previous paragraphs is quite general. The diagrammatic expansion of Fig. 7.12 can be summarized in the following equation in real space (**r**-representation)

$$G(\mathbf{x},\mathbf{x}') = G^{(0)}(\mathbf{x},\mathbf{x}') + \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, G^{(0)}(\mathbf{x},\mathbf{x}_1)\Sigma_I(\mathbf{x}_1,\mathbf{x}_2)G^{(0)}(\mathbf{x}_2,\mathbf{x}'). \tag{7.181}$$

The equation in momentum-energy space (for a homogeneous case) reads as follows

$$G(\mathbf{k},E) = G^{(0)}(\mathbf{k},E) + G^{(0)}(\mathbf{k},E)\Sigma_I(\mathbf{k},E)G^{(0)}(\mathbf{k},E). \tag{7.182}$$

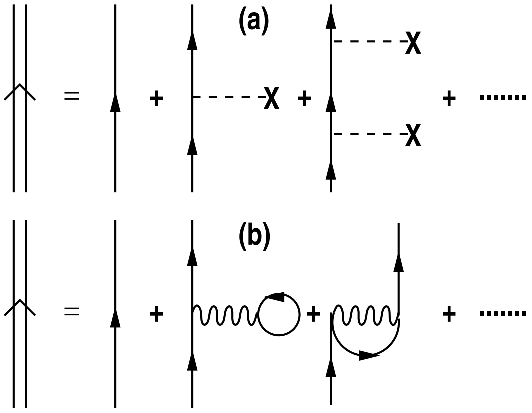

Fig. 7.12 Diagrammatic expansion for the propagator for (a) an external potential and (b) the electron-electron interaction.

In the case of a localized basis (like in a tight-binding model), the previous equation adopts the form:

$$G_{ij}(E) = G_{ij}^{(0)}(E) + \sum_{kl} G_{ik}^{(0)}(E)\Sigma_{I,kl}(E)G_{lj}^{(0)}(E). \tag{7.183}$$

To avoid explicit reference to any particular representation or space, we shall write the previous equation in matrix form:

$$\mathbf{G} = \mathbf{G}^{(0)} + \mathbf{G}^{(0)}\mathbf{\Sigma}_I\mathbf{G}^{(0)}, \tag{7.184}$$

where the internal integrals and sums are implicitly assumed. It is possible to write this equation in a more convenient way by inspection of the perturbative series of $\mathbf{G}$ or $\mathbf{\Sigma}_I$. Let us illustrate this fact first with the example of an external potential. As we explained in previous sections, the diagrammatic expansion has in this case the form of a geometrical series where the diagram of order $n$ is simply the repetition of $n$ identical pieces. If we define in this case the *proper self-energy*, $\Sigma$, as the part of the diagram

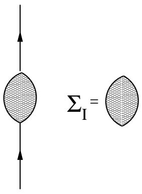

Fig. 7.13 Self-energy insertion.

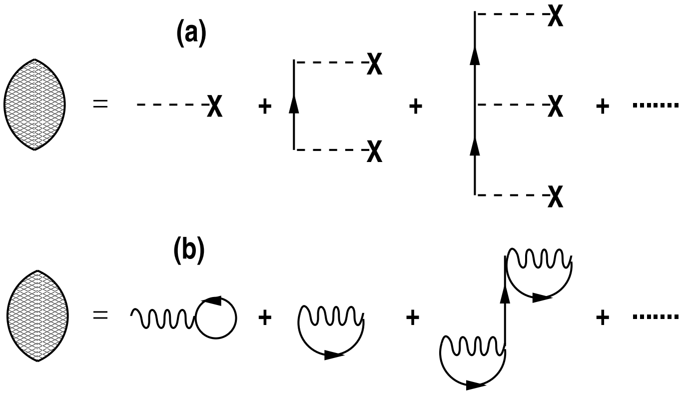

Fig. 7.14 Diagrammatic expansion for the self-energy insertion. (a) External potential. (b) Electron-electron interaction.

that includes only a single scattering process, which in this case is simply the external potential, we have the following identity

$$\mathbf{\Sigma}_I \mathbf{G}^{(0)} = \mathbf{\Sigma}\mathbf{G}. \tag{7.185}$$

This is evident when it is expressed diagrammatically as in Fig. 7.15.

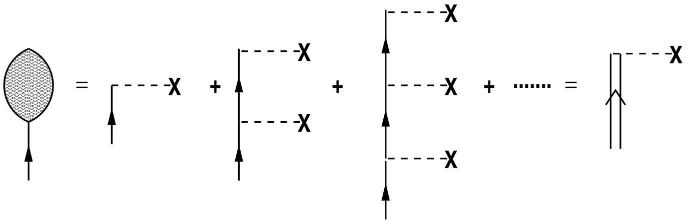

Fig. 7.15 Relation between the self-energy insertion, $\mathbf{\Sigma}_I$ and the proper self-energy, $\mathbf{\Sigma}$.

The proper self-energy, or from now on just self-energy, does not contain repetitions of the same process, but only one scattering event. Then, Eq. (7.184) can be written in terms of the self-energy as

$$\mathbf{G} = \mathbf{G}^{(0)} + \mathbf{G}^{(0)}\mathbf{\Sigma}\mathbf{G}, \tag{7.186}$$

which constitutes the so-called *Dyson's equation* and was first obtained by F. Dyson in 1949 in the context of the quantum electrodynamics.

Let us now discuss the derivation of this result in the case of the electron-electron interaction. Notice first that in this case the diagrams that contribute to the self-energy insertion to all orders can be classified in two different ways. On the one hand, we have diagrams that cannot be separated in two parts by cutting a propagator line, i.e. they do not contain repetitions of the same elementary process. These diagrams are called *irreducible* [see Fig. 7.16(a)]. On the other hand, we have diagrams that can be divided into parts of lower order by cutting a propagator line, these are called *reducible* diagrams [see Fig. 7.16(b)].

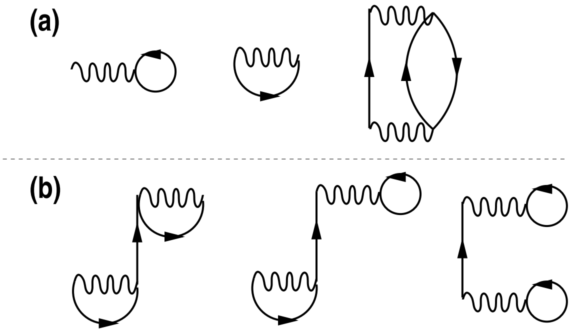

Fig. 7.16 (a) Examples of irreducible self-energy diagrams for the electron-electron interaction. (b) Reducible diagrams.

We define the proper self-energy (or simply self-energy) in this case as the sum of all the irreducible self-energy diagrams. With this definition, the Dyson's equation is also verified in this case. The proof is more complicated than in the case of an external potential and it will not be detailed here.

The Dyson's equation can be represented graphically as shown in Fig. 7.17. Notice that the due to the symmetry of the diagrammatic series, we could have chosen to close the Dyson's equation in an alternative way:

$$\mathbf{G} = \mathbf{G}^{(0)} + \mathbf{G}\mathbf{\Sigma}\mathbf{G}^{(0)}. \tag{7.187}$$

On the other hand, notice that the Dyson's equation obtained in the previous section for single-electron problems, see Eq. (7.37), is just a particular example of Eq. (7.186), which is valid for any electronic system.

For systems in equilibrium it is convenient to write the Dyson's equation in energy space

$$\mathbf{G}(E) = \mathbf{G}^{(0)}(E) + \mathbf{G}^{(0)}(E)\mathbf{\Sigma}(E)\mathbf{G}(E), \tag{7.188}$$

which will be our starting point for the description of the equilibrium properties of any system.

Taking into account the definition of the single-particle Green's function in energy space introduced in the previous section, we can rewrite the

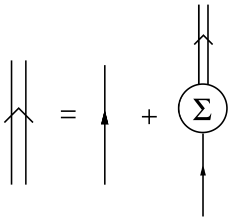

Fig. 7.17 Pictorial representation of the Dyson's equation.

previous Dyson's equation as

$$\left[\mathbf{G}^{(0)}(E)\right]^{-1}\mathbf{G}(E) = \mathbf{1} + \mathbf{\Sigma}(E)\mathbf{G}(E) \tag{7.189}$$

$$\left[E\mathbf{1} - \mathbf{H}_0\right]\mathbf{G}(E) = \mathbf{1} + \mathbf{\Sigma}(E)\mathbf{G}(E),$$

which allows us to write the Green's function matrix of the full system as

$$\mathbf{G}(E) = \left[E\mathbf{1} - \mathbf{H}_0 - \mathbf{\Sigma}(E)\right]^{-1}. \tag{7.190}$$

From this expression, one can interpret the self-energy as the matrix whose elements renormalize dynamically the matrix elements of the unperturbed system. Thus for instance, for the homogeneous electron gas with electron-electron interaction, the problem is diagonal in the plane wave basis that diagonalizes $\mathbf{H}_0$ and the previous Dyson's equation becomes

$$G(\mathbf{k}, E) = \frac{1}{E - \epsilon_k - \Sigma(\mathbf{k}, E)}. \tag{7.191}$$

In summary, the perturbative analysis reduces to the evaluation of the proper self-energy (or just self-energy) of the electronic system. For the two cases considered in the last sections, namely external potential and electron-electron interaction, this implies to calculate the diagrammatic series depicted in Fig. 7.18.

Finally, let us conclude this section with some comments and the main analytical properties of the electronic self-energy:

- The Dyson's equation relates directly the self-energy with the full Green's function. Therefore, the analytical properties of $\mathbf{\Sigma}(E)$ can be derived from those of $\mathbf{G}(E)$.
- One can interpret Eq. (7.190) as a definition of $\mathbf{\Sigma}(E)$ in terms of $\mathbf{G}(E)$. Thus, it is also possible to define a retarded and advanced self-energy.
- From Lehmann's representation of the Green's functions, one can deduce the following properties that we state here without any proof:

$$\mathrm{Im}\left\{\Sigma^r_{ii}(E)\right\} \leq 0 \; ; \; \mathrm{Im}\left\{\Sigma^a_{ii}(E)\right\} \geq 0 \tag{7.192}$$

$$\mathrm{Im}\left\{\Sigma^c_{ii}(E)\right\} \geq 0 \;\text{ if }\; E < \mu \; ; \; \mathrm{Im}\left\{\Sigma^c_{ii}(E)\right\} \leq 0, \;\text{ if }\; E > \mu.$$

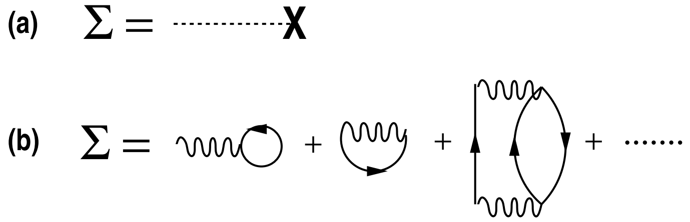

Fig. 7.18 Diagrammatic expansion for the proper self-energy. (a) External potential and (b) electron-electron interaction.

- $\text{Im}\Sigma_{ii}(E)$ and $\text{Re}\Sigma_{ii}(E)$ are related through a Hilbert transformation:

$$\begin{aligned} \text{Re}\left\{\Sigma^{r;a}_{ii}(E)\right\} &= \mp \mathcal{P} \int \frac{dE'}{\pi} \, \frac{\text{Im}\left\{\Sigma^{r;a}_{ii}(E')\right\}}{E - E'} \\ \text{Re}\left\{\Sigma^{c}_{ii}(E)\right\} &= -\mathcal{P} \int \frac{dE'}{\pi} \, \frac{\text{Im}\left\{\Sigma^{c}_{ii}(E')\right\} \text{sgn}(E' - \mu)}{E - E'} . \end{aligned} \quad (7.193)$$

### 7.2.8 *Example: Anderson model and Kondo effect*

The goal of this section is two-fold. On the one hand, we shall use the Anderson model, already discussed in section 7.1.4.3, to illustrate the perturbative approach described in this section. On the other hand, we shall use this model to get a flavor of the Kondo effect. This is a many-body phenomenon which can appear in molecular junctions and it will be described in more detail later in this course.

The Anderson model describes the interaction of a localized level with electron-electron interaction with the continuum of states of a metallic system. It was introduced by Anderson to describe a magnetic impurity in a metal host, but it can also be used to describe a metal-molecule-metal junction, which is the problem that we are interested in. In this model, the Hamiltonian is given by Eq. (7.118), where in particular, the $U$-term describes the electron-electron interaction in this level. In the absence of this interaction, this model reduces to the resonant tunneling model of section 7.1.3.3.

Our goal now is to study the influence of the electron-electron interaction in the equilibrium properties of a molecular junction, with special attention to the local density of states. For this purpose, we shall make use of the perturbative approach described in this section. In this approach we shall consider the entire system without electron-electron interaction as the unperturbed system and this interaction, i.e. the last term in Eq. (7.118), will be considered as the perturbation. The unperturbed Green's functions projected onto the localized level were already obtained in section 7.1.3.3, see Eq. (7.65). In particular, the causal function adopts the following form in the wide-band approximation[17]

$$G_{00}^{(0)}(E) = \frac{1}{E - \epsilon_0 + i\mathrm{sgn}(E-\mu)\Gamma}, \tag{7.194}$$

where $\mu$ is the chemical potential of the system and $\Gamma = \Gamma_L + \Gamma_R$ is the total broadening of the level acquired via the interaction with the metal electrodes. In what follows, we shall only consider symmetric situations ($\Gamma_L = \Gamma_R$). As we saw in section 7.1.3.3, in this approximation the density of states in the localized level is a Lorentzian with $\Gamma$ as its half width at half maximum.

In the rest of this section, and in order to study the effect of the electron-electron interaction, we shall first discuss the so-called Friedel sum rule, which is an exact result that relates the local density of states at the Fermi energy to the occupation of the level, and then we shall do a perturbative analysis up to second order in the interaction $U$.

### 7.2.8.1 *Friedel sum rule*

We discuss now an important exact result, known as Friedel' sum rule, which is a consequence of the Fermi liquid properties of the system described by the Anderson model.[18] This sum rule can be derived as follows. The effect of the electron-electron interaction in the localized level can be included via the exact self-energy of the problem, $\Sigma_{00,\sigma}(E)$.[19] The (retarded) full Green function projected onto the level can written in terms of the self-energy as

$$G_{00,\sigma}^{r}(E) = \frac{1}{E - \epsilon_0 + i\Gamma - \Sigma_{00,\sigma}^{r}(E)}. \tag{7.195}$$

Taking now into account that the density of states in the level is given by $\rho_{0\sigma}(E) = -(1/\pi)\mathrm{Im}G_{00,\sigma}^{r}(E)$, the corresponding occupation can be expressed as

$$\langle n_{0\sigma}\rangle = \int_{-\infty}^{\mu} dE\, \rho_{0\sigma}(E) = -\frac{1}{\pi}\int_{-\infty}^{\mu} dE\, \frac{1}{E - \epsilon_0 + i\Gamma - \Sigma_{00,\sigma}^{r}(E)}. \tag{7.196}$$

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[17] Notice that this function is independent of the spin.

[18] Although we have not discussed the Fermi liquid theory in this course, we find important to introduce this discussion about Friedel sum rule because it provides a simple way to understand the appearance of the Kondo effect.

[19] Notice that we have now included the spin index $\sigma$ in the self-energy.

We can now use the relation

$$\frac{1}{E-\epsilon_0+i\Gamma-\Sigma^r_{00,\sigma}(E)} = \frac{\partial}{\partial E}\ln\left[E-\epsilon_0+i\Gamma-\Sigma^r_{00,\sigma}(E)\right] + \frac{\partial\Sigma^r_{00,\sigma}(E)/\partial E}{E-\epsilon_0+i\Gamma-\Sigma^r_{00,\sigma}(E)} \qquad (7.197)$$

together with the Ward identity

$$\int_{-\infty}^{\mu} dE\; G^r_{00,\sigma}(E)\frac{\partial\Sigma^r_{00,\sigma}(E)}{\partial E} = 0, \qquad (7.198)$$

to write the occupation as

$$\langle n_{0\sigma}\rangle = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\mu} dE\; \frac{\partial}{\partial E}\ln\left[E-\epsilon_0+i\Gamma-\Sigma^r_{00,\sigma}(E)\right]. \qquad (7.199)$$

Integrating this expression we arrive at

$$\langle n_{0\sigma}\rangle = \frac{1}{2}-\frac{1}{\pi}\tan^{-1}\left[\frac{\epsilon_0-\mu-\mathrm{Re}\Sigma^r_{00,\sigma}(\mu)}{\Gamma}\right]. \qquad (7.200)$$

Here, we have used the fact that in a Fermi liquid $\mathrm{Im}\Sigma^r_{00,\sigma}(\mu)=0$, which physically means that the quasiparticles have an infinite lifetime at the Fermi energy.

Thus, we can write the local density of states as

$$\rho_{0\sigma}(E) = \frac{1}{\pi}\frac{\Gamma+\mathrm{Im}\Sigma^r_{00,\sigma}(E)}{\left[E-\epsilon_0-\mathrm{Re}\Sigma^r_{00,\sigma}(\mu)\right]^2+\left[\Gamma+\mathrm{Im}\Sigma^r_{00,\sigma}(E)\right]^2}. \qquad (7.201)$$

Using Eq. (7.200), we can relate the exact density of states at the Fermi energy with the occupation of the level as follows

$$\rho_{0\sigma}(\mu) = \frac{1}{\pi\Gamma}\sin^2\left[\pi\langle n_{0\sigma}\rangle\right], \qquad (7.202)$$

which is known as *Friedel sum rule.* In a case with electron-hole symmetry and $\langle n_{0\sigma}\rangle = 1/2$, the previous expression reduces to

$$\rho_{0\sigma}(\mu) = \frac{1}{\pi\Gamma}. \qquad (7.203)$$

Notice that this equation implies that in the symmetric case, the density of states at the Fermi energy coincides with the corresponding one in the unperturbed problem, i.e. $\rho_{0\sigma}(\mu)=\rho^{(0)}_{0\sigma}(\mu)$.

Friedel sum rule implies the appearance of a narrow peak in the density of states in the limit $U/\Gamma\to 0$. Let us discuss how this comes about. In section 7.1.4.3 we saw that the level Green's function in the limit $U/\Gamma\to 0$ (atomic limit) is given by Eq. (7.121). This equation suggests that when

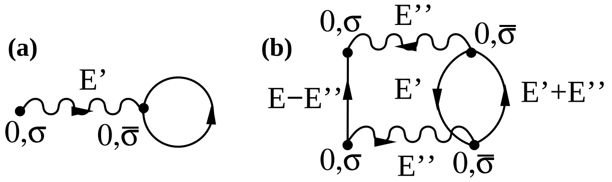

Fig. 7.19 First (a) and second (b) order self-energy diagrams in the Anderson model.

$U \gg \Gamma$, the density of states consists mainly of two subbands (of width $\sim \Gamma$) around $\epsilon_0$ and $\epsilon_0 + U$, which have most of the total spectral weight. However, Eq. (7.203) tells us that there is a finite density at the Fermi energy. Therefore, the exact density of states must exhibit a narrow peak at the Fermi energy, known as *Kondo peak* or *Kondo resonance*, the width of which tends to zero in the limit $U/\Gamma \to 0$. Indeed, it can be shown that this weight decays exponentially in this limit.

### 7.2.8.2 *Perturbative analysis*

We now want to calculate the properties of the system via a perturbative expansion of the Green's functions. For this purpose, we need an approximation for the self-energy, which can be obtained from the lowest-order diagrams. Expanding up to second order in $U$, one finds only two self-energy diagrams that give a finite contribution, namely those depicted in Fig. 7.19. The first-order diagram, see Fig. 7.19(a), is the Hartree diagram and it yields the following contribution

$$\Sigma^{(1)}_{00,\sigma}(E) = U \int_{-\infty}^{\infty} \frac{dE'}{2\pi} G^{(0)}_{00,\bar{\sigma}}(E') e^{iE'\eta} = U\langle n_{0\bar{\sigma}}\rangle. \tag{7.204}$$

The standard Hartree approximation requires to determine the occupation $\langle n_{0\bar{\sigma}}\rangle$ in a self-consistent manner, i.e. by dressing the Green's function line in the Hartree diagram.

The level Green's function can then be written within this approximation as

$$G_{00,\sigma}(E) = \frac{1}{E - \epsilon_0 + i\Gamma \mathrm{sgn}(E) - U\langle n_{0\bar{\sigma}}\rangle}, \tag{7.205}$$

where we have set $\mu = 0$. Notice that the role of the interaction is to shift the position of the resonant level, which moves to $\epsilon_0 + U\langle n_{0\bar{\sigma}}\rangle$. In the special case in which $\epsilon_0 = -U/2$, known as the symmetric case, the self-consistent solution, assuming that there is no magnetic solution, is $\langle n_{0\sigma}\rangle = \langle n_{0\bar{\sigma}}\rangle = 1/2$. The problem exhibits in this case electron-hole

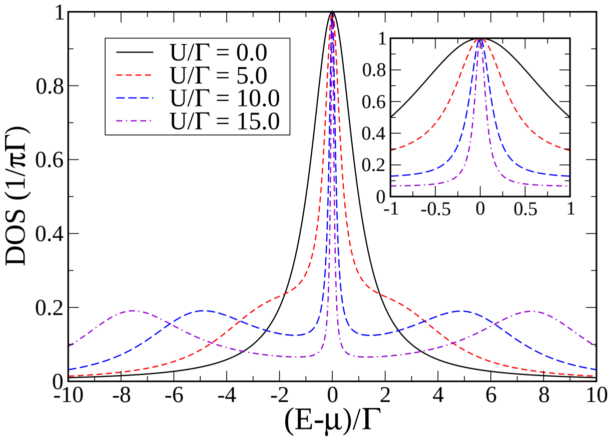

Fig. 7.20 Density of states projected onto the localized level as a function of the energy in the Anderson model for $\epsilon_0 = -U/2$ and different values of the ratio $U/\Gamma$. The calculation has been done including the self-energy diagrams up to second order. The inset shows a blow-up of the energy region close to the Fermi energy.

symmetry around $\mu = 0$ and the density of states is still described by a Lorentzian of width $\Gamma$.

Let us now analyze the contribution of the second-order diagram, see Fig. 7.19(b). Such contribution is given by

$$\Sigma^{(2)}_{00,\sigma}(E) = U^2 \int_{-\infty}^{\infty} \frac{dE''}{2\pi} \int_{-\infty}^{\infty} \frac{dE'}{2\pi} \, G^{(0)}_{00\sigma}(E - E'') G^{(0)}_{00\bar{\sigma}}(E') G^{(0)}_{00\bar{\sigma}}(E' + E''). \tag{7.206}$$

This expression is not easy to evaluate, but the main features of this self-energy can be reproduced in a simple analytical calculation in which one assumes a constant density of states for the unperturbed problem.

If in the diagram of Fig. 7.19(b) the Green's function line is dressed with the Hartree diagram and one considers the symmetric case ($\epsilon_0 = -U/2$), the second-order approximation preserves the electron-hole symmetry around $\mu = 0$ and one has $\langle n_{0\sigma} \rangle = \langle n^{(0)}_{0\sigma} \rangle$. Moreover, in this case one can show that $\mathrm{Re}\Sigma^{(2)}_{00,\sigma}(\mu) = \mathrm{Im}\Sigma^{(2)}_{00,\sigma}(\mu) = 0$. This implies that $\rho_{0\sigma} = \rho^{(0)}_{0\sigma}$ and therefore the Friedel sum rule is satisfied. This is one of the reasons why this second-order approximation gives an excellent description in the symmetric case, even if $U$ is not too small in comparison with $\Gamma$.

In order to illustrate the effect of the electron-electron interaction in the density of states, we have computed it numerically in the symmetric case using the second-order self-energy of Eq. (7.206). The results for different values of the ratio $U/\Gamma$ are shown in Fig. 7.20.[20] As one can see, as the $U/\Gamma$ increases, the density of states exhibits two subbands around $\epsilon_0$ and $\epsilon_0 + U$ and a narrow peak at the Fermi energy (the Kondo peak). Notice that the height of this peak remains constant and it is equal to $1/(\pi\Gamma)$, as in the case without electron-electron interaction. The appearance of this peak at the Fermi energy has very important consequences for the low-temperature transport properties of molecular junctions.

### 7.2.9 *Final remarks*

In this section we have presented a systematic perturbative approach to compute zero-temperature Green's functions of an electronic system. The next natural step in most textbooks is to discuss the generalization of this approach to finite temperatures. However, we shall skip this extension and jump in the next section to the nonequilibrium formalism in which the temperature will enter in a natural manner. Anyway, you are now in position to study the finite-temperature formalism, which can be found in different textbooks, see e.g. Refs. [2, 3, 6, 9].

It is worth stressing that in this section we have focused on the description of electronic systems, but a similar perturbative approach can be extended to other types of systems. For instance, in nanoscale junctions phonons or local vibrations play an important role both in the electronic and thermal transport properties. In this sense, it is interesting to learn how the diagrammatic formalism can be applied to phonons and other bosonic degrees of freedom. This subject will not be address in this monograph and if you are interested in this topic we recommend Refs. [2, 3, 6, 9].

Finally, we would like to emphasize that at this stage you are ready to study many important topics in solid state physics which are out of the scope of this course. For instance, the formalism detailed in this section is the starting point to understand the Fermi liquid theory, which is very important to get a deeper insight into the physics of metals. You are now also prepared to study the physics of the homogeneous electron gas, which is a model system where one can learn many important lessons related to the relevance of electronic correlations. Again, Refs. [2, 3, 6, 9] are very recommendable for studying these topics.

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[20] In this figure we explore cases in which $U$ is considerably larger than $\Gamma$, which in principle should be out of the scope of this second-order approximation. However, as stated above, this approximation works nicely in the symmetric case and it reproduces the main features of the exact solution [19].

## 7.3 Nonequilibrium Green's function formalism

So far we have shown how the Green's function techniques can help us to understand the physics of systems in equilibrium. Since our goal is the analysis of the transport properties of molecular contacts, we have to generalize those techniques to deal with situations in which the systems are driven out of equilibrium. This is the goal of this section in which we shall discuss the so-called *nonequilibrium Green's function formalism* (NEGF). This formalism was developed independently by Kadanoff and Baym [10] and Keldysh [11] in the early 1960's. Here we shall follow Keldysh formulation of this approach and we shall refer to it as the *Keldysh formalism.* This formalism is a natural extension of the diagrammatic theory that we have presented in the previous section. The importance of the Keldysh formalism lies in the fact that it allows us to go beyond the usual linear response in a systematic manner. Since its appearance, it has been used in a great variety of topics and, in particular, it has been applied to the study of electronic transport in many types of nanoscale devices and it constitutes a basic tool that will be used throughout the rest of this course.

Apart from the original paper [11], there exist a number of excellent reviews devoted to the Keldysh formalism in the literature [12, 13]. We try to present it here in a didactic manner, concentrating ourselves on its application to the problems of molecular electronics that we have in mind, rather than entering into very technical discussions about its foundation. Bearing this in mind, we have organized this section as follows. We first present the general ideas of the Keldysh formalism. Then, we shall briefly discuss how to perform the diagrammatic expansion within this formalism. We shall finish the formal discussion by reviewing both the main properties of the functions appearing in this nonequilibrium formalism and the main practical equations. Finally, the last part of this section is devoted to the application of the Keldysh formalism to some simple transport problems and we shall also present a derivation of a general version Landauer formula that can be applied to any nanocontact.

### 7.3.1 *The Keldysh formalism*

In an out-of-equilibrium situation the perturbative approach is not applicable. However, its generalization to nonequilibrium situations is straightforward. Let us consider an electron system that is described by the following

Hamiltonian

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}(t), \tag{7.207}$$

where $\mathbf{H}_0$ is a noninteracting Hamiltonian and $\mathbf{V}(t)$ is a time-dependent perturbation that can contain external potentials and interaction terms.

As in the equilibrium case, we are interested in the calculation of expectation values of operators like the following one

$$\langle \mathbf{A} \rangle = \frac{\langle \Psi_{\mathrm{H}} | \mathbf{A}_{\mathrm{H}}(t) | \Psi_{\mathrm{H}} \rangle}{\langle \Psi_{\mathrm{H}} | \Psi_{\mathrm{H}} \rangle}, \tag{7.208}$$

where, for the sake of clarity, we consider the expectation value of a single operator rather than the usual product of two of them.

We now change to the interaction picture, where this expectation value becomes

$$\langle \mathbf{A} \rangle = \frac{\langle \Psi_{\mathrm{I}} | \mathbf{A}_{\mathrm{I}}(t) | \Psi_{\mathrm{I}} \rangle}{\langle \Psi_{\mathrm{I}} | \Psi_{\mathrm{I}} \rangle}. \tag{7.209}$$

Although the perturbation in this case may depend on time, one can still assume that the interaction is adiabatically switched on and off at $t = -\infty$ and $t = \infty$, respectively. As usual, this can be done by the replacement $\mathbf{V}(t) \rightarrow \exp(-\epsilon|t|)\mathbf{V}(t)$, where $\epsilon$ is an infinitesimally small positive parameter. In the equilibrium case, the time symmetry is preserved and at time $t = \infty$ we recover the same noninteracting state $|\phi_0\rangle$ that we had at $t = -\infty$ (apart from a phase factor). However, out of equilibrium this symmetry is in general broken and the starting point for the perturbative expansion must be the following one

$$\langle \mathbf{A} \rangle = \frac{\langle \phi_0 | \mathbf{S}(-\infty, t) \mathbf{A}_{\mathrm{I}}(t) \mathbf{S}(t, -\infty) | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}(-\infty, t) \mathbf{S}(t, -\infty) | \phi_0 \rangle}. \tag{7.210}$$

At a first glance, one might think that now the perturbative expansion becomes very cumbersome because we cannot group all the pieces of the time-evolution operator into a single one. Keldysh showed that one can still order the time arguments along a modified time contour. This contour is referred to as *the Keldysh contour* and it is depicted in Fig. 7.21.

On this contour, the time runs from $-\infty$ to $+\infty$ in the upper branch, whereas it does it backwards in the lower one, i.e. from $+\infty$ to $-\infty$. In order to indicate in which branch the time arguments lie, we introduce a subindex that will be equal to $+$ for the upper branch and $-$ for the lower one. With this notation, we can write now the expectation value of Eq. (7.210) as

$$\langle \mathbf{A} \rangle = \frac{\langle \phi_0 | \mathbf{S}_-(-\infty, \infty) \mathbf{S}_+(\infty, t) \mathbf{A}_{\mathrm{I}}(t) \mathbf{S}_+(t, -\infty) | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}_-(-\infty, \infty) \mathbf{S}_+(\infty, t) \mathbf{S}_+(t, -\infty) | \phi_0 \rangle}, \tag{7.211}$$

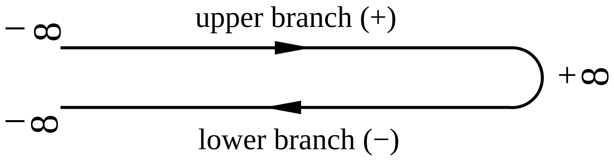

Fig. 7.21 The Keldysh contour.

if $t$ lies in the upper branch or

$$\langle \mathbf{A} \rangle = \frac{\langle \phi_0 | \mathbf{S}_-(-\infty, t) \mathbf{A}_{\rm I}(t) \mathbf{S}_-(t,\infty) \mathbf{S}_+(\infty,-\infty) | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}_-(-\infty, t) \mathbf{S}_-(t,\infty) \mathbf{S}_+(\infty,-\infty) | \phi_0 \rangle}, \tag{7.212}$$

if $t$ lies in the lower one. Defining the operator $\mathbf{T}_c$ that orders the time arguments along the Keldysh contour, we can rewrite the expectation value as

$$\langle \mathbf{A} \rangle = \frac{\langle \phi_0 | \mathbf{T}_c \left[ \mathbf{A}_{\rm I}(t) \mathbf{S}_-(-\infty,\infty) \mathbf{S}_+(\infty,-\infty) \right] | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}_-(-\infty,\infty) \mathbf{S}_+(\infty,-\infty) | \phi_0 \rangle}. \tag{7.213}$$

This expression can be in turn rewritten in a more familiar way by defining the operator that describes the time-evolution along the Keldysh contour

$$\mathbf{S}_c(\infty,-\infty) \equiv \mathbf{S}_-(-\infty,\infty) \mathbf{S}_+(\infty,-\infty). \tag{7.214}$$

With this definition we can finally write the expectation value $\langle \mathbf{A} \rangle$ as follows

$$\langle \mathbf{A} \rangle = \frac{\langle \phi_0 | \mathbf{T}_c \left[ \mathbf{A}_{\rm I}(t) \mathbf{S}_c(\infty,-\infty) \right] | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}_c(\infty,-\infty) | \phi_0 \rangle}. \tag{7.215}$$

Analogously, one can express the expectation value of any operator product.

The expectation value of Eq. (7.215) has formally the same structure as in an equilibrium situation. The main difference is the fact that one has to keep track of the branch in which the time arguments lie ($t_+$ and $t_-$). This implies that when defining the propagators in this formalism, there are four different possibilities depending on the two time arguments. These definitions are analogous to those of the causal function in the equilibrium formalism

$$G_{ij}(t_\alpha, t'_\beta) = -i \frac{\langle \Psi_{\rm H} | \mathbf{T}_c \left[ \mathbf{c}_{i\sigma}(t_\alpha) \mathbf{c}^\dagger_{j\sigma}(t'_\beta) \right] | \Psi_{\rm H} \rangle}{\langle \Psi_{\rm H} | \Psi_{\rm H} \rangle} \tag{7.216}$$

$$G(\mathbf{r}t_\alpha, \mathbf{r}'t'_\beta) = -i \frac{\langle \Psi_{\rm H} | \mathbf{T}_c \left[ \mathbf{\Psi}_\sigma(\mathbf{r}t_\alpha) \mathbf{\Psi}^\dagger_\sigma(\mathbf{r}'t'_\beta) \right] | \Psi_{\rm H} \rangle}{\langle \Psi_{\rm H} | \Psi_{\rm H} \rangle}, \tag{7.217}$$

depending on whether we use the representation $|i\rangle$ or $|\mathbf{r}\rangle$. The subindexes $\alpha$ and $\beta$ take the values $+$ and $-$ and indicate in which branch the time arguments lie. Let us now discuss in detail the expression for the four possible functions:

(1) $\underline{t = t_+ \text{ and } t' = t'_+}$:
In this case both time arguments lie in the upper branch and the corresponding Green's function reads (for a discrete representation)

$$G_{ij}^{++}(t,t') = -i\langle \mathbf{T}\left[\mathbf{c}_{i\sigma}(t)\mathbf{c}_{j\sigma}^{\dagger}(t')\right]\rangle, \tag{7.218}$$

where, from now on, the subindexes $\alpha, \beta = +, -$ will appear as superindexes of the Green's functions. Moreover, in order to simplify the notation, we shall drop the wave functions in the expectation values and we shall not include the denominator $\langle \Psi_{\mathrm{H}} | \Psi_{\mathrm{H}} \rangle$, which indeed turns out to be equal to 1 (see discussion below). Notice that this function is nothing else but the causal Green's function.

(2) $\underline{t = t_+ \text{ and } t' = t'_-}$:
In this case, since any time in the lower branch of the Keldysh contour is "larger" than any time in the upper branch, one has

$$G_{ij}^{+-}(t,t') = i\langle \mathbf{c}_{j\sigma}^{\dagger}(t')\mathbf{c}_{i\sigma}(t)\rangle. \tag{7.219}$$

This function plays a fundamental role in the nonequilibrium Green's functions theory and, as we shall see later, it contains information about the distribution function of the electrons.

(3) $\underline{t = t_- \text{ and } t' = t'_+}$:
In this case we have

$$G_{ij}^{-+}(t,t') = -i\langle \mathbf{c}_{i\sigma}(t)\mathbf{c}_{j\sigma}^{\dagger}(t')\rangle. \tag{7.220}$$

This function contains essentially the same information as $G_{ij}^{+-}(t,t')$.

(4) $\underline{t = t_- \text{ and } t' = t'_-}$
In this last possibility, both time arguments lie in the lower branch, where the arguments are ordered in an antichronological way. Therefore, this new function reads

$$G_{ij}^{--}(t,t') = -i\langle \bar{\mathbf{T}}\left[\mathbf{c}_{i\sigma}(t)\mathbf{c}_{j\sigma}^{\dagger}(t')\right]\rangle, \tag{7.221}$$

where the operator $\bar{\mathbf{T}}$ orders the time arguments in the opposite way as compared with the usual time-ordering operator $\mathbf{T}$, i.e. in a antichronological order.

The four Green's functions defined above can be grouped in a matrix as follows

$$\check{\mathbf{G}} = \begin{pmatrix} \mathbf{G}^{++} & \mathbf{G}^{+-} \\ \mathbf{G}^{-+} & \mathbf{G}^{--} \end{pmatrix}, \tag{7.222}$$

where the check symbol (ˇ) indicates that we are dealing with a $2 \times 2$ matrix in *Keldysh space*. The perturbative expansion couples the different components of this matrix, which effectively leads to an enlargement of the propagator space in a factor of 2. This enlargement is indeed quite natural since in an out-of-equilibrium situation we have to determine not only the states, the information of which is contained in the causal function, but also the distribution function that describes how such states are occupied. This latter information is provided by the off-diagonal functions in Eq. (7.222).

Formally speaking, the perturbative expansion is very similar to the equilibrium one, and one has only to keep track of the matrix structure. An additional complication is that in time-dependent problems, the products are replaced by convolutions over intermediate arguments, which makes the calculations considerably more complicated. Fortunately, transport problems often admit a stationary solution and then, the application of the nonequilibrium formalism is not more complicated than the equilibrium one.

As stated above, apart from the matrix structure introduced by the Keldysh formalism, the rest of the perturbative approach is very similar to the equilibrium one. To derive the perturbative expansion of the matrix propagator of Eq. (7.222), one can use the expression of Eq. (7.215) and expand the operator $\mathbf{S}_c$. Let us recall that $\mathbf{S}_c(\infty,-\infty) \equiv \mathbf{S}_-(-\infty,\infty)\mathbf{S}_+(\infty,-\infty)$ and the perturbative expansions of both time-evolution operators are given by

$$\mathbf{S}_+(\infty,-\infty) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \mathbf{T} \left[ \mathbf{V}_{\mathrm{I}}(t_1) \cdots \mathbf{V}_{\mathrm{I}}(t_n) \right] \quad (7.223)$$

$$\mathbf{S}_-(-\infty,\infty) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{\infty}^{-\infty} dt_1 \cdots \int_{\infty}^{-\infty} dt_n \bar{\mathbf{T}} \left[ \mathbf{V}_{\mathrm{I}}(t_1) \cdots \mathbf{V}_{\mathrm{I}}(t_n) \right].$$

After expanding the operators $\mathbf{S}_+$ and $\mathbf{S}_-$, one applies the Wick's theorem in the standard way. Therefore, the resulting diagrammatic structure is analogous to the one in equilibrium, the main difference being the enlargement of the space that is encoded in the indexes $\alpha$ and $\beta$. We shall discuss the peculiarities of the nonequilibrium diagrammatic expansion in the next section.

Finally, since the structure of the diagrammatic expansion is identical to the equilibrium one, such an expansion can be also summarized in a Dyson's equation, which in the nonequilibrium case has the following matrix form

$$\check{\mathbf{G}}(t,t') = \check{\mathbf{g}}(t,t') + \int dt_1 \int dt_2 \; \check{\mathbf{g}}(t,t_1)\check{\mathbf{\Sigma}}(t_1,t_2)\check{\mathbf{G}}(t_2,t'). \quad (7.224)$$

Here, we have denoted the unperturbed propagators by $\check{\mathbf{g}}$ instead of $\check{\mathbf{G}}^{(0)}$ to simplify the notation. Here, the self-energy has a $2 \times 2$ matrix structure in Keldysh space analogous to Eq. (7.222). In general, the functions appearing in Eq. (7.224) depend on two time arguments and the Dyson's equation is an integral equation. However, in many stationary situations, both the propagators and the self-energies depend on the time difference and, after Fourier transforming, Eq. (7.224) recovers its standard equilibrium form of an algebraic equation with the frequency as the argument, i.e.

$$\check{\mathbf{G}}(E) = \check{\mathbf{g}}(E) + \check{\mathbf{g}}(E)\check{\mathbf{\Sigma}}(E)\check{\mathbf{G}}(E). \tag{7.225}$$

### 7.3.2 *Diagrammatic expansion in the Keldysh formalism*

Let us discuss now some of the peculiarities of the diagrammatic expansion in the Keldysh formalism. One of them is the fact that in this formalism the denominator of the Green's functions does not play any role (indeed $\langle \phi_0 | \mathbf{S}_c | \phi_0 \rangle = 1$). One can show that in the expansion of $\mathbf{S}_c$ the terms of order higher than zero cancel each other order by order. One might think that this fact creates a problem related to the cancellation of the disconnected diagrams. However, this is not the case because, as it is easy to show by applying Wick's theorem, these diagrams also cancel each other. Therefore, as in equilibrium, one needs to consider the topologically distinct diagrams only once.

Let us discuss the diagrammatic structure in two situations of interest:

- **Case 1: Time-dependent external potential.**
  Let us consider a system with $N$ noninteracting electrons subjected to an external potential that can be time-dependent. The Hamiltonian in first quantization reads in this case

  $$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}(t), \tag{7.226}$$

  where

  $$\mathbf{V}(t) = \sum_{i=1}^{N} V(\mathbf{r}_i, t). \tag{7.227}$$

  The diagrams in this case are trivial because, as in the case of a static potential, they consist of the repetition of identical scattering events. The matrix self-energy is therefore given by

  $$\check{\Sigma}(\mathbf{r}, t) = \begin{pmatrix} V(\mathbf{r}, t) & 0 \\ 0 & -V(\mathbf{r}, t) \end{pmatrix}. \tag{7.228}$$

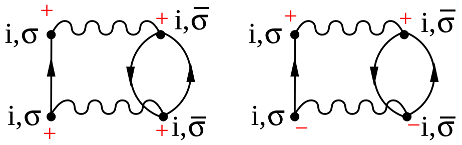

Fig. 7.22 Examples of second-order self-energy diagrams in the Keldysh space for the electron-electron interaction. The indexes + and − indicate in which branch the time arguments lie.

It is interesting to note that for this single-electron perturbation the components $\Sigma^{+-}$ and $\Sigma^{-+}$ vanish. The existence of off-diagonals components of the self-energies in the Keldysh space is only possible in the case of inelastic mechanisms such as electron-electron interaction or electron-phonon interaction (see next case).

- **Case 2: Electron-electron interaction.**
  Let us consider an electronic system where the electron-electron interaction is assumed to be the perturbation. The system might be out of equilibrium due to, for instance, the presence of a current. For the sake of concreteness, let us assume that the unperturbed system can be described by a tight-binding Hamiltonian and the interaction is Hubbard-like

$$\mathbf{H} = \mathbf{H}_0 + \sum_i U \mathbf{n}_{i\uparrow} \mathbf{n}_{i\downarrow}. \qquad (7.229)$$

The diagrams are topologically identical to the equilibrium ones and the only difference is the fact that one has to indicate where the time arguments reside on the Keldysh contour. In this respect, every equilibrium diagram gives rise to several diagrams for the different components of the self-energy in Keldysh space. We illustrate this fact in Fig. 7.22, where we show the self-energy diagrams of second order in $U$ for the components $\Sigma^{++}$ and $\Sigma^{+-}$. The expression of the self-energy $\Sigma^{+-}_{ii}$, for instance, would be (ignoring the spin dependence)

$$\Sigma^{+-}_{ii}(t,t') = U^2 \left[ g^{+-}_{ii}(t,t') \right]^2 g^{-+}_{ii}(t',t). \qquad (7.230)$$

### 7.3.3 *Basic relations and equations in the Keldysh formalism*

In the previous section we have seen that the Dyson's equation has acquired an additional 2 × 2 matrix structure, which gives the impression that one has to solve four times more equations than in the equilibrium case. Indeed, one can show that the different functions in the $2 \times 2$ matrix of Eq. (7.222) are not independent and the number of equations that one has to solve in practice can be reduced to only two. In this sense, the goal of this section is to derive those equations and to discuss the general properties of the Keldysh-Green's functions.

#### 7.3.3.1 *Relations between the Green's functions*

Let us explore the different relations between the functions appearing in the Keldysh formalism. We start by showing that the four Green's functions $G^{++}$, $G^{+-}$, $G^{-+}$ and $G^{--}$ are not independent, but satisfy

$$\mathbf{G}^{++} + \mathbf{G}^{--} = \mathbf{G}^{+-} + \mathbf{G}^{-+}. \tag{7.231}$$

This is a direct consequence of the definition of these functions. Thus for instance,

$$\begin{aligned} G^{++}_{ij}(t,t') &= -i\theta(t-t')\langle \mathbf{c}_{i\sigma}(t)\mathbf{c}^{\dagger}_{j\sigma}(t')\rangle + i\theta(t'-t)\langle \mathbf{c}^{\dagger}_{j\sigma}(t')\mathbf{c}_{i\sigma}(t)\rangle \\ &= \theta(t-t')G^{-+}_{ij}(t,t') + \theta(t'-t)G^{+-}_{ij}(t,t'). \end{aligned} \tag{7.232}$$

Analogously,

$$G^{--}_{ij}(t,t') = \theta(t-t')G^{+-}_{ij}(t,t') + \theta(t'-t)G^{-+}_{ij}(t,t'). \tag{7.233}$$

Adding these two equations, we obtain the relation stated above.

On the other hand, from this relation and using the Dyson's equation in Keldysh space, see Eq. (7.224), one can show the following relation between the different elements of the self-energy matrix in Keldysh space

$$\mathbf{\Sigma}^{++} + \mathbf{\Sigma}^{--} = -\left(\mathbf{\Sigma}^{+-} + \mathbf{\Sigma}^{-+}\right). \tag{7.234}$$

Other important relations are those between the Keldysh-Green's functions and the advanced and retarded functions $G^a$ and $G^r$. Such relations can be found as follows. Using the expression of Eq. (7.232), one obtains

$$G^{++}_{ij}(t,t') - G^{+-}_{ij}(t,t') = -\theta(t-t')\left[G^{+-}_{ij}(t,t') - G^{-+}_{ij}(t,t')\right], \tag{7.235}$$

and using the definitions of $G^{+-}$ and $G^{+-}$, we arrive at

$$\begin{aligned} G^{++}_{ij}(t,t') - G^{+-}_{ij}(t,t') &= -i\theta(t-t')\langle \mathbf{c}_{i\sigma}(t)\mathbf{c}^{\dagger}_{j\sigma}(t') + \mathbf{c}^{\dagger}_{j\sigma}(t')\mathbf{c}_{i\sigma}(t)\rangle \\ &= G^{r}_{ij}(t,t') \end{aligned} \tag{7.236}$$

Proceeding in an analogous way, one can show the following relations

$$\mathbf{G}^{r} = \mathbf{G}^{++} - \mathbf{G}^{+-} = \mathbf{G}^{-+} - \mathbf{G}^{--} \tag{7.237}$$

$$\mathbf{G}^{a} = \mathbf{G}^{++} - \mathbf{G}^{-+} = \mathbf{G}^{+-} - \mathbf{G}^{--}. \tag{7.238}$$

These relations are crucial for the discussion of next section.

### 7.3.3.2 *The triangular representation*

As we have seen above, there are redundancies in the Green's functions and in that sense it is natural to try to get rid of them to simplify the equations as much as possible. In what follows, we shall try to eliminate $G^{++}$ and $G^{--}$ in favor of $G^r$ and $G^a$. For this purpose, we will apply a unitary transformation to perform the following change

$$\begin{pmatrix} \mathbf{G}^{++} & \mathbf{G}^{+-} \\ \mathbf{G}^{-+} & \mathbf{G}^{--} \end{pmatrix} \longrightarrow \begin{pmatrix} \mathbf{0} & \mathbf{G}^a \\ \mathbf{G}^r & \mathbf{G}^K \end{pmatrix}, \tag{7.239}$$

where $\mathbf{G}^K = \mathbf{G}^{++} + \mathbf{G}^{--} = \mathbf{G}^{+-} + \mathbf{G}^{-+}$ is known as the Keldysh function.

It is easy to show that the unitary transformation has the form

$$\check{\mathbf{R}} = \frac{1}{\sqrt{2}} \begin{pmatrix} \mathbf{1} & -\mathbf{1} \\ \mathbf{1} & \mathbf{1} \end{pmatrix} = \frac{1}{\sqrt{2}} (\check{\mathbf{1}} - i\check{\sigma}_y), \tag{7.240}$$

where $\check{\sigma}_y$ is the corresponding Pauli matrix. The representation above is known as the *triangular representation* and it is important from the practical point of view. Let us now denote the standard Keldysh matrix by $\check{\mathbf{G}}$ and the corresponding matrix in the triangular representation as $\tilde{\mathbf{G}}$. They are related by $\tilde{\mathbf{G}} = \check{\mathbf{R}}\check{\mathbf{G}}\check{\mathbf{R}}^{-1}$. Applying the transformation $\check{\mathbf{R}}$ to the Dyson's equation[21]

$$\check{\mathbf{G}} = \check{\mathbf{g}} + \check{\mathbf{g}}\check{\mathbf{\Sigma}}\check{\mathbf{G}}, \tag{7.241}$$

we obtain the corresponding Dyson's equation in the triangular representation

$$\tilde{\mathbf{G}} = \tilde{\mathbf{g}} + \tilde{\mathbf{g}}\tilde{\mathbf{\Sigma}}\tilde{\mathbf{G}}, \tag{7.242}$$

where the self-energy in this representation has the form

$$\tilde{\mathbf{\Sigma}} = \begin{pmatrix} \mathbf{\Sigma}^K & \mathbf{\Sigma}^r \\ \mathbf{\Sigma}^a & 0 \end{pmatrix}. \tag{7.243}$$

Here, the new self-energy components are expressed in terms of those of the original representation as follows

$$\mathbf{\Sigma}^K = \mathbf{\Sigma}^{++} + \mathbf{\Sigma}^{--} = -\left(\mathbf{\Sigma}^{+-} + \mathbf{\Sigma}^{-+}\right) \tag{7.244}$$

$$\mathbf{\Sigma}^r = \mathbf{\Sigma}^{++} + \mathbf{\Sigma}^{+-} = -\left(\mathbf{\Sigma}^{--} + \mathbf{\Sigma}^{-+}\right) \tag{7.245}$$

$$\mathbf{\Sigma}^a = \mathbf{\Sigma}^{++} + \mathbf{\Sigma}^{-+} = -\left(\mathbf{\Sigma}^{--} + \mathbf{\Sigma}^{+-}\right). \tag{7.246}$$

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[21] In this equation, as in the next ones, the integrations over the intermediate arguments are implicitly assumed.

From Eqs. (7.242) and (7.243) one can show that the advanced and retarded Green's functions satisfy independent Dyson's equations, i.e.

$$\mathbf{G}^{r,a} = \mathbf{g}^{r,a} + \mathbf{g}^{r,a}\mathbf{\Sigma}^{r,a}\mathbf{G}^{r,a}. \tag{7.247}$$

Notice that this equation is formally identical to the equilibrium one. In the case in which the perturbation is an external potential, as we showed in the previous section, the corresponding self-energies reduce to $\Sigma^a(\mathbf{r},t) = \Sigma^r(\mathbf{r},t) = V(\mathbf{r},t)$, i.e. like in equilibrium.

On the other hand, the Keldysh function $\mathbf{G}^K$ fulfills the following equation

$$\mathbf{G}^K = \mathbf{g}^K + \mathbf{g}^K\mathbf{\Sigma}^a\mathbf{G}^a + \mathbf{g}^r\mathbf{\Sigma}^r\mathbf{G}^K + \mathbf{g}^r\mathbf{\Sigma}^K\mathbf{G}^a. \tag{7.248}$$

Notice now that $\mathbf{G}^K$ is coupled to $\mathbf{G}^{r,a}$ and this equation requires to solve first Dyson's equation for these latter functions. Let us recall that the retarded and advanced functions are related, which in practice means that there are only two functions to be determined, as we stated at the beginning of this section.

The previous equation can be written in a more symmetric way as follows. We first group on the left hand side all the terms containing $\mathbf{G}^K$ and then we multiply from the left by $(\mathbf{1} - \mathbf{g}^r\mathbf{\Sigma}^r)^{-1}$ on both sides of the equation to arrive at

$$\mathbf{G}^K = (\mathbf{1} - \mathbf{g}^r\mathbf{\Sigma}^r)^{-1}\mathbf{g}^K(\mathbf{1} + \mathbf{\Sigma}^a\mathbf{G}^a) + (\mathbf{1} - \mathbf{g}^r\mathbf{\Sigma}^r)^{-1}\mathbf{g}^r\mathbf{\Sigma}^K\mathbf{G}^a. \tag{7.249}$$

Then, using the Dyson's equation for the retarded function, we finally obtain

$$\mathbf{G}^K = (\mathbf{1} + \mathbf{G}^r\mathbf{\Sigma}^r)\,\mathbf{g}^K(\mathbf{1} + \mathbf{\Sigma}^a\mathbf{G}^a) + \mathbf{G}^r\mathbf{\Sigma}^K\mathbf{G}^a. \tag{7.250}$$

In this course, we shall mainly use the function $\mathbf{G}^{+-}$, rather than the Keldysh function $\mathbf{G}^K$. For this reason, we now proceed to derive the corresponding equation for $\mathbf{G}^{+-}$. We first take the element $+-$ in the Dyson's equation, i.e.

$$\mathbf{G}^{+-} = \mathbf{g}^{+-} + (\mathbf{g}\mathbf{\Sigma}\mathbf{G})^{+-}. \tag{7.251}$$

Then, we make use of the relations derived above between the different functions to arrive at

$$\mathbf{G}^{+-} = \mathbf{g}^{+-} + \mathbf{g}^{+-}\mathbf{\Sigma}^a\mathbf{G}^a + \mathbf{g}^r\mathbf{\Sigma}^r\mathbf{G}^{+-} - \mathbf{g}^r\mathbf{\Sigma}^{+-}\mathbf{G}^a. \tag{7.252}$$

The function $G^{-+}$ fulfills a similar equation that can be obtained from the previous one by exchanging + by − and vice versa. Eq. (7.252) for $\mathbf{G}^{+-}$ can be written in a more symmetric way, in analogy with what we did for the function $\mathbf{G}^K$. Thus, we obtain finally

$$\boxed{\mathbf{G}^{+-} = (\mathbf{1} + \mathbf{G}^r\mathbf{\Sigma}^r)\,\mathbf{g}^{+-}(\mathbf{1} + \mathbf{\Sigma}^a\mathbf{G}^a) - \mathbf{G}^r\mathbf{\Sigma}^{+-}\mathbf{G}^a} \tag{7.253}$$

The function $\mathbf{G}^{-+}$ satisfies a similar equation given by

$$\boxed{\mathbf{G}^{-+} = (\mathbf{1} + \mathbf{G}^r\mathbf{\Sigma}^r)\,\mathbf{g}^{-+}(\mathbf{1} + \mathbf{\Sigma}^a\mathbf{G}^a) - \mathbf{G}^r\mathbf{\Sigma}^{-+}\mathbf{G}^a} \tag{7.254}$$

#### 7.3.3.3 *Unperturbed Keldysh-Green's functions*

In the Keldysh formalism the time dependence is introduced through the perturbation and the unperturbed Hamiltonian $\mathbf{H}_0$ must correspond to a noninteracting electron system in equilibrium. Thus, all unperturbed Green's functions depend only on the time difference and they are easy to obtain in energy space. The form and properties of the unperturbed retarded, advanced and causal functions in energy space were studied in detail in section 7, whereas the properties of the functions $\mathbf{g}^{--}(E)$ can be easily deduced from those of $\mathbf{g}^{++}(E)$. Thus, we concentrate now on the analysis of the functions $\mathbf{g}^{+-}(E)$ and $\mathbf{g}^{-+}(E)$. From its definition in the time domain (and in a discrete basis)

$$G_{ij}^{+-}(t) = i\langle \mathbf{c}_{j\sigma}^{\dagger}(0)\mathbf{c}_{i\sigma}(t)\rangle, \tag{7.255}$$

it is obvious that this function is related to the electron distribution in equilibrium. Although the temperature does not appear explicitly in the Keldysh formalism, one uses the previous fact to introduce it. Thus, the previous expression for $t = 0$ and $i = j$ reads

$$G_{ii}^{+-}(0) = i\langle \mathbf{n}_{i\sigma}\rangle = \int_{-\infty}^{\infty} \frac{dE}{2\pi} G_{ii}^{+-}(E). \tag{7.256}$$

This implies that $G_{ii}^{+-}(E) = 2\pi i \rho_i(E) f(E)$, where $f(E)$ is the Fermi function and $\rho_i(E)$ is the local density of states in the site $i$. In the same way, one can show that $G_{ii}^{-+}(E) = -2\pi i \rho_i(E)[1 - f(E)]$. Taking into account this result, it is clear that $G^{+-} \propto f(E)$ and $G^{-+} \propto 1 - f(E)$. This fact together with the general relation

$$\mathbf{G}^a(t) - \mathbf{G}^r(t) = \mathbf{G}^{+-}(t) - \mathbf{G}^{-+}(t), \tag{7.257}$$

leads to the following relations

$$\mathbf{G}^{+-}(E) = [\mathbf{G}^a(E) - \mathbf{G}^r(E)]\, f(E) \tag{7.258}$$

$$\mathbf{G}^{-+}(E) = -[\mathbf{G}^a(E) - \mathbf{G}^r(E)]\,[1 - f(E)]\,. \tag{7.259}$$

It is worth stressing that we have written the previous expressions using capital letters to indicate that these expressions are always valid in equilibrium, even in an interacting case. In the Keldysh formalism the unperturbed system is moreover non-interacting, which implies that in a basis $|i\rangle$ one has

$$\begin{aligned} g_{ij}^{+-}(E) &= \left[g_{ij}^a(E) - g_{ij}^r(E)\right] f(E) \\ g_{ij}^{-+}(E) &= -\left[g_{ij}^a(E) - g_{ij}^r(E)\right]\left[1 - f(E)\right]. \end{aligned} \tag{7.260}$$

As a consequence, these functions are proportional to the spectral densities and to the thermal distribution function. The way in which we have introduced the temperature in the Keldysh formalism is certainly not very satisfactory. However, one can show that a rigorous derivation leads exactly to the result that we have just described.

#### 7.3.3.4 *Some comments on the notation*

The notation used here for the different Keldysh-Green's functions is not shared by all the authors. In this sense, it is important to devote a few lines to make contact with other texts where the Keldysh formalism is described.

Frequently, the functions $G^{+-}$ and $G^{-+}$ are denoted by $G^{<}$ and $G^{>}$, respectively. Sometimes, the Keldysh function $G^K$ is denoted by $G^F$ or simply by $F$. On the other hand, the triangular representation is often written in a slightly different way. One first defines a new matrix function as $\bar{\mathbf{G}} = \sigma_z \check{\mathbf{G}}$, where $\sigma_z$ is the Pauli matrix, and then the unitary transformation of Eq. (7.240) is applied. This leads to a $2 \times 2$ matrix with the form

$$\begin{pmatrix} \mathbf{G}^r & \mathbf{G}^K \\ \mathbf{0} & \mathbf{G}^a \end{pmatrix}, \tag{7.261}$$

which is often used in the field of superconductivity.

### 7.3.4 *Application of Keldysh formalism to simple transport problems*

In this section we shall illustrate the utility of the Keldysh formalism by applying it to the description of the electronic transport in some simple situations of special interest. Our goal is two-fold. First, we want to illustrate how this formalism is used in practice and second, we want to show how the elastic transmission can be computed from an atomistic point of view.

Most of the systems that we have in mind (atomic contacts, molecular junctions, etc.) are conveniently described by a tight-binding Hamiltonian of the following form

$$\mathbf{H} = \sum_{i\sigma} \epsilon_i \mathbf{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} \left( \mathbf{c}^{\dagger}_{i\sigma} \mathbf{c}_{j\sigma} + \mathbf{c}^{\dagger}_{j\sigma} \mathbf{c}_{i\sigma} \right), \tag{7.262}$$

where we have assumed, without loss of generality, that the hopping elements $t_{ij}$ are real. Our first task is to derive an expression for the electrical current operator in this local basis. For this purpose, we first consider the

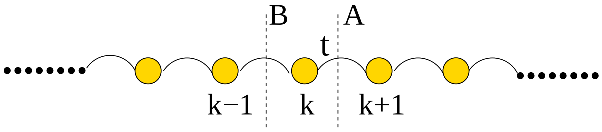

Fig. 7.23 Schematic representation of a linear chain with only nearest-neighbor hoppings.

simple case of a tight-binding chain with only nearest-neighbor hoppings, denoted by $t$. Such a chain is schematically represented in Fig. 7.23. Let us compute now the current between the sites $k$ and $k+1$. Without doing any calculation, one can guess that the operator must adopt somehow the following form[22]

$$\mathbf{I} \propto t \sum_{\sigma} \left[ \mathbf{c}^{\dagger}_{k\sigma}(t)\mathbf{c}_{k+1\sigma}(t) - \mathbf{c}^{\dagger}_{k+1\sigma}(t)\mathbf{c}_{k\sigma}(t) \right] , \tag{7.263}$$

where the first term in the sum represents the current flowing in one direction and second one corresponds to the current flowing in the opposite one. Let us see if a rigorous calculation confirms our intuition.

The current operator must be obtained from the continuity equation that describes the charge conservation. Such equation can be written in a discrete representation as

$$\mathbf{I}_A - \mathbf{I}_B + \frac{\partial \rho_k}{\partial t} = 0, \tag{7.264}$$

where $A$ represents a point between the sites $k$ and $k+1$ and $B$ a point between $k-1$ and $k$, see Fig. 7.23. Here, $\rho_k$ is the operator that describes the charge in the site $k$

$$\rho_k = e \sum_{\sigma} \mathbf{c}^{\dagger}_{k\sigma}\mathbf{c}_{k\sigma} \tag{7.265}$$

and satisfies the equation of motion of Heisenberg operators

$$\frac{\partial \rho_k}{\partial t} = -\frac{i}{\hbar} \left[ \rho_k, \mathbf{H} \right] . \tag{7.266}$$

Notice that we have reintroduced $\hbar$, and we shall write it explicitly from now on. Using the expression of Eq. (7.262) for the homogeneous chain that we are considering, it is straightforward to compute the commutator that appears in the previous equation of motion and thus, one arrives at

$$\frac{\partial \rho_k}{\partial t} = \frac{-iet}{\hbar} \sum_{\sigma} \left\{ \mathbf{c}^{\dagger}_{k\sigma}\mathbf{c}_{k+1\sigma} - \mathbf{c}^{\dagger}_{k+1\sigma}\mathbf{c}_{k\sigma} + \mathbf{c}^{\dagger}_{k\sigma}\mathbf{c}_{k-1\sigma} - \mathbf{c}^{\dagger}_{k-1\sigma}\mathbf{c}_{k\sigma} \right\} .$$

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[22] We believe that no confusion can arise between the hopping $t$ and the time appearing as an argument in the creation and annihilation operators.

Rewriting this expression in the form of the continuity equation, see Eq. (7.264), we can identify the current operator, which at point $A$ takes the form

$$\mathbf{I}_A(t) = \frac{iet}{\hbar} \sum_\sigma \left\{ \mathbf{c}^\dagger_{k\sigma}(t)\mathbf{c}_{k+1\sigma}(t) - \mathbf{c}^\dagger_{k+1\sigma}(t)\mathbf{c}_{k\sigma}(t) \right\}. \qquad (7.267)$$

Notice that this has exactly the intuitive form that we had anticipated above.

This expression can be easily generalized to any 3D system described by a tight-binding Hamiltonian as in Eq. (7.262). The electrical current through an arbitrary surface that separates two regions A and B is given by

$$\mathbf{I}(t) = \frac{ie}{\hbar} \sum_{i\in A; j\in B} \sum_\sigma t_{ij} \left\{ \mathbf{c}^\dagger_{i\sigma}(t)\mathbf{c}_{j\sigma}(t) - \mathbf{c}^\dagger_{j\sigma}(t)\mathbf{c}_{i\sigma}(t) \right\}. \qquad (7.268)$$

Let us now compute the expectation value of the current operator, for instance, for the case of the chain. According to Eq. (7.267), one can write (dropping the subindex $A$)

$$\langle \mathbf{I}(t) \rangle = \frac{iet}{\hbar} \sum_\sigma \left\{ \langle \mathbf{c}^\dagger_{k\sigma}(t)\mathbf{c}_{k+1\sigma}(t) \rangle - \langle \mathbf{c}^\dagger_{k+1\sigma}(t)\mathbf{c}_{k\sigma}(t) \rangle \right\}. \qquad (7.269)$$

The expectation values appearing in the previous equation can be expressed in terms of the Keldysh functions $G^{+-}$ as follows

$$\langle \mathbf{I}(t) \rangle = \frac{e}{\hbar} t \sum_\sigma \left\{ G^{+-}_{k+1,k}(t,t) - G^{+-}_{k,k+1}(t,t) \right\}, \qquad (7.270)$$

and there is a similar expression for the most general case of Eq. (7.268). In many situations, for instance when there is a constant voltage applied in a junction, the problem admits a stationary solution and the Green's functions depend exclusively on the difference of the time arguments. In those cases, Eq. (7.270) can be written in terms of the Green's functions in energy space as

$$\langle \mathbf{I} \rangle = \frac{e}{\hbar} t \sum_\sigma \int_{-\infty}^{\infty} \frac{dE}{2\pi} \left\{ G^{+-}_{k+1,k}(E) - G^{+-}_{k,k+1}(E) \right\}. \qquad (7.271)$$

We are now in position to discuss the electronic transport in some simple examples of special interest.

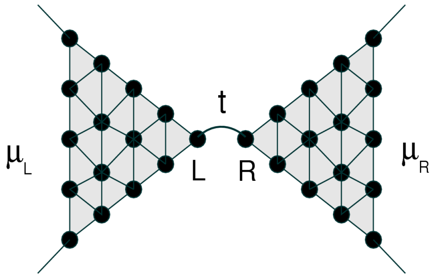

Fig. 7.24 Schematic representation of a single-channel atomic contact. The electrodes are coupled via the hopping element $t$ that describes the coupling between the two outermost atoms of both leads, denoted by $L$ and $R$. There is a bias voltage applied across the system giving rise to a difference in the chemical potential of the electrodes: $eV = \mu_L - \mu_R$.

### 7.3.4.1 *Electrical current through a metallic atomic contact*

As a first example, we consider an atomic constriction. For the sake of simplicity, we consider the case of a metal described by a tight-binding Hamiltonian with a single relevant atomic orbital per site. We assume that the two electrodes forming the atomic junction are only coupled through their outermost atoms, denoted as $L$ and $R$, via a single hopping element $t$. This situation is schematically represented in Fig. 7.24. Here, the specific shape of the electrodes is irrelevant for our discussion. As it will become clear later, this is a model for a contact with a single conduction channel and if everything is consistent, we should arrive at the Landauer formula. However, contrary to the scattering approach, we will now be able to obtain a microscopic expression for the transmission coefficient in terms of the coupling element $t$ and the local electronic structure of the electrodes.

This model system is described by the following tight-binding Hamiltonian

$$\mathbf{H} = \mathbf{H}_L + \mathbf{H}_R + \sum_{\sigma} t \left( \mathbf{c}^{\dagger}_{L\sigma} \mathbf{c}_{R\sigma} + \mathbf{c}^{\dagger}_{R\sigma} \mathbf{c}_{L\sigma} \right), \tag{7.272}$$

where $\mathbf{H}_L$ and $\mathbf{H}_R$ are the Hamiltonians describing the left and right electrodes, respectively. We assume that there is a bias voltage $V$ applied across the contact and that the potential drops abruptly in the interface region. The task in this example is to compute the current-voltage characteristics. According to Eqs. (7.269-7.271), the current evaluated at the interface between the electrodes is given by[23]

$$I = \langle \mathbf{I} \rangle = \frac{2et}{h} \int_{-\infty}^{\infty} dE \left[ G_{RL}^{+-}(E) - G_{LR}^{+-}(E) \right], \tag{7.273}$$

where the factor 2 is due to the spin degeneracy in this problem. At this stage the problem is to determine the Green's functions appearing in Eq. (7.273). For this purpose, we employ the perturbative method that we have just described in the previous sections. Therefore, the first thing that we need to do is to choose the perturbation. Let us remind that in the Keldysh formalism the unperturbed system has to be in equilibrium. One possibility would be to introduce the voltage as a perturbation, but this is not very convenient because such a perturbation is extended over the whole system and the calculation would be rather cumbersome. The most convenient choice is to treat the coupling term in Eq. (7.272) as the perturbation and include the voltage in the unperturbed Hamiltonians by shifting the corresponding chemical potential (e.g. $\mu_L = eV$ and $\mu_R = 0$).[24]

With this choice, the retarded and advanced self-energies associated to this single-particle perturbation adopt the form

$$\Sigma_{LR}^{r,a} = \Sigma_{RL}^{r,a} = t, \tag{7.274}$$

while the Keldysh self-energies vanish: $\Sigma^{+-} = \Sigma^{-+} = 0$ (there are no inelastic interactions). Now, the functions $G_{LR}^{+-}$ and $G_{RL}^{+-}$ appearing in the expression of the current can be determined in terms of the Green's functions of the uncoupled electrodes (unperturbed functions) using Eq. (7.253). But before doing so, we can simplify the algebra by writing the current in terms of the diagonal Green's functions of both electrodes. For this purpose, we compute $G_{LR}^{+-}$ making use of Eq. (7.252) by writing it as (remember that $\Sigma^{+-} = 0$ in this problem)

$$\mathbf{G}^{+-} = \mathbf{g}^{+-} + \mathbf{g}^{+-} \mathbf{\Sigma}^a \mathbf{G}^a + \mathbf{g}^r \mathbf{\Sigma}^r \mathbf{G}^{+-}, \tag{7.275}$$

while we compute $G_{RL}^{+-}$ using this equation, but written in the following alternative form:

$$\mathbf{G}^{+-} = \mathbf{g}^{+-} + \mathbf{G}^{+-} \mathbf{\Sigma}^a \mathbf{g}^a + \mathbf{G}^r \mathbf{\Sigma}^r \mathbf{g}^{+-}. \tag{7.276}$$

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[23] We assume that the voltage is time-independent and therefore the problem admits a stationary solution. This allows us to write the current in terms of the Fourier transform of the Green's functions with respect to the difference of the time arguments.

[24] This does not mean that the unperturbed system is out of equilibrium since in the absence of coupling, there is no current and the electron distributions in both leads are the equilibrium ones.

It is important to emphasize that these equations are algebraic equations in energy space and we shall often omit, as we have just done, the energy argument of the Green's functions, $E$, to abbreviate the notation.

Using the last two equations, we can write $G^{+-}_{LR}$ and $G^{+-}_{RL}$ as

$$G^{+-}_{LR} = g^{+-}_{LL}\Sigma^a_{LR}G^a_{RR} + g^r_{LL}\Sigma^r_{LR}G^{+-}_{RR}, \tag{7.277}$$

$$G^{+-}_{RL} = G^{+-}_{RR}\Sigma^a_{RL}g^a_{LL} + G^r_{RR}\Sigma^r_{RL}g^{+-}_{LL}. \tag{7.278}$$

Substituting now $G^{+-}_{LR}$ and $G^{+-}_{RL}$ in Eq. (7.273) and using the general relation $\mathbf{G}^a - \mathbf{G}^r = \mathbf{G}^{+-} - \mathbf{G}^{-+}$, one arrives at

$$I = \frac{2e}{h}t^2\int_{-\infty}^{\infty} dE\left[g^{+-}_{LL}(E)G^{-+}_{RR}(E) - g^{-+}_{LL}(E)G^{+-}_{RR}(E)\right]. \tag{7.279}$$

We now compute the functions $G^{+-}_{RR}$ and $G^{-+}_{RR}$ by using Eqs. (7.253) and (7.254)

$$G^{+-/-+}_{RR} = \left(1 + G^r_{RL}\Sigma^r_{LR}\right) g^{+-/-+}_{RR}\left(1 + \Sigma^a_{RL}G^a_{LR}\right) + \tag{7.280}$$

$$G^r_{RR}\Sigma^r_{RL}g^{+-/-+}_{LL}\Sigma^a_{LR}G^a_{RR}. \tag{7.281}$$

Introducing these expressions in Eq. (7.279) we obtain

$$I = \frac{2e}{h}t^2\int_{-\infty}^{\infty} dE\,\left|1 + tG^r_{RL}(E)\right|^2\left[g^{+-}_{LL}(E)g^{-+}_{RR}(E) - g^{-+}_{LL}(E)g^{+-}_{RR}(E)\right]. \tag{7.282}$$

Here, we have used the explicit expression of the self-energies, see Eq. (7.274), and the fact that $\mathbf{G}^a(E) = [\mathbf{G}^r(E)]^\dagger$ (thus e.g., $G^a_{LR}(E) = [G^r_{RL}(E)]^*$).

To complete the calculation we still have to determine the retarded function $G^r_{RL}(E)$. This can be done, very much like in equilibrium, using its Dyson's equation, see Eq. (7.247). Taking the element $(R, L)$ we arrive at

$$G^r_{RL} = g^r_{RR}\Sigma^r_{RL}G^r_{LL}. \tag{7.283}$$

To close this equation, we need now an equation for $G^r_{LL}$, which is obtained by taking the element $(L, L)$ in the Dyson's equation, i.e.

$$G^r_{LL} = g^r_{LL} + g^r_{LL}\Sigma_{LR}G^r_{RL}. \tag{7.284}$$

Substituting back into the equation for $G^r_{RL}$, we obtain finally

$$G^r_{RL} = \frac{tg^r_{RR}g^r_{LL}}{1 - t^2g^r_{RR}g^r_{LL}} \text{ and } 1 + tG^r_{RL} = \frac{1}{1 - t^2g^r_{RR}g^r_{LL}}. \tag{7.285}$$

Before coming back to the expression of current, let us remind that the unperturbed Keldysh functions $\mathbf{g}^{+-/-+}$ can be expressed in terms of the retarded and advanced ones using Eq. (7.260). Thus, the functions appearing in Eq. (7.282) can be written as

$$\begin{aligned} g^{+-}_{LL}(E) &= \left[g^a_{LL}(E-eV) - g^r_{LL}(E-eV)\right] f(E-eV) \\ &= 2\pi i \rho_L(E-eV) f(E-eV) \\ g^{-+}_{LL}(E) &= -\left[g^a_{LL}(E-eV) - g^r_{LL}(E-eV)\right]\left[1 - f(E-eV)\right] \\ &= -2\pi i \rho_L(E-eV)\left[1 - f(E-eV)\right] \\ g^{+-}_{RR}(E) &= \left[g^a_{RR}(E) - g^r_{RR}(E)\right] f(E) = 2\pi i \rho_R(E) f(E) \\ g^{-+}_{RR}(E) &= -\left[g^a_{RR}(E) - g^r_{RR}(E)\right]\left[1 - f(E)\right] = -2\pi i \rho_R(E)\left[1 - f(E)\right], \end{aligned} \tag{7.286}$$

where $f(E)$ is the Fermi function and $\rho_{L/R}$ is the local density of states of the leads projected onto the sites $L$ and $R$. Notice that we have already taken into account the relative shift of the chemical potentials due to the bias voltage $V$.

Using Eqs. (7.285) and (7.286), we can finally write the current as follows[25]

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \, \frac{4\pi^2 t^2 \rho_L(E-eV)\rho_R(E)}{|1 - t^2 g_{LL}(E-eV) g_{RR}(E)|^2} \left[f(E-eV) - f(E)\right]. \tag{7.287}$$

Notice that Eq. (7.287) has exactly the form of the Landauer formula, i.e.

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \, T(E,V) \left[f(E-eV) - f(E)\right], \tag{7.288}$$

where we can identify $T(E,V)$ as an energy and voltage-dependent transmission probability given by

$$T(E,V) = \frac{4\pi^2 t^2 \rho_L(E-eV)\rho_R(E)}{|1 - t^2 g_{LL}(E-eV) g_{RR}(E)|^2}. \tag{7.289}$$

As it can be seen, the transmission depends primarily on the coupling element $t$ and the local electronic structure of the leads.

For sufficiently low voltages, there is a linear regime where the current is proportional to the voltage. In this limit, the conductance is given by $G = (2e^2/h) T(E_\mathrm{F}, V=0)$, where $T(E_\mathrm{F}, V=0)$ is the zero-bias transmission at the Fermi energy given by

$$T(E_\mathrm{F}, V=0) = \frac{4\pi^2 t^2 \rho_L(E_\mathrm{F})\rho_R(E_\mathrm{F})}{|1 - t^2 g_{LL}(E_\mathrm{F}) g_{RR}(E_\mathrm{F})|^2}. \tag{7.290}$$

One can often consider that the Green's functions are constant around the Fermi energy and one can also neglect their real part (this is the wide-band

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[25] This expression for the current was first derived in Ref. [14] for a more realistic model.

approximation introduced in section 7). This means that the lead Green's functions can be approximated by

$$g^a_{LL} \approx \frac{i}{W}, \tag{7.291}$$

where $W = 1/\pi \rho_{L/R}(E_\mathrm{F})$ (we are assuming that the contact is symmetric, $g_{LL} = g_{RR}$, for simplicity). Within this approximation, one obtains the following expression for the transmission

$$T = \frac{4t^2/W^2}{(1+t^2/W^2)^2}. \tag{7.292}$$

This expression illustrates the transition from the tunnel regime, when the electrodes are separated by a large distance, to the contact regime at small distances. In the former limit, the transmission given in Eq. (7.292) can be approximated by $4t^2/W^2$. This means that the dependence of the transmission on the distance between the electrodes, and therefore that of the linear conductance, is determined by $t^2$. At large distances, a hopping element is roughly proportional to the overlap of the atomic orbitals and decays exponentially with the distance between the corresponding atoms. This is how the exponential length dependence in a tunnel junction comes about from an atomistic point of view.

When the electrodes approach each other the hopping $t$ becomes of the same order as the energy scale $W$ and the transmission can reach unity and in turn the conductance approaches the quantum of conductance $G_0 = 2e^2/h$. The transition from tunnel has been extensively studied in the context of the STM (for a recent overview, see Refs. [15, 16]).

Let us now study in more detail the tunnel limit ($t \to 0$). In this case, the non-linear current of Eq. (7.287) can be approximated by

$$I = \frac{8\pi^2 e}{h} t^2 \int_{-\infty}^{\infty} dE \; \rho_L(E-eV)\rho_R(E) \left[ f(E-eV) - f(E) \right], \tag{7.293}$$

which tell us that the current in this limit is determined by the convolution of the local density of states of both electrodes. This well-known expression is a fundamental result for the theory of STM and provides a simple interpretation of the STM images. Assuming that the left electrode represents a STM tip with a constant density of states around the Fermi energy, the differential conductance at low temperatures is simply given by

$$G(V) = \frac{dI}{dV} = \frac{2e^2}{h} 4\pi^2 t^2 \rho_L(E_\mathrm{F}) \rho_R(E_\mathrm{F} + eV), \tag{7.294}$$

i.e. the conductance is a measure of the local density of states of the sample (or of the right electrode in our case).

### 7.3.4.2 *Current through a resonant level*

Let us now discuss the calculation of the current for the resonant level model discussed in section 7.1.3.3. Let us remind that in this model a single quantum level is coupled to two metallic electrodes and the corresponding Hamiltonian is given by

$$\begin{aligned}\mathbf{H} = \mathbf{H}_L + \mathbf{H}_R + \sum_\sigma \epsilon_0 \mathbf{n}_{0\sigma} + \qquad\qquad\qquad\qquad\qquad\qquad \qquad (7.295)\\ \sum_\sigma t_L \left( \mathbf{c}^\dagger_{L\sigma}\mathbf{c}_{0\sigma} + \mathbf{c}^\dagger_{0\sigma}\mathbf{c}_{L\sigma} \right) + \sum_\sigma t_R \left( \mathbf{c}^\dagger_{R\sigma}\mathbf{c}_{0\sigma} + \mathbf{c}^\dagger_{0\sigma}\mathbf{c}_{R\sigma} \right),\end{aligned}$$

where $\epsilon_0$ is the position of the resonant level, which in principle can also depend on the bias voltage, and $t_{L,R}$ are the matrix elements describing the coupling to the reservoirs. Here, $L$ and $R$ denote the outermost sites of the left and right electrodes, respectively. On the other hand, we now assume that there is a constant bias voltage across the system and our task is to compute the current-voltage characteristics.

We start by evaluating the current at the interface between the left electrode and the level, which in terms of the Green's functions $G^{+-}$ can be written as follows

$$I = \frac{2et_L}{h} \int_{-\infty}^{\infty} dE \, \left[ G^{+-}_{L0}(E) - G^{+-}_{0L}(E) \right]. \qquad (7.296)$$

In order to determine the Green's functions in the previous expression, we use again the Keldysh formalism and we treat the coupling terms between the level and the electrodes, i.e. the second line in Eq. (7.295), as a perturbation. With this choice the only non-vanishing elements of the self-energy are: $\Sigma^{r,a}_{L0} = \Sigma^{r,a}_{0L} = t_L$ and $\Sigma^{r,a}_{R0} = \Sigma^{r,a}_{0R} = t_R$.

Following now the same steps as in section 7.3.4.1, we can write the current in terms of diagonal elements of the Green's functions as

$$I = \frac{2et_L^2}{h} \int_{-\infty}^{\infty} dE \, \left[ g^{+-}_{LL}(E) G^{-+}_{00}(E) - g^{-+}_{LL}(E) G^{+-}_{00}(E) \right]. \qquad (7.297)$$

Now, to determine the full Green's functions, we use the Dyson's equation, Eq. (7.253), to write

$$\begin{aligned}G^{+-/-+}_{00} = \left(\mathbf{1} + \mathbf{G}^r\boldsymbol{\Sigma}^r\right)_{00} g^{+-/-+}_{00} \left(\mathbf{1} + \boldsymbol{\Sigma}^a\mathbf{G}^a\right)_{00} + \qquad (7.298)\\ G^r_{00}\Sigma^r_{0L} g^{+-/-+}_{LL} \Sigma^a_{L0} G^a_{00} + G^r_{00}\Sigma^r_{0R} g^{+-/-+}_{RR} \Sigma^a_{R0} G^a_{00}.\end{aligned}$$

If we now substitute this expression into the current formula, the term containing $g^{+-/-+}_{LL}$ is canceled. Moreover, the term proportional to $g^{+-/-+}_{00}$ does not contribute either. The reason is that $g^{+-/-+}_{00}(E) \propto \delta(E - \epsilon_0)$ and the prefactor of this term vanishes at $E = \epsilon_0$.[26] Thus, the current can now be expressed as

$$I = \frac{2e}{h} 4\pi^2 t_L^2 t_R^2 \int_{-\infty}^{\infty} dE \; \rho_L(E) \rho_R(E) |G_{00}^r(E)|^2 \left[ f_L(E) - f_R(E) \right], \quad (7.299)$$

where it is implicitly assumed that the density of states (and distribution function) of the left electrode is shifted by $eV$. Notice that we have already used the expression of the lead Green's functions in terms of the local density of states and Fermi functions.

At this point, the only remaining task is the calculation of $G_{00}^r(E)$, but this is something that we have already done in section 7.1.3.3 and we just recall here the result

$$G_{00}^r(E) = \frac{1}{E - \epsilon_0 - t_L^2 g_L^r(E) - t_R^2 g_R^r(E)}. \quad (7.300)$$

Therefore, the current adopts again the form of the Landauer formula

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \; T(E,V) \left[ f(E - eV) - f(E) \right], \quad (7.301)$$

where this time the transmission $T(E,V)$ is given by

$$T(E,V) = \frac{4\pi^2 t_L^2 t_R^2 \rho_L(E - eV) \rho_R(E)}{|E - \epsilon_0 - t_L^2 g_L^r(E - eV) - t_R^2 g_R^r(E)|^2}. \quad (7.302)$$

To simplify this expression, we use now as in section 7.1.3.3 the wide-band approximation and neglect the energy dependence introduced by the leads. This way, $g_{L/R}^r \approx -i\pi \rho_{L/R}(E_\mathrm{F})$ and we define the scattering rates $\Gamma_{L/R} = \pi t_{L/R}^2 \rho_{L/R}(E_\mathrm{F})$. In this approximation the transmission can be written as

$$T(E,V) = \frac{4\Gamma_L \Gamma_R}{(E - \epsilon_0)^2 + (\Gamma_L + \Gamma_R)^2}. \quad (7.303)$$

In this case, the voltage dependence of the transmission may only stem from the eventual voltage dependence of the level position. This expression is the well-known Breit-Wigner or resonant tunneling formula that is known from the scattering approach.

Again, in the linear regime the low-temperature conductance is simply given by $G = (2e^2/h) T(E_\mathrm{F}, 0)$. This expression shows that the maximum conductance is reached when $E_\mathrm{F} = \epsilon_0$, which is the resonant condition. In the symmetric case ($\Gamma_L = \Gamma_R$), this maximum is equal to $G_0 = 2e^2/h$, irrespectively of the value of the scattering rates. These facts are illustrated in Fig. 7.25. The non-linear current-voltage characteristics of this model will be discussed in detail later on in this course.

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[26] Physically speaking, it is quite reasonable that this term does not contribute to the current. It makes no sense that the current depends on the occupation of the level before being coupled to the electrodes.

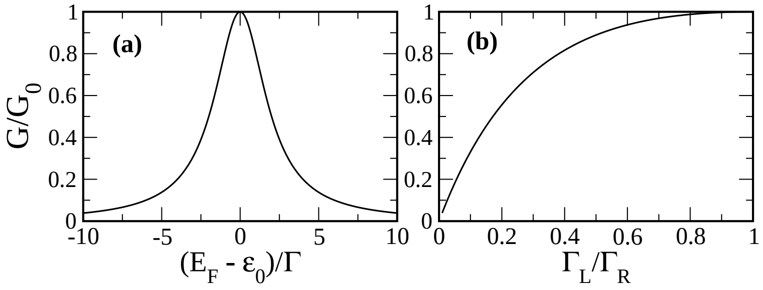

Fig. 7.25 Zero-temperature linear conductance in the resonant tunneling model. (a) Linear conductance (normalized by $G_0 = 2e^2/h$) as a function of the level position, $\epsilon_0$ for a symmetric contact $\Gamma_L = \Gamma_R = \Gamma$. (b) Linear conductance at resonance ($\epsilon_0 = E_{\mathrm{F}}$) as a function of the ratio between the scattering rates.

### 7.3.5 *Microscopic derivation of Landauer formula*

In the previous section we have discussed two simple examples of atomic-scale contacts. In both cases we ended up with a Landauer-like formula for the elastic current, the only difference being the expression for the transmission coefficient. In this section we shall demonstrate that this was not a coincidence and we shall derive a general expression for the elastic current valid for any type of atomic and molecular junction.

Let us consider a contact with arbitrary geometry like the one depicted in Fig. 7.26. Such a contact can be either an atomic contact or a molecular junction. Since we shall ignore inelastic interaction in this discussion, one can describe the system in terms of the following generic tight-binding Hamiltonian

$$\mathbf{H} = \sum_{ij,\alpha\beta,\sigma} h_{i\alpha,j\beta}\; \mathbf{c}^{\dagger}_{i\alpha,\sigma}\mathbf{c}_{j\beta,\sigma}, \tag{7.304}$$

where $i, j$ run over the atomic sites and $\alpha, \beta$ denote the different atomic

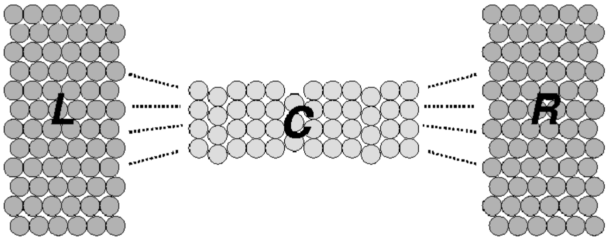

Fig. 7.26 Schematic representation of an atomic-scale contact of arbitrary geometry. We divide this system into three parts: a central region, $C$, and the two leads, $L$ and $R$.

orbitals. The number of orbitals in each site can be arbitrary. For the sake of simplicity, we assume that the local basis is orthogonal. Later in this section, we shall generalize the results to the case of nonorthogonal basis sets. Notice also that we are assuming that matrix elements are independent of the spin, i.e. we do not consider magnetic situations.

We now distinguish three different parts in this contact: the reservoirs $L$ and $R$, and a central region that can have arbitrary size and shape. In principle, the reservoirs $L$ and $R$ could also have an arbitrary shape and we assume that an electron in these subsystems has a well-defined temperature and chemical potential. In other words, these regions play the role of electron reservoirs, in the spirit of the scattering approach of Chapter 3 of this course. The separation of the contact in these three subsystems is somewhat arbitrary, especially in the linear response regime, and one can play with that, as we shall discuss below. We also assume that there is no direct coupling between the reservoirs. With this assumption the Hamiltonian above can be written in the following matrix form

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_{LL} & \mathbf{t}_{LC} & 0 \\ \mathbf{t}_{CL} & \mathbf{H}_{CC} & \mathbf{t}_{CR} \\ 0 & \mathbf{t}_{RC} & \mathbf{H}_{RR} \end{pmatrix}, \tag{7.305}$$

where the diagonal terms $\mathbf{H}_{XX}$ with $X = L, C, R$ are the Hamiltonian of the three subsystems and the $\mathbf{t}$'s describe the coupling between them.

Our aim is to determine the current through the contact induced by a constant bias voltage, $eV = \mu_L - \mu_R$. For this purpose, we first evaluate the current at the interface between the left lead $L$ and central region $C$, which in the tight-binding representation adopts the form (see section 7.3.4)

$$I = \frac{ie}{\hbar} \sum_{i \in L; j \in C; \alpha, \beta, \sigma} \left( h_{i\alpha,j\beta} \langle \mathbf{c}^{\dagger}_{i\alpha,\sigma} \mathbf{c}_{j\beta,\sigma} \rangle \; - \; h_{j\beta,i\alpha} \langle \mathbf{c}^{\dagger}_{j\beta,\sigma} \mathbf{c}_{i\alpha,\sigma} \rangle \right), \tag{7.306}$$

where $i$ runs over the atoms of the left electrode which are connected with the atoms in the central region $C$, and $j$ runs over the atoms of the central region coupled to the left electrode (in principle, all of them). The indexes $\alpha$ and $\beta$ indicate the different atomic orbitals in every site.

Following the ideas of the last section, we make use of nonequilibrium Green's function techniques to calculate the current. First of all, we express the expectation values appearing in the current expression in terms of the Keldysh-Green's function $G^{+-}$. This function gives information about the distribution function of the system and in a local basis it adopts the following form

$$G^{+-,\sigma\sigma'}_{i\alpha,j\beta}(t,t') = i \langle \mathbf{c}^{\dagger}_{j\beta,\sigma'}(t') \mathbf{c}_{i\alpha,\sigma}(t) \rangle. \tag{7.307}$$

Using this expression one can write the current as

$$I = \frac{e}{\hbar} \sum_{i \in L; j \in C; \alpha, \beta, \sigma} \left[ t_{i\alpha, j\beta} G^{+-,\sigma\sigma}_{j\beta, i\alpha}(t,t) \; - \; t_{j\beta, i\alpha} G^{+-,\sigma\sigma}_{i\alpha, j\beta}(t,t) \right] . \tag{7.308}$$

The current can be expressed in a more compact way in terms of the hopping matrices $\mathbf{t}_{LC}$ and $\mathbf{t}_{CL}$ [see Eq. (7.305)] whose elements are given by

$$\begin{aligned} (\mathbf{t}_{LC})_{i\alpha, j\beta} &= h_{i\alpha, j\beta} \;\; \text{with} \;\; i \in L; \; j \in C \\ (\mathbf{t}_{CL}) &= (\mathbf{t}_{LC})^{\dagger}. \end{aligned} \tag{7.309}$$

Analogously, one can define similar matrices for the Green's functions $G^{+-}$. With this new notation, one can express the current as

$$I = \frac{2e}{\hbar} \mathrm{Tr} \left[ \mathbf{G}^{+-}_{CL}(t,t) \mathbf{t}_{LC} \; - \; \mathbf{t}_{CL} \mathbf{G}^{+-}_{LC}(t,t) \right] , \tag{7.310}$$

where Tr denotes the trace over atoms and orbitals in the central region $C$. The prefactor 2 comes from the sum over spins, since for the moment we do not consider any magnetic situation. For the same reason, we drop the superindex $\sigma$ in the Green's functions.

This transport problem admits a stationary solution and therefore, the different Green's functions only depend on the difference of time arguments. Thus, we can Fourier transform with respect to the difference of the time arguments and write the current as

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \; \mathrm{Tr} \left[ \mathbf{G}^{+-}_{CL}(E) \mathbf{t}_{LC} \; - \; \mathbf{t}_{CL} \mathbf{G}^{+-}_{LC}(E) \right] . \tag{7.311}$$

Notice that the current is expressed in terms of the trace of a matrix whose dimension is the number of orbitals in the central region, which we denote as $N_C$. At this stage, the problem has been reduced to the determination of the functions $G^{+-}$ in terms of matrix elements of the Hamiltonian of Eq. (7.304). We shall calculate these functions considering the coupling terms between the electrodes and the central region as a perturbation. Then, starting from the Green's functions for the three isolated systems, we shall determine the corresponding functions for the whole system. With this choice, the self-energies of the problem are the hopping matrices defined in Eq. (7.309) and the equivalent ones for the interface between the central region and the right electrode $R$.

We now follow the ideas of section 7.3.4.2 and make use of Dyson's equation in Keldysh space, see Eq. (7.252), to write the functions $G^{+-}$ as follows[27]

$$\begin{aligned} \mathbf{G}_{LC}^{+-} &= \mathbf{g}_{LL}^{+-}\mathbf{t}_{LC}\mathbf{G}_{CC}^{a} \ + \ \mathbf{g}_{LL}^{r}\mathbf{t}_{LC}\mathbf{G}_{CC}^{+-} \\ \mathbf{G}_{CL}^{+-} &= \mathbf{G}_{CC}^{+-}\mathbf{t}_{CL}\mathbf{g}_{LL}^{a} \ + \ \mathbf{G}_{CC}^{r}\mathbf{t}_{CL}\mathbf{g}_{LL}^{+-}, \end{aligned} \tag{7.312}$$

where $\mathbf{g}_{XX}^{r,a}$ are the (retarded, advanced) Green's functions of the uncoupled reservoirs ($X = L, R$). Introducing this equation in the current expression and making use of the relation $\mathbf{G}^{+-} - \mathbf{G}^{-+} = \mathbf{G}^{a} - \mathbf{G}^{r}$, we obtain

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE \ \mathrm{Tr}\left[\mathbf{G}_{CC}^{-+}\mathbf{t}_{CL}\mathbf{g}_{LL}^{+-}\mathbf{t}_{LC} \ - \ \mathbf{G}_{CC}^{+-}\mathbf{t}_{CL}\mathbf{g}_{LL}^{-+}\mathbf{t}_{LC}\right]. \tag{7.313}$$

Then, we determine $\mathbf{G}^{+-/-+}$ by means of the relation

$$\mathbf{G}^{+-/-+} = (\mathbf{1} + \mathbf{G}^{r}\mathbf{t})\, \mathbf{g}^{+-/-+} (\mathbf{1} + \mathbf{t}\mathbf{G}^{a}). \tag{7.314}$$

Taking the element (C,C) in this expression we obtain

$$\mathbf{G}_{CC}^{+-/-+} = \mathbf{G}_{CC}^{r}\mathbf{t}_{CL}\mathbf{g}_{LL}^{+-/-+}\mathbf{t}_{LC}\mathbf{G}_{CC}^{a} + \mathbf{G}_{CR}^{r}\mathbf{t}_{CR}\mathbf{g}_{RR}^{+-/-+}\mathbf{t}_{RC}\mathbf{G}_{CC}^{a}. \tag{7.315}$$

Notice that there is an additional contribution containing $\mathbf{g}_{CC}^{+-/-+}$ that was left out in the previous expression. The reason for this is that, in analogy with our discussion of the resonant tunneling model in section 7.3.4.2, one can show that such a term does not contribute to the final expression of the current.

Substitution of the previous equation in the expression of the current yields

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE \ \mathrm{Tr}\left[\mathbf{G}_{CC}^{r}\mathbf{t}_{CR}\mathbf{g}_{RR}^{-+}\mathbf{t}_{RC}\mathbf{G}_{CC}^{a}\mathbf{t}_{CL}\mathbf{g}_{LL}^{+-}\mathbf{t}_{LC} - \mathbf{G}_{CC}^{r}\mathbf{t}_{CR}\mathbf{g}_{RR}^{+-}\mathbf{t}_{RC}\mathbf{G}_{CC}^{a}\mathbf{t}_{CL}\mathbf{g}_{LL}^{-+}\mathbf{t}_{LC}\right]. \tag{7.316}$$

Let us recall that the unperturbed functions $\mathbf{g}^{+-}$ and $\mathbf{g}^{-+}$ satisfy the following relations[28]

$$\begin{aligned} \mathbf{g}^{+-} &= (\mathbf{g}^{a} - \mathbf{g}^{r})\, f = 2i \ \mathrm{Im}\,(\mathbf{g}^{a})\, f \\ \mathbf{g}^{-+} &= (\mathbf{g}^{a} - \mathbf{g}^{r})\,(f-1) = 2i \ \mathrm{Im}\,(\mathbf{g}^{a})\,(f-1), \end{aligned} \tag{7.317}$$

where $f$ is the Fermi function. Thus, the current can be expressed as

$$I = \frac{8e}{h}\int_{-\infty}^{\infty} dE \ \mathrm{Tr}\left[\mathbf{G}_{CC}^{r}\mathbf{t}_{CR}\mathrm{Im}\left\{\mathbf{g}_{RR}^{a}\right\}\mathbf{t}_{RC}\mathbf{G}_{CC}^{a}\mathbf{t}_{CL}\mathrm{Im}\left\{\mathbf{g}_{LL}^{a}\right\}\mathbf{t}_{LC}\right] \times (f_L - f_R). \tag{7.318}$$

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[27] In order to abbreviate the notation, we do not write the energy argument $E$ explicitly. Moreover, since there are no inelastic processes involved in this model, the self-energies $\Sigma^{+-}$ associated with them vanish.

[28] Notice that in Eq. (7.317) we have assumed that that Hamiltonian is real, i.e. there is time reversal symmetry. One can easily show that this implies that $\mathbf{g}^{r}(E) = [\mathbf{g}^{a}(E)]^{*}$.

Here, $f_{L/R}$ is the Fermi function of the corresponding electrode, which takes into account the shift of the chemical potential induced by the voltage.

One can further simplify the expression of the current by defining

$$\mathbf{\Sigma}_L^{r,a} = \mathbf{t}_{CL}\mathbf{g}_{LL}^{r,a}\mathbf{t}_{LC} \text{ and } \mathbf{\Sigma}_R^{r,a} = \mathbf{t}_{CR}\mathbf{g}_{RR}^{r,a}\mathbf{t}_{RC}, \tag{7.319}$$

These matrices are nothing else but the self-energies of this problem for the subspace of the central region. These self-energies describe the influence of the reservoir in the central region and they depend both on the coupling between the reservoirs and the central region and on the local electronic structure of the leads. Notice that these matrices have a dimension equal to the number of orbitals in the central region. Using these definitions, the current can now be rewritten in the following familiar form

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE\, T(E,V)\,(f_L - f_R)\,, \tag{7.320}$$

where $T(E,V)$ is the energy- and voltage-dependent total transmission probability of the contact given by

$$\boxed{T(E,V) \equiv 4\mathrm{Tr}\left[\mathbf{\Gamma}_L \mathbf{G}_{CC}^r \mathbf{\Gamma}_R \mathbf{G}_{CC}^a\right]} \tag{7.321}$$

where we have defined the scattering rate matrices as $\mathbf{\Gamma}_{L,R} \equiv \mathrm{Im}\{\mathbf{\Sigma}_{L,R}^a\}$.[29] The voltage dependence of the transmission comes through the scattering rates (i.e. via the leads), but also through the possible voltage dependence of the Hamiltonian matrix elements of the central region.

We can further symmetrize this expression by using the cyclic property of the trace and write $T(E,V) = \mathrm{Tr}\left[\mathbf{t}(E,V)\mathbf{t}^\dagger(E,V)\right] = \mathrm{Tr}\left[\mathbf{t}^\dagger(E,V)\mathbf{t}(E,V)\right]$, where

$$\boxed{\mathbf{t}(E,V) = 2\mathbf{\Gamma}_L^{1/2}\mathbf{G}_{CC}^r\mathbf{\Gamma}_R^{1/2}} \tag{7.322}$$

is the transmission matrix of the system. The existence of $\mathbf{\Gamma}^{1/2}$ as a real matrix is warranted by $\mathbf{\Gamma}$ being positive definite.

Finally, the current adopts the form

$$\boxed{I = \frac{2e}{h}\int_{-\infty}^{\infty} dE\, \mathrm{Tr}\left[\mathbf{t}^\dagger(E,V)\mathbf{t}(E,V)\right](f_L - f_R)} \tag{7.323}$$

valid for arbitrary bias voltage. In the linear regime this expression reduces to the standard Landauer formula for the zero-temperature conductance

$$\boxed{G = \frac{2e^2}{h}\mathrm{Tr}\left[\mathbf{t}^\dagger(E_\mathrm{F},0)\mathbf{t}(E_\mathrm{F},0)\right] = \frac{2e^2}{h}\sum_{i=1}^{N} T_i} \tag{7.324}$$

---

[29] We have assumed without loss of generality that the hopping matrix elements are real.

where $T_i$ are the eigenvalues of $\hat{\mathbf{t}}^\dagger \mathbf{t}$ (or $\mathbf{t}\hat{\mathbf{t}}^\dagger$) at the Fermi level. As one can see, in principle the number of channel would be $N_C$, which is the dimension of the matrix $\mathbf{t}^\dagger \mathbf{t}$. However, as we stated at the beginning of this section, the separation in three subsystems in somewhat arbitrary and one can evaluate the current at any point. Thus, it is evident that the actual number of channels is controlled by the narrowest part of the junction. This fact will be very important in our discussion of the conduction channels in metallic single-atom contacts. Notice also that in this formulation, the conduction channels, defined as the eigenfunctions of $\mathbf{t}^\dagger \hat{\mathbf{t}}$, are linear combinations of the atomic orbitals in the central system.

As a result of the discussion above, we have not only re-derived the Landauer formula, but more importantly, we have also obtained an explicit formula for the transmission as a function of the microscopic parameters of the system. As one can see in Eq. (7.321) or in Eq. (7.322), the determination of the transmission requires the calculations of both the retarded/advanced Green's functions of the central system and the scattering rate matrices. These functions can be determined from their Dyson's equation

$$\mathbf{G}^a_{CC} = (\mathbf{G}^r_{CC})^\dagger = \left[(E - i0^+)\mathbf{1} - \mathbf{H}_{CC} - \mathbf{\Sigma}^a_L - \mathbf{\Sigma}^a_R\right]^{-1}, \qquad (7.325)$$

where $\mathbf{H}_{CC}$ is the Hamiltonian of the central region and the self-energies $\mathbf{\Sigma}_X$ $(X = L, R)$ are given by Eq. (7.319).

On the other hand, the calculation of the scattering rate matrices, which are the imaginary part of the self-energies of Eq. (7.319), requires the knowledge of the Green's functions of the uncoupled reservoirs, $\mathbf{g}_{XX}$ (with $X = L, R$). The leads are semi-infinite systems and thus they cannot possess in practice a very complicated geometry. A typical option is to describe these leads as ideal surfaces of the corresponding material and the unperturbed Green's functions are then computed using special recursive techniques like the so-called *decimation* [17].

Let us end this section with a brief technical discussion. The quantity $\mathbf{t}(E, V)$ appearing in Eq. (7.322) has been called transmission matrix without a real justification. We should demonstrate that this matrix fulfills the properties of a transmission matrix. In particular, we should at least prove that the eigenvalues of $\mathbf{t}\mathbf{t}^\dagger$ are bounded between 0 and 1. Indeed, this property can be shown using a few algebraic manipulations. Another way of showing that $\mathbf{t}(E, V)$ in Eq. (7.322) is indeed the transmission matrix of the contact is via the so-called Fisher-Lee relation [18], which expresses the elements of the scattering matrix in terms of Green's functions. If you are interested in this route, we recommend you the original work of Ref. [18]

and the discussion on this matter in Chapter 3 of Ref. [20].

#### 7.3.5.1 *An example: back to the resonant tunneling model*

As an application of the general formula derived above and in order to illustrate its use, let us now re-derive the current formula for the resonant tunneling model considered in section 7.3.4.2.

Our starting point is the expression for the transmission of Eq. (7.321). We need first to compute the retarded/advanced Green's functions of the central region. In this case this region consists of a single site with an on-site energy $\epsilon_0$. Therefore, the Green's functions of the central region are scalars with the following form

$$G^{r,a}_{CC} = \left[E \pm i0^+ - \epsilon_0 - \Sigma^{r,a}_L - \Sigma^{r,a}_R\right]^{-1}, \tag{7.326}$$

where the self-energies are the scalars $\Sigma^{r,a}_{L/R} = t^2_{L/R} g^{r,a}_{LL/RR}$. Assuming as in section 7.3.4.2 that the local Green's functions $g^{r,a}_{LL/RR}$ are purely imaginary and independent of the energy around $E_{\rm F}$, the advanced self-energies reduce to $\Sigma^a_{L/R} = i\Gamma_{L/R}$, where $\Gamma_{L/R} = t^2_{L/R}\text{Im}\{g^a_{LL/RR}(E_{\rm F})\}$ are the scattering rates at the Fermi energy. Substituting now Eq. (7.326) and the expressions of the self-energy in Eq. (7.321), we arrive again at the well-known Breit-Wigner formula

$$T(E) = \frac{4\Gamma_L\Gamma_R}{(E-\epsilon_0)^2 + (\Gamma_L+\Gamma_R)^2}. \tag{7.327}$$

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