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3 Introduction to the Keldysh Formalism

R. van Leeuwen, N.E. Dahlen, G. Stefanucci, C.-O. Almbladh,
and U. von Barth

3.1 Introduction

In this chapter we give an introduction to the Keldysh formalism, which is an extremely useful tool for first-principles studies of nonequilibrium many-particle systems. Of particular interest for TDDFT is the relation to nonequilibrium Green functions (NEGF), which allows us to construct exchange-correlation potentials with memory by using diagrammatic techniques. For many problems, such as quantum transport or atoms in intense laser pulses, one needs exchange-correlation functionals with memory, and Green function techniques offer a systematic method for developing these. The Keldysh formalism is also necessary for defining response functions in TDDFT and for defining an action functional needed for deriving TDDFT from a variational principle. In this chapter, we give an introduction to the nonequilibrium Green function formalism, intended to illustrate the usefulness of the theory. The formalism does not differ much from ordinary equilibrium theory, the main difference being that all time-dependent functions are defined for time-arguments on a contour, known as the Keldysh contour.

The Green function $G(\mathbf{r}t, \mathbf{r}'t')$ is a function of two space- and time-coordinates, and is obviously more complicated than the one-particle density $n(\mathbf{r}, t)$, which is the main ingredient of TDDFT. However, the advantage of NEGF methods is that we can systematically improve the approximations by taking into account particular physical processes (represented in the form of Feynman diagrams) that we believe to be important. The Green function provides us directly with all expectation values of one-body operators (such as the density and the current), and also the total energy, ionization potentials, response functions, spectral functions, etc. In relation to TDDFT, this is useful not only for developing orbital functionals and exchange-correlation functionals with memory, but also for providing insight in the exact properties of the noninteracting Kohn-Sham system.

In the following, we shall focus on systems that are initially in thermal equilibrium. We will start by introducing the Keldysh contour and the nonequilibrium Green function, which is one particular example of a function defined on the contour. In Sect. 3.4 we will explain how to combine and manipulate functions of time variables on the contour. These results, that are summarized in Table 3.1, are highly important, since the class of functions

also include response functions and self-energies. The results derived in this section are essential for defining action functionals and response functions, as we will do in Sect. 3.9, and are also used extensively in Chap. 32. The equations of motion for the Green function, known as the Kadanoff-Baym equations, are explained in Sect. 3.5. While in TDDFT we take exchange and correlation effects into account through $v_{xc}[n]$, the corresponding quantity in Green function theory is the self-energy $\Sigma[G]$. Just like v_{xc} , the self-energy functional must be approximated. For a given functional $\Sigma[G]$, it is important that the resulting observables obey the macroscopic conservation laws, such as the continuity equation. These approximations are known as *conserving*, and will be discussed briefly in Sect. 3.7. In the last part of this chapter we discuss the applications of the Keldysh formalism in TDDFT, including the relation between Σ and v_{xc} , the derivation of the Kohn-Sham equations from an action functional, and the derivation of an f_{xc} functional. As an illustrative example, we discuss the time-dependent exchange-only optimized effective potential approximation.

3.2 The Keldysh Contour

In quantum mechanics we associate with any observable quantity O a Hermitian operator \hat{O} . The expectation value $\text{Tr}\{\hat{\rho}_0\hat{O}\}$ gives the value of O when the system is described by the density operator $\hat{\rho}_0$ and the trace denotes a sum over a complete set of states in Hilbert space. For an isolated system the Hamiltonian \hat{H}_0 does not depend on time, and the expectation value of *any* observable quantity is constant, provided that $[\hat{\rho}_0, \hat{H}_0] = 0$. In the following we want to discuss how to describe systems that are isolated for times $t < 0$, such that $\hat{H}(t < 0) = \hat{H}_0$, but disturbed by an external time-dependent field at $t > 0$. The expectation value of \hat{O} at $t > 0$ is then given by the average on the initial density operator $\hat{\rho}_0$ of the operator \hat{O} in the Heisenberg representation,

$$O(t) = \langle \hat{O}_H(t) \rangle \equiv \text{Tr}\{\hat{\rho}_0\hat{O}_H(t)\} = \text{Tr}\{\hat{\rho}_0\hat{U}(0,t)\hat{O}\hat{U}(t,0)\}, \quad (3.1)$$

where the operator in the Heisenberg picture has a time-dependence according to $\hat{O}_H(t) = \hat{U}(0,t)\hat{O}\hat{U}(t,0)$. The evolution operator $\hat{U}(t,t')$ is the solution of the equations

$$i\frac{d}{dt}\hat{U}(t,t') = \hat{H}(t)\hat{U}(t,t') \quad \text{and} \quad i\frac{d}{dt'}\hat{U}(t,t') = -\hat{U}(t,t')\hat{H}(t'), \quad (3.2)$$

with the boundary condition $\hat{U}(t,t) = 1$. It can be formally written as

$$\hat{U}(t,t') = \begin{cases} \hat{T} \exp[-i \int_{t'}^t d\bar{t} \hat{H}(\bar{t})] & t > t' \\ \hat{\bar{T}} \exp[-i \int_{t'}^t d\bar{t} \hat{H}(\bar{t})] & t < t' \end{cases}. \quad (3.3)$$

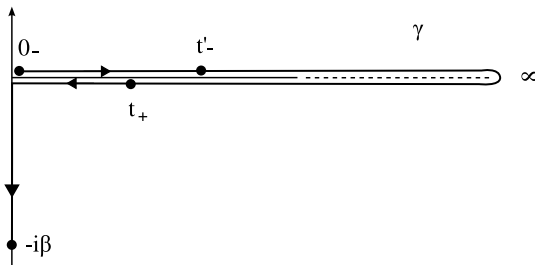


Fig. 3.1. The Keldysh contour in the complex time-plane, starting at $t = 0$, and ending at $t = -i\beta$, with t on the backward branch and t' on the forward branch. By definition, any point lying on the vertical track is later than a point lying on the forward or backward branch

In (3.3), $\hat{\mathcal{T}}$ is the time-ordering operator that rearranges the operators in chronological order with later times to the left; $\hat{\bar{\mathcal{T}}}$ is the anti-chronological time-ordering operator. The evolution operator satisfies the group property $\hat{U}(t, t_1) \hat{U}(t_1, t') = \hat{U}(t, t')$ for any t_1 . Notice that if the Hamiltonian is time-independent in the interval between t and t' , then the evolution operator becomes $\hat{U}(t, t') = \exp[-i\hat{H}(t-t')]$. If we now let the system be initially in thermal equilibrium, with an inverse temperature $\beta \equiv 1/k_B T$ and chemical potential μ , the initial density matrix is $\hat{\rho}_0 = \exp[-\beta(\hat{H}_0 - \mu\hat{N})] / \text{Tr}\{\exp[-\beta(\hat{H}_0 - \mu\hat{N})]\}$. Assuming that \hat{H}_0 and \hat{N} commute, $\hat{\rho}_0$ can be rewritten using the evolution operator \hat{U} with a complex time-argument, $t = -i\beta$, according to $\hat{\rho}_0 = \exp[\beta\mu\hat{N}]\hat{U}(-i\beta, 0) / \text{Tr}\{\exp[\beta\mu\hat{N}]\hat{U}(-i\beta, 0)\}$. Inserting this expression in (3.1), we find

$$O(t) = \frac{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \hat{U}(0, t) \hat{O} \hat{U}(t, 0) \right\}}{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\}}. \quad (3.4)$$

Reading the arguments in the numerator from the right to the left, we see that we can design a time-contour γ with a forward branch going from 0 to t , a backward branch coming back from t and ending in 0, and a branch along the imaginary time-axis from 0 to $-i\beta$. This contour is illustrated in Fig. 3.1. Note that the group property of \hat{U} means that we are free to extend this contour up to infinity. We can now generalize (3.4), and let z be a time-contour variable on γ . We will in the following stick to the notation that the time-variable on the contour is denoted z unless we specify on which branch of the contour it is located. This time-variable can therefore be real or complex. Letting the variable \bar{z} run along this same contour, (3.4) can be formally recast as

$$O(z) = \frac{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{\mathcal{T}}_c e^{-i \int_{\gamma} d\bar{z} \hat{H}(\bar{z})} \hat{O}(z) \right\}}{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{\mathcal{T}}_c e^{-i \int_{\gamma} dz \hat{H}(z)} \right\}}. \quad (3.5)$$

The contour ordering operator \hat{T}_c moves the operators with “later” contour variable to the left. In (3.5), $\hat{O}(z)$ is *not* the operator in the Heisenberg representation [the latter is denoted with $\hat{O}_H(t)$]. The contour-time argument in \hat{O} is there only to specify the position of the operator \hat{O} on γ . A point on the real axis can be either on the forward (we denote these points t_-), or on the backward branch (denoted t_+), and a point which is earlier in real time, can therefore be later on the contour, as illustrated in Fig. 3.1.

If z lies on the vertical track, then there is no need to extend the contour along the real axis. Instead, we have

$$O(z) = \frac{\text{Tr} \left\{ e^{\beta\mu\hat{N}} e^{-i\int_z^{-i\beta} d\bar{z}\hat{H}_0} \hat{O} e^{-i\int_0^z d\bar{z}\hat{H}_0} \right\}}{\text{Tr} \left\{ e^{-\beta(\hat{H}_0-\mu\hat{N})} \right\}} = \frac{\text{Tr} \left\{ e^{-\beta(\hat{H}_0-\mu\hat{N})} \hat{O} \right\}}{\text{Tr} \left\{ e^{-\beta(\hat{H}_0-\mu\hat{N})} \right\}}, \quad (3.6)$$

where the cyclic property of the trace has been used. The right hand side is independent of z and coincides with the thermal average $\text{Tr}\{\hat{\rho}_0\hat{O}\}$. It is easy to verify that (3.5) would give exactly the same result for $O(t)$, where t is real, if the Hamiltonian was time-independent, i.e., $\hat{H}(t) = \hat{H}_0$ also for $t > 0$.

To summarize, in (3.5) the variable z lies on the contour of Fig. 3.1; the r.h.s. gives the time-dependent statistical average of the observable O when z lies on the forward or backward branch, and the statistical average before the system is disturbed when z lies on the vertical track.

3.3 Nonequilibrium Green Functions

We now introduce the NEGF, which is a function of two contour time-variables. In order to keep the notation as light as possible, we here discard the spin degrees of freedom; the spin index may be restored later as needed. The field operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^\dagger(\mathbf{r})$ destroy and create an electron in \mathbf{r} and obey the anticommutation relations $\{\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')\} = \delta(\mathbf{r} - \mathbf{r}')$. We write the Hamiltonian $\hat{H}(t)$ as the sum of a quadratic term

$$\hat{h}(t) = \int d^3r \int d^3r' \hat{\psi}^\dagger(\mathbf{r}) \langle \mathbf{r} | \mathbf{h}(t) | \mathbf{r}' \rangle \hat{\psi}(\mathbf{r}'), \quad (3.7)$$

and the interaction operator

$$\hat{V}_{ee} = \frac{1}{2} \int d^3r \int d^3r' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') v_{ee}(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}). \quad (3.8)$$

We use boldface to indicate matrices in one-electron labels, e.g., \mathbf{h} is a matrix and $\langle \mathbf{r} | \mathbf{h} | \mathbf{r}' \rangle$ is the $(\mathbf{r}, \mathbf{r}')$ matrix element of \mathbf{h} . When describing electrons in an electro-magnetic field, the quadratic term is given by $\langle \mathbf{r} | \mathbf{h}(t) | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') \{ [-i\nabla + \mathbf{A}_{\text{ext}}(\mathbf{r}, t)]^2 / 2 + v_{\text{ext}}(\mathbf{r}, t) \}$.

The definition of an expectation value in (3.1) can be generalized to the expectation value of two operators. The Green function is defined as

$$G(\mathbf{r}z, \mathbf{r}'z') = \langle \mathbf{r} | \mathbf{G}(z, z') | \mathbf{r}' \rangle \equiv -i \langle \hat{\mathcal{T}}_c \hat{\psi}_H(\mathbf{r}, z) \hat{\psi}_H^\dagger(\mathbf{r}', z') \rangle, \quad (3.9)$$

where the contour variable in the field operators specifies the position in the contour ordering. The operators have a time-dependence according to the definition of the Heisenberg picture, e.g., $\hat{\psi}_H^\dagger(\mathbf{r}, z) = \hat{U}(0, z) \hat{\psi}^\dagger(\mathbf{r}) \hat{U}(z, 0)$. Notice that if the time-argument z is located on the real axis, then $\hat{\psi}_H(\mathbf{r}, t_+) = \hat{\psi}_H(\mathbf{r}, t_-)$. If the time-argument is on the imaginary axis, then $\hat{\psi}(\mathbf{r}, -i\tau)$ is *not* the adjoint of $\hat{\psi}(\mathbf{r}, -i\tau)$ since $\hat{U}^\dagger(-i\tau, 0) \neq \hat{U}(0, -i\tau)$. The Green function can be written

$$\mathbf{G}(z, z') = \theta(z, z') \mathbf{G}^>(z, z') + \theta(z', z) \mathbf{G}^<(z, z'). \quad (3.10)$$

The function $\theta(z, z')$ is defined to be 1 if z is later on the contour than z' , and 0 otherwise.¹ From the definition of the time-dependent expectation value in (3.4), it follows that the greater Green function $\mathbf{G}^>(z, z')$, where z is later on the contour than z' , is

$$iG^>(\mathbf{r}z, \mathbf{r}'z') = \frac{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \hat{\psi}_H(\mathbf{r}, z) \hat{\psi}_H^\dagger(\mathbf{r}', z') \right\}}{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\}}. \quad (3.11)$$

If z' is later on the contour than z , then the Green function equals

$$iG^<(\mathbf{r}z, \mathbf{r}'z') = - \frac{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \hat{\psi}_H^\dagger(\mathbf{r}', z') \hat{\psi}_H(\mathbf{r}, z) \right\}}{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\}}. \quad (3.12)$$

The extra minus sign on the right hand side comes from the contour ordering. More generally, rearranging the field operators $\hat{\psi}$ and $\hat{\psi}^\dagger$ (later arguments to the left), we also have to multiply by $(-1)^P$, where P is the parity of the permutation. From the definition of the Green function, it is easily seen that the electron density, $n(\mathbf{r}, z) = \langle \hat{\psi}_H^\dagger(\mathbf{r}, z) \hat{\psi}_H(\mathbf{r}, z) \rangle$ and current are obtained according to

$$n(\mathbf{r}, z) = -iG(\mathbf{r}z, \mathbf{r}z^+), \quad (3.13)$$

and

$$\mathbf{j}(\mathbf{r}, z) = - \left\{ \left[-i \frac{\nabla}{2} + i \frac{\nabla'}{2} + \mathbf{A}_{\text{ext}}(\mathbf{r}, z) \right] iG(\mathbf{r}z, \mathbf{r}'z') \right\}_{z'=z^+}. \quad (3.14)$$

where z^+ indicates that this time-argument is infinitesimally later on the contour.

The Green function $\mathbf{G}(z, z')$ obeys an important cyclic relation on the Keldysh contour. Choosing $z = 0_-$, which is the earliest time on the contour, we find $\mathbf{G}(0_-, z') = \mathbf{G}^<(0, z')$, given by (3.12) with $\hat{\psi}_H(\mathbf{r}, 0) = \hat{\psi}(\mathbf{r})$.

¹ This means that if z is parametrized according to $z(s)$, where the parameter s runs from linearly from s_i to s_f , then $\theta(z, z') = \theta(s - s')$.

Inside the trace we can move $\hat{\psi}(\mathbf{r})$ to the left. Furthermore, we can exchange the position of $\hat{\psi}(\mathbf{r})$ and $\exp\{\beta\mu\hat{N}\}$ by noting that $\hat{\psi}(\mathbf{r})\exp\{\beta\mu\hat{N}\} = \exp\{\beta\mu(\hat{N} + 1)\}\hat{\psi}(\mathbf{r})$. Using the group identity $\hat{U}(-i\beta, 0)\hat{U}(0, -i\beta) = 1$, we obtain

$$\begin{aligned} iG(\mathbf{r}0_-, \mathbf{r}'z') &= -\frac{\text{Tr}\left\{\hat{\psi}_H(\mathbf{r})e^{\beta\mu\hat{N}}\hat{U}(-i\beta, 0)\hat{\psi}_H^\dagger(\mathbf{r}', z')\right\}}{\text{Tr}\left\{e^{\beta\mu\hat{N}}\hat{U}(-i\beta, 0)\right\}} \\ &= -e^{\beta\mu}\frac{\text{Tr}\left\{e^{\beta\mu\hat{N}}\hat{U}(-i\beta, 0)\hat{\psi}_H(\mathbf{r}, -i\beta)\hat{\psi}_H^\dagger(\mathbf{r}', z')\right\}}{\text{Tr}\left[e^{\beta\mu\hat{N}}\hat{U}(-i\beta, 0)\right]}. \end{aligned} \quad (3.15)$$

The r.h.s. equals $-e^{\beta\mu}\langle\mathbf{r}|i\mathbf{G}(-i\beta, z')|\mathbf{r}'\rangle$. Together with a similar analysis for $\mathbf{G}(z, 0_-)$, we conclude that

$$\mathbf{G}(0_-, z') = -e^{\beta\mu}\mathbf{G}(-i\beta, z') \quad \text{and} \quad \mathbf{G}(z, 0_-) = -e^{-\beta\mu}\mathbf{G}(z, -i\beta). \quad (3.16)$$

These equations constitute the so called Kubo-Martin-Schwinger (KMS) boundary conditions [Kubo 1957, Martin 1959]. From the definition of the Green function in (3.9), it is easily seen that the $\mathbf{G}(z, z)$ has a discontinuity at $z = z'$,

$$\mathbf{G}^>(z, z) = \mathbf{G}^<(z, z) - i\mathbf{1}. \quad (3.17)$$

Furthermore, for both time-arguments on the real axis we have the important symmetry $[\mathbf{G}^{\leq}(t', t)]^\dagger = -\mathbf{G}^{\leq}(t, t')$. As we shall see, these relations play a crucial role in solving the equation of motion.

3.4 The Keldysh Book-Keeping

The Green function belongs to a larger class of functions of two time-contour variables that we will refer to as Keldysh space. These are functions that can be written on the form

$$k(z, z') = \delta(z, z')k^\delta(z) + \theta(z, z')k^>(z, z') + \theta(z', z)k^<(z, z'), \quad (3.18)$$

where the δ -function on the contour is defined as $\delta(z, z') = d\theta(z, z')/dz$.² The Green function, as defined in (3.10), has no such singular part. Another example of a function belonging to the Keldysh space, is the self-energy Σ , which will be discussed below. The singular part, Σ^δ , of the self-energy is the Hartree-Fock self-energy, while the terms Σ^{\leq} represent the correlation part.

² In general, functions containing singularities of the form $d^n\delta(z, z')/dz^n$ belong to the Keldysh space (see [Danielewicz 1984]). Notice that if the contour variable z is parametrized according to $z(s)$, where the parameter s runs linearly from some value s_i to s_f , we have $\delta(z, z') = [dz/ds]^{-1}d\Theta(s - s')/ds = [dz/ds]^{-1}\delta(s - s')$.

The functions in Keldysh space are somewhat complicated due to the fact that each of the time-arguments can be located on three different branches of the contour, as illustrated in Fig. 3.1. Below we systematically derive a set of identities that are commonly used for dealing with such functions and will be used extensively in the following sections. Most of the relations are well known [Langreth 1976], while others, equally important [Wagner 1991], are not. Our aim is to provide a self-contained derivation of all of them. A table at the end of the section summarizes the main results. For those who are not familiar with the Keldysh contour, we strongly recommend to scan what follows with pencil and paper.

It is straightforward to show that if $a(z, z')$ and $b(z, z')$ belong to the Keldysh space, then

$$c(z, z') = \int_{\gamma} d\bar{z} a(z, \bar{z})b(\bar{z}, z') \quad (3.19)$$

also belongs to the Keldysh space. For any $k(z, z')$ in the Keldysh space we define the *greater* and *lesser* functions on the physical time axis

$$k^>(t, t') \equiv k(t_+, t'_-), \quad k^<(t, t') \equiv k(t_-, t'_+). \quad (3.20)$$

We also define the following two-point functions with one argument t on the physical time axis and the other τ on the vertical track

$$k^{\lceil}(t, \tau) \equiv k(t_{\pm}, \tau), \quad k^{\lceil}(\tau, t) \equiv k(\tau, t_{\pm}). \quad (3.21)$$

In the definition of k^{\lceil} and k^{\lceil} we can arbitrarily choose t_+ or t_- since τ is later than both of them. The symbols “ \lceil ” and “ \lceil ” have been chosen in order to help the visualization of the time arguments. For instance, “ \lceil ” has a horizontal segment followed by a vertical one; correspondingly, k^{\lceil} has a first argument which is real (and thus lies on the horizontal axis) and a second argument which is imaginary (and thus lies on the vertical axis). We will also use the convention of denoting the real time with latin letters and the imaginary time with greek letters.

If we write out the contour integral in (3.19) in detail, we see – with the help of Fig. 3.1 – that the integral consists of four main parts. First, we must integrate along the real axis from $\bar{z} = 0_-$ to $\bar{z} = t'_-$, for which $a = a^>$ and $b = b^<$. Then, the integral goes from $\bar{z} = t'_-$ to $\bar{z} = t_+$, where $a = a^>$ and $b = b^>$. The third part of the integral goes along the real axis from $\bar{z} = t_+$ to $\bar{z} = 0_+$, with $a = a^<$ and $b = b^>$. The last integral is along the imaginary track, from 0_+ to $-i\beta$, where $a = a^{\lceil}$ and $b = b^{\lceil}$. In addition, we have the contribution from the singular parts, a^{δ} and b^{δ} , which is trivial since these integrals involve a δ -function. With these specifications, we can drop the “ \pm ” subscripts on the time-arguments and write

$$\begin{aligned}
c^>(t, t') &= a^>(t, t')b^\delta(t') + a^\delta(t)b^>(t, t') \\
&+ \int_0^{t'} d\bar{t} a^>(t, \bar{t})b^<(\bar{t}, t') + \int_{t'}^t d\bar{t} a^>(t, \bar{t})b^>(\bar{t}, t') \\
&+ \int_t^0 d\bar{t} a^<(t, \bar{t})b^>(\bar{t}, t') + \int_0^{-i\beta} d\bar{\tau} a^{\lceil}(t, \bar{\tau})b^{\lceil}(\bar{\tau}, t'). \quad (3.22)
\end{aligned}$$

The second integral on the r.h.s. is an ordinary integral on the real axis of two well defined functions and may be rewritten as

$$\int_{t'}^t d\bar{t} a^>(t, \bar{t})b^>(\bar{t}, t') = \int_{t'}^0 d\bar{t} a^>(t, \bar{t})b^>(\bar{t}, t') + \int_0^t d\bar{t} a^>(t, \bar{t})b^>(\bar{t}, t'). \quad (3.23)$$

Using this relation, the expression for $c^>$ becomes

$$\begin{aligned}
c^>(t, t') &= a^>(t, t')b^\delta(t') + a^\delta(t)b^>(t, t') - \int_0^{t'} d\bar{t} a^>(t, \bar{t})[b^>(\bar{t}, t') - b^<(\bar{t}, t')] \\
&+ \int_0^t d\bar{t} [a^>(t, \bar{t}) - a^<(t, \bar{t})]b^>(\bar{t}, t') + \int_0^{-i\beta} d\bar{\tau} a^{\lceil}(t, \bar{\tau})b^{\lceil}(\bar{\tau}, t'). \quad (3.24)
\end{aligned}$$

Next, we introduce two other functions on the physical time axis

$$k^{\text{R}}(t, t') \equiv \delta(t, t')k^\delta + \theta(t - t')[k^>(t, t') - k^<(t, t')], \quad (3.25a)$$

$$k^{\text{A}}(t, t') \equiv \delta(t, t')k^\delta - \theta(t' - t)[k^>(t, t') - k^<(t, t')]. \quad (3.25b)$$

The *retarded* function $k^{\text{R}}(t, t')$ vanishes for $t < t'$, while the *advanced* function $k^{\text{A}}(t, t')$ vanishes for $t > t'$. The retarded and advanced functions can be used to rewrite (3.24) in a more compact form

$$c^>(t, t') = \int_0^\infty d\bar{t} [a^>(t, \bar{t})b^{\text{A}}(\bar{t}, t') + a^{\text{R}}(t, \bar{t})b^>(\bar{t}, t')] + \int_0^{-i\beta} d\bar{\tau} a^{\lceil}(t, \bar{\tau})b^{\lceil}(\bar{\tau}, t'). \quad (3.26)$$

It is convenient to introduce a short hand notation for integrals along the physical time axis and for those between 0 and $-i\beta$. The symbol “ \cdot ” will be used to write $\int_0^\infty d\bar{t} f(\bar{t})g(\bar{t})$ as $f \cdot g$, while the symbol “ \star ” will be used to write $\int_0^{-i\beta} d\bar{\tau} f(\bar{\tau})g(\bar{\tau})$ as $f \star g$. Then

$$c^> = a^> \cdot b^{\text{A}} + a^{\text{R}} \cdot b^> + a^{\lceil} \star b^{\lceil}. \quad (3.27)$$

Similarly, one can prove that

$$c^< = a^< \cdot b^{\text{A}} + a^{\text{R}} \cdot b^< + a^{\lceil} \star b^{\lceil}. \quad (3.28)$$

Equations (3.27)–(3.28) can be used to extract the retarded and advanced component of c . By definition

$$\begin{aligned}
 c^{\text{R}}(t, t') &= \delta(t - t')c^\delta(t) + \theta(t - t')[c^>(t, t') - c^<(t, t')] \\
 &= a^\delta(t)b^\delta(t')\delta(t - t') + \theta(t - t') \int_0^\infty d\bar{t} a^{\text{R}}(t, \bar{t})[b^>(\bar{t}, t') - b^<(\bar{t}, t')] \\
 &\quad + \theta(t - t') \int_0^\infty d\bar{t} [a^>(t, \bar{t}) - a^<(t, \bar{t})]b^{\text{A}}(\bar{t}, t'). \quad (3.29)
 \end{aligned}$$

Using the definitions (3.25a) and (3.25b) to expand the integrals on the r.h.s. of this equation, it is straightforward to show that

$$c^{\text{R}} = a^{\text{R}} \cdot b^{\text{R}}. \quad (3.30)$$

Proceeding along the same lines, one can show that the advanced component is given by $c^{\text{A}} = a^{\text{A}} \cdot b^{\text{A}}$. It is worth noting that in the expressions for c^{R} and c^{A} no integration along the imaginary track is required.

Next, we show how to extract the components c^\parallel and c^\lceil . We first define the Matsubara function $k^{\text{M}}(\tau, \tau')$ with both arguments in the interval $(0, -i\beta)$:

$$k^{\text{M}}(\tau, \tau') \equiv k(z = \tau, z' = \tau'). \quad (3.31)$$

Let us focus on k^\parallel . Without any restrictions we may take t_- as the first argument in (3.21). In this case, we find

$$\begin{aligned}
 c^\parallel(t, \tau) &= a^\delta(t)b^\parallel(t, \tau) + \int_{0_-}^{t_-} d\bar{z} a^>(t_-, \bar{z})b^<(\bar{z}, \tau) \\
 &\quad + \int_{t_+}^{0_+} d\bar{z} a^<(t_-, \bar{z})b^<(\bar{z}, \tau) + \int_{0_+}^{-i\beta} d\bar{z} a^<(t_-, \bar{z})b(\bar{z}, \tau). \quad (3.32)
 \end{aligned}$$

Converting the contour integrals in integrals along the real time axis and along the imaginary track, and taking into account the definition (3.25a)

$$c^\parallel = a^{\text{R}} \cdot b^\parallel + a^\lceil \star b^{\text{M}}. \quad (3.33)$$

The relation for c^\lceil can be obtained in a similar way and reads $c^\lceil = a^\lceil \cdot b^{\text{A}} + a^{\text{M}} \star b^\lceil$. Finally, it is straightforward to prove that the Matsubara component of c is simply given by $c^{\text{M}} = a^{\text{M}} \star b^{\text{M}}$.

There is another class of identities we want to discuss for completeness. We have seen that the convolution (3.19) of two functions belonging to the Keldysh space also belongs to the Keldysh space. The same holds true for the product

$$c(z, z') = a(z, z')b(z', z). \quad (3.34)$$

Omitting the arguments of the functions, one readily finds (for $z \neq z'$)

$$c^> = a^>b^<, \quad c^< = a^<b^>, \quad c^\parallel = a^\parallel b^\lceil, \quad c^\lceil = a^\lceil b^\parallel, \quad c^{\text{M}} = a^{\text{M}}b^{\text{M}}. \quad (3.35)$$

The retarded function is then obtained exploiting the identities (3.35). We have (for $t \neq t'$)

Table 3.1. Table of definitions of Keldysh functions and identities for the convolution and the product of two functions in the Keldysh space

Definition	$c(z, z') = \int_{\gamma} d\bar{z} a(z, \bar{z})b(\bar{z}, z')$	$c(z, z') = a(z, z')b(z', z)$
$k^>(t, t') = k(t_+, t'_-)$	$c^> = a^> \cdot b^A + a^R \cdot b^> + a^{\lceil} \star b^{\lceil}$	$c^> = a^>b^<$
$k^<(t, t') = k(t_-, t'_+)$	$c^< = a^< \cdot b^A + a^R \cdot b^< + a^{\lceil} \star b^{\lceil}$	$c^< = a^<b^>$
$k^R(t, t') = \delta(t - t')k^{\delta}(t) + \theta(t - t')[k^>(t, t') - k^<(t, t')]$	$c^R = a^R \cdot b^R$	$c^R = \begin{cases} a^R b^< + a^< b^A \\ a^R b^> + a^> b^A \end{cases}$
$k^A(t, t') = \delta(t - t')k^{\delta}(t) - \theta(t' - t)[k^>(t, t') - k^<(t, t')]$	$c^A = a^A \cdot b^A$	$c^A = \begin{cases} a^A b^< + a^< b^R \\ a^A b^> + a^> b^R \end{cases}$
$k^{\lceil}(t, \tau) = k(t_{\pm}, \tau)$	$c^{\lceil} = a^R \cdot b^{\lceil} + a^{\lceil} \star b^M$	$c^{\lceil} = a^{\lceil} b^{\lceil}$
$k^{\rceil}(\tau, t) = k(\tau, t_{\pm})$	$c^{\rceil} = a^{\rceil} \cdot b^A + a^M \star b^{\rceil}$	$c^{\rceil} = a^{\rceil} b^{\lceil}$
$k^M(\tau, \tau') = k(z = \tau, z' = \tau')$	$c^M = a^M \star b^M$	$c^M = a^M b^M$

$$c^R(t, t') = \theta(t - t')[a^>(t, t')b^<(t', t) - a^<(t, t')b^>(t', t)]. \quad (3.36)$$

We may get rid of the θ -function by adding and subtracting $a^<b^<$ or $a^>b^>$ to the above relation and rearranging the terms. The final result is

$$c^R = a^R b^< + a^< b^A = a^R b^> + a^> b^A. \quad (3.37)$$

Similarly one finds $c^A = a^A b^< + a^< b^R = a^A b^> + a^> b^R$. The time-ordered and anti-time-ordered functions can be obtained in a similar way and the Reader can look at Table 3.1 for the complete list of definitions and identities.

For later purposes, we also consider the case of a Keldysh function $k(z, z')$ multiplied on the left by a scalar function $l(z)$. The scalar function is equivalent to the singular part of a function belonging to Keldysh space, $\tilde{l}(z, z') = l(z)\delta(z, z')$, meaning that $\tilde{l}^{R/A} = \tilde{l}^M = \tilde{l}$ and $\tilde{l}^{\lessgtr} = \tilde{l}^{\lceil} = \tilde{l}^{\rceil} = 0$. Using Table 3.1, one immediately realizes that the function l is simply a prefactor: $\int_{\gamma} d\bar{z} \tilde{l}(z, \bar{z})k^x(\bar{z}, z') = l(z)k^x(z, z')$, where x is one of the Keldysh components ($\lessgtr, R, A, \lceil, \rceil, M$). The same is true for $\int_{\gamma} d\bar{z} k^x(z, \bar{z})\tilde{r}(\bar{z}, z') = k^x(z, z')r(z')$, where $\tilde{r}(z, z') = r(z)\delta(z, z')$ and $r(z)$ is a scalar function.

3.5 The Kadanoff-Baym Equations

The Green function, as defined in (3.10), satisfies the equation of motion

$$i \frac{d}{dz} \mathbf{G}(z, z') = \mathbf{1} \delta(z, z') + \mathbf{h}(z) \mathbf{G}(z, z') + \int_{\gamma} d\bar{z} \mathbf{\Sigma}(z, \bar{z}) \mathbf{G}(\bar{z}, z'), \quad (3.38)$$

as well as the adjoint equation

$$-i \frac{d}{dz'} \mathbf{G}(z, z') = \mathbf{1} \delta(z, z') + \mathbf{G}(z, z') \mathbf{h}(z') + \int_{\gamma} d\bar{z} \mathbf{G}(z, \bar{z}) \mathbf{\Sigma}(\bar{z}, z'). \quad (3.39)$$

The external potential is included in \mathbf{h} , while the self-energy Σ is a functional of the Green function, and describes the effects of the electron interaction. The self-energy belongs to Keldysh space and can therefore be written in the form $\Sigma(z, z') = \delta(z, z')\Sigma^\delta(z) + \theta(z, z')\Sigma^>(z, z') + \theta(z', z)\Sigma^<(z, z')$. The singular part of the self-energy can be identified with the Hartree–Fock potential, $\Sigma^\delta(z) = \mathbf{v}_H(z) + \Sigma_x(z)$. The self-energy obeys the same anti-periodic boundary conditions at $z = 0_-$ and $z = -i\beta$ as \mathbf{G} . We will discuss self-energy approximations in more detail below.

Calculating the Green function on the time-contour now consists of two steps: (i) First one has to find the Green function for imaginary times, which is equivalent to finding the equilibrium Matsubara Green function $\mathbf{G}^M(\tau, \tau')$. This Green function depends only on the difference between the time-coordinates, and satisfies the KMS boundary conditions according to $\mathbf{G}^M(\tau+i\beta, \tau') = -e^{\beta\mu N}\mathbf{G}^M(\tau, \tau')$. Since the self-energy depends on the Green function, this amounts to solving the finite-temperature Dyson equation to self-consistency. (ii) The Green function with one or two time-variables on the real axis can now be found by propagating according to (3.38) and (3.39). Starting from $t = 0$, this procedure corresponds to extending the time-contour along the real time-axis. The process is illustrated in Fig. 3.2. Writing out the equations for the components of \mathbf{G} using Table 3.1, we obtain the equations known as the Kadanoff-Baym equations [Kadanoff 1962],

$$i\frac{d}{dt}\mathbf{G}^{\lessgtr}(t, t') = \mathbf{h}(t)\mathbf{G}^{\lessgtr}(t, t') + [\Sigma^R \cdot \mathbf{G}^{\lessgtr}](t, t') + [\Sigma^{\lessgtr} \cdot \mathbf{G}^A](t, t') + [\Sigma^{\lrcorner} \star \mathbf{G}^{\lrcorner}](t, t'), \quad (3.40a)$$

$$-i\frac{d}{dt'}\mathbf{G}^{\lessgtr}(t, t') = \mathbf{G}^{\lessgtr}(t, t')\mathbf{h}(t') + [\mathbf{G}^{\lessgtr} \cdot \Sigma^A](t, t') + [\mathbf{G}^R \cdot \Sigma^{\lessgtr}](t, t') + [\mathbf{G}^{\lrcorner} \star \Sigma^{\lrcorner}](t, t'), \quad (3.40b)$$

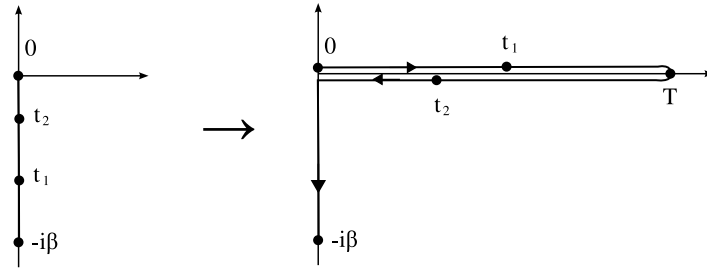


Fig. 3.2. Propagating the Kadanoff-Baym equations means that one first determines the Green function for time-variables along the imaginary track. One then calculates the Green function with one or two variables on an expanding time-contour

$$i \frac{d}{dt} \mathbf{G}^{\downarrow}(t, \tau) = \mathbf{h}(t) \mathbf{G}^{\downarrow}(t, \tau) + [\boldsymbol{\Sigma}^{\text{R}} \cdot \mathbf{G}^{\downarrow}](t, \tau) + [\boldsymbol{\Sigma}^{\downarrow} \star \mathbf{G}^{\text{M}}](t, \tau), \quad (3.40\text{c})$$

$$-i \frac{d}{dt} \mathbf{G}^{\uparrow}(\tau, t) = \mathbf{G}^{\uparrow}(\tau, t) \mathbf{h}(t) + [\boldsymbol{\Sigma}^{\uparrow} \cdot \mathbf{G}^{\text{A}}](\tau, t) + [\boldsymbol{\Sigma}^{\text{M}} \star \mathbf{G}^{\uparrow}](\tau, t). \quad (3.40\text{d})$$

The equations (3.40a) and (3.40c) can both be written on the form

$$i \frac{d}{dt} \mathbf{G}^{\text{x}}(t, z') = \mathbf{h}^{\text{HF}}(t) \mathbf{G}^{\text{x}}(t, z') + \mathbf{I}^{\text{x}}(t, z'), \quad (3.41)$$

while (3.40b) and (3.40d) can be written as the adjoint equations. The term proportional to $\mathbf{h}^{\text{HF}} \equiv \mathbf{h} + \boldsymbol{\Sigma}^{\delta}$ describes a free-particle propagation, while \mathbf{I}^{x} is a collision term, which accounts for electron correlation and introduces memory effects and dissipation. Considering the function $\mathbf{G}^{\lessgtr}(t, t')$, it is easily seen that if we denote by T the largest of the two time-arguments t and t' , then the collision terms $\mathbf{I}^{\lessgtr}(t, t')$ depend on $\mathbf{G}^{\lessgtr}(t_1, t_2)$, $\mathbf{G}^{\uparrow}(\tau_1, t_2)$ and $\mathbf{G}^{\downarrow}(t_1, \tau_2)$ for $t_1, t_2 \leq T$. In other words, given the functions $\mathbf{G}^{\text{x}}(t, t')$ for time arguments up to T , we can calculate $\mathbf{I}^{\text{x}}(t, t')$, and consequently find \mathbf{G}^{x} for time-arguments $t + \Delta$ and $t' + \Delta$, by a simple time-stepping procedure based on (3.41). The Green function $\mathbf{G}^{\lessgtr}(t, t')$ is thus obtained for time-arguments within the expanding square given by $t, t' \leq T$. Simultaneously, one calculates $\mathbf{G}^{\downarrow}(t, \tau)$ and $\mathbf{G}^{\uparrow}(\tau, t)$ for $t \leq T$. The resulting \mathbf{G} then automatically satisfies the KMS boundary conditions.

When propagating the Kadanoff-Baym equations one therefore starts at $t = t' = 0$, with the initial conditions given by $\mathbf{G}^{<}(0, 0) = \lim_{\eta \rightarrow 0} \mathbf{G}^{\text{M}}(0, -i\eta)$, $\mathbf{G}^{>}(0, 0) = \lim_{\eta \rightarrow 0} \mathbf{G}^{\text{M}}(-i\eta, 0)$, $\mathbf{G}^{\uparrow}(\tau, 0) = \mathbf{G}^{\text{M}}(\tau, 0)$ and $\mathbf{G}^{\downarrow}(0, \tau) = \mathbf{G}^{\text{M}}(0, \tau)$. As can be seen from (3.40a)–(3.40d), the only contribution to $\mathbf{I}^{\text{x}}(0, 0)$ comes from terms containing time-arguments on the imaginary axis. These terms therefore contain the effect of initial correlations, since the time-derivative of \mathbf{G} would otherwise correspond to that of an uncorrelated system, i.e., $\mathbf{I}^{\text{x}}(0, 0) = 0$.

3.6 Example: H₂ in An Electric Field

We can illustrate the procedure outlined in the previous section by a simple example. We consider an H₂ molecule, which is initially (at $t = 0$) in its ground-state. At $t = 0$ we then switch on an additional electric field, which is directed along the molecular axis and will remain constant, adding a term $v'(\mathbf{r}, t) = -zE_0\theta(t)$ to the Hamiltonian. We will here focus on the electron dynamics, and let the nuclei remain fixed in their equilibrium positions. The functions \mathbf{G} , $\boldsymbol{\Sigma}$, \mathbf{h} and \mathbf{I} defined in the previous section are all expanded in a molecular orbital basis, and the first step therefore consists of choosing these orbitals, e.g. by performing a Hartree-Fock calculation. The resulting Green function is independent of this choice of orbitals. Given this basis, the Green function is represented on matrix form,

$\langle \mathbf{r} | \mathbf{G}(z, z') | \mathbf{r}' \rangle = \sum_{ij} \varphi_i(\mathbf{r}) G_{ij}(z, z') \varphi_j^*(\mathbf{r}')$, where the indices i refer to the molecular orbitals $\varphi_i(\mathbf{r}) = \langle \mathbf{r} | \varphi_i \rangle$. We then solve the Dyson equation for the ground state, when the Hamiltonian (without the additional electric field) is time-independent. The Matsubara Green function only depends on the difference between the two imaginary time-coordinates, and we consequently have to solve the equation³

$$i \frac{d}{d\tau} \mathbf{G}^M(\tau - \tau') = \mathbf{1} \delta(\tau, \tau') + \mathbf{h} \mathbf{G}^M(\tau) + [\boldsymbol{\Sigma}^M \star \mathbf{G}^M](\tau - \tau') \quad (3.42)$$

with the anti-periodic boundary condition $\mathbf{G}^M(\tau + i\beta) = -e^{-\beta\mu} \mathbf{G}^M(\tau)$. In this example, we have used the second-order approximation to the self-energy $\boldsymbol{\Sigma}$, as illustrated in Fig. 3.4(b). Since the self-energy depends on the Green function, the Dyson equation should be solved to self-consistency, which can be done with an iterative procedure [Dahlen 2005b, Ku 2002]. The Matsubara Green function itself contains a wealth of information about the ground state system, and quantities such as the energy, ionization potential and the density matrix are readily given.

The time-propagation of the time-dependent matrix equations (3.40a)–(3.40d) is relatively straightforward, the main difficulty rising from the fact that the Green function G^{\lessgtr} has to be stored for all times $t, t' \leq T$. The self-energy approximation used here, is given by the same second-order diagrams that was used for the ground-state calculation. The plots in Fig. 3.3 show the imaginary part of the matrix element $G_{\sigma_g, \sigma_g}^<(t, t')$ calculated for time-variables within the square $t, t' \leq T = 20.0$ a.u., i.e., we have extended the contour in Fig. 3.2 to $T = 20$ a.u. The time-variables are here represented on an even-spaced grid. In the plot to the left, there is no added external potential and the molecule remains in equilibrium. This means that the Green function depends only on the difference $t_2 - t_1$ (for $t_1, t_2 \geq 0$) precisely like the ordinary equilibrium Green functions. Time-propagation without any added time-dependent field can in this way provide us with information about the ground state of the system. For instance, the Fourier transformed Green function $\mathbf{G}(\omega) = \int dt_1 dt_2 e^{i\omega(t_1 - t_2)} \mathbf{G}(t_1 - t_2)$ has poles at the ionization potentials and electron affinities of the system [Fetter 1971]. The density matrix at a time t is given by the time-diagonal, $-i\mathbf{G}^<(t, t)$, and one can therefore define time-dependent natural orbitals (and corresponding natural orbital occupation numbers) by diagonalizing the time-dependent density matrix. As the Green function illustrated in Fig. 3.3(a) is largely diagonal in the HF orbital indices, the frequency of the oscillations in the matrix element $G_{\sigma_g, \sigma_g}(t_1, t_2)$ is for this reason practically identical to the first ionization potential of the molecule. Also the value of $-iG_{\sigma_g, \sigma_g}^<(t_1, t_1) = \text{Im}G_{\sigma_g, \sigma_g}^<(t_1, t_1)$ (the Green function is imaginary on the diagonal), which is constant along the diagonal

³ This equation looks slightly different from how it usually appears in textbooks, e.g. in [Fetter 1971]. The conventional form is obtained by redefining $\mathbf{G}^M \rightarrow -i\mathbf{G}^M$, $\boldsymbol{\Sigma}^M \rightarrow -i\boldsymbol{\Sigma}^M$ and $\tau \rightarrow -i\tau$. The new quantities are then all real.

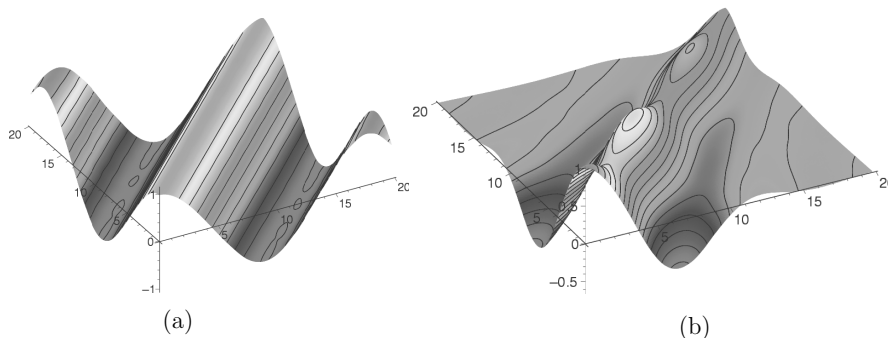


Fig. 3.3. The figures show the Green function $\text{Im } G_{\sigma_g, \sigma_g}^<(t_1, t_2)$ in the double time-plane, where the matrix indices refer to the groundstate σ_g Hartree–Fock orbital of the molecule. The figure on the *left* shows the system in equilibrium, while the system on the *right* has an additional electric field, $\theta(t)E_0$ along the molecular axis. The times t_1 and t_2 on the axes are given in atomic units

ridge in Fig. 3.3, is almost identical to the occupation number of the $1\sigma_g$ natural orbital.

The figure on the right shows the same matrix element, but now in the presence of an additional electric field which is switched on at $t = 0$. The oscillations along the ridge $t_1 = t_2$ can be interpreted as oscillations in the occupation number. We emphasize that Fig. 3.3 only shows the evolution of one matrix element. To calculate observables from the Green function we must of course take all matrix elements into account.

3.7 Conserving Approximations

In the Dyson–Schwinger equations (3.38) and (3.39), we introduced the electronic self-energy functional Σ , which accounts for the effects of the electron interaction. The self-energy is a functional of the Green function, and will have to be approximated in practical calculations. Diagrammatic techniques provide a natural scheme for generating approximate self-energies and for systematically improving these approximations. There are no general prescriptions for how to select the relevant diagrams, which means that this selection must be guided by physical intuition. There are, however, important conservation laws, like the number conservation law or the energy conservation law, that should always be obeyed. We will in the following discuss an exact framework for generating such *conserving approximations*.

Let us first discuss the conservation laws obeyed by a system of interacting electrons in an external field given by the electrostatic potential $v_{\text{ext}}(\mathbf{r}, t)$ and vector potential $\mathbf{A}_{\text{ext}}(\mathbf{r}, t)$. An important relation is provided by the continuity equation

$$\frac{d}{dt}n(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0. \quad (3.43)$$

The density and the current density can be calculated from the Green function using (3.13) and (3.14). Whether these quantities will obey the continuity equation will depend on whether the Green function is obtained from a conserving self-energy approximation. If we know the current density we can also calculate the total momentum and angular momentum expectation values in the system from the equations

$$\mathbf{P}(t) = \int d^3r \mathbf{j}(\mathbf{r}, t) \quad \text{and} \quad \mathbf{L}(t) = \int d^3r \mathbf{r} \times \mathbf{j}(\mathbf{r}, t). \quad (3.44)$$

For these two quantities the following relations should be satisfied

$$\frac{d}{dt}\mathbf{P}(t) = - \int d^3r \{n(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t) + \mathbf{j}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)\} \quad (3.45a)$$

$$\frac{d}{dt}\mathbf{L}(t) = - \int d^3r \{n(\mathbf{r}, t) \mathbf{r} \times \mathbf{E}(\mathbf{r}, t) + \mathbf{r} \times [\mathbf{j}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)]\}. \quad (3.45b)$$

where \mathbf{E} and \mathbf{B} are the electric and magnetic fields calculated from

$$\mathbf{E}(\mathbf{r}, t) = \nabla v_{\text{ext}}(\mathbf{r}, t) - \frac{d}{dt}\mathbf{A}_{\text{ext}}(\mathbf{r}, t) \quad \text{and} \quad \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}_{\text{ext}}(\mathbf{r}, t). \quad (3.46)$$

The (3.45a) and (3.45b) tell us that the change in momentum and angular momentum is equal to the total force and total torque on the system. In the absence of external fields these equations express momentum and angular momentum conservation. Since the right hand sides of (3.45a) and (3.45b) can also directly be calculated from the density and the current and therefore from the Green function, we may wonder whether they are satisfied for a given approximation to the Green function.

Finally we consider the case of energy conservation. Let $E(t) = \langle \hat{H}(t) \rangle$ be the energy expectation value of the system, then we have

$$\frac{d}{dt}E(t) = - \int d^3r \mathbf{j}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t). \quad (3.47)$$

This equation tells us that the energy change of the system is equal to the work done on the system. The total energy is calculated from the Green function using the expression

$$E(t) = -\frac{i}{2} \int d^3r \langle \mathbf{r} | \left[i \frac{d}{dt} + \mathbf{h}(t) \right] \mathbf{G}^<(t, t') | \mathbf{r} \rangle \Big|_{t'=t}. \quad (3.48)$$

The question is now whether the energy and the current calculated from an approximate Green function satisfy the relation in (3.47).

Baym and Kadanoff [Baym 1961, Baym 1962] showed that conserving approximations follow immediately if the self-energy is obtained as the functional derivative,

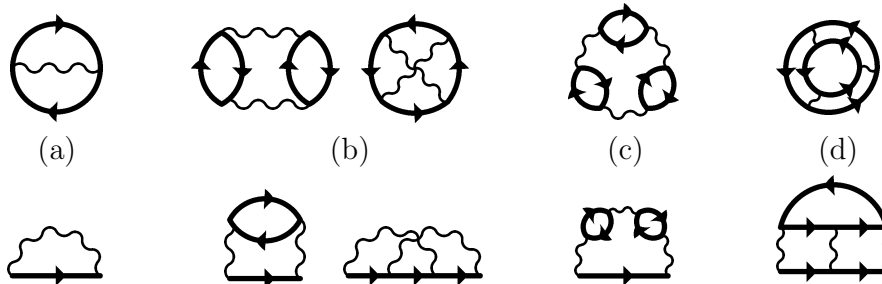


Fig. 3.4. Diagrams for the generating functional $\Phi[G]$, and the corresponding self-energy diagrams. In (a) we have the exchange diagram, and (b) the second order approximation. The diagrams in (c) and (d) belong to the GW approximation and the T -matrix approximation respectively

$$\Sigma(1, 2) = \frac{\delta\Phi[G]}{\delta G(2, 1)}. \quad (3.49)$$

Here, and in the following discussion, we use numbers to denote the contour coordinates, such that $1 = (\mathbf{r}_1, z_1)$. A functional $\Phi[G]$ can be constructed, as first shown in a seminal paper by Luttinger and Ward [Luttinger 1960], by summing over irreducible self-energy diagrams closed with an additional Green function line and multiplied by appropriate numerical prefactors,

$$\Phi[G] = \sum_{n,k} \frac{1}{2n} \int d\bar{1} \int d\bar{2} \Sigma_n^{(k)}(\bar{1}, \bar{2}) G(\bar{2}, \bar{1}). \quad (3.50)$$

In this summation, $\Sigma_n^{(k)}$ denotes a self-energy diagram of n -th order, i.e., containing n interaction lines. The time-integrals go along the contour, but the rules for constructing Feynman diagrams are otherwise exactly the same as those in the ground-state formalism [Fetter 1971]. Notice that the functional derivative in (3.49) may generate other self-energy diagrams in addition to those used in the construction of $\Phi[G]$ in (3.50). In Fig. 3.4 we show some examples of typical $\Phi[G]$ diagrams. Examples of Φ -derivable approximations include Hartree–Fock, the second order approximation (also known as the second Born approximation), the GW approximation and the T -matrix approximation.

When the Green function is calculated from a conserving approximation, the resulting observables agree with the conservation laws of the underlying Hamiltonian, as given in (3.43), (3.45a), (3.45b), and (3.47). This guarantees the conservation of particles, energy, momentum, and angular momentum. All these conservation laws follow from the invariance of $\Phi[G]$ under specific changes in G . We will here only outline the principles of the proofs, without going into the details, which can be found in [Baym 1961, Baym 1962].

- *Number conservation* follows from the gauge invariance of $\Phi[G]$. A gauge transformation $\mathbf{A}_{\text{ext}}(1) \rightarrow \mathbf{A}_{\text{ext}}(1) + \nabla\Lambda(1)$, where $\Lambda(\mathbf{r}, 0_-) = \Lambda(\mathbf{r}, -i\beta)$

leaves $\Phi[G]$ unchanged. A consequence of the gauge invariance is that a pure gauge cannot induce a change in the density or current. The invariance is therefore closely related to the Ward-identities and to the f -sum rule for the density response function [van Leeuwen 2004a].

- *Momentum conservation* follows from the invariance of $\Phi[G]$ under spatial translations, $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}(z)$. The invariance is a consequence of the electron interaction $v(1, 2) = \delta(z_1, z_2)/|\mathbf{r}_1 - \mathbf{r}_2|$ being instantaneous and only depending on the difference between the spatial coordinates.
- *Angular momentum conservation* follows from the invariance of $\Phi[G]$ under a rotation of the spatial coordinates.
- *Energy conservation* follows from the invariance of $\Phi[G]$ when described by an observer using a “rubbery clock”, measuring time according to the function $s(z)$. The invariance relies on the electron interaction being instantaneous.

3.8 Noninteracting Electrons

In this section we focus on noninteracting electrons. This is particularly relevant for TDDFT, where the electrons are described by the noninteracting Kohn-Sham system. While the Kohn-Sham Green function differs from the true Green function, they both produce the same time-dependent density. This is important since the density is not only an important observable in, e.g., quantum transport, but also since the density is the central ingredient in TDDFT. The use of NEGFs in TDDFT is therefore important due to the relation between v_{xc} and the self-energy.

For a system of noninteracting electrons $\hat{V}_{ee} = 0$ and it is straightforward to show that the Green function obeys the equations of motion (3.38) and (3.39), with $\Sigma = 0$. For any $z \neq z'$, the equations of motion can be solved by using the evolution operator on the contour,

$$\mathbf{U}(z, z') = \hat{\mathcal{T}}_c \left\{ e^{-i \int_z^{z'} d\bar{z} \mathbf{h}(\bar{z})} \right\}, \quad (3.51)$$

which solves $i \frac{d}{dz} \mathbf{U}(z, z') = \mathbf{h}(z) \mathbf{U}(z, z')$ and $-i \frac{d}{dz'} \mathbf{U}(z, z') = \mathbf{U}(z, z') \mathbf{h}(z')$. Therefore, any Green function

$$\mathbf{G}(z, z') = \theta(z, z') \mathbf{U}(z, 0_-) \mathbf{f}^> \mathbf{U}(0_-, z') + \theta(z', z) \mathbf{U}(z, 0_-) \mathbf{f}^< \mathbf{U}(0_-, z'), \quad (3.52)$$

satisfying the constraint (3.17) on the form

$$\mathbf{f}^> - \mathbf{f}^< = -\mathbf{i}1, \quad (3.53)$$

is a solution of (3.38)–(3.39). In order to fix the matrix $\mathbf{f}^>$ or $\mathbf{f}^<$ we impose the KMS boundary conditions. The matrix $\mathbf{h}(z) = \mathbf{h}_0$ for any z on the vertical track, meaning that $\mathbf{U}(-i\beta, 0_-) = e^{-\beta \mathbf{h}_0}$. Equation (3.16) then implies

$\mathbf{f}^< = -e^{-\beta(\mathbf{h}_0 - \mu)} \mathbf{f}^>$, and taking into account the constraint (3.53) we conclude that

$$\mathbf{f}^< = \frac{i}{e^{\beta(\mathbf{h}_0 - \mu)} + 1} = i f(\mathbf{h}_0), \quad (3.54)$$

where $f(\omega) = 1/[e^{\beta(\omega - \mu)} + 1]$ is the Fermi distribution function. The matrix $\mathbf{f}^>$ takes the form $\mathbf{f}^> = i[f(\mathbf{h}_0) - \mathbf{1}]$.

The Green function $\mathbf{G}(z, z')$ for a system of noninteracting electrons is now completely fixed. Both $\mathbf{G}^>$ and $\mathbf{G}^<$ depend on the initial distribution function $f(\mathbf{h}_0)$, as it should according to the discussion of Sect. 3.3. Another way of writing $-i\mathbf{G}^<$ is in terms of the eigenstates $|\varphi_n\rangle \equiv |\varphi_n(0)\rangle$ of \mathbf{h}_0 with eigenvalues ε_n . From the time-evolved eigenstate $|\varphi_n(t)\rangle = \mathbf{U}(t, 0)|\varphi_n\rangle$ we can calculate the time-dependent wavefunction $\varphi_n(\mathbf{r}, t) = \langle \mathbf{r} | \varphi_n(t) \rangle$. Inserting $\sum_n |\varphi_n(0)\rangle \langle \varphi_n(0)|$ in the expression for $\mathbf{G}^<$ we find

$$\begin{aligned} -i\mathbf{G}^<(\mathbf{r}t, \mathbf{r}'t') &= -i \sum_{m,n} \langle \mathbf{r} | \mathbf{U}(t, 0) | \varphi_m \rangle \langle \varphi_m | \mathbf{f}^< | \varphi_n \rangle \langle \varphi_n | \mathbf{U}(0, t) \mathbf{r}' \rangle \\ &= \sum_n f(\varepsilon_n) \varphi_n(\mathbf{r}, t) \varphi_n^*(\mathbf{r}', t'), \end{aligned} \quad (3.55)$$

which for $t = t'$ reduces to the time-dependent density matrix. The Green function $\mathbf{G}^>$ becomes

$$-i\mathbf{G}^>(\mathbf{r}t, \mathbf{r}'t') = - \sum_n [1 - f(\varepsilon_n)] \varphi_n(\mathbf{r}, t) \varphi_n^*(\mathbf{r}', t'). \quad (3.56)$$

Knowing the greater and lesser Green functions we can also calculate $\mathbf{G}^{\text{R,A}}$. By definition we have

$$\mathbf{G}^{\text{R}}(t, t') = \theta(t - t') [\mathbf{G}^>(t, t') - \mathbf{G}^<(t, t')] = -i\theta(t - t') \mathbf{U}(t, t'), \quad (3.57)$$

and similarly

$$\mathbf{G}^{\text{A}}(t, t') = i\theta(t' - t) \mathbf{U}(t, t') = [\mathbf{G}^{\text{R}}(t', t)]^\dagger. \quad (3.58)$$

In the above expressions the Fermi distribution function has disappeared. The information carried by $\mathbf{G}^{\text{R,A}}$ is the same contained in the one-particle evolution operator. There is no information on how the system is prepared (how many particles, how they are distributed, etc). We use this observation to rewrite \mathbf{G}^{\leq} in terms of $\mathbf{G}^{\text{R,A}}$

$$\mathbf{G}^{\leq}(t, t') = \mathbf{G}^{\text{R}}(t, 0) \mathbf{G}^{\leq}(0, 0) \mathbf{G}^{\text{A}}(0, t'). \quad (3.59)$$

Thus, \mathbf{G}^{\leq} is completely known once we know how to propagate the one-electron orbitals in time and how they are populated before the system is perturbed [Blandin 1976, Cini 1980, Stefanucci 2004a]. We also observe that an analogous relation holds for \mathbf{G}^{\geq} ,

$$\mathbf{G}^{\lceil}(t, \tau) = i\mathbf{G}^{\text{R}}(t, 0)\mathbf{G}^{\lceil}(0, \tau), \quad \mathbf{G}^{\lceil}(\tau, t) = -i\mathbf{G}^{\lceil}(\tau, 0)\mathbf{G}^{\text{A}}(0, \tau). \quad (3.60)$$

Let us now focus on a special kind of disturbance, namely $\mathbf{h}(t) = \mathbf{h}_0 + \theta(t)\mathbf{h}_1$. In this case

$$\mathbf{G}^{\text{R}}(t, t') = -i\theta(t - t')e^{-i(\mathbf{h}_0 + \mathbf{h}_1)(t - t')} \quad (3.61)$$

depends only on the difference between the time arguments. Let us define the Fourier transform of $\mathbf{G}^{\text{R,A}}$ from

$$\mathbf{G}^{\text{R,A}}(t, t') = \int \frac{d\omega}{2\pi} e^{-i\omega(t - t')} \mathbf{G}^{\text{R,A}}(\omega). \quad (3.62)$$

The step function can be written as $\theta(t - t') = \int \frac{d\omega}{2\pi i} \frac{\exp\{i\omega(t - t')\}}{\omega - i\eta}$, with η an infinitesimally small positive constant. Substituting this representation of the θ -function into (3.61) and shifting the ω variable one readily finds

$$\mathbf{G}^{\text{R}}(\omega) = \frac{1}{\omega - \mathbf{h}_0 - \mathbf{h}_1 + i\eta}, \quad (3.63)$$

and therefore $\mathbf{G}^{\text{R}}(\omega)$ is analytic in the upper half plane. On the other hand, from (3.58) it follows that $\mathbf{G}^{\text{A}}(\omega) = [\mathbf{G}^{\text{R}}(\omega)]^\dagger$ is analytic in the lower half plane. What can we say about the greater and lesser components? Do they also depend only on the difference $t - t'$? The answer to the latter question is negative. Indeed, we recall that they contain information on how the system is prepared before \mathbf{h}_1 is switched on. In particular the original eigenstates are eigenstates of \mathbf{h}_0 and in general are not eigenstates of the Hamiltonian $\mathbf{h}_0 + \mathbf{h}_1$ at positive times. From (3.59) one can see that $\mathbf{G}^{\lessgtr}(t, t')$ cannot be expressed only in terms of the time difference $t - t'$. For instance

$$\mathbf{G}^{\text{<}}(t, t') = e^{-i(\mathbf{h}_0 + \mathbf{h}_1)t} \mathbf{1} f(\mathbf{h}_0) e^{i(\mathbf{h}_0 + \mathbf{h}_1)t'}, \quad (3.64)$$

and, unless \mathbf{h}_0 and \mathbf{h}_1 commute, it is a function of t and t' separately.

It is sometimes useful to split $\mathbf{h}(t)$ in two parts⁴ and treat one of them perturbatively. Let us think, for instance, of a system composed of two connected subsystems $A + B$. In case we know how to calculate the Green function of the isolated subsystems A and B , it is convenient to treat the connecting part as a perturbation. Thus, we write $\mathbf{h}(t) = \mathcal{E}(t) + \mathcal{V}(t)$, and we define \mathbf{g} as the Green function when $\mathcal{V} = 0$. The function \mathbf{g} is a solution of

$$\left\{ i \frac{d}{dz} - \mathcal{E}(z) \right\} \mathbf{g}(z, z') = \mathbf{1} \delta(z, z'), \quad (3.65)$$

and of the corresponding adjoint equation of motion. Furthermore, the Green function \mathbf{g} obeys the KMS boundary conditions. With these we can use \mathbf{g} to convert the equations of motion for \mathbf{G} into integral equations

⁴ This can be done using projection operators. See [Stefanucci 2004a].

$$\begin{aligned}
\mathbf{G}(z, z') &= \mathbf{g}(z, z') + \int_{\gamma} d\bar{z} \mathbf{g}(z, \bar{z}) \mathbf{V}(\bar{z}) \mathbf{G}(\bar{z}, z') \\
&= \mathbf{g}(z, z') + \int_{\gamma} d\bar{z} \mathbf{G}(z, \bar{z}) \mathbf{V}(\bar{z}) \mathbf{g}(\bar{z}, z') ; \quad (3.66)
\end{aligned}$$

the integral on \bar{z} is along the generalized Keldysh contour of Fig. 3.1. One can easily check that this \mathbf{G} satisfies both (3.38) and (3.39). \mathbf{G} also obeys the KMS boundary conditions since the integral equation is defined on the contour of Fig. 3.1.

In order to get some familiarity with the above perturbation scheme, we consider explicitly the system $A + B$ already mentioned. We partition the one-electron Hilbert space in states of the subsystem A and states of the subsystem B . The ‘‘unperturbed’’ system is described by \mathcal{E} , while the connecting part by \mathbf{V} and

$$\mathcal{E} = \begin{bmatrix} \mathcal{E}_{AA} & 0 \\ 0 & \mathcal{E}_{BB} \end{bmatrix}, \quad \mathbf{V} = \begin{bmatrix} 0 & \mathbf{V}_{AB} \\ \mathbf{V}_{BA} & 0 \end{bmatrix}. \quad (3.67)$$

Taking into account that \mathbf{g} has no off-diagonal matrix elements, the Green function projected on one of the two subsystems, e.g., \mathbf{G}_{BB} , is

$$\mathbf{G}_{BB}(z, z') = \mathbf{g}_{BB}(z, z') + \int_{\gamma} d\bar{z} \mathbf{g}_{BB}(z, \bar{z}) \mathbf{V}_{BA}(\bar{z}) \mathbf{G}_{AB}(\bar{z}, z') \quad (3.68)$$

and

$$\mathbf{G}_{AB}(z, z') = \int_{\gamma} d\bar{z} \mathbf{g}_{AA}(z, \bar{z}) \mathbf{V}_{AB}(\bar{z}) \mathbf{G}_{BB}(\bar{z}, z'). \quad (3.69)$$

Substituting this latter equation into the first one, we obtain a closed equation for \mathbf{G}_{BB} :

$$\mathbf{G}_{BB}(z, z') = \mathbf{g}_{BB}(z, z') + \int_{\gamma} d\bar{z} \int_{\gamma} d\bar{z}' \mathbf{g}_{BB}(z, \bar{z}) \mathbf{\Sigma}_{BB}(\bar{z}, \bar{z}') \mathbf{G}_{BB}(\bar{z}', z'), \quad (3.70)$$

with

$$\mathbf{\Sigma}_{BB}(\bar{z}, \bar{z}') = \mathbf{V}_{BA}(\bar{z}) \mathbf{g}_{AA}(\bar{z}, \bar{z}') \mathbf{V}_{AB}(\bar{z}') \quad (3.71)$$

the embedding self-energy. The retarded and advanced component can now be easily computed. With the help of Table 3.1 one finds

$$\mathbf{G}_{BB}^{\text{R,A}} = \mathbf{g}_{BB}^{\text{R,A}} + \mathbf{g}_{BB}^{\text{R,A}} \cdot \mathbf{\Sigma}_{BB}^{\text{R,A}} \cdot \mathbf{G}_{BB}^{\text{R,A}}. \quad (3.72)$$

Next, we have to compute the lesser or greater component. As for the retarded and advanced components, this can be done starting from (3.70). The reader can soon realize that the calculation is rather complicated, due to the mixing of pure real-time functions with functions having one real time argument and one imaginary time argument, see Table 3.1. Below, we

use (3.59) as a feasible short-cut. A closed equation for the retarded and advanced component has been already obtained. Thus, we simply need an equation for $\mathbf{G}^{\lessgtr}(0,0)$. Let us focus on the lesser component $\mathbf{G}^<(0,0) = i\mathbf{f}^<$. Assuming that the Hamiltonian \mathbf{h}_0 is hermitian, the matrix $(\omega - \mathbf{h}_0)^{-1}$ has poles at frequencies equal to the eigenvalues of \mathbf{h}_0 . These poles are all on the real frequency axis, and we can therefore write

$$\mathbf{G}^<(0,0) = i\mathbf{f}(\mathbf{h}_0) = \int_{\gamma} \frac{d\zeta}{2\pi} f(\zeta) \frac{1}{\zeta - \mathbf{h}_0}, \quad (3.73)$$

where the contour γ encloses the real frequency axis.

3.9 Action Functional and TDDFT

We define the action functional

$$\tilde{A} = i \ln \text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\}, \quad (3.74)$$

where the evolution operator \hat{U} is the same as defined in (3.3). The action functional is a tool for generating equations of motion, and is not interesting *per se*. Nevertheless, one should notice that the action, as defined in (3.74) has a numerical value equal to $\tilde{A} = i \ln Z$, where Z is the thermodynamic partition function. In the zero temperature limit, we then have $\lim_{\beta \rightarrow \infty} i\tilde{A}/\beta = E - \mu N$.

It is easy to show that if we make a perturbation $\delta\hat{V}(z)$ in the Hamiltonian, the change in the evolution operator is given by

$$i \frac{d}{dz} \delta\hat{U}(z, z') = \delta\hat{V}(z) \hat{U}(z, z') + \hat{H}(z) \delta U(z, z'). \quad (3.75)$$

A similar equation for the dependence on z' , and the boundary condition $\delta\hat{U}(z, z) = 0$ gives

$$\delta\hat{U}(z, z') = -i \int_{z'}^z d\bar{z} \hat{U}(z, \bar{z}) \delta\hat{V}(\bar{z}) \hat{U}(\bar{z}, z'). \quad (3.76)$$

We stress that the time-coordinates are on a contour going from 0 to $-i\beta$. The variation in, e.g., $V(t_+)$ is therefore independent of the variation in $V(t_-)$. If we let $\delta\hat{V}(z) = \int d^3r \delta v(\mathbf{r}, z) \hat{n}(\mathbf{r})$, a combination of (3.74) and (3.76) yields [compare to (3.4)] the expectation values of the density,

$$\begin{aligned} \frac{\delta\tilde{A}}{\delta v(\mathbf{r}, z)} &= \frac{i}{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\}} \frac{\delta}{\delta v(\mathbf{r}, z)} \text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\} \\ &= \frac{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \hat{U}(0, z) \hat{n}(\mathbf{r}) \hat{U}(z, 0) \right\}}{\text{Tr} \left\{ e^{\beta\mu\hat{N}} \hat{U}(-i\beta, 0) \right\}} = n(\mathbf{r}, z). \end{aligned} \quad (3.77)$$

A physical potential is the same on the positive and on the negative branch of the contour, and the same is true for the corresponding time-dependent density, $n(\mathbf{r}, t) = n(\mathbf{r}, t_{\pm})$. A density response function defined for time-arguments on the contour is found by taking the functional derivative of the density with respect to the external potential. Using the compact notation $1 = (\mathbf{r}_1, z_1)$, the response function is written

$$\chi(1, 2) = \frac{\delta n(1)}{\delta v(2)} = \frac{\delta^2 \tilde{A}}{\delta v(1) \delta v(2)} = \chi(2, 1). \quad (3.78)$$

This response function is symmetric in the space and time-contour coordinates. We again stress that the variations in the potentials at t_+ and t_- are independent. If, however, one uses this response function to calculate the density response to an actual physical perturbing electric field, we obtain

$$\delta n(\mathbf{r}, t) = \delta n(\mathbf{r}, t_{\pm}) = \int_{\gamma} dz' \int d^3 r' \chi(\mathbf{r}t_{\pm}, \mathbf{r}'z') \delta v(\mathbf{r}', z'), \quad (3.79)$$

where γ indicates an integral along the contour. In this expression, the perturbing potential (as well as the induced density response) is independent of whether it is located on the positive or negative branch, i.e., $\delta v(\mathbf{r}', t'_{\pm}) = \delta v(\mathbf{r}', t')$. We consider a perturbation of a system initially in equilibrium, which means that $\delta v(\mathbf{r}', t') \neq 0$ only for $t' > 0$, and we can therefore ignore the integral along the imaginary track of the time-contour. The contour integral then consists of two parts: (i) First an integral from $t' = 0$ to $t' = t$, in which $\chi = \chi^>$, and (ii) an integral from $t' = t$ to $t' = 0$, where $\chi = \chi^<$. Writing out the contour integral in (3.79) explicitly then gives

$$\begin{aligned} \delta n(\mathbf{r}, t) &= \int_0^t dt' \int d^3 r' [\chi^>(\mathbf{r}t, \mathbf{r}'t') - \chi^<(\mathbf{r}t, \mathbf{r}'t')] \delta v(\mathbf{r}', t') \\ &= \int_0^{\infty} dt' \int d^3 r' \chi^R(\mathbf{r}t, \mathbf{r}'t') \delta v(\mathbf{r}', t'). \end{aligned} \quad (3.80)$$

The response to a perturbing field is therefore given by the retarded response function, while $\chi(1, 2)$ defined on the contour is symmetric in $(1 \leftrightarrow 2)$.

If we now consider a system of noninteracting electrons in some external potential v_{KS} , we can similarly define a noninteracting action-functional \tilde{A}_{KS} . The steps above can be repeated to calculate the noninteracting response function. The derivation is straightforward, and gives

$$\chi_{\text{KS}}(1, 2) = \frac{\delta^2 \tilde{A}_{\text{KS}}}{\delta v_{\text{KS}}(1) \delta v_{\text{KS}}(2)} = -i G_{\text{KS}}(1, 2) G_{\text{KS}}(2, 1). \quad (3.81)$$

The noninteracting Green function G_{KS} has the form given in (3.52), (3.55) and (3.56). The retarded response-function is

$$\begin{aligned}
\chi_{\text{KS}}^{\text{R}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= -i\theta(t_1 - t_2) [G_{\text{KS}}^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) G_{\text{KS}}^<(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) \\
&\quad - G_{\text{KS}}^<(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) G_{\text{KS}}^>(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1)] \\
&= i \sum_{n,m} [f(\varepsilon_m) - f(\varepsilon_n)] \\
&\quad \times \varphi_n(\mathbf{r}_1, t_1) \varphi_m^*(\mathbf{r}_1, t_1) \varphi_m(\mathbf{r}_2, t_2) \varphi_n^*(\mathbf{r}_2, t_2), \quad (3.82)
\end{aligned}$$

where we have used (3.55) and (3.56) in the last step.

Having defined the action functional for both the interacting and the noninteracting systems, we now make a Legendre transform, and define

$$A[n] = -\tilde{A}[v] + \int d1 n(1)v(1), \quad (3.83)$$

which has the property that $\delta A[n]/\delta n(1) = v(1)$. We also observe that the functional $A_{v_0}[n] = A[n] - \int d1 n(1)v_0(1)$, where v_0 is a fixed potential, is variational in the sense that

$$\frac{\delta A_{v_0}[n]}{\delta n(1)} = v(1) - v_0(1) = 0 \quad (3.84)$$

when $v = v_0$. This equation can be used as a basis for a variational principle in TDDFT [von Barth 2005]. Similar to the Legendre transform in (3.83), we define the action functional

$$A_{\text{KS}}[n] = -\tilde{A}_{\text{KS}}[v_{\text{KS}}] + \int d1 n(1)v_{\text{KS}}(1). \quad (3.85)$$

with the property $\delta A_{\text{KS}}[n]/\delta n(1) = v_{\text{KS}}(1)$. The Legendre transforms assume the existence of a one-to-one correspondence between the density and the potential. From these action functionals, we now define the exchange-correlation part to be

$$A_{\text{xc}}[n] = A_{\text{KS}}[n] - A[n] - \frac{1}{2} \int d1 \int d2 \delta(z_1, z_2) \frac{n(1)n(2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (3.86)$$

Taking the functional derivative with respect to the density gives

$$v_{\text{KS}}[n](1) = v(1) + v_{\text{H}}(1) + v_{\text{xc}}[n](1) \quad (3.87)$$

where $v_{\text{H}}(1)$ is the Hartree potential and $v_{\text{xc}}(1) = \delta A_{\text{xc}}/\delta n(1)$. Again, for time-arguments on the real axis, these potentials are independent of whether the time is on the positive or the negative branch. If we, however, want to calculate the response function from the action functional, then it is indeed important which part of the contour the time-arguments are located on.

As mentioned in the beginning in the section, we can make a connection to ground state DFT if we restrict ourselves to a time-independent Hamiltonian. In that case, the Kohn-Sham action takes the numerical value

$\lim_{\beta \rightarrow \infty} i\tilde{A}_{\text{KS}}/\beta = \sum_{i=1}^N (\epsilon_i - \mu) = T_{\text{KS}}[n] + \int d^3r n(\mathbf{r})v_{\text{KS}}(\mathbf{r}) - \mu N$. Using $i/\beta \int d1 n(1)v_{\text{KS}}(1) = \int d^3r n(\mathbf{r})v_{\text{KS}}(\mathbf{r})$, we can obtain, for a fixed potential v_0 ,

$$E_{v_0}[n] - \mu N = - \lim_{\beta \rightarrow \infty} \frac{i}{\beta} A_{v_0}[n] = T_{\text{KS}}[n] + \int d^3r n(\mathbf{r})v_0(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \lim_{\beta \rightarrow \infty} \frac{i}{\beta} A_{\text{xc}} - \mu N \quad (3.88)$$

from which we identify the relation

$$E_{\text{xc}}[n] = \lim_{\beta \rightarrow \infty} \frac{i}{\beta} A_{\text{xc}}[n]. \quad (3.89)$$

As an example, we can consider the ALDA action functional defined according to

$$A_{\text{xc}}^{\text{ALDA}}[n] = \int d1 n(1)e_{\text{xc}}(n(1)) \quad (3.90)$$

where e_{xc} is the exchange-correlation energy density. The resulting energy expression is

$$E_{\text{xc}}^{\text{LDA}}[n] = \lim_{\beta \rightarrow \infty} \frac{i}{\beta} \int_0^{-i\beta} d\tau \int d^3r n(\mathbf{r})e_{\text{xc}}(n(\mathbf{r})) = \int d^3r n(\mathbf{r})e_{\text{xc}}(n(\mathbf{r})). \quad (3.91)$$

We mention that much more sophisticated approximations to the exchange-correlation action functional can be derived using Green function techniques [von Barth 2005].

We already described how to define response function on the contour, both in the interacting (3.78) and the noninteracting (3.81) case. Given the exact Kohn-Sham potential, the TDDFT response function should give exactly the same density change as the exact response function,

$$\delta n(1) = \int d2 \chi(1, 2)\delta v(2) = \int d2 \chi_{\text{KS}}(1, 2)\delta v_{\text{KS}}(2). \quad (3.92)$$

The change in the Kohn-Sham potential is given by

$$\begin{aligned} \delta v_{\text{KS}}(1) &= \delta v(1) + \int d2 \frac{\delta v_{\text{H}}(1)}{\delta n(2)} \delta n(2) + \int d2 \frac{\delta v_{\text{xc}}(1)}{\delta n(2)} \delta n(2) \\ &= \delta v(1) + \int d2 f_{\text{Hxc}}(1, 2)\delta n(2) \\ &= \delta v(1) + \int d2 \int d3 f_{\text{Hxc}}(1, 2)\chi(2, 3)\delta v(3), \end{aligned} \quad (3.93)$$

where $f_{\text{Hxc}}(1, 2) = \delta(z_1, z_2)/|\mathbf{r}_1 - \mathbf{r}_2| + \delta v_{\text{xc}}(1)/\delta n(2)$. Inserted in (3.92), we obtain

$$\chi(1, 2) = \chi_{\text{KS}}(1, 2) + \int d3 \int d4 \chi_{\text{KS}}(1, 3) f_{\text{Hxc}}(3, 4) \chi(4, 2) . \quad (3.94)$$

This is the response function defined for time-arguments on the contour. If we want to calculate the response induced by a perturbing potential, the density change will be given by the retarded response function. Using Table 3.1, we can just write down

$$\begin{aligned} \chi^{\text{R}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \chi_{\text{KS}}^{\text{R}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) + \int dt_3 \int dt_4 \int d^3 r_3 \int d^3 r_4 \\ &\quad \chi_{\text{KS}}^{\text{R}}(\mathbf{r}_1 t_1, \mathbf{r}_3 t_3) f_{\text{Hxc}}^{\text{R}}(\mathbf{r}_3 t_3, \mathbf{r}_4 t_4) \chi^{\text{R}}(\mathbf{r}_4 t_4, \mathbf{r}_2 t_2) . \end{aligned} \quad (3.95)$$

The time-integrals in the last expression go from 0 to ∞ . As expected, only the retarded functions are involved in this expression. We stress the important result that while the function $f_{\text{Hxc}}(1, 2)$ is symmetric under the coordinate-permutation ($1 \leftrightarrow 2$), it is the retarded function

$$f_{\text{Hxc}}^{\text{R}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{\delta(t_1, t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{\text{xc}}^{\text{R}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) , \quad (3.96)$$

which is used when calculating the response to a perturbing potential.

3.10 Example: Time-Dependent OEP

We will close this section by discussing the time-dependent optimized effective potential (TDOEP) method in the exchange-only approximation. This is a useful example of how to use functions on the Keldysh contour. While the TDOEP equations can be derived from an action functional, we use here the time-dependent Sham-Schlüter equations as starting point [van Leeuwen 1996]. This equation is derived by employing a Kohn-Sham Green function, $G_{\text{KS}}(1, 2)$ which satisfies the equation of motion

$$\left\{ i \frac{d}{dz_1} + \frac{\nabla_1^2}{2} - v_{\text{KS}}(\mathbf{r}_1, z_1) \right\} G_{\text{KS}}(\mathbf{r}_1 z_1, \mathbf{r}_2 z_2) = \delta(z_1, z_2) \delta(\mathbf{r}_1 - \mathbf{r}_2) , \quad (3.97)$$

as well as the adjoint equation. The Kohn-Sham Green function is given by (3.55) and (3.56) in terms of the time-dependent Kohn-Sham orbitals. Comparing (3.97) to the Dyson-Schwinger (3.38), we see that we can write an integral equation for the interacting Green function in terms of the Kohn-Sham quantities,

$$\begin{aligned} G(1, 2) &= G_{\text{KS}}(1, 2) + \\ &\quad \int d\bar{1} \int d\bar{2} G_{\text{KS}}(1, \bar{1}) \{ \Sigma(\bar{1}, \bar{2}) + \delta(\bar{1}, \bar{2}) [v_{\text{ext}}(\bar{1}) - v_{\text{KS}}(\bar{1})] \} G(\bar{2}, 2) . \end{aligned} \quad (3.98)$$

It is important to keep in mind that this integral equation for $G(1, 2)$ differs from the differential equations (3.38) and (3.39) in the sense that we have imposed the boundary conditions of G_{KS} on G in (3.98). This means that if $G_{\text{KS}}(1, 2)$ satisfies the KMS boundary conditions (3.16), then so will $G(1, 2)$.

If we now assume that for any density $n(1) = -iG(1, 1^+)$ there is a potential $v_{\text{KS}}(1)$ such that $n(1) = -iG_{\text{KS}}(1, 1^+)$, we obtain the time-dependent Sham-Schlüter equation,

$$\int d\bar{1} \int d\bar{2} G_{\text{KS}}(1, \bar{1}) \Sigma(\bar{1}, \bar{2}) G(\bar{2}, 1) = \int d\bar{1} G_{\text{KS}}(1, \bar{1}) [v_{\text{KS}}(\bar{1}) - v_{\text{ext}}(\bar{1})] G(\bar{1}, 1). \quad (3.99)$$

This equation is formally correct, but not useful in practice since solving it would involve first calculating the nonequilibrium Green function. Instead, one sets $G = G_{\text{KS}}$ and $\Sigma[G] = \Sigma[G_{\text{KS}}]$. For a given self-energy functional, we then have an integral equation for the Kohn-Sham equation. This equation is known as the time-dependent OEP equation. Defining $\Sigma = v_H + \Sigma_{\text{xc}}$ and $v_{\text{KS}} = v_{\text{ext}} + v_H + v_{\text{xc}}$, the TDOEP equation can be written

$$\int d\bar{1} \int d\bar{2} G_{\text{KS}}(1, \bar{1}) \Sigma_{\text{xc}}[G_{\text{KS}}](\bar{1}, \bar{2}) G_{\text{KS}}(\bar{2}, 1) = \int d\bar{1} G_{\text{KS}}(1, \bar{1}) v_{\text{xc}}(\bar{1}) G_{\text{KS}}(\bar{1}, 1). \quad (3.100)$$

In the simplest approximation, Σ_{xc} is given by the exchange-only self-energy of Fig. 3.4a,

$$\Sigma_{\text{x}}(1, 2) = iG_{\text{KS}}^<(1, 2)v_{\text{ee}}(1, 2) = - \sum_j n_j \varphi_j(1) \varphi_j^*(2) v_{\text{ee}}(1, 2) \quad (3.101)$$

where n_j is the occupation number. This approximation leads to what is known as the exchange-only TDOEP equations [Ullrich 1995a, Ullrich 1995b, Görling 1997] (see Chap. 9). Since the exchange self-energy Σ_{x} is local in time, there is only one time-integration in (3.100). The x-only solution for the potential will be denoted v_{x} . With the notation $\tilde{\Sigma}(3, 4) = \Sigma_{\text{x}}(\mathbf{r}_3 t_3, \mathbf{r}_4 t_3) - \delta(\mathbf{r}_3 - \mathbf{r}_4) v_{\text{x}}(\mathbf{r}_3 t_3)$ we obtain from (3.100)

$$0 = \int_0^{t_1} dt_3 \int d^3 r_3 \int d^3 r_4 \left[G_{\text{KS}}^<(1, 3) \tilde{\Sigma}(3, 4) G_{\text{KS}}^>(4, 1) - G_{\text{KS}}^>(1, 3) \tilde{\Sigma}(3, 4) G_{\text{KS}}^<(4, 1) \right] \\ + \int_0^{-i\beta} dt_3 \int d^3 r_3 \int d^3 r_4 G_{\text{KS}}^{\lceil}(1, 3) \tilde{\Sigma}(3, 4) G_{\text{KS}}^{\lceil}(4, 1). \quad (3.102)$$

Let us first work out the last term which describes a time-integral from 0 to $-i\beta$. On this part of the contour, the Kohn-Sham Hamiltonian is time-independent, with $v_{\text{x}}(\mathbf{r}, 0) \equiv v_{\text{x}}(\mathbf{r})$, and $\varphi_i(\mathbf{r}, t) = \varphi_i(\mathbf{r}) \exp(-i\varepsilon_i t)$. Since Σ_{x} is time-independent on this part of the contour, we can integrate

$$\begin{aligned} & \int_0^{-i\beta} dt_3 G_{\text{KS}}^{\downarrow}(1, \mathbf{r}_3 t_3) G_{\text{KS}}^{\uparrow}(\mathbf{r}_4 t_3, 1) \\ &= -i \sum_{i,k} n_i (1 - n_k) \varphi_i(1) \varphi_i^*(\mathbf{r}_3) \varphi_k(\mathbf{r}_4) \varphi_k^*(1) \frac{e^{\beta(\varepsilon_i - \varepsilon_k)} - 1}{\varepsilon_i - \varepsilon_k}. \end{aligned} \quad (3.103)$$

If we then use $n_i(1 - n_k)(e^{\beta(\varepsilon_i - \varepsilon_k)} - 1) = n_k - n_i$ and define the function $u_{x,j}$ by

$$u_{x,j}(1) = -\frac{1}{\varphi_j^*(1)} \sum_k n_k \int d^2 \varphi_j^*(2) \varphi_k(2) \varphi_k^*(1) v_{\text{ee}}(1, 2), \quad (3.104)$$

we obtain from (3.103) and (3.101)

$$\begin{aligned} & \int_0^{-i\beta} dt_3 \int d^3 r_3 \int d^3 r_4 G_{\text{KS}}^{\downarrow}(1, 3) \tilde{\Sigma}(3, 4) G_{\text{KS}}^{\uparrow}(4, 1) \\ &= - \int d^3 r_2 \sum_j n_j \sum_{k \neq j} \frac{\varphi_j^*(\mathbf{r}_2) \varphi_k(\mathbf{r}_2)}{\varepsilon_j - \varepsilon_k} \varphi_j(1) \varphi_k^*(1) [u_{x,j}(\mathbf{r}_2) - v_x(\mathbf{r}_2)] + \text{c.c.} \end{aligned} \quad (3.105)$$

The integral along the real axis on the l.h.s. of (3.102) can similarly be evaluated. Collecting our results we obtain the OEP equations on the same form as in [Görling 1997],

$$\begin{aligned} 0 &= i \sum_j \sum_{k \neq j} n_j \int_0^{t_1} dt_2 \int d^3 r_2 [v_x(2) - u_{x,j}(2)] \varphi_j(1) \varphi_j^*(2) \varphi_k^*(1) \varphi_k(2) + \text{c.c.} \\ &+ \sum_j \sum_{k \neq j} n_j \frac{\varphi_j(1) \varphi_k^*(1)}{\varepsilon_j - \varepsilon_k} \int d^3 r_2 \varphi_j^*(\mathbf{r}_2) [v_x(\mathbf{r}_2) - u_{x,j}(\mathbf{r}_2)] \varphi_k(\mathbf{r}_2). \end{aligned} \quad (3.106)$$

The last term represents the initial conditions, expressing that the system is in thermal equilibrium at $t = 0$. The equations have exactly the same form if the initial condition is specified at some other initial time t_0 . The second term on the r.h.s. can be written as a time-integral from $-\infty$ to 0 if one introduces a convergence factor. In that case the remaining expression equals the one given in [van Leeuwen 1996, Ullrich 1995a, Ullrich 1995b]. The OEP equation (3.106) in the so-called KLI approximation have been successfully used by Ullrich et al. [Ullrich 1995b] to calculate properties of atoms in strong laser fields (see Chap. 24).