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Nonequilibrium Green function theory for excitation and transport in atoms and molecules

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Abstract. In this work we discuss the application of nonequilibrium Green functions theory to atomic and molecular systems with the aim to study charge and energy transport in these systems. We apply the Kadanoff-Baym equations to atoms and diatomic molecules initially in the ground state. The results obtained for the correlated initial states are used to analyze variational energy functionals of the Green function which are shown to perform very well. We further show an application of the Kadanoff-Baym equations to a molecule exposed to an external laser field. Finally we discuss the connection between nonequilibrium Green function theory and time-dependent density-functional theory with the aim to develop better density functionals in order to treat larger systems than those attainable with the nonequilibrium Green function method.

1. Introduction

We will give an overview of the application of the Kadanoff-Baym equations to molecular systems. This research is motivated by the recent developments in the new field of molecular electronics. Important topics in this field are the study of charge transport through single molecules attached to macroscopic electrodes [1] and the study of energy transport in molecular chains as well as the study of short laser pulse excitation of molecules. Especially the theoretical description of molecular conduction is challenging as one needs to take into account both the detailed electronic structure of the molecule as well as to take into account the macroscopic electrodes. Very little (also experimentally) is known about the microscopic processes that play a role in molecular conduction. It is clear that dissipative processes (due to electron-electron and electron-phonon interactions) play an essential role in attaining a final steady current, but almost nothing is known about how such a current builds up in time and what the relative importance is of electron-electron and electron-phonon interactions. Another very exciting new topic is the investigation of possible new ultrafast electron transport mechanisms in molecules that happen on a timescale of less than a femtosecond (several hundreds of attoseconds). A typical example is that of hole migration after short pulse laser ionization [2]. Virtually nothing is known about these processes.

In this work we will discuss two methods that can deal with these processes, nonequilibrium Green function theory [3, 4, 5, 6] and time-dependent density functional theory [7, 8]. In the first section of the paper we discuss the Kadanoff-Baym equations and the self-energy approximations that we will use to study diatomic molecules in external fields. A nice feature of these calculations is that dissipative effects that arise from the self-energy memory kernels is naturally introduced in the formalism. Apart from discussing the time-propagation we will

also discuss how to calculate in an efficient way total energies for atoms and molecules from an approximate Green function using variational energy functionals. Finally we will discuss time-dependent density-functional theory (TDDFT). This method can deal with much larger systems than are computationally attainable with the nonequilibrium Green function method. However, the time-dependent density functionals are not always accurate enough to deal with the problem at hand. We will therefore make a connection to nonequilibrium Green function theory and analyze the density functionals in terms of Green function quantities in order to develop better density functionals. Finally we will present our conclusions and outlook.

2. Nonequilibrium Green function theory

2.1. The temperature contour

We will study a system of interacting electrons in a time-dependent external potential $v(\mathbf{r}, t)$, where the single-particle part of the Hamiltonian is given by

$$h(\mathbf{r}, t) = -\frac{1}{2}\nabla^2 + v(\mathbf{r}, t) - \mu. \quad (1)$$

We use atomic units $\hbar = m = e = 1$. In the following, we are mainly interested in systems that evolve from an equilibrium state at some time t_0 , a choice which is reflected in the inclusion of the chemical potential μ in h_0 . Most of the theory can be generalized to much more general initial conditions, but this is a topic that deserves a more thorough discussion [3, 9, 10, 11]. The total Hamiltonian is written in second-quantization as

$$\hat{H}(t) = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) h_0(\mathbf{r}, t) \hat{\psi}(\mathbf{x}) + \frac{1}{2} \int \int d\mathbf{x}_1 d\mathbf{x}_2 \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}^\dagger(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1), \quad (2)$$

where we use the notation $\mathbf{x} = (\mathbf{r}, \sigma)$ where σ is a spin coordinate and $d\mathbf{x}$ denotes integration over \mathbf{r} as well as a summation over the spin indices. We now consider the expectation value of an operator \hat{O} for the case that the system is initially in an equilibrium state before a certain time t_0 . For $t < t_0$ the expectation value of operator \hat{O} in the Schrödinger picture is then given by $\langle \hat{O} \rangle = \text{Tr} \{ \hat{\rho} \hat{O} \}$ where $\hat{\rho} = e^{-\beta \hat{H}_0} / \text{Tr} e^{-\beta \hat{H}_0}$ is the density matrix and \hat{H}_0 is the time-independent Hamiltonian that describes the system before the perturbation is switched on. We further defined $\beta = 1/k_B T$ to be the inverse temperature, and the trace involves a summation over a complete set of states in the Hilbert space. After we switch on the field the expectation value becomes

$$\langle \hat{O}(t) \rangle = \text{Tr} \left\{ \hat{\rho} \hat{O}_H(t) \right\} \quad (3)$$

where $\hat{O}_H(t) = \hat{U}(t_0, t) \hat{O}(t) \hat{U}(t, t_0)$ is the operator in the Heisenberg picture. The evolution operator \hat{U} of the system is defined as the solution to the equations

$$i\partial_t \hat{U}(t, t') = \hat{H}(t) \hat{U}(t, t') \quad i\partial_{t'} \hat{U}(t, t') = -\hat{U}(t, t') \hat{H}(t') \quad (4)$$

with the boundary condition $\hat{U}(t, t) = 1$. The formal solution of Eq. (4) can be obtained by integration to yield (for $t > t'$) $\hat{U}(t, t') = T \exp(-i \int_{t'}^t d\tau \hat{H}(\tau))$. The operator $e^{-\beta \hat{H}_0}$ can now be regarded as an evolution operator in imaginary time, i.e. $\hat{U}(t_0 - i\beta, t_0) = e^{-\beta \hat{H}_0}$, if we define $\hat{H}(t)$ to be equal to \hat{H}_0 on the contour running straight from t_0 to $t_0 - i\beta$ in the complex time plane. We can therefore rewrite our expression for the expectation value as

$$\langle \hat{O}(t) \rangle = \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \hat{U}(t_0, t) \hat{O} \hat{U}(t, t_0) \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} \quad (5)$$

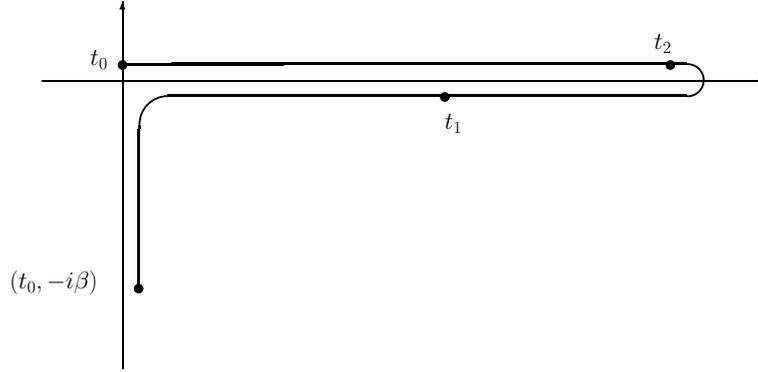


Figure 1. Keldysh contour in the complex time plane.

If we read the time arguments of the evolution operators in the numerator of this expression from right to left we may say that the system evolves from t_0 along the real time axis to t after which the operator \hat{O} acts. Then the system evolves back along the real axis from time t to t_0 and finally parallel to the imaginary axis from t_0 to $t_0 - i\beta$. A corresponding time contour is displayed in Fig. 1. From this observation we see that we can write the expectation value equivalently as

$$\langle \hat{O}(t) \rangle = \frac{\text{Tr} \left\{ T_C [\exp(-i \int_C d\bar{t} \hat{H}(\bar{t})) \hat{O}(t)] \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} \quad (6)$$

where we define the evolution operator on the contour as

$$\hat{U}(t_0 - i\beta, t_0) = T_C \exp(-i \int dt \hat{H}(t)). \quad (7)$$

and

$$T_C [\exp(-i \int_C d\bar{t} \hat{H}(\bar{t})) \hat{O}(t)] \equiv \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int d\bar{t}_1 \dots d\bar{t}_n T_C [\hat{H}(\bar{t}_1) \dots \hat{H}(\bar{t}_n) \hat{O}(t)] \quad (8)$$

Here the integrals in Eqs.(7) and (8) are taken on the contour and T_C denotes time-ordering along the contour of Fig.(1). For instance, time t_1 in Fig. 1 is later than time t_2 on the contour. With the compact notation $1 = (\mathbf{x}_1, t_1)$ we now define the one-particle Green's function G as

$$\begin{aligned} G(1, 2) &= \frac{1}{i} \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) T_C [\hat{\psi}_H(1) \hat{\psi}_H^\dagger(2)] \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} \\ &= -i \langle T_C [\hat{\psi}_H(1) \hat{\psi}_H^\dagger(2)] \rangle, \end{aligned} \quad (9)$$

This Green function is thus defined for time-arguments on the contour. We can illustrate the effect of contour ordering by considering the situation in Fig. 1. In the figure, t_1 is later on the contour than t_2 and hence $U(t_0 - i\beta, t_0) T_C [\hat{\psi}_H(1) \hat{\psi}_H^\dagger(2)] = U(t_0 - i\beta, t_1) \hat{\psi}(\mathbf{x}_1) U(t_1, t_2) \hat{\psi}^\dagger(\mathbf{x}_2) U(t_2, t_0)$. Let us now derive the boundary conditions that G satisfies. If we consider the Green function at $t_1 = t_0 - i\beta$ and use the cyclic property of the trace we find

$$G(\mathbf{x}_1 t_0 - i\beta, 2) = \frac{1}{i} \frac{\text{Tr} \left\{ \hat{\psi}(\mathbf{x}_1) \hat{U}(t_0 - i\beta, t_2) \hat{\psi}^\dagger(\mathbf{x}_2) \hat{U}(t_2, t_0) \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}}$$

$$= \frac{1}{i} \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_2) \hat{\psi}^\dagger(\mathbf{x}_2) \hat{U}(t_2, t_0) \hat{\psi}(\mathbf{x}_1) \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} = -G(\mathbf{x}_1 t_0, 2). \quad (10)$$

The Green function defined in Eq. (9) therefore obeys the boundary condition $G(\mathbf{x}_1 t_0, 2) = -G(\mathbf{x}_1 t_0 - i\beta, 2)$. The property $G(1, \mathbf{x}_2 t_0) = -G(1, \mathbf{x}_2 t_0 - i\beta)$ for the other argument is likewise easily verified. These boundary conditions are sometimes referred to as the Kubo-Martin-Schwinger (KMS) conditions [12, 13, 9]. Similar boundary conditions are satisfied by the usual equilibrium temperature Green function which, in fact, is obtained for the special case where the time arguments are located on the contour along the imaginary axis t_0 to $t_0 - i\beta$, where the Hamiltonian is time-independent.

2.2. The Kadanoff-Baym equations

We now study the equation of motion for the Green function. For this purpose, we introduce the functions $G^>$ and $G^<$ according to

$$G^>(1, 1') = -i \langle \hat{\psi}_H(1) \hat{\psi}_H^\dagger(1') \rangle \quad (11)$$

$$G^<(1, 1') = i \langle \hat{\psi}_H^\dagger(1') \hat{\psi}_H(1) \rangle \quad (12)$$

such that we can write

$$G(1, 1') = \theta(t_1, t_{1'}) G^>(1, 1') + \theta(t_{1'}, t_1) G^<(1, 1'). \quad (13)$$

Here we use the step function θ generalized to arguments on the contour [3],

$$\theta(t_1, t_{1'}) = \begin{cases} 1 & \text{if } t_1 \text{ is later than } t_{1'} \text{ on the contour} \\ 0 & \text{otherwise} \end{cases} \quad (14)$$

It is further useful to define a notation for the Green functions when one of the arguments is real and one is on the vertical part of the contour [14]:

$$G^\lceil(1, 1') = G^<(\mathbf{x}_1 t_1, \mathbf{x}'_1 t_0 - i\tau'_1) \quad (15)$$

$$G^\rfloor(1, 1') = G^>(\mathbf{x}_1 t_0 - i\tau_1, \mathbf{x}'_1 t'_1) \quad (16)$$

where $0 \leq \tau_1, \tau'_1 \leq \beta$. This notation is quite suggestive when one reads the symbols \lceil and \rfloor from left to right. For instance, \lceil has a horizontal segment followed by a vertical one; correspondingly G^\lceil has a first argument that is real (and thus lies on the horizontal axis) and a second argument with an imaginary part (which lies on the vertical part of the contour). Finally there is the case that both time arguments are on the imaginary part of the contour. We then have the equilibrium Matsubara Green function

$$G^M(1, 1') = \theta(\tau_1 - \tau'_1) G^>(\mathbf{x}_1 t_0 - i\tau_1, \mathbf{x}'_1 t_0 - i\tau'_1) + \theta(\tau'_1 - \tau_1) G^<(\mathbf{x}_1 t_0 - i\tau_1, \mathbf{x}'_1 t_0 - i\tau'_1) \quad (17)$$

where θ is now an ordinary Heaviside function. Since the Hamiltonian on the vertical branch of the contour is time-independent $G^M(1, 1')$ depends only on time through the combination $\tau = \tau_1 - \tau'_1$. We finally note that the formalism discussed here has been elaborated in references [15, 16]. With these preliminaries we are now ready to discuss the equations of motion:

$$(i\partial_{t_1} - h(1))G(1, 1') = \delta(1, 1') + \int d2 \Sigma(1, 2)G(2, 1') \quad (18)$$

$$(-i\partial_{t'_1} - h(1'))G(1, 1') = \delta(1, 1') + \int d2 G(1, 2)\hat{\Sigma}(2, 1') \quad (19)$$

where $\delta(1, 1') = \delta(t_1, t'_1)\delta(\mathbf{x}_1 - \mathbf{x}'_1)$ and $\delta(t_1, t'_1)$ is the contour delta function [3]. The term Σ is the self-energy operator, which is a functional of the Green function, and $\hat{\Sigma}$ is its adjoint. For systems initially in equilibrium one can prove using the KMS conditions that $\Sigma = \hat{\Sigma}$; however, this is not the case for more general initial conditions where Σ and $\hat{\Sigma}$ differ at the initial time. The self-energy has the following general structure [3]

$$\Sigma(1, 2) = \Sigma^{\text{HF}}(1, 2) + \theta(t_1, t_2)\Sigma^>(1, 2) + \theta(t_2, t_1)\Sigma^<(1, 2) \quad (20)$$

where the time-local part (i.e. proportional to $\delta(t_1, t_2)$) is given by the Hartree-Fock part

$$\Sigma^{\text{HF}}(1, 2) = \Sigma^{\text{HF}}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_1)\delta(t_1, t_2) \quad (21)$$

where

$$\Sigma^{\text{HF}}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_1) = iG^<(\mathbf{x}_1 t_1, \mathbf{x}_2 t_1)w(\mathbf{x}_1, \mathbf{x}_2) - i\delta(\mathbf{x}_1 - \mathbf{x}_2) \int d\mathbf{x}_3 w(\mathbf{x}_1, \mathbf{x}_3)G^<(\mathbf{x}_3 t_1, \mathbf{x}_2 t_1) \quad (22)$$

and $w(\mathbf{x}_1, \mathbf{x}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ is the two-particle interaction. Using Eq.(20) we can carry out the contour integration. For real times we obtain

$$\begin{aligned} & [i\partial_{t_1} - h(1)] G^{\lessgtr}(1, 1') - \int d\mathbf{x}_2 \Sigma^{\text{HF}}(1, \mathbf{x}_2 t_1) G^{\lessgtr}(\mathbf{x}_2 t_1, 1') = \\ & = \int_{t_0}^{t_1} d2 [\Sigma^>(1, 2) - \Sigma^<(1, 2)] G^{\lessgtr}(2, 1') - \int_{t_0}^{t'_1} d2 \Sigma^{\lessgtr}(1, 2) [G^>(2, 1') - G^<(2, 1')] \\ & + \int_{t_0}^{t_0 - i\beta} d2 \Sigma^{\lrcorner}(1, 2) G^{\lrcorner}(2, 1') \end{aligned} \quad (23)$$

and

$$\begin{aligned} & [-i\partial_{t'_1} - h(1')] G^{\lessgtr}(1, 1') - \int d\mathbf{x}_2 G^{\lessgtr}(1, 2) \Sigma^{\text{HF}}(\mathbf{x}_2 t'_1, 1') = \\ & = \int_{t_0}^{t_1} d2 [G^>(1, 2) - G^<(1, 2)] \Sigma^{\lessgtr}(2, 1') - \int_{t_0}^{t'_1} d2 G^{\lessgtr}(1, 2) [\Sigma^>(2, 1') - \Sigma^<(2, 1')] \\ & + \int_{t_0}^{t_0 - i\beta} d2 G^{\lrcorner}(1, 2) \Sigma^{\lrcorner}(2, 1'). \end{aligned} \quad (24)$$

while for the Green functions with a real and an imaginary argument we have

$$\begin{aligned} & [i\partial_{t_1} - h(1)] G^{\lrcorner}(1, 1') - \int d\mathbf{x}_2 \Sigma^{\text{HF}}(1, \mathbf{x}_2 t_1) G^{\lrcorner}(\mathbf{x}_2 t_1, 1') = \\ & = \int_{t_0}^{t_1} d2 [\Sigma^>(1, 2) - \Sigma^<(1, 2)] G^{\lrcorner}(2, 1') + \int_{t_0}^{t_0 - i\beta} d2 \Sigma^{\lrcorner}(1, 2) G^M(2, 1') \end{aligned} \quad (25)$$

and

$$\begin{aligned} & [-i\partial_{t'_1} - h(1')] G^{\lrcorner}(1, 1') - \int d\mathbf{x}_2 G^{\lrcorner}(1, 2) \Sigma^{\text{HF}}(\mathbf{x}_2 t'_1, 1') = \\ & = - \int_{t_0}^{t'_1} d2 G^{\lrcorner}(1, 2) [\Sigma^>(2, 1') - \Sigma^<(2, 1')] + \int_{t_0}^{t_0 - i\beta} d2 G^M(1, 2) \Sigma^{\lrcorner}(2, 1'). \end{aligned} \quad (26)$$

Finally on the imaginary part of the contour we have an equation of motion for the Matsubara Green function

$$(-\partial_\tau - h(1))G^M(\mathbf{x}_1, \mathbf{x}'_1; \tau) = i\delta(\tau)\delta(\mathbf{x}_1 - \mathbf{x}'_1) + \int_{t_0}^{t_0 - i\beta} d2\Sigma^M(1, 2)G^M(2, 1') \quad (27)$$

where $\tau = \tau_1 - \tau'_1$. The Eqs. (23) to (27) are known as the Kadanoff-Baym equations [17, 6]. We have solved these equations by time-propagation for the two conserving approximations of $\Sigma[G]$ to be discussed in the next section. We first solve the equilibrium equation (27) using the KMS conditions. Then Eqs.(23)-(26) are solved with the initial conditions

$$G^{\lceil}(t_0, \tau) = G^M(0, \tau) \quad (28)$$

$$G^{\lceil}(\tau, t_0) = G^M(\tau, 0) \quad (29)$$

$$G^<(t_0, t_0) = G^M(0, 0^+) \quad (30)$$

$$G^>(t_0, t_0) = G^M(0^+, 0) \quad (31)$$

where for the ease of notation we only indicated the time arguments. For details regarding to the numerical implementation of these equations we refer to ref.[18].

2.3. Conserving approximations

If the self-energy Σ is obtained from an underlying functional $\Phi[G]$, according to

$$\Sigma(1, 2) = \frac{\delta\Phi}{\delta G(2, 1)}, \quad (32)$$

then the self-energy is said to be Φ -derivable. Baym [19] has proven the important result that when the self-energy is Φ -derivable then the observables calculated from G satisfy the macroscopic conservation laws. The functional Φ can be constructed, as first shown by Luttinger and Ward [20], by summing over irreducible self-energy diagrams closed with an additional Green function line and multiplied by appropriate numerical factors,

$$\Phi[G] = \sum_{n,k} \frac{1}{2n} \int d1d2 \Sigma_k^{(n)}(1, 2)G(2, 1^+) = \sum_{n,k} \frac{1}{2n} \text{tr} \left[\Sigma_k^{(n)}G \right]. \quad (33)$$

The term n indicates the number of interaction lines and k labels Σ -diagrams. The trace tr indicates an integration over all variables (in contrast to the trace Tr that denotes a summation over a complete set of states in the Hilbert space). Some of the low-order diagrams are shown in Fig. 2, together with some of the corresponding self-energy diagrams. In our calculations we have used two approximate forms of Σ . The first approximation we use is a self-energy that includes all second order diagrams

$$\begin{aligned} \Sigma^{(2)}(1, 2) &= \Sigma^{\text{HF}}(1, 2) + i^2 \int d3d4 G(1, 3)w(1, 4)G(3, 4)G(4, 2)w(3, 2) \\ &\quad - i^2 \int d3d4 G(1, 2)w(1, 3)w(2, 4)G(4, 3)G(3, 4) \end{aligned} \quad (34)$$

where $w(1, 2) = \delta(t_1, t_2)w(\mathbf{x}_1, \mathbf{x}_2)$. As a second approximation we use the so-called GW approximation [21]

$$\Sigma_{\text{GW}}(1, 2) = -i\delta(1, 2) \int d\mathbf{x}_3 w(\mathbf{x}_1, \mathbf{x}_3)G^<(\mathbf{x}_3 t_1, \mathbf{x}_3 t_1) + i \int d3 G(1, 3)W(3, 2) \quad (35)$$

$$\begin{aligned}
\Phi &= -\frac{1}{2} \text{ (Hartree)} - \frac{1}{2} \text{ (screened)} - \frac{1}{4} \text{ (bubbles)} - \frac{1}{4} \text{ (bubbles)} \\
&\quad - \frac{1}{6} \text{ (bubbles)} - \frac{1}{6} \text{ (bubbles)} - \frac{3}{6} \text{ (bubbles)} + \dots \\
\Sigma &= \text{ (Hartree)} + \text{ (screened)} + \text{ (bubbles)} + \text{ (bubbles)} + \text{ (bubbles)} \\
&\quad + \text{ (bubbles)} + \text{ (bubbles)} + \text{ (bubbles)} + \text{ (bubbles)} + \dots
\end{aligned}$$

Figure 2. Some of the low-order Φ diagrams, and some of the self-energy diagrams obtained from $\Sigma = \delta\Phi/\delta G$.

The first term is simply the Hartree potential. The second term contains the dynamically screened interaction $W(1, 2)$ which satisfies

$$W(1, 2) = w(1, 2) + i \int d3d4 w(1, 3)G(3, 4)G(4, 3)W(4, 2) \quad (36)$$

i.e. it corresponds to an infinite sum of bubble diagrams. The GW approximation is most relevant in extended systems where long range interactions need to be screened. The second order diagrams are most relevant in small finite systems where long range interactions play a much smaller role.

2.4. Variational functionals of the Green function

As has been shown by Luttinger and Ward [20], the total energy of a system in equilibrium can be written as

$$E[G] = \Phi[G] - \text{tr} [\Sigma G + \ln(\Sigma - G_0^{-1})] + \mu N \quad (37)$$

where G_0 is the noninteracting Green function, N the number of particles in the system, and the trace is defined as an integration over spatial coordinates and summation over Matsubara frequencies, i.e. $\text{tr} A = 1/\beta \sum_n \int d\mathbf{x} e^{i\omega_n \eta} A(\mathbf{x}, \mathbf{x}, \omega_n)$. Here we already consider the $T \rightarrow 0$ (or equivalently $\beta \rightarrow \infty$) limit. If we make a variation δG in the Green function we see that

$$\begin{aligned}
\delta E &= \delta\Phi - \text{tr} [\Sigma\delta G + G\delta\Sigma + (\Sigma - G_0^{-1})^{-1}\delta\Sigma] \\
&= \text{tr} [\{(1 - G_0\Sigma)^{-1}G_0 - G\} \delta\Sigma] = 0
\end{aligned} \quad (38)$$

whenever the Dyson equation

$$G = G_0 + G_0\Sigma[G]G \quad (39)$$

is obeyed with $\Sigma[G] = \delta\Phi[G]/\delta G$. This is a very interesting property since it offers the possibility to obtain good total energies without going through the considerable computational cost of solving the Dyson equation selfconsistently. This can be seen as follows. We let G be the Green function corresponding to a self-consistent solution of the Dyson equation for some Φ -derivable Σ and let \tilde{G} be some approximation to G . Let $\Delta G = \tilde{G} - G$ be the difference between these Green functions. Then

$$E[\tilde{G}] = E[G + \Delta G] = E[G] + \frac{1}{2} \text{tr} \left\{ \Delta G \frac{\delta^2 E}{\delta G \delta G} \Delta G \right\} + \dots \quad (40)$$

	$E_{\text{LW}}^{(2)}[G_{\text{HF}}]$	SC(2)	$E_{\text{LW}}^{\text{GW}}[G_{\text{HF}}]$	SC-GW
He	-2.8969	-2.8969	-2.9277	-2.9278
Be	-14.6405	-14.6409	-14.7017	-14.7024
Ne	-128.8332	-128.8339	-129.0492	-129.0499
Mg	-199.9093	-199.9097	-200.1752	-200.1762
Mg ²⁺	-199.1025	-199.1027	-199.3453	-199.3457
H ₂	-1.1658	-1.1659	-1.1888	-1.1887
LiH	-8.0526	-8.0528	-8.0997	-8.0995

Table 1. Total energies (in atomic units) for a number of atoms and molecules calculated from a completely self-consistent (SC) solution of the Dyson equation within the second Born (denoted as (2)) and GW approximation compared to those from the Luttinger-Ward (LW) functional with a Hartree-Fock input Green function

Therefore, due to the variational property, the errors one makes in the energy are only of second order in ΔG . We tested this idea for some atoms and molecules using for Σ the second order and the GW approximation. As an approximate input Green function we used $\tilde{G} = G_{\text{HF}}$, which is the Green function obtained from the solution of the Dyson equation within the Hartree-Fock approximation. The results for the second order and the GW approximation to the self-energy are displayed in table 1. We see that the Luttinger-Ward functional performs extremely well (for more extensive discussion and details see refs. [22, 23, 24]). The energies obtained from a fully self-consistent calculation and from the Luttinger-Ward expression $E[G_{\text{HF}}]$ are virtually on top of each other. This is very exciting since $E[G_{\text{HF}}]$ can be evaluated at a fraction of the computing time of a fully self-consistent solution of the Dyson equation. The main question is then which Φ -functional to use in a particular application. The variational functionals are especially promising in chemistry in the calculation of molecular bond energies and potential energy surfaces that play an essential role in chemical reactions.

2.5. Kadanoff-Baym equations applied to molecules

After having solved the ground state problem we are now ready to solve the Kadanoff-Baym equations for our molecular systems. We will consider a molecule excited by a laser pulse where we use the second order approximation $\Sigma^{(2)}$ for the self-energy. All our calculations so far have been carried out for diatomic molecules in which the external potential is given by

$$v(\mathbf{r}t) = -\frac{Z_{\text{A}}}{|\mathbf{r} - \mathbf{R}_{\text{A}}|} - \frac{Z_{\text{B}}}{|\mathbf{r} - \mathbf{R}_{\text{B}}|} + \mathbf{r} \cdot \mathbf{E}(t) \quad (41)$$

Here \mathbf{R}_{A} and \mathbf{R}_{B} are the positions of the atomic nuclei with charge Z_{A} and Z_{B} . The remaining term describes the external laser pulse within the dipole approximation, where $\mathbf{E}(t)$ is the electric field which is switched on at $t = t_0$. In our calculations the Green functions are expanded in a basis of the Hartree-Fock orbitals $\phi_i(\mathbf{x})$ of the stationary system

$$G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) = \sum_{i,j} \phi_i(\mathbf{x}_1) \phi_j^*(\mathbf{x}_2) G_{ij}(t_1, t_2) \quad (42)$$

We can then interpret the coefficients G_{ij} as the Green function with respect to annihilation and creation operators \hat{a}_i and \hat{a}_i^\dagger with respect to this basis

$$G_{ij}(t_1, t_2) = -i \langle T_C [\hat{a}_{i,H}(t_1) \hat{a}_{i,H}^\dagger(t_2)] \rangle \quad (43)$$

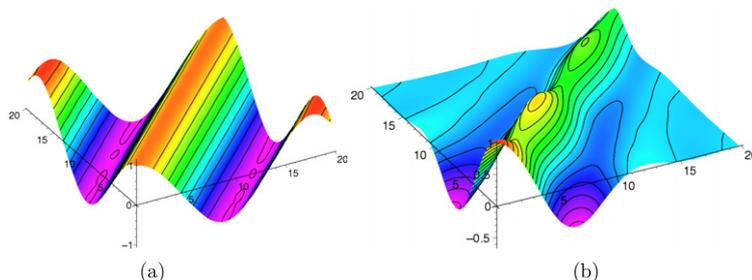


Figure 3. $\text{Im} G_{\sigma_g \sigma_g}^<(t_1, t_2)$ in the double time plane. The left hand figure (a) shows the field free propagation, whereas in the right hand figure (b) there is sudden switch-on of the field at $t = 0$. The times are in atomic units.

From this it follows that

$$\text{Im} G_{ii}^<(t_1, t_2) = \langle \hat{a}_{i,H}^\dagger(t_2) \hat{a}_{i,H}(t_1) \rangle \quad (44)$$

Therefore $n_i(t) = \text{Im} G_{ii}^<(t, t)$ can be interpreted as the time-dependent occupation number of state i . As an example we discuss the hydrogen molecule H_2 in a suddenly switched on potential. The external electric field is aligned with the bond-axis of the molecule which is pointed in z -direction and is of the form $\mathbf{E}(t) = \hat{\mathbf{z}} E_0 \theta(t)$. Fig 3 shows the matrix element $\text{Im} G_{\sigma_g \sigma_g}^<(t_1, t_2)$ where σ_g is the lowest occupied Hartree-Fock orbital. In the right panel of the figure we display the field free propagation of the Green function. One clearly sees an oscillation in terms of the relative time variable $t_1 - t_2$ with a frequency that coincides closely with the ionization energy of the molecule as it should. In the right hand panel the external field was switched on at $t = 0$. Now the oscillations are strongly damped and one further clearly sees Rabi-type of oscillations in the occupation number on the time diagonal. We refrain here from a more thorough discussion of the numerical results since these data are recent and currently subject of a more extensive investigation. We mainly wanted to point out here that it is quite feasible to solve the Kadanoff-Baym equations for finite systems such as atoms, molecules or quantum dots.

3. Time-dependent density-functional theory

3.1. Introduction

In this section we will discuss the basic features of time-dependent density-functional theory (TDDFT) and the close relations between TDDFT and nonequilibrium Green function theory. The most important feature of TDDFT is that it provides an exact treatment of nonequilibrium systems in terms of an effective noninteracting system in which the effective field is a functional of the time-dependent electron density. This one-particle description of the theory makes it of great practical use. For this reason the method has been widely used to calculate time-dependent properties of atoms, molecules and solids. The disadvantage of the method is that good approximate time-dependent functionals are not always available for the problem that one wishes to apply it to. This is notably the case beyond the linear response regime in the case of molecular transport or for molecules in strong short pulse laser fields. For this reason it is very useful to relate the effective potentials of TDDFT to nonequilibrium Green functions which allow for a systematic diagrammatic treatment of the many-body problem.

Since the main features of TDDFT are not well-known to the nonequilibrium Green function community we will present here a brief discussion of the basics of TDDFT. Subsequently we will make a connection to nonequilibrium Green functions.

3.2. The action functional and the Kohn-Sham equations

We start out from the action functional on the contour [25, 26]

$$\tilde{A}[v] = i \ln \text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\} \quad (45)$$

This expression is a functional of the external field $v(\mathbf{x}, t)$ present in the Hamiltonian. If we take the functional derivative of \tilde{A} with respect to the external field we obtain the time-dependent density of the system

$$n(1) = \frac{\delta \tilde{A}}{\delta v(1)} \quad (46)$$

To show this one needs to consider changes in \hat{U} which are readily evaluated using Eq.(4). For instance, when we make a perturbation $\delta \hat{V}(t)$ in the Hamiltonian we have using Eq.(4)

$$i\partial_t \delta \hat{U}(t, t') = \delta \hat{V}(t) \hat{U}(t, t') + \hat{H}(t) \delta U(t, t') \quad (47)$$

with a similar differential equation with respect to t' and boundary condition $\delta \hat{U}(t, t) = 0$. The solution to this equation is given by

$$\delta \hat{U}(t, t') = -i \int_{t'}^t d\tau \hat{U}(t, \tau) \delta \hat{V}(\tau) \hat{U}(\tau, t') \quad (48)$$

from which variations in the action can be calculated. If we choose

$$\delta \hat{V}(t) = \int d\mathbf{x} \delta v(\mathbf{x}t) \hat{n}(\mathbf{x}) \quad (49)$$

where $\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x})$ is the density operator we immediately obtain Eq.(46). We can now construct a functional of the density with the help of a Legendre transform and define

$$A[n] = -\tilde{A}[v] + \int_C d1 n(1)v(1) \quad (50)$$

where the latter integral is on the Keldysh contour. This functional then has the property that

$$\frac{\delta A}{\delta n(1)} = v(1) \quad (51)$$

which is readily derived from Eq.(46). It is important to note that in order to carry out the Legendre transform there must exist a one-to-one correspondence between the density and the potential. This is guaranteed by the Runge-Gross theorem. For the details we refer to ref [28, 8]. The definition and Legendre transform of the action that we carried out were independent of the form of the two-particle interactions in the Hamiltonian. Therefore in particular we can apply them to a noninteracting system with external potential v_s and action functionals $\tilde{A}_s[v_s]$. A similar Legendre transform then yields a density functional $A_s[n]$

$$A_s[n] = -\tilde{A}_s[v_s] + \int_C d1 n(1)v_s(1) \quad (52)$$

with the property $\delta A_s / \delta n(1) = v_s(1)$. From the two action functionals (50) and (52) we can then define the exchange-correlation part of the action to be

$$A_{xc}[n] = A_s[n] - A[n] - \frac{1}{2} \int d1 d2 \delta(t_1, t_2) \frac{n(1)n(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (53)$$

where we subtracted out the contribution of the Hartree interaction. Note that by writing down Eq.(53) we assumed that the functionals $A[n]$ and $A_s[n]$ are defined on the same domain of densities. In other words, we assume that for any time-dependent density $n(\mathbf{1})$ of an interacting many-body system we can find a noninteracting system (with an external potential $v_s(\mathbf{1})$) with same density. This so-called noninteracting v -representability condition can be proven by providing an explicit construction of $v_s(\mathbf{1})$ for a given density $n(\mathbf{1})$ [8, 29]. If we now take the functional derivative of Eq.(53) at the density n of an interacting system with external potential $v(\mathbf{1})$ we find that

$$v_s[n](\mathbf{1}) = v(\mathbf{1}) + v_H[n](\mathbf{1}) + v_{xc}[n](\mathbf{1}) \quad (54)$$

where we defined the Hartree and exchange-correlation (xc) potentials as

$$v_H[n](\mathbf{1}) = \int d\mathbf{x}_2 \frac{n(\mathbf{x}_2 t_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (55)$$

$$v_{xc}[n](\mathbf{1}) = \frac{\delta A_{xc}}{\delta n(\mathbf{1})} \quad (56)$$

Now since $v_s[n]$ is the potential of a noninteracting system the density can now be obtained from the following set of self-consistent one-particle equations

$$0 = (i\partial_t + \frac{1}{2}\nabla^2 - v(\mathbf{1}) - v_H[n](\mathbf{1}) - v_{xc}[n](\mathbf{1}))\phi_i(\mathbf{1}) \quad (57)$$

$$n(\mathbf{1}) = \sum_i n_i |\phi_i(\mathbf{1})|^2 \quad (58)$$

Here $n_i = 1/(e^{\beta\epsilon_i} + 1)$ is the Fermi-Dirac distribution which represents the occupation numbers that are given in terms of the eigenvalues ϵ_i of the initial orbitals before the external field is switched on. In the zero-temperature limit the n_i will become either zero or one. The set of equations (57) and (58) are the so-called time-dependent Kohn-Sham equations. For a given approximation to the functional $v_{xc}[n]$ they can be solved to self-consistency to give the time-dependent density. The density can then be used to calculate a variety of quantities. From it we can, for instance, directly calculate the amount of charge that flows through a molecule attached to leads. Another common application involves the calculation of the first order change in the dipole moment of the molecule. By Fourier-transforming this quantity one then directly obtains the excitation energies of the system [30]. At this point it is also useful to make a connection to the familiar ground state density functional theory introduced by Hohenberg, Kohn and Sham [31, 32]. To do this we note that the functional

$$A_{v_0}[n] = -A_s[n] + \int d\mathbf{1} n(\mathbf{1})v_0(\mathbf{1}) + \frac{1}{2} \int d\mathbf{1}d\mathbf{2} \delta(t_1, t_2) \frac{n(\mathbf{1})n(\mathbf{2})}{|\mathbf{r}_1 - \mathbf{r}_2|} + A_{xc}[n] \quad (59)$$

for a *fixed* potential v_0 is stationary whenever

$$0 = \frac{\delta A_{v_0}}{\delta n(\mathbf{1})} = -v_s(\mathbf{1}) + v_0(\mathbf{1}) + v_H(\mathbf{1}) + \frac{\delta A_{xc}}{\delta n(\mathbf{1})} \quad (60)$$

So the functional $A_{v_0}[n]$ specifies the Kohn-Sham potential v_s from a variational principle whenever we have an approximate form for $A_{xc}[n]$. One can readily verify from the definitions above that $A_{v_0}[n]$ can be expressed as

$$A_{v_0}[n] = \tilde{A}[v] + \int d\mathbf{1} n(\mathbf{1})(v_0(\mathbf{1}) - v(\mathbf{1})) \quad (61)$$

and therefore at the stationary point we have $A_{v_0}[n] = \tilde{A}[v_0]$. Let us now turn to the static limit and consider a time-independent system. Let us therefore calculate

$$\begin{aligned} \lim_{\beta \rightarrow \infty} -\frac{i}{\beta} A_s[n] &= \lim_{\beta \rightarrow \infty} \frac{i}{\beta} \tilde{A}_s[v_s] - \frac{i}{\beta} \lim_{\beta \rightarrow \infty} \int_0^{-i\beta} dt d\mathbf{r} n(\mathbf{r}) v_s(\mathbf{r}) \\ &= E_s - \mu N - \int d\mathbf{r} n(\mathbf{r}) v_s(\mathbf{r}) = T_s[n] - \mu N \end{aligned} \quad (62)$$

where $T_s[n]$ is the kinetic energy of the static Kohn-Sham system and we used that

$$\lim_{\beta \rightarrow \infty} \frac{i}{\beta} \tilde{A}_s[v_s] = \lim_{\beta \rightarrow \infty} -\frac{1}{\beta} \ln \text{Tr} \left\{ e^{-\beta \hat{H}_s} \right\} = \lim_{\beta \rightarrow \infty} \Omega_s = E_s - \mu N \quad (63)$$

where Ω_s is the grand potential of the Kohn-Sham system. If we therefore multiply the variational functional of Eq.(59) with i/β and take the zero-temperature limit we obtain the familiar energy expression of stationary density-functional theory

$$E_{v_0}[n] = T_s[n] + \int d\mathbf{r} n(\mathbf{r}) v_0(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_{xc}[n] \quad (64)$$

where we defined the exchange-correlation energy functional as

$$E_{xc}[n] = \lim_{\beta \rightarrow \infty} \frac{i}{\beta} A_{xc}[n] \quad (65)$$

and the energy functional as

$$E_{v_0}[n] - \mu N = \lim_{\beta \rightarrow \infty} \frac{i}{\beta} A_{v_0}[n] \quad (66)$$

Indeed, when we evaluate $A_{v_0}[n] = \tilde{A}[v_0]$ at the solution point we obtain in the zero-temperature limit

$$\lim_{\beta \rightarrow \infty} \frac{i}{\beta} \tilde{A}[v_0] = \lim_{\beta \rightarrow \infty} -\frac{1}{\beta} \ln \text{Tr} \left\{ e^{-\beta \hat{H}} \right\} = \lim_{\beta \rightarrow \infty} \Omega = E - \mu N \quad (67)$$

where Ω is the grand potential. This justifies the definitions in Eq.(65) and (66). We now turn back to the time-dependent case and we will investigate the exchange-correlation functionals in detail. Most of the applications sofar have used approximate functionals derived for the homogeneous or weakly perturbed electron gas. A commonly used functional is the adiabatic local density approximation (ALDA) for which the exchange-correlation action functional is given by

$$A_{\text{xc,ALDA}}[n] = \int d1 e_{\text{xc}}(n(1)) \quad (68)$$

where $e_{\text{xc}}(n)$ is the exchange-correlation energy per volume unit of a homogeneous electron gas of density n . For inhomogeneous and time-dependent systems this function is simply evaluated at the inhomogeneous and time-dependent density $n(1)$, i.e. it is an approximation that is local in space and in time and does not contain any memory effects. In the limit of stationary system the ALDA functional of Eq.(68) reduces to the familiar local density approximation

$$E_{\text{xc,LDA}}[n] = \lim_{\beta \rightarrow \infty} \frac{i}{\beta} \int_0^{-i\beta} dt d\mathbf{r} e_{\text{xc}}(n(\mathbf{r})) = \int d\mathbf{r} e_{\text{xc}}(n(\mathbf{r})) \quad (69)$$

The local density approximation has had many successes. However, there are also many cases in which the ALDA and the LDA functionals fail and therefore there is a clear need for better functionals. It is clear, for instance, that the ALDA functional will fail in any situation where memory effects are important, such as in the description of dissipation in quantum transport theory. For this reason we will connect TDDFT to nonequilibrium Green function theory in order to provide a more systematic approach to the construction of approximate density functionals.

3.3. The Sham-Schlüter equation

We now make a connection to nonequilibrium Green functions. Let us first consider a noninteracting system (which we will later identify with the Kohn-Sham system). To this noninteracting system there corresponds a Green function G_s with the equations of motion

$$(i\partial_{t_1} - h_s(1))G_s(1, 2) = \delta(1, 2) \quad (70)$$

$$(-i\partial_{t_2} - h_s(2))G_s(1, 2) = \delta(1, 2) \quad (71)$$

where h_s is of the form

$$h_s(\mathbf{x}t) = -\frac{\nabla^2}{2} + v_s(\mathbf{x}t) \quad (72)$$

At $t = t_0$ the system is in equilibrium. The system is then described by one-particle orbitals that satisfy.

$$h_s(\mathbf{x}t_0)\varphi_j(\mathbf{x}) = \epsilon_j\varphi_j(\mathbf{x}) \quad (73)$$

On the imaginary part of the contour where the Hamiltonian is time-independent the orbitals are given by $\phi_i(\mathbf{x}t) = \varphi_i(\mathbf{x}) \exp(-i\epsilon_i(t - t_0))$. For real times we define the orbitals to be the solution of

$$(i\partial_t - h_s(\mathbf{x}t))\phi_j(\mathbf{x}t) = 0 \quad (74)$$

with boundary condition $\phi_i(\mathbf{x}t_0) = \varphi_i(\mathbf{x})$. If we further define $n_j = (e^{\beta\epsilon_j} + 1)^{-1}$ then the Green function

$$G_s(1, 2) = -i\theta(t_1, t_2) \sum_j \phi_j(1)\phi_j^*(2)(1 - n_j) + i\theta(t_2, t_1) \sum_j \phi_j(1)\phi_j^*(2)n_j \quad (75)$$

satisfies the equations of motion Eq.(70) and Eq.(71), with the boundary conditions

$$G_s(\mathbf{x}_1t_0 - i\beta, 2) = -G_s(\mathbf{x}_1t_0, 2) \quad (76)$$

$$G_s(1, \mathbf{x}_2t_0 - i\beta) = -G_s(1, \mathbf{x}_2t_0) \quad (77)$$

We can now express the Green function G of an interacting system with external potential v in terms of G_s . We can easily check that

$$G(1, 1') = G_s(1, 1') + \int d2d3G_s(1, 2)[\Sigma(2, 3) - \delta(2, 3)(v_s(2) - v(2))]G(3, 1') \quad (78)$$

is a solution of Eq.(18) and (19) with similar boundary conditions as in Eqs.(76) and (77). We can now, as a particular noninteracting system, choose the Kohn-Sham system of TDDFT and write v_s as follows

$$v_s(1) = v(1) + v_H(1) + v_{xc}(1) \quad (79)$$

where v_H is the Hartree potential and v_{xc} the exchange-correlation potential. Then we must require that the noninteracting system will have the same density as the interacting one. We therefore require $n(1) = -iG(1, 1^+) = -iG_s(1, 1^+)$ which together with Eq.(78) leads to the following integral equation for v_{xc} :

$$\int d2G_s(1, 2)G(2, 1)v_{xc}(2) = \int d2d3G_s(1, 2)(\Sigma(2, 3) - \delta(2, 3)v_H(2))G(3, 1) \quad (80)$$

This equation is known as the time-dependent Sham-Schlüter equation [27]. The equation in this form is not useful as such as we can only calculate v_{xc} when we know G and Σ . This will,

however, change when we look at some approximate solutions of Eq.(78). A first iteration of Eq.(78) leads to

$$\tilde{G}(1, 1') = G_s(1, 1') + \int d2d3 G_s(1, 2)(\Sigma[G_s](2, 3) - \delta(2, 3)(v_s(2) - v(2)))G_s(3, 1') \quad (81)$$

It is important to note that the Green function \tilde{G} for a Φ -derivable $\Sigma = \delta\Phi[G_s]/\delta G_s$ where Σ is expressed in terms of G_s rather than G , also satisfies all conservation laws. This follows from similar derivations as in the work of Baym [19]. The Sham-Schlüter equation corresponding to Eq.(81) is given by

$$\int d2 G_s(1, 2)G_s(2, 1)v_{xc}(2) = \int d2d3 G_s(1, 2)(\Sigma[G_s](2, 3) - \delta(2, 3)v_H(2))G_s(3, 1) \quad (82)$$

In the simplest approximation, $\Sigma - v_H$ is given by the exchange-only self-energy of Eq.(21),

$$\Sigma_x(1, 2) = - \sum_j n_j \phi_j(1)\phi_j^*(2)w(1, 2) \quad (83)$$

where n_j is the occupation number. This approximation leads to what is known as the time-dependent optimized effective potential (TDOEP) equations [33, 34, 35] in the exchange-only approximation. Since the exchange self-energy Σ_x is local in time, there is only one time-integration in Eq. (82). The exchange-only solution for the potential will be denoted v_x . With the notation $\tilde{\Sigma}(3, 4) = \Sigma_x(\mathbf{x}_3 t_3, \mathbf{x}_4 t_3) - \delta(\mathbf{x}_3 - \mathbf{x}_4)v_x(\mathbf{x}_3 t_3)$ we obtain from Eq.(82)

$$\begin{aligned} 0 = & i \int_{t_0}^{t_1} dt_3 \int d\mathbf{x}_3 d\mathbf{x}_4 \left[G_s^>(1, 3)\tilde{\Sigma}(3, 4)G_s^<(4, 1) - G_s^<(1, 3)\tilde{\Sigma}(3, 4)G_s^>(4, 1) \right] \\ & + i \int_{t_0}^{t_0-i\beta} dt_3 \int d\mathbf{x}_3 d\mathbf{x}_4 G_s^{\lceil}(1, 3)\tilde{\Sigma}(3, 4)G_s^{\lceil}(4, 1). \end{aligned} \quad (84)$$

Let us first work out the last term which describes a time-integral from t_0 to $t_0 - i\beta$. On this part of the contour we have $\phi_i(\mathbf{x}, t) = \phi_i(\mathbf{x}, t_0) \exp(-i\epsilon_i(t - t_0))$ and since Σ_x is time-independent on this part of the contour, we can integrate

$$i \int_{t_0}^{t_0-i\beta} dt_3 G_s^{\lceil}(1, 3)G_s^{\lceil}(\mathbf{x}_4 t_3, 1) = \sum_{i,k} n_i(1 - n_k)\phi_i(1)\phi_i^*(\mathbf{x}_3, t_0)\phi_k(\mathbf{x}_4, t_0)\phi_k^*(1) \frac{e^{\beta(\epsilon_i - \epsilon_k)} - 1}{\epsilon_i - \epsilon_k} \quad (85)$$

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

$$u_{x,j}(1) = - \frac{1}{\phi_j^*(1)} \sum_k n_k \int d2 \phi_j^*(2)\phi_k(2)\phi_k^*(1)w(1, 2) \quad (86)$$

we obtain from Eq.(85) and Eq.(83)

$$\begin{aligned} & i \int_{t_0}^{t_0-i\beta} dt_3 \int d\mathbf{x}_3 d\mathbf{x}_4 G_s^{\lceil}(1, 3)\tilde{\Sigma}(3, 4)G_s^{\lceil}(4, 1) \\ & = - \int d\mathbf{x}_2 \sum_j n_j \sum_{k \neq j} \frac{\phi_j^*(\mathbf{x}_2 t_0)\phi_k(\mathbf{x}_2 t_0)}{\epsilon_j - \epsilon_k} \phi_j(1)\phi_k^*(1) [u_{x,j}(\mathbf{x}_2 t_0) - v_x(\mathbf{x}_2 t_0)] + c.c. \end{aligned} \quad (87)$$

The integral along the real axis on the lhs of Eq. (84) can similarly be evaluated. Collecting our results we obtain the OEP equations on the same form as in Ref. [35],

$$\begin{aligned}
0 = & i \sum_j \sum_{k \neq j} n_j \int_{t_0}^{t_1} dt_2 \int d\mathbf{x}_2 [v_x(2) - u_{x,j}(2)] \phi_j(1) \phi_j^*(2) \phi_k^*(1) \phi_k(2) + c.c. \\
& + \sum_j \sum_{k \neq j} n_j \frac{\phi_j(1) \phi_k^*(1)}{\epsilon_j - \epsilon_k} \int d\mathbf{x}_2 \phi_j^*(\mathbf{x}_2, t_0) [v_x(\mathbf{x}_2 t_0) - u_{x,j}(\mathbf{x}_2 t_0)] \phi_k(\mathbf{x}_2, t_0) \quad (88)
\end{aligned}$$

These equations, together with the Kohn-Sham equations (57) and (58), form a self-consistent scheme to calculate the time-dependent density. The exchange-only TDOEP-equations (88) in approximate form have been successfully used by Ullrich et al.[34] to calculate properties of atoms in strong laser fields. In a similar way, by taking more advanced forms of the self-energy in the Sham-Schlüter equation, we can derive more advanced TDOEP equations, in particular ones that contain proper memory effects which are important in transport phenomena. Although such TDOEP equations are far from trivial, they are still of one-particle form which is a great computational advantage.

We finally note that, apart from using the Sham-Schlüter equation, as we did here, there is a different route to constructing approximate density functionals. This is based on the extension of the Luttinger-Ward energy expression of Eq.(37) to an expression for an action functional on the Keldysh contour. One can then construct an OEP-scheme by inserting into the action Green functions coming from a noninteracting system with a local potential. By requiring stationarity with respect to changes in this potential one then obtains variational equations for the Kohn-Sham potential. We will not go into the details here and refer to reference [36].

4. Conclusions

We have discussed the application of the Kadanoff-Baym equations to atoms and molecules. In our time propagations we used a self-energy approximation that contains all diagrams to second order. The ground state calculations were also performed fully self-consistently within the GW approximation. These results we used to test variational energy functionals of the Green function. The variational functionals performed very well: with simple Hartree-Fock input Green function we obtained results in close agreement with computationally much more expensive self-consistent solutions of the Dyson equation. We further made a connection between nonequilibrium Green function theory and time-dependent density-functional theory. These relations are important to develop better approximate density functionals for future transport calculations, especially when memory effects are important. Our future research will focus on a more careful analysis of our preliminary results on the time-propagation of the Green functions and on extensions of our calculations to larger molecules. Another important goal will be to include the macroscopic electrodes to study charge transport through molecules. Also applications to quantum dot systems will be part of our future research. In general we can conclude that it is feasible to solve the Kadanoff-Baym equations for finite systems and to use nonequilibrium Green functions to develop better density functionals.

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