8 An Essential Introduction to NEGF Methods for Real-Time Simulations

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1 Introduction

We often hear about *strongly correlated systems* as opposed to weakly correlated ones. Strictly speaking, however, the adjective "correlated" is not a feature of the system, rather of the *state of the system*. Consider for instance a Hubbard dimer at half-filling with on-site repulsion U and hopping integral t. For $U/t \to \infty$ the ground state is a singlet with no double occupancy; such singlet is certainly a strongly correlated state since mean-field treatments predict that the ground state has a finite and U-independent double occupation. Does this mean that the Hubbard dimer is a strongly correlated system? Of course not. The same system does indeed admit a triplet excited state of zero energy which is identical to the triplet excited state of the noninteracting ($U = 0$) Hubbard dimer. Another example is provided by organic molecules. The majority of them have a weakly correlated ground state but highly correlated excited states.

In dealing with out-of-equilibrium problems it is crucial to have some physical intuition about the amount of correlation carried by *all* eigenstates involved in the dynamics. Not only that, different excited states may experience different correlation effects, meaning that several state-specific correlation mechanisms must be simultaneously taken into account. For these reasons the development of approximated methods is generally more difficult than for equilibrium problems.

In this chapter we introduce a versatile formalism to deal with any quantum system in arbitrary nonequilibrium situations. The formalism is dubbed Nonequilibrium Green Functions (NEGF) [1] and it is essentially the extension of many-body diagrammatic theory to systems driven by external time-dependent fields. We show how to convert a generic nonequilibrium process into a mathematical expression and hence how to build approximation schemes from our physical intuition. Finally we present recent advances for efficient real-time NEGF simulations of systems of interacting electrons and bosons, e.g., phonons or photons [2–6]. These progresses make NEGF competitive with the fastest quantum method today available, i.e., time-dependent density functional theory. Implementations in high performance computer facilities will more likely open the door to first-principles investigations of a wide range of nonequilibrium correlated phenomena.

2 The contour idea

In almost all approaches to quantum matter the very first approximation is the truncation of the one-particle Hilbert space. For solids this is usually done by ignoring planewaves with momentum higher than a certain cutoff and by choosing a certain discretization of momenta in the first Brillouin zone. In finite systems like atoms and molecules the truncation consists in considering only a certain number of localized orbitals, e.g., Slater type orbitals or Gaussian type orbitals or splines etc. Many kinds of one-particle bases are of course available in the market, their suitability depending on the system under investigation *and* on the external perturbing fields. In this chapter we do not specify the basis set and let the reader choose his/her favorite one. Only in the last section we shall introduce two different kind of bases for the discussion of recent

implementation strategies of the NEGF equations. We assume, however, that the chosen basis is orthonormal and we denote by $\hat{d}_i$ and $\hat{d}_i^\dagger$ the fermionic operators annihilating and creating an electron in the i-th basis function: hence the anticommutation rules read $\{\hat{d}_i,\, \hat{d}_j^\dagger\} = \delta_{ij}$. Notice that the label i includes, in general, both orbital and spin degrees of freedom.
In second quantization the fermionic operators are used to construct operators associated to observable quantities, hence the Hamiltonian too. For a self-contained presentation we consider a system of interacting electrons subject to external classical fields. However, we mention that the NEGF formalism can deal with more realistic situations where an interaction between electrons and quantized phonons and photons is present [7–9]. The purely electronic Hamiltonian reads

$$\hat{H}(t) = \hat{H}_0(t) + \hat{H}_{\text{int}} = \sum_{ij} h_{ij}(t)\, \hat{d}_i^\dagger \hat{d}_j + \frac{1}{2} \sum_{ijmn} v_{ijmn}\, \hat{d}_i^\dagger \hat{d}_j^\dagger \hat{d}_m \hat{d}_n \,. \tag{1}$$

Henceforth we shall use the hat symbol "ˆ" for *all* operators written in second quantization. The noninteracting part $\hat{H}_0(t)$ is a quadratic form of fermionic operators and it contains information on how electrons are coupled to external static potentials, e.g., the nuclear potential, and time-dependent fields, e.g., laser pulses. The interacting part $\hat{H}_{\text{int}}$ is a two-body operator describing, e.g., the Coulomb interaction between electrons. We specialize the discussion to an initial state which is the ground state $|\Psi_g\rangle$ of $\hat{H}_0 + \hat{H}_{\text{int}}$ and, without any loss of generality, we take $t = 0$ as the initial time. The average of any operator $\hat{O}$ at times $t > 0$ is given by

$$O(t) = \langle \Psi_g | \hat{U}(0,t)\, \hat{O}\, \hat{U}(t,0) | \Psi_g \rangle, \tag{2}$$

where $\hat{U}(t,t')$ is the evolution operator from time t' to time t. Let us manipulate Eq. (2).
Although the assumption of the adiabatic connection is not necessary to develop the NEGF formalism we here assume that it is fulfilled as it shortens the derivations. What is this assumption about? Let us first define it mathematically and then explore its physical content. The adiabatic Hamiltonian

$$\hat{H}_\eta(t) = \hat{H}_0 + e^{-\eta|t|} \hat{H}_{\text{int}} \tag{3}$$

coincides with the noninteracting part $\hat{H}_0$ in the remote past ($t \to -\infty$) and, for an infinitesimal energy η, it approaches (adiabatically) the full interacting Hamiltonian at time $t = 0$. Let $|\Phi_g\rangle$ be the (noninteracting) ground state of $\hat{H}_0$ and let $\hat{U}_\eta(t,t')$ be the evolution operator from time t' to time t associated to the Hamiltonian $\hat{H}_\eta(t)$. According to the Gell-Mann-Low theorem [10–12] the state $|\Psi\rangle = \hat{U}_\eta(0,-\infty)|\Phi_g\rangle$ is an eigenstate of $\hat{H}_0 + \hat{H}_{\text{int}}$. The adiabatic connection is fulfilled if $|\Psi\rangle = |\Psi_g\rangle$, i.e., if the interacting ground state can be obtained from the noninteracting one by an adiabatic switch-on of the interaction. The adiabatic connection allows for rewriting Eq. (2) in terms of the *non*-interacting state $|\Phi_g\rangle$, the price to pay being that the evolution starts at $t = -\infty$ instead of $t = 0$:

$$O(t) = \langle \Phi_g | \hat{U}_\eta(-\infty,0)\, \hat{U}(0,t)\, \hat{O}\, \hat{U}(t,0)\, \hat{U}_\eta(0,-\infty) | \Phi_g \rangle. \tag{4}$$

We could compress this result if we extend the definition of the time-dependent Hamiltonian in Eq. (1) to negative times: $\hat{H}(t<0) = \hat{H}_\eta(t)$. Then the group property of the evolution operator

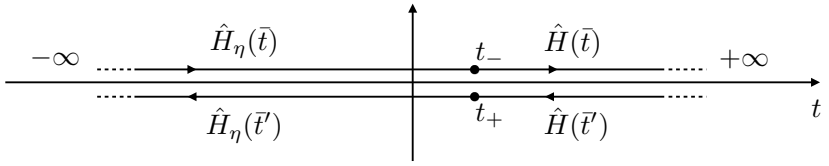

Fig. 1: *The contour γ, starting at $t=-\infty$, going all the way to $t=+\infty$ and then back to $t=-\infty$. By definition, any point lying on the forward branch is earlier than a point lying on the backward branch.*

implies $\hat{U}(t,0)\hat{U}_\eta(0,-\infty)=\hat{U}(t,-\infty)$ and Eq. (4) becomes

$$O(t)=\langle\Phi_g|\hat{U}(-\infty,t)\,\hat{O}\,\hat{U}(t,-\infty)|\Phi_g\rangle. \tag{5}$$

The *forward* evolution operator has a simple mathematical form in terms of the time-ordering operator $\mathcal{T}$. For any $t>t'$ (forward evolution)

$$\hat{U}(t,t')=\mathcal{T}\left\{e^{-\mathrm{i}\int_{t'}^{t}d\bar{t}\,\hat{H}(\bar{t})}\right\}. \tag{6}$$

In fact, $\mathcal{T}$ is not at all an operator, rather it is a rule according to which the operators in the curly bracket must be ordered with *later* times to the *left* (or equivalently earlier times to the right). We can better visualize the action of $\mathcal{T}$ if we write the integral in Eq. (6) as a Riemann sum over the discrete times $t_n=t'+n\delta$, where n varies from zero to $N=\mathrm{Int}[(t-t')/\delta]$ and $\delta\to 0$. Then t_n is later than t_m if $n>m$ and

$$\mathcal{T}\left\{e^{-\mathrm{i}\int_{t'}^{t}d\bar{t}\,\hat{H}(\bar{t})}\right\}=\lim_{\delta\to0}\mathcal{T}\left\{e^{-\mathrm{i}\delta\sum_{n=0}^{N}\hat{H}(t_n)}\right\}=\lim_{\delta\to0}e^{-\mathrm{i}\delta\hat{H}(t_N)}e^{-\mathrm{i}\delta\hat{H}(t_{N-1})}\cdots e^{-\mathrm{i}\delta\hat{H}(t_1)}e^{-\mathrm{i}\delta\hat{H}(t_0)}. \tag{7}$$

From this "unzipped" expression of the forward operator $\hat{U}(t,t')$ we can immediately find an expression for the *backward* evolution operator $\hat{U}(t',t)$. Taking into account the group property $\hat{U}(t,t')\hat{U}(t',t)=\hat{1}$ we have

$$\hat{U}(t',t)=\lim_{\delta\to0}e^{\mathrm{i}\delta\hat{H}(t_0)}e^{\mathrm{i}\delta\hat{H}(t_1)}\cdots e^{\mathrm{i}\delta\hat{H}(t_{N-1})}e^{\mathrm{i}\delta\hat{H}(t_N)}=\bar{\mathcal{T}}\left\{e^{\mathrm{i}\int_{t'}^{t}d\bar{t}\,\hat{H}(\bar{t})}\right\}=\bar{\mathcal{T}}\left\{e^{-\mathrm{i}\int_{t}^{t'}d\bar{t}\,\hat{H}(\bar{t})}\right\}, \tag{8}$$

where $\bar{\mathcal{T}}$ is the so called anti-time-ordering operator, i.e., a rule according to which the operators in the curly bracket must be ordered with later times to the right. Inserting these results into Eq. (5) we get

$$O(t)=\langle\Phi_g|\bar{\mathcal{T}}\left\{e^{-\mathrm{i}\int_{t}^{-\infty}d\bar{t}'\,\hat{H}(\bar{t}')}\right\}\hat{O}\,\mathcal{T}\left\{e^{-\mathrm{i}\int_{-\infty}^{t}d\bar{t}\,\hat{H}(\bar{t})}\right\}|\Phi_g\rangle. \tag{9}$$

Pay now attention to the ordering of times. If we define the oriented contour $\gamma=(-\infty,+\infty)\cup(+\infty,-\infty)$, see Fig. 1, and we place the times $\bar{t}$ on the upper, or forward, branch and the times $\bar{t}'$ on the lower, or backward, branch then the string of operators in Eq. (9) appears ordered on the contour γ. This observation is at the basis of the *contour idea* developed independently by Keldysh [13], Schwinger [14], and Konstantinov and Perel' [15], see also Refs. [16, 17] for a more recent discussion. Let us introduce the contour-variable, or better the contour-time $z\in\gamma$; z can lie either on the forward branch or on the backward branch and once the branch is specified it can assume any value between $-\infty$ and $+\infty$. To specify the branch we add a "+"

or "$-$" subscript to the times; thus $z = t_-$ is a time t on the forward branch and $z = t_+$ is a time t on the backward branch, see again Fig. 1. We also define operators with argument on the contour like

$$\hat{O}(t_-) = \hat{O}(t_+) \equiv \hat{O}(t) \quad \Rightarrow \quad \hat{O}(z) = \hat{O}(t). \tag{10}$$

In Fig. 1 we show how the Hamiltonian $\hat{H}(z)$ varies along the contour. Equation (9) can then be rewritten as

$$O(t) = \langle \Phi_g | \mathcal{T}_\gamma \left\{ e^{-\mathrm{i}\int_\gamma d\bar{z}\, \hat{H}(\bar{z})} \hat{O}(z) \right\} | \Phi_g \rangle, \tag{11}$$

where $\mathcal{T}_\gamma$ is the contour-ordering operator, i.e., a rule according to which the operators in the curly bracket must be ordered with later contour-times to the left. A contour-time is earlier than another if it is closer to the starting point, which in our notation is $\lim_{t\to-\infty} t_-$. Therefore, $\mathcal{T}_\gamma$ acts like the time-ordering operator $\mathcal{T}$ for arguments on the forward branch and like the anti-time-ordering operator $\bar{\mathcal{T}}$ for arguments on the backward branch. Let us verify Eq. (11). Suppose that $z = t_-$. Then Eq. (11) implies

$$\begin{aligned} O(t) &= \langle \Phi_g | \underbrace{\bar{\mathcal{T}} \left\{ e^{-\mathrm{i}\int_\infty^{-\infty} d\bar{t}'\, \hat{H}(\bar{t}')} \right\}}_{\hat{U}(-\infty,\infty)} \underbrace{\mathcal{T} \left\{ e^{-\mathrm{i}\int_t^{\infty} d\bar{t}\, \hat{H}(\bar{t})} \right\}}_{\hat{U}(\infty,t)} \hat{O} \underbrace{\mathcal{T} \left\{ e^{-\mathrm{i}\int_{-\infty}^{t} d\bar{t}\, \hat{H}(\bar{t})} \right\}}_{\hat{U}(t,-\infty)} | \Phi_g \rangle \\ &= \langle \Phi_g | \hat{U}(-\infty, t)\, \hat{O}\, \hat{U}(t, -\infty) | \Phi_g \rangle, \end{aligned} \tag{12}$$

which is the same as Eq. (5). Similarly the reader can verify that choosing $z = t_+$ the result does not change.

A remark about Eq. (11) is important at this point. If the operator $\hat{O}$ does not depend explicitly on time, like it is our operator, then we can safely write $\hat{O}(t) = \hat{O}$ in Eq. (12). However, if we do so in Eq. (11) then it is not possible to establish where to place the operator $\hat{O}$ when acted upon by $\mathcal{T}_\gamma$. The reason to give a contour argument even to operators that do not have an explicit time dependence (like the fermionic operators $\hat{d}_i$ and $\hat{d}_i^\dagger$) stems from the need of specifying their position along the contour, thus rendering unambiguous the action of $\mathcal{T}_\gamma$. Once the operators are ordered we can omit the time arguments if there is no time dependence.

We conclude this section with a brief comment on the necessity of introducing a contour for nonequilibrium situations. In the *absence* of external fields the Hamiltonian at positive times is constant and given by $\hat{H} = \hat{H}_0 + \hat{H}_{\rm int}$. For any finite $t > 0$ we can choose the infinitesimal energy η such that the equality $\hat{H} = \hat{H}_\eta(t)$ is fulfilled with arbitrary precision. Hence we can calculate time-dependent averages using the Hamiltonian $\hat{H}(t) = \hat{H}_\eta(t)$ for negative *and* positive times. For a nondegenerate ground state the Gell-Mann-Low theorem implies that $\langle \Phi_g | \hat{U}(\infty, -\infty) = \langle \Phi_g | e^{\mathrm{i}\alpha_g}$ where $e^{\mathrm{i}\alpha_g}$ is a phase factor. Physically this means that by switching on and then off the interaction we end up in the same state up to a phase factor $e^{\mathrm{i}\alpha_g} = \langle \Phi_g | \hat{U}(\infty, -\infty) | \Phi_g \rangle$. Substituting this result into Eq. (5) and using the group property of the evolution operator we get

$$O(t) = \frac{\langle \Phi_g | \hat{U}(\infty, t) \hat{O} \hat{U}(t, -\infty) | \Phi_g \rangle}{\langle \Phi_g | \hat{U}(\infty, -\infty) | \Phi_g \rangle}\,. \tag{13}$$

Reading the time arguments from right to left we see that they are ordered on the real axis. In equilibrium there is no need of introducing a contour. A more detailed discussion can be found in Ref. [1].

3 Nonequilibrium Green function

The NEGF formalism is a *nonperturbative* approach to calculate averages like in Eq. (11). Its power and versatility stems from the possibility of including only a (well thought) selection of scattering channels in the time-evolution. The fundamental bit in NEGF is the contour Green function

$$G_{ij}(z,z') \equiv \frac{1}{\mathrm{i}}\langle \Phi_g|\mathcal{T}_\gamma\left\{e^{-i\int_\gamma d\bar{z}\,\hat{H}(\bar{z})}\,\hat{d}_i(z)\,\hat{d}_j^\dagger(z')\right\}|\Phi_g\rangle, \tag{14}$$

where $\mathcal{T}_\gamma$ is the contour-ordering operator with an extra rule: after the reordering the sign changes if z' is later than z. This extra rule can be shown to simplify the math enormously [1]. Equation (14) is a two-point correlator on the contour. For both z and z' on the forward branch the contour Green function coincides with the more familiar time-ordered Green function. However other choices of contour-times are possible. Let us get acquainted with Eq. (14).
If z is earlier than z' we have (notice the sign change due to the extra rule)

$$G_{ij}(z,z') = -\frac{1}{\mathrm{i}}\langle \Phi_g|\hat{U}(-\infty,t')\,\hat{d}_j^\dagger\,\hat{U}(t',t)\,\hat{d}_i\,\hat{U}(t,-\infty)|\Phi_g\rangle \equiv G^<_{ij}(t,t'). \tag{15}$$

The last equality defines the *lesser* Green function. Notice that $G^<$ is a function of the physical times t and t'. One way to get this function for *all* times t and t' consists in evaluating the contour Green function for $z = t_-$ (forward branch) and $z' = t'_+$ (backward branch); in this case z would indeed be always earlier than z'. However, if $t < t'$ then we can get $G^<$ also choosing $z = t_-$ and $z' = t'_-$ whereas if $t > t'$ then we can get $G^<$ also choosing $z = t_+$ and $z' = t'_+$. The lesser Green function is proportional to the probability amplitude that a hole created at time t in the basis function i is found at time t' in the basis function j. In other words $G^<$ describes how an added hole (or a removed electron) propagates in the system.
The *greater* Green function is defined as the contour Green function evaluated at the contour-time z later than z'

$$G_{ij}(z,z') = \frac{1}{\mathrm{i}}\langle \Phi_g|\hat{U}(-\infty,t)\,\hat{d}_i\,\hat{U}(t,t')\,\hat{d}_j^\dagger\,\hat{U}(t',-\infty)|\Phi_g\rangle \equiv G^>_{ij}(t,t'). \tag{16}$$

Again this is a function of the physical times t and t' and it is proportional to the probability amplitude that an electron created at time t' in the basis function j is found at time t in the basis function i. Hence $G^>$ describes how an added electron propagates in the system. The lesser and greater Green functions can be used to rewrite the contour Green function as

$$G_{ij}(z,z') \equiv \Theta(z,z')\,G^>_{ij}(t,t') + \Theta(z',z)\,G^<_{ij}(t,t'), \tag{17}$$

where the Heaviside function on the contour $\Theta(z,z')$ has value 1 if z is later than z' and zero otherwise. In Eq. (17) the contour time z can be either t_- or t_+ and similarly the contour time z' can be either t'_- or t'_+.
From the equal-time lesser Green function we can calculate the time-dependent average of any one-body operator $\hat{O} = \sum_{ij} O_{ij}\hat{d}_i^\dagger\hat{d}_j$. To show it we observe that Eq. (15) for $t = t'$ yields

$$G^<_{ij}(t,t) = -\frac{1}{\mathrm{i}}\langle \Phi_g|\hat{U}(-\infty,t)\,\hat{d}_j^\dagger\,\hat{d}_i\,\hat{U}(t,-\infty)|\Phi_g\rangle = \mathrm{i}\rho_{ij}(t), \tag{18}$$

where $\rho(t)$ is the one-particle density matrix. Taking into account Eq. (5)

$$O(t) = \sum_{ij} O_{ij} \langle \Phi_g | \hat{U}(-\infty, t)\, \hat{d}_i^\dagger\, \hat{d}_j \hat{U}(t, -\infty) | \Phi_g \rangle = -\mathrm{i} \sum_{ij} O_{ij} G^<_{ji}(t,t) = \sum_{ij} O_{ij} \rho_{ji}(t). \quad (19)$$

Examples of one-body operators are the noninteracting part of the Hamiltonian, the particle density, the particle current, the local magnetic moment, the dipole moment, etc. From the time off-diagonal values of $G^<$ it is also possible to calculate the average of the interaction part of the Hamiltonian. This non trivial result is known as the Galitskii-Migdal formula

$$H_{\text{int}}(t) = \langle \Phi_g | \hat{U}(-\infty, t) \hat{H}_{\text{int}} \hat{U}(t, -\infty) | \Phi_g \rangle = \frac{1}{4\mathrm{i}} \sum_{ij} \left[\mathrm{i} \left(\frac{d}{dt} - \frac{d}{dt'} \right) \delta_{ij} - 2 h_{ij}(t) \right] G^<_{ji}(t,t') \Big|_{t=t'}. \quad (20)$$

The lesser and greater Green functions contain also information on the spectral properties, such as those probed in photoemission or inverse photoemission experiments. Let $D_{\mathbf{k}i}(t)$ be the matrix element of the light-matter interaction operator between the i-th state of our basis set and a photoelectron state of momentum $\mathbf{k}$ and energy $\varepsilon_{\mathbf{k}}$. The current of photoelectrons of momentum $\mathbf{k}$ measured at time t is then given by [18]

$$I_{\mathbf{k}}(t) = 2 \sum_{ij} \int d\bar{t}\, \mathrm{Re} \left(\Sigma_{ij,\mathbf{k}}(t, \bar{t})\, G^<_{ji}(\bar{t}, t) \right) \quad (21)$$

where $\Sigma_{ij,\mathbf{k}}(t,\bar{t}) = -\mathrm{i}\Theta(t-\bar{t})\, D_{i\mathbf{k}}(t) D^*_{j\mathbf{k}}(t) e^{-\mathrm{i}\varepsilon_{\mathbf{k}}(t-\bar{t})}$.
In the next sections we lay down the basis for the calculation of the lesser and greater Green function.

4 Noninteracting systems

A noninteracting system is described by a Hamiltonian with $\hat{H}_{\text{int}} = 0$. In this case the calculation of the Green function is elementary. The evolution operator in Eqs. (6) and (8) satisfies *for all* t and t'

$$\mathrm{i} \frac{d}{dt} \hat{U}(t,t') = \hat{H}(t) \hat{U}(t,t'), \qquad -\mathrm{i} \frac{d}{dt'} \hat{U}(t,t') = \hat{U}(t,t') \hat{H}(t'). \quad (22)$$

We then see that the derivative of Eq. (15) with respect to, e.g., t generates a commutator between $\hat{H}(t)$ and $\hat{d}_i$. For noninteracting Hamiltonians this commutator is simply given by $[\hat{H}_0(t),\, \hat{d}_i] = -\sum_m h_{im}(t)\, \hat{d}_m$. Similarly, the derivative with respect to t' generates the commutator between $\hat{H}(t')$ and $\hat{d}_j^\dagger$ which for noninteracting Hamiltonians is simply $[\hat{H}_0(t'),\, \hat{d}_j^\dagger] = \sum_m h_{mj}(t')\, \hat{d}_m^\dagger$. Therefore

$$\mathrm{i} \frac{d}{dt} G^<_{ij}(t,t') = \sum_m h_{im}(t)\, G^<_{mj}(t,t'), \qquad -\mathrm{i} \frac{d}{dt'} G^<_{ij}(t,t') = \sum_m G^<_{im}(t,t')\, h_{mj}(t'). \quad (23)$$

An analogous derivation for $G^>$ leads to the same equations of motion (23). Let us rewrite them in matrix form

$$\mathrm{i} \frac{d}{dt} G^\lessgtr(t,t') = h(t) G^\lessgtr(t,t'), \qquad -\mathrm{i} \frac{d}{dt'} G^\lessgtr(t,t') = G^\lessgtr(t,t') h(t'). \quad (24)$$

The most general solution of these equations is $G^{\lessgtr}(t,t') = u(t)\,Q^{\lessgtr}\,u^\dagger(t')$ where $Q^<$ and $Q^>$ are arbitrary matrices whereas u is the unitary time-evolution matrix in the *one-particle* Hilbert space

$$u(t) \equiv \mathcal{T}\left\{e^{-\mathrm{i}\int_{-\infty}^{t} d\bar{t}\, h(\bar{t})}\right\} \qquad \Rightarrow \qquad \mathrm{i}\frac{d}{dt}u(t) = h(t)u(t). \tag{25}$$

To find the matrices $Q^{\lessgtr}$ we need an initial condition. We observe that $\lim_{t\to-\infty} u(t) = 1$ and therefore $Q^{\lessgtr} = \lim_{t\to-\infty} G^{\lessgtr}(t,t)$. From Eq. (15) this limit is given by

$$Q^<_{ij} = \lim_{t\to-\infty} G^<_{ij}(t,t) = \mathrm{i}\langle\Phi_g|\hat{d}^\dagger_j\hat{d}_i|\Phi_g\rangle \equiv \mathrm{i}\rho^g_{ij}, \tag{26}$$

$$Q^>_{ij} = \lim_{t\to-\infty} G^>_{ij}(t,t) = -\mathrm{i}\langle\Phi_g|\hat{d}_i\hat{d}^\dagger_j|\Phi_g\rangle = -\mathrm{i}\big(\delta_{ij}-\rho^g_{ij}\big), \tag{27}$$

where ρ^g_{ij} is the one-particle density matrix in the remote past, which is also the one-particle density matrix associated to the noninteracting ground state $|\Phi_g\rangle$. The noninteracting Green function is therefore known once we know ρ^g.

The ρ^g can easily be calculated from the eigenvectors of the (equilibrium) one-particle hamiltonian: $h\,\vec{\varphi}^{(\lambda)} = \varepsilon_\lambda\vec{\varphi}^{(\lambda)}$. Let us see how. We construct the fermionic operators $\hat{c}^\dagger_\lambda \equiv \sum_m \varphi^{(\lambda)}_m \hat{d}^\dagger_m$ that create an electron in the basis vector $\vec{\varphi}^{(\lambda)}$. Using the orthonormality of the eigenvectors the inverse relation reads $\hat{d}^\dagger_m = \sum_\lambda \varphi^{(\lambda)*}_m \hat{c}^\dagger_\lambda$ and the noninteracting Hamiltonian can be rewritten as

$$\hat{H}_0 = \sum_{\lambda\lambda'}\sum_{ij}\hat{c}^\dagger_\lambda\varphi^{(\lambda)*}_i h_{ij}\varphi^{(\lambda')}_j\hat{c}_{\lambda'} = \sum_{\lambda\lambda'}\sum_{i}\hat{c}^\dagger_\lambda\varphi^{(\lambda)*}_i\varepsilon_{\lambda'}\varphi^{(\lambda')}_i\hat{c}_{\lambda'} = \sum_{\lambda\lambda'}\hat{c}^\dagger_\lambda\varepsilon_\lambda\delta_{\lambda\lambda'}\hat{c}_{\lambda'} = \sum_\lambda\varepsilon_\lambda\hat{c}^\dagger_\lambda\hat{c}_\lambda. \tag{28}$$

According to the aufbau principle the noninteracting ground-state $|\Phi_g\rangle$ of the system with N particles is constructed by filling the first N levels of h, i.e., $|\Phi_g\rangle = \hat{c}^\dagger_1\ldots\hat{c}^\dagger_N|0\rangle$ where $|0\rangle$ is the empty state. We then have

$$\rho^g_{ij} = \langle 0|\hat{c}_N\ldots\hat{c}_1\,\hat{d}^\dagger_j\hat{d}_i\,\hat{c}^\dagger_1\ldots\hat{c}^\dagger_N|0\rangle = \sum_{\lambda=1}^{N}\varphi^{(\lambda)*}_j\varphi^{(\lambda)}_i. \tag{29}$$

To summarize the noninteracting lesser and greater Green functions have the following analytic expression (in matrix form)

$$G^<(t,t') = \mathrm{i}\,u(t)\,\rho^g\,u^\dagger(t'), \qquad G^>(t,t') = -\mathrm{i}\,u(t)\big(1-\rho^g\big)u^\dagger(t'). \tag{30}$$

We can use the property of the evolution operator $u^\dagger(\tau)u(\tau) = 1$ for any time τ to rewrite Eq. (30) in terms of the *equal-time* lesser and greater Green functions $G^{\lessgtr}(t,t)$

$$\begin{aligned} G^{\lessgtr}(t,t') &= \Big(\Theta(t-t') + \Theta(t'-t)\Big)G^{\lessgtr}(t,t') \\ &= \Theta(t-t')\,u(t)u^\dagger(t')G^{\lessgtr}(t',t') + \Theta(t'-t)\,G^{\lessgtr}(t,t)\,u(t)u^\dagger(t'). \end{aligned} \tag{31}$$

This rewriting brings out two functions, i.e., the retarded and advanced Green functions

$$G^{\mathrm{R}}(t,t') = -\mathrm{i}\Theta(t-t')\,u(t)\,u^\dagger(t') = -\mathrm{i}\Theta(t-t')\,\mathcal{T}\left\{e^{-\mathrm{i}\int_{t'}^{t} d\bar{t}\, h(\bar{t})}\right\}, \tag{32}$$

$$G^{\mathrm{A}}(t,t') = \quad \mathrm{i}\Theta(t'-t)\,u(t)\,u^\dagger(t') = \quad \mathrm{i}\Theta(t'-t)\,\bar{\mathcal{T}}\left\{e^{-\mathrm{i}\int_{t'}^{t} d\bar{t}\, h(\bar{t})}\right\} = \big(G^{\mathrm{R}}(t',t)\big)^\dagger. \tag{33}$$

The retarded and advanced Green functions carry no information on how the noninteracting levels are initially populated. They only contain information on how to propagate one-particle states – sometimes we shall refer to $G^{\rm R}$ and $G^{\rm A}$ as propagators. Using the propagators we can rewrite Eq. (31) as

$$G^{\lessgtr}(t,t') = {\rm i}G^{\rm R}(t,t')\,G^{\lessgtr}(t',t') - {\rm i}G^{\lessgtr}(t,t)\,G^{\rm A}(t,t'). \tag{34}$$

This result has inspired an important ansatz in NEGF; we come back to it in section 8.

5 Dyson equation on the contour

The analytic calculation of the interacting Green function defined in Eq. (14) is possible only in special cases like, e.g., integrable models or systems with only a few particles. In most cases the interacting Green function must be approximated. In this section we discuss a scheme to evaluate $G(z,z')$ using an arbitrary subset of scattering processes. Accurate approximations can then be generated by selecting those processes that dominate over the others.
The starting point is the observation that inside the contour ordering the operators can be treated as commuting operators. Consider for instance the contour ordered product of $\hat{H}_0(z)$ (noninteracting part of the Hamiltonian) and $\hat{H}_{\rm int}(z')$ (interaction Hamiltonian). Then

$$\mathcal{T}_\gamma\left\{\hat{H}_0(z)\hat{H}_{\rm int}(z')\right\} = \mathcal{T}_\gamma\left\{\hat{H}_{\rm int}(z')\hat{H}_0(z)\right\}. \tag{35}$$

Indeed for, e.g., z later than z' Eq. (35) yields $\hat{H}_0(t)\hat{H}_{\rm int}(t')$ no matter if we use the expression in the left hand side or in the right hand side – remember the rule: operators with later contour-times must be placed to the left. We can then manipulate the interacting Green function in Eq. (14) as follows

$$\begin{aligned} G_{ij}(z,z') &= \frac{1}{\rm i}\langle\Phi_g|\mathcal{T}_\gamma\left\{e^{-{\rm i}\int_\gamma d\bar{z}\,\hat{H}_0(\bar{z})}e^{-{\rm i}\int_\gamma d\bar{z}\,\hat{H}_{\rm int}(\bar{z})}\hat{d}_i(z)\hat{d}_j^\dagger(z')\right\}|\Phi_g\rangle, \\ &= \frac{1}{\rm i}\sum_{n=0}^{\infty}\frac{(-{\rm i})^n}{n!}\int_\gamma dz_1\cdots dz_n\langle\Phi_g|\mathcal{T}_\gamma\left\{e^{-{\rm i}\int_\gamma d\bar{z}\,\hat{H}_0(\bar{z})}\hat{H}_{\rm int}(z_1)\cdots\hat{H}_{\rm int}(z_n)\hat{d}_i(z)\hat{d}_j^\dagger(z')\right\}|\Phi_g\rangle. \end{aligned} \tag{36}$$

In the first equality we used that for two commuting operators $\hat{A}$ and $\hat{B}$ we have $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}$. In the second equality we expanded the exponent containing the interaction Hamiltonian in a Taylor series. Comparing Eq. (36) with the expansion of the more familiar time-ordered Green function we notice that the only difference is in the domain of integration: in Eq. (36) all integrals are over the contour while in the time-ordered Green function all integrals are between $-\infty$ and $+\infty$ (real axis). We can then recycle all results of the time-ordered formalism; it will be enough to change the time domain from the real axis to the contour. In particular the integrand in Eq. (36) is the noninteracting average of a string of fermionic operators, which can be broken into products of Green functions using the Wick theorem [19]. This innocent-looking observation implies that we can represent the expansion of Eq. (36) in terms of the same Feynman diagrams as the time-ordered Green function! The only difference in NEGF is that the

oriented lines are contour Green functions and the times of each internal vertex are integrated over the contour. A few diagrammatic examples are given in the next section.
It is textbook knowledge that the diagrammatic expansion of G highlights the occurrence of an important mathematical unit repeated to infinite order, i.e., the self-energy Σ. In NEGF the self-energy, like the Green function, depends on two contour-times and the relation between G and Σ is given by the Dyson equation (in matrix form)

$$\begin{aligned} G(z,z') &= G_0(z,z') + \int_\gamma dz_1 dz_2\, G_0(z,z_1)\Sigma(z_1,z_2)G(z_2,z') \\ &= G_0(z,z') + \int_\gamma dz_1 dz_2\, G(z,z_1)\Sigma(z_1,z_2)G_0(z_2,z'), \end{aligned} \tag{37}$$

where the Green function G_0 is the noninteracting Green function discussed in section 4. We can transform the Dyson equation into two integro-differential equations that, as we shall see, are easier to handle. For this purpose we derive below the equation of motion of $G_0(z,z')$ on the contour. Using the decomposition in Eq. (17) we have

$$\mathrm{i}\frac{d}{dz}G_0(z,z') = \mathrm{i}\delta(z,z')\Big[G_0^>(t,t) - G_0^<(t,t)\Big] + \Theta(z,z')\frac{d}{dt}G_0^>(t,t') + \Theta(z',z)\frac{d}{dt}G_0^<(t,t'), \tag{38}$$

where

$$\delta(z,z') = \frac{d}{dz}\Theta(z,z') = -\frac{d}{dz}\Theta(z',z) \tag{39}$$

is the Dirac delta on the contour. From Eq. (30) the term in the square bracket is simply

$$G_0^>(t,t) - G_0^<(t,t) = -\mathrm{i}u(t)\Big(1-\rho^g+\rho^g\Big)u^\dagger(t) = -\mathrm{i}. \tag{40}$$

Taking into account Eq. (24), i.e., the time derivative of $G_0^{\lessgtr}$, we can then rewrite Eq. (38) as

$$\mathrm{i}\frac{d}{dz}G_0(z,z') = \delta(z,z') + h(t)G_0(z,z'). \tag{41}$$

With similar steps we can calculate the derivative with respect to z' and find

$$-\mathrm{i}\frac{d}{dz'}G_0(z,z') = \delta(z,z') + G_0(z,z')h(t'). \tag{42}$$

These last two equations are the equations of motion (on the contour) for the noninteracting Green function. As anticipated, they are useful to transform the Dyson equation into two integro-differential equations for G. Deriving the first line of Eq. (37) with respect to z and the second line of the same equation with respect to z' we find

$$\Big(\mathrm{i}\frac{d}{dz} - h(t)\Big)G(z,z') = \delta(z,z') + \int_\gamma d\bar{z}\,\Sigma(z,\bar{z})G(\bar{z},z'), \tag{43}$$

$$G(z,z')\Big(-\mathrm{i}\frac{\overleftarrow{d}}{dz'} - h(t')\Big) = \delta(z,z') + \int_\gamma d\bar{z}\,G(z,\bar{z})\Sigma(\bar{z},z'). \tag{44}$$

Before discussing the numerical strategies to solve the equations of motion (43) and (44) let us have a closer look at the self-energy and its lesser and greater components.

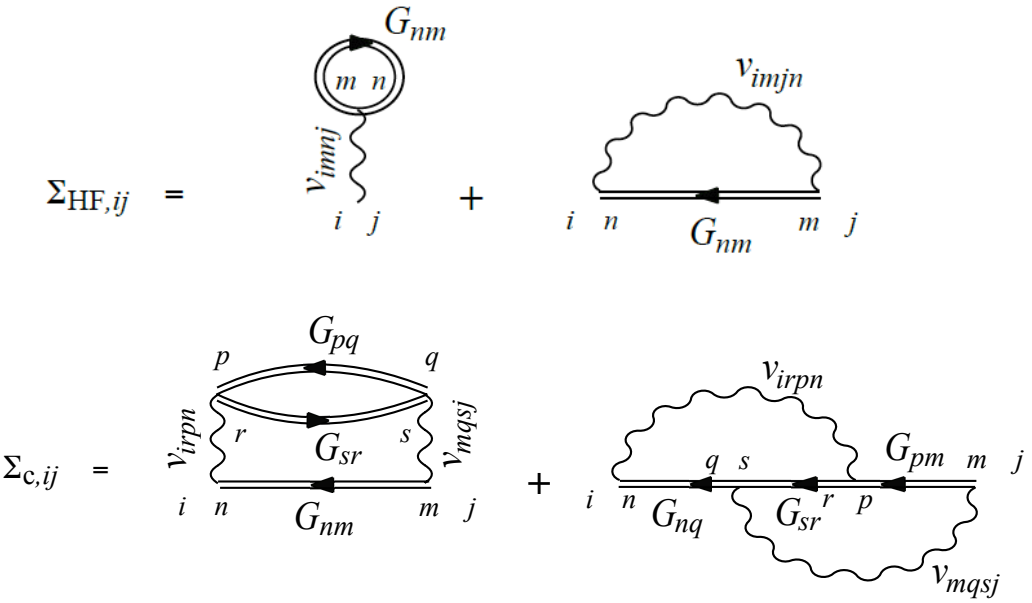

Fig. 2: *Diagrams for the Hartree-Fock self-energy (top) and for the correlation self-energy in the 2nd Born approximation (bottom).*

6 Simple diagrammatic approximations

In Fig. 2 we show a couple of diagrammatic approximations to Σ. To first order in the electron-electron interaction v only two diagrams contribute, see Fig. 2 (top). The resulting Σ is the so called Hartree-Fock (HF) self-energy

$$\Sigma_{\mathrm{HF},ij}(z,z') = \underbrace{-\mathrm{i}\,\delta(z,z')\sum_{mn} v_{imnj}\,G_{nm}(z,z^+)}_{\text{Hartree}} + \underbrace{\mathrm{i}\delta(z,z')\sum_{mn} v_{imjn}\,G_{nm}(z,z^+)}_{\text{Fock}}$$
$$\equiv \delta(z,z')\,V_{\mathrm{HF},ij}(t), \tag{45}$$

where we have denoted by z^+ a contour-time infinitesimally later than z and we have defined the HF potential in the second line of Eq. (45). From Eq. (17) we see that $G(z,z^+) = G^<(t,t) = \mathrm{i}\rho(t)$. The HF potential is therefore a linear function of the one-particle density matrix; explicitly we have

$$V_{\mathrm{HF},ij}(t) = \sum_{mn} \big(v_{imnj} - v_{imjn}\big)\rho_{nm}(t). \tag{46}$$

The HF self-energy diagrams are the only self-energy diagrams proportional to the Dirac delta on the contour. This time-locality of Σ_{HF} prevents the description of, e.g., quasi-particle lifetimes (which are always infinite in HF) and quasi-particle satellites like those emerging from the dressing of electrons with plasmons. The Green function in the HF approximation is the solution of the equations of motion (43) and (44) when Σ is approximated with Σ_{HF}. The contour integral is in this case trivial and the equations of motion reduce to

$$\left(\mathrm{i}\frac{d}{dz} - h(t) - V_{\mathrm{HF}}(t)\right)G(z,z') = \delta(z,z'), \tag{47}$$

$$G(z,z')\left(-\mathrm{i}\frac{\overleftarrow{d}}{dz'}-h(t')-V_{\rm HF}(t')\right)=\delta(z,z'). \tag{48}$$

These equations have the same mathematical structure as those of the noninteracting Green function, see Eqs. (41) and (42). The only difference is that the one-particle Hamiltonian $h(t)$ is replaced by the HF Hamiltonian

$$h_{\rm HF}(t)\equiv h(t)+V_{\rm HF}(t). \tag{49}$$

In essence the HF world is a world where an electron does not collide with other electrons but it rather moves in the mean-field potential $V_{\rm HF}$ generated by all other electrons. The lesser and greater components are therefore given by Eq. (30) with evolution operator $u(t)=\mathcal{T}\{e^{-\mathrm{i}\int_{-\infty}^{t}d\bar{t}\,h_{\rm HF}(\bar{t})}\}$. This implies that the HF retarded and advanced Green functions read

$$G^{\rm R}(t,t')=\mathrm{i}\Theta(t-t')\mathcal{T}\{e^{-\mathrm{i}\int_{t'}^{t}d\bar{t}\,h_{\rm HF}(\bar{t})}\},\qquad G^{\rm A}(t,t')=\big(G^{\rm R}(t',t)\big)^{\dagger}, \tag{50}$$

and that Eq. (34) for $G^{\lessgtr}$ is valid in the HF approximation too.

Higher-order self-energy diagrams are nonlocal in time and contribute to the so called *correlation* self-energy $\Sigma_{\rm c}$. The splitting of the full self-energy $\Sigma=\Sigma_{\rm HF}+\Sigma_{\rm c}$ into a HF part and a correlation part is extremely convenient for computational purposes, see section 10. In Fig. 2 we show the second-order (in the interaction) diagrams for the correlated self-energy, also known as the 2nd Born (2B) approximation. In the 2B world an electron can collide only once with another electron; this is however enough to change its quantum number like, e.g., the momentum, and hence to generate a finite life-time.

Converting the diagrams of Fig. 2 into a mathematical expression we get

$$\begin{aligned}
&\Sigma_{{\rm c},ij}(z,z')=\\
&=\mathrm{i}^2\sum_{rpn}\sum_{mqs}v_{irpn}v_{mqsj}\big[-G_{nm}(z,z')G_{sr}(z',z)G_{pq}(z,z')+G_{nq}(z,z')G_{sr}(z',z)G_{pm}(z,z')\big]\\
&=\mathrm{i}^2\sum_{rpn}\sum_{mqs}v_{irpn}\big(v_{qmsj}-v_{mqsj}\big)G_{nm}(z,z')G_{sr}(z',z)G_{pq}(z,z'),
\end{aligned} \tag{51}$$

where in the last step we renamed $m\leftrightarrow q$ in the second term of the square bracket. As anticipated this self-energy is nonlocal in time, i.e., it is not proportional to $\delta(z,z')$, and the equations of motion for G remain integro-differential equations. The corresponding greater and lesser Green functions cannot be written as in Eq. (30) and, consequently, Eq. (34) is no longer valid. The lesser and greater components of the self-energy are defined similarly to the lesser and greater components of the Green function

$$\Sigma_{\rm c}^{<}(t,t')\equiv\Sigma_{\rm c}(t_-,t'_+),\qquad \Sigma_{\rm c}^{>}(t,t')\equiv\Sigma_{\rm c}(t_+,t'_-). \tag{52}$$

Both $\Sigma^{<}$ and $\Sigma^{>}$ are functions of the real times t and t'. From their definition we see that these functions are simply obtained from Eq. (51) with the replacement

$$G_{nm}(z,z')G_{sr}(z',z)G_{pq}(z,z')\ \to\ G^{\lessgtr}_{nm}(t,t')G^{\gtrless}_{sr}(t',t)^{\lessgtr}G^{\lessgtr}_{pq}(t,t'). \tag{53}$$

Like the Green function, see discussion below Eq. (15), if $t<t'$ then the lesser self-energy is also given by $\Sigma_{\rm c}^<(t,t')=\Sigma_{\rm c}^<(t_-,t'_-)$ whereas if $t>t'$ then we have $\Sigma_{\rm c}^<(t,t')=\Sigma_{\rm c}^<(t_+,t'_+)$. Analogous considerations apply to the greater self-energy. Choosing z and z' on different branches, like we have done in Eq. (52), returns the lesser and greater self-energy for all times t and t'.
In the next section we describe how to calculate the Green function with a nonvanishing correlation self-energy.

7 Kadanoff-Baym equations

Let us start by rewriting the equations of motion (43), (44) with the self-energy $\Sigma=\Sigma_{\rm HF}+\Sigma_{\rm c}$

$$\left(\mathrm{i}\frac{d}{dz}-h_{\rm HF}(t)\right)G(z,z')=\delta(z,z')+\int_\gamma d\bar z\,\Sigma_{\rm c}(z,\bar z)\,G(\bar z,z'), \tag{54}$$

$$G(z,z')\left(-\mathrm{i}\frac{\overleftarrow{d}}{dz'}-h_{\rm HF}(t')\right)=\delta(z,z')+\int_\gamma d\bar z\,G(z,\bar z)\,\Sigma_{\rm c}(\bar z,z'). \tag{55}$$

As pointed out in section 3, see discussion below Eq. (15), the lesser Green function $G^<(t,t')$ is equal (for all t and t') to the contour Green function $G(z,z')$ when $z=t_-$ and $z'=t'_+$. Making this choice of contour-times in, e.g., Eq. (54) we find

$$\left(\mathrm{i}\frac{d}{dt}-h_{\rm HF}(t)\right)G^<(t,t')=\int_\gamma d\bar z\,\Sigma_{\rm c}(t_-,\bar z)\,G(\bar z,t'_+). \tag{56}$$

The Dirac delta vanishes since z lies on the forward branch and z' lies on the backward branch (hence they can never coincide). To work out the integral over the contour we break it up into four different pieces, two per branch. The integral over the forward branch is performed from $-\infty$ to t and then from t to $+\infty$ whereas the integral over the backward branch is performed from $+\infty$ to t' and then from t' to $-\infty$

$$\begin{aligned}\int_\gamma d\bar z\,\Sigma_{\rm c}(t_-,\bar z)G(\bar z,t'_+)=&\int_{-\infty}^{t}d\bar t\,\underbrace{\Sigma_{\rm c}(t_-,\bar t_-)G(\bar t_-,t'_+)}_{\Sigma_{\rm c}^>(t,\bar t)G^<(\bar t,t')}+\int_{t}^{\infty}d\bar t\,\underbrace{\Sigma_{\rm c}(t_-,\bar t_-)G(\bar t_-,t'_+)}_{\Sigma_{\rm c}^<(t,\bar t)G^<(\bar t,t')}\\&+\int_{\infty}^{t'}d\bar t\,\underbrace{\Sigma_{\rm c}(t_-,\bar t_+)G(\bar t_+,t'_+)}_{\Sigma_{\rm c}^<(t,\bar t)G^<(\bar t,t')}+\int_{t'}^{-\infty}d\bar t\,\underbrace{\Sigma_{\rm c}(t_-,\bar t_+)G(\bar t_+,t'_+)}_{\Sigma_{\rm c}^<(t,\bar t)G^>(\bar t,t')}.\end{aligned} \tag{57}$$

In this equation the integrand of the second and third terms is the same. We can then use $\int_t^\infty+\int_\infty^{t'}=\int_t^{t'}=\int_{-\infty}^{t'}-\int_{-\infty}^{t}$ and rewrite the contour integral as

$$\begin{aligned}\int_\gamma d\bar z\,\Sigma_{\rm c}(t_-,\bar z)G(\bar z,t'_+)=&\int_{-\infty}^{t}d\bar t\Big(\Sigma_{\rm c}^>(t,\bar t)-\Sigma_{\rm c}^<(t,\bar t)\Big)G^<(\bar t,t')\\&-\int_{-\infty}^{t'}d\bar t\,\Sigma_{\rm c}^<(t,\bar t)\Big(G^>(\bar t,t')-G^<(\bar t,t')\Big).\end{aligned} \tag{58}$$

For any two-times correlator $C(z,z')$ we define the retarded and advanced components as

$$C^{\rm R}(t,t') = \quad \Theta(t{-}t')\Big(C^{>}(\bar{t},t') - C^{<}(\bar{t},t')\Big), \tag{59}$$

$$C^{\rm A}(t,t') = -\Theta(t'{-}t)\Big(C^{>}(\bar{t},t') - C^{<}(\bar{t},t')\Big). \tag{60}$$

One important property following from these definitions is that

$$C^{\rm R} - C^{\rm A} = C^{>} - C^{<}. \tag{61}$$

Using the retarded and advanced functions we can transform the equation of motion (56) in a form containing only integrals and functions on the real axis

$$\left({\rm i}\frac{d}{dt} - h_{\rm HF}(t)\right)G^{<}(t,t') = \int_{-\infty}^{\infty} d\bar{t}\,\Big(\Sigma_{\rm c}^{\rm R}(t,\bar{t})G^{<}(\bar{t},t') + \Sigma_{\rm c}^{<}(t,\bar{t})G^{\rm A}(\bar{t},t')\Big). \tag{62}$$

With similar manipulations we obtain the equation of motion for the greater Green function. We choose $z = t_+$ and $z' = t'_-$, use Eq. (55), and find

$$G^{>}(t,t')\left(-{\rm i}\frac{\overleftarrow{d}}{dt'} - h_{\rm HF}(t')\right) = \int_{-\infty}^{\infty} d\bar{t}\,\Big(G^{\rm R}(t,\bar{t})\Sigma_{\rm c}^{>}(\bar{t},t') + G^{>}(t,\bar{t})\Sigma_{\rm c}^{\rm A}(\bar{t},t')\Big). \tag{63}$$

Equations (62) and (63) are known as the *Kadanoff-Baym equations* (KBE) [20]. They form a closed system of integro-differential equations since (i) the lesser and greater self-energies are functions (or better functionals) of $G^{<}$ and $G^{>}$, see for instance the 2B self-energy in Eq. (51), and (ii) the lesser and greater Green functions are anti-hermitian, see the definitions in Eqs. (15) and (16), i.e.,

$$G^{\lessgtr}(t',t) = -\Big(G^{\lessgtr}(t,t')\Big)^{\dagger}. \tag{64}$$

Due to the cubic scaling with the maximum propagation time, the KBE are rather burdensome to solve numerically. Their use has been so far restricted to atoms, diatomic molecules, or model systems [21–24]. Details on available implementations strategies can be found in [1, 25, 26].

Before concluding this section we would like to observe that the retarded and advanced correlators defined in Eqs. (59) and (60) agree with the previous definition of $G^{\rm R}$ and $G^{\rm A}$ in noninteracting systems. The noninteracting lesser and greater Green functions are given in Eq. (30) and therefore the noninteracting retarded Green function calculated according to Eq. (59) is

$$G^{\rm R}(t,t') = -{\rm i}\Theta(t{-}t')u(t)\big(1-\rho^g+\rho^g\big)u^{\dagger}(t') = -{\rm i}\Theta(t{-}t')u(t)u^{\dagger}(t'), \tag{65}$$

which is the same as Eq. (32). Similarly one can show that the advanced noninteracting Green functions defined as in Eq. (60) agrees with Eq. (33).

8 The Generalized Kadanoff-Baym Ansatz

In the mid-1980s Lipavsky *et al.* [27] proposed the so called Generalized Kadanoff-Baym Ansatz (GKBA) to collapse the KBE for the two-times Green functions into a single equation for the one-particle density matrix $\rho(t)$, reducing the computational cost drastically. The

NEGF+GKBA approach has been successfully applied to the nonequilibrium dynamics [28,29] and many-body localization [30] of Hubbard clusters, time-dependent quantum transport [31, 32] equilibrium absorption of sodium clusters [33], real-time dynamics of the Auger decay [34], transient absorption [35–38] and carrier dynamics [18, 39] of semiconductors, excitonic insulators out of equilibrium [40] as well as charge transfer [41] and charge migration [42–44] in molecular systems.

The basic idea of the GKBA is to approximate the lesser and greater Green functions *inside* the collision integral with the expression in Eq. (34), which we have demonstrated to be valid only for noninteracting systems or in the HF approximation. In terms of the one-particle density matrix $\rho(t) = -\mathrm{i}G^<(t,t) = 1 - \mathrm{i}G^>(t,t)$ defined in Eq. (18) we can write the GKBA as

$$G^<(t,t') = -G^{\rm R}(t,t')\,\rho(t') \quad + \quad \rho(t) \quad G^{\rm A}(t,t'), \tag{66}$$

$$G^>(t,t') = -G^{\rm R}(t,t')(\rho(t')-1) + (\rho(t)-1)G^{\rm A}(t,t'). \tag{67}$$

Through the GKBA the time off-diagonal lesser and greater Green functions are expressed in terms of ρ *and* the propagators. Assuming that the average time between two consecutive collisions of an electron in the medium is longer than the quasiparticle life-time we can further approximate the propagators with their HF expression, see Eq. (50). In this way the full $G^{\lessgtr}(t,t')$ depends only on the density matrix since $h_{\rm HF}$ is a functional of ρ through the HF potential, see again Eq. (46). We mention here that other approximations to the propagators have been proposed in the literature with the aim of accounting for finite quasi-particle life-times [31,45–47]. In all cases, however, the approximated propagators are functionals of ρ only.

Let us see how to reduce the KBE to a single equation for $\rho(t)$ using the GKBA. Consider Eq. (62) and the adjoint equation where the lesser Green function $G^<(t,t')$ is derived with respect to t'. The adjoint equation is the same as Eq. (63) with $> \to <$. Subtracting the two equations and setting $t = t'$ we get

$$\mathrm{i}\left(\frac{d}{dt} + \frac{d}{dt'}\right) G^<(t,t')\big|_{t=t'} - \big[h_{\rm HF}(t),\, G^<(t,t)\big] = I(t) + I^\dagger(t), \tag{68}$$

where $I(t)$ is the collision integral on the right hand side of Eq. (62) calculated at $t = t'$. To show that the collision integral of the adjoint equation is the hermitian conjugate of $I(t)$ one can use the anti-hermiticity of the Green function, i.e., Eq. (64), and of the self-energy. In this chapter there is not enough space for the general proof of the property $\Sigma^<(t,t') = -\big(\Sigma^<(t',t)\big)^\dagger$; however, the reader can verify that this property is fulfilled by the 2B self-energy in Eq. (51); see Ref. [1] for the general proof. The crucial observation is now that the first term in Eq. (68) is nothing but the time derivative of the one-particle density matrix ρ, whereas the second term is the commutator between the HF Hamiltonian and ρ. Hence

$$\frac{d}{dt}\rho(t) + \mathrm{i}\big[h_{\rm HF}[\rho](t),\, \rho(t)\big] = -I[\rho](t) - I^\dagger[\rho](t). \tag{69}$$

We have highlighted that $h_{\rm HF}$ is a functional of ρ through the HF potential in Eq. (46) and that the collision integral I is a functional of ρ through the GKBA. Therefore Eq. (69) is a closed

equation for the one-particle density matrix! The numerical solution scales quadratically with the maximum propagation time since ρ depends on one time only. To better appreciate the computational gain let us work out the collision integral $I(t)$ for the 2B self-energy.
We begin by observing that for $t=t'$ the right hand side of Eq. (62) can be written as

$$I(t) = \int_{-\infty}^{t} d\bar{t}\left(\Big(\Sigma_{\rm c}^{>}(t,\bar{t})-\Sigma_{\rm c}^{<}(t,\bar{t})\Big)G^{<}(\bar{t},t)-\Sigma_{\rm c}^{<}(t,\bar{t})\Big(G^{>}(\bar{t},t)-G^{<}(\bar{t},t)\Big)\right)$$
$$= \int_{-\infty}^{t} d\bar{t}\,\Big(\Sigma_{\rm c}^{>}(t,\bar{t})\,G^{<}(\bar{t},t)-\Sigma_{\rm c}^{<}(t,\bar{t})\,G^{>}(\bar{t},t)\Big). \tag{70}$$

Using Eq. (51) a matrix element of the product $\Sigma_{\rm c}^{>}(t,\bar{t})\,G^{<}(\bar{t},t)$ reads

$$\Big(\Sigma_{\rm c}^{>}(t,\bar{t})G^{<}(\bar{t},t)\Big)_{il} = \sum_j \Sigma^{>}_{{\rm c},ij}(t,\bar{t})\,G^{<}_{jl}(\bar{t},t)$$
$$= {\rm i}^2\sum_{rpn} v_{irpn}\sum_{jmqs}\big(v_{qmsj}-v_{mqsj}\big)G^{>}_{nm}(t,\bar{t})G^{<}_{sr}(\bar{t},t)G^{>}_{pq}(t,\bar{t})G^{<}_{jl}(\bar{t},t). \tag{71}$$

Similarly, the matrix element of the product $\Sigma_{\rm c}^{<}(t,\bar{t})\,G^{>}(\bar{t},t)$ is obtained from Eq. (71) by interchanging $>\leftrightarrow<$. The mathematical structure underlying these expressions emerges clearly if we introduce the Coulomb tensor

$$w_{\substack{qj\\sm}} \equiv v_{mqsj}-v_{qmsj} = w^{*}_{\substack{jq\\ms}} \tag{72}$$

and the response function

$$\chi^{0,\gtrless}_{\substack{pq\\rs}}(t,t') \equiv -{\rm i}G^{\gtrless}_{pq}(t,t')G^{\lessgtr}_{sr}(t',t). \tag{73}$$

We then see that Eq. (70) becomes [2–4]

$$I_{il}(t) = {\rm i}^2\sum_{rpn} v_{irpn}\int_{-\infty}^{t} d\bar{t}\sum_{jmqs}\Big[\chi^{0,>}_{\substack{pq\\rs}}(t,\bar{t})w_{\substack{qj\\sm}}\chi^{0,<}_{\substack{jl\\mn}}(\bar{t},t)-\chi^{0,<}_{\substack{pq\\rs}}(t,\bar{t})w_{\substack{qj\\sm}}\chi^{0,>}_{\substack{jl\\mn}}(\bar{t},t)\Big]$$
$$\equiv -{\rm i}\sum_{rpn} v_{irpn}\,\mathcal{G}_{\substack{pl\\rn}}(t). \tag{74}$$

The square bracket is the sum of simple products between matrices in the two-particle space. Using greek letters for superindices composed by pairs of one-particle indices, e.g., $\alpha=(p,r)$, $\beta=(l,n)$, etc., the matrix elements of $\mathcal{G}$ can also be written as [4]

$$\mathcal{G}_{\alpha\beta}(t) = -{\rm i}\int_{-\infty}^{t} d\bar{t}\sum_{\mu\nu}\Big[\chi^{0,>}_{\alpha\mu}(t,\bar{t})w_{\mu\nu}\chi^{0,<}_{\nu\beta}(\bar{t},t)-\chi^{0,<}_{\alpha\mu}(t,\bar{t})w_{\mu\nu}\chi^{0,>}_{\nu\beta}(\bar{t},t)\Big]. \tag{75}$$

We point out that up to this point we have not yet used the GKBA to transform the collision integral, or equivalently $\mathcal{G}$, into a functional of the density matrix. Evaluating the greater response function for $t>t'$ using the GKBA we get

$$\chi^{0,>}_{\substack{pq\\rs}}(t,t') = {\rm i}\underbrace{\sum_a G^{\rm R}_{pa}(t,t')\big(\rho_{aq}(t')-\delta_{aq}\big)}_{-G^{>}_{pq}(t,t')}\underbrace{\sum_b \rho_{sb}(t')G^{\rm A}_{br}(t',t)}_{G^{<}_{sr}(t',t)} = \sum_{ab} P^{\rm R}_{\substack{pa\\rb}}(t,t')\rho^{(2)>}_{\substack{aq\\bs}}(t'), \tag{76}$$

where we have defined

$$P^{\rm R}_{\substack{pa\\rb}}(t,t') \equiv {\rm i}\, G^{\rm R}_{pa}(t,t')\, G^{\rm A}_{br}(t',t), \qquad \rho^{(2)>}_{\substack{aq\\bs}}(t') \equiv \big(\rho_{aq}(t')-\delta_{aq}\big)\rho_{sb}(t'). \tag{77}$$

The two-time function $P^{\rm R}$ can be interpreted as the propagator of an electron-hole pair. Notice that $G^{\rm R}(t^+,t) = -{\rm i}$ and $G^{\rm A}(t,t^+) = {\rm i}$, and hence

$$P^{\rm R}_{\substack{pa\\rb}}(t^+,t) = {\rm i}\delta_{pa}\delta_{rb} \tag{78}$$

or equivalently

$$P^{\rm R}_{\alpha\beta}(t^+,t) = {\rm i}\delta_{\alpha\beta}. \tag{79}$$

For $t < t'$ the GKBA implies

$$\chi^{0,>}_{\substack{pq\\rs}}(t,t') = {\rm i}\underbrace{\sum_a \big(\rho_{pa}(t)-\delta_{pa}\big)G^{\rm A}_{aq}(t,t')}_{G^{>}_{pq}(t,t')}\underbrace{\sum_b G^{\rm R}_{sb}(t',t)\rho_{br}(t)}_{-G^{<}_{sr}(t',t)} = -\sum_{ab}\rho^{(2)>}_{\substack{pa\\rb}}(t)P^{\rm A}_{\substack{aq\\bs}}(t,t'), \tag{80}$$

where

$$P^{\rm A}_{\substack{aq\\bs}}(t,t') \equiv -{\rm i}\, G^{\rm A}_{aq}(t,t')G^{\rm R}_{sb}(t',t) = \Big(P^{\rm R}_{\substack{qa\\sb}}(t',t)\Big)^*. \tag{81}$$

Using the superindex convention, the greater response function in GKBA for any t and t' then reads

$$\chi^{0,>}_{\alpha\beta}(t,t') = \sum_\mu \Big(P^{\rm R}_{\alpha\mu}(t,t')\rho^{(2)>}_{\mu\beta}(t') - \rho^{(2)>}_{\alpha\mu}(t)P^{\rm A}_{\mu\beta}(t,t')\Big). \tag{82}$$

An analogous derivation can be carried out for the lesser response function. The final result is identical to Eq. (82) but the matrix $\rho^{(2)>}$ is replaced by the matrix

$$\rho^{(2)<}_{\substack{aq\\bs}}(t) \equiv \rho_{aq}(t)\big(\rho_{sb}(t)-\delta_{sb}\big). \tag{83}$$

Hence

$$\chi^{0,<}_{\alpha\beta}(t,t') = \sum_\mu \Big(P^{\rm R}_{\alpha\mu}(t,t')\rho^{(2)<}_{\mu\beta}(t') - \rho^{(2)<}_{\alpha\mu}(t)P^{\rm A}_{\mu\beta}(t,t')\Big). \tag{84}$$

We are now ready to transform $\mathcal{G}$ into an explicit functional of the one-particle density matrix. Taking into account that $\bar{t} < t$ in Eq. (75), we obtain (in matrix form) [2–4]

$$\boldsymbol{\mathcal{G}}(t) = {\rm i}\int_{-\infty}^{t} d\bar{t}\, \boldsymbol{P}^{\rm R}(t,\bar{t})\Big(\boldsymbol{\rho}^{(2)>}(\bar{t})\boldsymbol{w}\boldsymbol{\rho}^{(2)<}(\bar{t}) - \boldsymbol{\rho}^{(2)<}(\bar{t})\boldsymbol{w}\boldsymbol{\rho}^{(2)>}(\bar{t})\Big)\boldsymbol{P}^{\rm A}(\bar{t},t), \tag{85}$$

where boldface letters are used to distinguish matrices in the two-particle space from matrices like G, h or Σ in the one-particle space. The quadratic scaling of the NEGF+GKBA approach is evident from Eq. (85): a time step from t to $t+\delta t$ necessitates the calculation of $\mathcal{G}(t)$, and $\mathcal{G}(t)$ contains an integral whose upper limit grows like t.

$$\begin{cases} \dfrac{d}{dt}\rho + \mathrm{i}\Big[h_{\rm HF},\rho\Big] = -(I+I^\dagger) \\ \dfrac{d}{dt}\mathcal{G} + \mathrm{i}\Big[h^{(2)}_{\rm HF},\mathcal{G}\Big] = \mathrm{i}\Psi \end{cases} \qquad \begin{cases} I_{il} = -\mathrm{i}\sum_{rpn} v_{irpn}\,\mathcal{G}^{\,pl}_{\,rn} \\ \Psi \equiv \rho^{(2)>} w \rho^{(2)<} - \rho^{(2)<} w \rho^{(2)>} \\ \rho^{(2)<}_{\substack{aq\\bs}} \equiv \rho_{aq}(\rho_{sb}-\delta_{sb}) \\ \rho^{(2)>}_{\substack{aq\\bs}} \equiv (\rho_{aq}-\delta_{aq})\rho_{sb} \\ h^{(2)}_{{\rm HF},\substack{pc\\rd}} = h_{{\rm HF},pc}\delta_{rd} - \delta_{pc}h_{{\rm HF},dr} \end{cases}$$

Fig. 3: *Summary of the fundamental equations and definitions for NEGF+GKBA simulations in the 2B approximation.*

9 Time-linear scaling and state-of-the-art approximations

Important progress has been recently achieved in reducing the computational scaling of the NEGF+GKBA equations to the ideal linear law [2], and in establishing that the time-linear scaling holds for the 2B approximation as well as for state-of-the-art diagrammatic methods like GW and T-matrix (both in the particle-hole and particle-particle channels) [3]. In Ref. [4] the time-linear scaling formulation has been further extended to GW plus exchange, T-matrix plus exchange and self-energies with three-particle correlations. Furthermore, in Ref. [5] a GKBA has been introduced also for *bosonic* Green functions, and a time-linear scaling formulation for real-time simulations of nonequilibrium systems of interacting electrons and bosons, e.g., phonons or photons, has been established here too.

The fundamental observation is that the two-particle propagator $\boldsymbol{P}^{\rm R}$ satisfies an elementary equation of motion. Taking into account that $G^{\rm R}$ and $G^{\rm A}$ are approximated at the HF level, see Eq. (50), we get for any $t > \bar{t}$

$$\mathrm{i}\frac{d}{dt}P^{\rm R}_{\substack{pa\\rb}}(t,\bar{t}) = \sum_c h_{{\rm HF},pc}(t)P^{\rm R}_{\substack{ca\\rb}}(t,\bar{t}) - \sum_d h_{{\rm HF},dr}(t)P^{\rm R}_{\substack{ca\\db}}(t,\bar{t}). \tag{86}$$

Introducing the HF Hamiltonian in the two-particle space

$$h^{(2)}_{{\rm HF},\substack{pc\\rd}}(t) = h_{{\rm HF},pc}(t)\delta_{rd} - \delta_{pc}h_{{\rm HF},dr}(t), \tag{87}$$

we can rewrite the equation of motion for $\boldsymbol{P}^{\rm R}$ in matrix form as follows

$$\mathrm{i}\frac{d}{dt}\boldsymbol{P}^{\rm R}(t,\bar{t}) = \boldsymbol{h}^{(2)}_{\rm HF}(t)\boldsymbol{P}^{\rm R}(t,\bar{t}), \qquad t > \bar{t}. \tag{88}$$

Let us now come to $\boldsymbol{P}^{\rm A}$. In matrix form Eq. (81) reads $\boldsymbol{P}^{\rm A}(\bar{t},t) = \big(\boldsymbol{P}^{\rm R}(t,\bar{t})\big)^\dagger$. Taking the hermitian conjugate of Eq. (88) we then get

$$-\mathrm{i}\frac{d}{dt}\boldsymbol{P}^{\rm A}(\bar{t},t) = \boldsymbol{P}^{\rm A}(\bar{t},t)\boldsymbol{h}^{(2)}_{\rm HF}(t), \qquad t > \bar{t}, \tag{89}$$

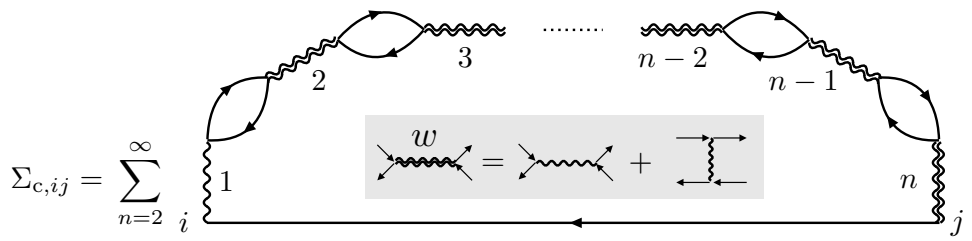

Fig. 4: *Diagrams for the GW+X self-energy.*

where we have observed that the matrix $\boldsymbol{h}^{(2)}_{\rm HF}$ is hermitian in the two-particle space, i.e., $h^{(2)}_{{\rm HF},\alpha\beta} = h^{(2)*}_{{\rm HF},\beta\alpha}$. The equations of motion for $\boldsymbol{P}^{\rm R}$ and $\boldsymbol{P}^{\rm A}$ can be used to construct an equation of motion for $\boldsymbol{\mathcal{G}}$. Recalling the rule

$$\frac{d}{dt}\int^t d\bar{t}\, f(t,\bar{t}) = f(t^+,t) + \int^t d\bar{t}\, \frac{d}{dt} f(t,\bar{t}), \tag{90}$$

where f is an arbitrary function of two times, we find from Eq. (85)

$$\mathrm{i}\frac{d}{dt}\boldsymbol{\mathcal{G}}(t) = -\boldsymbol{\Psi}(t) + \boldsymbol{h}^{(2)}_{\rm HF}(t)\boldsymbol{\mathcal{G}}(t) - \boldsymbol{\mathcal{G}}(t)\boldsymbol{h}^{(2)}_{\rm HF}(t), \tag{91}$$

with

$$\boldsymbol{\Psi}(t) \equiv \boldsymbol{\rho}^{(2)>}(t)\boldsymbol{w}\boldsymbol{\rho}^{(2)<}(t) - \boldsymbol{\rho}^{(2)<}(t)\boldsymbol{w}\boldsymbol{\rho}^{(2)>}(t). \tag{92}$$

Equation (91) together with the equation of motion for ρ, see Eq. (69), form a closed system of ordinary differential equations [2, 3]. Thus the numerical solution of the time-dependent 2B approximation in NEGF+GKBA scales linearly with the maximum propagation time, which was to be demonstrated. For the benefit of the reader we summarize in Fig. 3 the main equations and definitions.

We have already mentioned that the linear scaling of the NEGF+GKBA equations is not limited to the 2B approximation. In what follows we derive the NEGF+GKBA equations for the GW plus exchange (GW+X) approximation. As we shall see the difference with the 2B approximation, Eq. (91), is only minor. Readers who wish to immediately compare 2B with GW+X or who prefer to go through the derivation in a second reading can jump directly to Eq. (110).

The GW+X self-energy is displayed in Fig. 4 where the double wiggly lines represent the tensor w defined in Eq. (72), see also the diagrammatic representation of w in the grey box of Fig. 4. The well known GW self-energy is recovered by neglecting the exchange contribution in w, i.e., by setting $w^{\ }_{\substack{qj\\sm}} = v_{mqsj}$ (first term on the right hand side of the diagrammatic equation in the grey box). The figure shows the diagrams of order n in the interaction strength. The first term of the sum has $n = 2$ and it coincides with the 2B self-energy of Fig. 2. Thus, the GW+X self-energy is obtained from the 2B self-energy of Eq. (51) upon replacing the bare response function $\chi^0_{\substack{pq\\rs}}(z,z') \equiv -\mathrm{i}G_{pq}(z,z')G_{sr}(z',z)$, cf. Eq. (73), with the RPA response function (in matrix form)

$$\boldsymbol{\chi}(z,z') = \boldsymbol{\chi}^0(z,z') + \int_\gamma d\bar{z}\, \boldsymbol{\chi}^0(z,\bar{z})\, \boldsymbol{w}\, \boldsymbol{\chi}(\bar{z},z'). \tag{93}$$

This implies that the collision integral can again be written as in Eq. (74), but the function $\mathcal{G}$ changes into

$$\mathcal{G}(t) = -\mathrm{i}\int_{-\infty}^{t} d\bar{t}\,\Big(\boldsymbol{\chi}^{>}(t,\bar{t})\,\boldsymbol{w}\,\boldsymbol{\chi}^{0,<}(\bar{t},t) - \boldsymbol{\chi}^{<}(t,\bar{t})\,\boldsymbol{w}\,\boldsymbol{\chi}^{0,>}(\bar{t},t)\Big). \tag{94}$$

We point out that at this point we have not yet used the GKBA to transform $\mathcal{G}$ into a functional of the density matrix.

Before using the GKBA we extract the lesser and greater components of the RPA response function. They follows from Eq. (93) when setting $z = t_{-/+}$ and $z' = t_{+/-}$. Manipulating the contour integral as we did in Eq. (57) until Eq. (62) we get

$$\boldsymbol{\chi}^{\lessgtr}(t,t') = \boldsymbol{\chi}^{0,\lessgtr}(t,t') + \int d\bar{t}\,\Big(\boldsymbol{\chi}^{0,\mathrm{R}}(t,\bar{t})\,\boldsymbol{w}\,\boldsymbol{\chi}^{\lessgtr}(\bar{t},t') + \boldsymbol{\chi}^{0,\lessgtr}(t,\bar{t})\,\boldsymbol{w}\,\boldsymbol{\chi}^{\mathrm{A}}(\bar{t},t')\Big). \tag{95}$$

Unless otherwise stated undefined integrals are over the entire real axis, i.e., $\int \equiv \int_{-\infty}^{\infty}$. We can use Eq. (95) to calculate the retarded and advanced components which, we recall, are defined for any two-times correlator in Eqs. (59) and (60). For the retarded response function we find

$$\begin{aligned}\boldsymbol{\chi}^{\mathrm{R}}(t,t') = \boldsymbol{\chi}^{0,\mathrm{R}}(t,t') &+ \Theta(t{-}t')\int d\bar{t}\,\boldsymbol{\chi}^{0,\mathrm{R}}(t,\bar{t})\,\boldsymbol{w}\,\Big[\boldsymbol{\chi}^{>}(\bar{t},t'){-}\boldsymbol{\chi}^{<}(\bar{t},t')\Big]\\ &+ \Theta(t{-}t')\int d\bar{t}\,\Big[\boldsymbol{\chi}^{0,>}(t,\bar{t}){-}\boldsymbol{\chi}^{0,<}(t,\bar{t})\Big]\,\boldsymbol{w}\,\boldsymbol{\chi}^{\mathrm{A}}(\bar{t},t').\end{aligned} \tag{96}$$

Consider the last term in this expression. It vanishes unless $t > t'$, due to the theta function $\Theta(t{-}t')$, and $t' > \bar{t}$, due to the theta function hidden in $\boldsymbol{\chi}^{\mathrm{A}}$. We can then multiply the integrand by $\Theta(t{-}\bar{t})$ and hence replace the square bracket with $\boldsymbol{\chi}^{0,\mathrm{R}}(t,\bar{t})$. Taking into account Eq. (61) to rewrite the square bracket in the second term we then see that the products $\boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\,\boldsymbol{\chi}^{\mathrm{A}}$ cancel off and we remain with

$$\boldsymbol{\chi}^{\mathrm{R}}(t,t') = \boldsymbol{\chi}^{0,\mathrm{R}}(t,t') + \int d\bar{t}\,\boldsymbol{\chi}^{0,\mathrm{R}}(t,\bar{t})\,\boldsymbol{w}\,\boldsymbol{\chi}^{\mathrm{R}}(\bar{t},t'). \tag{97}$$

The advanced response function can be worked out similarly; the result is the same as Eq. (97) with $\mathrm{R} \to \mathrm{A}$.

The equations for $\boldsymbol{\chi}^{\mathrm{R/A}}$ are useful to isolate $\boldsymbol{\chi}^{\lessgtr}$ in Eq. (95). To lighten the notation let us denote with a dot the convolution between two functions. Thus Eq. (95) can be shorten into $\boldsymbol{\chi}^{\lessgtr} = \boldsymbol{\chi}^{0,\lessgtr}{+}\boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}{\cdot}\boldsymbol{\chi}^{\lessgtr}{+}\boldsymbol{\chi}^{0,\lessgtr}\,\boldsymbol{w}{\cdot}\boldsymbol{\chi}^{\mathrm{A}}$ and similarly Eq. (97) becomes $\boldsymbol{\chi}^{\mathrm{R}} = \boldsymbol{\chi}^{0,\mathrm{R}}{+}\boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}{\cdot}\boldsymbol{\chi}^{\mathrm{R}}$. The dot can of course go to the left of $\boldsymbol{w}$ as well. Notice that the retarded equation can be solved iteratively to give

$$\begin{aligned}\boldsymbol{\chi}^{\mathrm{R}} &= \boldsymbol{\chi}^{0,\mathrm{R}} + \boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}} + \boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}} + \ldots\\ &= \boldsymbol{\chi}^{0,\mathrm{R}} + \big(\boldsymbol{\chi}^{0,\mathrm{R}} + \boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}} + \ldots\big)\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}}\\ &= \boldsymbol{\chi}^{0,\mathrm{R}} + \boldsymbol{\chi}^{\mathrm{R}}\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}}.\end{aligned} \tag{98}$$

In other words $\boldsymbol{\chi}^{\mathrm{R}}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\mathrm{R}} = \boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{\mathrm{R}}$. Let us go back to Eq. (95). Isolating $\boldsymbol{\chi}^{\lessgtr}$ we get

$$\big(\boldsymbol{\delta} - \boldsymbol{\chi}^{0,\mathrm{R}}\,\boldsymbol{w}\big)\cdot\boldsymbol{\chi}^{\lessgtr} = \boldsymbol{\chi}^{0,\lessgtr}\cdot\big(\boldsymbol{\delta} + \boldsymbol{w}\,\boldsymbol{\chi}^{\mathrm{A}}\big), \tag{99}$$

where $\boldsymbol{\delta}$ stands for the Dirac delta, hence for any two-times correlator $\boldsymbol{\mathcal{C}}$ we have $[\boldsymbol{\delta}\cdot\boldsymbol{\mathcal{C}}](t,t') = \int d\bar{t}\,\boldsymbol{\delta}(t-\bar{t})\,\boldsymbol{\mathcal{C}}(\bar{t},t') = \boldsymbol{\mathcal{C}}(t,t')$. Next we observe that

$$\big(\boldsymbol{\delta}+\boldsymbol{\chi}^{\rm R}\,\boldsymbol{w}\big)\cdot\big(\boldsymbol{\delta}-\boldsymbol{\chi}^{0,\rm R}\,\boldsymbol{w}\big) = \boldsymbol{\delta}+\big(\boldsymbol{\chi}^{\rm R}-\boldsymbol{\chi}^{0,\rm R}-\boldsymbol{\chi}^{\rm R}\,\boldsymbol{w}\cdot\boldsymbol{\chi}^{0,\rm R}\big)\,\boldsymbol{w} = \boldsymbol{\delta}, \tag{100}$$

since the term in parenthesis vanish, see Eq. (98). Convoluting Eq. (99) with $\big(\boldsymbol{\delta}+\boldsymbol{\chi}^{\rm R}\,\boldsymbol{w}\big)$ on the right we then find

$$\boldsymbol{\chi}^{\lessgtr} = \big(\boldsymbol{\delta}+\boldsymbol{\chi}^{\rm R}\,\boldsymbol{w}\big)\cdot\boldsymbol{\chi}^{0,\lessgtr}\cdot\big(\boldsymbol{\delta}+\boldsymbol{w}\,\boldsymbol{\chi}^{\rm A}\big). \tag{101}$$

At this point we have all ingredients to evaluate $\boldsymbol{\mathcal{G}}$ using the GKBA. From Eqs. (82) and (84) we first obtain the GKBA expression of the retarded/advanced bare response functions

$$\boldsymbol{\chi}^{0,\rm R}(t,t') = \boldsymbol{P}^{\rm R}(t,t')\boldsymbol{\rho}^{(2),\Delta}(t'), \qquad \boldsymbol{\chi}^{0,\rm A}(t,t') = \boldsymbol{\rho}^{(2),\Delta}(t)\boldsymbol{P}^{\rm A}(t,t'), \tag{102}$$

where we have defined

$$\boldsymbol{\rho}^{(2),\Delta}(t) \equiv \boldsymbol{\rho}^{(2),>}(t) - \boldsymbol{\rho}^{(2),<}(t). \tag{103}$$

Inserting Eq. (102) into Eq. (97) and in the analogous equation for $\boldsymbol{\chi}^{\rm A}$ we obtain the GKBA expression for the retarded/advanced RPA response functions

$$\boldsymbol{\chi}^{\rm R}(t,t') = \boldsymbol{\Pi}^{\rm R}(t,t')\boldsymbol{\rho}^{(2),\Delta}(t'), \qquad \boldsymbol{\chi}^{\rm A}(t,t') = \boldsymbol{\rho}^{(2),\Delta}(t)\boldsymbol{\Pi}^{\rm A}(t,t'), \tag{104}$$

where the dressed electron-hole propagators satisfy the integral equation

$$\boldsymbol{\Pi}^{\rm R} = \boldsymbol{P}^{\rm R} + \boldsymbol{P}^{\rm R}\cdot\boldsymbol{\rho}^{(2),\Delta}\,\boldsymbol{w}\,\boldsymbol{\Pi}^{\rm R} = \boldsymbol{P}^{\rm R} + \boldsymbol{\Pi}^{\rm R}\cdot\boldsymbol{\rho}^{(2),\Delta}\,\boldsymbol{w}\,\boldsymbol{P}^{\rm R}, \tag{105a}$$

$$\boldsymbol{\Pi}^{\rm A} = \boldsymbol{P}^{\rm A} + \boldsymbol{P}^{\rm A}\cdot\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\Delta}\boldsymbol{\Pi}^{\rm A} = \boldsymbol{P}^{\rm A} + \boldsymbol{\Pi}^{\rm A}\cdot\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\Delta}\boldsymbol{P}^{\rm A}. \tag{105b}$$

Here and below the product of a one-time function A and a two-times function B is intended as $[AB](t,t') \equiv A(t)B(t,t')$ and $[BA](t,t') = B(t,t')A(t')$. Thus in Eqs. (105) the convolution dot could actually be placed anywhere between $\boldsymbol{P}^{\rm R/A}$ and $\boldsymbol{\Pi}^{\rm R/A}$. Using the GKBA expression for $\boldsymbol{\chi}^{0,\lessgtr}$ in Eqs. (82) and (84) as well as the GKBA expression for $\boldsymbol{\chi}^{\rm R/A}$ in Eq. (104) the lesser/greater RPA response function in Eq. (101) becomes

$$\begin{aligned}\boldsymbol{\chi}^{\lessgtr} &= \big(\boldsymbol{\delta}+\boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),\Delta}\,\boldsymbol{w}\big)\cdot\big(\boldsymbol{P}^{\rm R}\boldsymbol{\rho}^{(2),\lessgtr} - \boldsymbol{\rho}^{(2),\lessgtr}\boldsymbol{P}^{\rm A}\big)\cdot\big(\boldsymbol{\delta}+\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\Delta}\boldsymbol{\Pi}^{\rm A}\big)\\ &= \boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),\lessgtr}\cdot\big(\boldsymbol{\delta}+\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\Delta}\boldsymbol{\Pi}^{\rm A}\big) - \big(\boldsymbol{\delta}+\boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),\Delta}\,\boldsymbol{w}\big)\cdot\boldsymbol{\rho}^{(2),\lessgtr}\boldsymbol{\Pi}^{\rm A}.\end{aligned} \tag{106}$$

This result allows for rewriting $\boldsymbol{\mathcal{G}}$ in Eq. (94) in a very elegant form. Taking into account that

for any $\bar{t} < t$ Eqs. (82) and (84) imply $\boldsymbol{\chi}^{0,\lessgtr}(\bar{t},t) = -[\boldsymbol{\rho}^{(2),\lessgtr}\boldsymbol{P}^{\rm A}](\bar{t},t)$ we find

$$
\begin{aligned}
\boldsymbol{\mathcal{G}}(t) &= \mathrm{i}\Big[\Big(\underbrace{\boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),>}\cdot\big(\boldsymbol{\delta}+\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\Delta}\boldsymbol{\Pi}^{\rm A}\big) - \big(\boldsymbol{\delta}+\boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),\Delta}\,\boldsymbol{w}\big)\cdot\boldsymbol{\rho}^{(2),>}\boldsymbol{\Pi}^{\rm A}}_{\boldsymbol{\chi}^{>}}\Big)\cdot\boldsymbol{w}\,\underbrace{\boldsymbol{\rho}^{(2),<}\boldsymbol{P}^{\rm A}}_{-\boldsymbol{\chi}^{0,<}}\Big](t,t)\\
&\quad - \Big[\,>\leftrightarrow<\,\Big]\\
&= \mathrm{i}\Big[\boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),>}\boldsymbol{w}\boldsymbol{\rho}^{(2),<}\cdot\boldsymbol{P}^{\rm A} + \boldsymbol{\Pi}^{\rm R}\big(\underbrace{\boldsymbol{\rho}^{(2),>}\boldsymbol{w}\boldsymbol{\rho}^{(2),\Delta} - \boldsymbol{\rho}^{(2),\Delta}\boldsymbol{w}\boldsymbol{\rho}^{(2),>}}_{-\boldsymbol{\Psi}}\big)\cdot\boldsymbol{\Pi}^{\rm A}\cdot\boldsymbol{w}\boldsymbol{\rho}^{(2),<}\boldsymbol{P}^{\rm A}\Big](t,t)\\
&\quad - \mathrm{i}\Big[\boldsymbol{\Pi}^{\rm R}\boldsymbol{\rho}^{(2),<}\boldsymbol{w}\boldsymbol{\rho}^{(2),>}\cdot\boldsymbol{P}^{\rm A} + \boldsymbol{\Pi}^{\rm R}\big(\underbrace{\boldsymbol{\rho}^{(2),<}\boldsymbol{w}\boldsymbol{\rho}^{(2),\Delta} - \boldsymbol{\rho}^{(2),\Delta}\boldsymbol{w}\boldsymbol{\rho}^{(2),<}}_{-\boldsymbol{\Psi}}\big)\cdot\boldsymbol{\Pi}^{\rm A}\cdot\boldsymbol{w}\boldsymbol{\rho}^{(2),>}\boldsymbol{P}^{\rm A}\Big](t,t)\\
&= \mathrm{i}\Big[\boldsymbol{\Pi}^{\rm R}\boldsymbol{\Psi}\cdot\boldsymbol{P}^{\rm A} + \boldsymbol{\Pi}^{\rm R}\boldsymbol{\Psi}\cdot\boldsymbol{\Pi}^{\rm A}\cdot\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\Delta}\boldsymbol{P}^{\rm A}\Big](t,t)\\
&= \mathrm{i}\Big[\boldsymbol{\Pi}^{\rm R}\boldsymbol{\Psi}\cdot\boldsymbol{\Pi}^{\rm A}\Big](t,t),
\end{aligned}
\tag{107}
$$

where in the second equality we have observed that $[\boldsymbol{\rho}^{(2),\gtrless}\boldsymbol{\Pi}^{\rm A}\cdot\boldsymbol{w}\,\boldsymbol{\rho}^{(2),\lessgtr}\boldsymbol{P}^{\rm A}](t,t) = 0$ since $\boldsymbol{\Pi}^{\rm A}$ contains a $\Theta(\bar{t}-t)$ and $\boldsymbol{P}^{\rm A}$ contains a $\Theta(t-\bar{t})$. We have also recognized the quantity $\boldsymbol{\Psi}$ defined in Eq. (92). Making explicit the time integration, the function $\boldsymbol{\mathcal{G}}$ in the GW+X approximation has the following compact and elegant form

$$
\boldsymbol{\mathcal{G}}(t) = \mathrm{i}\int_{-\infty}^{t} d\bar{t}\;\boldsymbol{\Pi}^{\rm R}(t,\bar{t})\,\boldsymbol{\Psi}(t)\boldsymbol{\Pi}^{\rm A}(\bar{t},t). \tag{108}
$$

It is now easy to prove that also the GW+X method scales linearly in time. Taking into account the equation of motion (88) for $\boldsymbol{P}^{\rm R}$ and the rule in Eq. (90) we find from Eq. (105a)

$$
\begin{aligned}
\mathrm{i}\frac{d}{dt}\boldsymbol{\Pi}^{\rm R}(t,t') &= \boldsymbol{h}^{(2)}_{\rm HF}(t)\boldsymbol{P}^{\rm R}(t,t') + \mathrm{i}\frac{d}{dt}\int_{-\infty}^{t} d\bar{t}\,\boldsymbol{P}^{\rm R}(t,\bar{t})\boldsymbol{\rho}^{(2),\Delta}(t)\,\boldsymbol{w}\,\boldsymbol{\Pi}^{\rm R}(\bar{t},t')\\
&= \Big(\boldsymbol{h}^{(2)}_{\rm HF}(t) - \boldsymbol{\rho}^{(2),\Delta}(t)\,\boldsymbol{w}\Big)\boldsymbol{\Pi}^{\rm R}(t,t').
\end{aligned}
\tag{109}
$$

Equation (105a) also implies that $\boldsymbol{\Pi}^{\rm R}(t^+,t) = \mathrm{i}$ and that $\boldsymbol{\Pi}^{\rm A}(t',t) = [\boldsymbol{\Pi}^{\rm R}(t,t')]^\dagger$. Thus, using again the rule in Eq. (90)

$$
\mathrm{i}\frac{d}{dt}\boldsymbol{\mathcal{G}}(t) = -\boldsymbol{\Psi}(t) + \boldsymbol{h}^{(2)}_{\rm eff}(t)\boldsymbol{\mathcal{G}}(t) - \boldsymbol{\mathcal{G}}(t)\boldsymbol{h}^{(2)\dagger}_{\rm eff}(t), \tag{110}
$$

where

$$
\boldsymbol{h}^{(2)}_{\rm eff}(t) \equiv \boldsymbol{h}^{(2)}_{\rm HF}(t) - \boldsymbol{\rho}^{(2),\Delta}(t)\,\boldsymbol{w}. \tag{111}
$$

Comparing this result with the 2B equation of motion (91) we conclude that the only change brought about by the GW+X approximation is the replacement of $\boldsymbol{h}^{(2)}_{\rm HF}$ with the effective Hamiltonian $\boldsymbol{h}^{(2)}_{\rm eff}$. The effective Hamiltonian is not hermitian and therefore the last two terms in Eq. (110) cannot be grouped to form a commutator.

Similar derivations can be carried out for the T-matrix approximation in the particle-particle and particle-hole channels (with and without exchange diagrams), see Refs. [2–4]. In Ref. [4] an

extension of the GKBA to higher order Green functions has been put forward to include three-particle correlations while preserving the linear time-scaling. Another promising extension is the GKBA for bosonic Green functions to deal with systems of electrons interacting with quantized photons or phonons [5]. In this case too it is possible to build propagation algorithms that scale linearly in time [5]. Importantly, these methodological advances can be merged to treat the electron-electron, electron-phonon and electron-photon interactions on equal footing [6], thus opening the door for the investigation of a broad range of nonequilibrium correlated phenomena. Implementations of the NEGF+GKBA equations in high performance computer facilities are therefore foreseeable in the next few years.

10 First-principles NEGF+GKBA implementations

The NEGF+GKBA equations can be applied to finite systems like atoms and molecules as well as to extended systems like solids and interfaces. Of course, the most suitable basis to describe a certain phenomenon depends on the system *and* on the external driving. For the sake of definiteness we consider a finite system subject to an external time-dependent electric field $\mathbf{E}(t)$. Treating the light-matter interaction in the dipole approximation the one-particle Hamiltonian reads

$$h_{ij}(t) = h^{\rm eq}_{ij} + \mathbf{E}(t)\cdot\mathbf{D}_{ij}, \tag{112}$$

where $\mathbf{D}_{ij} = (D^x_{ij}, D^y_{ij}, D^z_{ij})$ is a matrix element of the dipole vector.
In general a finite system is described by a one-particle basis made of active states and core states. The population of the active states is different from 0 or 1 because of dynamical correlations or thermal fluctuations or external fields whereas the population of the core states is frozen to unity. We can work in the truncated space spanned by the active states provided that the HF potential of the core electrons is added to $h^{\rm eq}$. Henceforth we use the letter c for indices running in the space of core states and the letters i, j, m, n for indices running in the active space. We split the Hartree and exchange potentials into a core-electrons (ce) contribution and an active-electrons (ae) contribution

$$\big(V_{\rm H,ce}[\rho]\big)_{ij} = \sum_{cc'} v_{icc'j}\rho_{c'c}, \qquad \big(V_{\rm H,ae}[\rho]\big)_{ij} = \sum_{mn} v_{imnj}\rho_{nm}, \tag{113}$$

$$\big(V_{\rm x,ce}[\rho]\big)_{ij} = -\sum_{cc'} v_{icjc'}\rho_{c'c}, \qquad \big(V_{\rm x,ae}[\rho]\big)_{ij} = -\sum_{mn} v_{imjn}\rho_{nm}. \tag{114}$$

The full HF potential with indices in the active space is simply given by $V_{\rm HF} = V_{\rm H,ce} + V_{\rm H,ae} + V_{\rm x,ce} + V_{\rm x,ae}$, see Eq. (46). Taking into account that $\rho_{cc'} = \delta_{cc'}$, the equilibrium HF Hamiltonian in Eq. (49) can be rewritten as

$$h_{\rm HF}[\rho] = h^{\rm eq+ce} + V_{\rm H,ae}[\rho] + V_{\rm x,ae}[\rho], \tag{115}$$

where

$$h^{\rm eq+ce} = h^{\rm eq} + V_{\rm H,ce} + V_{\rm x,ce} \tag{116}$$

is the one-particle Hamiltonian plus the HF potential generated by the frozen core-electrons. Thus, replacing $h^{\rm eq}$ with $h^{\rm eq+ce}$ in Eq. (112) we can solve the NEGF+GKBA equations directly in the active space.
In the next sections we shall describe how to perform first-principles NEGF+GKBA simulations using two different types of basis. More details can be found in Ref. [48].

10.1 Kohn-Sham basis

We here consider the case of a Kohn-Sham (KS) basis [49–51] and assume that electrons in the KS core orbitals remain frozen and do not participate to the dynamics. The equilibrium KS one-particle density matrix in the KS basis reads $\rho_{{\rm KS},nm}=\delta_{nm}$. The equilibrium KS Hamiltonian in the same basis is diagonal and reads

$$h_{\rm KS}=h^{\rm eq}+V_{\rm H,ce}+V_{\rm H,ae}[\rho_{\rm KS}]+V_{\rm xc}, \tag{117}$$

where $V_{\rm xc}$ is the exchange-correlation (xc) potential of Density Functional Theory (DFT). In general, $V_{\rm H,ce}+V_{\rm xc}$ is given by the sum of the pseudopotential and the xc potential generated by the active electrons. A comparison with Eq. (115) allows us to express $h^{\rm eq+ce}$ in terms of the KS Hamiltonian according to

$$h^{\rm eq+ce}=h_{\rm KS}-V_{\rm xc}-V_{\rm H,ae}[\rho_{\rm KS}]+V_{\rm x,ce}. \tag{118}$$

Thus a first-principles NEGF+GKBA simulation needs as input the KS eigenvalues $\varepsilon_i^{\rm KS}$ (needed to construct the KS Hamiltonian $h_{{\rm KS},ij}=\delta_{ij}\varepsilon_i^{\rm KS}$), the matrix elements $V_{{\rm xc},ij}$, $\mathbf{D}_{ij}$ and the Coulomb integrals v_{ijmn} for the evaluation of the Hartree potential $V_{\rm H,ae}[\rho_{\rm KS}]$ generated by the active KS electrons, see Eq. (118), as well as for the evaluation of the functionals $V_{\rm H,ae}[\rho]$ and $V_{\rm x,ae}[\rho]$, see Eq. (115), and for the quantities $\boldsymbol{\Psi}$, see Eq. (92), and $\boldsymbol{h}^{(2)}_{\rm eff}$, see Eq. (111). In this way the only remaining unknown is $V_{\rm x,ce}$ which, however, is usually small and can be neglected. One could estimate this quantity by performing an all-electron KS calculation without pseudopotentials.

10.2 Localized basis

For a description in terms of N one-particle localized states $\{|i\rangle\}$ like, e.g., the Slater type orbitals (STO) [52, 53] or the Gaussian type orbitals (GTO) [54], we need the matrix elements of the equilibrium Hamiltonian $h^{\rm eq}_{ij}=\langle i|\frac{\hat{p}^2}{2m}+\hat{V}_{\rm n}|j\rangle$ ($V_{\rm n}$ being the nuclear potential), dipole vector $\mathbf{D}_{ij}=\langle i|\hat{\mathbf{r}}|j\rangle$, overlap matrix $S_{ij}=\langle i|j\rangle$ and Coulomb integrals $v_{ijmn}=\langle ij|\hat{v}|mn\rangle$. As our equations have been formulated in an *orthonormal* basis the very first step consists in the orthonormalization of the localized (STO or GTO) basis

$$|i\rangle\to\sum_m|m\rangle\,S^{-1/2}_{mi}, \tag{119}$$

and in expressing the matrices $h^{\rm eq}$, $\mathbf{D}$ and the Coulomb tensor v in the new orthonormal basis. To reduce the dimensionality of the one-particle Hilbert space we must perform a preliminary

self-consistent HF calculation in the orthonormal basis of Eq. (119), and then construct the orthonormal HF vectors $|i_{\rm HF}\rangle = \sum_m \varphi_m^{(i)}|m\rangle$ with HF energies $\varepsilon_i^{\rm HF}$. The HF states $|i_{\rm HF}\rangle = |c_{\rm HF}\rangle$ of energy $\varepsilon_c^{\rm HF} < \Lambda$ are considered as core states. Setting the vacuum energy at zero the energy cut-off Λ is typically of the order of -10^2 eV. The best way to exploit the fixed occupation of the core states is then to work in the HF basis since in this basis $\rho_{cc'} = \delta_{cc'}$. This means that we must calculate the matrix elements $h_{ij}^{\rm eq}$, $\mathbf{D}_{ij}$ and the Coulomb tensor v_{ijmn} in the HF basis. To determine $h^{\rm eq+ce}$ we use its definition in Eq. (116) which in the HF basis yields

$$h_{ij}^{\rm eq+ce} = h_{ij}^{\rm eq} + \sum_{cc'} \big(v_{icc'j} - v_{icjc'}\big)\rho_{c'c} = h_{ij}^{\rm eq} + \sum_{c} \big(v_{iccj} - v_{icjc}\big). \tag{120}$$

This equation tells us that in addition to v_{ijmn} with all indices in the active space we also need to calculate v_{iccj} and v_{icjc} for all core indices c and for all active indices i, j.

The main limitation of the STO or GTO basis is that the continuum part of the one-particle spectrum is, in general, poorly described and hence phenomena like photo-induced ionization and Auger decay cannot be simulated. In phenomena like electron transport or photoabsorption the electrons do instead remain bound to the system and a description in terms of localized orbitals can be made accurate at will.

References

[1] G. Stefanucci and R. van Leeuwen: *Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction* (Cambridge University Press, 2013)

[2] N. Schlünzen, J.P. Joost, and M. Bonitz, Phys. Rev. Lett. **124**, 076601 (2020)

[3] J.P. Joost, N. Schlünzen, and M. Bonitz, Phys. Rev. B **101**, 245101 (2020)

[4] Y. Pavlyukh, E. Perfetto, and G. Stefanucci, Phys. Rev. B, in press (2021)

[5] D. Karlsson, R. van Leeuwen, Y. Pavlyukh, E. Perfetto, and G. Stefanucci, Phys. Rev. Lett., in press (2021)

[6] Y. Pavlyukh, D. Karlsson, R. van Leeuwen, E. Perfetto, and G. Stefanucci, in preparation

[7] N. Säkkinen, Y. Peng, H. Appel, and R. van Leeuwen, J. Chem. Phys. **143**, 234102 (2015)

[8] P.M.M.C. de Melo and A. Marini, Phys. Rev. B **93**, 155102 (2016)

[9] M. Schüler, J. Berakdar, and Y. Pavlyukh, Phys. Rev. B **93**, 054303 (2016)

[10] M. Gell-Mann and F. Low, Phys. Rev. **84**, 350 (1951)

[11] A.L. Fetter and J.D. Walecka: *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971)

[12] L.G. Molinari, J. Math. Phys. **48**, 052113 (2007)

[13] L.V. Keldysh et al., Sov. Phys. JETP **20**, 1018 (1965)

[14] J. Schwinger, J. Math. Phys. **2**, 407 (1961)

[15] O. Konstantinov and V. Perel, Sov. Phys. JETP **12**, 142 (1961)

[16] M. Wagner, Phys. Rev. B **44**, 6104 (1991)

[17] G. Stefanucci and C.O. Almbladh, Phys. Rev. B **69**, 195318 (2004)

[18] E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci, Phys. Rev. B **94**, 245303 (2016)

[19] R. van Leeuwen and G. Stefanucci, Phys. Rev. B **85**, 115119 (2012)

[20] L.P. Kadanoff and G.A. Baym: *Quantum statistical mechanics: Green's function methods in equilibrium and nonequilibirum problems* (Benjamin, 1962)

[21] N.H. Kwong and M. Bonitz, Phys. Rev. Lett. **84**, 1768 (2000)

[22] N.E. Dahlen and R. van Leeuwen, Phys. Rev. Lett. **98**, 153004 (2007)

[23] P. Myöhänen, A. Stan, G. Stefanucci, and R. van Leeuwen, EPL **84**, 67001 (2008)

[24] M.P. von Friesen, C. Verdozzi, and C.O. Almbladh, Phys. Rev. Lett. **103**, 176404 (2009)

[25] A. Stan, N.E. Dahlen, and R. van Leeuwen, The J. Chem. Phys. **130**, 224101 (2009)

[26] K. Balzer and M. Bonitz: *Nonequilibrium Green's Functions Approach to Inhomogeneous Systems* (Springer, 2013)

[27] P. Lipavský, V. Špička, and B. Velický, Phys. Rev. B **34**, 6933 (1986)

[28] S. Hermanns, N. Schlünzen, and M. Bonitz, Phys. Rev. B **90**, 125111 (2014)

[29] N. Schlünzen and M. Bonitz, Contrib. Plasma Phys. **56**, 5 (2016)

[30] Y. Bar Lev and D.R. Reichman, Phys. Rev. B **89**, 220201 (2014)

[31] S. Latini, E. Perfetto, A.M. Uimonen, R. van Leeuwen, and G. Stefanucci, Phys. Rev. B **89**, 075306 (2014)

[32] R. Tuovinen, R. van Leeuwen, E. Perfetto, and G. Stefanucci, J. Chem. Phys. **154**, 094104 (2021)

[33] G. Pal, Y. Pavlyukh, W. Hübner, and H.C. Schneider, Eur. Phys. J. B **79**, 327 (2011)

[34] F. Covito, E. Perfetto, A. Rubio, and G. Stefanucci, Phys. Rev. A **97**, 061401 (2018)

[35] E. Perfetto, A.M. Uimonen, R. van Leeuwen, and G. Stefanucci, Phys. Rev. A **92**, 033419 (2015)

[36] E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci, Phys. Rev. B **92**, 205304 (2015)

[37] D. Sangalli, S. Dal Conte, C. Manzoni, G. Cerullo, and A. Marini, Phys. Rev. B **93**, 195205 (2016)

[38] E.A.A. Pogna, M. Marsili, D. De Fazio, S. Dal Conte, C. Manzoni, D. Sangalli, D. Yoon, A. Lombardo, A.C. Ferrari, A. Marini, G. Cerullo, and D. Prezzi, ACS Nano **10**, 1182 (2016)

[39] Sangalli, D. and Marini, A., EPL **110**, 47004 (2015)

[40] R. Tuovinen, D. Golež, M. Eckstein, and M.A. Sentef, Phys. Rev. B **102**, 115157 (2020)

[41] E.V. Boström, A. Mikkelsen, C. Verdozzi, E. Perfetto, and G. Stefanucci, Nano Lett. **18**, 785 (2018)

[42] E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci, J. Physical Chem. Lett. **9**, 1353 (2018)

[43] E. Perfetto, D. Sangalli, M. Palummo, A. Marini, and G. Stefanucci, J. Chem. Theory Comput. **15**, 4526 (2019)

[44] E. Perfetto, A. Trabattoni, F. Calegari, M. Nisoli, A. Marini, and G. Stefanucci, J. Phys. Chem. Lett. **11**, 891 (2020)

[45] H. Haug, Phys. Status Solidi B **173** (1992)

[46] M. Bonitz, D. Semkat, and H. Haug, Eur. Phys. J. B **9**, 309 (1999)

[47] A. Marini, Phys. Rev. Lett. **101**, 106405 (2008)

[48] E. Perfetto and G. Stefanucci, J. Phys: Condens. Matter **30**, 465901 (2018)

[49] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A.D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, and R.M. Wentzcovitch, J. Phys.: Condens. Matter **21**, 395502 (2009)

[50] X. Andrade, D. Strubbe, U. De Giovannini, A.H. Larsen, M.J.T. Oliveira, J. Alberdi-Rodriguez, A. Varas, I. Theophilou, N. Helbig, M.J. Verstraete, L. Stella, F. Nogueira, A. Aspuru-Guzik, A. Castro, M.A.L. Marques, and A. Rubio, Phys. Chem. Chem. Phys. **17**, 31371 (2015)

[51] D. Sangalli, A. Ferretti, H. Miranda, C. Attaccalite, I. Marri, E. Cannuccia, P. Melo, M. Marsili, F. Paleari, A. Marrazzo, G. Prandini, P. Bonfà, M.O. Atambo, F. Affinito, M. Palummo, A. Molina-Sánchez, C. Hogan, M. Grüning, D. Varsano, and A. Marini, J. Phys.: Condens. Matter **31**, 325902 (2019)

[52] J. Fernández Rico, I. Ema, R. López, G. Ramírez and K. Ishida, in *Recent Advances in Computational Chemistry: Molecular Integrals over Slater Orbitals*, eds. T. Ozdogan and M.B. Ruiz (Transworld Research Network, 2008), pp. 145.

[53] J.F. Rico, R. López, I. Ema, and G. Ramírez, J. Comp. Chem. **25**, 1987 (2004)

[54] Y. Pavlyukh and J. Berakdar, Comp. Phys. Commun. **184**, 387 (2013)