I. INTRODUCTION

Charge transfer through nanoscale interfaces is an ubiquitous dynamical process in molecular electronics, photovoltaics, electroluminescence and transient spectroscopy, to mention a few emerging fields of research.\(^1,2\) The complexity of the molecules (or molecular aggregate) and of the contacts to a source/drain electrode, as well as the simultaneous interplay of Coulomb repulsion and vibrational effects make these research fields an interdisciplinary topic where physics, chemistry and engineering meet. Reliable theoretical predictions require an accurate description of the nuclear degrees of freedom, a careful selection of the electronic basis functions and a proper treatment of correlation effects.

Among the \textit{ab initio} methods, Density Functional Theory\(^3,4\) (DFT) and its Time Dependent extension\(^5,6\) (TDDFT) stand out for the advantageous scaling of the computational cost with increasing the system size and the propagation time. However, as for any other method, a (TD)DFT implementation is based on some approximation and, at present, the available approximations are inadequate to capture correlation effects like the Coulomb blockade\(^7\)–\(^9\) or the polarization-induced renormalization of the molecular levels.\(^10\)–\(^14\) These effects are particularly important in a donor-acceptor complex, in a molecular junction in the weak-coupling regime and more generally when the transition rate for an electron to move from one atom to another is small. Many-body approaches based on Nonequilibrium Green’s Functions\(^15\) (NEGF) offer a promising alternative as the relevant scattering processes to describe the aforementioned effects can be incorporated either through a proper selection of Feynman diagrams or through a decoupling scheme for the higher order Green’s functions. Real-time simulations within the NEGF are performed by solving the Kadanoff-Baym equations\(^15\)–\(^18\) (KBE), which are a set of coupled nonlinear integro-differential equations for the one-particle Green’s function. Unfortunately, the price to pay in solving the KBE is that the computational time scales cubically with the propagation time (given the self-energy) whereas in TDDFT the scaling is linear (given the exchange-correlation potential).

In the mid eighties Lipavsky et al.\(^19\) proposed an approximation to scale down the computational time (from cubic to quadratic) of the KBE. This approximation is known as the Generalized Kadanoff-Baym Ansatz (GKBA) and has been successfully applied to strongly interacting nuclear matter,\(^20\) electron plasma,\(^21\)–\(^24\), carrier dynamics of semiconductors,\(^8\)\(^,\)\(^25\)\(^,\)\(^26\) optical absorption spectra,\(^27\) quasi-particle spectra,\(^28\) and more recently excited Hubbard clusters.\(^29\)\(^,\)\(^30\) In all these cases the system is either a bulk periodic system or a finite system. It is currently unknown how the GKBA performs for nanoscale structures chemically bonded to or adsorbed on a surface (open system). In fact, in open systems a number of issues have to be addressed before a GKBA calculation can be carried out. For instance the GKBA remains an approximation even in a noninteracting (or mean-field) treatment whereas in closed systems it is exact. Furthermore the performance of the GKBA strongly depends on the quality of the quasi-particle propagator and, as we shall see, in open systems the available approximations perform rather poorly.

This work contains a thorough study of the GKBA in open systems. In Section II we derive the fundamental equations and present a few exact properties. Here the discussion is mainly focussed on noninteracting and mean-field electrons. Important aspects of the GKBA like the construction of a mean-field propagator as well as issues related to relaxation and local thermalization are analyzed and addressed. This preliminary investigation...
II. GKBA IN OPEN SYSTEMS

In this Section we briefly review the KBE for open systems and discuss in detail the simplifications brought about by the GKBA. The most general Hamiltonian which describes a molecular junction in contact with $M$ electronic reservoirs has the form

$$\hat{H} = \sum_{\alpha=1}^{M} \hat{H}_\alpha + \hat{H}_J + \hat{H}_T. \quad (1)$$

In Eq. (1) the Hamiltonian of the $\alpha$ reservoir reads

$$\hat{H}_\alpha = \sum_{k\sigma} \varepsilon_{k\alpha} \hat{d}_{k\alpha}^\dagger \hat{d}_{k\alpha} \quad (2)$$

with $\hat{d}_{k\sigma}$ the annihilation operator for electrons of spin $\sigma$ and energy $\varepsilon_{k\alpha}$. The Hamiltonian of the molecular junction is expressed in terms of the operators $\hat{d}_{i\sigma}$ for electrons of spin $\sigma$ in the $i$-th localized molecular orbital

$$\hat{H}_J = \sum_{ij} h_{ij} \hat{d}_{i\sigma}^\dagger \hat{d}_{j\sigma} + \frac{1}{2} \sum_{ijmn} v_{ijmn} \hat{d}_{i\sigma}^\dagger \hat{d}_{j\sigma} \hat{d}_{m\sigma'} \hat{d}_{n\sigma} \quad (3)$$

where $h_{ij}$ are the one-electron matrix elements of the one-body part (kinetic plus potential energy) and $v_{ijmn}$ are the two-electron Coulomb integrals. The last term in Eq. (1) is the tunneling Hamiltonian between the different subsystems and reads

$$\hat{H}_T = \sum_{k\sigma} \sum_i \left( T_{k\alpha,i} \hat{d}_{k\alpha}^\dagger \hat{d}_{i\sigma} + \text{H.c.} \right) \quad (4)$$

with $T_{k\alpha,i}$ the tunneling amplitude between the $i$-th state of the molecular junction and the $k$ state of the $\alpha$ reservoir.

Initially, say at time $t = 0$, the system is in equilibrium at inverse temperature $\beta$ and chemical potential $\mu$. We assume that this equilibrium state can be reached starting from the uncontacted ($T_{k\alpha,i} = 0$) and noninteracting ($v_{ijmn} = 0$) system in the remote past, $t = -\infty$, and then propagating forward in time with the full interacting and contacted Hamiltonian until $t = 0$. This amounts to assume that initial-correlation and memory effects are washed out. In our experience this assumption is always verified. At time $t = 0$ the system is driven out of equilibrium by external electromagnetic fields, $\varepsilon_{k\alpha} \to \varepsilon_{k\alpha} + V_n(t)$ and $h_{ij} \to h_{ij}(t)$. We are interested in monitoring the evolution of the electronic degrees of freedom through the calculation of observable quantities like, e.g., the local occupation and current.

A. Green’s function and KBE

The building block of any diagrammatic many-body approach is the Green’s function defined according to

$$G_{ij}(z, z') = \frac{1}{i} \langle T \{ \hat{d}_{i\sigma}^\dagger H z \hat{d}_{j\sigma}^{'}(z') \} \rangle. \quad (5)$$

In this definition the symbol “(...)” denotes a grandcanonical average, and $T$ is the contour ordering acting on operators in the Heisenberg picture. The Green’s function has arguments $z$ and $z'$ on the contour $\gamma$ going from $-\infty$ to $\infty$ (forward branch) and back from $\infty$ to $-\infty$ (backward branch). On this contour $G_{ij}$ satisfies the equations of motion (in matrix form)

$$\left[ dz - h_{\text{HF}}(z) \right] \nabla z G(z, z') = \delta(z, z') + \int_\gamma dz' \Sigma(z, z') G(z, z') \quad (6)$$

and its adjoint. Let us describe the various quantities in this equation. The Hartree-Fock (HF) single-particle Hamiltonian is the sum of $h$ and the HF potential

$$h_{\text{HF},ij} = h_{ij} + \sum_{mn} (2v_{imnj} \rho_{nm} - v_{imjn} \rho_{nm}) \quad (7)$$

where

$$\rho_{nm}(z) \equiv -i G_{nm}(z, z^+) \quad (8)$$

is the time-dependent single-particle density matrix. The kernel $\Sigma = \Sigma_{\text{em}} + \Sigma_{\text{c}}$ is the sum of the so called embedding self-energy and the correlation self-energy. The former can be calculated directly from the parameters of the Hamiltonian and reads

$$\Sigma_{\text{em},ij}(z, z') = \sum_{k\alpha} T_{k\alpha,i} g_{k\alpha}(z, z') T_{k\alpha,j} \quad (9)$$

where

$$g_{k\alpha}(z, z') = \frac{1}{i} \left\{ \theta(z, z') \tilde{f}(\varepsilon_{k\alpha}) - \theta(z', z) f(\varepsilon_{k\alpha}) \right\} e^{-i\phi_{k\alpha}(z, z')} \quad (10)$$
Fig. 1. Diagrams for the 2B correlation self-energy.

is the Green’s function of the disconnected α reservoir. In Eq. (10) \( f(\epsilon) = 1/(e^{\beta(\epsilon-\mu)} + 1) \) is the Fermi function, \( \tilde{f}(\epsilon) = 1 - f(\epsilon) \) and the phase \( \phi_{\kappa\alpha}(z,z') = \int_z^\infty d\tilde{z}(\epsilon_{\kappa\alpha} + V_\alpha(\tilde{z})) \). The expression of the correlation self-energy depends on the choice of diagrams that we decide to include. In this work we consider the second-Born (2B) approximation which has been shown to produce results very close to those of the GW approximation, and to those of numerically exact techniques in model systems. The 2B self-energy is given by the sum of the lowest order bubble diagram plus the second-order exchange diagram, see Fig. 1.

\[
\Sigma_{\epsilon,ij}(z,z') = \sum_{nmpqrs} v_{mpq} v_{mnpqij}
\times [2G_{nm}(z,z')G_{pq}(z',z')G_{sr}(z',z)
- G_{nq}(z,z')G_{sr}(z',z)G_{pm}(z,z')]
\]

To solve Eq. (6) we convert it into a set of coupled equations, known as the KBE, for real time (as opposed to contour time) quantities. This is done by letting \( z \) vary on the forward (backward) branch and \( z' \) to vary on the backward (forward) branch of the contour \( \gamma \). Using the Langreth rules to convert contour-time convolutions into real-time convolutions we find (in matrix form)

\[
\begin{bmatrix}
\frac{d}{dt} & -i & \frac{d}{dt'} & -h_{HF}(t)
\end{bmatrix}
\begin{bmatrix}
I^<(t,t')
\end{bmatrix}
= \begin{bmatrix}
I^<(t,t')
\end{bmatrix}
\]

(12)

\[
\begin{bmatrix}
\frac{d}{dt} & -i & \frac{d}{dt'} & -h_{HF}(t')
\end{bmatrix}
\begin{bmatrix}
I^>(t,t')
\end{bmatrix}
= \begin{bmatrix}
I^>(t,t')
\end{bmatrix}
\]

(13)

with collision integrals

\[
I^<(t,t') = \int_{-\infty}^{\infty} dt \left[ \Sigma^<(t,\bar{t})G^A(\bar{t},t') + \Sigma^R(t,\bar{t})G^<(\bar{t},t') \right]
\]

(14)

\[
I^>(t,t') = \int_{-\infty}^{\infty} dt \left[ G^>(t,\bar{t})\Sigma^A(\bar{t},t') + G^R(t,\bar{t})\Sigma^>(\bar{t},t') \right]
\]

(15)

Here the superscripts “>, <, R, A” refer to the lesser, greater, retarded and advanced Keldysh components. Equations (12,13) are solved by a time stepping technique, starting from a value \( G^>(t_{in},t_{in}) \) at some initial time \( t_{in} < 0 \) and then evolving along the directions \( t \) and \( t' \) until a maximum propagation time \( t_{max} \). The time \( t_{in} \) is chosen remotely enough in the past in order to have full relaxation at \( t = 0 \), time at which the external fields are switched on. As \( I^>(t,t') \) in Eqs. (14,15) involves integrals between \( t_{in} \) (the self-energy vanishes for times smaller than \( t_{in} \) since the system is initially uncontacted and noninteracting) and either \( t \) or \( t' \), the numerical effort in solving the KBE scales like \( t_{max}^3 \).

B. GKBA

The GKBA allows us to reduce drastically the computational time. The basic idea consists in obtaining a closed equation for the equal time \( G^< \) from which to calculate the time-dependent averages of all one-body observables like, e.g., density, current, dipole moment, etc. The GKBA is therefore an ansatz for the density matrix \( \rho(t) = -iG^<(t,t) \), not for the spectral function which has to be approximated separately, see below.

The exact equation for \( \rho(t) \) follows from the difference between Eq. (12) and its adjoint, and reads

\[
\frac{d}{dt} \rho(t) + i [h_{HF}(t), \rho(t)] = - (I^<(t,t) + H.c.) \]  

(16)

This is not a closed equation for \( \rho \) as the collision integral contains the off-diagonal (in time) \( G^S \). To close Eq. (16) we make the GKBA

\[
G^<(t,t') = iG^R(t,t')G^<(t',t') - iG^<(t,t)G^A(t,t')
= -G^R(t,t')\rho(t') + \rho(t)G^A(t,t')
\]

(17)

and similarly

\[
G^>(t,t') = G^R(t,t')\rho(t') - \rho(t)G^A(t,t')
\]

(18)

where \( \rho(t) = 1 - \rho(t) = iG^>(t,t) \). However, the GKBA alone is not enough to close Eq. (16) since the quasiparticle propagator \( G^R \) (and hence \( G^A = [G^R]^{\dagger} \)), or equivalently the spectral function, remains unspecified. The possibility of using the GKBA in open systems strongly relies on the choice of \( G^R \). This is an important point which we thoroughly address in the next Section.

For the time being we observe that the numerical effort in solving Eq. (16) scales like \( t_{max}^2 \) provided that the calculation of \( G^R \) does not scale faster.

1. Exact properties

Among the properties of the GKBA we mention the fulfillment of the relation \( G^R - G^A = G^> - G^< \) for any choice of \( G^R \), and the fact that Eqs. (17,18) become an identity in the limit \( t \to t' \) since \( G^R(t',t) = -i \). Another valuable feature (in systems out of equilibrium) is that the GKBA preserves the continuity equation. There is, however, an even more important property from which the physical contents of the GKBA become evident. In closed systems (\( \Sigma_{em} = 0 \)) and for HF electrons (\( \Sigma_c = 0 \)) the collision integrals vanish and Eqs. (17,18) are the solution of Eqs. (12,13) provided that \( G^R \) is the HF propagator.

\[
G^R(t,t') = -i\theta(t-t') T e^{-i \int_{t'}^t dh_{HF}(i)}
\]  

(19)
where $T$ is the time-ordering operator. Therefore, the more the quasi-particle picture is valid the more the GKBA is accurate. A more exhaustive discussion on the range of applicability of the GKBA in closed systems can be found in Refs. 19 and 39.

In open systems the GKBA is not the solution of the HF equations since $\Sigma_{em} \neq 0$ and hence the collision integral is nonvanishing. The reliability of the GKBA in open systems needs to be investigated already at the HF level. In HF the collision integrals are evaluated with $\Sigma = \Sigma_{em}$ and $G^R$ being the solution of

$$\left[i\frac{d}{dt} - h_{HF}(t)\right]G^R(t, t') = \delta(t, t') + \int dt' \Sigma_{em}(t, t')G^R(t', t').$$

(20)

In HF-GKBA the collision integrals are evaluated with $\Sigma = \Sigma_{em}$, $G^R(t, t') = \rho(i)G^A(i, t')$ and $G^A = [G^R]^{\dagger}$ some suitable propagator. If we calculate $G^R$ from Eq. (20) then the numerical advantage of the GKBA is lost since the computational cost of solving this equation scales like $t_{max}^3$. Thus the question is: can a “computationally cheap” propagator be constructed for open systems? If so, how accurate is the solution of the HF-GKBA equation?

To answer these questions we consider a Wide Band Limit (WBL) embedding self-energy $\Sigma_{em}(t, t') = -(i/2)\Gamma\delta(t - t')$ where $\Gamma$ is a positive-semidefinite self-adjoint matrix. In this case the solution of Eq. (20) is

$$G^R(t, t') = -i\theta(t - t') T e^{-i\int dt' \left(h_{HF}(t') - \Gamma/2\right)}$$

(21)

which has the same mathematical structure of Eq. (19). In particular it has the group property

$$G^R(t + \delta, t') = iG^R(t + \delta, t)G^R(t, t')$$

(22)

and hence the number of operations to calculate $G^R$ for all $t < t_{max}$ and $t' < t$ scales like $t_{max}^2$. The HF collision integral reads

$$I^<(t, t) = \int_{-\infty}^{\infty} dt' \Sigma_{em}(t, t')G^A(i, t') - \frac{i}{2}\Gamma G^<(t, t),$$

(23)

whereas the HF-GKBA collision integral reads

$$I^<(t, t) = \int_{-\infty}^{\infty} dt' \Sigma_{em}(t, t')G^A(i, t') - \frac{i}{2}\Gamma \rho(t)G^<(t, t).$$

(24)

If in Eq. (24) we use for $G^A = [G^R]^{\dagger}$ the HF result in Eq. (21) then the collision integrals are identical since $G^A(t^- , t) = i$ and $i\rho(t) = G^<(t, t)$. We conclude that the $G^<(t, t)$ that solves the HF and HF-GKBA equations is the same provided that we use the same $G^R$ of Eq. (21). This observation contains useful hints on how to approximate the quasi-particle propagator of open systems without paying a too high computational price. We emphasize that the locality in time of the retarded embedding self-energy and of the HF self-energy $\Sigma_{HF}(z, z') = \delta(z, z')\left[h_{HF}(z) - h(z)\right]$ are distinct and should not be lumped together. The former is purely imaginary and hence $\Sigma_{em} \neq 0$ whereas the latter is purely real and hence $\Sigma_{HF} = 0$. Alternatively we can say that $\Sigma_{HF}$ is local on the contour whereas $\Sigma_{em}$ is not. This is a crucial difference: in closed systems the off-diagonal HF-GKBA $G^<(t, t')$ is the same as the HF $G^<(t, t')$ whereas in open systems it remains an approximation even for a WBL embedding self-energy. Only the diagonal HF and HF-GKBA $G^<(t, t)$ are identical in this case.

2. An approximate propagator for mean-field electrons

In most physical situations the removal and addition energies relevant to describe the electron dynamics of the molecular junction after the application of a voltage difference or a laser pulse are well inside the continuum spectrum of the reservoirs. It is therefore natural to study how well the GKBA equation performs when $G^R$ is chosen as in Eq. (21) with

$$\Gamma = i \left[\Sigma_{em}^R(\mu) - \Sigma_{em}^A(\mu)\right].$$

(25)

In Eq. (25) the quantity $\Sigma_{em}^R(\mu)$ is the Fourier transform of the equilibrium embedding self-energy evaluated at the chemical potential. This choice of $\Gamma$ is expected to yield accurate results whenever $\Sigma_{em}^R(\omega)$ depends weakly on $\omega$ for frequencies around $\mu$. Let us address this issue numerically. We consider a class of systems consisting of two reservoirs, $\alpha = L, R$, with $N_r$ transverse channels and a nanostructure with a chain geometry, see Fig. 2. We use a tight-binding representation and characterize the Hamiltonian of the reservoirs by a transverse hopping $T_z$ and a longitudinal hopping $T_\lambda$ between nearest neighboring sites, and an onsite energy $\epsilon = \mu$ (half-filled reservoirs). The molecular chain has matrix elements $h_{ij} = T_n$ between nearest neighboring sites $i$ and $j$ and $h_{ii} = \epsilon_n$ on the diagonal. The left reservoir is contacted through its middle terminal site to the leftmost site of the chain while the right reservoir is contacted through its middle terminal site to the rightmost site of the chain. We denote by $T$ the corresponding matrix elements of the Hamiltonian.

In Fig. 3 we compare GKBA versus full KBE results for noninteracting and HF electrons. In all cases the
The parameters (in arbitrary units) are Coulomb integrals \( v_{ij} = \delta_{in}\delta_{jm}v_{ij} \). The top panels refer to a system with \( N_v = 1 \) and a single-site chain driven out of equilibrium by a bias \( V_L = 2 \) and \( V_R = 0 \). The parameters (in arbitrary units) are \( \mu = \epsilon_n = 0 \), \( v_{ij} = 0 \), and \( T = \sqrt{|T\lambda|/2} \) with \( \gamma = 0.4 \). From Eq. (25) we find \( \Gamma = 2\gamma \). The simulations have been performed at zero temperature for three different values of \( T = -9, -5, -2 \), and are compared with exact numerical results obtained using the algorithm of Ref. 41. As expected the agreement deteriorates with decreasing the bandwidth \( W = 4|T\lambda| \) of the reservoirs since \( \sum_{\text{eim}}(\omega) \) acquires a strong dependence on \( \omega \) for \( \omega \) in the bias window. The dashed lines indicate the steady-state value of \( n_1 \) for one-dimensional reservoirs and for WBL reservoirs. KBE correctly approaches the one-dimensional steady-state in all cases whereas GKBA approaches the WBL steady-state only in the limit \( |T\lambda| \to \infty \). In the bottom left panel we consider a two-site chain driven out of equilibrium by a bias \( V_L = -V_R = 1 \) and again connected to one-dimensional reservoirs.\(^{31}\) In this case, however, the system is interacting and treated in the HF approximation. The chemical potential is chosen in the middle of the HOMO-LUMO gap of the disconnected chain with two electrons. For \( T = -1, \epsilon_n = 0 \), and Coulomb integrals \( v_{11} = v_{22} = 2, v_{12} = v_{21} = 1 \) one finds \( \mu = 2 \). The rest of the parameters are \( T_L = 1.5 \) and \( T = -0.5 \) which, from Eq. (25), implies \( \Gamma \approx 0.67 \) for the GKBA simulations. Even though the HOMO-LUMO gap \( \Delta_{HL} = 2 \) is not much smaller than the bandwidth \( W = 4|T\lambda| = 6 \) we still observe a satisfactory agreement for the density of site 1 (a similar agreement is found for site 2, not shown). The damping time as well as the amplitude and frequency of the transient oscillations are well reproduced; furthermore the GKBA steady-state value differs by less than 1\% from the corresponding KBE value. The accuracy of the HF-GKBA is not limited to the diagonal matrix elements of the density matrix. This is exemplified in the bottom right panel where we show the current flowing at the right interface of the four-site chain of Fig. 2 with \( N_v = 9 \) transverse channels, bias \( V_L = -V_R = 0.8, 1.2 \), and Coulomb potential \( \mu = 2.26 \) (chosen in the middle of the HOMO-LUMO gap of the disconnected chain with 4 electrons), \( T = -1, T_L = T_R = -2, T = -0.5, \epsilon_n = 0 \) and Coulomb integrals \( v_{ij} = v = 1.5 \) and \( v_{ij} = (v/2)/|i-j| \) for \( i \neq j \).\(^{33}\) The GKBA and KBE currents are in excellent agreement except for a slight overestimation of the GKBA steady-state value at small bias.

In conclusion the GKBA equation with \( GR \) from Eq. (21) and \( \Gamma \) from Eq. (25) is a good approximation to study the HF dynamics of open systems provided that the embedding self-energy of the reservoirs has a weak frequency dependence around the chemical potential.

### 3. Relaxation and local thermalization

For the GKBA results of Fig. 3 we started the propagation at time \( t_0 < 0 \) with the HF density matrix of the uncontacted system and let \( \rho(t) \) thermalize in the absence of external fields until \( t = 0 \) when a bias is switched on. For \( t_0 \) sufficiently remote in the past the density matrix attains a steady value \( \rho_{\text{eq}} \) before the system is biased. By definition \( \rho_{\text{eq}} \) is the static solution of Eq. (16) with \( d\rho/dt = 0 \); therefore if we start with \( \rho(t_0) = \rho_{\text{eq}} \) then the density matrix remains constant in the interval \( (t_0, 0) \). In the left panel of Fig. 4 we plot the time-dependent density of the noninteracting one-site chain of Fig. 3 for different initial values; we see that \( n_1(t) = \rho_{11}(t) = 1/2 \) for...
all \( t < 0 \) if \( n_1(t_{in} = -6) = 1/2 \) is the thermalized value. It is tempting to reduce the computational time (provided that one finds a simpler way to determine \( \rho_{eq} \) by starting the propagation at \( t = 0 \) with \( \rho(0) = \rho_{eq} \). This initial condition guarantees the local thermalization of all one-time observables. However, in a fully relaxed system any two-time correlator depends on the time-difference only, and to achieve this relaxation a “memory buffer” is needed. Suppose that we start the propagation with \( G^<(t_{in}, t_{in}) = i\rho_{eq} \). Then the equal-time \( G^>(t, t) \) remains constant but the \( G^<(t, t') \) depends on \( t \) and \( t' \) separately. It is only for \( t, t' \) large enough that \( G^<(t, t') \) depends on \( t - t' \). This concept is explained in the right panel of Fig. 4 where we display \( n_1(t) \) when a bias \( V_L = 2 \) is switched on at \( t = 0 \). In all cases \( \rho(t_{in}) = \rho_{eq} = 1/2 \) but the initial time \( t_{in} \) is varied. The absence of relaxation for too small \( |t_{in}| \) is evident from the strong dependence of the transient behavior on \( t_{in} \). The curves \( n_1(t > 0) \) become independent of \( t_{in} \) only for \( t_{in} < \approx -4 \).

The concept of relaxation, and hence of the memory buffer, has been illustrated in a simple model system but its importance is completely general and is not limited to systems in thermal equilibrium. Suppose that the physical system is in some excited state \( \rho_{ex} \). If we start the propagation at time \( t = 0 \) with initial condition \( \rho(0) = \rho_{ex} \) then the transient behavior is affected by spurious relaxation processes. The proper way of performing GKBA simulations consists in driving the relaxed system toward \( \rho_{ex} \) with some suitable external fields.

4. Damping

For bulk systems like an electron gas the inclusion of damping in the propagator worsens the agreement with the KBE results.\(^{24} \) In fact, the use of a non-Hermitian quasi-particle Hamiltonian \( \hat{H}_{HF} - i\Gamma/2 \) in \( G^R \) is a distinctive feature of open systems. Here we address how sensitive the results are to different values of \( \Gamma \). We consider again the noninteracting one-site chain of Fig. 3 with \( T_A = -9 \), for which Eq. (25) yields \( \Gamma = 0.8 \). In all cases we set the initial condition \( n_1(t_{in}) = 1 \). In Fig. 5 (left panel) we show the relaxation dynamics, starting from \( t_{in} = -8 \), of the unperturbed system for three different \( \Gamma \); the curves are essentially on top of each other. This may suggest that the dependence on \( \Gamma \) is weak. However, if we switch on a bias in the left lead \( V_L = 2 \) at time \( t = 0 \) (middle panel) we appreciate a strong \( \Gamma \)-dependence. We may argue that for small \( \Gamma \) the relaxation time is longer and hence that the curves with \( \Gamma = 0.0, 0.4 \) approach the curve with \( \Gamma = 0.8 \) by reducing \( t_{in} \). This is not the case as clearly illustrated in the right panel where \( t_{in} = -12 \). The curve with \( \Gamma = 0.4 \) is already converged whereas the one with \( \Gamma = 0 \) is not but the trend is to separate further from the curve with \( \Gamma = 0.8 \). The apparent weak \( \Gamma \)-dependence in the left panel is simply due to the alignment of the on-site energy to the chemical potential, \( \mu = \epsilon_n = 0 \). In general a proper choice of the quasi-particle damping is crucial for a correct description of the system evolution. In HF theory the damping is only due to embedding effects and the \( \Gamma \) of Eq. (25) is the most accurate. The inclusion of correlation effects introduces an extra damping. Is it possible to maintain the simple form in Eq. (21) for the quasi-particle propagator and still have good agreement with the KBE results? In the next Section we discuss two different correlated quasi-particle Hamiltonians to insert in Eq. (21).

III. CORRELATED APPROXIMATIONS TO THE PROPAGATOR

In the interacting case the exact equation of motion for \( G^R \) reads

\[
\left[ \frac{i}{\hbar} \frac{d}{dt} - \hat{H}_{HF}(t) \right] G^R(t, t') = \delta(t, t') + \int dt' \Sigma^R(t, \bar{t}) G^R(\bar{t}, t') \tag{26}
\]

with \( \Sigma^R = \Sigma^R_{em} + \Sigma^R_{c} \). If we approximate

\[
\Sigma^R_{em}(t, t') \simeq -(i/2)\Gamma \delta(t-t'), \tag{27}
\]

with \( \Gamma \) from Eq. (25), we find the approximate equation

\[
\left[ \frac{i}{\hbar} \frac{d}{dt} - h_{qp}^{(0)}(t) \right] G^R(t, t') = \delta(t, t') + \int dt' \Sigma^R_{c}(t, \bar{t}) G^R(\bar{t}, t') \tag{28}
\]

where

\[
h_{qp}^{(0)}(t) \equiv \hat{H}_{HF}(t) - i\Gamma/2 \tag{29}
\]

is the HF quasi-particle Hamiltonian. Discarding the integral on the right hand side of Eq. (28) one finds the HF solution of Eq. (21). We refer to the GKBA with HF propagators as the GKBA0 scheme. Unfortunately the GKBA0 scheme performs rather poorly, see Section IV, indicating that \( G^R \) has to incorporate correlation effects to some extent. Below we propose two schemes to
approximate the convolution $\Sigma^R G^R$ and reduce Eq. (28) to a quasi-particle equation of the form

$$\left[\frac{d}{dt} - h_{qp}(t)\right] G^R(t, t') = \delta(t, t').$$

The solution of Eq. (30) is

$$G^R(t, t') = -i\theta(t - t') T e^{-i \int_0^t dt' h_{qp}(t')},$$

and satisfies the group property of Eq. (22). Therefore, if we are successful in this task the calculation of $G^R$ will scale like $t_{\text{max}}^3$.

### A. Static correlation approximation

In open systems the correlation self-energy decays to zero when the separation between its time arguments approaches infinity. If $G^R(i, i') > G^R(t, t')$ for $t - i$ smaller than the decay time of $\Sigma^R$ we can approximately write

$$\int dt \Sigma^R_c(t, i) G^R(i, i') \approx \left[\int dt \Sigma^R_c(t, i)\right] G^R(t, t').$$

To evaluate the integral in the square brackets we make an adiabatic approximation on top of the GKBA, i.e., we replace $G^R$ with the equilibrium propagator of a system described by the Hamiltonian $\hat{H}(t)$. Let us consider, for simplicity, an interaction $v_{ij,mn} = \delta_{in}\delta_{jm}v_{ij}$. Then the Langreth rules\textsuperscript{15,36} provide us with the following expression of the retarded 2B self-energy, see Eq. (11),

$$\Sigma^R_{c,ij}(t, t') = \sum_{kl} v_{ik} v_{jl} [G^R_{ij}(t, t')G^R_{kl}(t', t)G^R_{kl}(t, t') + G^R_{kl}(t', t)G^R_{kl}(t', t)G^R_{kl}(t, t')] - \sum_{kl} v_{ik} v_{jl} [G^R_{ik}(t, t')G^R_{kl}(t', t)G^R_{kl}(t, t') - G^R_{kl}(t', t)G^R_{kl}(t', t)G^R_{kl}(t, t')].$$

As $\Sigma^R(t, t')$ vanishes for $t < t'$, the GKBA transforms this quantity into a function of $\rho(t)$ and $G^R(t, t') = [G^A(t', t)]^R$. The adiabatic approximation consists in evaluating the GKBA form of Eq. (33) using an equilibrium propagator

$$\tilde{G}^R(t, t-t') = \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(t-t')}}{\omega - h_{qp}(t) + i\eta},$$

where we use the matrix notation $1/A = A^{-1}$ for any matrix $A$. The resulting expression, which we denote by $\tilde{\Sigma}(t, t-t')$, depends implicitly on $t$ through the dependence on $\rho(t)$ and $h_{qp}(t)$ and explicitly on $t-t'$. If we define

$$\tilde{\Sigma}(t) = \int dt \tilde{\Sigma}(t, t-i)$$

then the right hand side of Eq. (32) becomes $\tilde{\Sigma}(t)G^R(t, t')$ and Eq. (28) is solved by Eq. (31) with

$$h_{qp}(t) = h_{HF}(t) - i\Gamma/2 + \tilde{\Sigma}(t).$$

In this way we generate a self-consistent equation for $\tilde{\Sigma}(t) = \tilde{\Sigma}(\rho(t), h_{qp}(t))$. In practice for a given $\tilde{\Sigma}(t_n)$ at the $n$-th time step we determine $\rho(t_{n+1})$ from Eq. (16), then calculate $h_{qp}(t_{n+1}) = h_{HF}(t_{n+1}) - i\Gamma/2 + \tilde{\Sigma}(t_n)$, hence $G^R(t_{n+1}, t_{n+1}-t')$ and finally $\tilde{\Sigma}(t_{n+1})$. Each time step can be repeated a few times to achieve convergence; in our experience two predictor correctors are typically enough. It is worth stressing that the propagator appearing in the collision integral is $G^R$ and not $\tilde{G}^R$. The latter is only an auxiliary quantity to calculate $\tilde{\Sigma}(t)$. In the following we refer to the combination of GKBA with the described propagator as the GKBA + Static Correlation (SC) scheme since Eq. (35) is the zero frequency value of the Fourier transform of $\tilde{\Sigma}(t, t-t)$. In this scheme the calculation of $\tilde{\Sigma}$ for a given $\tilde{G}^R$ scales like $N^5$ where $N$ is the number of basis functions in the molecular junction.

### B. Quasi-particle approximation

An alternative way to introduce correlation effects in the propagator is again based on the adiabatic approximation but uses the concept of quasi-particles. Let us represent operators in the one-particle Hilbert space with a hat, e.g., $\hat{h}_{qp}$ or $\hat{\Sigma}_c^R$, and denote by $|i\rangle$ the basis ket of the molecular junction so that $\langle i|\hat{\Sigma}_c^R=j\rangle = \hat{\Sigma}_c^{R,ij}$, etc.. For an isolated molecule in equilibrium the quasi-particle equation reads

$$[\hat{h}_{HF} + \hat{\Sigma}_c^R(\epsilon)]|\varphi\rangle = \epsilon|\varphi\rangle$$

where $\hat{\Sigma}_c^R(\epsilon)$ is the Fourier transform of the equilibrium self-energy. To lowest order in $\Sigma^R_c$ this equation implies that the correction to the HF energies $\epsilon_{HF,n}$ is

$$\epsilon_{qp,n} = \epsilon_{HF,n} + \langle \varphi_n | \hat{\Sigma}_c^R(\epsilon_{HF,n}) | \varphi_n \rangle$$

where $|\varphi_n\rangle$ is the eigenket of $\hat{h}_{HF}$ with eigenvalue $\epsilon_{HF,n}$. Equation (38) suggests to construct a quasi-particle Hamiltonian in the following manner. We evaluate again the GKBA form of Eq. (33) using the propagator of Eq. (34) and then calculate

$$\hat{\Sigma}(t, \omega) = \int dt e^{i\omega(t-t')} \tilde{\Sigma}(t, t-t').$$

From this quantity we construct the one-particle operator $\hat{\Sigma}(t, \omega) = \sum_{ij} |i\rangle \langle i| \hat{\Sigma}_c(t, \omega) |j\rangle$ and subsequently the diagonal self-energy operator in the HF basis

$$\hat{\tilde{\Sigma}}(t) = \sum_n |\varphi_n\rangle \langle \varphi_n | \hat{\Sigma}(t, \epsilon_{HF,n}) |\varphi_n\rangle \langle \varphi_n |.$$
Imposing now that $\hat{h}_{qp}(t) = \hat{h}_{qp}(0) + \hat{\Sigma}(t)$ we get a self-consistent equation for $\hat{\Sigma}(t)$. We refer to this procedure as the GKBA + Quasi-Particle (QP) scheme. As the Fourier transform of $\hat{\Sigma}(t, t-t')$ has to be evaluated in $N$ different energies the calculation of $\hat{\Sigma}(t)$ in the GKBA+QP scheme scales like $N^6$. The 2B steady current is larger (smaller) than the HF steady current at bias smaller (larger) than the HF HOMO-LUMO gap, see bottom-right panel of Fig. 4.

In Fig. 6 we compare the current at small (left panel) and large (right panel) bias using KBE and different GKBA schemes. Even though the correlation-induced enhancement (at small bias $V_L - V_R = 1.6$ the HF steady current is $\sim 0.023$) and suppression (at large bias $V_L - V_R = 2.4$ the HF steady current is $\sim 0.11$) of the steady current relative to the HF values is qualitatively captured by all GKBA schemes, quantitative differences emerge. GKBA0 is rather close to KBE during the initial transient but considerably overestimates the steady state. GKBA+QP corrects too much this deficiency and the steady current is appreciably underestimated. Furthermore the transient behavior worsens: the first peak is absent and the current saturates too fast. This is due to a general problem of the GKBA+QP scheme. The equilibrium $\Sigma$ is too large or, equivalently, equilibrium correlations are overestimated. GKBA+SC gives an overall improvement. The transient current reproduces several KBE features (oscillation frequency and relative height of the peaks) and the steady current is very close to the KBE value.

By construction the GKBA schemes guarantee the satisfaction of the continuity equation. The rate of change of the total number of electrons in the nanostructure, $dN/dt$, is equal to the sum of the currents flowing through the left and right interface, $I_L + I_R$. In Fig. 7 we show that this analytic property is numerically confirmed with high accuracy in the GKBA+QP and GKBA+SC schemes.

B. Photovoltaic junction

We consider a more complicated open system with the features of a photovoltaic molecular junction. Inspired by a paper by Li et al.\textsuperscript{43} we model the junction as a donor–acceptor complex connected to a left and right...
The donor is described by HOMO \( (h) \) and LUMO \( (l) \) levels and the LUMO is connected to a chain of four acceptor levels each described by a single localized orbital. These orbitals are mixed by the acceptor Hamiltonian and form two valence and two conduction levels. The junction is connected to the left electrode through the HOMO with tunneling amplitude \( T_{L,h} \) and to the right electrode through the rightmost acceptor site with tunneling amplitude \( T_{R,L} \). The explicit form of the Hamiltonian of the donor–acceptor complex is

\[
\hat{H}_J = \varepsilon_h \hat{n}_h + \varepsilon_l \hat{n}_l + \varepsilon_A \sum_{a=1}^{4} \hat{n}_a \\
+ T_{DA} \sum_\sigma \left( \hat{d}_{a\sigma}^\dagger \hat{d}_{3\sigma} + \hat{d}_{1\sigma}^\dagger \hat{d}_{1\sigma} \right) \\
+ T_A \sum_{a=1}^{3} \sum_\sigma \left( \hat{d}_{a\sigma}^\dagger \hat{d}_{a+1\sigma} + \hat{d}_{a+1\sigma}^\dagger \hat{d}_{a\sigma} \right) \\
+ U_{DA} \left( \hat{n}_a - \frac{1}{2} \right),
\]

where \( \hat{n}_x = \sum_\sigma \hat{d}_{x\sigma}^\dagger \hat{d}_{x\sigma} \) is the occupation operator for \( x = h, l, a \). The interaction between the excess charges of the donor and acceptor chain implicitly fixes the condition of charge neutrality. For one-dimensional reservoirs with longitudinal hopping integral \( T_\lambda = -9 \), tunneling amplitudes \( T_{L,h} = T_{R,L} = -0.3 \), donor levels \( \varepsilon_h = -2.92, \varepsilon_l = -0.92 \), acceptor levels \( \varepsilon_A = -2.08 \), donor-acceptor hopping \( T_{DA} = -0.1 \), intra-acceptor hopping \( T_A = -0.2 \) and interaction \( U_{DA} = 0.5 \), the chemical potential \( \mu = 0.04 \) is in the middle of the HF gap between the valence and conduction acceptor levels. The equilibrium system has HOMO and LUMO occupations \( 2 \) and \( 0 \) respectively and the two valence levels of the acceptor chain completely filled. The photovoltaic junction is driven out of equilibrium by irradiation with monochromatic light. For simplicity we assume that the light couples only to the donor dipole moment and hence

\[
\hat{H}_{\text{light}}(t) = s(t)T_{hl} \sum_\sigma \left( e^{i\omega t} \hat{d}_{h\sigma}^\dagger \hat{d}_{l\sigma} + e^{-i\omega t} \hat{d}_{l\sigma}^\dagger \hat{d}_{h\sigma} \right),
\]

where \( s(t) \) is a switching function. We consider \( T_{hl} = 0.3 \), \( \omega = 2 = |\varepsilon_h - \varepsilon_l| \) and study a pulse, \( s(t) = 1 \) for \( 0 < t < \pi/T_{hl} \) and zero otherwise, as well as continuous radiation, \( s(t) = 1 \) for \( t > 0 \) and \( s(t) = 0 \) for \( t < 0 \).

In order to apply many-body perturbation theory we rewrite \( \hat{H}_J \) in the form of Eq. (3). The one-particle Hamiltonian \( h_{ij} \) with \( i, j = h, l, a \) then reads

\[
h = \begin{pmatrix}
\varepsilon_h & 0 & 0 & 0 & 0 & 0 \\
0 & \tilde{\epsilon}_l & T_{DA} & 0 & 0 & 0 \\
0 & T_{DA} & \varepsilon_{A1} & T_A & 0 & 0 \\
0 & 0 & T_A & \varepsilon_{A2} & T_A & 0 \\
0 & 0 & 0 & T_A & \varepsilon_{A3} & T_A \\
0 & 0 & 0 & 0 & T_A & \varepsilon_{A4}
\end{pmatrix}
\]

with \( \tilde{\epsilon}_l = \varepsilon_l + \frac{25}{12} U_{DA} \), \( \varepsilon_{Aa} = \varepsilon_A + \frac{25}{6} U_{DA} - 2 U_{DA}/a \). For the Coulomb integrals we find \( \delta_{im} \delta_{jm} \varepsilon_{ij} \)

\[
v = U_{DA} \begin{pmatrix}
0 & 0 & 1 & 1/2 & 1/3 & 1/4 \\
0 & 0 & 1 & 1/2 & 1/3 & 1/4 \\
1 & 1 & 0 & 0 & 0 & 0 \\
1/2 & 1/2 & 0 & 0 & 0 & 0 \\
1/3 & 1/3 & 0 & 0 & 0 & 0 \\
1/4 & 1/4 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

Let us start with the mean-field analysis of the light pulse. The duration \( \pi/T_{hl} \) has been chosen to get a population inversion of the HOMO and LUMO levels. In Fig. 9 we show the HF occupations of the donor (top panel) and acceptor (bottom panel) levels in GKBA and KBE. The impressive agreement is due to the fact that for \( T_\lambda = -9 \) the WBL approximation is extremely good. The depletion of charge on the first acceptor site (A1) is a consequence of the repulsive interaction \( U_{DA} \). During the pulse the HOMO level is partially refilled by the left reservoir and the total charge on the donor overcomes 2. This excess charge is instantaneously felt by A1 which starts expelling electrons at a rate larger than the tunneling rate from LUMO to A1. We also observe that the charge transfer between LUMO and A1 is not effective. The inset shows the LUMO occupation on a longer time scale. Electrons remain trapped and slosh around along the junction. In fact, in HF no steady-state is reached. The occurrence of self-sustained charge oscillations in mean-field treatments has been observed in similar contexts and is most likely an artifact of the approximation. As we shall see, the correlated KBE results are very different. Therefore the collision integral and the correlated propagator of the GKBA approach...
have to correct the HF theory in a substantial manner.

With the inclusion of correlations a deficiency of the GKBA+QP scheme emerges already during the thermalization process. In Fig. 10 the donor and acceptor occupations are propagated within different schemes in the absence of external fields using the HF value of the uncontacted system and \( \Sigma(t_{in}) = 0 \) as initial conditions. Both GKBA0 and GKBA+SC thermalize, similarly to HF, to values very close to the equilibrium values of the correlated (2B) KBE approach (dotted horizontal line). In fact, in KBE the HF and 2B equilibrium occupations are essentially the same since the correlation self-energy, except for a slight renormalization of the quasi-particle energies (image charge effect), does not affect the width of the spectral peaks. For the GKBA to reproduce the KBE thermalized values the imaginary part of \( \Sigma \) has to tend to increase thus broadening the HOMO and LUMO spectral peaks. Hence the HOMO looses charge whereas the LUMO acquires charge and the donor polarizability increases. This makes the first bubble diagram of the 2B self-energy larger, and therefore the HOMO and LUMO spectral peaks more broadened. In a separate calculation (not shown) we simulated the GKBA+QP thermalization and found that the thermalization process is extremely slow, \( t_{in} \lesssim -1000 \), and that the thermalized value of, e.g., the LUMO occupation is \( \sim 0.7 \), well above the KBE result.

We are now ready to show the correlated results in the case of a light pulse. The KBE occupations are shown in Fig. 11 and are considerably different from the HF occupations of Fig. 9. The GKBA+SC scheme is in fairly good agreement with KBE for all occupations. To illustrate the crucial role played by our correlated propagator we also display the LUMO and A1 occupations in the GKBA0 scheme (dotted-dashed line). Even though the initial transient is acceptable the GKBA0 occupations become soon inaccurate. Therefore the evaluation of the GKBA collision integral with HF propagator performs rather poorly in open systems. The GKBA+SC scheme has the merit of working both in and out of equilibrium.

Like the only goal of TDDFT is to reproduce the density of an interacting system, so the only goal of the GKBA is to reproduce the density matrix of an interacting system. The TDDFT or GKBA spectral function

\[
A(t, t') = i[G^R(t, t') - G^A(t, t')]
\]

can be very different from the true one. This is, however, not always the case. In Fig. 12 we show the time evolution of the KBE and GKBA+SC total spectral function defined according to

\[
A(T, \omega) = -2\text{Im} \int d\tau e^{i\omega\tau} \text{Tr} \left[ G^R(T + \frac{\tau}{2}, T - \frac{\tau}{2}) \right],
\]

where \( T = (t + t')/2 \) is the center of mass time and \( \tau = t - t' \) is the relative time. Remarkably the two spectral functions have several common features. The most important one is the broadening of the spectral peaks after the pulse and the long elapsing time to relax back to the equilibrium state. Another common feature is the drift of the acceptor peaks toward higher energy and the merging of the two middle peaks of the acceptor chain. In GKBA0 the spectral peaks are sharp at all times whereas in GKBA+QP they are broadened at all times (not shown).

To end our discussion on the performance of GKBA in open systems we consider in Fig. 13 the occupations for the continuous radiation. Here GKBA+SC is not as accurate as in the case of the light pulse. However, the agreement with KBE remains satisfactory. The HOMO and LUMO occupations are essentially indistinguishable from the KBE values (top panel). The occupations of the acceptor sites next to the right electrode (A3 and A4)
FIG. 12. Time-dependent KBE (top panel) and GKBA+SC (bottom panel) spectral functions for the photovoltaic junction subject to a light pulse. The light pulse is switched on at time \( t = 40 \) for the KBE and \( t = 75 \) for the GKBA+SC. The parameters are the same as in Fig. 11.

are slightly underestimated in GKBA+SC but the overall trend (transient oscillations and steady-state value) are correctly reproduced (middle panel). A more quantitative agreement is observed for the acceptor sites next to the donor (A1 and A2). For the A1 occupation we also show the GKBA0 occupation (bottom panel) and we note again that after a short time the result deviates considerably from the KBE result.

Is there any possibility of improving over the GKBA+SC scheme using a different \( \Sigma \), or the only way is to go beyond the GKBA? In the bottom panel of Fig. 13 we display the A1 occupations for a hybrid scheme in which \( \Sigma \) is calculated from GKBA+SC at negative times (thermalization) and from GKBA+QP at positive times. The improvement up to times \( t \sim 200 \) is impressive and extend to all acceptor occupations (not shown). Instead, for times \( t > 200 \) the KBE results are closer to those of the GKBA+SC scheme. More generally for \( t \lesssim 200 \) we observed that the hybrid scheme performs better than GKBA+SC for \( \omega \sim \epsilon_h - \epsilon_l \) (large current in the junction) and worse otherwise (small current in the junction). The purpose of this investigation is to provide numerical evidence of the existence of a \( \Sigma \) for accurate GKBA simulations, and hence the possibility of improving the GKBA+SC scheme without increasing the computational cost.

V. SUMMARY AND OUTLOOK

We demonstrated that time-dependent NEGF simulations of molecular junctions (and more generally open quantum systems) can be considerably speeded up. Different GKBA-based schemes have been proposed and subsequently benchmarked against full KBE calculations. The GKBA+SC scheme turned out to be the most accurate both in and out of equilibrium, while still offering a significant computational gain (for the longest propagation \( (t_{\text{max}} = 300) \) of the photovoltaic junction the CPU time is \( \sim 10 \) minutes in GKBA+SC and \( \sim 20 \) hours in KBE). We also showed that the GKBA+SC scheme can, in principle, be further improved without rising the computational price.

All calculations have been performed within the 2B approximation for the correlation self-energy but the GKBA+SC scheme is completely general and not limited to this special case. Clearly, in large nanostructures screening is important and the interaction should be treated, at least, within the GW approximation. Another urgent extension of the GKBA+SC scheme is the inclusion of the interaction between electrons and nuclei.
This can be done either at the level of the Ehrenfest approximation\textsuperscript{45,46} or by adding diagrams with electron-phonon vertices to the correlation self-energy.\textsuperscript{26}

The GKBA+SC scheme, its extensions and refinements can be implemented in \textit{ab initio} molecular codes\textsuperscript{47} to perform first principle time-dependent simulations of open nanostructures. Foreseeable applications are, e.g., in the field of molecular photovoltaics and molecular electronics. Here there is much interest in developing efficient quantum simulation methods for an accurate description of the electron-hole formation, recombination and separation as well as of charge transfer and possibly ionic reorganization or isomerization. In molecular photovoltaics ab-initio studies have focused on the optical spectra using linear response TDDFT\textsuperscript{48} or the Bethe-Salpeter equation.\textsuperscript{49} Real-time simulations remain, however, the most powerful tool to resolve the different competing processes up to the ps time scale. State-of-the-art simulations treat the contacts as finite-size clusters while taking into account the full atomistic structure either semi-empirically\textsuperscript{50} or fully \textit{ab initio}.\textsuperscript{51,52} However, these studies suffer from spurious boundary effects like the formation of artificial electric fields and reflection of charge after a few tens of fs. There are no such limitations in the GKBA for open systems as the electrodes are described in a virtually exact way through the embedding self-energy. Furthermore the effects of the Coulomb interaction can be systematically included through the diagrammatic expansion of the correlation self-energy. The encouraging results presented in this work should foster advances in the development of a NEGF approach to ultrafast processes at the nanoscale.

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