Single molecule bridge as a testing ground for using NGF outside of the steady current regime

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Abstract

The simplest nanoscopic system, a molecular bridge consisting of a molecular island with one or few electronic or vibronic levels coupled to non-interacting leads can be treated using non-equilibrium Green's functions (NGF). We follow the well known procedure of Jauho, Wingreen and Meir (JWM). In the present work, we concentrate on the little investigated transient behavior of the molecular bridge undergoing abrupt changes. The transient process depends on the initial conditions at a finite time which may incorporate initial correlations. As an example, we study the electron response to sudden connecting the molecule to one or both leads. To obtain explicit solutions, we neglect all interactions at the island, whose role is mimicked by the island-leads coupling. We explore this analogy and obtain a complete solution for the transient NGF for abitrary "initial correlations" represented by off-diagonal coherences between the initial electron state of the island and of the leads. This direct one-electron solution is confronted with the field theoretic approach in the particular case of the switch-on states, for which the initial correlations result from the previous history of the system. This is formally captured by the partitioning-in-time of the NGF, which we combine with the JWM theory. It is the virtue of partitioning method to express the transient NGF in terms of the building blocks of stationary-state NGF with zero, one or both leads connected. The direct and the partitioning solutions are reduced explicitly one to another, clarifying thus the meaning of the singular terms of the self-energy for correlated initial conditions.

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1. Introduction

An important issue in the NGF technique [1–12] is a proper inclusion of the correlated initial conditions (CIC) for a transient process starting at a finite initial time. The problem of CIC has two sides. On the formal side, the CIC are an obstacle for a straightforward use of the Wick theorem on the Schwinger-Keldysh time contour. The self-energy has to be augmented by additional terms singular at the initial time, whose role is to reflect the initial time correlations [13,14]. This aspect has a long history and several methods of construction of NGF with initial correlations have been developed, some using a time contour augmented either on the real time axis [15,16] or by an imaginary "time" stretch [1,17,18], other employing a limited information on the

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initial time correlations [19–24]. We will not dwell on reviewing this vast field [9,11]. On the physical side, the CIC control the short time development of a transient process, roughly on the order of the relaxation time in the system. For fast transients, explicit incorporation of CIC becomes mandatory. A need emerges for a model system, which would be tractable and sufficiently flexible, on which these issues could be studied efficiently without resort to heavy numerical work.

One good candidate is the molecular bridge model: a (mesoscopic) bridge island (molecule, dot, ...) connects, through tunnelling contacts, two "leads", representing simply two reservoirs of, often non-interacting, electrons [25–27]. This model structure has been the subject of an extensive work employing the NGF to describe the electronic structure and the dynamic behavior of the bridge molecule in dependence on the interactions acting within the molecule. We follow the general line of study starting from the classical papers [28] by Meir and Wingreen for steady state, and notably [29] by Jauho, Wingreen and Meir (JWM) for transients. For recent research in this direction see [30]. It may be said that the famous Meir-Wingreen formula or similar results for the NGF of the electrons at the central bridge are obtained by down-folding the NGF for the global system. The island self-energy due to many-body interactions is enriched by the effects of the coupling of the bridge island to the environment of the leads. The system becomes particularly simple, if also the electrons at the bridge are free of any many-particle effects. Remarkably enough, the NGF of the central bridge retains most of its general structure and behavior: The true many particle processes are mimicked by the tunnelling through the contacts.

As will be shown, the NGF can in this case be solved for on the one-particle level and this solution offers a "backstage" insight into the structure of the NGF viewed from the systematic many-body perspective. This may be particularly illuminating for the short time transient processes we intend to examine, namely those evolving from an arbitrarily correlated initial condition of the electrons in response to sudden changes in the lead/central island coupling and gradually evolving to a non-equilibrium quasi-particle state.

The initial state for the global NGF of a non-interacting system is given by the one-particle density matrix (OEDM). The down-folding (Hilbert space partitioning) yields the self-energy for the central island, and it turns out that the CIC terms are expressed in terms of the OEDM off-diagonal elements (coherences) between the bridge and the leads. These correction terms reduce to zero for an entirely uncoupled bridge representing thus the uncorrelated initial state (this is the particular situation studied in [30]). The outlined approach can be made more systematic as a "bridge analogy". We obtain the desired link with the standard field theoretic formulation, represented by JWM, by solving for the bridge NGF in an alternative two-step way. First, the JWM solution for a switch-on process, starting at a remote past from an uncorrelated state, is reproduced. Then, the technique of partitioning-in-time[10,31] is used to construct from the JWM solution the NGF for an embedded process starting at a given initial time and identical with the transient under consideration. This NGF can be transformed to the direct one-particle solution explicitly and this rounds off the bridge analogy.

The paper is structured as follows. In Sec. 2, we first describe the bridge analogy (2.1), then introduce the NGF for non-interacting systems (2.2) and finally define the abstract bridge model Hamiltonian (2.3). In Sec. 3 we obtain Dyson Equations for the Bridge Model by constructing explicit expressions for all components of the real time NGF using the direct method. First, the DE for propagators are shown to be insensitive to the initial conditions (3.1), then the particle correlation function with all CIC terms is given (3.2). Finally, the UIC NGF is derived as a special case (3.3). A generally tuned Section 4 relates the NGF by direct method with the field-theoretic approaches to the correlated initial conditions. In Sec. 4.1 we classify these approaches to diachronous with an augmented Schwinger-Keldysh loop and synchronous employing the higher order correlations at one initial time. After that, the JWM solution for a switch-on process with the Keldysh initial condition is obtained by a limiting transition from our general solution (4.2). Then, there follows the key Section 5. First, the NGF with CIC at a finite initial time is obtained from the JWM switch-on solution by time partitioning (5.1). This solution conveys well how the UIC are concentrated to a sharp instant, the initial time, while the CIC are anchored to a whole time range around the initial time, in other parlance, a blurred boundary between the Past and the Future with respect to the fixed "Present", i.e., "initial" time of the Future. Finally, this diachronous structure is obtained

once more in Sec. 5.2, by transforming the direct solution of Sec. 3, which is of the synchronous type. In the final Sec. 6, the theory is applied to the example of coupling transients generated by a sudden change in the couplings between the central bridge island and the leads. The CIC and UIC cases can be clearly contrasted.

2. General picture of a bridge structure without interactions

The whole structure of the bridge model considered here is the standard one [25]:

Two leads, left and right, are connected to the central island each by its own independent tunnelling junction. This graphic description does not tell much about the electronic structure of the system. In general, the charge self-consistence should be mandatory everywhere including the leads, in particular in the case of transient processes leading to time dependent capacitance effects at each of the junctions. This fully systematic approach has been undertaken in [27] within the framework of the modern time-dependent density functional theory. In this context, it is natural that the authors look upon the system as a unified whole and find that an adiabatic incorporation of the coupling between the leads and the central bridge island is an alien element to the self-consistent description. We will be more conservative and follow the common simplification heralded in [28] and JWM. The leads will be viewed as reservoirs of independent electrons and all many body interactions will be concentrated to the central island. It makes sense to consider the electron orbitals at the island as relevant and find their NGF which have a privileged position. This suggests a more abstract picture of the bridge model, which we will introduce and employ first, adding more specific features of the system step by step.

In the new representation of the model, the NGF describe a propagation of electrons seated at the island states. An interaction can be described as a coupling of these single electron states to a continuum of decay states, to which the electron makes occasional virtual trips or a real irreversible transition. As an example, the purely one electron state may be excited to vibronic states by the electron-lattice interaction and to many particle excited states by the electron-electron interactions. In this context, it is obvious that the coupling (or hybridisation) of the central island states to the band of electron orbitals at the leads represents a perfect analogue and can be treated in very much the same formal manner. If then, at the end, also the interactions within the island will be neglected, the couplings remain and, as said above, do mimick the true many particle processes leading thus to the self-energy corrections to the propagation of the electrons.

2.1. *Coupled bridge as an analogy of interacting systems*

It will be convenient to refer to the one-particle formalism using a metaphorical language based on the above analogy between the many-particle excitations in the general case and the lead single-particle states, both acting as the decay states for the single-particle excitations at the bridge. The transitions between the single-particle excitations and the decay states is caused by the interactions in the former case, by the lead-bridge molecule coupling in the latter. We may expand this analogy as listed in a short table,

one-electron excitations	bridge molecule states
multi-particle excitations	lead one-electron states
many-body interactions	bridge-lead coupling ("*bonding*")
adiabatic transient	wide band limit (WBL)
many-body statistical operator	global one-electron density matrix
one-electron density matrix (OEDM)	bridge one-electron density matrix
correlated initial state	bridge & leads coupled
uncorrelated initial state	bridge & leads uncoupled

The first three entries need no further comment. We mention adiabatic transients for completeness. These are processes driven by external influences varying in time slowly enough in comparison with the formation time of non-equilibrium quasiparticles. As we will show in the forthcoming paper, adiabatic regime is achieved for the bridge model by making the lead bands ex-

tremely wide in the spectral representation. This is the WBL of [29].

As pointed out in the Introduction, a proper inclusion of the correlated initial conditions (CIC) for a transient process starting at a finite initial time represents an important issue in the NGF technique. Employing the bridge analogy, in which the correlated state is paralleled by the initial OEDM with off-diagonal elements (coherences) between the bridge and the leads, we get a chance to explicitly investigate full formal solutions with CIC incorporated and interpret the outcome on an analytic level.

2.2. *NGF for non-interacting electrons*

Consider the NGF for an arbitrary non-equilibrium process, [1–12],

$$G(1,1') = -\mathrm{i}\langle\, \boldsymbol{T}_{\mathbb{C}}\{\psi(1|t_{\mathrm{I}})\psi^{\dagger}(1'|t_{\mathrm{I}})\}\rangle_{\mathrm{I}} \tag{1}$$

with the Heisenberg field operators ψ, $\psi^{\dagger}$ anchored at t_{I} and the time-ordering operator $\boldsymbol{T}_{\mathbb{C}}$ acting along the closed time path $\mathbb{C}$ extending from t_{I} to $+\infty$ and back. The $\langle\cdots\rangle_{\mathrm{I}}$ average is performed over an arbitrary initial many-body state at the time t_{I}. In the standard Langreth-Wilkins representation [2,3,7–10] G is described by three real-time GF components, the *less*-correlation function $G^{<}$ and two (equivalent) propagators, $G^{A}(1,2) = [G^{R}(2,1)]^{\dagger}$. For a system of non-interacting electrons, our NGF can be quite generally reduced to a description within the space of one-electron states spanned over the whole nanoscopic structure. To indicate the global nature of these one-electron quantities, we will use calligraphic letters:

$$\begin{aligned} \mathcal{G}^{R}(t,t') &= -\mathrm{i}\mathcal{S}(t,t')\vartheta(t-t'), \\ \mathcal{G}^{A}(t,t') &= \mathrm{i}\mathcal{S}(t,t')\vartheta(t'-t) \end{aligned} \tag{2}$$

$$\mathcal{G}^{<}(t,t') = \mathrm{i}\mathcal{S}(t,t_{\mathrm{I}})\mathcal{P}_{\mathrm{I}}\mathcal{S}(t_{\mathrm{I}},t') \tag{3}$$

Here, $\mathcal{S}$ denotes the one-electron evolution operator, which is specified by the one-electron Hamiltonian $\mathcal{H}(t)$,

$$\mathrm{i}\hbar\partial_t\,\mathcal{S}(t,t') = \mathcal{H}(t)\mathcal{S}(t,t'); \quad \mathcal{S}(t',t') = 1_{\mathrm{op}} \tag{4}$$

The symbol $\mathcal{P}_{\mathrm{I}}$ denotes the initial OEDM whose choice is quite arbitrary. It puts a constraint on the many-body initial state from which it might derive:

$$\mathcal{P}_{\mathrm{I}}(x,x') = -\mathrm{i}\langle\, \psi^{\dagger}(x')\psi(x)\rangle_{\mathrm{I}} \tag{5}$$

2.3. *Bridge model*

An entirely general approach to the bridge model starts by singling out a group of orbitals $\{|b\rangle\}$ considered as "relevant". All the rest of the orbital space will be lumped together to the sub-space of decay states. The two groups of orbitals do not overlap. Later, the decay states will be divided into those belonging to the two leads, but the present basic division is conveniently expressed in terms of projectors

$$\begin{aligned} 1_{\mathrm{op}} &= \mathcal{P} + \mathcal{Q}, \quad \mathcal{P}\mathcal{Q} = 0 \\ \mathcal{P} &= \sum_{b} |b\rangle\langle b| \\ \mathcal{Q} &= \sum_{a} |a\rangle\langle a| \end{aligned} \tag{6}$$

The one-electron Hamiltonian for the bridge model becomes the form

$$\begin{aligned} \mathcal{H}(t) &= \mathcal{H}_0(t) + \mathcal{H}'(t) \\ \mathcal{H}_0 &= \mathcal{P}\mathcal{H}_0\mathcal{P} + \mathcal{Q}\mathcal{H}_0\mathcal{Q} \\ \mathcal{H}' &= \mathcal{P}\mathcal{H}'\mathcal{Q} + \mathcal{Q}\mathcal{H}'\mathcal{P} \end{aligned} \tag{7}$$

Here, $\mathcal{H}_0$ describes the bridge molecule and the leads as insular objects, while $\mathcal{H}'$ represents their mutual coupling. To make the model easier for handling and relevant to the true bridge structures, we make two assumptions: There will be a single b orbital on the bridge, $\mathcal{P} = |b\rangle\langle b|$, while the $\{\mathcal{Q}\}$ sub-space will consist of band (quasi-) continua of lead orbitals.

3. Dyson equations for the bridge model

The "true" NGF for the bridge are obtained by the $\mathcal{P}$-projection of the GF defined in Eqs. (2),(3)

$$\begin{aligned} \mathcal{G}^{\natural} &\to \mathcal{P}\mathcal{G}^{\natural}\mathcal{P} \\ &= |b\rangle\langle b|\mathcal{G}^{\natural}|b\rangle\langle b| \equiv \mathcal{P}G^{\natural} \\ G^{\natural} &= \langle b|\mathcal{G}^{\natural}|b\rangle, \quad \natural = R,\, A,\, < \end{aligned} \tag{8}$$

3.1. *Dyson equations for propagators*

Now, we follow the standard route, which ends by deriving the well known partitioning expressions for the self-energy for the propagators [32]. This is achieved

in three steps. First, unperturbed NGF are associated with $\mathcal{H}_0$. This permits to write the global purely unitary Dyson equations

$$\begin{aligned}\mathcal{G}^{R,A} &= \mathcal{G}_0^{R,A} + \mathcal{G}_0^{R,A}\mathcal{H}'\mathcal{G}^{R,A}\\ \mathcal{G}^{R,A} &= \mathcal{G}_0^{R,A} + \mathcal{G}^{R,A}\mathcal{H}'\mathcal{G}_0^{R,A}\end{aligned} \tag{9}$$

The time arguments are not shown explicitly, but it is understood that the external ones are fixed, while an integration in the natural limits is performed over all internal times, like

$$\begin{aligned}&\mathcal{G}^R = \cdots + \mathcal{G}_0^R\mathcal{H}'\mathcal{G}^R \rightarrow\\ &\mathcal{G}^R(t,t') = \cdots + \int \mathrm{d}\bar{t}\, \mathcal{G}_0^R(t,\bar{t})\mathcal{H}'(\bar{t})\mathcal{G}^R(\bar{t},t')\end{aligned}$$

In the second step, the block diagonality of $\mathcal{G}_0^{R,A}$ is employed to obtain the partitioning expressions

$$\begin{aligned}\mathcal{Q}\mathcal{G}^{R,A}|b\rangle &= \mathcal{Q}\mathcal{G}_0^{R,A}\mathcal{Q}\mathcal{H}'|b\rangle\langle b|\mathcal{G}^{R,A}|b\rangle\\ \langle b|\mathcal{G}^{R,A}\mathcal{Q} &= \langle b|\mathcal{G}^{R,A}|b\rangle\langle b|\mathcal{H}'\mathcal{Q}\mathcal{G}_0^{R,A}\mathcal{Q},\end{aligned} \tag{10}$$

altogether four of them. This finally leads to four counterparts of Eqs. (9) for the bridge GF. Thus, the first identity of (10) yields a genuine Dyson equation

$$\begin{aligned}G^R &= G_0^R + G_0^R\Sigma^R G^R\\ \Sigma^R &= \langle b|\mathcal{H}'\mathcal{Q}\mathcal{G}_0^R\mathcal{Q}\mathcal{H}'|b\rangle\end{aligned} \tag{11}$$

This expression has the interpretation described above: an electron in the bridge state is virtually scattered to the lead states and back. This is a textbook example of the parallel hybridization $\|$ many-body interactions, familiar from the mean field treatments of the Anderson Hamiltonian. The parallel is not complete, as the exact self-energy is expressed in terms of the unperturbed GF and has thus an appearance of a second order perturbation term. This is a substantial practical advantage, but such self-energy misses the feature of self-consistency with respect to the exact propagator.

3.2. $G^<$ *with "correlated initial condition"*

The same elementary procedure permits to obtain the Dyson equation for the particle correlation function $G^< = \langle b|\mathcal{G}^<|b\rangle$. The general structure of this equation is [17,20,31,9,10]

$$\begin{aligned}G^< &= G^R\Xi^<G^A,\\ \Xi^< &= {}_\circ\Sigma_\circ^< + {}_\circ\Sigma_\bullet^< + {}_\bullet\Sigma_\circ^< + {}_\bullet\Sigma_\bullet^<\end{aligned} \tag{12}$$

Here, $\Xi^<$ denotes the complete *less* self-energy, the symbolic multiplications involve integrations starting at $t_{\rm I}$. The four components of $\Xi^<$ differ by the degree of singularity at the initial time, as indicated by circles [10]. Open circles symbolize a time variable fixed at $t_{\rm I}$, the filled ones a time variable continuous in $(t_{\rm I},\infty)$.

The regular term ${}_\bullet\Sigma_\bullet^<$ (called $\breve{\Sigma}^<$ in [20]) corresponds to the Dyson equation as it is usually written for $t_{\rm I}\to-\infty$, namely $G^< = G^R\Sigma^<G^A$. The other components have the form

$$\begin{aligned}{}_\circ\Sigma_\circ^<(t,t') &= \mathrm{i}\rho(t_{\rm I})\delta(t-t_{\rm I}-0)\delta(t'-t_{\rm I}-0),\\ {}_\circ\Sigma_\bullet^<(t,t') &= {}_\circ\Lambda^<(t_{\rm I},t')\delta(t-t_{\rm I}-0),\\ {}_\bullet\Sigma_\circ^<(t,t') &= \Lambda_\circ^<(t,t_{\rm I})\delta(t'-t_{\rm I}-0)\end{aligned} \tag{13}$$

In the first line, we see the initial occupation of the b orbital,

$$\rho(t_{\rm I}) \equiv \rho_{\rm I} = \langle b|\mathcal{P}_{\rm I}|b\rangle \tag{14}$$

The other two lines introduce two single-time Λ functions entering ${}_\bullet\Sigma_\circ^<$ and ${}_\circ\Sigma_\bullet^<$, which appear in addition to the regular self-energy ${}_\bullet\Sigma_\bullet^<$ as a consequence of the initial correlations.

To derive expressions for these quantities, we first rewrite Eq. (3) for $\mathcal{G}^<$. The definitions (2) are used and a new quantity ${}_\circ\mathcal{P}_\circ$ is introduced permitting to switch to a compact form, where all multiplications involve also time integrations, with the lower integration limits set to $t_{\rm I}$:

$$\begin{aligned}\mathcal{G}^<(t,t') &= \mathrm{i}\mathcal{S}(t,t_{\rm I})\mathcal{P}_{\rm I}\mathcal{S}(t_{\rm I},t')\\ \mathcal{G}^<(t,t') &= \mathrm{i}\mathcal{G}^R(t,t_{\rm I})\mathcal{P}_{\rm I}\mathcal{G}^A(t_{\rm I},t')\\ \mathcal{G}^< &= \mathrm{i}\mathcal{G}^R\,{}_\circ\mathcal{P}_\circ\,\mathcal{G}^A\\ {}_\circ\mathcal{P}_\circ &= \mathcal{P}_{\rm I}\delta(t-t_{\rm I}-0)\delta(t'-t_{\rm I}-0)\end{aligned} \tag{15}$$

Then equation changed

$$\begin{aligned}G^< &= \langle b|\mathcal{G}^<|b\rangle\\ &= \mathrm{i}\langle b|\mathcal{G}^R\,{}_\circ\mathcal{P}_\circ\,\mathcal{G}^A|b\rangle\\ &= \mathrm{i}\langle b|\mathcal{G}^R(\mathcal{P}+\mathcal{Q})\,{}_\circ\mathcal{P}_\circ\,(\mathcal{P}+\mathcal{Q})\mathcal{G}^A|b\rangle\end{aligned} \tag{16}$$

The four term structure of $\Xi^<$ results immediately by multiplying through the 2×2 parentheses in Eq. (16) followed by another use of the partitioning expressions (10) on the off-diagonal blocks of propagators. The singular behavior of a particular term is determined by the position of ${}_\circ\mathcal{P}_\circ$:

$$\begin{aligned}
{}_\circ\Sigma^<_\circ &= \mathrm{i}\langle b|{}_\circ\mathcal{P}_\circ|b\rangle \\
{}_\circ\Sigma^<_\bullet &= \mathrm{i}\langle b|{}_\circ\mathcal{P}_\circ\mathcal{Q}\mathcal{G}_0^A\mathcal{Q}\mathcal{H}'|b\rangle \\
{}_\bullet\Sigma^<_\circ &= \mathrm{i}\langle b|\mathcal{H}'\mathcal{Q}\mathcal{G}_0^R\mathcal{Q}_\circ\mathcal{P}_\circ|b\rangle \\
{}_\bullet\Sigma^<_\bullet &= \mathrm{i}\langle b|\mathcal{H}'\mathcal{Q}\mathcal{G}_0^R\mathcal{Q}_\circ\mathcal{P}_\circ\mathcal{Q}\mathcal{G}_0^A\mathcal{Q}\mathcal{H}'|b\rangle
\end{aligned} \tag{17}$$

Here, the "mixed" terms ${}_\bullet\Sigma^<_\circ$, ${}_\circ\Sigma^<_\bullet$ depend on the off-diagonal blocks of $\mathcal{P}_{\mathrm{I}}$ and vanish together with them. Within the presently discussed analogy, these blocks of $\mathcal{P}_{\mathrm{I}}$ are a signature of CIC, just like the interactions are modelled by the off-diagonal $\mathcal{P}-\mathcal{Q}$ mixing. The two remaining terms, ${}_\circ\Sigma^<_\circ$ and ${}_\bullet\Sigma^<_\bullet$, correspond roughly to the self-energy for uncorrelated initial conditions. They depend on the diagonal blocks of $\mathcal{P}_{\mathrm{I}}$ and do not vanish even if it is block-diagonal. A full definition of an uncorrelated initial state for the present model is given in the next paragraph. We conclude by returning to expressions indicating the initial time explicitly

$$\begin{aligned}
\rho_{\mathrm{I}} &= \langle b|\mathcal{P}_{\mathrm{I}}|b\rangle \\
{}_\circ\Lambda^<(t_{\mathrm{I}},t') &= \mathrm{i}\langle b|\mathcal{P}_{\mathrm{I}}\mathcal{Q}\mathcal{G}_0^A(t_{\mathrm{I}},t')\mathcal{Q}\mathcal{H}'(t')|b\rangle \\
\Lambda^<_\circ(t,t_{\mathrm{I}}) &= \mathrm{i}\langle b|\mathcal{H}'(t)\mathcal{Q}\mathcal{G}_0^R(t,t_{\mathrm{I}})\mathcal{Q}\mathcal{P}_{\mathrm{I}}|b\rangle \\
{}_\bullet\Sigma^<_\bullet(t,t') &= \\
&\mathrm{i}\langle b|\mathcal{H}'(t)\mathcal{Q}\mathcal{G}_0^R(t,t_{\mathrm{I}})\mathcal{Q}\mathcal{P}_{\mathrm{I}}\mathcal{Q}\mathcal{G}_0^A(t_{\mathrm{I}},t')\mathcal{Q}\mathcal{H}'(t')|b\rangle
\end{aligned} \tag{18}$$

The first line just repeats (14) and is quoted for convenience.

3.3. *Uncorrelated initial condition as a special case*

The definition of UIC for NGF is a subtle problem in the general case. For our model, where the role of the correlative interactions is played by the lead-central island coupling, an uncorrelated initial state $\mathcal{P}_{0\mathrm{I}}$ will be defined by the equation

$$\mathcal{P}\mathcal{P}_{0\mathrm{I}}\mathcal{Q} = \mathcal{Q}\mathcal{P}_{0\mathrm{I}}\mathcal{P} = 0 \quad \ldots \text{ UIC limit} \tag{19}$$

For consistency reasons, it is required that such initial state remain uncorrelated for all times under the free evolution. This is satisfied for the reference problem of particles without interactions and, by Eq. (7), also for the bridge model without coupling. With the conditions (19), it is apparent that the $\mathcal{P}$-$\mathcal{Q}$ hybridization is mediated only through the dynamical coupling $\mathcal{H}'$, not through the initial condition. The Dyson equation then reduces to the popular Keldysh UIC form. Firstly, by (18),

$$\begin{aligned}
{}_\circ\Lambda^< &= \Lambda^<_\circ = 0 \;\Rightarrow \\
{}_\bullet\Sigma^<_\circ &= {}_\circ\Sigma^<_\bullet = 0 \quad \ldots \text{ UIC limit}
\end{aligned} \tag{20}$$

Also the ${}_\bullet\Sigma^<_\bullet$ term simplifies substantially: because $\mathcal{P}_{0I}$ is block diagonal, we obtain

$$\begin{aligned}
{}_\bullet\Sigma^<_\bullet(t,t') &= \\
&\mathrm{i}\langle b|\mathcal{H}'(t)\mathcal{Q}\mathcal{G}_0^R(t,t_{\mathrm{I}})\mathcal{P}_{0I}\mathcal{G}_0^A(t_{\mathrm{I}},t')\mathcal{Q}\mathcal{H}'(t')|b\rangle \\
&= \langle b|\mathcal{H}'(t)\mathcal{Q}\mathcal{G}_0^<(t,t')\mathcal{Q}\mathcal{H}'(t')|b\rangle \\
{}_\bullet\Sigma^<_\bullet(t,t') &\to \Sigma^<(t,t')
\end{aligned} \tag{21}$$

This expression has a form fully consistent with that of the propagator components of the self-energy (11), in the sense of the usual Langreth rule [2,3,7–10]. We suppress the black dot code, because now the initial time is hidden in the inner Green function and the appearance of the self-energy is the "usual" one. On top of that, for times t, t' greater than t_{I}, the free *less* function can be cast *exactly* into a form identical with the usual GKBA [33,34,7–10], so that the resulting self-energy is shown to be truly t_{I}-independent:

$$\begin{aligned}
\Sigma^<(t,t') = &-\mathrm{i}\langle b|\mathcal{H}'(t)\mathcal{Q}\{\mathcal{G}_0^R(t,t')\mathcal{P}_0(t') \\
&-\mathcal{P}_0(t)\mathcal{G}_0^A(t,t')\}\mathcal{Q}\mathcal{H}'(t')|b\rangle
\end{aligned} \tag{22}$$

With the definition $\rho_{0\mathrm{I}} = \langle b|\mathcal{P}_{0\mathrm{I}}|b\rangle$ consistent with the general Eq. (14), our UIC Dyson equation reads

$$G^< = G^R\mathrm{i}\rho_{0\mathrm{I}}G^A + G^R\Sigma^<G^A \tag{23}$$

It has just two terms, the coherent initial transient and the "transport" term which gradually prevails at long times, at least under normal circumstances. The

transient term can easily be manipulated into the form given first by Keldysh:

$$\begin{aligned} G^< &= G^R(G_0^R)^{-1}G_0^R\mathrm{i}\rho_{0\mathrm{I}}G_0^A(G_0^A)^{-1}G^A + G^R\Sigma^<G^A \\ &= (1+G^R\Sigma^R)G_0^<(1+\Sigma^AG^A) + G^R\Sigma^<G^A \end{aligned} \tag{24}$$

Several comments may be added. First, this derivation is obviously not limited to the somewhat trivial single level case. Second, the Keldysh form (24) has little theoretical or practical advantage. The simple equation (23) hints at the origin of the initial transient which becomes dominant for weak interactions and describes a free flight of the initial distribution of particles.

The third comment needs a more detailed introduction. In the UIC Eqs. (23), (24), the general form ${}_\bullet\Sigma_\bullet^<$ of the self-energy, as given by Eq. (18), is simplified to $\Sigma^<$ which does not depend on the initial time t_{I} by(22). This dependence creeps in, however, because it is necessary to determine $\mathcal{P}_0(t)$ by solving the appropriate EOM starting from $\mathcal{P}_0(t_{\mathrm{I}}) = \mathcal{P}_{0I}$. A broad class of processes exists, for which this problem is avoided. This class is defined by the condition additional to and amplifying on Eq. (19):

$$[\mathcal{H}_0(t), \mathcal{P}_{0\mathrm{I}}] = 0 \tag{25}$$

This condition has two related consequences. Firstly, $\mathcal{P}_{0\mathrm{I}}$ commutes also with the free propagators. Secondly, free propagation of the initial state leaves it time independent, $\mathcal{P}_0(t) = \mathcal{P}_{0\mathrm{I}}$. Employing these features, we merge both propagators in (22) to the free spectral density operator, which does not depend on t_{I} either:

$$\mathcal{A}_0(t,t') = \mathrm{i}\{\mathcal{G}_0^R(t,t') - \mathcal{G}_0^A(t,t')\} \tag{26}$$

This permits to finally identify ${}_\bullet\Sigma_\bullet^<$ with the "usual" *less* self-energy:

$$\begin{aligned} {}_\bullet\Sigma_\bullet^<(t,t') &\xrightarrow{(25)} \Sigma^<(t,t') \\ \Sigma^<(t,t') &= \langle b|\mathcal{H}'(t)\mathcal{Q}\mathcal{A}_0(t,t')\mathcal{P}_{0\mathrm{I}}\mathcal{Q}\mathcal{H}'(t')|b\rangle \end{aligned} \tag{27}$$

This is basically the expression given for $\Sigma^<$ in [29], for example. In another context, the condition (25) appears to permit a reduction of the more general Eq. (22) employing the GKBA form of $\mathcal{G}_0^<$ to (27), where $\mathcal{G}_0^<$ is reminiscent of the original KB Ansatz.

The condition (25) is quite restrictive. It would be enough to require it for the $\mathcal{Q}$-block of $\mathcal{H}_0$ and $\mathcal{P}_{0I}$ only. Apart from some special choices of $\mathcal{P}_{0I}$, the generic way of satisfying (25) is to assume a common time independent basis of all operators involved and letting just the eigen-energies vary in time (*cf.* Eqs. (6), (7)):

$$\begin{aligned} \mathcal{H}_0(t) &= \sum_a |a\rangle\epsilon_a(t)\langle a| \\ \mathcal{P}_{0I} &= \sum_a |a\rangle\mathcal{P}_{0I;a}\langle a| \end{aligned} \tag{28}$$

The bridge model with leads whose energy zero is floating arbitrarily in time under the influence of an external bias [29] is a specific instance of Eq. (28).

4. Comparison of the direct method with the field-theoretic approaches to the correlated initial conditions

In the preceding sections, we were able to give a full NGF solution for the special model of a molecular bridge without interactions for entirely general "correlated initial conditions". This solution may be called a direct, or an *ad hoc* one, as it was not obtained within the formal field theoretical machinery. In this section, we want to link the two approaches, or rather to put the direct method into the context of a systematic NGF treatment of CIC. In doing that, we will not aim at a complete historical overview. We will rather concentrate on the approaches relevant today. The definition (1) contains, of course, the most complete answer to the problem of finite time CIC, but in a form, which makes the answers inaccessible. Several related problems include: ⋄ The correlated many-body initial state $\mathcal{P}_{\mathrm{I}}$ is an extremely complex quantity, in practice never known, unless it is selected arbitrarily and put in by hand. ⋄ At the same time, it contains excessively much information about the many body correlations. In fact a massive reduction is necessary to obtain $\Xi^<$, the self-energy with initial correlations. ⋄ An extension is required of the usual Wick theorem which fails for a general $\mathcal{P}_{\mathrm{I}}$, so that we could get a perturbation expansion in term of modified diagrams for the NGF.

4.1. *NGF techniques incorporating the correlated initial conditions*

The existing methods of treating the CIC for NGF can be classified into two groups, synchronous and di-

achronous. They are complementary. In a synchronous technique, the initial correlations (*i.e.* general initial conditions) are taken into account in their literal sense: higher and higher correlation functions confined to the sharp initial time $t_{\rm I}$ are invoked. In the diachronous approach, the initial correlations are given in terms of single particle quantities only, but these must be specified as a function of time extending sufficiently far back into the past. The two groups intersect at a single point, for the uncorrelated initial conditions. The UIC are fully specified by the single particle density matrix at the instant of the initial time $t_{\rm I}$.

4.1.1. *Synchronous picture of CIC*

In the synchronous treatment, we rely on the fact that, by (1), the complete initial many body state is specified at a sharply defined single time instant $t_{\rm I}$ and this in turn defines the complete NGF for all subsequent times. It may be hoped that the information actually needed as CIC for NGF can be reduced in dependence on a specific physical situation – as hinted by the case of UIC. This idea was initiated in the paper [24] whose authors adopted the synchronous approach and formulated the principle that the CIC should be consistent with the physical approximation employed to construct the NGF. In particular, they showed that the T-matrix (pair collision) approximation for the GF is consistent with, and can be developed from, an initial condition containing the static pair correlation function. It may be said that our direct method also falls among the synchronous techniques, if the analogy interaction - hybridization is recalled. When determining the NGF for the central island, we have found that the correlated initial condition is specified by the complete single-particle density matrix involving also the lead orbitals and this information cannot be reduced further in general. Only for the UIC we need just the central island projection of the single-particle density matrix.

4.1.2. *Diachronous picture of CIC*

The diachronous techniques are based on the notion that a physically admissible initial state is an outcome of previous history ("preparation") of the system. From this, we should seek to determine its future evolution. Historically, this concept has been introduced already by Keldysh [15,4]. In his real time NGF theory, he starts from an UIC at a distant past, $t_{\rm I} \to -\infty$. This is termed the Keldysh initial condition, The interactions responsible for the correlations are turned on adiabatically and we can start the transient of interest from the correlated state at $t = 0$. The Green's function for the future times is found in one process with the GF for the past and in fact, the future development stems from the past process. While physically appealing, the described procedure has some drawbacks. First, it is inconvenient to integrate from $-\infty$ over and over again for processes starting from the same CIC and changing, say, parameters of the ensuing transient. Second, the integrations along the real time axis are inconvenient in general, and this brings to mind the alternative of extending the transient process back into an imaginary time interval. This notion has been introduced by Kadanoff and Baym [1]. It is interesting to note that the Keldysh method is equivalent with that of Kadanoff and Baym for $t_{\rm I} \to -\infty$. For finite initial times, the appropriate formalism in the presently used form has been developed by Danielewicz [17] and further generalized by M. Wagner [18]: the real time ℂloop is extended by a Matsubara-like imaginary time stretch 𝕄 and the perturbation expansion of G is performed along this augmented open time "loop". As shown by M. Wagner, this formalism is suited for an arbitrary many-body $\mathcal{P}$, the Hamiltonian along the imaginary "time" axis is purely formal, and the original KB notion of an analytical continuation between the real and imaginary time axis need not be used.

4.2. *JWM solution of the bridge model: switch-on process with the Keldysh Initial condition*

The general considerations of the preceding section will be illustrated on the bridge model. As is apparent, our bridge model comes as close as possible to that of Refs. [28,29]. Our treatment has been somewhat different, however. Namely, we have obtained the NGF for a finite initial time with arbitrary correlated initial conditions. A recipe for formalizing such initial conditions suitable for a prescribed physical situation is an extra task to be added.

The physically appealing method employed by JWM represents a direct use of the fundamental approach to NGF introduced by Keldysh [15], with some important but congenial modifications. In JWM, the initial

state is uncorrelated, that is with the leads and central island disconnected, but the initial time is shifted to $-\infty$. The interaction – hybridization is turned on adiabatically and at finite times, say around $t-0$, the system is already in a correlated state, which can subsequently undergo any further dynamical process. In addition, however, also the unperturbed lead Hamiltonian is allowed to change in time (independently floating grounding of both leads). The states thus attained cannot be arbitrary, as argued above, and form a subclass belonging to the so-called switch-on states.

We may reproduce $G^<$ as given by JWM from the results of the section 3.3 in a straightforward way. It is enough to send the initial time to a distant past, $t_{\rm I} \to -\infty$ and to replace the interaction by its adiabatic approximant:

$$\mathcal{H}'(t) \to \mathcal{H}'_{\rm ad}(t) \equiv \mathcal{H}'(t)\mathrm{e}^{\imath t}$$

where $\imath > 0$ is infinitesimal. The self-energy $_\bullet\Sigma^<_\bullet$ is given by the general expression (21) for the UIC limit and it can be constructed beforehand, because it does not depend of the NGF self-consistently. It is this rather special feature of the bridge model (and of all models falling under the heading of the "abstract Anderson model") which makes it more or less soluble. Turning now to Eq. (23), we may see that for $t_{\rm I} \to -\infty$ the initial transient evanesces for all finite times, if only there are some damping processes in the system, and the final expression for $G^<$ given in JWM is simply

$$G^< = G^R\Sigma^< G^A \tag{29}$$

It is necessary, of course, to know the propagators. These are in their turn obtained from the Dyson equation (11) with the self-energy depending again on the free propagator and, therefore, known already. The equations (11), (29) jointly provide a complete NGF solution of JWM.

5. Time partitioning

With the JWM solution at hand, we may attack the problem of CIC in yet another way proposed recently, namely using partitioning-in-time, as announced in [10] and treated in detail in [31]. As will become apparent, this technique is particularly suitable for the transient coupling processes treated here. The problem we will attack here is the construction of the *less*-self-energy $\Xi^<$ in the diachronous technique, in particular for the switch-on states. We will use $t_{\rm I}$ as a sharp dividing time separating the time domains, "Past" or "*p*", $t < t_{\rm I}$, from the "Future" or "*f*" , $t > t_{\rm I}$. The switch-on process appears then as a host process starting in the distant past, in which the actual process of interest is embedded as an event unfolding in the Future . For possible generalizations, the reader is referred to [31]. It is interesting that this idea escaped attention for the real time NGF, although an analogous consideration has been performed for the imaginary time case: From the self-energy along the augmented $\mathbb{C}\cup\mathbb{M}$ loop, a contraction over the imaginary times yields $\Xi^<$ as a function of real times only . Similarly, in the real-time partitioning, the $\Xi^<$ self-energy concerning only the future with respect to the initial time, is obtained by a contraction over the times lying in the past. Full information contained in the many body state at the initial time is thus replaced by a reduced information employing only the Green's function, which must be known for all times in the past, that is preceding $t_{\rm I}$.

5.1. *Explicit form of the time partitioned NGF*

In this section we quote some results for NGF from [10,31]. Time partitioning is similar to the usual partitioning in Hilbert space [32] as has been used is Sec. 3.1. Now, however, the GF is partitioned not as an operator, but as an operator-valued matrix labelled by two times; the four blocks of such matrix then mean restriction of the time variables to the past and to the future as defined above, with diagonal combinations *p-p, f-f* and off-diagonal blocks *p-f, f-p*. The partitioning applies to all components of the NGF. The *p-p* blocks of all components naturally coincide with their complete counterparts. For propagators, the same is true for the *f-f* block because of the causal structure of the Dyson equation, and of the off-diagonal blocks, one is always zero , while the remaining one is given by a time-partitioning identity. For the retarded propagator, this is the *f-p* block:

$$\begin{aligned} &G^R(t,t') = \mathrm{i}G^R(t,t_{\rm I})G^R(t_{\rm I},t') \\ &+\int_{t_{\rm I}}^{t}\mathrm{d}\bar{t}\int_{t'}^{t_{\rm I}}\mathrm{d}\bar{\bar{t}}G^R(t,\bar{t})\Sigma^R(\bar{t},\bar{\bar{t}})G^R(\bar{\bar{t}},t') \quad t \geq t_{\rm I} \geq t' \end{aligned} \tag{30}$$

This equation, the so-called Renormalized Semi-Group Rule [36], is a corollary of the Dyson equation, so that it holds quite generally. It has a number of contexts. It generalizes the true semi-group multiplicative property of free propagators to the case, when the renormalizations are important, it serves as a necessary condition for validity of the non-equilibrium Ward identity [35] and it provides means for introducing the notion of quasi-particles out of equilibrium [36]. Here, Eq. (30) is shown as the simplest case showing the general structure of the time-partitioning expressions for Green's functions: in the product $G\Sigma G$, one GF lies in the *p-p* sector, the other one in *f-f*. Only the self-energy straddles the dividing time $t_{\rm I}$. The self-energy $\Sigma(t,t')$ is expected to be substantially non-zero only in a strip $|t-t'| < \mathcal{O}(\tau_{_Q})$, where $\tau_{_Q}$ is the presumably short quasi-particle formation time. This means that the integrations in (30) extend also over a similarly narrow area around the dividing time $t_{\rm I}$. This is the main advantage of the partitioning reformulation of the Dyson equation.

Next, we get to the core of this section, the expressions for the *f-f* block of $G^<$. First, Eq. (12) is written in a more explicit form:

$$\begin{aligned} G^<(t,t') &= \mathrm{i}G^R(t,t_{\rm I})\rho(t_{\rm I})G^A(t_{\rm I},t') \\ &+G^R(t,t_{\rm I})\times\int_{t_{\rm I}}^{t'}\mathrm{d}u\ {}_{\circ}\Lambda^<(t_{\rm I},u)G^A(u,t') \\ &+\int_{t_{\rm I}}^{t}\mathrm{d}v G^R(t,v)\,\Lambda^<_{\circ}(v,t_{\rm I})\times G^A(t_{\rm I},t') \\ &+\int_{t_{\rm I}}^{t}\mathrm{d}v\int_{t_{\rm I}}^{t'}\mathrm{d}u\, G^R(t,v){}_{\bullet}\Sigma^<_{\bullet}(v,u)G^A(u,t') \\ &\qquad\qquad t>t_{\rm I},\ t'>t_{\rm I} \end{aligned} \tag{31}$$

This equation does not depend on the partitioning method, but it illustrates the integration ranges for various terms, all in the *f-f* sector. The propagators can be taken over from the host switch-on process; as said above, they are the same. The individual contributions to the self-energy $\Xi^<$ corresponding to the process beginning at $t_{\rm I}$ can be expressed in terms of various blocks of the quantities belonging to the host process – this is the result of time partitioning:

$$\begin{aligned} {}_{\circ}\Lambda^<(t_{\rm I},u) &= \mathrm{i}\int_{-\infty}^{t_{\rm I}}\mathrm{d}\bar{t}\,\{G^R\Sigma^< + G^<\Sigma^A\} \\ \Lambda^<_{\circ}(v,t_{\rm I}) &= -\mathrm{i}\int_{-\infty}^{t_{\rm I}}\mathrm{d}\bar{\bar{t}}\,\{\Sigma^<G^A + \Sigma^RG^<\} \\ {}_{\bullet}\Sigma^<_{\bullet}(v,u) &= \Sigma^<(v,u) \\ &+\int_{-\infty}^{t_{\rm I}}\mathrm{d}\bar{t}\int_{-\infty}^{t_{\rm I}}\mathrm{d}\bar{\bar{t}}\,\{\Sigma^RG^R\Sigma^< + \Sigma^RG^<\Sigma^A + \Sigma^<G^A\Sigma^A\} \\ &\quad \Sigma^RG^R\Sigma^< \mapsto \Sigma^R(u,\bar{t})G^R(\bar{t},\bar{\bar{t}})\Sigma^<(\bar{\bar{t}},v),\ \text{etc.} \end{aligned} \tag{32}$$

The external arguments u, v are always greater than $t_{\rm I}$, while the integration variables denoted for clarity by $\bar{t}$, $\bar{\bar{t}}$ belong entirely to the past. The integrations are indicated in a condensed symbolic form, but it is easy to see that the argument about straddling the dividing time applies now again. The only difference is the appearance of $\Sigma^<$. If the usual assumption is made that a characteristic "collision duration time" $\tau_{_C}$ exists also for $\Sigma^<$, we see that the conclusion about a restricted integration area remains valid for (32). A more detailed inspection of the expressions shows that neither the self-energies nor the Green's functions have to be known deeper into the past than to $t_{\rm I}-\mathcal{O}(\tau_{_Q},\tau_{_C})$. By the same token, all integral terms in Eq. (32) will be vanishingly small for their external arguments greater than $t_{\rm I}+\mathcal{O}(\tau_{_Q},\tau_{_C})$. Beyond certain time characterizing the decay of correlations in the system, only $\Sigma^<(u,v)$ of the host process will survive. By this, we may conclude that the initial transient in Eq. (31) will vane out over a period of the propagator relaxation time beyond $t_{\rm I}$. After that, the common form $G^< = G^R\Sigma^<G^A$ will prevail. To conclude, there are two time scales to be distinguished for the initial time transient. There is a fast decay of initial correlations in the self-energy $\Xi^<$ on the time scale of the collision duration time, and the usually slower decay of the initial transient in the Green's function $G^<$ governed by the quasi-particle relaxation time. The latter estimate is equally valid also for the uncorrelated initial condition, while the UIC self-energy assumes its asymptotic shape instantaneously.

5.2. *Time partitioning for $G^<$ derived from the direct solution: relation between the diachronous and the synchronous approaches*

The bridge model offers an exceptional chance of a detailed comparison between the synchronous and diachronous expressions for NGF. In fact, it is possible to transform one set of the expressions into the other one. As the simplest yet typical example how to derive the time partitioning expressions for the future-future block of the particle correlation function, we will perform the transformation for $\Lambda_{\rm o}^<$. We start from the general "synchronous" expression for the bridge model, Eq. (18), but with the time arguments like in (32):

$$\Lambda_{\rm o}^<(u,t_{\rm I}) = {\rm i}\langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,t_{\rm I})\mathcal{Q}\mathcal{P}_{\rm I}|b\rangle \qquad (33)$$

The correlated initial condition enters the r.h.s. only through $\mathcal{P}_{\rm I}$. The first basic step in the transformation is to view this quantity as the end point of the p stage of a switch-on process. This is formalized by observing that $\mathcal{P}_{\rm I} = -{\rm i}\mathcal{G}^<(t_{\rm I},t_{\rm I})$, so that, by (15),

$$\Lambda_{\rm o}^<(u,t_{\rm I}) = {\rm i}\langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,t_{\rm I})\mathcal{Q}\mathcal{G}^R(t_{\rm I},t_{\text{-}\infty})\mathcal{P}_{\text{-}\infty}\mathcal{G}^A(t_{\text{-}\infty},t_{\rm I})|b\rangle \qquad (34)$$

Here, we employ the label $_{\text{-}\infty}$ for the initial time and the initial state of the full switch-on process to distinguish it from the initial state for the transient labelled by $_{\rm I}$. $\Lambda_{\rm o}^<$ is now expressed in terms of the ancient uncorrelated initial state $\mathcal{P}_{\text{-}\infty}$ and of the propagators, as is proper for the time partitioning approach.

In the second step, all propagators are expressed as a series of diagonal propagations, $\mathcal{P}$-propagations within the island and $\mathcal{Q}$-propagations in the leads. The latter are collected inside the expressions slated to become self-energies of the host process. This requires several manipulations. First, we substitute for $\mathcal{G}^R$ from the DE, Eq. (9), and obtain two terms:

$$\begin{aligned}\Lambda_{\rm o}^<(u,t_{\rm I}) = {}& {\rm i}\langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,t_{\rm I})\mathcal{Q}\mathcal{G}_0^R(t_{\rm I},t_{\text{-}\infty})\mathcal{P}_{\text{-}\infty}\mathcal{G}^A(t_{\text{-}\infty},t_{\rm I})|b\rangle \\ & + {\rm i}\int_{\text{-}\infty}^{t_{\rm I}}{\rm d}\bar{t}\,\langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,t_{\rm I})\mathcal{Q}\mathcal{G}_0^R(t_{\rm I},\bar{t})\mathcal{H}'(\bar{t}) \\ & \qquad\cdot\,\mathcal{G}^R(\bar{t},t_{\text{-}\infty})\mathcal{P}_{\text{-}\infty}\mathcal{G}^A(t_{\text{-}\infty},t_{\rm I})|b\rangle\end{aligned} \qquad (35)$$

After formal rearrangements, this becomes

$$\begin{aligned}\Lambda_{\rm o}^<(u,t_{\rm I}) = {}& \langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,t_{\text{-}\infty})\mathcal{P}_{\text{-}\infty}\mathcal{Q}\mathcal{G}^A(t_{\text{-}\infty},t_{\rm I})|b\rangle \\ & + \int_{\text{-}\infty}^{t_{\rm I}}{\rm d}\bar{t}\,\underbrace{\langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,\bar{t})\mathcal{H}'(\bar{t})|b\rangle}_{\Sigma^R(u,\bar{t})} \\ & \qquad\cdot\underbrace{\langle b|\mathcal{G}^R(\bar{t},t_{\text{-}\infty})\mathcal{P}_{\text{-}\infty}\mathcal{G}^A(t_{\text{-}\infty},t_{\rm I})|b\rangle}_{-{\rm i}G^<(\bar{t},t')}\end{aligned} \qquad (36)$$

The second line, by (11), is already one of the desired terms of $\Lambda_{\rm o}^<$ in (32). Reading the line from the right, we see first the "true" Green's function $G^<$ projected into the $\mathcal{P}$-space. The particle flight ends at a virtual time $\bar{t}$ and it immediately continues by propagation in the $\mathcal{Q}$ space of "excitations", to which it has been promoted by the interaction $\mathcal{H}'$. This virtual flight ends in the $\mathcal{P}$ space again, the return being produced by another interaction process in which $\mathcal{H}'$ causes deexcitation. These elementary processes contributing to the correlated motion are lumped together into the Σ^R component of the self-energy. The original initial correlations given by a single time structure transgressing the $\mathcal{P}$ space are thus dissolved into the purely single particle quantities, which have to be known over the whole integration range extending into the past.

We continue our task on the first line by substituting for $\mathcal{Q}\mathcal{G}^A|b\rangle$ from Eq. (10), that is using the Hilbert space partitioning for the off-diagonal propagation:

$$\begin{aligned}\Lambda_{\rm o}^<(u,t_{\rm I}) = {}& \int_{\text{-}\infty}^{t_{\rm I}}{\rm d}\bar{t}\,\langle b|\mathcal{H}'(u)\mathcal{Q}\mathcal{G}_0^R(u,t_{\text{-}\infty})\mathcal{P}_{\text{-}\infty}\,\mathcal{Q}\mathcal{G}_0^A(t_{\text{-}\infty},\bar{t})\mathcal{H}'(\bar{t})|b\rangle \\ & \qquad\cdot\langle b|\mathcal{G}^A(\bar{t},t_{\rm I})|b\rangle \\ & + \int_{\text{-}\infty}^{t_{\rm I}}{\rm d}\bar{t}\,(-{\rm i})\Sigma^R(u,\bar{t})G^<(\bar{t},t_{\rm I})\end{aligned} \qquad (37)$$

Final identification using Eq. (21) recovers the time partitioning expression (32) for $\Lambda_{\rm o}^<$:

$$\Lambda_{\rm o}^{<}(u,t_{\rm I}) = \int_{-\infty}^{t_{\rm I}} {\rm d}\bar{t}\,(-{\rm i})\Sigma^{<}(u,\bar{t})G^{A}(\bar{t},t_{\rm I}) + \int_{-\infty}^{t_{\rm I}} {\rm d}\bar{t}\,(-{\rm i})\Sigma^{R}(u,\bar{t})G^{<}(\bar{t},t_{\rm I}) \tag{38}$$

The outlined procedure will clearly work for any other of the expressions (32) with the same success and it hints at an analogous transformation process for a system with true correlations, like that studied in [24].

6. Example: NGF for coupling transients

In this section we consider an example of transient effects in the bridge model, which can be really fast, namely electron response to changes in the bridge island-leads coupling. Such coupling variations may occur inadvertently in a mechanically loose system, or they may be controlled. This type of problem has been attacked in the recent paper [30]. The authors consider the simplest possible case: the bridge molecule is decoupled from the leads up to the initial time $t_{\rm I}$, when the coupling is suddenly turned on. Here, we will also study the NGF for a system in which one or both leads are suddenly coupled to the bridge molecule. In contrast to [30], we put emphasis on the asymmetrical case, in which the island is originally coupled with one of the leads and only the other one is suddenly attached as well. This case is substantially more involved, as explained below.

We will use both techniques available, the direct method and the time partitioning. For the latter, we will use the JWM NGF as an input into the time partitioning equations (30), (32). The $t_{\rm I}$ time serving to split the whole time axis into the past ($t < t_{\rm I}$) and the future ($t > t_{\rm I}$) will be set at the instant of the jump in the coupling strength. The complete NGF will be constructed from time blocks, like Past-Past etc. of GF and self-energies belonging to the auxiliary process, which are stationary and none, one, or two leads are coupled to the bridge molecule. We start by writing down the necessary self-energies and describing the cases of time dependent coupling to be studied.

For the general considerations of the preceding sections it was sufficient to introduce the gross structure of the bridge model by dividing all orbitals into the central island subspace $\{\,|b\rangle\}$ and the rest forming together the sub-space of decay states – Eq. (6). Now, the decay states will be divided into those belonging to the two leads: $\{\,|a\rangle\} = \{\,|\ell\rangle\} \oplus \{\,|r\rangle\}$. In terms of projectors:

$$\begin{aligned} 1_{\rm op} &= \mathcal{P} + \mathcal{Q}, \quad \mathcal{P}\mathcal{Q} = 0 \\ \mathcal{Q} &= \mathcal{Q}_{L} + \mathcal{Q}_{R}, \quad \mathcal{Q}_{L}\mathcal{Q}_{R} = 0 \\ \mathcal{P} &= \sum_{b} |b\rangle\langle b| \\ \mathcal{Q}_{L} &= \sum_{\ell} |\ell\rangle\langle\ell|, \quad \mathcal{Q}_{R} = \sum_{r} |r\rangle\langle r| \end{aligned} \tag{39}$$

The one-electron Hamiltonian (7) for the bridge model will be taken in its simplest possible form

$$\begin{aligned} \mathcal{H}(t) &= \mathcal{H}_0 + \mathcal{H}'(t) \\ \mathcal{H}_0 &= \mathcal{H}_{0L} + \mathcal{H}_{0B} + \mathcal{H}_{0R} \\ \mathcal{H}'(t) &= \alpha_{L}(t)\mathcal{V}_{L} + \alpha_{R}(t)\mathcal{V}_{R} \end{aligned} \tag{40}$$

The specific choice of various parts of the Hamiltonian is as follows. The three parts of the structure, taken as separate, have no time dependence. The leads couple only to the bridge, but not one to another. The coupling is specified by time independent operator amplitudes $\mathcal{V}_{L,\,R}$. All time dependence in the model is concentrated into two scalar functions $\alpha_{L,\,R}(t)$. These assumptions parallel those of [29]. We further assume a single-level bridge. For all components of the Hamiltonian we have the following explicit expressions:

$$\begin{aligned} \mathcal{H}_{0L} &= \sum_{\ell} |\ell\rangle\varepsilon_{\ell}\langle\ell|, \quad \varepsilon_{\ell} = \hat{\varepsilon}_{\ell} - e\Delta\phi_{\ell},\ e > 0 \\ \mathcal{H}_{0R} &= \sum_{r} |r\rangle\varepsilon_{r}\langle r|, \quad \varepsilon_{r} = \hat{\varepsilon}_{r} - e\Delta\phi_{r} \\ \mathcal{H}_{0B} &= \quad |b\rangle\varepsilon_{b}\langle b| \end{aligned} \tag{41}$$

Here, the level shifts $-e\Delta\phi_{\ell},\ -e\Delta\phi_{r}$, correspond to the independently floating grounding of both leads considered as extended electron reservoirs.

$$\begin{aligned} \mathcal{V}_{L} &= \sum_{\ell} |\ell\rangle v_{\ell}\langle b| + H.\,c. \\ \mathcal{V}_{R} &= \sum_{r} |r\rangle v_{r}\langle b| + H.\,c. \end{aligned} \tag{42}$$

6.1. *All components of the JWM self-energy.*

For any switch-on process, we have the general expressions (11) for propagator components of the self-energy and, as follows from the analysis of Sects. 3.3, 4.2, a similarly structured Eq. (21) for the *less* component. They all hold for all times from $-\infty$ to $+\infty$. Introducing the particular form (40) of the interaction Hamiltonian into these equations, we have

$$\begin{aligned}
\Sigma^\natural(t,t') &= \langle b|\mathcal{H}'(t)\mathcal{Q}\mathcal{G}_0^\natural\mathcal{Q}\mathcal{H}'(t')|b\rangle \\
\Sigma^\natural(t,t') &= \alpha_{_L}(t)\tilde{\Sigma}_{_L}^\natural(t,t')\alpha_{_L}(t') + \alpha_{_R}(t)\tilde{\Sigma}_{_R}^\natural(t,t')\alpha_{_R}(t') \\
\tilde{\Sigma}_{_L}^\natural(t,t') &= \langle b|\mathcal{V}_{_L}\,\mathcal{Q}_{_L}\,\mathcal{G}_0^\natural(t,t')\mathcal{Q}_{_L}\,\mathcal{V}_{_L}|b\rangle \\
\tilde{\Sigma}_{_R}^\natural(t,t') &= \langle b|\mathcal{V}_{_R}\,\mathcal{Q}_{_R}\mathcal{G}_0^\natural(t,t')\mathcal{Q}_{_R}\,\mathcal{V}_{_R}|b\rangle, \qquad \natural = R,\, A,\, <
\end{aligned} \tag{43}$$

Altogether, we have six time-independent building blocks $\tilde{\Sigma}_{_{L,R}}^\natural$ of the self-energy.

The JWM *less* self-energy for our model satisfies the condition (25), so that we may write also expressions resembling (27):

$$\begin{aligned}
\tilde{\Sigma}_{_L}^<(t,t') &= \langle b|\mathcal{V}_{_L}\,\mathcal{Q}_{_L}\,\mathcal{A}_0(t,t')\mathcal{Q}_{_L}\,\mathcal{P}_{0\mathrm{I}}\,\mathcal{Q}_{_L}\,\mathcal{V}_{_L}|b\rangle \\
\tilde{\Sigma}_{_R}^<(t,t') &= \langle b|\mathcal{V}_{_R}\,\mathcal{Q}_{_R}\mathcal{A}_0(t,t')\mathcal{Q}_{_R}\,\mathcal{P}_{0\mathrm{I}}\,\mathcal{Q}_{_R}\,\mathcal{V}_{_R}|b\rangle
\end{aligned} \tag{44}$$

6.2. *Sudden coupling transients*

The α time dependence is, so to say, under our control: the dimension-less coupling constants may describe various processes of coupling and decoupling the junctions, varying the coupling strength and similar. Today, we will study two processes, in which the coupling changes suddenly at a selected time $t_{_\mathrm{I}}$:

Definition of processes			
process	$\alpha_{_L}(t)$	$\alpha_{_R}(t)$	GF
U	$\breve{\alpha}_{_L}\vartheta(t-t_{_\mathrm{I}})$	$\breve{\alpha}_{_R}\vartheta(t-t_{_\mathrm{I}})$	$G_{_\mathsf{U}}$
C	$\breve{\alpha}_{_L}$	$\breve{\alpha}_{_R}\vartheta(t-t_{_\mathrm{I}})$	$G_{_\mathsf{C}}$
OFF	0	0	G_0
right OFF	$\breve{\alpha}_{_L}$	0	$G_{\dashv}$
ON	$\breve{\alpha}_{_L}$	$\breve{\alpha}_{_R}$	G_{+}
$\breve{\alpha}_\natural$ $(\natural = L,R)$ dimensionless coupling strengths			

(45)

The two processes are labelled U and C to indicate that the first one starts from uncorrelated initial conditions, while the other from correlated initial conditions. We will assume the evolution of the bridge system to be known up to $t_{_\mathrm{I}}$ and ask about its continuation for times $t > t_{_\mathrm{I}}$. The answer will be constructed from blocks of steady state GF and self-energies. Three steady state processes needed are listed at the bottom of the table. They are labelled as though the junctions were switches. It is easy to see that the Past - Past block of $G_{_\mathsf{U}}$ coincides with the unperturbed G_0, while for $G_{_\mathsf{C}}$ the Past - Past block is that of $G_{\dashv}$. Further identifications will be made below as far as will be necessary.

Concerning references to our list of processes, there is none to C, the U process is treated in [30], the OFF process is trivial, right OFF resembles the adsorbate model of Grimley and Newns without interactions [37] and, finally, ON is the system of [28].

6.3. *Sudden coupling transients by time partitioning for NGF*

Time partitioning for propagators

The causal structure of the propagators simplifies their construction. Namely, the propagator wholly in the future depends only on the self-energy block wholly in the future, in addition to the similar generally valid statement about the past. Only the past-future and future-past blocks have to be constructed. Consider, for example, the C-process. We have at once, with the use of Eq. (43) for the self-energy,

$\boldsymbol{\Sigma}_{_\mathsf{C}}^{\boldsymbol{R}}$	$t' > t_{_\mathrm{I}}$	$\vdots$	$t' < t_{_\mathrm{I}}$
$t > t_{_\mathrm{I}}$	Σ_{+}^R	$\vdots$	$\Sigma_{\dashv}^R$
$t < t_{_\mathrm{I}}$	0	$\vdots$	$\Sigma_{\dashv}^R$

$\boldsymbol{G}_{_\mathsf{C}}^{\boldsymbol{R}}$	$t' > t_{_\mathrm{I}}$	$\vdots$	$t' < t_{_\mathrm{I}}$
$t > t_{_\mathrm{I}}$	G_{+}^R	$\vdots$	?
$t < t_{_\mathrm{I}}$	0	$\vdots$	$G_{\dashv}^R$

(46)

The remaining off-diagonal block of the propagator is easily obtained using one of the time-partitioning identities, the Renormalized Semi-Group Rule (30): Introducing (46) into (30), we obtain the desired part and hence the whole propagator built up from a "building block kit" of stationary processes as listed in (45).

$$
\begin{aligned}
\text{"?"} \equiv G^R_{\mathsf{C}}(t,t') &= \mathrm{i}G^R_{+}(t,t_{\mathrm{I}})G^R_{\dashv}(t_{\mathrm{I}},t') \\
&\quad + \int_{t_{\mathrm{I}}}^{t} \mathrm{d}\bar{t}\, G^R_{+}(t,\bar{t})\Theta^R_{\dashv}(\bar{t},t') \quad t \geq t_{\mathrm{I}} \geq t' \\
\Theta^R_{\dashv}(\bar{t},t') &= \int_{t'}^{t_{\mathrm{I}}} \mathrm{d}\bar{\bar{t}}\, \Sigma^R_{\dashv}(\bar{t},\bar{\bar{t}})G^R_{\dashv}(\bar{\bar{t}},t')
\end{aligned}
\tag{47}
$$

The multiplicative term in (47) alone would mean a kink in the GF as an instantaneous response of the system to the sudden onset of the right coupling. Memory effects smooth this transition out, as measured by the integral term. We abandon the symmetric form of the general relation (30): The inner integral, composed entirely of blocks belonging to the past, is condensed to the Θ-kernel for the outer integral, which expresses how the tentacles of the past stretch in a coherent fashion forward into the future. This extends over a time region with the temporal width $\mathcal{O}(\tau_{Q\dashv})$ comparable with that of the $\dashv$ self-energy. A quantitative analysis could only be based on explicit expressions for the self-energy .

An equation like (47) could also be written for $G^R_{\dashv}$. For the related steady state process, t_{I} has no exceptional role and the integral term simply compensates the kink in the multiplicative term to make the full propagator smooth. Such compensation of an artificial singularity must be a part of (47) as well. We subtract both relations with the result describing the true reaction of the system to the jump in the lead- central island coupling:

$$
\begin{aligned}
G^R_{\mathsf{C}}(t,t') &= G^R_{\dashv}(t,t') + \mathrm{i}\left\{G^R_{+} - G^R_{\dashv}\right\}(t,t_{\mathrm{I}})G^R_{\dashv}(t_{\mathrm{I}},t') \\
&\quad + \int_{t_{\mathrm{I}}}^{t} \mathrm{d}\bar{t}\, \left\{G^R_{+} - G^R_{\dashv}\right\}(t,\bar{t})\Theta^R_{\dashv}(\bar{t},t') \\
&\quad t \geq t_{\mathrm{I}} \geq t'
\end{aligned}
\tag{48}
$$

This form is ideally suited for t times close to t_{I}, more or less uniformly in the choice of the t' time. Considering first the second term in (48), it may be shown that the short time expansions of both $G^R_{\dashv}$ and G^R_{+} start from the same linear function and a difference occurs only in the quadratic terms. The onset of the second term is thus smooth. The same is true even more about the third term, where the integration leads to further smoothing.

For the uncorrelated case, the U-process, the considerations simplify. The time-partitioned matrices read

$\boldsymbol{\Sigma}^{\boldsymbol{R}}_{\mathsf{U}}$	$t' > t_{\mathrm{I}}$	$\vdots$	$t' < t_{\mathrm{I}}$
$t > t_{\mathrm{I}}$	Σ^R_{+}	$\vdots$	0
$t < t_{\mathrm{I}}$	0	$\vdots$	0

$\boldsymbol{G}^{\boldsymbol{R}}_{\mathsf{U}}$	$t' > t_{\mathrm{I}}$	$\vdots$	$t' < t_{\mathrm{I}}$
$t > t_{\mathrm{I}}$	G^R_{+}	$\vdots$	$\mathrm{i}G^R_{+}\times G^R_{0}$
$t < t_{\mathrm{I}}$	0	$\vdots$	G^R_{0}

(49)

There are no time off-diagonal contributions to the self-energy and this leads to the future-past element of the propagator at once. In (30), the integral term becomes zero and we are left with the product $\mathrm{i}G^R_{+}(t,t_{\mathrm{I}})G^R_{0}(t_{\mathrm{I}},t')$, as indicated in the propagator matrix. The Renormalized Semi-Group Rule is thus exact in this case.

Time partitioning for $G^<$

To obtain the correlation functions $G^<_{\mathsf{U}}$ and $G^<_{\mathsf{C}}$ in the Future - Future sector, we repeat the procedure for propagators, departing this time from Eqs. (31) and (32). Considering first (31), we see that all propagators have both times in the f f quadrant, so that, by (49) and (46),

$$
\begin{aligned}
G^{R,A}_{\mathsf{U}} &= G^{R,A}_{+}, \\
G^{R,A}_{\mathsf{C}} &= G^{R,A}_{+},
\end{aligned}
\qquad t,\, t' \geq t_{\mathrm{I}}
\tag{50}
$$

In Eq. (32), we will need, first of all, $\Sigma^<$ for the host process in the f f quadrant. From (43),

$$
\begin{aligned}
\Sigma^<_{\mathsf{U}} &= \Sigma^<_{+}, \\
\Sigma^<_{\mathsf{C}} &= \Sigma^<_{+},
\end{aligned}
\qquad t,\, t' \geq t_{\mathrm{I}}
\tag{51}
$$

Finally, we need the f p and p f blocks of the self-energy and the p p blocks of the host GF. Just like in (47), we find from (43) again that

$$
\begin{aligned}
\Sigma^{\natural}_{\mathsf{U}} &= 0, \\
\Sigma^{\natural}_{\mathsf{C}} &= \Sigma^{\natural}_{\dashv},
\end{aligned}
\qquad
\begin{aligned}
&(t > t_{\mathrm{I}} > t') \wedge (t < t_{\mathrm{I}} < t') \\
&\natural = R, A, <
\end{aligned}
\tag{52}
$$

The UIC correlation function follows from Eq. (31) at once:

$$
\begin{aligned}
G^<_{\mathsf{U}}(t,t') &= \mathrm{i}G^R_{+}(t,t_{\mathrm{I}})\rho(t_{\mathrm{I}})G^A_{+}(t_{\mathrm{I}},t') \\
&\quad + \int_{t_{\mathrm{I}}}^{t}\mathrm{d}v \int_{t_{\mathrm{I}}}^{t'}\mathrm{d}u\, G^R_{+}(t,v)\Sigma^<_{+}(v,u)G^A_{+}(u,t') \\
&\qquad\qquad t > t_{\mathrm{I}},\, t' > t_{\mathrm{I}}
\end{aligned}
\tag{53}
$$

This result deserves several comments. It clearly has the general structure of $G^<$ for uncorrelated initial

conditions, as given by Eq. (23). The past of the host process penetrates into (53) only through the value of $\rho(t_{\rm I})$. We will return to this at once. The other term should contain the propagators and self-energy of the U host process in general. It is, in fact, expressed in terms of the steady state $+$ quantities pertinent to the f f sector, as the UIC prevent any dynamic coupling between the Past and the Present. In fact, the $G\Sigma G$ term in (53) looks like the r.h.s. of the Dyson equation (29) for $G^<_+$ with a suitably trimmed integration area. For increasing upper integration limits, this trimming becomes less and less important and the whole term gradually approaches $G^<_+$. At the same time the coherent transient in (53) dies out to zero. The two terms are not mutually coupled, so that the initial occupation $\rho(t_{\rm I})$ of the island level can be chosen at will. The level occupation then changes from the initial value $\rho(t_{\rm I})$ to the saturation value $\rho(\infty) = -{\rm i}G^<_+(\infty,\infty)$. We note that the initial occupation need not be only 1 or 0, as a fractional occupation can be achieved by an infinitesimal coupling to the leads in the past, which has no dynamical meaning, but allows particle exchange between the central island and the lead reservoirs.

The CIC correlation function in the present case is also obtained as a special simplified form of Eq. (31):

$$\begin{aligned} G^<_{\rm C}(t,t') &= {\rm i}G^R_+(t,t_{\rm I})\rho(t_{\rm I})G^A_+(t_{\rm I},t') \\ &+ \int_{t_{\rm I}}^{t}{\rm d}v\int_{t_{\rm I}}^{t'}{\rm d}u\, G^R_+(t,v)\Sigma^<_+(v,u)G^A_+(u,t') \\ &+ \int_{t_{\rm I}}^{t}{\rm d}v\int_{t_{\rm I}}^{t'}{\rm d}u\, G^R_+(t,v)\{\text{CIC terms}\}G^A_+(u,t') \\ &\qquad\qquad t>t_{\rm I},\, t'>t_{\rm I} \end{aligned} \tag{54}$$

The time partitioning permits to replace the host propagators and the "regular" part of the *less* self-energy by the respective *f-f* blocks of the $+$ quantities. The first two lines are then identical with $G^<_{\rm U}$ as given by (53). The initial occupation $\rho(t_{\rm I})$ is now fixed, however, as the final outcome of the host process preceding the $t_{\rm I}$ time. This uncorrelated behavior of $G^<$ is modified by the additional CIC terms of the self-energy. They are of a transient nature and so it may be concluded that after elapse of a time of the order of the relaxation time the correlation function will nearly coincide with the steady state $G^<_+$ and the initial conditions and the initial formation process will be forgotten. For shorter times, the CIC terms are important. To obtain their explicit form, we invoke Eqs. (13), (32) and (52). The overall structure of the CIC terms remains, but all entering quantities, by Eq. (52), relate to the steady $\dashv$ process. This means, of course, that they refer to the past of the host process without any outreach into the future. We give the list of these CIC terms in a compact tabular form:

$_\bullet\Sigma^<_\circ$	$\Lambda^<_\circ = \int \Sigma^<_\dashv G^A_\dashv + \Sigma^R_\dashv G^<_\dashv$
$_\circ\Sigma^<_\bullet$	$_\circ\Lambda^< = \int G^R_\dashv \Sigma^<_\dashv + G^<_\dashv \Sigma^A_\dashv$
$_\bullet\Sigma^<_\bullet$ - $\Sigma^<_+$	$\iint \Sigma^R_\dashv G^R_\dashv \Sigma^<_\dashv + \Sigma^R_\dashv G^<_\dashv \Sigma^A_\dashv + \Sigma^<_\dashv G^A_\dashv \Sigma^A_\dashv$

(55)

More explicit expressions are easily inferred from the equations (13), (32). In particular, the integrations are performed over all inner times in the limits from $-\infty$ to $t_{\rm I}$. The actual integration limits are expected to be significantly less wide, because the self-energies should have a finite width in the double time plane and the outer times fall into the future, above $t_{\rm I}$.

7. Summary

In this paper, we have studied the simplest nanoscopic system, a molecular bridge consisting of a molecular island with discrete electronic levels coupled to non-interacting leads with continuous bands of one-electron states, using the non-equilibrium Green's functions. The details of the model and the general approach followed the procedure of Jauho, Wingreen and Meir. Specifically, we analyzed the transient behavior of electrons residing at the molecular bridge which undergoes abrupt changes. The induced transient process depends on the initial conditions at a finite starting time which may incorporate initial correlations. The particular topic addressed was the electron response to a sudden connection of the molecule to one or both leads. We neglected all interactions at the island, yet the NGF projected on the island one-electron states retains all salient features, because the role of the interactions is to a large extent taken over by the island-leads coupling. Guided by this analogy, we have obtained a complete solution for the transient

NGF for arbitrary initial correlations. These could be represented by off-diagonal coherences between the initial electron states of the island and of the leads. The resulting direct one-electron solution has been cast into the form of explicit formulas for self-energies, including the singular terms in the *less* self-energy.In the particular case of the switch-on states, for which the initial correlations result from the previous history of the system, we were able to obtain the transient NGF through a different route, close to the usual field theoretic techniques. This alternative solution was produced by partitioning-in-time of the NGF, applied on the JWM solution for a complete switch-on process. The time partitioning formalism incorporates only the propagation taking place entirely in the past, or entirely in the future. As a consequence, we were able to express the transient NGF in terms of the building blocks of stationary-state NGF with zero, one or both leads connected. Finally, the direct and the partitioning solutions were converted explicitly one to another. This shed some light on the meaning of the singular terms of the self-energy for correlated initial conditions.

Compared with the other work, our results for the correlated initial conditions seem to be given here for the first time. The special case of uncorrelated initial conditions gave results in agreement with JWM in the limit of a very remote initial time, while for a finite initial time, our results and the solution given in [30] appear to be equivalent. Finally, we want to return to the paper [27] referred to at the beginning of Sec. 2. As pointed out there, we do not prefer either of the possibilities, initially coupled or initially uncoupled leads. Our aim was to compare these two cases with the more complex situation of one-sided coupling of the lead as the initial state. One outcome of our work, which is, of course, only proved for a non-interacting system, is an asymptotic equivalence of all initial states. The only condition is an identical behavior of the external parameters of the system for the f times, after $t_{\rm I}$. The other result for non-interacting systems is the explicit proof of equivalence of the direct method and of the time partitioning for the switch-on states. It can be reinterpreted as a proof of equivalence of the adiabatic turning-on of the couplings with the situation where the couplings are on from the outset. All this reasoning is based on the assumption that there is some damping in the system leading to the loss of memory of the distant past; the cases of bound states lasting forever or of persistent currents require a separate analysis and there the warnings made in [27] keep their acuteness.

For the future work, the first obvious step will be to use the present formal framework to study, mostly numerically, electronic transients caused by the sudden changes in the coupling. For each of the stationary processes involved, we have to deal with two distinct time scales, the decay of correlations, and the decay of quasiparticle states. These dynamic characteristics can then be expressed in terms of the electronic structure of the leads and the bridge molecule, and of the coupling strengths. This permits to explore several general questions, in particular formation of the "quasiparticle" excitations, saturation to a steady state and validity of the non-equilibrium Ward identities which have a direct bearing on the possibility of simplifying the general NGF expressions to quantum transport equations by means of a modified Generalized Kadanoff-Baym ansatz [9,10].

In the next step, the model should be extended. First, still on the one-electron level, the jump in the coupling strength may take place over a finite time, not "suddenly". This will certainly bring the model closer to reality. The third additional time scale will permit to analyze the concept of sudden *vs.* adiabatic change of the coupling by varying the jump duration with the time of decay of the correlations. Only then, it will be meaningful to study the role of the WBL as used in JWM (ref. [29]). The other extension goes beyond the one-electron level, but using a mean-field approximation. this should be used not only on the central island levels like in [30], but also on the transient charge depletion cloud at the leads. This step makes the task less clearly defined, but it is necessary in order to make the theory conserving.

Note Added In Proof After completion of this manuscript, R. van Leeuwen kindly brought to our attention the paper by P. Myohanen et al., *A many-body approach to quantum transport dynamics: Initial correlations and memory effects* in Eur. Phys. Lett. 84, (2008) 67001 dealing with correlated initial conditions for a molecular bridge structure handled in the TDDFT framework. This valuable work will be discussed in the context of our investigation in the forthcoming communication.

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References

[1] L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics, Benjamin, New York, 1962.

[2] D. C. Langreth and G. Wilkins, Phys. Rev. B 6 (1972) 3189.

[3] D. C. Langreth, in Linear and Nonlinear Electron Transport in Solids (J. T. Devreese and E. van Boren, eds.), Plenum, New York, 1976.

[4] E.M. Lifshitz, L.P. Pitaevskii, Physical Kinetics, L.D.Landau and E.M. Lifshitz Course of Theoretical Physics, Vol.10, Pergamon Press 1981.

[5] J. Rammer, H. Smith, Rev. Mod. Phys. 58 (1986) 323.

[6] G.D. Mahan, Many Particle Physics, (Plenum Press, New York, 1990).

[7] H. Haug, A.P. Jauho, Quantum Kinetics in Transport and Optics of Semiconductors, Springer, Berlin, 1997.

[8] M. Bonitz, Quantum Kinetic Theory, Teubner, Stuttgart, 1998.

[9] V. Špička, B. Velický and A. Kalvová, Physica E 29 (2005) 154, ibid 175, ibid 196.

[10] B. Velický, A. Kalvová and V. Špička, J.Phys: Conference Series 35 (2006) 1.

[11] M. Bonitz, A. Filinov (eds.), Progress in Non-equilibrium Green's Functions III, J.Phys: Conference Series **35**, 2006.

[12] M. Bonitz, D. Semkat (eds.), Introduction to Computational Methods in Many Body Physics, Rinton Press, Inc., New Jersey 2006

[13] S. Fujita, Phys. Rev. A bf 4 (1971) 1114.

[14] A.G. Hall, J. Phys. A 8 (1975) 214.

[15] L.V. Keldysh, Zh. Exp. Teor. Fiz. 47 (1964) 1515. [Sov. Phys. JETP 20 (1965) 1018]

[16] Yu.A. Kukharenko, S.G. Tikhodeev, Soviet. Phys. JETP 56 (1982), 831.

[17] P. Danielewicz, Ann. Phys. (N.Y.) 152 (1984) 239.

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

[19] D. Semkat, D. Kremp, and M. Bonitz, Phys. Rev. E 59 (1999) 1557.

[20] V.G. Morozov, G. Ropke, Ann. Phys. 278 (1999) 127.

[21] D. Semkat, D. Kremp, and M. Bonitz, J. Math. Phys. 41 (2000) 7458.

[22] K. Morawetz, M. Bonitz, V.G. Morozov, G. Ropke, and D. Kremp Phys. Rev. E bf 63 (2001) 020102-1.

[23] D. Semkat, D. Kremp, and M. Bonitz, Contrib. Plasma Phys. 43 (2003) 321.

[24] D. Kremp, D. Semkat and M. Bonitz, J. Phys.: Conference Series 11(2005) 1.

[25] M. Galperin, M. A. Ratner and A. Nitzan, J. Phys.: Cond. Matt. 19 (2007) 103201

[26] A. Goker, B.A. Friedman, and P. Nordlander, J. Phys.: Condens. Matter 19 (2007) 376206.

[27] G. Stefanucci, Phys. Rev. B75 (2007) 1955115.

[28] Y. Meir, N.S. Wingreen, Phys. Rev. Lett. 68 (1992) 2512

[29] A. P. Jauho, N.S. Wingreen and Y. Meir, Phys. Rev. B 50 (1994) 5528.

[30] T.L. Schmidt, P. Werner, L. Muhlbacher, and A. Komnik, Phys. Rev. B78 (2008) 235110.

[31] B. Velický, A. Kalvová and V. Špička, Phys. Rev. B (2009), to appear.

[32] A. Messiah, Quantum Mechanics, Dover, 1999.

[33] P. Lipavský,V. Špička, and B. Velický Phys. Rev. B 29 (1986) 6933 .

[34] A.V. Vinogradov, Trudy Fiz. Inst. Im. P.N. Lebedeva 187(1988) 117.

[35] B. Velický, A. Kalvová and V. Špička, Phys. Rev. B 77 (2008) 041201 (R).

[36] B. Velický, A. Kalvová and V. Špička, Phys. Rev. B 75 (2007) 195125 .

[37] D.M. Newns, Phys. Rev. 178 (1969) 1123, Grimley T B., J. Vac. Sci. Technol. 8 (1971) 31.