

# Linear optical response of current-carrying molecular junction: A nonequilibrium Green's function–time-dependent density functional theory approach

Michael Galperin<sup>a)</sup> and Sergei Tretiak

Theoretical Division, Center for Integrated Nanotechnologies,  
Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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We propose a scheme for calculation of linear optical response of current-carrying molecular junctions for the case when electronic tunneling through the junction is much faster than characteristic time of external laser field. We discuss relationships between nonequilibrium Green's function (NEGF) and time-dependent density functional theory (TDDFT) approaches and derive expressions for optical response and linear polarizability within NEGF-TDDFT scheme. Corresponding results for isolated molecule, derived within TDDFT approach previously, are reproduced when coupling to contacts is neglected. © 2008 American Institute of Physics.  
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## I. INTRODUCTION

Rapid progress of experimental capabilities in the field of molecular electronics necessitates development of theoretical (and calculational) tools capable of explaining existing data and predicting (proposing) future experiments. While initial focus of both experimental and theoretical studies was on ballistic current-voltage characteristic of molecular junctions,<sup>1</sup> today, more complicated phenomena are on the forefront of research. This includes inelastic transport (inelastic electron tunneling spectroscopy both far-off<sup>2</sup> and at resonance<sup>3</sup>), current-induced motion,<sup>4</sup> nonlinear conductance (negative differential resistance,<sup>5</sup> hysteresis,<sup>6</sup> and switching<sup>7</sup>), shot noise,<sup>8</sup> Coulomb blockade,<sup>9</sup> Kondo effect,<sup>10,11</sup> heating of molecular junctions,<sup>12,13</sup> etc. Recently, optical properties of molecular junctions started to attract attention of researchers. Application of external laser field promises ability to effectively control transport properties of molecular devices,<sup>14</sup> while Raman spectroscopy, together with scanning tunneling microscopy and inelastic electron tunneling spectroscopy (IETS) can serve as a diagnostic tool.<sup>15,16</sup> First experimental data in this direction include light induced switching behavior of molecular junctions,<sup>17–19</sup> voltage effects on fluorescence<sup>20</sup> of molecules in nanojunctions, and surface enhanced Raman scattering from molecules positioned in narrow gaps between metal nanoparticles.<sup>21–24</sup> Theoretically, optoelectronic properties of current-carrying molecular junctions have been studied mostly within simple models.<sup>25–28</sup> Here, we make a first step in direction of *ab initio* calculations of optical properties of such junctions.

Transport properties of molecular junctions are naturally described within non-equilibrium Green's function (NEGF) approach.<sup>29,30</sup> A consistent way to treat transport of molecular junction within NEGF implies using many-body Green's

functions approach. However, complexity of the schemes limits applicability of this treatment to relatively simple molecular models only.<sup>31–34</sup> Density functional theory (DFT) is a well-established tool for accurate calculation of ground state electronic properties of isolated systems (atoms, molecules, and solids).<sup>35–38</sup> DFT ability to deal with relatively extended realistic systems made the idea of merging the two approaches very appealing. First, NEGF-DFT was implemented to steady-state ballistic (Landauer) transport calculations.<sup>39–41</sup> Later, the calculations were extended to the case of inelastic electron transport in the weak electron-phonon coupling limit.<sup>42–46</sup> For detailed discussion on different approaches to transport through molecular junctions, see Ref. 47. While NEGF-DFT calculations modeling IETS reported good agreement with experimental data,<sup>43,44</sup> results for ballistic current-voltage calculations are not always in quantitative agreement. Sometimes, experimental data are reproduced by NEGF-DFT approach,<sup>48,49</sup> while in other cases, calculations yield a current that is orders of magnitude larger than experimental values.<sup>50,51</sup>

Besides obvious uncertainties inherent for molecular junction simulations, such as influence of contact geometry<sup>52,53</sup> and local environment<sup>54</sup> on transport, a methodological DFT problem (when applied to transport situation) was pointed as a possible source of discrepancy.<sup>55–58</sup> Possible errors can be grouped into several categories: (1) Use of inappropriate exchange-correlation (XC) functional (ground state and/or spatially local character of functionals used, self-interaction errors, absence of derivative discontinuity, and xc contribution to the electric field response), (2) inherent time-dependent character of transport, which goes beyond validity of DFT, (3) DFT [as well as time-dependent DFT (TDDFT) discussed below] is a theory which works for finite systems (external disturbance local in space) only, and (4) unphysical separation of the system into disconnected

<sup>a)</sup>Electronic addresses: galperin@lanl.gov and mishagalperin@gmail.com.

parts (contacts and molecule) at infinite past within NEGF. For a detailed discussion on application of DFT in transport calculations, see Refs. 59–61.

Optical response of the system is defined by its electronic excitations. In order to calculate excited states, two main approaches can be implemented. One is based on a many-body theory, where solution of the Bethe-Salpeter equation is needed. Its computationally expensive character limits applicability of the approach to a relatively narrow range of problems (see, e.g., Refs. 62–64). A much more numerically efficient alternative is the TDDFT. For a review comparing these two techniques, see Ref. 65. TDDFT is an extension of density functional theory,<sup>66,67</sup> which properly treats correlated excited states and where electronic excitations are associated with the poles of exact charge density response. TDDFT is known for successful calculations of optical spectra in many finite molecular systems.<sup>65,68</sup> Its numerical simplicity allows treating systems that involve hundreds of atoms, and a lot of work within the approach has been done for isolated molecules.<sup>69–76</sup> Taking into account size of realistic systems (molecules) used in molecular devices, TDDFT is the only tool available today capable of dealing with such calculations.

Transport calculation schemes based on TDDFT were proposed as an alternative to NEGF-DFT method. Main differences are time-dependent character of the TDDFT scheme (TDDFT instead of DFT), absence of system partitioning, and finite size of the system under study. In particular, one of the proposed schemes, time-dependent Kohn-Sham master equation approach, utilizes ring geometry, and linearly increasing magnetic field in the center of the ring provides driving force.<sup>59,60</sup> Another TDDFT-NEGF approach considers time evolution of finite linear system initially at equilibrium under influence of external field (battery discharge).<sup>61,77–79</sup> While these approaches seem to solve (at least partially) problems of NEGF-DFT, some questions still exist. For example, in the master equation approach, finite size of the ring forces to apply artificially large coupling between electrons and the bath in order to achieve thermalization in the part of the ring representing contact, which raises question of physicality of charge distribution in the contacts and, hence, current through the device part of the ring. TDDFT-NEGF also implements system of finite size; i.e., continuum character of states in the electrodes is questionable. Thus, equivalence of transient current calculated within the approach and realistic steady-state current is not obvious. The approaches still have to be tested on the problems where NEGF-DFT failed. Note also that TDDFT has its own limitations (nonuniqueness of the excited-state potentials, question of stability, and chaos of the mapping of densities on potentials).<sup>80,81</sup>

While agreement on existence of methodological pitfalls of NEGF-DFT exists, the importance of those errors (i.e., if they are the cause of discrepancy between NEGF-DFT results and experimental data) is not completely understood yet.<sup>58</sup> Besides, within TDDFT-NEGF approach, it was shown that after initial correlations die out and steady-state current is established, the last is given by Landauer-like formula with chemical potentials in Fermi distribution functions be-

ing shifted in accordance with extra exchange-correlation term originating from response to external field (bias).<sup>59,61</sup> The problems of NEGF-DFT and TDDFT-NEGF schemes seem to stem from essentially different basic assumptions of the two (NEGF and DFT) theories; compatibility of those is not clear. However, this is the only practical tool available today capable of dealing with realistic simulations of molecular junctions.

In this paper, we consider optical response of current-carrying molecular junction within NEGF-TDDFT approach. We assume that initially, steady-state current across the junction is established and then, the system is probed by an external laser field. The last is assumed to be a weak perturbation on top of the nonequilibrium steady state. The assumption works in the case when time scale for electron transport is much shorter than the characteristic time of external field. In the opposite case (both times are comparable or the field is quicker), one would need to consider time-dependent transport, either within TDDFT-NEGF (Refs. 61 and 77–79) or time-dependent NEGF (Ref. 82) approach, explicitly. We postpone such consideration for future research. In treating steady-state flux, we assume that Landauer formula is correct, while *xc* and chemical potential are adjusted properly, as is discussed in Refs. 59 and 61. So, the treatment formally looks similar to the standard NEGF-DFT; however, one has to keep in mind points mentioned above.

The ability to predict electro-optical response of molecular junctions potentially has important practical applications: From molecular optical switches and photodiodes to diagnostic tools capable of providing specific information on properties of the molecule in the junction. Optical spectrum calculated for isolated molecule often will be inadequate to describe the situation in the junction. The most obvious consequences of molecular coupling to contacts are smearing of the discrete optical spectrum into continuum (in complete analogy to broadening of energy levels) and an additional source of memory (due to presence of one more interaction). The stronger the coupling to the contacts is, the more pronounced the effects are. Nonequilibrium character of the system brings in fractional average population of the levels (probability to find a molecular level being populated or empty at different times), which results both in alternation of the optical spectrum due to highest occupied molecular orbital (HOMO) being distributed over set of levels and possible interference effects due to temporal dependence of occupation and emptying of different levels (not considered here).

In Sec. II, we introduce model of molecular junction. Section III briefly discusses general differences between NEGF and TDDFT approaches and proposes a way to describe the latter in terms of the former. In Sec. IV, we derive expressions for steady-state flux, while Sec. V deals with optical response of the current-carrying junction. Section VI summarizes our findings.

## II. MODEL

The model we employ consists of a molecule coupled to two contacts (left *L* and right *R*). Each contact is a reservoir

of free charge carriers at its equilibrium, i.e., characterized by its own electrochemical potential  $\mu_K$  ( $K=L,R$ ). We introduce second quantization field operators for electrons in the molecule  $\hat{\psi}_\sigma$  and in the contacts  $\hat{\psi}_{\sigma,K}$  ( $\sigma$  is electron spin and  $K=L,R$ ) with the usual anticommutation relations,

$$\{\hat{\psi}_{\sigma_1}(\mathbf{r}_1; \mathbf{R}); \hat{\psi}_{\sigma_2}^\dagger(\mathbf{r}_2; \mathbf{R})\} = \delta_{\sigma_1, \sigma_2} \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (1)$$

$$\{\hat{\psi}_{\sigma_1, K_1}(\mathbf{r}_1); \hat{\psi}_{\sigma_2, K_2}^\dagger(\mathbf{r}_2)\} = \delta_{\sigma_1, \sigma_2} \delta_{K_1, K_2} \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (2)$$

and all other anticommutators being zero. Note that molecular field operators depend parametrically on the nuclear configuration  $\mathbf{R}=\{\mathbf{R}_\alpha\}$  (Born-Oppenheimer approximation).

Many-body electronic Hamiltonian of the system in the second quantization is

$$\hat{H}(\mathbf{R}) = \hat{H}_L + \hat{H}_R + \hat{H}_M(\mathbf{R}) + \hat{V}_L(\mathbf{R}) + \hat{V}_R(\mathbf{R}), \quad (3)$$

where the contact Hamiltonian is given by

$$\hat{H}_K = \sum_\sigma \int d\mathbf{r}_k \hat{\psi}_{\sigma, K}^\dagger(\mathbf{r}_k) \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_k^2} \right] \hat{\psi}_{\sigma, K}(\mathbf{r}_k) \quad (4)$$

(here and below,  $K=L,R$ ), coupling between molecule and contact  $K$  is (no spin-flip transitions)

$$\hat{V}_K(\mathbf{R}) = \sum_\sigma \int d\mathbf{r} \int d\mathbf{r}_k [\hat{\psi}_\sigma^\dagger(\mathbf{r}; \mathbf{R}) V_{\sigma, K}(\mathbf{r}, \mathbf{r}_k; \mathbf{R}) \hat{\psi}_{\sigma, K}(\mathbf{r}_k) + \text{H.c.}], \quad (5)$$

and molecular Hamiltonian is

$$\begin{aligned} \hat{H}_M(\mathbf{R}) = & \sum_\sigma \int d\mathbf{r} \hat{\psi}_\sigma^\dagger(\mathbf{r}; \mathbf{R}) \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} \right. \\ & \left. - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} - e\mathbf{E}(t)\mathbf{r} \right] \hat{\psi}_\sigma(\mathbf{r}; \mathbf{R}) \\ & + \frac{e^2}{2} \sum_{\sigma_1, \sigma_2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \hat{\psi}_{\sigma_1}^\dagger(\mathbf{r}_1; \mathbf{R}) \hat{\psi}_{\sigma_2}^\dagger(\mathbf{r}_2; \mathbf{R}) \\ & \times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \hat{\psi}_{\sigma_2}(\mathbf{r}_2; \mathbf{R}) \hat{\psi}_{\sigma_1}(\mathbf{r}_1; \mathbf{R}). \end{aligned} \quad (6)$$

Here,  $\alpha$  indicates sum over nuclei of the molecule,  $Z_\alpha$  is a charge of the nucleus  $\alpha$ , and  $\mathbf{E}(t)$  is external laser field. Note that we intentionally started from the Hamiltonian in the second quantization form and used explicit partition of the system into contacts and a molecule. Since this is a standard NEGF approach, it makes the following connection to TDDFT clearer. At the same time, NEGF partitioning scheme by Caroli *et al.*<sup>31</sup> and partitionless approach by Cini<sup>83</sup> implemented in TDDFT-NEGF schemes for time-dependent transport<sup>59–61,77–79</sup> in the steady-state case, which we are going to consider, were shown to be equivalent.<sup>77</sup> Note that below, we will consistently use atomic units, i.e.,  $\hbar=e=m=1$ , and drop  $\mathbf{R}$ , keeping in mind that all the quantities depend on positions of nuclei parametrically.

Now in the spirit of DFT (and TDDFT) theory, we replace the true many-body molecular Hamiltonian [Eq. (6)] by fictitious single-particle Kohn-Sham Hamiltonian, which in the second quantization form is

$$\begin{aligned} \hat{H}_M^{(KS)} = & \sum_\sigma \int d\mathbf{r} \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left[ -\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}^2} + v^{\text{ext}}(\mathbf{r}) + v^{\text{cl}}(\mathbf{r}, t) \right. \\ & \left. + v_\sigma^{\text{xc}}(\mathbf{r}, t) - \mathbf{E}(t)\mathbf{r} \right] \hat{\psi}_\sigma(\mathbf{r}). \end{aligned} \quad (7)$$

Here,

$$v^{\text{ext}}(\mathbf{r}) = - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \quad (8)$$

is external potential due to electron-nuclear interaction,

$$v^{\text{cl}}(\mathbf{r}, t) = \sum_{\sigma_1} \int d\mathbf{r}_1 \frac{n_{\sigma_1}(\mathbf{r}_1, t)}{|\mathbf{r} - \mathbf{r}_1|} \quad (9)$$

is electron-electron Coulomb interaction, and

$$v_\sigma^{\text{xc}}(\mathbf{r}, t) = \frac{\delta A^{\text{xc}}[n]}{\delta n_\sigma(\mathbf{r}, t)} \quad (10)$$

is the exchange-correlation potential. Here,  $A^{\text{xc}}[n]$  is the exchange-correlation action, which should be defined on the Keldysh contour.<sup>84</sup> In Eqs. (9) and (10),  $n_\sigma(r, t)$  is an electron density of spin  $\sigma$  in position  $\mathbf{r}$  at time  $t$ .

Below, we will represent molecular electron subspace in some finite basis set  $\{\phi_{i\sigma}\}$ , where  $i$  is some quantum number (or set of quantum numbers) and  $\sigma$  is spin. As a basis, one can use atomic or molecular single-particle states (orbitals), or any other convenient basis set. In this basis set representation,

$$\hat{\psi}_\sigma(\mathbf{r}) = \sum_i \hat{c}_{i\sigma} \phi_{i\sigma}(\mathbf{r}), \quad (11)$$

$$\hat{\psi}_\sigma^\dagger(\mathbf{r}) = \sum_i \hat{c}_{i\sigma}^\dagger \phi_{i\sigma}^*(\mathbf{r}), \quad (12)$$

where  $\hat{c}_{i\sigma}$  ( $\hat{c}_{i\sigma}^\dagger$ ) is electron annihilation (creation) operator for state  $i\sigma$ . Kinetic energy and potentials in Eqs. (7)–(10) become matrices in Hilbert space. Similar basis set representation will be used for electrons in contacts.

### III. DENSITY MATRIX FORMULATION OF NEGF

Central quantity of interest within NEGF is an electron GF, defined on the Keldysh contour as

$$G_{ij\sigma}(\tau, \tau') = -i \langle T_c \hat{c}_{i\sigma}(\tau) \hat{c}_{j\sigma}^\dagger(\tau') \rangle, \quad (13)$$

where  $\tau$  and  $\tau'$  are contour variables,  $T_c$  is a contour ordering operator, and operators  $c_{i\sigma}$  are given in the Heisenberg representation. Applying standard perturbation theory and assuming that initial correlations died out, one arrives at the Dyson equation on the contour

$$\left[ i \frac{\partial}{\partial \tau} - H \right] G(\tau, \tau') = \delta(\tau, \tau') + \int_c d\tau_1 \Sigma(\tau, \tau_1) G(\tau_1, \tau') \quad (14)$$

or relative to the other variable

$$G(\tau, \tau') \left[ -i \frac{\partial}{\partial \tau'} - H \right] = \delta(\tau, \tau') + \int_c d\tau_1 G(\tau, \tau_1) \Sigma(\tau_1, \tau'). \quad (15)$$

In Eqs. (14) and (15),  $H$  is Hamiltonian of the part of the system under study, while  $\Sigma$  is self-energy (SE) which represents influence of all other parts (and processes). Here and below, we suppress matrix indices keeping in mind that Hamiltonian, GFs, and SEs are matrices in the Hilbert space. In the model introduced in Sec. II,  $H$  corresponds to  $H_M$  [Eq. (6)] and  $\Sigma$  represents contacts and coupling to them [Eqs. (4) and (5)],

$$\Sigma_{ij\sigma}(\tau_1, \tau_2) = \sum_{K=L,R} \sum_{k \in K} V_{ik,\sigma} g_{k\sigma}(\tau_1, \tau_2) V_{kj,\sigma}, \quad (16)$$

where  $g_{k\sigma}(\tau_1, \tau_2) = -i \langle T_c \hat{c}_{k\sigma}(\tau_1) \hat{c}_{k\sigma}^\dagger(\tau_2) \rangle$  is GF for free electrons in the contacts. Generally,  $\Sigma$  should include also contributions from many-body processes, such as electron-electron interaction in Eq. (6); however, in an attempt to combine NEGF with TDDFT, the last is introduced through potentials (9) and (10) in the Kohn-Sham Hamiltonian [Eq. (7)].

In what follows, we will need lesser projection of Eqs. (14) and (15),

$$\left[ i \frac{\partial}{\partial t} - H \right] G^<(t, t') = \int_{-\infty}^{+\infty} dt_1 [\Sigma^r(t, t_1) G^<(t_1, t') + \Sigma^<(t, t_1) G^a(t_1, t')], \quad (17)$$

$$G^<(t, t') \left[ -i \frac{\partial}{\partial t'} - H \right] = \int_{-\infty}^{+\infty} dt_1 [G^<(t, t_1) \Sigma^a(t_1, t') + G^r(t, t_1) \Sigma^<(t_1, t')], \quad (18)$$

and retarded projection of Eq. (14)

$$\left[ i \frac{\partial}{\partial t} - H \right] G^r(t, t') = \delta(t - t') + \int_{-\infty}^{+\infty} dt_1 \Sigma^r(t, t_1) G^r(t_1, t'), \quad (19)$$

while advanced GF is

$$G_{ij\sigma}^a(t, t') = [G_{ji\sigma}^r(t', t)]^*. \quad (20)$$

Note,  $t$  and  $t'$  in Eqs. (17)–(20) are time variables. In order to get time-dependent solution (without initial correlations) within NEGF, one has to solve Eqs. (17) and (19) simultaneously, while SE should also represent electron-electron interaction.

While in NEGF, one deals with retarded and lesser GFs,

$$G_{ij\sigma}^<(t, t') = i \langle \hat{c}_{j\sigma}^\dagger(t') \hat{c}_{i\sigma}(t) \rangle, \quad (21)$$

central object of TDDFT is single-electron density matrix (DM),

$$\rho_{ij\sigma}(t) = \langle \hat{c}_{j\sigma}^\dagger(t) \hat{c}_{i\sigma}(t) \rangle \equiv -i G_{ij\sigma}^<(t, t). \quad (22)$$

Note that rigorous foundations of TDDFT formalism<sup>66</sup> establish correspondence only between densities of real and non-interacting (Kohn-Sham) systems. However, in practice non-diagonal elements of the Kohn-Sham DMs are also used in calculations of optical properties. Moreover, approaches explicitly utilizing DM within time-dependent functional theory (TDDMFT) were also proposed.<sup>85–87</sup>

Time evolution of DM,

$$\frac{\partial}{\partial t} \rho(t) = -i \left[ \frac{\partial}{\partial t} G^<(t, t') + \frac{\partial}{\partial t'} G^<(t, t') \right]_{t=t'}, \quad (23)$$

can be obtained from Eqs. (17) and (18) (approximately) expressed in terms of  $G^<(t, t)$  only. In order to do so, we employ generalized Kadanoff-Baym ansatz<sup>88</sup> (GKBA) in the right side of Eqs. (17) and (18), thus partly loosing nonlocality in time. This leads to

$$\begin{aligned} & i \frac{\partial}{\partial t} G^<(t, t) - [H; G^<(t, t)] \\ & - \int_{-\infty}^{+\infty} dt_1 [\Sigma^r(t, t_1) G^<(t_1, t_1) - G^<(t_1, t_1) \Sigma^a(t_1, t)] \\ & = \int_{-\infty}^{+\infty} dt_1 [G^r(t, t_1) \Sigma^<(t_1, t) - \Sigma^<(t, t_1) G^a(t_1, t)]. \end{aligned} \quad (24)$$

Note that in the absence of contacts (i.e., when all SEs are zero) and substituting  $H_M^{(KS)}$  [Eq. (7)] in place of  $H$ , we recover the standard TDDFT formulation in terms of DM.<sup>70</sup> Equation (24) together with Eqs. (19) and (20) are the approximate formulation for NEGF in terms of DM evolution. Below, we use these expressions in order to get first a steady-state transport through the junction and then optical response of such current-carrying junction to an external laser field.

Summarizing, NEGF-TDDFT is superior over NEGF-DFT due to the ability of treating both time-dependent transport and/or optical response of current-carrying molecular junctions. Still, as is indicated above, it misses nonlocality in time due to GKBA applied and keeps limitations of TDDFT. Also, fundamental question of combining the two ideologically different schemes remains. Ideological difference of the two approaches stems from the fact that NEGF is based on many-body approaches, while DFT methods are effectively single particle. Both approaches have rigid foundations and methods to take many-body correlations into account. These methods are different, however. Mixture of the two approaches when applied to one problem (usual situation in any NEGF-DFT or NEGF-TDDFT scheme) is at least questionable, since there is no proof that introduction of different correlations (in our case, effects of contacts and interactions on the bridge) by different methods within one problem is justified.

#### IV. STEADY-STATE CURRENT

First, we consider steady-state current through the junction in the absence of an external field,  $\mathbf{E}(t)=0$ . In the steady-state situation, GFs and SEs in Eqs. (19) and (24) depend on the time difference only, and DM becomes time independent,  $\bar{\rho}=-i\bar{G}^<(t=0)$ . In order to simplify notation, we further consider contacts within wide-band approximation (WBA), when

$$\Sigma^r(t_1-t_2) \approx -\frac{i}{2}\Gamma\delta(t_1-t_2). \quad (25)$$

Here,

$$\Gamma_{ij\sigma} = 2\pi \sum_{K=L,R} \sum_{k \in K} V_{ik\sigma} V_{kj\sigma} \delta(E - \varepsilon_{k\sigma}) \equiv \Gamma_{ij\sigma}^L + \Gamma_{ij\sigma}^R \quad (26)$$

is assumed to be constant, independent of energy  $E$ , and  $\varepsilon_{k\sigma}$  is energy of the state  $k\sigma$ . The WBA is valid when bandwidth in the contacts is the largest energy scale of the problem, which is the usual case for metallic electrodes. Note that WBA is used only in order to simplify notation. In principle, the approximation can be relaxed, then one has to deal with the full expression for the retarded (advanced) SE  $\Sigma^r(t_1-t_2)$  in place of  $-i\Gamma\delta(t_1-t_2)/2$ .

In this case, Eq. (24) yields [for brevity, we write  $\bar{G}^<$  keeping in mind that this is  $\bar{G}^<(t=0)$ ]

$$\begin{aligned} i\frac{\partial}{\partial t}\bar{G}^< - [\bar{H}; \bar{G}^<] + \frac{i}{2}\{\Gamma; \bar{G}^<\} \\ = \int_{-\infty}^{+\infty} dt_1 [\bar{G}^r(t-t_1)\Sigma^<(t_1-t) - \Sigma^<(t-t_1)\bar{G}^a(t_1-t)], \end{aligned} \quad (27)$$

where  $[\dots; \dots]$  is a commutator, while  $\{\dots; \dots\}$  is an anticommutator. Note,  $i(\partial/\partial t)\bar{G}^<=0$  and is written here only in order to keep similarity to the structure to Eq. (24). Here,

$$\bar{H}_{ij\sigma} = (H_M^{(KS)}[\bar{\rho}])_{ij\sigma} = h_{ij\sigma} + \bar{v}_{ij\sigma}^{\text{cl}} + \bar{v}_{ij\sigma}^{\text{xc}}, \quad (28)$$

with

$$h_{ij\sigma} = \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left[ -\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}^2} - v^{\text{ext}}(\mathbf{r}) \right] \phi_{j\sigma}(\mathbf{r}), \quad (29)$$

$$\bar{v}_{ij\sigma}^{\text{cl}} = \sum_{m,n\sigma'} (ij\sigma | nm\sigma') \bar{\rho}_{mn\sigma'}, \quad (30)$$

$$\begin{aligned} (ij\sigma | nm\sigma') &= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_{i\sigma}^*(\mathbf{r}_1) \phi_{j\sigma}(\mathbf{r}_1) \\ &\times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{n\sigma'}^*(\mathbf{r}_2) \phi_{m\sigma'}(\mathbf{r}_2). \end{aligned} \quad (31)$$

Note that  $\bar{v}^{\text{xc}}$  generally is not a ground state xc functional. In order to estimate it, one can follow the approach described in Ref. 92 and utilize formal equivalence (in particular cases) between partitionless TDDFT and partitioned NEGF schemes for the case of established steady-state current.<sup>78</sup>

For details of approximate way to estimate  $\bar{v}^{\text{xc}}$ , see Appendix.

Fourier transform (FT) of lesser SE entering Eq. (27) is

$$\Sigma^<(E) = i[f_L(E)\Gamma^L + f_R(E)\Gamma^R], \quad (32)$$

where  $f_K(E)$  is the Fermi distribution in the contact  $K$ , and retarded GF  $\bar{G}^r$  can be obtained from FT of Eq. (19),

$$\bar{G}^r(E) = [E - \bar{H} + i\Gamma/2]^{-1}. \quad (33)$$

Note that chemical potentials in the contacts should be shifted to take into account xc response to bias induced field.<sup>77</sup>

Integral version of Eq. (27) (Keldysh equation),

$$\bar{G}^<(t=0) = \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \bar{G}^r(E) \Sigma^<(E) \bar{G}^a(E), \quad (34)$$

together with Eq. (33) yield the standard NEGF-DFT approach to steady-state transport. Note, however, that in the last case,  $\bar{v}_{\text{xc}}$  is substituted by ground state xc potential, and xc corrections to chemical potentials of the contacts are neglected.

#### V. LINEAR OPTICAL RESPONSE

Here, we consider linear optical response to weak external laser field  $\mathbf{E}(t)$ . In contrast to previous TDDFT considerations<sup>70,71</sup> the response is calculated on top of non-equilibrium steady state (rather than ground state) of the system.

Upon introduction of the time-dependent external field, Eqs. (19) and (24) yield (within WBA)

$$\begin{aligned} i\frac{\partial}{\partial t}G^<(t,t) - [H; G^<(t,t)] + \frac{i}{2}\{\Gamma; G^<(t,t)\} \\ = \int_{-\infty}^{+\infty} dt_1 [G^r(t,t_1)\Sigma^<(t_1-t) - \Sigma^<(t-t_1)G^a(t_1,t)], \end{aligned} \quad (35)$$

$$G^r(t,t') = \bar{G}^r(t-t') + \int_{-\infty}^{+\infty} dt_1 \bar{G}^r(t-t_1)[H - \bar{H}]G^r(t_1,t'). \quad (36)$$

Note, in Eq. (35), we assume that contacts are not influenced by an external field (SEs are the same), and Eq. (36) is an integral variant of Eq. (19). Here,

$$H_{ij\sigma} = (H_M^{(KS)}[\rho(t)])_{ij\sigma} = h_{ij\sigma} + v_{ij\sigma}^{\text{cl}}(t) + v_{ij\sigma}^{\text{xc}}(t) - \boldsymbol{\mu}_{ij\sigma} \cdot \mathbf{E}(t), \quad (37)$$

with  $h_{ij\sigma}$  defined in Eq. (29),  $v_{ij\sigma}^{\text{cl}}(t)$  defined similar to Eq. (30) with  $\bar{\rho}$  replaced by  $\rho(t)$ ,  $v_{ij\sigma}^{\text{xc}}(t)$  is xc potential when both bias and external optical fields are applied to the junction, and the matrix element of molecular dipole,

$$\boldsymbol{\mu}_{ij\sigma} = \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \mathbf{r} \phi_{j\sigma}(\mathbf{r}), \quad (38)$$

$\bar{H}$  is defined in Eq. (28)

Assuming that external optical field is a weak perturbation, we linearize Eqs. (35) and (36) in  $\mathbf{E}(t)$ . Introducing response to the field,

$$\delta G^<(t, t) = G^<(t, t) - \bar{G}^< \equiv i \delta \rho(t), \quad (39)$$

$$\delta G^{r,a}(t, t') = G^{r,a}(t, t') - \bar{G}^{r,a}(t - t'), \quad (40)$$

linearizing Eqs. (35) and (36) in the field and response to it, and subtracting Eq. (27) from the linearized version of Eq. (35), we obtain

$$\begin{aligned} i \frac{\partial}{\partial t} \delta G^<(t, t) - [\bar{H}; \delta G^<(t, t)] + \frac{i}{2} [\Gamma; \delta G^<(t, t)] \\ - [\delta v^{\text{cl}}(t) + \delta v^{\text{xc}}(t); \bar{G}^<] + \mathbf{E}(t) [\boldsymbol{\mu}; \bar{G}^<] \\ = \int_{-\infty}^{+\infty} dt_1 [\delta G^r(t, t_1) \Sigma^<(t_1 - t) - \Sigma^<(t - t_1) \delta G^a(t_1, t)], \end{aligned} \quad (41)$$

$$\begin{aligned} \delta G^r(t, t') = \int_{-\infty}^{+\infty} dt_1 \bar{G}^r(t - t_1) [\delta v^{\text{cl}}(t_1) + \delta v^{\text{xc}}(t_1) \\ - \mathbf{E}(t_1) \boldsymbol{\mu}] \bar{G}^r(t_1 - t'). \end{aligned} \quad (42)$$

Here,

$$\delta v_{ij\sigma}^{\text{cl}}(t) = v_{ij\sigma}^{\text{cl}}(t) - \bar{v}_{ij\sigma}^{\text{cl}} = \sum_{m,n,\sigma'} (ij\sigma | nm\sigma') \delta \rho_{mn\sigma'}(t), \quad (43)$$

$$\begin{aligned} \delta v_{ij\sigma}^{\text{xc}}(t) = v_{ij\sigma}^{\text{xc}}(t) - \bar{v}_{ij\sigma}^{\text{xc}} \\ \approx \sum_{m,n,\sigma'} \int_{-\infty}^{+\infty} dt_1 f_{ij\sigma, nm\sigma'}^r(t - t_1) \delta \rho_{mn\sigma'}(t_1), \end{aligned} \quad (44)$$

where superscript  $r$  on xc response function  $f^r(t - t_1)$  indicates its retarded character, i.e., for  $t < t_1$ ,  $f^r(t - t_1) = 0$ . Since steady state can be (approximately) mapped to an effective equilibrium,<sup>89-91</sup>  $\delta v^{\text{xc}}(t)$ , in principle, can be estimated following procedure of Ref. 92 when equilibrium is understood as an effective equilibrium corresponding to a particular steady state.

Substituting Eq. (42) and its advanced analog into Eq. (41) and rearranging terms so that all source terms (terms containing external field) are in the right-hand side, we obtain final result, which in Liouville space is given by

$$\begin{aligned} \left[ i \frac{\partial}{\partial t} - L_0 \right] \delta \rho^<(t) - \int_{-\infty}^{+\infty} dt_1 L_1^r(t - t_1) \delta \rho(t_1) \\ = \int_{-\infty}^{+\infty} dt_1 \mathcal{E}^r(t - t_1) \mathbf{E}(t_1), \end{aligned} \quad (45)$$

where superscript  $r$  again indicates retarded character of the corresponding functions. Fourier transform of Eq. (45) is

$$[\omega - L_0 - L_1^r(\omega)] \delta \rho(\omega) = \mathcal{E}^r(\omega) \mathbf{E}(\omega). \quad (46)$$

Here, Markovian part of the Liouvillian is

$$\begin{aligned} [L_0]_{ij\sigma, mn\sigma'} = \left\{ \left[ \bar{H}_{im\sigma} - \frac{i}{2} \Gamma_{im\sigma} \right] \delta_{nj} \right. \\ \left. - \left[ \bar{H}_{nj\sigma} + \frac{i}{2} \Gamma_{nj\sigma} \right] \delta_{im} \right\} \delta_{\sigma\sigma'}, \end{aligned} \quad (47)$$

frequency-dependent Liouvillian is

$$\begin{aligned} [L_1^r(\omega)]_{ij\sigma, mn\sigma'} \\ = \sum_p [f_{ip\sigma, nm\sigma'}^r(\omega) \bar{\rho}_{pj\sigma} - \bar{\rho}_{ip\sigma} f_{pj\sigma, nm\sigma'}^r(\omega)] \\ - i \sum_{p,q,r} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \{ \bar{G}_{ip\sigma}^r(E + \omega) \bar{G}_{qr\sigma}^r(E) \Sigma_{rj\sigma}^<(E) \\ \times [(pq\sigma | nm\sigma') + f_{pq\sigma, nm\sigma'}^r(\omega)] \\ - \Sigma_{ir\sigma}^<(E) \bar{G}_{rq\sigma}^a(E) \bar{G}_{pj\sigma}^a(E - \omega) \\ \times [(qp\sigma | nm\sigma') + f_{qp\sigma, nm\sigma'}^r(\omega)] \}, \end{aligned} \quad (48)$$

and frequency-dependent coefficient of the source term is

$$\begin{aligned} \mathcal{E}_{ij}^r(\omega) = \sum_{p,\sigma} [\boldsymbol{\mu}_{ip\sigma} \bar{\rho}_{pj\sigma} - \bar{\rho}_{ip\sigma} \boldsymbol{\mu}_{pj\sigma}] - i \sum_{p,q,r,\sigma} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \\ \times [\bar{G}_{ip\sigma}^r(E + \omega) \bar{G}_{qr\sigma}^r(E) \Sigma_{rj\sigma}^<(E) \boldsymbol{\mu}_{pq\sigma} \\ - \Sigma_{ir\sigma}^<(E) \bar{G}_{rq\sigma}^a(E) \bar{G}_{pj\sigma}^a(E - \omega) \boldsymbol{\mu}_{qr\sigma}]. \end{aligned} \quad (49)$$

Since in the linear optical response, only particle-hole,  $\bar{\rho}_{ii\sigma} > \bar{\rho}_{jj\sigma}$ , and hole-particle,  $\bar{\rho}_{ii\sigma} < \bar{\rho}_{jj\sigma}$ , elements of  $\delta \rho_{ij\sigma}(t)$  are nonzero,<sup>93</sup> size of the matrix Eq. (46) can be reduced. Following Ref. 93, we order the basis, such that  $i < j$  for  $\bar{\rho}_{ii\sigma} \geq \bar{\rho}_{jj\sigma}$ , and divide  $\delta \rho(t)$  into particle-hole and hole-particle parts. Introducing matrices in the ordered basis, so that  $i < j$  and  $m < n$ ,

$$A_{ij\sigma, mn\sigma'}(\omega) = [L_0 + L_1^r(\omega)]_{ij\sigma, mn\sigma'}, \quad (50)$$

$$B_{ij\sigma, mn\sigma'}(\omega) = [L_0 + L_1^r(\omega)]_{ij\sigma, nm\sigma'}, \quad (51)$$

and using general relations,

$$\delta \rho_{ij\sigma}(\omega) = \delta \rho_{ji\sigma}^*(-\omega), \quad (52)$$

$$[L_0]_{ij\sigma, mn\sigma'} = -[L_0]_{ji\sigma, nm\sigma'}^*, \quad (53)$$

$$[L_1^r(\omega)]_{ij\sigma, mn\sigma'} = -[L_1^r(-\omega)]_{ji\sigma, nm\sigma'}^*, \quad (54)$$

$$\mathcal{E}_{ij}^r(\omega) = -[\mathcal{E}_{ji}^r(-\omega)]^*, \quad (55)$$

we get matrix equation of the form

$$\begin{aligned} \begin{bmatrix} \omega - \mathbf{A}(\omega) & -\mathbf{B}(\omega) \\ \mathbf{B}^*(-\omega) & \omega + \mathbf{A}^*(-\omega) \end{bmatrix} \begin{bmatrix} \delta \rho(\omega) \\ \delta \rho^*(-\omega) \end{bmatrix} \\ = \begin{bmatrix} \mathbf{S}^r(\omega) \\ -[\mathbf{S}^r(-\omega)]^* \end{bmatrix}, \end{aligned} \quad (56)$$

where

$$\mathbf{S}^r(\omega) \equiv \boldsymbol{\mathcal{E}}^r(\omega)\mathbf{E}(\omega). \quad (57)$$

Equation (56) is reduced dimension form of Eq. (46). In the case when contacts are absent and real molecular orbitals are chosen as a basis, matrices  $\mathbf{M}=\{\mathbf{A}, \mathbf{B}, \mathbf{S}^r\}$  satisfy

$$\mathbf{M}^*(-\omega) = \mathbf{M}(\omega) \quad (58)$$

and Eq. (56) reduces to the result derived within TDDFT approach previously.<sup>71</sup>

Polarization of the molecule is

$$P_{\alpha}(t) = \text{Tr}[\mu_{\alpha}\delta\rho(t)] = \sum_{\beta} \int_{-\infty}^t dt_1 R_{\alpha\beta}^{(1)}(t-t_1) E_{\beta}(t_1), \quad (59)$$

where  $\alpha, \beta=(x, y, z)$ ,  $R_{\alpha\beta}^{(1)}(t-t_1)$  is the time-domain linear response function (tensor in  $x, y, z$ ), and trace is over molecular electronic basis ( $\text{Tr}[\dots]=\sum_{i\sigma}[\dots]_{ii\sigma}$ ). Equation (46) yields for the frequency-domain linear polarizability [FT of  $R_{ij}^{(1)}(t-t_1)$ ],

$$\alpha_{\alpha\beta}(\omega) = -\text{Tr}\{\mu_{\alpha}[\omega - L_0 - L_1^r(\omega)]^{-1}\boldsymbol{\mathcal{E}}_{\beta}^r(\omega)\}. \quad (60)$$

Excitation energies (continuous spectrum of excitation energies) and oscillator strengths can be obtained from the poles and residues of the polarizability. In the absence of contacts, Eq. (60) reduces to the result derived previously.<sup>70</sup>

## VI. CONCLUSION

We discuss correspondence between NEGF and TDDFT approaches and derive approximate DM representation for NEGF equations. Thus, derived NEGF-TDDFT approach is superior over NEGF-DFT due to ability to treat both time-dependent transport and/or optical response of current-carrying molecular junctions. However, it partially misses nonlocality in time, inherent to NEGF. Also, fundamental question of combining the two ideologically different schemes (NEGF and TDDFT) remains open. We further propose a practical scheme for calculation of linear optical response of current-carrying molecular junctions. Situation considered corresponds to the case when an electron transport through the junction is much faster than the characteristic time of an external laser field (e.g., a pulse length).

First, we derive expression for the steady-state current through the junction within NEGF-TDDFT scheme and discuss its correspondence to the TDDFT-NEGF approaches to time-dependent transport of Refs. 59–61 and 77–79. Formal equivalence of NEGF-TDDFT and TDDFT-NEGF schemes in the case of established steady-state flux permits us to propose a way to estimate xc potential and, thus, go beyond ground state xc potential implemented in the standard NEGF-DFT transport schemes.

After that, we consider response of such current-carrying junction to weak external laser fields. We derive expressions for linear response and polarizability, which in the absence of contacts reduce to previously obtained TDDFT results for optical response of isolated molecules. The presence of the contacts introduces memory in both Liouvillian and source terms due to external field. Equation for response DM is then expressed in reduced (particle-hole and hole-particle) basis, which allows direct comparison to corresponding isolated molecule expression obtained previously.

The proposed approach allowing to calculate optical response of current-carrying junctions is a first step in direction of *ab initio* calculations of such kind, with the final goal to go beyond model based studies of optical properties of current-carrying junctions available in the literature. Development of such *ab initio* schemes is especially important in light of experimental data on optoelectronic properties of molecular junctions which start to appear.<sup>17–24</sup> In contrast to optical response of an isolated molecule, the presence of contacts will smear discrete excitation spectrum into a continuous one, which is in complete analogy to smearing of discrete energy spectrum of isolated molecule into continuous density of states upon attaching to the contacts. The presence of contacts also allows for charge transfer transitions upon optical excitation—process absent in the isolated molecule case, and thus, changing the optical response of the molecule. Finally, nonequilibrium character of the junction will alternate optical response. An obvious change is the presence of electronic density in an extended energy region, defined by difference of electrochemical potentials of the two contacts, opposed to well-defined ground state energy in the case of isolated molecule. For example, this may lead to appearance of additional (inverse) Raman scattering channel (situation when initial and final electronic state is lowest unoccupied MO rather than HOMO in the isolated molecule case) and to interference between the two (normal and inverse) channels, as is discussed in detail elsewhere.<sup>94</sup>

Consideration of situation, when time of electron tunneling and characteristic time of external field change are comparable, is a subject of future studies.

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## APPENDIX: APPROXIMATE WAY TO ESTIMATE $\bar{v}^{xc}$

Here, we discuss an approximate way to estimate  $\bar{v}^{xc}$  for current-carrying molecular junction in steady state. We follow approach by van Leeuwen,<sup>92</sup> where connection between xc potential and standard diagrammatic technique was established. Reference 92 considers a system both within full many-body approach and within TDDFT, where true Hamiltonian  $\hat{H}$  is replaced by fictitious single-particle Kohn-Sham Hamiltonian  $\hat{H}^{(KS)}$  with some xc potential  $v^{xc}$  to be found. Then, adiabatic switching on of the interaction,  $\hat{H} - \hat{H}^{(KS)}$ , is considered, which leads to connection between full many-body GF  $G$  and single-particle Kohn-Sham GF  $G_{KS}$  in the form

$$\begin{aligned}
G(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) &= G_{\text{KS}}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) + \int d\mathbf{r}_3 \int_c d\tau_3 \int d\mathbf{r}_4 \int_c d\tau_4 \\
&\times G_{\text{KS}}(\mathbf{r}_1, \tau_1; \mathbf{r}_3, \tau_3) [\Sigma_{\text{xc}}(\mathbf{r}_3, \tau_3; \mathbf{r}_4, \tau_4) \\
&- \delta(\mathbf{r}_3 - \mathbf{r}_4) \delta(\tau_3, \tau_4) v^{\text{xc}}(\mathbf{r}_3, \tau_3)] G(\mathbf{r}_4, \tau_4; \mathbf{r}_2, \tau_2), \quad (\text{A1})
\end{aligned}$$

with  $\Sigma_{\text{xc}}$  being xc part of the SE due to electron-electron interaction. Since the two approaches are assumed to give the same electron density,

$$n(\mathbf{r}, t) = -iG^<(\mathbf{r}, t; \mathbf{r}, t) = -iG_{\text{KS}}^<(\mathbf{r}, t; \mathbf{r}, t), \quad (\text{A2})$$

lesser projection of Eq. (A1) provides a (self-consistent) expression for xc potential  $v^{\text{xc}}$  in terms of SE  $\Sigma_{\text{xc}}$ ,

$$\begin{aligned}
&\int d\mathbf{r}_1 \int_{-\infty}^{+\infty} dt_1 [G_{\text{KS}}(\mathbf{r}, t; \mathbf{r}_1, t_1) v^{\text{xc}}(\mathbf{r}_1, t_1) G(\mathbf{r}_1, t_1; \mathbf{r}, t)]^< \\
&= \int d\mathbf{r}_1 \int_{-\infty}^{+\infty} dt_1 \int d\mathbf{r}_2 \int_{-\infty}^{+\infty} dt_2 \\
&\times [G_{\text{KS}}(\mathbf{r}, t; \mathbf{r}_1, t_1) \Sigma_{\text{xc}}(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) G(\mathbf{r}_2, t_2; \mathbf{r}, t)]^<, \quad (\text{A3})
\end{aligned}$$

where

$$[G_{\text{KS}} v^{\text{xc}} G]^< = G_{\text{KS}}^< v^{\text{xc}} G^a + G_{\text{KS}}^r v^{\text{xc}} G^<, \quad (\text{A4})$$

$$[G_{\text{KS}} \Sigma_{\text{xc}} G]^< = G_{\text{KS}}^< \Sigma_{\text{xc}}^a G^a + G_{\text{KS}}^r \Sigma_{\text{xc}}^< G^a + G_{\text{KS}}^r \Sigma_{\text{xc}}^r G^<. \quad (\text{A5})$$

Equation (A3) is our starting point.

Now, we consider a situation of established steady-state current in the system. In this case, it was shown that  $v^{\text{xc}}$  becomes constant far from the device region.<sup>78</sup> Accordingly, we formally partition the system into three parts: two contacts ( $K=L, R$ ), where  $v^{\text{xc}}$  is constant, and device (molecule,  $M$ ), where it varies in space. Then, integral over space in the left of Eq. (A3) splits into two parts (integration over contacts  $V_K$  and over device  $V_M$ ), while double space integral in the right will have four contributions: two over  $V_K$  and  $V_M$  and two mixed ones. The last may be neglected (especially when device is well separated from the contacts), taking into account relatively short range of xc interaction. This approximation yields additive (in  $K$  and  $M$ ) structure of Eq. (A3) and obviously, one can equate corresponding parts separately. As a result, one gets for the device region only expression similar to Eq. (A3), where  $v^{\text{xc}}$  is time independent and where GFs are restricted to the device region only. As was demonstrated in Ref. 78, the last are given formally from the usual NEGF expressions for GFs of the device region in terms of SEs due to coupling to the contacts, when appropriate constant shift of chemical potentials in the contacts due to xc response is taken into account. Moreover, while this shift generally may depend on the history of appearance of the steady state, in local-density approximation, it depends only on the instantaneous local density and has no memory at all;<sup>78</sup> i.e., instantaneous (and constant in time) potential and instantaneous (and constant in time) density uniquely define each other. In this case, we can assume that the correct

(shifted by xc response) chemical potentials in the contacts are some predefined boundary conditions, as is usually done within NEGF, which determines situation in the device region. In other words, we assume equivalence of partitioned NEGF and partitionless TDDFT approaches in this case. Then, after introducing some basis within the device region (so that GFs, SEs, and  $v^{\text{xc}}$  are matrices in Hilbert space), Eq. (A3) yields

$$\int \frac{dE}{2\pi} [G_{\text{KS}}(E) \bar{v}^{\text{xc}} G(E)]^< = \int \frac{dE}{2\pi} [G_{\text{KS}}(E) \Sigma_{\text{xc}}(E) G(E)]^<, \quad (\text{A6})$$

with GFs given by usual NEGF expressions. Equation (A6) is an approximate way to estimate  $\bar{v}^{\text{xc}}$  in the steady-state situation. Explicit expression for  $\bar{v}^{\text{xc}}$  is obtained by rewriting Eq. (A6) in Liouville space.

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