Научном већу Института за физику, Београд

Прегревица 118, Земун

Предмет: Реизбор Милоша Дражића у звање истраживач сарадник

Молба

Молим Научно веће Института за физику да покрене поступак за мој реизбор у звање истраживач сарадник.

Прилажем:

- Мишљење руководиоца
- Стручну биографију
- Списак објављених радова
- Кратак преглед научне активности
- Фотокопије објављених радова
- Уверење о уписаним докторским студијама
- Копију решења о претходном избору у звање истраживач сарадник

У Београду

01. 06. 2017. године

Подносилац молбе

Милош Дражић

Милош Дражић

Научном већу Института за физику, Београд

Предмет: Мишљење руководиоца пројекта о реизбору
Милоша Дражића у звање истраживач сарадник

Милош Дражић је од јануара 2011. године запослен у Институту за физику у Београду где је ангажован на пројекту основних истраживања ОИ171033 „Електронске, транспортне и оптичке особине нанофазних материјала“ Министарства просвете, науке и технолошког развоја. Докторске студије на Физичком факултету је уписао 2008. године. До сада је публиковао два рада у међународним часописима, један категорије $\mathbf{M}_{21}$ и један категорије $\mathbf{M}_{22}$. Докторска дисертација под називом „Теорија електронског транспорта кроз квантне тачке и молекуле“ је предата Физичком факултету Универзитета у Београду. Комисија за одбрану је сачинила позитиван референт и дисертација са рефератом је била на увиду јавности у периоду 12.4-12.5.2017. Одбрана дисертације се очекује током лета, или на јесен.

У закључку, с обзиром да су испуњени сви критеријуми прописани од стране Министарства просвете, науке и технолошког развоја, сагласан сам са покретањем поступка за реизбор Милоша Дражића у звање истраживач сарадник.

За састав Комисије предлажем:

1. др Радомир Жикић, научни саветник, Институт за физику, Београд
2. др Радош Гајић, научни саветник, Институт за физику, Београд
3. др Дејан Тимотијевић, научни саветник, Институт за физику, Београд
4. др Марко Спасеновић, виши научни сарадник, Институт за физику, Београд

У Београду,

01. 06. 2017. године

др Радомир Жикић

Руководилац пројекта ОИ171033

СТРУЧНА БИОГРАФИЈА

Образовање:

Милош Дражић рођен је 06.07.1978. у Земуну. Основну школу и Гимназију завршио је у Земуну.

Физички факултет у Београду уписао је школске 1997/1998. године. Дипломски рад на тему „Пфафијанска квантна Холова стања“ под менторством др Милице Миловановић одбранио је 2008. године са оценом 10 и стекао звање: дипломирани физичар. Физички факултет је завршио са просечном оценом 9,42.

Докторске студије на Физичком факултету на смеру „Физика кондензованог стања материје“, уписао је школске 2008/2009. године. Наставно научно веће Физичког факултета му је одобрило израду дисертације под називом „Теорија електронског транспорта кроз квантне тачке и молекуле“, а након њене израде и оцене Комисије, одређена је Комисија за одбрану.

Радно искуство:

Од краја 2008. до краја 2010. године као стипендиста Министарства науке био је ангажован на пројекту основних истраживања „Моделирање и нумеричке симулације сложених система“ (ОИ141035-руководилац др Александар Белић) а потом на пројекту основних истраживања „Динамика атомских, молекулских и мезоскопских система“ (ОИ141029-руководилац др Таско Гроздановˈ), као и на међународном FP7 пројекту „Nano Tools for Ultra Fast DNA Sequencing“ под руководством др Радомира Жикића.
Од јануара 2011. године као истраживач приправник запослен је на Институту за физику у Београду на пројекту основних истраживања (ОИ171033) „Електронске, транспортне и оптичке особине нанофазних материјала“ под руководством др Радомира Жикића. Научно веће Института за физику на седници одржаној 23. 09. 2014. донело је одлуку о стицању звања истраживач сарадник за сарадника Института за физику Милоша Дражића.

Кандидат до сада има два рада публикована у међународним часописима, категорија $\mathbf{M_{21}}$ и $\mathbf{M_{22}}$.

Списак публикација кандидата

Радови у врхунским међународним часописима (M21):

M. S. Dražić, Viktor Z. Cerovski, Radomir Zikic, *Theory of time-dependent nonequilibrium transport through a single molecule in a nonorthogonal basis set*, International Journal of Quantum Chemistry **117** (2017) 57-73.

Радови у истакнутим међународним часописима (M22):

M. S. Dražić , Viktor Z. Cerovski, and Radomir Žikić, *Non-equilibrium linear-response transport through quantum dot beyond time homogeneity at Hartree–Fock level*, Physica Status Solidi B **251** (2014) 1438–1450.

Саопштења са међународних скупова штампана у целини (M33):

N. N. Nedeljković, Lj. D. Nedeljković, M. D. Majkić, and **M. S. Dražić**, *Neutralization in Quantum Teleology of the Ion-Surface Interaction, Proc. 23rd Symposium on the Physics of Ionized Gases* – SPIG 2006, Contributed Papers and Abstracts of Invited Lectures, Topical Invited Lectures and Progress Reports, August 28th- September 1st 2006, Kopaonik, Serbia, Ed. Nenad S. Simonović, Bratislav P. Marinković and Ljupčo Hadžijevski (Belgrade, Institute of Physics) Contributed Paper, pp. 171 – 174.
http://www.phy.bg.ac.rs/~spig2006/Papers.htm#Section221

Саопштења са међународних скупова штампана у изводу (M34):

Miloš S. Dražić, Ivana Đurišić, Viktor Z. Cerovski and Radomir Žikić,
The nonorthogonality effects on capacitive behaviour of quantum dot, Serbian Ceramic Society Conference ADVANCED CERAMICS AND APPLICATION V: Program and the Book of Abstracts, pp. 46.

Саопштења са скупа националног значаја штампаног у целини (M63):

М. С. Дражић, В. З. Церовски и Р. Жикић, *Теорија микроскопског неравнотежног временски нехомогеног транспорта кроз молекул у линеарном одзиву у Хатри-Фоковој апроксимацији,* XII Конгрес физичара Србије, 28. април- 2. Мај 2013, Врњачка бања, Србија
Зборник радова-Усмена предавања, предавања по секцијама, усмена и постер саппштења
Постер у секцији: 3. Физика кондензоване материје и статистичка физика стр. 268-271.
http://www.dfs.rs/kongres/index.htm;
http://www.dfs.rs/kongres/Posteri_Kongres.pdf

Научна активност кандидата

Област истраживања Милоша Дражића је физике кондензованог стања, а посебно област квантног електронског транспорта кроз наноструктуре и молекуле/квантне тачке. У раду користи методе аналитичког и нумеричког описа квантног транспорта кроз молекул који је постављен између две проводне електроде, користећи формализам Гринових функција дефинисаних на Келдишовој контури као и теорију функционала густине (DFT-density functional theory).

Тема досадашњег истраживања је испитивање утицаја временски променљивог напона мале амплитуде на транспортне особине произвољног молекула који је постављен између две добро проводне електроде. Поступак који се уводи јесте да се познати и ефикасни DFT методи користе за рачунање временски хомогених Гринових функција као и стационарног потенцијала у молекулу.

Прва целина досадашњег рада се односила на одређивање динамичке корекције временски хомогених Гринових функција и стационарног потенцијала молекула *у Хартри-Фоковој апроксимацији у ортогоналном базису*. Фоков члан не уноси додатну грешку услед самоинтеракције, мимо оне коју практична употреба DFT-а производи. Уведена је саоусаглашена схема којом се динамичке корекције добијају у функцији временски хомогених Гринових функција, стационарног потенцијала и временски зависних потенцијала у електродама.

Друга целина се бави одређивањем динамичке корекције временски хомогених Гринових функција и стационарног потенцијала *у Хартријевој апроксимацији у неортогоналном базису*. Добијена веза између временски хомогених Гринових функција и њихових динамичких корекција отвара могућност нумеричког рачунања временски променљивих транспортних особина уз помоћ DFT-а, где су кодови стандардно базирани на коришћењу неортогоналних базисних скупова . Избегавањем ортогонализационих схема, карактеристичних за постојеће кодове који се користе у опису временски зависног транспорта, добијени резултат постаје погодан за рачунарску примену.

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FULL PAPER

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Theory of time-dependent nonequilibrium transport through a single molecule in a nonorthogonal basis set

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Abstract

A microscopic theory of nonequilibrium electronic transport under time-dependent bias through a molecule (or quantum dot) embedded between two semi-infinite metallic electrodes is developed in a nonorthogonal single-particle basis set using an *ab initio* formalism of Green's functions. The equilibrium zeroth order electron Green's function and self-energy are corrected by the corresponding time-inhomogeneous dynamical contributions derived in the Hartree approximation in a steady-state linear-response regime. Nonorthogonality contributes to dynamical response by introducing terms related to the central region-electrode interface, which appears only in the time-dependent case. The expression for current is also derived, where a nonorthogonality-induced dynamical correction gives an additional current that is not present in the orthogonal description. It is shown that the obtained expression for current is gauge-invariant and demonstrated that the omission of the additional current violates charge conservation. The additional current term vanishes in an orthogonal basis set.

KEYWORDS
time-dependent nonequilibrium electron transport

1 | INTRODUCTION

Numerical codes for the calculation of electronic transport are based on theories derived for orthogonal basis sets, but their implementation is realized using a nonorthogonal basis.[1,2] Numerical calculations of electronic transport under time-independent bias (i.e., steady state current) are invariant with respect to the choice of an orthogonal basis set. In the time-dependent (TD) case, a number of studies have demonstrated that the exact treatment of nonorthogonality (i.e., the use of a nonorthogonal basis without any transformations) in electronic transport is necessary for reliable results.[3–11] Since the early days of molecular orbital theory, there was a strong and prominent advocacy that nonorthogonality is not just a mathematical convenience.[12–17] The nonorthogonality of atomic orbital basis sets in electronic transport theories is typically handled via Löwdin[18] or lead-device orthogonalization.[19,20] However, Löwdin orthogonalization should be applied with care in the case of electronic transport of small open-shell systems since orthogonal functions have wider spatial extents than nonorthogonal functions.[21–23] Working directly with a nonorthogonal set is a natural alternative. In the present work, we develop a theory of TD nonequilibrium electronic transport through a molecule in a two-probe geometry formulated in a nonorthogonal basis set. The derived theory shows that new terms appear in the nonorthogonal case that are present in neither the orthogonal nor the time-independent case. The origin of these terms is in the displacement current, as will be shown in detail.

Atomic orbitals appear to be a natural basis for a theoretical description of atoms and molecules, but because of the nonorthogonality of single-electron states, a number of conceptual difficulties arise: discrepancy in the description of the chemical bonds strengths and the resonance molecular energies,[12–15] sensitivity of bond orders and charge densities in heteromolecules to the value of the overlap,[16] and dependence of the description of atomic force attraction of molecules.[17] Additionally, nonorthogonality is strongly involved in the population analysis problem.[24–28] Further, it leads to various possible Hamiltonian projections where the appearance of ambiguity in the obtained eigenvalues, local density of states and partial charges is caused by nonorthogonality between complementary subspaces.[29,30] In a recent series of papers,[31–33] many-body nonorthogonal theory was developed and applied to valence bond theory, giving the enhanced Wick's theorem.

In electronic transport theories, nonorthogonality has also been the subject of research, and Prange[3] considered it an elementary problem of thin-barrier tunneling of electrons, showing that conceptual difficulties with the transfer Hamiltonian can be overcome if one includes nonorthogonality between the states left and right of the barrier. In addition, nonorthogonality has been proposed as a solution to the problem of transferability appearing in orthogonal basis sets.[21,34,35] In his papers, Stuchebrukhov[4–6] developed a method for calculating the tunneling currents in electron transfer reactions. Because of the overlap of the atomic orbitals, the currents between atoms are nonuniquely defined. However, the balance equation demonstrated that the Mulliken population gives a well-defined theory. Important insights concerning the nonorthogonality related appearance of anti-resonances and its effects on a diminishing of electron transfer are achieved by introducing a revised Hilbert space by Emberly,[7,8] where new orthogonal states appears and the Hamiltonian matrix elements associated with noninteracting electrodes become energy-dependent. The anti-resonances can be reproduced within the tight binding scheme. This scheme has highlighted the equivalence between the nonorthogonal description with nearest neighbor hopping and the orthogonal description with second neighbor hopping.[9] Such a conclusion is known from earlier studies.[36] Additionally, the theoretical studies showed an asymmetric band structure and an effective mass decrease/increase at the band top/bottom. The asymmetry of the transmission curves relative to the band center was obtained using a tensorial approach,[10] which showed an energy dependence of the overlap effect. The nonorthogonality effects were examined on the T-junction structure[37] indicating that anti-resonance increases inside the band and at the band edges. Fransson[11] studied weak coupling of a dot and electrode in a nonorthogonal case for an extended Anderson Hamiltonian with a large Coulomb intra-dot repulsion by analyzing one-particle Hamiltonian of a single-barrier tunneling structure. In that case, transformation of the tunneling coefficient decreased the coupling strength. Thygesen[20] used the contravariant states of the central region and achieved mutual orthogonality of the electrode's and central region's subspaces, also known as electrode-central region orthogonalization. This result represents a generalization of Meir-Wingren[38] in the steady state case for an arbitrary type of interaction in the central region. Within the TD density functional theory (TDDFT) scheme, based on the hierarchical equations of motion, the problem of electrode-central region overlap is solved by embedding the overlap in the self-energy (SE). This transformation has been shown to be equivalent to electrode-central region orthogonalization.[19] The electrode's time dependency can be treated as a perturbation. In orthogonal formalism this dependence is removed by using a proper unitary transformation, giving a phase factor that is acquired in hopping between the electrodes and the central region. The nonorthogonal extension is developed[18] to approximate the exact noninteracting result[39] and has been shown to be applicable after the Hamiltonian orthogonalization. In strongly correlated electronic systems, Haldane used the nonorthogonality of localized states to construct an extensive Hilbert space of topological states of the quantum Hall effect, leading to a generalization of the Pauli Principle.[40]

This work studies quantum electronic transport in a standard two-probe geometry when the entire system is decomposed into three parts: the left and right electrodes and a molecule placed between them. In this case, the Hamiltonian and the overlap matrices have a block form induced by the system partition, where the central region Green's function (GF), electrode (surface) GF, and junction (interface) SE are obtained from the matrix equations within the formalism of nonequilibrium GFs, leading to computational applications in which the numerical codes rely on coupling with DFT to treat the interaction.[1,2,41–43] In this context, nonorthogonality was also shown to be a solution to the lack of transferability of orthogonal basis sets and instrumental to developing order-N methods.[22,23,44] The main advance made by this work is that the nonequilibrium theory of TD electronic transport is formulated starting from a nonorthogonal single-particle basis set. Our approach does not rely on electrode-central region orthogonalization[19,20] or on unitary transformation.[18] Instead, working directly with a nonorthogonal set, we obtained dynamical corrections of the GFs, the SE, and the current. The dynamical corrections of the GFs and SEs we will call the time-inhomogeneous (TIH). The effects of the displacement current are accounted for in a self-consistent manner. Our primary goal was to obtain linear dynamical corrections and responses accordingly. Additionally, our method can be perturbatively expanded to include nonlinearities. Since the TD contributions of the GFs and the SEs are obtained in terms of time translational invariant quantities, which we will call the time-homogeneous (TH) quantities, this method is suitable for use in combination with DFT. From a theoretical point of view, it is shown that nonorthogonality introduces a nontrivial contribution to the current caused by its coupling to the electrodes.

2 | METHODOLOGY

The formalism of GFs is the main method used to describe electronic transport through mesoscopic and nano-structures, particularly in systems of molecule/interface/dot between two metallic electrodes.[38,42,43,45–56] Such systems have been successfully coupled with both DFT[1,2,41–43] and TDDFT.[19,57–60] The significance of GFs in the description of quantum transport is that they provide both microscopic and phenomenological theories of the time-evolutions of many particle systems through their particle and current densities, momentums and energies. In the microscopic case considered here, a general form of the one-particle GF is defined through the field operators given in the Heisenberg picture.[61,62] From the equation of motion (EOM) of a one-particle GF, and in addition to the one-particle kinetic energy and external potential, there are two-body contributions caused by the Coulomb interaction, which is expressed by a two-particle GF, which indicate a BBGKY hierarchy.[61–64] In this work, interaction is treated at the level of the mean-field Hartree approximation[62,65] and is expressed in terms of characteristic potentials.[43,66–68] To obtain a closed-form GF equation, SE is introduced, which in its exact form can be perturbatively expanded to obtain approximations that conserve current, momentum and energy.[62,65] In the case of electronic transport, in addition to the particle-interaction related SE, there is an additional contribution associated with the coupling of the central region and the electrode: the junction (i.e., interface) SE.

Defined through the field operators, the GF depends on two time-position variables. The representation of the GF in a set of one-particle creation/annihilation operators requires an expansion of the field operators of the many-particle state over a basis of single-particle states. DFT based numerical calculations of electronic transport for time-independent bias expand wavefunctions in nonorthogonal basis sets,[1,2,41,69] which raises a question regarding the nature of the creation and annihilation operators; that is, what are the states created (annihilated) by these operators and how are related to the field expansion coefficients (functions).

When expanding an electronic wavefunction in a given nonorthogonal basis set, the relations between this set and the one created by the operators given in the field operator expansion concern the problem of the existence of a biorthonormal basis, where creation (annihilation) operators create (annihilate) the given nonorthogonal basis set state, leading to the conclusion (Riesz lemma) that the expansion functions are isomorphic to the space of linear functionals (the dual space),[70] and biorthonormalization is related to the inversion of the overlap matrix of the given basis.[71–74] There is a nonunique resolution of identity, which provides Hermitian projectors[29,75] only in the Löwdin case.[14,15]

2.1 | Hamiltonian

The Hamiltonian of Coulomb-interacting electrons in the second quantization formalism is

$$H=\int \hat{\psi}^{\dagger}(\mathbf{r})h(\mathbf{r}t)\hat{\psi}(\mathbf{r})d\mathbf{r}+\frac{e^2}{2}\int\int \hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})d\mathbf{r}d\mathbf{r}', \tag{1}$$

where the electron field operators satisfy the fermionic anti-commutation relations

$$\{\hat{\psi}(\mathbf{r}),\hat{\psi}^{\dagger}(\mathbf{r}')\}=\delta(\mathbf{r}-\mathbf{r}'),\ \{\hat{\psi}(\mathbf{r}),\hat{\psi}(\mathbf{r}')\}=0,\ \{\hat{\psi}^{\dagger}(\mathbf{r}),\hat{\psi}^{\dagger}(\mathbf{r}')\}=0, \tag{2}$$

and time dependency is introduced through one-particle contributions arising from TD external perturbation. For simplicity, spin indices are omitted and $\hbar=1$.

The system naturally decomposes into three coupled subsystems of left- and right-lead and the central region, with respective single-particle basis sets of $\{\psi_{i_\alpha}(\mathbf{r}),\alpha=L,R,i_\alpha=1,\ldots\}$ and $\{\psi_n(\mathbf{r}),n=1,\ldots\}$. The standard assumption is taken that there is no interaction between the leads. The central region consists of the molecule with the electrode termini (which will be defined more precisely in a later section).

2.2 | Nonorthogonal basis set field operator expansion

The completeness relations (i.e., resolution of identity) in a nonorthogonal single-particle basis set $\{|\psi_i\rangle\}$ is given by[70]

$$I=\sum_{ij}|\psi_i\rangle(S^{-1})_{ij}\langle\psi_j| \tag{3}$$

where S is the overlap matrix, $S_{ij}=\langle\psi_i|\psi_j\rangle$, of the corresponding two states.

In the system studied here S has a 3 × 3 block form that is naturally induced by the system decomposition into left-lead/dot/right-lead, where the blocks are matrices $S_{\alpha\beta},S_{\alpha C},S_{C\alpha},S_C$ with matrix elements equal to the overlaps of the lead-lead ($S_{i_\alpha j_\beta}$), lead-dot ($S_{i_\alpha n}$, S_{nj_α}) and dot-dot (S_{nm}) basis vectors.

To simplify the notation, the overlap matrix and its inverse can be presented as a covariant and contravariant tensor, respectively, where the tensor element S^{ij} equals the matrix element $(S^{-1})_{ij}$. The property $S^{-1}S=I$ gives the connection between the upper and lower indices $S^{ij}S_{jk}=\delta^i_k$, where the Einstein summation convention is used.

The introduction of S^{ij} now induces the contravariant basis-set,

$$|\psi^i\rangle=S^{ij}|\psi_j\rangle, \tag{4}$$

and the completeness identity in Equation 3 can now be written as

$$I=|\psi_i\rangle S^{ij}\langle\psi_j|=|\psi_i\rangle\langle\psi^i|=|\psi^i\rangle\langle\psi_i|, \tag{5}$$

or equivalently, the orthogonality of the covariant and contravariant states,

$$\langle\psi_i|\psi^j\rangle=\langle\psi^j|\psi_i\rangle=\delta^j_i, \tag{6}$$

which provides an interpretation of $\{|\psi^i\rangle\}$ as a biorthogonal basis.

Any operator O now has contravariant (O^{ij}), covariant (O_{ij}), and mixed (O^i_j) representations, which are connected through the metric tensors S_{ij} and S^{ij} in the standard fashion. In particular, Equation 3 gives expansions[76] for the electron field creation operator

$$\hat{\psi}^{\dagger}(\mathbf{r})=c_i^{\dagger}S^{ij}\psi_j^*(\mathbf{r})=c^{i\dagger}\psi_i^*(\mathbf{r}) \tag{7}$$

and annihilation operator,

$$\hat{\psi}(\mathbf{r})=\psi_i(\mathbf{r})S^{ij}c_j=c^i\psi_i(\mathbf{r}) \tag{8}$$

where the operators $c^{i\dagger}$ (c^i) create (annihilate) the corresponding one-particle state $|\psi_i\rangle=\psi_i(\mathbf{r})$, with anti-commutators

$$\{c^{i\dagger},c_j\}=\{c_j^{\dagger},c^i\}=\delta^i_j \tag{9}$$

$$\{c^i,c_j\}=\{c_j,c^i\}=0, \tag{10}$$

and the operators c_i ($c_i^{\dagger}$) create (annihilate) the state $|\psi^i\rangle=S^{ij}|\psi_i\rangle$, with the remaining anti-commutators

$$\{c^i,c^{j\dagger}\}=S^{ij},\ \{c^i,c^j\}=\{c^{i\dagger},c^{j\dagger}\}=0, \tag{11}$$

$$\{c_i,c_j^{\dagger}\}=S_{ij},\ \{c_i,c_j\}=\{c_i^{\dagger}c_j^{\dagger}\}=0. \tag{12}$$

The assumption of no-overlap between the leads can be simply stated as $S_{i_\alpha j_\beta}=0,\alpha\neq\beta$. However, nonorthogonality implies that $S^{i_\alpha j_\beta}$ does not necessarily vanish, since it is determined by the inverse of S.

2.3 | Green's functions in a nonorthogonal basis

GFs of the electronic system are defined as

$$G(\mathbf{r}t;\mathbf{r}'t')=-i\langle T_c(\hat{\psi}(\mathbf{r}t)\hat{\psi}^{\dagger}(\mathbf{r}'t'))\rangle, \tag{13}$$

where T_c represents time-ordering on the Keldysh contour,[61–63] with the equations of motion (EOM)

$$\begin{aligned}i\partial_t G(\mathbf{r}t;\mathbf{r}'t')&=\delta(t-t')\delta(\mathbf{r}-\mathbf{r}')+h(\mathbf{r}t)G(\mathbf{r}t;\mathbf{r}'t')\\&+\int d\mathbf{r}_1\int_c dt_1\Sigma^{\mathrm{int}}(\mathbf{r}t;\mathbf{r}_1t_1)G(\mathbf{r}_1t_1;\mathbf{r}'t'),\end{aligned} \tag{14}$$

$$i\partial_{t'}G(\mathbf{r}t;\mathbf{r}'t')=-\delta(t-t')\delta(\mathbf{r}-\mathbf{r}')-h(\mathbf{r}'t')G(\mathbf{r}t;\mathbf{r}'t')$$
$$-\int d\mathbf{r}_1\int_c dt_1 G(\mathbf{r}t;\mathbf{r}_1t_1)\Sigma^{\text{int}}(\mathbf{r}_1t_1;\mathbf{r}'t'), \tag{15}$$

where Σ^{int} is the Coulomb interaction SE and the time integration is along the Keldysh contour.

We proceed by using a contravariant representation of GF,

$$G(\mathbf{r}t,\mathbf{r}'t')=\psi_i(\mathbf{r})G^{ij}(t,t')\psi_j^*(\mathbf{r}'), \tag{16}$$

which is also used in numerical implementations in a time-independent regime.[1,2] This approach has the advantage that the Hamiltonian is represented in the given nonorthogonal basis; consequently, the screening in the dot region, where the interaction plays an important role, has an intuitive description.

The replacement of Equation 16 into the EOM Equations 14 and 15 gives

$$iS_{ij}\partial_t G^{jk}(t,t')=\delta(t-t')\delta_i^k+H_{ij}(t)G^{jk}(t,t')+\int_c dt_1\,\Sigma_{ij}^{\text{int}}(t,t_1)G^{jk}(t_1,t') \tag{17}$$

$$-i\partial_{t'}G^{ij}(t,t')S_{jk}=\delta(t-t')\delta_k^i+G^{ij}(t,t')H_{jk}(t')+\int_c dt_1\,G^{ij}(t,t_1)\Sigma_{jk}^{\text{int}}(t_1,t'),. \tag{18}$$

To emphasize the dot-leads structure Equation 17 can be written in block-form, standardly written as

$$\begin{bmatrix} S_L & S_{LC} & 0 \\ S_{CL} & S_C & S_{CR} \\ 0 & S_{RC} & S_R \end{bmatrix} i\partial_t \begin{bmatrix} G^L & G^{LC} & G^{LR} \\ G^{CL} & G^C & G^{CR} \\ G^{RL} & G^{RC} & G^R \end{bmatrix}(t,t')=$$
$$\delta(t-t')\begin{bmatrix} \delta_{i_L}^{i_L} & 0 & 0 \\ 0 & \delta_n^n & 0 \\ 0 & 0 & \delta_{i_R}^{i_R} \end{bmatrix}+\begin{bmatrix} H_L & H_{LC} & 0 \\ H_{CL} & H_C & H_{CR} \\ 0 & H_{RC} & H_R \end{bmatrix}(t)\begin{bmatrix} G^L & G^{LC} & G^{LR} \\ G^{CL} & G^C & G^{CR} \\ G^{RL} & G^{RC} & G^R \end{bmatrix}(t,t')$$
$$+\int_c dt_1\begin{bmatrix} \Sigma_L^{\text{int}} & \Sigma_{LC}^{\text{int}} & 0 \\ \Sigma_{CL}^{\text{int}} & \Sigma_C^{\text{int}} & \Sigma_{CR}^{\text{int}} \\ 0 & \Sigma_{RC}^{\text{int}} & \Sigma_R^{\text{int}} \end{bmatrix}(t,t_1)\begin{bmatrix} G^L & G^{LC} & G^{LR} \\ G^{CL} & G^C & G^{CR} \\ G^{RL} & G^{RC} & G^R \end{bmatrix}(t_1,t'), \tag{19}$$

where each letter in subscript/superscript of a matrix refers to a block formed by the covariant/contravariant indices of the subsystem marked by the letter and the zero block-matrices of H and Σ arise from the assumption of no interaction between different electrodes.[1,2,42] The similar block-matrix expression for GF EOM in t' (i.e., Equation 15) is straightforward to write, which we omit for brevity.

Projections of GF satisfy the trace property, $\int d\mathbf{r}G(\mathbf{r}t,\mathbf{r}t')=\text{Tr}\,G(t,t')$, in which the nonorthogonal basis adopts tensor notation for the subsystems,

$$\begin{aligned} &\int d\mathbf{r}\,G^{\alpha\beta}(\mathbf{r}t;\mathbf{r}t')=S_{i_\beta i_\alpha}G^{i_\alpha i_\beta}(t,t') \\ &\int d\mathbf{r}\,G^{\alpha C}(\mathbf{r}t;\mathbf{r}t')=S_{ni_\alpha}G^{i_\alpha n}(t,t') \\ &\int d\mathbf{r}\,G^{C\alpha}(\mathbf{r}t;\mathbf{r}t')=S_{i_\alpha n}G^{ni_\alpha}(t,t') \\ &\int d\mathbf{r}\,G^{C}(\mathbf{r}t;\mathbf{r}t')=S_{nm}G^{mn}(t,t'), \end{aligned} \tag{20}$$

where the l.h.s. are defined as Equation 16 over the set of basis vectors given by indices.

Electronic transport is described by the continuity equation

$$\partial_t n(\mathbf{r}t)+\nabla\mathbf{j}(\mathbf{r}t)=0, \tag{21}$$

where electron density and electron current are given, respectively, as

$$n(\mathbf{r}t)=-iG(\mathbf{r}t,\mathbf{r}t^+), \tag{22}$$

$$\mathbf{j}(\mathbf{r}t)=\frac{1}{2mi}(\nabla-\nabla')(-iG(\mathbf{r}t,\mathbf{r}'t^+))|_{\mathbf{r}=\mathbf{r}'}, \tag{23}$$

where t^+ implies the value of G obtained on the Keldysh contour.[61]

2.4 | Time-dependent external potential

The special case of great interest that is studied here concerns electrodes with good screening properties.[68] In this case, TD potentials are spatially constant in the electrodes because of screening, giving an overall shift of their energy levels. This is satisfied for metallic leads in a periodic external driving field of frequency below the leads plasma frequency.[48]

Near the molecule, the constant potential shift is violated and the TD potential profile along the transport direction changes depending on the injected and the induced TD charge. This defines the central region as the molecule together with parts of the electrodes where the screening occurs, and outside of which the TD potentials of the electrodes are unperturbed.

The induced charge generation restores the charge neutrality within the central region whose boundaries are determined by parts of the leads near the physical molecule where the potential begins to deviate from the bulk.[77–79] Time dependency in the central region and at its interface with the rest of the electrodes then arise from the dynamical contributions of the interaction SEs, Σ_C^{int} and $\Sigma_{C\alpha(\alpha C)}^{\text{int}}$, respectively, whereas the time dependency in the electrodes is integrated into their one-particle Hamiltonian.

The mean-field approximation for the interaction SE,

$$\Sigma_\alpha^{\text{int}}(t,t') \approx \Sigma_\alpha^{\text{int}}(t,t')\delta(t-t'), \tag{24}$$

introduces time-homogeneity of SEs, giving

$$H_\alpha(t)=H_\alpha+S_\alpha v_\alpha(t), \tag{25}$$

where a spatially uniform TD potential is introduced through the second term. The TD bias arises from the sum of an external field and the dynamical (TIH) contribution of the electrode's interaction SE. Furthermore, the mean-field approximation allows the inclusion of the interaction TH SE, $\Sigma_\alpha^{\text{int}}$, into the one-particle Hamiltonian Equation 25,

$$H_\alpha^{\text{tot}}(t)=H_\alpha+\Sigma_\alpha^{\text{int}}+S_\alpha v_\alpha(t). \tag{26}$$

The isolated electrode GFs, $G^{0\alpha}$, has matrix elements defined as

$$G^{0i_\alpha j_\alpha}(t,t')=-i\langle T_c c^{0i_\alpha}(t)c^{0j_\alpha\dagger}(t')\rangle, \tag{27}$$

with operators

$$c^{0i_\alpha}=S_\alpha^{i_\alpha j_\alpha}c_{j_\alpha},\ c^{0j_\alpha\dagger}=c_{i_\alpha}^\dagger S_\alpha^{i_\alpha j_\alpha}, \tag{28}$$

where the time evolution is governed by the evolution operator of Hamiltonian Equation 26,

$$c^{0i_\alpha}(t)=U^{\dagger}_{H^0_\alpha}(t,t_0)c^{0i_\alpha}U_{H^0_\alpha}(t,t_0), \tag{29}$$

with EOM,

$$\begin{aligned} i\partial_t U_{H^0_\alpha}(t,t_0)&=H^0_\alpha(t)U_{H^0_\alpha}(t,t_0)\\ H^0_\alpha(t)&=c^{0i_\alpha\dagger}[H^{\mathrm{tot}}_\alpha(t)]_{i_\alpha j_\alpha}c^{0j_\alpha}. \end{aligned} \tag{30}$$

At present, the steady-state regime is considered; therefore, the EOM of lead GFs, Equation 27, become

$$\begin{aligned} (S_\alpha\, i\overrightarrow{\partial_t}-H^{\mathrm{tot}}_\alpha(t))G^{0\alpha}(t,t')&=I^\alpha_\alpha\delta(t-t')\\ G^{0\alpha}(t,t')(i\overleftarrow{\partial_{t'}}\, S_\alpha+H^{\mathrm{tot}}_\alpha(t'))&=-I^\alpha_\alpha\delta(t-t'), \end{aligned} \tag{31}$$

which gives the following system of GF EOM for the whole system, which are decomposed into contributions from the subsystems,

$$\begin{aligned} G^{\alpha\beta}(t,t')&=G^{0\alpha}(t,t')\delta_{\alpha\beta}\\ &+\int_c\int_c G^{0\alpha}(t,t_1)\vec{V}_{\alpha C}(t_1,t_2)(G^{C\alpha}(t_2,t')\delta^\beta_\alpha+G^{C\beta}(t_2,t')(1-\delta^\alpha_\beta))dt_1dt_2 \end{aligned} \tag{32}$$

$$G^{C\alpha}(t,t')=\int_c G^C(t,t_1)\vec{V}_{C\alpha}(t_1,t_2)G^{0\alpha}(t_2,t')dt_1dt_2 \tag{33}$$

$$G^{\alpha C}(t,t')=\int_c G^{0\alpha}(t,t_1)\vec{V}_{\alpha C}(t_1,t_2)G^C(t_2,t')dt_1dt_2 \tag{34}$$

$$S_C i\partial_t G^C(t,t')=I^C_C\delta(t,t')+H_C G^C(t,t')+\int_c(\Sigma^{\mathrm{int}}_C(t,t_1)+\Sigma^{\mathrm{junct}}_C(t,t_1))G^C(t_1,t')dt_1 \tag{35}$$

$$\Sigma^{\mathrm{junct}}_C(t,t')=\sum_\alpha\Sigma^{\mathrm{junct}}_{C_\alpha}(t,t')=\sum_\alpha\int_c\int_c\vec{V}_{C\alpha}(t,t_1)G^{0\alpha}(t_1,t_2)\vec{V}_{\alpha C}(t_2,t')dt_1dt_2, \tag{36}$$

where

$$\begin{aligned} \vec{V}_{\alpha C}(t,t')&=\delta(t,t')(H_{\alpha C}-S_{\alpha C}i\overrightarrow{\partial_t})+\Sigma^{\mathrm{int}}_{\alpha C}(t,t')\\ \vec{V}_{C\alpha}(t,t')&=\delta(t,t')(H_{C\alpha}-S_{C\alpha}i\overrightarrow{\partial_t})+\Sigma^{\mathrm{int}}_{C\alpha}(t,t'). \end{aligned} \tag{37}$$

Similarly, the derivative over the time argument t' gives

$$\begin{aligned} G^{\alpha\beta}(t,t')&=\delta_{\alpha\beta}G^{0\alpha}(t,t')\\ &+\int_c\int_c G^{\alpha C}(t,t_1)(\overleftarrow{V}_{C\alpha}(t_1,t_2)G^{0\alpha}(t_2,t')\delta^\beta_\alpha+\overleftarrow{V}_{C\beta}(t_1,t_2)G^{0\beta}(t_2,t')(1-\delta^\alpha_\beta))dt_1dt_2 \end{aligned} \tag{38}$$

$$G^{C\alpha}(t,t')=\int_c\int_c G^C(t,t_1)\overleftarrow{V}_{C\alpha}(t_1,t_2)G^{0\alpha}(t_2,t')dt_1dt_2 \tag{39}$$

$$G^{\alpha C}(t,t')=\int_c\int_c G^{0\alpha}(t,t_1)\overleftarrow{V}_{\alpha C}(t_1,t_2)G^C(t_2,t')dt_1dt_2 \tag{40}$$

$$i\partial_{t'}G^C(t,t')S_C=-I^C_C\delta(t-t')-G^C(t,t')H_C-\int_c G^C(t,t_1)(\Sigma^{\mathrm{int}}_C(t_1,t')+\Sigma^{\mathrm{junct}}_C(t_1,t'))dt_1 \tag{41}$$

$$\Sigma^{\mathrm{junct}}_C(t,t')=\sum_\alpha\Sigma^{\mathrm{junct}}_{C_\alpha}(t,t')=\sum_\alpha\int_c\int_c\overleftarrow{V}_{C\alpha}(t,t_1)G^{0\alpha}(t_1,t_2)\overleftarrow{V}_{\alpha C}(t_2,t')dt_1dt_2, \tag{42}$$

where

$$\begin{aligned} \overleftarrow{V}_{\alpha C}(t,t')&=(H_{\alpha C}+i\overleftarrow{\partial_{t'}}\,S_{\alpha C})\delta(t,t')+\Sigma^{\mathrm{int}}_{\alpha C}(t,t')\\ \overleftarrow{V}_{C\alpha}(t,t')&=(H_{C\alpha}+i\overleftarrow{\partial_{t'}}\,S_{C\alpha})\delta(t,t')+\Sigma^{\mathrm{int}}_{C\alpha}(t,t'). \end{aligned} \tag{43}$$

Despite a similarity to the orthogonal states description,[48–50] there are some important differences. In addition to the use of a biorthogonal basis set, where the Hamiltonian and GFs are represented in dual basis sets, the hopping matrices now contain two additional terms: the mixed overlap matrices with time-derivative operators and the interaction SE projected onto the interface Equations 37 and 43. The appearance of the mixed overlap matrices is the result primarily known from steady state transport in the energy domain.[1,2,42] The interface interaction SEs affect the form of the junction SEs, Equations 36 and 42. The TD component of these interface interaction SEs, $\Sigma_{C\alpha(\alpha C)}$, contributes to the total induced potential within the region where charge neutrality is conserved. These dynamical corrections, originating in the dot-leads hopping terms (Equations 37 and 43) also affect the TD contributions of the junction SE (Equations 36 and 42) by making them different from the same quantities described in an orthogonal set.

2.5 | Coulomb interaction

In GFs formalism, the interaction SE represents the Coulomb (two-particle) interaction. The EOM (we take only the first time argument derivative since the second time argument derivative leads to the same result) of GF Equation 13 of the system described with Hamiltonian Equation 1 is[61,62]

$$\begin{aligned} i\partial_t G(\mathbf{r}t;\mathbf{r}'t')&=\delta(t-t')\delta(\mathbf{r}-\mathbf{r}')+h(\mathbf{r}t)G(\mathbf{r}t;\mathbf{r}'t')\\ &-i\int W(|\mathbf{r}-\mathbf{r}_1|)G_2(\mathbf{r}t,\mathbf{r}_1t;\mathbf{r}'t',\mathbf{r}_1t^+)d\mathbf{r}_1, \end{aligned} \tag{44}$$

where W is the Coulomb interaction and the two particle GF is

$$G_2(\mathbf{r}t,\mathbf{r}_1t_1;\mathbf{r}'t',\mathbf{r}_2t_2)=(-i)^2\langle T_c(\psi(\mathbf{r}t)\psi(\mathbf{r}_1t_1)\psi^\dagger(\mathbf{r}_2t_2)\psi^\dagger(\mathbf{r}'t'))\rangle. \tag{45}$$

The time argument t^+ in Equation 44 equals $t+\delta$ on the Keldysh contour for an infinitesimal δ. The interaction SE represents the Coulomb interaction via

$$\int\int_c\Sigma^{\mathrm{int}}(\mathbf{r}t;\mathbf{r}_1t_1)G(\mathbf{r}_1t_1;\mathbf{r}'t')d\mathbf{r}_1dt_1=-i\int W(|\mathbf{r}-\mathbf{r}_1|)G_2(\mathbf{r}t,\mathbf{r}_1t;\mathbf{r}'t',\mathbf{r}_1t^+)d\mathbf{r}_1, \tag{46}$$

The form of the SE depends on the procedure to acquire the two-particle GF expansion over the one-particle GFs. We consider the Hartree approximation, which is mean-field and leads to the following expansion of two-particle GF in terms of single-particle GFs[62]

$$G_2(\mathbf{r}t,\mathbf{r}_1t_1;\mathbf{r}'t',\mathbf{r}_2t_2)=G(\mathbf{r}t;\mathbf{r}'t')G(\mathbf{r}_1t_1;\mathbf{r}_2t_2), \tag{47}$$

giving

$$\begin{aligned} \Sigma^{\mathrm{int}}_{\mathrm{H}}(\mathbf{r}t;\mathbf{r}t)&=-i\int W(|\mathbf{r}-\mathbf{r}_1|)G^<(\mathbf{r}_1t;\mathbf{r}_1t)d\mathbf{r}_1,\\ G^<(\mathbf{r}_1t;\mathbf{r}_1t)&=G(\mathbf{r}_1t;\mathbf{r}_1t^+). \end{aligned} \tag{48}$$

Finally, we consider the linear-response regime of the molecule to the external bias, that is, that the dynamical corrections of equilibrium quantities will be small, and GF and SE can be separated,[43,49,50]

$$\begin{aligned} G(t,t')&=G(t-t')+g(t,t')\\ \Sigma(t,t')&=\Sigma(t-t')+\sigma(t,t'), \end{aligned} \tag{49}$$

into the TH quantities and additional TIH corrections represented by the first and second terms on the r.h.s., respectively.

This splits the system of the EOM Equations 31–37 into functions that consider TH and TIH contributions.

3 | RESULTS

The following subsections are devoted to a derivation for a closed system of equations of the entire system. The results are presented in the energy domain by Fourier transforms of the results obtained by application of Langreth rules,[63,80] where to simplify notation,[50] we drop explicitly writing the energy dependence; the bar over a quantity represents its dependence on $E+\omega$. The TIH quantities g and σ have $(E+\omega, E)$ dependence, and v_α, i_α in the energy domain indicate $v_\alpha(\omega), i_\alpha(\omega)$, respectively. The indices α, β, and ρ enumerate electrodes and are not tensor quantities; thus, there is no implicit summation when the same index is repeated. Finally, the index γ is often used in superscript to denote a type of GF, either retarded (R), lesser (<), or advanced (A).

3.1 | Time-homogeneous contributions

The TH contributions of the dot-leads interaction, Equations 36 and 37, are

$$\begin{gathered} V_{\alpha C}=H_{\alpha C}+\Sigma^{\text{int}}_{\alpha C}-ES_{\alpha C} \\ V_{C\alpha}=H_{C\alpha}+\Sigma^{\text{int}}_{C\alpha}-ES_{C\alpha} \\ \Sigma^{\text{junct}\gamma}_{C}=\sum_{\alpha}\Sigma^{\text{junct}\gamma}_{C_\alpha}=\sum_{\alpha}V_{C\alpha}G^{0\alpha\gamma}V_{\alpha C};\gamma=\mathrm{R},\mathrm{A},<, \end{gathered} \tag{50}$$

and equations for the TH EOM of G^γ, $\gamma=\mathrm{R},\mathrm{A}$, follow from Equations 33–35,

$$G^{C\gamma}=\left(ES_C-H_C-\Sigma^{\text{int}}_{c}-\Sigma^{\text{junct}\gamma}_{C}\right)^{-1}, \tag{51}$$

$$G^{C\alpha\gamma}=G^{C\gamma}V_{C\alpha}G^{0\alpha\gamma} \tag{52}$$

$$G^{\alpha C\gamma}=G^{0\alpha\gamma}V_{\alpha C}G^{C\gamma} \tag{53}$$

$$G^{\alpha\beta\gamma}=G^{0\alpha\gamma}\delta^{\beta}_{\alpha}+G^{0\alpha\gamma}V_{\alpha C}(G^{C\alpha\gamma}\delta^{\beta}_{\alpha}+G^{C\beta\gamma}(1-\delta^{\alpha}_{\beta})) \tag{54}$$

$$=G^{0\alpha\gamma}\delta^{\beta}_{\alpha}+G^{\alpha C\gamma}(V_{C\alpha}G^{0\alpha\gamma}\delta^{\beta}_{\alpha}+V_{C\beta}G^{0\beta\gamma}(1-\delta^{\alpha}_{\beta})) \tag{55}$$

and the lesser GF,

$$G^{C<}=G^{CR}\Sigma^{\text{junct}<}_{C}G^{CA}\quad(\text{Keldysh Eq.}) \tag{56}$$

$$G^{C\alpha<}=G^{CR}V_{C\alpha}G^{0\alpha<}+G^{C<}V_{C\alpha}G^{0\alpha A} \tag{57}$$

$$G^{\alpha C<}=G^{0\alpha R}V_{\alpha C}G^{C<}+G^{0\alpha<}V_{\alpha C}G^{CA} \tag{58}$$

$$\begin{gathered} G^{\alpha\beta<}=G^{0\alpha<}\delta^{\beta}_{\alpha}+G^{0\alpha R}V_{\alpha C}(G^{C\alpha<}\delta^{\beta}_{\alpha}+G^{C\beta<}(1-\delta^{\alpha}_{\beta})) \\ +G^{0\alpha<}V_{\alpha C}(G^{C\alpha A}\delta^{\beta}_{\alpha}+G^{C\beta A}(1-\delta^{\alpha}_{\beta})) \end{gathered} \tag{59}$$

$$\begin{gathered} =G^{0\alpha<}\delta^{\beta}_{\alpha}+G^{\alpha CR}(V_{C\alpha}G^{0\alpha<}\delta^{\beta}_{\alpha}+V_{C\beta}G^{0\beta<}(1-\delta^{\alpha}_{\beta})) \\ +G^{\alpha C<}(V_{C\alpha}G^{0\alpha A}\delta^{\beta}_{\alpha}+V_{C\beta}G^{0\beta A}(1-\delta^{\alpha}_{\beta})). \end{gathered} \tag{60}$$

In Equation 80, retarded, advanced, and lesser TH GFs are simply the EOM of an isolated electrode, Equation 31,

$$\begin{gathered} (S_\alpha E-H_\alpha-\Sigma^{\text{int.}}_{\alpha})G^{0\alpha R(A)}=I_\alpha \\ (S_\alpha E-H_\alpha-\Sigma^{\text{int.}}_{\alpha})G^{0\alpha<}=0, \end{gathered} \tag{61}$$

with solutions

$$\begin{gathered} G^{0\alpha R}=(S_\alpha(E+i\delta)-H_\alpha-\Sigma^{\text{int.}}_{\alpha})^{-1} \\ G^{0\alpha A}=[G^{0\alpha R}]^{\dagger} \\ G^{0\alpha<}=f(G^{0\alpha A}-G^{0\alpha R}), \end{gathered} \tag{62}$$

where f is the Fermi distribution.

The standard result Equation 62, which uses the regularity of the retarded (advanced) GFs in the upper (lower) half-plane, is obtained.

3.2 | Time-inhomogeneous contribution of electrodes

Linearization, Equation 49, of the EOM of the electrodes GF for the TIH part Equation 31 gives

$$(S_\alpha i\vec{\partial}_t-H_\alpha-\Sigma^{\text{int}}_{\alpha})G^{0\alpha}(t-t')=I^{\alpha}_{\alpha}\delta(t-t') \tag{63}$$

$$G^{0\alpha}(t-t')(i\overleftarrow{\partial}_{t'}S_\alpha+H_\alpha+\Sigma^{\text{int}}_{\alpha})=-I^{\alpha}_{\alpha}\delta(t-t') \tag{64}$$

$$(S_\alpha i\vec{\partial}_t-H_\alpha-\Sigma^{\text{int}}_{\alpha})g^{0\alpha}(t,t')=S_\alpha v_\alpha(t)G^{0\alpha}(t-t'), \tag{65}$$

$$g^{0\alpha}(t,t')(i\overleftarrow{\partial}_{t'}S_\alpha+H_\alpha+\Sigma^{\text{int}}_{\alpha})=-v_\alpha(t')G^{0\alpha}(t-t')S_\alpha \tag{66}$$

where the last two Equations represent TIH contributions.

Equation 66 provides the connection between the TH and TIH quantities

$$g^{0\alpha}(t,t')=\int_{\mathrm{c}}dt_1G^{0\alpha}(t-t_1)S_\alpha v_\alpha(t_1)G^{0\alpha}(t_1-t'). \tag{67}$$

This can be further simplified by making the transformation

$$G^{0\alpha}(t,t')\mapsto e^{-i\int_{t'}^{t}v_\alpha(\tau)d\tau}G^{0\alpha}(t,t'),$$

which gives

$$(S_\alpha i\vec{\partial}_t-H^{\text{tot}}_{\alpha}(t))e^{-i\int_{t'}^{t}v_\alpha(\tau)d\tau}G^{0\alpha}(t,t')=\delta(t,t')I^{\alpha}_{\alpha}+S_\alpha v_\alpha(t)e^{-i\int_{t'}^{t}v_\alpha(\tau)d\tau}G^{0\alpha}(t,t'). \tag{68}$$

Alternatively, from the EOM of the leads, Equation 31, follows

$$e^{-i\int_{t'}^{t}v_\alpha(\tau)d\tau}G^{0\alpha}(t,t')=G^{0\alpha}(t,t')+\int_{\mathrm{c}}G^{0\alpha}(t,t_1)S_\alpha v_\alpha(t_1)e^{-i\int_{t'}^{t_1}V_\alpha(\tau)d\tau}G^{0\alpha}(t_1,t')dt_1, \tag{69}$$

which, after linearization, gives

$$-i\int_{t'}^{t}d\tau v_\alpha(\tau)G^{0\alpha}(t-t')=\int_{\mathrm{c}}dt_1G^{0\alpha}(t-t_1)S_\alpha v_\alpha(t_1)G^{0\alpha}(t_1-t'), \tag{70}$$

Therefore, the expression for the TIH portion of the GFs of the leads follows from Equations 67 and 70,

$$g^{0\alpha}(t,t')=-i\int_{t'}^{t}d\tau v_\alpha(\tau)G^{0\alpha}(t-t'). \tag{71}$$

The above procedure produces a dynamical correction that is simply linear in the TD potentials. However, this result can be easily extended to obtain the full dynamical response

$$g^{0\alpha}_{\text{full}}(t,t')=(e^{-i\int_{t'}^{t}d\tau v_\alpha(\tau)}-1)G^{0\alpha}(t-t').$$

In the energy domain, Equations 70 and 71 become

$$g^{0\alpha<}=\frac{v_\alpha}{\varepsilon}(G^{0\alpha<}-\bar{G}^{0\alpha<})=v_\alpha(\bar{G}^{0\alpha R}S_\alpha G^{0\alpha<}+\bar{G}^{0\alpha<}S_\alpha G^{0\alpha A}) \tag{72}$$

$$g^{0\alpha\gamma}=\frac{v_\alpha}{\varepsilon}(G^{0\alpha\gamma}-\bar{G}^{0\alpha\gamma})=v_\alpha\bar{G}^{0\alpha\gamma}S_\alpha G^{0\alpha\gamma},\ \gamma=\mathrm{R,A}, \tag{73}$$

These equations express the TIH GF contribution of the electrodes in terms of the TH GF. These expressions will be useful later when the dynamical corrections of the junction SEs and the GFs are rearranged in a way that is suitable for comparison with the orthogonal results and in proving gauge-invariance.

3.3 | Interaction time-inhomogeneous contributions

In the Hartree case, Büttiker connects[68] the potential induced in the central caused by an external bias (i.e., TIH interaction SE) and the external potential via characteristic potentials, $a^{[\alpha]}(\mathbf{r})$,

$$\sigma^{\mathrm{int}}(\mathbf{r}t;\mathbf{r}t)=V_{\mathrm{H}}(\mathbf{r}t)=\sum_\alpha a^{[\alpha]}(\mathbf{r})v_\alpha(t), \tag{74}$$

with the property that, in the case of well-screening electrodes α, the TIH SE in the bulk of α must match $v_\alpha(t)$, that is, $a^{[\alpha]}(\mathbf{r})$ changes from 0 to 1 on going from a bulk of $\beta\neq\alpha$ to a bulk of α. The gauge invariance condition requires that

$$\sum_\alpha a^{[\alpha]}(\mathbf{r})=1. \tag{75}$$

We generalize these expressions for the nonorthogonal case by considering the following normalization conditions

$$\sum_\alpha a_C^{[\alpha]}=S_C,\ \sum_\alpha a_{\beta C}^{[\alpha]}=S_{\beta C},\ \sum_\alpha a_{C\beta}^{[\alpha]}=S_{C\beta},\ \sum_\alpha a_\beta^{[\alpha]}=\delta_{\alpha\beta}S_\beta, \tag{76}$$

and explicitly prove the gauge-invariance of the obtained theory.

The only remaining TIH quantity related to the interaction is the TIH contribution of the junction SE, Equation 36, $\sigma^{\mathrm{junct}}(t,t')$, which is related to the TIH GFs of the isolated electrodes and, in the nonorthogonal case, to TIH hopping, Equation 37. The latter is nothing but the TIH contribution of the interaction SE projected onto the interface.

3.4 | Time-inhomogeneous contributions to GF

The TIH correction of the central region GF, which is obtained after substituting Equation 49 into the GF (Equations 35 and 41), are given in the energy domain as

$$g^C=\bar{G}^C(U_C+\sigma_C^{\mathrm{junct}})G^C, \tag{77}$$

where the form of U_C is given in Equation 84. Derivation of an expression for $g^<$, the most important quantity in the formalism related to electron transport, as well as $g^{\mathrm{R/A}}$ are quite involved, and the details are given in the Appendix. The result can be expressed rather succinctly in coordinate-free expressions,

$$\begin{aligned}g^<&=\sum_\alpha v_\alpha(\bar{G}^{\mathrm{R}}a^{[\alpha]}G^<+\bar{G}^<a^{[\alpha]}G^{\mathrm{A}})\\&=\frac{v_\alpha}{\omega}(G^<-\bar{G}^<)+(v_\beta-v_\alpha)(\bar{G}^{\mathrm{R}}a^{[\beta]}G^<+\bar{G}^<a^{[\beta]}G^{\mathrm{A}})\end{aligned} \tag{78}$$

$$\begin{aligned}g^\gamma&=\sum_\alpha v_\alpha(\bar{G}^\gamma a^{[\alpha]}G^\gamma)\\&=\frac{v_\alpha}{\omega}(G^\gamma-\bar{G}^\gamma)+(v_\beta-v_\alpha)(\bar{G}^\gamma a^{[\beta]}G^\gamma),\ \gamma=\mathrm{R,A}.\end{aligned} \tag{79}$$

These contributions are via Equations 32–34 and 38–40 connected with the GFs of the isolated electrodes,

$$\begin{aligned}g^{0\alpha<}&=v_\alpha(\bar{G}^{0\alpha R}S_\alpha G^{0\alpha<}+\bar{G}^{0\alpha<}S_\alpha G^{0\alpha A})\\&=\frac{v_\alpha}{\omega}(G^{0\alpha<}-\bar{G}^{0\alpha<}),\\g^{0\alpha,\gamma}&=v_\alpha\,\bar{G}^{0\alpha,\gamma}S_\alpha G^{0\alpha,\gamma}\\&=\frac{v_\alpha}{\omega}(G^{0\alpha,\gamma}-\bar{G}^{0\alpha,\gamma}),\ \gamma=\mathrm{R,A}.\end{aligned} \tag{80}$$

where the second row in each case is obtained from Equation 70. The corrections resemble the orthogonal ones,[43,49] where the only difference is that both the TH and TIH GFs are represented in a contravariant basis.

Linearization of $\Sigma_{C_\alpha}^{\mathrm{junct}}$, Equation 36, in the energy domain, α,

$$\sigma_{C_\alpha}^{\mathrm{junct}\gamma}=\bar{V}_{C\alpha}\bar{G}^{0\alpha,\gamma}U_{\alpha C}+U_{C\alpha}G^{0\alpha,\gamma}V_{\alpha C}+\bar{V}_{C\alpha}g^{0\alpha,\gamma}V_{\alpha C}, \tag{81}$$

contains $g^{0\alpha}$ which is transformed using Equation 80 to obtain

$$\sigma_{C_\alpha}^{\mathrm{junct}\gamma}=\frac{v_\alpha}{\omega}(\Sigma_{C_\alpha}^{\mathrm{junct}\gamma}-\bar{\Sigma}_{C_\alpha}^{\mathrm{junct}\gamma})+\bar{V}_{C\alpha}\bar{G}^{0\alpha,\gamma}(U_{\alpha C}-v_\alpha S_{\alpha C})+(U_{C\alpha}-v_\alpha S_{C\alpha})G^{0\alpha,\gamma}V_{\alpha C}, \tag{82}$$

where $\gamma=\mathrm{R,A},<$ and with a first term that is equal to the orthogonal case.[43,49] The difference being the energy dependent junction SE caused by the overlap, Equation 50, whereas the last two terms are obtained from $\Sigma^{\mathrm{junct.}}$, Equations 36 and 42, in the energy domain, and transformed via Equation 70. The TIH contribution of the dot SE from the junction with lead α, Equation 82, introduces new terms recognized in explicit dependence of the characteristic potential projections onto the interfaces, Equation 83. In the wide-band limit,[48] the difference $\Sigma_{C_\alpha}^{\mathrm{junct}\gamma}-\bar{\Sigma}_{C_\alpha}^{\mathrm{junct}\gamma}$ vanishes.[48] Therefore, the TIH SE also vanishes in the orthogonal case because of the junction, whereas the second and the third terms in Equation 82 remain nonvanishing in the nonorthogonal case.

Finally, dynamically induced TIH potentials in the nonorthogonal case have a dot and junction contribution, both of which are expressed through characteristic potentials,

$$U_{C\alpha(\alpha C)}=\frac{1}{2\pi}\int\sigma_{C\alpha(\alpha C)}^{\mathrm{int}}dE=\sum_\beta a_{C\alpha(\alpha C)}^{[\beta]}v_\beta \tag{83}$$

$$U_C=\frac{1}{2\pi}\int\sigma_C^{\mathrm{int}}dE=\sum_\beta a_C^{[\beta]}v_\beta. \tag{84}$$

This closes the GF EOM where all the TIH quantities are represented through TH quantities. What remains is to determine the spatial shape of the characteristic potentials.

3.5 | Time-inhomogeneous contributions in the space domain

Characteristic potentials are present in a self-consistent relation with $g^<$, which means that their spatial dependence is obtained as a solution of the Poisson equation,

$$\Delta V_H(\mathbf{r}t)=-4\pi e^2\,\delta n(\mathbf{r}t), \tag{85}$$

$$\delta n(\mathbf{r}t)=n(\mathbf{r}t)-n_{\mathrm{eq}}(\mathbf{r}), \tag{86}$$

where both the Hartree potential, V_H, and the electron density fluctuations caused by the TD bias, δn, are related to $a^{[\alpha]}$. The former is given by definition, Equation 74, and the latter is given through $g^{<}$, Equation 78.

However, the nonorthogonality introduces a complication when determining the electron densities of the subsystems. In the orthogonal case, the particle number operator for the electrodes is $N_\alpha = \sum_{i_\alpha} c^\dagger_{i_\alpha} c_{i_\alpha}$, and for the dot, it is $N_C = \sum_n c^\dagger_n c_n$. However, the trace of the corresponding lesser GF provides the formal framework for the particle number and current calculation. In the nonorthogonal case, the total number of particles operator, $\hat{N}$, can be expressed as a scalar Hermitian operator in two manifestly basis-independent ways,

$$\hat{N} = c^{i\dagger} c_i = c^{n\dagger} c_n + \sum_\alpha c^{i_\alpha \dagger} c_{i_\alpha}, \tag{87}$$

$$= c_i^\dagger c^i = c_n^\dagger c^n + \sum_\alpha c^\dagger_{i_\alpha} c^{i_\alpha} = \hat{N}^\dagger, \tag{88}$$

which, again, express the decomposition of the total number of electrons across the subsystems but in two ways as $\hat{N} = \hat{N}_C + \sum_\alpha \hat{N}_\alpha$, and $\hat{N} = \hat{N}^\dagger = \hat{N}_C^\dagger + \sum_\alpha \hat{N}_\alpha^\dagger$, where

$$\hat{N}_C = c_n^\dagger c^n, \ \hat{N}_\alpha = c^\dagger_{i_\alpha} c^{i_\alpha}, \tag{89}$$

represent the operators of the number of electrons in the corresponding subsystem. It is straightforward to verify that both of these operators are non-Hermitian, with the consequence that every linear combination of the form

$$x\hat{N}_C + (1-x)\hat{N}_C^\dagger, \ 0 \le x \le 1$$

provides a possible number operator of the dot (and is similarly true for $\hat{N}_\alpha$). Among those, however, there is a unique x when both operators are Hermitian, $x = 1/2$, when N_C and N_α can be obtained as eigenvalues of Hermitian operators,

$$\frac{1}{2}(\hat{N}_C + \hat{N}_C^\dagger), \ \frac{1}{2}(\hat{N}_\alpha + \hat{N}_\alpha^\dagger), \tag{90}$$

respectively. Therefore, $x = 1/2$ is used in the following calculations.

Accordingly, the deviation of the particle number near the equilibrium value, $\delta N(\omega) = N(\omega) - N$, can be determined for each subsystem,

$$\begin{aligned} \delta N_\alpha(\omega) &= -\frac{i}{2\pi}\int \mathrm{Tr}(S_\alpha g^{\alpha<})dE - \frac{i}{4\pi}\int \mathrm{Tr}(S_{\alpha C} g^{C\alpha<} + S_{C\alpha} g^{\alpha C<})dE \\ \delta N_C(\omega) &= -\frac{i}{2\pi}\int \mathrm{Tr}(S_C g^{C<})dE - \frac{i}{4\pi}\sum_\alpha \int \mathrm{Tr}(S_{\alpha C} g^{C\alpha<} + S_{C\alpha} g^{\alpha C<})dE \end{aligned} \tag{91}$$

After expressing GF in the space domain, Equations 16 and 20, projections of the Poisson equation on the central region gives

$$\sum_\alpha \Delta a^{[\alpha]}(\mathbf{r}) v_\alpha = 2ie^2 \int \Big(g^{C<}_{\mathbf{rr}} + \frac{1}{2}\sum_\beta (g^{C\beta<}_{\mathbf{rr}} + g^{\beta C<}_{\mathbf{rr}})\Big)dE, \tag{92}$$

with the boundary conditions set by the requirement of charge neutrality,

$$\int \sum_\alpha \Delta a^{[\alpha]}(\mathbf{r}) v_\alpha d\mathbf{r} = 0 = \int \mathrm{Tr}\Big(S_C g^{C<} + \frac{1}{2}\sum_\beta (S_{\beta C} g^{C\beta<} + S_{C\beta} g^{\beta C<})\Big)dE. \tag{93}$$

Using the obtained expression for $g^{<}$, Equation 78, to express the TIH contribution in terms of G, the charge neutrality condition decouples into independent equations for each component of the characteristic potential,

$$\begin{aligned} \Delta a^{[\alpha]}(\mathbf{r}) = 2ie^2 \Bigg[&\int \psi_n(\mathbf{r})(\bar{G}^R a^{[\alpha]} G^< + \bar{G}^< a^{[\alpha]} G^A)^{nm} \psi^*_m(\mathbf{r})dE \\ &+ \frac{1}{2}\int \psi_n(\mathbf{r})(\bar{G}^R a^{[\alpha]} G^< + \bar{G}^< a^{[\alpha]} G^A)^{nj_\beta} \psi^*_{j_\beta}(\mathbf{r})dE \\ &+ \frac{1}{2}\int \psi_{i_\beta}(\mathbf{r})(\bar{G}^R a^{[\alpha]} G^< + \bar{G}^< a^{[\alpha]} G^A)^{i_\beta m} \psi^*_m(\mathbf{r})dE \Bigg]. \end{aligned} \tag{94}$$

Since the results are obtained in the Hartree approximation which is charge-conserving,[62] summing both sides over α must equal zero. In particular, because of the characteristic potential normalization, Equation 76, the sum of the r.h.s. gives,

$$\begin{aligned} \sum_\alpha \Delta a^{[\alpha]} = 2ie^2 \Bigg[&\int \psi_n(\mathbf{r})(\bar{G}^R S G^< + \bar{G}^< S G^A)^{nm} \psi^*_m(\mathbf{r})dE \\ &+ \frac{1}{2}\Big(\int \psi_n(\mathbf{r})(\bar{G}^R S G^< + \bar{G}^< S G^A)^{nj_\beta} \psi^*_{j_\beta}(\mathbf{r})dE + \int \psi_{j_\beta}(\mathbf{r})(\bar{G}^R S G^< + \bar{G}^< S G^A)^{j_\beta n} \psi^*_n(\mathbf{r})dE\Big)\Bigg], \end{aligned} \tag{95}$$

Transforming this expression is performed using a result derived in the Appendix, Equation A21, which, in essence, expresses the $\bar{G}SG$ terms as differences $G^< - \bar{G}^<$ to obtain

$$\frac{2ie^2}{\omega}\left[\int (G^{C<}_{\mathbf{rr}} - \bar{G}^{C<}_{\mathbf{rr}})dE + \frac{1}{2}\sum_\beta \int (G^{C\beta<}_{\mathbf{rr}} - \bar{G}^{C\beta<}_{\mathbf{rr}} + G^{\beta C<}_{\mathbf{rr}} - \bar{G}^{\beta C<}_{\mathbf{rr}})dE\right].$$

The integrals in the last expression vanish because all their differences are of the form $\int_{-\infty}^{\infty}(F - \bar{F})dE$, which equals 0, thereby proving the charge-neutrality condition of the Poisson equation. This also proves that $\sum_\alpha \Delta a^\alpha(\mathbf{r}) = 0$.

The total dynamical charge density within the central region is contained in the r.h.s. of the Poisson Equation 92, which contains contributions from both the injected and the induced charge densities. Contributions from the former occur via the terms with characteristic potentials projected onto the electrodes (giving $\delta_{\alpha\beta} S_\beta$), whereas contributions from the latter occur via the terms with characteristic potentials projected onto the interfaces and the dot.

With each of the characteristic potentials obtained, Equation 94 can be formulated in the form of the Lindhard equation[43,68]

$$\Delta a^{[\alpha]}(\mathbf{r}) = 4\pi e^2\left(-\frac{dn(\mathbf{r},\alpha)}{dE} + \int \Pi(\mathbf{r},\mathbf{r}',\omega) a^{[\alpha]}(\mathbf{r}')d\mathbf{r}'\right), \tag{96}$$

where we obtain the following for the injectivity of lead α (i.e., its density of states)

$$\begin{aligned} \frac{dn(\mathbf{r},\alpha)}{dE} = -\frac{i}{2\pi}\int\int \Big[&\bar{G}^{C\alpha R}_{\mathbf{rr}'} G^{\alpha C<}_{\mathbf{r}'\mathbf{r}} + \bar{G}^{C\alpha<}(\mathbf{rr}') G^{\alpha CA}_{\mathbf{r}'\mathbf{r}} \\ &+ \frac{1}{2}\sum_\gamma (\bar{G}^{C\alpha R}_{\mathbf{rr}'} G^{\alpha\gamma<}_{\mathbf{r}'\mathbf{r}} + \bar{G}^{C\alpha<}_{\mathbf{rr}'} G^{\alpha\gamma A}_{\mathbf{r}'\mathbf{r}} + \bar{G}^{\gamma\alpha R}_{\mathbf{rr}'} G^{\alpha C<}_{\mathbf{r}'\mathbf{r}} + \bar{G}^{\gamma\alpha<}_{\mathbf{rr}'} G^{\alpha CA}_{\mathbf{r}'\mathbf{r}})\Big] dE d\mathbf{r}'. \end{aligned} \tag{97}$$

The polarization, $\Pi(\mathbf{r},\mathbf{r}',\omega)$, has dot-dot ($\pi_C$), dot-lead ($\pi_\alpha$) and lead-lead ($\pi_{\alpha\beta}$) contributions,

$$\Pi(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int dE\left(\pi_C(\mathbf{r},\mathbf{r}',\omega) + \sum_\alpha \pi_\alpha(\mathbf{r},\mathbf{r}',\omega) + \frac{1}{2}\sum_{\alpha\beta}\pi_{\alpha\beta}(\mathbf{r},\mathbf{r}',\omega)\right), \tag{98}$$

where

$$
\begin{aligned}
\pi_C(\mathbf{r},\mathbf{r}',\omega) &= \bar{G}^{CR}_{\mathbf{rr}'}G^{C<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C<}_{\mathbf{rr}'}G^{CA}_{\mathbf{r}'\mathbf{r}}\\
\pi_\alpha(\mathbf{r},\mathbf{r}',\omega) &= \frac{1}{2}(\bar{G}^{CR}_{\mathbf{rr}'}G^{C\alpha<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C<}_{\mathbf{rr}'}G^{C\alpha A}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{\alpha CR}_{\mathbf{rr}'}G^{C<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{\alpha C<}_{\mathbf{rr}'}G^{CA}_{\mathbf{r}'\mathbf{r}})\\
&\quad+\bar{G}^{CR}_{\mathbf{rr}'}G^{\alpha C<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C<}_{\mathbf{rr}'}G^{\alpha CA}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C\alpha R}_{\mathbf{rr}'}G^{C<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C\alpha<}_{\mathbf{rr}'}G^{CA}_{\mathbf{r}'\mathbf{r}}\\
\pi_{\alpha\beta}(\mathbf{r},\mathbf{r}',\omega) &= \bar{G}^{CR}_{\mathbf{rr}'}G^{\alpha\beta<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C<}_{\mathbf{rr}'}G^{\alpha\beta A}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C\alpha R}_{\mathbf{rr}'}G^{C\beta<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{C\alpha<}_{\mathbf{rr}'}G^{C\beta A}_{\mathbf{r}'\mathbf{r}}\\
&\quad+\bar{G}^{\alpha CR}_{\mathbf{rr}'}G^{\beta C<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{\alpha C<}_{\mathbf{rr}'}G^{\beta CA}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{\alpha\beta R}_{\mathbf{rr}'}G^{C<}_{\mathbf{r}'\mathbf{r}}+\bar{G}^{\alpha\beta<}_{\mathbf{rr}'}G^{CA}_{\mathbf{r}'\mathbf{r}}.
\end{aligned}
$$

With the Lindhard Equation 96 determining the characteristic potentials design, the theory is closed. We now proceed to derive the expression for the TD current through the molecule.

3.6 | Time dependent current

The electronic current is driven by the external TD potentials $v_\alpha(t), \alpha = L, R$. To provide the current conservation, the displacement current, which is caused by charge accumulation in the central region, must be considered.[81] A self-consistent treatment of the response potential incorporates the effects of the Coulomb interaction, thus creating a feedback. That is, the induced charge density screens the charge injected from the electrodes, giving a zero net charge. Consequently, integration of the continuity equation over the volume of the central region provides a conserved current. Inclusion of the Coulomb interaction in the particle current expression ensures that the displacement current effects are not neglected,[68,81] so the total current can be obtained as a time derivative of the particle current where the displacement current contribution arises from its explicit dependence on the induced potential constituents (i.e., the characteristic potentials). A time derivative over the dynamical contribution of charge density in electrode α will give the corresponding TD current density plus the TD current after integration over the region of interest. Using a nonorthogonal basis set, this approach imposes the question regarding lead population, which was addressed in the previous section, giving the following result for the TD current from δN_α

$$
\begin{aligned}
i_\alpha(t) &= 2ei[\mathrm{Tr}(S_\alpha\partial_t g^{\alpha<}(t,t))+\frac{1}{2}\mathrm{Tr}(S_{\alpha C}\partial_t g^{C\alpha<}(t,t))+\frac{1}{2}\mathrm{Tr}(S_{C\alpha}\partial_t g^{\alpha C<}(t,t))]\\
&= 2ei[\mathrm{Tr}(S_\alpha(\partial_t+\partial_{t^+})g^\alpha(t,t^+))+\frac{1}{2}\mathrm{Tr}(S_{\alpha C}(\partial_t+\partial_{t^+})g^{C\alpha}(t,t^+))\\
&\quad+\frac{1}{2}\mathrm{Tr}(S_{C\alpha}(\partial_t+\partial_{t^+})g^{\alpha C}(t,t^+))]\\
&= 2e\mathrm{Tr}[(H_{\alpha C}+\Sigma^{\mathrm{int}}_{\alpha C}-S_{\alpha C}i\partial_t)g^{C\alpha}(t,t^+)+\sigma^{\mathrm{int}}_{\alpha C}(t,t)G^{C\alpha}(t-t^+)\\
&\quad-g^{\alpha C}(t,t^+)(H_{C\alpha}+\Sigma^{\mathrm{int}}_{C\alpha}+i\overleftarrow{\partial}_{t^+}S_{\alpha C})-G^{\alpha C}(t-t^+)\sigma^{\mathrm{int}}_{C\alpha}(t^+,t^+) \qquad (99)\\
&\quad+\frac{i}{2}(S_{\alpha C}(\partial_t+\partial_{t^+})g^{C\alpha}(t,t^+)+S_{C\alpha}(\partial_t+\partial_{t^+})g^{\alpha C}(t,t^+))], \qquad (100)
\end{aligned}
$$

where the leading coefficient 2 arises from the spin. In the energy-domain,

$$
\begin{aligned}
i_\alpha(\omega) &= \frac{e}{\pi}\int\mathrm{Tr}[(H_{\alpha C}+\Sigma^{\mathrm{int}}_{\alpha C}-(E+\omega)S_{\alpha C})g^{C\alpha<}+U_{\alpha C}G^{C\alpha<}\\
&\quad-g^{\alpha C<}(H_{C\alpha}+\Sigma^{\mathrm{int}}_{C\alpha}-ES_{C\alpha})-\bar{G}^{\alpha C<}U_{C\alpha}]dE\\
&\quad+\omega\frac{e}{2\pi}\int\mathrm{Tr}(g^{C\alpha<}S_{\alpha C}+S_{C\alpha}g^{\alpha C<})dE.
\end{aligned} \tag{101}
$$

After some algebra involving expressions for the TIH contribution $g^<$ from the dot and leads, Equations 78 and 80, and the TIH contribution σ from the junction to the dot SE, Equation 82, we obtain

$$
\begin{aligned}
i_\alpha &= \frac{e}{\pi}\int\mathrm{Tr}(\bar{G}^{CR}\sigma^{\mathrm{junct}<}_{C_\alpha}+\bar{G}^{C<}\sigma^{\mathrm{junctA}}_{C_\alpha}+g^{CR}\Sigma^{\mathrm{junct}<}_{C_\alpha}+g^{C<}\Sigma^{\mathrm{junctA}}_{C_\alpha}\\
&\quad-\sigma^{\mathrm{junctR}}_{C_\alpha}G^{C<}-\sigma^{\mathrm{junct}<}_{C_\alpha}G^{CA}-\bar{\Sigma}^{\mathrm{junctR}}_{C_\alpha}g^{C<}-\bar{\Sigma}^{\mathrm{junct}<}_{C_\alpha}g^{CA})dE\\
&\quad-\omega\frac{e}{2\pi}\int\mathrm{Tr}(g^{C\alpha<}S_{\alpha C}+S_{C\alpha}g^{\alpha C<})dE,
\end{aligned} \tag{102}
$$

Together with equations that express the TIH quantities over the TH quantities, Equations 78–80 and 82, these equations constitute the main results of this article. The first integral of Equation 102 formally contains the same terms as in the orthogonal case, only with contravariant GFs (i.e., represented in a dual basis[43,50]). The second integral of Equation 102, which is absent in the orthogonal case, arises from the TD charge at the interfaces because of the nonorthogonality of the dot and leads states, which are introduced by nonzero $S_{\alpha C}, S_{C\alpha}$.

4 | DISCUSSION

Since the results are obtained in the Hartree approximation, which is one of a few known conserving approximations,[62] we next explicitly verify the current conservation and gauge invariance of the result and then discuss the importance of the second integral, which relates to the nonorthogonality by considering both the orthogonal case and the limit of vanishing nonorthogonality.

4.1 | Current conservation and gauge invariance

The sum of the lead currents, Equation 99,

$$
\begin{aligned}
\sum_\alpha i_\alpha(t) &= -2e\sum_\alpha\mathrm{Tr}((H_{C\alpha}+\Sigma^{\mathrm{int}}_{C\alpha}-i\partial_t S_{C\alpha})g^{\alpha C}(t,t^+)+\sigma^{\mathrm{int}}_{C\alpha}(t^+,t^+)G^{\alpha C}(t-t^+)\\
&\quad-g^{C\alpha}(t,t^+)(H_{\alpha C}+\Sigma^{\mathrm{int}}_{\alpha C}+i\overleftarrow{\partial}_{t^+}S_{\alpha C})-G^{C\alpha}(t-t^+)\sigma^{\mathrm{int}}_{\alpha C}(t,t)\\
&\quad+\frac{i}{2}(S_{\alpha C}(\partial_t+\partial_{t^+})g^{C\alpha}(t,t^+)+S_{C\alpha}(\partial_t+\partial_{t^+})g^{\alpha C}(t,t^+))),
\end{aligned} \tag{103}
$$

can be transformed by rewriting the first two rows using the GF EOM Equation 19, to obtain

$$
\begin{aligned}
\sum_\alpha i_\alpha(t) &= -2ei\mathrm{Tr}[S_C(\partial_t+\partial_{t^+})g^C(t,t^+)\\
&\quad+\sum_\alpha\frac{1}{2}(S_{\alpha C}(\partial_t+\partial_{t^+})g^{C\alpha}(t,t^+)+S_{C\alpha}(\partial_t+\partial_{t^+})g^{\alpha C}(t,t^+))],
\end{aligned}
$$

which in the energy domain becomes

$$
\sum_\alpha i_\alpha(\omega) = -\frac{e}{\pi}\omega\int\mathrm{Tr}(S_C g^{C<})dE-\frac{e}{2\pi}\omega\sum_\alpha\int\mathrm{Tr}(S_{\alpha C}g^{C\alpha<}+g^{\alpha C<}S_{C\alpha})dE, \tag{104}
$$

where the first term is simply (negative) current through the central region. The charge neutrality condition in Equation 93 ensures that $\sum_\alpha i_\alpha(\omega)=0$. To verify gauge invariance, the potentials are shifted by a constant, $v_\alpha \mapsto v_\alpha + K$, and the resulting i_α are calculated. The shift changes the TIH quantities, Equations 78, 79, and 82,

$$
\begin{aligned}
&g^{\gamma} \mapsto g^{\gamma} + K(\bar{G}SG)^{\gamma} = g^{\gamma} + \frac{K}{\omega}(G^{\gamma} - \bar{G}^{\gamma}),\ \gamma = <, \mathrm{A}, \mathrm{R};\\
&\sigma_{C_\alpha}^{\mathrm{junct}\gamma} \mapsto \sigma_{C_\alpha}^{\mathrm{junct}\gamma} + \frac{K}{\omega}(\Sigma_{C_\alpha}^{\mathrm{junct}\gamma} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}\gamma}),
\end{aligned}
\tag{105}
$$

where the normalization property of the characteristic potentials, Equation 76, has been used, whereas the equality

$$
(\bar{G}SG)^{\gamma} = \frac{1}{\omega}(G^{\gamma} - \bar{G}^{\gamma}),
$$

is proved in the Appendix. By recalling the results for the TIH contributions $g^{<}$ and σ^{junct}, Equation 105, the current changes as

$$
\begin{aligned}
i_\alpha \mapsto i_\alpha &+ \frac{eK}{\pi\omega}\int \mathrm{Tr}(\bar{G}^{C\mathrm{R}}(\Sigma_{C_\alpha}^{\mathrm{junct}<} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}<}) + \bar{G}^{C<}(\Sigma_{C_\alpha}^{\mathrm{junctA}} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junctA}}) + (G^{C\mathrm{R}} - \bar{G}^{C\mathrm{R}})\Sigma_{C_\alpha}^{\mathrm{junct}<}\\
&+ (G^{C<} - \bar{G}^{C<})\Sigma_{C_\alpha}^{\mathrm{junctA}} - (\Sigma_{C_\alpha}^{\mathrm{junctR}} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junctR}})G^{C<}\\
&- (\Sigma_{C_\alpha}^{\mathrm{junct}<} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}<})G^{C\mathrm{A}} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junctR}}(G^{C<} - \bar{G}^{C<}) - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}<}(G^{C\mathrm{A}} - \bar{G}^{C\mathrm{A}}))dE\\
&- \frac{eK}{2\pi}\int \mathrm{Tr}((G^{C\alpha<} - \bar{G}^{C\alpha<})S_{\alpha C} + S_{C\alpha}(G^{\alpha C<} - \bar{G}^{\alpha C<}))dE,
\end{aligned}
\tag{106}
$$

where only terms of the form $\int_{-\infty}^{\infty}(F - \bar{F})dE = 0$ appear under both integrals, thereby proving that $i_\alpha \mapsto i_\alpha$.

4.2 | Importance of dot-interface projections

To demonstrate that the gauge invariance would have been violated if the interface SE projections Equation 83 were not included, we calculate dynamical corrections that neglect the interface projections when only $a_C^{[\alpha]}$ remains in a self-consistent manner. The hopping and junction quantities, Equations 50 and 82, then become

$$
\begin{aligned}
V_{C\alpha(\alpha C)} &= H_{C\alpha(\alpha C)} - ES_{C\alpha(\alpha C)}\\
\Sigma_{C_\alpha}^{\mathrm{junct}\gamma} &= V_{C\alpha}G^{0\alpha,\gamma}V_{\alpha C}\\
\sigma_{C_\alpha}^{\mathrm{junct}\gamma} &= \bar{V}_{C\alpha}g^{0\alpha,\gamma}V_{\alpha C},
\end{aligned}
$$

whereas the TIH contributions become

$$
\begin{aligned}
&\sigma_{C_\alpha}^{\mathrm{junct}\gamma} = \frac{v_\alpha}{\omega}(\Sigma_{C_\alpha}^{\mathrm{junct}\gamma} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}\gamma}) - v_\alpha(S_{C\alpha}G^{0\alpha,\gamma}V_{\alpha C} + \bar{V}_{C\alpha}\bar{G}^{0\alpha,\gamma}S_{\alpha C}),\ \gamma = \mathrm{R}, \mathrm{A}, <\\
&g^{<} = \sum_{\beta} v_\beta((\bar{G}^{\mathrm{R}}(a_C^{[\beta]} + S_\beta)G^{<}) + (\bar{G}^{<}(a_C^{[\beta]} + S_\beta)G^{\mathrm{A}}))\\
&g^{\gamma} = \sum_{\beta} v_\beta\bar{G}^{\gamma}(a_C^{[\beta]} + S_\beta)G^{\gamma}.
\end{aligned}
\tag{107}
$$

To verify the gauge invariance of the obtained current, we again make a shift of v_α by K and calculate the resulting current change. Quantities in Equation 107 change after the shift as

$$
\begin{aligned}
&\sigma_{C_\alpha}^{\mathrm{junct}\gamma} \mapsto \sigma_{C_\alpha}^{\mathrm{junct}\gamma} + \frac{K}{\omega}(\Sigma_{C_\alpha}^{\mathrm{junct}\gamma} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}\gamma}) - K(S_{C\alpha}G^{0\alpha\gamma}V_{\alpha C} + \bar{V}_{C\alpha}\bar{G}^{0\alpha\gamma}S_{\alpha C})\\
&g^{ij<} \mapsto g^{ij<} + \frac{K}{\omega}(G^{ij<} - \bar{G}^{ij<})\\
&- K\sum_{\rho}(\bar{G}^{iC\mathrm{R}}S_{C\rho}G^{\rho j<} + \bar{G}^{i\rho\mathrm{R}}S_{\rho C}G^{Cj<} + \bar{G}^{iC<}S_{C\rho}G^{\rho j\mathrm{A}} + \bar{G}^{i\rho<}S_{\rho C}G^{Cj\mathrm{A}})\\
&g^{ij\gamma} \mapsto g^{ij\gamma} + \frac{K}{\omega}(G^{ij\gamma} - \bar{G}^{ij\gamma}) - K\sum_{\rho}(\bar{G}^{iC\gamma}S_{C\rho}G^{\rho j\gamma} + \bar{G}^{i\rho\gamma}S_{\rho C}G^{Cj\gamma}),\ \gamma = \mathrm{R}, \mathrm{A}.
\end{aligned}
\tag{108}
$$

For comparison, the shift changes the same quantities in the full description, Equations 78, 79, and 82, as

$$
\begin{aligned}
&g^{ij\gamma} \mapsto g^{ij\gamma} + \frac{K}{\omega}(G^{ij\gamma} - \bar{G}^{ij\gamma}),\ \gamma = <, \mathrm{A}, \mathrm{R};\\
&\sigma_{C_\alpha}^{\mathrm{junct}\gamma} \mapsto \sigma_{C_\alpha}^{\mathrm{junct}\gamma} + \frac{K}{\omega}(\Sigma_{C_\alpha}^{\mathrm{junct}\gamma} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}\gamma}),
\end{aligned}
\tag{109}
$$

which reveals that all three TIH quantities after the potential shift acquire additional terms with respect to the full description scenario. This difference arises from neglecting $U_{C\alpha}, U_{\alpha C}$ in $\sigma_{C_\alpha}^{\mathrm{junct},\gamma}$, Equation 81, which consequently influences all other TIH quantities through Equations 78, 79, and 82. The current changes after the shift again by acquiring two additional contributions,

$$
i_\alpha \mapsto i_\alpha - K\frac{e}{\pi}i'_\alpha + K\,\omega\,\frac{e}{2\pi}i''_\alpha,
\tag{110}
$$

where

$$
\begin{aligned}
i'_\alpha = \int \mathrm{Tr}\Big[&\bar{G}^{C\alpha<}S_{\alpha C} - S_{C\alpha}G^{\alpha C<} + \bar{G}^{C\mathrm{R}}S_{C\alpha}G^{0\alpha<}V_{\alpha C} + \bar{G}^{C<}S_{C\alpha}G^{0\alpha\mathrm{A}}V_{\alpha C}\\
&- \bar{V}_{C\alpha}\bar{G}^{0\alpha\mathrm{R}}S_{\alpha C}G^{C<} - \bar{V}_{C\alpha}\bar{G}^{0\alpha<}S_{\alpha C}G^{C\mathrm{A}}\\
&+ \sum_{\beta}(\bar{G}^{C\mathrm{R}}S_{C\beta}G^{\beta C\mathrm{R}} + \bar{G}^{C\beta\mathrm{R}}S_{\beta C}G^{C\mathrm{R}})\Sigma_{C_\alpha}^{\mathrm{junct}<}\\
&- \bar{\Sigma}_{C_\alpha}^{\mathrm{junct}<}\sum_{\beta}(\bar{G}^{C\mathrm{A}}S_{C\beta}G^{\beta C\mathrm{A}} + \bar{G}^{C\beta\mathrm{A}}S_{\beta C}G^{C\mathrm{A}})\\
&+ \sum_{\beta}(\bar{G}^{C\mathrm{R}}S_{C\beta}G^{\beta C<} + \bar{G}^{C<}S_{C\beta}G^{\beta C\mathrm{A}} + \bar{G}^{C\beta\mathrm{R}}S_{\beta C}G^{C\beta<} + \bar{G}^{C\beta<}S_{\beta C}G^{C\beta\mathrm{A}})\\
&(\Sigma_{C_\alpha}^{\mathrm{junctA}} - \bar{\Sigma}_{C_\alpha}^{\mathrm{junctR}})\Big]dE
\end{aligned}
\tag{111}
$$

and

$$
\begin{aligned}
i''_\alpha = \int \mathrm{Tr}\Big[&\sum_{\beta}(\bar{G}^{C\beta\mathrm{R}}S_{\beta C}G^{C\alpha<} + \bar{G}^{C\mathrm{R}}S_{C\beta}G^{\beta\alpha<} + \bar{G}^{C\beta<}S_{\beta C}G^{C\alpha\mathrm{A}} + \bar{G}^{C<}S_{C\beta}G^{\beta\alpha\mathrm{A}})S_{\alpha C}\\
&+ S_{C\alpha}\sum_{\beta}(\bar{G}^{\alpha\beta\mathrm{R}}S_{\beta C}G^{C<} + \bar{G}^{\alpha C\mathrm{R}}S_{C\beta}G^{\beta C<} + \bar{G}^{\alpha\beta<}S_{\beta C}G^{C\mathrm{A}} + \bar{G}^{\alpha C<}S_{C\beta}G^{\beta C\mathrm{A}})\Big]dE,
\end{aligned}
\tag{112}
$$

neither of which are zero. Therefore, omitting the interface-induced potentials in the dot, $U_{C\alpha}$ and $U_{\alpha C}$, in the nonorthogonal case gives a nongauge-invariant theory.

4.3 | From nonorthogonal to orthogonal basis

If the overlap matrix S is the unit matrix, the known results for the orthogonal case of Wei et al.[43] are recovered. The TIH GF contributions g derived here, Equations 78, 79, and 82, depend on the dot-leads interaction electron SEs $\Sigma_{C\alpha(\alpha C)}^{\mathrm{int}}$. In the previous section it is explicitly shown that they cannot be neglected in the nonorthogonal case if the theory is to be gauge-invariant. In the orthogonal case, the gauge-breaking currents, Equations 111 and 112, equal 0 when the basis-set overlap matrices between the central region and electrodes, $S_{\alpha C}, S_{C\alpha}$, equal 0. However, this only demonstrates that neglecting the dot-leads SE in the orthogonal case does not violate gauge-invariance. We now derive the expression for current in the orthogonal case when the central-region-electrodes SE are *not* neglected. The result for the current Equation 102 in the orthogonal case, using Equations 78, 79, and 82 with $S_{\alpha C} = S_{C\alpha} = 0$, becomes

$$i_\alpha^{\text{ortho}}=(v_\beta-v_\alpha)\frac{e}{\pi}\int \mathrm{Tr}(\bar{G}_{C\alpha}^{<}a_{\alpha C}^{[\beta]}-a_{C\alpha}^{[\beta]}G_{\alpha C}^{<}+\bar{G}_C^{R}a_{C\alpha}^{[\beta]}G_\alpha^{0<}V_{\alpha C}+\bar{G}_C^{<}a_{C\alpha}^{[\beta]}G_\alpha^{0A}V_{\alpha C}$$
$$-V_{C\alpha}\bar{G}_\alpha^{0R}a_{\alpha C}^{[\beta]}G_C^{<}-V_{C\alpha}\bar{G}_\alpha^{0<}a_{\alpha C}^{[\beta]}G_C^{A}$$
$$+(\bar{G}^{R}a^{[\beta]}G^{R})_C\Sigma_{C_\alpha}^{\text{junct}<}-\bar{\Sigma}_{C_\alpha}^{\text{junct}<}(\bar{G}^{A}a^{[\beta]}G^{A})_C$$
$$+(\bar{G}^{R}a^{[\beta]}G^{<}+\bar{G}^{<}a^{[\beta]}G^{A})_C(\Sigma_{C_\alpha}^{\text{junctA}}-\bar{\Sigma}_{C_\alpha}^{\text{junctR}}))dE, \tag{113}$$

where all the indices are written in subscript since the covariant and contravariant formulations are identical because of the trivial metric $S=S^{-1}=I$ of the orthogonal single-particle basis. Because of the zero overlap of the basis states in the dot and leads, the hopping matrices $V_{C\alpha(\alpha C)}$, Equation 50, are now energy independent. The current again can be split into the particle, i_α^{p}, dot-dot, $i_\alpha^{d'}$, dot-leads, $i^{d''}$, and displacement current contributions,

$$i_\alpha^{\text{ortho}}=i_\alpha^{p}+i_\alpha^{d'}+i_\alpha^{d''},$$

where the first two terms,

$$i_\alpha^{p}=(v_\beta-v_\alpha)\frac{e}{\pi}\int \mathrm{Tr}[\bar{G}_{C\beta}^{R}G_{\beta C}^{R}\Sigma_{C_\alpha}^{\text{junct}<}-\bar{\Sigma}_{C_\alpha}^{\text{junct}<}\bar{G}_{C\beta}^{A}G_{\beta C}^{A}$$
$$+(\bar{G}_{C\beta}^{R}G_{\beta C}^{<}+\bar{G}_{C\beta}^{<}G_{\beta C}^{A})(\Sigma_{C_\alpha}^{\text{junctA}}-\bar{\Sigma}_{C_\alpha}^{\text{junctR}})]dE,$$
$$i_\alpha^{d'}=(v_\beta-v_\alpha)\frac{e}{\pi}\int \mathrm{Tr}[\bar{G}_C^{R}a_C^{[\beta]}G_C^{R}\Sigma_{C_\alpha}^{\text{junct}<}-\bar{\Sigma}_{C_\alpha}^{\text{junct}<}\bar{G}_C^{A}a_C^{[\beta]}G_C^{A}+$$
$$+(\bar{G}_C^{R}a_C^{[\beta]}G_C^{<}+\bar{G}_C^{<}a_C^{[\beta]}G_C^{A})(\Sigma_{C_\alpha}^{\text{junctA}}-\bar{\Sigma}_{C_\alpha}^{\text{junctR}})]dE,$$

correspond to the standard orthogonal result[43] and both currents are clearly gauge-invariant. Clearly, the additional dot-lead interface contribution to the total current,

$$i_\alpha^{d''}=(v_\beta-v_\alpha)\frac{e}{\pi}\int \mathrm{Tr}[\bar{G}_C^{R}a_{C\alpha}^{[\beta]}G_\alpha^{0<}V_{\alpha C}+\bar{G}_C^{<}a_{C\alpha}^{[\beta]}G_\alpha^{0A}V_{\alpha C}-V_{C\alpha}\bar{G}_\alpha^{0R}a_{\alpha C}^{[\beta]}G_C^{<}-V_{C\alpha}\bar{G}_\alpha^{0<}a_{\alpha C}^{[\beta]}G_C^{A}$$
$$+\sum_\rho(\bar{G}_{C\rho}^{R}a_{\rho C}^{[\beta]}G_C^{R}+\bar{G}_C^{R}a_{C\rho}^{[\beta]}G_{\rho C}^{R})\Sigma_{C_\alpha}^{\text{junct}<}-\bar{\Sigma}_{C_\alpha}^{\text{junct}<}\sum_\rho(\bar{G}_{C\rho}^{A}a_{\rho C}^{[\beta]}G_C^{A}+\bar{G}_C^{A}a_{C\rho}^{[\beta]}G_{\rho C}^{A})$$
$$+\sum_\rho(\bar{G}_{C\rho}^{R}a_{\rho C}^{[\beta]}G_C^{<}+\bar{G}_C^{R}a_{C\rho}^{[\beta]}G_{\rho C}^{<}+\bar{G}_{C\rho}^{<}a_{\rho C}^{[\beta]}G_C^{A}+\bar{G}_C^{<}a_{C\rho}^{[\beta]}G_{\rho C}^{A})(\Sigma_{C_\alpha}^{\text{junctA}}-\bar{\Sigma}_{C_\alpha}^{\text{junctR}})$$
$$+\bar{G}_{C\alpha}^{<}a_{\alpha C}^{[\beta]}-a_{C\alpha}^{[\beta]}G_{\alpha C}^{<}]dE, \tag{114}$$

is also gauge-invariant. It consists solely of terms containing characteristic potentials $a_{C\alpha}^{[\beta]}, a_{\alpha C}^{[\beta]}$, which, in turn, are determined self-consistently. The normalization condition on the characteristic potentials, Equation 76, in the orthogonal case becomes

$$\sum_\beta a_{\alpha C}^{[\beta]}=\sum_\beta a_{C\alpha}^{[\beta]}=0, \tag{115}$$

which, notably, does not rigorously guarantee that each summand is zero. Indeed, although each a goes from 0 to a positive value ≤ 1 when going from one electrode through the central region to the other electrode, it is at present not known whether they are also, for example, strictly non-negative, which would be a sufficient condition for their vanishing under the orthogonal case condition, Equation 115. To estimate the value of these potentials, we use the block-form of S, Equation 19, which is decomposed via the identity[82] $S=S_D+S_O$ into its block-diagonal, S_D, and block-off-diagonal, S_O, parts,

$$S=\frac{1}{2}(S_D(I+S_D^{-1}S_O)+(I+S_OS_D^{-1})S_D),$$

$$S_D=\begin{pmatrix} S_L & 0 & 0 \\ 0 & S_C & 0 \\ 0 & 0 & S_R \end{pmatrix},\ S_O=\begin{pmatrix} 0 & S_{LC} & 0 \\ S_{CL} & 0 & S_{CR} \\ 0 & S_{RC} & 0 \end{pmatrix}.$$

Using the condition of $a_\beta^{[\alpha]}=0$ in electrode $\beta\neq\alpha$, $a_{C\beta}^{[\alpha]}$ and $a_{\beta C}^{[\alpha]}$ can be written, after some algebra, as

$$\begin{aligned} a_{C\beta}^{[\alpha]}&=\frac{1}{2}(a_C^{[\alpha]}S_C^{-1}+\delta_{\alpha\beta})S_{C\beta} \\ a_{\beta C}^{[\alpha]}&=\frac{1}{2}S_{\beta C}(\delta_{\alpha\beta}+S_C^{-1}a_C^{[\alpha]}), \end{aligned} \tag{116}$$

which shows that in the limit of vanishing nonorthogonality, when $S_O\to 0$, they are expected to also go to zero. Therefore, the additional current $i_\alpha^{d''}\to 0$ recovers the orthogonal case result.

4.4 | The model and numerical results

Regarding the numerical aspects of our work, the central quantities that have to be determined are the characteristic potentials. As we show, every other time inhomogeneous contribution depends directly on the characteristic potentials and the TH GFs. The Lindhard equation must be solved with charge neutrality as a boundary condition. DFT is suitable for determining/establishing the TH GFs, including the central region GF, the mixed GF and the GF of the isolated electrodes. The latter, also called the surface GF, can be determined by a separate calculation, which is possible because of the screening approximation. Within this separate calculation, the junction SEs are determined as well. Although the components necessary to solve the Lindhard equation are provided, in principle, the involvement of the polarization kernel can be computationally cumbersome. The first step toward simplification would be to localize the polarization kernel, that is, to adopt the Thomas–Fermi approximation. As a quasi-static approximation, it is expected that this framework will omit some effects, such as Friedel oscillations. Nevertheless, the Thomas–Fermi approximation can be a good choice for an acceptable range of frequencies. Furthermore, the quasi-neutrality condition can be imposed. Another huge simplification would be to neglect the energy dependence of the electrodes-central region couplings (wide band limit,-WBL), which can be justified as long as the width of the conduction band significantly exceeds the values of the bias amplitudes and the width of the resonances. Still, the calculation within the microscopic theory remains highly demanding even with all these approximations because it must be performed at every real space point. It is much easier to begin with the phenomenological approach where the explicit dynamical response is neglected; thus, the displacement current partition is determined by the gauge invariance requirement. The advantage of the phenomenological theory is a low computational cost since the calculation must be performed in the orbital space. We have developed a toy model in the nonorthogonal basis to test our theory using the phenomenological approach. In this subsection, we present the toy model to consist of an interacting system connected to noninteracting one-dimensional tight-binding chains. The interacting system consists of two sites C^L and C^R. We consider that their states are $|C^L\rangle$ and $|C^R\rangle$ in the orthogonal description, whereas the chain sites are denoted with $|i\rangle$, where i goes from $-\infty$ to -1 and from 1 to ∞ for the left and the right chains, respectively. The nonorthogonality is introduced through linear combinations[9]

$$\begin{aligned} |C_n^L\rangle &= \sin\phi\sin\theta|-1\rangle+\cos\theta|C^L\rangle+\cos\phi\sin\theta|C^R\rangle;\\ |C_n^R\rangle &= \sin\phi\sin\theta|1\rangle+\cos\phi\sin\theta|C^L\rangle+\cos\theta|C^R\rangle. \end{aligned} \tag{117}$$

It is easy to see that

$$\begin{aligned} \langle -1_n|C_n^L\rangle=\langle 1_n|C_n^R\rangle &= \sin\phi\sin\theta\cos\alpha=\bar{s};\\ \langle C_n^L|C_n^R\rangle &= \sin 2\theta\cos\phi=S, \end{aligned} \tag{118}$$

represent the overlap between the central region and the chains, $\bar{s}$, as well as the overlap within the central region, S. We adopted the following for the Hamiltonian matrix elements, given in an orthogonal basis,[52]

$$\begin{gathered} H_{C_{ij}}=h_{C_{ij}}+v_{ij};\ h_{C_{ij}}=\delta_{ij}-1;\ v_{ij}=1.5+0.75(1-\delta_{ij}),\\ h_{-1C^L}=h_{C^L-1}=h_{1C^R}=h_{C^R1}=-\bar{t}=-0.5,\\ -t=h_{ii\pm1}=-2. \end{gathered}$$

Above, H_C denotes the Hamiltonian in the central region, where the one-particle contribution h_C, and the Coulomb contribution v_{ij} are presented. Additionally, the dot-electrodes hopping $\bar{t}$ and the next neighbor hopping in wires t are introduced. The on-site energy ε equals the Fermi energy. In the nonorthogonal description, the hopping matrix elements are

$$\begin{gathered} V_{C_n^R,1}=\langle C_n^R|h-E|1\rangle=\langle C_n^L|h-E|-1\rangle=V_{C_n^L,-1}=\bar{s}(\varepsilon-E)-\bar{t}\cos\theta;\\ V_{C_n^R,2}=\langle C_n^R|h-E|2\rangle=\langle C_n^L|h-E|-2\rangle=V_{C_n^L,-2}=-t\bar{s};\\ V_{C_n^L,1}=\langle C_n^L|h-E|1\rangle=\langle C_n^R|h-E|-1\rangle V_{C_n^R,-1}=-\bar{t}\sin\theta\cos\phi. \end{gathered}$$

From the above, it is straightforward to find the junction SEs

$$\Sigma_{C_n}^{R(A)}=\sum_{\alpha}V_{C_n\alpha}G_{\alpha}^{0R(A)}V_{\alpha C_n}$$

where the isolated electrode GFs are obtained from the half-infinite matrix

$$\hat{h}=\begin{bmatrix} \varepsilon & -t & 0 & 0 & 0\ldots & & \\ -t & \varepsilon & -t & 0 & 0 & 0\ldots & \\ 0 & -t & \varepsilon & -t & 0 & 0 & 0\\ . & . & . & . & . & & \end{bmatrix}, \tag{119}$$

where

$$\begin{aligned} G_{ij}^{0R(A)}(E) &= \mathrm{P.V.}\sum_k U_{ik}\frac{1}{E-\varepsilon_k}(U^\dagger)_{kj}\\ &\quad \mp i\pi\sum_k U_{ik}\delta(E-\varepsilon_k)(U^\dagger)_{kj}\\ G_{ij}^{0<}(E) &= if(E)2\pi\sum_k U_{ik}\delta(E-\varepsilon_k)(U^\dagger)_{kj}, \end{aligned} \tag{120}$$

and the matrix $U_{ij}=\sin\frac{ij\pi}{M+1}$ diagonalizes the Hamiltonian. The eigenvalue problem

$$\hat{h}|\bar{k}\rangle=\varepsilon_k|\bar{k}\rangle,$$

gives

$$|\bar{k}\rangle=\sqrt{\frac{2}{M+1}}\begin{bmatrix} \sin\frac{k\pi}{M+1}\\ \sin\frac{2k\pi}{M+1}\\ .\\ .\\ .\\ \sin\frac{Mk\pi}{M+1} \end{bmatrix}, \tag{121}$$

with eigenvalues

$$\varepsilon_k=\varepsilon-2t\cos\frac{k\pi}{M+1}.$$

Releasing the infinite sum in Equation 120 to a continuum, is obtained using contour integration

$$\begin{gathered} G_{11}^{0R(A)}=\frac{1}{t}\left(\frac{E-\varepsilon}{2t}\mp i\sqrt{1-\left(\frac{E-\varepsilon}{2t}\right)^2}\right)\Theta(2t-|E-\varepsilon|)\\ +\frac{1}{t}\left(\frac{E-\varepsilon}{2t}-\sqrt{\left(\frac{E-\varepsilon}{2t}\right)^2-1}\right)(1-\Theta(2t-|E-\varepsilon|))\\ G_{12}^{0R(A)}=G_{21}^{0R(A)}=G_{-1,-2}^{0R(A)}=G_{-2,-1}^{0R(A)}=-2\left(\frac{E-\varepsilon}{2t}\right)G_{11}^{0R(A)}+\frac{1}{t}\\ G_{22}^{0R(A)}=g_{-2-2}^{0R(A)}=-2\left(\frac{E-\varepsilon}{2t}\right)G_{12}^{0R(A)}\\ G_{ij}^{0<}=f(E)(G_{ij}^{0A}-G_{ij}^{0R}). \end{gathered} \tag{122}$$

To determine the central region GF, we derived the Hamiltonian

$$\begin{gathered} (H_C)_{C_n^L,C_n^L}=(H_C)_{C_n^R,C_n^R}=\bar{s}^2\varepsilon-2\bar{s}\bar{t}\cos\theta+(1-\bar{s}^2)(h_{C_{11}}+v_{11})+S(h_{C_{12}}+v_{12})\\ (H_C)_{C_n^R,C_n^L}=(H_C)_{C_n^LC_n^R}=-2\bar{s}\bar{t}\sin\theta\cos\phi+(1-\bar{s}^2)(h_{C_{12}}+v_{12})+S(h_{C_{11}}+v_{11}). \end{gathered} \tag{123}$$

Knowing that

$$(E\hat{S}-H_{C_n}-\Sigma_{C_n})G_{C_n}=I,$$

where

$$\begin{aligned} A &\overset{\text{def.}}{=} E-(H_C)_{C_n^{L(R)},C_n^{L(R)}}-\Sigma^{R(A)}_{C_n^{L(R)},C_n^{L(R)}}\\ &=(1-\bar{s}^2)(E-(h_C)_{11}-v_{11}-g_{11}^{0R(A)}\bar{t}^2)-S((h_C)_{12}+v_{12}),\\ B &\overset{\text{def.}}{=} \mathrm{E}S-(H_C)_{C_n^{L(R)},C_n^{R(L))}}-\Sigma^{R(A)}_{C_n^{L(R)},C_n^{R(L))}}\\ &=S(E-(h_C)_{11}-v_{11}-g_{11}^{0R(A)}\bar{t}^2)-(1-\bar{s}^2)((h_C)_{12}+v_{12}), \end{aligned}$$

we obtain

$$G_{C_n}=(A^2-B^2)^{-1}\begin{bmatrix} A & -B\\ -B & A \end{bmatrix}. \tag{124}$$

Here, we adopted the phenomenological theory.[50] This method is equivalent to a microscopic self-consistent model in the quasi-neutrality approximation where the charge polarization in the central region is neglected. Since the dynamically induced charge is not considered, the total displacement current is partitioned into each electrode, giving for the conductance

$$G_{\alpha\beta}=G_{\alpha\beta}^p-G_\beta^d\frac{\sum_\gamma G_{\alpha\gamma}^p}{\sum_\gamma G_\gamma^d},$$

where

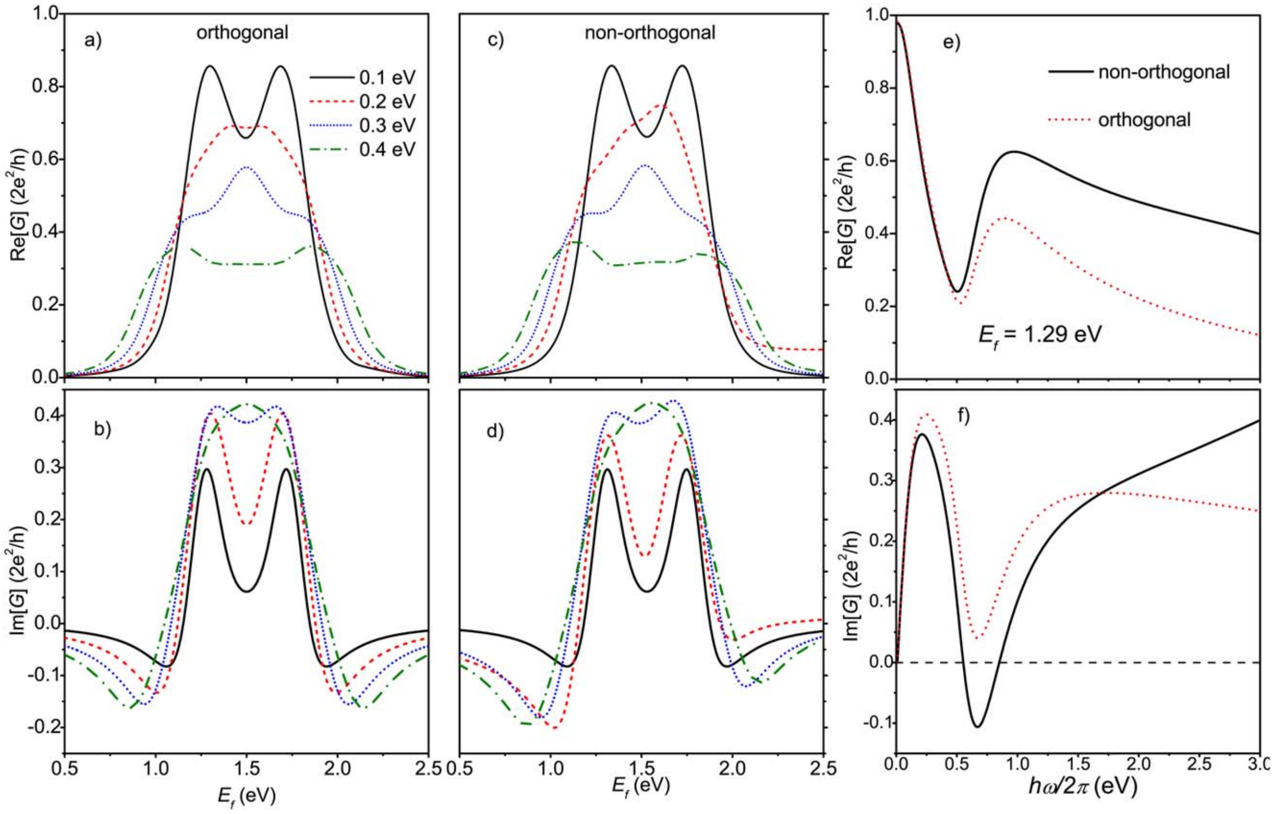

FIGURE 1 The conductance, G, of a two state central region coupled with two semi-infinite leads. (a) Real and (b) imaginary parts of G in an orthogonal basis for different frequencies (eV) as functions of the Fermi energy E_f (c) Real and (d) imaginary parts of G in a nonorthogonal basis for different frequencies (eV) as functions of the Fermi energy E_f (e) Real and (f) imaginary parts of G for $E_f = 1.29$ eV as functions of frequency in nonorthogonal and orthogonal cases. To describe nonorthogonality we choose $(\theta, \phi) = (\pi/6, \pi/8)$

$$
\begin{aligned}
G^{p}_{\alpha\beta} &= \frac{2e^2}{h}\mathrm{Tr}\int dE((\bar{G}I_\beta G)^<_{\alpha C_n} + 1/2(\bar{G}S_{C_n\beta}G)^<_{\alpha C_n} + 1/2(\bar{G}S_{\beta C_n}G)^<_{\alpha C})\left(V_{C_n\alpha} - \frac{\hbar\omega}{2}S_{C_n\alpha}\right)\\
&-(V_{\alpha C_n} - \frac{\hbar\omega}{2}S_{\alpha C_n})((\bar{G}I_\beta G)^<_{C_n\alpha} + 1/2(\bar{G}S_{C_n\beta}G)^<_{C_n\alpha} + 1/2(\bar{G}S_{\beta C_n}G)^<_{C\alpha})\\
&+1/2\delta_{\alpha\beta}\frac{2e^2}{h}\mathrm{Tr}\int dE(\bar{G}^<_{\alpha C_n}S_{C_n\alpha} - S_{\alpha C_n}G^<_{C_n\alpha})\\
G^{d}_{\beta} &= -\hbar\omega\frac{e^2}{h}\mathrm{Tr}\sum_\alpha\int[S_{\alpha C_n}((\bar{G}I_\beta G)^<_{C_n\alpha} + 1/2(\bar{G}S_{C_n\beta}G)^<_{C_n\alpha} + 1/2(\bar{G}S_{\beta C_n}G)^<_{C_n\alpha})\\
&+((\bar{G}I_\beta G)^<_{C_n\alpha} + 1/2(\bar{G}S_{C_n\beta}G)^<_{\alpha C_n} + 1/2(\bar{G}S_{\beta C_n}G)^<_{\alpha C_n})S_{C_n\alpha}]\\
&-\hbar\omega\frac{2e^2}{h}\mathrm{Tr}\int S_{C_n}((\bar{G}I_\beta G)^<_{C_n} + 1/2(\bar{G}S_{C_n\beta}G)^<_{C_n} + 1/2(\bar{G}S_{\beta C_n}G)^<_{C_n}),
\end{aligned}
\tag{125}
$$

$G^p_{\alpha\beta}$ and $G^d_{\alpha\beta}$ are the particle and the displacement current related conductance, respectively. The above expressions for conductance are derived from our microscopic theory. Using the expressions (78 and 79), the current can be expanded over the voltages

$$
i_\alpha = \sum_\beta G_{\alpha\beta}V_\beta.
$$

The voltage is $V_\alpha = -v_\alpha/e$, where v_α is the external potential. Since the dynamical self-consistent response is neglected, charge neutrality does not hold any more. This is the reason for partitioning the term from the right side of Equation 104, to separate contributions of the left and the right electrode. This leads to interface projections of the characteristic potentials Equation 116,

$$
a^{[\alpha]}_{C_n\beta} = \frac{1}{2}\delta_{\alpha\beta}S_{C_n\beta};\ \ a^{[\alpha]}_{\beta C_n} = \frac{1}{2}S_{\beta C_n}\delta_{\alpha\beta}. \tag{126}
$$

This is the reason for the coefficient 1/2 in front of the interface terms in Equation 125. In our model $S_{\beta C_n} = S_{C_n\beta} = \bar{s};\ S_{C_n} = S$. In the left panel of Figure 1, the real and imaginary parts of the conductance (G) obtained in the orthogonal and nonorthogonal description are plotted. Even a phenomenological theory applied to a simple model exhibits clear differences between an orthogonal and nonorthogonal description. Nonorthogonality introduces an asymmetric response relative to the minimum between the two peaks. This result is consistent with earlier studies.[36,37] The behavior of the real part of the conductance around the resonance energies where inductive responses occur is expected[50] and can be understood through a classical explanation where the current lags the voltage because of electron inertia.[53] Additionally, the increasing frequency causes the imaginary part to become more pronounced. On the right side of Figure 1, the frequency response for the orthogonal and nonorthogonal case is represented for a fixed Fermi energy of 1.29 eV. The imaginary part of the conductance in the orthogonal description is always positive, which is a hallmark of inductive behavior. However, in the nonorthogonal description, there is a range of frequencies where the imaginary part is negative, meaning that the capacitive response dominates. Compared with the orthogonal case, the nonorthogonal description gives rise to an additional displacement current (i.e., the charging capacitor current). With a further increase in the frequency, the inductive behavior becomes more pronounced in the nonorthogonal description, which could be related to an increase of the electron effective mass. The above figure clearly demonstrates that the orthogonal and nonorthogonal descriptions do not produce the same result for dynamical currents in linear response theory.

5 | CONCLUSIONS

We have derived expressions for current in the bounds of a microscopic theory of nonequilibrium time-dependent electronic transport through a molecule using a nonorthogonal basis. The first-order response of the central region to external potential of well-screening electrodes was determined within the Hartree approximation. A nontrivial current contribution is generated using a nonorthogonal basis for the case of a time-dependent bias. If these terms are omitted from the expression for current, the gauge invariance is violated. Their physical meaning can be related to the fraction of displacement current through the electrode-central region interfaces. The orthogonal case result is recovered for both zero and the limit of vanishingly small overlap. The presented theory is suitable for coupling with density functional theory in the standard way, which would make it practical to describe time-dependent electronic transport through atoms, molecules and junctions for a wide variety of systems.

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APPENDIX

Obtaining the expression for the TIH GFs, Equations 78 and 79 requires a rather long derivation and, as a first step, we derive an auxiliary result,

$$g^{\gamma}=\sum_{\alpha} v_{\alpha}(\bar{G}a^{[\alpha]}G)^{\gamma};\ \gamma=\mathrm{R},\mathrm{A},<. \tag{A1}$$

The derivation was done for the TIH GFs projection on the electrode α (i.e., $g^{\alpha,\gamma}$), because this step is the most demanding of all necessary projections. The derivation will also give the expression for $g^{C\alpha}$, whereas the remaining projections may be obtained in a similar way.

The superscript γ will be omitted in the following presentation in order to simplify the notation, since the following expressions are valid for all three types (i.e., R, A and $<$) of the GFs individually. The product $(\bar{G}a^{[\alpha]}G)^{\gamma}$ was expanded and expressed according to the Langreth rules in the energy-domain via the Fourier transformation. The GFs and the SEs, contained in the EOM of $G^{\alpha\beta}$, Equation 32, were separated into the TH and TIH parts according to Equation 49. This leads to the TIH contribution

$$g^{\alpha}=g^{0\alpha}+\bar{G}^{0\alpha}\bar{V}_{\alpha C}g^{C\alpha}+\bar{G}^{0\alpha}U_{\alpha C}G^{C\alpha}+g^{0\alpha}V_{\alpha C}G^{C\alpha}. \tag{A2}$$

The above expression contains the TIH contributions $g^{0\alpha}$, $g^{C\alpha}$, $U_{\alpha C}$, and each of them must be found. The TIH GF of the isolated electrode α is obtained from Equation 67 in energy domain

$$g^{0\alpha}=v_{\alpha}\bar{G}^{0\alpha}S_{\alpha}G^{0\alpha}. \tag{A3}$$

The TIH part of the mixed GF is obtained from Equation 33

$$g^{C\alpha}=\bar{G}^{C}\bar{V}_{C\alpha}g^{0\alpha}+\bar{G}^{C}U_{C\alpha}G^{0\alpha}+g^{C}V_{C\alpha}G^{0\alpha}, \tag{A4}$$

which together with Equation A3 transforms the first two terms on the r.h.s. of Equation A4 into

$$v_{\alpha}\bar{G}^{C\alpha}S_{\alpha}G^{0\alpha}+\sum_{\beta} v_{\beta}\bar{G}^{C}a^{[\beta]}_{C\alpha}G^{0\alpha}, \tag{A5}$$

where U is expressed through characteristic potentials. The third term, $g^{C}V_{C\alpha}G^{0\alpha}$, is more difficult to transform due to the presence of g^{C}, Equation 77. Starting from Equations 52, 54, 55, 82, and 84, for the third term on the r.h.s. of Equation A4 the following is obtained

$$\begin{aligned}\bar{G}^{C}U_{C}G^{C\alpha}+\bar{G}^{C}\sigma^{\mathrm{junct}}_{C}G^{C\alpha}=&\sum_{\beta}(v_{\beta}\bar{G}^{C}a^{[\beta]}_{C}G^{C\alpha}+\bar{G}^{C\beta}U_{\beta C}G^{C\alpha}\\&+\bar{G}^{C}U_{C\beta}(G^{\beta\alpha}-\delta^{\alpha}_{\beta}G^{0\beta})+v_{\beta}\bar{G}^{C\beta}S_{\beta}(G^{\beta\alpha}-\delta^{\alpha}_{\beta}G^{0\beta})).\end{aligned} \tag{A6}$$

Collecting terms from Equations A5 and A6, gives

$$g^{C\alpha}=\sum_{\beta} v_{\beta}(\bar{G}a^{[\beta]}G)^{C\alpha}, \tag{A7}$$

proving the Equation A1 for $g^{C\alpha}$.

We proceed with derivation in order to prove Equation A1 for the expression $g^{\alpha,\gamma}$ with $\gamma=\mathrm{R},\mathrm{A},<$. The sum of the first and fourth term on the r.h.s of Equation A2, which we denote with X, is

$$\begin{aligned}\mathrm{X}&=g^{0\alpha}+g^{0\alpha}V_{\alpha C}G^{C\alpha}\\&=v_{\alpha}\bar{G}^{0\alpha}S_{\alpha}G^{0\alpha}+v_{\alpha}\bar{G}^{0\alpha}S_{\alpha}(G^{\alpha}-G^{0\alpha})\\&=v_{\alpha}\bar{G}^{0\alpha}S_{\alpha}G^{\alpha},\end{aligned} \tag{A8}$$

the third term, expressed through characteristic potentials and denoted with Y, is

$$Y=\bar{G}^{0\alpha}U_{\alpha C}G^{C\alpha}=\sum_{\beta} v_{\beta}\bar{G}^{0\alpha}a^{[\beta]}_{\alpha C}G^{C\alpha}, \tag{A9}$$

and, by using Equation A7, for the second term (denoted with Z) it is obtained

$$\begin{aligned}Z=\bar{G}^{0\alpha}\bar{V}_{\alpha C}g^{C\alpha}&=\sum_{\beta} v_{\beta}\bar{G}^{\alpha C}(a^{[\beta]}G)^{C\alpha}+\sum_{\beta} v_{\beta}\sum_{\rho}(\bar{G}^{\alpha\rho}-\delta_{\alpha\rho}\bar{G}^{0\rho})(a^{[\beta]}G)^{\rho\alpha}\\&=\sum_{\beta} v_{\beta}(\bar{G}^{\alpha C}(a^{[\beta]}G)^{C\alpha}+\sum_{\rho}\bar{G}^{\alpha\rho}(a^{[\beta]}G)^{\rho\alpha})-\sum_{\beta}\bar{G}^{0\alpha}(a^{[\beta]}G)^{\rho\alpha}\\&=\sum_{\beta} v_{\beta}(\bar{G}a^{[\beta]}G)^{\alpha}-\mathrm{X}-\mathrm{Y}.\end{aligned} \tag{A10}$$

Summary of these terms, $\mathrm{X}+\mathrm{Y}+\mathrm{Z}=g^{\alpha}$, is valid for the index $\gamma=\mathrm{R},\mathrm{A},<$, which proves Equation A1.

What remains is to prove expressions given in the second row in Equations 78 and 79 and for this purpose it is considered the case of lesser TIH GF. By tranforming Equation A1 using the property $\sum_{\gamma} a^{[\gamma]}=S$, it is obtained

$$g^{\alpha<}=v_\beta(\bar{G}SG)^{\alpha<}+(v_\alpha-v_\beta)(\bar{G}a^{[\alpha]}G)^{\alpha<}. \tag{A11}$$

In the following procedure we will use explicit denoting of terms obtained after the Langreth rules. The next necessary step it to calculate $(\bar{G}SG)^{\alpha<}$, which will be done by analyzing its contributions, one by one. The first one (denoted with A_1),

$$A_1=(\bar{G}^{\alpha C}S_C G^{C\alpha})^{<},$$

after the Langreth expansion contains terms $\bar{G}^{CR(A)}S_C G^{CR(A)}$, $\bar{G}^{CR}S_C G^{C<}$, and $\bar{G}^{C<}S_C G^{CA}$. Referring expressions for R/A GFs, Equation 51, the following is obtained

$$[\bar{G}^{CR(A)}]^{-1}-[G^{CR(A)}]^{-1}=\omega S_C+\Sigma_C^{\mathrm{junctR(A)}}-\bar{\Sigma}_C^{\mathrm{junctR(A)}}. \tag{A12}$$

After multiplying it with $\bar{G}^{CR(A)}$ from the left and with $G^{CR(A)}$ from the right the following is gained

$$\bar{G}^{CR(A)}S_C G^{CR(A)}=\frac{G^{CR(A)}-\bar{G}^{CR(A)}}{\omega}-\bar{G}^{CR(A)}\frac{\Sigma_C^{\mathrm{junctR(A)}}-\bar{\Sigma}_C^{\mathrm{junctR(A)}}}{\omega}G^{CR(A)}. \tag{A13}$$

By multiplying the obtained expression with $\bar{G}^{CR}\bar{\Sigma}_C^{\mathrm{junct}<}$ from the left, in the case of advanced GF, and with $\Sigma_C^{\mathrm{junct}<}G^{CA}$ from the right, in the case of retarded GF, and by referring to the Keldysh Equation 56, the following is obtained

$$\begin{aligned}\bar{G}^{CR}S_C G^{C<}&=\frac{G^{C<}-\bar{G}^{CR}\Sigma_C^{\mathrm{junct}<}G^{CA}}{\omega}-\bar{G}^{CR}\frac{\Sigma_C^{\mathrm{junctR}}-\bar{\Sigma}_C^{\mathrm{junct,R}}}{\omega}G^{C<}\\ \bar{G}^{C<}S_C G^{CA}&=\frac{\bar{G}^{CR}\bar{\Sigma}_C^{\mathrm{junct}<}G^{CA}-\bar{G}^{C<}}{\omega}-\bar{G}^{C<}\frac{\Sigma_C^{\mathrm{junctA}}-\bar{\Sigma}_C^{\mathrm{junctA}}}{\omega}G^{CA}.\end{aligned} \tag{A14}$$

Equations A13 and A14 were used to transform the TH expressions for $G^{C\alpha}, G^{\alpha C}$, Equations 52, 53, 57, and 58 and the following was found

$$\begin{aligned}A_1=\;&\bar{G}^{\alpha CR}S_C G^{C\alpha<}+\bar{G}^{\alpha C<}S_C G^{C\alpha A}\\ =\;&\bar{G}^{0\alpha R}\bar{V}_{\alpha C}(\bar{G}^{CR}S_C G^{CR})V_{C\alpha}G^{0\alpha<}+\bar{G}^{0\alpha R}\bar{V}_{\alpha C}(\bar{G}^{CR}S_C G^{C<})V_{C\alpha}G^{0\alpha A}\\ &+\bar{G}^{0\alpha R}\bar{V}_{\alpha C}(\bar{G}^{C<}S_C G^{CA})V_{C\alpha}G^{0\alpha A}+\bar{G}^{0\alpha<}\bar{V}_{\alpha C}(\bar{G}^{CA}S_C G^{CA})V_{C\alpha}G^{0\alpha A}\\ =\;&\frac{1}{\omega}(\bar{G}^{0\alpha R}\bar{V}_{\alpha C}G^{C\alpha<}+\bar{G}^{0\alpha<}\bar{V}_{\alpha C}G^{C\alpha A}-\bar{G}^{\alpha CR}V_{C\alpha}G^{0\alpha<}-\bar{G}^{\alpha C<}V_{C\alpha}G^{0\alpha A}\\ &+\bar{G}^{\alpha CR}(\bar{\Sigma}_C^{\mathrm{junctR}}-\Sigma_C^{\mathrm{junctR}})G^{C\alpha<}+\bar{G}^{\alpha CR}(\bar{\Sigma}_C^{\mathrm{junct}<}-\Sigma_C^{\mathrm{junct}<})G^{C\alpha A}\\ &+\bar{G}^{\alpha C<}(\bar{\Sigma}_C^{\mathrm{junctA}}-\Sigma_C^{\mathrm{junctA}})G^{C\alpha A}).\end{aligned} \tag{A15}$$

The second characteristic contribution (denoted with A_2) resulting from $(\bar{G}SG)^{\alpha<}$ is

$$\begin{aligned}A_2=&\sum_\beta\bar{G}^{\alpha CR}S_{C\beta}G^{\beta\alpha<}+\bar{G}^{\alpha C<}S_{C\beta}G^{\beta\alpha A}+\bar{G}^{\alpha\beta R}S_{\beta C}G^{C\alpha<}+\bar{G}^{\alpha\beta<}S_{\beta C}G^{C\alpha A}\\ =&\sum_\beta\bar{G}^{\alpha CR}S_{C\beta}(G^{0\alpha}\delta_\alpha^\beta+G^{0\beta}V_{\beta C}G^{C\alpha})^{<}+\bar{G}^{\alpha C<}S_{C\beta}(G^{0\alpha}\delta_\alpha^\beta+G^{0\beta}V_{\beta C}G^{C\alpha})^{A}\\ &+(\bar{G}^{\alpha C}\bar{V}_{C\beta}\bar{G}^{0\beta}+\bar{G}^{0\alpha}\delta_\alpha^\beta)^{R}S_{\beta C}G^{C\alpha<}+(\bar{G}^{\alpha C}\bar{V}_{C\beta}\bar{G}^{0\beta}+\bar{G}^{0\alpha}\delta_\alpha^\beta)^{<}S_{\beta C}G^{C\alpha A},\end{aligned} \tag{A16}$$

which is obtained by using Equations 54 and 59 for $G^{\beta\alpha A}$ and $G^{\beta\alpha<}$, respectively, and by applying Equations 55 and 60 for $\bar{G}^{\alpha\beta R}$ and $\bar{G}^{\alpha\beta<}$, respectively. After the multiplication and the application of Langreth rules, the above expression was transformed into

$$\begin{aligned}A_2=\;&\bar{G}^{\alpha CR}S_{C\alpha}G^{0\alpha<}+\bar{G}^{\alpha C<}S_{C\alpha}G^{0\alpha A}+\bar{G}^{0\alpha R}S_{\alpha C}G^{C\alpha<}+\bar{G}^{0\alpha<}S_{\alpha C}G^{C\alpha A}\\ &+\frac{1}{\omega}\sum_\beta(\bar{G}^{\alpha CR}(\omega S_{C\beta}G^{0\beta R}V_{\beta C}+\bar{V}_{C\beta}\bar{G}^{0\beta R}\omega S_{\beta C})G^{C\alpha<}\\ &\qquad+\bar{G}^{\alpha CR}(\omega S_{C\beta}G^{0\beta<}V_{\beta C}+\bar{V}_{C\beta}\bar{G}^{0\beta<}\omega S_{\beta C})G^{C\alpha A}\\ &\qquad+\bar{G}^{\alpha C<}(\omega S_{C\beta}G^{0\beta A}V_{\beta C}+\bar{V}_{C\beta}\bar{G}^{0\beta A}\omega S_{\beta C})G^{C\alpha A}).\end{aligned} \tag{A17}$$

The only remaining contribution (denoted with A_3),

$$A_3=\sum_\beta(\bar{G}^{\alpha\beta R}S_\beta G^{\beta\alpha<}+\bar{G}^{\alpha\beta<}S_\beta G^{\beta\alpha A}), \tag{A18}$$

is transformed in the same way as A_2, giving

$$\begin{aligned}A_3=\;&\bar{G}^{0\alpha R}S_\alpha G^{0\alpha<}+\bar{G}^{0\alpha<}S_\alpha G^{0\alpha A}+\bar{G}^{0\alpha R}S_\alpha G^{0\alpha R}V_{\alpha C}G^{C\alpha<}\\ &+(\bar{G}^{0\alpha R}S_\alpha G^{0\alpha<}+\bar{G}^{0\alpha<}S_\alpha G^{0\alpha A})V_{\alpha C}G^{C\alpha A}\\ &+\bar{G}^{\alpha C<}\bar{V}_{C\alpha}\bar{G}^{0\alpha A}S_\alpha G^{0\alpha A}+\bar{G}^{\alpha CR}\bar{V}_{C\alpha}(\bar{G}^{0\alpha R}S_\alpha G^{0\alpha<}+\bar{G}^{0\alpha<}S_\alpha G^{0\alpha A})\\ &+\sum_\beta[\bar{G}^{\alpha CR}\bar{V}_{C\beta}\bar{G}^{0\beta R}S_\beta G^{0\beta R}V_{\beta C}G^{C\alpha<}+\bar{G}^{\alpha C<}\bar{V}_{C\beta}\bar{G}^{0\beta A}S_\beta G^{0\beta A}V_{\beta C}G^{C\alpha A}\\ &\qquad+\bar{G}^{\alpha CR}\bar{V}_{C\beta}(\bar{G}^{0\beta R}S_\beta G^{0\beta<}+\bar{G}^{0\beta<}S_\beta G^{0\beta A})V_{\beta C}G^{C\alpha A}].\end{aligned} \tag{A19}$$

The sum A_1+A_2 can be simplified via Equation 50 for the TH $\Sigma_C^{\mathrm{junct}}$,

$$\begin{aligned}A_1+A_2\;=&\sum_\beta\Bigg[\bar{G}^{\alpha CR}\bar{V}_{C\beta}\frac{\bar{G}^{0\beta R}-G^{0\beta R}}{\omega}V_{\beta C}G^{C\alpha<}+\bar{G}^{\alpha CR}\bar{V}_{C\beta}\frac{\bar{G}^{0\beta<}-G^{0\beta<}}{\omega}V_{\beta C}G^{C\alpha A}\\ &\qquad+\bar{G}^{\alpha C<}\bar{V}_{C\beta}\frac{\bar{G}^{0\beta A}-G^{0\beta A}}{\omega}V_{\beta C}G^{C\alpha A}\Bigg]\\ &-\frac{1}{\omega}[\bar{G}^{\alpha CR}\bar{V}_{C\alpha}G^{0\alpha<}+\bar{G}^{\alpha C<}\bar{V}_{C\alpha}G^{0\alpha A}-\bar{G}^{0\alpha R}V_{\alpha C}G^{C\alpha<}-\bar{G}^{0\alpha<}V_{\alpha C}G^{C\alpha A}].\end{aligned} \tag{A20}$$

The importance of Equations 72 and 73 becomes obvious because they show that the corresponding terms in the sums over β of A_3, Equation A19, and β of A_1+A_2, Equation A20, sum up to zero. The remaining terms of $A_1+A_2+A_3$, via Equations 54, 55, 59, and 60, together with Equations 72 and 73 give simply the following: $(G^{\alpha<}-\bar{G}^{\alpha<})/\omega$. To summarize,

$$(\bar{G}^{R}SG^{<})^{\alpha}+(\bar{G}^{<}SG^{A})^{\alpha}=A_1+A_2+A_3=\frac{G^{\alpha<}-\bar{G}^{\alpha<}}{\omega}. \tag{A21}$$

By applying the above equation to Equation A11, it is confirmed that

$$g^{\alpha<}=v_\alpha\frac{G^{\alpha<}-\bar{G}^{\alpha<}}{\omega}+(v_\beta-v_\alpha)(\bar{G}^{R}a^{[\beta]}G^{<}+\bar{G}^{<}a^{[\beta]}G^{A})^{\alpha},$$

which is just sought Equation 78. Using the similar derivation it is somewhat easier to prove Equation 79.

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Non-equilibrium linear-response transport through quantum dot beyond time homogeneity at Hartree–Fock level

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The expression for current, induced by finite bias with additional time-dependent (TD) external perturbation, through a molecule/dot is derived using the non-equilibrium Green's function (GF) formalism in the standard two-probe geometry. The GFs as well as self energies (SEs) are split into time-homogeneous (TH) and time-inhomogeneous (TIH) contributions, where the former are obtained as a result of zeroth-order expansion of the full, two-time corresponding quantities and the latter we find as linear corrections. The TD charge in the dot consists of a charge that is injected from the electrodes and the charge that is induced in the dot. The TD potential, induced in the dot due to dot TD charge, was treated self consistently at Hartree–Fock (HF) level as a TIH part of Coulomb interaction related SE. It is assumed that TH quantities are solved either exactly or approximately, i.e., using density functional theory (DFT). The theory is charge conserving and its gauge invariance is explicitly shown. The contribution of TD HF potential to the total Coulomb interaction energy vanishes in the case of one-electron existence, i.e., the self-interaction error (SIE), beyond the one associated with the DFT, was not introduced. Known results in a special case of time homogeneity are recovered and extended to TIH transport. The issues of current partitioning and the displacement current are resolved naturally, without any additional assumptions about any of quantities, due to explicit inclusion of dot potential. The special cases of wide-band limit, zero bias, and zero-bias wide-band limit are also considered and in each case the corresponding expression for the TD current is derived. The theory is particularly suitable for use in connection with DFT when it provides a first-principle microscopic linear-response description of the non-equilibrium TIH quantum transport useful for calculation of TD current through quantum dots, molecules, junctions, or devices at the nano-scale.

1 Introduction One of the main challenges of the microscopic description of current flow through a quantum system is how to treat Coulomb interaction. Since the pioneering work of Landauer [1], the scattering formalism was used to formulate the theory of transport through quantum-coherent systems coupled to electronic reservoirs. In the equilibrium case, the transport is described using the concept of conducting channels, directly related to the conductance of the system [2, 3]. In the non-equilibrium case, the approach was extended to the non-equilibrium quantum-coherent case in the mesoscopic regime using the scattering formalism in the presence of a time-dependent (TD) potential of small frequency for quantum dots, which intra-dot interaction is treated at the Hartree (random phase approximation, RPA) level [4], leading to the recent experimental finding of the quantization of conductance in the alternating current regime [5]. The quantum mesoscopic system in the presence of the incoherent scattering was studied as well, extending results to the case of dephasing processes, using the formalism of non-equilibrium Green's functions (NEGFs) [6], which was also used to formulate a current-conserving gauge-invariant theory without explicit treatment of TD potential induced by TD injected charge [7]. The connection between the scattering and NEGF results for electronic current in the Hartree case has been established as well [8].

The treatment of non-equilibrium transport in the finite-bias stationary state by combining NEGFs and density functional theory (DFT) has also been used to numerically compute conductance and direct current [9–11], by expressing electronic density through NEGFs and treating Coulomb interaction at the DFT level, through Hartree and (semi-)local exchange-correlation (XC) functionals.

The DFT can be used so that GFs are associated directly with the effective one-particle, Kohn–Sham (KS) Hamiltonian. From the equations of motion of the GFs, the treatment of interaction also includes an expansion of the two-particle GF to obtain the interaction self energy (SE) [12], while the conservation relations [13, 14] provide a specific form of the SE. All higher orders of the two-particle GF expansion beyond the Hartree contribution lead to the spatially non-local SE, which is furthermore time non-local beyond the Fock contribution [15]. Our approach is to make a connection between time-homogeneous (TH) and time-inhomogeneous (TIH) parts of GFs and consequently TH and TIH parts of all relevant quantities derived from GFs using the Keldysh technique [15, 16] applied to the Kadanoff–Baym (KB) formalism [12–14]. Assuming that the ratio between amplitude of the TD voltage and frequency is much smaller than $\hbar/e$, where $\hbar$ is Planck's constant and e elementary charge, it is possible to neglect the voltage-nonlinear contribution to the current [6, 17]. We adopted the picture in Ref. [18], where it was assumed that due to good screening properties of the electrodes, a time-varying field causes a spatially homogeneous shift of energy levels in the electrodes. This picture is spoiled when the driving frequency exceeds the metallic plasma frequency. For this reason, the sudden application of the TD voltage cannot be described properly within our approach. The TD voltage rise time has to be slower than the plasma frequency period. The coupling of DFT and NEGFs is achieved through the DFT treatment of the TH contribution of the GFs, while the KB/NEGF approach provides the TIH part of the interaction SE, which is just the TD potential in the dot, calculated self consistently at the Hartree–Fock (HF) level. The starting point is the standard partitioning scheme where the Hamiltonian of the whole system is represented by separate Hamiltonians of electrode, dot, and junction regions [18, 19].

It is not necessary to consider the equation of motion of GFs in order to describe the steady-state regime, where it is possible to work directly with the matrix equation in the energy domain. The GF of the whole system is the resolvent of the total Hamiltonian; the connection between block matrices, associated with subsystems and contained in the equation, provides relevant equations for the dot, electrode, and junction regions; and, the junction SE is obtained as a function of surface (isolated electrode) GF, hopping, and mixed overlap matrices [9, 11]. In the non-steady regime working with the equation of motion is very useful because it facilitates computations with two-particle GFs [12, 15], and for this reason we use creation/annihilation operators of orthogonal states in the second quantization [6, 7, 18].

Working with two-particle GFs allows us to trivially demonstrate the current conservation, i.e., validity of the continuity equation, using the GF equation of motion. In order to satisfy the request of current conservation (as well as momentum and energy conservation), the approximate SE, stemming from two-particle GF expansion, has to take particular forms [13, 14]. Therefore, some basic physics was preserved, and the need for current-conserving theory was the motive for introducing the DFT, coupled with NEGFs, in our description. Namely, combining the two methods, treating the steady state in one way (DFT) and the TD contribution in another way, i.e., using HF expansion of the two-particle GFs and keeping its TIH part, provides the current conservation, as we will demonstrate explicitly. In addition to being current conserving, our approach is advantageous compared with Hartree self-consistent treatment of the TD internal potential, because the HF potential does not introduce a self-interaction error (SIE). Namely, the energy of the Coulomb interaction, within the linear-response description of TD systems, consists of contributions associated with time-independent and TD charge density that interact via TH, Coulomb interaction related, SE and contributions due to time-independent charge density that interact via TIH, Coulomb interaction related, SE. Within the proposed scheme, TH GFs are treated in the DFT manner, while the linear TIH corrections are adopted from perturbation expansion in the HF approximation. The consequences of such approximation are a replacement of TH SE by the Hartree plus exchange-correlation (H + XC) part of the KS Hamiltonian. In the one-electron case, the first two contributions are not zero (constant), which is the intrinsic DFT property, i.e., SIE, but the third term goes to zero, due to cancelation of Hartree and Fock contributions. The need for the current-conserving description, as well as the possibility of self-interaction-free TD transport theory, was a motivation for us to propose this hybrid approach.

The rest of the paper is organized as follows: in Section 2, the model and notation are introduced; the equation of motion of GFs in the presence of an external TD potential is discussed; in Section 3, the connections between TIH and TH quantities are established and a set of equations for their determination is derived, while the use of DFT to calculate TH quantities is discussed in Section 3.1; in Section 3.2, we point out the SIE problem as well as the benefit of our method associated with SIE reduction; in Section 4, expressions for both direct (Section 4.1) and alternating (Sections 4.2 and 4.3) currents are derived, and the solution to the current-partitioning problem within the theory is also given; gauge invariance of the obtained expressions is shown in Section 4.3; special cases of wide-band limit (WBL), zero bias, and zero-bias WBL are considered in Section 5, where corresponding expressions for TD current in each of the three cases are derived; and, Section 6 summarizes the main results of the paper.

2 Hamiltonian

The standard model of two probes with TD energy levels coupled to a quantum dot (molecule), described by the Hamiltonian

$$H = H_{\mathrm{L}} + H_{\mathrm{LD}} + H_{\mathrm{D}} + H_{\mathrm{RD}} + H_{\mathrm{R}}, \tag{1}$$

is considered, where $H_{\mathrm{L/R}}$ are Hamiltonians of the left/right lead, H_{D} is the dot Hamiltonian, and $H_{\mathrm{LD/RD}}$ are Hamiltonians describing the interaction of the left/right lead and the dot, which in the second quantization take the following forms:

$$H_\alpha = \sum_{k\alpha} \epsilon_{k\alpha}(t) c^\dagger_{k\alpha} c_{k\alpha}, \tag{2}$$

$$H_{\mathrm{D}} = \sum_{nm} \varepsilon_{nm} d^\dagger_n d_m + \frac{1}{2} \sum_{mnkl} W_{mn,kl}\, d^\dagger_m d^\dagger_n d_l d_k, \tag{3}$$

$$H_{\alpha\mathrm{D}} = \sum_{k\alpha,n} \left(V_{k\alpha,n} c^\dagger_{k\alpha} d_n + \mathrm{h.c.} \right), \tag{4}$$

where k is a wave vector such that $k\alpha$ counts eigenstates of the probe $\alpha = \mathrm{L}, \mathrm{R}$; the index n labels basis vectors of the dot, the Hamiltonian H_{D} is assumed to be Hermitian, represented in a basis $\{\phi_n(\mathbf{r})\}$, with particles interacting via two-particle interaction described by the matrix W, while the spin indices are not written since it is assumed that the system is non-magnetic. Creation and annihilation operators in the dot, $d_n(t)$ and $d^\dagger_n(t)$, respectively, as well as creation and annihilation operators in the leads, $c_{k\alpha}(t)$ and $c^\dagger_{k\alpha}(t)$, respectively, all satisfy fermionic commutation relations, while operators of the dot and leads anti-commute, i.e., $\{c^\dagger_{k\alpha}(t), d^\dagger_n(t)\} = 0$. We set $\hbar = 1$ hereafter to simplify notation without loss of generality. One-particle, kinetic with additional external potential, energy matrix elements are

$$\varepsilon_{\mathrm{nm}} = \int \mathrm{d}\mathbf{r}\, \phi^*_n(\mathbf{r}) \big(-\frac{1}{2m} \Delta_{\mathbf{r}} + u(\mathbf{r}) \big) \phi_m(\mathbf{r}) \tag{5}$$

and the Coulomb repulsion of electrons is represented via matrix elements of W as

$$W_{mn,kl} = \mathrm{e}^2 \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\, \frac{\phi^*_m(\mathbf{r})\phi^*_n(\mathbf{r}')\phi_k(\mathbf{r})\phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{6}$$

It is furthermore adopted that the standard assumption is that the two probes do not interact one with another and that the only interaction between the probes and the dot is through the coupling $V_{k\alpha,n}$, typically representing tunneling amplitudes across the junction between lead α and the molecule D.

3 Time dependence

An externally applied voltage in the lead α, $V_\alpha(t)$, induces time dependence of probe energy levels $\epsilon_{k\alpha} = \epsilon_{k\alpha}(t)$, thus making H time dependent as well. As a consequence, the first concern is how this introduces TD potential in the dot, and it is analyzed by using Dyson's equation. The GF of H_{D} is

$$G_{nm}(t, t') = -i \big\langle\, T_C\, d_n(t) d^\dagger_m(t') \big\rangle, \tag{7}$$

where d_n ($d^\dagger_m(t')$) is an annihilation (creation) operator in the Heisenberg picture, and the time ordering T_C is on the Keldysh contour C, where also lie time arguments [15, 16]. The equation of motion of d_n is

$$i\, \dot{d}_n(t) = [d_n(t), H(t)]. \tag{8}$$

The evaluation of the commutator is simplified because $[d_n(t), H_\alpha] = 0$ due to $\{d_n(t), c_{k\alpha}(t)\} = 0$. The commutator $[d_n(t), H_{\alpha\mathrm{D}}(t)]$ gives a contribution to the SE of the junction, while $[d_n(t), H_{\mathrm{D}}(t)]$ gives SE coming from the interaction part of H_{D} (the second sum of Eq. (3)). The junction SE, Σ^{jnc}, comes from its surface GF [18],

$$g_{k\alpha}(t, t') = -i \big\langle\, T_C\, c^{(\mathrm{H}_\alpha)}_{k\alpha}(t) c^{(\mathrm{H}_\alpha)\dagger}_{k\alpha}(t') \big\rangle, \tag{9}$$

where operators are in the Heisenberg picture according to the electrode Hamiltonian $H_\alpha(t)$, while the dot-interaction SE time dependence comes from the two-particle GF [12]

$$\begin{aligned} &G_2(nt, mt', n_1 t_1, m_1 t'_1) \\ &\quad = (-i)^2 \left\langle\, T_C\, d_n(t) d_m(t') d^\dagger_{m_1}(t'_1) d^\dagger_{n_1}(t_1) \right\rangle. \end{aligned} \tag{10}$$

The last GF can be in principle represented as a one-particle GF multiplying the dot-interaction SE Σ^{int} that is generally difficult to calculate. The standard assumption of non-interacting electrons in the leads is used, while the dot interaction remains Coulomb. Therefore, TD potential will exist in the dot due to potentials in electrodes coupled to the dot, which can be in principle found knowing Σ^{int}. It is important to emphasize that, due to the coupling of the dot and probes, the TD potential introduced in the probes will make the dot-interaction GF and the SE time dependent. Therefore, the problem is approached by decomposing all quantities into TH and TIH parts [6], expanding the two-particle GF up to the Hartree–Fock level [12], and then treating the TH parts of the obtained expressions using a different theory, in this case DFT [20–22], which solves, in principle exactly or in practice approximately, ground-state properties of interacting electrons in the dot through KS single-particle solutions. In other words, a perturbative technique is used to find the TD potential in the dot (related to TIH Σ^{int}), while DFT deals with the Coulomb interaction in the dot (related to TH Σ^{int}).

The TH part of Σ^{int} can be taken into account by decomposing it into the HF local part and the non-local remainder [15]:

$$\begin{aligned} \Sigma^{\mathrm{int}}(t, t') = {} & \Sigma^{\mathrm{int,HF}}(t, t')\delta(t - t') + \Sigma^{\mathrm{int,>}}(t, t')\theta(t - t') \\ & + \Sigma^{\mathrm{int,<}}(t, t')\theta(t' - t), \end{aligned} \tag{11}$$

obtained from the expansion of the two-particle GF, where the lowest-order term gives the HF part, and the remaining two terms contain the contribution from the two-particle interaction.

The concern is with the linear-response regime, where Dyson's equation for the TIH part is derived assuming that the

TIH contribution is small and depends on time-varying voltage up to the linear term [6, 8], giving the following equation of motion of the GF, written in matrix form as

$$i\frac{\partial G(t,t')}{\partial t} = \delta(t-t')I + \varepsilon\, G(t,t') + \int_C \mathrm{d}t_1\, \Sigma(t,t_1)G(t_1,t'), \tag{12}$$

where I is the unity matrix, and Σ is the total SE, which can be split into the interaction and junction parts, $\Sigma = \Sigma^{\mathrm{int}} + \Sigma^{\mathrm{jnc}}$, with the following equations for each contribution:

$$\begin{aligned}\sum_l \int_C \mathrm{d}t_1\, \Sigma^{\mathrm{int}}_{nl}(t,t_1)G_{lm}(t_1,t')\\ = -i\sum_{jkl} W_{njkl}G_2(kt, lt; mt', jt^+),\end{aligned} \tag{13}$$

$$\Sigma^{\mathrm{jnc}}_{nl}(t,t_1) = \sum_{k\alpha} V^*_{k\alpha,n}\, g_{k\alpha}(t,t_1)V_{k\alpha,m}, \tag{14}$$

where Eq. (13) describes the intra-dot Coulomb interaction of electrons, Eq. (14) describes the coupling between the dot and leads, and g is the surface GF, Eq. (9). The time argument t^+ means $t+\delta$ for infinitesimal $\delta > 0$, and the time integration is along the Keldysh contour C. Similarly, both G and Σ are decomposed into TH and TIH parts:

$$G(t,t') = G^{\mathrm{h}}(t-t') + G^{\mathrm{i}}(t,t'), \tag{15}$$

$$\Sigma(t,t') = \Sigma^{\mathrm{h}}(t-t') + \sigma(t,t'). \tag{16}$$

Equation (15) allows separation of the equation of motion of the GF, Eq. (12), into two equations, for TH and TIH parts,

$$\begin{aligned}i\frac{\partial G^{\mathrm{h}}(t-t')}{\partial t} &= \delta(t-t')I + \varepsilon\, G^{\mathrm{h}}(t-t')\\ &\quad + \int_C \mathrm{d}t_1\, \Sigma^{\mathrm{h}}(t-t_1)G^{\mathrm{h}}(t_1-t'),\end{aligned} \tag{17}$$

$$\begin{aligned}i\frac{\partial G^{\mathrm{i}}(t,t')}{\partial t} &= \varepsilon\, G^{\mathrm{i}}(t,t') + \int_C \mathrm{d}t_1\, \Sigma^{\mathrm{h}}(t-t_1)G^{\mathrm{i}}(t_1,t')\\ &\quad + \int_C \mathrm{d}t_1 \sigma(t,t_1)G^{\mathrm{h}}(t_1-t')\end{aligned} \tag{18}$$

with the following particular solution for the TIH part:

$$G^{\mathrm{i}}(t,t') = \int_C \mathrm{d}t_1 \int_C \mathrm{d}t_2\ G^{\mathrm{h}}(t-t_1)\sigma(t_1,t_2)G^{\mathrm{h}}(t_1-t'). \tag{19}$$

The TIH SE of the junction, $\sigma^{\mathrm{jnc}}(t,t')$, directly follows from Eq. (14),

$$\sigma^{\mathrm{jnc}}_{mn}(t,t') = \sum_{k\alpha} V^*_{k\alpha,m}\, g^{\mathrm{i}}_{k\alpha}(t,t')V_{k\alpha,n}, \tag{20}$$

where the TIH part is now contained in the surface GF. Evolution of g in the Heisenberg picture of H_α is given by

$$\begin{aligned}g_{k\alpha}(t,t') &= \theta(t-t')(-i)\langle c_{k\alpha}c^\dagger_{k\alpha}\rangle \mathrm{e}^{-i\left(\epsilon_{k\alpha}(t-t')+\int_{t'}^{t}\mathrm{d}\tau V_\alpha(\tau)\right)}\\ &\quad + \theta(t'-t)i\langle c^\dagger_{k\alpha}c_{k\alpha}\rangle \mathrm{e}^{-i\left(\epsilon_{k\alpha}(t-t')+\int_{t'}^{t}\mathrm{d}\tau V_\alpha(\tau)\right)}\end{aligned} \tag{21}$$

with retarded, advanced, and lesser GFs given by

$$\begin{aligned}g^{\mathrm{R}}_{k\alpha}(t,t') &= -i\theta(t-t')\mathrm{e}^{-i\epsilon_{k\alpha}(t-t')}\\ &\quad -i\theta(t-t')\mathrm{e}^{-i\epsilon_{k\alpha}(t-t')}\sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\Big(\int_{t'}^{t}\mathrm{d}\tau V_\alpha(\tau)\Big)^n,\\ g^{\mathrm{A}}_{k\alpha}(t,t') &= i\theta(t'-t)\mathrm{e}^{-i\epsilon_{k\alpha}(t-t')}\\ &\quad +i\theta(t'-t)\mathrm{e}^{-i\epsilon_{k\alpha}(t-t')}\sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\Big(\int_{t'}^{t}\mathrm{d}\tau V_\alpha(\tau)\Big)^n,\\ g^{<}_{k\alpha}(t,t') &= i\langle c^\dagger_{k\alpha}c_{k\alpha}\rangle\mathrm{e}^{-i\epsilon_{k\alpha}(t-t')}\\ &\quad + i\langle c^\dagger_{k\alpha}c_{k\alpha}\rangle\mathrm{e}^{-i\epsilon_{k\alpha}(t-t')}\sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\Big(\int_{t'}^{t}\mathrm{d}\tau V_\alpha(\tau)\Big)^n.\end{aligned} \tag{22}$$

Within the linear-response regime, we keep only the first term ($n = 1$) of each series, which gives the TIH part of SE, Eq. (14), expressed through the TH part

$$\sigma^\gamma(t,t') = -i\sum_\alpha \int_{t'}^{t}\mathrm{d}\tau V_\alpha(\tau)\Sigma^{\gamma\mathrm{h}}_\alpha(t-t'), \tag{23}$$

where γ stands for R, A, or <. Furthermore, assuming that the leads contain non-interacting fermions, we can associate a Fermi distribution with the average number of electrons in a single-particle state $k\alpha$:

$$\langle c^\dagger_{k\alpha}c_{k\alpha}\rangle = f_\alpha(\epsilon_{k\alpha}). \tag{24}$$

Now that TIH junction SEs are expressed in the linear-response approximation, attention is paid to Σ^{int}. As announced, it will be treated in the HF approximation [12],

$$\begin{aligned}G_2(kt, lt; mt', jt^+) &\approx G_{km}(t,t')G_{lj}(t,t^+)\\ &\quad - G_{kj}(t,t^+)G_{lm}(t,t'),\end{aligned} \tag{25}$$

where two terms on the right-hand side represent, respectively, the Hartree and the Fock terms. Inserting this approximate expression into Eq. (13), we get the interaction

SE in the HF approximation

$$\Sigma^{\mathrm{int}}_{nl}(t,t_1) = \delta(t-t_1)\sum_{jk}\big(2W_{njlk} - W_{njkl}\big)\big\langle d_j^{\dagger}(t) d_k(t_1)\big\rangle. \tag{26}$$

The result is time local, as expected within the HF approximation, and can be conveniently expressed as

$$\Sigma^{\mathrm{int}}_{nl}(t,t) = -i\sum_{jk}\big(2W_{njlk} - W_{njkl}\big) G^{<}_{kj}(t,t). \tag{27}$$

Prior to the further derivation, a remark about Eq. (19) will be made. It is a linear TD correction to the zeroth-order TH GF due to external TD perturbation σ^{jnc} and induced field σ^{int}, and the total TD SE can be recognized as the effective field in the dot. This is analogous to the random phase approximation (RPA) [23], the difference being that the explicit external potential influences the dot through the junction TIH SE, Eq. (23), and that the induced field is TD HF while in the RPA it is TD Hartree potential. The induced field can be understood as a shielding potential that screens the particle interaction [23]. Then, non-inclusion of short-range effects in RPA leads to the overestimation of the screening.

Our aim is to find the TIH part of the HF SE, using the decomposition $G^{<}(t,t') = G^{<\mathrm{h}}(t-t') + G^{<\mathrm{i}}(t,t')$. Obviously, the TIH part of the interaction SE is related to the TIH lesser GF through

$$\sigma^{\mathrm{int}}_{nm}(t,t) = -i\sum_{jk}\big(2W_{njmk} - W_{njkm}\big) G^{<\mathrm{i}}_{kj}(t,t), \tag{28}$$

while another connection is provided by applying Langreth rules [16] on Eq. (19), leading to

$$\begin{aligned} G^{<\mathrm{i}}(t,t) = \iint \mathrm{d}t_1 \mathrm{d}t_2 \big[&G^{\mathrm{Rh}}(t-t_1)\sigma^{\mathrm{R}}(t_1,t_2)G^{<\mathrm{h}}(t_2-t) \\ &+ G^{\mathrm{Rh}}(t-t_1)\sigma^{<}(t_1,t_2)G^{\mathrm{Ah}}(t_2-t) \\ &+ G^{<\mathrm{h}}(t-t_1)\sigma^{\mathrm{A}}(t_1,t_2)G^{\mathrm{Ah}}(t_2-t)\big] \\ &+ \int \mathrm{d}t_1 \big[G^{\mathrm{Rh}}(t-t_1)\sigma^{\mathrm{int}}(t_1,t_1)G^{<\mathrm{h}}(t_1-t) \\ &+ G^{<\mathrm{h}}(t-t_1)\sigma^{\mathrm{int}}(t_1,t_1)G^{\mathrm{Ah}}(t_1-t)\big]. \end{aligned} \tag{29}$$

The first term can be interpreted as the contribution to the TD charge density in the dot due to charge injection, as a consequence of the external TD potentials, while the second term is the charge density induced as a response, which depends on the internal, screening HF potential. Finally, lesser TH GFs are expressed through the Keldysh equation [16, 18], valid for a non-interacting system

$$G^{<}(t-t') = \iint \mathrm{d}t_1 \mathrm{d}t_2 G^{\mathrm{R}}(t-t_1)\Sigma^{<}(t_1-t_2)G^{\mathrm{A}}(t_2-t'). \tag{30}$$

From the expressions derived so far, it is possible to formulate a self-consistent scheme for deriving the dot potential, Eq. (28): what is needed is the TIH part of the lesser GF, Eq. (29), which depends on TH retarded, advanced, and lesser GFs, TIH retarded, advanced, and lesser junction SEs as well as TIH interaction SE, i.e., the TD dot potential. This brings us back to Eq. (28) as the new input for Eq. (29). The TH expression for SE, Eq. (23), as a consequence of the linear-response approximation, provides the TIH junction SE, contained in Eq. (29), and the TH lesser GF, also included in Eq. (29), is through Eq. (30) described in terms of TH retarded and advanced GFs, and TH lesser junction SE.

3.1 Time-homogeneous quantities of the dot

The set of equations derived in the previous section forms the basis for alternating current calculation, where TIH quantities are reduced to TH quantities. Now the TH quantities, that is, TH dot's GF and TH isolated electrode's GF, are addressed, where the latter will provide the TH junction SE.

Fourier transformation (FT) of the equation of motion of the TH GF, Eq. (17), gives the well-known result

$$G(E) = \big(E - \varepsilon - \Sigma^{\mathrm{jnc}} - \Sigma^{\mathrm{int}}\big)^{-1}. \tag{31}$$

At this point, DFT can be used to provide an effective single-electron Hamiltonian, the so-called KS Hamiltonian, of the system in the ground state, by mapping an interacting to an effective non-interacting, KS electronic system. This system is influenced by a (semi-)local potential generated from the electron density. The potential consists of external, Hartree, and exchange-correlation (XC) contributions. The key point here is that the GF related to H_{eff} and the GF related to the KS Hamiltonian provide densities that are equal. This feature has a benefit as it allows the use of the GF related to the KS Hamiltonian to find the density, Eq. (55). At the same time, a determinantal (Slater) shape of the many-electron function can be used due to an effectively non-interacting description.

The KS states, which build the Slater determinant, are solutions of the following eigenproblem [20]:

$$\big(-\frac{1}{2m}\Delta + u[n] + v_{\mathrm{H}}[n] + v_{\mathrm{XC}}[n]\big)\phi^{\mathrm{KS}}_{\mu}(\mathbf{r}) = \varepsilon^{\mathrm{KS}}_{\mu}\phi^{\mathrm{KS}}_{\mu}(\mathbf{r}), \tag{32}$$

where n is the electron density $n(\mathbf{r}) = \sum_{\mu}|\phi^{\mathrm{KS}}_{\mu}(\mathbf{r})|^2$, with corresponding GF

$$G = \big(E - \varepsilon^{\mathrm{KS}} - \Sigma^{\mathrm{jnc}}\big)^{-1}. \tag{33}$$

The KS matrix elements in the dot basis are

$$\varepsilon^{\mathrm{KS}}_{nm} = \int \mathrm{d}\mathbf{r}\, \phi^{*}_{n}(\mathbf{r})\big(-\frac{1}{2m}\Delta_{\mathbf{r}} + u + v_{\mathrm{H}} + v_{\mathrm{XC}}\big)\phi_{m}(\mathbf{r}). \tag{34}$$

KS orbitals can be expanded in an orthonormal basis $\{\phi_n(\mathbf{r})\}$ of the dot,

$$\phi_\mu^{\rm KS}(\mathbf{r}) = \sum_n C_{n\mu}\phi_n(\mathbf{r}), \tag{35}$$

where orthonormality provides the constraint that expansion coefficients in Eq. (35) have to satisfy [24]:

$$\sum_{nm} C_{n\beta}^{*}\varepsilon_{nm}^{\rm KS}C_{m\alpha} = \varepsilon_\alpha^{\rm KS}\delta_{\alpha\beta},\ \sum_n C_{n\beta}^{*}C_{n\alpha} = \delta_{\alpha\beta}. \tag{36}$$

What remains is to find a description of the junction SE, which depends on the isolated electrode's GF. In practice, this is the first step in obtaining the dot GF [25]. The iterative procedure developed in Ref. [9] then finds the initial electron density from the electric field between the electrodes at the Hartree level, providing the initial KS Hamiltonian matrix, Eq. (32). The matrix and junction SE determine the initial GF, Eq. (33), which is then used to calculate the density matrix D and from it the electron density $n = \mathrm{Tr}\, D$. The process is then iteratively repeated until the convergence of n. The scheme remains valid in the present theory as well, insofar as it solves the Hartree part of the problem and with it the associated direct current, to which we will return in Section 4.1.

3.2 Self interaction The reducing of SIE will be demonstrated. It is necessary to find the Coulomb interaction related potential energy. By observing Eqs. (17) and (18), it is possible to find the total energy by taking the trace of the time derivative of lesser GFs over the first time argument, repeating the same procedure with the time derivative over the second time argument, and finding the difference of the obtained derivatives [12]. The total energy will include kinetic, lead–dot interaction, and Coulomb interaction energies. For the last, it can be found that

$$E_{\rm int}(t) \sim \mathrm{Tr}\int \mathrm{d}t'[(\Sigma^{\rm int}(t,t')G(t',t))^{<} + (G(t,t')\Sigma^{\rm int}(t',t))^{<}]. \tag{37}$$

Decomposing both G and $\Sigma^{\rm int}$ into TH and TIH parts, Eqs. (15) and (16), adopting the DFT description of TH GF and SE, and treating the TIH SE at the HF approximation, it can be observed that Eq. (37) consists of the following parts: (i) a contribution due to stationary (obtained from lesser TH GF) charge interacting via effective H + XC potential

$$\mathrm{Tr}[(\varepsilon_{\rm H}^{\rm KS} + \varepsilon_{\rm XC}^{\rm KS})G^{<}],$$

(ii) a contribution due to dynamic (obtained from lesser TIH GF) charge interacting via effective H + XC potential

$$\mathrm{Tr}[(\varepsilon_{\rm H}^{\rm KS} + \varepsilon_{\rm XC}^{\rm KS})G^{<\rm i}(t,t)],$$

(iii) a contribution due to stationary charge interacting via internal HF time-dependent potential

$$\mathrm{Tr}[\sigma^{\rm int}(t,t)G^{<}].$$

Taking the existence of one electron only, it is, recalling Eq. (28), possible to straightforwardly see that the third contribution is zero (the prefactor 2 at the Hartree term came because of spin summation, but in the single-electron case this summation does not exist). The problem of SIE remains due to the fact that in DFT, moving of a single electron is influenced by the external potential, i.e., the junction SE, but also to a certain extent by H + XC potential. This is in contrast to the physical picture, in which this potential would have to be constant (there should be no Coulomb force acting on the single electron), namely,

$$\begin{aligned} &v_{\rm eff}(\mathbf{r}) = v_{\rm H}(\mathbf{r}) + v_{\rm X}(\mathbf{r}) + v_{\rm C}(\mathbf{r});\\ &v_{\rm H}(\mathbf{r}) + v_{\rm X}(\mathbf{r}) = \text{const.};\\ &v_{\rm C}(\mathbf{r}) = 0. \end{aligned} \tag{38}$$

If this were satisfied, then the first two contributions to the interaction energy would be

$$\text{const.}\sum_{n,m}\delta_{nm}G^{<}(t,t)_{mn} = \text{const.}, \tag{39}$$

where the unity value of the trace of the total lesser GF was taken, according to the existence of one electron only. In order to avoid the problem of SIE, the DFT SIC scheme [26, 27] (SIC – self-interaction correction) has to be adopted. In that case, the first and the second contributions could be zero (constant), and this is what knowing the exact functionals guarantees. However, it is important to point out that even in the case of DFT that is free of SIE, the linear-response, time-dependent theory would be free of SIE only within the proposed HF treatment of the time-dependent internal potential. Throughout the rest of the paper the symbol for SE (TH, TIH, or total) means junction SE, unless otherwise noted.

4 Current Electrical current originates in the leads that are kept at a finite potential difference, the externally controlled bias V, where additionally the potential V_α of lead α changes in time. The standard adopted assumption is of noninteracting Fermi-distributed electrons in the leads when the difference in chemical potentials between the left and the right electrodes is due to the bias, i.e., $\mu_L - \mu_R = eV$. At some time, assumed to be in the remote past, reservoirs providing electrons to the leads are exposed to the influence of time-dependent potential. The total electron flow through the system then is the sum of the time-independent currents due to the finite bias and the time-dependent currents due to the varying potential, which were each determined separately, starting from the definition of the electrical current in the lead α:

$$I_\alpha(t) = -e\frac{d}{dt}\big\langle N_\alpha(t)\big\rangle = -ie\big\langle [H(t), N_\alpha(t)]\big\rangle, \tag{40}$$

where $N_\alpha(t) = \sum_{k\alpha} c^\dagger_{k\alpha}(t)c_{k\alpha}(t)$ is the total number of electrons in the lead α. The evaluation of the commutator in Eq. (40) gives

$$I_\alpha(t) = ie\sum_{kn}\big(V_{k\alpha,n}\langle c^\dagger_{k\alpha}(t)d_n(t)\rangle - V^*_{k\alpha,n}\langle d^\dagger_n(t)c_{k\alpha}(t)\rangle\big). \tag{41}$$

The last sum can be expressed with the lesser form of the mixed GF, which involves analytical continuation on the real-time axis [16], transforming Eq. (41) into

$$\begin{aligned} I_\alpha(t) = 2e\int_{-\infty}^{t} \mathrm{d}t' \mathrm{Tr}\big[&G^{\mathrm{R}}(t,t')\Sigma^<_\alpha(t',t) + G^<(t,t')\Sigma^{\mathrm{A}}_\alpha(t',t) \\ &- \Sigma^{\mathrm{R}}_\alpha(t,t')G^<(t',t) - \Sigma^<_\alpha(t,t')G^{\mathrm{A}}(t',t)\big]. \end{aligned} \tag{42}$$

Double counting, due to spin summation, is included in the above equation. Partitioning of GFs and SEs into TH and TIH parts done in Section 3 gives two contributions to the total current $I_\alpha(t)$, namely a time-independent direct current (DC) I_α and a time-dependent alternating current (AC) $i_\alpha(t)$, respectively, as follows:

$$I_\alpha(t) = I_\alpha + i_\alpha(t), \tag{43}$$

$$\begin{aligned} I_\alpha = 2e\int \mathrm{d}t' \,\mathrm{Tr}\big[&G^{\mathrm{R}}(t-t')\Sigma^<_\alpha(t'-t) \\ &+ G^<(t-t')\Sigma^{\mathrm{A}}_\alpha(t'-t) - \Sigma^{\mathrm{R}}_\alpha(t-t')G^<(t'-t) \\ &- \Sigma^<_\alpha(t-t')G^{\mathrm{A}}(t'-t)\big], \end{aligned} \tag{44}$$

$$\begin{aligned} i_\alpha(t) = 2e\int \mathrm{d}t' \,\mathrm{Tr}\big[&G^{\mathrm{R}}(t,t')\Sigma^<_\alpha(t'-t) + G^{\mathrm{R}}(t-t')\sigma^<_\alpha(t',t) \\ &+ G^<(t-t')\sigma^{\mathrm{A}}_\alpha(t',t) + G^<(t,t')\Sigma^{\mathrm{A}}_\alpha(t'-t) \\ &- \Sigma^{\mathrm{R}}_\alpha(t-t')G^<(t',t) - \sigma^{\mathrm{R}}_\alpha(t,t')G^<(t'-t) \\ &- \Sigma^<_\alpha(t-t')G^{\mathrm{A}}(t',t) - \sigma^<_\alpha(t,t')G^{\mathrm{A}}(t'-t)\big], \end{aligned} \tag{45}$$

where the index α denotes the contribution from the lead α. Langreth rules [16] provide the retarded and advanced forms of the TIH contribution of the dot GF, Eq. (19), as

$$\begin{aligned} G^{\gamma\mathrm{i}}(t,t') = \iint \mathrm{d}t_1\mathrm{d}t_2\, G^{\gamma\mathrm{h}}(t-t_1)\big[&\sigma^\gamma(t_1,t_2) \\ &+ \sigma^{\mathrm{int}}(t_1,t_2)\delta(t_1-t_2)\big]G^{\gamma\mathrm{h}}(t_2-t'), \end{aligned} \tag{46}$$

where γ stands for R or A. Note that in this expression all one- and two-time quantities correspond to TH and TIH terms, respectively, which remains true for all the expressions in the rest of the paper, and thus explicit writing of ‘h’ and ‘i’ hereafter is omitted.

4.1 Direct current After FT of the expression for DC, Eq. (44), it is obtained that

$$I_\alpha = \frac{e}{\pi}\int \mathrm{Tr}\big[G^{\mathrm{R}}\Sigma^<_\alpha + G^<\Sigma^{\mathrm{A}}_\alpha - \Sigma^{\mathrm{R}}_\alpha G^< - \Sigma^<_\alpha G^{\mathrm{A}}\big]\,\mathrm{d}E, \tag{47}$$

where, to simplify the notation, explicit dependence of quantities under the integral on E is omitted. From Eq. (20), it follows that

$$\Sigma^\gamma_\alpha = V^\dagger_{\alpha\mathrm{D}}\, g^\gamma_\alpha\, V_{\alpha\mathrm{D}}, \quad \gamma = \mathrm{R, A,} < \tag{48}$$

and, from Eqs. (22) and (24), SE matrices describing the influence of electrodes are obtained as follows:

$$\Sigma^{\mathrm{A}}_\alpha - \Sigma^{\mathrm{R}}_\alpha = i\,\Gamma_\alpha, \tag{49}$$

$$\Sigma^<_\alpha = if_\alpha\Gamma_\alpha, \tag{50}$$

where the bandwidth Γ is defined as

$$\Gamma = \sum_\alpha \Gamma_\alpha; \quad \Gamma_\alpha(E) = 2\pi V^\dagger_{\alpha\mathrm{D}}\Delta_\alpha(E)V_{\alpha\mathrm{D}} \tag{51}$$

and $\Delta_\alpha(E)$ is the density of states matrix of the isolated electrode α.

From Eq. (49), it follows that

$$\Gamma_\alpha(E) = -2\mathrm{Im}\,\Sigma^{\mathrm{R}}_\alpha(E) \tag{52}$$

and, recalling Eqs. (33) and (49), it is straightforward to show that

$$\begin{aligned} [G^{\mathrm{R}}]^{-1} - [G^{\mathrm{A}}]^{-1} &= \Sigma^{\mathrm{A}} - \Sigma^{\mathrm{R}}, \\ i(G^{\mathrm{R}} - G^{\mathrm{A}}) &= G^{\mathrm{R}}\Gamma G^{\mathrm{A}}, \end{aligned} \tag{53}$$

which, together with the TH part of the Keldysh equation (30), gives the expression for DC, Eq. (47), in the well-known Caroli form [19]

$$I_\alpha = \frac{e}{\pi}\int \mathrm{d}E(f_\alpha - f_\beta)\mathrm{Tr}[\Gamma_\beta G^{\mathrm{R}}\Gamma_\alpha G^{\mathrm{A}}], \quad \alpha \neq \beta. \tag{54}$$

This equation was obtained before using the scattering formalism of Büttiker [28, 29], where particle interaction in the dot was treated up to the elastic one-particle interaction level, the connection between S-matrix and GF was established viathe Fisher–Lee relation [3], and the transmission recognized in the term $\mathrm{Tr}[\Gamma_\alpha G^{\mathrm{R}} \Gamma_\beta G^{\mathrm{A}}]$. Beyond elastic mean-field potential scattering, however, equality between this expression and the transmission coefficient does not hold any longer.

The expressions for the TH lesser GF, Eq. (30), and the lesser SE, Eq. (50), together with Eq. (53), determine the electron density matrix as

$$D = -iG^{<}(t - t^{+}) = \frac{1}{2\pi i} \int \mathrm{d}E\, G^{<}(E). \tag{55}$$

The Fourier-transformed Keldysh equation (30), together with Eq. (49), expresses the lesser TH GF as

$$\begin{aligned} G^{<} &= G^{\mathrm{R}} \Sigma^{<} G^{\mathrm{A}} \\ &= G^{\mathrm{R}} \sum_{\beta} i f_\beta \Gamma_\beta G^{\mathrm{A}} \\ &= i f_\beta G^{\mathrm{R}} \Gamma G^{\mathrm{A}} + i(f_\alpha - f_\beta) G^{\mathrm{R}} \Gamma_\alpha G^{\mathrm{A}}. \end{aligned} \tag{56}$$

It is assumed here that $\mu_\alpha > \mu_\beta$ for definiteness, two terms of the TH lesser GF, respectively, are the equilibrium density matrix associated with lead states $k\beta$ up to μ_β and the non-equilibrium part with the energy values between chemical potentials. Due to Eq. (53), the equilibrium part is simply

$$i f_\beta G^{\mathrm{R}} \Gamma G^{\mathrm{A}} = -2 i f_\beta \mathrm{Im} G^{\mathrm{R}}, \tag{57}$$

which is analytical in the complex upper half-plane except at poles of the Fermi distribution at the imaginary axis, and the integral can be calculated by contour integration [9, 10]. The non-equilibrium part of the density matrix is not analytical due to the presence of both retarded and advanced GFs, so the integration is done along the real axis [9–11].

The DC is conserved, which can be demonstrated by taking the sum over left and right current contributions, Eq. (47), to obtain

$$\sum_{\alpha=\mathrm{R,L}} I_\alpha = \frac{e}{\pi} \int \mathrm{Tr}[(G^{\mathrm{R}} - G^{\mathrm{A}})\Sigma^{<} + (\Sigma^{\mathrm{A}} - \Sigma^{\mathrm{R}})G^{<}]\, \mathrm{d}E. \tag{58}$$

The first rows of Eqs. (53) and (56) then trivially lead to the DC conservation.

4.2 Alternating current

The expression for the alternating current, Eq. (45), can be transformed recalling Eqs. (29), (28), (23), and (46), to obtain an expression involving only TH quantities. To this end, first the double FT is applied to all two-times quantities, which transforms the expression for AC, Eq. (45), into a sum of four contributions

$$\begin{aligned} i_\alpha(\omega) &= \frac{e}{\pi} \int \mathrm{d}E\, \mathrm{Tr}\left[i_\alpha^{(1)} + i_\alpha^{(2)} + i_\alpha^{(3)} + i_\alpha^{(4)} \right], \\ i_\alpha^{(1)} &= [G^{\mathrm{R}}(E_+) - G^{\mathrm{A}}(E)] \sigma_\alpha^{<}(E_+, E), \\ i_\alpha^{(2)} &= [\Sigma_\alpha^{\mathrm{A}}(E) - \Sigma_\alpha^{\mathrm{R}}(E_+)] G^{<}(E_+, E), \\ i_\alpha^{(3)} &= G^{\mathrm{R}}(E_+, E) \Sigma_\alpha^{<}(E) - \Sigma_\alpha^{<}(E_+) G^{\mathrm{A}}(E_+, E), \\ i_\alpha^{(4)} &= G^{<}(E_+) \sigma_\alpha^{\mathrm{A}}(E_+, E) - \sigma_\alpha^{\mathrm{R}}(E_+, E) G^{<}(E), \end{aligned} \tag{59}$$

where E_+ stands for $E + \omega$ (notation adopted from Ref. [6]). The first three terms agree with the results previously obtained by Anantram and Datta (see Eq. (22) of Ref. [6]), who provided also their interpretation – the first term, $i_\alpha^{(1)}$, corresponds to the correlated injection of electrons from electrode α at energies E and E_+, while the second, $i_\alpha^{(2)}$, describes the correlated injection of the electrons in the other direction, from the dot into the lead; the third term, $i^{(3)}$, corresponds to the injection of the electron from one energy from the leads to the changing density of states in the dot.

The fourth term, $i^{(4)}$, also presented in Refs. [7, 8], can be interpreted by tracing back its origin to the expression for the TIH junction SE, Eq. (60) – if, for the sake of simplicity, $\Sigma(E)$ changes linearly with E, then $\sigma_\alpha(E_+, E) = (-\partial \Sigma_\alpha(E)/\partial E) V_\alpha$, i.e., TIH SE is produced by the change of the TH junction SE with energy. The change of the real part is associated with the shifting of energy levels in the dot, while the change of the imaginary part with the change of width of dot levels. Since these changes originate in the leads, the fourth term describes the process that is the third process reversed, namely an injection of the electron from the dot into the lead due to the altering density of states in the leads. This term gives the contribution beyond the WBL approximation, which is discussed later (Section 5.1) considering it a special case of the general expression (59).

Subsequently, the four contributions to the current can be grouped into two types of processes: $i^{(1)} + i^{(3)}$ corresponds to the transfer of the electron from the leads into the dot, while $i^{(2)} + i^{(4)}$ corresponds to the transfer of the electron from the dot into the leads.

4.3 Expression for current

Now, what follows is the derivation of the final expression for the dynamical current starting with the FT of Eq. (23):

$$\sigma_\alpha^{\gamma}(E_+, E) = \frac{V_\alpha(\omega)}{\omega} [\Sigma_\alpha^{\gamma}(E) - \Sigma_\alpha^{\gamma}(E_+)], \tag{60}$$

where γ stands for A, R, or $<$. The FT of Eq. (46) is

$$G^{\gamma}(E_+, E) = G^{\gamma}(E_+)[U(\omega) + \sigma^{\gamma}(E_+, E)] G^{\gamma}(E), \tag{61}$$

where γ stands for A or R, and U is the time-dependent potential at the HF level

$$U_{nm}(\omega) = \frac{1}{2\pi} \int \mathrm{d}E\, \sigma_{nm}^{\mathrm{int}}(E_+, E), \tag{62}$$

determined self consistently. The FT of the TIH contribution of the lesser GF of the dot, Eq. (29), is

$$\begin{aligned}G^{<}(E_{+},E) = {}& G^{\mathrm{R}}(E_{+})\sigma^{\mathrm{R}}(E_{+},E)G^{<}(E)\\ &+G^{\mathrm{R}}(E_{+})\sigma^{<}(E_{+},E)G^{\mathrm{A}}(E)\\ &+G^{<}(E_{+})\sigma^{\mathrm{A}}(E_{+},E)G^{\mathrm{A}}(E)\\ &+G^{\mathrm{R}}(E_{+})U(\omega)G^{<}(E)\\ &+G^{<}(E_{+})U(\omega)G^{\mathrm{A}}(E).\end{aligned} \tag{63}$$

The self-consistent set of equations now involves the use of Eqs. (60), (62), and (63) to express TIH quantities through TH ones, resulting in the expression for the current where all the quantities are functions of either E or $E+\omega$. For this reason, to simplify notation, the writing of explicit dependence on E is dropped, while the explicit dependence on $E+\omega$ is indicated by the subscript $+$, while V and U depend on ω only, which is also not explicitly written. Using this notation, the derivation of the expression for dynamical current at the frequency ω is given in the Appendix, with the following result:

$$\begin{aligned}i_{\alpha}(\omega) = {}& \frac{e}{\pi}\int \mathrm{d}E\,\mathrm{Tr}\big(G^{\mathrm{R}}_{+}\widetilde{U}^{\mathrm{R}}_{\alpha}G^{\mathrm{R}}\Sigma^{<}_{\alpha} - \Sigma^{<}_{\alpha+}G^{\mathrm{A}}_{+}\widetilde{U}^{\mathrm{A}}_{\alpha}G^{\mathrm{A}}\big)\\ &+\frac{e}{\pi}\int \mathrm{d}E\,\mathrm{Tr}\{[\Sigma^{\mathrm{A}}_{\alpha}-\Sigma^{\mathrm{R}}_{\alpha+}][G^{\mathrm{R}}_{+}\widetilde{U}^{\mathrm{R}}_{\alpha}G^{<}\\ &+G^{<}_{+}\widetilde{U}^{\mathrm{A}}_{\alpha}G^{\mathrm{A}}+G^{\mathrm{R}}_{+}\frac{V_{\beta}-V_{\alpha}}{\omega}(\Sigma^{<}_{\beta}-\Sigma^{<}_{\beta+})G^{\mathrm{A}}]\},\end{aligned} \tag{64}$$

$$\widetilde{U}^{\gamma}_{\alpha} = \frac{V_{\beta}-V_{\alpha}}{\omega}\big(\Sigma^{\gamma}_{\beta}-\Sigma^{\gamma}_{\beta+}\big)+U-V_{\alpha};\quad \gamma=\mathrm{R},\mathrm{A};\ \beta\neq\alpha, \tag{65}$$

where $\widetilde{U}_{\alpha}$ can be perceived as an effective potential that includes TIH self energy as well as the induced dot potential, all shifted by the potential of the corresponding lead.

The first integral of Eq. (64) contains the AC contribution from leads-to-dot processes $i^{(1,3)}_{\alpha}$. Presence of the in-scattering rate $\Sigma^{<}$ in the integral shows that the described process is not only due to external potentials but also due to internal ones [30]. The second integral of Eq. (64), corresponding to the contribution of dot-to-leads processes $i^{(2,4)}_{\alpha}$, is due to the presence of the dissipative term $G^{<}$ [30].

The gauge-invariant current theory is the one where simultaneous shift of all potentials by the same amount has no observable effect on current, i.e., the current depends only on voltage differences [4, 7, 8, 28, 31]. Both of these contributions to the total AC show that the current depends on potential differences, which is the hallmark of gauge invariance, and clearly point out the necessity of the explicit introduction of internal potential in order to preserve gauge invariance.

4.3.1 Admittance

Although expressions for AC and DC have been derived and the scheme for the calculation of all relevant quantities developed, no connection to the conductance has been made so far. Büttiker established a connection between time-dependent Hartree potential and electrode potentials via conductance using the formalism of characteristic potentials [4], and proved the gauge invariance with respect to constant potential shifts of V. To better understand the obtained result, Eq. (64), especially the role of the displacement current, the expression can be formally rewritten in terms of the transport coefficient, the particle current associated admittance $\tilde{G}^{\mathrm{p}}(\omega)$, and the displacement current i^{d}_{α} as

$$i_{\alpha}(\omega) = \sum_{\alpha\beta}\tilde{G}^{\mathrm{p}}_{\alpha\beta}(\omega)V_{\beta}(\omega)+i^{\mathrm{d}}_{\alpha}(\omega) \tag{66}$$

or, in matrix form, as

$$\begin{bmatrix} i_{\mathrm{L}}\\ i_{\mathrm{R}}\end{bmatrix} = \begin{bmatrix}\tilde{G}^{\mathrm{p}}_{\mathrm{L}} & \tilde{G}^{\mathrm{p}}_{\mathrm{LR}}\\ \tilde{G}^{\mathrm{p}}_{\mathrm{RL}} & \tilde{G}^{\mathrm{p}}_{\mathrm{R}}\end{bmatrix}\begin{bmatrix}V_{\mathrm{L}}\\ V_{\mathrm{R}}\end{bmatrix}+\begin{bmatrix}i^{\mathrm{d}}_{\mathrm{L}}\\ i^{\mathrm{d}}_{\mathrm{R}}\end{bmatrix}, \tag{67}$$

where corresponding components of the admittance matrix can be easily extracted from Eq. (64). The obtained expression appears non-homogeneous in V_{α} due to the displacement-current term $i^{\mathrm{d}}_{\alpha}(\omega)$, equal to the contribution of the first four terms in Eq. (64) containing all the contributions of the TD potential in the molecule $U(\omega)$. This potential, however, is determined self consistently and therefore also indirectly depends on V_{α}. This can be seen by considering first the limit of vanishing amplitudes of electrode potentials V_{α}. In this case, for small frequencies the response of the dot to the external field will also be small, and expansion of U in V_{α} would provide a constant term in the lowest order, which can be removed by choosing a suitable gauge, and terms linear in V_{α} as the largest non-trivial corrections, thus making the displacement current also linearly dependent on V_{α},

$$i^{\mathrm{d}}_{\alpha} = \sum_{\beta}\tilde{G}^{\mathrm{d}}_{\alpha\beta}V_{\beta}.$$

Therefore, the main effect of the displacement current is the renormalization of the total admittance of the molecule,

$$i_{\alpha}(\omega) = \sum_{\alpha\beta}\tilde{G}_{\alpha\beta}(\omega)V_{\beta}(\omega),\qquad \tilde{G}(\omega)=\tilde{G}^{\mathrm{p}}(\omega)+\tilde{G}^{\mathrm{d}}(\omega). \tag{68}$$

In this limit of vanishing $V_{\alpha}(\omega)$, the current will be vanishing as well so long as ω is smaller than the molecular gap. When the two energies are comparable, however, there is a possibility of forming transient excited states, which are not well described in the formalism of linear response [16]. This sets the upper limit for the frequency of the driving field to about the (effective) level spacing near the Fermi energy of the dot or, alternatively, the HOMO–LUMO gap of the molecule.

In general, if $V(\omega)$ is non-vanishing, $U(\omega)$ does not have to be linear in $V_{\alpha}(\omega)$ even when all TIH quantities are, where the source of nonlinearities is the intra-dot Coulomb interaction. Then, due to TH contributions of U nonlinear in V_α, a simple relation (68) is only an approximation and would acquire additional nonlinearity in V_α terms, which are taken into account with the presented formalism and already included in the expression for dynamical current, Eq. (64).

4.3.2 Current partition When talking about the electron injection between the dot and the lead, it should be stated that the four terms in Eq. (59) include not only the particle current, but also the current due to charge accumulation in the dot induced by the external potential, the displacement current i_d. This is due to the fact that the system of equations developed in Section 3 includes also the intra-dot interaction, whose TIH contribution is exactly the TD potential in the dot. The left and right AC contributions to Eq. (59) are

$$i(\omega) = i_\mathrm{L}(\omega) + i_\mathrm{R}(\omega). \tag{69}$$

Taking the GFs in a Kohn–Sham form, Eq. (33), the above sum is

$$\begin{aligned}\sum_{\alpha=\mathrm{R,L}} i_\alpha(\omega) = {}& -e\frac{\omega}{\pi}\int \mathrm{d}E\,\mathrm{Tr}\big[G_+^\mathrm{R}\sigma^<(E_+,E)G^\mathrm{A} \\ &+ G_+^<\sigma^\mathrm{A}(E_+,E)G^\mathrm{A} + G_+^\mathrm{R}\sigma^\mathrm{R}(E_+,E)G^<\big] \\ &- e\frac{\omega}{\pi}\int \mathrm{d}E\,\mathrm{Tr}\big[G_+^<U(\omega)G^\mathrm{A} + G_+^\mathrm{R}U(\omega)G^<\big],\end{aligned} \tag{70}$$

where U is the HF time-dependent potential, Eq. (62). The above result is easy to obtain if the sum of left and right contributions of the second term of Eq. (59) is transformed:

$$\begin{aligned}&(\Sigma^\mathrm{A} - \Sigma_+^\mathrm{R})G^<(E_+,E) \\ &\quad = -\omega G^<(E_+,E) + ([G_+^\mathrm{R}]^{-1} - [G^\mathrm{A}]^{-1})G^<(E_+,E).\end{aligned} \tag{71}$$

Using Eq. (63), in the second term on the right-hand side, it can be found that this term is canceled by the left and right sums of the first, third, and fourth terms of Eq. (59), giving Eq. (70). The right-hand side of Eq. (70) also equals

$$-2ei\hbar\frac{\partial}{\partial t}\mathrm{Tr}\,G^<(t,t).$$

Equation (70) consists of two contributions: the current associated with injected charge where the external potential was recognized in the TIH junction SE, and the current associated with induced charge with corresponding internal potential, Eq. (62). The displacement current density is the divergence of the time derivative of the electric field generated by charge density. This charge density is composed from injected and induced charge densities in the dot.

The molecule–lead coupling affects both the molecule and the leads. For metallic leads, effects of this coupling are expected to be screened at the depth of the Thomas–Fermi length, which is at most a few lattice constants, with bulk-like properties deeper in the conductor, which in the case of finite bias means the uniform electro-chemical potentials in the bulk. This is then used to impose the correct boundary conditions: the system is divided into the central region, the so-called extended molecule (EM), containing the molecule and parts of the electrodes, with the requirements that its potential and non-equilibrium distribution match with those in both electrodes. Due to the screening of field lines, the charge neutrality is maintained in the central region if sufficiently large parts of the leads are included [9, 11, 32].

This approach is extended to the TD transport in Hartree approximation by the introduction of characteristic potentials [4, 8, 17, 31].

At the HF level studied in this research, inclusion of the internal potential U into the system of equations determining the current does not require use of characteristic potentials and, since inclusion of the exchange through the Fock term results in the reduced interaction of half of the electrons [33, 34], the screening is expected to be slightly weakened compared to the Hartree case. As a consequence, the size of the central region, where charge neutrality is maintained, should be larger than in the RPA description. As far as our model is concerned, the exchange contribution to the internal potential is localized within the EM. With this in mind, the proper boundary conditions thus should include: matching of the TD Hartree potential, vanishing TD Fock contribution, and imposing the EM charge-neutrality condition, $\mathrm{Tr}[G^{<\mathrm{i}}(t,t)] = 0$.

It can be stated that the right-hand side of Eq. (70) is a time derivative of the volume integral of the TD charge density, which is, due to EM charge neutrality, zero. In other words [4, 17, 31], field lines, stemming from the charge density, do not penetrate the surface which encloses the EM. The charge neutrality of the central region, besides providing boundary conditions, means that the voltages of contacts are well defined [35]. Therefore, Eq. (70) represents the current conservation as well as the current partition on left and right terms. The effects of the displacement current are self-consistently included during the determination of the time-dependent dot potential via implicit inclusion of the Coulomb interaction (which is responsible for the displacement current [4, 8, 17, 31] in the first place).

5 Wide-band limit and zero bias Generally, whenever the leads are connected to the electronic reservoir and good featureless conductors, one may expect fast screening of the external electric field by a large electronic density of states at the leads' surface, effectively creating a capacitor-like system with the dot/molecule in the middle and approximately constant density of states at the surface. In this case one expects the wide-band-limit approximation to be adequate, simplifying the derived expressions. Another interesting case is that of voltage without any bias, corresponding to a time-dependent-only driving voltage on the leads. We therefore consider these cases separately and derive the appropriate expressions for i_α.

5.1 Current in the WBL

As discussed earlier (Section. 4.2), the fourth contribution $i^{(4)}$ of the dynamical current, Eq. (59), corresponds to the charge injection from the dot into the changing density of states in the leads.

The WBL consists then in the assumption that there is no such density change, so, in this case, the alternating current is Eq. (59) without the fourth term, which leads to the result as in Ref. [6], with a caveat that the here derived expression for the current is more general due to the self-consistent inclusion of dot interaction. To derive the expression for AC in WBL, we start with the TH self energy, Eq. (14), which after FT can be written in matrix form as

$$\Sigma_\alpha^\gamma(E) = V_\alpha^\dagger\, g_\alpha^\gamma(E) V_\alpha, \quad \gamma = \mathrm{R}, \mathrm{A}.$$

The k index labelling the wave vector, can be expressed via the density of states, with explicitly separated real and imaginary parts of the above equation,

$$\begin{aligned}\Sigma_\alpha^\gamma(E) = &\int_{-W}^{W} \mathrm{d}\epsilon\, \Delta_\alpha(\epsilon) V_\alpha^\dagger(\epsilon)\big[\mathrm{Re}\, g_\alpha^\gamma(E,\epsilon) \\ &+ \mathrm{Im}\, g_\alpha^\gamma(E,\epsilon)\big]\, V_\alpha(\epsilon),\end{aligned}$$

where W is the band half-width. After finding of separate contributions to the SE from the real and imaginary parts of the isolated electrode TH retarded GF, Eq. (9), and using the standard principal value (PV) representation of the Fourier-transformed GF

$$\begin{aligned}g_\alpha^{\mathrm{R/A}}(E,\epsilon) &= \frac{1}{E-\epsilon \pm i\delta} \\ &= \mathrm{PV}\left(\frac{1}{E-\epsilon}\right) \mp i\pi\delta(E-\epsilon),\end{aligned}$$

we obtain

$$\begin{aligned}\Sigma_\alpha^{\mathrm{R}/A}(E) = &\mp i\pi V_\alpha^\dagger(E)\Delta_\alpha(E)V_\alpha^\dagger(E) \\ &+ \mathrm{PV}\int_{-W}^{W} \mathrm{d}\epsilon\, \Delta_\alpha(\epsilon)V_\alpha^\dagger(\epsilon)\frac{1}{E-\epsilon}V_\alpha(\epsilon).\end{aligned} \qquad (72)$$

The imaginary part is associated with the dot bandwidth, Eq. (51), assumed within WBL to be energy independent throughout the band, thus giving

$$\Sigma_\alpha^{\mathrm{R/A}}(E) = \left(\frac{1}{2\pi}\ln\left|\frac{W+E}{W-E}\right| \mp \frac{i}{2}\right)\Gamma_\alpha. \qquad (73)$$

When it is furthermore assumed that the electrode bandwidth is much larger than any other relevant energy scale, such as amplitudes of time-dependent potentials and the dot bandwidth Γ, the real part of SE goes to zero.

As mentioned in the introduction, the TIH SE acts as a TD external perturbation. By its construction, Eq. (14), the junction SE is expected to vanish in leads away from the molecule. In general, the evolution of the EM is non-unitary due to interaction and junction self energies. The continuity equation for closed systems is preserved by the current-conservation condition. In the case of the open system, this condition affects only the interaction SE, while the presence of junction SE breaks the continuity equation as a consequence of boundaries where particles emerge or disappear.

The WBL approximation significantly overestimates the electrode density of states and consequently screening effects, which leads to the neglect of the external perturbing potential, i.e., changes of the TIH junction SE. Besides the vanishing $i_\alpha^{(4)}$, WBL reduces the changes of the density of states within the EM (without self-consistent potential inclusion, there would be no changes at all), and affects the correlated electron injection from the dot to the leads by removing the effects of external potentials on the electron correlation function $G^<$. The expression for AC in the WBL again consists of two contributions, due to the particle current, associated with terms containing external potentials only, and the displacement current containing the internal potential only,

$$\begin{aligned}i_\alpha(\omega) = \frac{e}{\pi}\int \mathrm{d}E\, \mathrm{Tr}\{ &i f_\alpha G_+^{\mathrm{R}}(U-V_\alpha)G^{\mathrm{R}} \\ &- i f_{\alpha+} G_+^{\mathrm{A}}(U-V_\alpha)G^{\mathrm{A}} - \sum_{\gamma=\mathrm{L,R}} G_+^{\mathrm{R}}[f_\gamma(U-V_\alpha)G^{\mathrm{R}}\Gamma_\beta \\ &+ f_{\gamma+}\Gamma_\gamma G_+^{\mathrm{A}}(U-V_\alpha)]G^{\mathrm{A}}\Gamma_\alpha \\ &- (f_\beta - f_{\beta+})\frac{V_\beta - V_\alpha}{\omega} G_+^{\mathrm{R}}\Gamma_\beta G^{\mathrm{A}}\Gamma_\alpha\}.\end{aligned}$$

Once again, it can be observed that the inclusion of displacement current through the self-consistent introduction of the internal field preserves the gauge invariance. The Fermi distributions come from Eq. (50). The first two terms under the integral are due to charge-correlated charge injection as well as injection with corresponding changing density of states within the dot, i.e., the EM, while the remaining terms correspond to correlated charge injections into the leads without changing their density of states. To the best of our knowledge, this expression has not been derived before.

5.2 Current in the zero-bias regime

Another important special case is that of the zero bias, when the molecule is exposed to the AC only. In this case chemical potentials of the leads are equal and Fermi distributions therefore unshifted, leading to the zero direct current and simplifying the expression for the dynamical current, Eq. (64), to obtain

$$\begin{aligned}i_\alpha = \frac{e}{\pi}\int \mathrm{d}E\, \mathrm{Tr}\Big[&(f\, \widetilde{U}_\alpha^{\mathrm{R}} - f_+\widetilde{U}_\alpha^{\mathrm{A}})G^{\mathrm{A}}(\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{R}})G_+^{\mathrm{R}} \\ &+ f_+\widetilde{U}_\alpha^{\mathrm{A}}G^{\mathrm{A}}(\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{A}})G_+^{\mathrm{A}} - f\,\widetilde{U}_\alpha^{\mathrm{R}}G^{\mathrm{R}}(\Sigma_\alpha^{\mathrm{R}} - \Sigma_{\alpha+}^{\mathrm{R}})G_+^{\mathrm{R}} \\ &+ \frac{V_\beta - V_\alpha}{\omega}G_+^{\mathrm{R}}(i f\Gamma_\beta - i f_+\Gamma_{\beta+})G^{\mathrm{A}}(\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{R}})\Big].\end{aligned} \qquad (74)$$

To the best of our knowledge, this result has also not been obtained yet.

5.3 Current in the zero-bias WBL Finally, we consider the case of applied AC only in the WBL, which greatly further simplifies the current expression, Eq. (64), to obtain

$$i_\alpha(\omega) = \frac{e}{\pi}\int \mathrm{d}E\,\mathrm{Tr}\{(f - f_+)\Gamma_\alpha G_+^\mathrm{R} \times \left[i(U - V_\alpha) + \frac{V_\alpha - V_\beta}{\omega}\Gamma_\beta\right] G^\mathrm{A}\}. \tag{75}$$

To compare the obtained expression with the zero-bias result, Eq. (27) of Ref. [6], it is convenient to work in a gauge corresponding to the experimental setup from the reference (which is in our case possible due to the gauge invariance), by setting $V_\alpha \mapsto V_\alpha - V_\beta$ and $V_\beta \mapsto 0$, i.e., by shifting external potentials of both electrodes by V_β. In this gauge, and by neglecting the TD potential in the dot, U, the two expressions agree.

6 Conclusions In conclusion, we have derived a set of equations describing non-equilibrium charge-conserving gauge-invariant transport through a quantum dot/molecule, including the time-dependent dot potential and with it the associated displacement current, at the Hartree–Fock level, and derived the expression for the frequency dependence of the dynamical current. The gauge invariance of the theory was explicitly shown and special cases of the wide-band limit, zero bias, as well as the zero-bias wide-band limit considered and corresponding expressions for the current derived. The theory is particularly suitable for use with the DFT, where the latter can provide the time-homogeneous contribution of the Coulomb interaction to the dot potential, thus providing a theoretical basis for the first-principle microscopic description of the non-equilibrium quantum transport in linear response and calculation of electronic current in molecules, dots, junctions, or nano-scale devices beyond the time homogeneity. Coupled with SIC DFT, the theory is free of a self-interaction error and suitable for the time-dependent transport description in the cases where the single-charge effects, for example in the regime of weak coupling between electrodes and the molecule, could be of interest. The current conservation based on the DFT coupling with GFs relies on the fact that the time-dependent internal potential was approximated at the mean-field level. Therefore, within our scheme, the possible systematic expansion of TIH interaction SE, with the aim to include time non-local contributions, would not provide current conservation. However, it does not mean that the description based on time local potentials was exhausted. It is our opinion that the mean-field approximation introduced in Ref. [34] leaves room for further progress.

Appendix In this appendix we will derive the expression for the dynamical current. We start with its expression, Eq. (59), and separately consider two contributions: the first one describing the charge injection,

$$i_\alpha^\mathrm{inj} = \frac{e}{2\pi}\int \mathrm{d}E\,\mathrm{Tr}\big(i_\alpha^{(1)} + i_\alpha^{(3)}\big) \tag{76}$$

and the second one related to charge emission,

$$i_\alpha^\mathrm{emi} = \frac{e}{2\pi}\int \mathrm{d}E\,\mathrm{Tr}\big(i_\alpha^{(2)} + i_\alpha^{(4)}\big). \tag{77}$$

Equation (76) is transformed using Eqs. (59), (60), (61), and (63) to obtain

$$\begin{aligned} i_\alpha^\mathrm{inj} = \frac{e}{2\pi}\int \mathrm{d}E\,\mathrm{Tr}\bigg[&\frac{V_\alpha}{\omega}(G_+^\mathrm{R} - G^\mathrm{A})(\Sigma_\alpha^< - \Sigma_{\alpha+}^<) \\ &+ G_+^\mathrm{R}\sigma^\mathrm{R}G^\mathrm{R}\Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^\mathrm{A}\sigma^\mathrm{A}G^\mathrm{A} \\ &+ G_+^\mathrm{R}UG^\mathrm{R}\Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^\mathrm{A}UG^\mathrm{A}\bigg]. \end{aligned} \tag{78}$$

Since the integration is over all energies, we can transform the first-term contribution on the right-hand side:

$$\begin{aligned} &\int \mathrm{d}E\,\mathrm{Tr}[(G_+^\mathrm{R} - G^\mathrm{A})(\Sigma_\alpha^< - \Sigma_{\alpha+}^<)] \\ &= \int \mathrm{d}E\,\mathrm{Tr}[(G_+^\mathrm{R} - G^\mathrm{R})\Sigma_\alpha^< - \Sigma_{\alpha+}^<(G_+^\mathrm{A} - G^\mathrm{A})]. \end{aligned} \tag{79}$$

The expressions

$$G_+^\gamma - G^\gamma, \quad \gamma = \mathrm{A}, \mathrm{R}, \tag{80}$$

can be transformed by recalling the definition of the KS GF, out of which directly follows

$$\big(G_+^\gamma\big)^{-1} - \big(G^\gamma\big)^{-1} = \omega + \Sigma^\gamma - \Sigma_+^\gamma, \tag{81}$$

which, after multiplying with G_+^γ from the left and with G^γ from the right, gives

$$G^\gamma - G_+^\gamma = \omega G_+^\gamma G^\gamma + G_+^\gamma(\Sigma^\gamma - \Sigma_+^\gamma)G^\gamma. \tag{82}$$

Finally, recalling Eq. (60), we obtain

$$\frac{V_\alpha}{\omega}(G_+^\gamma - G^\gamma) = -G_+^\gamma\Big(V_\alpha + \sigma_\alpha^\gamma + \frac{V_\alpha}{V_\beta}\sigma_\beta^\gamma\Big)G^\gamma, \tag{83}$$

where $\alpha \neq \beta$. This result is inserted on the right-hand side of Eq. (79) and the obtained expression is added to the rest of Eq. (78) to obtain

$$i_\alpha^\mathrm{inj} = \frac{e}{2\pi}\int \mathrm{d}E\,\mathrm{Tr}\big(G_+^\mathrm{R}\widetilde{U}_\alpha^\mathrm{R}G^\mathrm{R}\Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^\mathrm{A}\widetilde{U}_\alpha^\mathrm{A}G^\mathrm{A}\big), \tag{84}$$

where $\widetilde{U}$ is the effective potential, Eq. (65). A similar procedure applied to Eq. (77) gives

$$i_\alpha^{\mathrm{emi}} = \frac{e}{2\pi}\int \mathrm{d}E\,\mathrm{Tr}[(\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{R}})(G_+^{\mathrm{R}}UG^< + G_+^<UG^{\mathrm{A}} + G_+^{\mathrm{R}}\sigma^{\mathrm{R}}G^< + G_+^<\sigma^{\mathrm{A}}G^{\mathrm{A}} + G_+^<\sigma^<G^{\mathrm{A}}) + G_+^<\sigma_\alpha^{\mathrm{A}} - G^<\sigma_\alpha^{\mathrm{R}}\big]. \tag{85}$$

The contribution from the last line is transformed as was done with Eq. (79),

$$\int \mathrm{d}E\,\mathrm{Tr}[G_+^<(\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{A}}) - G^<(\Sigma_\alpha^{\mathrm{R}} - \Sigma_{\alpha+}^{\mathrm{R}})] = \int \mathrm{d}E\,\mathrm{Tr}[(G_+^< - G^<)(\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{R}})]. \tag{86}$$

In order to find a suitable expression for lesser GFs, we use the Keldysh equation (30). In the case of $G_+^<$, Eq. (82), where γ stands for advanced functions, will be useful. Taking the product of both sides of this equation with V_α/ω and then with $G_+^{\mathrm{R}}\Sigma_+^<$ acting from the left, we obtain

$$\frac{V_\alpha}{\omega}G_+^< = \frac{V_\alpha}{\omega}G_+^{\mathrm{R}}\Sigma_+^<G^{\mathrm{A}} - G_+^<\big(V_\alpha + \sigma_\alpha^{\mathrm{A}} + \frac{V_\alpha}{V_\beta}\sigma_\beta^{\mathrm{A}}\big)G^{\mathrm{A}}. \tag{87}$$

We follow the same route for $G^<$, with those differences that in Eq. (82), γ stands for retarded functions, and that we take the both sides product with $\Sigma^<G^{\mathrm{A}}$ acting from the right. This leads to

$$\frac{V_\alpha}{\omega}G^< = \frac{V_\alpha}{\omega}G_+^{\mathrm{R}}\Sigma^<G^{\mathrm{A}} + G_+^{\mathrm{R}}\big(V_\alpha + \sigma_\alpha^{\mathrm{R}} + \frac{V_\alpha}{V_\beta}\sigma_\beta^{\mathrm{R}}\big)G^<. \tag{88}$$

The insertion of Eqs. (87) and (88) into the right-hand side of (86), and the obtained result into Eq. (85), leads to

$$i_\alpha^{\mathrm{emi}} = \frac{e}{2\pi}\int \mathrm{d}E\,\mathrm{Tr}\{[\Sigma_\alpha^{\mathrm{A}} - \Sigma_{\alpha+}^{\mathrm{R}}] \times [G_+^{\mathrm{R}}\widetilde{U}_\alpha^{\mathrm{R}}G^< + G_+^<\widetilde{U}_\alpha^{\mathrm{A}}G^{\mathrm{A}} + G_+^{\mathrm{R}}(V_\beta - V_\alpha)\frac{\Sigma_\beta^< - \Sigma_{\beta+}^<}{\omega}G^{\mathrm{A}}]\}. \tag{89}$$

Taking the sum of Eqs. (84) and (89), we arrive at Eq. (64).

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На основу члана 161 Закона о општем управном поступку и службене евиденције издаје се

УВЕРЕЊЕ

Дражић (Слободан) Милош, бр. индекса 2015/8028, рођен 06.07.1978. године, Земун, Београд-Земун, Република Србија, уписан школске 2016/2017. године, у статусу: самофинансирање; тип студија: докторске академске студије; студијски програм: Физика.

Према Статуту факултета студије трају (број година): три.
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18-06-2014 го. год.

Научно веће Института за физику је на седници одржаној 17.06.2014. године покренуло поступак за избор **Милоша Дражића у звање истраживач сарадник.**

У Комисију за писање извештаја су именовани:

др Радомир Жикић, виши научни сарадник, Институт за физику, 1. референт

др Таско Грозданов, научни саветник, Институт за физику

др Жељко Шљиванчанин, научни саветник, Институт за нуклеарне науке ВИНЧА

др Дејан Тимотијевић, виши научни сарадник, Институт за физику

Комисија је дужна да у року од 30 дана од када је образована поднесе извештај Научном већу ИФ.

Прилог за 1. референта:

материјали за избор

Председник Научног већа ИФ

др Љубинко Игњатовић

за