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Density-functional theory of nonequilibrium tunneling

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Nanoscale optoelectronics and molecular-electronics systems operate with current injection and nonequilibrium tunneling—phenomena that challenge consistent descriptions of the steady-state transport. The current affects the electron-density variation and hence the intermolecular and intramolecular bondings which in turn determine the transport magnitude. The standard approach for efficient characterization of steady-state tunneling combines ground-state density-functional theory (DFT) calculations (of an effective scattering potential) with a Landauer-type formalism and ignores all actual many-body scattering. The standard method also lacks a formal variational basis. This paper formulates a Lippmann-Schwinger (LS) collision density-functional theory (LSC DFT) for tunneling transport with full electron-electron interactions. Quantum-kinetic (Dyson) equations are used for an exact reformulation that expresses the variational noninteracting and interacting many-body scattering T matrices in terms of universal density functionals. The many-body LS variational principle defines an implicit equation for the exact nonequilibrium density.

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I. INTRODUCTION

The function of heterostructure-based optoelectronics and of future molecular electronics[1] rests on current injection and tunneling transport that causes genuinely nonequilibrium conditions. The systems are nanoscale and the performance is sensitive to the atomic configuration. The technologies define difficult theory problems of calculating nonequilibrium tunneling in the presence of electron-electron or boson scattering. A quantum-cascade laser[2] (QCL) produces optical transitions in repeated stages with current injection in resonant-tunneling structures. The electron-electron interaction is ubiquitous, causes strong many-body scattering out of equilibrium,[3] and directly affects the QCL operation. This is because electrons which exit one QCL stage must be recycled for current injection in subsequent stages and because the optical activity depends on details of the energy distribution of injected electrons. Similarly, a current-driven molecular-electronics switch[4] positions a nanoscale molecule between leads and uses charge-transfer processes to adjust the intramolecular and intermolecular bondings and morphology. Understanding details of the current-induced changes in the interacting electron distribution is also important here because the molecular morphology (and nature of bonds) determines the magnitude of the nonequilibrium tunneling. Deriving a quantum-physical description that provides *ab initio* predictive and self-consistent accounts of nonequilibrium tunneling with full electron-electron interaction is very desirable.

For equilibrium systems it is possible to rely on the traditional *ground-state* density-functional theory[5,6] (DFT) to provide a material-specific or system-specific account. The ground-state DFT is formulated in the canonical ensemble, conserves the total number of electrons, and takes as input only the potential defined by the nuclei. The approach uses predefined approximations for a universal functional that expresses contributions of the electron-electron interaction to the total interacting ground-state energy for a system in equilibrium. Traditional implementations of ground-state DFT calculations, using the local-density approximation[7] or the generalized-gradient approximation,[8] provide a rich description of the bonding inside materials with a dense electron-density distribution and within molecules. Recent extensions[9–11] of the density functionals that include accounts of dispersive interactions allow descriptions of van der Waals bonding and organization in sparse materials[12] and in (as well as of) macromolecules.[13] The ground-state DFT calculations define an *ab initio level* (as opposed to a model level) of details in the description of materials-physics or molecular-physics properties and are extremely useful for they allow a transferable description of specific systems. It is this *ab initio* level of detail that we seek also for the open nonequilibrium tunneling systems. Unfortunately, the openness and transport invalidate the assumptions of traditional DFT which rests in a *ground-state total-energy* variation principle that applies in equilibrium.

There is exciting recent progress toward *ab initio* calculations of steady-state interacting tunneling even if consistent quantum-physical calculations of open nonequilibrium systems are challenging. The nonequilibrium tunneling problem is difficult because the finite applied bias makes phase space available for actual electron-scattering processes (which are normally suppressed in equilibrium). It is also difficult because it is essential (but hard) to ensure conservation rules[14] in accounts of the nonequilibrium and interacting electron dynamics. The Landauer-type formulations,[15] characterizing tunneling transport in terms of ballistic propagation of individual particles moving in an effective potential, constitute a simple approximation. They can formally be derived[16–18] for the linear-response regime or in the absence of many-body scattering using the nonequilibrium Green's functions[19,20] (NEGF) within the so-called partition scheme introduced by Caroli *et al.*,[21] but they only have limited applicability. One solution strategy for *ab initio* calculations of nonequilibrium interacting tunneling involves use of quantum-kinetic equations[20] for conserving calculations, and there exists a number of formal results[17,18,22–25] extending and correcting the Landauer-type formulation. Several explicit calculations for nonequilibrium tunneling with electron-electron interactions focus on correlated-electron systems such as the Kondo problem and use both diagrammatic approaches (for example, see Refs. 17, 26, and 27) and exact reformulations[24,28] of the quantum-kinetic equations. Tunneling through molecular systems has been investigated on an *ab initio* level diagrammatically starting from either Hartree-Fock eigenstates of the molecular system[29] or by applying a conserving GW formulation.[30] A second solution strategy for interacting steady-state tunneling invokes time-dependent (TD) DFT (Ref. 31) either in combination with a master-equation approach for a finite closed-loop system[32,33] or with the NEGF formulation in an infinite open partition-free formulation with an explicit time evolution in the applied bias.[25,34] Traditional TD DFT contains no implicit dephasing and describes coherent evolution of the (interacting) many-body wave function for finite systems. Explicit and implicit dephasing mechanisms must be carefully analyzed[25,33] in these applications to steady-state tunneling. Both of the TD-DFT-based methods allow calculations of interacting tunneling transport that are in principle exact, and the TD-DFT basis should make it simpler to achieve an *ab initio* level of details. All of the above-mentioned solution strategies for *ab initio* nonequilibrium calculations are computationally intensive.

The standard method for efficient calculations of steady-state tunneling with an *ab initio* level of detail combines ground-state DFT with a Landauer-type formulation,[15] computing tunneling transport as an independent-particle transmission problem. The resulting ballistic-transport (BT)-DFT approach was introduced by Lang[35] and uses the ground-state DFT exchange-correlation energy to define an effective potential for scattering of independent particles. The BT DFT represents a natural (but *ad hoc*) extension of the Poisson-Landauer-type transport solvers.[36] It is a meaningful approximation because electron conservation is automatic in the ballistic single-particle description. There exist efficient implementations[37,38] and BT-DFT calculations provide valuable theory characterizations of tunneling systems. However, the BT-DFT approach also constitutes an uncontrolled approximation. Stefanucci *et al.*[25] identified implicit (memory-loss) conditions under which their TD-DFT single-particle description will relax to noninteracting steady-state scattering of fictitious particles. However, this scattering dynamics is given by the functional derivative of the TD-DFT action *not* by the exchange-correlation potential of ground-state DFT. Use of a ground-state DFT formulation to determine an effective scattering potential must be discussed even in linear response.[39] Use of the Landauer-type formulation, ignoring all actual many-body scattering events and assuming that quasiparticle properties remain unchanged from equilibrium conditions, is problematic for fully nonequilibrium conditions. Analysis[40] of the frequency-resolved current density shows that nonequilibrium electron-phonon scattering causes distribution changes that are inconsistent with Landauer-type descriptions (corresponding problems for nonequilibrium electron-electron scattering can be inferred from Ref. 3). The use of a Landauer-type formulation prevents BT DFT from consistent calculations of current-induced changes in the electron distribution and hence of effects that are important for nanoscale optoelectronics and molecular electronics. The fact that BT DFT lacks a formal variational basis motivates a continued search for efficient *ab initio* calculations of nonequilibrium tunneling with full electron-electron interaction.

This paper formulates a Lippmann-Schwinger (LS) collision (LSC) DFT for steady-state nonequilibrium tunneling systems treated in the Born-Oppenheimer approximation. The LSC DFT is based on formal collision theory[41] for the interacting many-body problem[42,43] and allows an exact discussion resting on the LS variational principle.[44–46] The LSC DFT is expressed through universal density functionals that characterize the variational form of the noninteracting and interacting many-body T matrices. The LSC DFT provides a formal solution in terms of an implicit equation for the exact electron density. The formal LSC-DFT solution constitutes a natural starting point in search for rigorous formulations of single-particle schemes based on the LS variational principle.

This paper is organized as follows. Section II defines the partition scheme and the Hamiltonian. It also discusses the general (nonequilibrium and interacting) tunneling problem as a complex many-body collision problem. Section III presents the formal density-functional basis for the theory while Sec. IV develops the LS T-matrix functional description. Finally, Sec. V contains a summary and outlook while the Appendix provides details of the uniqueness-of-density proof for the time-dependent interacting tunneling problem.

II. PARTITION SCHEME, HAMILTONIAN, AND COLLISION THEORY

It is convenient to utilize the partition framework of Caroli *et al.*[21] but retain the full level of details of atomistic many-body calculations everywhere close to the tunneling region $\mathbf{r}\sim 0$ at all physically relevant times $t\sim 0$ in the collision problem.[47] For simplicity, the tunneling structure only comprises a left (right) lead $\mathbf{r}<z_L(>z_R)$ plus a central tunneling region "C" in $z_L<\mathbf{r}<z_R$. Atomic units will be used throughout and the full kinetic energy is written as

$$\sum_s \int d\mathbf{r}' \int d\mathbf{r}\, \hat{\psi}_s^{+}(\mathbf{r}') \left\{ -\frac{1}{2}[\nabla \delta(\mathbf{r}-\mathbf{r}')]^2 \right\} \hat{\psi}_s(\mathbf{r}) \equiv K_L + K_R + K_C + \delta K, \tag{1}$$

where $K_{L,R,C}$ have support strictly confined to separate spatial regions,

$$K_L = \sum_s \int_{z'<z_L} d\mathbf{r}' \int d\mathbf{r}\, \hat{\psi}_s^{+}(\mathbf{r}') \left\{ -\frac{1}{2}[\nabla \delta(\mathbf{r}-\mathbf{r}')]^2 \right\} \hat{\psi}_s(\mathbf{r}), \tag{2}$$

$$K_R = \sum_s \int_{z'>z_R} d\mathbf{r}' \int d\mathbf{r}\, \hat{\psi}_s^{+}(\mathbf{r}') \left\{ -\frac{1}{2}[\nabla \delta(\mathbf{r}-\mathbf{r}')]^2 \right\} \hat{\psi}_s(\mathbf{r}), \tag{3}$$

$$K_C=\sum_s \int_{z_L<z'<z_R} d\mathbf{r}' \int d\mathbf{r}\, \hat{\psi}_s^{+}(\mathbf{r}')\left\{-\frac{1}{2}[\nabla\delta(\mathbf{r}-\mathbf{r}')]^2\right\}\hat{\psi}_s(\mathbf{r}), \tag{4}$$

and where

$$\delta K=\sum_{i=L/R}\sum_s \int d\mathbf{r}'\,\delta(\mathbf{r}'-z_i)\int d\mathbf{r}\,\hat{\psi}_s^{+}(\mathbf{r}') \times\left\{-\frac{1}{2}[\nabla\delta(\mathbf{r}-\mathbf{r}')]^2\right\}\hat{\psi}_s(\mathbf{r}). \tag{5}$$

At time $t\to-\infty$ the partition scheme assumes that each of the disconnected subsections of the partitioned system $H_d=\Sigma_{i=L,C,R}H_i$ is in equilibrium at (generally) different chemical potentials[48] $\mu_{L/C/R}$. The operators $N_{L/C/R}$ describe the electron count in each of the three subcomponents. Initially, at $t\to-\infty$, the system is described by a static potential $v_0(\mathbf{r})$ and corresponding operator

$$V_0=\int d\mathbf{r}\, v_0(\mathbf{r})\hat{n}(\mathbf{r}), \tag{6}$$

where $\hat{n}(\mathbf{r})\equiv\Sigma_s\hat{\psi}_s^{+}(\mathbf{r})\hat{\psi}_s(\mathbf{r})$ denotes the electron-density operator. I assume, for simplicity, that $v_0(\mathbf{r})$ reduces to a uniform background potential $\phi_{L/R}$ (with a value set by the average electron concentration) far in the leads. The choice of initial Hamiltonian,

$$H_d=\sum_{i=L/R/C}K_i+V_0, \tag{7}$$

ensures an automatic charge neutrality at $t\to-\infty$ (and at $z\to\pm\infty$ even at finite t). The equilibrium distribution at $t\to-\infty$ is specified by a Gibbs energy weighting $H_d-\mu_L N_L-\mu_R N_R-\mu_C N_C$, which is independent of the value of the applied bias $\phi_{\text{bias}}\equiv\mu_L-\mu_R$ and exclusively depends on the initial electron concentration in the leads (and on the initial electron occupation of the central island C).

The LSC DFT further assumes an adiabatic turning on of the tunneling, of the electron-electron interaction W, and of the static electron-scattering potential $v_{\text{sc}}(\mathbf{r})$ which includes the effects of the applied bias and of the set of atomic potentials. One can also allow for an addition of a time-dependent potential $\phi_g(\mathbf{r},t>t_0)$ that describes a possible gate operation starting at some finite time t_0. The time-dependent collision potential is

$$v_{\text{col}}(\mathbf{r},t)=[v_{\text{sc}}(\mathbf{r})+\phi_g(\mathbf{r},t)]\exp(\eta t) \tag{8}$$

and the collision problem is formally described by the Hamiltonian

$$H(t)=H_d+H_1(t), \tag{9}$$

$$H_1(t)=[\delta K+W]\exp(\eta t)+\delta V(t), \tag{10}$$

$$V_{\text{col}}(t)=\delta V(t)=\int d\mathbf{r}\, v_{\text{col}}(\mathbf{r},t)\hat{n}(\mathbf{r}), \tag{11}$$

where the factor $\exp(\eta t), \eta\to 0^+$ expresses the adiabatic turning on. The collision term that drives the dynamics is $H_1(t)$. One may, without lack of generality, assume that the collision potential $v_{\text{col}}(\mathbf{r},t)$ also contains an implicit multiplicative factor that restricts the support to a finite but very large region (much larger than $z_L<z<z_R$); given the choice for $v_0(|\mathbf{r}|\to\infty)$ this assumption simply amounts to treating the remote part of the leads as jellium.

The expectation value of the electron density is defined,[20]

$$n(\mathbf{r},t)=\langle\hat{n}(\mathbf{r})\rangle(t)\equiv\frac{\text{Tr}\{\hat{\rho}_0\hat{n}_H(\mathbf{r};t)\}}{\text{Tr}\{\rho_0\}}, \tag{12}$$

$$\hat{n}_H(\mathbf{r};t)\equiv\hat{U}(t,-\infty)^{+}\hat{n}(\mathbf{r})\hat{U}(t,-\infty), \tag{13}$$

by establishing the initial (equilibrium) density matrix $\hat{\rho}(t\to-\infty)=\hat{\rho}_0$ and by formally solving for the ensuing (nonequilibrium) dynamics described by[44]

$$i\frac{\partial\hat{U}(t,-\infty)}{\partial t}=H(t)\hat{U}(t,-\infty). \tag{14}$$

This applies to general quantum-statistical problems but it is important to provide consistent (conserving) approximations to the time evolution $\hat{U}(t,-\infty)$ of the systems. Such approximations are notoriously difficult to obtain for interacting systems out of equilibrium.

In this paper, I use the LS many-body collision theory[44–46] and describe the interacting tunneling problem as a complex collision problem[42,43] in which (an ensemble of) fully interacting many-body electronic states of the leads encounter and scatter off a potential in some central tunneling region. For any initial many-body state $|\Phi_\xi\rangle$ (eigenstate of H_d) one may formally obtain the many-body collision state[44]

$$|\Psi_{\xi,+}(t)\rangle=\hat{U}(t,-\infty)|\Phi_\xi\rangle \tag{15}$$

from a direct application of the temporal-evolution operator (14). The case of a purely static scattering potential is then described as an elastic many-body collision but the finite bias still causes actual electron-electron scattering[3] that invalidates assumptions of ballistic transport. An inelastic collision event arises when the ensemble of many-body states scatters off a corresponding time-dependent collision potential.[49,50] An effective time-dependent potential may also arise in the description of tunneling in the presence of a quantized boson field[40,51–53] as is relevant for further investigations of optoelectronic devices, for example, lasers under typical operating conditions.

The many-body collision problem (for tunneling) is from the outset specified by the choice of partitioning, that is, (i) a specific choice of Hamiltonian H_d with an interrupted kinetic energy $K-\delta K$, (ii) the lead electron concentration, and (iii) the choice of an initial state $|\Phi_0\rangle$ (or ensemble of initial states $\hat{\rho}_0$) that also formally depends on the initial distribution in the central region C.

III. DENSITY-FUNCTIONAL THEORY OF INTERACTING TUNNELING

For a time-dependent collision potential it is relatively simple to generalize the TD-DFT analysis[31,54] to the many-body collision theory of nonequilibrium interacting tunneling (Appendix). This demonstrates that the time-dependent density is a unique functional of the time-dependent collision potential. The time-dependent collision density-functional theory contains the steady-state formulation of LSC DFT as a limiting case under some conditions.

A. Density-functional theory of time-dependent tunneling

Applying a time-dependent gate voltage to a nonequilibrium tunneling system probes a response[49,50] that reflects electron correlations. It is interesting in itself to develop a formal density-functional theory basis for such time-dependent many-body collision problems. I note that solving these collision problems for the electron density defines a mapping $\mathcal{N}: v_{\rm col}(\mathbf{r},t) \rightarrow n(\mathbf{r},t)$.

Observation 1. The electron density $n(\mathbf{r},t)$ is a unique functional of the collision potential $v_{\rm col}(\mathbf{r},t)$ for a given bias and partitioning of the general time-dependent collision problem.

For the collision problem the goal is to determine the nonequilibrium time evolution of a single state (or a grand-canonical ensemble) of an infinite open system under a collision term $H_1(t)$ which includes an adiabatic turning on of both tunneling, δK, the electron-electron interaction W, and a time-dependent potential $\delta V(t)$ (with a finite support). In contrast, TD DFT considers a single state which from the outset is described by $K+W$ and which evolves under an external potential $V(t)$ and demonstrates uniqueness of the time-dependent density when the system is finite[31] or when the external potential $V(t)$ has a finite support.[54] However, it is straightforward to generalize the reductio ad absurdum argument from TD DFT to the present many-body collision formulation of interacting nonequilibrium tunneling described in a partition scheme. This is because the *difference* of collision terms, $H_1(t)-H_1'(t)$, remains exclusively specified by the difference in collision potentials, $v_{\rm col}(\mathbf{r},t) - v'_{\rm col}(\mathbf{r},t)$ (and this difference may be assumed to have a finite support).

Formally the observation (1) only establishes the uniqueness of the density variation and history for a given bias and for a given choice of partition scheme (that is, choice of $z_{L/R}$ and choice of the initial occupation in the central region C). A different partition scheme produces a different unique mapping $\tilde{\mathcal{N}}$ (as well as corresponding T-matrix functionals for the scattering behavior). However, the choice of partition scheme must become irrelevant for very large $z_R - z_L$ and a very large support of the collision term $\delta V(t)$. This is argued on physical grounds for tunneling systems that lack singular responses: since dephasing eventually decouples the time and spatial correlations[24] the solution $n(\mathbf{r},t)$ must eventually become insensitive to memory effects as well as details of the potential far in the leads.[25,38]

B. Density-functional theory of steady-state tunneling

For static collision problems the four-dimensional variational space of a general density history $n(\mathbf{r},t)$ naturally becomes over complete in its definition of the scattering potential $v_{\rm sc}(\mathbf{r})$. The mapping $\mathcal{N}^{-1}: n(\mathbf{r},t) \rightarrow v_{\rm col}(\mathbf{r},t)$ shows that a general density history causes potential variations,

$$\delta v = \frac{\delta \mathcal{N}^{-1}}{\delta n} \delta n(\mathbf{r},t) = \frac{\delta \mathcal{N}^{-1}}{\delta n}\left[\nabla n \, \delta \mathbf{r} + \frac{\partial n}{\partial t}\delta t\right], \qquad (16)$$

that are incompatible with the steady-state transport assumption.

Observation 2. The time-independent scattering potential $v_{\rm sc}(\mathbf{r})$ is uniquely determined by the steady-state density $n(\mathbf{r}) \equiv n(\mathbf{r},0)$ for time-independent collision problems that have a steady-state solution, $n(\mathbf{r},t) = n(\mathbf{r},0)$.

The adiabatic turning on of the static scattering potential $v_{\rm sc}(\mathbf{r})$ can be viewed as a limiting case of a time-dependent tunneling problem with the restricted variation,

$$\delta v_{\rm col} = \nabla v_{\rm sc} \exp(\eta t)\delta \mathbf{r} + \eta\, v_{\rm sc} \exp(\eta t)\delta t \rightarrow \nabla v_{\rm sc}\ \delta \mathbf{r}. \qquad (17)$$

The unique mapping $\mathcal{N}: v_{\rm col}(\mathbf{r},t) \rightarrow n(\mathbf{r},t)$ identifies the corresponding set of relevant density variations. If the steady-state tunneling problem is characterized by nondivergent values of $\delta \mathcal{N}/\delta v$, we have[55]

$$\frac{\partial n}{\partial t} = \frac{\delta \mathcal{N}}{\delta v}\ \eta v_{\rm sc} \exp(\eta t) \rightarrow 0. \qquad (18)$$

This is the condition that specifies the steady-state scattering solutions, $\delta n(\mathbf{r}) = \delta n(\mathbf{r}, t=0)$.

Observation 2 permits formulation of universal density functionals that characterize variational expressions for the noninteracting and interacting T matrices in LSC DFT. Formally these universal functionals also depend on the assumptions that are built into the partition scheme. For some tunneling problems it may be important to retain a functional dependence on the initial island occupation μ_C. Here I assume that the solution of the steady-state LSC-DFT problem is a functional only of the density (for a given applied bias and choice of μ_L and μ_R).

IV. LIPPMANN-SCHWINGER *T*-MATRIX FUNCTIONAL DESCRIPTION

Formulation of a single-particle scheme with independent dynamics of fictitious particles is important for an accurate and efficient evaluation of the electron density in interacting nonequilibrium tunneling problems. Prerequisites for such a formulation are (a) corresponding variational expressions of a many-body quantity evaluated both in the interacting and noninteracting cases, and (b) universal density functionals to characterize those variational physical quantities. The LSC DFT uses the many-body LS variation principles for the interacting and noninteracting many-body T matrices as well as exact reformulations to satisfy those necessary conditions. The LS variational properties also permit the LSC DFT to specify an exact implicit equation for the nonequilibrium electron density.

A. Lippmann-Schwinger variation principle

In their seminal paper Lippmann and Schwinger[44] identified a set of variational properties for the collision problems.

The original theory ignores the self-energy shifts associated with the adiabatic tuning on of the collision term $H_1(t)$ but the work was soon after supplemented and regularized by additional analysis.[45,46] The LS variational principle[41] applies for any combination of collision states and it should be straightforward to generalize the following also to finite-temperature tunneling problems. Like in traditional equilibrium DFT, however, the focus will likely remain on zero-temperature properties. It is natural to build a functional that reflects the evolution of the ground-state $|\Phi_0\rangle$ of the original disconnected system.

The LSC DFT provides an exact variational evaluation of the ground-state-to-ground-state transition matrix element $T_V[n]$ with usual definition $T_V[n]=\langle\Phi_0|H_1|\Psi_{0,+}[n]\rangle$. This matrix element is a functional of the tunneling electron density because the scattering state $|\Psi_{0,+}[n]\rangle$ is specified by the choice of external potential. Through the optical theorem,[56] this T-matrix element characterizes the total rate of tunneling (a charge-transfer process) arising in the presence of full electron-electron interaction.

The LS variational principle is expressed using the notation of Ref. 44. I generally follow the discussion in Ref. 41 and introduce $G^d_\pm=(E_0-H_d\pm i\eta)^{-1}$ as the retarded (+) and advanced (−) Green's function operators of the original disconnected Hamiltonian H_d while

$$|\Psi_{0,\pm}[n]\rangle = |\Phi_0\rangle + G^d_\pm H_1|\Psi_{0,\pm}[n]\rangle \tag{19}$$

identifies the many-body (collision) state that evolves forward or backward in time under the collision term H_1. These states are functionals exclusively of the density $n(\mathbf{r})$ [or $n(\mathbf{r},t)$ in the wider problems beyond the present scope]. I further introduce

$$\Xi_-[n,V] \equiv \langle\Psi_{0,-}[n]|H_1|\Phi_0\rangle, \tag{20}$$

$$\Xi_+[n,V] \equiv \langle\Phi_0|H_1|\Psi_{0,+}[n]\rangle, \tag{21}$$

$$\Upsilon[n,V] \equiv \langle\Psi_{0,-}[n]|H_1 - H_1G^d_+H_1|\Psi_{0,+}[n]\rangle, \tag{22}$$

which, like the compensated form

$$T_V[n] = \Xi_-[n,V] + \Xi_+[n,V] - \Upsilon[n,V], \tag{23}$$

are functionals of the density n but also contain an explicit dependence on $V=V_0+\delta V$ through the collision term H_1. All four functionals represent a correct evaluation of the T-matrix behavior when evaluated at the correct density n (the density n that results under the collision term H_1). For $\Upsilon[n,V]$ this follows by a simple application of the Dyson equation, $T_+=1-H_1G^d_+=1-G^d_+H_1$, see Refs. 42 and 44.

The key observation for the LSC-DFT formulation is that the extremum identified by the variational condition,

$$\frac{\delta T_V[n]}{\delta n} = \frac{\delta T_V}{\delta\Psi_{0,-}}\frac{\delta\Psi_{0,-}}{\delta n} + \frac{\delta T_V}{\delta\Psi_{0,+}}\frac{\delta\Psi_{0,+}}{\delta n} = 0, \tag{24}$$

identifies the electron density n that solves the collision problem H_1. This follows from the (many-body) LS variational principle[42,44] because the derivative $\delta T_V/\delta\Psi_{0,-(+)}$ is directly proportional to the many-body LS equation for scattering states $|\Psi_{0,+(-)}\rangle$ (Ref. 44).

The noninteraction collision problem, defined by $H_1^0=\delta K+\delta V$, has a corresponding density-functional description. It has a different unique mapping between the density and the potential δV and different scattering states $|\Psi^0_{0,\pm}\rangle$, and this mapping defines other (related) functionals

$$\Xi^0_-[n,V] \equiv \langle\Psi^0_{0,-}[n]|H^0_1|\Phi_0\rangle, \tag{25}$$

$$\Xi^0_+[n,V] \equiv \langle\Phi_0|H^0_1|\Psi^0_{0,+}[n]\rangle, \tag{26}$$

$$\Upsilon^0[n,V] \equiv \langle\Psi^0_{0,-}[n]|H^0_1 - H^0_1G^d_+H^0_1|\Psi^0_{0,+}[n]\rangle, \tag{27}$$

$$T^0_V[n] = \Xi^0_-[n,V] + \Xi^0_+[n,V] - \Upsilon^0[n,V]. \tag{28}$$

The extremum, identified by the variational condition

$$\delta T^0_V[n] = 0, \tag{29}$$

identifies the density that solves the noninteracting problem $H^0_1=\delta K+\delta V$.

B. Universality of *T*-matrix functionals in LSC DFT

To obtain a description given in terms of universal functionals it is necessary to identify the partial contributions that arise from the kinetic-energy addition, the electron-electron interaction, and the potential scattering and to find a method to evaluate the difficult many-electron effects once and for all. This is possible by formal manipulation using the Dyson equation and by use of the LS equation itself. By construction, the formal manipulation does not invalidate the underlying variational character of the LS formulation (23).

I first introduce scattering states and the Green's function operators for the set of partial collision problems defined at $\delta V\equiv 0$. I use $|\chi^0_{0,\pm}\rangle$ and $|\chi_{0,\pm}\rangle$ to denote the collision states for the $\delta V\equiv 0$ noninteracting and interacting connected problems given by $H_d+\delta K$ and $H_d+\delta K+W$, respectively. Also, $G^0_\pm=[E_0-(H_d+\delta K)\pm i\eta]^{-1}$ and $G_\pm=[E_0-(H_d+\delta K+W)\pm i\eta]^{-1}$ identify the noninteracting and interacting Green's function operators at $\delta V=0$. These noninteracting and interacting collision problems contain an implicit choice of potential V_0 while the general noninteracting and interacting collision problems are described by $V=V_0+\delta V\equiv V_{\mathrm{col}}$. Neither $\chi_{0,\pm}$ nor $\chi^0_{0,\pm}$ are therefore functionals of n (and the same applies for all the Green's functions in use).

For the matrix element $\Xi^0_+[n]=\langle\Phi_0|(\delta K+\delta V)|\Psi^0_{0,+}[n]\rangle$ I use a simple formal manipulation of the "ket" state,

$$\begin{aligned}|\Psi^0_{0,+}[n]\rangle &= |\Phi_0\rangle + G^d_+(\delta K+\delta V)|\Psi^0_{0,+}[n]\rangle\\ &= |\chi^0_{0,+}\rangle + G^0_+\delta V|\Psi^0_{0,+}[n]\rangle,\end{aligned} \tag{30}$$

as can be verified by a direct application of the LS equation.[41] The resulting separation

$$\Xi^0_+[n,V] = \langle\Phi_0|\delta K|\chi^0_{0,+}\rangle + \langle\chi^0_{0,-}|\delta V|\Psi^0_{0,+}[n]\rangle \tag{31}$$

can, of course, be repeated for a separation also of $\Xi^0_-[n]$ and of the corresponding interacting expression $\Xi_\pm[n,V]$, for example,

$$\Xi_{+}[n,V] = \langle \Phi_0 | (\delta K + W) | \chi_{0,+} \rangle + \langle \chi_{0,-} | \delta V | \Psi_{0,+}[n] \rangle. \tag{32}$$

This reformulation can also be derived [Eqs. (XIX.9) and (XIX.120) of Ref. 41] by applying the Green's theorem on the weighted overlap between the two collision states. The Green's theorem plays a central role in NEGF calculations for the open tunneling systems and enters, for example, in the quantum-kinetic based derivation of resonant-tunneling rate equations.[23]

For the noninteracting matrix element $\Upsilon^0[n,V] = \langle \Psi^0_{0,-}[n] \| (\delta K + \delta V)\{1 - G^d_{+}(\delta K + \delta V)\} | \Psi^0_{0,+}[n] \rangle$ (and for $\Upsilon[n,V]$) it is necessary to first expand the "bra" and ket collision states by the LS equation. I collect terms involving either a $\langle \chi^0_{0,-}|$ or a $\langle \Psi^0_{0,-}[n]\|$ bra state and either a $|\chi^0_{0,+}\rangle$ or a $|\Psi^0_{0,+}[n]\rangle$ ket state separately, and I use the underlying quantum-kinetic (Dyson) equation for simplification. Taking one of the cross terms as an example, one obtains

$$\langle \chi^0_{0,-} | \delta K \{ G^0_{+}[V_0] - G^d_{+} \delta K G^0_{+}[V_0] - G^d_{+} \} \delta V | \Psi^0_{0,+}[n] \rangle \equiv 0. \tag{33}$$

Repeated applications of the Dyson equation completes the separation

$$\Upsilon^0[n,V] = \langle \chi^0_{0,-} | \delta K \{ 1 - G^d_{+} \delta K \} | \chi^0_{0,+} \rangle + \langle \Psi^0_{0,-}[n] \| \delta V \{ 1 - G^0_{+} \delta V \} \times | \Psi^0_{0,+}[n] \rangle. \tag{34}$$

A corresponding expansion applies, of course, also for the interacting matrix element

$$\Upsilon[n,V] = \langle \chi_{0,-} | (\delta K + W) \{ 1 - G^d_{+}(\delta K + W) \} | \chi_{0,+} \rangle + \langle \Psi_{0,-}[n] \| \delta V \{ 1 - G_{+} \delta V \} | \Psi_{0,+}[n] \rangle. \tag{35}$$

The electron-electron interaction effects on the many-body scattering problem can now be expressed in universal functionals. A set of complex constants,

$$a_{-} \equiv \langle \chi_{0,-} | (\delta K + W) | \Phi_0 \rangle, \tag{36}$$

$$a_{+} \equiv \langle \Phi_0 | (\delta K + W) | \chi_{0,+} \rangle, \tag{37}$$

$$b \equiv \langle \chi_{0,-} | (\delta K + W) [1 - G^d_{+}(\delta K + W)] | \chi_{0,+} \rangle, \tag{38}$$

(along with corresponding definitions $a^0_{\pm}, b^0$ for the noninteracting case) characterizes the dynamics in the absence of the collision potential (at $\delta V = 0$). More importantly, a set of collision-state matrix elements,

$$\mathcal{A}_{-}[n](\mathbf{r}) \equiv \langle \Psi_{0,-}[n] \| \hat{n}(\mathbf{r}) | \chi_{0,+} \rangle, \tag{39}$$

$$\mathcal{A}_{+}[n](\mathbf{r}) \equiv \langle \chi_{0,-} | \hat{n}(\mathbf{r}) | \Psi_{0,+}[n] \rangle, \tag{40}$$

$$\mathcal{B}_1[n](\mathbf{r}) \equiv \langle \Psi_{0,-}[n] \| \hat{n}(\mathbf{r}) | \Psi_{0,+}[n] \rangle, \tag{41}$$

$$\mathcal{B}_2[n](\mathbf{r},\mathbf{r}') \equiv \langle \Psi_{0,-}[n] \| \hat{n}(\mathbf{r}) G_{+} \hat{n}(\mathbf{r}') | \Psi_{0,+}[n] \rangle, \tag{42}$$

represents universal density functionals that determine the many-body dynamics when the collision potential is included in the presence of full electron-electron interaction (while corresponding universal functionals $\mathcal{A}^0_{\pm}[n]$ and $\mathcal{B}^0_{1,2}[n]$ characterize the full collision problem at $W=0$). The variational form of the interacting and noninteracting T matrices can thus be reformulated as

$$T_V[n] = a_{-} + a_{+} - b + \int d\mathbf{r} v_{\mathrm{sc}}(\mathbf{r}) \mathcal{K}_V[n](\mathbf{r}), \tag{43}$$

$$T^0_V[n] = a^0_{-} + a^0_{+} - b^0 + \int d\mathbf{r} v_{\mathrm{sc}}(\mathbf{r}) \mathcal{K}^0_V[n](\mathbf{r}), \tag{44}$$

$$\mathcal{K}^{(0)}_V[n](\mathbf{r}) = \mathcal{A}^{(0)}_{+}[n](\mathbf{r}) + \mathcal{A}^{(0)}_{-}[n](\mathbf{r}) - \mathcal{B}^{(0)}_1[n](\mathbf{r}) + \int d\mathbf{r}' \mathcal{B}^{(0)}_2[n](\mathbf{r},\mathbf{r}') v_{\mathrm{sc}}(\mathbf{r}'). \tag{45}$$

In essence, calculation of a set of universal functionals (for relevant choices of chemical potentials $\mu_{L/R}$) permits a simple general evaluation of the interacting T matrix for arbitrary scattering potentials $v_{\mathrm{sc}}(\mathbf{r})$.

The LSC-DFT description also permits a succinct formulation of the interaction effects on the T-matrix functional derivatives,

$$\frac{\delta(T_V[n] - T^0_V[n])}{\delta n(\mathbf{r})} = v_{\mathrm{sc}}(\mathbf{r}) \frac{\delta(\mathcal{K}_V[n] - \mathcal{K}^0_V[n])}{\delta n(\mathbf{r})} \equiv v_{\mathrm{sc}}(\mathbf{r}) \frac{\delta \Delta \mathcal{K}_V[n]}{\delta n(\mathbf{r})}. \tag{46}$$

The interaction effect is expressed as a complex function of **r** and it is entirely specified by suitable approximations to universal density functionals.

C. Variational solution of the interacting collision problem

Separating out the noninteracting dynamics (for which we can seek highly accurate characterizations) and the interaction effect (46) defines a formal LSC-DFT solution,

$$\frac{\delta T_V[n]}{\delta n(\mathbf{r})} = \frac{\delta T^0_V[n]}{\delta n(\mathbf{r})} + v_{\mathrm{sc}}(\mathbf{r}) \frac{\delta \Delta \mathcal{K}_V[n]}{\delta n(\mathbf{r})}, \tag{47}$$

which constitutes an exact but implicit equation for the nonequilibrium electron density.

The formal LSC-DFT solution (47) serves as a natural starting point of search for a single-particle scheme for calculations of the density in specific nonequilibrium tunneling systems. The possibility is exciting for a rigorous single-particle scheme would permit efficient and exact calculations of $\delta T^0_V[n]$ and would ensure automatic current conservation in *ab initio* calculations specified by universal functionals. The single-particle LS equation certainly determines the noninteracting many-body dynamics described by $\delta T^0_V[n]/\delta n$. It is not *a priori* clear that the interaction term (46) represents an additional effect caused by some *effective single-particle scattering* and it is not *a priori* clear that a single-particle scheme exists for the LSC DFT. However, the present results show that the LSC DFT satisfies necessary conditions and motivate a search for rigorous single-particle formulations.

V. SUMMARY AND OUTLOOK

This paper formulates a Lippmann-Schwinger collision density-functional theory (LSC DFT) for nonequilibrium interacting steady-state tunneling. The theory rests on the Lippmann-Schwinger variational principle for the interacting and noninteracting many-body T matrices and includes exact reformulations that express the variational T-matrix forms through universal density functionals. The variational property of the LSC DFT specifies an exact implicit Eq. (47) for the electron density. The LSC DFT furthermore fulfills *necessary* conditions for a possible formulation of a rigorous single-particle scheme. The present results motivate a future study [using the formal LSC-DFT solution (47) and the LS variational properties of single-particle scattering] to explore conditions on the dynamics and to test if a rigorous single-particle scheme can be defined in LSC DFT.

It is important to stress that the underlying (many-body) T-matrix variational principle of LSC DFT is, in principle, different from the wave-function action variational principle exploited in TD DFT. It is not clear that one will be able to derive an explicit mapping between the T-matrix functionals of LSC DFT and the action functionals of TD DFT. The TD-DFT f_{xc} kernel is defined by the (nonequilibrium) density-density correlation function. However, a nonequilibrum problem has no fluctuation-dissipation theorem and there is no reason to expect a simple connection of this correlation function to the variational formulations of the many-body T-matrix behavior (and hence to the LSC-DFT functionals). On the other hand, one can expect the LSC-DFT (with its formal connections to the open-system many-body Green's functions) and the TD-DFT functionals to supplement each other in the descriptions of steady-state nonequilibrium tunneling.

Any implementation of a LSC-DFT method must rely on successful formulation of a good approximation for the universal functionals $\mathcal{A}_{\pm}[n]$ and $\mathcal{B}_{1,2}[n]$ that characterize the complex many-electron collision behavior. The formulation of TD-DFT-based *ab initio* calculations[25,32] facilitates a program to explore the T-matrix behavior for a range of scattering potentials and thereby deconvolutes approximations for the universal functionals $\mathcal{A}_{\pm}[n](\mathbf{r})$ and $\mathcal{B}_{1,2}[n](\mathbf{r})$. The partition-scheme method for time propagation of the tunneling many-body wave function[34] may allow a direct extraction of T matrices and simplify the task. Calculations of interacting steady-state and weakly time-dependent nonlinear transport in periodic or even homogeneous systems[57] may offer an alternative approach by characterizing local charge-transfer rates (and hence T-matrix behavior) as a function of a homogenous electron density and of the electric field (local voltage drop). Either way it is natural to first seek functionals that have a local-density flavor in the parametrization of Eqs. (39)–(42), in essence, assuming that $\mathcal{A}_{\pm}[n](\mathbf{r})$ and $\mathcal{B}_{1,2}[n](\mathbf{r})$ depend only on $n(\mathbf{r})$ and the local field. It is also possible that more complex functional forms must be explored. Exact solutions of nonequilibrium correlated-electron model systems[28] present possibilities for further refining parametrizations of approximations for the universal functionals. There is value in building good approximations to the universal T-matrix functionals of LSC DFT from a range of calculations obtained using a range of different (consistent) theoretical descriptions of nonequilibrium tunneling dynamics.

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APPENDIX: UNIQUENESS OF DENSITY IN COLLISION THEORY

I argue uniqueness of the time-dependent density, observation 1, for the complex LS collision problem of open tunneling systems in the partition scheme as a relatively straightforward generalization of the TD-DFT analysis for finite[31] and for infinite systems with a restricted support of the single-particle potential.[54] The grand-canonical foundation, the use of the partition scheme, and the basis in quantum-kinetic equations make the analysis of the many-body collision problem slightly different from that of Ref. 54, and the argument is included here for completeness.

For a specific partition with given initial configuration and initial density-matrix operator $\hat{\rho}(t\to-\infty)=\hat{\rho}_0$, I consider the time evolution

$$i\frac{\partial\hat{\rho}(t)}{\partial t}=[H(t),\hat{\rho}(t)], \tag{A1}$$

with formal solution given by the many-body evolution operator

$$\hat{\rho}(t)=\hat{U}(t,-\infty)^{+}\hat{\rho}_0\hat{U}(t,-\infty). \tag{A2}$$

I compare two similar systems given by $H_1(t)$ and $H_1'(t)$ for which the kth time derivative of the collision potential begins to differ at some time t_i [Eq. (3) of Ref. 31]. The current-density operator,

$$\hat{j}(\mathbf{r})=(2i)^{-1}\sum_s[\nabla\hat{\psi}_s^{+}(\mathbf{r})]\psi_s(\mathbf{r})-\hat{\psi}_s^{+}(\mathbf{r})[\nabla\psi_s(\mathbf{r})], \tag{A3}$$

constitutes a sensitive probe of system differences at times immediately thereafter, $t=t_i^{+}$.

The density matrices $\hat{\rho}(t)$ and $\hat{\rho}'(t)$ that correspond to $H_1(t)$ and $H_1(t)$ must, of course, agree at t_i. Use of Eq. (A1) permits the evaluation,

$$\begin{aligned}i\frac{\partial}{\partial t}\Delta j(\mathbf{r},t_i)&=\mathrm{Tr}\{[H_1(t_i)-H_1'(t_i),\hat{\rho}(t_i)]\hat{j}(\mathbf{r})\}\\&=\int d\mathbf{r}'[v_{\text{col}}(\mathbf{r}',t_i)-v_{\text{col}}'(\mathbf{r}',t_i)]\\&\quad\times\mathrm{Tr}\{\hat{\rho}(t_i)[\hat{j}(\mathbf{r}),\hat{n}(\mathbf{r}')]\}\\&=i\mathrm{Tr}[\hat{\rho}(t_i)\hat{n}(\mathbf{r})]\nabla[v_{\text{col}}(\mathbf{r},t_i)-v_{\text{col}}'(\mathbf{r},t_i)],\end{aligned} \tag{A4}$$

of the system differences in time evolution of the current expectation values. The third line of Eq. (A4) results from an operator identity and by partial integration in formal manipulations that directly mirror those of the TD-DFT analysis. It applies because the finite (but assumed very large) support for $v_{\mathrm{col}}(\mathbf{r},t)$ and for $v'_{\mathrm{col}}(\mathbf{r},t)$ eliminates surface contributions.

If the potentials themselves differ at t_i it follows directly that the current densities must differ at a time immediately thereafter. If instead the potentials only differ at some derivative of order $k \geq 1$, we proceed by direct differentiation of Eq. (A4),

$$i\frac{\partial}{\partial t}\left(i\frac{\partial}{\partial t}\right)^{k}\Delta j(\mathbf{r},t_i) = i\mathrm{Tr}\{\hat{\rho}(t_i)\hat{n}(\mathbf{r})\}\,\nabla\left(i\frac{\partial}{\partial t}\right)^{k}[v_{\mathrm{col}}(\mathbf{r},t_i) - v'_{\mathrm{col}}(\mathbf{r},t_i)] \neq 0. \tag{A5}$$

It follows that the current densities must differ at time t_i^+.

Finally, uniqueness of the electron density $n(\mathbf{r},t)$ results by direct application of the reductio ad absurdum argument given for infinite-system TD DFT in Ref. 54. Using $n(\mathbf{r},t_i) = \mathrm{Tr}\{\hat{\rho}(t)\hat{n}(\mathbf{r})\}$ and the continuity equation gives

$$\frac{\partial^{k+2}}{\partial t^{k+2}}[n(\mathbf{r},t_i) - n'(\mathbf{r},t_i)] = -\nabla\cdot[n(\mathbf{r},t)\,\nabla\,u(\mathbf{r},t_i)], \tag{A6}$$

$$u(\mathbf{r},t_i) = \frac{\partial^{k}}{\partial t^{k}}[v_{\mathrm{col}}(\mathbf{r},t_i) - v'_{\mathrm{col}}(\mathbf{r},t_i)], \tag{A7}$$

that is in agreement with Eq. (6) of Ref. 31. Use of Green's first identity shows that

$$-\int d\mathbf{r}u(\mathbf{r},t_i)\,\nabla\,\cdot[n(\mathbf{r},t)\,\nabla\,u] = \int d\mathbf{r}n(\mathbf{r},t_i)[\nabla u(\mathbf{r},t_i)]^2 \tag{A8}$$

because our collision problem permits us to make an implicit assumption of a finite support for $v_{\mathrm{col}}(\mathbf{r},t)$ so that $u(|\mathbf{r}| \to \infty) = 0$. As in Refs. 31 and 54 it follows that the difference (A6) must be nonzero since $n(\mathbf{r},t_i)[\nabla u(\mathbf{r},t_i)]^2 \geq 0$ and since $n(\mathbf{r},t_i)[\nabla u(\mathbf{r},t_i)]^2$ cannot vanish identically. In summary, a reductio ad absurdum argument shows (observation 1) that the time-dependent density variation $n(\mathbf{r},t)$ is a unique functional of the collision potential $v_{\mathrm{col}}(\mathbf{r},t)$ in the many-body LS collision problem that is used here to describe nonequilibrium interacting tunneling.

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