

Density Functional Theory of the Electrical Conductivity of Molecular Devices

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Time-dependent density functional theory is extended to include dissipative systems evolving under a master equation, providing a Hamiltonian treatment for molecular electronics. For weak electric fields, the isothermal conductivity is shown to match the adiabatic conductivity, thereby recovering the Landauer result.

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Much recent interest has focused on using single molecules as transistors for a new breed of computers [1]. The complex nature of these devices, especially the leads, suggests that their properties can be sensitive to chemical details. Thus we wish to model the transport characteristics of such devices with first-principles electronic structure methods, such as density functional theory (DFT). However, the traditional theorems of DFT do not apply to extended systems carrying current in finite homogeneous electric fields.

Valid applications of DFT are derived from exact principles of quantum mechanics. These involve proofs of a one-to-one correspondence between densities and potentials, i.e., that a given one-electron density can only be produced by at most a single one-body potential, under a given set of restrictions. Ground-state DFT was established by Hohenberg and Kohn [2] by proving that, for interacting electrons, a given ground-state density can be produced by at most one ground-state one-body potential. The one-body potential, and hence all other properties, is a *functional* of the ground-state density. Similarly, Runge and Gross (RG) showed [3] that, for interacting electrons in a given initial state, a given evolution of the one-body density can be produced by at most one *time-dependent* one-body potential, thus establishing the validity of time-dependent density functional theory (TDDFT). TDDFT has become very popular as a method for calculating electronic transition frequencies [4] and for atoms and molecules in intense laser fields [5].

On the other hand, transport problems are usually handled within the Landauer formalism [6]. The molecule and contacts are placed between two infinite reservoirs at chemical potentials that differ by the voltage drop across the molecule. A standard integral over the Green's function and coupling to the reservoirs then yields the current, and thus the conductance. This can be made exact by using nonequilibrium Keldysh Green's functions [7]. In a modern DFT calculation [8,9], a self-consistent Kohn-Sham (KS) calculation is performed and the scattering states

are inserted into the (two-terminal) Landauer formula to calculate the conductance. At finite fields, the KS Green's function is significantly distorted from its zero-field value. As is well recognized [9], use of the ground-state KS Green's function in place of the exact nonequilibrium Green's function is an unjustified approximation. For example, the poles of this Green's function, representing resonances of the molecule, are at the KS orbital energy differences, *not* the true excitations of the system.

Acknowledging such limitations, there have been several recent attempts to go beyond this picture [10–12], but always in terms of the electrons alone. In this Letter, we prove a new density functional theorem that encompasses transport at finite electric fields by including dissipation to phonons via a master equation. We derive the associated KS master equation. The new exchange-correlation (XC) potential reduces to that of TDDFT in the limit of zero dissipation. The new formalism is naturally suited to periodic boundary condition codes, and we show how all the ingredients for a realistic calculation can be constructed. Finally, we show how the Kubo response is recovered in the limit of weak bias.

We consider only symmetric leads. To avoid the use of reservoirs, put the entire system on a long thin ring and thread through the center a solenoidal magnetic field. This produces a spatially uniform electric field throughout the entire system, and is equivalent to a change of gauge [13]. The system is finite, and nowhere are there two different chemical potentials. However, an important difficulty arises when the field is finite. For a purely electronic system, the electrons will accelerate indefinitely and the current will grow infinitely. In nature, there is dissipation due to scattering with phonons that brings the system to equilibrium. This phenomenon is described by the quantum Liouville equation for the density matrix of the entire system of electrons and phonons, S_{tot} :

$$dS_{\text{tot}}/dt = -i[H_{\text{tot}}, S_{\text{tot}}(t)]. \quad (1)$$

(We use atomic units, so $e^2 = m = \hbar = 1$). In the case of

bulk transport, Kohn and Luttinger [14] showed how, for scattering from dilute impurities in weak fields, Eq. (1) recovers the Boltzmann equation, identifying the diagonal elements of the electronic density matrix with the distribution function.

In the quantum mechanics of dissipative systems, there is a well-established procedure for incorporating the effects of inelastic scattering with a reservoir into the long-time evolution of a system. In our case, the total Hamiltonian consists of the system Hamiltonian H (the electrons) and a reservoir Hamiltonian R (the phonons), coupled by K . The system Hamiltonian contains N interacting electrons. The coupling is linear in the phonon coordinates, and involves only one-body forces on the system. Before an initial time ($t = 0$), both electrons and phonons are in thermal equilibrium at temperature T . The exact system density matrix $S (= \text{tr} S_{\text{tot}}$, where tr denotes a trace over the reservoir alone) satisfies

$$dS(t)/dt = -i[H(t), S(t)] - i\text{tr}[K, S_{\text{tot}}(t)]. \quad (2)$$

To derive a master equation for S , we coarse grain over a time scale Δt that is long compared to electronic transitions and phonon correlations, but short compared to the relaxation time [15], i.e., the time scale on which the electrons are losing energy to the reservoir. This yields a master equation for \bar{S} , the coarse-grained S ,

$$d\bar{S}/dt = -i[H, \bar{S}(t)] + C[\bar{S}(t)], \quad (3)$$

where C is a superoperator, found by applying Fermi's golden rule to the scattering process, and determined by the coupling K and the reservoir spectral density. It is usually written in a basis of eigenstates of the time-independent (many-body) Hamiltonian, $H|A\rangle = E_A|A\rangle$:

$$C[\bar{S}] = -\sum_{A,B} \Gamma_{A \rightarrow B} (L_{AB} L_{BA} \bar{S} + \bar{S} L_{AB} L_{BA} - 2L_{BA} \bar{S} L_{AB}), \quad (4)$$

where the operators L_{BA} represent a transition from state A to state B , with transition probability:

$$\Gamma_{A \rightarrow B} = \begin{cases} \mathcal{D}(\omega_{AB}) |\gamma_{AB}|^2 (\bar{n}(\omega_{AB}) + 1) & E_A > E_B \\ \mathcal{D}(\omega_{BA}) |\gamma_{AB}|^2 \bar{n}(\omega_{BA}) & E_A < E_B \end{cases} \quad (5)$$

in terms of the electron-phonon coupling elements γ_{AB} , where $\mathcal{D}(\omega)$ is the density of states of phonons with frequency ω ($\omega_{AB} = E_A - E_B$), and $\bar{n}(\omega) = 1/(e^{\omega/kT} - 1)$ is the thermal occupation factor. Detailed balance requires:

$$\exp(-E_A/k_B T) \Gamma_{A \rightarrow B} = \exp(-E_B/k_B T) \Gamma_{B \rightarrow A}, \quad (6)$$

so that the steady-state solution of Eq. (3) yields the thermal equilibrium density matrix of H . No matter what the initial density matrix, the steady-state solution is always the same. Thus the master equation couples statistical mechanics to quantum mechanics and, by including only secular contributions, builds in irreversibility.

In the prototype of the radiative lifetime of a two-level atom coupled to the electrodynamic continuum [15], the range of frequencies of photons includes the transition frequency. Although electronic transitions are much higher than phonons, the metal of the leads means there is no gap in our band structure, producing transitions all the way down to zero frequency. Thus the reservoir can slowly drain energy from the system. As long as the coupling to the reservoir is weak, the rate at which the system relaxes back to equilibrium (the relaxation time) will be much longer than all other scales, and the master equation applies. While there is much discussion about the validity of the master equation [15] and what physics it contains, we take Eq. (3) as given and show how to map the system to an effective single-particle system.

Our goal is describe a many-electron system, evolving under a master equation, by a collection of noninteracting electrons. In the usual derivation of a master equation, the system Hamiltonian is time independent and any time dependence is generated by, e.g., starting in a nonequilibrium density matrix. For our purposes, we allow the one-body potential of H to be time dependent. This breaks the connection between C and H , since the final H might have an external electric field turned on, but the initial H might not. We now show that, for fixed electron-electron interaction and superoperator C , and for a given initial density matrix S_0 , no two one-body potentials can give rise to the same time-dependent density $n(\mathbf{r}t)$. We assume that the potentials are Taylor-series expandable around $t = 0$, and that some coefficient in the expansion is not uniform in space. The equation of motion is:

$$\begin{aligned} \frac{d\langle \mathbf{j}(\mathbf{r}) \rangle}{dt} &= \text{Tr} \left[\mathbf{j}(\mathbf{r}) \frac{d\bar{S}}{dt} \right] \\ &= -i\text{Tr} [\mathbf{j}(\mathbf{r}) [H, \bar{S}]] + \text{Tr} [\mathbf{j}(\mathbf{r}) C(\bar{S})], \end{aligned} \quad (7)$$

where $\mathbf{j}(\mathbf{r}) = \frac{1}{2} \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{p}_i + \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i)$ is the current-density operator. Since cyclic permutation does not alter the trace, the first term on the right is $i\text{Tr} ([H, \mathbf{j}(\mathbf{r})] \bar{S})$, the usual contribution from evolution under a Hamiltonian. Evaluating everything at $t = 0$, and considering two systems with possibly different potentials but the same initial density matrix and coupling, we find

$$\left. \frac{d\Delta\langle \mathbf{j}(\mathbf{r}) \rangle}{dt} \right|_{t=0} = -n_0(\mathbf{r}) \Delta \nabla v_{\text{ext}}(\mathbf{r}t=0), \quad (8)$$

just as in RG. Thus two potentials that differ at $t = 0$ give rise to two different currents.

For two systems whose initial Hamiltonians are the same, and two operators that are identical initially but whose time evolution differs,

$$\left. \frac{d\Delta\langle A \rangle}{dt} \right|_{t=0} = \text{Tr} \left[\left. \frac{d\Delta A}{dt} \right|_{t=0} \bar{S}(0) \right] \quad (9)$$

within the master equation, because both the commutator and C are identical in both systems at $t = 0$. Applying this

result to the equation of motion for the k th derivative of the currents,

$$\partial_0^{k+1} \Delta \mathbf{j}(\mathbf{r}t) = -n_0(\mathbf{r}) \nabla \partial_0^k \Delta v_{\text{ext}}(\mathbf{r}t), \quad (10)$$

where $\partial_0^k = (\partial^k / \partial t^k)|_{t=0}$. Thus, any difference in any derivative of the potentials (other than a constant) produces two different currents. This establishes a one-to-one correspondence between densities and currents.

We could stop here, as it is TD current DFT that is more natural for the optical response of extended systems [16] and for transport calculations [17]. But, for generality, we also wish to establish a *density* functional theory. The equation of motion for $n(\mathbf{r}t)$ is

$$\frac{d\langle n(\mathbf{r}) \rangle}{dt} \Big|_{t=0} = -\text{Tr}(\nabla \mathbf{j}(\mathbf{r}) \bar{S}(0)) + \text{Tr}(n(\mathbf{r}) C[\bar{S}(0)]) \quad (11)$$

and the last term is the same in both systems. The usual arguments about the vanishing of the potentials sufficiently rapidly at large distances then suffice for finite systems [18], or single-valuedness for periodic systems [16]. Breakdown of continuity in the master equation occurs because, in Eq. (11), the superoperator provides a correction to the usual statement under Hamiltonian evolution; i.e., some momentum is transferred to the reservoir. But use of Eq. (11) restores continuity, and the correction can even be written in terms of a current [19].

We have established that the potential is a functional of the time-dependent current density for a given interaction, statistics, initial density matrix, and coupling. In principle, we can apply the same argument with the interaction set to zero to produce a set of time-dependent KS equations whose one-body potential, $v_S[n, S_S(0), C](\mathbf{r}t)$, is defined to yield the exact $n(\mathbf{r}t)$ when evolved under the master equation. By subtracting the external potential and Hartree contribution, we find an XC potential that has the same dependencies as the KS potential, but also depends on the initial density matrix of the interacting system. Fortunately, we can subsume all dependence on the initial density matrices into the functional itself by beginning in an equilibrium distribution for both the interacting and non-interacting systems. In that case, the Mermin functional, which is just a functional of the initial density, determines the initial density matrix [20].

Constructed this way, the KS system has certain pathologies. The superoperator in the many-body master equation is guaranteed to vanish only on the many-body equilibrium density matrix, not its KS doppelgänger. To compensate for this, the corresponding KS potential might need to evolve forever, even after the KS system has settled into a steady state [21]. Nevertheless, we can construct a practical KS scheme by constructing a KS superoperator, C_S . To do so, we define $v_S(T)(\mathbf{r})$ as the KS potential in the Mermin functional at temperature T , i.e., the potential that, when thermally occupied with noninteracting electrons, reproduces the exact one-electron density at thermal equi-

librium. We apply perturbation theory for a weak interaction between noninteracting electrons in this potential and the phonons in the reservoir, yielding the analogs to Eqs. (5) above:

$$\Gamma_{i \rightarrow j} = \begin{cases} \mathcal{D}(\omega_{ij}) |\gamma_{ij}|^2 (\bar{n}(\omega_{ij}) + 1) & \epsilon_i > \epsilon_j \\ \mathcal{D}(\omega_{ji}) |\gamma_{ij}|^2 \bar{n}(\omega_{ji}) & \epsilon_i < \epsilon_j \end{cases} \quad (12)$$

where ϵ_i are the eigenvalues of $-\nabla^2/2 + v_S(T)(\mathbf{r})$. The matrix elements γ_{ij} are now evaluated for the interaction between the KS system and the bath. To find the KS master equation itself, we reduce the many-body Eq. (3) to a single-particle form by tracing out all other degrees of freedom, and using a Hartree-style approximation for the two-particle correlation functions appearing in $C[\bar{S}]$. In the basis of the single-particle KS orbitals, we find [22]:

$$\begin{aligned} ds_{nm}/dt = & -i \sum_p (h_{np} s_{pm} - s_{np} h_{pm}) \\ & + (\delta_{nm} - s_{nm}) \sum_p (\Gamma_{p \rightarrow n} + \Gamma_{p \rightarrow m}) s_{pp} \\ & - s_{nm} \sum_p (\Gamma_{n \rightarrow p} + \Gamma_{m \rightarrow p}) (1 - s_{pp}). \end{aligned} \quad (13)$$

In this KS master equation, the steady-state equilibrium has a static potential. The approach rate, determined by Γ , might not match that of the true system, but such effects are absorbed in the XC potential. The important point is that, if such a KS system exists, it is unique for the given coupling by the theorem proven above.

Next we discuss the XC functional, which depends on the coupling to the reservoir. One could imagine performing accurate wave function calculations for a uniform gas on a ring, with the given coupling, to produce a local density approximation for the master equation. But we argue that the usual TDDFT approximations, such as the adiabatic local density approximation, are likely to suffice, because the KS master equation includes dissipation and drives the system to the thermodynamic steady state. The effect of dissipation on XC should be small, and might even vanish in the limit of weak coupling to the reservoir. The important XC effects are to correct the electronic transition frequencies into the true transitions, and this is captured exactly by such an approximation.

The dissipative matrix elements of the KS master equation, defined in Eqs. (12), depend only on phonon frequencies ω , densities of state $\mathcal{D}(\omega)$, and coupling matrix elements γ_{nm} . All these quantities can be extracted from first-principles density functional linear response calculations [23]. This allows for a fully consistent DFT implementation of the dissipative dynamics by making minor modifications to existing plane-wave codes.

Next, we discuss the limit of weak bias. For a given master equation, assume the density matrix has evolved into its steady state, \bar{S}_0 , so that

$$[H_0, \bar{S}_0] = -iC(\bar{S}_0) = 0. \quad (14)$$

If C has been constructed to thermalize the eigenstates of H_0 , both sides of this equation vanish. Now imagine perturbing the system with a weak time-dependent potential ΔV , which becomes constant after a finite time. Allow the system to relax back to its new steady state, with density matrix $\bar{S}_0 + \Delta S$. Equating equal powers in the perturbation:

$$[H_0, \Delta S] + i\eta[\bar{S}_0] \cdot \Delta S = -[\Delta V, \bar{S}_0], \quad (15)$$

where η is the first derivative of C_S . Expanding all quantities in eigenstates of H_0 and solving, we find

$$\Delta S_{AB} = \frac{f_A \Delta V_{AB} - f_B \Delta V_{BA}}{E_A - E_B + i\eta_{AB}}, \quad (16)$$

where $\bar{S}_0 = \sum |A\rangle f_A \langle A|$; i.e., f_A is the Fermi occupation factor of $|A\rangle$. Calculating the density change by tracing the density operator with ΔS , we find it related to the perturbation by the usual Kubo density-density response function [24]. The same derivation applies to the KS master equation, yielding the noninteracting KS response function, and the usual Dyson-like equation at the heart of TDDFT linear response follows.

To understand what this means, consider a KS master equation with weak dissipation ($\eta_{ij} \ll \omega_{ij}$) on an infinite ring. Turn on a small but finite electric field, and evolve the system into a steady state. The ratio of the current to the voltage drop across the system is the isothermal conductivity [14], found from the steady-state solution for the electrons coupled to the phonons. The derivation above shows that, in the zero-field limit, this reduces to the adiabatic conductivity as given by the usual Kubo response formula. This agrees with the Landauer formula for non-interacting electrons [25], and the KS version of this is under study [17].

Although we introduce dissipation in our formalism and are currently performing realistic calculations with finite couplings [26], we can imagine running the calculation for even smaller (but always finite) Γ (after taking limits of infinite ring size, zero temperature, etc.) for finite bias. The steady-state solution(s) of our KS master equation should become independent of the strength of the dissipation, yielding predictions for the conductance that do not depend on any details of the reservoir (just that it exists). This is analogous to the weak bias limit treated above. An interesting question is how this compares with the present standard nonequilibrium Green's function calculations based on the Landauer formalism, or other formulations of the problem [11,12].

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