Relaxation in Time-Dependent Current-Density-Functional Theory

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We apply the time-dependent current-density-functional theory to the study of the relaxation of a closed many-electron system evolving from a nonequilibrium initial state. We show that the self-consistent unitary time evolution generated by the exchange-correlation vector potential irreversibly drives the system to equilibrium. We also show that the energy dissipated in the Kohn-Sham system, i.e., the noninteracting system whose particle and current densities coincide with those of the physical system under study, is related to the entropy production in the real system.

The irreversible time evolution of a many-electron system which is initially prepared in a nonequilibrium state is the subject of strong research interest [1]. The system might be, for example, a large molecule [2] or the electron liquid in a quantum well, and the initial nonequilibrium state might be created by laser excitation or by the application and subsequent removal of an electric field [3]. From experience, we know that, even if the system is closed and isolated, i.e., no exchanges of particles and energy are allowed, the interaction between the particles drives the system towards the state of maximum entropy, i.e., the equilibrium state. When this happens, we say that the system has relaxed [4]. At each stage of the relaxation process, the system has a certain amount of "mechanical energy" which could, in principle, be channeled into work. One of the tasks of theory is to develop efficient tools—as an alternative to the solution of the many-body Schrödinger equation—to calculate the time evolution of the mechanical energy. One would like to do this starting from first principles yet without knowing the exact state of the many-body system as a function of time.

Various formulations of the problem of relaxation of a quantum system have been proposed over the years. Most of these formulations couple the system of interest to some kind of external environment—the so-called thermal bath [5]. When the information about the microscopic state of the thermal bath is discarded, this approach leads to an effective dynamics of the system that is no longer unitary. The main weakness of this approach lies in the fact that the thermal bath and its coupling to the system must be modeled in an essentially *ad hoc* manner. In this Letter, we will describe an alternative approach, based on the time-dependent current-density-functional theory (TDCDFT) [6–10], which allows a first-principle treatment of relaxation in terms of a self-consistent unitary time evolution [11].

We assume that the external potential acting on the system does not depend on time and that the system is closed and isolated. We thus consider the time evolution of a many-electron system described by the Hamiltonian

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + \hat{W} + \int dr V(r)\hat{n}(r), \qquad (1)$$

where $\hat{n}(r)$ is the density operator, $V(r)$ is the external potential, and $\hat{W}$ describes the electron-electron interaction (here and in the following, $\hbar = 1$). A possible way to generate the initial nonequilibrium state $|\psi_i\rangle$ is by applying an external potential at $t = -\infty$ and allowing the system to relax in the presence of this potential. The external potential is then switched off at the initial time $t = 0$, and the system evolves henceforth according to the Schrödinger equation $i\partial_t|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$. Because of the presence of the electron-electron interaction, the system will relax to an equilibrium state of $\hat{H}$. Because the system is closed and isolated during its time evolution, the energy is conserved and equal to its initial value $E_i = \langle\psi_i|\hat{H}|\psi_i\rangle$. This implies that the final equilibrium state will not be the ground state of $\hat{H}$ but the most probable state with total energy E_i. In this final state, the entropy, as well as the temperature, will have finite values. Our task is to calculate the time evolution of the mechanical energy between the initial and the final states of this evolution.

The central tenet of TDCDFT is that the correct time evolution of the particle and current densities of the many-electron system can be obtained from the time evolution of a *noninteracting* reference system, known as the Kohn-Sham (KS) system, described by the state $|\Psi_{KS}(t)\rangle$. This state evolves from an initial state $|\Psi_{KS,i}\rangle$—constructed to give the initial density and energy of the system—according to the equation

$$i\partial_t|\Psi_{KS}(t)\rangle = \hat{H}_{KS}(t)|\Psi_{KS}(t)\rangle, \qquad (2)$$

where the KS Hamiltonian is

$$\hat{H}_{KS}(t) = \sum_i \frac{1}{2m}[\hat{p}_i + eA_{xc}(\hat{r}_i, t)]^2 + \int dr\hat{n}(r)V_{hxc}(r, t)$$
$$+ \int dr\hat{n}(r)V(r). \qquad (3)$$

$V_{hxc}(r, t)$ is an effective scalar potential that includes the

Hartree potential (h) as well as the ground-state exchange-correlation (xc) potential of static density-functional theory (DFT) evaluated at the instantaneous density $n(r, t)$. $A_{xc}(r, t)$ is the xc vector potential, which is a functional of the density and of the time-dependent current density $j(r, t)$ and whose role is to enforce the correct time evolution of the current. The time dependence of $\hat{H}_{KS}$ arises from its being a functional of n and j. In practice, both $V_{hxc}(r, t)$ and $A_{xc}(r, t)$ need to be approximated, but these approximations are nonempirical, in the sense that they are based on exact physical constraints. The simplest and most popular approximation is the local density approximation (LDA), which expresses the xc potential as a functional of the density in the following manner:

$$V_{hxc}(r, t) = \int dr' \frac{e^2}{|r - r'|} n(r', t) + \mu_{xc}(n(r, t)), \quad (4)$$

where $\mu_{xc}(n) = d\epsilon_{xc}(n)/dn$ and $\epsilon_{xc}(n)$ is the xc energy density of a uniform electron gas [10]. As for A_{xc}, a quasilocal approximation in terms of the current density was derived by Vignale and Kohn [12] and can be cast in the form [13]

$$e \frac{d}{dt} A_{xc,k}(r, t) = \frac{1}{n(r, t)} \nabla_i \sigma_{xc}^{ik}(r, t), \quad (5)$$

where i, k denote Cartesian components and the stress tensor σ_{xc} is given by

$$\sigma_{xc}^{ik}(r, t) = \zeta(r, t)\delta_{ik}\nabla \cdot v + \eta(r, t)$$
$$\times (\nabla_i v_k + \nabla_k v_i - \tfrac{2}{3}\delta_{ik}\nabla \cdot v), \quad (6)$$

where $v(r, t) = j(r, t)/n(r, t)$ is the velocity, and we have, for simplicity, neglected retardation effects in the relation between σ_{xc} and the velocity. The quantities η and ζ are the viscoelastic constants of the homogeneous electron liquid and can be calculated from the linear response functions of the latter [10], evaluated at the instantaneous density $n(r, t)$. We want to point out that Eqs. (2)–(6) define a self-consistent unitary evolution which is designed to approximate the true density and current of the system. It is the dependence of the xc vector potential on the velocity that breaks the time-reversal invariance of the KS Hamiltonian and allows for the possibility of irreversible relaxation.

We now define the key quantity of this Letter, the "Kohn-Sham energy"

$$E(t) \equiv \langle\Psi_{KS}(t)|\hat{T}_{A_{xc}} + \hat{V}|\Psi_{KS}(t)\rangle + E_{hxc}[n(t)]$$
$$= \langle\Psi_{KS}(t)|\hat{H}_{KS}(t)|\Psi_{KS}(t)\rangle$$
$$- \int dr V_{hxc}(r, t)n(r, t) + E_{hxc}[n(t)], \quad (7)$$

where $\hat{T}_{A_{xc}} = \sum_i (\hat{p}_i + eA_{xc}(\hat{r}_i, t))^2/2m$ is the kinetic energy operator, and E_{hxc} is the Hartree + xc energy functional of the ground-state DFT. E_{hxc} and V_{hxc} are related by the identity $V_{hxc} = \delta E_{hxc}(n)/\delta n$. In static DFT, $E(t)$ is just

the familiar expression from which the ground-state energy is calculated. In TDCDFT, $E(t)$ is not the true energy of the interacting many-particle system, but, as we will show below, it decreases monotonically with time going from E_i at $t = 0$ to some final value $E_f \geq E_0$ at $t = +\infty$, E_0 being the true ground-state energy of the system.

To prove this point, we observe that a straightforward calculation shows that (we used $\delta\hat{H}_{KS}/\delta A_{xc} = \hat{j}$)

$$\frac{dE}{dt} = \int dr j(r, t) \cdot \frac{dA_{xc}}{dt}. \quad (8)$$

Equation (8) immediately allows us to identify dE/dt as the work done on the system by the self-consistent xc vector potential. By putting Eq. (5) in Eq. (8), we get

$$\frac{dE}{dt} = -2 \int dr \eta \operatorname{Tr}(\omega - \tfrac{1}{3}\operatorname{Tr}\omega)^2 - \int dr \zeta(\operatorname{Tr}\omega)^2, \quad (9)$$

where $\omega_{ij} = (\nabla_i v_j + \nabla_j v_i)/2$. The nonpositivity of $dE(t)/dt$ follows from the fact that the viscosity constants η and ζ are positive [10].

Next we prove that $E(t) \to E_f \geq E_0$ for $t \to \infty$. We begin by observing that, at a fixed time t [14],

$$E(t) \geq \min_{\Psi \to n(t)} \langle\Psi(t)|\hat{T}_{A_{xc}(t)} + \hat{V}|\Psi(t)\rangle + E_{hxc}[n(t)]$$
$$\geq E_0[A_{xc}(t), V] + E_{hxc}[n(t)] - E_{hxc}[n(t), A_{xc}(t)], \quad (10)$$

where $E_0[A, V]$ is the instantaneous ground-state energy of the system, in the presence of static potentials V and A. $E_{hxc}[n, A]$ is the Hartree + xc energy functional of the system in the presence of a static vector potential $A(r)$. Now it is known [15] that, in LDA and up to second order in $B(r) \equiv \nabla \times A(r)$, one has $E_{hxc}[n] - E_{hxc}[n, A] = \int dr c(n(r))B^2(r) > 0$, because $c(n)$ (equals one-half the difference between the orbital magnetic susceptibilities of the interacting and noninteracting homogeneous electron liquid [15]) is a positive quantity. Assuming that this inequality is generally true [16], we can then neglect the last two terms on the right-hand side of Eq. (10) to arrive at $E(t) \geq E_0[A_{xc}(t), V]$. We now observe that, because the electron-electron Coulomb interaction is a positive operator, the ground-state energy of an interacting many-particle system is always greater than the ground-state energy of the same system where electron-electron interaction is turned off. We then conclude that $E_0[A_{xc}, V] \geq E_0^{ni}[A_{xc}, V]$, where E_0^{ni} is the instantaneous ground-state energy of the noninteracting system. On the other hand, the ground-state energy of a noninteracting fermion system is always greater than the ground-state energy $E_{0,b}^{ni}$ of a noninteracting boson system in the same external potentials. We then have

$$E(t) \geq E_0^{ni}[A_{xc}, V] \geq E_{0,b}^{ni}[A_{xc}, V] \geq E_{0,b}^{ni}[A_{xc} = 0, V], \quad (11)$$

where we have used in the last step the diamagnetic inequality, which states that the ground-state energy of a spinless boson system in the presence of a vector potential is always greater than the ground-state energy of the

same system without the vector potential [17]. Because $E_{0,b}^{ni}[A_{xc} = 0, V]$ is a time-independent quantity, we have arrived at our conclusion that $E(t)$ is bounded. Equations (9) and (11) allow us to conclude that the limit $t \to \infty$ of $E(t)$ is finite and that $\lim_{t\to\infty} dE/dt = 0$. From Eq. (9) and the requirement that j vanishes at infinity, we deduce that we can have $dE/dt = 0$ if and only if $\nabla \cdot v = 0$ and $\nabla \times v = 0$, which imply $v = 0$ everywhere (we consider only simply connected geometries). In turn, this implies that the current j is zero everywhere, and, therefore, through the continuity equation, the density approaches a stationary limit $n_f(r)$. This can happen only if the asymptotic state is one of the eigenstates of the KS Hamiltonian with density $n_f(r)$. In the following, we will disregard the unlikely cases when the system gets stuck in some excited state [18], and we will assume $n_f(r) = n_0(r)$, where $n_0(r)$ is the ground-state density. The time evolution of Eq. (2) will then drive the KS system to the ground state of the corresponding KS Hamiltonian.

To demonstrate the above ideas in a concrete example, we have computed numerically the time evolution of the electronic dipole moment $d(t) = \int dz\, z\, n(z, t)$ [Fig. 1(a)] and the energy $E(t) - E_0$ [Fig. 1(b)] in a one-dimensional quantum well, such that the electrons are confined in the z direction and yet are free to move in the x-y plane [19]. The single-particle states for this system are of the form $\psi_n(z)e^{ik\cdot r}$, where k and r are vectors in the x-y plane. The system is initially prepared in a state that corresponds to the KS ground state in the presence of a uniform electric field $\mathcal{E} = 0.01$ mV/nm in the z direction. This state is homogeneous in the x-y plane, and this property is maintained throughout the subsequent time evolution. This means that all the electrons share the same state of motion in the z direction—a time-dependent state that can be written as a linear superposition of the lowest-lying stationary states $\psi_n(z)$ (typically the two lowest ones suffice). The xc vector potential A_{xc} has been approximated in the

form of Eq. (5) [20]. We see from Fig. 1 that the condition $dE/dt \leq 0$ is verified at all times. Moreover, the energy $E(t)$ is well approximated by the analytic form

$$E(t) - E_0 = (E_i - E_0)e^{-\Gamma t}, \quad (12)$$

where the parameter Γ can be estimated from the slope of the curve in Fig. 1.

We now wish to argue that $E(t) - E_0$ is the maximum work that can be extracted from the system at a given time and that its time derivative is related to the rate of entropy production [21]. To do this, let us take a closer look to the quantum well (see Fig. 2). In the 3D system, we separate two different sets of degrees of freedom: the motion in the z direction confined in the quantum well and the free motion in the x-y plane. These two sets of degrees of freedom can be studied as two coupled "subsystems" (see Fig. 2). The coupling is induced by the electron-electron Coulomb interaction: No empirical modeling is needed. As the macroscopic state of motion in the z direction evolves with time, energy is transferred from this motion into low-lying excitations of the two-dimensional electron gas (2DEG) in the x-y plane. These excitations are, in the simplest case, double electron-hole pairs with zero total momentum.

We start from an initial state in which the 2DEG is in the ground state but all the electrons occupy an excited state of motion in the z direction. At the end of the relaxation, all the electrons are in lowest energy state in the z direction, but the 2DEG is in an excited state. In the process, we have transferred energy from a macroscopic state to the many degrees of freedom of the 2DEG. The total energy is conserved and given by E_i. On the other hand, the infinite-time limit of $E(t)$ is the ground-state energy of the system E_0, as one can see by noting that the final Kohn-Sham Hamiltonian, according to Eq. (3), coincides
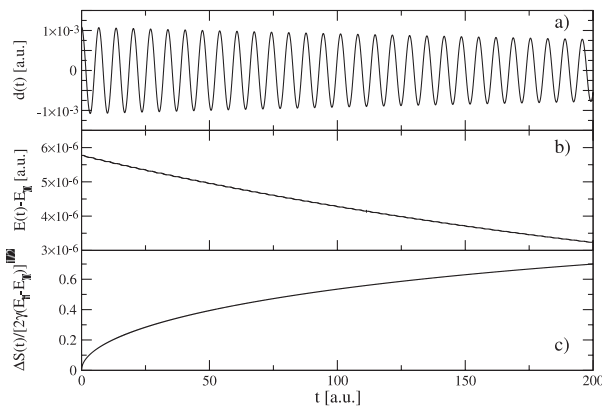

FIG. 1. (a) Plot of the dipole moment $d(t)$ for the electrons in the quantum well as described in the text. (b) Plot of the Kohn-Sham energy $E(t) - E_0$. (c) Plot of $\Delta S(t)/\sqrt{2\gamma(E_i - E_0)}$ as given by Eqs. (12) and (15). A fit of $E(t)$ using the data in (b) gives $\Gamma = 0.0034$ a.u.
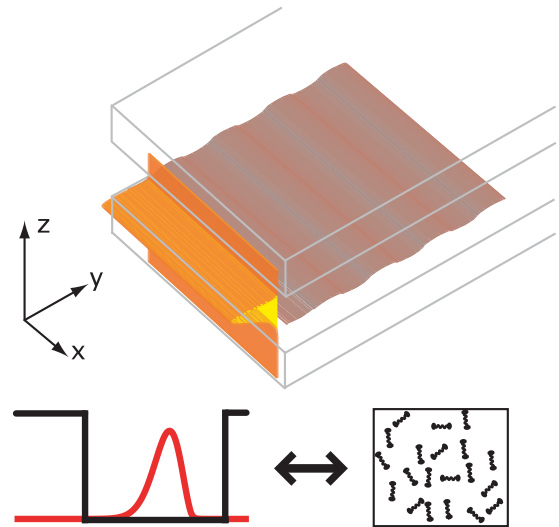

FIG. 2 (color online). The motion in the z direction is coupled through the Coulomb interaction to a 2DEG in the x-y plane. The energy is lost to the motion in the z direction at a rate given by dE/dt.

with the Kohn-Sham Hamiltonian of static DFT which, by definition, yields the correct ground-state energy. Since the electrons are finally at rest in the z direction, the difference $E_i - E_0$ must be entirely ascribed to the excitation of the 2DEG; i.e., $E_i - E_0$ is the total heat Q, transferred from the macroscopic motion in the z direction to the many degrees of freedom of the 2DEG. Denoting by T_i and T_f the initial and final temperatures of the 2DEG, respectively, we have

$$Q = \int_{T_i}^{T_f} dT C_V(T), \tag{13}$$

where $C_V(T)$ is the heat capacity of the 2DEG. At low temperature, we have $C_V(T) = \gamma T$, with $\gamma = \pi \mathcal{A} m^* k_B / 3$, where $\mathcal{A}$ is the area occupied by the gas in the x-y plane and m^* is the particle mass renormalized by electron-electron interactions. Because in our model calculation $T_i = 0$, we get for the final temperature $T_f = \sqrt{(2/\gamma)(E_i - E_0)}$, and, by recalling that $C_V/T = dS/dT$, we get the increase in entropy $\Delta S = \gamma T_f$. The fact that the energy $E_i - E_0$ is converted into heat that increases the temperature and entropy of the 2DEG allows us to identify $E_i - E_0$ as the maximum energy that could, in principle, be extracted from the motion in the z direction to do work.

We can also use Eq. (13) to define a suitable "temperature" for nonequilibrium states. We observe that Eq. (13) can be cast in the form $\int_0^\infty dt [\frac{dE}{dt} + T(t)\frac{dS}{dt}] = 0$, which simply states the global conservation of energy. This suggests that we *define* the nonequilibrium temperature of the system in such a way that the equation

$$\frac{dE}{dt} = -T(t)\frac{dS}{dt} \tag{14}$$

is satisfied at all t. The possibility of this definition stems from the fact that we can always follow a nonequilibrium thermodynamical transformation through a series of small quasiequilibrium transformations. Equation (14) is, in fact, a differential equation for the temperature that can be easily solved to give $T(t) = \sqrt{(2/\gamma)[E_i - E(t)]}$ [we have used again $C_V(T) = \gamma T$ for a 2DEG] and, finally [see Fig. 1(c)],

$$\Delta S(t) = \sqrt{2\gamma[E_i - E(t)]}. \tag{15}$$

In conclusion, we have shown that the time-dependent current-density-functional theory naturally opens the possibility of a first-principle description of relaxation in many-body systems. To show this, we have identified a quantity, the Kohn-Sham energy, that defines a "time arrow" in the evolution of the system by monotonically decreasing with time. We are also able to relate the energy dissipated to the increase in entropy and temperature. This thermodynamical approach allows us to identify the Kohn-Sham energy with the maximum amount of work that can be extracted from the system.

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