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 an non-equilibrium initial state. We show that the self-consistent unitary time evolution generated by the time dependent exchange-correlation vector potential irreversibly drives the system to equilibrium. We also show that the energy dissipated in the Kohn-Sham system is related to the entropy production in the real system.

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The irreversible time evolution of a many-electron system, which is initially prepared in a non-equilibrium 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 non-equilibrium 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 [16]. 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 –in 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 [4]. 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 paper we will describe an alternative approach, based on the time-dependent current-density functional theory (TDCDFT) [5, 6, 7, 8, 9], which allows a first-principle treatment of relaxation in terms of a self-consistent unitary time evolution [17].

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

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

(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 non-equilibrium 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 $i\partial_t |\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$. Due to 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 state 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 non-interacting 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

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

(2)

where the KS Hamiltonian is

$$\hat{H}_{KS}(t) = \sum_i \frac{1}{2m} [\hat{p}_i + eA_{xc}(\hat{r}_i, t)]^2$$

(3)

$$+ \int dr \, \hat{n}(r)V_{hxc}(r, t) + \int dr \, \hat{n}(r)V(r).$$

$V_{hxc}(r, t)$ is an effective scalar potential that includes the Hartree potential ($h$) as well as the ground-state
The current density was derived by Vignale and Kohn in the following manner:

\[ j = \langle j(r), t \rangle = \mu_{xc}(n(r, t)) \left( \int d\nu^{2} - \frac{1}{\nu^{2}} \right) n(r, t) + \mu_{xc}(n(r, t)) \right), \]

where \( \mu_{xc}(n) = d\epsilon_{xc}(n)/dn \) and \( \epsilon_{xc}(n) \) is the xc energy density of a uniform electron gas \( \xi \). For \( V_{hxc}(r, t) \) 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:

\[ V_{hxc}(r, t) = \int d\nu \frac{\epsilon^{2}}{v^{2}} n(r', t) + \mu_{xc}(n(r, t)) \left( \int d\nu^{2} - \frac{1}{\nu^{2}} \right) n(r, t) + \mu_{xc}(n(r, t)) \right), \]

where \( \mu_{xc}(n) = d\epsilon_{xc}(n)/dn \) and \( \epsilon_{xc}(n) \) is the xc energy density of a uniform electron gas \( \xi \). As for \( A_{xc} \), a quasi-local approximation in terms of the current density was derived by Vignale and Kohn [10], and can be cast in the form [11]

\[ e \frac{d}{dt} A_{xc,k}(r, t) = \frac{1}{n(r, t)} \left( \nabla_{i} \sigma_{xc}^{ik}(r, t) \right) \]

where \( i, k \) denote cartesian components and the stress tensor \( \sigma_{xc} \) is given by

\[ \sigma_{xc}^{ik}(r, t) = \zeta(r, t) (\eta + \frac{2}{3} \delta_{ik} \nabla \cdot v) \]

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 \( \sigma_{xc} \) and the velocity. The quantities \( \eta \) and \( \zeta \) are the visco-elastic constants of the homogeneous electron liquid and can be calculated from the linear response functions of the latter \( \xi \), evaluated at the instantaneous density \( n(r, t) \).

We want to point out that the Eqs. (2)-(6) define a key quantity of this paper, the “Kohn-Sham energy”

\[ E(t) = (\Psi_{KS}(t)|H_{KS}(t)|\Psi_{KS}(t)) \]

where \( H_{hxc} \) is the Hartree + xc energy functional of the ground-state DFT. \( H_{hxc} \) and \( V_{hxc} \) are related by the identity \( V_{hxc} = \delta H_{hxc}(n)/\delta n \). 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 \( E_{t} \) to some final value \( E_{f} \). Finally, \( E_{0} \) is the true ground-state energy of the system.

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

\[ \frac{dE}{dt} = \int dr j(r, t) \cdot \frac{dA_{xc}}{dt}. \]

Eq. (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. (9) in Eq. (8) we get

\[ \frac{dE}{dt} = -2 \int dr \zeta(\omega) - \frac{1}{3} Tr(\omega)^{2} - \int dr \zeta(\omega)^{2}, \]

where, \( \omega_{ij} = (\nabla_{i} v_{j} + \nabla_{j} v_{i})/2 \). The non-positivity of \( dE/dt \) follows from the fact that the viscosity constants \( \eta \) and \( \zeta \) are positive \( \xi \).

Next we prove that \( E(t) \to E_{f} \geq E_{0} \) for \( t \to \infty \). We begin by observing that, if \( \nabla \cdot v = 0 \), then \( E_{hxc} = \sum_{i} (\frac{1}{2} m \omega_{ij}^{2} + \hat{h}_{xc} n^{i}) \) is the KS kinetic energy, then at a fixed time \( t \) [18],

\[ E(t) \geq \min_{\Psi \rightarrow n(t)} (\Psi(t)|\hat{T}_{hxc}(t) + \hat{V}(\Psi(t)) + h_{hxc} n(t)) \]

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 [12] 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 \( c(n) \) is one half the difference between the orbital magnetic susceptibilities of the interacting and non-interacting homogeneous electron liquid [12] is a positive quantity. Assuming that this inequality is generally true 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 \( E_{0}[A_{xc}, V] \geq E_{0}[A_{xc}, V] \) where \( E_{0} \) is the instantaneous ground state energy of the non-interacting system. On the other hand, the ground state energy of a non-interacting fermion system is always greater than the ground state energy, \( E_{0}[A_{xc}, V] \), of a non-interacting boson system in the same external potentials. We then have

\[ E(t) \geq E_{0}[A_{xc}, V] \geq E_{0}[A_{xc}, V] \geq E_{0}[A_{xc}, V] = 0, V]. \]
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 \[13\]. Because

\[
E_{0_{\text{exc}}}[A_{xc}, 0, V] \text{ is a time-independent quantity we have arrived at our conclusion that } E(t) \text{ is bounded. Eqs. } \[10\] \text{ and } \[11\] \text{ allow us to conclude that the limit } t \to \infty \text{ of } E(t) \text{ is finite and that } \lim_{t \to \infty} dE/dt = 0. \text{ From Eq. } \[9\] \text{ and the requirement that } j \text{ vanishes at infinity, we deduce that we can have } dE/dt = 0 \text{ if and only if } \nabla \cdot v = 0 \text{ and } \nabla \times v = 0, \text{ which imply } v = 0 \text{ everywhere (we consider only simply connected geometries). } \text{ In turn this implies that the current } j \text{ is zero everywhere, and therefore, through the continuity equation, the density approaches a stationary limit } n_f(r). \text{ This can only happen if the asymptotic state is one of the eigenstates of the KS Hamiltonian with density } n_f(r). \text{ In the following, we will disregard the unlikely cases when the system gets stuck in some excited state, and we will assume } n_f(r) = n_0(r), \text{ where } n_0(r) \text{ is the ground-state density. The time evolution of Eq. } \[2\] \text{ 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 \( d(t) = \int dz n(z, t) \) (Fig. 1 panel a) and the energy \( E(t) - E_0 \) (Fig. 1 panel 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 \[14\]. The single-particle states for this system are of the form \( \psi_n(z) e^{ikr} \) 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 \( \mathcal{E} = 0.01 \text{ mV/nm} \) 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. \[5\] \[10\]. 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

\[
E(t) - E_0 = (E_t - E_0)e^{-\Gamma t}, \tag{12}
\]

where the parameter \( \Gamma \) 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 \[15\]. To do this, let us take a closer look to our quantum well system (see Fig. 1). In this system we can recognize a macroscopic degree of freedom—the \( z \)-dependent wave function in which all the electrons reside—and a “thermal bath”—the two-dimensional electron-gas (2DEG) in the \( x - y \) plane. The coupling between the two is induced by the 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 2DEG in the \( x - y \) plane. These excitations are, in the simplest case, double electron-hole pairs with zero total momentum. Let us study in detail this energy exchange.

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. The total energy is conserved and given by \( E_t \). 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 with the Kohn-Sham hamiltonian of static DFT.

FIG. 1: a) Plot of the dipole moment \( d(t) = \int dz n(z, t) \). b) Plot of the Kohn-Sham energy \( E(t) - E_0 \). c) Plot of \( \Delta S(t)/\sqrt{2\gamma(E_t - E_0)} \) as given by Eqs. \[10\] and \[12\]. A fit with \( E(t) \) in Eq. \[12\] of the data in plot b) gives \( \Gamma = 0.0034 \text{ a.u.} \) We have always used \( \mathcal{E} = 0.01 \text{ mV/nm} \).

FIG. 2: 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 \( dE/dt \).
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. This means that $E_i - E_0$ is the total heat, $Q$, transferred from the macroscopic motion in the z-direction to the 2DEG.

Denoting by $T_i$ and $T_f$ the initial and final temperature of the 2DEG we have

$$Q = \int_{T_i}^{T_f} dT \ C_V(T) \ .$$  \hspace{1cm} (13)

where $C_V(T)$ is the heat capacity of the 2DEG. At low temperature we have $C_V(T) = \gamma T$ with $\gamma = \pi a^2 k_B/3$ where $\Lambda$ is the area occupied by the gas in the $x-y$ plane and $m^*$ is the particle mass renormalized by electron-electron interactions. Eq. (13) provides a quantitative relation between the increase in temperature of the “thermal bath” and the energy that is lost to the macroscopic motion in the z-direction. Because in our model calculation $T_i = 0$ we get for the final temperature $T_f = (\frac{2}{3} \gamma (E_i - E_0)$ 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 [20]. In other words, $E_i - E_0$ is the work we would extract from the system if we could prevent excitation of the 2DEG during the relaxation of the motion in the z-direction. Any excitation of the 2DEG will necessarily result in less work obtained from the system.

We can also use Eq. (13) to define a suitable “temperature” for non-equilibrium states. We begin with the observation that Eq. (13) can be cast in the form [21]

$$\int_0^\infty dt \left[ \frac{dE}{dt} + T(t) \frac{dS}{dt} \right] = 0,$$  \hspace{1cm} (14)

which simply states the global conservation of energy. This suggest that we define the non-equilibrium temperature of the system in such a way that the equation

$$\frac{dE}{dt} = -T(t) \frac{dS}{dt}$$  \hspace{1cm} (15)

is satisfied at all $t$. The possibility of this definition stems from the fact that we can always follow a non-equilibrium thermodynamical transformation through a series of small quasi-equilibrium transformations. Then Eq. (15) is sufficient for the Eq. (14) to be satisfied. Eq. (15) is in fact a differential equation [22] for the temperature that can be easily solved to give $T(t) = \sqrt{\frac{2}{\gamma} [E_i - E(t)]}$ (we have used again $C_V(T) = \gamma T$ for a 2DEG) and finally (see Fig. 1 panel c)

$$\Delta S(t) = \sqrt{2\gamma [E_i - E(t)]}.$$  \hspace{1cm} (16)

This is the desired connection between $E(t)$ and $\Delta S(t)$.

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. Indeed we have proved that this energy monotonically decreases with time until an equilibrium state is reached. 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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[18] We have \( E(t) = \langle \Psi_{KS}(t) | \tilde{T}_{Axc} + \tilde{V} | \Psi_{KS}(t) \rangle + E_{hxc}[n(t)] \) and \( E_0[A,V] = \min_{\Psi} \{ \langle \Psi | \tilde{T}_A + \tilde{V} | \Psi \rangle + E_{hxc}[n, A] \} \).

[19] A more accurate study of this system, including the frequency-dependence of the visco-elastic coefficients has been recently presented in Ref. 14.

[20] In the motion in the z-direction the entropy is constant.

[21] We have \( E_0 - E_i = \int_0^\infty dt \; dE/dt \).

[22] Observe that from \( C_V/T = dS/dT \) follows \( T dS/dt = C_V dT/dt \).