

Mapping from Densities to Potentials in Time-Dependent Density-Functional Theory

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We show that a time-dependent particle density $n(\mathbf{r}t)$ obtained from a given many-particle system can, under mild restrictions on the initial state, always be reproduced by an external potential $v'(\mathbf{r}t)$ in a many-particle system with different two-particle interactions. Given the initial state of this other many-particle system, the potential $v'(\mathbf{r}t)$ is unique up to a purely time-dependent function. As a special case we obtain the well-known Runge-Gross theorem. [S0031-9007(99)09067-5]

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In this work we will discuss the relation between the density and potential of time-dependent many-particle systems. We will show that a time-dependent particle density $n(\mathbf{r}t)$ obtained from a given many-particle system can, under mild restrictions on the initial state, always be reproduced by an external potential $v'(\mathbf{r}t)$ in a many-particle system with different two-particle interactions. Given the initial state of this other many-particle system the potential $v'(\mathbf{r}t)$ is unique up to a purely time-dependent function.

If we specialize to two systems with identical initial states and identical two-particle interactions this statement reduces to the well-known Runge-Gross theorem [1]. This work therefore represents an extension of the theorem by Runge and Gross. Another special case is obtained if we take the two-particle interactions of the second system to be zero. In that case we obtain the result that the density of an interacting system can be reproduced by a one-body potential in a noninteracting system. This result has important consequences for time-dependent density functional theory (TDDFT).

TDDFT [2–5] has turned out to be a successful approach to the calculation of time-dependent properties of many-particle systems. The rigorous foundation of the TDDFT approach is based on the Runge-Gross theorem [1]. This theorem states that, for a fixed initial many-body state, there is a one-to-one correspondence between the time-dependent external field $v(\mathbf{r}t)$ and the time-dependent density $n(\mathbf{r}t)$. This is made into a practical scheme by means of the so-called Kohn-Sham equations. In the Kohn-Sham approach one introduces a noninteracting many-particle system with the same density $n(\mathbf{r}t)$ as the fully interacting system. This noninteracting Kohn-Sham system has a local potential that incorporates all the exchange-correlation effects and is obtained as a density derivative of the action [6]. The fact that the Kohn-Sham equations constitute a set of one-particle equations makes them of great practical use. However, it has still been an unproven assumption that such a noninteracting system, with the same density as the fully interacting system at all times, exists. If, for a certain density $n(\mathbf{r}t)$, such a noninteracting system exists then this density is called noninteracting v -representable.

There are, however, some differences between the use of this concept in stationary and time-dependent systems. For stationary systems a density $n(\mathbf{r})$ is called noninteracting v representable if this density can be obtained as a *ground state* density of a noninteracting system. Even for smooth densities this is not always possible. The counterexamples are provided by densities constructed from degenerate ensembles [7,8]. However, it is generally believed that smooth (i.e., normalizable and twice differentiable) densities are noninteracting ensemble- v -representable (i.e., densities corresponding to a ground state ensemble of a noninteracting system). In a time-dependent system the situation is different, since in that case we are solving an initial-value problem. The initial state of the noninteracting system need not be an eigenstate of the system (and need not even be a Slater determinant wave function). If this initial state has the right specified density, then we can ask ourselves the question whether, in a noninteracting system with this initial state, a time-dependent one-body potential $v_s(\mathbf{r}t)$ exists that reproduces a given smooth density $n(\mathbf{r}t)$ at all times. In this work we will show that this, under mild restrictions on the initial state, is always possible. We will give a constructive proof of this statement. We furthermore show that, given the initial state, this potential is unique up to a purely time-dependent function. This result therefore provides rigorous support for the time-dependent Kohn-Sham formalism. The result also elucidates the initial-state dependence of the time-dependent density functionals.

Let us begin by proving the statement announced at the beginning of the introduction. We start from a Hamiltonian \hat{H} of a finite many-particle system

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}, \quad (1)$$

where \hat{T} is the kinetic energy, $\hat{V}(t)$ the external potential, and \hat{W} the two-particle interaction. In second quantization the constituent terms are written as usual as

$$\hat{T} = -\frac{1}{2} \int d^3r \hat{\psi}^\dagger(\mathbf{r}) \nabla^2 \hat{\psi}(\mathbf{r}), \quad (2)$$

$$\hat{V}(t) = \int d^3r v(\mathbf{r}t) \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}), \quad (3)$$

$$\hat{W} = \int d^3r d^3r' w(|\mathbf{r} - \mathbf{r}'|) \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}). \quad (4)$$

We take the external potential $v(\mathbf{r}t)$ to be of the form

$$v(\mathbf{r}t) = \int d^3r' \frac{Z(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|}, \quad (5)$$

where $Z(\mathbf{r}t)$ describes a finite but arbitrarily large charge distribution. The external potential is thus assumed to be generated by some finite, and in general time-dependent, charge distribution. This form is chosen to make the integrals in our following discussion well defined. However, the form is not particularly restrictive as it encompasses most cases of physical interest. For instance, if $Z(\mathbf{r}t)$ is a delta-function-like distribution of point charges, then $v(\mathbf{r}t)$ describes a molecular framework. The form Eq. (5) excludes some commonly used external fields, such as the potential of a spatially homogeneous electric field. However, for practical purposes these fields can always be approximated to arbitrary accuracy by considering very large but finite charge distributions (which is actually closer to the real physical situation). We further assume $v(\mathbf{r}t)$ to be an analytic function of time t , i.e., $v(\mathbf{r}t)$ must have a Taylor expansion with finite convergence radius for each time t .

We now specify an initial state $|\Psi_0\rangle$ at $t = t_0$ and evolve the wave function with the Hamiltonian $\hat{H}(t)$. From this wave function we can subsequently calculate the density $n(\mathbf{r}t)$. In the following, we consider two continuity equations. If $|\Psi(t)\rangle$ is the state evolving from $|\Psi_0\rangle$ under the influence of Hamiltonian $\hat{H}(t)$ we have the usual continuity equation

$$\partial_t n(\mathbf{r}t) = -i \langle \Psi(t) | [\hat{n}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle = -\nabla \cdot \mathbf{j}(\mathbf{r}t), \quad (6)$$

where the current operator is defined as

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \{ \hat{\psi}^\dagger(\mathbf{r}) \nabla \hat{\psi}(\mathbf{r}) - [\nabla \hat{\psi}^\dagger(\mathbf{r})] \hat{\psi}(\mathbf{r}) \} \quad (7)$$

and has expectation value

$$\mathbf{j}(\mathbf{r}t) = \langle \Psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle. \quad (8)$$

We can further consider an analogous continuity equation for the current itself. We have

$$\partial_t \mathbf{j}(\mathbf{r}t) = -i \langle \Psi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle. \quad (9)$$

If we work out this equation in more detail, we find

$$\partial_t j_k(\mathbf{r}t) = -n(\mathbf{r}t) \partial_k v(\mathbf{r}t) - \sum_i \partial_i T_{ik}(\mathbf{r}t) - W_k(\mathbf{r}t). \quad (10)$$

Here we defined the momentum-stress tensor (part of the energy-momentum tensor) as

$$\hat{T}_{ik}(\mathbf{r}) = \frac{1}{2} \left\{ \partial_i \hat{\psi}^\dagger(\mathbf{r}) \partial_k \hat{\psi}(\mathbf{r}) + \partial_k \hat{\psi}^\dagger(\mathbf{r}) \partial_i \hat{\psi}(\mathbf{r}) - \frac{1}{2} \partial_i \partial_k [\hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r})] \right\} \quad (11)$$

and the quantity \hat{W}_k as

$$\hat{W}_k(\mathbf{r}) = \int d^3r' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \partial_k w(|\mathbf{r} - \mathbf{r}'|) \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}), \quad (12)$$

where the derivative ∂_k is with respect to the variable \mathbf{r} . Their expectation values are defined as

$$T_{ik}(\mathbf{r}t) = \langle \Psi(t) | \hat{T}_{ik} | \Psi(t) \rangle, \quad (13)$$

$$W_k(\mathbf{r}t) = \langle \Psi(t) | \hat{W}_k | \Psi(t) \rangle. \quad (14)$$

Taking the divergence of Eq. (10) and using the continuity Eq. (6) we find

$$\partial_t^2 n(\mathbf{r}t) = \nabla \cdot [n(\mathbf{r}t) \nabla v(\mathbf{r}t)] + q(\mathbf{r}t), \quad (15)$$

with $q(\mathbf{r}t)$ defined as

$$q(\mathbf{r}t) = \langle \Psi(t) | \hat{q}(\mathbf{r}) | \Psi(t) \rangle, \quad (16)$$

and where the operator $\hat{q}(\mathbf{r})$ is defined as

$$\hat{q}(\mathbf{r}) = \sum_{i,k} \partial_i \partial_k \hat{T}_{ik}(\mathbf{r}) + \sum_k \partial_k \hat{W}_k(\mathbf{r}). \quad (17)$$

Equation (15) is the central equation of our discussion as it represents a differential equation which directly relates the external potential and the electron density.

We now ask ourselves the central question: Can the same density $n(\mathbf{r}t)$ be reproduced by an external potential $v'(\mathbf{r}t)$ in a system with a given two-particle interaction $w'(|\mathbf{r} - \mathbf{r}'|)$? We will answer this question affirmatively by means of a constructive procedure for the potential $v'(\mathbf{r}t)$. The only further constraint we will put on the potential $v'(\mathbf{r}t)$ is that it vanishes at infinity, as does potential $v(\mathbf{r}t)$ of Eq. (5). We further notice that if such a $v'(\mathbf{r}t)$ exists then also the potential $v'(\mathbf{r}t) + C(t)$, where $C(t)$ is a purely time-dependent function, will reproduce the required density. This is because the function $C(t)$ only changes the phase of the wave function and does not affect the density. We will show that this is the only ambiguity that can arise, i.e., $v'(\mathbf{r}t)$ is uniquely determined modulo $C(t)$.

We now consider a second system with Hamiltonian

$$\hat{H}'(t) = \hat{T} + \hat{V}'(t) + \hat{W}'. \quad (18)$$

The terms $\hat{V}'(t)$ and \hat{W}' represent again the one- and two-body potentials. We denote the initial state by $|\Phi_0\rangle$ at $t = t_0$ and time-evolved state by $|\Phi(t)\rangle$. The form of \hat{W}' is assumed to be such that $\hat{W}'_k(\mathbf{r}t)$ and its derivatives are finite. For the most important case of interest, i.e., $\hat{W}' = \lambda \hat{W}$ with $0 \leq \lambda \leq 1$, this is automatically satisfied. We will discuss some special cases of this type later on. For the system described by Hamiltonian \hat{H}' we have an analogous equation to Eq. (15). Assuming that the other system has identical density, i.e., $n'(\mathbf{r}t) = n(\mathbf{r}t)$, we have

$$\partial_t^2 n(\mathbf{r}t) = \nabla \cdot [n(\mathbf{r}t) \nabla v'(\mathbf{r}t)] + q'(\mathbf{r}t), \quad (19)$$

where $q'(\mathbf{r}t)$ is the expectation value

$$q'(\mathbf{r}t) = \langle \Phi(t) | \hat{q}(\mathbf{r}) | \Phi(t) \rangle. \quad (20)$$

By subtracting Eqs. (15) and (19), we find

$$\nabla \cdot [n(\mathbf{r}t)\nabla\omega(\mathbf{r}t)] = \zeta(\mathbf{r}t), \quad (21)$$

where $\omega(\mathbf{r}t) = v(\mathbf{r}t) - v'(\mathbf{r}t)$ and $\zeta(\mathbf{r}t) = q'(\mathbf{r}t) - q(\mathbf{r}t)$. Equation (21) is the equation we will use to construct $v'(\mathbf{r}t)$. First we need to discuss some initial and boundary conditions. As a necessary condition for the potential v' to exist, we must obviously require that the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$ yield the same initial density, i.e.,

$$\langle\Phi_0|\hat{n}(\mathbf{r})|\Phi_0\rangle = \langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_0\rangle. \quad (22)$$

We now note that the basic equation, Eq. (15), we used is a second-order differential equation in time for $n(\mathbf{r}t)$. This means that we still need the additional requirement of $\partial_t n'(\mathbf{r}t) = \partial_t n(\mathbf{r}t)$ at $t = t_0$. With the help of the continuity equation (6) this yields the condition

$$\langle\Phi_0|\nabla \cdot \hat{\mathbf{j}}(\mathbf{r})|\Phi_0\rangle = \langle\Psi_0|\nabla \cdot \hat{\mathbf{j}}(\mathbf{r})|\Psi_0\rangle. \quad (23)$$

This constraint also implies the weaker requirement that the initial state $|\Phi_0\rangle$ must be chosen in such a way that the initial momenta $\mathbf{P}(t_0)$ of both systems are the same. This follows directly from the fact that the momentum of the system is given by

$$\mathbf{P}(t) = \int d^3r \mathbf{j}(\mathbf{r}t) = \int d^3r r \partial_t n(\mathbf{r}t). \quad (24)$$

The equality of the last two terms in this equation follows directly from the continuity equation (6) and the fact that we are dealing with finite systems (i.e., currents and densities are zero at infinity). This also helps us to understand the physics behind constraint (23). If the densities of both systems described by Hamiltonian \hat{H} and \hat{H}' are the same at all times, then the above equation (24) implies that also the momenta of both systems are equal at all times. This clearly cannot be satisfied if the initial momenta of both systems are different, since it would require an infinite force to make them equal for $t > t_0$.

With the initial conditions Eqs. (22) and (23), we now discuss the solution of Eq. (21). We first notice that this equation contains no time derivatives and the time variable can therefore be treated as a parameter. We further notice that this equation is of a well-known Sturm-Liouville type, which has a unique solution for $\omega(\mathbf{r}t)$ if $n(\mathbf{r}t)$ and $\zeta(\mathbf{r}t)$ are given, and we further specify the boundary condition that $\omega(\mathbf{r}t)$ approaches zero at infinity. Imposing the latter boundary condition at infinity also means that we choose a particular gauge for the potential $v'(\mathbf{r}t)$, i.e., we fix the arbitrary time-dependent function $C(t)$ mentioned above. Note that this boundary condition at infinity is also satisfied for the potential $v(\mathbf{r}t)$ of Eq. (5). At $t = t_0$ we have

$$\nabla \cdot [n(\mathbf{r}t_0)\nabla\omega(\mathbf{r}t_0)] = \zeta(\mathbf{r}t_0). \quad (25)$$

Since $n(\mathbf{r}t)$ is known at all times and $\zeta(\mathbf{r}t_0)$ can be calculated from the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$ there

is, when taking into account the boundary condition, a unique solution $\omega(\mathbf{r}t_0)$. This means that we have determined $v'(\mathbf{r}t_0) = v(\mathbf{r}t_0) - \omega(\mathbf{r}t_0)$. In the next step we take the time derivative of Eq. (21) at $t = t_0$ and obtain

$$\nabla \cdot [n(\mathbf{r}t_0)\nabla\omega^{(1)}(\mathbf{r})] = \zeta^{(1)}(\mathbf{r}) - \nabla \cdot [n^{(1)}(\mathbf{r})\nabla\omega(\mathbf{r}t_0)], \quad (26)$$

where we introduced the following notation for the k th time derivative at $t = t_0$:

$$f^{(k)}(\mathbf{r}) = \partial_t^k f(\mathbf{r}t)|_{t=t_0}. \quad (27)$$

Now all quantities on the right-hand side of Eq. (26) are known, since $n(\mathbf{r}t)$ is known at all times and $\omega(\mathbf{r}t_0)$ was already determined from Eq. (25). The quantity $\zeta^{(1)}(\mathbf{r})$ is calculated from the commutators:

$$\begin{aligned} \zeta^{(1)}(\mathbf{r}) &= \partial_t \zeta(\mathbf{r}t)|_{t=t_0} \\ &= i\langle\Psi_0|[\hat{q}(\mathbf{r}), \hat{H}(t_0)]|\Psi_0\rangle \\ &\quad - i\langle\Phi_0|[\hat{q}(\mathbf{r}), \hat{H}'(t_0)]|\Phi_0\rangle, \end{aligned} \quad (28)$$

where $\hat{H}'(t_0)$ is known from our previous calculation of $v'(\mathbf{r}t_0)$. From Eq. (26), which is of the same Sturm-Liouville type as Eq. (25), we can therefore calculate (with the same boundary condition at infinity as before) $\omega^{(1)}(\mathbf{r})$ and hence $\partial_t v'(\mathbf{r}t)$ at $t = t_0$. We can now take the second time derivative of Eq. (21) and repeat the above procedure to determine $\partial_t^2 v'(\mathbf{r}t)$ at $t = t_0$. In general, if we take the k th time derivative of Eq. (21), we obtain

$$\nabla \cdot [n(\mathbf{r}t_0)\nabla\omega^{(k)}(\mathbf{r})] = Q^{(k)}(\mathbf{r}), \quad (29)$$

where the inhomogeneity $Q^{(k)}(\mathbf{r})$ is given by

$$Q^{(k)}(\mathbf{r}) = \zeta^{(k)}(\mathbf{r}) - \sum_{l=0}^{k-1} \binom{k}{l} \nabla \cdot [n^{(k-l)}(\mathbf{r})\nabla\omega^{(l)}(\mathbf{r})]. \quad (30)$$

The term $\zeta^{(k)}$ involves multiple commutators of the operator $\hat{q}(\mathbf{r})$ with the Hamiltonians \hat{H} and \hat{H}' and their time derivatives up to order $k - 1$, sandwiched between the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$. The structure of the iteration procedure is now clear. The inhomogeneity $Q^{(k)}(\mathbf{r})$ is completely determined by the density $n(\mathbf{r}t)$, the potential $v(\mathbf{r}t)$, the initial states $|\Psi_0\rangle$ and $|\Phi_0\rangle$, and the time derivatives $\partial_t^{(l)} v'(\mathbf{r}t)$ at $t = t_0$ up to order $k - 1$. Equation (29) therefore allows complete determination of $\partial_t^k v'(\mathbf{r}t)$ at $t = t_0$ for arbitrary value of k . We can therefore construct $v'(\mathbf{r}t)$ from its Taylor series as

$$v'(\mathbf{r}t) = \sum_{k=0}^{\infty} \frac{1}{k!} \partial_t^k v'(\mathbf{r}t)|_{t=t_0} (t - t_0)^k. \quad (31)$$

This determines $v'(\mathbf{r}t)$ completely within the convergence radius of the Taylor expansion. If this convergence radius is nonzero but finite, we can propagate $|\Phi_0\rangle$ to $|\Phi(t_1)\rangle$

at a finite time $t_1 > t_0$ within the convergence radius and repeat the whole procedure above from $t = t_0$ by regarding $|\Phi(t_1)\rangle$ as the initial state. This amounts to analytic continuation along the whole real time axis and a complete determination of $v'(\mathbf{r}t)$ at all times. There is, of course, the possibility that the convergence radius is zero. However, this would mean that $v'(\mathbf{r}t)$ and hence $n(\mathbf{r}t)$ and $v(\mathbf{r}t)$ would be nonanalytic at $t = t_0$. Since we consider only analytical densities we disregard this possibility. We can now make the following statement: We specify a given density $n(\mathbf{r}t)$ obtained from a many-particle system with Hamiltonian \hat{H} and initial state $|\Psi_0\rangle$. If one chooses an initial state $|\Phi_0\rangle$ of a many-particle system with two-particle interaction \hat{W}' in such a way that it yields the correct initial density and initial time derivative of the density, then, for this system, there is a unique external potential $v'(\mathbf{r}t)$ [determined up to a purely time-dependent function $C(t)$] that reproduces the given density $n(\mathbf{r}t)$.

Let us now specify some special cases. We take $\hat{W}' = 0$. We conclude that for a given initial state $|\Phi_0\rangle$, having the correct initial density and initial time derivative of the density, there is a unique potential $v_s(\mathbf{r}t)$ [modulo $C(t)$] in a noninteracting system that produces the given density $n(\mathbf{r}t)$ at all times. This solves the noninteracting v -representability problem, provided we can find an initial state with the required properties. If the many-body system described by Hamiltonian \hat{H} is stationary for times $t < t_0$, the initial state $|\Psi_0\rangle$ at t_0 leads to a density with zero time derivative at $t = t_0$. In that case a noninteracting state with the required initial density and initial time derivative of the density (namely zero) can be obtained via the so-called Harriman [8,9] construction. Therefore for this kind of switch-on processes a Kohn-Sham potential always exists. The additional question of whether this initial state can be chosen as a ground state of a noninteracting system is equivalent to the currently unresolved noninteracting v -representability question for stationary systems.

We now take $\hat{W}' = \hat{W}$. We therefore consider two many-body systems with the same two-particle interac-

tion. We find that, for a given v -representable density $n(\mathbf{r}t)$ [corresponding to initial state $|\Psi_0\rangle$ and potential $v(\mathbf{r}t)$] and a given initial state $|\Phi_0\rangle$ (with the same initial density and initial time derivative of the density as the state $|\Psi_0\rangle$) there is a unique external potential $v'(\mathbf{r}t)$ [modulo $C(t)$] that yields this given density $n(\mathbf{r}t)$. The case $|\Psi_0\rangle = |\Phi_0\rangle$ (in which the constraints on the initial state $|\Phi_0\rangle$ are trivially satisfied) corresponds to the well-known Runge-Gross theorem.

We can summarize our results as follows: We have generalized the well-known Runge-Gross theorem of time-dependent density functional theory. This is achieved through an analysis of the continuity equations for the density and the current. Our results furthermore demonstrate the noninteracting v -representability of the density of many-particle systems and have elucidated the density-potential relation and initial-state dependence of time-dependent density functionals.

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