

Density-Functional Theory for Time-Dependent Systems

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A density-functional formalism comparable to the Hohenberg-Kohn-Sham theory of the ground state is developed for arbitrary time-dependent systems. It is proven that the single-particle potential $v(\vec{r}t)$ leading to a given v -representable density $n(\vec{r}t)$ is uniquely determined so that the corresponding map $v \rightarrow n$ is invertible. On the basis of this theorem, three schemes are derived to calculate the density: a set of hydrodynamical equations, a stationary action principle, and an effective single-particle Schrödinger equation.

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Density-functional methods have become an important tool in the treatment of many-body problems in atomic, molecular, solid state, and nuclear physics.¹ The successful application to stationary systems has recently sparked new interest in treating time-dependent (td) problems in terms of density functionals: Atomic² and nuclear³ scattering processes, photoabsorption in atoms,⁴ and the dynamical response of inhomogeneous metallic systems^{5,6} have been successfully discussed.

However, as yet, a fundamental existence theorem comparable to the theorem of Hohenberg and Kohn⁷ (HK) could not be demonstrated for arbitrary td systems. To illustrate the difficulties involved we shall first give an outline of how such a

theorem should look in a general td situation. The starting point is the td Schrödinger equation (SE)

$$i\partial\Phi(t)/\partial t = \hat{H}(t)\Phi(t), \quad \Phi(t_0) = \Phi_0 \quad (1)$$

(atomic units are used throughout this paper). The Hamiltonian $\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$ is assumed to consist of the kinetic energy

$$\hat{T} = \sum_s \int d^3r \hat{\psi}_s^\dagger(\vec{r}) \left(-\frac{1}{2}\nabla^2\right) \hat{\psi}_s(\vec{r}),$$

a td, local, and spin-independent single-particle potential

$$\hat{V}(t) = \sum_s \int d^3r v(\vec{r}t) \hat{\psi}_s^\dagger(\vec{r}) \hat{\psi}_s(\vec{r}),$$

and some spin-independent particle-particle interaction

$$\hat{W} = \frac{1}{2} \sum_s \sum_{s'} \int d^3r \int d^3r' \hat{\psi}_s^\dagger(\vec{r}) \hat{\psi}_{s'}^\dagger(\vec{r}') w(\vec{r}, \vec{r}') \hat{\psi}_{s'}(\vec{r}') \hat{\psi}_s(\vec{r}).$$

By solving the td SE (1) with various potentials $v(\vec{r}t)$ and a fixed initial state Φ_0 we obtain a map $F: v(\vec{r}t) \rightarrow \Phi(t)$. Next we calculate the densities $n(\vec{r}t) = \langle \Phi(t) | \hat{n}(\vec{r}) | \Phi(t) \rangle$ with $\hat{n}(\vec{r}) = \sum_s \hat{\psi}_s^\dagger(\vec{r}) \times \hat{\psi}_s(\vec{r})$ for all the td wave functions resulting from F . This defines another map $G: v(\vec{r}t) \rightarrow n(\vec{r}t)$. In order to establish a td version of the HK theorem one has to show that G is invertible. Of course, we cannot expect an exact 1-1 correspondence since for two potentials $\hat{V}(t)$ and $\hat{V}'(t)$ differing by an additive merely td scalar function $C(t)$ the corresponding wave functions will differ by a merely td phase $\tilde{\Phi}(t) = e^{-i\alpha(t)}\Phi(t)$ with $\dot{\alpha}(t) = C(t)$, so that the resulting densities will be identical, $\tilde{n}(\vec{r}t) = n(\vec{r}t)$. However, if it is possible to establish the invertibility of G up to such an additive td function then the wave function is fixed by the density up to a td phase via $\Phi(t) = FG^{-1}n(\vec{r}t)$ and any expectation value $\langle \Phi(t) | \hat{O} | \Phi(t) \rangle$ can be regarded as a functional of the density (the ambiguity in the phase cancels out

provided \hat{O} contains no time derivatives).

The proof of the traditional HK theorem is based on the Rayleigh-Ritz principle. The difficulty for td systems arises from the fact that no minimum principle is available; the action integral

$$A = \int_{t_0}^{t_1} dt \langle \Phi(t) | i\partial/\partial t - \hat{H}(t) | \Phi(t) \rangle \quad (2)$$

provides only a stationary point (but, in general, no minimum) at the solution of the td SE (1). So far, a HK-type theorem has been proven only for two special cases⁸: (a) If the potentials $v(\vec{r}t)$ are restricted to functions having a periodic dependence on time the proof can be based either on the Rayleigh-Ritz principle for steady states⁹ or on the minimum property of the "adiabatic" td ground-state energy.¹⁰ (b) For potentials consisting of a fixed static part and a small td perturbation $v(\vec{r}t) = v_0(\vec{r}) + v_{\text{ext}}(\vec{r}t)$ the inverse of G can be constructed within linear-response theory.^{11,12}

The aim of this paper is to establish a general theory for v -representable densities which applies to *arbitrary* 1d situations: In the first part (theorem 1) we shall prove the invertibility of G . Except for the requirement of being expandable into a Taylor series with respect to the time coordinate, no restrictions will be imposed on the set of admissible potentials. The second part of the paper (consisting of three further theorems) will provide a theoretical basis for practical schemes to calculate the 1d density.

Theorem 1.—For every single-particle potential $v(\vec{r}t)$ which can be expanded into a Taylor series with respect to the time coordinate around $t = t_0$, a map $G: v(\vec{r}t) \rightarrow n(\vec{r}t)$ is defined by solving the time-dependent Schrödinger equation with a fixed initial state $\Phi(t_0) = \Phi_0$ and calculating the corresponding densities $n(\vec{r}t)$. This map can be inverted up to an additive merely time-dependent function in the potential.

Proof.—Let $v(\vec{r}t)$ and $v'(\vec{r}t)$ be two potentials

which differ by more than a 1d function, i.e., $v(\vec{r}t) - v'(\vec{r}t) \neq c(t)$. This does of course not exclude that the potentials are identical at $t = t_0$. However, since the potentials can be expanded into a Taylor series around t_0 , there must exist some minimal nonnegative integer k such that

$$\frac{\partial^k}{\partial t^k} [v(\vec{r}t) - v'(\vec{r}t)]|_{t=t_0} \neq \text{const.} \quad (3)$$

The only thing to prove is that the densities $n(\vec{r}t)$ and $n'(\vec{r}t)$ corresponding to $v(\vec{r}t)$ and $v'(\vec{r}t)$ are different if (3) is fulfilled with some $k \geq 0$. In a first step, we show that the corresponding current densities $j(\vec{r}t)$ and $j'(\vec{r}t)$ are different. It should be noted that the particle and current densities corresponding to $v(\vec{r}t)$ and $v'(\vec{r}t)$ are of course identical at the initial time t_0 since we consider only wave functions which evolve from a fixed initial state Φ_0 .

The time evolution of the current density is most easily discussed by means of the equation of motion

$$i \frac{d}{dt} \langle \Phi(t) | \hat{O}(t) | \Phi(t) \rangle = \langle \Phi(t) | i \frac{\partial}{\partial t} \hat{O}(t) + [\hat{O}(t), \hat{H}(t)] | \Phi(t) \rangle. \quad (4)$$

Using $\vec{j}(\vec{r}t) = \langle \Phi(t) | \hat{\vec{j}}(\vec{r}) | \Phi(t) \rangle$ with

$$\hat{\vec{j}}(\vec{r}) = (2i)^{-1} \sum_s [[\nabla \hat{\psi}_s^\dagger(\vec{r})] \hat{\psi}_s(\vec{r}) - \hat{\psi}_s^\dagger(\vec{r}) [\nabla \hat{\psi}_s(\vec{r})]],$$

one obtains

$$i \partial \vec{j}(\vec{r}t) / \partial t = \langle \Phi(t) | [\hat{\vec{j}}(\vec{r}), \hat{H}(t)] | \Phi(t) \rangle. \quad (5)$$

Since $\Phi(t)$ and $\Phi'(t)$ evolve from the same initial state Φ_0 , Eq. (5) leads to

$$i \frac{\partial}{\partial t} [\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)]|_{t=t_0} = \langle \Phi_0 | [\hat{\vec{j}}(\vec{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Phi_0 \rangle = in(\vec{r}t_0) \nabla [v(\vec{r}t_0) - v'(\vec{r}t_0)].$$

If the potentials differ at $t = t_0$ [i.e., if (3) holds for $k = 0$] then the right-hand side of this equation will be different from zero and thus $\vec{j}(\vec{r}t)$ and $\vec{j}'(\vec{r}t)$ will become different infinitesimally later than t_0 . If the minimum integer k for which (3) holds is greater than zero then Eq. (4) has to be applied k times. Derivatives of the potentials with respect to space coordinates [as far as required to calculate the commutators in (4)] are assumed to exist. After some straightforward algebra one obtains

$$\left(i \frac{\partial}{\partial t} \right)^{k+1} [\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)]|_{t=t_0} = in(\vec{r}t_0) \nabla \left\{ \left(i \frac{\partial}{\partial t} \right)^k [v(\vec{r}t) - v'(\vec{r}t)]|_{t=t_0} \right\} \neq 0.$$

Again this means that $\vec{j}(\vec{r}t)$ and $\vec{j}'(\vec{r}t)$ will become different infinitesimally later than t_0 which completes the proof for the current vectors.

Next we consider the corresponding densities. By use of the continuity equation we have

$$(\partial/\partial t)[n(\vec{r}t) - n'(\vec{r}t)] = -\text{div}[\vec{j}(\vec{r}t) - \vec{j}'(\vec{r}t)].$$

Taking the $(k+1)$ st derivative of this equation and using the above result for the current densities we obtain

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [n(\vec{r}t) - n'(\vec{r}t)]|_{t=t_0} = -\text{div} n(\vec{r}t_0) \cdot \nabla \left\{ \frac{\partial^k}{\partial t^k} [v(\vec{r}t) - v'(\vec{r}t)]|_{t=t_0} \right\}. \quad (6)$$

It remains to be shown that the right-hand side of (6) cannot vanish if (3) holds. The proof is by *reductio ad absurdum*: Assume that $\text{div}[n(\vec{r}, t_0)\nabla u(\vec{r})] = 0$ with $u(\vec{r}) \neq \text{const}$; then

$$0 = \int d^3r u(\vec{r}) \text{div}[n(\vec{r}, t_0)\nabla u(\vec{r})] = - \int d^3r n(\vec{r}, t_0) [\nabla u(\vec{r})]^2 + \frac{1}{2} \oint n(\vec{r}, t_0) [\nabla u^2(\vec{r})] \cdot d\vec{r}.$$

If the initial density $n(\vec{r}, t_0)$ falls off rapidly enough to ensure that the surface integral vanishes we can conclude $n(\vec{r}, t_0) [\nabla u(\vec{r})]^2 \equiv 0$. This is in contradiction to $u(\vec{r}) \neq \text{const}$ provided $n(\vec{r}, t_0)$ is reasonably well behaved (we merely have to exclude that the initial density vanishes in precisely those subregions of space where $u = \text{const}$, if such regions exist at all). Thus, the right-hand side of (6) cannot vanish which proves that the densities $n(\vec{r}, t)$ and $n'(\vec{r}, t)$ become different infinitesimally later than t_0 .

Theorem 2.—There exists a three-component density functional $\vec{P}[n](\vec{r}, t)$ which depends parametrically on (\vec{r}, t) such that the exact particle and current densities can be determined from a set of “hydrodynamical” equations

$$\partial n(\vec{r}, t)/\partial t = -\text{div} \vec{j}(\vec{r}, t), \quad (7)$$

$$\partial \vec{j}(\vec{r}, t)/\partial t = \vec{P}[n](\vec{r}, t), \quad (8)$$

with initial conditions $n(\vec{r}, t_0) = \langle \Phi_0 | \hat{n}(\vec{r}) | \Phi_0 \rangle$ and $\vec{j}(\vec{r}, t_0) = \langle \Phi_0 | \hat{\vec{j}}(\vec{r}) | \Phi_0 \rangle$.

Proof.—Since the exact particle and current densities always satisfy the continuity equation (7) it is sufficient to prove Eq. (8). From theorem 1 we know that the potential is determined by the density up to an additive td function $C(t)$. This in turn fixes the wave function within a td phase factor: $\Phi(t) = e^{-i\alpha(t)} \Psi[n](t)$ where $\Psi[n](t)$ is defined as the wave function obtained for the choice $C(t) = 0$. By insertion into (5) the desired Eq. (8) is immediately obtained if the functional \vec{P} is chosen as

$$\begin{aligned} \vec{P}[n](\vec{r}, t) \\ = -i \langle \Psi[n](t) | [\hat{\vec{j}}(\vec{r}), \hat{H}(t)] | \Psi[n](t) \rangle. \end{aligned} \quad (9)$$

Theorem 3.—The action integral (2) can be represented as a functional of the density $A[n]$. If the potential $v(\vec{r}, t)$ is chosen such that no additive time-dependent function can be split, the total action can be written as

$$A[n] = B[n] - \int_{t_0}^{t_1} dt \int d^3r n(\vec{r}, t) v(\vec{r}, t), \quad (10)$$

where $B[n]$ is a universal functional of the density

$$A_{xc}[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | \hat{W} | \Psi[n](t) \rangle - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' n(\vec{r}, t) w(\vec{r}, \vec{r}') n(\vec{r}', t) + S_0[n] - S_W[n]. \quad (14)$$

Theorem 4.—The exact time-dependent density of the system can be computed from

$$n(\vec{r}, t) = \sum \phi_j^*(\vec{r}, t) \phi_j(\vec{r}, t). \quad (15)$$

in the sense that the same dependence on $n(\vec{r}, t)$ holds for all external potentials $v(\vec{r}, t)$. $A[n]$ has a stationary point at the exact density of the system, i.e., the exact density can be computed from the Euler equation

$$\delta A / \delta n(\vec{r}, t) = 0. \quad (11)$$

Proof.—Although the wave function $\Phi(t)$ is fixed by the density only within a td phase factor, the matrix element

$$\langle \Phi(t) | i\partial/\partial t - \hat{T} - \hat{W} - \hat{V}(t) | \Phi(t) \rangle$$

is uniquely determined since the function $C(t)$ contained in the potential $\hat{V}(t)$ is precisely cancelled by the time derivative of the phase $\dot{\alpha}(t) = C(t)$ [see discussion following Eq. (1)]. Therefore, the action (2) is a unique functional of the density and can be written as (10) if $B[n]$ is chosen as

$$B[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i\partial/\partial t - \hat{T} - \hat{W} | \Psi[n](t) \rangle. \quad (12)$$

The universality of B follows trivially from the construction. Since the action (2) is stationary for the exact solution of the td SE (1), the corresponding density functional (10) must be stationary for the exact td density of the system.

In order to derive a practical scheme comparable to the Kohn-Sham formalism¹³ we first define another density functional by

$$S[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i\partial/\partial t - \hat{T} | \Psi[n](t) \rangle \quad (13)$$

which is, of course, universal in the same sense as $B[n]$. It should be pointed out that the particle-particle interaction has been kept fixed so far. If we compare two different interactions \hat{W} and \hat{W}' then the corresponding functionals $S_W[n]$ and $S_{W'}[n]$ will in general be different. Now let $S_0[n]$ be the particular functional (13) for the case $\hat{W} = 0$, i.e., for noninteracting particles. Then, in analogy to the stationary case, the “exchange-correlation” part of the action can be defined as

where the single-particle orbitals $\phi_j(\vec{r}t)$ fulfill the time-dependent Schrödinger equation

$$(i\partial/\partial t + \frac{1}{2}\nabla^2)\phi_j(\vec{r}t) = v_{\text{eff}}[\vec{r}t; n(\vec{r}t)]\phi_j(\vec{r}t) \quad (16)$$

with an effective one-particle potential given by

$$v_{\text{eff}}[\vec{r}t; n(\vec{r}t)] = v(\vec{r}t) + \int d^3r' n(\vec{r}'t) w(\vec{r}, \vec{r}') + \delta A_{\text{xc}}/\delta n(\vec{r}t). \quad (17)$$

Proof.—With use of the definition of the exchange-correlation functional (14), the stationary action principle (11) yields

$$\delta A/\delta n(\vec{r}t) = 0 = \delta S_0/\delta n(\vec{r}t) - [v(\vec{r}t) + \int d^3r' n(\vec{r}'t) w(\vec{r}, \vec{r}') + \delta A_{\text{xc}}/\delta n(\vec{r}t)].$$

This is precisely the Euler equation for a system of *independent* particles moving in the effective potential (17). Therefore, the exact density of the system can be obtained from a set of single-particle orbitals fulfilling the effective td SE (16).

It should be emphasized that the functionals $P[n]$, $B[n]$, and $A_{\text{xc}}[n]$ as given by (9), (12), and (14), respectively, are defined only for v -representable densities. The functionals remain undefined for those densities $n(\vec{r}t)$ which do not correspond to some potential $v(\vec{r}t)$. This fact may cause mathematical problems, e.g., when variations $\delta A[n]$ with respect to *arbitrary* densities are required. At present, it is not clear how large the set of v -representable td densities is.

In the theory presented here, Φ_0 is an arbitrary but *fixed* initial state. Therefore, the functionals $P[n]$, $B[n]$, etc., are defined only for td densities which all have the *same* initial shape $n(\vec{r}t_0)$. For this reason, td theory presented above cannot be compared directly to the stationary Hohenberg-Kohn-Sham theory since the initial densities corresponding to stationary ground states are of course all different. However, if the initial state Φ_0 is allowed to *vary* within the set of nondegenerate ground-state wave functions, it is easy to prove invertibility of the extended map $\hat{G}:(\Phi_0, v(\vec{r}t)) \rightarrow n(\vec{r}t)$.¹⁴ For the set of densities obtained in this way, theorems 2, 3, and 4 hold in precisely the form given above and can be shown to reduce to the common Hohenberg-Kohn-Sham theory in the limit of stationary ground states.¹⁵

Theorems 2, 3, and 4 provide a theoretical basis for three different practical schemes: If one is able to construct the functionals $P[n]$, $B[n]$, or $A_{\text{xc}}[n]$ within a reasonable approximation then the corresponding densities can be calculated from (7) and (8), (11), and (15)–(17), respectively. On the *exact* level the three schemes proven here are, of course, completely equivalent. However, the most attractive alternative to calculate *approximate* densi-

ties is provided by the td Kohn-Sham scheme (theorem 4) since it will produce a quantum mechanical (wiggle) structure in the most natural way.

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