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Time-Dependent Density-Functional Theory: Conceptual and Practical Aspects

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We sketch the proof of an existence theorem for a time-dependent density-functional theory on the set of N -representable densities, extending the constrained-search formulation of Levy into the time-dependent domain, and add a brief comment on practical issues.

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Stationary density-functional theory (DFT) is well established as a powerful tool to discuss ground-state properties of Coulomb systems and atomic nuclei.¹ Formal justification of this theory is provided by the theorem of Hohenberg and Kohn.² The universal functional of Hohenberg and Kohn (HK) is, however, defined only for densities that are ν -representable. For purposes of variational approaches there thus remains the question of whether the domain of the HK functional is adequate. The question has been resolved in two points. Kohn³ was able to show for problems defined on a cubic lattice that the set of ν -representable densities is dense. On the other hand, Levy⁴ demonstrated in his constrained-search formulation that there exists a proper universal functional representing the kinetic energy and the two-particle interaction, which is N -representable and reduces to the HK functional for ν -representable densities.

For the discussion of scattering and excitation processes, an extension of the theory to time-dependent (TD) situations is required (see, e.g., Lundquist⁵). On the level of existence theorems a general TD extension of the HK theorem has been established recently by Runge and Gross.^{1,6} This theorem supersedes earlier efforts for restricted classes of problems with periodic potentials^{7,8} or small TD perturbations.^{9,10} The functionals of Runge and Gross are, like those of the original HK formulation, only defined for ν -representable densities. We note that there have been objections concerning some technical details of the proof in Ref. 6, which gave rise to some controversy.¹¹ In this note we briefly sketch a simple

proof of the existence of a TD DFT on the set of N -representable densities, which reduces in the stationary limit to the scheme of Levy. To be specific, we sketch the theorem for a scattering situation in a Coulomb system. At time $t=0$ the ground state of the electrons is characterized by the Hamiltonian

$$\hat{H} = \hat{T} + \hat{C} + \hat{V}(t=0).$$

[\hat{T} is the kinetic energy, \hat{C} the Coulomb repulsion, and $\hat{V}(t=0)$ the external potentials.] For later times we have

$$\hat{H}(t) = \hat{T} + \hat{C} + \hat{V}(t).$$

Let $|\Psi_0\rangle$ be the initial ground state and $|\Psi_t\rangle$ the solution of the TD Schrödinger equation that develops from this state. We attempt to show that

$$\langle \Psi_t | \hat{O} | \Psi_t \rangle = O[\rho(t)],$$

that is, the expectation value of an operator \hat{O} can be considered to be a functional of the TD one-particle density. The proof proceeds by explicit construction.

Let P be the set of N -representable densities at an arbitrary time t . For each trial density $\rho \in P$, construct the (auxiliary) set S_ρ^t containing all antisymmetric N -particle states giving the density ρ at time t . This set usually contains a large number of states. As ρ is assumed to be N -representable, it will at least contain one state. The task is to select, in a reasonable way, one state $|\Psi\rangle \in S_\rho^t$ with which the expectation values can be calculated and the functionals be defined. We set up the selection principle in two steps.

Define the operator

$$\hat{K}(t) = \hat{U}(t)[\hat{T} + \hat{C} + \hat{V}(t=0)]\hat{U}^\dagger(t),$$

$\hat{U}(t)$ being the full time-evolution operator of the system. With each state $|\Psi\rangle \in S_{\hat{\Psi}}^{\rho}$, calculate the matrix element $\langle\Psi|\hat{K}(t)|\Psi\rangle$.

As $\hat{K}(t)$ provides an isospectral deformation of the ground-state Hamiltonian,¹² the selection can be based on the usual Rayleigh-Ritz principle. The correct state is selected from $S_{\hat{\Psi}}^{\rho}$ via

$$K[\rho] = \inf_{|\Psi\rangle \in S_{\hat{\Psi}}^{\rho}} \langle\Psi|\hat{K}(t)|\Psi\rangle. \quad (1)$$

The functionals $O[\rho]$ defined with the help of the states determined in this way are, however, not universal. The operator $\hat{K}(t)$ depends on $\hat{V}(t)$ via $\hat{U}(t)$ and hence on the history of the system for a given external potential.

To construct a universal functional of the density $\rho \in P$ we consider the set of potentials W which contains all TD potentials $\hat{v}(t)$ such that $\hat{v}(t=0) = \hat{V}(t=0)$ and for which a time evolution operator $\hat{U}_v(t)$ with the Hamiltonian $\hat{H}_v = \hat{T} + \hat{C} + \hat{v}(t)$ exists. Defining the operators

$$\hat{K}_v(t) = \hat{U}_v(t)[\hat{T} + \hat{C} + \hat{V}(t=0)]\hat{U}_v^\dagger(t), \quad \hat{v} \in W,$$

we use the selection principle

$$K[\rho] = \inf_{|\Psi\rangle \in S_{\hat{\Psi}}^{\rho}} \inf_{\hat{v} \in W} \langle\Psi|\hat{K}_v(t)|\Psi\rangle. \quad (2)$$

To avoid the situation that two states $|\Psi_1\rangle, |\Psi_2\rangle \in S_{\hat{\Psi}}^{\rho}$ can be mapped onto the same initial state by two operators $\hat{U}_{v_1}^\dagger$ and $\hat{U}_{v_2}^\dagger$, one must consider all elements in W differing only by a time-dependent function as being equivalent.

In principle, the (rather strange) case could occur that for two states $|\Psi_1\rangle, |\Psi_2\rangle \in S_{\hat{\Psi}}^{\rho}$ one has

$$\inf_{\hat{v} \in W} \langle\Psi_1|\hat{K}_v(t)|\Psi_1\rangle = \inf_{\hat{v} \in W} \langle\Psi_2|\hat{K}_v(t)|\Psi_2\rangle. \quad (3)$$

If degeneracies of the initial ground state are excluded, however, this can never happen on the set $S_{\hat{\Psi}}^{\rho}$ if ρ is the true density. For an arbitrary density ρ the states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ for which this happens should be excluded from $S_{\hat{\Psi}}^{\rho}$ to make the functional unique.

We add the following remarks:

(i) At time $t=0$ we have $\hat{U}_v(0) = 1$ for all $v \in W$; thus the principle (1) as well as (2) reduce to the constrained search recipe of Levy with

$$Q[\rho] = K[\rho] - \int V\rho d^3r.$$

(ii) For v -representable densities the functionals defined via Eq. (2) contain those of Ref. 6.

(iii) We recall that even for time-independent systems, there are still a number of open questions con-

cerning mathematical rigor (see, e.g., the contribution of Lieb in Ref. 1). We do not claim to have covered all the points which a rigorous approach will have to address. For example, we have not touched the question of domains for the operators \hat{K}_v and \hat{O} .

(iv) Existence theorems of the HK type do not readily provide a practical guide to the construction of the functional in question. The time-independent constrained-search formulation, on the other hand, has been implemented directly by Zumbach and Maschke.¹³ One can hope that the search recipe (2) could open the way for an analogous approach in TD DFT, although some new ideas will be needed to make it a working tool.

(v) Presently there is a trend to treat explicitly time-dependent systems within the phase-space formulation of quantum theory. It should be obvious, then, that the sketch of an existence theorem for TD DFT implies that *in principle* all information can be extracted from the one-particle Wigner function. This may help to give a conceptual basis to several (*ad hoc*) truncations of the quantum Bogoliubov-Born-Green-Kirkwood-Yvon chain.

We would like to point out that invariant operators like $\hat{K}(t)$ do give some insight into how functionals can be set up in a practical situation or, at least, which specific problems may appear in their determination. To illustrate this point briefly we confine ourselves to a system of noninteracting particles evolving from a ground state by an external time-dependent potential $V(t)$. The density operator for such a system is

$$\begin{aligned} \hat{\rho}(t) &= \hat{U}(t)\theta(\epsilon_F - \hat{H}(t=0))\hat{U}^\dagger(t) \\ &= \theta(\epsilon_F - \hat{I}(t)), \end{aligned} \quad (4)$$

ϵ_F being the Fermi energy of the ground state. The operator $\hat{I}(t) = \hat{U}(t)\hat{H}(t=0)\hat{U}^\dagger(t)$ satisfies the equation of motion

$$i\hbar \partial \hat{I} / \partial t + [\hat{I}, \hat{H}(t)] = 0, \quad (5)$$

$$\hat{I}(t=0) = \hat{H}(t=0).$$

There are time-integrable systems for which the solution of this equation can be given (e.g., Kohl and Dreizler¹⁴). The corresponding density operator (4) is then the starting point for the determination of the functionals. To obtain some idea as to what happens in the general case, assume the *Ansatz*

$$\hat{H}(t) = \sum_{k=0}^{\infty} \frac{t^k}{k!} \hat{H}_k, \quad \hat{I}(t) = \sum_{k=0}^{\infty} \frac{t^k}{k!} \hat{I}_k. \quad (6)$$

Introduction of Eqs. (6) into Eq. (5) leads to a recursion formula for the operators \hat{I}_k ,

$$\hat{I}_{n+1} = \frac{i}{\hbar} \sum_{k=0}^n \binom{n}{k} [\hat{I}_k, \hat{H}_{n-k}], \quad \hat{I}_0 = \hat{H}_0. \quad (7)$$

In principle, this recursion formula gives a Taylor series expansion of $\hat{I}(t)$ up to arbitrary order. Considering for simplicity a one-dimensional system, one has

$$\hat{I}(t) = \frac{p^2}{2m} + V(\hat{q}, t=0) + \frac{it^2}{4m\hbar} [\hat{p}^2, \dot{V}]_{t=0} + \dots \quad (8)$$

Using the $\hbar=0$ limit of the time-dependent Wigner function $\theta(\epsilon - I(p, q, t))$, $I(p, q, t)$ being the Weyl transformation of the first three terms in Eq. (8), one can derive, e.g., the functional for the kinetic energy density:

$$\tau[\rho, j] = \frac{\hbar^2}{24m} \rho^3 + \frac{m}{2} \frac{j^2}{\rho}, \quad (9)$$

j being the current density of the system. As follows from the derivation, this functional holds strictly only for short times after the time dependence of the Hamiltonian sets in. A detailed investigation of several specific situations like adiabatic and sudden transition systems is in progress.

The main topic of the present paper was, however, to point out that operators like $\hat{K}(t)$ and $\hat{K}_v(t)$ as defined in the text can be used to define a *minimum principle on a set of time-dependent states* (searching over equivalence classes of density operators is possible too). There are still many technical questions to be answered in further work on the subject, as, for instance, how the set W of time-dependent potentials $v(t)$ should or could be reasonably constrained and defined more explicitly.

Note added.—It follows directly from Eq. (2) that a possible degeneracy as indicated in Eq. (3) cannot occur if ρ is a v -representable density. Furthermore, if one is willing to do without the condition of universality of the functionals, the search recipe (1) is sufficient and does lead to a unique state $|\Psi^{\min}(t)\rangle \in S_{\Psi}^{\rho}$ in any case. In fact, the situation is rather tricky and there

are several good reasons why the concept of *universal functionals* for time-dependent systems will play a less important role in *general* practice than in the time-independent case.

¹For a recent review and detailed references, see *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia, NATO Advanced Study Institute Series B, Vol. 123 (Plenum, New York, 1985).

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¹²Some important properties of such operators have been pointed out by H. R. Lewis and W. B. Riesenfeld [J. Math. Phys. **10**, 1458 (1969)]. One can prove directly the following assertions: $i\hbar \partial \hat{K} / \partial t + [\hat{K}(t), \hat{H}(t)] = \hat{0}$. For each solution $|E_n, t\rangle$ of the time-dependent Schrödinger equation evolving from an eigenstate $|E_n, t=0\rangle$ of $\hat{H}(0)$ the equation $\hat{K}(t)|E_n, t\rangle = E_n|E_n, t\rangle$ holds, E_n being the energy corresponding to the state at time $t=0$.

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