

## Orbital-free tensor density functional theory

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We propose a family of time-dependent orbital-free density-based theories that go beyond the usual current-density description of electrons or other particles. The theories deal with physical quantities that characterize the one-particle density matrix and consequently the kinetics of the particles. We analyze the first two theories in the family. The “lowest-order” theory is quantum hydrodynamics. The second one yields not only the longitudinal plasmon collective excitations, but also the transverse phonon modes that are associated with elementary excitations in Fermi liquids. The theories should make it feasible to do large orbital-free simulations of time-dependent and stationary systems. © 2006 American Institute of Physics. [DOI: [10.1063/1.2148953](https://doi.org/10.1063/1.2148953)]

### I. INTRODUCTION

Density-based orbital-free methods<sup>1,2</sup> have been very successful for the past several decades in studying meso- and macroscopic many-particle stationary quantum systems.<sup>3–6</sup> In the time-dependent case, the only density-based orbital-free method used is quantum hydrodynamics (QH),<sup>7–13</sup> in which the hydrodynamics analogy is based on the de Broglie–Bohm formulation of quantum mechanics.<sup>14</sup> In QH, the one-particle density matrix is factorized as though the system consists of only one particle. As a result, the kinetics of the system is described by the spatial particle and current densities (or velocity potential), and an analogy with hydrodynamics arises. In QH, a relatively small amount of information is needed to model a system. Therefore, QH is specifically advantageous numerically, especially in combination with recent methods for its solution.<sup>15–18</sup>

QH is a useful but restrictive approximation. In fact, the kinetics of the particles in the system is entirely described only by the whole one-particle density matrix. The density and the current are just two parameters based on the density matrix. For some problems, however, consideration only of the density and current is not satisfactory. For example, QH may not treat transverse modes in the system, which nevertheless exist in Fermi liquids. Therefore, topologically non-trivial movements in the system, such as vortices, are not treated.

In this paper, we propose a family of time-dependent orbital-free density-based theories, which go beyond the usual density-current description of a Fermi system. The theories deal with tensors that characterize the one-particle density matrix and consequently the kinetics of the particles. We analyze the first two theories in the family. The “lowest-order” theory appears to be quantum hydrodynamics. The second one enables us to obtain not only the longitudinal plasmon collective excitations, but also the transverse phonon modes that should be associated with elementary excita-

tions in Fermi liquids. The resulting equations should be directly applicable to time-dependent and stationary simulations of large electronic systems.

In this paper, we analyze the theory for a general tensor (Sec. II), present the limiting cases of quantum hydrodynamics (Sec. III), and then extend it to the next order, tensor-current-density (Sec. IV), where the general equations and their linear response are presented. Conclusions follow in Sec. V.

### II. GENERAL FORMULATION

We start from the secondary quantized Hamiltonian of an inhomogeneous time-dependent Fermi liquid (using  $m = 1$ ,  $\hbar = 1$ ,  $e = 1$ ):

$$\hat{H} = \hat{K} + \hat{V} + \hat{U},$$

$$\hat{K} = \frac{1}{2} \int d^3x [i\partial_\alpha \hat{\psi}^\dagger(\vec{x})] [-i\partial_\alpha \hat{\psi}(\vec{x})],$$

$$\hat{V} = \int d^3x V(\vec{x}, t) \hat{\rho}(\vec{x}),$$

$$\hat{U} = \int d^3x d^3x' : \delta \hat{\rho}(\vec{x}') U(|\vec{x} - \vec{x}'|) \delta \hat{\rho}(\vec{x}) :,$$

where  $\partial_\alpha = \partial / \partial x_\alpha$ ,  $\hat{\psi}$ 's are the electron annihilation operators,  $\hat{\rho}(\vec{x}) = \hat{\psi}^\dagger \hat{\psi}(\vec{x})$  is the density operator,  $V(\vec{x}, t)$  is the external potential, which is generally time-dependent,  $U(|\vec{x} - \vec{x}'|)$  is the two-body interaction potential,  $\delta \hat{\rho}(\vec{x}) = \hat{\rho}(\vec{x}) - \rho_0(\vec{x})$  with  $\rho_0(\vec{x})$  being the spatial density of the positive background charges, and the columns mean normal operator ordering. Hereafter, a summation over repeated Greek indices is assumed.

As mentioned, the quantity that completely characterizes the kinetics of the electrons is the one-particle density matrix, defined conveniently in terms of difference and average positions:

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$$\rho^{(1)}(\vec{R}, \vec{s}) = \langle \hat{\psi}^\dagger(\vec{R} - \vec{s}/2) \hat{\psi}(\vec{R} + \vec{s}/2) \rangle. \quad (1)$$

The time evolution of the one-particle density matrix is governed by the Liouville equation,

$$\frac{\partial}{\partial t} \rho^{(1)} = -D_\alpha (-i\partial_\alpha) \rho^{(1)} - i[\tilde{V}(\vec{R} + \vec{s}/2) - \tilde{V}(\vec{R} - \vec{s}/2)] \rho^{(1)}. \quad (2)$$

Here  $D_\alpha$  and  $\partial_\alpha$  denote the differentiation over  $R_\alpha$  and  $s_\alpha$ , respectively;  $\tilde{V}(\vec{R})$  is the effective potential, which also takes into account two-body interactions,

$$\tilde{V}(\vec{R}) = \int \frac{\rho(\vec{R}') - \rho_0(\vec{R}')}{|\vec{R} - \vec{R}'|} d^3R' + \frac{\delta E_{xc}}{\delta \rho(\vec{R})} + V(\vec{R}), \quad (3)$$

where  $\rho(\vec{R}) = \rho^{(1)}(\vec{R}, \vec{0})$  is the spatial electron density, the first term is the direct interaction between the electrons and the positive background, and  $E_{xc}$  is the exchange-correlation energy of the system. We use the local-density approximation (LDA) for the exchange-correlation energy, so that it is the functional of  $\rho(\vec{R})$ ,

$$E_{xc} = \int e_{xc}[\rho(\vec{R})] d^3R,$$

where  $e_{xc}(\rho)$  is some function of the density. There are a variety of functions  $e_{xc}$  in the literature (see, e.g., Ref. 6 and refs. therein). For us, however, the specific form of  $e_{xc}$  is not relevant so we do not specify it. Further, a better choice of the exchange-correlation functional would in principle be developed in terms of the current and the kinetic energy tensor introduced below as would be pursued in future publications.

The one-particle density matrix can be obtained by solving Eq. (2). Alternatively, the entire information on the density matrix is contained in the infinite number of differentials over  $\vec{s}$  at  $\vec{s}=\vec{0}$ ,

$$\Phi_{i_1 \dots i_N}^{(N)}(\vec{R}) = (-i\partial_{i_1}) \dots (-i\partial_{i_N}) \rho^{(1)}(\vec{R}, \vec{s})|_{\vec{s}=\vec{0}}. \quad (4)$$

All the  $\Phi$ 's are functions of  $\vec{R}$  only, unlike the one-particle density matrix, which is a function of both  $\vec{R}$  and  $\vec{s}$ . The set of all  $\Phi$ 's contains the same information as the entire one-particle density matrix.

In the usual orbital-free approaches, only the first two (zeroth- and first-order) derivatives are considered—the particle density and the current density:

$$\Phi^{(0)}(\vec{R}) = \rho(\vec{R}), \quad \Phi_i^{(1)}(\vec{R}) = J_i(\vec{R}). \quad (5)$$

Here we derive equations for the time evolution of the system that include higher-order  $\Phi$ 's. These higher-order derivatives contain more information on the electron movement than the density and current alone. Nevertheless, for any physical problem a few orders of  $\Phi$ 's are needed and not the entire infinite set of them. Therefore, the numerical solution of the set of equations proposed in this paper could be more economical than the solution of the Liouvillian Eq. (2), because less information is needed (a finite number of functions of only one 3D continuous variable  $\vec{R}$  versus the den-

sity matrix, which is a function of two 3D continuous variables,  $\vec{R}$  and  $\vec{s}$ ).

From Eq. (2) we find an infinite set of equations that connect the quantities  $\rho, J_i, \Phi^{(2)}, \Phi^{(3)}, \dots$ ,

$$\frac{\partial}{\partial t} \rho = -D_\alpha J_\alpha, \quad (6a)$$

$$\frac{\partial}{\partial t} J_i = -D_\alpha \Phi_{i\alpha}^{(2)} - \rho D_i \tilde{V}, \quad (6b)$$

$$\frac{\partial}{\partial t} \Phi_{ij}^{(2)} = -D_\alpha \Phi_{ij\alpha}^{(3)} - J_i D_j \tilde{V} - J_j D_i \tilde{V}, \quad (6c)$$

$$\begin{aligned} \frac{\partial}{\partial t} \Phi_{ijk}^{(3)} = & -D_\alpha \Phi_{ijk\alpha}^{(4)} - \Phi_{ij}^{(2)} D_k \tilde{V} - \Phi_{ik}^{(2)} D_j \tilde{V} - \Phi_{jk}^{(2)} D_i \tilde{V} \\ & + \frac{1}{4} \rho D_i D_j D_k \tilde{V}, \end{aligned} \quad (6d)$$

...

The generic set of equations needs to be truncated to be useful. Usually, this is done by factorizing a function  $\Phi^{(N+1)}$  at some  $N$  into functions  $\Phi^{(k)}$ ,  $k \leq N$ . Then, the set of equations will close and one will end up with  $N$  equations involving  $N$  orders of functions  $\Phi$ . Such a set of equations could later be solved numerically. The order  $N$  at which we truncate the set of equations controls the precision with which we treat the system.

Further, so far the set of Eqs. (6) does not distinguish between fermions and bosons. Therefore, another very important issue is that the desired factorization *should reflect the fermionic nature of the electrons*.

To come up with such a factorization method, we parametrize the one-particle density matrix in the following way:

$$\rho^{(1)}(\vec{R}, \vec{s}) = \rho(\vec{R}) \exp[\phi(\vec{R}, \vec{s})] f_0(\rho, \vec{s}), \quad (7a)$$

where

$$\phi(\vec{R}, \vec{s}) = 0|_{\vec{s}=\vec{0}},$$

and  $f_0$  is the one-particle density matrix of a free fermion liquid with density  $\rho(\vec{R})$ ,

$$f(\rho, \vec{s}) = 3 \frac{\sin(k_F s) - (k_F s) \cos(k_F s)}{(k_F s)^3},$$

normalized such that

$$f_0(\rho, \vec{s})|_{\vec{s}=\vec{0}} = 1,$$

where  $k_F = (3\pi^2\rho)^{1/3}$  is the local Fermi wave vector.

The one-particle density matrix is Hermitian, i.e.,

$$\rho^{(1)}(\vec{R}, \vec{s}) = \rho^{(1)}(\vec{R}, -\vec{s})^*.$$

This condition implies that the function  $\phi$  generally could be given as a Taylor series of the complex variable  $(i\vec{s})$ ,

$$\phi(\vec{R}, \vec{s}) = \sum_{\alpha \geq 1} \frac{1}{\alpha!} \phi_{i_1 i_2 \dots i_\alpha}^{(\alpha)}(\vec{R})(i s_{i_1})(i s_{i_2}) \cdots (i s_{i_\alpha}) \quad (7b)$$

with all the  $\phi^{(\alpha)}$  real.

The parametrization (7a) is not general. In the general case, one should also include operators that move the one-particle density matrix in  $\vec{s}$  space, so that, for example, the nodes of  $f_0$  are also changed. Nevertheless, the proposed parametrization of the density matrix is a reasonable starting approximation; future papers will include more general expansions.

It is also important to stress that  $\phi$ 's from Eq. (7b) and  $\Phi$ 's from Eq. (4) are not equal. The relations between the  $\phi$ 's and  $\Phi$ 's are analogous to the coupled cluster method, where in order to take into account an infinite series of specific diagrams one uses the exponent function. In our case, for example,

$$\Phi_{ij}^{(2)} = \rho \phi_{ij}^{(2)} + \rho \phi_i^{(1)} \phi_j^{(1)} + E_{ij}(\rho), \quad (8)$$

where the matrix  $E$  is defined as a tensor characterizing the spatial kinetic energy density of a homogeneous electron liquid at rest,

$$E_{ij} = \frac{2}{3} E_{\text{TF}}(\rho) \delta_{ij}. \quad (9)$$

$E_{\text{TF}}$  is the spatial density of the Thomas-Fermi kinetic energy,

$$E_{\text{TF}}(\rho) = C_k \rho^{5/3}, \quad C_k = (3/10)(3\pi^2)^{2/3}.$$

In fact,

$$E_{ij} = \langle p_i p_j \rangle_{\text{FS}},$$

where  $p_i$  is the  $i$ th spatial component of a fermion momentum and the subscript FS denotes averaging over the unperturbed Fermi sea. Note that it is the factor  $f_0$  in Eq. (7a), representing the Fermi distribution in momentum space, that adds the Thomas-Fermi energy into Eq. (8). This term would not appear in a bosonic system, though one could parametrize the boson one-particle density matrix in a way similar to Eqs. (7).

For higher  $N$ , the higher-order averages over the Fermi sea, e.g.,

$$E_{ijkl} = \langle p_i p_j p_k p_l \rangle_{\text{FS}},$$

$$E_{ijklmn} = \langle p_i p_j p_k p_l p_m p_n \rangle_{\text{FS}}, \dots,$$

appear in the relations between  $\Phi$ 's and  $\phi$ 's. We are not going to consider these averages in the rest of this paper.

The relation between the function  $\Phi^{(N)}$  at some  $N$  and all the functions  $\phi^{(\alpha)}$  does not include  $\phi^{(\alpha)}$ 's of orders higher than  $N$ . The same is true for the reverse relations. Therefore, when terminating the set of Eqs. (6) at some order  $N$ , the function  $\phi$  [Eq. (7b)] should also be an  $N^{\text{th}}$ -order polynomial.

### III. QUANTUM HYDRODYNAMICS

We have just described the general recipe for constructing a closed system of dynamic equations. As a first example, we consider the lowest-order ( $N=1$ ) approximation,

or the usual current-density description of the system. The “phase” function  $\phi$  in the definition of one-particle density function (7a) is

$$\phi(\vec{R}, \vec{s}) = i \frac{J_\alpha}{\rho} s_\alpha. \quad (10)$$

Only two equations remain in the whole set (6):

$$\frac{\partial}{\partial t} \rho = -D_\alpha J_\alpha, \quad (11a)$$

$$\frac{\partial}{\partial t} J_i = -D_\alpha \left( \frac{J_i J_\alpha}{\rho} + E_{i\alpha}(\rho) \right) - \rho D_i \tilde{V}. \quad (11b)$$

The factorization of  $\Phi^{(2)}$  in the equation for  $\vec{J}$  comes from Eq. (8) with  $\phi^{(2)}$  equal to zero.

Now, if one assumes that the current could be given through the so-called velocity potential  $\chi$ ,

$$J_i = \rho D_i \chi, \quad (12)$$

then the usual continuity equation and the Euler equation of motion of QH are obtained (see, e.g., Ref. 7),

$$\frac{\partial}{\partial t} \rho + D_\alpha (\rho D_\alpha \chi) = 0, \quad (13a)$$

$$\frac{\partial}{\partial t} \chi + \frac{1}{2} (D \chi)^2 + \frac{\delta K}{\delta \rho} + \tilde{V} = 0, \quad (13b)$$

where  $K = \int E_{\text{TF}}[\rho(\vec{R})] d^3 R$  is the Thomas-Fermi kinetic energy functional. This kinetic energy functional, however, does not include the von Weizsäcker contribution.

## IV. TENSOR-CURRENT-DENSITY

### A. The equations

Next we go one step further ( $N=2$ ) beyond the current-density description. We keep in the “phase” part of the density matrix the terms up to the second order in  $\vec{s}$  [compare with Eq. (8)]:

$$\phi(\vec{R}, \vec{s}) = i \frac{J_\alpha s_\alpha}{\rho} - \frac{1}{2\rho} \left( \Phi_{\alpha\beta}^{(2)} - \frac{J_\alpha J_\beta}{\rho} - E_{\alpha\beta}(\rho) \right) s_\alpha s_\beta.$$

For such a “phase” function,  $\Phi^{(3)}$  in the equation for  $\Phi^{(2)}$  factorizes as

$$\Phi_{ijk}^{(3)} = \Phi_{ij}^{(2)} \frac{J_k}{\rho} + \Phi_{ik}^{(2)} \frac{J_j}{\rho} + \Phi_{jk}^{(2)} \frac{J_i}{\rho} - 2 \frac{J_i J_j J_k}{\rho^2}, \quad (14)$$

so that the whole system of equations becomes

$$\frac{\partial}{\partial t} \rho = -D_\alpha J_\alpha, \quad (15a)$$

$$\frac{\partial}{\partial t} J_i = -D_\alpha \Phi_{i\alpha}^{(2)} - \rho D_i \tilde{V}, \quad (15b)$$

$$\begin{aligned} \frac{\partial}{\partial t} \Phi_{ij}^{(2)} = & -D_\alpha \left( \Phi_{ij}^{(2)} \frac{J_\alpha}{\rho} + \Phi_{i\alpha}^{(2)} \frac{J_j}{\rho} + \Phi_{\alpha j}^{(2)} \frac{J_i}{\rho} - 2 \frac{J_i J_j J_\alpha}{\rho^2} \right) \\ & - J_i D_j \tilde{V} - J_j D_i \tilde{V}. \end{aligned} \quad (15c)$$

This set of equations is ready to be numerically propagated, as will be done in a future paper. Here, we study the system by linear response.

## B. Linear response

Using Eqs. (15), we study the linear response of a stationary homogeneous electron liquid at rest. In this case, the stationary values of the functions involved are

$$\rho = \rho_0, \quad J_i = 0, \quad \Phi_{ij}^{(2)} = \rho_0 \frac{1}{5} v_F^2 \delta_{ij}, \quad D_i \tilde{V} = 0,$$

where we used  $2E_{\text{TF}}(\rho_0)/(3\rho_0) = 1/5 v_F^2$  with  $v_F$  being the Fermi velocity. Then, we let the values vary with the infinitesimally small deviations from their stationary values,

$$\rho = \rho_0 + \rho(\omega, \vec{q}) e^{-i(\omega t - \vec{q}\vec{R})},$$

$$J_i = J_i(\omega, \vec{q}) e^{-i(\omega t - \vec{q}\vec{R})},$$

$$\Phi_{ij}^{(2)} = \frac{1}{5} v_F^2 \delta_{ij} + \Phi_{ij}^{(2)}(\omega, \vec{q}) e^{-i(\omega t - \vec{q}\vec{R})},$$

$$D_i \tilde{V} = i q_i \left( U(q) + \frac{\partial^2 e_{\text{xc}}(\rho)}{\partial \rho^2}(\rho_0) \right) \rho(\omega, \vec{q}) e^{-i(\omega t - \vec{q}\vec{R})},$$

where  $U(q)$  is the Fourier component of the Coulomb potential,

$$U(q) = \frac{4\pi}{q^2}.$$

The linearization yields

$$\omega \rho(\omega, \vec{q}) = q_\alpha J_\alpha \rho(\omega, \vec{q}), \quad (16a)$$

$$\begin{aligned} \omega J_i(\omega, \vec{q}) = & q_\alpha \Phi_{i\alpha}^{(2)}(\omega, \vec{q}) \\ & + \rho_0 q_i \left( U(q) + \frac{\partial^2 e_{\text{xc}}(\rho)}{\partial \rho^2}(\rho_0) \right) \rho(\omega, \vec{q}), \end{aligned} \quad (16b)$$

$$\begin{aligned} \omega \Phi_{ij}^{(2)}(\omega, \vec{q}) = & \frac{1}{5} v_F^2 q_\alpha [\delta_{ij} J_\alpha(\omega, \vec{q}) + \delta_{j\alpha} J_i(\omega, \vec{q}) \\ & + \delta_{i\alpha} J_j(\omega, \vec{q})]. \end{aligned} \quad (16c)$$

Combining the above equations, one gets the final equation for the three current-density components:

$$\begin{aligned} \omega^2 J_i(\omega, \vec{q}) = & \frac{1}{5} v_F^2 q^2 J_i(\omega, \vec{q}) \\ & + \left[ \frac{2}{5} v_F^2 + \rho_0 \left( U(q) + \frac{\partial^2 e_{\text{xc}}(\rho)}{\partial \rho^2}(\rho_0) \right) \right] \\ & \times q_i q_\alpha J_\alpha(\omega, \vec{q}). \end{aligned} \quad (17)$$

There are two types of solutions. When the current is parallel to momentum  $\vec{q}$  [ $J_i = (q_i/q) J_\parallel$ ], then the combination  $q_i q_\alpha J_\alpha$  in the last term of Eq. (17) simplifies as  $q^2 J_i$ . As a result, one finds the dispersion of these longitudinal excitations in the following form:

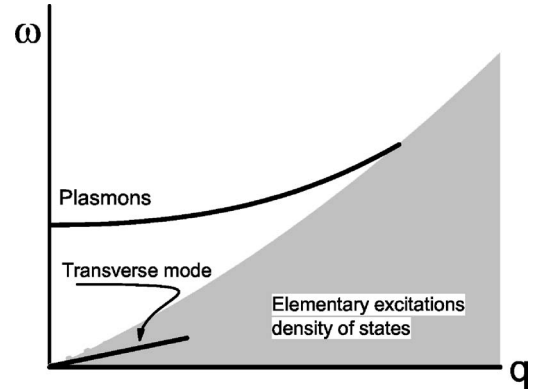


FIG. 1. The excitations of a Fermi liquid consist of the collective plasmon mode, which corresponds to longitudinal oscillations, and of elementary excitations, which correspond to the two transverse phononic modes found. The plasmon mode and the center of the elementary excitation band are reproduced by the  $N=2$  case developed here.

$$\omega_\parallel^2(q) = \omega_0^2 + q^2 \left( \frac{3}{5} v_F^2 + \rho_0 \frac{\partial^2 e_{\text{xc}}(\rho)}{\partial \rho^2}(\rho_0) \right), \quad (18)$$

where  $\omega_0^2 = 4\pi\rho_0$  is the plasma oscillations frequency. These excitations are the collective plasma excitations (plasmons) in the Fermi liquid with Coulomb repulsion. Note that the random-phase approximation result for the plasmon dispersion is

$$\omega_{\text{RPA},\parallel}^2(q) = \omega_0^2 + q^2 \frac{3}{5} v_F^2.$$

The difference comes from contributions from the exchange-correlation energy, for which we used the LDA; however, the LDA is justified only in the high-density limit, where the exchange correlation is smaller than the kinetic and direct energies. In this sense, one might say that the theory reproduces the RPA result for the plasmon dispersion.

The other two solutions are the two transverse oscillations of the current. When the current is transverse ( $q_\alpha J_\alpha = 0$ ), then the last term in Eq. (17) drops out. The dispersion of these transverse phonons is

$$\omega_\perp^2(q) = v_\perp^2 q^2, \quad (19)$$

where the sound velocity is  $v_\perp = v_F/5^{1/2}$ . These oscillations should be associated with elementary excitations in Fermi liquids.

Our result has a physical interpretation. The longitudinal oscillations involve the spatial density, which feels the Coulomb interaction. Therefore, the longitudinal oscillations get renormalized and move up on the energy scale, become gapped, and gain mass. In contrast, the transverse oscillations leave the density intact (at least at the linear-response level). Therefore, they do not get renormalized by the Coulomb interactions. The transverse oscillations consequently remain the elementary excitations of a noninteracting Fermi liquid.

Surprisingly, the dispersion of the transverse mode we got lies almost in the middle of the RPA density of states. In our case, however, these phonons have a dispersion instead of having the smeared density of states between  $0 < \omega < v_F q$  as predicted by the RPA (see Fig. 1). We expect that as one goes to higher- $N$  theories, new phonon modes should

arise. The phonon modes will gradually cover the entire elementary excitations density of states area ( $\Phi^{(3)}$  theory confirms this conjecture, as will be shown later). Furthermore, as one takes into account nonlinearities, the transverse modes' dispersions should get smeared. This smearing should also contribute to the covering of the density-of-states area. Either way, the  $N=2$  theory discussed is the first orbital-free density-based method which gives the transverse excitation mode.

## V. CONCLUSIONS

In conclusion, we proposed a family of orbital-free density-based methods that go beyond the widespread orbital-free current-density description. We analyzed the two first theories in the family. At the simplest  $N=1$  level, the set of equations reproduces the usual quantum hydrodynamics. The  $N=2$  theory gives not only the plasmon longitudinal collective mode, but for the first time the transverse phonon mode, which should be associated with the elementary excitations in a Fermi liquid.

In the future, we plan to extend the theory to the cases in which spin polarization may occur; exploit the proposed approach to numerical studies of realistic finite systems, specifically concentrating on the problem of topologically non-trivial excitations; and study large molecular aggregates and clusters, and their interaction with light and magnetic fields. We also plan to study the stationary states and the time-dependent response for conducting systems, where the stationary state has nonzero current (and possibly vortices). The study would be done by imposing boundary conditions on the set of Eqs. (15), solving that in the stationary case (where all the time derivatives are zero), and then studying linear response. There are also methodological improvements needed. The theory shall be extended to the cases in which the system is exposed to an external magnetic field, and the exchange-correlation contribution  $e_{xc}$  shall be described in terms of  $\rho$ ,  $\vec{J}$ , and kinetic energy tensor  $\Phi^{(2)}$ .

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