

Hydrodynamic tensor density functional theory with correct susceptibility

Igor V. Ovchinnikov, Lizette A. Bartell, and Daniel Neuhauser^{a)}*Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California, 90095-1569*

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In a previous work the authors developed a family of orbital-free tensor equations for the density functional theory [J. Chem. Phys. **124**, 024105 (2006)]. The theory is a combination of the coupled hydrodynamic moment equation hierarchy with a cumulant truncation of the one-body electron density matrix. A basic ingredient in the theory is how to truncate the series of equation of motion for the moments. In the original work the authors assumed that the cumulants vanish above a certain order (N). Here the authors show how to modify this assumption to obtain the correct susceptibilities. This is done for $N=3$, a level above the previous study. At the desired truncation level a few relevant terms are added, which, with the right combination of coefficients, lead to excellent agreement with the Kohn-Sham Lindhard susceptibilities for an uninteracting system. The approach is also powerful away from linear response, as demonstrated in a nonperturbative study of a jellium with a repulsive core, where excellent matching with Kohn-Sham simulations is obtained, while the Thomas-Fermi and von Weiszacker methods show significant deviations. In addition, time-dependent linear response studies at the new $N=3$ level demonstrate the author's previous assertion that as the order of the theory is increased new additional transverse sound modes appear mimicking the random phase approximation transverse dispersion region. © 2007 American Institute of Physics. [DOI: 10.1063/1.2716667]

I. INTRODUCTION

The development of new methods for quantum dynamics based upon hydrodynamic representations is very promising. In hydrodynamics the kinetics of the system is defined by a lesser number of variables than the number of variables required to define the complete one-particle density matrix (which contains all the information on off-diagonal quantum coherence as in, e.g., the Kohn-Sham approach). For stationary studies the hydrodynamics approach is related to orbital-free density functional theory.^{1–25} It is the reduced number of variables depicting the system that makes hydrodynamical theories applicable for numerical studies of relatively large systems.

The simplest hydrodynamical approach is similar to the de Broglie–Bohm formulation of one-particle quantum mechanics.^{26–33} In this approximation the complete complex-valued one-particle density matrix is substituted by two real valued fields ρ and ϕ , which are combined in an order parameter $\psi = \sqrt{\rho} \exp(i\phi)$. The equations of motion are obtained by minimizing a Ginzburg-Landau-type functional on ψ . In addition the density matrix is assumed to possess long-range off-diagonal one-particle correlations.

A more rigorous and asymptotically exact approach is an infinite hierarchy of coupled hydrodynamic moment (CHM) equations.^{34–38} The moments come from a Taylor expansion of the one-particle density matrix with respect to the off-diagonal variable. To get a tractable system of equations the infinite hierarchy must be truncated. The most physically meaningful truncation is a cumulant expansion for the den-

sity matrix.³⁴ Specifically, one decides on an order to terminate the method at; a low order will be less numerically demanding but less accurate than a higher one. Then, at that order, labeled N , the $(N+1)$ th order moment is expanded in terms of the previous set of moments, through the use of the cumulant expansion.

The CHM theory and the accompanying cumulant truncation have been applied so far to systems where particle statistics does not play an important role. In Ref. 39 we have generalized the CHM theory and cumulant expansion to statistically degenerate fermions. The main point has been the modification of the unperturbed one-particle density matrix of a locally homogenous electron gas by using the cumulants. Since the approach uses successive tensors, we labeled it as hydrodynamic tensor density functional theory (HTDFT).

It turns out that the lowest level of truncation, $N=1$, HTDFT corresponds to a de Broglie–Bohm quantum hydrodynamics and in addition naturally incorporates the Thomas-Fermi⁴⁰ kinetic energy term into the energy functional. At the next level, $N=2$, HTDFT starts reproducing the spectrum of a homogenous Fermi liquid, i.e., it gets transverse excitations, rather than just classical plasmonic longitudinal excitations. The transverse sound mode mimics the elementary excitations' density of states.

A crucial feature of HTDFT is the value of the cumulant used at the truncation. In Ref. 39 we assumed that the $(N+1)$ th order cumulant is zero. It turns out, however, as we show here that this assumption leads to a wrong susceptibility for a homogenous electron gas, i.e., to a wrong linear response to a perturbation, even for a noninteracting system of electrons. We show here how to remedy this problem. This

^{a)}Electronic mail: dxn@chem.ucla.edu

is exemplified below for truncation at the $N=3$ level, which is the first level where the method will yield different ground state results from the Thomas-Fermi approach. Specifically, the fourth order cumulant is written as a sum of terms involving the gradients of the previous moments. The coefficients of these terms are obtained by fitting to the exact susceptibility of a noninteracting set of electrons (the Lindhard function).

The balance of the paper is as follows. The general methodology is first developed in Sec. II. In Sec. III the derivation of a correct susceptibility is done. Section IV applies the methodology to a static nonperturbative numerical study of a jellium with a deep spherically symmetric hole, where we show that the agreement with Kohn-Sham results is excellent while the Thomas-Fermi and the von Weiszacker methods have significant errors. Section V is a linear response time-dependent study of the approach for $N=3$ as a function of frequency and wave vector. This latter part is a direct continuation of our work in Ref. 39 for $N=2$, and proves that there is an additional sound mode with respect to the $N=2$ case, just as suggested in Ref. 39. Conclusions follow in Sec. VI.

II. THE SYSTEM AND TENSOR-DFT FORMULATION

A. Coupled hydrodynamic moment hierarchy

For completeness, we rederive the basic aspects of the theory (see Ref. 39). We assume that the many electron system can be described by the one-particle density matrix $\rho^{(1)}$. The one-electron Hamiltonian governing this system h is, as usual, composed of kinetic terms and local potential terms.

The one-particle density matrix is then expressed in terms of average and difference coordinates as

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

The time evolution of the one-particle density matrix is governed by the Heisenberg equation, $i\dot{\rho} = [h, \rho]$, which in those coordinates takes the following form:

$$i \frac{\partial}{\partial t} \rho^{(1)}(\mathbf{R}, s) = \hat{P}_\alpha \hat{p}_\alpha \rho^{(1)} + (\tilde{V}(\mathbf{R} + s/2) - \tilde{V}(\mathbf{R} - s/2)) \rho^{(1)}. \quad (2)$$

Here \hat{P}_α and \hat{p}_α stand for the derivatives over the coordinates R_α and s_α ,

$$\hat{P}_\alpha = -i\partial/\partial R_\alpha, \quad \hat{p}_\alpha = -i\partial/\partial s_\alpha, \quad (3)$$

and $\tilde{V}(\mathbf{R})$ is the effective potential, which also takes into account the two-body interactions,

$$\tilde{V}(\mathbf{R}) = \int \frac{\rho(\mathbf{R}') - \rho_0(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} d^3R' - \frac{\delta E_{xc}}{\delta \rho(\mathbf{R})} + V_{\text{ext}}(\mathbf{R}), \quad (4)$$

where $\rho(\mathbf{R}) = \rho^{(1)}(\mathbf{R}, 0)$ is the spatial electron density, $\rho_0(\mathbf{R})$ is the positive nuclear charge density, V_{ext} is any external potential, E_{xc} is the exchange-correlation energy, and ρ_0 is the nuclei density. There are a variety of functions $V_{xc} \equiv \delta E_{xc} / \delta \rho$ in the literature (see, e.g., Refs. 2–4). For us, however, the specific form of V_{xc} is not important. [In future

works we will aim to derive a form of V_{xc} which depends also on other moments in addition to $\rho(\mathbf{R})$.]

The particle kinetics in the system can be exactly described by the complete infinite set of hydrodynamic moments (dynamic tensors),^{34–39} which are the derivatives of the one-particle density matrix with respect to the off-diagonal distance s at $s=0$,

$$\Phi_{i_1 \dots i_N}^{(N)}(\mathbf{R}) = \hat{p}_{i_1} \dots \hat{p}_{i_N} \rho^{(1)}(\mathbf{R}, s)|_{s=0}. \quad (5)$$

The particle and the current spatial densities are merely the first two tensors in the family,

$$\Phi^{(0)}(\mathbf{R}) = \rho(\mathbf{R}), \quad \Phi_i^{(1)}(\mathbf{R}) = J_i(\mathbf{R}). \quad (6)$$

By using Eq. (2) one derives an infinite set of equations which connects the moments at different orders,

$$\frac{\partial}{\partial t} \rho = -\nabla_\alpha J_\alpha, \quad (7a)$$

$$\frac{\partial}{\partial t} J_i = -\nabla_\alpha \Phi_{i\alpha}^{(2)} - \rho \nabla_i \tilde{V}, \quad (7b)$$

$$\frac{\partial}{\partial t} \Phi_{ik}^{(2)} = -\nabla_\alpha \Phi_{ik\alpha}^{(3)} - J_i \nabla_k \tilde{V} - J_k \nabla_i \tilde{V}, \quad (7c)$$

$$\begin{aligned} \frac{\partial}{\partial t} \Phi_{ikl}^{(3)} = & -\nabla_\alpha \Phi_{ikl\alpha}^{(4)} - \Phi_{ik}^{(2)} \nabla_l \tilde{V} - \Phi_{il}^{(2)} \nabla_k \tilde{V} - \Phi_{lk}^{(2)} \nabla_i \tilde{V} \\ & + \frac{1}{4} \rho \nabla_i \nabla_k \nabla_l \tilde{V}, \end{aligned} \quad (7d)$$

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This generic set of equations is correct for both fermions and bosons. For this set to be useful one should terminate it at some level. As usual, this termination is actually a method for factorizing a moment $\Phi^{(N+1)}$ at some N into moments $\Phi^k, k \leq N$. In addition, this truncation reflects the Fermi statistics of the particles. The order N at which one terminates controls the precision with which we treat the system.

B. Fermi factorization of higher order dynamic tensors

In Ref. 39 we proposed a factorization procedure for the lowest order dynamic tensors ($N=2, 3$). Here we describe in detail how the factorization of the higher order dynamic tensors works in the Fermi case. The method proposed is based on the following general parametrization of the one-particle density matrix:

$$\rho^{(1)}(\mathbf{R}, s) = \rho \exp\{\phi(\mathbf{R}, s)\} f_0(\rho, s), \quad (8a)$$

$$\phi(\mathbf{R}, s) = \sum_{\alpha \geq 1} \frac{1}{\alpha!} \phi_{i_1 i_2 \dots i_\alpha}^{(\alpha)}(\mathbf{R})(i s_{i_1})(i s_{i_2}) \dots (i s_{i_\alpha}), \quad (8b)$$

$$f_0(\rho, s) = 3 \frac{\sin(k_F s) - (k_F s) \cos(k_F s)}{(k_F s)^3}, \quad (8c)$$

$$k_F = (3\pi^2\rho)^{1/3}. \quad (8d)$$

Here, f_0 is the normalized one-particle density matrix of a free fermion liquid with density $\rho(\mathbf{R})$ and k_F is the local (density-dependent) Fermi wave vector. All the cumulants $\phi^{(\alpha)}$, are symmetric in all the indices because they are convolved with the symmetric tensors $s_{i_1} \dots s_{i_n}$ and all the $\phi^{(\alpha)}$ are real as the one-particle density matrix is hermitian. The same is true for the tensors $\Phi^{(\alpha)}$.

The physical meaning of this parametrization is as follows. If $\phi \equiv 0$, then we end up with the Thomas-Fermi approximation of a locally homogeneous Fermi liquid. The ϕ function perturbs this steady liquid picture, and the tensors $\phi^{(\alpha)}$'s and/or $\Phi^{(\alpha)}$'s determine different dynamic characteristics of the flowing electron liquid. The function f_0 assures the Fermi statistics of the particles at the one-particle level.

For brevity we introduce below the tensors

$$\mathcal{F}^{(\alpha)} \equiv \Phi^{(\alpha)}/\rho, \quad (9)$$

instead of $\Phi^{(\alpha)}$. The tensors $\mathcal{F}^{(\alpha)}$ and $\phi^{(\alpha)}$ are interrelated. The relations between $\mathcal{F}^{(\alpha)}$'s and $\phi^{(\alpha)}$'s for the lowest order tensors are given below for the first four relations:

$$\mathcal{F}^{(1)} = \phi^{(1)}, \quad (10a)$$

$$\mathcal{F}^{(2)} = \phi^{(2)} + \overline{\phi^{(1)}\phi^{(1)}} + e^{(2)}, \quad (10b)$$

$$\mathcal{F}^{(3)} = \phi^{(3)} + 3\overline{\phi^{(1)}\phi^{(2)}} + 3\overline{\phi^{(1)}e^{(2)}} + \overline{\phi^{(1)}\phi^{(1)}\phi^{(1)}}, \quad (10c)$$

$$\begin{aligned} \mathcal{F}^{(4)} = & \phi^{(4)} + 4\overline{\phi^{(1)}\phi^{(3)}} + 3\overline{\phi^{(2)}\phi^{(2)}} + 6\overline{\phi^{(1)}\phi^{(1)}\phi^{(2)}} \\ & + 6\overline{\phi^{(2)}e^{(2)}} + 6\overline{\phi^{(1)}\phi^{(1)}e^{(2)}} + \overline{\phi^{(1)}\phi^{(1)}\phi^{(1)}\phi^{(1)}} + e^{(4)}, \end{aligned} \quad (10d)$$

etc. Here all terms are absolutely symmetric tensors of their indices so that there is no need to write down the indices explicitly; a bar denotes here a complete symmetrization, e.g., for a product of $a_{i_1 \dots i_K}$ and $b_{i_1 \dots i_M}$,

$$\overline{ab}_{i_1 \dots i_{K+M}} = \frac{1}{(K+M)!} \sum_p a_{p(i_1) \dots p(i_K)} b_{p(i_{K+1}) \dots p(i_{K+M})},$$

where summation is assumed over all $(K+M)!$ permutations of the indices and p denotes a permutation. The symmetrized multiplication is associative and it can be considered a multiplication on a ring of symmetric tensors (note that in Ref. 39 a somewhat different symmetrization was used). Here is an explicit example of the symmetrized multiplication as follows:

$$\begin{aligned} \overline{\phi^{(1)}\phi^{(1)}\phi^{(2)}} \equiv & \frac{1}{6}(\phi_i^{(1)}\phi_j^{(1)}\phi_k^{(2)} + \phi_i^{(1)}\phi_k^{(1)}\phi_j^{(2)} + \phi_i^{(1)}\phi_l^{(1)}\phi_{jk}^{(2)} \\ & + \phi_k^{(1)}\phi_l^{(1)}\phi_{ij}^{(2)} + \phi_j^{(1)}\phi_l^{(1)}\phi_{ik}^{(2)} \\ & + \phi_j^{(1)}\phi_k^{(1)}\phi_{il}^{(2)}). \end{aligned} \quad (11)$$

In Eqs. (10) the tensors $e^{(2)}$ and $e^{(4)}$ come from differentiating the function f_0 , so that they have the physical meaning of averaging the particle momenta products over the unperturbed Fermi sea (ufs):

$$e_{ij}^{(2)} = \rho^{-1} \langle p_i p_j \rangle_{ufs} = c_2 \delta_{ij}, \quad (12)$$

$$\begin{aligned} e_{ijkl}^{(4)} &= \rho^{-1} \langle p_i p_j p_k p_l \rangle_{ufs} \\ &= 3c_4 \overline{\delta \delta}_{ijkl} \\ &\equiv c_4 (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \end{aligned} \quad (13)$$

where the kinetic coefficients are defined as

$$c_2 = \frac{1}{5} k_F^2, \quad c_4 = \frac{1}{35} k_F^4. \quad (14)$$

All the odd order e 's vanish.

The general recipe for how to express $\mathcal{F}^{(N)}$ in terms of $\phi^{(\alpha)}$'s is as follows. $\mathcal{F}^{(N)}$ is the sum of all the different symmetrized (in the sense discussed above) products of $\phi^{(\alpha)}$ and $e^{(\alpha)}$, $\alpha \leq N$. An additional rule is that each term may include one (and only one) e tensor.

The relations inverse to Eqs. (10) are

$$\mathcal{F}^{(1)} - \phi^{(1)} = 0, \quad (15a)$$

$$\mathcal{F}^{(2)} - \phi^{(2)} = \overline{\mathcal{F}^{(1)}\mathcal{F}^{(1)}} + e^{(2)}, \quad (15b)$$

$$\mathcal{F}^{(3)} - \phi^{(3)} = 3\overline{\mathcal{F}^{(1)}\mathcal{F}^{(2)}} - 2\overline{\mathcal{F}^{(1)}\mathcal{F}^{(1)}\mathcal{F}^{(1)}}, \quad (15c)$$

$$\begin{aligned} \mathcal{F}^{(4)} - \phi^{(4)} = & 4\overline{\mathcal{F}^{(1)}\mathcal{F}^{(3)}} - 12\overline{\mathcal{F}^{(1)}\mathcal{F}^{(1)}\mathcal{F}^{(2)}} \\ & + 6\overline{\mathcal{F}^{(1)}\mathcal{F}^{(1)}\mathcal{F}^{(1)}\mathcal{F}^{(1)}} + 3\overline{\mathcal{F}^{(2)}\mathcal{F}^{(2)}} - 3\overline{e^{(2)}e^{(2)}} \\ & + e^{(4)}. \end{aligned} \quad (15d)$$

The inversion of the infinite set of relations [Eq. (10)] is possible since an expression for any $\mathcal{F}^{(N)}$ in terms of $\phi^{(\alpha)}$'s contains only $\phi^{(\alpha)}$, $\alpha \leq N$. This means that if one knows the expressions for the first N $\phi^{(\alpha)}$ tensors [e.g. Eqs. (15a)–(15c) for $N=3$] then by substituting all the lower order $\phi^{(\alpha)}$'s, $\alpha \leq N$, in the relation for $\mathcal{F}^{(N+1)}$ [Eq. (10d)] with corresponding expressions in terms of $\mathcal{F}^{(\alpha)}$'s one gets the inverse relation for $\phi^{(N+1)}$ (Eq. (15)).

The factorization for the tensor $\Phi^{(N+1)}$ is then simply given by the $(N+1)$ th equation in Eqs. (15). The expression for the $\Phi^{(N+1)}$ tensor contains only kinetic tensors of order $n \leq N$, as well as the $(N+1)$ th order cumulant. Once this cumulant is known the system of Eqs. (8) closes and one arrives at the N th order tensor DFT theory.

C. $N=3$ hydrodynamic tensor DFT

At the $N=3$ level the factorization of $\Phi^{(4)}$ is given by Eq. (15d) with $\phi^{(4)}$ set to zero, or

$$\begin{aligned} \Phi^{(4)} = & 4\rho^{-1} \overline{J\Phi^{(3)}} - 12\rho^{-2} \overline{JJ\Phi^{(2)}} + 6\rho^{-3} \overline{JJJ} \\ & + 3\rho^{-1} \overline{\Phi^{(2)}\Phi^{(2)}} - 3\rho \overline{e^{(2)}e^{(2)}} + \rho e^{(4)} + \rho \phi^{(4)}. \end{aligned} \quad (16)$$

In order to complete the theory we need to obtain $\phi^{(4)}$. For this, we study the static linear response of a homogeneous electron gas. In the ground state all the odd order $\Phi^{(\alpha)}$ tensors vanish (a ground state has no currents as its wave function is real when there is no magnetic field and no degeneracy), so that the first three terms in Eq. (16) would give only nonlinear contributions and can be neglected. As a

result, the required factorization for static studies simplifies as (here we restore the indices)

$$\Phi_{ijkl}^{(4)} = 3\rho^{-1}\overline{\Phi_{ij}^{(2)}\Phi_{kl}^{(2)}} + 3\rho(c_4(\rho) - c_2^2(\rho))\overline{\delta_{ij}\delta_{kl}} + \phi_{ijkl}^{(4)}. \quad (17)$$

III. STATIC LINEAR RESPONSE OF HOMOGENEOUS FERMIONS AND ADJUSTMENT TO THE LINDHARD STRUCTURE FACTOR

The static properties of a homogeneous electron liquid are determined by the structure factor $\chi(\mathbf{q})$. The structure factor is actually the static limit of the density-density correlation function $\chi(\mathbf{q}) = \langle \hat{\rho}(-\mathbf{q}, -\omega)\hat{\rho}(\mathbf{q}, \omega) \rangle_{\omega \rightarrow i0}$. The physical meaning of $\chi(\mathbf{q})$ is the ratio between the amplitude of the infinitesimal harmonic change in electron density $\underline{\rho}(\mathbf{q})$ and that of the external potential $\underline{v}_{\text{ext}}(\mathbf{q})$, which induces the change in the electron density,

$$\delta v_{\text{ext}}(\mathbf{R}) = \underline{v}_{\text{ext}} \exp(i\mathbf{q} \cdot \mathbf{R}) + \text{c.c.}, \quad (18a)$$

$$\delta \rho(\mathbf{R}) = \underline{\rho} \exp(i\mathbf{q} \cdot \mathbf{R}) + \text{c.c.}, \quad (18b)$$

$$\underline{\rho} = \frac{\chi(\mathbf{q})}{\rho_0} \underline{v}_{\text{ext}} + C \underline{v}_{\text{ext}}^3 + \dots \quad (18c)$$

In the ground state of a homogeneous liquid the nonzero values at the $N=3$ level are the density ρ_0 and the second and the fourth order dynamic tensors $\Phi_{ij}^{(2)} = \rho_0 c_2(\rho_0) \delta_{ij}$ and $\Phi_{ijkl}^{(4)} = \rho_0 c_4(\rho_0) \overline{\delta_{ij}\delta_{kl}}$. In a static linear response problem all the odd order kinetic tensors remain zero. Therefore, to study the static linear response of the system we let the values of ρ , $\Phi^{(2)}$, and $\Phi^{(4)}$ vary harmonically in space around their stationary values,

$$\underline{v}_{\text{ext}} = \underline{v}_{\text{ext}} e^{i\mathbf{q} \cdot \mathbf{R}} + \text{c.c.}, \quad (19a)$$

$$\underline{\rho} = \underline{\rho} + (\underline{\rho} e^{i\mathbf{q} \cdot \mathbf{R}} + \text{c.c.}), \quad (19b)$$

$$\underline{\Phi}_{ij}^{(2)} = c_2 \rho_0 \delta_{ij} + (\underline{\Phi}_{ij}^{(2)} e^{i\mathbf{q} \cdot \mathbf{R}} + \text{c.c.}), \quad (19c)$$

$$\underline{\Phi}_{ijkl}^{(4)} = 3c_4 \rho_0 \overline{\delta_{ij}\delta_{kl}} + (\underline{\Phi}_{ijkl}^{(4)} e^{i\mathbf{q} \cdot \mathbf{R}} + \text{c.c.}) + \rho_0 \phi_{ijkl}^{(4)}, \quad (19d)$$

$$\underline{\nabla}_i \underline{\tilde{v}} = q_i (i(\underline{\tilde{v}}(q) \underline{\rho} + \underline{v}_{\text{ext}}) e^{i\mathbf{q} \cdot \mathbf{R}} + \text{c.c.}), \quad (19e)$$

where the underlined variables are the linear response coefficients, while

$$\underline{\tilde{v}}(q) = \frac{4\pi}{q^2} - \frac{\partial V_{\text{xc}}(\rho)}{\partial \rho}(\rho_0). \quad (20)$$

With the use of Eq. (16) the infinitesimal deviation of $\Phi^{(4)}$ has the following form:

$$\underline{\Phi}_{ijkl}^{(4)} = 3D \underline{\rho} \overline{\delta_{ij}\delta_{kl}} + 6c_2 \underline{\delta_{ij}} \overline{\Phi_{kl}^{(2)}} + \rho_0 \phi_{ijkl}^{(4)}, \quad (21)$$

where

$$D = \left. \frac{\partial(\rho(c_4 - c_2^2))}{\partial \rho} \right|_{\rho=\rho_0} - c_2^2 = -\frac{1}{15} k_F^4.$$

Next we consider what terms can be in $\phi^{(4)}$. Our purpose is to make sure that the static response in the noninteracting case would resemble the Lindhard function (static density response of free electrons). The terms added should include the derivative of the available quantities, i.e., the density and the stress tensor, so that they will be vanishing for uniform densities. Further, since $\phi^{(4)}$ is a fourth order tensor, it needs to be constructed from available tensors; the only ones available in the static limit are $\underline{\nabla}_i$, ρ , Φ_{kl} , and δ_{jl} . It is easy to see by inspection that only the following local terms are available to first order in the perturbation and to lowest orders needed in $\underline{\nabla}_i$:

$$\rho_0 \phi_{ijkl}^{(4)}(\mathbf{R}) = \Lambda \overline{\underline{\nabla}_i \underline{\nabla}_j \underline{\nabla}_k \underline{\nabla}_l \rho} - 6f \overline{\underline{\nabla}_i \underline{\nabla}_j \Phi_{kl}^{(2)}} - 6c_2 h \overline{\delta_{ij} \underline{\nabla}_k \underline{\nabla}_l \rho}, \quad (22)$$

where Λ , f , and h are dimensionless parameters. Even in linear response these terms can be augmented by terms involving further derivatives, e.g., terms involving a Laplacian of the components in Eq. (22), (i.e., q^2 in Fourier space), but as orbital-free methods should be primarily geared towards the long-wavelength limit we do not consider here such higher order terms in q .

The additional terms yield the following relation between the linear response coefficients $\underline{\rho}$, $\underline{\Phi}^{(2)}$, and $\underline{\Phi}^{(4)}$:

$$\underline{\Phi}_{ijkl}^{(4)}(\mathbf{q}) = 6(c_2 \delta_{ij} + f q_i q_j) \overline{\Phi_{kl}^{(2)}} + 3D \underline{\rho} \overline{\delta_{ij}\delta_{kl}} + \Lambda \underline{\rho} q_i q_j q_k q_l + 6c_2 h \underline{\rho} q_i q_j \delta_{kl}. \quad (23)$$

Finally, the linearized equations read

$$q_\alpha \underline{\Phi}_{i\alpha}^{(2)} + q_i \rho_0 \underline{\tilde{v}} + q_i \rho_0 \underline{v}_{\text{ext}} = 0, \quad (24a)$$

and

$$\begin{aligned} & 3(c_2 \delta_{ij} + f q_i q_j) (q_\alpha \underline{\Phi}_{k\alpha}^{(2)}) + 3(c_2 + f q^2) q_i \overline{\Phi_{kl}^{(2)}} \\ & + (3(D + c_2 \rho_0 \underline{\tilde{v}} + h c_2 q^2) \overline{\delta_{ij} q_k}) \\ & + (\frac{1}{4} \rho_0 \underline{\tilde{v}} + \Lambda q^2 + 3h c_2) q_i q_j q_k \underline{\rho} \\ & + (3c_2 \overline{\delta_{ij} q_k} + \frac{1}{4} q_i q_j q_k) \rho_0 \underline{v}_{\text{ext}} = 0, \end{aligned} \quad (24b)$$

where the index α is summed over. The only preferential direction in the problem is the momentum vector \mathbf{q} so that the dynamic tensor $\underline{\Phi}^{(2)}$ can be decomposed into the following two form factors:

$$\underline{\Phi}_{ij}^{(2)} = \delta_{ij} \underline{\Phi}^{(0)} + \frac{q_i q_j}{q^2} \underline{\Phi}^{(1)}.$$

Upon substituting this resolution into the initial equations and equating independent spatial tensor components we arrive at three equations for $\underline{\rho}$, $\underline{\Phi}^{(0)}$, and $\underline{\Phi}^{(1)}$,

$$\Phi^{(0)} + \Phi^{(1)} + \rho_0 \tilde{\nu} \rho = -\rho_0 \underline{\nu}_{\text{ext}},$$

$$\begin{aligned} &(-\rho_0 \underline{\nu}_{\text{ext}} - \rho_0 \tilde{\nu} \rho) + \left(1 + \frac{f}{c_2} q^2\right) \Phi^{(0)} \\ &+ \left(-\frac{k_F^2}{3} + \rho_0 \tilde{\nu} + h q^2\right) \rho = -\rho_0 \underline{\nu}_{\text{ext}}, \end{aligned}$$

$$\begin{aligned} &3f(-\rho_0 \underline{\nu}_{\text{ext}} - \rho_0 \tilde{\nu} \rho) + 3\frac{c_2}{q^2} \left(1 + \frac{f}{c_2} q^2\right) \Phi^{(0)} \\ &+ \left(\frac{1}{4} \rho_0 \tilde{\nu} + \Lambda q^2 + 3hc_2\right) \rho = -\frac{1}{4} \rho_0 \underline{\nu}_{\text{ext}}. \end{aligned}$$

Upon solving these linear equations one gets

$$\rho = -\chi \rho_0 \underline{\nu}_{\text{ext}}, \quad (25a)$$

$$-\chi^{-1} = -\chi_0^{-1} + \tilde{\nu}, \quad (25b)$$

where

$$-\frac{\pi^2}{k_F} \chi_0 = \frac{1 + 20(2f - 1/12)\eta^2}{1 - 24h\eta^2 - 80\Lambda\eta^4}, \quad (25c)$$

and we introduced the following dimensionless momentum:

$$\eta = \frac{q}{2k_F}.$$

Equation (25b) is the definition of the structure factor renormalized with respect to two-body interactions. Therefore χ_0 should be the structure factor of noninteracting electrons. In order to adjust our theory to the realistic description of electrons one should compare χ_0 to the following Lindhard function:

$$-\frac{\pi^2}{k_F} \chi_{\text{Lind}} = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right|. \quad (26)$$

The freedom in choosing the parameters Λ , f , and h allows us to fit our structure factor to the Lindhard function. The Lindhard function has the following properties:

$$-\frac{\pi^2}{k_F} \chi_{\text{Lind}} = \begin{cases} \frac{1}{3} \eta^{-2}, & \eta \rightarrow \infty \\ 1 - \frac{1}{3} \eta^2, & \eta \rightarrow 0 \\ \frac{1}{2}, & \eta = 1. \end{cases} \quad (27)$$

In order for our function χ_0 to possess these properties we should choose

$$\Lambda = -\frac{1}{80}, \quad f = \frac{1}{20}, \quad \text{and } h = -\frac{1}{36}. \quad (28)$$

A comparison between the resulting structure factor of the proposed theory with the Lindhard function and the structure factor provided by the 1/9 von Weiszacker theory is given in Fig. 1.

IV. APPLICATION TO THE GROUND STATE PROBLEM

We applied the $\Phi^{(3)}$ theory to a ground state study of a nonperturbative nonhomogeneous jellium. We chose a spherically symmetric infinite electron system in the following positive jellium background density profile:

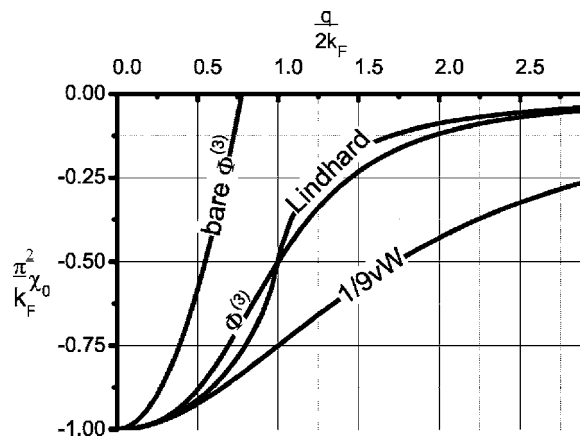


FIG. 1. The bare structure factors χ_0 on a scaled momentum scale $q/2k_F$ for the 1/9 von Weiszacker approach, bare and adjusted $\Phi^{(3)}$ HTDFT theories, and the Lindhard function (free-electron gas static density-density correlator). The $\Phi^{(3)}$ HTDFT is fitted to have the three properties of the Lindhard function given in Eq. (27).

$$\rho_0(r) = \rho_\infty + \Delta\rho(r),$$

$$\Delta\rho(r) = -\zeta\rho_\infty \left(1 - \frac{r^2}{3r_0^2}\right) e^{-r^2/2r_0^2}, \quad (29)$$

where we took $\rho_\infty = 0.01$, $\zeta = 0.9$, and $r_0 = 3$ and 2 (all in a.u.). The additional nonhomogeneous part of jellium density $\Delta\rho$ integrates to zero so we avoid complications connected with an overall non-neutral system. Alternatively this system can be viewed as having constant jellium background density ρ_∞ but with an external Gaussian potential,

$$V_b(r) = r_0^2 \zeta \rho_\infty \frac{4\pi}{3} e^{-r^2/2r_0^2}, \quad (30)$$

which is related to $\Delta\rho(r)$ by the Poisson equation,

$$\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} V_b(r) = 4\pi \Delta\rho(r). \quad (31)$$

The Dirac exchange is used here,

$$V_{\text{xc}}(\mathbf{R}) = \frac{(3\pi^2)^{1/3}}{\pi} \rho(\mathbf{R})^{1/3}. \quad (32)$$

No correlation energy was employed (its contribution is very small; it will be included in future studies). The simulations were performed by adiabatical turning on the nonhomogeneous part of the jellium positive background density $\Delta\rho$. Initially the electron and the jellium densities are homogeneous, ρ_∞ . The odd order kinetic tensors J_i and $\Phi_{ijk}^{(3)}$ are zero and the even order tensors are those of a homogeneous electron liquid $\Phi_{ij}^{(2)} = \rho_\infty e_{ij}^{(2)}$ and $\Phi_{ijkl}^{(4)} = \rho_\infty e_{ijkl}^{(4)}$ with the e tensors given in Eq. (13).

We then propagate the set of Eqs. (7) while the jellium density gradually changes from homogenous to the final $\rho_0(r)$; this ensures that the system remains at the ground state for all times. We implemented the adiabatic density by setting

$$\rho_0(R, t) = (1 - g(t))\rho_0(R) + g(t)\rho_\infty,$$

where $g(t)$ is a smooth function rising from 0 to 1; we chose here, quite arbitrarily,

$$g(t) = \frac{1}{1 + \exp((t_0 - t/\tau)^3)},$$

and used

$$t_0 = 3\tau.$$

The width parameter τ was typically taken as 50 a.u.; this value was more than sufficient for adiabatic convergence. $\rho_0(R, t)$ is then used for the definition of the time-dependent potential [Eq. (4)].

The evolution of the system is then determined from the four first equations in Eq. (7), with the $\Phi^{(4)}$ tensor given by Eqs. (16) and (22). The three dimensional equations were discretized and the derivative were evaluated by Fourier transforms, as was the Coulomb integral. Grid spacings of 1.6–2 a.u. were sufficient to converge when the hole width parameter r_0 was set at 2.0 or 3.0 a.u., respectively. A simple fixed step Runge-Kutta algorithm with $dt=0.2$ a.u. was used to evolve the equations in time.

We compared the results to Thomas-Fermi, von Weiszacker, and plane wave Kohn-Sham simulations. The latter were done by a standard plane wave code; interestingly, we found that the grid spacing needed to converge the Kohn-Sham plane wave simulations had to be smaller by about 20% than those needed in the HFDFD code, so that they were about 1.3 and 1.6 a.u. for $r_0=2.0$ and 3.0, respectively. The grids contained typically $(20)^3$ points.

Figure 2 shows that HTDFT gives essentially the same density as the Kohn-Sham approach, while the von Weiszacker and Thomas-Fermi results deviate significantly. Since the two-body interaction is treated the same in all four simulations, this proves that the hydrodynamic approach yields, even for this system which is shifted strongly away from uniformity, the same densities as the essentially exact description of the kinetic energy in the Kohn-Sham approach.

V. TIME-DEPENDENT LINEAR RESPONSE AND THE COLLECTIVE MODES

In our previous paper³⁹ we studied the ground state of a homogenous electron gas at the $N=2$ level, with the assumption that $\phi^{(N+1)}$ is zero. Here we extend the studies to $N=3$, with $\phi^{(4)}$, as given by Eqs. (22) and (28). We derive the governing formulas in general, and arrive at analytical limits in the long-wavelength limit (where ϕ^4 is not contributing), showing new kinds of excitations.

In the ground state of a homogeneous liquid the nonzero values at the $N=3$ level are the density ρ_0 and the second and the fourth order dynamic tensors $\Phi_{ij}^{(2)} = \rho_0 c_2(\rho_0) \delta_{ij}$ and $\Phi_{ijkl}^{(4)} = \rho_0 c_4(\rho_0) \delta_{ij} \delta_{kl}$, respectively. To study the linear response of the system we let all the values in the problem vary harmonically around their stationary values,

$$\rho = \rho_0 + (\rho e^{-i(\omega t - \mathbf{q} \cdot \mathbf{R})} + \text{c.c.}), \quad (33a)$$

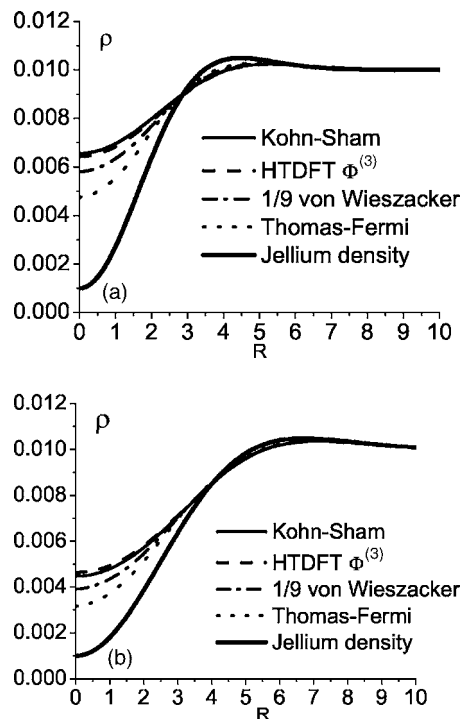


FIG. 2. The electron density profiles for a jellium model with background positive density (lower solid line) given by Eq. (29) with $\zeta=0.9$ and $r_0 = 2, 3$ [(a) and (b) graphs, respectively] for Thomas-Fermi, $\Phi^{(3)}$ HTDFT, and the Kohn-Sham orbital based approaches. All quantities are in a.u.

$$J_i = \underline{J}_i e^{-i(\omega t - \mathbf{q} \cdot \mathbf{R})} + \text{c.c.}, \quad (33b)$$

$$\Phi_{ij}^{(2)} = c_2 \rho_0 \delta_{ij} + (\Phi_{ij}^{(2)} e^{-i(\omega t - \mathbf{q} \cdot \mathbf{R})} + \text{c.c.}), \quad (33c)$$

$$\Phi_{ijk}^{(3)} = \Phi_{ijk}^{(3)} e^{-i(\omega t - \mathbf{q} \cdot \mathbf{R})} + \text{c.c.}, \quad (33d)$$

$$\nabla_i \tilde{V} = q_i \tilde{v}(q) (i \rho e^{-i(\omega t - \mathbf{q} \cdot \mathbf{R})} + \text{c.c.}), \quad (33e)$$

After linearizing Eqs. (7) one gets

$$\omega \underline{\rho} = q_\alpha \underline{J}_\alpha, \quad (34a)$$

$$\omega \underline{J}_i = q_\alpha \Phi_{i\alpha}^{(2)} + \rho_0 q_i \tilde{v}(q) \underline{\rho}, \quad (34b)$$

$$\omega \Phi_{ij}^{(2)} = q_\alpha \Phi_{ij\alpha}^{(3)}, \quad (34c)$$

$$\begin{aligned} \omega \Phi_{ijk}^{(3)} = & \overline{3(c_2 \delta_{ij} + f q_i q_j)(q_\alpha \Phi_{k\alpha}^{(2)})} + 3(c_2 + f q^2) \overline{q_i \Phi_{jk}^{(2)}} \\ & + (3(D + c_2 \rho_0 \tilde{v} + h c_2 q^2) \delta_{ij} \overline{q_k}) \\ & + (\frac{1}{4} \rho_0 \tilde{v} + \Lambda q^2 + 3 h c_2) q_i q_j \overline{q_k} \rho, \end{aligned} \quad (34d)$$

where the linearized variation of $\Phi^{(4)}$ is taken from Eq. (23), and α is again summed over. This is a system of linear homogeneous equations, and to find its solutions we have to diagonalize it.

All the variables in Eqs. (34) could be expressed in terms of $\underline{\rho}$ and $\Phi_{ij}^{(2)}$. Therefore, we can consider the equations on $\Phi^{(2)}$ and $\underline{\rho}$ only without losing any solutions. In matrix form these equations read

$$\frac{\omega^2}{q^2} \underline{\rho} = \text{Tr}(\underline{\Phi}^{(2)} \underline{Q}) + \rho_0 \tilde{v}(q) \underline{\rho}, \quad (35a)$$

$$\begin{aligned} \frac{\omega^2}{q^2} \underline{\Phi}^{(2)} &= (c_2 + fq^2)(\underline{\Phi}^{(2)} + 2\{\underline{\Phi}^{(2)}, \underline{Q}\}) \\ &+ (c_2 \mathbf{I} + fq^2 \underline{Q}) \text{Tr}(\underline{\Phi}^{(2)} \underline{Q}) \\ &+ (\mathbf{I}Z(q) + \underline{Q}Z'(q)) \underline{\rho}, \end{aligned} \quad (35b)$$

where

$$Z(q) = D + c_2 \rho_0 \tilde{v} + hc_2 q^2,$$

$$Z'(q) = 2Z + \frac{1}{4} \rho_0 \tilde{v}(q) q^2 + \Lambda q^4 + 3hc_2 q^2,$$

and Tr means a matrix trace, $I_{ij} \equiv \delta_{ij}$ is the 3×3 unity matrix, $Q_{ij} = q_i q_j / q^2$, curly brackets denote an anticommutator, and capital bold face letters refer here to matrices. Without loss of generality we can always assume that the wave vector \mathbf{q} is directed along the x axis ($\mathbf{q} = (q, 0, 0)^T$), so that

$$\underline{Q} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (36)$$

There are several solutions for these equations. The first three solutions are decoupled from the density fluctuations so that $\underline{\rho} = 0$ for all of them. They are

$$\underline{\Phi}^{(2)} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad (37a)$$

which corresponds to the following dispersion relation:

$$\omega^2 = 3/5 k_F^2 q^2, \quad (37b)$$

and

$$\underline{\Phi}^{(2)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad (38a)$$

with a dispersion of

$$\omega^2 = 1/5 k_F^2 q^2. \quad (38b)$$

The first two solutions [Eq. (37a)] correspond to transverse sound as the current is given as

$$\omega(q) \underline{J}_i = q_j \underline{\Phi}_{ij}^{(2)} = \begin{pmatrix} 0 \\ q \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ q \end{pmatrix}. \quad (39)$$

Note, however, that the velocity of this transverse sound mode is different from the one found for the same mode within the $N=2$ theory.³⁹ The third solution in Eq. (38) is a new sound mode. This mode involves neither density nor current fluctuations and corresponds to transverse quadrupole fluctuations of the Fermi sea.

The next three solutions are found by representing the tensor $\underline{\Phi}^{(2)}$ in terms of the remaining diagonal tensors (\mathbf{I} and \underline{Q}),

$$\underline{\Phi}^{(2)} = \alpha \underline{Q} + \beta (\mathbf{I} - \underline{Q}), \quad (40)$$

which leads, upon insertion into Eqs. (35), to the following equations for α , β , and $\underline{\rho}$:

$$\frac{\omega^2}{q^2} \alpha = 6(c_2 + fq^2) \alpha + (Z(q) + Z'(q)) \underline{\rho}. \quad (41a)$$

$$\frac{\omega^2}{q^2} \beta = c_2 \alpha + (c_2 + fq^2) \beta + Z(q) \underline{\rho}, \quad (41b)$$

$$\frac{\omega^2}{q^2} \underline{\rho} = \alpha + \rho_0 \tilde{v}(q) \underline{\rho}. \quad (41c)$$

This set of equations has complicated solutions, which, however, could be simplified in low-wavelength limit. In this limit, we can leave only the leading terms in q ; in the effective potential it is the divergent Fourier components of the Coulomb potential. In the long-wavelength limit the system of equations has the following form:

$$\begin{pmatrix} 6 & 0 & 3 \\ 1 & 1 & 1 \\ a(q) & 0 & a(q) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \underline{\rho}' \end{pmatrix} = \omega'^2 \begin{pmatrix} \alpha \\ \beta \\ \underline{\rho}' \end{pmatrix}, \quad (42)$$

where $a(q) = 4\pi\rho_0/(q^2 c_2)$, $\omega'^2 = \omega^2/(q^2 c_2)$, $\underline{\rho}' = 4\pi\rho_0 \underline{\rho}/q^2$, and $a(q) \gg 1$. Dropping the terms of order $a(q)^{-1}$ and smaller, the three eigenvalues and corresponding eigenvectors are

$$\omega^2 = \frac{1}{5} k_F^2 q^2, \quad (\alpha, \beta, \underline{\rho}') = (1, 2/3, -1); \quad (43a)$$

$$\omega^2 = \frac{3}{5} k_F^2 q^2, \quad (\alpha, \beta, \underline{\rho}') = (1, 0, -1); \quad (43b)$$

$$\omega^2 = \omega_p^2 + \frac{3}{5} k_F^2 q^2, \quad (\alpha, \beta, \underline{\rho}') = (0, 0, 1), \quad (43c)$$

where $\omega_p^2 = 4\pi\rho_0$ is the plasmon frequency. Note that the first two of the three modes [Eq. (43a) and (43b)] have the same eigenvalues as the transverse modes in Eqs. (37b) and (38b).

The total spectrum given by $N=3$ HTDFT for elementary excitations in the homogeneous electron gas is given in Fig. 3. The spectrum found differs from that of the $N=2$ approach by an additional sound mode with velocity $\sqrt{3/5} k_F$ and by shifting the previous sound modes from $\sqrt{3/5} k_F$ to $\sqrt{1/5} k_F$. This result confirms the conjecture made in Ref. 39, that with increasing N new sound modes should appear, and that they will gradually cover the entire continuous random phase approximation (RPA) density of states in the Fermi liquid.

VI. CONCLUSIONS

In conclusion, we have shown that HTDFT can also be used for time-independent studies. We have supplanted our previous conjecture where we assumed that the terms in the equation of motion hierarchy should be terminated with the next relevant cumulant [i.e., $\phi^{(N+1)}$] being zero; instead, we now derived $\phi^{(N+1)}$ from fitting the linear response to a HEG. The resulting set of equations [given at the $N=3$ level by Eqs. (22), (7), and (16)] is closed and can be propagated forward in time.

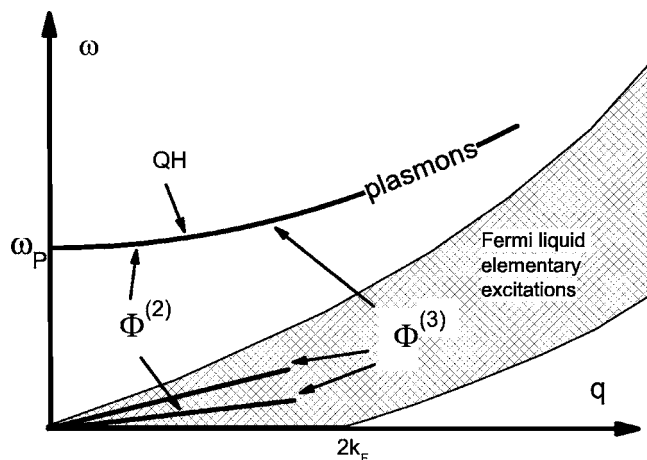


FIG. 3. The elementary excitation spectrum provided by quantum hydrodynamics, HTDFT $\Phi^{(2)}$, and HTDFT $\Phi^{(3)}$ theories. QH gives only a plasmon mode. HTDFT also gives transverse sound modes which mimic the RPA elementary excitations in Fermi liquid. $\Phi^{(3)}$ HTDFT gives additional sound modes with respect to $\Phi^{(2)}$ HTDFT confirming the conjecture made in Ref. 39 that when increasing the order of HTDFT new sound modes should appear, and they will gradually cover the entire continuous RPA density of states of Fermi liquid.

The linear response in the static limit is fitted to the Lindhard function homogeneous electron gas (HEG) for both short, intermediate, and long wavelengths (for comparison, the 1/9 in the von Weizsacker approach is obtained to fit long wavelengths, while a fit to long wavelengths would have required replacing the 1/9 by 1 in the von Weizsacker theory). We have then applied HTDFT away from equilibrium, for a case of a jellium density with a deep hole in the middle, and have shown excellent agreement with the Kohn-Sham results, in a case where more approximate theories such as Thomas-Fermi and von Weizsacker fail; this is directly due to the fact that their structure factor do not follow the Lindhard function except at low wavelengths.

The last part of the paper dealt with time-dependent linear response studies at the present level $N=3$. The analytical studies have confirmed our previous assertion that as the level of the theory increases more and more transverse excitations are found. A new excitation at the $N=3$ level couples neither to the current nor to the density. All excitations, including the new ones, lie within the RPA density of states of elementary excitations in a Fermi liquid.

Future works will study the applicability of the approach to covalent chemical systems, where the directionality of the tensors should enable a correct description even at a low N , possibly as low as $N=3$. Further, dynamic susceptibilities will be studied so that further terms, depending on J , $\Phi^{(3)}$, etc., will be included in the terminating cumulant [ϕ^4 here, $\phi^{(N+1)}$ in general] so that the theory will be valid over a wide range of frequencies and wave vectors. Of course, it will be very interesting and challenging for the theory to get the correct material-specific band gaps, since in many covalent systems the band gap is extremely material dependent. Therefore, the earliest efforts in the theory will be towards quasifree metallic systems, such as metallic dots and their interaction. The basic formalism developed here and in forthcoming work will be useful in developing applications to

dynamical problems which straddle the transition between molecular system and nanostructures, at least for metallic systems.

Another direction is the application to magnetic phenomena. We have separately shown that the HTDFT approach is naturally appropriate to describe magnetic vortices and the transition between different ferromagnetic phases. This will be presented in a separate publication.

We note that other applications to fermionic systems can also be envisioned. For example, by replacing the zeroth order HEG density matrix with a temperature-dependent density matrix and fitting the coefficients of the derivative terms in the cumulant to a temperature dependent Lindhard expression, we will get a temperature-dependent HTDFT theory which can be applied to plasmas and to studies of narrow conduction bands. Similarly, applications to nuclear systems can also be envisioned.

Other future improvements will include better methods to solve the time-dependent HTDFT equations. One approach will be to include external electric fields that will have dipole and quadruple (or higher) components that will be time dependent. The electric fields will be chosen, at each time instant, to remove energy from the system [i.e., to reduce the trace of $\Phi^{(2)}$ plus the total potential].

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