Transport Properties and a Current-Functional Theory in the Linear-Response Regime

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The possibility of formulating a time-dependent current-functional theory which describes the linear responses of systems of inhomogeneous, interacting electron gas to an arbitrary form of time-dependent electromagnetic field is studied. A Kohn-Sham-type theory for the dynamical electronic conductivity tensor is derived and a local-density type of approximation for the resulting exchange-correlation electric field is constructed.

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Since the original papers of Hohenberg and Kohn¹ and Kohn and Sham,² density-functional theory has become one of the most widely used tools in the treatment of electron-electron interaction in condensed matter physics.^{3,4} Recently, the formulation has been generalized to systems under large, static magnetic field in the form of a current-density-functional theory,⁵ and also to the time-dependent linear-response regime under a very general thermodynamic condition.⁶ The content of this Letter is divided into two parts. In the first part, we show that the time-dependent density-functional theory of Ng and Singwi,⁶ which describes linear responses of electronic systems to external time-dependent *longitudinal* electric fields, can be generalized to describe (linear) responses of electronic systems to an *arbitrary* form of time-dependent electromagnetic field, in the form of a current-functional theory. The consequences of this result are discussed. In the second part, we formulate a Kohn-Sham-type theory for the dynamical electronic conductivity tensor and construct a "local-density" type of approximation for the resulting exchange-correlation electric field. Some general comments are also given.

A time-dependent electromagnetic field can be specified by its electric field component, $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, \omega)e^{i\omega t}$ [notice that $i\omega\mathbf{B}(\mathbf{r}, \omega) = -c\nabla \times \mathbf{E}(\mathbf{r}, \omega)$ from Maxwell's equation, thus the magnetic field is also specified], up to an unimportant gauge factor. We shall prove the following theorem: For a system with fixed number of electrons, there is a one-to-one mapping between the induced current distribution $\mathbf{j}(\mathbf{r}, \omega)$ and the applied electric field $\mathbf{E}(\mathbf{r}, \omega)$ for nonzero ω in the linear-response regime if the system under consideration obeys the second law of thermodynamics, and is at *stable* thermal equilibrium. (The work done by the external potential $\Delta W \geq 0$ to second order of the external potential.⁷)

Notice that in the linear-response regime, we can generally write

$$j_i(\mathbf{r}, \omega) = \sum_j \int \sigma'_{ij}(\mathbf{r}, \mathbf{r}', \omega) E_j(\mathbf{r}', \omega) d\mathbf{r}', \quad (1)$$

where σ'_{ij} is the conductivity tensor for the external elec-

tric field and $i, j = x, y, z$ are direction indices. To prove that there is a one-to-one mapping between $\mathbf{j}$ and $\mathbf{E}$, it is sufficient to prove that there exists no external field $\mathbf{E}'(\mathbf{r}, \omega)$ such that⁶

$$0 \equiv \sum_j \int \sigma'_{ij}(\mathbf{r}, \mathbf{r}', \omega) E'_j(\mathbf{r}', \omega) d\mathbf{r}'. \quad (2)$$

To prove this theorem, we follow Ref. 6 and consider the total work done by the external potential,⁸

$$\Delta W = \int dt \int d\mathbf{r} \left\{ \mathbf{j}(\mathbf{r}, t) \cdot \frac{-1}{c} \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} + n(\mathbf{r}, t) \frac{\partial \phi(\mathbf{r}, t)}{\partial t} \right\}, \quad (3)$$

where $\mathbf{A}$ and ϕ are the external vector and scalar electromagnetic potentials and $\mathbf{j}$ and n are the induced current and density fluctuations. Integrating by parts and using the continuity equation on the second term, we obtain after Fourier transforming in time

$$\Delta W = \int \frac{d\omega}{2\pi} \int d\mathbf{r} \mathbf{j}(\mathbf{r}, \omega) \cdot \mathbf{E}(\mathbf{r}, \omega), \quad (4)$$

where $\mathbf{j}$ is given by Eq. (1) to second order in $\mathbf{E}$.

From thermodynamics, $\Delta W \geq 0$. The equality sign holds only for reversible processes, which are quasistatic (i.e., $\omega = 0$). For $\omega \neq 0$ processes, $\Delta W > 0$ which implies from Eqs. (1) and (4) that $\mathbf{j}(\mathbf{r}, \omega)$ cannot be identically zero in Eq. (1), as long as the external field perturbs the system. This completes the proof of the theorem.

Naively, one expects as a consequence of this theorem that a Kohn-Sham-type theory can be constructed for the (linear) current responses of the system to external time-dependent electromagnetic fields. However, notice that a fundamental assumption we have made in proving the present theorem is that the system under consideration obeys the second law of thermodynamics, whereas the Hohenberg-Kohn-Sham theory involves the Schrödinger equation only. The second law of thermodynamics requires the existence of time-irreversible processes whereas the Schrödinger equation is time reversible. Thus, the present theorem does not necessarily im-

ply the existence of one-to-one mapping between induced current distribution and applied external electromagnetic field for a system which obeys the Schrödinger equation only (see Refs. 7 and 9 for an example). In particular, it does not guarantee the validity of a straightforward Kohn-Sham-type of approach (it is not certain that the Kohn-Sham approach obeys the second law of thermodynamics).

In practice, this difficulty can be overcome by introducing a small imaginary frequency to the response function evaluated in the Kohn-Sham theory; i.e., $\omega \rightarrow \omega + i\delta$ in $\sigma'_{ij}(\mathbf{r}, \mathbf{r}', \omega)$, where $\delta > 0$, which phenomenologically couples the system to an external heat bath, and our theorem is valid as long as $\delta > 0$. (In fact, this result can be proved directly from the Kubo formula for the current-current response function,¹⁰ without involving directly the second law of thermodynamics.) Thus a Kohn-Sham-type theory can be constructed for *finite* δ , of which the current-current correlation function can be computed, and the physical result can be obtained by analytic continuation (extrapolation) to the $\delta \rightarrow 0$ limit. Notice that this procedure is actually the *standard* one of which a retarded response function is being defined. Thus our analytic continuation procedure gives the correct result as long as the standard procedure of defining a retarded response function remains valid.

With this procedure in mind, we now turn to the formulation of the one-particle Kohn-Sham equation. First, we make the necessary assumption that the density distribution function $n_0(\mathbf{r}) + n(\mathbf{r}, \omega)$ and current distribution function $\mathbf{j}_0(\mathbf{r}) + \mathbf{j}(\mathbf{r}, \omega)$, where $n_0(\mathbf{r})$ and $\mathbf{j}_0(\mathbf{r})$ are the density and current distribution functions of the system in the absence of the time-dependent perturbing potential [here we shall only consider nonmagnetic systems such that $\mathbf{j}_0(\mathbf{r}) \equiv 0$],⁵ are *v* representable;¹¹ i.e., they can be reproduced by a system of noninteracting electrons moving in appropriate single-particle potentials $\phi_{\text{eff}}(\mathbf{r})$ and electric field $\mathbf{E}_{\text{eff}}(\mathbf{r}, \omega)$. Notice that the separation of the current and density variables into a dominant $\omega = 0$ part plus small time-dependent fluctuations is a special feature of the linear-response regime only, and is not possible in a general time-dependent theory. Notice also that in the limit $\mathbf{E}(\mathbf{r}, \omega) = 0$, $\phi_{\text{eff}}(\mathbf{r})$ must reproduce the correct ground-state density distribution $n_0(\mathbf{r})$ and is thus the ordinary Kohn-Sham potential. For $\omega \neq 0$, $n(\mathbf{r}, \omega)$ is completely determined by $\mathbf{j}(\mathbf{r}, \omega)$ by the continuity equation. Therefore it is sufficient to consider only the induced current $\mathbf{j}(\mathbf{r}, \omega)$. From the linear-response requirement, we must have

$$j_i(\mathbf{r}, \omega) = \sum_j \int d\mathbf{r}' \sigma_{ij}^{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) E_{\text{eff},j}(\mathbf{r}', \omega), \quad (5)$$

where σ^{KS} is the conductivity tensor for a system of noninteracting electrons moving in the Kohn-Sham potential $\phi_{\text{eff}}(\mathbf{r})$. The effective electric field $\mathbf{E}_{\text{eff}}$ can be

written as

$$\mathbf{E}_{\text{eff}}(\mathbf{r}, \omega) = \mathbf{E}(\mathbf{r}, \omega) + \nabla_{\mathbf{r}} \int d\mathbf{r}' \frac{n(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} + \mathbf{E}_{\text{xc}}(\mathbf{r}, \omega), \quad (6)$$

where $\mathbf{E}(\mathbf{r}, \omega)$ is the external electric field and the second term is the polarization field. The first and second terms on the right-hand side of Eq. (6) together form the *total* electric field $\mathbf{E}_t(\mathbf{r}, \omega)$ felt by electrons in the system. The exchange-correlation electric field $\mathbf{E}_{\text{xc}}(\mathbf{r}, \omega)$ is defined by Eqs. (5) and (6) and incorporates all other interaction effects. The exact form of $\mathbf{E}_{\text{xc}}$ is unknown except that from the existence theorem, we know that it can be expressed as linear functional of $\mathbf{j}(\mathbf{r}, \omega)$,

$$E_{\text{xc},i}(\mathbf{r}, \omega) = \sum_k \int d\mathbf{r}' \xi_{ik}(\mathbf{r}, \mathbf{r}', \omega) j_k(\mathbf{r}', \omega), \quad (7)$$

where ξ_{ik} is a functional of the unperturbed ground-state particle density $n_0(\mathbf{r})$. Thus Eqs. (5)–(7) together with the continuity equation define a scheme where the induced current fluctuation $\mathbf{j}(\mathbf{r}, \omega)$ and density fluctuation $n(\mathbf{r}, \omega)$ can be determined self-consistently. Notice that in general, we do not know how to construct the tensor ξ_{ik} except that it can be formally defined through Eqs. (1) and (5)–(7) as

$$\xi(\mathbf{r}, \mathbf{r}', \omega) = \sigma^{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega)^{-1} - \sigma(\mathbf{r}, \mathbf{r}', \omega)^{-1}, \quad (8)$$

where $\sigma(\mathbf{r}, \mathbf{r}', \omega)$ is the (exact) usual conductivity tensor for the interacting system which relates the induced current distribution to the *total* electric fields; i.e., $\mathbf{j} = \sigma \cdot \mathbf{E}_t$ and σ^{KS} is the corresponding quantity for the system of noninteracting electrons moving in the Kohn-Sham potential, provided that these inverse functions exist.

We now proceed to the discussion of the local-density type of approximation for ξ . For this purpose we first consider ξ for the homogeneous [$n_0(\mathbf{r}) = \text{const}$] situation.

For homogeneous systems, the conductivity tensor σ has the general form

$$\sigma_{ij}^h(\mathbf{q}, \omega) = \sigma_T(q, \omega) \left[\delta_{ij} - \frac{q_i q_j}{q^2} \right] + \sigma_L(q, \omega) \frac{q_i q_j}{q^2}, \quad (9)$$

where σ_T and σ_L are scalar functions describing the response of the system to transverse and longitudinal electric fields, respectively. Thus from Eq. (8), we obtain for homogeneous systems

$$\begin{aligned} \xi_{ij}^h(\mathbf{q}, \omega) &= \left[\frac{1}{\sigma_T^0(q, \omega)} - \frac{1}{\sigma_T(q, \omega)} \right] \left[\delta_{ij} - \frac{q_i q_j}{q^2} \right] \\ &\quad + \left[\frac{1}{\sigma_L^0(q, \omega)} - \frac{1}{\sigma_L(q, \omega)} \right] \frac{q_i q_j}{q^2} \\ &= \xi_T(q, \omega) \left[\delta_{ij} - \frac{q_i q_j}{q^2} \right] + \xi_L(q, \omega) \frac{q_i q_j}{q^2}, \end{aligned} \quad (10)$$

where $\sigma_{L(T)}^0$ is the conductivity tensor for the corresponding noninteracting electron gas. The longitudinal con-

ductivity $\sigma_L(q, \omega)$ is related to the scalar dielectric function $\epsilon(q, \omega)$ through

$$\epsilon(q, \omega) = 1 + \frac{4\pi i \sigma_L(q, \omega)}{\omega} = 1 - \frac{v_q \chi_0(q, \omega)}{1 + v_q G(q, \omega) \chi_0(q, \omega)}, \quad (11)$$

where $\chi_0(q, \omega)$ is the Lindhard function and $G(q, \omega)$ is the so-called local-field factor.^{11,12} From Eqs. (10) and (11), we obtain

$$\xi_L(q, \omega) = \frac{q^2}{i\omega} v_q G(q, \omega). \quad (12)$$

The $q \rightarrow 0$, $\omega \gg q$ limit of $\xi_{L(T)}(q, \omega)$ is of particular interest since it will enter in the local-density type of approximation. In the longitudinal case, it is known that $v_q G(q, \omega) \rightarrow \alpha_L(\omega)$ as $q \rightarrow 0$,¹¹⁻¹³ where $\alpha_L(\omega)$ is finite as $\omega \rightarrow 0$, so that $\xi_L(q, \omega) \rightarrow q^2 \alpha_L(0)/i\omega$ in this limit. The transverse conductivity is also known to have the form^{14,15} (see also Ref. 5)

$$\sigma_T(q, \omega) \sim \frac{ine^2}{m\omega} \left[1 + q^2 \frac{\alpha_T(\omega)}{\omega^2} \right], \quad (13)$$

in this limit, where $\alpha_T(0)$ is finite. With these results, it is easy to see from Eq. (10) that both $\xi_L(q, \omega)$ and $\xi_T(q, \omega)$ vanish as q^2 as $q \rightarrow 0$ (ω finite), so that the exchange-correlation field $\mathbf{E}_{xc}$ is identically zero for a constant current flow in a homogeneous system. Notice that this is just a direct consequence of the translational invariance for a homogeneous system.

An immediate consequence of this result is that at finite ω a local-density type of approximation, where $\mathbf{E}_{xc}(\mathbf{r}, \omega)$ depends locally only on the current $\mathbf{j}(\mathbf{r}, \omega)$ and density $n_0(\mathbf{r})$, does not exist (see also Ref 5). However, a local-density approximation for the curl and divergence of the current exists, which can be constructed in the following way.

First of all, we construct the current functional

$$I_{xc}[\mathbf{j}, \omega] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \mathbf{j}(\mathbf{r}, \omega) \cdot \xi(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{j}(\mathbf{r}', \omega), \quad (14)$$

such that

$$\mathbf{E}_{xc}(\mathbf{r}, \omega) = \delta I_{xc} / \delta \mathbf{j}(\mathbf{r}, \omega). \quad (15)$$

I_{xc} can be considered as the exchange-correlation part of the action integral^{16,17} for our system in the time-dependent linear-response regime. For a homogeneous electron gas, I_{xc} can be written as [using Eq. (10)]

$$I_{xc}^h = \frac{1}{2} \int d\mathbf{q} \{ \xi_L(q, \omega) |\mathbf{j}_L(q, \omega)|^2 + \xi_T(q, \omega) |\mathbf{j}_T(q, \omega)|^2 \} = \frac{1}{2} \int d\mathbf{q} \left\{ \frac{\xi_L(q, \omega)}{q^2} [\mathbf{q} \cdot \mathbf{j}(q, \omega)]^2 + \frac{\xi_T(q, \omega)}{q^2} [\mathbf{q} \times \mathbf{j}(q, \omega)]^2 \right\}, \quad (16)$$

where $\mathbf{j}_L$ and $\mathbf{j}_T$ are the longitudinal and transverse parts of the current, respectively. Notice that ξ_L/q^2 and ξ_T/q^2 are nonsingular functions in the $q \rightarrow 0$ ($\omega \neq 0$) limit.

Equation (16) suggests that one can make the following local-density type of approximation for I_{xc} in the general, inhomogeneous situation (see also Ref. 11). We assume that (i) the local density $n_0(\mathbf{r})$ is a slowly varying function in space so that one can replace the function ξ by the corresponding function ξ^h for a homogeneous electron gas *locally*, and (ii) the induced current distribution $\mathbf{j}(\mathbf{r}, \omega)$ also varies slowly in space so that only the $q \rightarrow 0$ limit of ξ^h needs to be considered.

With these assumptions, we arrive at the following approximation:

$$I_{xc} \sim \frac{1}{2} \int d\mathbf{r} \{ \xi_L^*(\omega; n_0(\mathbf{r})) |\nabla \cdot \mathbf{j}(\mathbf{r}, \omega)|^2 + \xi_T^*(\omega; n_0(\mathbf{r})) |\nabla \times \mathbf{j}(\mathbf{r}, \omega)|^2 \}, \quad (17)$$

where

$$\xi_{L(T)}^*(\omega; n) = \lim_{q \rightarrow 0} \frac{\xi_{L(T)}(q, \omega)}{q^2},$$

for a homogeneous electron gas with density n . The exchange-correlation electric field is given from straightforward functional derivatives of I_{xc} [Eq. (15)] by

$$\mathbf{E}_{xc}(\mathbf{r}, \omega) = -\nabla \{ \xi_L^*(\omega; n_0(\mathbf{r})) \nabla \cdot \mathbf{j}(\mathbf{r}, \omega) \} - \nabla \times \{ \xi_T^*(\omega; n_0(\mathbf{r})) \nabla \times \mathbf{j}(\mathbf{r}, \omega) \}. \quad (18)$$

Equations (5), (6), and (18) now form a self-consistent, approximate scheme in which the dynamical conductivity of electronic systems can be calculated. Notice that in the case $\nabla \times \mathbf{j} \equiv 0$ (i.e., only longitudinal current present), we have [using Eq. (12) and the continuity equation]

$$\mathbf{E}_{xc}(\mathbf{r}, \omega) = -\nabla \{ \lim_{q \rightarrow 0} [v_q G(q, \omega; n_0(\mathbf{r}))] n(\mathbf{r}, \omega) \}, \quad (19)$$

in agreement with the approximate expression for the exchange-correlation potential derived by Gross and Kohn¹¹ for the case of a time-dependent scalar perturbing potential. An approximate expression for ξ_L^* [or $v_q G(q, \omega)$] has been ob-

tained by these authors, which is convenient to use. The corresponding approximation for ξ_T^* is still missing and is at present under study.

We would now like to make a few comments about our formulation, and about the local-density approximation.

It is important to keep in mind that our formulation is valid only for frequencies $\omega \neq 0$, where $\Delta W > 0$. In fact, Vignale and Rasolt⁵ have shown that for electrons in static, external potentials, the ground state is a functional of the static density $n_0(\mathbf{r})$ and paramagnetic current $\mathbf{j}_p(\mathbf{r})$, instead of just the total current $\mathbf{j}(\mathbf{r})$. This difference arises because in the static case, the $\mathbf{E}$ and $\mathbf{B}$ fields are independent, and so are the particle density $n_0(\mathbf{r})$ and current density $\mathbf{j}(\mathbf{r})$. However, in the dynamic case, the $\mathbf{B}$ field is completely determined by the $\mathbf{E}$ field via the Maxwell equation, and the density fluctuation $n(\mathbf{r}, \omega)$ is completely determined by $\mathbf{j}(\mathbf{r}, \omega)$ via the continuity equation. Thus the nonequilibrium fluctuation is completely determined by the $\mathbf{E}$ field, or current $\mathbf{j}$, in contrast to the ground-state situation.

We would also like to make a few comments on our local-density approximation. An implicit assumption we have made in defining $\xi_{L(T)}^*(\omega; n)$ [Eq. (17)] is that $q \ll \omega$ in the functions $\xi_{L(T)}(q, \omega)$. However, the existence of nonzero $\nabla \cdot \mathbf{j}(\mathbf{r})$ or $\nabla \times \mathbf{j}(\mathbf{r}, \omega)$ terms implies that there exists a characteristic nonzero wave vector $\mathbf{q}_0(\mathbf{r})$ which measures the "size" of the divergence or curl of the current at any local space point $\mathbf{r}$ and our approximation for $\xi_{L(T)}$ is valid only when $\omega \gg q_0(\mathbf{r})$. This is not expected to be always satisfied for a realistic system under low-frequency external perturbation and therefore our approximation is expected to be satisfactory only for the calculation of high-frequency conductivity. In particular, our local-density approximation for $\xi_{L(T)}$ is not expected to be satisfactory for the calculation of dc conductivities. The approximate method for calculating dc conductivities has been constructed in the case of electrons moving in *weakly* disordered potentials and will be discussed elsewhere.

In summary, we have shown that under a very general thermodynamic condition (or in practice, letting $\omega \rightarrow \omega + i\delta$, with $\delta > 0$ in the response function), a current-functional theory can be constructed to compute transport properties of electronic systems in the linear-response regime. A local-density type of approximation

for the resulting exchange-correlation electric field is constructed for this purpose. We have also pointed out that there are strong limitations to our local-density type of approximation, which demands care in realistic applications.

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