PHYSICAL REVIEW B **87**, 165125 (2013)

Time-dependent effective potential and exchange kernel of homogeneous electron gas

V. U. Nazarov

Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan

(Received 30 January 2013; revised manuscript received 4 March 2013; published 19 April 2013)

By minimizing the difference between the left- and the right-hand sides of the many-body time-dependent Schrödinger equation with the Slater-determinant wave function, we derive a nonadiabatic and self-interaction-free time-dependent single-particle effective potential, which is the generalization to the time-dependent case of the so-called localized Hartree-Fock potential. The new potential can be efficiently used within the framework of the time-dependent density-functional theory as we demonstrate by the evaluation of the wave vector and frequency-dependent exchange kernel $f_x^h(q,\omega)$ of the homogeneous electron gas. This is found to be nonsingular and causal, and it satisfies the positiveness of the dissipation, in contrast to the earlier known kernel from the first-order perturbation theory, which makes our f_x^h promising for applications.

DOI: 10.1103/PhysRevB.87.165125 PACS number(s): 31.15.ee

I. INTRODUCTION

Time-dependent (TD) density-functional theory (DFT)[1] is in the perpetual search for effective single-particle potentials which accurately (ideally, exactly) map the propagation of an interacting many-body system onto that of a noninteracting one. While the exchange-correlation (xc) functionals based on the local-density approximation (LDA)[2,3] and its semilocal refinement of the generalized gradient approximation (GGA)[4–6] have proven very successful in the ground-state DFT, in TDDFT the usefulness of (semi)local approaches is limited due to the fundamental spatial nonlocality of the exact TD xc functional.[7]

Beyond LDA and GGA, the concept of the optimized effective potential (OEP)[8,9] plays one of the key roles in the systematic nonheuristic construction of DFT. In the ground-state case, OEP is defined as a single-particle potential which minimizes the many-body Hamiltonian expectation value taken on the Slater-determinant wave function. From the DFT perspective, OEP is the first term in the adiabatic connection series in the powers of the interaction constant [exact exchange (EXX)].[10] The generalization of the OEP to the time-dependent case has been proposed[11,12] but is impractical for applications due to the formidable complexity of the integral equation involved.

In this paper we propose and implement an alternative approach to the development of the time-dependent single-particle effective potential for many-body problems. This is based on the variational principle of the minimization of the difference between the left- and right-hand sides of the time-dependent Schrödinger equation, which we had introduced almost three decades ago.[13] By this and with no further approximations or *ad hoc* assumptions, we derive a time-dependent effective potential with the following useful properties: (i) It is free of self-interaction; (ii) it is expressed in terms of an equation easily solvable for both a finite and an infinite periodic (or homogeneous) problems; and (iii) in the static case, our effective potential reduces to the previously known so-called localized Hartree-Fock (HF) potential.[14,15] As an immediate application of this approach, we derive the dynamic exchange kernel $f_x(q,\omega)$ of the homogeneous electron gas (HEG).

This paper is organized as follows: In Sec. II we introduce the variational principle of the minimization of the difference between the left- and right hand sides of TD Schrödinger equation and we work out the TD effective potential. In Sec. III we use this potential to evaluate the exchange kernel of the homogeneous electron gas. In Appendix A we give details of the derivation of the effective potential. In Appendix B we give an alternative derivation of the effective potential. In Appendix C we evaluate integrals involved in the expression of $f_x(q,\omega)$. In Appendix D we analytically derive the infinite-frequency limit $f_x(q,\infty)$. Atomic units are used throughout.

II. TIME-DEPENDENT VARIATIONAL PRINCIPLE AND SINGLE-PARTICLE EFFECTIVE POTENTIAL

A. Formalism

We are considering an N-electron system with the TD Hamiltonian

$$\hat{H}(t) = \sum_i \left[-\frac{1}{2}\Delta_i + v_{ext}(\mathbf{r}_i,t) \right] + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{1}$$

The many-body wave function $\Psi(t)$ propagates according to the Schrödinger equation

$$i\frac{\partial \Psi(t)}{\partial t} = \hat{H}(t)\Psi(t).$$

We ask the question: What is the potential $v_{eff}(\mathbf{r},t)$ such that the functional

$$\int \left| i\frac{\partial \Psi_s(t)}{\partial t} - \hat{H}(t)\Psi_s(t) \right|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N \tag{2}$$

is minimal at a given arbitrary time t, where $\Psi_s(t)$ is the Slater determinant built with the single-particle orbitals $\psi_\alpha(\mathbf{r},t)$, the latter satisfying the single-particle Schrödinger equation

$$i\frac{\partial \psi_\alpha(\mathbf{r},t)}{\partial t} = \left[-\frac{1}{2}\Delta + v_{eff}(\mathbf{r},t) \right] \psi_\alpha(\mathbf{r},t)? \tag{3}$$

Let us assume that the TD part of $v_{ext}(\mathbf{r},t)$ was absent at $t < 0$, and we have already solved the static problem of determining $v_{eff}(\mathbf{r})$ at $t < 0$ and the corresponding orbitals $\psi_\alpha(\mathbf{r},t)$ at

$t \leqslant 0$. At $t = 0$, the time dependence of the potential is switched on. Knowing the orbitals $\psi_\alpha(\mathbf{r},0)$, we find $v_{eff}(\mathbf{r},0)$ which, by determining $\partial\psi_\alpha(\mathbf{r},t)/\partial t|_{t=0}$ using Eq. (3), minimizes the functional (2) at $t = 0$. We then find $\psi_\alpha(\mathbf{r},\Delta t) \approx \psi_\alpha(\mathbf{r},0) + \partial\psi_\alpha(\mathbf{r},t)/\partial t|_{t=0}\Delta t$, where Δt is a small time increase. The procedure is repeated up to an arbitrary time t.

In the $\Delta t \to 0$ limit, this scheme reads as follows: With fixed (but yet unknown) orbitals $\psi_\alpha(\mathbf{r},t)$, we are looking for the potential $v_{eff}(\mathbf{r},t)$, which, by determining $\partial\psi_\alpha(\mathbf{r},t)/\partial t$ using Eq. (3), minimizes the functional (2). This gives $v_{eff}(\mathbf{r},t)$ as a functional of the orbitals, and, finally, the orbitals themselves are found by the self-consistent solution of Eqs. (3).

We emphasize that in the above procedure $\Psi_s(t)$ is unaffected by the variation of $v_{eff}(\mathbf{r},t')$ at $t \leqslant t'$. Indeed, due to causality, $\Psi_s(t)$ does not depend on $v_{eff}(\mathbf{r},t')$ at $t < t'$. Moreover, because of the very structure of the Schrödinger equation for Ψ_s

$$i\frac{\partial\Psi_s(t)}{\partial t} = \sum_i \left[-\frac{1}{2}\Delta_i + v_{eff}(\mathbf{r}_i,t)\right]\Psi_s(t) \tag{4}$$

as the first-order differential equation with respect to time, $\Psi_s(t)$ does not depend on $v_{eff}(\mathbf{r},t)$ at the same moment t: Even if $v_{eff}(\mathbf{r},t)$ experiences a jump at the moment t, only $\Psi_s(t'),t' > t$ would be affected, not $\Psi_s(t)$. This property can be referred to as the "inertia" of the wave function. In contrast, $\partial\Psi_s(t)/\partial t$ is affected instantaneously by the change in $v_{eff}(\mathbf{r}_i,t)$ according to Eq. (4).

Exploiting this property, at every particular moment t, we adjust $v_{eff}(\mathbf{r},t)$ and, therefore, by Eq. (4), $\partial\Psi_s(t)/\partial t$ to make the functional (2) minimal. According to this procedure, globally in time $\Psi_s(t)$ remains a functional of $v_{eff}(\mathbf{r},t')$ at $t' < t$ as causality dictates. We note that a procedure of the minimization of the same functional (2) with respect to $\partial\psi_\alpha/\partial t$ as independently varied functions retrieves the TD HF equations.[13]

By using Eq. (4) the functional (2) can be rewritten as

$$\int \left[\sum_i \tilde{v}(\mathbf{r}_i,t) - \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]^2 |\Psi_s(t)|^2 d\mathbf{r}_1 \ldots d\mathbf{r}_N, \tag{5}$$

where $\tilde{v} = v_{eff} - v_{ext}$. By equating to zero the first variation of Eq. (5) with respect to $\delta\tilde{v} = \delta v_{eff}$, where the expression in the brackets but *not* $\Psi_s(t)$ is varied, we find

$$\int \left[\sum_i \tilde{v}(\mathbf{r}_i,t) - \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] \times |\Psi_s(t)|^2 \sum_i \delta\tilde{v}(\mathbf{r}_i,t) d\mathbf{r}_1 \ldots d\mathbf{r}_N = 0,$$

which can be rewritten using the permutational symmetry of the wave function as

$$\int \left[\sum_i \tilde{v}(\mathbf{r}_i,t) - \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] |\Psi_s(t)|^2 \delta\tilde{v}(\mathbf{r}_1,t) d\mathbf{r}_1 \ldots d\mathbf{r}_N = 0,$$

and, due to the arbitrariness of $\delta\tilde{v}$,

$$\int \left[\sum_i \tilde{v}(\mathbf{r}_i,t) - \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] |\Psi_s(t)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N = 0. \tag{6}$$

Straightforward but rather lengthy transformations carried out in Appendix A lead from Eq. (6) to the following equation for the exchange potential $v_x = \tilde{v} - v_H$, where v_H is the Hartree potential:

$$n(\mathbf{r},t)v_x(\mathbf{r},t) = \int \left[v_x(\mathbf{r}_1,t) - \frac{1}{|\mathbf{r} - \mathbf{r}_1|}\right] |\rho(\mathbf{r},\mathbf{r}_1,t)|^2 d\mathbf{r}_1 + \int \frac{\rho(\mathbf{r},\mathbf{r}_1,t)\rho(\mathbf{r}_1,\mathbf{r}_2,t)\rho(\mathbf{r}_2,\mathbf{r},t)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \tag{7}$$

where

$$n(\mathbf{r},t) = \sum_{\alpha=1}^{N} |\psi_\alpha(\mathbf{r},t)|^2, \tag{8}$$

$$\rho(\mathbf{r},\mathbf{r}_1,t) = \sum_{\alpha=1}^{N} \psi_\alpha(\mathbf{r},t)\psi_\alpha^*(\mathbf{r}_1,t) \tag{9}$$

are the particle density and the single-particle density matrix, respectively.[16] Equation (7) is the main result of this paper.

B. Properties of the effective potential

First, we note that the only difference of Eq. (7) from the earlier known *static* localized HF potential (see Refs. 14 and 15 for spin-neutral and spin-polarized cases, respectively) is the time dependence of all the quantities involved. However, it must be emphasized that without the derivation from the time-dependent variational principle the generalization of the static localized HF potential to the time-dependent case by just inserting the time variable into the static equation would have been ungrounded. Trivially, Eq. (7) reduces to the equation for the localized HF potential in the time-independent case. Therefore, as a by-product, our method provides an alternative derivation of the localized HF potential of the stationary problem, treating it as a specific case of the TD problem and requiring the minimal violation of TD Schrödinger equation, rather than doing it from the approximation of the equality of HF and EXX orbitals.[14] Comparison of the two methods of the derivation of Eq. (7) is carried out in Appendix B.

The solution of Eq. (7) in the case of a few-body system does not present a difficulty, as has already been pointed out in Ref. 14 in conjunction with the time-independent case: Due to Eq. (9), the kernel $|\rho(\mathbf{r},\mathbf{r}_1,t)|^2$ of the integral equation (7) is a separable function with respect to $\mathbf{r}$ and $\mathbf{r}_1$ variables. It also does not present a difficulty in the case of infinite periodic systems, when the equation reduces to the matrix one. The fact that $v_x(\mathbf{r},t)$ is free of self-interaction can be demonstrated by substituting $\rho(\mathbf{r},\mathbf{r}_1,t) = \psi(\mathbf{r},t)\psi^*(\mathbf{r}_1,t)$ into Eq. (7) for a one-particle system, which gives $v_x(\mathbf{r},t) = -v_H(\mathbf{r},t) + A(t)$, where $A(t)$ is a time-dependent constant, and, moreover, $A(t) = 0$ by Eq. (A10) of the Appendix A.

Equation (7) admits an explicit solution in the simplest nontrivial case of a two-body system propagating in a singlet state. By substituting

$$\rho(\mathbf{r}\sigma,\mathbf{r}'\sigma',t) = \psi(\mathbf{r},t)\psi^*(\mathbf{r}',t)[\delta_{\uparrow\sigma}\delta_{\uparrow\sigma'} + \delta_{\downarrow\sigma}\delta_{\downarrow\sigma'}],$$

where the coordinate and spin variables are written explicitly and $\delta_{\sigma\sigma'}$ is the Kronecker δ, into Eq. (7), we obtain

$$v_x(\mathbf{r},t) = -\frac{1}{2}\int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \frac{1}{8}\int \frac{n(\mathbf{r}',t)n(\mathbf{r}'',t)}{|\mathbf{r}'-\mathbf{r}''|}d\mathbf{r}'d\mathbf{r}'', \tag{10}$$

where the second term is a time-dependent constant. Equation (10) shows that in a singlet state of two particles our exchange potential is effectively minus one half of the Hartree potential, which coincides exactly with both HF and EXX results.[17]

We conclude this section by noting that the variational principle we employ to derive the TD exchange potential of Eq. (7) is the *minimum* principle, which is in contrast to the *stationary* variational principle used to derive the conventional OEP.[11]

III. DYNAMIC EXCHANGE KERNEL OF THE HOMOGENEOUS ELECTRON GAS

We now apply our effective potential to obtain the wave vector and frequency-dependent exchange kernel $f_x(q,\omega)$ of HEG, which, being a fundamental quantity by itself,[18] is also an important input in the theory of optical response of a weakly inhomogeneous interacting electron gas.[19] In the case of HEG and a weak externally applied potential $\delta v_{ext}(\mathbf{r},t) = \delta v_{ext}(\mathbf{q},\omega)e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$, we linearize Eq. (7) with respect to the latter. The zeroth-order orbitals are plane waves,[20] and to the zeroth and first orders we have for the density matrix

$$\rho_0(\mathbf{r},\mathbf{r}_1) = \frac{2}{V}\sum_{\mathbf{k}}\int f(\epsilon_{\mathbf{k}})e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_1)},$$

$$\delta\rho(\mathbf{r},\mathbf{r}_1,\omega) = \delta v_s(\mathbf{q},\omega)\, e^{i\mathbf{q}\cdot\mathbf{r}}\frac{2}{V} \times \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}}) - f(\epsilon_{\mathbf{k+q}})}{\omega - \epsilon_{\mathbf{k+q}} + \epsilon_{\mathbf{k}} + i\eta}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_1)}, \tag{11}$$

where $\epsilon_{\mathbf{k}} = k^2/2$ are free-particle eigenenergies, $f(\epsilon_{\mathbf{k}})$ are their occupation numbers, $\delta v_s(\mathbf{q},\omega)$ is the perturbation of the Kohn-Sham (KS) potential, V is the normalization volume, and η is an infinitesimal positive. After the linearization, Eq. (7) yields

$$\frac{\delta v_x(q,\omega)}{\delta v_s(q,\omega)} = \frac{4\pi}{(2\pi)^3 A(q)}\int \left[\frac{1}{\omega - \epsilon_{\mathbf{k+q}} + \epsilon_{\mathbf{k}} + i\eta} - \frac{1}{\omega + \epsilon_{\mathbf{k+q}} - \epsilon_{\mathbf{k}} + i\eta}\right]\{f(\epsilon_{\mathbf{k}})B(\mathbf{q},\mathbf{k}) - f(\epsilon_{\mathbf{k+q}})[f(\epsilon_{\mathbf{k}}) - 1]C(k)\}d\mathbf{k}, \tag{12}$$

where

$$A(q) = n_0 - \frac{2}{(2\pi)^3}\int f(\epsilon_{\mathbf{k}})f(\epsilon_{\mathbf{k+q}})d\mathbf{k}, \tag{13}$$

$$B(\mathbf{q},\mathbf{k}) = \frac{2}{(2\pi)^3}\int \frac{f(\epsilon_{\mathbf{k}_1})f(\epsilon_{\mathbf{k}_1+\mathbf{q}})}{|\mathbf{k}-\mathbf{k}_1|^2}d\mathbf{k}_1, \tag{14}$$

$$C(k) = \frac{2}{(2\pi)^3}\int \frac{f(\epsilon_{\mathbf{k}_1})}{|\mathbf{k}-\mathbf{k}_1|^2}d\mathbf{k}_1. \tag{15}$$

With the use of Eq. (12), the exchange kernel is now found as

$$f_x^h(q,\omega) \equiv \frac{\delta v_x(q,\omega)}{\delta n(q,\omega)} = \frac{\delta v_x(q,\omega)}{\delta v_s(q,\omega)}\frac{\delta v_s(q,\omega)}{\delta n(q,\omega)} = \frac{\delta v_x(q,\omega)}{\delta v_s(q,\omega)}\left(\chi_s^h\right)^{-1}(q,\omega), \tag{16}$$

where $\chi_s^h(q,\omega)$ is the Lindhard density-response function[21]

$$\chi_s^h(q,\omega) = \frac{2}{V}\sum_{\mathbf{k}}\frac{f(\epsilon_{\mathbf{k}}) - f(\epsilon_{\mathbf{k+q}})}{\omega - \epsilon_{\mathbf{k+q}} + \epsilon_{\mathbf{k}} + i\eta}. \tag{17}$$

In Appendix C, we evaluate the integrals (13) and (15) analytically and reduce the integral (14) to a single-fold one.

It can be seen from Eqs. (12) and (16) that Im f_x^h is nonzero inside the single particle-hole excitation continuum only and shares this property with its counterpart from the first-order perturbation theory.[22] This deficiency of f_x derived from our effective potential is not limited to HEG but, as can be easily seen, persists for any extended (periodic) system. Therefore, such subtle effect as the high-frequency tail of Im f_x of HEG[23] cannot be accounted for within the present approach. Instead, we now show that f_x derived from our effective potential significantly corrects the Lindhard dielectric function of HEG within the single particle-hole continuum. We also note that our $f_x^h(q,\omega)$ does not have singularities, is causal, and satisfies the requirement of the positivity of dissipation, all of which are violated by the first-order perturbation theory.[18,22]

In Fig. 1, the exchange kernel $f_x^h(q,\omega)$ obtained by the use of Eqs. (12) and (16) is plotted at $q = 0.5 \times k_F$ for $r_s = 2$ and 5. With the inclusion of f_x, the dielectric function of HEG can be written as

$$\epsilon^h(q,\omega) = 1 - \frac{4\pi}{q^2}\frac{\chi_s^h(q,\omega)}{1 + \chi_s^h(q,\omega)f_x^h(q,\omega)}. \tag{18}$$

In Fig. 2, the dielectric function of HEG of $r_s = 5$ obtained through Eq. (18) is plotted together with the Lindhard dielectric function. From this we judge that the dynamic exchange plays

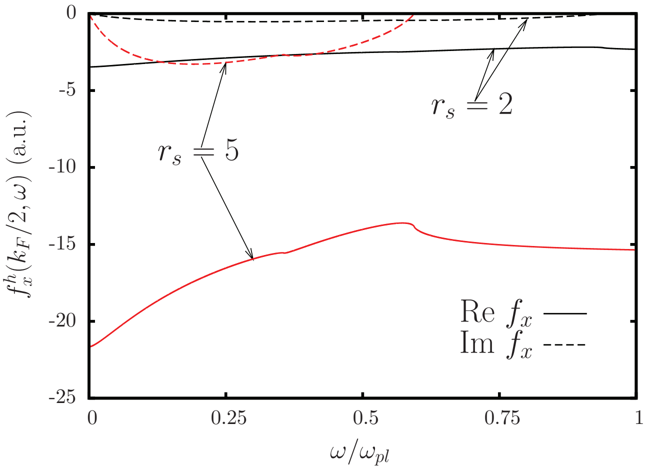

FIG. 1. (Color online) Exchange kernel $f_x^h(q,\omega)$, $q = 0.5 \times k_F$, of HEG of $r_s = 2$ (black curves) and $r_s = 5$ (red [gray] curves). Solid and dashed curves are real and imaginary parts of f_x^h, respectively.

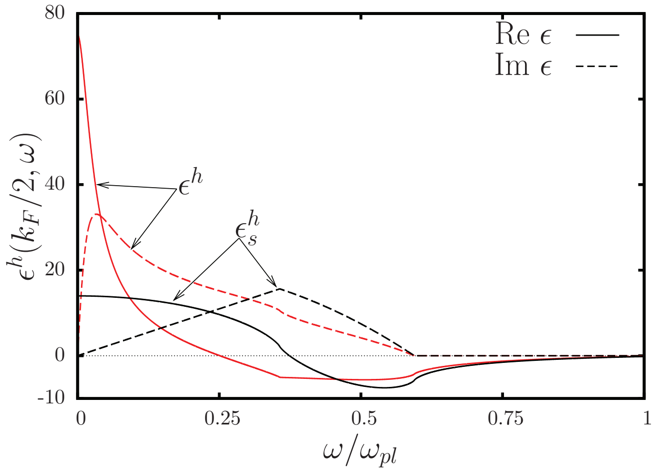

FIG. 2. (Color online) Dielectric function $\epsilon^h(q,\omega), q = 0.5 \times k_F$, of HEG of $r_s = 5$ evaluated by the use of Eq. (18) with the exchange kernel f_x^h included (red [gray] curves) and its Lindhard counterpart $\epsilon_s^h(q,\omega)$ (black curves). Solid and dashed curves are real and imaginary parts of the dielectric function, respectively.

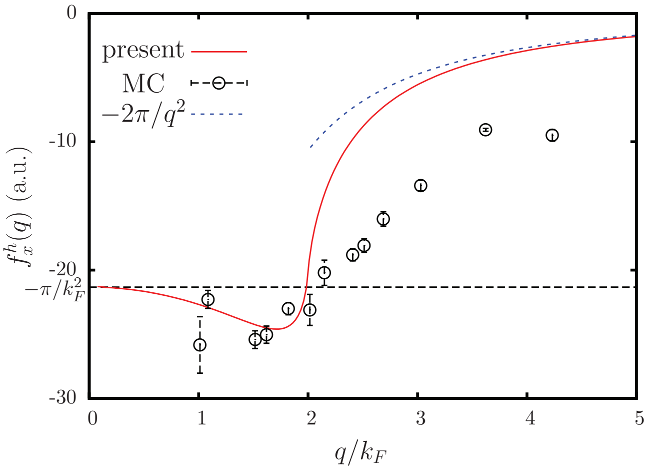

FIG. 3. (Color online) Static exchange kernel $f_x^h(q)$ of HEG of $r_s = 5$. Solid line (red [gray]) is the present result. Symbols with error bars are $f_{xc}^h(q)$ by MC simulations from Ref. 24. The dashed line (blue [dark gray]) shows the asymptotic behavior at large q, as stipulated by Eq. (21).

a significant role at this density and can hardly be considered as a weak perturbation.

In Fig. 3, the static exchange kernel $f_x^h(q)$ is plotted for HEG of $r_s = 5$ as a function of the wave vector, where we find a qualitative agreement with the Monte Carlo (MC) simulations of $f_{xc}^h(q,0)$ of Ref. 24.

The following limiting cases can be further worked out from Eqs. (12)–(15):[25]

$$f_x^h(0,\omega \neq 0) = -\frac{3\pi}{4k_F^2}, \tag{19}$$

$$\lim_{q\to 0} f_x^h(q,0) = -\frac{\pi}{k_F^2}, \tag{20}$$

$$\lim_{q\to \infty} f_x^h(q,0) = -\frac{2\pi}{q^2}, \tag{21}$$

and the infinite-frequency limit at an arbitrary wave vector $f_x^h(q,\infty)$ is given in Appendix D. Equation (19) suggests that, similar to the first-order perturbation theory,[22] our $f_x(0,\omega)$ is purely real and frequency independent. More refined theories taking correlations into account[26] but restricted to the $q = 0$ case, do account for the imaginary part of $f_{xc}(0,\omega)$. We note that the value in the right-hand side of Eq. (19) is somewhat greater than the EXX value $-3\pi/(5k_F^2)$ derived from the exact relation between $f_{xc}^h(0,\infty)$ and the xc energy per particle ϵ_{xc},[26,27] with the substitution of the exchange-only $\epsilon_x = -3k_F/(4\pi)$ for the latter. Since both EXX and our scheme are approximate approaches, this discrepancy must not be a surprise. On the other hand, the limit of Eq. (20) is in the perfect agreement with the compressibility sum rule[26,27] in the exchange-only case.

IV. CONCLUSIONS

Within the well-defined procedure of the minimization of the difference between the left- and right-hand sides of the time-dependent Shrödinger equation, we have derived a time-dependent single-particle effective potential for a system of an arbitrary number of electrons under the action of a time-dependent external field. This potential is nonadiabatic and free of self-interaction. At the same time, our effective potential is comparatively easy to evaluate, which is in contrast to previously known TD optimized effective potentials. These properties open a way to efficiently use this potential within the context of the time-dependent density-functional theory, as we demonstrate by the derivation of the exchange kernel $f_x^h(q,\omega)$ of the homogeneous electron gas. This f_x^h is found to be nonsingular and causal and satisfies the requirement of the positivity of the dissipation, which makes it superior to the earlier known kernel by the first-order perturbation theory and opens up a way to use our kernel in applications.

ACKNOWLEDGMENT

We acknowledge support from National Science Council, Taiwan, Grant No. 100-2112-M-001-025-MY3.

APPENDIX A: DETAILS OF THE DERIVATION OF EQ. (7).

Using permutational symmetry, we can rewrite Eq. (6) as

$$\tilde{v}(\mathbf{r}_1,t)\int |\Psi_s(t)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N + \int \left[(N-1)\tilde{v}(\mathbf{r}_2,t) - \frac{(N-1)}{|\mathbf{r}_1-\mathbf{r}_2|} - \frac{(N-1)(N-2)}{2|\mathbf{r}_2-\mathbf{r}_3|}\right]|\Psi_s(t)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N = 0, \tag{A1}$$

or

$$\frac{\tilde{v}(\mathbf{r}_1,t)n(\mathbf{r}_1,t)}{N} + (N-1)\int \left[\tilde{v}(\mathbf{r}_2,t) - \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} - \frac{N-2}{2|\mathbf{r}_2-\mathbf{r}_3|}\right]|\Psi_s(t)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N = 0, \tag{A2}$$

where $n(\mathbf{r},t)$ is the particle density. Further simplifications give

$$\frac{\tilde{v}(\mathbf{r}_1,t)}{N(N-1)} + \int \left[\tilde{v}(\mathbf{r}_2,t) - \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right] \frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2;t)}{n(\mathbf{r}_1,t)} d\mathbf{r}_2 - \frac{(N-2)}{2} \int \frac{\rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)}{n(\mathbf{r}_1,t)|\mathbf{r}_2-\mathbf{r}_3|} d\mathbf{r}_2 d\mathbf{r}_3 = 0, \tag{A3}$$

where the k-particle density matrix is

$$\rho_k(\mathbf{r}_1,\ldots\mathbf{r}_k;\mathbf{r}'_1,\ldots\mathbf{r}'_k;t) = \int \Psi_s(\mathbf{r}_1\ldots\mathbf{r}_k,\mathbf{r}''_{k+1}\ldots\mathbf{r}''_N,t)\Psi_s^*(\mathbf{r}'_1\ldots\mathbf{r}'_k,\mathbf{r}''_{k+1}\ldots\mathbf{r}''_N,t)d\mathbf{r}''_{k+1}\ldots d\mathbf{r}''_N. \tag{A4}$$

For the Slater-determinant wave function $\Psi_s(t)$ the equalities hold

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2;t) = \frac{1}{N(N-1)}[n(\mathbf{r}_1,t)n(\mathbf{r}_2,t) - |\rho(\mathbf{r}_1;\mathbf{r}_2,t)|^2], \tag{A5}$$

$$\begin{aligned}\rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t) = {}& \frac{1}{N(N-1)(N-2)}[n(\mathbf{r}_1,t)n(\mathbf{r}_2,t)n(\mathbf{r}_3,t) - n(\mathbf{r}_2,t)|\rho(\mathbf{r}_1;\mathbf{r}_3,t)|^2 - n(\mathbf{r}_3,t)|\rho(\mathbf{r}_1;\mathbf{r}_2,t)|^2 \\ & - n(\mathbf{r}_1,t)|\rho(\mathbf{r}_2;\mathbf{r}_3,t)|^2 + \rho(\mathbf{r}_1;\mathbf{r}_2,t)\rho(\mathbf{r}_2;\mathbf{r}_3,t)\rho(\mathbf{r}_3;\mathbf{r}_1,t) + \rho(\mathbf{r}_1;\mathbf{r}_3,t)\rho(\mathbf{r}_3;\mathbf{r}_2,t)\rho(\mathbf{r}_2;\mathbf{r}_1,t)],\end{aligned} \tag{A6}$$

where

$$\rho(\mathbf{r};\mathbf{r}',t) = N\rho_1(\mathbf{r};\mathbf{r}',t) = \sum_\alpha \psi_\alpha(\mathbf{r},t)\psi_\alpha^*(\mathbf{r}',t). \tag{A7}$$

Therefore

$$\begin{aligned}&\tilde{v}(\mathbf{r}_1,t) - V_H(\mathbf{r}_1,t) - \int \left[\tilde{v}(\mathbf{r}_2,t) - \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\frac{|\rho(\mathbf{r}_1;\mathbf{r}_2;t)|^2}{n(\mathbf{r}_1,t)} d\mathbf{r}_2 + \int \frac{n(\mathbf{r}_2,t)|\rho(\mathbf{r}_1;\mathbf{r}_3,t)|^2}{n(\mathbf{r}_1,t)|\mathbf{r}_2-\mathbf{r}_3|} d\mathbf{r}_2 d\mathbf{r}_3 \\ &- \int \frac{\rho(\mathbf{r}_1;\mathbf{r}_2,t)\rho(\mathbf{r}_2;\mathbf{r}_3,t)\rho(\mathbf{r}_3;\mathbf{r}_1,t)}{n(\mathbf{r}_1,t)|\mathbf{r}_2-\mathbf{r}_3|} d\mathbf{r}_2 d\mathbf{r}_3 + C(t) = 0,\end{aligned} \tag{A8}$$

where

$$V_H(\mathbf{r},t) = \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \tag{A9}$$

$$\begin{aligned}C(t) = {}& \int \tilde{v}(\mathbf{r}_2,t)n(\mathbf{r}_2,t)d\mathbf{r}_2 - \frac{1}{2}\int \frac{n(\mathbf{r}_2,t)n(\mathbf{r}_3,t)}{|\mathbf{r}_2-\mathbf{r}_3|} d\mathbf{r}_2 d\mathbf{r}_3 \\ & + \frac{1}{2}\int \frac{|\rho(\mathbf{r}_2;\mathbf{r}_3,t)|^2}{|\mathbf{r}_2-\mathbf{r}_3|} d\mathbf{r}_2 d\mathbf{r}_3 = 0,\end{aligned} \tag{A10}$$

and the second equality in Eq. (A10) follows from Eq. (A8). Equations (A8) and (A10) give immediately Eq. (7).

APPENDIX B:DIFFERENT METHOD OF DERIVATION OF EQ. (7)

In this Appendix we outline the derivation of the effective potential of Eq. (7) in the same spirit as has been done in Ref. 14 in application to the time-independent case. HF and EEX determinant wave functions, Ψ_{HF} and Ψ_{EXX}, respectively, satisfy the equations

$$i\frac{\partial \Psi_s(t)}{\partial t} = \hat{H}_{HF}(t)\Psi_s(t), \tag{B1}$$

$$i\frac{\partial \Psi_s(t)}{\partial t} = \hat{H}_{EXX}(t)\Psi_s(t), \tag{B2}$$

where $\hat{H}_{HF}$ and $\hat{H}_{EXX}$ are HF and EXX Hamiltonians, respectively, and the approximation of Ref. 14, $\Psi_{HF} = \Psi_{EXX} (= \Psi_s)$, has been applied. By subtracting Eq. (B2) from Eq. (B1), multiplying by Ψ_s^*, and integrating over all but one particle's coordinates, we arrive at Eq. (7) in the similar way as has been done in Ref. 14 in the time-independent case. It must be noted, however, that Eqs. (B1) and (B2) cannot hold simultaneously except in trivial cases. We, therefore, consider the derivation from the time-dependent variational principle preferential with respect to the mathematical formulation, as it also is with respect to the physical insight it imparts.

APPENDIX C: INTEGRALS (13)–(15)

For integrals (13) and (15) we have straightforwardly

$$A(q) = n_0 - \frac{1}{48\pi^2}\Theta(2k_F - q)(2k_F - q)^2(4k_F + q), \tag{C1}$$

$$C(k) = \frac{2}{(2\pi)^3} H(k,k_F), \tag{C2}$$

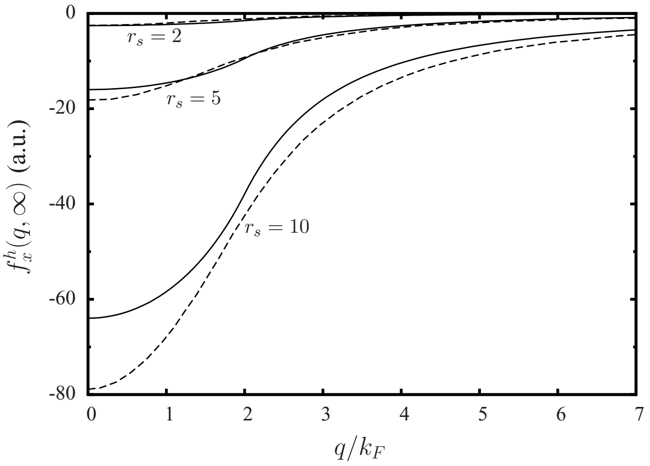

FIG. 4. Exchange kernel as a function of the wave vector q at infinite frequency. Solid lines are results from Eq. (D2) for $r_s = 2,5,$ and 10. Dashed lines are $f_{xc}^h(q,\infty)$ with the neglect of the correlation kinetic energy taken from Ref. 28.

where $\Theta(x)$ is the Heaviside step function and

$$H(k,p)=\frac{\pi}{k}\left[(p^2-k^2)\log\left|\frac{p+k}{p-k}\right|+2kp\right]. \tag{C3}$$

For integral (14) we have

$$B(\mathbf{q},\mathbf{k})=\frac{2}{(2\pi)^3}\Theta(k_F-q)H(k,k_F-q)+\frac{2}{(2\pi)^2}\Theta(2k_F-q)\int_{|k_F-q|}^{k_F}P\left(k,k_1,\frac{k_F^2-k_1^2-q^2}{2k_1q},\frac{\mathbf{k}\cdot\mathbf{q}}{kq}\right)dk_1, \tag{C4}$$

where

$$\begin{aligned}P(k,k_1,x,y)=\frac{k_1}{2k}\Big\{&\log\Big[\sqrt{k^4+4k^2k_1^2x^2+2kk_1\big[kk_1(2y^2-1)-2xy\big(k^2+k_1^2\big)\big]+k_1^4}+2kk_1x-y\big(k^2+k_1^2\big)\Big]\\&-\log((1-y)(k-k_1)^2)\Big\}.\end{aligned} \tag{C5}$$

APPENDIX D: INFINITE-FREQUENCY LIMIT OF $f_x(q,\omega)$

By expanding Eq. (12) to the second order in ω^{-1}, we have

$$\begin{aligned}\frac{\delta v_x(q,\omega)}{\delta v_s(q,\omega)}=&\frac{16\pi}{(2\pi)^6A(q)\omega^2}\int\frac{\mathbf{q}\cdot\mathbf{k}}{k^2}f(\epsilon_{\mathbf{k}+\mathbf{k}_1})f(\epsilon_{\mathbf{k}_1+\mathbf{q}})\\&\times\left[f\left(\epsilon_{\mathbf{k}_1}\right)-\frac{1}{2}\right]d\mathbf{k}d\mathbf{k}_1+O(\omega^{-4}).\end{aligned} \tag{D1}$$

Equation (D1) can be analytically evaluated. With the use of Eq. (16), for the kernel this gives

$$\begin{aligned}f_x(q,\infty)=&-\frac{k_F}{560\pi\tilde{q}^3A(q)}\{[Z(\tilde{q})+Z(-\tilde{q})-4\tilde{q}^6\\&+10\tilde{q}^4(13+14\log 2)-8\tilde{q}^2(3+28\log 2)\\&+192\log(2)]\Theta(2-\tilde{q})+[Z(\tilde{q})-Z(-\tilde{q})\\&+2(28-\tilde{q}^2)\tilde{q}^5\log\tilde{q}+4(\tilde{q}^4+44\tilde{q}^2+24)\tilde{q}]\\&\Theta(\tilde{q}-2)\},\end{aligned} \tag{D2}$$

where $\tilde{q}=q/k_F$, $A(q)$ is given by Eq. (C1), and

$$Z(x)=(x+2)^4[(x-6)(x-2)x-6]\log|x+2|. \tag{D3}$$

In Fig. 4 we plot $f_x(q,\infty)$ of Eq. (D2) and compare it with $f_{xc}(q,\infty)$ of Ref. 28 [$f_{xc}^{(1)}(q,\infty)$] calculated with the neglect of the correlation kinetic energy and with the use of the static structure factor of Ref. 29. The two are found to be in reasonable agreement.

[1] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980); E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); E. K. U. Gross and W. Kohn, *ibid.* **55**, 2850 (1985); **57**, 923 (1986).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[3] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[4] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[5] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1996).

[6] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997).

[7] G. Vignale, Phys. Lett. A **209**, 206 (1995).

[8] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[9] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[10] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

[11] C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **74**, 872 (1995).

[12] R. van Leeuwen, Phys. Rev. Lett. **76**, 3610 (1996).

[13] V. U. Nazarov, Math. Proc. Cambridge Philos. Soc. **98**, 373 (1985).

[14] F. Della Sala and A. Gorling, J. Chem. Phys. **115**, 5718 (2001).

[15] Z. Zhou and S.-I. Chu, Phys. Rev. A **71**, 022513 (2005).

[16] In Eq. (7), the integration over the space coordinates also implies the summation over spin indices.

[17] While generally there is no single-particle effective potential in HF theory, in the particular case of a singlet state of a two-electron system such a potential exists.

[18] G. F. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge, 2005).

[19] V. U. Nazarov, G. Vignale, and Y.-C. Chang, Phys. Rev. Lett. **102**, 113001 (2009).

[20] Caution must be exercised when solving the ground-state problem for HEG with Eq. (7): Although the ground-state effective potential is constant, it is infinite for the infinite system. A proper limiting procedure, however, of starting from a finite volume resolves this difficulty unambiguously.

[21] J. Lindhard, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. **28**, 1 (1954).

[22] A. Holas, P. K. Aravind, and K. S. Singwi, Phys. Rev. B **20**, 4912 (1979).

[23] K. Sturm and A. Gusarov, Phys. Rev. B **62**, 16474 (2000).

[24] S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995).

[25] It must be noted that in Eq. (20) we have not been able to evaluate the numerator analytically, but rather, having evaluated it numerically to 3.1415, surmised it to be π. This does not affect the following discussion at all.

[26] Z. Qian and G. Vignale, Phys. Rev. B **65**, 235121 (2002).

[27] S. Conti and G. Vignale, Phys. Rev. B **60**, 7966 (1999).

[28] V. U. Nazarov, I. V. Tokatly, S. Pittalis, and G. Vignale, Phys. Rev. B **81**, 245101 (2010).

[29] P. Gori-Giorgi, F. Sacchetti, and G. B. Bachelet, Phys. Rev. B **61**, 7353 (2000).