

Exact exchange in linear-response theory

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(Received 4 September 1998; revised manuscript received 20 January 1999)

An exact formalism for excitation energies of any interacting N -electron system has recently been derived from the linear-response limit of time-dependent Kohn-Sham theory. A response kernel is determined in this theory by the functional derivative of the ground-state Kohn-Sham potential function with respect to electron density. It is shown here that the exchange part of this response kernel is a linear operator determined exactly by the underlying second-quantized Hamiltonian. If correlation response is neglected, the theory reduces to the random-phase approximation including exchange. This formalism justifies methods that combine this exact exchange kernel with density-functional approximations to the correlation kernel. [S1050-2947(99)50111-X]

PACS number(s): 31.10.+z, 31.50.+w

Introduction. Density-functional theory (DFT), originally restricted to ground states [1,2], has recently been extended to excitation energies by Petersilka *et al.* [3], using time-dependent linear-response theory [4]. An alternative formalism, exact for exchange, is well-established as the linear-response limit of time-dependent Hartree-Fock theory (TDHF) [5], equivalent to the random-phase approximation (RPA) with exchange [6]. Since the DFT and RPA expressions for the exchange response kernel f_x defined in this theory appear to differ, it is important to determine whether this difference is significant, and if so, the source of the difference.

The ability to compute excitation energies within a formally exact linear-response theory is a potentially very great extension of the area of applicability of density-functional methods, already widely used in atomic, molecular, and solid-state physics. In this theory [3,4], excitation frequencies are determined by

$$\sum_{q'} \{ \delta_{qq'} - M_{qq'}(\omega) / (\omega - \omega_{q'} + i\eta) \} \xi_{q'}(\omega) = 0 \quad (1)$$

for spin-indexed ground-state electron density $\rho = \sum_i n_i \phi_i^* \phi_i$ in an exact Kohn-Sham orbital basis, obtained by minimizing the Hohenberg-Kohn energy functional. The index q denotes a virtual excitation $i \rightarrow a$, defining $\omega_q = \epsilon_a - \epsilon_i$ and $\alpha_q = n_i - n_a$, and similarly for $q' : j \rightarrow b$.

The first application of this theory [3] approximated the exchange part of the response kernel and neglected the correlation part. In this exchange-only limit,

$$M_{qq'}(\omega) = \alpha_{q'} (aj|u + f_x|ib), \quad (2)$$

in the usual notation for matrix elements of $u = 1/|\mathbf{r} - \mathbf{r}'|$. The corresponding formula in the RPA [6] is

$$M_{qq'}(\omega) = \alpha_{q'} [(aj|u|ib) - (aj|u|bi)]. \quad (3)$$

These equations agree if the exchange response kernel is the linear operator,

$$\hat{f}_x = - (1/|\mathbf{r} - \mathbf{r}'|) \mathcal{P}(\mathbf{r}, \mathbf{r}'), \quad (4)$$

where \mathcal{P} permutes the indicated coordinates for equal spin. Using the exchange-only optimized effective potential (OEP) for v_x^{stat} in the Krieger-Li-Iafrate (KLI) [7] approximation, Petersilka *et al.* [3] derive the formula

$$f_x^{OEP}(\mathbf{r}\mathbf{r}') \approx -2 \left| \sum_k n_k \phi_k(\mathbf{r}) \phi_k^*(\mathbf{r}') \right|^2 / |\mathbf{r} - \mathbf{r}'| \rho(\mathbf{r}) \rho(\mathbf{r}'). \quad (5)$$

The textbook derivations of RPA or TDHF are unlikely to be wrong. The question of why Eqs. (4) and (5) are so different is examined here. A general principle can be stated that determines the exchange part of the two-electron Coulomb interaction in any exact theory derived from the N -electron nonrelativistic Hamiltonian: the only matrix elements of the Coulomb interaction that occur in the second-quantized Hamiltonian are linear combinations of integrals of the form $(ij|\bar{u}|kl) = (ij|u|kl) - (ij|u|lk)$. No exact theory can be derived in conflict with this formal structure. This principle determines an exact expression for the exchange part of the response kernel in linear-response theory in agreement with Eq. (4).

Equivalence to TDHF or RPA theories in the pure-exchange limit, as established here, implies that the formal linear-response theory is free of mathematical difficulties, except possibly for the correlation response. A further implication is that systematic corrections to the RPA can be deduced by analysis of effective correlation potentials derived in density-functional theory. By establishing an exact form for the exchange term, the residual mathematical and computational difficulties of the linear-response theory are relegated to this less well characterized correlation term. In practice, this development should make the theory more accurate and more widely applicable.

Section II summarizes the recently derived DFT linear-response theory [4]. Section III presents a fundamental argument that establishes an exact universal expression for the exchange kernel in this theory. Questions relevant to consistent definitions [8] are considered in Sec. IV. A detailed comparison with local-exchange theory [3] is made in Sec. V. Principal conclusions are summarized in Sec. VI.

Summary of linear response theory. The formalism of time-dependent density-functional linear response theory is developed in detail in a recent review [4]. The essential equations describing this formalism will be summarized here in order to establish the context of the present proposal for exact exchange.

Following Ref. [4], starting from a stationary ground state, the first-order density change $\rho_1(\mathbf{r}t)$ in the limit

of linear response is related to a first-order perturbing potential $v_1(\mathbf{r}t)$ by the density-density response function $\chi(\mathbf{r}t; \mathbf{r}'t') = \delta\rho(\mathbf{r}t)/\delta v(\mathbf{r}'t')|_{v_1 \rightarrow 0}$, such that $\rho_1(\mathbf{r}t) = \int dt' \int d^3\mathbf{r}' \chi(\mathbf{r}t; \mathbf{r}'t') v_1(\mathbf{r}'t')$. The response function χ_s of a noninteracting Kohn-Sham system can be expressed in terms of the orbital functions ϕ_i , eigenvalues ϵ_i , and occupation numbers n_i . When Fourier-transformed from time to frequency,

$$\begin{aligned} \chi_s(\mathbf{r}\mathbf{r}'\omega) &= \sum_{j,k} (n_k - n_j) \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta} \\ &= \sum_q \alpha_q \frac{\Xi_q(\mathbf{r})\Xi_q^*(\mathbf{r}')}{\omega - \omega_q + i\eta} \end{aligned} \quad (6)$$

for $\eta \rightarrow 0+$. All spin indices are suppressed here and a notation for excitations has been introduced, such that index q denotes a virtual excitation $k \rightarrow j$, $\Xi_q(\mathbf{r}) = \phi_j(\mathbf{r})\phi_k^*(\mathbf{r})$, $\alpha_q = n_k - n_j$, and $\omega_q = \epsilon_j - \epsilon_k$. The formal argument relates $\chi(\mathbf{r}t; \mathbf{r}'t')$ to the noninteracting response function $\chi_s(\mathbf{r}t; \mathbf{r}'t')$ by an integral equation whose kernel contains the functional derivative $f_{xc}(\mathbf{r}t; \mathbf{r}'t') = \delta v_{xc}(\mathbf{r}t)/\delta\rho(\mathbf{r}'t')$. This equation, similar to a Dyson equation, is

$$\begin{aligned} \chi(\mathbf{r}t; \mathbf{r}'t') &= \chi_s(\mathbf{r}t; \mathbf{r}'t') + \int d^3\mathbf{x} \int d\tau \int d^3\mathbf{x}' \int d\tau' \\ &\quad \times \chi_s(\mathbf{r}t; \mathbf{x}\tau) \left(\frac{\delta(\tau - \tau')}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}(\mathbf{x}\tau; \mathbf{x}'\tau') \right) \\ &\quad \times \chi(\mathbf{x}'\tau'; \mathbf{r}'t'). \end{aligned} \quad (7)$$

In a simplified notation, the defining equation $\rho_1 = \int \chi v_1$ takes the form

$$\begin{aligned} \rho_1 &= \int \chi_s \left\{ v_1 + \int \left(\frac{\delta}{|\mathbf{x} - \mathbf{x}'|} + f_{xc} \right) \int \chi v_1 \right\} \\ &= \int \chi_s \left\{ v_1 + \int \left(\frac{\delta}{|\mathbf{x} - \mathbf{x}'|} + f_{xc} \right) \rho_1 \right\}, \end{aligned} \quad (8)$$

equivalent to the inhomogeneous integral equation

$$\int \left\{ \delta - \chi_s \int \left(\frac{\delta}{|\mathbf{x} - \mathbf{x}'|} + f_{xc} \right) \right\} \rho_1 = \int \chi_s v_1. \quad (9)$$

When the time variable is Fourier-transformed to frequency ω this becomes

$$\begin{aligned} \int d^3\mathbf{x} \int d^3\mathbf{x}' \left\{ \delta(\mathbf{r} - \mathbf{x})\delta(\mathbf{r} - \mathbf{x}') - \chi_s(\mathbf{r}\mathbf{x}\omega) \left(\frac{1}{|\mathbf{x} - \mathbf{x}'|} \right. \right. \\ \left. \left. + f_{xc}(\mathbf{x}\mathbf{x}'\omega) \right) \right\} \rho_1(\mathbf{x}'\omega) = \int d^3\mathbf{x} \chi_s(\mathbf{r}\mathbf{x}\omega) v_1(\mathbf{x}\omega). \end{aligned} \quad (10)$$

Excitation energies occur for frequencies $\omega = \Omega$ for which this integral equation is singular, as determined by the non-linear eigenvalue equation

$$\begin{aligned} \int d^3\mathbf{x} \int d^3\mathbf{x}' \left\{ \delta(\mathbf{r} - \mathbf{x})\delta(\mathbf{r} - \mathbf{x}') - \chi_s(\mathbf{r}\mathbf{x}\omega) [1/|\mathbf{x} - \mathbf{x}'| \right. \\ \left. + f_{xc}(\mathbf{x}\mathbf{x}'\omega)] \right\} \zeta(\mathbf{x}'\omega) = 0. \end{aligned} \quad (11)$$

On defining the integral $\xi_q(\omega) = \int d^3\mathbf{x} \int d^3\mathbf{x}' \Xi_q^*(\mathbf{x}) [1/|\mathbf{x} - \mathbf{x}'| + f_{xc}(\mathbf{x}\mathbf{x}'\omega)] \zeta(\mathbf{x}'\omega)$ and substituting Eq. (6) for χ_s , excitation frequencies $\omega = \Omega$ are determined by Eq. (1), in which

$$M_{qq'}(\omega) = \alpha_{q'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \Xi_q^*(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc} \right) \Xi_{q'}(\mathbf{r}'). \quad (12)$$

The summation in Eq. (1) becomes an integral for a system whose unoccupied one-electron states lie in the energy continuum. Equation (12) completes the formal derivation [3,4].

Exchange kernel implied by exact N-electron theory. In the theory of N -electron wave functions, it is well known [9] that all matrix elements of the Coulomb interaction between Slater determinants constructed from a common basis of spin-indexed orthonormal orbital wave functions are linear combinations of two-electron integrals of $u = 1/r_{12}$ in the form

$$(ij|\bar{u}|kl) = (ij|u|kl) - (ij|u|lk). \quad (13)$$

This is a consequence of the fact that the Coulomb interaction in the second-quantized many-electron Hamiltonian is the sum $\frac{1}{2} \sum_{ijkl} (ij|u|kl) \eta_j^\dagger \eta_i^\dagger \eta_k \eta_l$, where η^\dagger and η , respectively, are elementary electron creation and annihilation operators [6]. Because η_k and η_l anticommute, this sum is identical to the form $\frac{1}{4} \sum_{ijkl} (ij|\bar{u}|kl) \eta_j^\dagger \eta_i^\dagger \eta_k \eta_l$, which implies that all two-electron matrix elements in any exact theory take the form $(ij|\bar{u}|kl)$. If a two-electron Coulomb integral $(ij|u|kl)$ occurs in any exact formula derived from many-body theory it must be accompanied by an exchange integral of the form $-(ij|u|lk)$.

An important purpose of the present paper is to point out that this rule determines the exchange term in Eq. (12). In order to be consistent with the general rule for two-electron matrix elements, the Coulomb and exchange part of the integrand in Eq. (12) must take the form

$$\begin{aligned} \Xi_q^*(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_x \right) \Xi_{q'}(\mathbf{r}') = \phi_j^*(\mathbf{r})\phi_k^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ \times \{ \phi_k(\mathbf{r})\phi_{j'}(\mathbf{r}') - \phi_{j'}(\mathbf{r})\phi_k(\mathbf{r}') \}. \end{aligned} \quad (14)$$

In agreement with the structure of the second-quantized Hamiltonian, this is equivalent to the linear operator expression

$$f_h + f_x = (1/r_{12}) \{1 - \mathcal{P}_{12}\}, \quad (15)$$

where the direct Coulomb response kernel is $f_h = 1/r_{12}$ and \mathcal{P}_{12} permutes the indicated coordinates. In integrals over this operator, summation over spin produces a Kronecker-delta factor in the spin indices. Equation (15) gives an exact and universal formula for the exchange kernel f_x .

This formula can be verified for two virtual excitations $q: i \rightarrow a$ and $q': j \rightarrow b$, where $i \neq j$, $a \neq b$, $n_i = n_j = 1$, and $n_a = n_b = 0$. The interaction matrix element between the uncorrelated wave functions denoted by Φ_i^a and Φ_j^b is [9]

$$(\Phi_i^a | H | \Phi_j^b) = (aj|\bar{u}|ib). \quad (16)$$

In the present notation, $\Xi_q^*(\mathbf{r}) = \phi_a^*(\mathbf{r})\phi_i(\mathbf{r})$, $\Xi_{q'}(\mathbf{r}') = \phi_b(\mathbf{r}')\phi_j^*(\mathbf{r}')$, and $\alpha_q = \alpha_{q'} = 1$. Substituting Eqs. (15) and (14) into Eq. (12), the matrix element for this example, omitting correlation, is

$$\begin{aligned} M_{qq'} &= \int d^3\mathbf{r} \int d^3\mathbf{r}' \phi_a^*(\mathbf{r})\phi_j^*(\mathbf{r}') 1/(|\mathbf{r}-\mathbf{r}'|) \\ &\quad \times [1 - \phi_b(\mathbf{r})\phi_i(\mathbf{r}')/\phi_i(\mathbf{r})\phi_b(\mathbf{r}')] \phi_i(\mathbf{r})\phi_b(\mathbf{r}') \\ &= (aj|\bar{u}|ib), \end{aligned} \quad (17)$$

in agreement with Eq. (16). In an orbital basis representation of Eq. (7), matrix elements of the Coulomb interaction can be modified to include exact exchange by using Eq. (15).

If the matrix elements given by Eq. (17) are substituted into Eqs. (1) this provides a theory that is valid when correlation response can be neglected. Comparison with time-dependent Hartree-Fock (TDHF) theory [5] shows that when Eqs. (1) are expressed in terms of coefficients $\xi/(\omega - \omega_{q'} + i\eta)$ these equations give exactly the linear-response limit of TDHF. As discussed by Thouless [6], these equations are equivalent to the random-phase approximation when exchange is included in the latter. As is well known in the theory of metals, an exact-exchange theory is not physically correct for any system with nonvanishing density of states at the Fermi surface, so parallel consideration of correlation response is needed, except for applications with discrete energy levels, and must be included in any theory intended to improve on the RPA.

Consistent definitions. It is widely assumed in the DFT literature that the exact ground-state energy functional established by Hohenberg-Kohn theory [1] defines a local exchange-correlation potential in exact Kohn-Sham equations [2]. By extension, the response kernel f_{xc} in Eq. (12) is expected to be defined as a c -number function in exact linear-response theory [3,4]. The exact exchange kernel defined by Eq. (15) is a nonlocal linear operator. It thus appears to be inconsistent with the DFT derivation of Eq. (12) [4]. This apparent inconsistency can be resolved in one of two ways: either an exact DFT c -number exchange response kernel exists, and is equivalent in the system of equations derived in linear-response theory to the exact nonlocal linear operator of Eq. (15), or else the assumption of locality fails. Evidence for the second conclusion exists, and is discussed below. However, the first conclusion cannot be ruled out without proof. Definitions needed to make this issue clear are summarized here.

While Eq. (15) is a necessary consequence of the structure of the second-quantized Hamiltonian, it requires a consistent definition of exchange and correlation energy in the energy functional [8]. This can be put into a general context by defining a reference state Φ , described by a single Slater determinant, determined by some rule from the exact correlated wave function Ψ . Hohenberg-Kohn theory implies for ground states that Φ and its set of occupied orbital functions $\{\phi_i\}$ are functionals of the density function. If Φ and Ψ are normalized so that $(\Phi|\Psi) = (\Phi|\Phi) = 1$, then $E = (\Phi|H|\Psi) = (\Phi|H|\Phi) + (\Phi|H|\Psi - \Phi)$ and $(\Phi|\Psi - \Phi) = 0$ by construction. This unsymmetric formula expresses any total energy eigenvalue in the form $E = (\Phi|H|\Phi) + E_c$, and provides a natural definition of correlation energy E_c for any

reference state Φ . E_x and all other terms in the energy functional are defined as reference-state mean values. In the basis of occupied orbitals of the reference state, this definition of E_c implies Eq. (15), because $(\Phi|H|\Phi)$ always has the same form.

In standard DFT [2], a model or reference state is defined by minimizing the kinetic energy $(\Phi|T|\Phi)$ while constraining the reference-state density function ρ_Φ to be identical with the correlated density function ρ_Ψ . This defines Φ as a functional of ρ_Ψ or ρ_Φ , consistent with the natural definition of E_c given above. Alternatively, in reference-state DFT (RDFT) [10], Φ is determined by maximum projection on Ψ , and the ground-state energy is a functional of ρ_Φ . In RDFT all one-electron terms drop out of E_c .

To discuss the locality of the DFT exchange-correlation potential, it is necessary to distinguish between the ‘‘Kohn-Sham construction’’ (minimizing reference-state kinetic energy with a density constraint) and the ‘‘exact Kohn-Sham equations’’ derived by minimizing the exact Hohenberg-Kohn energy functional with respect to variations of the occupied orbital functions of the Kohn-Sham reference state. The coupled equations for occupied orbitals derived in these two formalisms differ if the effective exchange-correlation potential in the exact Kohn-Sham equations is a linear operator that is not equivalent to a local potential function in the context of these equations. Effective potentials in the exact Kohn-Sham equations take the form of density-functional derivatives. The relevant mathematical issue is whether a definition of functional derivatives restricted to local potential functions is appropriate to the variational theory of these equations. In the case of the kinetic-energy functional, the assumption of locality implies the equivalence of Thomas-Fermi theory and exact Kohn-Sham theory, if both are derived from the same Hohenberg-Kohn energy functional. This assumption is negated by the fact that these theories are inconsistent unless all Kohn-Sham one-electron energies are equal [13]. Kohn and Sham [2] follow standard variational theory in using the linear operator $-\frac{1}{2}\nabla^2$ of Schrödinger, rather than assuming that the density-functional derivative of the kinetic energy functional defines a local potential. They also consider a variant of DFT ([2], Sec. II B) in which ‘‘exact’’ exchange is represented by the nonlocal Fock exchange operator.

Comparison with local-exchange theory. In Eq. (6) [4], χ_s is evaluated using exact Kohn-Sham orbitals computed for a stationary ground state. This is justified in the linear-response limit, assuming that the unperturbed external potential is time independent. The functional derivative $f_{xc}(\mathbf{r};\mathbf{r}'t')$ is also to be evaluated in the limit of vanishing perturbing field. In Coulomb gauge, if the electromagnetic radiation field is neglected, Coulomb interactions are instantaneous. Even for nonzero frequencies, it can be expected for instantaneous interactions that

$$f_{xc}(\mathbf{r}\mathbf{r}'\omega) \approx f_{xc}(\mathbf{r}\mathbf{r}'0) = \delta^2 E_{xc} / \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}'). \quad (18)$$

For example, given the classical Coulomb (Hartree) energy $E_h = \frac{1}{2} \int [\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|] d^3\mathbf{r}d^3\mathbf{r}'$, the functional second derivative is $f_h = \delta^2 E_h / \delta\rho^2 = 1/|\mathbf{r}-\mathbf{r}'|$, which describes an instantaneous interaction. For a system with continuous energy levels at the Fermi level, single-electron states acquire a lifetime and the response kernel must be considered to be

frequency dependent. Otherwise, it is consistent to include the exchange kernel required in Eq. (12) in the form $(\delta^2/\delta\rho^2)(E_h + E_x) = 1/|\mathbf{r} - \mathbf{r}'| + f_x(\mathbf{r}\mathbf{r}'0)$.

A relationship can be established between TDHF-RPA equations and the expression $f_x = \delta^2 E_x / \delta\rho^2$ derived from exact Kohn-Sham theory. For any orbital functional F that is also a density functional, the infinitesimal variation generated by orbital variations is given by

$$\begin{aligned} \delta F &= \sum_i \int \{ \delta\phi_i^* (\delta F / \delta\phi_i^*) + \text{c.c.} \} d^3\mathbf{r} \\ &= \sum_i n_i \int \{ \delta\phi_i^*(\mathbf{r}) [\delta F / \delta\rho(\mathbf{r})] \phi_i(\mathbf{r}) + \text{c.c.} \} d^3\mathbf{r}. \end{aligned} \quad (19)$$

This is expressed in a form valid for linear operators, but reduces to the usual definition $\delta F = \int (\delta F / \delta\rho) \delta\rho$ if the functional derivative is a local function. The implied chain rule for functional derivatives is $\delta F / \delta\phi_i^* = n_i (\delta F / \delta\rho) \phi_i$. For example, using the natural definition of correlation energy, the sum of Coulomb and exchange energies for ground states determines the density functional

$$U[\rho] = (\Phi | U | \Phi) = \frac{1}{2} \sum_{i,j} n_i n_j (ij | \bar{u} | ij), \quad (20)$$

in the notation of Eq. (13). When evaluated in a basis of orbital functions derived from exact Kohn-Sham equations, functional derivatives of this explicit orbital functional are determined by the chain rule given above. Thus in ground-state theory,

$$\delta U / \delta\phi_j^* = n_j (\delta U / \delta\rho) \phi_j = n_j \sum_i n_i (i | \bar{u} | i) \phi_j, \quad (21)$$

which defines $\delta U / \delta\rho$ as the linear operator of Fock. Since this expression is itself an orbital functional, the functional second derivative is

$$\begin{aligned} \frac{\delta^2 U}{\delta\phi_i^*(1) \delta\phi_j^*(2)} &= \frac{n_i n_j \delta^2 U}{\delta\rho(1) \delta\rho(2)} \phi_i(1) \phi_j(2) \\ &= \frac{n_i n_j}{r_{12}} [\phi_i(1) \phi_j(2) - \phi_j(1) \phi_i(2)]. \end{aligned} \quad (22)$$

Terms with $i=j$ drop out because of antisymmetry. This is equivalent to the linear operator expression given in Eq. (15),

$$f_h + f_x = \delta^2 U / \delta\rho(1) \delta\rho(2) = (1/r_{12}) \{1 - \mathcal{P}_{12}\}, \quad (23)$$

and agrees with Eq. (4), which gives the RPA formula for $M_{qq'}(\omega)$ in Eq. (3).

Using the exchange-only optimized effective potential [11,12] for v_x^{stat} in the KLI [7] approximation, Petersilka *et al.* [3] derive Eq. (5), which clearly differs from Eq. (4). Although Eq. (5) is itself an approximation of the OEP theory, it is an important question whether a result derived from such a theory, based on a local-exchange potential, could be equivalent to the exact expression for f_x given by the linear exchange operator in Eq. (4). The assumption that a density-functional derivative must yield a local potential function for ground states has recently been shown to be false in the case of the kinetic-energy functional in DFT and Thomas-Fermi theory [13]. Numerical criteria computed in unrestricted Hartree-Fock theory indicate that density-functional derivatives are not in general equivalent to local potential functions for either kinetic or exchange energy functionals [14]. Other results in existing literature imply that an exact theory cannot be based on the optimized effective potential model. This model is known to be inexact for exact-exchange (Hartree-Fock) ground states. OEP ground-state energies computed by Aashamar *et al.* [15] and with improved accuracy by Engel and Vosko [16] are -14.5724 for Be and -128.5455 for Ne in Hartree units, above the Hartree-Fock energies -14.57302 for Be and -128.54710 for Ne [17] by amounts greater than the expected residual numerical inaccuracy. It is unlikely that an exact theory of linear response and excitation can be based on a model that is inexact for ground states.

Conclusions. It has been shown here that an exact expression exists for the exchange part of the response kernel in linear-response theory based on density-functional theory. Using this exact-exchange expression, the theory becomes equivalent to the RPA or linear-response limit of time-dependent Hartree-Fock theory if the electronic correlation part of the response kernel is neglected. This exact-exchange kernel retains its form when correlation energy is included in the theory, consistent with the ‘‘natural’’ definition of correlation energy discussed in Sec. IV [8].

The integrals in Eq. (2) are no easier to compute using Eq. (5) than Eq. (4). Even if a practical way were found to eliminate the KLI approximation and to use the full OEP theory in Eq. (5), it might not offer any practical advantage over the RPA formula. In view of this, one might as well use the nonlocal RPA expression, Eq. (4), for the exchange response kernel, augmenting it with a correlation kernel obtained from DFT.

The author is grateful to R. Colle for discussions and to the Scuola Normale Superiore (Pisa) for support.

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