The Sham-Schlüter Equation in Time-Dependent Density-Functional Theory

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We present an exact equation for the exchange-correlation potential of time-dependent density-functional theory. This relation is derived using a many-particle Green's function formalism due to Keldysh. We furthermore show how this equation can be derived from an action principle. The method presented provides a systematic way to derive correlation contributions to the time-dependent exchange-correlation potential. [S0031-9007(96)00144-5]

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In recent years a wealth of new physical phenomena has been observed in the study of atoms and molecules in strong laser fields [1–3]. These phenomena cannot be explained theoretically using traditional perturbation theory, due to the high strengths of the electric fields involved. In order to be able to calculate the properties of atomic and molecular systems in strong external fields a completely nonperturbative treatment of the external field is therefore called for.

Time-dependent density-functional theory (TDDFT) [4–6] is a method of this type. The rigorous foundations of TDDFT were first established by Runge and Gross [7]. In the TDDFT formalism one can transform the interacting many-particle problem into an equivalent problem of noninteracting particles with the same time-dependent density $n(\mathbf{r}t)$. The effective potential v_s for this noninteracting system is known as the Kohn-Sham potential. By subtracting from v_s both the Hartree potential and the external potential of the interacting system one obtains the exchange-correlation potential v_{xc} incorporating all the exchange and correlation effects of the system. The formalism has been successfully applied to the case of atoms in strong laser fields [8,9] and in the calculation of atomic excitation energies [10] using the exchange-only (x-only) time-dependent optimized potential method (TDOPM) [11]. The TDOPM has important advantages over other common approaches, such as the adiabatic local density approximation (ALDA) [10]. In contrast to ALDA the TDOPM is self-interaction free and incorporates memory effects. In this Letter we develop a theoretical approach in which we make a connection between the many-particle Green's function theory and TDDFT. This enables one to extend the above-mentioned x-only TDOPM calculations and include correlation effects.

Conventional methods treat the external time-dependent field perturbatively. However, the perturbation series breaks down when the expansion parameter (the external field) becomes large. Our approach will be to find an exact solution for the time evolution of the noninteracting (zeroth-order) system in the presences of the external field. The external field is thereby treated completely nonperturbatively. The two-particle interactions, on the other hand, are treated perturbatively using Green's function techniques. This requires the use of a Green's function formalism in which the zeroth-order system is already a nonstationary time-dependent system. Such a formalism has been developed by Keldysh and elaborated on by others [12–17]. In this Letter we will demonstrate its usefulness in connection with the TDDFT of atoms and molecules in strong fields.

We discuss an interacting system of N electrons with the Hamiltonian

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}, \tag{1}$$

where $\hat{T}$ represents the kinetic energy operator, $\hat{V}$ the time-dependent external field, and $\hat{W}$ the Coulombic interparticle repulsion. The external field is assumed to be constant in time for times $t < t_0$ when the system is assumed to be in its ground state. We are therefore also describing switch-on processes. The time evolution of the system under influence of the time-dependent external field is described by the time-evolution operator

$$\hat{V}(t_2, t_1) = T \exp\left[-i \int_{t_1}^{t_2} \hat{H}(t)\, dt\right], \tag{2}$$

where T is the usual time-ordering operator. In TDDFT the system is also described by the time-dependent Kohn-Sham Hamiltonian

$$\hat{H}_s(t) = \hat{T} + \hat{V}_s(t), \tag{3}$$

where $\hat{V}_s$ is the one-particle operator representing the Kohn-Sham potential. The Kohn-Sham noninteracting state can be represented by a Slater determinant wave function whose orbitals satisfy the time-dependent Kohn-Sham equations [5,6]

$$\begin{gathered}[-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r}t)]\phi_i(\mathbf{r}t) = i\partial_t \phi_i(\mathbf{r}t), \\ n(\mathbf{r}t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}t)|^2, \\ v_s(\mathbf{r}t) = v(\mathbf{r}t) + v_H(\mathbf{r}t) + v_{\mathrm{xc}}(\mathbf{r}t),\end{gathered} \tag{4}$$

where $v_H(\mathbf{r}t) = \int d^3r'\, n(\mathbf{r}'t)/|\mathbf{r} - \mathbf{r}'|$ denotes the time-dependent Hartree potential and $v(\mathbf{r}t)$ represents the time-dependent external field. The quantity $v_{\mathrm{xc}}(\mathbf{r}t)$ denotes the time-dependent exchange-correlation potential, the determination of which is a central problem in TDDFT.

The time evolution of the Kohn-Sham noninteracting state is determined by the evolution operator

$$\hat{U}_s(t_2, t_1) = T \exp\left[-i \int_{t_1}^{t_2} \hat{H}_s(t)\, dt \right]. \tag{5}$$

We can now express the expectation value of any operator $\hat{A}$ at time t' in terms of Kohn-Sham quantities by

$$\langle \hat{A}(t') \rangle = \langle \Phi_0 | \hat{S}(-\infty, t') \hat{A}_I(t') \hat{S}(t', -\infty) | \Phi_0 \rangle . \tag{6}$$

Here $\hat{A}_I$ and $\hat{S}$ are, respectively, the operator $\hat{A}$ and the time-evolution operator in the interaction picture defined by

$$\hat{A}_I(t) = \hat{U}_s(t_0, t) \hat{A}(t) \hat{U}_s(t, t_0) , \tag{7}$$

$$\begin{aligned} \hat{S}(t_2, t_1) &= \hat{U}_s(t_0, t_2) \hat{V}(t_2, t_1) \hat{U}_s(t_1, t_0) \\ &= T \exp\left[-i \int_{t_1}^{t_2} (\hat{H} - \hat{H}_s)_I(t)\, dt \right]. \end{aligned} \tag{8}$$

Equation (6) also includes an adiabatic switching on of the interaction (for times $t < t_0$) of the form $\exp[\epsilon(t - t_0)](\hat{H} - \hat{H}_s)$. This relates the interacting stationary state $|\Psi_0\rangle$ at t_0 to a noninteracting state $|\Phi_0\rangle$ at $t \longrightarrow -\infty$. We must also introduce a static external potential v_ϵ defined by the requirement that for $t < t_0$ the density of the system with the adiabatically switched on two-particle interaction remains equal to the density of the Kohn-Sham system for all values of ϵ. For times $t < t_0$ this density is constant in time. The use of such an adiabatic connection formula is common practice in DFT for stationary systems. It follows that $|\Phi_0\rangle$ can be identified with the Kohn-Sham state of the interacting system at $t \longrightarrow -\infty$. The limit $\epsilon \downarrow 0$ is taken after evaluation of the expectation value Eq. (6).

At this point an important difference with respect to the case of stationary systems becomes apparent. For these systems we turn off the interaction adiabatically and return to the noninteracting ground state. If we use this property, we can make the time variable in Eq. (6) run from $-\infty$ to $+\infty$ and expand in time-ordered products with the help of Wick's theorem. This is, however, not possible for the case of time-dependent systems. Because of the external field being switched on at $t = t_0$ the system will always end up in a nonstationary state, even if we turn off the interaction adiabatically. In order to still be able to apply the usual many-body techniques we use a method due to Keldysh [12,14,17]. We parametrize the physical time $t(\tau)$ by a pseudotime τ in such a way that if τ runs from $-\infty$ to 0 then t runs from $-\infty$ to t' and if τ runs from 0 to $+\infty$ then t runs back from t' to $-\infty$. The actual form of the parametrization $t(\tau)$ is not important since our final results will be independent of it. We now define a time ordering T_C (where C stands for contour) in the pseudotime variable τ. Then Eq. (6) becomes

$$\langle \hat{A}(t') \rangle = \langle \Phi_0 | T_C [\hat{S}_C(+\infty, -\infty) \hat{A}(t')] | \Phi_0 \rangle , \tag{9}$$

where

$$S_C(\tau_2, \tau_1) = T_C \exp\left[-i \int_{\tau_1}^{\tau_2} d\tau\, t'(\tau)\, (\hat{H} - \hat{H}_s)_I [t(\tau)] \right], \tag{10}$$

where $t'(\tau) = dt/d\tau$. If we further define $t_i = t(\tau_i)$ then the one-particle Green's function is defined by

$$\begin{aligned} iG(\mathbf{r}_1 \tau_1, \mathbf{r}_2 \tau_2) = {}& \theta(\tau_1 - \tau_2) \langle \Psi_0 | \psi_H(\mathbf{r}_1 t_1) \psi_H^\dagger(\mathbf{r}_2 t_2) | \Psi_0 \rangle \\ & - \theta(\tau_2 - \tau_1) \langle \Psi_0 | \psi_H^\dagger(\mathbf{r}_2 t_2) \psi_H(\mathbf{r}_1 t_1) | \Psi_0 \rangle , \end{aligned} \tag{11}$$

where $\psi_H^\dagger$ and ψ_H are the creation and annihilation operators in the Heisenberg picture. With the definitions (9) and (11) we can carry out the usual diagrammatic perturbation theory. The only difference is that time integrations in the diagrams must be replaced by contour integrations in the pseudotime τ. The Green's function satisfies the equation of motion

$$\begin{aligned} [i\partial_{t_1} - h_s(\mathbf{r}_1 t_1)] G(\mathbf{r}_1 \tau_1, \mathbf{r}_2 \tau_2) = {}& \delta_C(t_1 - t_2) \\ & + \int_{-\infty}^{+\infty} d\tau_3\, t'(\tau_3) \int d^3 r_3 [\Sigma_{xc}(\mathbf{r}_1 \tau_1, \mathbf{r}_3 \tau_3) \\ & - \delta_C(t_1 - t_3) \delta(\mathbf{r}_1 - \mathbf{r}_3) v_{xc}(\mathbf{r}_1 t_1)] G(\mathbf{r}_3 \tau_3, \mathbf{r}_2 \tau_2) , \end{aligned} \tag{12}$$

where h_s is the Kohn-Sham Hamiltonian and v_{xc} is the exchange-correlation (xc) potential of time-dependent Kohn-Sham theory [5,6]. We further defined a contour delta function [14] by $\delta_C(t_1 - t_2) = \delta(\tau_1 - \tau_2)/t'(\tau_1)$. The term Σ_{xc} represents the xc parts of the self-energy Σ (that is, all diagrams except those involving the external potential difference $v - v_s$ and the Hartree potential). When we use the Dyson equation and the fact that the electron density is given by

$$n(\mathbf{r} t_1) = -i \lim_{\tau_2 \downarrow \tau_1} G(\mathbf{r} \tau_1, \mathbf{r} \tau_2) = -i \lim_{\tau_2 \downarrow \tau_1} G_s(\mathbf{r} \tau_1, \mathbf{r} \tau_2) \tag{13}$$

for both the interacting system and the Kohn-Sham system we obtain the required integral equation for $v_{\mathrm{xc}}(\mathbf{r} t)$

$$\begin{aligned} & \int_{-\infty}^{+\infty} d\tau_2 \int d^3 r_2\, t'(\tau_2) G(\mathbf{r}_1 \tau_1, \mathbf{r}_2 \tau_2) G_s(\mathbf{r}_2 \tau_2, \mathbf{r}_1 \tau_1) v_{\mathrm{xc}}(\mathbf{r}_2 \tau_2) \\ & \quad = \int_{-\infty}^{+\infty} d\tau_3 \int_{-\infty}^{+\infty} d\tau_4 \int d^3 r_3 \int d^3 r_4\, t'(\tau_3) t'(\tau_4) G_s(\mathbf{r}_1 \tau_1, \mathbf{r}_3 \tau_3) \Sigma_{\mathrm{xc}}(\mathbf{r}_3 \tau_3, \mathbf{r}_4 \tau_4) G(\mathbf{r}_4 \tau_4, \mathbf{r}_1 \tau_1) , \end{aligned} \tag{14}$$

where G_s is the Green's function of the time-dependent Kohn-Sham system, explicitly given in terms of the Kohn-Sham orbitals ϕ_i of Eq. (4) by

$$iG_s(\mathbf{r}_1\tau_1,\mathbf{r}_2\tau_2) = \theta(\tau_1 - \tau_2)\sum_{i>N}\phi_i(\mathbf{r}_1t_1)\phi_i^*(\mathbf{r}_2t_2) - \theta(\tau_2 - \tau_1)\sum_{i=1}^{N}\phi_i(\mathbf{r}_1t_1)\phi_i^*(\mathbf{r}_2t_2)\,. \tag{15}$$

Equation (14) is the main result of this Letter. It represents the generalization to time-dependent systems of the integral equation derived by Sham and Schlüter [18,19] for the case of stationary systems.

Equation (14) is a convenient starting point for making successive approximations within time-dependent density-functional theory. In the x-only case for instance, where we replace Σ_{xc} by Σ_x and G by G_s, this equation reduces to the x-only equations of the TDOPM [11]. In this approximation we have

$$\Sigma_x(\mathbf{r}_3\tau_3,\mathbf{r}_4\tau_4) = -\frac{\delta(\tau_3 - \tau_4)}{t'(\tau_4)}\sum_{i=1}^{N}\frac{\phi_i(\mathbf{r}_3t_3)\phi_i^*(\mathbf{r}_4t_4)}{|\mathbf{r}_3 - \mathbf{r}_4|}\,. \tag{16}$$

Insertion of Eqs. (16) and (15) into Eq. (14) then yields the x-only TDOPM equations [11] for the exchange potential v_x

$$\sum_{i=1}^{N}\int_{-\infty}^{+\infty}dt_2\int d^3r_2[v_x(\mathbf{r}_2t_2) - u_{x,i}(\mathbf{r}_2t_2)]\phi_i(\mathbf{r}_1t_1)\phi_i^*(\mathbf{r}_2t_2) \times G_R(\mathbf{r}_1t_1,\mathbf{r}_2t_2) + \text{c.c.} = 0\,, \tag{17}$$

where

$$u_{x,i}(\mathbf{r}t) = -\frac{1}{\phi_i^*(\mathbf{r}t)}\sum_{k=1}^{N}\int d^3\mathbf{r}'\,\frac{\phi_i^*(\mathbf{r}'t)\phi_k(\mathbf{r}'t)\phi_k^*(\mathbf{r}t)}{|\mathbf{r} - \mathbf{r}'|} \tag{18}$$

and

$$iG_R(\mathbf{r}_1t_1,\mathbf{r}_2t_2) = \theta(t_1 - t_2)\sum_{i=1}^{+\infty}\phi_i(\mathbf{r}_1t_1)\phi_i^*(\mathbf{r}_2t_2)\,. \tag{19}$$

The Green's function G_R is the retarded Kohn-Sham Green's function. This Green's function appears in the above expression as a result of the fact that the $\tau_2 > \tau_1$ integration leads to a relative minus sign as compared to the integration over $\tau_2 < \tau_1$ when the integration in the pseudotime τ_2 is replaced by integration in the physical time t_2. The occurrence of retarded Green's functions is a typical feature of the Keldysh formalism. It implies that physical quantities, such as response functions, have the correct physical causality properties. In the case of the x-only TDOPM equations the presence of the retarded Green's function implies that the determination of $v_x(\mathbf{r}t_1)$ at time t_1 requires knowledge of the system for all times $t_2 < t_1$. We can proceed further and systematically go beyond the x-only TDOPM approximation by making successively better approximations for the self-energy Σ_{xc} and Green's function G in the central equation [Eq. (14)]. Electron correlation may have a large influence on the physically interesting memory effects in v_{xc}. Therefore our Keldysh diagrammatic method, which in principle allows an exact treatment of electron correlations, provides a direct means for a systematic study of these memory effects.

As a final remark we mention that Eq. (14) can also be obtained from a variational principle in the same spirit as in the work by Sham and Schlüter [18,19]. For reasons that soon will become evident we define an action functional of G and G_s as

$$A[G,G_s] = A_0[G_s] + \Phi[G] - \int_{-\infty}^{+\infty}d\tau\,t'(\tau) \times \int d^3r\,\langle\mathbf{r}\tau|\ln(1 - \Sigma G_s)|\mathbf{r}\tau\rangle\,, \tag{20}$$

where the mathematical meaning of the last term is defined by its Taylor series and insertion of complete sets $|\mathbf{r}\tau\rangle\langle\mathbf{r}\tau|$. The functional A_0 is defined by

$$A_0[G_s] = \int_{-\infty}^{+\infty}d\tau_1t'(\tau_1) \times \lim_{\tau_2\downarrow\tau_1}\left[i\partial_{t_1} - \left(-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}t_1)\right)\right]G_s(\mathbf{r}_1\tau_1,\mathbf{r}_2\tau_2)\,, \tag{21}$$

where v is the external potential of the interacting system. For this functional it follows from the equation of motion for G_s that

$$\frac{\delta A_0}{\delta G_s(\mathbf{r}_1\tau_1,\mathbf{r}_2\tau_2)} = \delta_C(t_1 - t_2)\delta(\mathbf{r}_1 - \mathbf{r}_2) \times [v(\mathbf{r}_1t_1) - v_s(\mathbf{r}_1t_1)]\,. \tag{22}$$

The functional Φ is defined by [20]

$$\Phi[G] = \sum_n\frac{1}{2n}\int_{-\infty}^{+\infty}d\tau_1\int_{-\infty}^{+\infty}d\tau_2\int d^3r_1 \times \int d^3r_2t'(\tau_1)t'(\tau_2)\Sigma^{(n)}(\mathbf{r}_1\tau_1,\mathbf{r}_2\tau_2)G(\mathbf{r}_2\tau_2,\mathbf{r}_1\tau_1)\,, \tag{23}$$

where $\Sigma^{(n)}$ represents the diagrams in Σ with n interaction lines and in which Green's function lines are given by the full Green's function G. The functional Φ has the property [20]

$$\frac{\delta\Phi}{\delta G(\mathbf{r}_2\tau_2,\mathbf{r}_1\tau_1)} = \Sigma(\mathbf{r}_1\tau_1,\mathbf{r}_2\tau_2) - \delta_C(t_1 - t_2)\delta(\mathbf{r}_1 - \mathbf{r}_2) \times [v(\mathbf{r}_1t_1) - v_s(\mathbf{r}_1t_1)] \tag{24}$$

at the solution point where G satisfies the Dyson equation. From the Runge-Gross theorem [7] we see that both G and G_s are functionals of the electron density or, equivalently, of the Kohn-Sham potential v_s. Therefore the functional (20) can be viewed as a functional of v_s. Requiring stationarity of this functional with respect to variations in v_s then yields

$$0 = \frac{\delta A}{\delta v_s} = \frac{\delta A}{\delta G_s}\frac{\delta G_s}{\delta v_s} + \frac{\delta A}{\delta G}\frac{\delta G}{\delta v_s}\,. \tag{25}$$

By working out the derivatives in this equation explicitly and using the fact that both G and G_s yield the same density one finds [19] the required Eq. (14). Our results can be summarized as follows: We have shown that one can derive an exact integral equation for v_{xc} within TDDFT using the Green's function formalism of Keldysh. We have further shown that one can derive this equation from an action principle.

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