Time-Dependent Optimized Effective Potential

C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross

Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

(Received 23 December 1993)

Given an expression for the quantum mechanical action $A[\phi_{j\sigma}]$ of an N-electron system as a functional of N time-dependent spin orbitals, we present a method of constructing the variationally best local time-dependent single-particle potentials $v_\sigma(\mathbf{r}t)$ which, when inserted in time-dependent single-particle Schrödinger equations for the spin-up and spin-down electrons yield orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$ that make $A[\phi_{j\sigma}]$ stationary. We also propose a simplification of this scheme leading to a time-dependent generalization of the static optimized effective potentials recently introduced by Krieger, Li, and Iafrate [Phys. Lett. A **146**, 256 (1990)].

PACS numbers: 31.10.+z, 03.65.–w, 31.15.Ew

Owing to rapid experimental progress in the field of laser physics, ultrashort laser pulses of very high intensity have become available in recent years. The electric field produced in such pulses can reach the strength of the electric field caused by atomic nuclei. If an atomic system is placed in the focus of such a laser pulse, one observes a wealth of new phenomena [1] which cannot be explained by perturbation theory. The nonperturbative quantum mechanical description of interacting particles moving in a very strong time-dependent external field therefore has become a prominent problem of theoretical physics.

Since its rigorous foundation by Runge and Gross [2], time-dependent density functional theory (TDDFT) [3–5] is available as a method to deal with time-dependent many-particle problems of this kind. The central statement of TDDFT is that the time-dependent density $n(\mathbf{r}t)$ of a system of *interacting* particles moving in an external potential $v_{\text{ext}}(\mathbf{r}t)$ can be calculated, in principle exactly, from a set of time-dependent *single-particle* equations which can be viewed as the time-dependent counterpart of the Kohn-Sham scheme. These single-particle equations involve an exchange-correlation potential, $v_{\text{xc}}(\mathbf{r}t)$, which is a functional of $n(\mathbf{r}t)$ and has to be approximated in practice. An extension of TDDFT to spin-polarized systems has been proposed by Liu and Vosko [6]. Neglecting magnetic effects associated with the orbital motion of the electrons, they consider external time-dependent potentials acting on electrons with spin σ only. In this case, two different $v_{\text{xc}\sigma}(\mathbf{r}t)$ corresponding to the two spin orientations are needed which are functionals of the spin densities $n_\sigma(\mathbf{r}t)$. Again, the key problem is to obtain good approximations of $v_{\text{xc}\sigma}(\mathbf{r}t)$. To date, only a rather crude *adiabatic* approximation is available which adopts the functional form of the *static* exchange-correlation potential.

The purpose of this paper is to introduce a different approach to the construction of $v_{\text{xc}\sigma}(\mathbf{r}t)$ which can be viewed as a time-dependent version of the so-called optimized potential method (OPM). The approach leads to $v_{\text{xc}\sigma}$ as a function of $(\mathbf{r}t)$ rather than to $v_{\text{xc}\sigma}$ as an explicit functional of the spin densities. The OPM of stationary systems [7,8] takes as starting point a given expression for the total energy $E[\varphi_{j\sigma}]$ of an N-electron system as a functional of a set of spin orbitals $\{\varphi_{j\sigma}(\mathbf{r})\}$ (e.g., the Hartree-Fock total energy functional in the exchange-only case). Then, the variationally best *local* effective potential is determined for each spin orientation such that, when inserted in a stationary single-particle Schrödinger equation, it yields the set of $N = \sum_\sigma N_\sigma$ eigenfunctions (corresponding to the N_σ lowest eigenvalues) that minimize $E[\varphi_{j\sigma}]$. In practice, the full OPM scheme is computationally quite involved since it requires the numerical solution of an integral equation for each $v_{\text{xc}\sigma}(\mathbf{r})$. As a consequence, complete OPM calculations have been performed mainly for problems where the potential is a function of a single variable, e.g., for spherically symmetric atoms [8–13]. There exists, however, an approximate OPM scheme, recently proposed by Krieger, Li, and Iafrate (KLI) [14–21], which is numerically as easy to handle as the ordinary Kohn-Sham scheme. This simplified OPM has been applied very successfully to the calculation of atomic properties.

In order to derive a time-dependent generalization of the OPM we consider an N-electron system at some finite time t_0 which, for all times up until t_0, has been in the ground state associated with an external potential $v_{0\sigma}(\mathbf{r})$ (e.g., a nuclear Coulomb potential plus a static magnetic field coupling to the electronic spins only). We assume that the corresponding stationary OPM problem has been solved for that system, i.e., a local effective potential for each spin orientation and a set of N spin orbitals $\{\varphi_{j\sigma}\}$ (with energy eigenvalues $\varepsilon_{j\sigma}$) minimizing a given energy functional $E[\varphi_{j\sigma}]$ are assumed to be known. At $t = t_0$ an additional time-dependent potential $v_{1\sigma}(\mathbf{r}t)$ is switched on. Our goal is to determine the time evolution of the system under the influence of the total external potential $v_{\text{ext}\sigma}(\mathbf{r}t) = v_{0\sigma}(\mathbf{r}) + v_{1\sigma}(\mathbf{r}t)$ from t_0 up until an arbitrary later time t_1. To construct an optimized local effective potential we start with the quantum mechanical action

 0031-9007/95/74(6)/872(4)$06.00

$$A[\phi_{j\sigma}] = \sum_\sigma \sum_j^{N_\sigma} \int_{-\infty}^{t_1} dt \int d^3r\, \phi_{j\sigma}^*(\mathbf{r}t)\,(i\partial/\partial t + \nabla^2/2)\phi_{j\sigma}(\mathbf{r}t) - \sum_\sigma \int_{-\infty}^{t_1} dt \int d^3r\, n_\sigma(\mathbf{r}t) v_{\mathrm{ext}\sigma}(\mathbf{r}t) - \frac{1}{2}\int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{n(\mathbf{r}t)n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} - A_{\mathrm{xc}}[\phi_{j\sigma}] \quad (1)$$

written as a functional of $N = \sum_\sigma N_\sigma$ time-dependent spin orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$, where $n(\mathbf{r}t) = \sum_\sigma n_\sigma(\mathbf{r}t) = \sum_\sigma \sum_j^{N_\sigma} |\phi_{j\sigma}(\mathbf{r}t)|^2$ [atomic (Hartree) units are used throughout]. In the following no specific approximation is used for the exchange-correlation functional $A_{\mathrm{xc}}[\phi_{j\sigma}]$, but we mention that in an exchange-only theory A_{xc} would be replaced by the time-dependent Hartree-Fock (TDHF) expression

$$A_{\mathrm{x}} = -\tfrac{1}{2}\sum_\sigma \sum_{i,j}^{N_\sigma} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r'\, \phi_{i\sigma}^*(\mathbf{r}'t)\phi_{j\sigma}(\mathbf{r}'t)\phi_{i\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}t) \Big/ |\mathbf{r}-\mathbf{r}'|\,. \quad (2)$$

The orbitals are solutions of the time-dependent Schrödinger equation

$$i(\partial/\partial t)\phi_{j\sigma}(\mathbf{r}t) = [-\nabla^2/2 + v_\sigma(\mathbf{r}t)]\phi_{j\sigma}(\mathbf{r}t), \qquad j = 1,\ldots,N_\sigma\,, \quad (3)$$

with the initial condition $\phi_{j\sigma}(\mathbf{r}t) = \varphi_{j\sigma}(\mathbf{r})\exp[-i\varepsilon_{j\sigma}(t-t_0)]$ for $-\infty < t \le t_0$. The local effective potential is given by

$$v_\sigma(\mathbf{r}t) = v_{\mathrm{ext}\sigma}(\mathbf{r}t) + \int d^3r'\, n(\mathbf{r}'t)/|\mathbf{r}-\mathbf{r}'| + v_{\mathrm{xc}\sigma}(\mathbf{r}t)\,, \quad (4)$$

$v_\sigma(\mathbf{r}t)$ has to be determined in such a way that the $\{\phi_{j\sigma}(\mathbf{r}t)\}$, resulting from Eq. (3), render the total action functional $A[\phi_{j\sigma}]$ stationary. Therefore, we have to solve the following variational problem:

$$\frac{\delta A[\phi_{j\sigma}]}{\delta v_\sigma(\mathbf{r}t)} = \sum_j^{N_\sigma} \int_{-\infty}^{+\infty} dt' \int d^3r' \left(\frac{\delta A[\phi_{j\sigma}]}{\delta \phi_{j\sigma}(\mathbf{r}'t')} \frac{\delta \phi_{j\sigma}(\mathbf{r}'t')}{\delta v_\sigma(\mathbf{r}t)} + \frac{\delta A[\phi_{j\sigma}]}{\delta \phi_{j\sigma}^*(\mathbf{r}'t')} \frac{\delta \phi_{j\sigma}^*(\mathbf{r}'t')}{\delta v_\sigma(\mathbf{r}t)} \right) = 0\,. \quad (5)$$

In order to compute the functional derivative $\delta A/\delta\phi_{j\sigma}$, the first term of Eq. (1) has to be integrated by parts with respect to the time coordinate. We impose the usual boundary condition on $\phi_{j\sigma}(\mathbf{r}t)$ at $t = t_1$, i.e., $\delta\phi_{j\sigma}(\mathbf{r}t_1) = 0$, thus obtaining a zero boundary contribution. The other boundary contribution at $t = -\infty$ vanishes, too, because the action functional (1), in order to be well defined, is to be calculated by introducing the usual factor $\exp(\eta t)$ in the integrand and taking $\lim_{\eta\to 0^+}$ after the integration. Then, substituting Eq. (4) and making use of the fact that $\phi_{j\sigma}^*$ solves the complex conjugate of the Schrödinger equation (3), we find

$$\frac{\delta A[\phi_{j\sigma}]}{\delta \phi_{j\sigma}(\mathbf{r}'t')} = [v_{\mathrm{xc}\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}j\sigma}(\mathbf{r}'t')] \times \phi_{j\sigma}^*(\mathbf{r}'t')\theta(t_1 - t')\,, \quad (6)$$

where

$$u_{\mathrm{xc}j\sigma}(\mathbf{r}t) = \frac{1}{\phi_{j\sigma}^*(\mathbf{r}t)} \frac{\delta A_{\mathrm{xc}}[\phi_{j\sigma}]}{\delta \phi_{j\sigma}(\mathbf{r}t)}\,, \quad (7)$$

and $\theta(x)$ denotes the usual step function (1 for $x > 0$, 0 for $x < 0$). An analogous expression is obtained for $\delta A/\delta\phi_{j\sigma}^*$, which, for all reasonable (i.e., real) functionals $A[\phi_{j\sigma}]$, is the complex conjugate of (6).

In order to evaluate $\delta A/\delta v_\sigma$ from Eq. (5), we further need the functional derivatives $\delta\phi_{j\sigma}/\delta v_\sigma$ and $\delta\phi_{j\sigma}^*/\delta v_\sigma$. To this end, we consider the orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$ as unperturbed states, remembering that at $t = t_1$ the orbitals are held *fixed* with respect to variations in the total potential. We therefore start from $t = t_1$, subject the system to an *additional* small perturbation $\delta v_\sigma(\mathbf{r}t)$ and let it evolve *backward* in time. The corresponding perturbed wave functions $\phi'_{j\sigma}(\mathbf{r}t)$ are determined by the backward Schrödinger equation

$$i(\partial/\partial t)\phi'_{j\sigma}(\mathbf{r}t) = [-\nabla^2/2 + v_\sigma(\mathbf{r}t) + \delta v_\sigma(\mathbf{r}t)]\phi'_{j\sigma}(\mathbf{r}t)\,, \qquad j = 1,\ldots,N_\sigma\,, \quad (8)$$

with the initial condition $\phi'_{j\sigma}(\mathbf{r}t_1) = \phi_{j\sigma}(\mathbf{r}t_1)$. This problem cannot be treated directly with time-dependent perturbation theory as described in standard textbooks because the unperturbed Hamiltonian is already time dependent. Nevertheless, Dirac's method of variation of constants can be applied in a straightforward manner. It follows [22] that the first-order correction to the wave function $\phi_{j\sigma}(\mathbf{r}t)$ under the influence of $\delta v_\sigma(\mathbf{r}t)$ is given by

$$\delta\phi_{j\sigma}(\mathbf{r}t) = i\sum_{k=1}^{\infty} \int_t^{t_1} dt' \int d^3r'\, \phi_{k\sigma}^*(\mathbf{r}'t')\delta v_\sigma(\mathbf{r}'t') \times \phi_{j\sigma}(\mathbf{r}'t')\phi_{k\sigma}(\mathbf{r}t)\,. \quad (9)$$

Therefore, the desired functional derivative is

$$\frac{\delta\phi_{j\sigma}(\mathbf{r}'t')}{\delta v_\sigma(\mathbf{r}t)} = i\sum_{k=1}^{\infty} \phi_{k\sigma}^*(\mathbf{r}t)\phi_{j\sigma}(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t') \times \theta(t_1 - t)\theta(t - t')\,. \quad (10)$$

Once again, $\delta\phi_{j\sigma}^*/\delta v_\sigma$ leads to the complex conjugate expression. We can now insert (6) and (10) in the variational equation (5), and the result is the time-dependent OPM (TDOPM) integral equation for the local exchange-correlation potential $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$:

$$i\sum_j^{N_\sigma} \int_{-\infty}^{t_1} dt' \int d^3r' [v_{\mathrm{xc}\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}j\sigma}(\mathbf{r}'t')] \times \phi_{j\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}'t')K_\sigma(\mathbf{r}t,\mathbf{r}'t') + \text{c.c.} = 0\,. \quad (11)$$

The kernel $K_\sigma(\mathbf{r}t,\mathbf{r}'t') = \sum_{k=1}^{\infty}\phi^*_{k\sigma}(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t')\theta(t-t')$ can be identified with the Green's function of the system, which satisfies the differential equation

$$\{i\partial/\partial t' - [-\nabla'^2/2 + v_\sigma(\mathbf{r}'t')]\}K_\sigma(\mathbf{r}t,\mathbf{r}'t') = -i\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \quad (12)$$

with the initial condition $K_\sigma(\mathbf{r}t,\mathbf{r}'t') = 0$ for $t' > t$. The TDOPM scheme is now complete: the integral equation (11) has to be solved for $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$ in combination with the Schrödinger equation (3) and the differential equation (12) for $K_\sigma(\mathbf{r}t,\mathbf{r}'t')$, both with the appropriate initial conditions. It is easy to show that in the time interval $[-\infty,t_1]$ the exchange-correlation potential $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$ is only determined up to within an additive, purely time-dependent function $c(t)$ (as expected in view of the time-dependent Hohenberg-Kohn theorem [2]). Also it can be demonstrated [22] that for time-independent external potentials $[v_{1\sigma}(\mathbf{r}t) \equiv 0]$ the TDOPM reduces to the stationary OPM.

The numerical implementation of the full TDOPM is an extremely demanding task. It is therefore most desirable to obtain a simplified scheme. To this end we shall perform a transformation of Eq. (11) similar to the one proposed by KLI in the stationary case [18,21]. This will lead to an alternative but still exact form of the TDOPM scheme which allows one to construct approximations of $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$ which are *explicit* functionals of the orbitals $\{\phi_{j\sigma}\}$, thereby avoiding the need to solve the integral equation. Following Refs. [18] and [21], we define

$$p_{j\sigma}(\mathbf{r}t) = \frac{-i}{\phi^*_{j\sigma}(\mathbf{r}t)}\int_{-\infty}^{t_1}dt'\int d^3r'[v_{\mathrm{xc}\sigma}(\mathbf{r}'t') - u_{\mathrm{xc}j\sigma}(\mathbf{r}'t')] \times \phi^*_{j\sigma}(\mathbf{r}'t')\sum_{\substack{k=1\\k\neq j}}^{\infty}\phi^*_{k\sigma}(\mathbf{r}t)\phi_{k\sigma}(\mathbf{r}'t')\theta(t-t'), \quad (13)$$

and

$$\overline{u}_{\mathrm{xc}j\sigma}(t) = \int d^3r\, n_{j\sigma}(\mathbf{r}t)u_{\mathrm{xc}j\sigma}(\mathbf{r}t), \quad (14)$$

where $n_{j\sigma}(\mathbf{r}t) = |\phi_{j\sigma}(\mathbf{r}t)|^2$. Equation (11) can then be written as

$$\sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)p_{j\sigma}(\mathbf{r}t) + \text{c.c.} = -i\sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\int_{-\infty}^{t}dt' \times [\overline{u}_{\mathrm{xc}j\sigma}(t') - \overline{u}^*_{\mathrm{xc}j\sigma}(t')], \quad (15)$$

and it is easy to show that

$$\int d^3r\, n_{j\sigma}(\mathbf{r}t)p_{j\sigma}(\mathbf{r}t) = 0. \quad (16)$$

Evaluating $\phi_{j\sigma}(\mathbf{r}t)[-i\partial/\partial t + \nabla^2/2 - v_\sigma(\mathbf{r}t)]\phi^*_{j\sigma}(\mathbf{r}t) \times p_{j\sigma}(\mathbf{r}t)$, we find after some straightforward algebra that $p_{j\sigma}(\mathbf{r}t)$ satisfies the following differential equation:

$$\nabla\cdot[n_{j\sigma}(\mathbf{r}t)\nabla p_{j\sigma}(\mathbf{r}t)]/2 - in_{j\sigma}(\mathbf{r}t)\partial p_{j\sigma}(\mathbf{r}t)/\partial t - i\mathbf{J}_{j\sigma}(\mathbf{r}t)\cdot\nabla p_{j\sigma}(\mathbf{r}t) = -n_{j\sigma}(\mathbf{r}t)\{v_{\mathrm{xc}\sigma}(\mathbf{r}t) - u_{\mathrm{xc}j\sigma}(\mathbf{r}t) - [\overline{v}_{\mathrm{xc}j\sigma}(t) - \overline{u}_{\mathrm{xc}j\sigma}(t)]\}, \quad (17)$$

with the current density $\mathbf{J}_{j\sigma}(\mathbf{r}t) = (2i)^{-1}[\phi^*_{j\sigma}(\mathbf{r}t)\nabla\phi_{j\sigma}(\mathbf{r}t) - \phi_{j\sigma}(\mathbf{r}t)\nabla\phi^*_{j\sigma}(\mathbf{r}t)]$ and $\overline{v}_{\mathrm{xc}j\sigma}(t) = \int d^3r\, n_{j\sigma}(\mathbf{r}t)v_{\mathrm{xc}\sigma}(\mathbf{r}t)$. Finally, operating with ∇^2 on Eq. (15) and using (17) we find

$$v_{\mathrm{xc}\sigma}(\mathbf{r}t) = \frac{1}{n_\sigma(\mathbf{r}t)}\sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\,\frac{1}{2}\,[u'_{\mathrm{xc}j\sigma}(\mathbf{r}t) + u'^*_{\mathrm{xc}j\sigma}(\mathbf{r}t)] + \frac{1}{n_\sigma(\mathbf{r}t)}\sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\left\{\overline{v}_{\mathrm{xc}j\sigma}(t) - \frac{1}{2}\,[\overline{u}_{\mathrm{xc}j\sigma}(t) + \overline{u}^*_{\mathrm{xc}j\sigma}(t)]\right\} + \frac{i}{4n_\sigma(\mathbf{r}t)}\sum_j^{N_\sigma}\nabla^2 n_{j\sigma}(\mathbf{r}t)\int_{-\infty}^{t}dt'[\overline{u}_{\mathrm{xc}j\sigma}(t') - \overline{u}^*_{\mathrm{xc}j\sigma}(t')], \quad (18)$$

where

$$u'_{\mathrm{xc}j\sigma}(\mathbf{r}t) = u_{\mathrm{xc}j\sigma}(\mathbf{r}t) + \frac{1}{n_{j\sigma}(\mathbf{r}t)}\left[\frac{1}{2}\nabla\cdot[p_{j\sigma}(\mathbf{r}t)\nabla n_{j\sigma}(\mathbf{r}t)] + in_{j\sigma}(\mathbf{r}t)\frac{\partial}{\partial t}\,p_{j\sigma}(\mathbf{r}t) + i\mathbf{J}_{j\sigma}(\mathbf{r}t)\cdot\nabla p_{j\sigma}(\mathbf{r}t)\right]. \quad (19)$$

Equations (18) and (19) together with the differential equation (17) for $p_{j\sigma}(\mathbf{r}t)$ and the condition (16) [which can be used to fix the constant left undetermined by Eq. (17)] represent an exact alternative formulation of the TDOPM scheme. The advantage of Eq. (18) lies in the fact that it is a very convenient starting point for constructing approximations of $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$ as explicit functionals of the $\{\phi_{j\sigma}(\mathbf{r}t)\}$: It is only necessary to approximate $p_{j\sigma}(\mathbf{r}t)$ in Eq. (19) by a suitably chosen functional of the orbitals. We can then readily solve Eq. (18) *analytically* for $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$, as we shall show below.

We expect an *approximate* potential $\tilde{v}_{\mathrm{xc}\sigma}(\mathbf{r}t)$ defined in this way to be close to the exact $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$. This conjecture is based on the observation that the difference between $\tilde{v}_{\mathrm{xc}\sigma}$ and $v_{\mathrm{xc}\sigma}$ is entirely accounted for by the differences $u'_{\mathrm{xc}j\sigma} - u_{\mathrm{xc}j\sigma}$, which are zero if averaged over the $j\sigma$th orbital:

$$\overline{u}'_{\mathrm{xc}j\sigma}(t) - \overline{u}_{\mathrm{xc}j\sigma}(t) = \tfrac{1}{2}\int d^3r\nabla\cdot[p_{j\sigma}(\mathbf{r}t)\nabla n_{j\sigma}(\mathbf{r}t)] + i\int d^3r\left[n_{j\sigma}(\mathbf{r}t)\frac{\partial}{\partial t}\,p_{j\sigma}(\mathbf{r}t) + \mathbf{J}_{j\sigma}(\mathbf{r}t)\cdot\nabla p_{j\sigma}(\mathbf{r}t)\right] = 0. \quad (20)$$

The last equality follows [22] by using the divergence theorem and the continuity equation for the $j\sigma$th orbital and then applying Eq. (16).

The simplest approximation is obtained by replacing $p_{j\sigma}$ by its average value, i.e., by setting $p_{j\sigma}(\mathbf{r}t) \equiv 0$. The resulting approximate potential $\tilde{v}_{\mathrm{xc}\sigma}$ is then determined by

$$\tilde{v}_{\mathrm{xc}\sigma}(\mathbf{r}t) = \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\, \frac{1}{2}\left[u_{\mathrm{xc}j\sigma}(\mathbf{r}t) + u^*_{\mathrm{xc}j\sigma}(\mathbf{r}t)\right] + \frac{1}{n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t) \left\{ \overline{\tilde{v}}_{\mathrm{xc}j\sigma}(t) - \frac{1}{2}\left[\overline{u}_{\mathrm{xc}j\sigma}(t) + \overline{u}^*_{\mathrm{xc}j\sigma}(t)\right]\right\} + \frac{i}{4n_\sigma(\mathbf{r}t)} \sum_j^{N_\sigma} \nabla^2 n_{j\sigma}(\mathbf{r}t) \int_{-\infty}^{t} dt' [\overline{u}_{\mathrm{xc}j\sigma}(t') - \overline{u}^*_{\mathrm{xc}j\sigma}(t')]. \quad (21)$$

This equation is still an integral equation for $\tilde{v}_{\mathrm{xc}\sigma}$. It can, however, be solved analytically [17]: Multiplying Eq. (21) by $n_{k\sigma}(\mathbf{r}t)$ and integrating over all space yields

$$\overline{\tilde{v}}_{\mathrm{xc}k\sigma}(t) = \overline{w}_{\mathrm{xc}k\sigma}(t) + \sum_j^{N_\sigma} M_{kj\sigma}(t)\overline{\tilde{v}}_{\mathrm{xc}j\sigma}(t), \quad (22)$$

where $w_{xc\sigma}(\mathbf{r}t)$ denotes the right-hand side of Eq. (21) minus $[n_\sigma(\mathbf{r}t)]^{-1}\sum_j^{N_\sigma} n_{j\sigma}(\mathbf{r}t)\overline{\tilde{v}}_{xcj\sigma}(t)$, and

$$M_{kj\sigma}(t) = \int d^3r\, \frac{n_{k\sigma}(\mathbf{r}t) n_{j\sigma}(\mathbf{r}t)}{n_\sigma(\mathbf{r}t)}. \quad (23)$$

Solving Eq. (22) for $\overline{\tilde{v}}_{\mathrm{xc}j\sigma}(t)$ requires inversion of the $N_\sigma \times N_\sigma$ matrix $A_{kj\sigma}(t) = \delta_{kj} - M_{kj\sigma}(t)$, and leads to

$$\overline{\tilde{v}}_{\mathrm{xc}j\sigma}(t) = \sum_k^{N_\sigma} [A^{-1}_\sigma(t)]_{jk} \overline{w}_{\mathrm{xc}k\sigma}(t). \quad (24)$$

When Eq. (24) is substituted into Eq. (21), one obtains $\tilde{v}_{\mathrm{xc}\sigma}(\mathbf{r}t)$ as an explicit functional of the orbitals $\{\phi_{j\sigma}(\mathbf{r}t)\}$. We point out that the construction of $\tilde{v}_{\mathrm{xc}\sigma}(\mathbf{r}t)$ does not involve the introduction of a corresponding approximate $\tilde{A}_{\mathrm{xc}}[\phi_{j\sigma}]$ in addition to the given $A_{\mathrm{xc}}[\phi_{j\sigma}]$. We emphasize, however, that, in contrast to the exchange-correlation energy of the *static* OPM, the functional A_{xc} is not a quantity of physical interest because the value of the exact total action is always zero at the stationary point. As the exact $v_{\mathrm{xc}\sigma}(\mathbf{r}t)$, which follows from Eq. (11), $\tilde{v}_{\mathrm{xc}\sigma}(\mathbf{r}t)$ is determined by Eq. (21) only up to within an additive, purely time-dependent function $c(t)$.

The last term of Eq. (21) vanishes identically for a large class of exchange-correlation functionals A_{xc}. This class includes all functionals depending on $\{\phi_{j\sigma}\}$ only through the combinations $\phi_{j\sigma}(\mathbf{r}t)\phi^*_{j\sigma}(\mathbf{r}'t)$ [such as the TDHF functional, Eq. (2)].

The time-dependent KLI (TDKLI) approximation consisting of Eq. (21), combined with the Schrödinger equation (3), represents a time-dependent scheme which is numerically less involved than, e.g., the TDHF method, because the optimized effective potential is local in configuration space. From experience with the static KLI scheme in the exchange-only limit [13,16–21], we expect the results of the full TDOPM scheme, the TDKLI approximation and the full TDHF method to agree very closely with each other. Atomic systems subject to intense laser pulses are currently being studied using the TDKLI approximation. Given an approximate functional for the correlation part of $A_{\mathrm{xc}}[\phi_{j\sigma}]$, the principal advantage of the TDOPM and TDKLI schemes is that the inclusion of time-dependent *correlation* effects does not increase the numerical effort involved in the exchange-only case.

We thank J. B. Krieger for very stimulating discussions and for giving us a preprint of his latest work. One of us (C. A. U.) acknowledges the support of a fellowship of the Studienstiftung des deutschen Volkes.

[1] *Atoms in Intense Laser Fields*, edited by M. Gavrila (Academic Press, Boston, 1992).
[2] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[3] E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985); **57**, 923(E) (1986).
[4] E. K. U. Gross and W. Kohn, Adv. Quant. Chem. **21**, 255 (1990).
[5] O.-J. Wacker, R. Kümmel, and E. K. U. Gross, Phys. Rev. Lett. **73**, 2915 (1994).
[6] K. L. Liu and S. H. Vosko, Can. J. Phys. **67**, 1015 (1989).
[7] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
[8] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[9] M. R. Norman and D. D. Koelling, Phys. Rev. B **30**, 5530 (1984).
[10] J. D. Talman, Comput. Phys. Commun. **54**, 85 (1989).
[11] Y. Wang, J. P. Perdew, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, Phys. Rev. A **41**, 78 (1990).
[12] E. Engel, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, Z. Phys. D **23**, 7 (1992).
[13] E. Engel and S.H. Vosko, Phys. Rev. A **47**, 2800 (1993).
[14] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Lett. A **146**, 256 (1990).
[15] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Lett. A **148**, 470 (1990).
[16] Y. Li, J. B. Krieger, M. R. Norman, and G. J. Iafrate, Phys. Rev. B **44**, 10 437 (1991).
[17] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).
[18] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).
[19] J. B. Krieger, Y. Li, and G. J. Iafrate, Chem. Phys. Lett. **191**, 38 (1992).
[20] Y. Li, J. B. Krieger, and G. J. Iafrate, Phys. Rev. A **47**, 165 (1993).
[21] J. B. Krieger, Y. Li, and G. J. Iafrate, in *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Plenum Press, New York, 1994), p. 191.
[22] E. K. U. Gross, C. A. Ullrich, and U. J. Gossmann, in *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Plenum Press, New York, 1994), p. 149.