

DENSITY-FUNCTIONAL APPROACH TO ATOMS IN STRONG LASER PULSES

C. A. Ullrich, U. J. Gossmann

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

and

E. K. U. Gross

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

and

Faculty of Science and Technology
Griffith University
Nathan, Queensland 4111
Australia

Abstract

A density functional formalism for time-dependent systems comparable to the theory of Hohenberg, Kohn and Sham is presented. In this approach, the time-dependent density can be obtained (in principle exactly) from a set of time-dependent single-particle (Kohn-Sham) equations. In order to apply the time-dependent Kohn-Sham scheme in practical calculations, an effective time-dependent single-particle potential is needed. Given an expression for the quantum mechanical action $A[\phi_1 \dots \phi_N]$ of an N -electron system as a functional of N time-dependent orbitals, we present a method of constructing the variationally best local time-dependent single-particle potential which, when inserted in a time-dependent single-particle Schrödinger equation yields orbitals $\{\phi_j\}$ that make $A[\phi_1 \dots \phi_N]$ stationary. We also propose a simplification of this scheme leading to a time-dependent generalization of the static optimized effective potential recently introduced by Krieger, Li and Iafrate [Phys. Lett. A **146**, 256 (1990)]. Applications of this scheme to the case of a beryllium atom in a strong laser pulse are presented.

1 Introduction

The response of an interacting many-particle system to a time-dependent external field can usually be treated within linear response theory. Due to rapid experimental progress in the field of laser physics, however, ultra-short 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 traditional perturbation theory. The non-perturbative quantum mechanical description of interacting particles moving in a very strong time-dependent external field therefore has become a prominent problem of theoretical physics. In principle, it requires a full solution of the time-dependent Schrödinger equation for the interacting many-body system, which is an exceedingly difficult task. In view of the success of density functional methods [2] in the treatment of stationary many-body systems and in view of their numerical simplicity, a time-dependent version of density functional theory appears highly desirable, both within and beyond the regime of linear response.

The first steps towards a time-dependent Kohn-Sham (KS) scheme were taken by Peuckert [3] and by Zangwill and Soven [4]. These authors treated the linear density response of rare-gas atoms to a time-dependent external potential as the response of non-interacting electrons to an effective time-dependent potential. In analogy to stationary KS theory, this effective potential was assumed to contain an exchange-correlation (xc) part, $v_{xc}(\mathbf{r}t)$, in addition to the time-dependent external and Hartree terms:

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}t) \quad . \quad (1)$$

Peuckert suggested an iterative scheme for the calculation of v_{xc} , while Zangwill and Soven adopted the functional form of the static exchange-correlation potential in LDA, i. e.

$$v_{xc}(\mathbf{r}t) = \left. \frac{de_{xc}^{hom}(n)}{dn} \right|_{n=n(\mathbf{r}t)} \quad , \quad (2)$$

where $e_{xc}^{hom}(n)$ is the xc energy per volume of the homogeneous electron gas. This approximation can be expected to be good only if the time dependence of $n(\mathbf{r}t)$ is sufficiently slow. In practice, however, it gave quite good results even for the case of rather rapid time dependence.

The approach of Zangwill and Soven is valid *under the assumption* that a time-dependent KS theorem exists. Significant steps towards a rigorous foundation of time-dependent density functional theory were taken by Deb and Ghosh [5]–[8] and by Bartolotti [9]–[12] who formulated and explored Hohenberg-Kohn (HK) and KS type theorems for the time-dependent density. Each of these derivations, however, was restricted to a rather narrow set of allowable time-dependent potentials (to potentials periodic in time in the theorems of Deb and Ghosh, and to adiabatic processes in the work of Bartolotti). A general formulation covering essentially all time-dependent potentials of interest was given by Runge and Gross [13]. A short description of the time-dependent density functional formalism will be presented in section 2. The central result is a set of time-dependent KS equations which are structurally similar to the time-dependent Hartree equations but include (in principle exactly) all many-body effects through a *local* time-dependent exchange-correlation potential. In practice, this

potential must be approximated.

In section 3, we present a new method of constructing approximations of the time-dependent xc potential. Finally, in section 4, the formalism is applied to the case of a beryllium atom in a superintense laser pulse.

2 Time-Dependent Density-Functional Formalism

In this section we deal with many-electron systems moving in an explicitly time-dependent potential

$$\hat{V}(t) = \sum_{\sigma=\uparrow\downarrow} \int d^3r v(\mathbf{r}t) \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \quad . \quad (3)$$

The total Hamiltonian is given by

$$\hat{H}(t) = \hat{T} + \hat{U} + \hat{V}(t) \quad , \quad (4)$$

where \hat{T} is the kinetic energy of the electrons

$$\hat{T} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \hat{\psi}_\sigma(\mathbf{r}) \quad (5)$$

and \hat{U} is the mutual Coulomb interaction

$$\hat{U} = \frac{1}{2} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma(\mathbf{r}) \quad (6)$$

(atomic units are used throughout). The number of electrons, N , is fixed.

Ordinary time-independent density functional theory is based on the existence of an exact mapping between densities and external potentials. In the ground state formalism, the existence proof relies on the Rayleigh-Ritz minimum principle for the energy. Straightforward extension to the time-dependent domain is not possible since a *minimum* principle is not available in this case. The existence proof for a 1–1 mapping between time-dependent potentials and time-dependent densities, first given by Runge and Gross [13], is somewhat more involved. Starting from the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Phi(t) = \hat{H}(t) \Phi(t) \quad , \quad (7)$$

the densities $n(\mathbf{r}t)$ of electronic systems evolving from a *fixed* initial (many-particle) state

$$\Phi(t_0) = \Phi_0 \quad (8)$$

under the influence of different external potentials $v(\mathbf{r}t)$ are investigated. For each fixed initial state Φ_0 , formal solution of the Schrödinger equation (7) defines a map

$$\mathcal{A} : v(\mathbf{r}t) \longrightarrow \Phi(t) \quad (9)$$

between the external potentials and the corresponding time-dependent many-particle wave functions and a second map

$$\mathcal{B} : \Phi(t) \longrightarrow n(\mathbf{r}t) = \langle \Phi(t) | \hat{n}(\mathbf{r}) | \Phi(t) \rangle \quad (10)$$

between the many-particle wave functions and the time-dependent densities. The aim is to prove invertibility of the complete map

$$\mathcal{G} : v(\mathbf{r}t) \longrightarrow n(\mathbf{r}t) \quad . \quad (11)$$

Runge and Gross have demonstrated [13] that if the potentials $v(\mathbf{r}t)$ are required to be expandable in a Taylor series with respect to the time coordinate around the initial time t_0 , then the map \mathcal{G} is indeed invertible up to within an additive, merely time-dependent function in the potential. In other words, two densities $n(\mathbf{r}t)$ and $n'(\mathbf{r}t)$ evolving from a common initial state Φ_0 under the influence of the potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ are always different provided that the potentials differ by more than a purely time-dependent function:

$$v(\mathbf{r}t) \neq v'(\mathbf{r}t) + c(t) \quad . \quad (12)$$

Having established the existence of the inverse map

$$\mathcal{G}^{-1} : n(\mathbf{r}t) \longrightarrow v(\mathbf{r}t) + c(t) \quad , \quad (13)$$

subsequent application of the map \mathcal{A} tells us that the many-particle wave function is a functional of the time-dependent density, unique up to within a purely time-dependent phase $\alpha(t)$:

$$\Phi(t) = e^{-i\alpha(t)}\Psi[n](t) \quad . \quad (14)$$

As a consequence, the expectation value of any quantum mechanical operator $\hat{Q}(t)$ is a *unique* functional of the density:

$$Q[n](t) = \langle \Psi[n](t) | \hat{Q}(t) | \Psi[n](t) \rangle \quad . \quad (15)$$

The ambiguity in the phase cancels out.

The 1–1 correspondence between time-dependent densities and time-dependent potentials can be established for any *given* interaction \hat{U} , in particular also for $\hat{U} \equiv 0$, i. e. for non-interacting particles. Therefore the external potential $v_s[n](\mathbf{r}t)$ of a non-interacting system reproducing a given density $n(\mathbf{r}t)$ is uniquely determined. However, the 1–1 correspondence only ensures the uniqueness of $v_s[n]$ for all v -representable densities but not its existence for an *arbitrary* $n(\mathbf{r}t)$. In order to derive a time-dependent KS scheme we have to assume, similar to the static case, non-interacting v -representability, i. e., we have to assume that v_s exists for the time-dependent density of the *interacting* system of interest. Under this assumption, the density of the interacting system can be obtained from

$$n(\mathbf{r}t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}t)|^2 \quad (16)$$

with orbitals $\varphi_j(\mathbf{r}t)$ satisfying the time-dependent KS equation

$$i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s[n](\mathbf{r}t) \right) \varphi_j(\mathbf{r}t) \quad . \quad (17)$$

As usual, the single-particle potential v_s is written as

$$v_s[n](\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}t) \quad , \quad (18)$$

where $v(\mathbf{rt})$ is the external time-dependent field. The second term on the right-hand side of Eq. (18) is the time-dependent Hartree potential while the third term is the xc potential which, in practice, has to be approximated. As in the static case, the great advantage of the time-dependent KS scheme lies in its computational simplicity compared to other methods such as time-dependent configuration interaction [14]–[19].

The time-dependent density functional formalism described above has been extended to a number of physically different situations. Those include spin-polarized systems [20], multicomponent systems [21], time-dependent ensembles [22, 23], external vector potentials [24, 25] as well as superconducting systems [26].

To date, most applications of the formalism fall in the regime of linear response [27]–[31]. The linear response limit of time-dependent density functional theory has been discussed in great detail in a review article by Gross and Kohn [32]. For a broad overview of applications the reader is referred to the textbook by Mahan and Subbaswamy [33].

3 Time-Dependent Optimized Effective Potential

Beyond the realm of linear response theory, the only approximation of v_{xc} used until today is the adiabatic approximation given by Eq. (2). In the following, a new approach to the construction of $v_{xc}(\mathbf{rt})$ will be developed which can be viewed as a time-dependent version of the so-called optimized potential method (OPM) [34]–[49]. The approach leads to v_{xc} as a function of (\mathbf{rt}) rather than to v_{xc} as an explicit functional of the density. The OPM of stationary systems [34, 35] takes as starting point a given expression for the total energy $E[\varphi_1 \dots \varphi_N]$ of an N -electron system as a functional of a set of single-particle orbitals $\{\varphi_j(\mathbf{r})\}$ (e. g. the Hartree-Fock (HF) total energy functional in the exchange-only case). Then, the variationally best *local* effective potential is determined such that, when inserted in a stationary single-particle Schrödinger equation, it yields the set of N eigenfunctions (corresponding to the N lowest eigenvalues) that minimize $E[\varphi_1 \dots \varphi_N]$. In practice, the full OPM scheme is computationally quite involved since it requires the numerical solution of an integral equation for $v_{xc}(\mathbf{r})$. 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 [35]–[40]. There exists, however, an approximate OPM scheme, recently proposed by Krieger, Li, and Iafrate (KLI) [41]–[49], which is numerically as easy to handle as the ordinary KS 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 $v_0(\mathbf{r})$ (e. g. a nuclear Coulomb potential). We assume that the corresponding stationary OPM problem has been solved for that system, i. e. a local effective potential and a set of N single-particle orbitals $\{\varphi_j\}$ (with energy eigenvalues ε_j) minimizing a given energy functional $E[\varphi_1 \dots \varphi_N]$ are assumed to be known. At $t = t_0$ an additional time-dependent potential $v_1(\mathbf{rt})$ is switched on. Our goal is to determine the time evolution of the system under the influence of the total external potential $v(\mathbf{rt}) = v_0(\mathbf{r}) + v_1(\mathbf{rt})$ 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

$$A[\phi_1 \dots \phi_N] = \sum_j^N \int_{-\infty}^{t_1} dt \int d^3r \phi_j^*(\mathbf{r}t) \left(i \frac{\partial}{\partial t} + \frac{\nabla^2}{2} \right) \phi_j(\mathbf{r}t) - \int_{-\infty}^{t_1} dt \int d^3r n(\mathbf{r}t) v(\mathbf{r}t) - \frac{1}{2} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{n(\mathbf{r}t)n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} - A_{xc}[\phi_1 \dots \phi_N] \quad (19)$$

written as a functional of N time-dependent single-particle orbitals $\{\phi_j(\mathbf{r}t)\}$ where $n(\mathbf{r}t) = \sum_j^N |\phi_j(\mathbf{r}t)|^2$. In the following no specific approximation is used for the exchange-correlation functional $A_{xc}[\phi_1 \dots \phi_N]$, but we mention that in an exchange-only theory A_{xc} would be replaced by the time-dependent Hartree-Fock (TDHF) expression

$$A_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j}^N \delta_{\sigma_i \sigma_j} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{\phi_i^*(\mathbf{r}'t) \phi_j(\mathbf{r}'t) \phi_i(\mathbf{r}t) \phi_j^*(\mathbf{r}t)}{|\mathbf{r} - \mathbf{r}'|} \quad (20)$$

(σ_j denotes the spin orientation of the j th orbital). The orbitals are solutions of the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \phi_j(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}t) \right) \phi_j(\mathbf{r}t) \quad , \quad j = 1, \dots, N \quad , \quad (21)$$

with $\phi_j(\mathbf{r}t) = \varphi_j(\mathbf{r}) \exp[-i\varepsilon_j(t - t_0)]$ for $-\infty < t \leq t_0$. The local effective potential is given by

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + v_{\text{H}}(\mathbf{r}t) + v_{xc}(\mathbf{r}t) \quad , \quad (22)$$

where $v_{\text{H}}(\mathbf{r}t) = \int d^3r' n(\mathbf{r}'t) / |\mathbf{r} - \mathbf{r}'|$ denotes the time-dependent Hartree potential. The total potential $v_s(\mathbf{r}t)$ has to be determined in such a way that the $\{\phi_j(\mathbf{r}t)\}$, resulting from Eq. (21), render the total action functional $A[\phi_1 \dots \phi_N]$ stationary. Therefore, we have to solve the following variational problem:

$$\begin{aligned} \frac{\delta A[\phi_1 \dots \phi_N]}{\delta v_s(\mathbf{r}t)} &= \sum_j^N \int_{-\infty}^{+\infty} dt' \int d^3r' \left(\frac{\delta A[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}'t')} \frac{\delta \phi_j(\mathbf{r}'t')}{\delta v_s(\mathbf{r}t)} + \frac{\delta A[\phi_1 \dots \phi_N]}{\delta \phi_j^*(\mathbf{r}'t')} \frac{\delta \phi_j^*(\mathbf{r}'t')}{\delta v_s(\mathbf{r}t)} \right) \\ &= 0 \quad . \end{aligned} \quad (23)$$

We first compute the functional derivatives $\delta A / \delta \phi_j$ and $\delta A / \delta \phi_j^*$: defining

$$u_{xcj}(\mathbf{r}t) = \frac{1}{\phi_j^*(\mathbf{r}t)} \frac{\delta A_{xc}[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}t)} \quad , \quad (24)$$

we obtain

$$\frac{\delta A[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}'t')} = \left[-i \frac{\partial}{\partial t'} - \left(-\frac{\nabla'^2}{2} + v(\mathbf{r}'t') + v_{\text{H}}(\mathbf{r}'t') + u_{xcj}(\mathbf{r}'t') \right) \right] \phi_j^*(\mathbf{r}'t') \theta(t_1 - t') \quad (25)$$

and an analogous expression for $\delta A / \delta \phi_j^*$ which, for all reasonable (i. e. real) functionals $A[\phi_1 \dots \phi_N]$, is the complex conjugate of (25). $\theta(x)$ denotes the usual step function (1 for $x > 0$, 0 for $x < 0$). To arrive at Eq. (25) the first term of Eq. (19) has to be integrated by parts with respect to the time coordinate. We impose the usual boundary condition on $\phi_j(\mathbf{r}t)$ at $t = t_1$, i. e. $\delta \phi_j(\mathbf{r}t_1) = 0$, thus obtaining a zero boundary contribution. The other boundary contribution at $t = -\infty$ vanishes, too,

because the action functional (19), in order to be well-defined, is to be calculated by introducing the usual factor $e^{\eta t}$ in the integrand and taking $\lim_{\eta \rightarrow 0^+}$ after the integration. Substituting Eq. (22) into (25) and making use of the fact that ϕ_j^* solves the complex conjugate of the Schrödinger equation (21), we find

$$\frac{A[\phi_1 \dots \phi_N]}{\delta \phi_j(\mathbf{r}'t')} = [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j^*(\mathbf{r}'t') \theta(t_1 - t') \quad . \quad (26)$$

In order to evaluate $\delta A/\delta v_s$ from Eq. (23), we further need the functional derivatives $\delta \phi_j/\delta v_s$ and $\delta \phi_j^*/\delta v_s$. The stationary OPM eigenfunctions $\{\varphi_j(\mathbf{r}), j = 1, \dots, \infty\}$ form a complete orthonormal set, and so do the time-evolved states $\{\phi_j(\mathbf{r}t), j = 1, \dots, \infty\}$ for any time $t \in [-\infty, t_1]$, and we denote this set by Φ_t . Now consider Φ_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 $\delta v_s(\mathbf{r}t)$ and let it evolve *backward* in time. The corresponding perturbed wave functions $\phi'_j(\mathbf{r}t)$ are determined by the backward Schrödinger equation

$$i \frac{\partial}{\partial t} \phi'_j(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}t) + \delta v_s(\mathbf{r}t) \right) \phi'_j(\mathbf{r}t) \quad , \quad j = 1, \dots, N \quad (27)$$

with the initial condition $\phi'_j(\mathbf{r}t_1) = \phi_j(\mathbf{r}t_1)$. This problem cannot be treated directly with time-dependent perturbation theory as described in standard text books because the unperturbed Hamiltonian is already time-dependent. Nevertheless, Dirac's method of variation of constants can be applied in a straightforward manner. We expand, at each given t , the perturbed wave function $\phi'_j(\mathbf{r}t)$ in terms of the set Φ_t ,

$$\phi'_j(\mathbf{r}t) = \sum_{k=1}^{\infty} c_{jk}(t) \phi_k(\mathbf{r}t) \quad , \quad (28)$$

and insert this expansion in (27), utilizing Eq. (21). The resulting equation

$$i \sum_{k=1}^{\infty} \dot{c}_{jk}(t) \phi_k(\mathbf{r}t) = \sum_{k=1}^{\infty} c_{jk}(t) \delta v_s(\mathbf{r}t) \phi_k(\mathbf{r}t) \quad (29)$$

is then multiplied by $\phi_l^*(\mathbf{r}t)$ and integrated over all space; the orthonormality of Φ_t yields

$$\dot{c}_{jl}(t) = \frac{1}{i} \sum_{k=1}^{\infty} c_{jk}(t) \int d^3r \phi_l^*(\mathbf{r}t) \delta v_s(\mathbf{r}t) \phi_k(\mathbf{r}t) \quad . \quad (30)$$

We now make the usual ansatz for a perturbation expansion,

$$c_{jk}(t) = c_{jk}^{(0)}(t) + c_{jk}^{(1)}(t) + \dots \quad (31)$$

and collect corresponding orders on each side of Eq. (30). This yields

$$\begin{aligned} \dot{c}_{jl}^{(0)}(t) &= 0 \\ \dot{c}_{jl}^{(1)}(t) &= \frac{1}{i} \sum_{k=1}^{\infty} c_{jk}^{(0)}(t) \int d^3r \phi_l^*(\mathbf{r}t) \delta v_s(\mathbf{r}t) \phi_k(\mathbf{r}t) \\ &\vdots \end{aligned} \quad (32)$$

Since, in our case, the wave function evolves backward from the fixed state $\phi_j(\mathbf{r}t_1)$ we find $c_{jk}^{(0)}(t) = \delta_{jk}$ and $c_{jk}^{(1)}(t_1) = 0$, leading to

$$c_{jl}^{(1)}(t) = \frac{1}{i} \int_{t_1}^t dt' \int d^3r \phi_l^*(\mathbf{r}t') \delta v_s(\mathbf{r}t') \phi_j(\mathbf{r}t') \quad . \quad (33)$$

It follows that the first-order correction to the wave function $\phi_j(\mathbf{r}t)$ under the influence of $\delta v_s(\mathbf{r}t)$ is given by

$$\delta \phi_j(\mathbf{r}t) = \sum_{k=1}^{\infty} c_{jk}^{(1)}(t) \phi_k(\mathbf{r}t) = i \sum_{k=1}^{\infty} \int_t^{t_1} dt' \int d^3r' \phi_k^*(\mathbf{r}'t') \delta v_s(\mathbf{r}'t') \phi_j(\mathbf{r}'t') \phi_k(\mathbf{r}t) \quad . \quad (34)$$

Therefore, the desired functional derivative is

$$\frac{\delta \phi_j(\mathbf{r}'t')}{\delta v_s(\mathbf{r}t)} = i \sum_{k=1}^{\infty} \phi_k^*(\mathbf{r}t) \phi_j(\mathbf{r}t) \phi_k(\mathbf{r}'t') \theta(t_1 - t) \theta(t - t') \quad . \quad (35)$$

Once again, $\delta \phi_j^* / \delta v_s$ leads to the complex conjugate expression. We can now insert (26) and (35) in the variational equation (23), and the result is the time-dependent OPM (TDOPM) integral equation for the local exchange-correlation potential $v_{xc}(\mathbf{r}t)$:

$$i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}'t') K(\mathbf{r}t, \mathbf{r}'t') + c.c. = 0 \quad . \quad (36)$$

The kernel

$$K(\mathbf{r}t, \mathbf{r}'t') = \sum_{k=1}^{\infty} \phi_k^*(\mathbf{r}t) \phi_k(\mathbf{r}'t') \theta(t - t') \quad (37)$$

can be identified with the Green's function of the system, which satisfies the differential equation

$$\left[i \frac{\partial}{\partial t'} - \left(-\frac{\nabla'^2}{2} + v_s(\mathbf{r}'t') \right) \right] K(\mathbf{r}t, \mathbf{r}'t') = -i \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (38)$$

with the initial condition $K(\mathbf{r}t, \mathbf{r}'t') = 0$ for $t' > t$. The TDOPM scheme is now complete: the integral equation (36) has to be solved for $v_{xc}(\mathbf{r}t)$ in combination with the Schrödinger equation (21) and the differential equation (38) for $K(\mathbf{r}t, \mathbf{r}'t')$, both with the appropriate initial conditions. It is easy to show that in the time interval $[-\infty, t_1]$ the exchange-correlation potential $v_{xc}(\mathbf{r}t)$ is only determined up to within an additive, purely time-dependent function $c(t)$ (as expected in view of the time-dependent HK theorem discussed in section 2).

We now demonstrate that for $t < t_0$ or for a time-independent external potential ($v_1(\mathbf{r}t) \equiv 0$) the TDOPM reduces to the stationary OPM. For this purpose we rewrite Eq. (36) in the following way (using the fact that v_{xc} is real):

$$\begin{aligned} & i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}'t') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \phi_k^*(\mathbf{r}t) \phi_k(\mathbf{r}'t') \theta(t - t') + c.c. \\ & = i \sum_j^N \phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}t) \int_{-\infty}^t dt' \int d^3r' (u_{xcj}(\mathbf{r}'t') - u_{xcj}^*(\mathbf{r}'t')) \phi_j(\mathbf{r}'t') \phi_j^*(\mathbf{r}'t') \quad . \quad (39) \end{aligned}$$

In the static case, the orbitals $\{\phi_j(\mathbf{r}t)\}$ are replaced by $\{\varphi_j(\mathbf{r}) \exp[-i\varepsilon_j(t - t_0)]\}$. It is reasonable to assume that the exchange-correlation functional A_{xc} then becomes

$$A_{xc}[\phi_1 \dots \phi_N] \longrightarrow \int_{-\infty}^{t_1} dt' E_{xc}[\phi_1(t') \dots \phi_N(t')] \quad , \quad (40)$$

where $E_{xc}[\varphi_1 \dots \varphi_N]$ is the corresponding ground state exchange-correlation energy functional. Definition (24) then yields

$$u_{xcj}^{static}(\mathbf{r}t) = \left[\frac{1}{\tilde{\varphi}_j^*(\mathbf{r})} \frac{\delta E_{xc}[\tilde{\varphi}_1 \dots \tilde{\varphi}_N]}{\delta \tilde{\varphi}_j(\mathbf{r})} \right]_{\tilde{\varphi}_j(\mathbf{r})=\varphi_j(\mathbf{r})e^{-i\varepsilon_j(t-t_0)}} \quad . \quad (41)$$

We assume that the value of $E_{xc}[\varphi_1 \dots \varphi_N]$ remains unchanged if the arguments $\{\varphi_j(\mathbf{r})\}$ are multiplied by phase factors $e^{i\alpha_j}$. If this is the case, we can use the identity

$$\phi_j(\mathbf{r}t) = \sqrt{\phi_j(\mathbf{r}t)\phi_j^*(\mathbf{r}t)} \frac{\phi_j(\mathbf{r}t)\phi_j^*(\mathbf{r}_0t)}{|\phi_j(\mathbf{r}t)\phi_j^*(\mathbf{r}_0t)|} e^{i \arg(\phi_j(\mathbf{r}_0t))} \quad (42)$$

(where \mathbf{r}_0 is an arbitrary reference point) and write E_{xc} in Eq. (40) as a functional of the combinations $\phi_j(\mathbf{r}t)\phi_j^*(\mathbf{r}'t)$. Then it is not difficult to show that u_{xcj}^{static} is independent of time and that the right-hand side of (39) is zero. We therefore obtain

$$i \sum_j^N \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}(\mathbf{r}') - u_{xcj}^{static}(\mathbf{r}')] \varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r}') e^{-i(\varepsilon_j - \varepsilon_k)(t-t')} \theta(t-t') \\ + c.c. = 0 \quad . \quad (43)$$

Performing the integration over t' we find the stationary OPM integral equation [35]

$$\lim_{\eta \rightarrow 0^+} \sum_j^N \int d^3r' [v_{xc}(\mathbf{r}') - u_{xcj}^{static}(\mathbf{r}')] \varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r}')}{\varepsilon_j - \varepsilon_k - i\eta} + c.c. = 0 \quad . \quad (44)$$

The derivation of Eq. (44) shows that in order to recover the static limit from the time-dependent formalism one had to extend the time integral in Eq. (19) to $-\infty$; a *finite* lower time boundary does not correctly account for memory effects in v_{xc} and therefore results in an unphysical time dependence even in the static case.

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. (36) similar to the one proposed by KLI in the stationary case [46, 49]. This will lead to an alternative but still exact form of the TDOPM scheme which allows one to construct approximations of $v_{xc}(\mathbf{r}t)$ which are *explicit* functionals of the orbitals $\{\phi_j\}$, thereby avoiding the need to solve the integral equation. Following Refs. [46] and [49], we define

$$p_j(\mathbf{r}t) = \frac{-i}{\phi_j^*(\mathbf{r}t)} \int_{-\infty}^{t_1} dt' \int d^3r' [v_{xc}(\mathbf{r}'t') - u_{xcj}(\mathbf{r}'t')] \phi_j^*(\mathbf{r}'t') \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \phi_k^*(\mathbf{r}t)\phi_k(\mathbf{r}'t') \theta(t-t') \quad (45)$$

and

$$\bar{u}_{xcj}(t) = \int d^3r n_j(\mathbf{r}t) u_{xcj}(\mathbf{r}t) \quad (46)$$

where $n_j(\mathbf{r}t) = |\phi_j(\mathbf{r}t)|^2$. Eq. (39) can then be written as

$$\sum_j^N n_j(\mathbf{r}t) p_j(\mathbf{r}t) + c.c. = -i \sum_j^N n_j(\mathbf{r}t) \int_{-\infty}^t dt' (\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t')) \quad , \quad (47)$$

and it is easy to show that

$$\int d^3r n_j(\mathbf{r}t) p_j(\mathbf{r}t) = 0 \quad . \quad (48)$$

Evaluating $\phi_j(\mathbf{r}t)[-i \partial/\partial t + \nabla^2/2 - v_s(\mathbf{r}t)]\phi_j^*(\mathbf{r}t)p_j(\mathbf{r}t)$ we find after some straightforward algebra that $p_j(\mathbf{r}t)$ satisfies the following differential equation:

$$\begin{aligned} \frac{1}{2}\nabla \cdot (n_j(\mathbf{r}t)\nabla p_j(\mathbf{r}t)) - i n_j(\mathbf{r}t) \frac{\partial}{\partial t} p_j(\mathbf{r}t) - i \mathbf{J}_j(\mathbf{r}t) \cdot \nabla p_j(\mathbf{r}t) \\ = -n_j(\mathbf{r}t) \left[v_{xc}(\mathbf{r}t) - u_{xcj}(\mathbf{r}t) - \left(\bar{v}_{xcj}(t) - \bar{u}_{xcj}(t) \right) \right] \end{aligned} \quad (49)$$

with the current density $\mathbf{J}_j(\mathbf{r}t) = (2i)^{-1} (\phi_j^*(\mathbf{r}t)\nabla\phi_j(\mathbf{r}t) - \phi_j(\mathbf{r}t)\nabla\phi_j^*(\mathbf{r}t))$ and $\bar{v}_{xcj}(t) = \int d^3r n_j(\mathbf{r}t)v_{xc}(\mathbf{r}t)$. Finally, operating with ∇^2 on Eq. (47) and using Eq. (49) we find

$$\begin{aligned} v_{xc}(\mathbf{r}t) &= \frac{1}{n(\mathbf{r}t)} \sum_j^N n_j(\mathbf{r}t) \frac{1}{2} \left(u'_{xcj}(\mathbf{r}t) + u_{xcj}^*(\mathbf{r}t) \right) \\ &+ \frac{1}{n(\mathbf{r}t)} \sum_j^N n_j(\mathbf{r}t) \left[\bar{v}_{xcj}(t) - \frac{1}{2} \left(\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t) \right) \right] \\ &+ \frac{i}{4n(\mathbf{r}t)} \sum_j^N \nabla^2 n_j(\mathbf{r}t) \int_{-\infty}^t dt' \left(\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t') \right) \end{aligned} \quad (50)$$

where

$$u'_{xcj}(\mathbf{r}t) = u_{xcj}(\mathbf{r}t) + \frac{1}{n_j(\mathbf{r}t)} \left[\frac{1}{2}\nabla \cdot (p_j(\mathbf{r}t)\nabla n_j(\mathbf{r}t)) + i n_j(\mathbf{r}t) \frac{\partial}{\partial t} p_j(\mathbf{r}t) + i \mathbf{J}_j(\mathbf{r}t) \cdot \nabla p_j(\mathbf{r}t) \right]. \quad (51)$$

Eqs. (50) and (51) together with the differential equation (49) for $p_j(\mathbf{r}t)$ and the condition (48) (which can be used to fix the constant left undetermined by Eq. (49)) represent an exact alternative formulation of the TDOPM scheme. The advantage of Eq. (50) lies in the fact that it is a very convenient starting point for constructing approximations of $v_{xc}(\mathbf{r}t)$ as explicit functionals of the $\{\phi_j(\mathbf{r}t)\}$: it is only necessary to approximate $p_j(\mathbf{r}t)$ in Eq. (51) by a suitably chosen functional of the orbitals. We can then readily solve Eq. (50) *analytically* for $v_{xc}(\mathbf{r}t)$, as we shall show below.

We expect an *approximate* potential $\tilde{v}_{xc}(\mathbf{r}t)$ defined in this way to be close to the exact $v_{xc}(\mathbf{r}t)$. This conjecture is based on the observation that the difference between \tilde{v}_{xc} and v_{xc} is entirely accounted for by the differences $u'_{xcj} - u_{xcj}$ which are zero if averaged over the j th orbital, as will be demonstrated in the following. From Eq. (51) we obtain

$$\begin{aligned} \bar{u}'_{xcj}(t) - \bar{u}_{xcj}(t) &= \\ \frac{1}{2} \int d^3r \nabla \cdot (p_j(\mathbf{r}t)\nabla n_j(\mathbf{r}t)) + i \int d^3r \left[n_j(\mathbf{r}t) \frac{\partial}{\partial t} p_j(\mathbf{r}t) + \mathbf{J}_j(\mathbf{r}t) \cdot \nabla p_j(\mathbf{r}t) \right] \end{aligned} \quad (52)$$

Using the divergence theorem, the first term on the right-hand side can be transformed into a surface integral which vanishes if the time-dependent orbitals decrease exponentially for $r \rightarrow \infty$. The contribution to the second integral containing $\mathbf{J}_j \cdot \nabla p_j$ is then integrated by parts. The surface term vanishes due to the same argument as

before, and the remaining term is transformed using the continuity equation for the j th orbital to replace $-\nabla \cdot \mathbf{J}_j(\mathbf{r}t)$ by $\partial n_j(\mathbf{r}t)/\partial t$. Hence we find

$$\bar{u}'_{xcj}(t) - \bar{u}_{xcj}(t) = i \frac{\partial}{\partial t} \int d^3r n_j(\mathbf{r}t) p_j(\mathbf{r}t) = 0 \quad , \quad (53)$$

where the last equality follows from Eq. (48).

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

$$\begin{aligned} \tilde{v}_{xc}(\mathbf{r}t) &= \frac{1}{n(\mathbf{r}t)} \sum_j^N n_j(\mathbf{r}t) \frac{1}{2} \left(u_{xcj}(\mathbf{r}t) + u_{xcj}^*(\mathbf{r}t) \right) \\ &+ \frac{1}{n(\mathbf{r}t)} \sum_j^N n_j(\mathbf{r}t) \left[\bar{v}_{xcj}(t) - \frac{1}{2} \left(\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t) \right) \right] \\ &+ \frac{i}{4n(\mathbf{r}t)} \sum_j^N \nabla^2 n_j(\mathbf{r}t) \int_{-\infty}^t dt' \left(\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t') \right) \quad . \end{aligned} \quad (54)$$

This equation is still an integral equation for \tilde{v}_{xc} . It can, however, be solved analytically [45]: multiplying Eq. (54) by $n_k(\mathbf{r}t)$ and integrating over all space yields

$$\bar{v}_{xck}(t) = \bar{w}_{xck}(t) + \sum_j^N M_{kj}(t) \bar{v}_{xcj}(t) \quad , \quad (55)$$

where we have defined

$$\begin{aligned} w_{xc}(\mathbf{r}t) &= \frac{1}{n(\mathbf{r}t)} \sum_j^N n_j(\mathbf{r}t) \frac{1}{2} \left(u_{xcj}(\mathbf{r}t) + u_{xcj}^*(\mathbf{r}t) \right) \\ &- \frac{1}{n(\mathbf{r}t)} \sum_j^N n_j(\mathbf{r}t) \frac{1}{2} \left(\bar{u}_{xcj}(t) + \bar{u}_{xcj}^*(t) \right) \\ &+ \frac{i}{4n(\mathbf{r}t)} \sum_j^N \nabla^2 n_j(\mathbf{r}t) \int_{-\infty}^t dt' \left(\bar{u}_{xcj}(t') - \bar{u}_{xcj}^*(t') \right) \end{aligned} \quad (56)$$

and

$$M_{kj}(t) = \int d^3r \frac{n_k(\mathbf{r}t) n_j(\mathbf{r}t)}{n(\mathbf{r}t)} \quad . \quad (57)$$

Solving Eq. (55) for $\bar{v}_{xcj}(t)$ requires inversion of the $N \times N$ matrix

$$A_{kj}(t) = \delta_{kj} - M_{kj}(t) \quad (58)$$

and leads to

$$\bar{v}_{xcj}(t) = \sum_k^N \left(A^{-1}(t) \right)_{jk} \bar{w}_{xck}(t) \quad . \quad (59)$$

When Eq. (59) is substituted into Eq. (54), one obtains $\tilde{v}_{xc}(\mathbf{r}t)$ as an explicit functional of the orbitals $\{\phi_j(\mathbf{r}t)\}$. As the exact $v_{xc}(\mathbf{r}t)$ which follows from Eq. (36), $\tilde{v}_{xc}(\mathbf{r}t)$ is determined by Eq. (54) only up to within an additive, purely time-dependent function $c(t)$.

The last term of Eqs. (54) and (56) vanishes identically for a large class of exchange-correlation functionals A_{xc} . This class includes all functionals depending on $\{\phi_j\}$ only through the combinations $\phi_j(\mathbf{r}t) \phi_j^*(\mathbf{r}'t)$ (such as the TDHF functional, Eq. (20)).

The time-dependent KLI (TDKLI) approximation consisting of Eq. (54) combined with the Schrödinger equation (21) 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 [40], [45]–[49], we expect the results of the full TDOPM scheme, the TDKLI approximation and the full TDHF method to agree very closely with each other. Given an approximate functional for the correlation part of $A_{xc}[\phi_1 \dots \phi_N]$, 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.

4 Application to Atoms in Strong Laser Pulses

As an example, we simulate the ionization process that a neutral beryllium atom, initially in its ground state, undergoes when irradiated by a linearly polarized laser pulse with wave length $\lambda = 227.8$ nm (5.44 eV photon energy) and peak intensity $I = 1.75 \times 10^{14}$ W/cm². In this intensity regime, a non-perturbative treatment of the system is mandatory [1]. The total external potential seen by the electrons is given by

$$v(\mathbf{r}t) = -\frac{Z}{r} - E_0 f(t) z \sin(\omega t) \quad (60)$$

where the nuclear charge Z equals 4 in the case of Be. The second term on the right-hand side of Eq. (60) is the potential due to the laser field in dipole approximation, written in the length form. Since the wavelength of currently used lasers is almost always very large compared to any characteristic length associated with an atomic system, the dipole approximation usually turns out to be very good in practice [50]. E_0 denotes the peak electric field strength and $f(t)$ characterizes the envelope function of the pulse, which in our calculations is linearly ramped to its peak value over the first 10 cycles and then held constant (one cycle corresponds to 0.76 fs). The field is assumed to be polarized along the z -direction.

In the following, we compare the results of a TDKLI calculation using the approximate potential (54) with an adiabatic LDA (ALDA) calculation using the potential (2), both for the exchange-only case. The numerical procedure to solve the single-particle equations for the Be 1s and 2s spin orbitals in TDKLI (21) and ALDA (17) is similar to the one presented in the pioneering work by Kulander [51, 52], who solved the time-dependent Schrödinger and TDHF equations for a hydrogen and helium atom in a laser pulse, respectively. The spin orbitals are expressed in cylindrical coordinates and, due to the linear polarization of the field, the spin as well as the angular part of the orbitals are preserved. Consequently, a fully three-dimensional treatment only requires a two-dimensional grid for the numerical integration and $\phi_{1s\uparrow}(\mathbf{r}t) = \phi_{1s\downarrow}(\mathbf{r}t) \equiv \phi_{1s}(\mathbf{r}t)$ and $\phi_{2s\uparrow}(\mathbf{r}t) = \phi_{2s\downarrow}(\mathbf{r}t) \equiv \phi_{2s}(\mathbf{r}t)$ for all t . The integration of the single-particle equations is performed using a finite-difference representation of the kinetic energy operator. The algorithm employed [53] ensures that the time propagation of the orbitals is always unitary.

In order to simulate ionization, the grid contains an absorbing boundary to remove the flux leaving the domain of the calculation. When some portion of the wave function propagates to the outer edges of the grid it is absorbed. We assume this flux corresponds to that part of the wave function which is in the continuum. Strictly

speaking, such a criterion is meaningful only after long times when the respective contributions have propagated very far away from the nucleus. For the wave length considered here, the probability to remain in a finite volume of space has nevertheless proven to be a useful definition of bound-state occupation probability which has been used in many successful applications [51, 52], [54]–[59], e. g., to extract single-particle ionization rates from the time change of the norm of the wave function [51].

The norm of the single-particle orbitals

$$p_j(t) = \int_{\text{finite volume}} d^3r |\phi_j(\mathbf{r}t)|^2, \quad j = (1s), (2s) \quad (61)$$

has been calculated in each time step (about 600 per cycle) by integrating the single-particle densities $|\phi_j(\mathbf{r}t)|^2$ over the finite volume of a cylindrical box (with a maximum radius of about 20 a.u. and a height of about 60 a.u.). Figs. 1 and 2 show the so defined norm of the Be 1s and 2s orbitals versus time. For $p_{1s}(t)$, the numerical integration from Eq. (61) yields oscillations with an amplitude of approximately 5×10^{-5} . These oscillations have been smoothed out in Fig. 1 because the numerical accuracy of our integration routine is of the same order of magnitude. For both orbitals it can be seen how the norm stays nearly unchanged during the first few cycles of the rise time of the pulse. Somewhat surprisingly, the ionization of the inner orbital seems to set in first (after the second cycle). However, this impression is due to the different scales used in Figs. 1 and 2, respectively. If we examine the first 3 cycles only and use the scale of Fig. 1 to plot both the 1s and 2s norm, we find a noticeable decrease for both orbitals after the second cycle. This delay between the switch-on of the pulse and the beginning of the decrease can be attributed to the finite time it takes the electrons which are released near the nucleus to reach the boundary of the grid.

In the following, the 1s norm decays steadily, until the ionization nearly saturates at about the 10th cycle. Parallel to this, the 2s orbital starts to ionize rapidly at the 5th cycle, the decrease then being almost four orders of magnitude faster than for the 1s orbital. The degree of ionization of the 2s orbital is about 90% after 19 cycles compared to only about 0.025% for the 1s orbital. This was to be expected, because the 1s orbital is much stronger bound on the scale of the applied photon energy.

In Table 1, the Be 1s and 2s binding energies in the KLI approximation and in LDA are compared with the HF orbital energies [60]. In LDA, the 1s and 2s binding energies are only 92% and 58%, respectively, of the HF value, whereas the KLI binding energies deviate from HF only by about 0.7% and 5%, respectively. The LDA and KLI orbital energies have been calculated using our two-dimensional grid in cylindrical coordinate representation. Since the grid must cover a very large region of space (20 a.u. \times 60 a.u.) the grid spacing has to be chosen relatively coarse (in the order of 0.1 a.u.) even close to the nucleus in order to keep the computational effort manageable. The resulting grid then has more than 30000 grid points. Compared to results in the literature [45], our LDA and KLI ionization potentials are therefore slightly too deep (by about 0.2 and 0.4 eV, respectively).

The differences between the TDKLI and ALDA results in Figs. 1 and 2 (in ALDA the atom can be seen to ionize faster) are due to the fact that in LDA the orbitals are generally much too weakly bound. Considering the photon energy of 5.44 eV which lies in between the TDKLI and ALDA ionization potentials of 8.85 and 4.85 eV, respectively, one would have expected a much larger difference of the two ionization rates, because in TDKLI the ionization requires at least two photons, whereas in ALDA

one photon is already sufficient to ionize the atom. The results of our calculations indicate, however, that in the intensity regime considered here this perturbative picture of the ionization process is no longer applicable.

In Fig. 3 we display how the differently charged states are populated during the time evolution of the system. To obtain these results, we have used the time dependence of the norm $p_{2s}(t)$ of the Be 2s orbital given by the TDKLI curve in Fig. 2, neglecting the very small decrease of the norm of the 1s orbital (and therefore higher than doubly ionized states). Keeping in mind that this time-dependent norm refers to spin (i. e. singly occupied) orbitals, the probabilities for the population of the differently charged states can be expressed as [61]

$$P(\text{Be}^0) = p_{2s}(t)^2 \quad (62)$$

$$P(\text{Be}^+) = 2p_{2s}(t)(1 - p_{2s}(t)) \quad (63)$$

$$P(\text{Be}^{2+}) = (1 - p_{2s}(t))^2 \quad (64)$$

It can be seen in Fig. 3 that, as the probability for the atom to stay neutral continuously decreases to nearly zero, first the number of singly ionized atoms rises. During the course of the pulse, however, this number saturates and goes down again as, beginning at about the 5th cycle, the probability for the atoms to suffer a second ionization starts to grow rapidly and finally dominates.

In conclusion we point out that our results have been obtained by performing non-perturbative time-dependent *all-electron* calculations in contrast to computational schemes [54, 55], [57]–[59] for multielectron systems where only one active electron is considered and all the others are kept frozen in their initial configuration. Calculations on other atomic systems with different laser parameters using the TDKLI and ALDA schemes are in progress.

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References

- [1] *Atoms in Intense Laser Fields*, edited by M. Gavrilu (Academic Press, Boston, 1992)
- [2] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990)
- [3] V. Peuckert, *J. Phys. C* **11**, 4945 (1978)
- [4] A. Zangwill and P. Soven, *Phys. Rev. A* **21**, 1561 (1980)
- [5] B. M. Deb and S. K. Ghosh, *J. Chem. Phys.* **77**, 342 (1982)
- [6] S. K. Ghosh and B. M. Deb, *Chem. Phys.* **71**, 295 (1982)
- [7] S. K. Ghosh and B. M. Deb, *Theor. Chim. Acta* **62**, 209 (1983)
- [8] S. K. Ghosh and B. M. Deb, *J. Mol. Struct.* **103**, 163 (1983)
- [9] L. J. Bartolotti, *Phys. Rev. A* **24**, 1661 (1981)
- [10] L. J. Bartolotti, *Phys. Rev. A* **26**, 2243 (1982)
- [11] L. J. Bartolotti, *J. Chem. Phys.* **80**, 5687 (1984)
- [12] L. J. Bartolotti, *Phys. Rev. A* **36**, 4492 (1987)
- [13] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984)
- [14] L. F. Errea, L. Méndez, A. Riera, M. Yáñez, J. Hanssen, C. Harel, and A. Salin, *J. Physique* **46**, 719 (1985)
- [15] I. L. Cooper, A. S. Dickinson, S. K. Sur, and C. T. Ta, *J. Phys. B* **20**, 2005 (1987)
- [16] A. Henne, H.-J. Lüdde, A. Toepfer, and R. M. Dreizler, *Phys. Lett. A* **124**, 508 (1987)
- [17] W. Fritsch and C. D. Lin, *Phys. Lett. A* **123**, 128 (1987)
- [18] J. F. Reading and A. L. Ford, *Phys. Rev. Lett.* **58**, 543 (1987)
- [19] J. F. Reading and A. L. Ford, *J. Phys. B* **20**, 3747 (1987)
- [20] K. L. Liu and S. H. Vosko, *Can. J. Phys.* **67**, 1015 (1989)
- [21] T.-C. Li and P.-Q. Tong, *Phys. Rev. A* **34**, 529 (1986)
- [22] T.-C. Li and P.-Q. Tong, *Phys. Rev. A* **31**, 1950 (1985)
- [23] T.-C. Li and Y. Li, *Phys. Rev. A* **31**, 3970 (1985)
- [24] S. K. Ghosh and A. K. Dhara, *Phys. Rev. A* **38**, 1149 (1988)
- [25] T. K. Ng, *Phys. Rev. Lett.* **62**, 2417 (1989)

- [26] O.-J. Wacker, R. Kümmel, and E. K. U. Gross, *Phys. Rev. Lett.* **73**, 2915 (1994)
- [27] A. Zangwill and P. Soven, *Phys. Rev. Lett.* **45**, 204 (1980)
- [28] Z. H. Levine and P. Soven, *Phys. Rev. Lett.* **50**, 2074 (1983)
- [29] E. K. U. Gross and W. Kohn, *Phys. Rev. Lett.* **55**, 2850 (1985); erratum: **57**, 923 (1986)
- [30] Z. H. Levine and D. C. Allan, *Phys. Rev. Lett.* **63**, 1719 (1989)
- [31] J. Dobson, *Phys. Rev. Lett.* **73**, 2244 (1994)
- [32] E. K. U. Gross and W. Kohn, *Adv. Quant. Chem.* **21**, 255 (1990)
- [33] G. D. Mahan and K. R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum Press, New York, 1990)
- [34] R. T. Sharp and G. K. Horton, *Phys. Rev.* **90**, 317 (1953)
- [35] J. D. Talman and W. F. Shadwick, *Phys. Rev. A* **14**, 36 (1976)
- [36] M. R. Norman and D. D. Koelling, *Phys. Rev. B* **30**, 5530 (1984)
- [37] J. D. Talman, *Comput. Phys. Commun.* **54**, 85 (1989)
- [38] Y. Wang, J. P. Perdew, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, *Phys. Rev. A* **41**, 78 (1990)
- [39] E. Engel, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, *Z. Phys. D* **23**, 7 (1992)
- [40] E. Engel and S. H. Vosko, *Phys. Rev. A* **47**, 2800 (1993)
- [41] J. B. Krieger, Y. Li, and G. J. Iafrate, *Phys. Lett. A* **146**, 256 (1990)
- [42] J. B. Krieger, Y. Li, and G. J. Iafrate, *Phys. Lett. A* **148**, 470 (1990)
- [43] Y. Li, J. B. Krieger, M. R. Norman, and G. J. Iafrate, *Phys. Rev. B* **44**, 10437 (1991)
- [44] J. B. Krieger, Y. Li, and G. J. Iafrate, *Int. J. Quantum Chem.* **41**, 489 (1992)
- [45] J. B. Krieger, Y. Li, and G. J. Iafrate, *Phys. Rev. A* **45**, 101 (1992)
- [46] J. B. Krieger, Y. Li, and G. J. Iafrate, *Phys. Rev. A* **46**, 5453 (1992)
- [47] J. B. Krieger, Y. Li, and G. J. Iafrate, *Chem. Phys. Lett.* **191**, 38 (1992)
- [48] Y. Li, J. B. Krieger, and G. J. Iafrate, *Phys. Rev. A* **47**, 165 (1993)
- [49] J. B. Krieger, Y. Li, and G. J. Iafrate, in *Density Functional Theory*, ed. by E. K. U. Gross and R. M. Dreizler (NATO ASI series, Plenum Press, 1994)
- [50] F. H. M. Faisal, *Theory of Multiphoton Processes* (Plenum Press, New York, 1987)

- [51] K. C. Kulander, Phys. Rev. A **35**, 445 (1987)
- [52] K. C. Kulander, Phys. Rev. A **36**, 2726 (1987)
- [53] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes*, 2nd edition, section 19.2 (Cambridge Univ. Press, Cambridge, 1992)
- [54] K. C. Kulander, Phys. Rev. A **38**, 778 (1988)
- [55] K. C. Kulander, K. J. Schafer, and J. L. Krause, in Ref. [1]
- [56] J. L. Krause, K. J. Schafer, and K. C. Kulander, Phys. Rev. A **45**, 4998 (1992)
- [57] M. S. Pindzola, T. W. Gorczyca, and C. Bottcher, Phys. Rev. A **47**, 4982 (1993)
- [58] H. Xu, X. Tang, and P. Lambropoulos, Phys. Rev. A **46**, R2225 (1992)
- [59] H. Xu, X. Tang, and P. Lambropoulos, Laser Phys. **3**, 759 (1993)
- [60] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974)
- [61] M. Horbatsch, H. J. Lüdde, and R. M. Dreizler, J. Phys. B: At. Mol. Opt. Phys. **25**, 3315 (1992)

Figure and Table Captions

Fig. 1. Time evolution of the norm $p_{1s}(t)$ of the Be 1s orbital subject to an intense laser pulse ($\lambda = 227.8$ nm, $I = 1.75 \times 10^{14}$ W/cm²)

Fig. 2. Time evolution of the norm $p_{2s}(t)$ of the Be 2s orbital (same laser parameters as in Fig. 1)

Fig. 3. Population of the differently charged states of the Be atom during the course of the pulse (calculated with TDKLI)

Table 1. Comparison of calculations of the Be 1s and 2s orbital energies ε_{1s} and ε_{2s} (in eV), in various exchange-only approximations

	HF	KLI	LDA
$-\varepsilon_{1s}$	128.78	129.74	118.34
$-\varepsilon_{2s}$	8.42	8.85	4.85