

# Many-electron atoms in strong femto-second laser pulses: a density-functional study

## Abstract

The fundamental concept of time-dependent density functional theory is to describe the dynamics of an interacting many-particle system exclusively and completely in terms of its time-dependent density. We give a short overview of the basic theorems including an extension of the formalism to a unified treatment of electronic and nuclear motion. The density-functional approach is then applied to describe neon atoms in strong laser fields on a non-perturbative all-electron level, i.e. beyond the so-called single-active electron approximation. We study multiphoton ionization and harmonic generation from 248-nm KrF laser pulses in neon and compare calculated harmonic spectra with recent experimental data.

KEY WORDS: DENSITY FUNCTIONAL THEORY, KOHN-SHAM EQUATIONS, OPTIMIZED POTENTIAL METHOD, ATOMS IN STRONG LASER FIELDS, MULTIPHOTON IONIZATION, HARMONIC GENERATION

# 1 Introduction

The great variety of new and often unexpected phenomena observed in experiments on atoms interacting with very strong laser pulses has stimulated a large number of theoretical studies in the last years.<sup>1,2</sup> In the high-intensity regime, perturbation theory must necessarily fail, so that one in principle has to solve the full time-dependent many-particle Schrödinger equation in order to arrive at a correct description of the electron dynamics of an atomic system in a strong laser field.

To date, most of the theoretical activity in this area has focused on the simplest system, the hydrogen atom, where the complications due to electron-electron interaction are absent and fully numerical solutions of the time-dependent Schrödinger equation can be obtained with comparatively low effort.<sup>3,4</sup> Such a strategy becomes of course tremendously involved as soon as one deals with atoms having more than one electron; some progress<sup>5</sup> has been made very recently, however, in propagating the full two-electron wave function of helium in all three spatial dimensions.

All other studies dealing with many-electron atoms in strong laser fields have made use of more or less severe approximations to reduce the problem to a tractable size. In the single-active electron (SAE) model,<sup>4,6,7</sup> for example, the time-dependent Schrödinger equation is solved for only one “active” electron while the remaining electrons are frozen in their initial configuration, their influence on the active electron being simulated by a *static* model potential. This strategy successfully models the screening of the nuclear charge by the inner electrons, but cannot describe collective effects arising from electronic correlation. More sophisticated methods such as the *R*-matrix Floquet formalism<sup>8</sup> allow for systematic improvement by including more field-free atomic basis states. Floquet methods, however, are only applicable to long laser pulses. Time-dependent configuration-interaction (CI) methods<sup>7,9</sup> are applicable to arbitrarily short pulses but they are limited by the speed and storage capacity of present-day computers to very small atoms. Other approaches reducing the complexity of the many-electron problem consist for example in the study of model systems with lower dimensionality<sup>10</sup> or a classical or semiclassical treatment of the electronic motion.<sup>11,12</sup>

In this paper we present an approach to study the electron dynamics of many-electron atoms in strong laser fields which is based on time-dependent density functional theory (TDDFT). The method allows for the interaction of *all* atomic electrons with the laser field and as such has some similarities with the time-dependent Hartree-Fock (TDHF) method.<sup>13,14,15</sup> In contrast to the latter, however, the TDDFT approach is embedded in a formal framework which makes it in principle exact and, besides that, it is also numerically easier to implement than TDHF. Density functional theory (DFT) is based on the insight<sup>16</sup> that an interacting many-particle system, usually characterized by its full many-body wave function, may as well be exclusively and completely described in terms of its density. The key point is that the latter can be obtained without solving the full many-body Schrödinger equation but rather as density of an auxiliary system of non-interacting particles moving in an effective *local* single-particle potential (the so-called Kohn-Sham<sup>17</sup> potential). In the original work of Hohenberg, Kohn and Sham<sup>16,17</sup> these theorems were

proven for the ground-state density of *static* many-body systems. On the basis of these theorems, DFT has provided an extremely successful description of ground-state properties of atoms, molecules and solids.<sup>18,19</sup> The accuracy of approximations for the Kohn-Sham potential has steadily improved over the years and the currently best functionals yield ground-state properties in very close agreement with configuration interaction results.<sup>20</sup>

DFT of time-dependent systems is of more recent origin.<sup>21-24</sup> The important theorems stated above have been shown to hold true for the time-dependent density as well.<sup>21</sup> An overview of the formal framework of TDDFT will be given in section 2. As a promising new development we include the extension of the formalism to treat electronic *and* nuclear motion in a unified way.

So far, TDDFT has been applied almost exclusively in the regime of linear response (for recent reviews see Refs. 22-26). There is, however, a growing activity in the field of cluster physics where non-perturbative TDDFT methods are used to describe effects such as collective oscillations<sup>27-29</sup> and electron escape.<sup>30</sup> In section 3, we present numerical results for multiphoton ionization and harmonic generation of the neon atom in intense 248-nm KrF laser fields obtained from non-perturbative all-electron TDDFT calculations.

## 2 Time-dependent density functional formalism

### 2.1 One-to-one mapping between time-dependent densities and potentials

The time evolution of a system of  $N$  electrons is governed by the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Phi(t) = \hat{H}(t)\Phi(t) \quad (1)$$

(atomic [Hartree] units are used throughout) with the total Hamiltonian  $\hat{H}(t)$  composed of the kinetic energy  $\hat{T}$  of the electrons, their mutual Coulomb interaction  $\hat{W}$  and an explicitly time-dependent external potential  $\hat{V}(t)$ :

$$\begin{aligned} \hat{H}(t) &= \hat{T} + \hat{W} + \hat{V}(t) \\ &= \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i t) \quad . \end{aligned} \quad (2)$$

If we describe for example an atom in a strong laser field,  $v_{\text{ext}}(\mathbf{r}t)$  consists of the static Coulomb potential of the nucleus plus a time-dependent part caused by the laser.

TDDFT is based on the existence of an exact one-to-one mapping between time-dependent densities and external potentials. We investigate the densities  $n(\mathbf{r}t)$  of electronic systems evolving from a *fixed* initial (many-particle) state  $\Phi(t_0) = \Phi_0$  under the influence of different external potentials  $v_{\text{ext}}(\mathbf{r}t)$ . Each external potential leads, via solution of the Schrödinger equation (1), to a time-dependent many-body wave function  $\Phi(t)$ . For a fixed initial state  $\Phi_0$ , this defines a map

$$\mathcal{A} : v_{\text{ext}}(\mathbf{r}t) \longrightarrow \Phi(t) \quad (3)$$

between the external potentials and the corresponding time-dependent many-particle wave

functions. By virtue of the density operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad , \quad (4)$$

a second map

$$\mathcal{B} : \Phi(t) \longrightarrow n(\mathbf{r}t) = \langle \Phi(t) | \hat{n}(\mathbf{r}) | \Phi(t) \rangle \quad (5)$$

is established between the many-particle wave functions and the time-dependent densities. The heart of TDDFT is the proof of invertibility of the combined map  $\mathcal{G} \equiv \mathcal{B} \circ \mathcal{A}$ :

$$\mathcal{G} : v_{\text{ext}}(\mathbf{r}t) \longrightarrow n(\mathbf{r}t) \quad . \quad (6)$$

The invertibility of this map was first proven by Runge and Gross.<sup>21</sup> Accordingly, two densities  $n(\mathbf{r}t)$  and  $n'(\mathbf{r}t)$  evolving from a common initial state  $\Phi_0$  under the influence of two potentials  $v_{\text{ext}}(\mathbf{r}t)$  and  $v'_{\text{ext}}(\mathbf{r}t)$  always become different infinitesimally later than  $t_0$ , provided that the potentials differ by more than a purely time-dependent function  $c(t)$ . The set of potentials for which invertibility can be shown comprises all potentials expandable in a Taylor series with respect to the time coordinate around the initial time  $t_0$ . Having established the existence of the inverse map

$$\mathcal{G}^{-1} : n(\mathbf{r}t) \longrightarrow v_{\text{ext}}(\mathbf{r}t) + c(t) \quad , \quad (7)$$

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

$$\Phi(t) = e^{-i\alpha(t)} \Psi[n](t) \quad . \quad (8)$$

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

$$Q[n](t) = \langle \Psi[n](t) | \hat{Q}(t) | \Psi[n](t) \rangle \quad . \quad (9)$$

The ambiguity in the phase cancels out (provided that  $\hat{Q}(t)$  contains no time derivatives). Moreover, any transition amplitude, i. e. any  $S$ -matrix element

$$\langle \Phi_f | \hat{S} | \Phi_i \rangle \quad (10)$$

between some initial many-body state  $\Phi_i$  and some final many-body state  $\Phi_f$  is a functional of the time-dependent density once the states  $\Phi_i$  and  $\Phi_f$  are specified. This is because the  $S$ -operator is uniquely determined by the Hamiltonian (2), i. e.  $S = S[H]$ , and the Hamiltonian, by virtue of the map (7), is uniquely fixed by the time-dependent density, so that

$$S = S[H[n]] \quad . \quad (11)$$

In practice, some quantities may be easily calculated from the density, while other observables are more difficult to extract. Examples for both cases will be found in section 3. But, as a matter of principle, *all* physical observables are determined by the time-dependent density alone.

## 2.2 Time-dependent Kohn-Sham scheme

The 1–1 correspondence between time-dependent densities and time-dependent potentials can be established for any *given* interaction  $\hat{W}$ , in particular also for  $\hat{W} \equiv 0$ , i. e. for non-interacting particles. Therefore, if  $n(\mathbf{r}t)$  is a *given* density, the potential  $v(\mathbf{r}t)$  of *non-interacting* particles that reproduces  $n(\mathbf{r}t)$  is *uniquely* determined,  $v(\mathbf{r}t) = v[n](\mathbf{r}t)$ , i. e. the given density  $n(\mathbf{r}t)$  can be calculated from

$$n(\mathbf{r}t) = \sum_{j=1}^N |\phi_j(\mathbf{r}t)|^2 \quad (12)$$

with the single-particle orbitals  $\phi_j(\mathbf{r}t)$  satisfying

$$i \frac{\partial}{\partial t} \phi_j(\mathbf{r}t) = \left( -\frac{\nabla^2}{2} + v[n](\mathbf{r}t) \right) \phi_j(\mathbf{r}t) \quad . \quad (13)$$

Whether or not  $v(\mathbf{r}t)$  actually *exists* for an *arbitrary* given density  $n(\mathbf{r}t)$  is an open question in the time-dependent case\*. But if it exists it is *unique*. If one chooses for  $n(\mathbf{r}t)$  the density of the *interacting* system of interest [i. e. the density of Coulomb-interacting particles moving in the external potential  $v_{\text{ext}}(\mathbf{r}t)$ ] then the potential  $v[n]$  is termed the time-dependent Kohn-Sham (TDKS) potential. The latter is usually decomposed into the external potential, a time-dependent Hartree part and the so-called exchange-correlation (xc) potential:

$$v[n](\mathbf{r}t) = v_{\text{ext}}(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r}t) \quad . \quad (14)$$

The xc potential is a *universal* functional of the density, i. e. it has the *same* functional dependence on  $n$  for *all* Coulomb systems, independent of the particular external potential  $v_{\text{ext}}$  of the system at hand.

As in the static case, the great advantage of the TDKS scheme lies in the fact that one can avoid solving the full Schrödinger equation (1) but still in principle obtains the *exact*  $n(\mathbf{r}t)$ . Besides, compared to other methods such as TDHF or time-dependent CI, the TDKS approach is computationally relatively simple due to the fact that  $v_{\text{xc}}$  is a *local* potential in configuration space.

The basic formalism is easily extended to spin-polarized systems.<sup>31</sup> In that case the xc potential depends on the spin densities

$$n_\sigma(\mathbf{r}t) = \sum_{j=1}^{N_\sigma} |\phi_{j\sigma}(\mathbf{r}t)|^2 \quad , \quad \sigma = \uparrow\downarrow \quad (15)$$

with  $N = \sum_\sigma N_\sigma$ , and the spin orbitals  $\phi_{j\sigma}(\mathbf{r}t)$  satisfy the single-particle equations

$$i \frac{\partial}{\partial t} \phi_{j\sigma}(\mathbf{r}t) = \left( -\frac{\nabla^2}{2} + v_\sigma[n_\uparrow, n_\downarrow](\mathbf{r}t) \right) \phi_{j\sigma}(\mathbf{r}t) \quad (16)$$

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\*This question is termed the *v-representability problem*. In the static case, the question could be answered in a satisfactory way. For a review of the static *v-representability* problem see, e. g., chapter 4.2 of Ref. 18.

with

$$v_\sigma[n_\uparrow, n_\downarrow](\mathbf{r}t) = v_{\text{ext}\sigma}(\mathbf{r}t) + \int d^3r' \frac{n_\uparrow(\mathbf{r}'t) + n_\downarrow(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}t) \quad . \quad (17)$$

In practice, the xc potential  $v_{\text{xc}\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}t)$  has to be approximated. The simplest possible form is the so-called adiabatic local density approximation (ALDA):

$$v_{\text{xc}\sigma}^{\text{ALDA}}[n_\uparrow, n_\downarrow](\mathbf{r}t) = \left. \frac{de_{\text{xc}}^{\text{hom}}(n_\uparrow, n_\downarrow)}{dn_\sigma} \right|_{n_\sigma = n_\sigma(\mathbf{r}t)}, \quad (18)$$

where  $e_{\text{xc}}^{\text{hom}}(n_\uparrow, n_\downarrow)$  is the xc energy per volume of the homogeneous spin-polarized electron gas. One might expect this approximation to be good only for systems where the  $n_\uparrow$  and  $n_\downarrow$  are sufficiently slowly varying in space as well as in time. However, contrary to this expectation, it is well known<sup>18</sup> that in the static limit the LDA performs quite well even for strongly inhomogeneous systems such as atoms, molecules and solids. Correspondingly, the ALDA in practice gives quite good results even for cases of rather rapid time dependence. In the exchange-only case (to which we shall restrict ourselves in the following), one explicitly obtains

$$v_{\text{xc}\sigma}^{\text{ALDA}}(\mathbf{r}t) = - (6n_\sigma(\mathbf{r}t)/\pi)^{\frac{1}{3}} \quad . \quad (19)$$

The ALDA is *local* both in space and time, i. e.  $v_{\text{xc}}(\mathbf{r}t)$  only depends on the density values at the very same time  $t$  and the very same location  $\mathbf{r}$ . Recently, a different time-dependent xc potential has been proposed which is tailored for the description of memory effects.<sup>24,32</sup> In this approximation  $v_{\text{xc}}(\mathbf{r}t)$  depends on the density values  $n(\mathbf{r}'t')$  at other locations  $\mathbf{r}'$  and earlier times  $t' \leq t$ . Both approximations have in common that they are based on the homogeneous electron gas.

### 2.3 Time-dependent optimized effective potential

We have recently developed a new method<sup>23,24,33,34</sup> of constructing approximations of  $v_{\text{xc}\sigma}$  which also takes memory effects into account but does not make use of the theory of the homogeneous electron gas. The approach can be viewed as a time-dependent extension of the so-called optimized potential method (OPM). As before, the description of the time evolution of an  $N$ -electron system with a given initial state is achieved in terms of a set of time-dependent spin orbitals  $\{\phi_{j\sigma}(\mathbf{r}t)\}$  obeying a single-particle Schrödinger equation (16). The difference compared to conventional density-functional schemes is that the time-dependent xc potential appearing in Eq. (17) will now be given as a functional of the *orbitals*  $\{\phi_{j\sigma}(\mathbf{r}t)\}$  rather than the spin densities. To construct it, we start with the total quantum mechanical action

$$\begin{aligned} A[\{\phi_{j\sigma}\}] &= \sum_\sigma \sum_j^{N_\sigma} \int_{-\infty}^{t_1} dt \int d^3r \phi_{j\sigma}^*(\mathbf{r}t) \left( i \frac{\partial}{\partial t} + \frac{\nabla^2}{2} - v_{\text{ext}\sigma}(\mathbf{r}t) \right) \phi_{j\sigma}(\mathbf{r}t) \\ &\quad - \frac{1}{2} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{n(\mathbf{r}t)n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} - A_{\text{xc}}[\{\phi_{j\sigma}\}] \end{aligned} \quad (20)$$

written as a functional of the spin orbitals  $\{\phi_{j\sigma}(\mathbf{r}t)\}$ . We associate the action functional (20) with a system which has been in its ground state for all times up until some finite time  $t_0$ . At  $t_0$ , the external potential becomes explicitly time-dependent, and we follow the time

evolution of the system up to some arbitrary later time  $t_1$ . The xc part  $A_{xc}[\{\phi_{j\sigma}\}]$  of the total action (20) has to be approximated in practice. If all correlation effects are neglected (x-only case) then  $A_{xc}$  is constructed from the usual Fock exchange energy functional as

$$A_x = -\frac{1}{2} \sum_{\sigma} \sum_{i,j}^{N_{\sigma}} \int_{-\infty}^{t_1} dt \int d^3r \int d^3r' \frac{\phi_{i\sigma}(\mathbf{r}t)\phi_{j\sigma}^*(\mathbf{r}t)\phi_{i\sigma}^*(\mathbf{r}'t)\phi_{j\sigma}(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} . \quad (21)$$

We now use a stationary action principle with respect to the orbitals under the constraint<sup>†</sup> that the orbitals satisfy the single-particle Schrödinger equation (16) featuring the *local* potential  $v_{\sigma}(\mathbf{r}t)$ . This leads to the following variational equation:

$$\frac{\delta A[\{\phi_{j\sigma}\}]}{\delta v_{\sigma}(\mathbf{r}t)} = \sum_j^{N_{\sigma}} \int_{-\infty}^{+\infty} dt' \int d^3r' \frac{\delta A[\{\phi_{j\sigma}\}]}{\delta \phi_{j\sigma}(\mathbf{r}'t')} \frac{\delta \phi_{j\sigma}(\mathbf{r}'t')}{\delta v_{\sigma}(\mathbf{r}t)} + c.c. = 0 , \quad (22)$$

where *c.c.* denotes the complex conjugate. The first functional derivative,  $\delta A/\delta \phi_{j\sigma}$ , is easily obtained from the given action functional, and to calculate  $\delta \phi_{j\sigma}/\delta v_{\sigma}$  one makes use of time-dependent perturbation theory. One thus arrives at the following integral equation for the optimized xc potential:<sup>33</sup>

$$i \sum_j^{N_{\sigma}} \int_{-\infty}^{t_1} dt' \int d^3r' \left[ v_{xc\sigma}^{\text{OPM}}(\mathbf{r}'t') \phi_{j\sigma}^*(\mathbf{r}'t') - \frac{\delta A_{xc}[\{\phi_{j\sigma}\}]}{\delta \phi_{j\sigma}(\mathbf{r}'t')} \right] \phi_{j\sigma}(\mathbf{r}t) K_{\sigma}(\mathbf{r}t, \mathbf{r}'t') + c.c. = 0 \quad (23)$$

with the kernel  $K_{\sigma}(\mathbf{r}t, \mathbf{r}'t') = \sum_{k=1}^{\infty} \phi_{k\sigma}^*(\mathbf{r}t) \phi_{k\sigma}(\mathbf{r}'t') \theta(t-t')$ . The numerical implementation of the full TDOPM scheme is an extremely demanding task: at each time step one has to solve the integral equation (23) for  $v_{xc\sigma}^{\text{OPM}}$ . For this reason, we have developed a simplified scheme<sup>33</sup> similar to the one proposed by Krieger, Li and Iafrate (KLI)<sup>35</sup> for the static case which yields approximations to  $v_{xc\sigma}^{\text{OPM}}$  as *explicit* functionals of the orbitals. In the x-only case, these approximations are given by

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}t) = w_{x\sigma}(\mathbf{r}t) + \frac{1}{n_{\sigma}(\mathbf{r}t)} \sum_j^{N_{\sigma}} n_{j\sigma}(\mathbf{r}t) \int d^3r' n_{j\sigma}(\mathbf{r}'t) v_{x\sigma}^{\text{KLI}}(\mathbf{r}'t) \quad (24)$$

with

$$w_{x\sigma}(\mathbf{r}t) = -\frac{1}{n_{\sigma}(\mathbf{r}t)} \sum_{j,k}^{N_{\sigma}} \left[ \phi_{j\sigma}(\mathbf{r}t) \phi_{k\sigma}^*(\mathbf{r}t) \int d^3r' \frac{\phi_{k\sigma}(\mathbf{r}'t) \phi_{j\sigma}^*(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} - n_{j\sigma}(\mathbf{r}t) \int d^3r'' \int d^3r' \frac{\phi_{j\sigma}(\mathbf{r}''t) \phi_{k\sigma}^*(\mathbf{r}''t) \phi_{k\sigma}(\mathbf{r}'t) \phi_{j\sigma}^*(\mathbf{r}'t)}{|\mathbf{r}''-\mathbf{r}'|} \right] , \quad (25)$$

where  $n_{j\sigma}(\mathbf{r}t) = |\phi_{j\sigma}(\mathbf{r}t)|^2$ . Eq. (24) still has to be solved for  $v_{x\sigma}^{\text{KLI}}$  which is done in analogy to the static case,<sup>35</sup> the solution only involving the inversion of a  $(N_{\sigma}-1) \times (N_{\sigma}-1)$  matrix.

The full x-only OPM potential constitutes the exact x-only limit of TDDFT. It is distinguished from TDHF by the fact that the OPM exchange potential is local and therefore numerically favourable. We emphasize that the x-only TDOPM should not be

<sup>†</sup>Without this constraint, one arrives at the TDHF equations (using Eq. (21) for  $A_{xc}$ ).

considered as merely a local approximation to TDHF. Apart from its numerical simplicity the x-only OPM is also *physically superior* to HF. This is most easily appreciated in the static limit: The static OPM orbitals (both occupied and unoccupied ones) are self-interaction free. By contrast, in HF only the occupied orbitals are self-interaction free while the unoccupied ones have a serious self-interaction error which causes them to be much too weakly bound. Since time-dependent external fields will cause transitions to the virtual orbitals (which are poorly represented in HF) we expect the x-only OPM to be more accurate than TDHF, even if the full OPM exchange potential is approximated by the KLI potential (24). The KLI potential (24) is significantly more accurate but also numerically more involved than the ALDA potential (19).

## 2.4 Motion of the nuclei

The formalism developed so far is adequate whenever the motion of the nuclei can be neglected. Then the electron-nucleus interaction only enters as a *static* contribution to  $v_{\text{ext}}$ . This is a good approximation for atoms in strong laser fields above the infrared frequency regime. When the nuclei are allowed to move, the nuclear motion couples dynamically to the electronic motion and the situation becomes more complicated.

We now present a TDDFT for systems consisting of  $N$  electrons and  $N_A$  nuclei of charge  $Z_A$  and mass  $M_A$  (in a.u.),  $A = 1, \dots, K$  ( $K$  is the number of different nuclear species). The configuration space vector of the  $\alpha$ th nucleus of species  $A$  is denoted by  $\mathbf{R}_{A\alpha}$ . Then the complete system of electrons and nuclei is described by the Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}, t) = \left[ \hat{H}_e(\mathbf{r}_1 \dots \mathbf{r}_N, t) + \hat{H}_n(\{\mathbf{R}_{A\alpha}\}, t) + \hat{H}_{en}(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}) \right] \Psi(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}, t) \quad (26)$$

with the electronic Hamiltonian

$$\hat{H}_e = \sum_{i=1}^N \left( -\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{ext}}(\mathbf{r}_i t) \right) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad , \quad (27)$$

the nuclear Hamiltonian

$$\hat{H}_n = \sum_{A=1}^K \sum_{\alpha=1}^{N_A} \left( -\frac{\nabla_{\mathbf{R}_{A\alpha}}^2}{2M_A} + V_{\text{ext}}^A(\mathbf{R}_{A\alpha} t) \right) + \frac{1}{2} \underbrace{\sum_{A=1}^K \sum_{\alpha=1}^{N_A} \sum_{B=1}^K \sum_{\beta=1}^{N_B} \frac{Z_A Z_B}{|\mathbf{R}_{A\alpha} - \mathbf{R}_{B\beta}|}}_{(A\alpha) \neq (B\beta)} \quad (28)$$

and the electron-nucleus interaction

$$\hat{H}_{en} = - \sum_{i=1}^N \sum_{A=1}^K \sum_{\alpha=1}^{N_A} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_{A\alpha}|} \quad . \quad (29)$$

Li and Tong<sup>36</sup> have extended the Runge-Gross theorem discussed in section 2.1 to arbitrary multicomponent systems. In the following we apply this work to the coupled system of electrons and nuclei described above. First of all, there exists a rigorous 1-1 mapping



between the set of external potentials and the set of electronic and nuclear densities:

$$\left\{ v_{\text{ext}}(\mathbf{r}t); V_{\text{ext}}^1(\mathbf{R}t), \dots, V_{\text{ext}}^K(\mathbf{R}t) \right\} \xleftrightarrow{1-1} \left\{ n(\mathbf{r}t); n_1(\mathbf{R}t), \dots, n_K(\mathbf{R}t) \right\} . \quad (30)$$

Once again, this 1-1 correspondence is valid for a fixed initial many-body state  $\Psi(\mathbf{r}_1 \dots \mathbf{r}_N, \{\mathbf{R}_{A\alpha}\}, t_0)$ . It is then possible to derive the following set of coupled TDKS equations featuring electronic and nuclear single-particle wave functions  $\phi_j$  and  $\psi_{A\alpha}$ :

$$i \frac{\partial}{\partial t} \phi_j(\mathbf{r}t) = \left( -\frac{\nabla_{\mathbf{r}}^2}{2} + v[n, \{n_B\}](\mathbf{r}t) \right) \phi_j(\mathbf{r}t), \quad j = 1, \dots, N \quad (31)$$

$$i \frac{\partial}{\partial t} \psi_{A\alpha}(\mathbf{R}t) = \left( -\frac{\nabla_{\mathbf{R}}^2}{2M_A} + V^A[n, \{n_B\}](\mathbf{R}t) \right) \psi_{A\alpha}(\mathbf{R}t), \quad \begin{cases} A = 1, \dots, K \\ \alpha = 1, \dots, N_A \end{cases} \quad (32)$$

with the electronic density (12), the nuclear densities

$$n_A(\mathbf{R}t) = \sum_{\alpha=1}^{N_A} n_{A\alpha}(\mathbf{R}t), \quad n_{A\alpha}(\mathbf{R}t) = |\psi_{A\alpha}(\mathbf{R}t)|^2 \quad (33)$$

and the KS potentials

$$v[n, \{n_B\}](\mathbf{r}t) = v_{\text{ext}}(\mathbf{r}t) + \int d^3 r' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} - \sum_{B=1}^K \int d^3 R \frac{Z_B n_B(\mathbf{R}t)}{|\mathbf{r} - \mathbf{R}|} + v_{\text{xc}}[n, \{n_B\}](\mathbf{r}t) \quad (34)$$

$$\begin{aligned} V^A[n, \{n_B\}](\mathbf{R}t) &= V_{\text{ext}}^A(\mathbf{R}t) - Z_A \int d^3 r' \frac{n(\mathbf{r}'t)}{|\mathbf{R} - \mathbf{r}'|} \\ &+ Z_A \sum_{B=1}^K \int d^3 R' \frac{Z_B n_B(\mathbf{R}'t)}{|\mathbf{R} - \mathbf{R}'|} + V_{\text{xc}}^A[n, \{n_B\}](\mathbf{R}t) . \end{aligned} \quad (35)$$

Clearly, a complete numerical solution of the coupled KS equations (31), (32) will be rather involved. As a first simplification, one could reserve a fully dynamic treatment to the valence electrons only and take the core electrons into account by suitably chosen pseudopotentials.<sup>37</sup> This procedure reduces the number of electronic KS equations considerably.

Further simplification can be achieved by treating the nuclear motion classically. Numerical schemes of this type have been derived in various ways.<sup>24,37-40</sup> One obtains a set of TDKS equations for the electrons coupled to a set of classical Newton equations describing the nuclear motion.

Regardless of the obvious numerical advantages one has to keep in mind that a classical treatment of nuclear motion is justified only if the probability densities  $n_{A\alpha}(\mathbf{R}t)$  remain narrow distributions during the whole process considered. The splitting of the nuclear wave packet as observed, e. g., in pump-probe experiments<sup>41-44</sup> or during the dissociation of  $\text{H}_2^+$  in strong fields<sup>45,46</sup> cannot properly be accounted for by treating the nuclear motion classically. In this case, one has to face the complete system (31)–(35) of coupled TDKS equations for electrons and nuclei.

### 3 Neon: beyond the single-active electron approximation

#### 3.1 Numerical method

In this section we present the results of full TDDFT calculations for the neon atom in a strong laser field. We have solved the TDKS equations (13) for the Ne valence electrons using the TDKLI and ALDA xc potentials in the x-only approximation. The external potential is given by

$$v_{\text{ext}}(\mathbf{rt}) = E_0 f(t) z \sin(\omega_0 t) - \frac{10}{r} . \quad (36)$$

The laser field, assumed to be linearly polarized along the  $z$  direction, has been written in dipole approximation in the usual length form, with peak field strength  $E_0$  and frequency  $\omega_0$ . The envelope function,  $f(t)$ , is such that the laser is linearly ramped to its maximum amplitude and then held constant.

Due to the linear polarization of the laser field, rotational symmetry of the system around the  $z$ -axis is preserved for all times. We thus solve the TDKS equations in two dimensions, using a finite-difference scheme in cylindrical coordinates following Kulander.<sup>3</sup> The calculation is done on a finite non-uniform grid (mesh spacings between 0.035 and 0.28  $a_0$ ) similar to Pindzola *et al.*<sup>15</sup> The spatial extent of the mesh is about 20 a.u.  $\times$  60 a.u., the number of grid points is 32010.

In Table 1 we give the energy eigenvalues resulting from a diagonalization of the stationary KS equations on our two-dimensional grid. We first note that there is a slight difference (about 3 mHartrees) between the eigenvalues of the 2p<sub>0</sub> and 2p<sub>1</sub> orbitals due to their different orientations on the grid: the 2p<sub>0</sub> orbital is oriented along the  $z$ -axis, the 2p<sub>1</sub> orbitals perpendicular to it. By choosing a larger grid size and smaller mesh spacings, this energy difference can be further reduced. A comparison with the exact values from the literature<sup>35,47</sup> shows that the average of the 2p orbital energies is too small by 4.9% (41 mHartrees) for KLI and 6.5% (29 mHartrees) for LDA. The 1s and 2s electrons, on the other hand, are overbound by about 12%. These deviations are due to the relative coarseness of the grid in the vicinity of the nucleus which keeps the number of grid points manageable.

For the case of neon and also in general, the KLI eigenvalues are found to be much closer to the HF results than the LDA eigenvalues. This difference is most important for the energy of the highest occupied orbital, which, in exact DFT, is identical with the first ionization potential.<sup>18</sup> The 2p LDA eigenvalue of Ne is too small by almost 50%, whereas the exact KLI result agrees with the HF ionization potential within 1 mHartree (0.1%). This is a direct consequence of the self-interaction error in LDA. We mention that the experimental ionization potential is 0.792 Hartrees.

The grid has an absorbing boundary which keeps the propagated orbitals from being reflected at the edges. The finite boundary also allows us to simulate ionization by calculating the number of electrons

$$N(t) = \int_{\text{finite volume}} d^3r n(\mathbf{rt}) \quad (37)$$

found at time  $t$  within the finite volume of the grid. Assuming that the electron flux absorbed at the grid boundary corresponds to the continuum part of the full time-dependent wave function, the quantity  $N(t)$  can be identified with the number of electrons remaining in a bound state at time  $t$ . This identification has proven to be a useful definition of the bound-state occupation probability in a number of applications.<sup>3,4,48</sup>

In the following, we label the TDKS single-particle orbitals in Eq. (13) by their ground state quantum numbers at the initial time  $t = 0$ . To simplify the calculation, the 1s electrons have been frozen, i. e. we propagate only the 2s and 2p electrons by solving the TDKS equations, whereas the time evolution of the 1s electrons is given by

$$\phi_{1s}(\mathbf{r}t) = \phi_{1s}(\mathbf{r}t_0) e^{-i\epsilon_{1s}(t-t_0)} \quad . \quad (38)$$

We emphasize that the only approximation made in this frozen-core prescription is to write the frozen orbitals in the form (38). The exchange between the frozen orbitals and the other orbitals is fully included in the TDKLI or ALDA potentials. In this respect, our scheme differs from other frozen-core prescriptions such as, e. g., used in the SAE approach.<sup>4,6,7</sup> In view of the high binding energy of the 1s electrons compared to the other electrons (see Table 1), freezing only the 1s electrons is expected to be a very good approximation for the neon atom. Later we shall discuss the effect of additionally freezing electrons of the valence shell and only propagating the most loosely bound, i. e. the 2p<sub>0</sub> orbital.

### 3.2 Ionization

Fig. 1 shows the time-dependent norm

$$N_j(t) = \int_{\text{finite volume}} d^3r |\phi_j(\mathbf{r}t)|^2 \quad (39)$$

of the Ne orbitals initially in the 2s, 2p<sub>0</sub> and 2p<sub>1</sub> states for the laser wave length  $\lambda = 248\text{nm}$  and intensity  $I = 3 \times 10^{15} \text{ W/cm}^2$ . The pulse has been linearly ramped over the first ten cycles and is then kept constant for another 15 cycles. As expected, the 2s orbital is the least ionized of the three orbitals (only 0.3% ionization for TDKLI and 1.9% for ALDA at the end of our calculation). A little surprising at first sight, the 2p<sub>0</sub> and 2p<sub>1</sub> orbitals differ by about an order of magnitude in their degree of ionization (60% for the 2p<sub>0</sub> orbital compared to only 4.75% for the 2p<sub>1</sub> orbital within TDKLI, and 56% for the 2p<sub>0</sub> compared to 7.7% for the 2p<sub>1</sub> orbital within the ALDA). This difference has been observed before by Kulander<sup>6,49</sup> for the case of xenon (within the SAE model). It is due to the fact that the 2p<sub>0</sub> orbital is oriented along the polarization direction of the laser field, which makes it easier for the electrons to escape the nuclear attraction than for the case of the 2p<sub>1</sub> orbital, which is oriented perpendicularly to the field polarization.

To explain the difference between the results obtained within the TDKLI and ALDA schemes shown in Fig. 1, let us again consider Table 1. Interpreting the KS energy eigenvalues in the spirit of Koopmans' theorem (though this is not rigorously justified except for the highest eigenvalue), we observe that it takes 5 photons to ionize the 2p orbitals in TDKLI compared to only 3 photons in ALDA. Similarly, it takes 11 photons to ionize the

2s orbital in TDKLI and only 9 in ALDA. The difference between the curves in Fig. 1A and C is thus hardly surprising. On the other hand, it seems quite unexpected that the ALDA and TDKLI curves cross in Fig. 1B so that the ALDA curve ends up lying *above* the TDKLI curve. This behaviour can be attributed to the fact that the other orbitals are ionized much more strongly in ALDA than in TDKLI, so that their electron density near the nucleus (and therefore their screening of the nuclear charge) is decreased. This makes it slightly more difficult for the 2p<sub>0</sub> electrons to escape within the ALDA scheme.

To establish a link with experiment, one wants to calculate probabilities of finding the neon atom at a time  $t > t_0$  in one of the possible charge states  $k$  to which it can ionize. According to the basic theorems of TDDFT stated in section 2.1, these probabilities  $P^k(t)$  are unique functionals of the total time-dependent density  $n(\mathbf{rt})$ ,

$$P^k(t) = P^k[n](t), \quad k = 0, \dots, +8 \quad . \quad (40)$$

Yet, these probabilities cannot be straightforwardly written as explicit functionals of  $n(\mathbf{rt})$  except for simple cases such as the helium atom<sup>48</sup> with only one occupied orbital. Instead, it is possible to derive explicit expressions for the  $P^k(t)$  in terms of the *orbital* densities  $n_j(\mathbf{rt})$ . Since the Kohn-Sham single-particle orbitals have no rigorous physical meaning, one must consider these  $P^k[\{n_j\}](t)$  only as a reasonable approximation to the exact probabilities (40). To obtain these expressions, we make use of some combinatorial considerations which, for closed-shell systems, lead us to the following identification:

$$\sum_k P^k(t) = \prod_j [N_j(t) + (1 - N_j(t))]^2 \quad . \quad (41)$$

The summation index  $k$  on the left-hand side of Eq. (41) runs over all possible charge states, and the index  $j$  in the product runs over all (doubly occupied) Kohn-Sham orbitals. It is easy to see that both sides of Eq. (41) are separately equal to unity. The factors  $[N_j(t) + (1 - N_j(t))]^2$  of the product account for the fact that each orbital represents two particles which, independently of each other, are either bound (probability  $N_j(t)$ ) or ionized (probability  $1 - N_j(t)$ ). For our case of the neon atom, we thus have (omitting the time argument of the  $N_j$ )

$$\sum_{k=0}^{+8} P^k(t) = [N_{2s} + (1 - N_{2s})]^2 [N_{2p_0} + (1 - N_{2p_0})]^2 [N_{2p_1} + (1 - N_{2p_1})]^4 \quad (42)$$

(remember that the 1s orbital is kept frozen). We then work out the right-hand side of Eq. (42) and rearrange the resulting terms, collecting terms containing  $k$  factors  $(1 - N_j)$  and  $(8 - k)$  factors  $N_j$ . These are then associated with the probabilities  $P^k(t)$ , and we obtain:

$$P^0(t) = N_{2s}^2 N_{2p_0}^2 N_{2p_1}^4 \quad (43)$$

$$P^{+1}(t) = 2N_{2s}(1 - N_{2s})N_{2p_0}^2 N_{2p_1}^4 + 2N_{2s}^2 N_{2p_0}(1 - N_{2p_0})N_{2p_1}^4 + 4N_{2s}^2 N_{2p_0}^2 N_{2p_1}^3 (1 - N_{2p_1}) \quad (44)$$

⋮

$$P^{+8}(t) = (1 - N_{2s})^2 (1 - N_{2p_0})^2 (1 - N_{2p_1})^4 \quad . \quad (45)$$

The populations of the charge states as calculated using TDKLI are displayed up to  $\text{Ne}^{+3}$  in Fig. 2 (same laser parameters as in Fig. 1) and up to  $\text{Ne}^{+4}$  in Fig. 3 (higher laser intensity,  $I = 5 \times 10^{15} \text{ W/cm}^2$ , linear ramp over the first 5 cycles). Higher charge states are not visible due to the linear scale of the plots. The results of the ALDA calculations are very similar to the TDKLI results. In Table 2 we give for both schemes the probabilities of finding the Neon atom in one of the charge states 0 through +8 for both sets of laser parameters after 25 and 20 optical cycles, respectively. We see that the values extend over more than 10 orders of magnitude. For the laser parameters used, a complete stripping of the valence shell is of course extremely unlikely.

Let us now consider Fig. 2. We see that the probability for  $\text{Ne}^{+1}$  has reached its maximum at about the 14th cycle and then slowly decreases, while the probability for  $\text{Ne}^{+2}$  is still growing. At the 25th cycle,  $P^{+1}$  is slightly higher than  $P^{+2}$  (0.419 compared to 0.378), and both are higher than  $P^0 = 0.130$ . The lowest probability visible on a non-logarithmic scale is  $P^{+3}$ , which is 0.0673 at the 25th cycle.

The distribution of the charge states is different at the higher laser intensity of  $I = 5 \times 10^{15} \text{ W/cm}^2$ , see Fig. 3. We have to keep in mind, however, that the switching-on of the pulse was performed with a shorter, 5-cycle ramp.  $P^{+1}$  reaches its maximum between the 6th and 7th cycle and then goes down again. In contrast to Fig. 2, the curves for  $P^{+1}$  and  $P^{+2}$  cross after about 9.5 optical cycles, and at the end of the simulation after the 20th cycle the doubly charged Ne ions clearly dominate:  $P^{+2} = 0.510$  compared to  $P^{+1} = 0.291$  and  $P^{+3} = 0.138$ . The probability for the Ne atom to stay neutral is only 0.0452 at the end of the calculation. The lowest visible charge state in our plot is now the +4 state with  $P^{+4} = 0.0151$  at the 20th cycle. Of course, for the parameters of Fig. 2, a cross-over between  $P^{+1}$  and  $P^{+2}$  will also occur, but for much later times ( $t > 25$  optical cycles).

In order to make contact with experimental ion yields<sup>50,51</sup> the above probabilities  $P^k(t)$  have to be calculated for various intensities and then folded with a realistic spatial pulse profile.

### 3.3 Harmonic generation

To simulate harmonic generation of the neon atom, we calculate the induced dipole moment  $d(t) = \int d^3r z n(\mathbf{r}, t)$  which is then Fourier transformed over the last 5 cycles of the constant-intensity interval. The square of the resulting Fourier transform,  $|d(\omega)|^2$ , has been shown<sup>52</sup> to be proportional to the experimentally observed harmonic distribution to within a very good approximation.

We have calculated the harmonic spectra for both sets of laser parameters (Figs. 4A and B). We see that for the lower intensity,  $I = 3 \times 10^{15} \text{ W/cm}^2$ , the plateau extends up to the 23rd harmonic, whereas for  $I = 5 \times 10^{15} \text{ W/cm}^2$  it goes up to the 33rd harmonic, both within ALDA and TDKLI.

We compare our calculated harmonic distributions with experimental data by Sarukura *et al.*<sup>53</sup> The experiment was performed with a KrF laser ( $\lambda = 248 \text{ nm}$ ) at a pulse duration of 280 femtoseconds and a peak intensity of  $4 \times 10^{17} \text{ W/cm}^2$ . The experimental peak

intensity is two orders of magnitude higher than the intensities used in our calculations. It is to be expected, however, that the atoms have become completely ionized by the time the pulse reaches its maximum. The detected harmonic radiation must therefore have been induced during the rise time of the pulse, probably in an intensity range close to the intensities used in our calculations.

The experimental data points shown in Figs. 4A and B have both been normalized to the value of the 17th harmonic (within TDKLI) in Fig. 4A. At  $3 \times 10^{15}$  W/cm<sup>2</sup>, we see that the calculated spectra can explain the measured harmonics 15 to 21, whereas the harmonics 17 to 25 (with the exception of the strongly suppressed 25th harmonic for ALDA and the a little less strongly suppressed 21st harmonic for both schemes) are explained by the spectrum at  $5 \times 10^{15}$  W/cm<sup>2</sup>. Hence, our calculations show that the generation of the harmonics 15 to 25 is dominated by the intensity range covered in our calculations. We can match this part of the experimental harmonic distribution pretty well by a superposition of the two TDKLI spectra with equal weights. This corresponds to the experimental situation where the harmonic photons generated on different positions in the laser focus (and, therefore, coming from regimes with different laser intensities) are superimposed in the detector. An equal-weight superposition of the two ALDA spectra agrees somewhat less accurately with the experimental spectrum.

In order to explain the same experimental data, Kondo *et al.*<sup>54</sup> have performed numerical simulations based on a simple atomic model (a single electron in a short-range model potential). They calculated the harmonic spectrum for neutral Ne at  $4.5 \times 10^{14}$  W/cm<sup>2</sup>, for Ne<sup>+1</sup> at  $1.8 \times 10^{15}$  W/cm<sup>2</sup> and for Ne<sup>+2</sup> at  $4.8 \times 10^{15}$  W/cm<sup>2</sup>. By a suitable superposition of these single-electron spectra, they reproduced the qualitative features of the experimental harmonic distribution. The authors attributed the harmonics above the 11th to Ne<sup>+1</sup> and the harmonics above the 21st to doubly charged Ne.

We come to a similar conclusion by considering the populations of the ionized states of the Ne atom as given in Figs. 2 and 3 and in Table 2. For the intensity  $3 \times 10^{15}$  W/cm<sup>2</sup>, we find a slightly higher probability for Ne<sup>+1</sup> than for Ne<sup>+2</sup>. Thus, the harmonics up to the 21st are most probably caused by Ne<sup>+1</sup>. At the higher intensity, we find that the doubly charged Ne ions are prevailing. We can therefore attribute the harmonics above the 21st to Ne<sup>+2</sup>, in accordance with Ref. 54.

The results of this section have received additional support by a very recent experimental study<sup>55</sup> performed under very similar conditions as in Ref. 53 but with improved detection techniques. A theoretical model of these experimental data based on the one-dimensional SAE approximation again ascribes the harmonics above the 21st to Ne<sup>+2</sup>.

### 3.4 A “single-active orbital” scheme

We found that the harmonic spectra displayed in Figs. 4A and B are dominated by the contribution of the 2p<sub>0</sub> orbital to the total dipole moment. This leads us to the following question: To what extent is the harmonic motion of the 2p<sub>0</sub> electrons influenced by the motion of the other electrons? In order to study this question, we have performed an additional TDKLI calculation with the same laser parameters as in Fig. 4A, this time

with all but the  $2p_0$  electrons frozen in their initial states. Fig. 5 shows a comparison of the time-dependent norm of the  $2p_0$  orbital calculated in the original scheme (i. e. all electrons are propagated under the influence of the laser except the  $1s$  electrons) and in the new frozen-core scheme (i. e. propagation of the  $2p_0$  orbital only). The difference between the two curves is very slight, implying that the *ionization* of the  $2p_0$  orbital can reliably be calculated with the new frozen-core prescription.

However, if we calculate the *harmonic spectrum* in the new frozen-core scheme, we find a strong deviation from the spectrum calculated in the original scheme. Comparing the two spectra in Fig. 6, we see that the effect of freezing the  $2s$  and  $2p_1$  electrons is twofold: First of all, the whole spectrum is slightly shifted towards lower values of  $|d(\omega)|^2$ . The second, more drastic effect is the appearance of a pronounced Lorentz-profile resonance peak just below the 7th harmonic at an energy of 1.18 Hartrees. This energy is very close to the difference of the Ne  $2s$  and  $2p_0$  KLI orbital eigenvalues given in Table 1 (1.14 Hartrees) which suggests that the peak in Fig. 6 is due to a resonance of the  $2s$  and  $2p_0$  KS orbitals.

This resonance is also present when all valence electrons are fully propagated, but it does not show up in the total harmonic spectrum. This is because the oscillating dipole moment of the  $2s$  orbital has a component with the same resonance frequency, but phase-shifted by  $\pi$  with respect to its counterpart in the  $2p_0$  orbital dipole moment. When summed up to the total dipole moment, these frequency components therefore cancel each other. The appearance of the resonance peak in the harmonic spectrum obtained with the “single-active orbital” approximation thus appears to be an artefact of the method.

This leads us to the conclusion that a reliable density-functional calculation of harmonic spectra requires simultaneously treating the time evolution of *all* electrons belonging to the outermost atomic shell. We claim that this observation is also relevant for the widely used SAE model, since a very similar resonance phenomenon has been observed by Kulan-der and Shore<sup>49</sup> for the case of Xenon, where a single  $5p_0$  electron was propagated only.

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	HF <sup>(exact)</sup>	KLI <sup>(exact)</sup>	LDA <sup>(exact)</sup>	KLI <sup>(grid)</sup>	LDA <sup>(grid)</sup>
$-\epsilon_{1s}$	32.77	30.80	30.24	35.13	34.47
$-\epsilon_{2s}$	1.930	1.707	1.266	1.951	1.522
$-\epsilon_{2p_0}$	0.8504	0.8494	0.4431	0.8098	0.4159
$-\epsilon_{2p_1}$	0.8504	0.8494	0.4431	0.8065	0.4126

Table 1: Ne orbital energies (in Hartrees) calculated in various exchange-only schemes: Hartree-Fock (HF), optimized potential method (KLI), local density approximation (LDA). The values calculated on the finite grid are compared with the exact values from the literature.<sup>35,47</sup>

charge	$I = 3 \times 10^{15} \text{ W/cm}^2$		$I = 5 \times 10^{15} \text{ W/cm}^2$	
	TDKLI	ALDA	TDKLI	ALDA
0	0.130	0.135	$4.52 \times 10^{-2}$	$5.46 \times 10^{-2}$
+1	0.419	0.394	0.291	0.288
+2	0.378	0.355	0.510	0.447
+3	$6.73 \times 10^{-2}$	0.101	0.138	0.177
+4	$5.04 \times 10^{-3}$	$1.36 \times 10^{-2}$	$1.51 \times 10^{-2}$	$3.03 \times 10^{-2}$
+5	$1.80 \times 10^{-4}$	$9.53 \times 10^{-4}$	$7.76 \times 10^{-4}$	$2.44 \times 10^{-3}$
+6	$2.82 \times 10^{-6}$	$3.50 \times 10^{-5}$	$1.67 \times 10^{-5}$	$8.12 \times 10^{-5}$
+7	$1.28 \times 10^{-8}$	$6.12 \times 10^{-7}$	$7.57 \times 10^{-8}$	$4.71 \times 10^{-7}$
+8	$1.75 \times 10^{-11}$	$3.98 \times 10^{-9}$	$9.74 \times 10^{-11}$	$7.53 \times 10^{-10}$

Table 2: Probabilities of finding the neon atom in one of the charge states 0 through +8 after 25 optical cycles (for  $I = 3 \times 10^{15} \text{ W/cm}^2$ ) and 20 optical cycles (for  $I = 5 \times 10^{15} \text{ W/cm}^2$ ), respectively.

## Abbreviations

ALDA	adiabatic local density approximation
CI	configuration-interaction
DFT	density functional theory
HF	Hartree-Fock
KLI	Krieger-Li-Iafrate
KS	Kohn-Sham
LDA	local density approximation
OPM	optimized potential method
SAE	single-active electron
TDDFT	time-dependent density functional theory
TDHF	time-dependent Hartree-Fock
TDKLI	time-dependent Krieger-Li-Iafrate
TDKS	time-dependent Kohn-Sham
TDOPM	time-dependent optimized potential method
x	exchange
xc	exchange-correlation

## Figure Captions

**Figure 1:** Time evolution of the norm of the Ne 2s orbital (A), the Ne 2p<sub>0</sub> orbital (B) and the Ne 2p<sub>1</sub> orbital (C), calculated in the x-only TDKLI and ALDA schemes. Laser parameters:  $\lambda = 248$  nm,  $I = 3 \times 10^{15}$  W/cm<sup>2</sup>, linear ramp over the first 10 cycles. One optical cycle corresponds to 0.82 femtoseconds.

**Figure 2:** Population of the ionized states of Ne calculated with TDKLI. Laser parameters as in Fig. 1 ( $\lambda = 248$  nm,  $I = 3 \times 10^{15}$  W/cm<sup>2</sup>, linear ramp over the first 10 cycles).

**Figure 3:** Population of the ionized states of Ne calculated with TDKLI. Laser parameters:  $\lambda = 248$  nm,  $I = 5 \times 10^{15}$  W/cm<sup>2</sup>, linear ramp over the first 5 cycles.

**Figure 4:** Harmonic distributions for Ne ( $\lambda = 248$  nm), calculated within the TDKLI and ALDA schemes at  $I = 3 \times 10^{15}$  W/cm<sup>2</sup> (A) and  $I = 5 \times 10^{15}$  W/cm<sup>2</sup> (B). The experimental data<sup>53</sup> were taken using 280 fs pulses at the same laser wave length but with  $I = 4 \times 10^{17}$  W/cm<sup>2</sup> peak intensity.

**Figure 5:** Time-dependent norm of the 2p<sub>0</sub> orbital, calculated with TDKLI in two different schemes (propagation of all valence electrons and of the 2p<sub>0</sub> orbital only, respectively). The laser parameters are  $\lambda = 248$  nm and  $I = 3 \times 10^{15}$  W/cm<sup>2</sup>.

**Figure 6:** Line: harmonic spectrum of Ne calculated by propagating the 2p<sub>0</sub> orbital only. Squares: harmonic distribution calculated by propagating all valence electrons (both calculations were done using TDKLI). Laser parameters as in Fig. 5.