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# Strong field ionization of linear molecules: a correlated three-dimensional calculation

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## Abstract

We introduce an implementation of the MCTDHF method in three dimensions restricted to cylindrical symmetry. Ionization yields for linear molecules in strong short laser pulses are calculated. We find a strong increase of ionization with molecule size, which is in striking disagreement with earlier results for one-dimensional model systems (Caillat *et al* 2005 *Phys. Rev. A* **71** 012712).

## 1. Introduction

Several experiments on the ionization of molecules by strong laser pulses show that these systems behave distinctly differently from atoms. There are the obvious effects of orientation of the molecule relative to the laser field, but also more subtle differences that are traced back to the in general more complex valence electronic structure. Most strikingly, it is consistently found [1, 2] that molecules resist ionization better than atoms with the same ionization potential, quite opposite to the naive expectation that the generally larger polarizability of molecules would enhance the effect of the laser on the molecule. Similar observations were made for metal clusters [3] and C<sub>60</sub> [4]. In all cases the laser field strengths are assumed to be large enough for dominant ionization by tunnelling or barrier suppression.

There are a variety of approaches to incorporate molecular effects into the theory of strong laser ionization. First, the Ammosov–Delone–Krainov (ADK) theory for the ionization of atoms was generalized to molecules by replacing the atomic orbital of the single active electron (SAE) by a suitable approximation for a molecular system [5]. These approaches may, in principle, explain the ionization of small molecules with little electron mobility. The enhanced resistance to ionization is generally attributed to multi-electron effects. The simplest multi-electron effect is screening, which reduces the effective field acting on a single electron and thus reduces tunnelling. Screening can be included into the SAE picture

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by the addition of suitable polarization terms to the potential that the electron sees during tunnelling [6]. The derivation of these corrections is exceedingly difficult and involves serious approximations. While the basic picture may well be correct, it is difficult to verify the approaches by comparison with experimental data only.

Numerical calculations can provide data on ionization that are of utmost importance, both, as input to experiments and to verify more intuitive physical pictures of the ionization mechanisms. So far, this was possible for a single or at most two active electrons in the field [7–10]. One method that would be applicable beyond the two-electron limit is time-dependent density functional theory. Unfortunately, until now the method is plagued by fundamental problems when applied to strongly ionizing systems [11, 12]. The problems seen in the time-dependent density functional theory are reminiscent of the shortcomings of the time-dependent Hartree–Fock method, which is known to fail for strong field phenomena [13]. The basic flaw of time-dependent Hartree–Fock appears already in strong ionization of a two-electron system: it cannot describe the transition from an initial state with two identical orbitals to a final state where the two orbitals strongly differ. This problem is overcome by the multi-configuration time-dependent Hartree–Fock (MCTDHF) method, which was first introduced and applied to strong laser-molecule interactions in [14]. Its rapid convergence to the exact solutions of the time-dependent Schrödinger equation was demonstrated for important observables such as total ionization, electron spectra and branching into channels with different ionic excitations [15, 16]. Meanwhile the method has found several more applications [17–19]. Except for [17], which was limited to bound state problems, all applications of MCTDHF so far were to one-dimensional (1D) model systems.

In the present paper, we introduce an extension of MCTDHF to three-dimensional (3D), cylindrically symmetric systems and apply it to the ionization of linear molecules with two, four, and six active electrons by strong short laser pulses. We show that results differ qualitatively from the one-dimensional models. The importance of correlation for total ionization is less pronounced in three dimensions compared to one-dimensional models. In addition, ionization increases with molecule size as expected, in contrast to the counter-intuitive behaviour found in the one-dimensional models.

## 2. The MCTDHF method

We review the principles of the MCTDHF method, as introduced for 1D in [16], to which the reader is referred for further details. Extending this work, we then present a 3D implementation.

While in time-dependent Hartree–Fock the wavefunction contains only a single Slater determinant, the MCTDHF ansatz for the  $f$ -electron wavefunction consists of a linear combination of all Slater determinants (configurations) that can be formed from a set of  $n$  time-dependent one-particle orbitals  $\Phi = \{\phi_j, j = 1, \dots, n\}$ . Denoting the spatial and spin coordinates collectively by  $q_i = (\vec{r}_i, s_i)$ , the ansatz reads

$$\Psi(q_1, \dots, q_f; t) = \sum_{j_1=1}^n \cdots \sum_{j_f=1}^n c_{j_1 \dots j_f}(t) \phi_{j_1}(q_1; t) \cdots \phi_{j_f}(q_f; t) \quad (1)$$

where the coefficients  $\mathbf{c} = \{c_{j_1, \dots, j_f}\}$  are taken to be totally antisymmetric with respect to their indices, which leaves only  $\binom{n}{f}$  independent coefficients. Increasing the number of orbitals  $n$  allows us to systematically include correlation effects. In the limit  $n \rightarrow \infty$  the exact wavefunction is recovered.

From the Dirac–Frenkel variational principle

$$\langle \delta \Psi(t) | i \frac{d}{dt} - H(t) | \Psi(t) \rangle = 0 \quad \forall t, \quad (2)$$

one derives the nonlinear and coupled equations of motion for the coefficients and orbitals

$$i\dot{\mathbf{c}}(t) = A[\Phi]\mathbf{c}(t) \quad i\dot{\Phi}(q, t) = B[\mathbf{c}, \Phi]\Phi(q, t)$$

(the linear operators  $A$  and  $B$  are given explicitly in [16]).

The antisymmetry of the wavefunction is due to the fermionic nature of the electrons and the exchange symmetry of the Hamiltonian (in atomic units)

$$H(t) = \sum_{l=1}^f \frac{1}{2} \left[ \frac{1}{i} \vec{\nabla}_l - \vec{A}(t) \right]^2 + V_n(\vec{r}_l) + \sum_{k=l+1}^f V_{ee}(|\vec{r}_l - \vec{r}_k|) + V_{\text{cap}}. \quad (3)$$

The laser field is represented in velocity gauge and dipole approximation.  $V_n(\vec{x}_j)$  is the nuclear potential (to be specified later) acting on the  $j$ th electron, and  $V_{ee}$  denotes the usual electron–electron Coulomb repulsion. To reduce the computational cost for the electron–electron interaction, we approximate  $V_{ee}$  by a lower-rank operator using the so-called Schmidt decomposition (or singular value decomposition). The full procedure is described in [16].

To suppress unphysical reflections at the boundaries, we include in  $H$  a complex absorbing potential (CAP), which we choose to be purely imaginary  $V_{\text{cap}} = -iW(\vec{r})$ . In cylindrical coordinates, we have

$$W(\vec{r}) = W^{(1)}(z) + W^{(1)}(\rho) \quad \xi = z, \rho$$

$$W^{(1)}(\xi) = \begin{cases} 0 & |\xi| < \xi_0 \\ \frac{W_\xi}{2} \left[ 1 - \cos \left( \pi \frac{|\xi| - \xi_0}{L_\xi} \right) \right] & \xi_0 \leq \xi < \xi_0 + L_\xi \\ W_\xi & \xi_0 + L_\xi \leq \xi. \end{cases}$$

The parameters  $W_z$ ,  $L_z$ ,  $z_0$  and  $W_\rho$ ,  $L_\rho$ ,  $\rho_0$  are adjusted empirically to minimize reflections for the physical situation at hand.

For the extension to 3D, cylindrical coordinates  $(z, \rho, \varphi)$  are suggested by the geometry of interactions with a strong linearly polarized laser field. Since we do not account for the  $\varphi$ -dependence of the orbitals, we have effectively a 2D problem. In restricting the  $z$ -component of angular momentum to  $\ell_z = 0$  for each orbital, we exclude the correlation of electrons on the  $\varphi$ -coordinate due to the coupling of different angular momenta  $\ell_z$  by the Coulomb interaction.

Our 2D orbitals are built from products of 1D primitive functions,

$$\phi_j(z, \rho; t) = \sum_{v_1=1}^{N_1} \sum_{v_2=1}^{N_2} \sum_{\lambda_1=1}^{L_1} \sum_{\lambda_2=1}^{L_2} \alpha_{v_1\lambda_1, v_2\lambda_2}^j(t) h_{v_1\lambda_1}^{(1)}(z) h_{v_2\lambda_2}^{(2)}(\rho), \quad (4)$$

which allows us to benefit from the tensor product structure of operators. Each coordinate  $z, \rho$  is divided into finite elements (FE) of equal length. On every FE  $v$ , the basis  $h_{v\lambda}^{(i)}$  consists of  $\lambda = 0, \dots, p$  polynomials up to degree  $p$ , which is the order of the FE. Internally, the basis is expressed in Legendre polynomials. Note that the support of the basis functions is confined to one FE. In general, the  $h_{v\lambda}^{(i)}$  also vanish at the endpoints of the FE, except for two of them, which are non-zero at the lower and upper boundaries, respectively. By matching the coefficients of the corresponding functions in adjacent FE's continuity of the orbitals is ensured. A big advantage of the FE approach is that local operators are represented by banded matrices, as functions on different FE's have no overlap. Actually, the matrices are block-diagonal, but the blocks are interlaced due to the continuity condition. Furthermore, since the orbitals are linear combinations of piecewise polynomials, integrations can be done quite accurately by Gauss quadrature. For matrix elements of arbitrary kernels, which do not correspond to any of the classical weight functions, optimal quadrature weights and base points can be constructed numerically (e.g. with the ORTHPOL package from netlib). A more detailed description of our implementation of the FE method can be found in [20].

**Table 1.**  $H_2$  ground-state energy at an internuclear distance of 1.4 au.

$n$	$f$	Configurations	$E$
2	2	1	−1.8466
4	2	6	−1.8652
6	2	15	−1.8725
8	2	28	−1.8732
Exact			−1.8887

Because of the serious computational effort involved, 2D calculations are only feasible on parallel machines in sensible time. For the parallelization we distribute the spatial domain over the processors by splitting the  $z$ -axis at finite element boundaries. Profiting from the banded structure of the matrices, communication between different nodes occurs only in two cases:

- To enforce continuity of the orbitals over CPU boundaries.
- For the electron–electron interaction, which requires the calculation of the mean-field potential.

The cost of the latter is by far dominant and reducing the rank as mentioned above is crucial.

In table 1 we show the convergence of the MCTDHF electronic ground state energy of  $H_2$  with increasing number of orbitals  $n$ . The difference to the exact electronic energy is about 25% of the total correlation energy, which must be ascribed to the absence of correlation on the  $\varphi$ -coordinate.

In the ionization computations presented in this paper, typical box dimensions are  $|z| \leq 100$  au and  $\rho \leq 20$  au. The basis sizes are chosen such that they admit a maximum momentum of about 15 au in  $z$  and 7.5 au in  $\rho$ . For performance reasons, the FE order in 2D calculation was set to 2, which keeps the bandwidth of matrices low.

### 3. Ionization of linear molecules

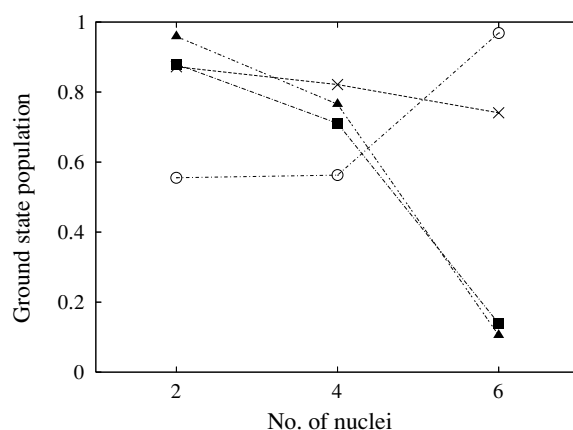
We investigate the ionization of 3D linear model molecules with two to six nuclei at a constant internuclear separation. It is assumed that there is one active electron per nucleus, while the remaining electrons only contribute through a screening of the nuclear potentials in the form

$$V_n = \sum_{k=1}^K \frac{1}{\sqrt{x^2 + y^2 + (z + kR)^2 + a^2}}. \quad (5)$$

The screening parameter  $a$  was adjusted to obtain a constant ionization potential of 0.3 atomic units ( $\approx 10$  eV), independent of the number of nuclei  $K$ . Two different internuclear separations  $R = 1.4$  and  $R = 3$  were used in the calculations. As initial states we used the singlet neutral ground states of the molecules. Note that in the 3D case screening is only needed to adjust ionization potentials. The specific form of the screening in equation (5) was chosen in order to have the closest possible analogy with the commonly used 1D screened Coulomb potentials that were also employed in [16]. We show below that our general conclusions are independent of that particular nuclear potential.

The model molecules are exposed to a laser pulse with linear polarization along the molecular axis ( $z$ -direction)

$$\vec{A}(t) = \vec{e}_z A_0(t) \sin(\omega_l t), \quad (6)$$



**Figure 1.** Residual ground-state population for 3D and 1D model molecules as a function of molecule size. In 3D, population decreases with molecule size for internuclear separations  $R = 1.4$  (crosses) and  $R = 3$  (full squares), and the Hartree–Fock result is similar to the correlated result (triangles,  $R = 3$ ). In contrast, 1D models show an increase of residual population with size (circles).

where we assumed Gaussian and  $\sin^2$  envelope functions  $A_0(t)$  with a width of 1 optical cycle. We use laser frequency  $\omega_l = 0.057$  ( $\lambda = 800$  nm) and intensity  $I = 2.5 \times 10^{13} \text{ W cm}^{-2}$  ( $7.1 \times 10^{-4}$  au), which leads to nearly 90% depletion for the largest molecule at  $R = 3$ . For  $R = 1.4$  a slightly higher intensity of  $I = 3.5 \times 10^{13} \text{ W cm}^{-2}$  ( $10^{-3}$  au) was used. Figure 1 shows the depletion of the ground state after passage of the laser pulse for molecules with an increasing number of nuclei. For both internuclear separations,  $R = 1.4$  and  $R = 3$ , depletion increases with the number of nuclei. For figure 1 we used a  $\sin^2$  pulse shape and pulse duration of 1 optical cycle. At the very short pulse duration used here the pulse shape becomes important, but it does not affect our results qualitatively. When a Gaussian pulse is used, the maximal change from 13% to 23% residual population occurs for the largest 3D molecule with internuclear separation  $R = 3$ .

The increase of depletion for long molecules is in accordance with naive expectations that larger molecules should respond more strongly to an external field because of their generally larger polarizability. It is, however, in striking disagreement with our findings for 1D model molecules with the same internuclear separation of  $R = 1.4$  au and at similar total depletion [16], where the opposite trend was observed: larger 1D molecules were harder to ionize. These findings are confirmed for 1D models with internuclear separation 3 and at the present laser pulse parameters (cf figure 1).

Another important difference between the 1D and 3D calculations is found in the *single-configuration* time-dependent Hartree–Fock (TDHF) approximation: in 1D, ionization yields calculated in TDHF were much below the correct yields [16]. In addition, the dependence of the TDHF yields on the molecule size was opposite of the MCTDHF yields. In 3D, TDHF qualitatively agrees with MCTDHF with TDHF yields typically only by about 10% below MCTDHF.

At present we cannot offer a conclusive explanation for these observations. Screening was suggested as the cause for the experimentally observed stability of multi-electron systems against ionization [2] and was identified qualitatively in 1D calculations [19]. In that picture, the electron density is enhanced near the tunnelling barrier, which raises the tunnel barrier

seen by a single electron, or, from an alternative point of view, reduces the local field strength. That mechanism exists in three dimensions as well. However, a closer inspection of the idea shows that (i) it is applicable only to static electric fields or at Keldysh parameters  $\gamma \ll 1$  and (ii) the Stark shift of the tunnelling electron energy relative to the top of the tunnelling barrier must be properly included. The constraint on the Keldysh parameter in molecules may be more stringent, as electron mobility is not so much characterized by the ionization potential  $I_p$ , but by the spacing between ground and excited electronic levels, which decreases with size. Even when the quasi-static tunnelling picture is applicable the interplay of screening on the one hand and adiabatic dc Stark shift on the other hand is complicated by the fact that both quantities enter exponentially into the tunnelling rate. A detailed analysis of that mechanism is beyond the scope of the present paper.

The 3D potentials (5) were used because of their similarity to the 1D model potentials of [16] which allowed us to more clearly expose effects due to dimensionality. We repeated the calculations with modified Coulomb potentials of the form

$$V_n = \sum_k V(\sqrt{x^2 + y^2 + (z + kR)^2}), \quad V(r) = -\frac{1}{r} + e^{-ar} \frac{b}{r}, \quad (7)$$

where the parameters  $a$  and  $b$  were adjusted to obtain ionization potentials of  $I_p = 0.3$  as for the potentials (5). We find that ionization rates are hardly affected by the exact shape of  $V_n$ .

#### 4. Conclusions

We have introduced the 3D MCTDHF method and demonstrated its application to realistic strong field ionization of molecules. Contrary to our own expectations, we find a strong influence of dimensionality on the ionization yields. Firstly, the importance of correlation is strongly exaggerated in commonly used 1D models. Here we define as the effect of correlation the difference in ionization found in a single- versus a multi-configuration time-dependent Hartree–Fock calculation. Secondly, 1D and 3D models show the opposite dependence of the ionization yield on molecule size.

The use of 1D models for the study of strong field ionization is put into serious doubt by our findings. Such models may only be used for quick studies, but always require independent confirmation by a more refined calculation. Also, we must re-raise the question about the unexpected stability of larger molecules when compared to atoms with the same ionization potential. At least for our 3D linear model molecules we cannot confirm such a tendency. Influence of core electrons cannot be excluded, but seems unlikely as ionization depends only weakly on the core screening. Laser pulse parameters used here were not fully realistic: although pulse shape has no influence on our conclusions, pulse duration is much shorter than in experiments. For a systematic comparison with experiments longer pulses and a more realistic modeling of the valence electrons will be required.

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