Single and Double Ionization of Atoms and Small Molecules by Short-Pulse Intense Laser Fields

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Abstract. Examples of recent calculations for the interaction of intense short-pulse laser fields with (quasi)one- and two-electron atomic (H, He, Li) and molecular (H\textsuperscript{+}, H\textsubscript{2}) targets are presented. In light of the often challenging parameter sets chosen in both experiment and other theoretical work, the need to carefully check both the numerical aspects and physical effects such as resonances is emphasized.

1. Introduction
The response of atoms and molecules irradiated by intense laser pulses has attracted growing interest in recent years (see, for example, [1] for a recent collection of papers). This is to a large extent due to the rapid progress in both experimental and theoretical/computational techniques regarding few-cycle infrared (IR) pulses, free-electron lasers (FELs) and high-harmonic generation (HHG) that can provide extreme ultraviolet (XUV) pulses, and supercomputer resources that allow for the direct solution of the time-dependent Schrödinger equation (TDSE) on a space-time grid using massively parallel machines. For (quasi)-one electron targets, very detailed information about the response of the active electron to single and multiple (e.g. in pump-probe setups) laser pulses can be obtained, while the correlated response of multi-electron targets to strong driving laser fields can also be studied in both the time and momentum domains.

Over the past few years, our group at Drake University has been engaged in performing a number of benchmark calculations for simple atoms and molecules, such as H, He, Li, H\textsubscript{2}\textsuperscript{+} and H\textsubscript{2}. An overview of our work (not a review of the field) with a few selected examples is presented in this paper. Work on heavier targets (Ne and Ar) can be found in refs. [2, 3]. Despite the apparent simplicity of these targets, it turns out that some of the parameters (central frequency, peak intensity, pulse length, pulse shape, etc.) chosen in many experiments, as well as other theoretical studies, make the calculations extremely challenging. Hence, we have put strong emphasis on developing accurate numerical methods and the accompanying computer programs. In rather extreme scenarios, somewhat surprising results were obtained. However, the extensive tests carried out give us confidence in our predictions.

In the following section, we briefly describe some of the numerical techniques implemented in our programs. This is followed by a few illustrative examples. Details can be found in the references given. Unless indicated otherwise, atomic units are used throughout this paper.
2. Numerical Methods

The results presented below were obtained with a number of different approaches. For H and Li, we employed the matrix iteration method (MIM) of Nurhuda and Faisal [4] to propagate the initial field-free state in time under the influence of a strong laser field. Depending on the peak intensity of the pulse(s), we use either the length or the velocity form of the electric dipole operator. Details were described by Grum-Grzhimailo et al [5]. The method is very efficient and numerically accurate. However, it requires the solution of a tridiagonal system of equations at every timestep, both in the radial coordinate (when using a finite-difference method) and in the angular momentum due to the dipole coupling of different partial-wave symmetries. Hence, special care has to be taken to ensure efficient parallelization of the computer code.

For He, we combined field-free and dipole matrices obtained with the B-spline R-matrix method [6, 7] with an efficient short-iterative Lanczos (SIL) [8] propagation scheme. This is an explicit method that effectively reduces to matrix-vector multiplications, for which highly optimized library routines are widely available. The computer code used for single ionization of Ne and Ar is published [9]. Such programs run efficiently on passively parallel machines using a hybrid technique of OpenMP and MPI parallelization.

Finally, for H_2^+ and H_2, we again employed the SIL technique, but this time combined with a finite-element discrete-variable representation (FE-DVR). Due to the lack of spherical symmetry and the entangled motions of the nuclei and the electrons, the situation in molecules is much more complicated than in atoms. The latter complication is often neglected by limiting the treatment to the fixed-nuclei approximation (FNA), which in turn limits the comparison with experiment. Even though the electron-electron interaction (needed for the H_2 problem) is complicated, formulating the problem in prolate-spheroidal coordinates and thereby exploring the natural symmetry of the problem is highly advantageous.

3. Example Results

This section provides an overview of some of the calculations that have been performed at Drake University over the past few years. As mentioned above, strong emphasis has been put on the numerical stability of the results, including those from essentially model problems for which experimental do not (yet) exist. We start with atomic hydrogen and lithium, assuming that the latter can effectively be described as a quasi-one-electron target with the inner two electrons being represented by a core potential. We then move on to helium as a two-electron target before going to the H_2^+ and H_2 molecules.

3.1. H and Li

Figure 1 shows an example for ionization of atomic hydrogen by a few-cycle 780 nm laser pulse of peak intensity of 10^{15} W/cm^2. Handling such a strong IR field far outside the perturbative regime represents a challenging numerical problem. Using the velocity gauge of the electric dipole operator, we could demonstrate the stability of our predictions against variations of various parameters, such as the number of coupled partial waves. Details can be found in [5].

The above work laid the foundations for several follow-up projects, including the necessary assistance from theory in calibrating absolute laser intensities at the 1% level [10]. It also led to the prediction of a displacement effect [11], i.e., a strong dependence of the photoelectron spectrum and the angular distribution on what on first sight seemed to be very small changes in the ramp-on and ramp-off characteristics of a laser pulse with a plateau of the envelope function in between. Figure 2 shows an example of two pulses denoted by “2-36-2 S-S” and “2-36-2 L-L”, respectively. Here “n_1-n_2-n_3” refers to the number of optical cycles (o.c.) in the ramp-on (n_1), the plateau (n_2), and the ramp-off (n_3), while “S” and “L” label sine-squared (S) or linear (L) ramp-on/off.
Figure 1. Photoelectron spectrum for ionization of atomic hydrogen in a 10-cycle laser pulse with a \( \sin^2 \) envelope for the vector potential, a peak intensity of \( 10^{15} \text{ W/cm}^2 \), and a central frequency of 0.057 a.u., corresponding to a wavelength of 780 nm. [5]. Left: Results obtained with the velocity form of the electric dipole operator for angular momenta up to \( \ell_{\text{max}} = 70 \) (solid line) and \( \ell_{\text{max}} = 50 \) (dots). Right: Similar results over an extended energy scale. The results for \( \ell_{\text{max}} = 40 \) (20) were multiplied by 0.1 (10) to make them distinguishable from those for \( \ell_{\text{max}} = 70 \).

Figure 2. Electric field (left) and Fourier spectrum (right) of 2-36-2 L-L and S-S pulses with central photon energy 0.7 a.u. and peak intensity \( 4.0 \times 10^{14} \text{ W/cm}^2 \) [11]. The inserts magnify the changes due to the small differences in the ramp-on/off cycles. The pulses are identical in the plateau regime.

Because of its universal nature, the displacement effect should be observable in any atom or molecule – provided pulses with non-zero displacement can be made experimentally. This question is currently under discussion among experimental experts, but the existence of such pulses per se does not seem to contradict Maxwell’s equations. Indeed, Fig. 3 displays ionization spectra and photoelectron angular distributions (PADs) for Li driven by a similar set of S-S and L-L pulses. The ramp-on/off effect in the energy spectra is very similar to that observed for hydrogen [11]. It manifests itself in the PADs integrated over the energy interval covering approximately half of the ionization peak in Fig. 3, while it essentially disappears if a symmetric energy window is used.

The left part of Fig. 4 illustrates the momentum distribution of the electron ejected from Li by a few-cycle single laser pulse of peak intensity \( \approx 4 \times 10^{11} \text{ W/cm}^2 \) and a sine-squared envelope of the electric field [12]. Relating it to the right part, where two pulses of peak intensity \( \approx 10^{11} \text{ W/cm}^2 \) delayed by 170 femtoseconds (fs) act on the system, a single pulse corresponds...
Figure 3. Left: Ejected-electron spectrum for ionization of Li by 2-36-2 S-S (solid line) and 2-36-2 L-L (dashed line) pulses with central photon energy 0.5 a.u. and peak intensity $4.0 \times 10^{14}$ W/cm$^2$ \cite{11}. Right: PADs for Li by pulses with central photon energy 0.5 a.u. and peak intensity $4.0 \times 10^{14}$ W/cm$^2$. Lines are for an asymmetric energy window, $0.25 \leq E \leq 0.30$ a.u., while symbols are for a symmetric energy window, $0.25 \leq E \leq 0.35$ a.u., around the central peak. The arrow indicates the direction of the laser polarization axis.

Figure 4. Left: Momentum distribution of the ejected electron after a single linearly polarized laser pulse of peak intensity $\approx 4 \times 10^{11}$ W/cm$^2$ as observed in experiment (a) and theory (b) \cite{12}. The respective peak normalized angular distributions (black: experiment; red: theory) are shown in (c). Right: Momentum distribution of the ejected electron for a delay of 170 fs between two linearly polarized laser pulses of 30 fs (FWHM) duration, as observed in experiment (top row) and theory (center row). The peak-normalized PADs are shown in the bottom row.

to two such pulses without delay. In the experimental momentum distribution, five angular maxima are clearly identified. The experimental momentum resolution of about 0.05 a.u. in longitudinal direction and 0.07 a.u. in transversal direction gives rise to a broadening of the
Two-Color Double Ionization of Helium with Variable Delay

- $\omega_1 = 35.3$ eV; $\tau_1 = 10$ o.c.; peak intensity of $10^{14}$ W/cm$^2$
- $\omega_2 = 57.1$ eV; $\tau_2 = 10$ o.c.; peak intensity of $10^{13}$ W/cm$^2$

Time delays between -121 and 605 atto-seconds

Figure 5. Energy distributions of the two escaping electrons from He in a two-color laser pulse scenario [14]. The laser parameters are: $\omega_1 = 35.3$ eV, $\tau_1 = 12$ o.c. at a peak intensity of $10^{14}$ W/cm$^2$ and $\omega_2 = 57.1$ eV, $\tau_2 = 14$ o.c. at a peak intensity of $10^{13}$ W/cm$^2$. The time delays between the two laser pulses are indicated in the panels.

peaks shown in the top row of Fig. 4 compared to the theoretical results in the middle row. A more quantitative comparison between experiment and theory is shown in the bottom row, where the PAD is displayed for the main photoline.

3.2. He

Double-ionization (DI) of He as the classic two-electron target is another highly challenging problem, due to the correlated behavior of the two electrons both in the initial and the final state consisting of three charged particles moving away from each other. One of the many issues concerns the extraction of the information after the laser field is switched off [13]. In one of our works on this particular problem [14], we investigated a two-color pump-probe scheme, in which two laser pulses with a tunable delay hit the atom. The central frequencies are chosen in such a way that one of the pulses could directly only eject an electron from the He(1s$^2$) ground state (ionization potential of 24.6 eV), while the other one could also eject the remaining electron from the He($^+1s$) ground state, which requires 54.4 eV of energy. Hence one would expect a non-sequential process if the pulse with the higher frequency comes first, while a sequential process appears possible otherwise. However, the latter is not obvious, since the outcome may also depend on the relaxation time of the singly-ionized state, i.e., the time it takes for the remaining electron after the first ionization to realize that it is in the “wrong” quantum state.

Figure 5 shows the energy distribution of the two escaping electrons for various delays between two pulses with central frequencies corresponding to 35.3 and 57.1 eV, respectively. A negative delay means that the higher-frequency pulse comes first. As seen from the figure, it takes several hundred attoseconds (as) before the sequential process is clearly established, i.e., the expected energies of two subsequently electrons are predicted with high probability.
3.3. $H_2^+$

Moving on to molecules, two immediate complications arise. First, the multi-center nature of the target allows for the study of orientation effects due to the relative directions of the linear laser polarization vector and the internuclear axis. Second, the nuclei will move in reality, but even in the FNA one can study potential interference effects, i.e., the results obtained with different values of the internuclear distance $R$ may vary substantially, since it is quantum mechanically impossible to assign which nucleus the electron came from.

Figure 6 displays the probability densities in configuration space and the momentum distributions at the end of the laser pulse, respectively, in the parallel geometry, where the electric field of the laser and internuclear axis are oriented along the same direction. Though the time-evolution of the wave packet in configuration space does not directly reveal the dominant momentum distribution of the photoelectron, it clearly shows both the preferred and forbidden emission directions. For some cases, the probability density for the electron ionized along the polarization axis is completely negligible [c.f. Fig. 6 (c) at $R = 2.0$]. This corresponds to the “confinement effect” [16] observed in the angular-resolved momentum distribution [c.f. Fig. 6 (g)]. Similar correspondences in the perpendicular geometry can also be established [15].
all previously published time-dependent results \[6, 9, 11\] employed an interaction time between 1.4-2.1 ... in the present work, combined with the way we extract the results, would not allow us to resolve possible

Figure 8. GTCS for two-photon DI of the H\(_2\) molecule. In panel (a), the molecular axis is oriented perpendicular to the linear polarization vector (represented by a double-headed arrow) of the laser pulse. Our results were obtained for pulse lengths of 10, 20, and 30 optical cycles. Also shown are the \emph{ab initio} and the model results of Simonsen \textit{et al.} [21], as well as the cross sections of Colgan \textit{et al.} [19] and Morales \textit{et al.} [20] at 30 eV. Panel (b) shows a comparison between our \emph{ab initio} results obtained in the perpendicular (⊥) and parallel (∥) geometries, and again the corresponding predictions from the simple model.

As mentioned previously, limiting the theoretical model to the FNA usually prevents direct comparison with experiment. For H\(_2^+\), indeed, this restriction can be relaxed [17]. Figure 7 shows preliminary results [18] for the survival probability of the H\(_2^+\) ground state (left panel) and the predicted sharing of the excess energy between the nuclei (\(E_u\)) and the ejected electron (\(E_{\text{elec}}\)) (right panel) when the H\(_2^+\) molecular ion is exposed to a pulse of central energy 0.6 a.u. or 0.8 a.u., respectively. The dominant process here is two-photon ionization. The FNA results clearly change when the nuclei are allowed to move. Hence, it is essential to treat this process in a more general way than in the FNA.

3.4. H\(_2\)

Finally, molecular hydrogen as a two-center two-electron problem remains a formidable challenge to theory. Several \emph{ab initio} calculations for this problem have been performed, using highly sophisticated methods such as time-dependent close-coupling (TDCC) [19] and exterior complex scaling (ECS) [20]. Unfortunately, the results for apparently similar parameters do not always agree with each other to the extent that one might have expected.

The angle-integrated generalized total cross sections (GTCSs) for double ionization of the H\(_2\) molecule for various cases are displayed in Fig. 8. At \(h\nu = 30\) eV, all previously published time-dependent calculations [19, 21, 22] employed an interaction time between 1.4-2.1 fs, i.e., 10-15 o.c. For the perpendicular geometry shown in Fig. 8 (a), the dependence of our results on the pulse length is small for central photon energies up to about 33 eV, as shown by examining predictions obtained with 10, 20, and 30 o.c. When approaching the threshold for sequential DI, on the other hand, the rapid increase of the GTCS is not at all captured by the 10 o.c. pulse. Our results for 20 o.c. are in excellent agreement with the \emph{ab initio} calculations by Simonsen \textit{et al.} [21], which were performed using an entirely independent method, but with similar laser parameters (15 o.c. as the pulse duration). The simplified model of Ref. [21] also does reasonably well. The time-dependent close-coupling (TDCC) results of Colgan \textit{et al.} [19] and the exterior complex scaling (ECS) predictions of Morales \textit{et al.} [20] for a photon energy of 30 eV, however, are about a factor of two larger than our TDSE results at this energy. In contrast to the parallel geometry where even larger discrepancies occur, resonance effects due to autoionizing states, which may affect the FNA results [22, 23], can be ruled out for the perpendicular case.
4. Conclusions and Outlook
We have presented a number of benchmark calculations for intense short-pulse laser interactions with small atoms and molecules. For the atoms, the TDSE can be solved with high accuracy and hence it is possible to reproduce experimental data in detail and also guide experiment where appropriate. Some of the experimental parameters chosen are computationally challenging, and hence great care must be taken to ensure numerical accuracy. For molecules, most calculations remain limited to the fixed-nuclei approximation, which makes a meaningful comparison with experiment difficult, if not impossible. As an important intermediate step towards the ultimate goal of accounting for the nuclear motion, calculations for a number of well-defined scenarios should be carried out by independent groups, and the results should be compared carefully.

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