Time-dependent multielectron dynamics of Ar in intense short laser pulses

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We have developed an *ab initio* *R*-matrix-based approach for the time-dependent description of the multi-electron response of complex atoms irradiated by intense ultrashort laser pulses. Ionization rates for Ar irradiated by intense 390 nm laser light are in excellent agreement with the most accurate rates available. The present approach shows how complex atomic structure affects the atomic response in the time domain. The approach extends the range of intensities, for which accurate ionization rates can be obtained for complex multielectron atoms, and the amount of atomic structure that can be included at high intensities, compared to the *R*-matrix Floquet approach. Because of these advantages, the approach is highly promising for the *ab initio* investigation of the multielectron response to intense ultrashort light pulses.

Investigations of the multielectron dynamics of atoms in strong light fields have become increasingly of interest with the development of ultrashort light pulses, lasting less than one period of visible light. Attosecond light pulses have, for example, been used to investigate the emission of Auger electrons in the time domain [1]. Other applications of ultrashort light pulses include the direct measurement of the electric field irradiated with a laser field [2], and the use of high harmonics to investigate proton dynamics on a subfemtosecond time scale [3].

Ultrashort light pulses pose new challenges to theoretical investigations. Ultrashort light pulses are formed by a superposition of high-frequency radiation. The atomic response to high-frequency light fields consists of the coherent response of many electrons, since the radiation may be sufficiently energetic to, for example, excite several electrons or cause inner-shell electrons to be emitted. Hence, an appropriate theoretical approach must be an explicit multielectron approach.

At present, the most advanced theoretical approaches for the description of atoms irradiated by intense light fields are approaches dedicated to pure two-electron systems. The most extensive description is provided by the so-called HELIUM code by Parker and Taylor and co-workers, in which the helium atom in a strong laser field is treated in a fully *ab initio* approach [4,5]. This approach has provided excellent agreement with experiment for He irradiated by 390 nm light [6]. Many other approaches have been developed for He, for example, the reduced-dimensionality approach, in which the interelectronic coordinate is treated in three dimensions, whereas the sum coordinate is treated in one dimension [7].

In order to describe the response of multielectron atoms, such as Ne and Ar, to intense ultrashort light pulses, an approach is needed which can accurately describe both the multielectron atomic structure and the multielectron response to the light field. For atoms subjected to long pulses, such an approach is provided by the *R*-matrix Floquet approach [8], which has proven to be capable, for example, of describing the response of both inner-shell and outer-shell electrons to an intense laser field [9]. As this approach assumes that the light field has a constant intensity, it cannot be applied to describe atoms irradiated by ultrashort pulses. However, several years ago, Burke and Burke proposed a different exten-

sion of *R*-matrix theory to enable the investigation of time-dependent processes [10]. This approach envisaged a simple description of the continuum electron in an outer region and a detailed description of electron-electron interactions in an inner region.

In the present paper, we describe an *ab initio* time-dependent approach, based on *R*-matrix theory and associated codes [11–13], which is capable of describing the multielectron atomic response to intense ultrashort light pulses. The approach solves the time-dependent Schrödinger equation within a box using *R*-matrix-based inner-region basis sets. To verify that this approach provides an appropriate means for theoretical investigation of intense-field processes, we investigate multiphoton ionization of Ar irradiated by intense laser light with a wavelength of 390 nm, and demonstrate the accuracy of the approach by comparing ionization rates with rates obtained using *R*-matrix Floquet theory [14]. We also show how the atomic structure, in combination with the laser pulse duration, affects the obtained ionization probabilities.

The approach we pursue solves the time-dependent Schrödinger equation directly. We propagate the wave function in time, following Ref. [10], by solving the following system of linear equations at each time step:

$$\left(1 + iH_{q+1/2}\frac{\Delta t}{2}\right)\psi_{q+1} = \left(1 - iH_{q+1/2}\frac{\Delta t}{2}\right)\psi_q, \qquad (1)$$

where ψ_q is the wave function at step q, Δt is the time step, and $H_{q+1/2}$ is the time-dependent Hamiltonian at the midpoint of t_q, and t_{q+1},

$$H_q \equiv H(t_q) = \sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \mathbf{E}(t_q) \cdot \sum_i \mathbf{r}_i. \qquad (2)$$

In the Hamiltonian, bold font indicates vector quantities $\mathbf{r}_i$ and $\mathbf{p}_i$ indicate the position and momentum of electron i, Z indicates the nuclear charge, and $\mathbf{E}(t)$ is the time-dependent light field. All sums are over all $(N+1)$ electrons, where N indicates the number of electrons in the residual ion.

FIG. 1. Structure of the time-dependent Hamiltonian in terms of couplings between different angular momenta.

The wave function ψ_q is expanded in term of eigenstates of the field-free Hamiltonian for each accessible $L \leq L_{\max}$:

$$\psi_q = \sum_{m,L} c_{qmL} \phi_{mL}, \qquad (3)$$

where m is a label indicating a particular eigenvector ϕ_{mL} of the field-free Hamiltonian with an angular-momentum L and c_{qmL} are the expansion coefficients. Each eigenvector ϕ_{mL} has an associated eigenenergy E_{mL}. The initial wavefunction ψ_0 for the Ar ground state is given by the eigenvector with lowest eigenenergy from a diagonalization of the field-free Hamiltonian for the $^1S^e$ symmetry ϕ_{1S}. Hence $c_{01S}=1$, and all other coefficients c_{0mL} are zero. The Hamiltonian in the presence of the field has a block-tridiagonal structure, as shown in Fig. 1, with the diagonal blocks containing the field-free Hamiltonian for each angular momentum, and the off-diagonal blocks containing the dipole couplings between the different angular momenta.

For the accurate solution of the time-dependent Schrödinger equation for multielectron systems, we find that the laser field is best described using the length form of the dipole operator. This is in contrast to strong-field calculations for one-electron and two-electron systems, in which the velocity-gauge form of the dipole operator is preferred. The velocity-gauge form is less appropriate for multielectron systems, since it emphasizes short-range excitations near the nucleus. Hence, the neglect of energetic three- and four-electron excitations would lead to significant loss of accuracy. As a consequence, the velocity-gauge description of the laser field requires a far better description of the atomic structure than the length-form description of the laser field. At present, such a description is not feasible and we therefore employ the length form of the dipole operator in the description of the laser field. We note that also in the R-matrix-Floquet approach [8], the length form of the dipole operator is used in the inner region.

While the length gauge form of the dipole operator must be used to limit the amount of atomic structure in the calculations, this form has drawbacks for the computational description of the laser-atom interactions: the basis used in the description of Ar must include many angular momenta. For the present calculations, we have used a maximum angular momentum $L_{\max}=12$, although for the higher intensities, we found it necessary to increase $L_{\max}$ to 18.

In order to set up the system of equations given in Eq. (1), we use the R-matrix II suite of codes [12,13]. This set of codes provides eigenenergies for an atomic system within a box for a range of angular momenta and reduced dipole matrix elements between all the eigenstates. The suite of codes were adapted in two ways. Firstly, in the time-dependent calculations, spurious reflections from the boundary need to be prevented. This is achieved by adding an absorbing boundary potential to the field-free Hamiltonian. Secondly, in order to improve the accuracy of the calculations, the standard R-matrix set of continuum functions was replaced by a set of continuum functions based on B splines [15]. The combination of R-matrix codes with B-spline basis sets has proven to be highly successful in obtaining, for example, precise electron-impact excitation and ionization cross sections [16–19]. However, the B-spline basis set must be able to describe wave functions with high angular momenta accurately. To ensure that the behaviour near the origin is sufficiently smooth, we use a set of high-order B splines with order $k > L_{\max}$.

To demonstrate the accuracy of the time-dependent approach, we study multiphoton ionization of Ar subjected to intense 390 nm laser light, for which ionization rates are available [14]. We use the R-matrix basis developed for single-photon ionization of Ar [20], although we extend the box size to a radius of 100 au, while the set of continuum orbitals contains 80–90 continuum functions for each available angular momentum of the continuum electron. We re-emphasize that all calculations are carried out within this box. Most of the results presented in this report have been obtained including only the $1s^2 2s^2 2p^6 3s^2 3p^5\,\,^2P^0$ ground state of Ar$^+$ as a target state, but for selected intensities we have also obtained ionization rates including the excited $1s^2 2s^2 2p^6 3s 3p^6\,\,^2S^e$ state of Ar$^+$ as a target state. A good description of the target states is obtained by including all single and double excitations from $3s3p^6$ and $3s^2 3p^5$ to a set of pseudo-orbitals $\overline{3d}$, $\overline{4s}$, and $\overline{4p}$. Details on all these orbital functions used can be found in Ref. [20]. The description of Ar includes all $1s^2 2s^2 2p^6 3s^2 3p^5 \varepsilon l$ channels up to $L=L_{\max}$. For the two-target-state calculations, all $1s^2 2s^2 2p^6 3s 3p^6 \varepsilon l'$ channels up to $L=L_{\max}$ are included as well. In addition, all single, double, and triple excitations from $3s^2 3p^6$ to $\overline{3d}$, $\overline{4s}$, and $\overline{4p}$ are also included.

In time-dependent calculations, a pulse shape needs to be specified for the laser field. We have used a three cycle $\sin^2$ turn-on of the electric field, followed by n, typically between 0 and 14, cycles of an oscillating electric field with constant amplitude, followed by a three-cycle $\sin^2$ turn-off. We typically use 2000 steps per cycle. This form of the electric field allows us to obtain ionization rates at a certain intensity, and to compare these rates with ionization rates obtained in other work. We obtain ionization rates in two different ways: we investigate the dependence of the survival probability as a function of n, the number of cycles during which a constant intensity is maintained, and we investigate the decrease in the norm of the wave function during the pulse.

Figure 2 shows how the norm of the total wave function and the population of the field-free ground state wave function change as a function of time for a pulse in which a constant intensity is maintained for 12 optical cycles. The norm $M(\psi_q)$ is given by
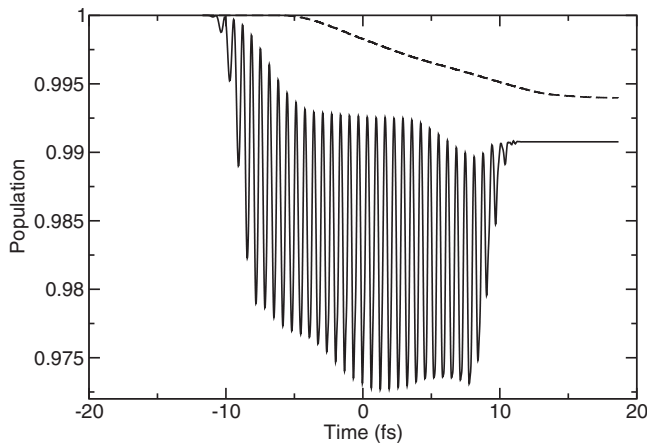
FIG. 2. Time dependence of the norm of the wave function and the population of the field-free ground-state wave function for Ar subjected to 390-nm laser light with a peak intensity of 0.70 $\times 10^{14}$ W/cm^2. The pulse has a three-cycle sin^2 turn-on at the start, maintains peak intensity for 12 cycles and has a three-cycle sin^2 turn-off at the end. At the end of the pulse, we continue to solve the Schrödinger equation for a duration corresponding to a further six cycles.

$$M(\psi_q) = \sum_{mL} |c_{qmL}|^2, \tag{4}$$

where c_{qmL} are the expansion coefficients from Eq. (3), and ψ_q is the wave function at time step q. These calculations are carried out including a single target state for Ar$^+$. The calculation extends beyond the end of the pulse, to demonstrate that it takes time for emitted electrons to be absorbed by the absorbing boundary. The ground-state population shows the behavior one expects to see during a laser pulse with a rapid depopulation and repopulation during the laser pulse (see, e.g., Ref. [21]). Furthermore, we have chosen the intensity such that the ground-state energy in the laser field is nearly resonant with the intermediate $3s^23p^53d$ ^1P and ^1F states [14]. The slow oscillation in the maximum population in the ground state as a function of time is due to resonant transfer of population into these excited states and back into the ground state. As a consequence, the amount of population in the ground state depends on the exact duration of the pulse. The norm of the wave function shows an exponential decay (with an additional oscillation due to the influence of an excited state), and the ionization rate can be estimated from the decay curve.

Figure 3 shows the total bound-state population of Ar at the end of the laser pulse as a function of the number of cycles at which the intenstity is kept constant. This population M_b is given by

$$M_b(\phi_q) = \sum_{mL, E_{mL}<0} |c_{qmL}|^2, \tag{5}$$

where c_{qmL} are the expansion coefficients in Eq. (3). To obtain the bound-state population at the end of the pulse, we evaluate this population only after the light field has been turned off completely. Populations are shown for three dif-
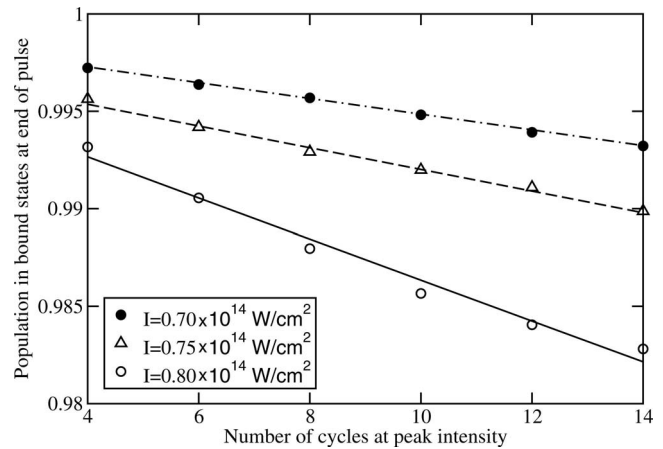

FIG. 3. Population of Ar bound states at the end of a laser pulse for Ar irradiated by 390-nm laser light as a function of number of optical cycles with constant peak intensity. All pulses have a three-cycle sin^2 turn-on at the start and a three-cycle sin^2 turn-off at the end. Results are shown for three different peak intensities 0.70 $\times 10^{14}$ W/cm^2 (filled circles), 0.75$\times 10^{14}$ W/cm^2 (open triangles), and 0.80$\times 10^{14}$ W/cm^2 (open circles). Ionization rates have been estimated by fitting exponential-decay curves to these populations, as shown in the figure.

ferent intensities 0.70×10^{14} W/cm^2, 0.75×10^{14} W/cm^2, and 0.80×10^{14} W/cm^2. The populations obtained for an intensity of 0.70×10^{14} W/cm^2 follow an exponential-decay curve well, and the ionization rate can be established with good accuracy. For the other intensities, Fig. 3 shows an exponential decay with a oscillation superimposed. Again, these oscillations are due to the $3s^23p^53d$ ^1P and ^1F resonances, which become resonant with the Ar ground state near this intensity [14].

Figure 4 shows the intensity dependence of the obtained ionization rates and compares these to rates obtained using R-matrix Floquet theory [14] and using the so-called Ammosov-Delone-Krainov (ADK) approach [22,23]. We
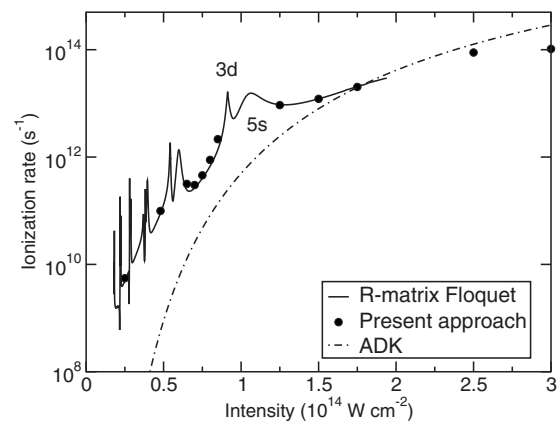

FIG. 4. Comparison of ionization rates for Ar irradiated by 390-nm laser light as a function of intensity. Rates from the present approach (solid circles) are compared to those obtained using the R-matrix Floquet approach [14] (solid line) and the ADK approach (dashed line). The intermediate $3s^23p^53d$ $^1P/^1F$ and $3s^23p^55s$ ^1P resonances have been indicated.

note that we have multiplied the ionization rates obtained in the ADK approach by 2 due to the presence of 2 $m=0$ electrons. The agreement with rates obtained by the R-matrix Floquet approach is excellent, typically well within 10%. Within the R-matrix Floquet approach, it was difficult to extend the calculations to intensities above 2×10^{14} W/cm^2 due to channel closing occurring at this intensity. The present time-dependent approach allows us to obtain rates at higher intensities, as evidenced by the ionization rates obtained at $I = 2.5 \times 10^{14}$ W/cm^2 and $I = 3.0 \times 10^{14}$ W/cm^2. However, the limitations of using the length form of the dipole operator become more apparent with an increased uncertainty in the obtained ionization rates of about 10% for $I = 2.5 \times 10^{14}$ W/cm^2 and 5% for $I = 3.0 \times 10^{14}$ W/cm^2. The calculations for $I = 2.5 \times 10^{14}$ W/cm^2 are more sensitive, as ionization is expected to be influenced by intermediate $3s^2 3p^5 nl$ resonances at this intensity.

At the higher intensities, the ionization rates are in surprisingly close agreement with ionization rates given by the ADK formula [22,23], although the ADK rates tend to increase more rapidly with increasing intensity. The close agreement is quite surprising, since the ADK approach is based on a static-field approach and does not take the detailed atomic structure into account. The ADK approach is, however, not universally applicable, as demonstrated, for example, by a rather poor estimate of ionization rates in open-shell systems, such as V and Ni [24]. At lower intensities, it can be seen that the differences between the present ionization rates and the ADK approach increase rapidly, as the ADK approach becomes less appropriate at lower intensities. From the comparison of the ionization rates obtained in the present approach with those obtained via other approaches, we can conclude that the present approach is capable of determining highly reliable ionization rates, while the main limitation on the calculations is the need to include more and more angular momenta for higher intensities.

As we have already indicated, the ionization rates and ionization yields are affected by resonances. Resonances affect the ionization yields in two different ways. Figure 4 shows that, near an intensity of 0.75×10^{14} W/cm^2, the ionization rates in the R-matrix Floquet approach are enhanced due to the $3s^2 3p^5 3d$ ^1P and ^1F resonances [14]. This enhancement is reproduced in the present time-dependent approach. However, due to the limited duration of the laser pulse, we expect that the appearance of the resonance in the present approach will be slightly broader than its appearance in the R-matrix Floquet approach, and this may be one of the reasons for the small differences between the two sets of calculations.

Other effects of the resonances appear in the final population of Ar bound states, as presented in Fig. 3. The global behavior of the norm of the wave function at the end of the pulse is an exponential decay with increasing pulse length. However, near a resonance, population will be resonantly transferred between the ground state and the resonance and vice versa. The net effect of this transfer process on the bound-state population at the end of a pulse appears in the ionization yields as an oscillation on top of the exponential decay. The frequency and amplitude of this oscillation depend on the detuning from resonance and the intensity. Fig-

TABLE I. Ionization rates for Ar irradiated by 390-nm laser light obtained in the present approach using either the $3s^2 3p^5$ ^5P target state only (one-target state) or both the $3s^2 3p^5$ ^2P and $3s3p^6$ ^2S target states (two-target state).

Intensity 10^{14} W/cm^2	One-target s^{-1}	Two-target s^{-1}
0.48	9.79×10^{10}	9.63×10^{10}
0.75	4.32×10^{11}	4.30×10^{11}
1.50	1.21×10^{13}	1.20×10^{13}

ure 3 shows that the frequency of the oscillations increases with increasing detuning away from resonance. The amplitude of the oscillations, on the other hand, decreases with increasing detuning away from resonance. These oscillations are more interesting to study using time-dependent methods, as they are a signature of the dynamics of the atomic response, while the overall decay rate can be determined equally well using the established time-independent R-matrix Floquet approach.

Although the results presented so far have employed only a single Ar$^+$ target state, the time-dependent R-matrix approach can be extended to include additional target states. Table I compares ionization rates for Ar subjected to 390-nm laser light obtained using a single-target-state expansion and a two-target-state expansion ($3s^2 3p^5$ $^2P^0$ and $3s3p^6$ $^2S^e$) for a small number of intensities. The table shows that the inclusion of an additional target state has only marginal influence on the ionization rates. The additional target state appears to lead to a slight reduction in the ionization rate of less than 2%. This is comparable to differences observed for He irradiated by 248.6 nm laser light [25]. For the present combination of intensity and wavelength, a single-target-state description is therefore appropriate. We note that the R-matrix Floquet approach to study Ar irradiated by 390-nm light was restricted to the use of a single-target-state expansion [14]. Inclusion of the $3s3p^6$ $^1S^e$ target state gives rise to strongly closed channels, which in turn lead to linear dependencies in the calculations. As a consequence, no accurate results could be obtained using the two-target-state description for intensities above approximately 0.4×10^{14} W/cm^2. The time-dependent R-matrix approach does not suffer from this problem and, hence, the approach can be used to verify that it is appropriate to include only the $3s^2 3p^5$ $^2P^0$ target state for substantially higher intensities.

In conclusion, we have developed an *ab initio* technique for the description of complex multielectron atoms in intense, short, laser fields based on the use of R-matrix theory. The approach is designed to be capable of describing the full multielectron response of real multi-electron atoms, such as Ne and Ar, to intense laser fields. We demonstrate the accuracy of the approach by determining multiphoton ionization rates for Ar irradiated by 390-nm laser light with intensity up to 3×10^{14} W/cm^2 within 10% of ionization rates obtained by other techniques. The present *ab initio* approach thus provides a highly accurate tool for investigating complex atoms in intense ultrafast light fields.

The present time-dependent approach may provide more flexibility in the investigation of intense-field processes than other approaches for complex multi-electron atoms, such as the R-matrix Floquet approach. We have demonstrated that the present approach is capable of investigating multiphoton processes at higher intensities, and of including more details of the atomic structure at these higher intensities. This is particularly important for atoms other than the noble gases. The residual Ar^+ ion is left in the ground state, which is well separated from the excited states. For other atoms, excited states of the residual ion may lie much closer to the ground state. When this is the case, the inclusion of these excited ionic states in the calculations becomes of significant importance. It is therefore of interest to extend the present approach to even more difficult studies, involving higher intensities and more complex targets. Such studies will, of course, require further code development.

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