A strong-field approach with realistic wave functions to the above-threshold ionization of Ba$^+$

B Böning$^{1,2,*}$, P Abele$^3$, W Paufler$^1$ and S Fritzsche$^{1,2,3}$

1 Helmholtz-Institut Jena, 07743 Jena, Germany
2 GSI Helmholtzzentrum für Schwerionenforschung GmbH, D-64291 Darmstadt, Germany
3 Theoretisch-Physikalisches Institut, Friedrich-Schiller-Universität Jena, 07743 Jena, Germany

E-mail: b.n.boening@gsi.de

Received 18 September 2020, revised 5 November 2020
Accepted for publication 27 November 2020
Published 18 January 2021

Abstract

We study the above-threshold ionization of atoms in intense circularly polarized laser pulses. In order to compute photoelectron energy spectra, we apply the strong-field approximation with different models for the initial state wave function. Specifically, we compare the spectra for singly ionized Barium (Ba$^+$) using hydrogenic wave functions and realistic one-particle wave functions obtained by multiconfiguration Dirac–Hartree–Fock computations, respectively. As a particular example, we discuss the dependence of the photoelectron spectra on the magnetic quantum number $m$ of the initial state and we reproduce the well known $m$-selectivity in strong-field ionization. Here, we show that the photoelectron spectra exhibit noticeable differences for the two models of the initial state and that the $m$-selectivity is enhanced when realistic wave functions are used. We conclude that the description of strong-field processes within the strong-field approximation will benefit from a realistic description of the initial atomic state.

Keywords: above-threshold ionization, strong-field approximation, initial-state dependence

(Some figures may appear in colour only in the online journal)

1. Introduction

Over the past decades, strong-field processes have deepened our understanding of electron dynamics in atoms and molecules. In particular, the above-threshold ionization (ATI, [1, 2]) and high-harmonic generation (HHG, [3, 4]) not only revealed many details of this dynamics but also helped to manipulate atoms on very short time scales down to the sub-femtosecond domain [5].

Several theoretical approaches have been worked out to describe strong-field (ionization) processes. Apart from the direct numerical solution of the time-dependent Schrödinger equation (TDSE) or the semiclassical description of the electron dynamics, the so-called strong-field approximation (SFA, [6–8]) has become a valuable tool that enables one to predict the ATI and HHG spectra for a wide range of laser parameters. Within the SFA, one assumes that the Coulomb potential of the parent ion is negligible compared to the driving electric field if the electron is in the continuum. In addition, the influence of the laser field on the initial-state wave function is omitted, such that it is an eigenstate of the atomic Hamiltonian, i.e. without the external field. With these assumptions in mind, the momentum distributions of the photoelectrons emitted in the ionization process can then often be evaluated analytically.

In most SFA-based studies, in addition, the target atom is assumed to be in a hydrogenic initial bound state but with an ionization potential that is matched to the target atoms in question. In this approach, the interactions between the active elec-
tron and the remaining bound electrons are ignored and, for the sake of simplicity, use is made of a 1s state in most cases. The assumption of a 1s orbital greatly simplifies the evaluation of the SFA transition amplitude, while keeping the essential dynamics of the photoelectron in the laser field [9]. In practice, however, strong-field experiments often use atomic targets for which hydrogenic orbitals provide only a rough approximation. It is therefore desirable to better understand the conditions under which this approximation is justified.

For the strong-field ionization, several authors have analyzed how the principal, orbital and magnetic quantum numbers \( n, \ell \) and \( m \), respectively, of hydrogenic initial states affect the photoelectron spectra computed within the SFA [10–12]. While noticeable differences were found in the spectra of photoelectrons that are emitted from different \((n, \ell)\) shells as well as for states with different magnetic quantum numbers \( m \), the focus of these studies lay on the gauge dependence of the SFA. It was shown, in particular, that only the length gauge agrees with the exact solution of the TDSE for odd-parity initial states. These results already demonstrate that the replacement of the hydrogenic 1s state by some excited hydrogenic wave functions has a significant influence on the physical results obtained within the SFA.

A further extensive work has explored the influence of the orbital function for the co- and counter-rotating \( p \)-orbitals with \( m = \pm 1 \), taken relative to the circularly-polarized driving field [13, 14]. For such a setup, the emission of photoelectrons from counter-rotating orbitals dominates over those from co-rotating ones, quite in contrast to one-photon ionization [13, 14]. For such a setup, the emission of photoelectrons is utilized in order to produce spin-polarized electrons, including the remaining core. We consider the ATI wave functions and discuss the conditions under which their use is necessary.

This paper is structured as follows. In section 2, we discuss the theoretical framework, including the SFA (section 2.1) and the realistic Hartree–Fock initial states used in our computations (section 2.2). Based on this framework, we present our results in section 3, where we compare the ATI spectra obtained from the hydrogenic and Hartree–Fock approaches (section 3.2) and discuss the \( m \)-selectivity for the ionization of the low-lying excited states of Ba\(^+\) (section 3.3). Finally, in section 4, we give our conclusions and an outlook to future work.

Note that atomic units \((m_e = e = \hbar = 4\pi\varepsilon_0 = 1)\) are used throughout the paper unless stated otherwise.

### 2. Theoretical framework

Figure 1 shows the geometry of the ATI process considered in this work. A (right-)circularly polarized laser pulse (orange) propagates in \(z\)-direction \((k = ke_z)\). The single atomic target is in the initial state \(|\psi_{\text{idm}}\rangle\), characterized by the principal quantum number \( n \), the orbital angular momentum \( \ell \) and the magnetic quantum number \( m \), with respect to the quantization \( z \)-axis. The emitted photoelectron is measured at the detector \( D \) with momentum \( p = (p, \vartheta_p, \varphi_p) \) in spherical coordinates.
Below, we will describe the ionization process within the dipole approximation that neglects the spatial dependence of the laser field. This assumption is justified in our case, since the wavelength $\lambda$ is much longer than the typical atomic length scale and short enough to neglect the influence of the magnetic field in the photoelectron continuum [18]. Accordingly, we write the electric field of the laser pulse in the dipole approximation as [9]

$$ E(t) = \frac{\mathcal{E}_0}{\sqrt{2}} \sin^2 \left( \frac{\omega t}{2n_p} \right) \left( \cos(\omega t) \hat{x} + \sin(\omega t) \hat{y} \right), \quad (1) $$

for $0 < t < T_p$ and $E(t) = 0$ otherwise. It is characterized by the wavelength $\lambda$, the number of optical cycles $n_p$ and the intensity $I = E_0^2/2$.

2.1. SFA transition amplitude

Our aim is to analyze the energy- and angle-differential photoionization probability $w(p)$ as a function of the asymptotic momentum $p$ of the photoelectron at the detector for a target atom in the initial state $|\psi_0\rangle = |\psi_{in}0\rangle$ that is ionized by the laser field (1). The probability for the emission of a photoelectron with energy $E = p^2/2$ into the solid angle element $d\Omega_p$ can be written in terms of the transition amplitude $M_p$ for the process as [9]

$$ w(p) = \frac{|M_p|^2}{dE/d\Omega_p} = p|M_p|^2, \quad (2) $$

where $p = |p|$ and $d^3p = p^2 dp d\Omega_p = p d\Omega_p$. In the following, we will refer to the energy- and angle-differential photoionization probability $w(E) = w(E, \theta p_0, \varphi p_0)$, measured under given polar and azimuthal angles $\theta p_0 = \theta p_0$ and $\varphi p_0 = \varphi p_0$, respectively, as the ATI spectrum.

According to (2), the ATI spectra are given in terms of the transition amplitude $M_p$ that we evaluate within the SFA, which we briefly describe in the following. Within the SFA, both the effect of the driving laser field $E(t)$ on the initial state as well as the Coulomb interaction between parent ion and photoelectron in the continuum are neglected. In order to derive an explicit expression for $M_p$, we start with the full Hamiltonian of the atom in the laser field, given in length gauge by

$$ H(t) = H_0 + r \cdot E(t) = H_0 + V_{le}(t), \quad (3) $$

where $H_0 = p^2/2 + V_{a}(r)$ is the field-free Hamiltonian with the atomic binding potential $V_{a}(r)$ and $V_{le}(t) = r \cdot E(t)$ is the laser-electron interaction potential.

The transition amplitude $M_p$ for ionization from the initial state $|\psi_0\rangle$ to a final (continuum) state $|\psi_p(t)\rangle$ with asymptotic momentum $p$ at the detector is then given by

$$ M_p = \lim_{t \to \infty, t' \to -\infty} \langle \psi_p(t)|\hat{U}(t, t')\hat{U}(t)|\psi_0(t')\rangle, \quad (4) $$

where $\hat{U}(t, t')$ is the time-evolution operator that corresponds to the full Hamiltonian (3). Making use of the Dyson equation, the time-evolution operator can be written as [9]

$$ \hat{U}(t, t') = \hat{U}_0(t, t') - i \int_{t'}^{t} dt'' \hat{U}(t, t'')\hat{H}(t'')\hat{U}_0(t'', t'), \quad (5) $$

with the time-evolution operator $\hat{U}_0(t, t')$ of the field-free Hamiltonian $H_0$. Upon insertion into (4), we obtain

$$ M_p = \lim_{t \to \infty, t' \to -\infty} \left[ \langle \psi_p(t)|\hat{U}(t, t')\hat{U}(t)|\psi_0(t')\rangle - i \int_{t'}^{t} dt'' \langle \psi_p(t)|\hat{U}(t, t'')\hat{V}(t'')\hat{U}_0(t'', t')|\psi_0(t')\rangle \right]. $$

Since, in general, both the initial and the final state are eigenstates of the full Hamiltonian, they are orthogonal,

$$ \langle \psi_p(t)|\hat{U}(t, t')\hat{U}(t)|\psi_0(t')\rangle = \langle \psi_p(t)|\psi_0(t')\rangle = 0, $$

and the transition amplitude reduces to

$$ M_p = -i \lim_{t \to \infty, t' \to -\infty} \int_{t'}^{t} dt'' \langle \psi_p(t)|\hat{U}(t, t'')\hat{V}(t'')|\psi_0(t')\rangle \hat{U}_0(t', t'). $$

Finally, we use the Dyson equation again, however, this time by decomposing the full Hamiltonian as $H(t) = H_0 + V_{le}(r)$ with the laser-electron interaction Hamiltonian $H_{le}(r) = p^2/2 + r \cdot E(t)$. Together with (6), we then arrive at

$$ M_p = -i \lim_{t \to \infty, t' \to -\infty} \int_{t'}^{t} dt'' \langle \psi_p(t)|\hat{U}(t, t'')\hat{V}(t'')|\psi_0(t')\rangle \hat{U}_0(t', t') $$

$$ + \langle k|A(t)\rangle e^{-iS(t)} \times \hat{V}_a(r) \hat{U}_{le}(t', t'') \hat{r} \cdot \hat{E}(t'')|\psi_0(t')\rangle, $$

where $\hat{U}_{le}(t', t'')$ is the time-evolution operator of the Hamiltonian $H_{le}(t)$. The first term in the transition amplitude (7) describes the so-called direct electrons, while the second term describes electrons that are rescattered at the parent ion of the target. For the circularly polarized laser pulse considered in this work, the rescattering term can be neglected [9] and we will approximate the transition amplitude by the direct term,

$$ M_p \approx M_{p}^{\text{dir}}. \quad (8) $$

In order to simplify expression (7) further, we decompose $\hat{U}_{le}(t, t')$ in the form

$$ \hat{U}_{le}(t, t') = \int d^3k |\chi_k(t)\rangle \langle \chi_k(t')|, \quad (9) $$

where $|\chi_k(t)\rangle$ are solutions to the Schrödinger equation describing an electron in the presence of the laser field,

$$ i\frac{d}{dt} |\chi_k(t)\rangle = \hat{H}_{le}|\chi_k(t)\rangle. $$

Its solutions are the so-called Volkov states [9, 19]

$$ |\chi_k(t)\rangle = |k + A(t)\rangle e^{-iS(t)}, \quad (10) $$

with plane waves $|k + A(t)\rangle$ and the Volkov phase

$$ S(t) = \frac{1}{2} \int_{0}^{t} dt' |k + A(t')|^2. \quad (11) $$

Here, $A(t)$ is the vector potential of the laser pulse, defined via $-\partial A(t) = E(t)$. In order to evaluate the time integral in
the direct transition amplitude (12), the Volkov phase needs to be evaluated for the vector potential corresponding to the electric field (1). By making use of a Fourier decomposition of the electric field, the vector potential can be found analytically (see [9]) and the integral in the Volkov phase can be explicitly evaluated. The calculation is straightforward but rather lengthy and we will not state it here.

Since in the SFA we assume that the final continuum state $|\psi_f(t)\rangle$ is not affected by the Coulomb potential of the parent ion, we can approximate it by a plane wave, $|\psi_f(t)\rangle \approx |p(t)\rangle$. Also, we neglect the influence of the laser field on the initial state, $|\psi_i(t)\rangle = |\psi_{i0}(t)\rangle = |\psi_{i0}\rangle e^{i\tilde{p} t}$, where $I_0$ is the corresponding ionization potential. Therefore, $|\psi_{i0}\rangle$ is an eigenstate of the field-free Hamiltonian $H_0$. Upon insertion of these approximations into (7) and by making use of the decomposition (9), the direct SFA transition amplitude finally reads

$$M_p \approx M_p^{(0)}$$

$$= -i \int_0^{T_p} dt \mathbf{E}(t) \cdot (\chi_p(t)) |\psi_i(t)\rangle$$

$$= \int_0^{T_p} dt e^{i\tilde{p}t} e^{i\tilde{p}t} |\psi_{i0}\rangle \cdot \nabla_{\tilde{q}} \psi_{i0}(q).$$ (12)

with $\tilde{p} = p - A(T_p)$ and $q = \tilde{p} + A(t)$ and where we used the Fourier space identity $r = i\nabla_q$ to rewrite the transition probability amplitude in terms of the momentum space wave function

$$\tilde{\psi}_{i0}(q) = \frac{1}{(2\pi)^{3/2}} \int d^3 r e^{-i\tilde{q}r} \psi_{i0}(r).$$ (13)

2.2. Initial state wave function

In order to compute the Fourier integral (13), we write the initial state wave function in position space as

$$\psi_{i0}(r) = R_{i0}(r) Y_{\ell0}^m(\tilde{r}),$$ (14)

with the spherical harmonics $Y_{\ell}^m$ and where we abbreviated $\tilde{r} = (\tilde{r}, \varphi_{\tilde{r}})$ with the polar and azimuthal angles $\tilde{r}$ and $\varphi_{\tilde{r}}$, respectively. Furthermore, we decompose the plane waves $e^{-i\tilde{q}r}$ in the form

$$e^{-i\tilde{q}r} = \frac{e^{-i\tilde{r} \cdot \tilde{q}}}{4\pi} = \sum_{\ell'=-\infty}^{\infty} \sum_{m=-\ell'}^{\ell'} (-i)^{\ell'} j_{\ell'}(q r) Y_{\ell'}^{m'}(\tilde{q}) Y_{\ell'}^{m*}(\tilde{r}),$$ (15)

where $j_{\ell'}$ are the spherical Bessel functions of the first kind. Insertion of equations (14) and (15) into the momentum space wave function (13) and integration over the angles $\tilde{r}$ and $\varphi_{\tilde{r}}$ yields

$$\tilde{\psi}_{i0}(q) = F_{i0}(q) Y_{\ell0}^m(\tilde{q}),$$ (16)

where $F_{i0}(q)$ is the remaining radial integral,

$$F_{i0}(q) = (-i)^\ell \sum_{r=0}^{\infty} \sum_{m=-\ell}^{\ell} \int_0^{2\pi} d\varphi_{\tilde{q}} \int_0^\infty dr r^2 R_{i0}(r) j_{\ell}(q r).$$ (17)

In the following, we will use two approaches to the description of the initial state: the hydrogenic and the Hartree–Fock approach. Both approaches treat the initial state in the single-active electron approximation, that is, the interaction between the laser field and other electrons bound in the target atom is neglected. In the first approach, we use a hydrogenic initial state that is an eigenstate of the Hamiltonian $H_0 = p^2/2 + V(r)$ with the Coulomb potential $V(r) = -Z'/r$ with an effective nuclear charge $Z'$ that is chosen such that the ionization potential $I_0 = Z'^2/(2n^2)$ matches that of the target atom. The radial wave functions are then given by

$$R_{i0}(q) = C_{i0} e^{-\rho}(2\rho)^n L_{n-\ell-1}^{\ell+1}(2\rho),$$

with a normalization constant $C_{i0}$ and $\rho = 2Z'r/n$. This hydrogenic description of the initial state is often used in the SFA, since it allows an analytical evaluation of the radial integral in (17) for all quantum numbers $n$ and $\ell$ [20] and also of the direct transition amplitude (12).

In the Hartree–Fock approach, we use a one-electron wave function obtained by numerical MCDHF computations using the GRASP code [21]. Here, in addition to the interaction with the nucleus, correlations with the remaining bound electrons are taken into account in the dynamics of the active electron. In our Hartree–Fock computations, we neglect the fine-structure splitting of the angular momentum states. For given atomic species and principal and angular momentum quantum numbers $n$ and $\ell$, these computations then yield the radial wave function $R_{i0}(r)$. The momentum space wave function (16) is subsequently obtained by numerical integration in (17).

3. Results

We now turn to the analysis of specific ATI spectra within the SFA formalism described above. In particular, we will compare the ATI spectra $\psi(E)$ obtained within the two approaches (hydrogenic and Hartree–Fock) to the description of the initial state described in section 2.2.

3.1. Atomic target, geometry and laser parameters

As atomic target species, we here assume singly-ionized Barium (Ba$^+$), which has one electron in the valence shell and can therefore be treated within the single-active electron approximation. We consider target atoms where the active electron is either in the 6s ground state or in one of the lowest-lying excited states 5d, 6p or 4f. The ionization potentials and effective nuclear charges corresponding to these states are listed in Table 1. Since we neglect the fine structure splitting of the initial state, the ionization potential $I_0$ does not depend on the magnetic quantum number $m$.

Since the driving laser pulse (1) is polarized in the $x$–$y$-plane, the photoelectrons are preferably emitted within this plane. Furthermore, the maximum ionization probability is found along the $x$-direction. Therefore, we consider a detector placed at $\vartheta_r = \pi/2$ and $\varphi_{\tilde{q}} = 0$ (cf figure 1). In order to compute ATI spectra for a given initial state and laser parameters, we numerically perform the time integration in the direct transition amplitude (12). The evaluation of the momentum space
wave function is either done analytically (in the hydrogenic approach) or numerically (in the Hartree–Fock approach). From the direct transition amplitude, the ATI spectra are then computed via (2).

In all our results below, we assume an \( n_p = 8 \)-cycle driving laser pulse with wavelength and intensity of \( \lambda = 800 \text{ nm} \) and \( I = 5 \times 10^{13} \text{ W cm}^{-2} \), respectively, which are values typically used in strong-field ionization experiments.

With the above choice of wavelength, the energy differences between low-lying states of Ba\(^+\) are close to the photon energy. In other words, these states might be coupled by the laser field. The SFA-based theory used here does not account for such a coupling and we note that the results presented below might change if a more sophisticated model is used. However, we expect that our general statements about the difference between the hydrogenic and Hartree–Fock approaches will still be valid.

### Table 1. Binding energies and effective nuclear charges for the lowest-lying states of the active electron in Ba\(^+\). All values were taken from [22].

| \( n\ell \) | \( J \) | \( I_p (\text{eV}) \) | \( Z' \) |
|---|---|---|---|
| 6s | 1/2 | 10.0038 | 5.1449 |
| 5d | 3/2 | 9.3995  | 4.1559 |
| 6p | 1/2 | 7.4917  | 4.4523 |
| 4f | 5/2 | 4.0205  | 2.1744 |

![Figure 2. Radial wave functions (left) and normalized ATI spectra (right) computed for the ionization of Ba\(^+\) from the 6s ground state with binding energy \( I_p = 10.0038 \text{ eV} \) and for different models of the initial state: 1s hydrogenic wave function with effective nuclear charge \( Z' = \sqrt{2I_p} \) (blue solid curves); 6s hydrogenic wave function with effective nuclear charge \( Z' = 6\sqrt{2I_p} \) (orange dashed curves); realistic 6s Hartree–Fock wave function for Ba\(^+\) (black dotted curves). The following parameters were used: \( \lambda = 800 \text{ nm} \, n_p = 8, I = 5 \times 10^{13} \text{ W cm}^{-2}, \theta_p = \pi/2, \varphi_p = 0 \). All ATI spectra in (b) are normalized to their respective maximum.](image)

#### 3.2. Comparison of ATI spectra from hydrogenic and Hartree–Fock approaches

In the ground state of Ba\(^+\), the active electron is in a 6s state with ionization potential \( I_p = 10.0038 \text{ eV} \). We here compare the ATI spectra from this ground state for three different models. First, as it is often done in SFA-based computations, we assume a hydrogenic 1s initial state with an effective quantum number \( Z' = \sqrt{2I_p} = 0.8574 \). In a second model, we improve this assumption by using a hydrogenic 6s initial state with effective nuclear charge \( Z' = 6\sqrt{2I_p} = 5.1449 \). Third, we use the Hartree–Fock approach described above to obtain a realistic one-electron wave function for the 6s ground state of Ba\(^+\). The radial wave functions for all three models are displayed in figure 2(a).

The corresponding ATI spectra, computed from the direct SFA transition amplitude (12), are shown in figure 2(b). While the positions of the characteristic ATI peaks are identical for all three curves (see also section 3.3), it can be easily observed that the relative magnitudes of the individual peaks differs considerably for all three models of the initial state. In particular, the use of a hydrogenic 6s initial state (orange dashed curve) instead of a 1s state (blue solid curve) leads to a suppression of several peaks over the full energy range shown in the figure. On the other hand, if the Hartree–Fock approach is used to obtain the radial wave function of the 6s initial state (black dotted curve), the ATI peaks in the low-energy part of the spectrum are reduced compared to the 1s hydrogenic approach, while the magnitudes of the peaks are enhanced for photoelectron energies \( E > 5\omega \). This difference can be understood from the radial wave functions in figure 2(a). While the active electron is bound close to the core in the hydrogenic 1s state, it is in fact further removed in Ba\(^+\), as can be seen in the black dotted curve. This leads to a larger overlap with the continuum wave function for higher photoelectron energies and, therefore, to a larger value of the radial integral (17) that determines the photoionization probability via the direct SFA transition amplitude (12).

From this first consideration, we can conclude that the ATI spectra as computed from the direct SFA amplitude, differ considerably between the often used hydrogenic (1s) approach
Figure 3. Radial wave functions (left column) and normalized ATI spectra (middle and right columns) computed for different Ba\textsuperscript{+} initial configurations [Xe]\textsuperscript{n}\ell with increasing orbital angular momentum quantum number \ell from top to bottom: top row 6\textit{p} (\ell = 1), middle row 5\textit{d} (\ell = 2), bottom row 4\textit{f} (\ell = 3). In the left column, the respective radial parts \(R_{\ell n}(r)\) of the one-electron initial state wave function [cf (14)] are shown for the hydrogenic approach (blue curves) and the Hartree–Fock approach (orange curves). In the middle and right columns, the ATI spectra are shown for co- (\(m = +\ell\)) and counter- (\(m = -\ell\)) rotating electrons computed using either the respective hydrogenic initial state (middle column) or the Hartree–Fock initial state (right column). All ATI spectra exhibit the characteristic \(\omega\)-spaced ATI-peaks and also an \(m\)-selectivity, i.e. the enhanced ionization rate from counter-rotating compared to co-rotating initial states. In the 4\textit{f} state, the Hartree–Fock wavefunction is well approximated by the hydrogenic wavefunction and the ATI spectra obtained in the two approaches are similar. Noticeable differences between the approaches can be seen for 6\textit{p} and 5\textit{d} initial states: the relative magnitude of the ATI peaks differs considerably. Also, the relative ionization probability between co- and counter-rotating initial states differs between the approaches. The following parameters were used: \(\lambda = 800\) nm, \(n_p = 8\), \(I = 5 \times 10^{13}\) W cm\textsuperscript{-2}, \(\varphi_p = \pi/2\), \(\varphi_p = 0\). All ATI spectra are normalized to the maximum of the two respective curves in each plot.

and the more realistic Hartree–Fock approach. While the dependence on the initial state wave function can be directly seen in the expression for the transition amplitude (12), it is not immediately clear how well a given model for the initial state works. Nonetheless, the results in figure 2 demonstrate that the use of a hydrogenic initial state might often be only a first approximation to the atomic target used in experiment.

3.3. \(m\)-selectivity

In order to discuss the dependence on the initial state wave function in more detail, we will now turn to the dependence of the ATI spectra on the magnetic quantum number \(m\). In particular, we will examine the ATI spectra computed for initial states with \(m = \pm m_{\text{max}} = \pm \ell\) for the low-lying excited states listed in table 1. The helicity of the circularly polarized laser pulse (1) is kept fixed and, hence, the sign of \(m\) defines the relative orientation of the electron orbital in the initial state and the circular polarization of the pulse. Accordingly, we will call an electron in the \(m = +\ell\) and \(m = -\ell\) initial states co- and counterrotating, respectively. In our discussion below, we will focus on the differences in the ATI spectra between co- and counterrotating initial states. Within the hydrogenic approach, this was studied in detail by Barth and Smirnova in [13, 14]. In order to obtain ATI spectra comparable to our results below from ionization experiments, the atoms comprising the target have to be prepared in a state with \(m = \pm \ell\). However, if the target
is not prepared and consists of a mixture of atoms in different \( m \) states, the \( m \) selectivity discussed implies different depletions rates for atoms in different \( m \) states, similar to the discussion in [13]. In addition, the initial state might be polarized in an experimental setup. This might alter the difference between \( m = \pm \ell \) states considered below when measured in an experiment. However, it should not alter our main point about the difference between hydrogenic and Hartree–Fock approaches.

The ATI spectra \( w(E) \) computed for the parameters discussed above and using either the hydrogenic or Hartree–Fock approach are presented in figure 3 for \( 6p \) (top row), \( 5d \) (center row) and \( 4f \) (bottom row) initial state wave functions. The center and right columns show the ATI spectra for the corresponding \( m = \pm \ell \) initial states. In addition, in the left column we show the respective radial parts \( R_w(r) \) of the hydrogenic and Hartree–Fock initial state wave functions. In all ATI spectra shown, the characteristic ATI peaks and the typical exponential cutoff of the magnitudes of the individual ATI peaks for increasing photoelectron energies can be seen.

In the SFA transition amplitude (12), the precise form of the ATI spectra is determined by the time dependence of the Volkov phase (11) and the (momentum-space) initial state wave function (13). The energy spacing of the ATI peaks results from superpositions of the emitted photoelectron wavepackets within different cycles of the laser pulse [23], which is included in the Volkov phase.

More importantly, in the present case, the influence of the precise form of the initial state wave function is pronounced in our results. A comparison of the two radial wave functions in the left column of figure 3 for each of the initial states shows that the Hartree–Fock wave functions of the states with higher binding energies (\( 6p \) and \( 5d \)) fall off for smaller \( r \) than those of the corresponding hydrogenic wave functions. That is, the active electron is confined to a smaller region around the nucleus in the Hartree–Fock approach than in the hydrogenic approach. Therefore, the corresponding momentum distribution, given by the momentum space wave function (13), is broader than in the hydrogenic state. As a consequence of this broader momentum space wave function, the ATI spectra computed on the basis of the Hartree–Fock wave functions differ considerably from those found with the hydrogenic wave functions for \( 6p \) and \( 5d \) states. While the ATI peaks lie at the same photoelectron energies, their number and relative magnitudes vary between the hydrogenic and the Hartree–Fock approaches. For instance, the hydrogenic approach for the \( 6p_\ell \) initial state (top row) predicts photoelectrons with a maximum energy of about \( 4\omega \), while the Hartree–Fock approach yields photoelectrons with an energy of up to about \( 7\omega \).

In contrast, for the weakly bound \( 4f \) initial states (bottom row in figure 3), the ATI spectra are almost identical when computed with the hydrogenic and Hartree–Fock initial states, since the corresponding radial wave functions are virtually identical. The description in terms of a hydrogenic wave function is therefore much better in this case than for the \( 6d \) and \( 5p \) initial states. Here, the valence electron in \( \text{Ba}^+ \) is further removed from the core (consisting of nucleus and inner-shell electrons) and therefore experiences a potential very similar to the hydrogenic Coulomb potential with an effective nuclear charge. Therefore, the hydrogenic initial state wave function is a good approximation to the Hartree–Fock wave function and the resulting ATI spectra computed within the SFA agree very well.

All ATI spectra shown in figure 3 exhibit an \( m \)-selectivity, that is, the ionization probability \( w(E) \) differs considerably between co- \((m = \ell)\) and counter-rotating \((m = -\ell)\) electrons. This \( m \)-selectivity was discussed in references [13, 14], based on hydrogenic initial states and within the PPT formalism. There, the authors showed that strong-field ionization from initial \( p \)-orbitals preferably removes the counter-rotating electrons. In order to test this statement in our framework, we consider the total ionization probability

\[
    w = \int_0^\infty dE \, w(E).
\]

In figure 4, we show the ratio \( w_-/w_+ \) of the total ionization probabilities \( w_- = w_{m=-1} \) and \( w_+ = w_{m=+1} \) from counter- to co-rotating electrons as a function of laser intensity \( I \) or, equivalently, the Keldysh parameter \( \gamma = \omega \sqrt{2I}/E_0 \). Contrary to the results in [13, 14], \( w_-/w_+ \approx 1 \) for the \( 6p \) orbital of \( \text{Ba}^+ \) [red curve in figure 4(a)], when computed within the SFA with a hydrogenic initial state. From this result, therefore, one would not expect a selectivity between co- and counter-rotating electrons. However, when the same quantity is computed within the SFA using the Hartree–Fock initial state wave functions [green curve in figure 4(a)], \( w_-/w_+ > 1 \) for low intensities and large Keldysh parameters, which confirms the statement that counter-rotating electrons are preferentially emitted. The ratio \( w_-/w_+ \) decreases when the intensity is increased and falls below unity at around \( 10^{14} \text{ W cm}^{-2} \). In general, this decrease is in agreement with the \( \gamma \)-dependence found in [14] within PPT theory [black dashed curve in figure 4(a)], although the authors did not find \( w_-/w_+ < 1 \) for higher intensities. Let us also note that, for all intensities shown in figure 4, the SFA always predicts a smaller ratio \( w_-/w_+ \) than the PPT theory and, hence, a smaller selectivity between counter- and co-rotating initial states. Figure 4(a) therefore leads to the conclusion that the SFA with hydrogenic initial states does not yield an \( m \)-selectivity in ATI from \( p \)-states, while the inclusion of realistic Hartree–Fock \( \text{Ba}^+ \) initial states is in qualitative agreement with the PPT results.

It is now an interesting question if and how the \( m \)-selectivity changes if the orbital angular momentum \( \ell \) of the initial state is increased. In references [13, 14], only the results for initial \( p \)-states were discussed. The ATI spectra computed within the SFA that we presented above in the second row of figure 3 indicate that, for the \( 5d \) initial state, the total ionization probabilities \( w_- = w_{m=-2} \) and \( w_+ = w_{m=+2} \) are different. Figure 4(b) again shows the ratio \( w_-/w_+ \) as a function of \( I \) and \( \gamma \), respectively. In contrast to the previous case, the SFA with hydrogenic (red curve) and realistic Hartree–Fock (green curve) initial states here predict a similar qualitative behavior: the ratio \( w_-/w_+ > 1 \) for low intensities and decreases when the

\[
\text{J. Phys. B: At. Mol. Opt. Phys. 54 (2021) 025602} \quad \text{B Böning et al}
\]
intensity is increased. The $m$-selectivity is always larger when computed using the Hartree–Fock initial state wave functions than for the hydrogenic ones. The black, dashed curve shows the result from the PPT theory that we obtained for $d$-states in analogy to the derivation leading to (110) for $p$-states in reference [14]. As in figure 4(a), the $m$-selectivity is always found to be larger within the PPT theory than within our SFA computations, while the dependencies on the intensity are in qualitative agreement. Most importantly, if we compare the results for initial $d$-states in figure 4(b) to those for initial $p$-states in figure 4(a), we see that the $m$-selectivity in ATI is enhanced for larger orbital angular momentum quantum number $\ell$ of the initial state. This is true both in our SFA computations with Hartree–Fock wave functions and in the PPT theory of [13, 14].

In general, we found that the SFA predicts that counter-rotating electrons are preferably emitted ($w_{-}/w_{+} > 1$) only when Hartree–Fock Ba$^+$ wave functions are used. Physically, the $m$-selectivity is a consequence of the fact that the tunneling process for typical experimental conditions (Keldysh parameter $\gamma \approx 1$) is not instantaneous, quite contrary to what is often assumed in the three-step model. Instead, if the electron is initially stronger bound, the relative motion of the electron in the orbital and the (rotating) potential barrier, formed by the Coulomb potential and the electric field of the circularly polarized laser pulse, has an increasing influence on the tunneling process. The difference between the hydrogenic and the Hartree–Fock approaches can then be understood by considering the shape of the radial wave functions in the left column in figure 3: in the Hartree–Fock wave function for $6p$ and $5d$ states, the electron is bound closer to the nucleus than in the hydrogenic approach. This implies that the potential barrier is broader and hence the interaction between electron motion and barrier rotation is stronger, which in turn leads to a larger $m$-selectivity in the ionization probability.

In summary, our SFA computations of the ATI spectra for a Ba$^+$ target demonstrate the circumstances under which a hydrogenic description of the initial state is justified within the SFA. As long as the electron is in an excited, weakly bound state ($4f$), correlations with the core electrons can be neglected and the initial state can be well approximated by a hydrogenic wave function with modified nuclear charge $Z'$. For lower lying initial states (6s, 6p and 5d), the correlations with other electrons become important and the realistic Hartree–Fock wave functions differ considerably from the hydrogenic approximation. The importance of this difference becomes visible both in the ATI spectra, i.e. the energy-differential ionization probabilities $w(E)$, and in the analysis of the different total ionization probabilities $w_{+}$ for co- and counter-rotating electrons from identical $nf$ initial states with different magnetic quantum numbers $m = \pm \ell$.

4. Conclusion

In this paper, we have investigated the ATI of Ba$^+$ atoms in ground and low-lying excited initial states with different principal and angular momentum quantum numbers $n$, $\ell$ and $m$, and driven by circularly polarized laser pulses. We analyzed the ATI spectra resulting from SFA computations with both hydrogenic initial state wave functions that are commonly used within the SFA and realistic Hartree–Fock initial state wave functions that also account for correlations between the active electron and the core electrons.

We found that the ATI spectra for 6s, 6p and 5d initial states with $|m| = \ell$ show pronounced differences between the two models for the initial state wave function, which is due to the fact that the electron is either further removed from the core (6s) or bound closer (6p and 5d) to the nucleus in the Hartree–Fock initial state than in the hydrogenic initial state. In contrast, the two descriptions of the initial state yield identical ATI spectra for 4f initial states, since the active

![Figure 4](image_url)

Figure 4. Ratio $w_{-}/w_{+}$ of the total ionization probability from counter- ($m = -\ell$) and co- ($m = +\ell$) rotating orbitals for (a) $6p$ ($\ell = 1$) and (b) $5d$ ($\ell = 2$) initial states of the Ba$^+$ atomic target as a function of intensity $I$. Each plot shows the results obtained within the SFA with hydrogenic initial state wave functions (circles, red) and with more realistic Hartree–Fock wave functions (squares, green). The black dashed curves show the respective approximate formulas for small Keldysh parameters $\gamma \ll 1$ obtained within PPT theory (see main text). The total ionization rates $w_{\pm}$ were obtained via integration of the corresponding ATI spectra $w(E)$ [cf figure 3] over the photoelectron energy $E$ for different intensities. All other parameters are the same as in figure 3.
electron is weaker bound and the nucleus together with the remaining core electrons can be well approximated by an effective Coulomb potential. Furthermore, we found that only the SFA with Hartree–Fock initial states predicts the correct $m$-selectivity in ATI, i.e. the ratio of the total ionization probabilities from counter- ($m = -\ell$) to co-rotating initial states ($m = +\ell$). Here, the results obtained with the Hartree–Fock initial state wave functions agree with previous findings from PPT theory for both $6p$ and $5d$ orbitals. Furthermore, we showed that the $m$-selectivity is enhanced for initial states with larger orbital angular momentum quantum number $\ell$, which was not discussed in previous studies. While we performed our calculations within the framework of the SFA, we note that the dependence of the $m$-selectivity on the atomic initial state might differ if other models are used. It would therefore be an important future task to investigate this dependence further.

Our findings underline the importance of a correct description of the initial bound state in SFA computations and that it is in general not sufficient to assume a hydrogenic initial state wave function. Since the SFA is often applied to ATI and HHG processes with a variety of atomic target species, we hope that our results lead to more precise theoretical predictions in particular polarized laser fields. II. Derivation of formulas for large-scale relativistic atomic structure calculations

Acknowledgments

BB and WP acknowledge support from the Helmholtz Institute Jena and the Research School of Advanced Photon Science of Germany.

ORCID iDs

B Bönig  https://orcid.org/0000-0001-6504-0300
W Paufler  https://orcid.org/0000-0001-6227-2915
S Fritzsche  https://orcid.org/0000-0003-3101-2824

References

[1] Agostini P, Fabre F, Mainfray G, Petite G and Rahman N K 1979 Free-free transitions following six-photon ionization of xenon atoms Phys. Rev. Lett. 42 1127–30
[2] Paulus G, Nicklich W, Xu H, Lambropoulos P and Walther H 1994 Plateau in above threshold ionization spectra Phys. Rev. Lett. 72 2851–4
[3] McPherson A, Gibson G, Jara H, Johann U, Luk T S, McIntyre I A, Boyer K and Rhodes C K 1987 Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases J. Opt. Soc. Am. B 4 595–601
[4] Ferry M, L’Huillier A, Li X F, Lompré L A, Mainfray G and Manus C 1988 Multiple-harmonic conversion of 1064 nm radiation in rare gases J. Phys. B: At. Mol. Opt. Phys. 21 L31–5
[5] Calegari F, Sansone G, Stagira S, Vozzi C and Nisoli M 2016 Advances in attosecond science J. Phys. B: At. Mol. Opt. Phys. 49 062001
[6] Keldysh L V 1965 Ionization in the field of a strong electromagnetic wave Sov. Phys.–JETP 20 1307
[7] Faisal F H M 1973 Multiphoton absorption of laser photons by atoms J. Phys. B: At. Mol. Phys. 6 L89
[8] Reiss H R 1980 Effect of an intense electromagnetic field on a weakly bound system Phys. Rev. A 22 1786–813
[9] Milošević D B, Paulus G G, Bauer D and Becker W 2006 Above-threshold ionization by few-cycle pulses J. Phys. B: At. Mol. Opt. Phys. 39 R203–62
[10] Bauer D, Milošević D B and Becker W 2005 Strong-field approximation for intense-laser-atom processes: the choice of gauge Phys. Rev. A 72 023415
[11] Bauer J H 2008 Comparison of two forms of the $S$-matrix element of strong-field photoionization J. Phys. B: At. Mol. Phys. 41 185003
[12] Bauer J H 2013 Comparison of two forms of the $S$-matrix element of strong-field photoionization: II. $(m, l, m)$ = $(2, 1, 1 \pm 1)$ states J. Phys. B: At. Mol. Opt. Phys. 46 045601
[13] Barth I and Smirnova O 2011 Nonadiabatic tunneling in circularly polarized laser fields: physical picture and calculations Phys. Rev. A 84 063415
[14] Barth I and Smirnova O 2013 Nonadiabatic tunneling in circularly polarized laser fields. II. Derivation of formulas Phys. Rev. A 87 013433
[15] Herath T, Yan L, Lee S K and Li W 2012 Strong-field ionization rate depends on the sign of the magnetic quantum number Phys. Rev. Lett. 109 043004
[16] Trabert D et al 2018 Spin and angular momentum in strong-field ionization Phys. Rev. Lett. 120 043202
[17] Perelomov A M, Popov V S and Terentev M V 1966 Ionization of atoms in an alternating electric field Sov. Phys.–JETP 23 924
[18] Bönig B, Paufler W and Fritzsche S 2019 Nondipole strong-field approximation for spatially structured laser fields Phys. Rev. A 99 035404
[19] Wolkow D M 1935 Über eine klasse von lösungen der dirac-netz wave J. Phys. 240 250–60
[20] Bransden B H and Joachain C J 2003 Theoretical Physics of Atoms and Molecules (Englewood Cliffs, NJ: Prentice Hall)
[21] Parpia F A, Fischer C F and Grant I P 1996 Grasp92: a package for large-scale relativistic atomic structure calculations Comput. Phys. Commun. 94 249–71
[22] Curry J J 2004 Compilation of wavelengths, energy levels, and transition probabilities for Ba I and Ba II J. Phys. Chem. Ref. Data 33 725–46
[23] Arbo D G, Yoshida S, Persson E, Dimitriou K I and Burgdörfer J 2007 Interference of electrons ionized by short laser pulses J. Phys.: Conf. Ser. 88 012054
[24] Fritzsche S 2019 A fresh computational approach to atomic structures, processes and cascades Comput. Phys. Commun. 240 1–14

9