Secondary peaks in the atomic ionization by a resonant laser pulse

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Abstract. The above-threshold ionization of atoms by XUV short laser pulses with frequencies resonant with a ground-excited state transition is investigated. A theory based on a variational expression with trial wave functions for the final and the initial states is presented. For the former we use a Coulomb-Volkov wave function, and for the latter a close-coupling solution of the time-dependent Schrödinger equation considering a few bound states and their depletion towards the continuum. We find that this discrete-continuum Coulomb-Volkov theory provides a very good description of the photoelectron spectrum. In particular it accounts for the splitting of the above-threshold ionization peaks by Rabi oscillations and the appearance of secondary-peaks observed in full numerical simulations.

1. Introduction

Resonances in above-threshold ionization (ATI) have been observed in different contexts. For instance, experiments with rare gases exhibit a rescattering plateau enhancement for sharply defined laser intensities [1, 2]. In a previous article [3], we reported the appearance of doublets in the photoelectron spectra of positronium irradiated by short laser pulses and showed that they are related to a bound–bound resonance known as Autler–Townes doublets [4]. Furthermore, the ATI peaks splitting, a consequence of Rabi oscillations, was described by means of a two-state Coulomb-Volkov approximation [3]. The ATI photoelectron spectrum also shows resonance enhancement effects as recently investigated [5]. Previous non-perturbative semi-analytical theories [6, 7], besides employing the Coulomb-Volkov approximation for describing the time-dependent final continuum wave function, have also relied on a field-unperturbed bound initial state. This simple description of the initial state is not reliable for processes where an intermediate field-dressed state is populated by a resonant tuned laser. For this reason, we have recently improved the description of the initial state by employing an exact two-state close-coupling calculation, and applied it to the analysis of the positronium 1s–2p\(_0\) transition [3]. The same calculation was also employed for hydrogen atoms [8]. These results might be interpreted by considering the Rabi flopping dynamics as a zeroth-order approximation of the problem of an infinite number of bound states coupled to the continuum under a rotating wave approximation.

In this article, we propose a further improvement over these previous approximations [3, 5]. Our new model accounts for the depletion of the initial state towards the continuum increased by
ionization from the resonant excited state. The paper is organized as follows. We introduce our theoretical formulation in section 2 and present the corresponding results in section 3. Finally, section 4 contains conclusions and perspectives. Atomic units are used throughout this article.

2. Theory

Under non-relativistic conditions and within the electric dipole approximation, the electron wave function $\Psi(r, t)$ for a hydrogenic atom satisfies the time-dependent Schrödinger equation (TDSE) which, written in the length gauge, reads

$$i \frac{d\Psi(r, t)}{dt} = [-\frac{1}{2} \nabla^2 + V(r) + r \cdot F(t)]\Psi(r, t). \tag{1}$$

Here $r$ is the position of the electron with respect to the positive ion and $V(r)$ is the interaction between the electron and the rest of the target. The external laser radiation is given by the electric field $F(t) = F_0 \sin(\omega t + \varphi) \sin^2(\pi t/\tau)$. The transition amplitude from the state $i$ at $t = 0$ to the state $f$ at $t = \tau$ can be approximated by the following variational expression [9]:

$$a_{fi} = \lim_{t \to 0} \langle \chi_f(t) | \chi_i(t) \rangle - i \int_0^\tau dt' \langle \chi_f(t') | H - i d/dt' | \chi_i(t') \rangle, \tag{2}$$

where the non-hermitian operator $H - i d/dt'$ applies onto $\chi_f(t')$. The trial wave functions $\chi_f(t)$ and $\chi_i(t)$ approximate the exact solutions to the TDSE (1), subject to the following initial and final conditions:

$$\lim_{t \to 0} \chi_i(t) = \phi_i^+(r, t) = \varphi_i^+(r) \exp(-i\epsilon_i t),$$
$$\lim_{t \to \tau} \chi_f(t) = \phi_f^+(r, t) = \varphi_f^-(r) \exp(-i\epsilon_f t).$$

Here, $\varphi_f^-(r)$ and $\varphi_i^+(r)$ are eigenfunctions of the atomic Hamiltonian associated with the eigenenergies $\epsilon_f$ and $\epsilon_i$, respectively. In references [5, 6, 7], the Coulomb-Volkov approximation was used to represent the final trial wavefunction

$$\chi_f(r, t) = \phi_f^+(r, t) \exp[iA(t) \cdot r - i \int_0^t dt' A(t')] ,$$

where $A(t) = \int_0^t dt' F(t')$ is the vector potential. Replacing in Eq. (2), we obtain

$$a_{fi} = \int_0^\tau dt \exp \left( i \frac{k^2}{2} t + i k \cdot \int_0^t dt' A(t') + \frac{i}{2} \int_0^t dt' A^2(t') \right) \int dr \chi_i^+(r, t) e^{iA(t') \cdot r} A(t) \cdot [i k + \nabla] \varphi_f^+(r). \tag{3}$$

The choice of the appropriate trial wave function $\chi_i^+(r, t)$ depends on the process to be described. For photon energies above the ionization threshold and for small enough intensities so as to ensure that the total ionization probability is far from the saturation regime, the unperturbed initial wave function $\varphi_f^-(r) \exp(-i\epsilon_f t)$ can be safely used. This has been done in the framework of the Coulomb-Volkov (CV$^2$) theory where a favorable comparison with exact TDSE computations has been found within the aforementioned conditions [6, 7]. However, for photon energies below the ionization threshold a better description of the initial trial wave function is required. In this case, the electron will absorb several photons during the ionization process, passing through many virtual intermediate states. Even when the photon energy is not in tune, the wide spectrum
of the short laser pulse enables the population of the excited states. This effect is observed in the appearance of secondary peaks on the ATI photoelectron spectrum and can be interpreted in terms of different multi-photon ionization channels launched from every relevant field-dressed excited state. A simple way to improve the CV2− taking these channels into account is to consider a different choice for the trial wave function \[10\], namely
\[ \chi^+_i(r,t) = \sum_j b_{ji}(t) \phi_j(r,t), \]
where \( b_{ji}(t) \) is the transition amplitude at time \( t \) from the initial state \( \phi_i \) to the intermediate state \( \phi_j \). In reference \[10\], \( b_{ji}(t) \) was evaluated within a first Born approximation giving place to the so called modified Coulomb-Volkov (MCV2−) approximation. Although MCV2− correctly describes the position of the emergent secondary peaks, some sizable quantitative differences with TDSE remains. In \[5\] some improvements were achieved by evaluating the amplitudes \( b_{ji}(t) \) with a close-coupling calculation involving some few bound states including the initial and the near resonant ones among others. This close-coupling Coulomb-Volkov (CC-CV2−) theory provides a correct treatment of atomic ionization processes induced by a laser resonant with a given ground-bound state transition. The laser intensities for these theoretical treatment should be relatively small since any population depletion towards the continuum is not accounted for.

In this work, we improve the CC-CV2− theory by allowing the coupling between discrete states and the continuum, and between discrete states. In particular, we take into account the coupling of the initial state \( i \) with the resonant state \( r \) as well as with some other bound states. On the other hand, we also account for the coupling between the resonant state \( r \) and the continuum. Using the set of close coupling equations we obtain two integro-differential equations system (IDEs) of Volterra type:

\[
\dot{a}_i(t) = -i F(t) z_{ir} e^{-i(\varepsilon_i - \varepsilon_r)t} a_r(t) - \int_0^t dt' F(t) F(t') e^{i(\varepsilon_i - \varepsilon_r)(t-t')} a_i(t') h^D_i(t-t') \tag{4}
\]

\[
\dot{a}_r(t) = -i F(t) z_{ri} e^{-i(\varepsilon_i - \varepsilon_r)t} a_i(t) - \int_0^t dt' F(t) F(t') e^{i(\varepsilon_i - \varepsilon_r)(t-t')} a_r(t') h^C_r(t-t'). \tag{5}
\]

In this case the laser pulse is assumed to be linearly polarized in the \( z \) direction. \( z_{ir} = |i|z|r \) is the corresponding matrix element for the transition between the initial and the resonant states.

The kernel of the first equation is obtained by adding over the discrete spectrum, while the kernel of the second equation can be computed by means of the Nordsieck method \[11\], namely

\[
h^D_i(t-t') = \sum_{n \neq r} |z_{in}|^2 e^{-i\varepsilon_n(t-t')} , \quad h^C_r(t-t') = \int dk |z_{rk}|^2 e^{-i\varepsilon_k(t-t')} .
\]

In these equations, the superscript \( D \) stands for Discrete and the \( C \) for Continuum. We solve these equations using the Goldfine method \[12\]; namely, we use a Taylor expansion to propagate the initial and resonant transition amplitudes from \( t \) to \( t + \delta t \). The required time derivatives are obtained using the original equations. Once \( a_i(t) \) and \( a_r(t) \) were obtained, we can calculate \( a_n(t) \) by direct integration,

\[
a_n(t) = -i \int_0^t dt' z_{ni} F(t') e^{-i(\varepsilon_i - \varepsilon_n)t'} a_i(t') .
\]

In terms of \( a_i(t) \), \( a_r(t) \) and \( a_n(t) \), the trial wave function reads

\[
\chi^+_i(r,t) = a_i(t) \phi_i(r,t) + a_r(t) \phi_r(r,t) + \sum_n a_n(t) \phi_n(r,t) , \tag{6}
\]

Finally, the transition amplitude for the new discrete-continuum Coulomb-Volkov theory (DC-CV2−) accounting for bound-state continuum coupling is obtained by replacing Eq. \( (6) \) in Eq. \( (3) \). The CD-CV2− transition amplitude represents a series of CV2−-like amplitudes for transitions starting from intermediate states \( n \). The interpretation is rather straightforward: every bound state is populated with an amplitude given by \( b_{ji}(t) \), where a multi-photon promotion to the continuum is considered by using a CV2−-like amplitude.
3. Results

We apply our model to the study of the ionization of Hydrogen by a laser pulse with a frequency \( \omega = 0.375 \) a.u., resonant with the \( 1s - 2p_0 \) transition \((i = 1s \text{ and } r = 2p_0)\). The pulse length is \( \tau = 670.2 \) a.u., i.e. corresponding to 40 cycles. The laser polarization is linear, and chosen in the z-direction. Therefore, the magnetic quantum number is a constant of motion in the present application. We examine two laser field amplitudes \( E_0 = 0.04 \) and 0.05 a.u., large enough to produce an appreciable depopulation towards the continuum. We included \( 3p_0, 4p_0 \) and \( 5p_0 \) bound non-resonant states and checked that the convergence is achieved for principal quantum numbers \( n \leq 5 \). We compare our results with those obtained by numerically solving the TDSE. For this latter purpose we use the QPROP code [13]. In this code the initial wave function for the system is expanded in spherical harmonics and propagated with the Crank-Nicholson approximation for the short-time propagator. The spectral analysis of the real-time propagation computed with the Qprop package is performed through the window-operator technique [13] allowing the computation of the total and the angular resolved ionization spectra without the knowledge of the eigenstates.

![Figure 1](image.png)

**Figure 1.** Transition probabilities as a function of time for a 40 cycles length laser pulse \((\tau = 670 \) a.u. = 16.25 fs.). The laser electric field intensities are \( E_0 = 0.04 \) a.u. (left panel) and 0.05 a.u. (right panel).

3.1. Ionization probabilities and ground state population decay

We first analyze the quality of the trial initial wave function obtained from the numerical solution of the IDEs of Eq. (5). The left panel of Figure 1 shows the elastic and transition probabilities as a function of time for a laser electric field intensity of \( E_0 = 0.04 \) a.u. Both, the \( 1s \) and the \( 2p_0 \) populations display a Rabi oscillations pattern. We can distinguish one and a half
Rabi oscillations. Since ionization is important, a considerable depletion of the bound states population \( \sum P_n \) is exhibited as a function of time. A small amplitude and high frequency oscillation behavior of the probabilities are due to counter-rotating terms. Also the transitions probabilities to \( 3p_0, 4p_0 \) and \( 5p_0 \) (bottom figure) exhibit Rabi like oscillations presenting two maxima before going to zero near the end of the pulse. Since the population of these states occurs via the \( 1s \) state, it is reasonable that the corresponding maxima are almost coincident in time. For times closer to the end of the pulse, the \( 1s \) state population does not increase and therefore all the \( np \) probabilities remain small. In the right panel we show similar results but for a larger laser field amplitude of \( E_0 = 0.05 \) a.u.. The features are similar but the Rabi frequency is slightly increased (\( \Omega_R \propto E_0 \)). In this case a full two cycles of Rabi oscillations is observed. The \( n = 3 - 5 \) excitation probabilities display three maxima. The total bound state population decreases to 0.53, that is considerably smaller than the value 0.67 corresponding to the smaller perturbation in the left panel. Since the \( 1s \) population shows three clear maxima, also the \( np \) probabilities do.

![Figure 2. Hydrogen ionization spectra for a 40 cycles laser pulse (t=670 u.a.=16.25 fs.) and two different laser electric field intensities. The present DC-CV2 theory (thick (blue) line) is compared with the solution of the TDSE obtained with the Qprop code (thin (red) line).](image)

3.2. Ionization spectra
The ionization spectra were computed with the new modified Coulomb-Volkov theory. The trial wave function for the initial state was approximated by an expansion up to the fifth excited bound eigenstate of the atomic Hamiltonian. The corresponding probability amplitudes were determined from the solution of the set of coupled IDEs in Eq. (5). In figure 2 the results obtained for photons with a frequency \( \omega = 0.375 \) a.u. and laser intensities \( E_0 = 0.04 \) and 0.05 a.u. are displayed. The first four principal ATI peaks are plotted in each spectrum. We clearly notice the peak splitting due to Rabi oscillations [3]. The separation between the subpeaks increases linearly with the maximum electric field amplitude. The presence of a secondary peak
structure to the right of the main secondary peaks can be clearly distinguished. The theory is clearly able to show this feature that can be related to excitation followed by subsequent ionization. To probe this hypothesis, we have checked that the structure disappears when the excited states are removed from the trial initial wave function.

In general the agreement with the quantum propagation provided by the Qprop package [13] is very good. This is a clear indication that the use of an improved initial wave function accounting for the bound state depletion towards the continuum is correct. Some differences between QPROP and DC-CV2 may be observed in the background where the former results display a smaller amplitude oscillation. Regarding this, we should remember that the QPROP results are convoluted with a window in energy that naturally tends to average faster oscillations. Furthermore, some numerical error might arise due to the quite small values of the spectral probabilities in the background.

4. Conclusions
By comparing our DC-CV2 approximation with the numerical solution of the TDSE, we have been able to establish the importance of including the pathways through the bound states when the laser frequency has been tuned accordingly. An excellent agreement is achieved in the description of the photoelectron spectrum. In particular the secondary peak spectrum is explained and related to the transient population of intermediate states followed by absorption of one or more photons. On the contrary, previous CC-CV2 models tend to underestimate both the ionization spectrum and the total ionization probabilities, and only achieve a quantitative agreement when the laser field amplitude is in a perturbative regime. This is a strong indication that the coupling with the continuum states should be included in the theory. This is particularly important when a higher bound state is populated under resonance condition.

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