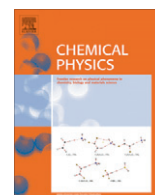




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Slow and fast multi-photon ionization of clusters in strong XUV and X-ray pulses

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ABSTRACT

The photo-electron spectrum resulting from multi-photon absorption of an extended target, such as an atomic cluster or a large molecule, from an intense laser pulse with photon energies larger than the ionization potential of the atomic constituents is discussed. We develop an approximate analytical framework and provide simple analytical expressions for the shape of the photo-electron spectrum in the limit of sequential and parallel ionization, realized by long and short pulses, respectively. The width of the spectrum provides valuable information about the absorbed photons of the target in relation to its extension.

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1. Introduction

With the impressive development of attosecond laser pulse technology increasing attention has been paid to identify ultrafast processes on the attosecond scale which are promising and worthwhile to detect experimentally. Using attosecond pulses for making microscopic time measurements requires typically a pump–probe scheme to start and stop the clock. In attosecond streaking the system is pumped by an attosecond extreme-ultraviolet (XUV) pulse and probed by a few-cycle near-infrared (NIR) pulse. In early experiments [1,2] the final electron momenta were measured, in which the excitation time is encoded by the instantaneous vector potential of the NIR pulse. In another setup [3], the ion yield was recorded, whereby the *nonlinear* dependence of the tunnel ionization on the instantaneous electric field of the NIR pulse allows one to determine the initial time with subfemtosecond resolution. Using elliptical polarization attosecond time intervals for ionized electrons could be determined [4] provoking, as often, questions about the tunneling process itself. One of the most puzzling experimental finding using the XUV pump NIR streaking technique was the difference in ionization times for electrons released from different orbitals from a surface atom as well as an isolated gas-phase atom [5,6]. It could be shown that these attosecond time difference can be traced back to energy-dependent complex scattering phases in a time-independent picture [7] and that in general, the asymptotic phases are quite delicate to deal with [8]. In a broader context, it can be argued that for all processes which remain coherent until detected (i.e., no information is lost) time-

domain and energy-domain measurements are equivalent and related to each other by Fourier transform. In reality, this Fourier transform needs to take into account physical boundary conditions such as causality. Yet, it has been demonstrated that starting from the energy domain, i.e., by taking a series of frequency-resolved absorption spectra, one can indeed synthesize by an appropriate Fourier transform the time evolution of an electron density on an attosecond time scale [9].

Hence the question arises, for which kind of processes attosecond laser pulses allow to retrieve new and otherwise not obtainable experimental information. From the deliberations above it follows that we have to look for situations where information is lost in the energy domain on the way to the detector. This is clearly the case for all kinds of transient processes which are over once measured very much later at the detector. One example is the charging of a cluster or large molecule during illumination of a short intense laser pulse which remains hidden in conventional detection of charged (and often partially recombined) fragments at the detector. In this situation, an XUV attosecond pulse with well-defined time delay with respect to the strong laser pulse, could probe the transient ionic states *during* charging [10].

However, this is only one interesting non-mainstream application of attosecond pulses in extended systems. Here, we would like to draw attention to another phenomenon which is generic for intense XUV or X-ray pulses. For photon energies larger than the ionization potential multi-photon ionization in an extended system containing many atoms proceeds by almost simultaneous single-photon ionization of many atoms. This can lead to a transient electron cloud in the continuum of condensed-phase density which we will discuss in the following and contrast this ultrafast, parallel ionization in extended systems with its opposite, namely ultra-slow, sequential ionization. The latter was observed first in clusters

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and found to be well describable by Monte Carlo simulations [11]. We will discuss sequential and parallel ionization in the context of the so called Coulomb complexes (CC) [12]. They allow for an approximate description which leads to simple analytical expressions for the photo-electron spectra, despite the fact that we deal with many-particle systems.

2. General considerations

2.1. Photo-activation

If an extended target is illuminated by a laser pulse, typically the electrons bound to individual atoms or small molecules within the large target absorb a photon and become thereby photo-activated. The process of photo-activation can be described in a simple way by taking the appropriate photo-ionization cross sections σ_ω for the atom species contained in the cluster since multiple absorption of high-frequency photons by a single electron is very unlikely if the first photon absorbed puts the electron already into the continuum with respect to its mother ion. The single-photon absorption rate is proportional to the intensity $I(t)$ of the pulse,

$$\frac{dn(t)}{dt} = N_{\text{at}} \sigma_\omega \frac{I(t)}{\omega} \quad (1)$$

with $n(t)$ the number of electrons that have absorbed a photon up to time t , while N_{at} is the number of atoms. For a Gaussian pulse with duration T we can integrate Eq. (1) analytically to get

$$n(t) = \frac{N_{\text{at}} \sigma_\omega I_0}{\omega} \int_{-\infty}^t dt' \exp(-(t'/T)^2) \quad (2a)$$

$$= \frac{Q}{2} [1 + \text{erf}(t/T)]; \quad (2b)$$

$$Q = N_{\text{at}} \sigma_\omega I_0 T \sqrt{\pi} / \omega, \quad (2c)$$

where Q is the total number of photons absorbed from the pulse. We use the variable Q to indicate that with Q photons absorbed the Coulomb complex becomes also Q -fold charged which we will need in the following. Clearly, taking a single-photon cross section is an idealization for several reasons. Yet, our main goal here is to achieve basic insight and keep the description as far as possible transparent and simple. Three snapshots before and during photo-activation are sketched in Fig. 1. Initially, the electrons (red) are bound by the ions (blue) which we will describe as a homogenous positive background charge, see Section 2.2. An electron i , bound by an atom with energy E_b , which has absorbed a photon (green) of energy ω would be measured at the detector with the excess energy (atomic units are used unless stated otherwise)

$$E^* = \omega - E_b. \quad (3)$$

If the electron is released from a cluster atom, this excess energy is modified by a potential

$$\tilde{E}^* = \omega - E_b + \tilde{V}(\mathbf{r}). \quad (4)$$

Hence, coming out of a cluster, the electron will only be detected if its absorbed photon energy is sufficient to overcome the atomic binding energy E_b and the additional potential \tilde{V} due to the nearby ions and electrons in the system. The cluster potential $\tilde{V}(\mathbf{r})$ depends on the position \mathbf{r} of the electron and, most importantly, on the other electrons and consequently, the history of photo-activations in the system. The latter are determined by the duration of the laser pulse as we will discuss in Section 3. Before doing so we develop the simpler part of this potential, which is given by the ionic background.

2.2. The ionic background potential

Since we do not require details about the ions and their positions we approximate them by a jellium potential of constant charge density such that a cluster of radius R carries the charge Q . The potential created by this charge follows from

$$V(r) = \frac{3Q}{R^3} \int_0^R dr' \frac{r'^2}{|\mathbf{r} - \mathbf{r}'|} \quad (5)$$

which can be solved analytically using the partial-wave decomposition [13] of $|\mathbf{r} - \mathbf{r}'|^{-1}$ to give

$$V(r) = \begin{cases} -\frac{3Q}{2R} + \frac{Q}{2R} \left[\frac{r}{R}\right]^2 & \text{for } r \leq R \quad (\text{a}) \\ -\frac{Q}{r} & \text{for } R \leq r. \quad (\text{b}) \end{cases} \quad (6)$$

The depth of the potential $V_0 \equiv \frac{3}{2}Q/R$, cf. Fig. 2, defines the energy scale of the extended system (note that this is not an absolute definition but depends on the photo-activation which generates Q charges, or from another perspective, deposits Q photons). The propagation of the photo-activated electrons can be done classically due to the high energies involved which can be measured by the excess energy $E^* \sim V_0$ relative to the harmonic curvature of the potential $\Omega = [Q/R^3]^{1/2}$, where $E^*/\Omega \sim (QR)^{1/2}$ which is of the order of 10^2 for 1000 photons absorbed by an extended system of a radius 1 nm ($\approx 20 a_0$).

Interestingly, for a large and reasonable parameter space, we do not need to describe the motion of the ions in a simple, yet realistic approach. This can be seen by comparing the time scales of the electronic and the ionic motion. A typical time of the electron motion (with the order of the kinetic energy given by V_0) is

$$\tau_{\text{el}} = \frac{R}{\sqrt{2V_0}} = \sqrt{\frac{R^3}{3Q}}, \quad (7)$$

which scales with the period of the harmonic potential (6a). The ions move due to Coulomb explosion whereby the surface ions would be the fastest. Estimating the time it would take to change the radius of the ionic background by δR one gets [14]

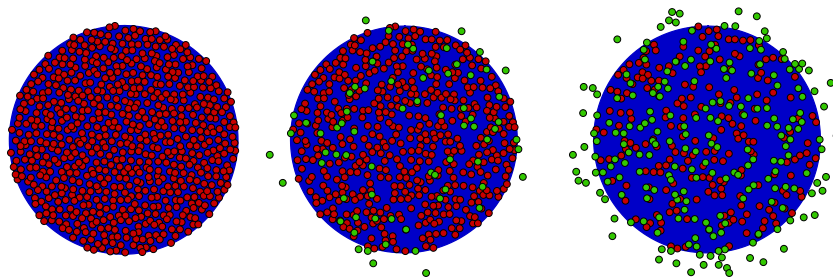


Fig. 1. Activation of photo-electrons in a Coulomb complex: bound electrons (red), activated electrons (green), ionic background potential (blue) for three different instances of time: $t \rightarrow -\infty$ (left), $t = -T/2$ (middle), and $t = +T/2$ (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

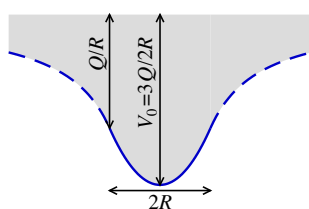


Fig. 2. Jellium-like ionic background potential as defined in Eq. (6).

$$\tau_{\text{ion}} = \sqrt{M \frac{R^2 \delta R}{2Q}} \quad (8)$$

with M the mass of the atomic constituents. Obviously $\tau_{\text{el}} \ll \tau_{\text{ion}}$ holds for typical atomic masses.

3. Multi-photon ionization

With the help of the jellium potential one can easily calculate the evolution of the photo-electron spectrum for various pulse durations T . Fig. 3 clearly shows a transition from a curved spectrum for short pulses to a plateau-like spectrum for longer pulses. The overall extension of the spectrum, which is about V_0 , is less sensitive to the pulse duration. The spectra for the limiting cases, which turn out to be due to sequential and parallel ionization (Fig. 3a and b), can be approximated analytically as we will derive below.

3.1. Sequential ionization

The picture behind sequential ionization is the assumption that electrons leave the cluster upon photo-ionization independently of each other. Were the atoms of the system far apart, this would be simply a multiple copy of atomic ionization. However, for a high density of atoms such as in clusters, already the second electron and after it all others which leave the cluster, have to overcome a positive background charge which increases with each electron leaving, cf. the potential \tilde{V} in Eq. (4). This is the reason, why in general photo-electrons reach the detector with energies less than the atomic photo-line at E^* . Characteristic for sequential ionization is in addition a plateau (see Fig. 3a) which is also found in simulations, e.g., for ionization of carbon by an X-ray pulse [15]. We will prove with analytical considerations the existence of the plateau.

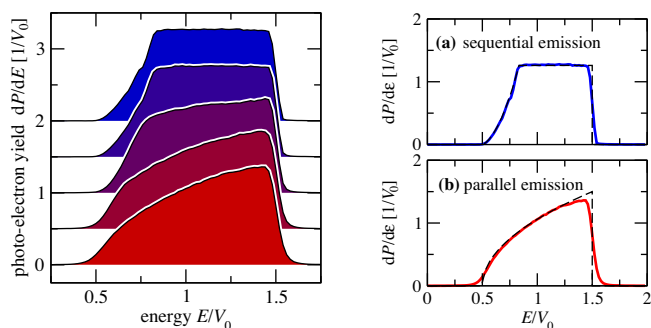


Fig. 3. Left: Illustration of the shape evolution of the photo-electron spectrum for Coulomb complexes activated over different time intervals increasing by a factor of $\sqrt{10}$ with an excess energy $E^*/V_0 = 3/2$, from fast activation (red, foreground) to slow activation (blue, background). Right: Comparison of the spectra for the shortest and the longest pulse, respectively, with the analytical expressions of the SES according to Eq. (13) and the PAS according to Eq. (15). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To be specific, the photo-spectrum in terms of a classical correlation function in phase space can be constructed in the following way: First we ask what is the probability to find an electron with final energy E after leaving the cluster which is already q -fold charged. If the initial photo-ionization from an atom in the cluster leads to an excess energy E^* and happens at r , the final energy is given by

$$E_q(r) = E^* + V(r) = E^* - \frac{q}{2R}(3 - r^2/R^2). \quad (9)$$

We do not know, from where the electron started. Therefore, we integrate over the cluster volume,

$$P_q(E) = \frac{3}{R^3} \int_0^R dr r^2 \delta(E - E_q(r)), \quad (10)$$

with $3/R^3$ as normalization factor. Since the intermediate charge state q of the cluster is normally not measured, we also have to integrate over it, $P(E) = (1/Q) \int_0^Q dq P_q(E)$. The flat plateau in Fig. 4 can most easily be demonstrated by interchanging the integration sequence over q and r . To evaluate the δ -function easily, we change additionally the integration variable from q to E_q . Since q and E_q are linearly related, cf. Eq. (9), the Jacobian $|dq/dE_q| = 2R/(3 - r^2/R^2)$ does not depend on E_q and can therefore be taken out of the integral over E_q ,

$$P(E) = \frac{3}{QR^3} \int_0^R dr r^2 |dq/dE_q| \int_0^{E_q} dE_q \delta(E - E_q). \quad (11)$$

The second integral simply gives unity for all curves $E_q(r)$ contributing to E (in Fig. 4 for energy E_2 those which are between the two green lines). Provided that these curves cover the whole range $r = 0 \dots R$, the first integral is constant, which explains the appearance of a plateau. Furthermore, it shows that the existence of the plateau does not depend on the particular shape of the background potential Eq. (6). Expression (9) looks different for other potentials, but the independence of the photo-electron spectrum of E over a finite energy interval Δ still holds, as long as the potential increases linearly with q . For final energies E outside the interval Δ , the integration is restricted to a certain region of r within the Coulomb complex and the spectrum does depend on the particular form of the potential through the Jacobian according to

$$\frac{dP(E)}{dE} = \frac{3}{QR^3} \int_{\max(0, r_{\min}(E))}^{\max(R, r_{\max}(E))} dr r^2 |dq/dE_q|. \quad (12)$$

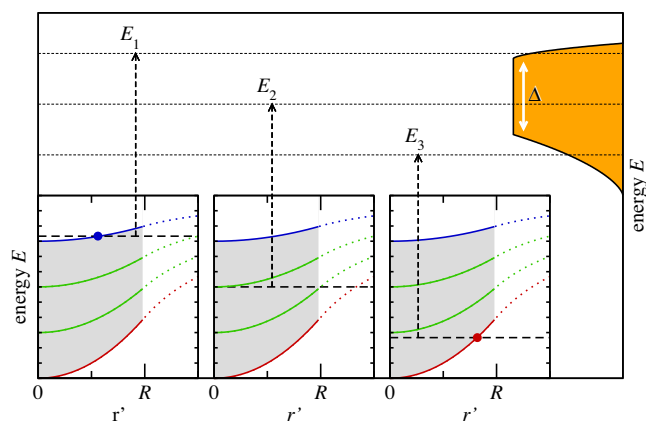


Fig. 4. Formation of the sequential spectrum (orange-shaded area). Insets show the contributions from various charge states between q_{\min} (blue line) and $q_{\max} = Q$ (red) and positions r according to Eq. (9). The integration region of Eq. (12) is marked by the gray-shaded area. For an initially neutral cluster ($q_{\min} = 0$) the spectra would show a sharp cutoff at the high-energy end. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 shows with the energies E_1 and E_3 two examples for such cases. If ionization starts from a neutral cluster as it is typically the case, the plateau ends with a sharp cutoff at the atomic photo-line $E = E^*$ and is preceded by a trailing continuous fall-off to zero. Such spectra have been measured at FLASH [11], where due to the high intensity the plateau reached down to $E = 0$. The explicit analytical expression for the SES (see also [12]) from Eq. (12) for the potential Eq. (9) reads with $\chi \equiv (E^* - E)/V_0$

$$\frac{dP(E)}{dE} = \begin{cases} \frac{9}{V_0} \left[\sqrt{3} \operatorname{arccoth}(\sqrt{3}) - 1 \right] & \text{for } 0 < \chi < \frac{2}{3} \\ \frac{9\sqrt{3}}{V_0} \left[\operatorname{arctanh}(\sqrt{1 - \chi(E)}) - \sqrt{1 - \chi(E)} \right] & \text{for } \frac{2}{3} < \chi < 1 \end{cases} \quad (13)$$

and is shown in Fig. 3a as the dashed black line in obvious good agreement with the numerical result (blue line).

3.2. Parallel ionization

We turn now to parallel ionization which is the limit of simultaneous photo-activation of all Q electrons. Fig. 3b shows the spectrum for a sufficiently short pulse. Due to the interaction of the parallel activated electrons, we see a distinctly different spectrum compared to the sequential case. While still mainly restricted to the energies $-1 \leq E/V_0 - E^*/V_0 \leq 0$, the plateau gets replaced by a square-root shape, characteristic for radial expansion of the electron cloud, dominantly driven by the mean-field of the interaction. The parallel emission spectrum (PAS) can be obtained analytically in the following way. The potential for an electron photo-activated with excess energy E^* at radial distance r from the center is $V_{\text{eff}}(r) = V(r) + V_{\text{rep}}(r)$, with V from Eq. (6) and $V_{\text{rep}}(r) = Q_e/r$ is the repulsive potential of the charge $Q_e = Q r^3/R^3$ created by all electrons within the sphere of radius r . To escape from the CC the electron has to overcome V_{eff} and its final energy is therefore

$$E(r) = E^* - V_0(r^2/R^2 - 1). \quad (14)$$

With the radial electron distribution $dP/dr = 3r^2/R^3$ and Eq. (14) we get with $dP/dE = [dP/dr] [dE/dr]^{-1}$ with the same abbreviation $\chi \equiv (E^* - E)/V_0$

$$\frac{dP(E)}{dE} = \frac{3}{2} \sqrt{1 - \chi(E)}, \quad (15)$$

within the interval $0 \leq \chi \leq 1$.

3.3. Width of the photo-electron spectra

From the analytical form of the SES in Eq. (13) it follows that the full width at half maximum of the distribution is $\Delta E_{\text{SES}} = 0.777 V_0$ or

$$\Delta E_{\text{SES}} \approx 1.165 Q/R. \quad (16)$$

Thereby, the number of ionized electrons Q is related to the size R of the cluster. If one of these quantities is known, the other one can be read off from the SES via ΔE_{SES} . If one has a valid description for the charging through the laser pulse, as, e.g., given in Eq. (2c) for a Gaussian pulse, one can also determine the peak intensity I_0 from ΔE_{SES} , as argued in a different way before [15].

In a similar spirit, we obtain from Eq. (15) for the full width at half maximum of the PAS

$$\Delta E_{\text{PAS}} = \frac{9}{8} Q/R = 1.125 Q/R, \quad (17)$$

providing the ratio of charging to radius of the illuminated cluster. In the regime of massively parallel ionization this result is again very useful to estimate the number of photons absorbed if the cluster size is known, or vice versa, determine the size of the cluster illuminated if one can measure how many electrons (their number Q equals the number of photons) have been ionized. Since the spectra for both, sequential and parallel ionization, have very similar width (Eqs. 16 and 17), and their shape evolves quite smoothly for finite photo-activation between these two limits (see Fig. 3) one may conclude that the width of the photo-electron spectrum for an extended system is to a good approximation given by $\Delta E \approx \frac{9}{8} Q/R$.

4. Summary

We have described the basic shape of the photo-electron spectrum which results from illuminating an extended system, such as a cluster or large molecule containing hundreds or thousands of atoms, with an intense laser pulse. We have focused on the two limiting cases of a slow rate of absorbed photons (long pulse) which allows the photo-electrons to leave one after another independently, and a fast activation of photo-electrons (short pulse) which leads to an interaction of the electrons even after photo-absorption. The shapes of both spectra, the sequential-emission shape and the parallel-emission shape, could be obtained in a simple approximate form analytically. The full width at half maximum of the spectra provides in both cases valuable information about the target, namely the ratio of its charge (or equivalently, the number of absorbed photons) to its radius.

How important analytical approximations can be is impressively illustrated by the influence of the so called “three-step model” for single-electron strong-field ionization dynamics at high energies [16,17] on the development of attosecond science. Even recently, a new phenomenon at low energies (the “low-energy structure”) in the strong-field atomic ionization spectrum was discovered experimentally [18] and eventually found its analytical description [19]. We hope that the analytical approximations discussed here provide a basis for analyzing in the future subtle effects of ultra-short time dynamics involving ionization in extended many-electron systems.

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