Slow electrons from clusters in strong x-ray pulses

A Camacho Garibay¹, U Saalmann¹ and J M Rost¹,²

¹ Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany
² PULSE Institute, Stanford University and SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA

E-mail: us@pks.mpg.de

Received 4 May 2015, revised 16 June 2015
Accepted for publication 17 June 2015
Published 17 July 2015

Abstract
Electrons released from clusters through strong x-ray pulses show broad kinetic-energy spectra, extending from the atomic excess energy down to the threshold, where usually a strong peak appears. These low-energy electrons are normally attributed to evaporation from the nano-plasma formed in the highly-charged clusters. Here, it is shown that also directly emitted photo-electrons generate a pronounced spectral feature close to threshold. Furthermore, we give an analytical approximation for the direct photo-electron spectrum.

Keywords: free-electron lasers, multiple ionization, highly-charged clusters, photo-electrons

1. Introduction
Recently, there has been increasing interest in slow electrons from photo-driven processes. While identified in strong-field ionization of atoms [1–3] as well as molecules [4], the mechanisms behind the production of slow electrons are very different for atoms in linearly polarized pulses [5] and molecules in elliptically polarized pulses [6], respectively. Crucial in both cases is the (single) electron dynamics in the combined potential of the ion left behind and the driving laser field.

Slow electrons can also emerge from soft and even hard x-ray pulses. At a first glance this is surprising, since the electronic excess energy $E^*$ (which is the photon energy reduced by the binding energy) is typically large, say a few hundred eV up to few keV, depending on the photon energy. Under such circumstances, the low-energy electrons can occur through non-adiabatic effects in very short pulses, when the pulse length becomes comparable with the orbital period of the bound orbital which is photo-ionized [7, 8].

While this effect is again essentially a single-electron phenomenon, another very common mechanism to produce slow electrons in intense x-ray pulses requires although not collective, yet multiple ionization: thereby, a complex of ions (either clusters or big molecules) staying behind forms a large background charge [9–17], which reduces the excess energy $E^*$. Hence, these kind of slow electrons can only emerge from large systems, which allow for high charging. In fact, the background charge may be so large that electrons are being trapped even for photons in the keV range [11]. The trapping leads to the formation of a so-called nano-plasma, which thermalizes quickly and consequently evaporates (slow) electrons. Since slow electrons are difficult to observe it is not surprising that only two of the papers cited above [12, 17] contain experimental results. However, as shown recently [17] Rydberg atoms, ionized in the detector, may serve as a sensitive probe of electrons near the threshold from a molecular complex.

Typically, the yield of the slow electrons shows an exponential decrease with an energy-scaling constant related to the plasma temperature according to common sense. However, this relation is tricky for two reasons. Firstly, due to the continuous excitation of electrons into the plasma its state may change considerably during the x-ray pulse violating the quasi-stationarity which is necessary to assign a temperature to the electron spectrum. Secondly, the photo-ionization process itself gives rise to directly ejected slow electrons.

This is illustrated in figure 1 with the electron spectrum resulting from the illumination of a generic (spherical) cluster with radius $R = 10$ by a short pulse with $T = 32$ duration and...
excess energy of \( E^* = 50 \). The direct electrons (red curve) show a clear peak at low energies, revealing that the slow electrons do not only result from the evaporation of the nano-plasma. Direct electrons are those which can leave the cluster without any additional interaction, see section 4 for a quantitative definition.

In order to understand the peak in the (numerically obtained) direct-electron yield in figure 1, we will provide in section 2 an analytical derivation of the direct-electron spectrum under the premise that these electrons leave the cluster sequentially and (indirect) plasma electrons remain in the cluster. Thereby, the origin of the slow direct electrons will become clear. With a surprisingly simple approximation, suggested by the form of the direct-electron spectrum, we can give a fully analytical formula (section 3). It is compared in section 4 to the numerical spectrum, revealing how the indirect plasma electrons influence the direct electrons.

The model calculations presented in figure 1 and section 4 are done in an arbitrary reference unit system. Other conditions can be reached by scaling positions, momenta, energy and time, respectively, according to [14]

\[
[r, p, E, t] \rightarrow \{\eta^{-1}r, \eta^{-1/2}p, \eta E, \eta^{-1/2}t\}. \tag{1}
\]

Note that choosing \( R \) and \( E^* \) fixes the intrinsic time scale to \( R/\sqrt{2E^*} \), the time it takes an electron to pass the cluster radius. For \( R = 10 \) and \( E^* = 50 \), used in figures 1 and 3, this unit is 1.

2. The direct photo-electron spectrum and the origin of slow direct electrons

We assume here for simplicity that the system is spherical with a radius \( R \) throughout the ionization process. The light pulse leads to random single-ionization events of atoms within the cluster, where we choose the intensity such that the system is far from saturation of complete single-photon ionization and the occurrence of any multiple ionization of cluster atoms. More explicitly, if the cluster contains \( N \) atoms and the pulse leads to \( Q \) ionization events, then in the end \( N - Q \approx N \) atoms of the cluster remain neutral. For the case of sequential ionization the photo-electron spectrum follows from integrating the spectra \( P_q \) for an instantaneous charge \( q \) ranging from \( q = 0 \) (for the initially neutral cluster) to \( q = Q \) (the highest possible charge state)

\[
P(E) = \int_0^Q dq P_q(E). \tag{2}
\]

The highest charge \( Q \) is reached when the cluster potential

\[
V_q(r) = \frac{q}{2R} \left( 3 - \frac{r^2}{R^2} \right) \tag{3}
\]

is so deep that absorption of a single photon (with excess energy \( E^* \)) is not sufficient to overcome the threshold. This occurs if \( V_0(R) = E^* \) which implies \( Q = E^*R \).

If the cluster potential \( V_q(r) \) is still shallow enough for all electrons in the cluster to escape by absorbing just one photon, the electron spectrum of a \( q \)-fold charged spherical cluster is given by [19]

\[
P_q(E) = \frac{3}{R} \int_0^R dr r^2 \delta(E - E_q(r)) \tag{4a}
\]

with

\[
E_q(r) = E^* - \frac{q}{2R} \left( 3 - \frac{r^2}{R^2} \right) \tag{4b}
\]

the final energy of an electron released at a distance \( r \) from the centre through the absorption of a photon. We obtain from equation (4)

\[
P_q(E) = \frac{3}{q/R} \sqrt{3 - 2E^* - E\frac{q}{q/R}} \tag{5a}
\]

for \( E_{\text{min}}(q) \leq E \leq E_{\text{max}}(q) \)

with \( E_{\text{min}}(q) \equiv E^* - 3q/2R \)

and \( E_{\text{max}}(q) \equiv E^* - q/R \) \tag{5b}

and \( P_q(E) = 0 \) elsewhere. Here, \( E_{\text{min}}(q) = E_q(0) \) is the energy from an electron released at the centre \( (r = 0) \), while an electron from the surface will appear at \( E_{\text{max}}(q) = E_q(R) \), cf equation (4b). The two lower blue dashed lines in figure 2(b) show as examples \( P_q(E) \) for \( q = 2Q/5 \) and \( q = 3Q/5 \), respectively.

Expression 5 has to be modified when the cluster potential becomes so deep that electrons—firstly those

3. At higher intensities ionization would saturate. Further, due to the larger ionization potential of atomic ions, there would be electrons with lower excess energies.

4. Note that higher charge states can be reached when electrons are excited below threshold and the nano-plasma, formed in the process, evaporates [9, 12, 18].
released at the centre—are trapped after single-photon absorption. This occurs at \( q_{\text{trap}} = E^*/3 = 2Q/3 \). Since these electrons do not increase the cluster charge, further charging is due to electrons located closer and closer to the surface. Hence, for charges \( q_{\text{trap}} \leq q \leq Q \) the instantaneous spectra become

\[
P_q(E) \rightarrow P_{q}^{\text{trap}}(E) = \frac{P_q(E)}{1 - \left[ 3 - \frac{E^*}{q/R} \right]^{1/2}}
\]

for \( 0 \leq E \leq E_{\text{max}}(q) \) and \( P_{q}^{\text{trap}}(E) = 0 \) elsewhere. The denominator in (6) normalizes the distribution \( P_q^{\text{trap}} \) for any \( q \) just as \( P_q \) above is normalized, i.e.

\[
\int_{0}^{
E^*} dE \ P_q(E) = \int_{0}^{
E^*} dE \ P_{q}^{\text{trap}}(E) = 1.
\]

One example for \( P_{q}^{\text{trap}}(E) \) is shown in figure 2(b) with the upper blue dashed line corresponding to \( q = 4Q/5 \). One can also see from the shaded area in figure 2(b) that the restriction of electron energies to the interval \( E_{\text{min}}(q) \leq E(q) \leq E_{\text{max}}(q) \) implies for the integral (2) a restriction to charges in the interval \( q_{\text{min}}(E) \leq q(E) \leq q_{\text{max}}(E) \) with

\[
q_{\text{min}}(E) \equiv \frac{2}{3} \left[ E^* - E \right] R \quad \text{and} \quad q_{\text{max}}(E) \equiv \left[ E^* - E \right] R,
\]

which follows directly from equation (5b). The abundance for a particular energy \( E \) finally reads

\[
P(E) = \int_{q_{\text{min}}}^{q_{\text{max}}} dq \ P_q(E)
\]

for \( E^*/3 \leq E \leq E^* \) (9a)

\[
P(E) = \int_{q_{\text{min}}}^{q_{\text{max}}} dq \ P_q(E) + \int_{q_{\text{trap}}}^{q_{\text{max}}} dq \ P_{q}^{\text{trap}}(E)
\]

for \( 0 \leq E \leq E^*/3 \). (9b)

Equation (9a) can be solved analytically and gives the energy-independent value \( P(E) = 3R \left[ \sqrt{3} \ln \left( 2 + \sqrt{3} \right) - 2 \right] \) corresponding to a plateau [14]. Equation (9b), on the other hand, does not allow for a compact analytically solution. Therefore, we provide with the blue dashed line in figure 2(a) the numerically integrated spectrum. One clearly sees an accumulation towards lower energies with a divergence at \( E = 0 \). With \( q_{\text{min}} \) and \( q_{\text{trap}} \) finite, this is due to the second term in (9b) and may be interpreted as follows: electrons with energies \( E \geq E^*/3 \) can escape from anywhere in the cluster for any (accessible) charge state, as described by equation (9a). For electrons with energies \( E < E^*/3 \) this is limited to clusters charged less than \( q_{\text{trap}} = 2Q/3 \), cf 1st integral in (9b). For clusters charged higher than \( q_{\text{trap}} \) direct electrons come from the outer regions of the cluster with ever decreasing energy as the cluster charge grows beyond \( q_{\text{trap}} \). This part of the spectrum is described by the 2nd integral in (9b).

3. Analytical approximation for the direct photo-electron spectrum

Interestingly, the exact shape of \( P_q(E) \) is not important for the final spectrum. One may choose any form for \( P_q \). As long as the shape for various values \( q \) can be obtained by a simple scaling the final spectrum is a plateau [19]. In order to obtain an analytical expression for all energies we approximate \( P_q(E) \) with the simplest form possible, namely a constant spectrum between \( E_{\text{min}} \) and \( E_{\text{max}} \). The \( q \)-dependence is then introduced via the normalization (7). With \( E_{\text{min}} \) and \( E_{\text{max}} \) given in (5b) this leads to

\[
P_q(E) = \frac{1}{E_{\text{max}} - E_{\text{min}}} = \frac{2R}{q}
\]

for \( 0 \leq q \leq q_{\text{trap}} \) (10a)

\[
P_q(E) = \frac{1}{E_{\text{max}}} = \frac{1}{E^* - q/R}
\]

for \( q_{\text{trap}} \leq q \leq Q \). (10b)

This distributions are shown in figure 2(b) as red solid lines. They allow for an integration of equation (9)

\[
P(E) = 2R \ln(3/2)
\]

for \( E^*/3 \leq E \leq E^* \) (11a)
which is shown as red solid line in figure 2(a). It reproduces the spectrum obtained with the blade-shaped instantaneous spectra (blue dashed line in figure 2(a)) extremely well. This applies to both, the absolute values of the plateau at large $E$, and the divergent behaviour around $E = 0$. Note, that the latter is indeed due to the second term in (11b) which represents the analytical approximation of the integral over $p_{\text{lep}}$ in (9b).

4. Comparison to numerical results from Coulomb complexes

The analytical expressions have been derived under the assumptions that photo-ionization occurs sequentially and that electrons excited to states below threshold remain trapped. In the following we will assess if and when these assumptions are justified by comparing the results from (11) to those of molecular dynamics calculations without those assumptions in the framework of so-called photo-activated Coulomb complexes [14]. This is a simple model, where electrons are treated as classical particles and ions form a spherical jellium, describing the attractive potential $V_Q$ of the charged cluster as given in equation (3). This potential as well as the electron-electron interaction are essential for understanding the formation of the broad electron spectra.

Initially $Q$ electrons are placed in the spherical background potential in such way that the total energy $E_{\text{tot}} = \sum_j V_Q(r_j) + \sum_{j<k} |r_j - r_k|^{-1}$ is minimized. Then the potential energy $W(r_j) = V_Q(r_j) + \sum_{k(\neq j)} |r_j - r_k|^{-1}$ is used to get the absolute value of the activation momentum $p_j^*$ for each electron from $p_j^* = \sqrt{2(E^* - W(r_j))}$. The activation direction is chosen randomly. It remains to define an activation time $t_j^*$ for each electron which is also chosen randomly with a distribution according to the instantaneous x-ray intensity $I$, which we assume to be a Gaussian $I(t) = \exp(-t^2/T^2)$. In order to obtain generic results we calculate 100 realizations which differs by the randomly chosen activation times and momentum directions.

Before the first activation event all electrons have the same energy $E = E^*$. Although an electron before activation remains on its initial position this energy will change in time since already activated electrons will escape thereby lower the electron-electron repulsion and thus $W(r_j)$. Therefore, electrons, activated later, will start with an energy $E_j^* \equiv E(t_j^*) < E^*$ and eventually $E_j^* < 0$. The energy of an electron at its time of activation $t_j^*$ is used to distinguish between direct (if $E_j^* > 0$) and plasma (if $E_j^* < 0$) electrons. The former may leave the cluster directly (without any interaction), the latter may only become free due to electron-electron collisions.

Once activated the electrons are propagated according to Newton’s equations with forces resulting from the jellium potential $V_Q$ and the electron-electron interaction. Thus, in contrast to the description of the previous section, here correlations (collisions) of the electrons are fully taken into account. The system is propagated sufficiently long (up to times $t = 10^4$ for the results presented) before spectra are calculated. These are obtained by folding the final (kinetic) energies $E_j$ of the electrons with a Gaussian

$$P(E) = \sum_j \exp \left( -\frac{(E_j - E)^2}{\delta E^2} \right)$$

of width $\delta E = 1$.

Figures 1 and 3 show such spectra for a Coulomb complex of radius $R = 10$ with $10^3$ electrons and $E^* = 50$. The photo-activation rate is proportional to $\exp(-t^2/T^2)$. One clearly sees a broad spectrum with a large peak at $E \approx 0$, a plateau at $E < E^*$ and a cutoff at $E = E^*$. These features have been observed [20] and discussed [12–15] before, interpreting the high-energy part (plateau) as a consequence of the direct photo-electrons and the low-energy part with its peak towards threshold as a consequence of the evaporation from the transient nano-plasma.

However, as already mentioned, figure 1 reveals that also direct electrons, defined as those electrons which have initially enough energy to escape from the cluster potential, contribute to the slow-electron peak. Their contribution to the low-energy spectrum is even larger in the analytical estimate considering only sequentially emitted electrons (see figure 3, gray-filled area) than from the numerically obtained direct electrons (red curve). The reason is that we do not take into account that initially trapped plasma electrons do eventually leave at a certain rate. If this rate is faster than the photo-ionization rate, direct photo electrons see an increased background charge reducing their yield at low energies since they get trapped. This effect should be least important for very short pulses when the direct electrons leave before plasma evaporation becomes important. However, for very short pulses, the second assumption made for the analytical direct electron spectrum is violated, namely, the sequential ionization: the photo-ionization rate is so large that the direct electrons interact and exchange energy before leaving the cluster. This indicates the onset of massively parallel ionization [21], which is accompanied by high-energy tails at $E \gtrsim E^*$ in the spectrum. Indeed, the red curves from the numerical calculation in figure 3 show these tails in contrast to the sharp cutoff of the analytical spectrum at $E = E^*$.

5. Summary

Comparing fully numerical spectra to those from photo-electrons only, we have shown that the low-energy peak observed in the photo-electron spectrum of multiple
ionization of clusters in strong x-ray pulses is not only generated by initially trapped plasma electrons but also by photoelectrons directly escaping. An understanding of the origin of slow direct electrons has been made possible by the formulation of the spectrum for the direct electrons alone down to threshold, including a fully analytical approximation—always under the assumption that the electrons leave the cluster sequentially. In the future it would be interesting to disentangle direct photo-electron dynamics from plasma-electron dynamics experimentally. This could be done by exploiting the fact that angular distributions may be different for photo-electrons (depending on the shape of the orbitals being ionized) and plasma-electrons (expected to be isotropic) or by using streaking techniques [22].

Figure 3. Electron spectra (red solid line) for the direct photo-electrons only, i.e. excluding plasma-electrons, as obtained from Coulomb complexes with $10^3$ electrons for an excess energy $E^* = 50$ and various pulse durations $T$. They should be compared to the analytical expressions (11), which is shown by the light grayshaded areas.

References

[1] Blaga C I et al 2009 Nat. Phys. 5 335
[2] Quan W et al 2009 Phys. Rev. Lett. 103 093001
[3] Mancuso C A et al 2015 Phys. Rev. A 91 031402
[4] Dimitrovski D, Maurer J, Stapefeldt H and Madsen L 2014 Phys. Rev. Lett. 113 103005
[5] Kästner A, Saalmann U and Rost J-M 2012 Phys. Rev. Lett. 108 033201
[6] Dimitrovski D and Madsen L B 2015 Phys. Rev. A 91 033409
[7] Toyota K, Tolstikhin O I, Morishita T and Watanabe S 2009 Phys. Rev. Lett. 103 153003
[8] Toyota K, Saalmann U and Rost J M 2015 New J. Phys. at press (arXiv:1408.4541 [physics])
[9] Saalmann U and Rost J M 2002 Phys. Rev. Lett. 89 143401
[10] Moribayashi K 2009 Phys. Rev. A 80 025403
[11] Gnodtke C, Saalmann U and Rost J M 2009 Phys. Rev. A 79 041201 (R)
[12] Bostedt C et al 2010 New J. Phys. 12 083004
[13] Arbeiter M and Fennel T 2010 Phys. Rev. A 82 013201
[14] Gnodtke C, Saalmann U and Rost J-M 2011 New J. Phys. 13 013028
[15] Arbeiter M and Fennel T 2011 New J. Phys. 13 053022
[16] Camacho Garibay A, Saalmann U and Rost J M 2014 Phys. Rev. Lett. 113 083001
[17] Schütte B et al 2014 Phys. Rev. Lett. 112 073003
[18] Yase S et al 2015 Phys. Rev. A 88 043203
[19] Gnodtke C, Saalmann U and Rost J-M 2013 Chem. Phys. 414 65
[20] Bostedt C et al 2008 Phys. Rev. Lett. 100 133401
[21] Gnodtke C, Saalmann U and Rost J-M 2012 Phys. Rev. Lett. 108 175003
[22] Krikunova M 2014 Private communication