Mechanisms for Multiple Ionization of Atoms by Strong Pulsed Lasers

P. Lambropoulos

Department of Physics, University of Southern California, Los Angeles, California 90089, and Department of Physics and Institute of Electronic Structure and Laser, University and Research Center of Crete, Iraklion, Crete, Greece

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It is shown that substantial ionization during the rise of the pulse of a strong laser is inevitable. Thus only multiply charged ions are likely to be exposed to fields above 10^{14} W/cm^2. The behavior of the N-photon generalized cross section for $N >> 1$ and its connection to tunneling are discussed.

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Two recent papers[1,2] in the pages of this journal highlight the significance and challenge of accumulating experimental results[3,4] on multiple ionization of atoms under strong lasers (peak intensities above 10^{11} W/cm^2). Some[3] of these data seem to be compatible with a multiphoton mechanism characterized by definite slopes of the curves representing ionization versus laser intensity (in a log-log plot) in accordance with the law $\hat{\sigma}_N F^N$, where $\hat{\sigma}_N$ is the generalized cross section (gcs) and F the photon flux. Other data,[4] however, seem to exhibit rather different behavior indicating incompatibility with this law. Such differences must of course be related to the different intensities and frequencies employed in the two sets of experiments which should play a role in any theoretical interpretation.

The elusiveness of a definitive interpretation is underscored by the fact that the two recent theoretical papers rely on diametrically opposite assumptions. One proposes[1] total coherence in some form of collective excitation, while the other[2] relies on a one-electron picture as obtained from the Hartree model of a multielectron atom. As is often the case with such complex problems, both pictures may well be valid under different experimental conditions or even for different stages in the process of the same experiment.

My purpose in this paper is twofold: to examine certain questions which have not been addressed, but have, as I show below, a decisive influence on the validity of any interpretation; and second, to argue that mechanisms having to do with the structure of the particular atoms cannot be ignored.

The basic question at hand is how a multielectron atom undergoes single or multiple ionization under the electromagnetic field of a strong laser (say above 10^{12} W/cm^2). First, I show that another question must be answered first: Can an atom be put in such a field? Experimentally, the atom is exposed to a pulsed laser of duration ranging from a few nanoseconds to a few picoseconds with rapid progress being made toward the few-femtosecond regime. To make my discussion quantitative, I first consider the Xe atom in the 5-psec pulse employed in the experiment of Luk *et al.*[4] where the photon wavelength was 193 nm, or $h\nu = 6.423$ eV. Let me assume for the moment a peak power of 10^{15} W/cm^2, which corresponds to a photon flux of 0.96×10^{33} photons/cm^2 sec. Neutral Xe which has ionization potential 12.127 eV is singly ionized by a two-photon process ($\mathrm{Xe} + 2h\nu + \mathrm{Xe}^+ + e^-$). The generalized cross section $\hat{\sigma}_2$ for this process has most recently been calculated by my collaborators[5] employing multichannel quantum-defect theory with the result $\hat{\sigma}_2 = 1.16 \times 10^{-49}$ cm^4 sec. Earlier calculations by McGuire[6] are in reasonable agreement with the result. Complete agreement is not expected since McGuire's calculation did not account for the autoionizing structure[7] between the $P_{3/2}$ and $P_{1/2}$ thresholds which is where the energy of the two photons falls. If I take a flux of 10^{31}, i.e., two orders of magnitude smaller than the above peak flux, I obtain $\hat{\sigma}_2 F^2 = 1.16 \times 10^{-49} \times (10^{31})^2 = 1.16 \times 10^{13}$ sec^{-1}. This shows that at a flux of 10^{31} ($\sim 10^{13}$ W/cm^2) the lifetime of Xe against single-electron ejection is less than 10^{-13} sec $= 0.1$ psec. It follows, therefore, that the neutral Xe atom cannot have "seen" a power more than 10^{13} W/cm^2 because it will ionize within 0.1 psec after that power is reached. It is ionized somewhere along the rise of the 5-psec pulse. The validity of the above calculation cannot be contested (to within a factor of 2) because it is employed in a regime of intensity where perturbation theory is expected to be valid on theoretical as well as experimental grounds.[8]

Let me now follow the fate of Xe^+ which is born at an intensity somewhere around 10^{13} W/cm^2 or less. Its ionization potential is 21.2 eV and for $\lambda = 193$ nm, Xe^+ is within four-photon ionization, i.e., $\mathrm{Xe}^+ + 4h\nu \rightarrow \mathrm{Xe}^{++} + e^-$. I do not know this particular four-photon generalized cross section as we have not calculated it yet. From our calculations of two- and three-photon gcs so far and those of McGuire,[6] I expect a typical number. I choose an extremely pessimistic number $\hat{\sigma}_4 \cong 10^{-115}$ cm^8 sec^3 and calculate the transition probability per unit time for an intensity 10^{14} W/cm^2 ($I = 10^{32}$ photons/cm^2 sec). This gives $\hat{\sigma}_4 F^4 = 10^{13}$ sec^{-1} which implies that as the intensity approaches 10^{14} W/cm^2, Xe^+ goes to Xe^{++} within 10^{-13} sec. Thus neither has Xe^+ the chance to see the peak of the pulse, which means that Xe^{++} is born at about an intensity of 10^{14} W/cm^2 or slightly before. Continuing with the same type of calculation, I find that $\mathrm{Xe}^{++}+5h\nu \rightarrow \mathrm{Xe}^{+++}+e^-$ takes place with a pessimistic probability $\hat{\sigma}_5F^5=10^{-147}\times 10^{160}=10^{13}$ sec^{-1}. Thus also Xe^{++} never sees the peak intensity.

My arguments up to this point show that neither the Xe atom nor its first two ions can be exposed to a field higher than about 10^{15} W/cm^2 if the pulse duration is 5 psec or longer. It might seem that for a pulse of about 100 fsec or less, neutral Xe might see the peak. But then, since $\hat{\sigma}_2(10^{32})^2=1.16\times 10^{-49}\times 10^{64}\cong 10^{15}$ sec^{-1}, the process $\mathrm{Xe}+2h\nu \rightarrow \mathrm{Xe}^{+}+e^-$ would occur just before the pulse reached 10^{14} W/cm^2. On the other hand, Xe^{+} or at least Xe^{++} might be exposed to an intensity near the peak intensity.

In view of the above results, we can also understand the behavior of Xe in pulses of peak power 10^{16} W/cm^2 and 10^{17} W/cm^2. It is not that Xe ever sees these powers. But as the pulse rises, the previous sequence of events takes place, except that now the 10^{14} and 10^{15} W/cm^2 are reached faster.

Although I have used Xe as an example in order to exhibit certain quantitative estimates, the overall situation is essentially the same for all atoms involved in the experiment of Luk *et al.*[4] Because of the relatively large photon energy (6.423 eV), the first and second ionization events were of relatively low order and would occur at or before 10^{14} W/cm^2. Even for He which has the highest ionization potential, the same analysis indicates successive peeling of He and He^{+} around 2×10^{16} W/cm^2. For this special case, however, it turns out[9] that He^{+} has a deep valley at that photon frequency which makes it possible to survive even around that intensity.

Let me turn now to the other set of data, by L'Huillier *et al.*[3] who employed a Nd laser ($h\nu \cong 1.17$ eV) and its second harmonic. Considering again the Xe atom, noting that it takes 11 photons of 1.17 eV to eject one electron, and employing $\hat{\sigma}_{11}=10^{-341}$ cm^{22} sec^{10} at an intensity 10^{13} W/cm^2 ($F\cong 5\times 10^{31}$ photons/cm^2 sec), I obtain $\hat{\sigma}_{11}F^{11}\cong 4.8\times 10^{7}$ sec^{-1} while for 5×10^{13} W/cm^2 ($F\cong 2.5\times 10^{32}$ photons/cm^2 sec) I obtain $\hat{\sigma}_{11}F^{11}\cong 2.4\times 10^{15}$ sec^{-1}. This shows that around 10^{13} W/cm^2 a slope of 11 is expected with total saturation occurring before 5×10^{13} W/cm^2 (except for the interaction-volume–expansion effect which I discuss below). The above picture is remarkably compatible with the data of Ref. 3, except for a discrepancy of a factor of 2 or 3 in the estimate of the saturation power, a discrepancy which is to be expected since I am employing pessimistic generalized cross sections. The data are in fact consistent with a $\hat{\sigma}_{11}$ slightly larger than the one I have used. Taking this one step further, let us consider $\mathrm{Xe}^{+}+19h\nu \rightarrow \mathrm{Xe}^{++}+e^-$. The pessimistic gcs now is $\hat{\sigma}_{19}=10^{-600}$ cm^{38} sec^{18} and for intensity 5×10^{13} W/cm^2 we have $\hat{\sigma}_{19}F^{19}=10^{-600}(2.5\times 10^{32})^{19}\cong 3.6\times 10^{15}$ sec^{-1}, suggesting that at about 5×10^{13} W/cm^2 or slightly before, saturation sets in for the ejection of one electron from Xe^{++}. This again is remarkably compatible with the data of L'Huillier *et al.*[3] Without elaborating on the arithmetic any further here, I simply point out that similar analysis of the data for $h\nu \cong 2.34$ eV ($\lambda = 532$ nm) shows that saturation should set in at an intensity about one order of magnitude smaller than in the previous case, and that is what the data show.

In comparing predictions of any theory with experimental data, one must not forget the ever present effect of the expansion of the interaction volume. In short, as the intensity in the focal region is raised beyond the value of total ionization of a certain species (say Xe^{++}), the intensity in the volume surrounding it becomes sufficiently large to contribute to ionization. This effect can be modeled in well-known ways.[10] Its main consequence is that the log-log curve of ionization versus intensity instead of becoming horizontal keeps increasing but more slowly. This is clearly evident in the data by L'Huillier *et al.* and is expected to always be present. For this reason, the ratio of ionization yields for an N-photon process at two intensities F and F' is not expected to be $(F/F')^N$ if one or both of these intensities is above the saturation value. This, being well-established experimentally as well as theoretically, shows that the departure of this ratio from $(F/F')^N$ does not necessarily imply that the process departs from the law $\hat{\sigma}_NF^N$. As I have shown above, saturation was surely present in the experiments of Luk *et al.*[4] and, as a consequence, the ratio of the signals for the same species at different intensities or different species at the same intensity cannot be used as direct input to any theory, unless the interaction volume and related instrumental problems can be unfolded which presupposes excruciatingly careful and controllable experimental characterization of the temporal and spatial pulse shape.

Let me now elaborate somewhat on what I have called pessimistic gcs and show some interesting conclusions that can be obtained. Karule[11] has some time ago calculated the gcs $\hat{\sigma}_N$ for the ground state of the hydrogen atom up to $N=16$. The summations over intermediate states have been performed by use of an explicit representation of the exact Green's function. These results are among the most accurate available and have been in good agreement with other calculations, notably those of Gontier and Trahin.[12] Over the years, calculations in other atoms, including those by my group, have shown that such hydrogenic gcs are among the smallest, for reasons expected on physical grounds. From Karule's cross sections, I have taken the low values for each order N and employed them for pessimistic calculations in the sense that they underestimate the transition probability. These numbers can also teach us something even more interesting.

Let us take $\hat{\sigma}_N$ in units of $\mathrm{cm}^{2N}\,\mathrm{sec}^{N+1}$ and calculate $(\hat{\sigma}_N)^{1/N}$ which I then write as $10^{-\Lambda_N}$. I have plotted Λ_N as a function of N from $N=2$ to 16 in Fig. 1. It is clear that after about $N=6$, Λ_N rises very slowly with a tendency to perhaps reach a constant value,[13] somewhere between 31 and 32. Physically this makes sense. For N larger than 10 or so, it does not really make that much of a difference whether one more photon is needed to ionize, since $h\nu$ is already much smaller than the ionization potential and for $N > 20$, $h\nu$ is also much smaller than the energy separation between the ground and first excited states. If Λ_N does tend to a constant Λ, its value must be related to tunneling. Indeed, if $\Lambda_N \rightarrow \Lambda$ for $N \gg 1$ then for a photon flux $F_0 = 10^{\Lambda}$, the transition probability $\hat{\sigma}_N F_0^N$ becomes independent of N (for large N) which corresponds to the limit in which the multiphoton picture is expected to merge with tunneling.

Thus the quantity $F \times 10^{-\Lambda}$ can be another parameter qualitatively characterizing the onset of tunneling. Note that the existing model for tunneling[14,15] under an ac field, as formulated by Keldysh[14] and extended by others,[16] introduces the parameter $\gamma = \frac{1}{2}(h\nu/I_0)E_0/E$ where I_0 is the ionization potential, E_0 an internal atomic field strength, and E the equivalent average strength of the externally imposed laser field. Tunneling is expected to prevail for $\gamma < 1$ and multiphoton ionization for $\gamma > 1$. The value $\gamma = 1$ ought to be understood as a characteristic region rather than a strict demarcation line since the model, idealized as it is, ignores the structure of a multielectron atom. For one electron bound in a Coulomb field, γ if taken literally scales as Z. It is evident, of course, that in a multielectron atom and its first several ions, screening would cause γ to scale much more slowly than Z.

In view of this behavior of $\hat{\sigma}_N$ for large N, it is not surprising that multiply charged ions seem to appear easily in the experiments of L'Huillier *et al.*[3] The assumption we have all been making, that as N increases the yield should drop rapidly, has been based on the tacit extrapolation of the steep part of the curve of Fig. 1 and on experience with intensities mostly below 10^{11} $\mathrm{W/cm^2}$. A gcs for ten-photon ionization of Xe^+ for $\lambda = 532$ nm obtained by L'Huillier *et al.*,[3] through a clever exploitation of the behavior of the data, gave the value 10^{-297} which is several orders of magnitude larger than my pessimistic value. Whether tunneling was in fact involved in some of the higher ionic species in those experiments is an interesting question which cannot be settled for the moment. It should be kept in mind, though, that as γ changes with the loss of each electron, the probability of ionization decreases because $h\nu$ and E remain unchanged.

The high-frequency experiments[4,17] ($\lambda = 193$ nm) involve lower-order processes. Successive ejection of electrons from the outer subshell, within a perturbation-theory regime during the rise of the pulse but under strong saturation and volume-expansion conditions, was certainly the dominant mechanism for the creation of the first few ionic species. It does not seem possible that either the atom or ions of the first few multiplicities could have been exposed to fields much above 10^{14} $\mathrm{W/cm^2}$.

It is certain, on the other hand, that the $5s^2$ subshell in Xe and the $4s^2$ in Kr played a significant role because of accidental two-photon near resonance of the singly charged ions. These specific processes are in the process of being calculated in detail and will be published separately.[18] What is surprising in the data by Luk *et al.*[4] is the difference in behavior between Xe and I (see Fig. 1 of Ref. 4). But this difference would point more toward the role of the detailed spectroscopic structure of the atoms (including saturation behavior) than collective behavior. Why would the presence of one more electron in Xe cause a significant difference in collective behavior, if the electrons could be assumed to be essentially free under the strong field? On the other hand, in some of the experiments by Boyer *et al.*[19] there has been strong evidence of doubly excited states involving one of the $4s^2$ electrons in Kr. In work on other atoms,[20] it has been shown that the behavior of two-electron excited states can undergo significant changes at intensities above 10^{11} $\mathrm{W/cm^2}$, and such effects would have a large impact on the ionization of Xe, Xe^+, Xe^{++}, and similarly for Kr. Thus not only the intensity but also the particular photon energy has played a decisive role in the experiments of Luk *et al.*[4] In addition to detailed theoretical studies, experiments at other frequencies (say $h\nu \cong 5$ or 4 eV) would be essential in disentangling the global aspects of the behavior from those which are specific to each atom.

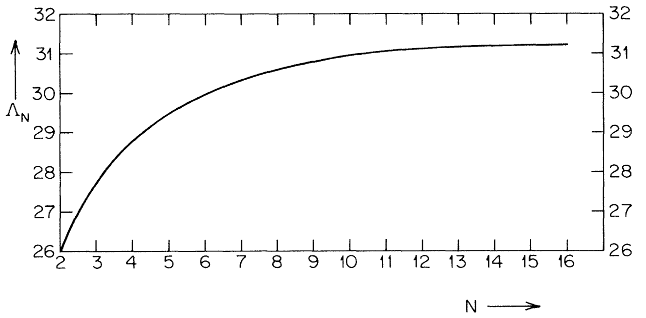

FIG. 1. Plot of $\Lambda_N = -(1/N)\log_{10}\hat{\sigma}_N$ obtained from average minimum values of the gcs $\hat{\sigma}_N$ for the hydrogen atom as calculated by Karule.

In conclusion, I have presented quantitative evidence suggesting that peeling of electrons during the rise of a laser pulse plays a principal role in multiple ionization. As a result, an atom cannot be realistically assumed to be exposed intact to laser intensities much higher than 10^{14} W/cm^2. It is worth emphasizing here that any calculation based on coupling an atom to a field $E(t)=\epsilon_0 e^{i\omega t}+\epsilon_0^* e^{-i\omega t}$, without addressing the problem of switching on (as well as off), is inherently a *weak*-field calculation because it contains the tacit assumption that nothing significant happens while the pulse is rising to its peak value. As I have shown, a lot happens during that time, when the peak intensity is above 10^{13} W/cm^2. Weak must of course be understood in context. Although the intensity may be strong by traditional standards, it is tacitly assumed to be sufficiently weak for most of the ionization to occur after the peak has been reached. It would of course be interesting to see what will happen as the pulse length approaches 10 fsec or so. It may well be, however, that no neutral atom can possibly be exposed intact to a peak power much above 10^{14} W/cm^2 at frequencies in the near infrared and above.

If this is the case, it does not seem possible that a whole atomic shell can be excited. Even if such an excitation channel exists within the appropriate energy range, it must compete with all other processes that occur much faster at lower intensities. As a result, multiple ionization alone is far from sufficient evidence of coherent excitation of a whole atomic shell.

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