Inner-Shell Ionization in Strong High-Frequency Laser Fields and Formation of “Hollow-Ions”

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Abstract—Inner-shell ionization of atoms in strong laser fields at high frequencies is investigated using a simple model formula relating intense-field N-photon ionization rates to those for weak-field one-photon ionization. The probabilities of a two-photon inner-shell ionization and the formation of a “hollow ion” are found to be most likely when the valence electron is weakly bound and the difference between the binding energies of the electron in the valence shell and the inner shell(s) is large, as for alkali atoms. A possible formation of hollow ions of the K atom is found to be very likely; it might be evidenced by detecting the subsequent fluorescence radiation due to the decay of an outer-shell electron into the inner-shell hole.

1. INTRODUCTION

In recent years, the rapid technological development of powerful laser systems generating femtosecond pulses in the optical frequency domain has stimulated great interest in the interaction of atoms, molecules, clusters, and solids with such strong electromagnetic fields. Currently, we are facing a new technological breakthrough, the development of strong high-order harmonic sources and free-electron lasers delivering pulses in the VUV- and XUV-wavelength regime. The large photon energies, together with the expected high intensities of these new light sources, will make it possible in the future, e.g., to study multiphoton processes in inner shells of atoms and molecules. An interesting aspect of such studies is the question of whether or not it is possible to efficiently ionize an electron from an inner shell of an atom via a multiphoton process while leaving the valence shell of the atom (almost) untouched. This would generate, in the ideal case, an inverted system with a single (or multiple) hole in one of the inner shells of the atom, a so-called “hollow ion.”

To date, there have been only a few successful attempts to observe nonlinear processes in the valence shell of noble gas atoms using intense VUV and XUV light. Ion yields for two- and three-photon ionization of noble gas atoms with low-order harmonics of KrF [2] and Ti:sapphire lasers [3, 4] have been reported recently. Furthermore, at the TESLA test facility in Hamburg, self-amplified spontaneous emission in a free-electron laser has been observed [5] and the first experiments with Xe atoms and clusters at about 100 nm and $10^{14}$ W/cm$^2$ have been performed very recently [6]. From these observations, one can anticipate technical difficulties in the observation of inner-shell processes. It is therefore desirable to provide theoretical support for such experiments.

Ab initio calculations of ionization rates and generalized cross sections for the hydrogen and the helium atom at high laser frequencies have been performed recently [7–10]. Similar studies with the same accuracy for heavier atoms under the inclusion of inner subshells have not been possible up to now [7]. It has been found [9] that the results of approximate model calculations using the so-called Keldysh–Faisal–Reiss (KFR) approach [11–13] are in good agreement with those of ab initio Floquet calculations for ionization of hydrogen provided the intensity of the high-frequency laser field is not too high. Such model calculations are easily extended towards inner-shell processes, and classes of atoms and wide laser parameter regimes can be investigated. In future, the results of these analyses could be of use for more elaborate numerical studies and experiments.

Below, we investigate the rate for inner-shell ionization of atoms in the high-frequency regime at laser intensities up to $10^{17}$ W/cm$^2$. For this purpose, we shall use a modification of the usual plane-wave KFR formula to approximately take account of the Coulomb tail effect for nonresonant ionization beyond the limit of validity of the former. This is necessary since the plane-wave KFR formula is originally suggested for the case of electron detachment and not for ionization as such [12, 13].

First, the results will be compared for one- and two-photon ionization of the valence shell of noble gas atoms with the results of more accurate calculations (within the lowest order perturbation theories) and the experimental data. Next, we apply the model formula to the ionization from an inner-shell of an atom and analyze the rates for different classes of atoms. Then, we use the basic rates in the rate equations in order to estimate the ion yields arising in a given temporal and spatial intensity distribution. Finally, we comment on the production of hollow ions in a laser pulse of high frequency.
2. A MODEL RATE FORMULA

Within the KFR approach [11–13], the ionization of an electron from one of the shells of the atom is described by its transition from the initial ground state to a final Volkov state. This approach is appropriate for situations when the internal level structure of the target may be neglected, e.g., for effective one-electron models of negative ions or for low frequency and high intensity, when the Keldysh gamma parameter, $\gamma = \sqrt{I_p/2U_p}$, is less than unity. The rate of absorption of $N$ photons from the field and ionization of the atom is then given by (Hartree atomic units, $\hbar = e = m = 1$, are used)

$$\Gamma_{KFR}^{(N)}(\omega, I) = 2\pi \int d\mathbf{k}_N k_N J_N^2\left(\alpha_0 \cdot \mathbf{k}_N; \frac{U_p}{2\omega}\right)$$

(1)

$$\times \left| (U_p - N\omega)\phi_0(\mathbf{k}_N, \mathbf{r}) \phi_\gamma(\mathbf{r}_2, \ldots, \mathbf{r}_n) \phi_\phi(\mathbf{r}_1, \ldots, \mathbf{r}_n) \right|^2,$$

where $\phi_0(\mathbf{k}, \mathbf{r})$ is the plane-wave function of momentum $\mathbf{k}$ and $\phi_\gamma$ and $\phi_\phi$ are the initial and final state wave function of the neutral atom and the (excited) ion, respectively. $J_N(a, b)$ is the generalized Bessel function of two arguments (e.g., [13]), $k_N^2/2 = N\omega - (U_p + E_B)$ is the kinetic energy of the electron, $\alpha_0 = \sqrt{I/\omega^2}$ is the quiver energy, $U_p = I/4\omega^2$ is the ponderomotive (or quiver) energy of an electron in a laser field of frequency $\omega$ and intensity $I$, and $E_B$ is the binding energy.

It is interesting to note that the formula (Eq. (1)) can be thought of as given by two parts: one arises from the rate of photoeffect at an effective frequency $\omega = N\omega - U_p$ calculated in the plane-wave Born approximation, weighted by the probability of finding the Volkov electron in the continuum after absorbing $N$ photons. This strongly suggests that an improved approximation for ionization might be obtained by replacing the first part by the actual rate of photoeffect without making the first Born approximation. This gives a simple model formula for the non-resonant cross section of ionization by the absorption of $N$ photons, $\sigma^{(N)}(\omega, I)$, as [14]:

$$\sigma^{(N)}(\omega, I) = 4\left(\frac{N\omega - U_p}{\omega}\right)^3 \int d\mathbf{k}_N k_N$$

$$\times J_N^2\left(\frac{U_p}{2\omega}\right) \frac{d\sigma^{(1)}(N\omega - U_p, I \rightarrow 0)}{d\mathbf{k}_N}$$

(2)

where the multiphoton ionization cross section is related to the corresponding rate by

$$\frac{dW^{(N)}(\omega, I)}{d\mathbf{k}} = F \frac{d\sigma^{(N)}(\omega, I)}{d\mathbf{k}}$$

(3)

respectively, and $F = I/\omega$ is the incident photon flux.

Here, we adopt Eq. (2) to get an order of magnitude estimate of the ionization rates of interest by making use of the large sets of available experimental data for the single-photon ionization cross section of atoms by weak synchrotron radiation. For the present calculation, we also found it convenient to use a fit formula by Verner et al. [15] that summarizes the single-photon ionization cross sections of atoms with up to 30 electrons; for the heavier noble gas atoms, we used the experimental photoionization data given by Sorokin et al. [16].

3. RESULTS AND DISCUSSION

3.1. One- and Two-Photon Valence-Shell Ionization

Before investigating the inner-shell ionization rates, we first test the model formula, Eq. (2), for several one- and two-photon ionization rates in weak and strong fields for which experimental data or results of ab initio calculations are available. In Fig. 1, we present the results of the present model formula along with recent experimental data (circles, [16]) for the ionization of Ar by weak synchrotron radiation. The model predictions, as well as the experimental data, are shown as cross sections vs. photon energy, where the partial contributions from all occupied subshells are calculated and added. It can be seen that the present results (solid line) are in good agreement with the experimental data (circles); they are also consistent with the data obtained by Verner et al. [15] from their fit formula. Note that, as expected, the plane-wave KFR rate, Eq. (1), shown by the dashed line, does not follow the trend of the experimental data at low photon energies without any Coulomb correction for ionization.

Next, we calculated the “generalized cross sections” for a number of $N$-photon ionization processes of noble gas atoms using Eq. (2). (The generalized cross sections of a $N$-photon process are obtained from the
respective rates by dividing by $F_{N-1}$. We show in Fig. 2, as examples, the calculated results for two-photon ionization of the He atom (panel a, solid line) and of the Xe atom (panel b, solid line). (Nominal “ionization” cross sections from Eq. (1) are also shown by the dashed lines.) For the generalized cross sections, elaborate numerical calculations [7, 17, 18] have been performed in the past. They show strong structures with several sharp maxima and minima at specific photon energies which are well understood to be due to the occurrence of intermediate one-photon resonances in the two-photon ionization processes. The present nonresonant model can provide only an average over the resonances; they (solid lines) are found, however, to be in agreement with the correct order of magnitude, as well as with the trend of the results of the more sophisticated calculations cited above. We shall, therefore, use the formula given by Eq. (2) for our estimates of the rates of ionization of inner-shell ionization of a whole class of atoms and apply them to assess the possibility of formation of hollow ions by interaction with intense laser radiation.

### 3.2. Two-Photon Inner-Shell Ionization of Atoms

Thus, in the context of inner-shell ionization, it is interesting to investigate the rates and yields at those photon energies for which the ionization of an electron from the inner shell requires the absorption of at least one more photons than for the ionization from the valence shell. Below, we will compare the calculated one-photon valence-shell rates with two-photon inner-shell rates for two different classes of atoms, namely, the noble gases and the alkali atoms. Alkalis have a rather weakly bound electron in the outer shell, as compared to those in the noble gas atoms, and are thus expected to behave differently than the noble gases in the present context.

In Fig. 3, the results obtained for (a) Ne at $\omega = 40$ eV and (b) Ar at $\omega = 20$ eV are presented as a function of the laser intensity. The comparison shows that the one-photon valence-shell ionization rates (solid lines) largely dominate over the two-photon inner-shell ionization rates (dashed lines) at all intensities. Even at $10^{16}$ W/cm² the valence-shell rates exceed the inner-shell rates by more than three orders of magnitude. Similar results are found for all photon energies investigated.

A qualitatively different behavior is found for the alkali atoms, as can be seen in Fig. 4 from the calculated rates for Li ($\omega = 40$ eV, panel a), Na ($\omega = 27$ eV, panel b), and K ($\omega = 13$ eV, panel c). Now, at the highest intensities, the two-photon ionization rates from the inner-shell are larger than those for one-photon ionization from the valence shell. Note also that the laser intensity at which the inner-shell rates start to dominate (from the crossing point above) decrease with increasing mass of the alkali atom. Thus, a large difference between the ionization energies of the outer and the inner shells, together with a low binding energy of the valence electron, seems to give a preferable condition for the formation of hollow ions by a two-photon inner-shell ionization process. In contrast, such an observation of inner-shell ionization in noble gas atoms is unlikely at the intensities considered.

We may ask now if the rates for two-photon ionization from even deeper lying inner shells can dominate over one-photon valence-shell ionization rates at these moderate laser intensities. In view of the above find-
ings, we have chosen to investigate this question for atoms with weakly bound electrons in the two outermost shells. In Fig. 5, we present an example of our calculated results for the ionization rates from the valence shell (solid line) and the next two successive inner shells of Al at $\omega = 55$ eV. It is seen from the figure that the two-photon ionization rate for the $2p$ shell dominates over the one-photon ionization rate for both subshells of the ($n = 3$) shell at intensities above $10^{17}$ W/cm$^2$.

The influence of the temporal and spatial distribution of the laser intensity plays a significant role in the actual yields of ions in an experiment. Therefore, we also calculated the (residual) ion yields using the basic rates for the valence- and inner-shell ionization of K and Al with the help of the rate equations for the yields. A Gaussian temporal pulse profile with a FWHM pulse width of $\tau = 20$ fs for a Gaussian beam (with a cylindrical spatial distribution having a constant intensity in the propagation direction) has been assumed. Yields for the creation of an ion with holes in the valence shell (solid lines) and in one of the inner shells (dashed and dotted lines) are plotted in Fig. 6 as a function of the peak intensity of the pulse. Note that, for K (panel a), the hollow-ion yields (i.e., an ion with a hole in the inner shell) via two-photon ionization exceed the yields of ground-state ions due to the one-photon ionization at higher intensities. We expect that, since the $3p$ hole would be filled subsequently by the single $4s$ electron by the emission of fluorescence radiation, the formation of an excess of hollow ions in the focal volume might be detected by observing an amplification of this emission line. We note that the Al$^+$($2p^{-1}$) yields (panel b) are close to but below the yields with holes in one of the outer shells. This is due to the depletion of neutral atoms in the focal volume at the saturation intensity, which occurs well below $10^{17}$ W/cm$^2$, at which the ionization rate for the inner-shell process starts to dominate (cf. Fig. 5). It would be interesting to see in future

![Fig. 5.](image5.png)

**Fig. 5.** Ionization rates for the emission of an electron from the valence and from the next two inner shells of Al at $\omega = 55$ eV.

![Fig. 6.](image6.png)

**Fig. 6.** Yields of (residual) ions in the ground state and in the excited states for ionization of (a) K at $\omega = 13$ eV and (b) Al at $\omega = 55$ eV by a Gaussian laser pulse with a duration $\tau = 20$ fs.
if possible experiments and/or more elaborate numerical calculations would confirm these predictions.

4. CONCLUSIONS

We have investigated two-photon ionization from inner shells of different classes of atoms in strong high-frequency laser fields using a simple model formula (Eq. (2)) that links intense-field \( N \)-photon ionization rates with the single-photon rates in weak fields. It is estimated that two-photon inner-shell ionization rates can exceed one-photon valence-shell rates at moderate intensities for a class of atoms with low binding energies of the electrons in the outer most shell(s), e.g., the alkali atoms. The creation of a hollow ion via two-photon inner-shell ionization is found to be very likely for the K atom. This may be detected in the subsequent fluorescence due to the decay of an outer-shell electron to fill the hole in the inner shell.

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