On the importance of inner-shell processes in two-photon ionization of Ne$^+$

Linda Hamonou, Michael A Lysaght and Hugo W van der Hart
Centre for Theoretical Atomic, Molecular and Optical Physics, Queen’s University Belfast, Belfast BT7 1NN, United Kingdom
E-mail: h.vanderhart@qub.ac.uk

Abstract. We have investigated two-photon ionization of ground-state Ne$^+$ using the time-independent R-matrix Floquet approach and the time-dependent R-matrix approach. The R-matrix Floquet approach enables the detailed study of the influence of atomic structure on the magnitude of the ionization rates. It is found that excitation processes involving the inner 2s electron substantially enhance the two-photon ionization rates of Ne$^+$. For photon energies above 37.5 eV, emission of the 2s electron becomes significant as demonstrated by the large probability that the residual Ne$^{2+}$ ion is left in the 2s2p$^5$ configuration. Time-dependent calculations of the ionization probability as a function of pulse length correspond well with the R-matrix Floquet ionization rates. However, the ionization probability is enhanced by single-photon ionization during the turn-on and turn-off of the laser pulse. In addition, the laser pulse leads to the population and depopulation of autoionizing states above the Ne$^{2+}$ ground state during the pulse, and the final population left in these states strongly depends on pulse length.

1. Introduction
One of the main developments in laser technology over the last years has been the development of free-electron lasers (FELs) operating in the VUV and X-ray regime. The free-electron laser in Hamburg (FLASH) has been in operation for a few years now, stimulating a wide range of new physics experiments [1, 2]. The first beam to users at the Linac Coherent Light Source (LCLS) in Stanford will occur in September 2009. The unique combinations of high intensity and high photon energy at these facilities (will) enable studies of light-matter interaction in an entire new regime. For example, whereas infra-red lasers predominantly interact with outer electrons, VUV and X-ray lasers will in addition also interact with inner-shell electrons.

Atomic physics is at the forefront of applications of new laser technology. The relative simplicity of atomic systems means that the detailed response of matter to intense laser light is easiest to investigate in these systems. An example of such an application to atomic systems are experimental studies of sequential and non-sequential double photoionization of Ne [3, 4, 5, 6]. These studies provided estimates for (generalised) cross sections of the various ionization processes and angular distributions of the emitted electrons.

For a full interpretation of the experimental results obtained during atomic physics experiments at FEL facilities, it is important to compare experiment and theory. For example, knowledge about the magnitude of a cross section does not necessarily imply knowledge about the physics leading to that particular cross section. Over the past few years, at Queen’s University Belfast we have investigated the importance of inner-shell excitation and emission processes. The
present report extends these studies to two-photon ionization of Ne$^+$, a process of experimental interest. For this, we need a theoretical approach capable of handling large amounts of atomic structure as well as multiphoton processes. Such an approach is provided by the R-matrix Floquet (RMF) approach, which has been applied previously to investigate various emission processes involving inner-shell electrons, such as inner-shell photodetachment of Li$^-$ [7] and the competition between emission of a 1s and of a 2s electron from 1s2s $^1$S in He [8, 9].

2. Theory

R-matrix Floquet theory combines standard R-matrix theory [10] with the Floquet Ansatz. This Ansatz transforms the time-dependent Schrödinger equation into a time-independent system of equations. However, the wavefunction is now described in terms of coupled Floquet blocks, where each Floquet block describes the wavefunction after absorption of a certain net number of photons [11, 12].

In R-matrix theory, configuration space is separated into an inner region and an outer region. The inner region is a box of radius $a$ which contains all electrons, and includes all interactions between all electrons. Ionization is described by allowing one electron to escape the inner region and enter the outer region. This electron is separated from the other electrons in the outer region, and exchange interactions involving this electron can thus be neglected. Diagonalization of the inner-region Floquet Hamiltonian, with the laser field described in the length form, yields the Floquet R-matrix at the inner region boundary. This R-matrix is then propagated through the outer region, in which the laser field is described in the velocity gauge, to a distance $a'$, where it is matched to asymptotic solutions. This matching procedure then yields the energy and width of an atomic state in the presence of the given laser field.

To estimate the effect of inner-shell processes, Ne$^{2+}$ is described using two different basis sets. The first basis set is a three-target-state basis, in which Ne$^+$ is described as a single electron attached to the Ne$^{2+}$ 1s$^2$2s$^2$2p$^4$ $^3$P$^c$, 1D$^c$, and $^1$S$^c$ states, with 1s, 2s and 2p given by Hartree-Fock orbitals [13]. In the second (five-target-state) basis set, Ne$^+$ is described as a single electron attached to the Ne$^{2+}$ 1s$^2$2s$^2$2p$^3$ $^3$P$^e$, 1D$^e$, and $^1$S$^e$ states, or to the Ne$^{2+}$ 1s$^2$2s2p$^5$ $^3$P$^o$ and $^1$P$^o$ states. Since the 2s and 2p orbitals in 2s2p$^5$ and 2s$^2$2p$^3$ differ, additional 3s, 3p, 3d, 4s, $^3$P, and $^4$D orbitals are included, taken from [14]. More detailed descriptions of these basis sets can be found in [15] for the three-state basis and [16] for the five-state basis.

The parameters in the R-matrix Floquet calculations are as follows: the intensity is set to $10^{14}$ W cm$^{-2}$. The maximum total angular momentum included, $L_{\text{max}}$, equals 5. The Floquet expansion includes 4 absorption blocks and 1 emission block for the five-state calculations and 2 emission blocks for the three-state calculations. The R-matrix is typically propagated to 55 au, although closer to thresholds the R-matrix is propagated further, up to 200 au.

3. Results and discussion

Figure 1 shows the ionization rates obtained for ground-state Ne$^+$ irradiated by laser light with an intensity of $10^{14}$ W cm$^{-2}$ as a function of photon energy. The 2s2p$^5$ $^3$P$^o$ threshold of Ne$^{2+}$ can be reached by two-photon absorption at a threshold photon energy of 33.29 eV, while the 2s2p$^3$ $^1$P$^o$ threshold is reached at a photon energy of 38.54 eV. These thresholds energies are slightly larger than the experimental ones, 33.16 eV and 38.42 eV, respectively. The Rydberg series leading up to the 2s2p$^5$ $^1$P$^o$ state of Ne$^{2+}$ can be clearly seen in figure 1. For photon energies above 38.6 eV, the Rydberg series converging to the 2s2p$^4$ $^3$P$^e$ threshold, reached after absorption of a single photon, can be observed.

The importance of excitation and emission processes involving inner-shell electrons can be determined from figure 1 by comparing the ionization rates obtained for the three-target-state basis and the five-target-state basis. In the former basis, excitation of a 2s electron is not allowed, while some of these excitation and emission processes are allowed in the latter basis. Over the
entire photon-energy range shown in figure 1, ionization has strongly increased by including excitation and emission of the inner 2s electron, typically by a factor five. Enhancement of the ionization rates is particularly noticeable for photon energies greater than 37.5 eV, which is the photon-energy range of experimental interest. Here, the enhancement may be by more than one order of magnitude. The enhancement is most obvious for the Rydberg series converging to the 2s2p4 3P0 threshold. In the three-state calculation, this series actually reduces ionization, whereas in the five-state calculation, the series substantially enhances ionization. Inner-shell processes thus need to be accounted for to obtain reliable intense-field ionization rates at high photon energies.

Figure 1 also compares the theoretical ionization rates with an ionization rate deduced from the experimentally reported generalised cross section for two-photon ionization of Ne+ [3]. The difference between the three-state calculation and experiment is quite significant with a difference of close to a factor 50 at 38.4 eV. Five-target-state calculations can not be performed reliably at 38.4 eV due to the proximity of the 2s2p3 1P0 threshold. However, figure 1 shows that the difference between experiment and theory has reduced significantly to about a factor eight. One of the main reasons for the enhancement near a photon energy of 38.4 eV is an increase in the photoionization width of the 2s2p4 (1D0)3d/4s resonances.

It is important to remember, however, that accurate experimental measurement of two-photon ionization cross sections is quite difficult. These difficulties are enhanced for FEL pulses due to the significant fluctuations in both photon energy and intensity profile of these pulses. In addition, FEL pulses are multimode, whereas in the RMF calculations, it is assumed that the laser field is monomode. The calculations are also performed at higher intensity than the ones reported experimentally. This may affect the importance of resonance enhancement of the ionization rates: at low intensities the two-photon ionization rates will scale as $I^2$, whereas at high intensities, when the interaction between the ground state and a resonance saturates, the two-photon ionization rates will scale as $I$. Hence, it is difficult to unambiguously assess the agreement between theory and experiment.

Figure 2 shows the distribution of population in the Ne2+ residual states after two-photon ionization of ground-state Ne+, with Ne+ described using the five-target-state basis. The figure shows that, around a photon energy of 37 - 38 eV, most of the residual Ne2+ ions are left in the 2s2p4 1D0 state. Thus the majority of residual ions is not left in the ground state, but instead in an excited state. For photon energies between 37.1 and 37.7 eV, figure 2 shows that the probability of leaving Ne2+ in an excited configuration is just below 20%, but, for photon energies between 37.7 and 38.3 eV, this probability increases to about 40%. At the experimental
photon energy of 38.4 eV, it can thus be expected that a substantial proportion of the residual Ne$^{2+}$ ions is left in an excited configuration.

One of the basic assumptions in the R-matrix-Floquet approach is that the laser pulse is infinitely long. In reality, however, FEL pulses have a finite duration, in the order of 10 - 30 fs. At a photon energy of 38.4 eV, this corresponds to approximately 100 - 300 optical cycles. For these numbers of cycles, it is generally assumed that the long-pulse approximation is valid. Nevertheless, it is of interest to investigate whether additional physical effects are present when the infinite-pulse approximation is removed by determining the solution to the time-dependent Schrödinger equation directly.

To solve the time-dependent Schrödinger equation, we use the time-dependent R-matrix (TDRM) approach. Recently, at Queen’s University Belfast, we have developed two different TDRM approaches. We first developed an approach in which the time-dependent Schrödinger equation is solved within an inner region only using R-matrix-based basis sets [17]. Subsequently, we have developed a full TDRM approach in which configuration space is split into an inner region and an outer region. These regions are now linked by the R-matrix, a T-vector and an F-vector. The time-dependent wavefunction is then obtained after propagating, for each time step, the R-matrix and T-vectors outwards and the F-vector inwards [18]. In the present calculations, we use the former approach. The inner-region boundary is moved outward to 120 au. In order to prevent reflections from the boundary we also include an absorbing boundary. The approach was first applied to multiphoton ionization of Ar at 390 nm and very good agreement between the TDRM approach and the RMF approach was obtained for strong-field ionization rates [17]. We note that a similar TDRM approach has also been developed by Guan et al [19].

Figure 3 shows the ionization probability for ground-state Ne$^+$ irradiated by 38.4 eV laser light with a peak intensity of $10^{14}$ W cm$^{-2}$. The pulse shape adopted consisted of a three-cycle $\sin^2$ turn-on of the electric field, followed by a given number of cycles at peak intensity and a three-cycle $\sin^2$ turn-off. At the end of the pulse, we determine the total population in all bound states, states below the Ne$^{2+}$ ground state. The missing population is considered to be ionization. This is the same approach as used in the multiphoton ionization calculations for Ar [17].

The behaviour of the ionization probability shown in figure 3 is not straightforward. Three different features can be seen in the figure. A substantial ionization probability is seen for very short pulse lengths. This is due to single-photon ionization. For very short pulses, the uncertainty in the photon energy is sufficiently large to allow single-photon ionization (the photon energy is 38.4 eV, whereas the single-photon ionization threshold is 41 eV). For longer
pulses, the behaviour of the ionization probability appears to follow a linear increase with pulse duration superimposed by substantial oscillations.

A linear increase with pulse duration is what one would expect for a constant ionization rate, and such a behaviour can be seen in figure 3 for pulses with more than six cycles at peak intensity. The associated slope corresponds to an ionization rate of $6.3 \times 10^{11} \text{s}^{-1}$. A direct comparison with the RMF calculations is not possible at 38.4 eV, since converged RMF calculations require propagation over a very long distance. However, figure 1 suggests that this ionization rate is quite similar to the rates obtained near a photon energy of 38.4 eV. Hence the TDRM and RMF calculations are consistent with each other.

Superimposed on the linear increase in the ionization probability in figure 3 are quite substantial oscillations. The magnitude of these oscillations suggests that these are due to processes occurring at the single-photon level. The ionization probability follows from the bound-state population below the $2s^22p^4 \, ^3P^e$ threshold of Ne$^{2+}$. However, just above this threshold lie the $2s^22p^4 \, ^1D^e$ and $2s^22p^4 \, ^1S^e$ thresholds. Rydberg series will be attached to these thresholds, but population transferring into these series may be classified as ionization. We therefore ascribe these oscillations to time-dependent population and depopulation of autoionizing states lying just above the Ne$^{2+}$ ground state. The time-dependent population of these states is not accounted for in RMF theory, since RMF theory assumes an infinite pulse length. However, the autoionizing states may have a substantial effect for finite pulses. The oscillations may still be significant when the pulse length is extrapolated to 250 cycles.

4. Conclusions

In conclusion, we have investigated the importance of inner-shell processes on strong-field ionization of atomic systems at high photon energies by determining ionization rates of Ne$^{2+}$. The two-photon ionization rates are substantially enhanced by excitation and/or emission of the inner 2s electron. The ionization rates can be enhanced by an order of magnitude, but a factor of five is more typical. The comparison with the experimental cross section is difficult due to the fluctuations in the photon energy and intensity of free-electron laser pulses. We have analysed the ionisation rates further by investigating the distribution of the final states of Ne$^{2+}$ left after two-photon ionization. The dominant final state is the $2s^22p^4 \, ^1D^e$ state, and hence Ne$^{2+}$ is predominantly left in an excited state. For photon energies larger than 37.7 eV, a substantial fraction of the Ne$^{2+}$ ions is left in the excited $2s2p^5$ configuration, demonstrating the importance of inner-shell emission processes.
A comparison between TDRM and RMF calculations shows that the two approaches are consistent with each other for the ionization rate. However, the two methods give complementary information regarding two-photon ionization. The RMF approach allows the investigation of the importance of various atomic structure contributions. On the other hand, the TDRM approach shows that the ionization probability can be substantially affected by a finite pulse duration. The application of both, complementary, approaches is thus beneficial for a full comprehension of the physics of intense-field processes at high photon energies.

Acknowledgments
LH is supported by the European Social Fund under its Building Sustainable Prosperity programme. MAL is supported by the Engineering and Physical Sciences Research Council of the UK under grant ref. no. GR/E000223/1.

References
[1] Ackermann W et al 2007 Nature Phot. 1 336
[2] Tiedtke K et al 2009 New J. Phys. 11 023029
[3] Sorokin A A, Wellhöfer M, Bobashev S V, Tiedtke K and Richter M 2007 Phys. Rev. A 75 051402(R)
[4] Moshammer R et al 2007 Phys. Rev. Lett. 98 203001
[5] Braune M, Reinköster A, Viehhaus J, Lohmann B and Becker U 2007 Proc. Int. Conf. on Photonic, Electronic and Atomic Collisions (ICPEAC), Freiburg, Germany, Book of Abstracts, Fr 034
[6] Kurka M et al 2007 J. Phys. B: At. Mol. Opt. Phys. 42 141002
[7] van der Hart H W 2005 Phys. Rev. Lett. 95 153001
[8] Madine M and van der Hart H W 2005 J. Phys. B: At. Mol. Opt. Phys. 38 3963
[9] Madine M and van der Hart H W 2006 J. Phys. B: At. Mol. Opt. Phys. 39 4049
[10] Burke P G and Berrington K A 1993 Atomic and Molecular Processes: An R-matrix Approach (Bristol: Institute of Physics Publishing)
[11] Burke P G, Francken P and Joachain C J 1991 J. Phys. B: At. Mol. Opt. Phys. 24 761
[12] Dörr M, Terao-Dunseath M, Purvis J, Noble C J, Burke P G and Joachain C J 1992 J. Phys. B: At. Mol. Opt. Phys. 25 2809
[13] Clementi E and Roetti C 1974 At. Data. Nucl. Data Tables 14 177
[14] McLaughlin B M and Bell K L 2000 J. Phys. B: At. Mol. Opt. Phys. 33 597
[15] Hamonou L, van der Hart H W, Dunseath K M and Terao-Dunseath M 2008 J. Phys. B: At. Mol. Opt. Phys. 41 015603
[16] Hamonou L and van der Hart H W 2008 J. Phys. B: At. Mol. Opt. Phys. 41 121001
[17] van der Hart H W, Lysaght M A and Burke P G 2007 Phys. Rev. A 76 043405
[18] Lysaght M A, Burke P G and Lysaght M A 2008 Phys. Rev. Lett. 101 253001
[19] Guan X, Zatsarinny O, Bartschat K, Schneider B I, Feist J, and Noble C J 2007 Phys. Rev. A 76 053411