LETTER TO THE EDITOR

Double shake-off model for triple photoionization of beryllium

A. S. Kheifets

Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia

E-mail: A.Kheifets@anu.edu.au

Igor Bray

Centre for Atomic, Molecular, and Surface Physics, School of Mathematical and Physical Sciences, Murdoch University, Perth, 6150 Australia

E-mail: I.Bray@murdoch.edu.au

Abstract. We propose a model of triple photoionization of Be in which the core $1s$ electron absorbs the photon $\gamma + 1s^2 2s^2$ Be $\rightarrow \epsilon_1 p + 1s2s^2$ Be^+ and the valence $2s^2$ electrons are shaken off into continuum due to a sudden change of the core potential. We decompose the double shake-off amplitude into a single shake-off $2s^2 \rightarrow ns\,\epsilon s$ and a subsequent electron impact ionization of the doubly charged Be^{2+} ion $\epsilon s + 1sns$ $Be^{2+} \rightarrow \epsilon_2 l + \epsilon_3 l + 1s$ Be^{3+} . The latter process is described by the T-matrix of inelastic electron scattering on the "semi-hollow" $1sns$ Be^{2+} ion in the monopole singlet channel. The convergent close-coupling (CCC) method is used to evaluate the T-matrix.

PACS numbers: 31.20.Tz, 32.80.Fb

Submitted to: *J. Phys. B: At. Mol. Phys.* 24 March 2003

During recent years, multiple photoionization processes have been under intensive scrutiny. The interest to these processes is motivated by the fact that a photon, outside the domain of superstrong laser fields, can only couple to a single atomic electron. Simultaneous ejection of two or more atomic electrons after absorption of a single photon is driven entirely by many-electron correlations. The many-body problem, especially with several electrons in the continuum, can only be solved in various approximations and extensive experimental studies are needed to find limitations of these approximate solutions.

The simplest direct multiple photoionization process is double photoionization (DPI) of helium. As a result of massive theoretical and experimental efforts during the past ten years, good understanding of this fundamental process now emerges. The mechanisms of helium double photoionziation are well understood. Cross-sections are established reliably in a wide photon energy range in a good accordance between theory and experiment. Some important aspects of helium DPI have been reviewed recently by Briggs and Schmidt (2000).

As the helium DPI problem is now close to being solved, researches divert their attention to other atomic targets. The beryllium atom is a very attractive choice. The core $1s^2$ and valence $2s^2$ shells of Be are well separated, both in energy and coordinate space. From the double ionization threshold at 27.5 eV up to the first autoionization resonance at about 115 eV, the core electrons remain spectators and take no direct part in photoionization. This allows to apply various frozen-core models and to treat DPI of Be similar to that of He (Kheifets and Bray 2002, Colgan and Pindzola 2002, Citrini *et al* 2003). Experimental data on direct DPI of Be became recently available (Wehlitz and Whitfield 2001). The total DPI cross-section in the range of photon energies between 32 and 80 eV was found in fair agreement with theoretical predictions (Wehlitz and Whitfield 2002). Hasegawa *et al* (2002) reported the total DPI cross-section of Be above 115 eV. This measurement fell into the region of autoionizing resonances and could not be compared with the theories of direct DPI. In general, for atoms with more than one electron shell, multiple photoionziation can proceed sequentially via Auger transitions or excitation of autoionizing resonances. These processes, interesting by themselves, are not strong markers of electron correlations and will be excluded from our further consideration.

The cross-section of direct DPI of Be was found to be smaller than that of He. This was interpreted by Wehlitz and Whitfield (2001) as the result of a larger separation and weaker correlation of the two valence $2s$ electrons. However, Kheifets and Bray (2002) observed a much stronger angular correlation between the photoelectrons in Be than that in He. The Gaussian width parameter, which governs the angular correlation at equal energy sharing between the photoelectrons, was found to be 68 and 90° for Be and He, respectively, at the same excess energy of 20 eV above the threshold. We remind the reader that the Gaussian width parameter converges to zero at the threshold which corresponds to the rigidly correlated back-to-back Wannier escape.

Another level of complexity is presented by the triple photoionization (TPI) in

which absorption of a single photon results in simultaneous ejection of three atomic electrons. The first TPI measurement was performed on Li by Wehlitz *et al* (1998). These authors suggested that for sufficient excess energy, triple photoionization of Li is reasonably well described by a double ionization of the inner electrons followed by a shake-off of the outer electron. This decomposition of the three-electron breakup process into a two-electron emission plus shake-off requires sufficiently large excess energy above the triple ionization threshold which should exceed the binding energy of the outer $2s$ electron: $\Delta E = \omega - IP^{3+} > |\epsilon_{2s}|$. The DPI of the $1s^2$ core of the Li^+ ion can be described accurately by non-perturbative models (Kornberg and Miraglia 1993, Kheifets and Bray 1998). As to the shake-off probability of the outer $2s$ electron, Wehlitz *et al* (1998) assumed that both inner-shell electrons are removed instantaneously which would be the case in the infinite photon energy limit. Various calculations (Wehlitz *et al* 1998, van der Hart and Greene 1998, Cooper 1999, Santos *et al* 2001) predicted different shake-off rates depending on the way they described the ground state of Li. The multi-configuration Dirack-Fock calculation of Santos *et al* (2001) seems to be in best agreement with experiment of Wehlitz *et al* (1998). A more realistic approach to the TPI of Li is taken by Pattard and Burgdorfer (2001). These authors suggested a so-called half-collision model (HCM) in which the two primary electrons ejected from the $1s^2$ shell collide with the $2s$ electron on their way out of the atom.

The TPI of Li is an analog of the DPI of He as both processes result in the complete fragmentation of the target atom. A similar, but somewhat more complex process is the TPI of Be. The Be atom has already been earmarked as a good candidate to study TPI (Wehlitz *et al* 2002). From the triple ionization threshold at 181.4 eV, there is a wide photon energy range of more than 100 eV where the TPI cross section is not affected by sequential or autoionization processes and where straightforward comparison between theory and experiment is possible.

In anticipation of forthcoming experiments, we propose a theoretical model of the TPI of Be in which we decompose this process into a single photoionization of the inner $1s^2$ shell $\gamma + 1s^2 2s^2$ Be $\rightarrow \epsilon_1\, p + 1s 2s^2$ Be^+ and a double shake-off (DSO) of the outer $2s^2$ shell. We do not assume an instantaneous departure of the two $2s^2$ electrons. Rather, we allow them to interact with each other and the nucleus on their way out of the atom. In this sense, our approach is similar to the HCM of Pattard and Burgdorfer (2001). However, instead of the time-dependent perturbation theory in coordinate space employed by these authors, we use the unperturbative convergent close-coupling (CCC) formalism in the momentum space. In our model, we further decompose the double shake-off into a single shake-off into a virtual intermediate state $2s^2 \rightarrow ns\,\epsilon s$ and a subsequent electron impact ionization of the doubly charged Be^{2+} ion leading to the triply ionized final state $\epsilon\, s + 1sns$ $Be^{2+} \rightarrow \epsilon_2\, l + \epsilon_3\, l + 1s$ Be^{3+} . The latter process is described by the T-matrix of inelastic electron scattering on the "semi-hollow" $1sns$ Be^{2+} ion in the monopole singlet channel.

We write the single photoionization cross-section of a closed ns^2 shell in atomic

units, as defined by Amusia (1990):

$$\sigma^{+}_{ns^2}(\omega) = \frac{8\pi^2\omega}{c} \int d^3k \; |\langle \boldsymbol{k}\, ns| \, D \, |ns^2\rangle|^2 \, \delta(\omega - E + \epsilon_{1s}) \qquad (1)$$

This expression corresponds to the momentum space normalization of the continuous wave function: $\langle \boldsymbol{k}|\boldsymbol{k}'\rangle = \delta(\boldsymbol{k} - \boldsymbol{k}')$. The dipole operator D is evaluated in the random phase approximation with exchange (RPAE) using the computer code of Chernysheva *et al* (1974). The photoionization cross-sections of the inner $1s^2$ shell as well as the outer $2s^2$ shell are presented in Figure 1. We see that at the photon energy range of our interest $\sigma^{+}_{1s^2} \gg \sigma^{+}_{2s^2}$. It is well known that the photoabsorption process takes place preferentially near the nucleus to accommodate the recoil momentum. At the same photon energy the probability of this process is much higher for inner-shell electrons than for outer-shell electrons. It is for this reason that we choose the $1s^2$ single photoionization as the most probable precursor of the TPI.

We write the triple photoionzziation cross-section as:

$$\sigma^{3+}(\omega) = \frac{8\pi^2\omega}{c} \sum_{\epsilon_f > 0} \int d^3\boldsymbol{k}_1 \; d^3\boldsymbol{k}_2 \; \left|\langle \boldsymbol{k}_1 1s \,|\, D \,|\, 1s^2\rangle\right|^2 \; \left|\langle \boldsymbol{k}_2 f \,|\, \mathcal{O} \,|\, 2s^2\rangle\right|^2 \qquad (2)$$
$$\times \; \delta(\omega - IP^{3+} - E_1 - E_2 - \epsilon_f)$$

Here $E_i = k_i^2/2$, $i = 1, 2$. Following the general philosophy of the CCC method, we introduce a complete set of pseudostates $|f\rangle$ diagonalizing the "semi-hollow" Be^{2+} Hamiltonian. Positive energy pseudostates $\epsilon_f > 0$ contribute to TPI. The DSO amplitude from the outer $2s^2$ shell is defined in Equation (2) as

$$\langle \boldsymbol{k}_2\, f|\mathcal{O}|2s^2\rangle = \langle \boldsymbol{k}_2\, f \,|\, 2s^2\rangle + \sum_j \sum\!\!\!\!\!\!\int d^3\boldsymbol{k} \; \frac{\langle \boldsymbol{k}\, j \,|\, 2s^2\rangle \langle \boldsymbol{k}_2\, f \,|\, T \,|\, j\, \boldsymbol{k}\rangle}{k_2^2/2 + \epsilon_f - k^2/2 - \epsilon_j + i\delta} \qquad (3)$$

The first term in the right hand side of Equation (3) corresponds to the direct (or "bare") shake-off whereas the second integral term describes the shake-off assisted by the inelastic electron scattering on the "semi-hollow" Be^{2+} ion. This process is evaluated via the half on-shell T-matrix which is found by solving the Lippmann-Scwinger equation in the monopole singlet channel. Equation (3) is analogous to the CCC expression of the amplitude of He DPI given by Kheifets and Bray (1996). However, in the latter case, the T-matrix is evaluated in the dipole, rather than monopole, singlet channel.

The bare shake-off amplitude $\langle \boldsymbol{k}\, j \,|\, 2s^2\rangle$ is calculated as an overlap between the valence $2s^2$ shell of the neutral Be atom and the two-electron state $|\boldsymbol{k}\, j\rangle$ which consists of a Coulomb wave and a pseudostate of the semi-hollow Be^{2+} ion. This overlap is sensitive to the ground state correlation as the valence electrons can be found, with finite probability, in virtual excited states nl^2, $l > 0$, $n \geq 2$. In the present calculation we account for all virtual excitations with $l \leq 4$ and $n \leq 5$ by constructing the multiconfiguration Hartree-Fock ground state (Dyall *et al* 1989).

To simplify notations in Equation (2) we introduce the DSO cross-section

$$\sum_{\epsilon_f > 0} \int d\boldsymbol{k}_2 \; \left|\langle \boldsymbol{k}_2 f \,|\, \mathcal{O} \,|\, 2s\rangle\right|^2 \delta(\omega - IP^{3+} - E_1 - E_2 - \epsilon_f) \equiv \sigma^{2+}_{2s^2}(\Delta E - E_1) \qquad (4)$$

where $\Delta E = \omega - IP^{3+}$ is the excess energy above the TPI threshold. Using expressions (1) and (4) we rewrite Equation (2) as

$$\sigma^{3+}(\omega) = \int_0^{\Delta E} dE_1 \, \frac{\omega}{\omega'} \, \sigma^{+}_{1s^2}(\omega') \, \sigma^{2+}_{2s^2}(\Delta E - E_1) \tag{5}$$

Here $\omega' = E_1 - \epsilon_{1s}$ is an equivalent photon energy corresponding to the energy of the primary photoelectron E_1.

The DSO cross-section (4) as well as the cross-sections of the single shake-off processes leaving the Be ion in various doubly charged states $1snl$, $n = 2 \ldots 6$ are shown in Figure 2. In the same figure we also draw the cross-sections of electron scattering on the "semi-hollow" Be^{2+} $1s2s$ ion leading to the same final states. These cross-sections are obtained from the monopole T-matrix $\langle \boldsymbol{k}_2 \, nl | \, T \, | 2s \, \boldsymbol{k} \rangle$ taken on the energy shell. We see that at small electron energies the shake-off cross-sections to higher excited states $n \geq 4$ and the double shake-off scale with the same constant to the corresponding electron scattering and electron impact ionization cross-sections in the monopole channel. This situation is very similar to photoionization-excitation and double photoionization processes which scale, near threshold, to corresponding electron scattering and electron impact ionization cross-sections in the dipole channel (Samson 1990, Samson *et al* 1992). This scaling can be interpreted as the dominance of the two-step double ionization, assisted by inelastic electron scattering, over the direct shake-off mechanism (Kheifets 2001).

The TPI cross-section of Be is shown in Figure 3. On the left panel we show the ratio of triple-to-single photoionziation cross-sections in comparison with the experimental (Wehlitz *et al* 1998) and calculated (Kheifets and Bray 1998) ratios for Li. The calculated triple-to-single ratio is fitted to the experiment by multiplying an *ab initio* double-to-single ratio of Li^+ by an empirical shake-off probability of the outer $2s$ electron. This fitted value of 0.0035 is to be compared with calculated values of 0.00174 (Wehlitz *et al* 1998), 0.00465 (Cooper 1999) and 0.00703 (Santos *et al* 2001). The triple-to-single ratio in Be is about the same as in Li. However, the absolute TPI cross-section is bigger by about a factor of 4 due to a large single photoionization cross-section. The triple-to-single ratio in Be reaches its peak value at about 100 eV above the triple ionization threshold as compared to 200 eV in Li. This faster onset of TPI in Be is explained by a smaller energy scale of the DSO from the outer $2s^2$ shell. Whereas in Li most of the energy dependence of TPI comes from the DPI of the inner $1s^2$ shell.

In conclusion, we propose a model of the TPI of Be in which we decompose this process into a single photoionization of the inner $1s^2$ shell and the DSO of the outer $2s^2$ shell. The latter is calculated using the CCC model of the electron impact ionization of the "semi-hollow" Be^{2+} ion. We predict a TPI cross-section of the peak value of several barns, slightly bigger than that of Li. This significant cross-section should render possible an experimental observation of the TPI on Be. As to other atomic targets, Suzuki *et al* (2002) reported first measurement of the TPI on Mg. The present theory can be easily modified to account for the DSO from the outer $3s^2$ shell of Mg.

However, due to proximity of the subvalent $2p^6$ shell, the TPI of Mg will be strongly effected by indirect processes not accounted by our model.

Another aspect of the present model which can affect its accuracy is explicit distinguishability of all three photoelectron. The "primary" electron is photoionized from the core and the two "secondary" electrons are shaken off from the valence shell subsequently. Of these two shake-off electrons, one "outer" electron is described by a true continuum state whereas another "inner" electron is represented by a positive energy pseudostate. The latter representation cannot lead to any significant error as the T-matrix is very small when the energy of the "inner" electron exeeds one half of the total electron pair energy. Unfortunately, there is no such a clear separation in energy between the "primary" electron and the "secondary" electron pair. Therefore, running the integration over E_1 across the whole excess energy range ΔE in Equation (5) can lead to certain double count and overestimation of the TPI cross-section.

Acknowledgments

One of the authors (ASK) expresses his gratitude to the Japan Society for the Promotion of Science for supporting his visit to the Photon Factory (PF-KEK). ASK also whishes to thank Prof. Y. Azuma and members of his group at PF-KEK for many stimulating discussions. The authors thank Dr. R. Wehlitz for critical reading of the manuscript. The Australian Partnership for Advanced Computing is acknowledged for providing access to the Compaq AlphaServer SC National Facility.

References

Amusia M Y 1990 *Atomic photoeffect* New York, Plenum Press

Briggs J S and Schmidt V 2000 *J. Phys. B* **33**(1), R1–R48

Chernysheva L V, Amusia M Y and Cherepkov N A 1974 Computer programs for atomic photoionization cross section calculations with correlations within one and two transitions Preprint 459 A. F. Ioffe Institute Leningrad, Russia

Citrini F, Malegat L, Selles P and Kazansky A K 2003 *Phys. Rev. A* p. to be published

Colgan J and Pindzola M S 2002 *Phys. Rev. A* **65**(2), 2709

Cooper J W 1999 *Phys. Rev. A* **59**(6), 4825–4828

Dyall K G, Grant I P, Johnson C T, Parpia F A and Plummer E P 1989 *Comp. Phys. Commun.* **55**, 425–456

Hasegawa S, Obara S, Yoshida F, Suzuki T, Azuma Y and Nagata T 2002 *in* 'International Workshop on Photoionization' SPring-8, Hyogo, Japan p. FA17

Kheifets A S 2001 *J. Phys. B* **34**(8), L247–L252

Kheifets A S and Bray I 1996 *Phys. Rev. A* **54**(3), R995–R997

Kheifets A S and Bray I 1998 *Phys. Rev. A* **58**(6), 4501–4511

Kheifets A S and Bray I 2002 *Phys. Rev. A* **65**(1), 2710

Kornberg M A and Miraglia J E 1993 *Phys. Rev. A* **48**(5), 3714–3719

Pattard T and Burgdorfer J 2001 *Phys. Rev. A* **63**(2), 701

Samson J A R 1990 *Phys. Rev. Lett.* **65**(23), 2861–2864

Samson J A R, Bartlett R J and He Z X 1992 *Phys. Rev. A* **46**(11), 7277–7280

Santos J P, Laranjeira M F and Parente F 2001 *Europhys. Lett.* **55**(4), 479–485

Suzuki T Y, Sullivan J, Harries J, Obara S and Azuma Y 2002 *in* 'International Workshop on Photoionization' SPring-8, Hyogo, Japan p. FA09

van der Hart H W and Greene C H 1998 *Phys. Rev. Lett.* **81**(20), 4333–4336

Wehlitz R and Whitfield S B 2001 *J. Phys. B* **34**(22), L719–L725

Wehlitz R and Whitfield S B 2002 *in* 'International Workshop on Photoionization' SPring-8, Hyogo, Japan p. FA18

Wehlitz R, Huang M T, Depaola B D, Levin J C, Sellin I A, Nagata T, Cooper J W and Azuma Y 1998 *Phys. Rev. Lett.* **81**(9), 1813–1816

Wehlitz R, Lukic D, Koncz C and Sellin I A 2002 *Rev. Sci. Instr.* **73**(3), 1671–1673

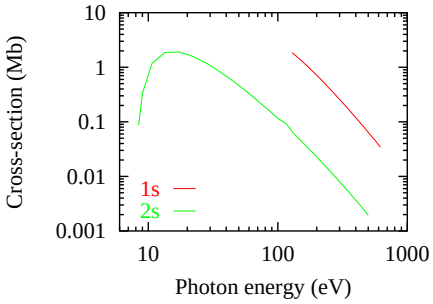

Figure 1. Single photoionization cross-sections of the $1s^2$ and $2s^2$ shells of Be.

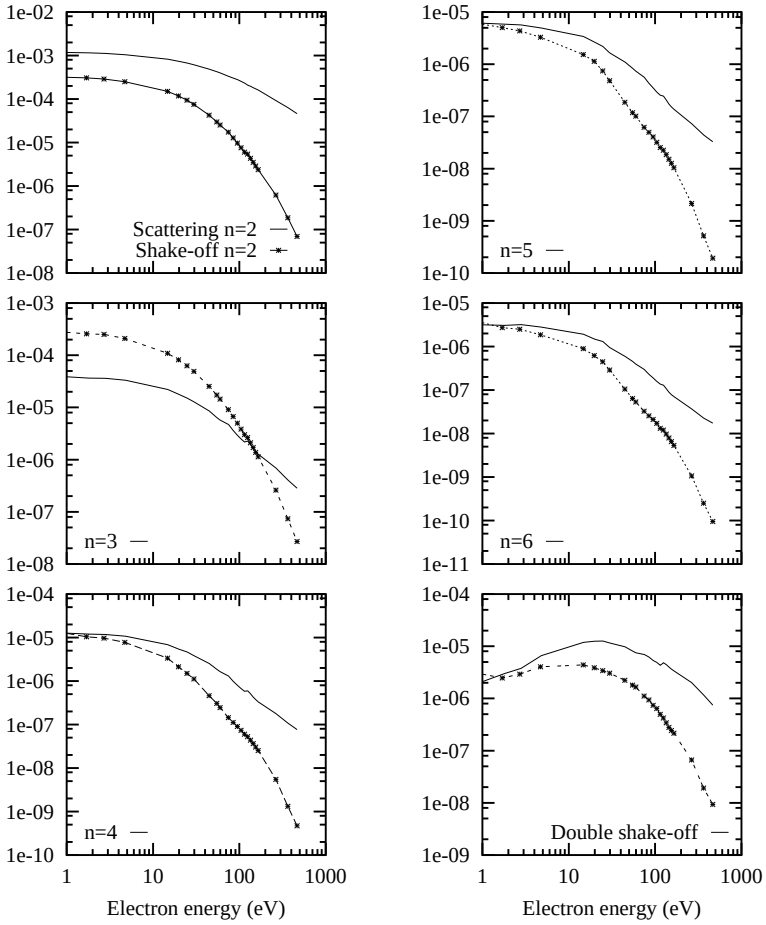

Figure 2. Shake-off cross-sections of the Be^{2+} ion leading to various doubly charged states $1snl$, $n = 2 \ldots 6$ and triply ionized state are shown by the dotted line. Cross-sections of the inelastic electron scattering on the semi-hollow Be^{2+} $1s2s$ ion leading to the same final states are drawn by the solid line. Same scaling constant is applied to all the graphs.

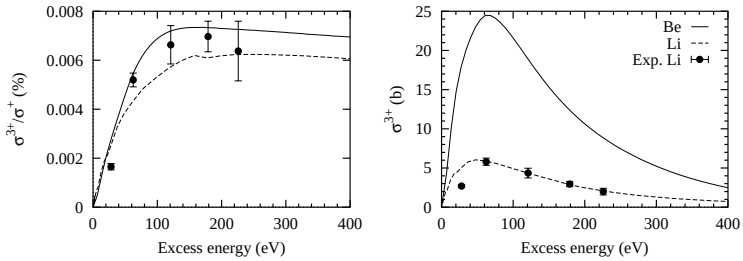

Figure 3. Left panel: triple-to-single photoionziation cross-sections ratio in Be (solid line) and Li (dashed line). Experimental ratio for Li is from Wehlitz *et al* (1998). Calculated ratio for Li is from Kheifets and Bray (1998). Right panel - same for the absolute triple photoionziation cross-section.