

# CONVERGENCE STUDIES OF THE DOUBLE PHOTOIONIZATION OF $\text{Li}^+$ AND He

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**Abstract:** We discuss the convergence of the time-dependent close-coupling approach to double photoionization of  $\text{Li}^+$  and He from the ground and first excited states. The triple differential cross sections are examined for double photoionization of these systems at equal energy sharing and for coplanar geometries, and as a function of the radial grids and number of coupled channels used in the calculations. These studies provide a useful guide to planned calculations of the triple photoionization of Li, where similar convergence trends are expected.

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## 1. INTRODUCTION

Investigations of the fragmentation of small atoms with a single photon has become an invaluable tool in analyzing the nature and strength of electron correlations in atoms. Double photoionization of helium (i.e. a single photon ejecting both bound electrons) is a process which cannot take place without electron correlation, since the photon can only be absorbed by one electron. This process has thus been the subject of intense investigations, which are well described in two recent reviews [1, 2]. Experimental investigations of the double photoionization process have been spurred by the continuing improvements in multi-coincidence technology, particularly the cold-target recoil-ion-momentum-spectroscopy (COLTRIMS) apparatus [3, 4], which have allowed detection of both outgoing electrons as a function of their energies and over a range of ejection angles, the so-called triple differential cross section (TDCS). On the theoretical front, several nonperturbative approaches can claim to have solved this three-body Coulomb problem numerically, without requiring any initial approximations [5, 6, 7, 8].

Similar investigations beyond helium have also taken place. For example, studies of double photoionization of molecular hydrogen have been reported recently, with advances in theory and experiment [9, 10] allowing new

phenomena to be uncovered and explained [11, 12, 13, 14, 15]. Several recent studies have also reported on the double photoionization of atomic lithium [16, 17]. Some initial work has also taken place to examine *triple* photoionization of lithium, i.e. the ejection of all three bound electrons after absorption of one photon. The total cross section for this process, which peaks at just a few barns, has been measured [18] and numerical calculations are in good agreement with this result [19]. Some semi-classical approaches have also investigated possible break-up mechanisms for the triple photoionization process [20, 21]. It is of considerable interest to completely characterize this process, i.e. to be able to predict the outgoing angles and energies of all three electrons after the single photon absorption. In the threshold region, this illuminates Wannier theory [22], and at higher photon energies, the competing electron correlation mechanisms can be explored. In pursuit of this goal, the time-dependent close-coupling (TDCC) approach is currently being extended to examine energy and angle differential cross sections for the triple photoionization of lithium. Our approach builds on previous work which calculated the total cross section for this process [9] and on a recent study of the electron-impact double ionization of helium [23], which results in a very similar final state: three electrons moving in the field of an atomic nucleus. Such

three-electron calculations are, however, extremely computationally expensive. Before beginning such studies, it is important to assess the likely convergence requirements of such a calculation. This paper thus reports on convergence properties of calculations of the TDCS for double photoionization of  $\text{Li}^+$  from its ground and first excited states using the time-dependent close-coupling approach. We study this process at a photon energy of 300 eV, which is a suitable photon energy at which to perform triple photoionization studies of neutral lithium, since it is near the peak of the total cross section. Also, the threshold energy for the double photoionization of  $\text{Li}^+$  is quite similar to that of the triple photoionization threshold for lithium (since the  $2s$  electron is so weakly bound). The first excited state of  $\text{Li}^+$  is of interest since the triple photoionization process in lithium is thought to proceed via absorption of the photon by an inner  $1s$  electron (so that the nucleus can absorb the recoil momentum), leaving a  $1s2s$  state which is then ejected by either a shake-off process or through electron-impact ionization by the returning photoelectron.

In the following section we give a very brief description of the important aspects of time-dependent close-coupling theory as applied to atomic double photoionization. We then discuss in detail the convergence properties of the TDCS for double photoionization of  $\text{Li}^+$ , and compare these cross sections to those from He. We discuss the implications for the planned calculations of the pentuple differential cross sections (PDCS) for the triple photoionization of lithium and end with a short conclusion.

## 2. THEORY

The time-dependent close-coupling approach to double photoionization of two-electron systems has been laid out in detail in several previous publications [5, 24, 25, 26]. Here we just state the main aspects of our method relevant to the subsequent discussion. The triple differential cross section for double photoionization can be written as

$$\frac{d^3\sigma}{dE_1 d\Omega_1 d\Omega_2} = \frac{\omega}{I} \frac{1}{k_1 k_2} \frac{\partial}{\partial t} \int_0^\infty dk_1 \int_0^\infty dk_2 \delta\left(\alpha - \tan^{-1}\left(\frac{k_2}{k_1}\right)\right) \times \left| \sum_{l_1, l_2} (-i)^{l_1 + l_2} e^{i(\sigma_{l_1} + \sigma_{l_2})} \bar{P}_{l_1 l_2}^{1P}(k_1, k_2, t) Y_{l_1 l_2}^{1P}(\hat{k}_1, \hat{k}_2) \right|, \quad \dots (1)$$

where  $\omega$  is the photon energy,  $I$  is the radiation field intensity,  $\sigma_l$  is the Coulomb phase shift,  $Y_{l_1 l_2}^{1P}(\hat{k}_1, \hat{k}_2)$  are coupled spherical harmonics, and integration over all solid angles and ejected energies recovers the total integral cross section. The outgoing electrons with momenta  $k_1$  and  $k_2$  share the excess energy  $E = \omega - IP$ , where  $IP$  is the double ionization potential for the atomic state under investigation.

The momentum space probability for double ionization is defined as

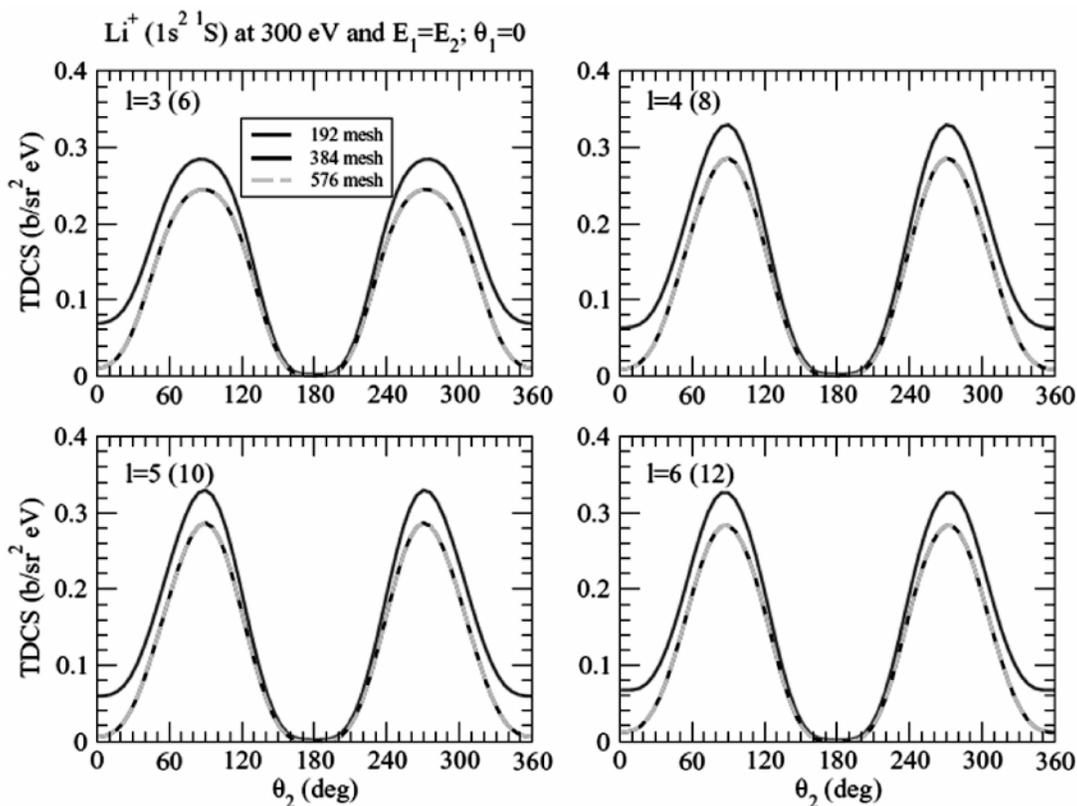
$$\bar{P}_{l_1 l_2}^{1P}(k_1, k_2, t) = \int_0^\infty dr_1 \int_0^\infty dr_2 P_{k_1 l_1}(r_1) P_{k_2 l_2}(r_2) P_{l_1 l_2}^{1P}(r_1, r_2, t),$$

where  $P_{l_1 l_2}^{1P}(r_1, r_2, t)$  are the two-dimensional radial wavefunctions that result from the expansion of the total time-dependent wavefunction, and  $P_{kl}(r)$  are radial continuum states [5]. As discussed below, we monitor the convergence of the TDCS calculations with respect to the radial mesh used in the time-dependent equations, and to the number of channels used in the expansion over  $l_1 l_2$  given in Eq. (1).

## 3. RESULTS AND DISCUSSION

In the discussion below, we restrict ourselves to studies of the triple differential cross sections (TDCS) for equal energy sharing outgoing electrons, in the coplanar geometry (i.e.  $\phi_1 = \phi_2 = 0^\circ$ ) and for  $\theta_1 = 0^\circ$ . This geometry is well-known to be the slowest to converge [2], due to the drop in the cross section as  $\theta_1$  is decreased and so is the most stringent test of the convergence of our calculations. For this geometry, the TDCS contains some general trends [5]. For example, the TDCS for  $\theta_2$  values near  $0^\circ$  should be close to zero, since this geometry implies both electrons being ejected along similar trajectories and at the same energy, which is highly constrained by the electron repulsion. Also, the TDCS for back-to-back ejection (i.e.  $\theta_1 = 0^\circ$ ,  $\theta_2 = 180^\circ$ ) is forbidden due to the well-known selection rules for outgoing electrons in an odd  $^1P$  final state [27]. Thus the TDCS in this geometry is expected to have a two-lobe structure, symmetric about  $\theta_2 = 180^\circ$ , very similar to that found previously, both theoretically and experimentally, for He [5].

In Fig. 1 we present time-dependent close-coupling calculations of the triple differential cross sections (TDCS) for double photoionization of  $\text{Li}^+$  at a photon



**Fig. 1:** Time-dependent close-coupling calculations of the triple differential cross sections for double photoionization of the  $\text{Li}^+$  ground state at a photon energy of 300 eV. The cross sections are presented for equal energy sharing outgoing electrons, in the coplanar geometry, and where one electron angle is fixed at  $0^\circ$ . Cross sections are presented for various mesh sizes as indicated. A mesh of 192 points is indicated by the solid red lines, a mesh of 384 points by the solid black lines, and a mesh of 576 points by the dashed green lines. In each case a mesh spacing of 0.1 a.u. was used. The 384 and 576 cases lie on top of each other in this figure. Each panel represents a calculation for a given maximum angular momentum value as indicated (with the number of coupled channels used in parentheses).

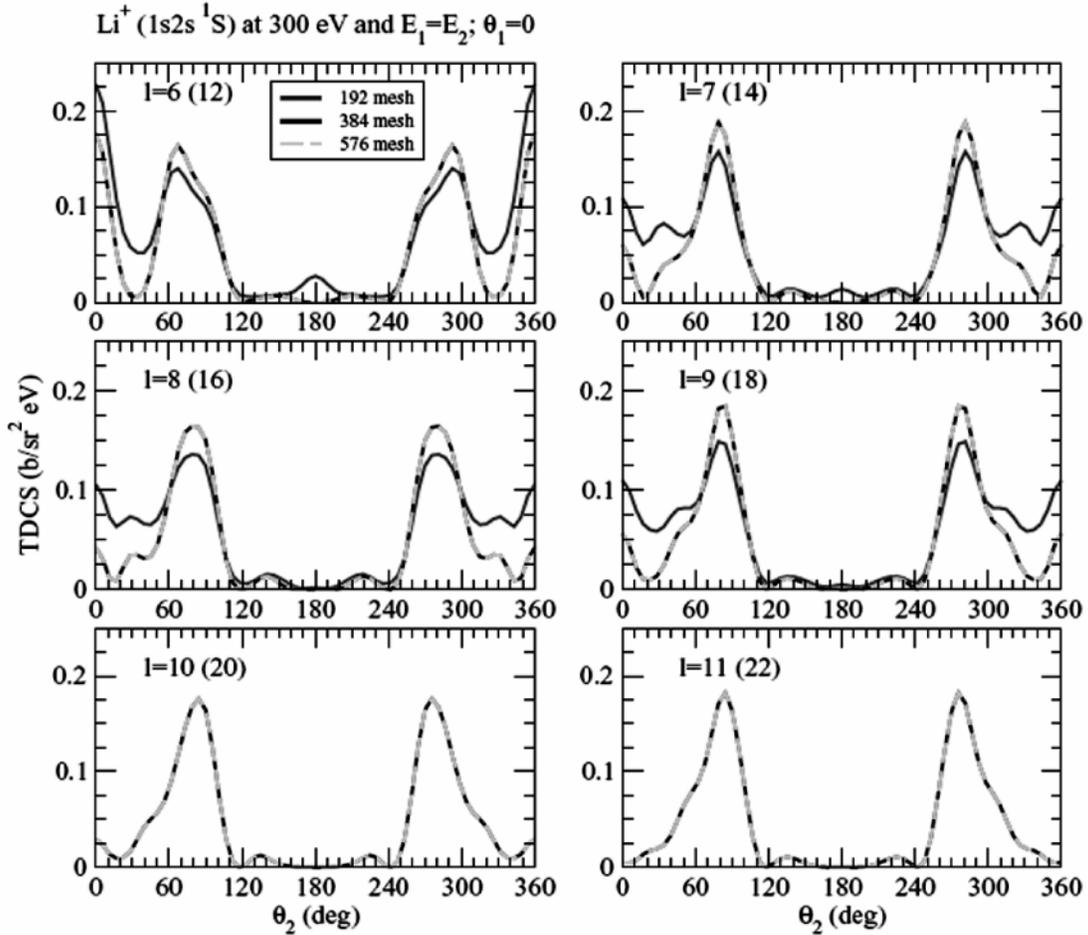
energy of 300 eV. The cross sections are presented for three different mesh sizes as indicated. In each case a mesh spacing of  $\Delta r = 0.1$  a.u. was used. Each panel represents a calculation for a given maximum angular momentum value as indicated, where the number of coupled channels retained is also shown in parentheses.

Our study reveals some important trends. We find that the TDCS for this case is well described using a radial grid of less than 40 a.u. ( $0.1 \times 384$  points) in the time-dependent close-coupling calculations, since increasing the mesh to 57.6 a.u. makes no difference to the TDCS. An even smaller grid extending to just 19.2 a.u. captures the shape of the TDCS very well, but overestimates slightly the magnitude. These modest grid size requirements are partly due to the small radial extent of the initial  $\text{Li}^+$  wavefunction.

We also find that the TDCS is well converged using only 8 coupled channels in the time-dependent close-

coupling expansion, corresponding to a maximum angular momentum value of four. Extending the number of channels retained to 10 or 12 (lower panels of Fig. 1) makes no noticeable difference to the TDCS for these geometries. A measure of the convergence of the calculation is found for the TDCS for  $\theta_2$  values close to  $0^\circ$ . The cross section in this region is slow to converge with respect to the radial grid size. On the other hand, the other expected “zero” in the TDCS, at  $\theta_2 = 180^\circ$ , is found for all calculations, no matter how small the various radial and angular expansions may be.

In Fig. 2 we present the TDCS at the same photon energy (300 eV) from the first excited state of  $\text{Li}^+$  ( $1s2s\ ^1S$ ). Again, we choose the equal energy sharing, coplanar case, with  $\theta_1 = 0^\circ$ . In this case, since the double photoionization threshold is lower (134 eV) compared to DPI from the ground state (193 eV), the outgoing electrons are more energetic, with around 83 eV of energy.

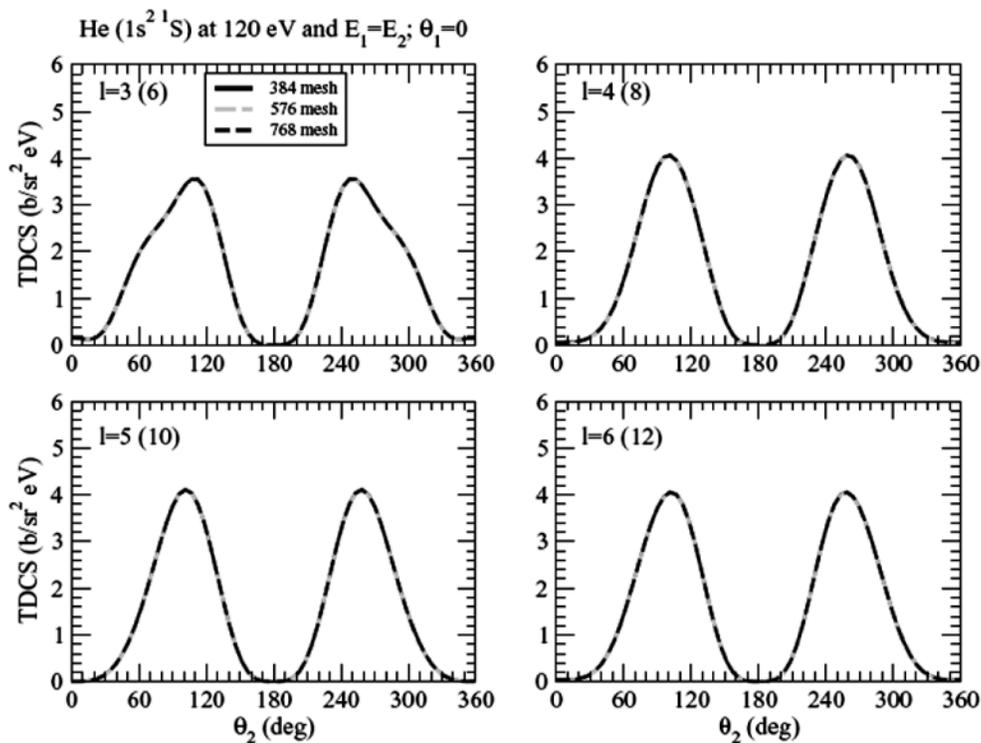


**Fig. 2:** As in Fig. 1, except from the first excited  $1s2s\ ^1S$  state of  $\text{Li}^+$ , also at a photon energy of 300 eV. For the lower two panels, no calculation using a 192 mesh is shown.

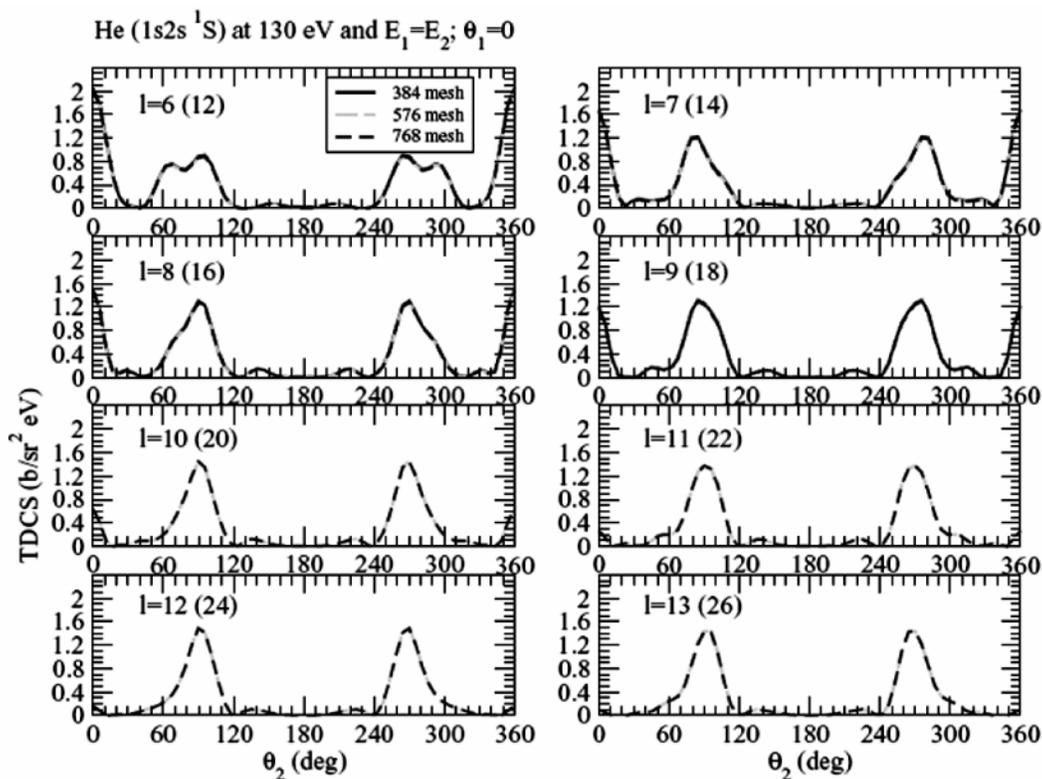
We find some notable convergence trends. The convergence with respect to the radial grid used appears to be similar to the convergence in the calculations from the ground state. Again, we find the calculations well converged using a box of around 40 a.u. A smaller box, of 19.2 a.u., again overestimates the cross section but captures the shape of the TDCS quite well. The convergence of the time-dependent close-coupling calculations with respect to the maximum angular momentum value used is, however, quite different from the ground state calculations. The top left panel shows the calculation with a maximum angular momentum ( $l$ ) value of 6, which was more than sufficient to converge the calculations from the ground state. In this case, although we do find a two-lobe structure as expected, we also observe a large unphysical cross section at  $\theta_2 = 0^\circ$ . The cross section near this region slowly decreases as the  $l$  value increases, but the calculations requires a

value of  $l = 11$  (22 coupled channel pairs) before the cross section is close to zero in this region, where the TDCS can be considered to be completely converged. The much slower convergence of the TDCS from the first excited state is most likely due to the more diffuse nature of the initial  $1s2s\ ^1S$  state, which is much less tightly bound than the ground state. The outgoing electrons have more energy available to them, so that higher angular momentum states may be accessed.

It is instructive to compare these calculations with similar studies on He. In Figs 3 and 4 we show the TDCS for double photoionization of He from its ground and first excited states, respectively, at photon energies of 120 eV (ground state) and 130 eV (first excited state). These energies were chosen as the excess energy available to the outgoing electrons, in threshold units, is similar to the corresponding cases for  $\text{Li}^+$ . Threshold units are defined as the photon energy divided by the double ionization



**Fig. 3:** As in Fig. 1, except from the ground state of He, and at a photon energy of 120 eV. A mesh of 384 points is indicated by the solid black lines, a mesh of 576 points by the dashed green lines, and a mesh of 768 points by the short-dashed blue lines. In each case a mesh spacing of 0.1 a.u. was used. The curves representing all 3 cases lie on top of each other in this figure.



**Fig. 4:** As in Fig. 3, except from the first excited  $1s2s \ ^1S$  state of He, and at a photon energy of 130 eV. For the lower four panels, no calculation using a 384 mesh is shown.

potential for a given state; thus for the first excited states we have  $300/134 = 2.23$  ( $\text{Li}^+$ ), which is similar to  $130/58$  for He.

For the TDCS from the ground state of He (Fig. 3), we found that, as in  $\text{Li}^+$ , a box of around 40 a.u. was sufficient to accurately describe the cross sections. Increasing the box to 57.6 or 76.8 a.u. made very little difference to the resulting TDCS, although we also note that smaller grid sizes (e.g. 20 a.u.) resulted in unphysical TDCS, presumably because the smaller box results in significant wavefunction reflections at these lower photon energies. As in  $\text{Li}^+$ , a maximum angular momentum of  $l = 4$  was found to be sufficient to fully converge the TDCS.

For the TDCS from the first excited state of He, as shown in Fig. 4, the convergence properties are also similar to the first excited state of  $\text{Li}^+$ . Retaining angular momentum values up to  $l = 6$  (upper left panel of Fig. 4), which was more than sufficient to converge the cross sections from the ground state, results in a clearly unconverted cross section, since a major feature in this distribution is a large peak at  $\theta_2 = 0^\circ$ , which is unphysical. Increasing the number of angular momentum terms included in the calculation lowers the peak at  $\theta_2 = 0^\circ$ , although the decrease with  $l$  is slow, so that it takes up to  $l = 13$  to calculate a TDCS which can be thought of as fully converged.

Several other points should be kept in mind. We note that our previous studies of the TDCS from the  $1s2s\ ^1S$  state of He [25] at lower photon energies, found that fewer angular momentum terms were required to fully converge the TDCS. At a photon energy of around 80 eV, angular momentum values up to  $l = 9$  were sufficient to fully converge the TDCS. As the ejected electrons have more energy available to them, the number of angular momentum values they can reach increases, so more terms must be included in the expansions of Eq. (1). We also note that the total double photoionization cross sections converge much more quickly than the TDCS. For example, in Table 1 we show the total double photoionization cross sections for  $\text{Li}^+$  from ground and first excited states as a function of the maximum angular momentum used in the expansions in Eq. (1). We find that the total cross section has essentially converged using up to  $l = 4$  from the ground state, and using  $l = 5$  from the first excited state. These cross sections are in excellent agreement with previous time-dependent close-coupling calculations [28].

**Table 1:** Convergence of the total double photoionization cross section for ground and first excited state  $\text{Li}^+$  as a function of the maximum angular momentum retained in the close-coupling expansions.

Maximum orbital angular momentum	Cross section (kb) $\text{Li}^+$ ( $1s^2$ )	$\text{Li}^+$ ( $1s2s\ ^1S$ )
3	1.311	
4	1.306	1.007
5	1.305	1.098
6	1.303	1.110
7	1.303	1.106
8		1.103
9		1.099
10		1.097
11		1.095

#### 4. CONCLUSION

Our study has several implications for the planned calculations of the pentuple differential cross sections for the triple photoionization of Li. As previously discussed, we might expect the convergence properties of these PDCS to be similar to those of the  $1s2s\ ^1S$  state of  $\text{Li}^+$ . Thus, a planned triple photoionization of Li calculation may require a reasonably small radial grid (although we remember that a three-electron calculation requires a 3-dimensional lattice), but may also require a significant number of angular momentum terms to fully converge the PDCS. This is somewhat problematic in the three continuum electron case, since the number of coupled channels available to three outgoing electrons with a total orbital angular momentum of  $L = 1$  is significantly larger than the number of channels available to two outgoing electrons with  $L = 1$  for a given maximum  $l$  value. For example, increasing the maximum  $l$  value from 3 to 4 implies two extra coupled channels in the two electron case, but in the three electron case implies an increase of 44 coupled channels. Such considerations mean that significant computational resources must be spent to fully converge the PDCS for triple photoionization of Li. A preliminary study of the double photoionization of  $\text{Li}^+$ , as outlined here, is therefore valuable before undertaking the much more challenging triple photoionization studies.

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## REFERENCES

- [1] J.S. Briggs and V. Schmidt, *J. Phys. B: At. Mol. Opt. Phys.*, **33**, R1 (2000).
- [2] L. Avaldi and A. Huetz, *J. Phys. B: At. Mol. Opt. Phys.*, **38**, S861, (2005).
- [3] R. Dörner, et. al., *Physics Reports*, **330**, 95, (2000).
- [4] H. Bräuning et. al., *J. Phys. B: At. Mol. Opt. Phys.*, **31**, 5149, (1998).
- [5] J. Colgan, M.S. Pindzola, and F. Robicheaux, *J. Phys. B: At. Mol. Opt. Phys.*, **34**, L457, (2001).
- [6] L. Malegat, P. Selles, and A.K. Kazansky, *Phys. Rev. Letts.*, **85**, 4450, (2000).
- [7] A.S. Kheifets and I. Bray, *Phys. Rev. A.*, **62**, 065402, (2000).
- [8] C.W. McCurdy, D.A. Horner, T.N. Rescigno, and F. Martin, *Phys. Rev. A.*, **69**, 032707, (2004).
- [9] T. Weber, A.O. Czasch, O. Jagutzki, A.K. Müller, V. Mergel, A. Kheifets, E. Rotenburg, G. Meigs, M.H. Prior, S. Daveau, A. Landers, C.L. Cocke, T. Osipov, R. Diez Mulho, H. Schmidt-Böcking, and R. Dörner, *Phys. Rev. Letts.*, **92**, 163001, (2004); *Nature*, **431**, 437, (2004); **443**, 1014, (2006).
- [10] M. Gisselbrecht, M. Lavollée, A. Huetz, P. Bolognesi, L. Avaldi, D.P. Seecombe, and T.J. Reddish, *Phys. Rev. Letts.*, **96**, 153002, (2006).
- [11] W. Vanroose, F. Martin, T.N. Rescigno, and C.W. McCurdy, *Science*, **310**, 1787, (2005).
- [12] W. Vanroose, D.A. Horner, F. Martin, T.N. Rescigno, and C.W. McCurdy, *Phys. Rev. A.*, **74**, 052702, (2006).
- [13] J. Colgan, M.S. Pindzola, and F. Robicheaux, *Phys. Rev. Letts.*, **98**, 153001, (2007).
- [14] D.A. Horner, W. Vanroose, T.N. Rescigno, F. Martin, and C.W. McCurdy, *Phys. Rev. Letts.*, **98**, 073001, (2007).
- [15] T.J. Reddish, J. Colgan, P. Bolognesi, L. Avaldi, M. Gisselbrecht, M. Lavollée, M.S. Pindzola, and A. Huetz, *Phys. Rev. Letts.*, **100**, 193001, (2008).
- [16] G. Zhu, M. Schuricke, J. Steinmann, J. Albrecht, J. Ullrich, I. Ben-Itzhak, T.J.M. Zouros, J. Colgan, M.S. Pindzola, and A. Dorn, *Phys. Rev. Letts.*, **103**, 103008, (2009).
- [17] A.S. Kheifets, D.V. Fursa, I. Bray, J. Colgan, and M.S. Pindzola, *Phys. Rev. A*, **82**, 023403, (2010).
- [18] R. Wehlitz, M.T. Huang, B.D. DePaola, J.C. Levin and I.A. Sellin, *Phys. Rev. Letts.*, **81**, 1813, (1998).
- [19] J. Colgan, M.S. Pindzola, and F. Robicheaux, *Phys. Rev. Letts.*, **93**, 053201, (2004).
- [20] A. Emmanouilidou, *Phys. Rev. A*, **75**, 042702, (2007).
- [21] A. Emmanouilidou, P. Wang and J.M. Rost, *Phys. Rev. Letts.*, **100**, 063002, (2008).
- [22] A. Emmanouilidou and J.M. Rost, *J. Phys. B: At. Mol. Opt. Phys.*, **39**, 063002, 4037, (2006).
- [23] M.S. Pindzola, F. Robicheaux, and J. Colgan, *J. Phys. B: At. Mol. Opt. Phys.*, **41**, 235202, (2008).
- [24] M.S. Pindzola et al., *J. Phys. B: At. Mol. Opt. Phys.*, **40**, R39, (2007).
- [25] J. Colgan and M.S. Pindzola, *Phys. Rev. A.*, **67**, 012711, (2003).
- [26] M. Foster and J. Colgan, *J. Phys. B: At. Mol. Opt. Phys.*, **39**, 5067, (2006).
- [27] F. Maulbetsch and J.S. Briggs, *J. Phys. B: At. Mol. Opt. Phys.*, **28**, 551, (1995).
- [28] U. Kleiman, M.S. Pindzola, and F. Robicheaux, *Phys. Rev. A.*, **72**, 022707, (2005).

