Evidence for a T-Shape Break-Up Pattern in the Triple Photoionization of Li

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We examine the angular distributions of all three electrons ionized from Li by a single photon near the triple ionization threshold using a fully quantum-mechanical treatment. We find strong evidence for a T-shape break-up pattern at a 5 eV excess energy as previously predicted by quasiclassical simulations [A. Emmanouilidou and J. M. Rost, J. Phys. B **39**, 4037 (2006); A. Emmanouilidou, P. Wang, and J. M. Rost, Phys. Rev. Lett. **100**, 063002 (2008)]. This finding is in conflict with the expected Wannier break-up dynamics of three electrons moving at mutual angles of 120°, which is expected to hold at energies a few eV above threshold. We use our quantum-mechanical approach to explore the physical mechanisms behind this unusual break-up configuration.

The breakup of atoms near the ionization threshold has been a topic of interest for many years. The pioneering work of Wannier [1,2], using classical mechanics, revealed the expected escape dynamics of two electrons moving in the field of an ion (the classic three-body Coulomb problem) as back-to-back emission, and led to a threshold law for the energy dependence of single ionization that was also applicable to double photoionization. Later work [3–6] extended this analysis to three outgoing electrons, where it was predicted that the three-electron breakup should proceed along the vertices of an equilateral triangle. The ''triangular'' breakup was verified experimentally in $(e, 3e)$ coincidence measurements of all three outgoing electrons arising from the electron-impact double ionization of He [7]. In contrast, the process of triple photoionization of Li, which leads to the same final state of three electrons moving in the field of a nucleus, has been predicted [8] to proceed via a T-shape breakup in the threshold region, that is, two electrons moving back to back (antiparallel) to the third electron which is at 90° to this direction. The T-shape breakup was attributed to the different initial state of the Li atom [9] (compared to an electron incident on He), and it was shown that the emission of three electrons is, in general, initial state dependent.

In this work, we use a fully quantum-mechanical approach using the time-dependent close-coupling (TDCC) method to probe the triple photoionization of Li and find strong evidence for the prevalence of a T-shape breakup at excess energies of 5 eV above the triple ionization threshold. We compare our calculations as far as possible with the quasiclassical predictions [8,9]. Such a comparison can be somewhat involved, for several reasons.

TDCC calculations become increasingly computationally intensive as the excess energy is lowered, due to the requirement of using large radial grid sizes and long propagation times to accurately treat the interaction of the slow outgoing electrons. The lowest excess energy we consider in this work is thus 5 eV, which is (just) a computationally feasible TDCC calculation, and which is a low enough energy at which the T-shape breakup should be visible, as predicted by the quasiclassical calculations. Also, in the quasiclassical simulations only the relative angle between any of the outgoing electrons has any meaning, because there is no reference from which to give an absolute angle. In the TDCC calculations (and in any measurement), such a reference is provided by the polarization direction, and the absolute angles of ejection of the ionized electrons are given with respect to this polarization direction. As we show below, the polarization direction can strongly influence the resulting angular distributions and therefore, any comparison that is possible between TDCC calculations and the quasiclassical simulations can only be approximate.

In this Letter, we extend an earlier TDCC approach [10] to examine the triple photoionization of Li at energies close to the triple ionization threshold (at 203.4 eV [11]). The TDCC approach [10,12] treats all three electrons equivalently, by expanding the three-electron Schrödinger equation in coupled spherical harmonics, leading to a set of time-dependent coupled partial differential equations that must be solved for the radial dimensions of all three electrons. We present calculations performed at excess energies (E) of 100, 30, 10, and 5 eV and various angular distributions for the outgoing electrons, and at all possible

energy sharings, using a form of the angular distributions described recently [10]. As the excess energy is lowered, the TDCC calculations become more challenging in that larger radial meshes and longer propagation times are required. In the calculations reported here, the largest mesh used was $(384)^3$, with a spacing of $\Delta r = 0.15$ a.u. Test calculations made at smaller mesh spacings of 0.1 a.u., did not change the resulting electron angular distributions, even though they resulted in a somewhat more accurate triple ionization threshold.

In Fig. 1 we present the angular distributions for triple ionization of Li at four excess energies of 100, 30, 10, and 5 eV. We show the angular distributions at equal energy sharing between the electrons $E_1 = E_2 = E_3$ and in the coplanar geometry (so that the plane of ejection of the electrons is in the polarization plane). Distributions are shown for fixed angles of electrons 1 and 2 at 45° and 135°, respectively. At 100 eV excess energy, the third electron is ejected at an angle of around 270°, which is the angle that maximizes the third electron's distance from the other two electrons. Smaller lobes are evident at angles near ~240° and ~300°. As the excess energy drops to 30 eV, these lobes become more prominent, and move slightly to ejection angles closer to the other (fixed) electrons. As the excess energy drops to 10 eV, these side lobes become the dominant feature of the angular distribution, with the ejection along 270° clearly suppressed. At the lowest excess energy considered of 5 eV, the side lobes again move slightly in angle, but are still the dominant
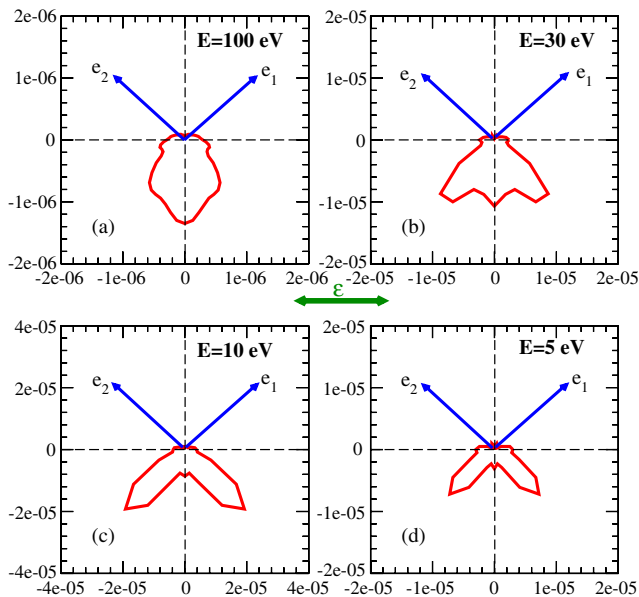
ejection feature. Calculations made at different energy sharings between the outgoing electrons are similar in shape to the distributions presented in Fig. 1.

The ejection angles made by the third electron at the lower excess energies are seen to be in antiparallel directions to the fixed electrons 1 and 2. They thus can be described as a T shape that is symmetric about the axis between the fixed electrons. This T-shape break-up pattern is precisely that predicted by the earlier quasiclassical calculations [9] and is characterized by two electrons leaving back to back, with the remaining electron perpendicular to this back-to-back axis. The distribution of the third electron shows no preference for antiparallel ejection with respect to either of the fixed electrons. The T-shape dominance seems to be well established at 10 eV above the (triple) ionization threshold (at least for the specific break-up configurations so far analyzed), which is not quite in the Wannier threshold region (usually characterized as several eV above the threshold).

In Fig. 2 we present more evidence for the dominance of the T shape, by looking at angular distributions with fixed electrons at 0° and 90°. This distribution is not identical to the distribution in Fig. 1, even though the relative angle between the fixed electrons is the same. This is due to the influence of the polarization axis on the angular distribution, something that has long been recognized in the simpler two-electron double photoionization [13]. At large excess energies, we see that the angular distribution of the third electron is peaked around angles of 200°
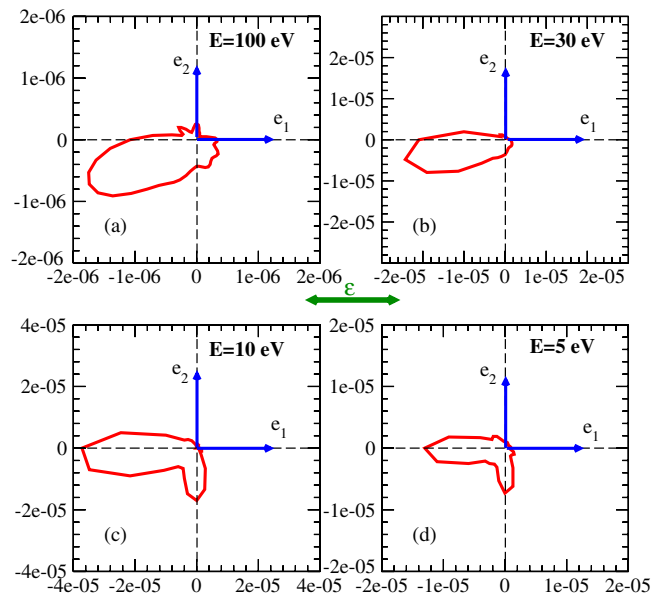

FIG. 1 (color online). Pentuple differential cross sections (PDCS) for triple photoionization of Li at four excess energies (E) as indicated, $E_1 = E_2 = E_3$, and for $\theta_1 = 45°$, $\theta_2 = 135°$, where ϵ is the field polarization direction. Results are presented as a function of θ_3 and for coplanar geometry. All cross sections are in units of b/(sr^{3}eV^2).

FIG. 2 (color online). PDCS for triple photoionization of Li at four excess energies (E) as indicated, $E_1 = E_2 = E_3$, and for $\theta_1 = 0°$, $\theta_2 = 90°$, where ϵ is the field polarization direction. Results are presented as a function of θ_3 and for coplanar geometry. All cross sections are in units of b/(sr^{3}eV^2).

to 220°, again close to the angle that maximizes the third electron's distance from the fixed electrons. As the excess energy is decreased, we find that this peak moves towards an ejection angle of 180°, a direction that is well established at excess energies of 10 and 5 eV, and forms a clear T shape with the fixed electrons. At these lower excess energies, we also find a small peak along ejection angles of 270°. This smaller peak also corresponds to a T-shape ejection, but the magnitude of the peak along this direction is much smaller than the peak along 180°, unlike the case examined in Fig. 1, where the two peaks were of identical size. The difference in this case is due to the polarization direction of the radiation field; the ejection along the field (which is horizontal in all the plots shown here) is more probable than ejection perpendicular to the polarization direction. Ejection along the field polarization direction is also more likely in (two-electron) double photoionization of a $1s2s$ electron pair, as discussed previously [14].

As final evidence for the dominance of the T-shape breakup, we present in Fig. 3 angular distributions that are for a fixed relative angle between the two fixed electrons of $\theta_{12} = 90°$, in the coplanar geometry, as a function of the relative angle between electrons 2 and 3, at an excess energy of 5 eV. Figure 3(a) shows TDCC calculations that have been summed over all values of θ_1 from 0° to 180°, so that the influence of the polarization field on the angular distribution is effectively averaged over. The figure shows the angular distribution for equal energy sharing case (solid red line) and for all possible energy sharings (dashed line); both sets of calculations are quite similar. We find
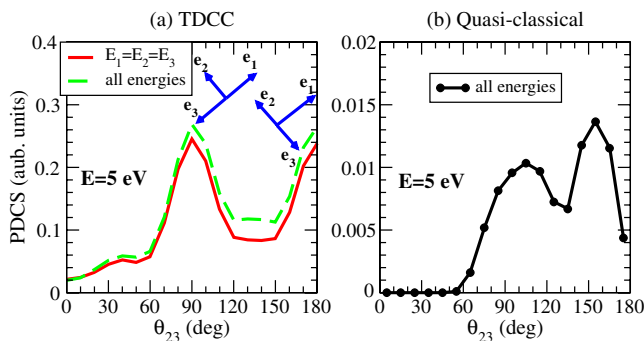

FIG. 3 (color online). (a) TDCC calculations of PDCS for triple photoionization of Li at a 5 eV excess energy, for fixed relative angle between electrons 1 and 2 of $\theta_{12} = 90°$, and as a function of the relative angle θ_{23} between electrons 2 and 3, all in the coplanar geometry. The cross section is summed over all possible θ_1 values with respect to the polarization direction (defined by $\theta_1 = 0°$). The red solid curve shows the equal energy sharing cross section and the green dashed curve shows the cross section summed over all possible electron energy sharings. (b) Quasiclassical calculations of the triple photoionization of Li where all electrons are ejected into a common plane. Only those events are included where the external product of two of the outgoing momenta vectors make an interelectronic angle between 87.5° and 92.5° with the third vector.

two prominent peaks in the distribution at $\theta_{23} = 90°$ and $\theta_{23} = 180°$; each of these corresponds to a T-shape breakup as indicated. The magnitude of the peaks at 90° and 180° are almost identical, showing that once the influence of the polarization direction is accounted for, the third electron is equally likely to form a T shape by moving antiparallel to electrons 1 or 2. Several further calculations performed in noncoplanar geometries (not shown) also find angular distributions that are similar to those shown in Fig. 3. We find that the T-shape break-up pattern is also evident for the angular distribution summed over all energy sharings (dashed line), allowing us to conclude that this break-up pattern is found at low excess energies irrespective of the energy sharing between the electrons. For such relative angle distributions, we may also compare with the predictions of quasiclassical calculations [8,9]. Figure 3(b) shows such a calculation where the electrons are ejected into a common plane [the polarization axis does not enter into the quasiclassical calculations so this plane cannot be identified with the coplanar case shown in Fig. 3(a)], for any possible energy sharing between the electrons. The quasiclassical prediction is also of two prominent peaks near relative angles of 90° and 180°, although not at quite the same relative angles as predicted in the TDCC calculations shown in Fig. 3(a). The difference between the TDCC quantal calculations and quasiclassical calculations may be due to the restriction made in the TDCC calculation to only a coplanar geometry, or it could be due to the neglect of the polarization axis influence within the quasiclassical approach. Convolution with the volume element $\sin\theta$ also leads to an appearance of the 180° peak at a smaller angle for the quasiclassical calculation. A complete set of TDCC calculations for all possible planes, which would be required for a direct comparison with the quasiclassical calculations [8,9], is a daunting task because it would require calculations for all possible relative angles for all three electrons, in all possible planes, and for all possible energy sharings. However, the good qualitative agreement between the TDCC calculations and quasiclassical predictions provides strong evidence for the dominance of the T-shape breakup at these excess energies.

Because we have now established that a T shape is the dominant break-up configuration at low excess energies, it is important to understand the physics behind such a pattern, as it contrasts with the general expectation that the Wannier threshold break-up pattern also holds a few eV above threshold, such as the 5 eV energy considered here. Our picture of the triple photoionization process is the following. The photon is absorbed by one of the $1s$ electrons and immediately ionized. Cross sections for single ionization from the $1s$ subshell at photon energies above 200 eV are several orders of magnitude larger than the cross sections for ionization from the $2s$ subshell. After this rapid ionization, there are several mechanisms through which the remaining $1s2s$ electron pair can escape.
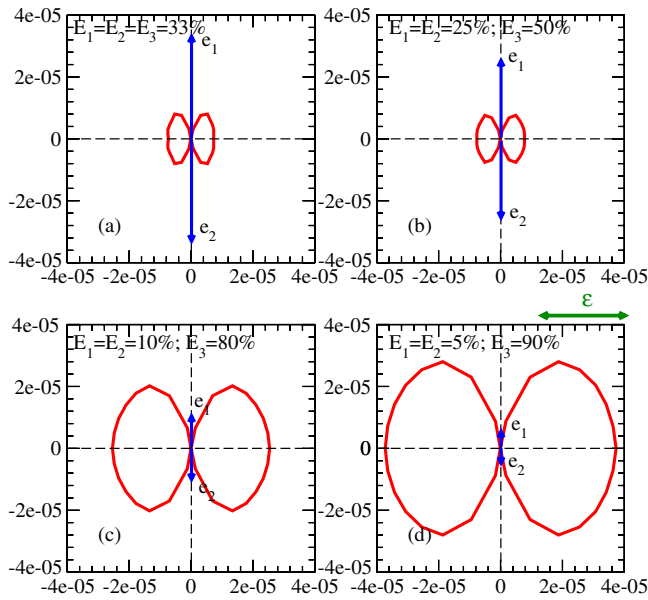
FIG. 4 (color online).   PDCS for triple photoionization of Li at an excess energy of 5 eV and for $\theta_1 = 90°$, $\theta_2 = 270°$, where ϵ is the field polarization direction. Results are presented as a function of θ_3, for coplanar geometry and for various excess energies as indicated. All cross sections are in units of b/(sr^{3}eV^2).

Shakeoff of the $2s$ electron after removal of both $1s$ electrons was proposed in early studies of this process [15,16], and a double shakeoff mechanism was postulated for the related process of triple photoionization of Be [17]. Both of these processes are expected to be significant at large photon energies, but not at the low excess energies currently considered. Successive knockout processes were also proposed [18], whereby the photoelectron knocks out the second $1s$ electron and then the remaining $2s$ electron as it leaves the atom. A similar process where the photoelectron knocks out the second $1s$ electron, and this second $1s$ electron removes the $2s$ electron was also considered. The signature of these break-up mechanisms should be reflected in the relative energies of the outgoing electrons; we should expect to find that triple ionization events where one electron has most of the excess energy, and the remaining two have smaller (approximately equal) energies, are more likely. This is indeed the case, as demonstrated in Fig. 4, where we show the angular distribution for fixed back-to-back electrons ($\theta_1 = 90°$; $\theta_2 = 270°$) and where the energy of the third electron is increased from 33% to 90% of the available excess energy. We find the shape of the distribution to be a broad T shape in all cases, but the magnitude of the cross section increases by over a factor of 4 as the third electron retains more of the available excess energy. Further analysis of the electron energetics at a fixed set of angles corresponding to the T shape reveals that the most probable configuration is where the third electron carries off most of the energy, and that the energy sharing between the remaining electron pair is less important. The $1s2s$ outgoing electron pair may have singlet or triplet characteristics, depending on their orientation with respect to the other $1s$ electron, but in either case, these electrons are likely to escape in a back-to-back configuration, because this maximizes their mutual angle, and because this electron pair has a total angular momentum of zero. Electron repulsion will also position this electron pair as far as possible from the direction of the first electron: this leads naturally to a T-shape break-up configuration. This conclusion was also previously reached in Ref. [9] where, after assuming that the $1s2s$ electron pair breaks up back to back, the T-shape break-up configuration was shown to be the most stable configuration. We finally note that consideration of the selection rules for two-electron ejection [19] that are very instructive in analyzing double photoionization angular distributions do not shed more light on the expected ejection patterns of the residual $1s2s$ electron pair. This is because the two electrons are in different subshells and because the overall symmetry of this $1s2s$ electron pair is $L = 0$ (because the photoelectron absorbs the photon and thus has the available one unit of angular momentum). The dominant emission pattern for the breakup of these two electrons is simply back to back, as we show.

Therefore, the T-shape break-up dynamic can arise from the rapid removal of a $1s$ electron followed by back-to-back ejection of the remaining electron pair. The T-shape formation results from the minimization of the energy of this configuration [9], which leads to the back-to-back electron pair oriented at 90° to the fast electron. At larger excess energies the T-shape breakup is also viable, but becomes one of several competing break-up configurations [10], resulting in more complicated angular distributions.

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