Double and Triple Photoionization of Ground-State Lithium

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The double and triple photoionization of ground-state lithium is investigated in the high-energy limit. Relative to the total photoionization cross section, the fraction of two-electron escape processes is 0.0325, while the fraction leading to triple escape is only 5.6×10^{-6}. Double ionization via Li^+ autoionizing states accounts for more than 40% of the two-electron escape processes. A comparison of the high-energy-limit calculations with experiments at 424 eV shows close agreement for double photoionization. A factor of 10 discrepancy exists for triple photoionization at 424 eV, however, which presumably indicates that the high-energy limit has not yet been reached. [S0031-9007(98)07694-7]

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Extensive research into the nature of two-electron ejection processes has dramatically improved theoretical and experimental capabilities just in the past few years [1–6]. Much of the experimental improvement derives from the higher brightness of third-generation synchrotron light sources. On the theory side, poor understanding of how to impose appropriate boundary conditions on a continuum state with two escaping electrons blocked progress for too many years. Some aspects require further improvement, of course, but our understanding is now in a far more satisfactory state than it was a mere five years ago. The recent progress opens up new questions about the ultimate capabilities and limitations of this new class of theoretical methods.

The improved capability of theory to predict the probability that one photon will eject two electrons from a simple system like He or H^- leads us to consider some theoretical issues relating to three-electron ejection processes. Experimental measurements of triple photoionization have recently been carried out for Li at photon energies well beyond the threshold for three-electron escape [7]. The only theoretical results available are calculations at the simplest nontrivial levels of approximation, based on the independent-electron model.

Three-electron systems immediately raise the possibility of qualitatively different physical processes possessing no analog in two-electron photophysics. Beyond the obvious additional process of triple photoionization, another major difference is the presence of indirect photoionization pathways in double photoionization. For instance, the initial photoionization of a three-electron atom like Li can produce a highly excited autoionizing state of Li^+. Since the autoionizing state of the ion will mainly decay by emitting another electron, this is a potentially important pathway to the double ionization continuum that is absent in helium. This subgroup of double photoionization events possesses a signature that is largely distinct from direct double photoionization, namely, the energy distribution between the two electrons is fixed by the energies of the autoionizing state and the energy of the Li^{++} state produced in the decay. At energies within the autoionization linewidth, of course, this two-step quantum mechanical amplitude $[h\nu + \mathrm{Li} \rightarrow (\mathrm{Li}^+)^{**} + e^- \rightarrow (\mathrm{Li}^+ + e^-) + e^-]$ can interfere with the direct amplitude $[h\nu + \mathrm{Li} \rightarrow \mathrm{Li}^+ + e^- + e^-]$. This discussion is meant to emphasize that, despite the recent progress in theoretical treatments of helium double ejection, new issues must still be addressed to handle multielectron ejection processes in Li and other multielectron atoms and ions.

A remarkable combination of theoretical and experimental results has already emerged in the low-energy limit. Klar and Schlecht predicted an $E^{2.162}$ threshold law for small E just above the triple ionization threshold [8]. This scaling law was experimentally confirmed in experiments on O and Ne [9], but at energies larger than 5.5 eV above threshold, a second threshold law was observed, $E^{1.86\pm0.09}$. A subsequent theoretical study confirmed this second threshold law, $E^{1.821}$, and explained it as excitation of a different mode of breakup [10].

In this Letter, we present theoretical results for double and triple photoionization of Li in the high-energy (but nonrelativistic) limit, adapting a formulation that was originally developed [11] to treat the high-energy limit of double photoionization. In this limit, the electron that absorbs the photon is emitted with a large energy, and its wave function is hence given by a plane wave. This approximation is valid, if the ejected-electron energy is much larger than the Li binding energy of 203.5 eV. We therefore expect the high-energy limit to be valid for photon energies beyond roughly 2000 eV.

In the high-energy limit, the nonrelativistic oscillator strength distribution for a two-electron atom behaves approximately as [12]

$$\frac{df^+}{d\epsilon} = C(ns)\epsilon^{-7/2} \tag{1}$$

with ϵ the photoelectron energy and $C(ns)$ a proportionality constant to leave the residual ion in the ns state, given in a.u. by [11]

$$C(ns) = \frac{128\pi Z^2}{3\sqrt{2}} |\langle \Psi(\vec{r}_1, \vec{r}_2)|\delta(\vec{r}_2)|\phi_{ns}(\vec{r}_1)\rangle|^2 \quad (2)$$

with ϕ_{ns} a hydrogenic wave function. The proportionality constant summed over all final states is then given by

$$C = \frac{128\pi Z^2}{3\sqrt{2}} \left| \int d\vec{r}_1 \Psi(\vec{r}_1, \vec{0}) \right|^2 . \quad (3)$$

For a three-electron system initially in the state $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)$, the equation for the sum over all proportionality constants changes into

$$C = \frac{64\pi Z^2}{\sqrt{2}} \left| \int d\vec{r}_1 \int d\vec{r}_2 \Psi(\vec{r}_1, \vec{r}_2, \vec{0}) \right|^2 \quad (4)$$

and the excitation of a residual Li^+ state is given by

$$C_n = \frac{64\pi Z^2}{\sqrt{2}} |\langle \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)|\delta(\vec{r}_3)|\Phi_n(\vec{r}_1, \vec{r}_2)\rangle|^2 \quad (5)$$

with Φ_n the nth state of Li^+. The change in coefficient between the two- and three-electron system is due to the normalization of the final-state wave function.

To determine the proportionality constants C_n, we first have to obtain the wave function for the Li ground state. Since the present interest is on the triple ionization of Li, it is crucial to include a complete description of single, double, and triple excitations. We have used a basis set including all partial waves up to $\ell = 2$, consisting of 17 B splines per partial wave defined in a box of 25 a.u. using an exponential distribution of the knot points, yielding an expansion length of 18 000 basis functions. After obtaining the ground-state wave function, it is projected onto a set of discretized Li^+ eigenfunctions as indicated in Eq. (5).

Only s wave functions have a nonzero value at $\vec{r} = 0$ and only the s-wave portions of the configuration interaction expansion contribute to electron ejection in the high-energy limit. The residual Li^+ eigenstates excited thus include only the ${}^1S^e$ and the ${}^3S^e$ symmetries. There is no interaction between these symmetries, and the following is thus performed twice, once for each symmetry. To obtain the proper Li^+ states, another B-spline basis set is employed, defined using a partially linear and partially exponential knot set distribution. The number of splines is increased to 58 per partial wave while the box size is varied from 30 to 200 a.u. in order to assess the convergence of the numerics. This different box size means that after obtaining the transition matrix elements, we have to transform these to the Li^+ basis set. This transformation only requires the calculation of overlap matrix elements.

After diagonalization of the Li^+ Hamiltonian, the excitation probability of each Li^+ box state is easily calculated. Now the correspondence of each Li^+ state with single, double, and triple photoionization has to be addressed unambiguously. The single photoionization can be derived by summing over all properly described Li^+ bound states including an n^{-3} extrapolation over the high n spectrum of the $1sns$ Rydberg series. The remaining photoionization originates from double and triple ionization.

Any photoionization event that produces a residual Li^+ eigenstate $|\alpha\rangle$ lying above the Li^{3+} threshold is assumed to contribute only to double or triple ionization, which should be an excellent approximation. To separate the double and triple ionization contributions to states with $E_\alpha > 0$, we ascertain for these states whether the less energetic electron is in a bound hydrogenic state or in a continuum state. To determine the probability that the less energetic electron is left in a box orbital $|\overline{n\ell}\rangle$, we have coherently transformed the amplitudes for excitation of Li^+ eigenstates $|\alpha\rangle$ having an energy $E_\alpha > E(\mathrm{Li}^{\,3+}) \equiv 0$ back into a representation $|\overline{n\ell n'\ell}\rangle$ formed with hydrogenic (noninteracting) box orbitals $|\overline{n\ell}\rangle$. This produces an amplitude given by the qualitative structure

$$A(\overline{n\ell}, \overline{n'\ell}) = \sum_{E_\alpha > 0} \langle \overline{n\ell n'\ell}|\alpha\rangle \langle \alpha|\delta(\vec{r}_3)|1s^2 2s\rangle . \quad (6)$$

The probability that the less energetic electron is in the box state $|\overline{n\ell}\rangle$ is given by

$$P(\overline{n\ell}) = \sum_{\overline{n'} \geq \overline{n}} \sum_{\overline{\ell}} |A(\overline{n\ell}, \overline{n'\ell})|^2 . \quad (7)$$

The final frame transformation to physical bound and continuum states should ideally be performed coherently [13]. For the present two-electron case, however, this would become a two-electron transformation, which is numerically complicated since the "exact" two-electron eigenstates are not known. This complication has forced us to perform instead a frame transition on the probabilities $P(\overline{n\ell})$, which, again, represent the contributions to double or triple ionization via the states $|\alpha\rangle$ with $E_\alpha > 0$. Near the Li^{3+} threshold these are smooth functions of $\overline{n}$. Since the coherence information has been lost after obtaining the values for $P(\overline{n\ell})$ following Eq. (7), the remaining single-electron frame transformation has been performed incoherently, as proposed in [14],

$$P(n\ell) = \sum_{\overline{n\ell}} P(\overline{n\ell}) |\langle n\ell|\overline{n\ell}\rangle|^2 , \quad (8)$$

where $|n\ell\rangle$ are the physical bound and continuum states of Li^{2+}. The triple ionization contribution is finally obtained by integrating over all states of the less energetic electron with energy $\epsilon > 0$,

$$P^{3+} = \sum_\ell \int_0^\infty P(\epsilon\ell)\, d\epsilon = \sum_{\overline{n\ell}} P(\overline{n\ell}) - \sum_{n\ell} P(n\ell) . \quad (9)$$

In practice, we have bypassed this continuum integration by subtracting the probabilities for bound-state excitation from the total continuum + bound-state excitation using a completeness argument. The resulting dependence on box size, which we interpret as a measure of the inaccuracy associated with this frame transformation, is small, approximately 5% of the triple ionization.

The calculation of the Li ground state in the three-electron B-spline approach gives an energy of $-7.476\,710$ a.u. Comparing the results with large-scale MCHF calculations [15] including a full description up to $\ell = 2$, $-7.476\,760$ a.u., shows good agreement for the energy of the Li ground state. The most important wave function contributions to the Li ground state are given in Table I.

In the calculation of the single photoionization of Li, it must be ensured that the summed excitation probability of the $1sns$ states of Li^+ has converged. We sum over all $1sns$ states that are contained within the box, and extrapolate over the remainder of the Rydberg series by assuming an n^{-3} behavior. By varying the box size, we find that a converged result is obtained at a box size of 200 a.u. Using this box size a value of the contribution of single ionization to the total ionization of 96.75% is obtained (see also Table II). This corresponds to a ratio of $(\sigma^{2+} + \sigma^{3+})/\sigma^+ = 0.0336$. As shown in Table II, triple ionization is a factor of 6000 smaller than the double ionization, so this ratio is essentially σ^{2+}/σ^+. In Table II, the probabilities for leaving Li^+ in various low-lying states are given as well.

The probability for exciting a triplet state is larger than for exciting a singlet state, 73.75% and 26.25%, respectively. This is due to the dominant emission of the $1s$ electron, which has the largest probability to be at $r = 0$. Emission of a $1s$ electron gives a 75% probability for leaving Li^+ in a triplet state and 25% for a singlet state. The emission of the $2s$ electron always leaves Li^+ in a singlet state, but from the expansion coefficients in Table I and the $n^{-3/2}$ behavior of the value of the ns wave function at $\vec{r} = 0$, it follows that this process is a factor of 60 less likely. This explains the relative magnitudes of the singlet and triplet state excitations.

The ratio between double ionization and single ionization is significantly larger for the ground state Li, 0.0336, than the one calculated for Li^+ in either the ground state, 0.0086, or the $1s2s\ {}^1S$ or ${}^3S$ states, 0.0120 and 0.0030, respectively [16]. In addition to direct double ionization, which accounts for all double ionization in two-electron systems, a second mechanism leading to double ionization in Li is hinted at in Table I. The coefficient of $1s2s({}^1S)3s$ is larger than 0.1. The electron most likely to be emitted from this configuration is the $1s$ electron, leaving Li^+ in the $2s3s$ state. This state lies above the $1s$ threshold of Li^{2+} and thus is metastable, decaying mainly by autoionization. Examining the $2\ell n\ell$ states of Li^+, we find that the $2\ell n\ell$ states contribute more than 1.4% to the total photoionization (see Table II), or over 40% of the total double ionization. This mechanism is thus essential for establishing accurate ratios between double and single photoionization of three-electron systems.

TABLE I. The most important contributions in the configuration interaction expansion of the Li ground-state wave function. The single-electron orbitals are Li^{2+} eigenfunctions.

Basis function	Amplitude
$1s^22s$	0.7165
$1s^23s$	−0.6721
$1s2s({}^{-1}S)3s$	0.1086

The ratio of triple and total ionization cross sections is also given in Table II. As a fraction of the total ionization, the singlet states of Li^+ contribute 3.1×10^{-6}, whereas the triplet states donate a comparable amount, 2.5×10^{-6}. The total contribution is 5.6×10^{-6}.

The accuracy of the triple ionization is studied by changing the box size for the initial state between 15 and 40 a.u. and the box size for the final state between 25 and 60 a.u. The number of splines for the final states has been varied between 38 and 58 per ℓ value. The largest uncertainty in the calculations derives from the box-size dependence, which is approximately at the 5% level.

Previously, Wehlitz *et al.* [7], using a shakeoff mechanism for the Hartree-Fock $2s$ orbital in the Li ground state and the ratio between double and single ionization for the Li^+ $1s^2$ core, estimated a ratio between triple and single photoionization of 1.5×10^{-5}. This model approximates the true physical situation in the high-energy limit by assuming that both $1s$ electrons are removed instantaneously. No interaction is included between any pair of electrons in the final state. In our high-energy limit, however, only the electron absorbing the photon is ejected instantaneously. The other emitted electrons are slow electrons, so that the Coulomb repulsion cannot be neglected for these electrons. We expect this Coulomb repulsion to reduce the

TABLE II. Probabilities for single, double, and triple ionization in the photoionization of ground-state Li. The individual contributions for excitation of various states of Li^+ are also indicated.

States	Contribution to total ionization %	Relative to single ionization
All singlet states	26.25	
All triplet states	73.75	
$1s^2\ {}^1S$	1.23	0.0127
$1s2s\ {}^1S$	20.89	0.2160
$1s3s\ {}^1S$	3.10	0.0321
$1s2s\ {}^3S$	54.09	0.5591
$1s3s\ {}^3S$	16.47	0.1702
Single ionization	96.75	1
$2s^2\ {}^1S$	0.36	0.0037
$2p^2\ {}^1S$	0.10	0.0011
$2s3s\ {}^3S$	0.66	0.0068
$2p3p\ {}^3S$	0.24	0.0025
Double ionization	3.25	0.0336
For singlet states	0.87	0.0090
For triplet states	2.38	0.0246
Triple ionization	0.000 56	0.000 005 8
For singlet states	0.000 32	0.000 003 3
For triplet states	0.000 24	0.000 002 5

TABLE III. Comparison of the photoionization properties in the high-energy limit with experimental ones at 424 eV.

Process	High-energy limit	Experiment at 424 eV[a]
σ^{2+}/σ^{+}	0.0337 ± 0.0003	0.0373 ± 0.002
σ^{3+}/σ^{+}	$(0.58 \pm 0.03) \times 10^{-5}$	$6.38 \pm 2.4 \times 10^{-5}$

[a] References [7,17].

shakeoff of the $2s$ electron, since the $2s$ orbital in $1s^2 2s$ should overlap the $2s$ orbital in $1s2s$ better than the hydrogenic $2s$ orbital. The present calculations therefore establish a factor of 3 smaller probability for triple ionization than the model estimates, since they describe the atomic structure more precisely.

A comparison with the experimental results in Table III, in which also the estimated accuracy of the calculations is indicated, shows that the high-energy-limit results are 15% off the experimental results at a photon energy of 424 eV for double ionization [17] and differ by about a factor of 10 for triple ionization [7]. The comparison of the high-energy limit and the experimental results at 424 eV is, however, not obvious. For He, the difference between the maximum contribution from double ionization to the total photoionization and the high-energy limit are a factor of 2.5 for $1s^2$, a factor of 4 for $1s2s\ {}^1S$, and a factor of 2 for $1s2s\ {}^3S$ [5,6,18]. The agreement between experiment and theory for the importance of double ionization in Li is therefore surprising. However, the excitation of autoionizing states is an important process leading to double ionization. This process is absent in He, and could significantly change the behavior of the double photoionization, both at the high-energy limit and at lower photon energies. The high-energy limit is clearly not valid for the triple ionization probability with a difference of a factor of 10. Regarding triple ionization as a product of two double ionization processes, we can use the He data given above to estimate a similar factor of 10 difference between the high-energy limit and the available finite-frequency experimental results for Li.

In conclusion, we have described an approach for determining the contributions of single, double, and triple photoionization to Li photoionization in the high-energy limit. The use of B-spline basis sets and transformation techniques allow us to accurately separate the different degrees of ionization. The predicted ratio between double and single ionization is 0.0336, while the predicted ratio between triple and single ionization is 5.8×10^{-6}. By examining the contribution from low-lying autoionizing states to the double ionization, it is found that an indirect mechanism through excitation of doubly excited states accounts for more than 40% of the double ionization. The triple ionization is a factor of 6 smaller than estimated in [7] based on a shakeoff mechanism, which suggests that full inclusion of the two-electron interactions in both the initial and final state is required in order to estimate the triple ionization cross sections.

It is difficult to compare these predictions with experiment, because the lone experiment has been performed at comparatively low photon energies. The experimental ratio, $\sigma^{2+}/\sigma^{+} = 0.0373 \pm 0.002$, at a photon energy of 424 eV [7] already agrees with the high-energy limit predicted here. This agreement between our asymptotic value and the experiment may be fortuitous because of the highly different photon energies. For the ratio σ^{3+}/σ^{+}, a difference of a factor of 10 is observed. If both the experimental measurement and theoretical high-energy limit are correct, this suggests an interesting qualitative difference between double and triple ionization. In He, the ratio between the maximum value of σ^{2+}/σ^{+} and its high-energy limit is around 2.5, whereas in Li the ratio between the maximum value of σ^{3+}/σ^{+} and its high-energy limit is apparently greater than 10. A nontrivial task is now to extend the double-ionization R-matrix techniques at lower frequencies to see whether this approach can describe triple ionization processes. The importance of autoionizing states versus the direct double and triple ionization processes remains important to assess at photon energies closer to those employed in the experiment.

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