Asymptotic ratios of single, double, and triple photoionization for lithium at high energies

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A method is proposed for calculating the ratio of triple to double ionization and a number of calculations of the ratios of double to single and triple to double ionization are given for neutral and singly ionized lithium. [S1050-2947(99)08306-7]

For helium, it has been established by a number of detailed calculations that the asymptotic ratio of double to single photoionization at high energies is 1.68% [1–3]. Although there is some controversy as to the ratio at higher energies where double ionization via Compton scattering is the dominant process, experiments seem to confirm that the photoionization cross section is approaching this limit at energies below 1 keV where the cross section for ionization via Compton scattering is small.

Recently, the ratio of double to single photoionization of lithium has been measured in the energy range from threshold (81.01 eV) [4] to 424 eV and, in addition, the ratio of triple to single ionization has been obtained from the threshold (203 eV) to 424 eV [5]. While no calculations of the cross sections for double or triple ionization of lithium are available, it should be possible to predict the asymptotic ratios of these cross sections in the high-energy limit in a manner similar to that used for two electron systems and, in fact, some estimates of these ratios have already been made [5,6]. It is the purpose of this paper to show how these estimates can be improved.

The calculation of the asymptotic ratio of multiple to single ionization for any atomic system is based on the assumption that one electron leaves the atom so rapidly that it does not interact with the rest of the system. Under these circumstances, the probability of the atom being left in state *n* will be [1]:

$$P_n^+(k) = \frac{|\langle \phi_n | \psi_0(k) \rangle|^2}{\langle \psi_0(k) | \psi_0(k) \rangle}. \qquad (1)$$

Here k is the momentum transferred to the outgoing electron, ϕ_n is the $N-1$ electron wave function representing a state n when one electron is ejected, and ψ_0 is the partial Fourier transform of the initial N electron atom; i.e.,

$$\psi_0(r_1, r_2, \ldots, r_{N-1}, k) = \int e^{-k \cdot r_N} \psi_0(r_1, r_2, r_N) dr_N. \qquad (2)$$

Using Eq. (1), the ratio of multiple to single ionization can be calculated simply by setting the total probability of ionization equal to 1. The ratio of multiple ionization to single ionization is then

$$P^{+m}(k)/P^+(k) = \frac{1 - \sum_n P_n^+(k)}{\sum_n P_n^+(k)}, \qquad (3)$$

where the sum is over all possible singly ionized bound states.

Equation (3) is useful since, in order to calculate the ratio of multiple to single ionization, one need not calculate ionization cross sections. All that is needed are accurate bound state wave functions for the initially ionized N electron system and for all of the discrete states of the $N-1$ ionized system. For two electron systems this can be done quite accurately since the single-electron ionized core wave functions are simply hydrogenic wave functions and highly accurate wave functions are available for two electron systems [7].

In order to obtain estimates of the high-energy limit (as $k \to \infty$), two procedures can be used, namely;

(A). One can integrate over the momentum distribution of Eq. (2). In this case the denominator of Eq. (1) becomes unity and Eq. (1) reduces to

$$P_n^+ = \int |\langle \phi_n | \psi_0 \rangle|^2 dr_N. \qquad (4)$$

(B). One can evaluate the partial Fourier transform of Eq. (2) and take its high-energy limit [1,8,9]. Eq. (1) may then be written as

$$P_n^+ = \frac{|\langle \phi_n(r_1, r_2, \ldots, r_{N-1}) | \psi_0(r_1, r_2, \ldots, r_{N-1}, 0) \rangle|^2}{\langle \psi_0(r_1, r_2, \ldots, r_{N-1}, 0) | \psi_0(r_1, r_2, r_{N-1}, 0) \rangle}. \qquad (5)$$

Equation (5) is the correct form to use for high-energy photoionization since the process takes place near the nucleus [8,9]. A number of calculations using it have been performed for two-electron systems [1,3,10]. Equation 4 has been used for estimates of the high-energy limit of Compton scattering from helium [11,12]. For wave functions, which are products of orbitals, Eqs. (4) and (5) give identical results since orbitals evaluated at the origin in Eq. (5) cancel in numerator and denominator. Equation (5) has also been used to obtain estimates of the ratio of multiple to single ionization of lithium [6].

In order to estimate the ratio of triple to double ionization for three-electron systems, it is desirable to have a formalism

similar to that outlined above for the ratio of multiple to single ionization. In analogy with the above, if we suppose that two electrons leave the system, the probability of the ion remaining in a doubly ionized state n may be written as

$$P_n^{++}(k_1,k_2) = \frac{|\langle \phi_n | \psi_0(k_1,k_2)\rangle|^2}{\langle \psi_0(k_1,k_2) | \psi_0(k_1,k_2)\rangle}. \tag{6}$$

Equation (6) is now a function of two momentum variables, k_1 and k_2, and $\psi_0(k_1,k_2)$ is now a partial Fourier transform of the initial state wave function over two variables that represent the momenta of the two emitted electrons and ϕ_n is a wave function representing a doubly ionized state.

There are three ways Eq. (6) may be further approximated to obtain the high-energy limit of the probability of a doubly charged ion being left in a state n. In analogy to Eq. (4), one can integrate over the momentum distributions of both electrons. In this case, Eq. (6) reduces to

$$P_n^{++} = \int \int |\langle \phi_n | \psi_0 \rangle|^2 dr_{N-1} dr_N, \tag{7}$$

where the bracket is evaluated over $N-2$ coordinates. In analogy to Eq. (5), if we assume that both outgoing electrons are fast, Eq. (6) reduces to a form similar to Eq. (5) where two electrons are assumed to be emitted from the region near the nucleus.

Neither of these two forms seem to be appropriate to photoionization in the energy range below 10 keV where

TABLE I. Ratios of double to single ionization for Li+ computed using various bound-state wave functions. The columns labeled $1s$ and $2s-\infty s$ give the probability (in %) of being left in the $1s$ or the sum of all other ns states when single ionization occurs. $\delta^3(r)$ is the relative probability of one electron being at $r=0$. Energy is the total energy of the bound state in atomic units.

Bound state	Ratio (%)	$1s$ (%)	$2s-\infty s$ (%)	$\delta^3(r)$	Energy
Hylleraas	0.89	97.15	1.95	6.659	7.2799
(20 term) [3,7]					
Ref. [6]	0.85				
Hylleraas [15]					
(4 term)	0.43	98.09	1.48		
HF (this paper)	0.30	98.65	1.95	6.845	7.2364
UHF [16]	0.58	95.98	3.44	6.69	7.2364
Hylleraas [17]					
(7 term)	1.04	95.34	3.63	6.55	7.2788
Exact [7]				6.852	7.2799

experiments are currently being performed, since experimentally it is known that when double ionization takes place, the emitted electrons share the available energy unequally, i.e., one is fast and the other slow [13]. To the extent that this is so, one can ignore the correlation between the two ejected electrons and evaluate the limit by integrating over the momentum distribution of one (slow) electron and assume that the fast electron is emitted from the region near the nucleus. Under these assumptions, Eq. (6) reduces to

$$P_n^{++} = \frac{\int |\langle \phi_n(r_1,r_2,\ldots,r_{N-2}) | \psi_0(r_1,r_2,\ldots,r_{N-1},0)\rangle|^2 dr_{N-1}}{\langle \psi_0(r_1,r_2,\ldots,r_{N-1},0) | \psi_0(r_1,r_2,\ldots,r_{N-1},0)\rangle}. \tag{8}$$

The ratio of multiple (triple or greater) to double ionization is then given by

$$\frac{P^{+m}}{P^{++}} = \frac{1 - \sum_n P_n^{++}}{\sum_n P_n^{++}}. \tag{9}$$

For lithium, accurate estimates of the probability of a doubly charged ion being left in a discrete state when two electrons are removed can be calculated using Eq. (8) [or alternatively Eq. (7)], since, in this case the $N-2$ electron states of the doubly charged ion will be one-electron hydrogenic wave functions and highly accurate ground-state wave functions for lithium are available. Note that, as for two-electron systems, if product wave functions are used for the lithium ground state and $2s$ ionization is ignored Eqs. (7) and (8) give identical results.

Two things are to be noted about Eqs. (5) and (8), which give, respectively, the probability of leaving a singly or doubly charged ion in a specific state following photoionization. The numerator is simply the square of the overlap of a wave

function representing a singly or doubly charged ion with a ground-state wave function evaluated with one electron at the origin. The denominator is the same in both cases and is simply the probability of one electron being at $r=0$, i.e., $\sum_i \langle \delta^3(r_i)\rangle$. Accurate values of this quantity are available for both two- [7] and three-electron [14] systems and can be used to judge the accuracy of other calculations.

The formalism described above has been applied using a number of wave functions available in the literature to obtain ionization ratios for neutral and singly ionized lithium. Similar results for helium are available in Ref. [1].

For singly ionized lithium there have been no experiments and only two calculations have been reported [3,6]. Some additional results for Li$^+$ ground-state ionization are given in Table I along with these previous estimates. One would expect that the most accurate value of the double to single ionization ratio is that of Dalgarno and Sadeghpour [3] based on the ground-state wave functions of Hart and Herzberg [7]. Note, however, that the value of $\sum_i \delta(r_i)$ is 3% lower than the ''exact'' value from Ref. [7]. If their value of the Li^{++}/Li$^+$ ratio is reduced by 3% it is in exact agreement with the value reported in Ref. [6]. The Hartree-Fock value

TABLE II. Percentages left in various final states of Li and the ratio of multiple to single ionization when single ionization of neutral lithium occurs.

Final State	% left in final state	
	(This paper)	(Ref. [6])
$1s^2\ ^1S$	1.22	1.23
$1s2s\ ^3S$	52.98	54.09
$1s2s\ ^1S$	21.61	20.89
$1s3s\ ^3S$	18.65	16.47
$1s3s\ ^1S$	2.88	3.10
$4s-\infty s\ ^{1,3}S$	0.88	2.20
Sum	98.22	96.75
Multiple ionization	1.78	3.25
$(Li^{++}+Li^{+++})/Li^+$	1.81	3.36

TABLE III. Percentages left in various final states of Li^{++} when double K-shell ionization takes place. Note: The value for triple ionization given in Ref. [5], .17% neglected some of the contributions of high-lying states and is incorrect.

Final state	% left in final state			
	HF (this paper)	HF [18]	UHF [19]	Ref. [6]
$1s$	0.1799	0.1874	0.1752	
$2s$	51.6877	51.6692	51.7095	
$3s$	47.6079	47.6172	47.5829	
$4s$	0.2928	0.2512	0.2913	
$5s-\infty s$	0.1842	0.1897	0.1849	
Sum	99.9535	99.9147	99.9421	
Triple ionization and Li^{+++}/Li^{++}	0.0465	0.0853	0.0579	0.0172

for the ratio is approximately $\frac{1}{3}$ of this, but the other values are closer. The table also shows why these deviations occur. As is the case for helium, over 90% of the ions are left in the ground state, but deviations of a few percent occur between the various calculations. It is interesting to note that the wave functions of Refs. [16] and [17], which include correlation, give a lower estimate of leaving the ion in its ground state but a higher value for discrete excitation.

To the extent that intershell correlation is not important, one can estimate the relative probability of $2s$ to $1s$ ionization as proportional to the probabilities of $2s$ and $1s$ electrons being at $r=0$. For lithium, the Hartree-Fock values are $\delta_{1s}(r)=6.8307$ and $\delta_{2s}(r)=.1660$. Their sum, 13.8274, is close to the exact value, 13.841 82 [14]. Using these values, the relative probability of $2s$ to $1s$ ionization is 1.22% in almost exact agreement with the recent calculation of Ref. [6].

In order to estimate the multiple-ionization probability term dependent numerical Hartree-Fock (HF) calculations for the $1sns\ ^{1,3}S$ states of Li^+ and the lithium ground state were made and Eq. (5) used to compute the probability of leaving the ion in singly excited states. The results were modified by using the ratios of the exact value of the denominator to the Hartree-Fock value i.e., 13.8272/13.841 82 to obtain a better estimate. The results are compared in Table II with the recent results of Ref. [6]. The result for the probability of multiple ionization, 1.78% is approximately $\frac{1}{2}$ of the value of Ref. [6], 3.25%.

The main purpose of the calculations reported above was to indicate that Hartree-Fock estimates made using Eqs. (4) and (5) provide a reasonably accurate estimate of the probability of leaving an ion in a singly excited state. However, since the probability of multiple ionization is small, deviations of a few percent in the estimates of the probability of leaving the singly charged ion in a particular excited state can lead to large deviations in the ratio of multiple to single ionization when Eq. (3) is used to obtain the ratio. One would expect the same to be true of the probability of leaving the ion in a doubly ionized state using Eq. (9).

If it is assumed that both K-shell electrons in lithium are ejected followed by relaxation or shakeoff of the outer valence electron when double ionization occurs, then the probability of being left in an excited state of Li^{++} given by Eq.

(8) reduces to a simple overlap of hydrogenic s orbitals of Li^{++} and the neutral $2s$ orbital and this is the approach used in the estimates given in Ref. [5]. This is expected to be a good approximation for the probability of the doubly charged ion being left in a particular state since it is known from previous work that in lithium there is little correlation between core and valence electrons [17]. The good agreement of the probability of the ion being left in its ground state when single ionization occurs of the simple Hartree-Fock estimate (which ignores intershell correlation) with the result of the more sophisticated calculation of Ref. [6] seems to confirm this.

In order to estimate the ratio of triple to double ionization of lithium calculations of the probability of being left in particular states when double ionization occurs in the K shell have been made using three different Hartree-Fock bound state wave functions and the results are given in Table III. The table shows that, although all of the calculations yield essentially the same results for the probability of leaving the doubly charged ion in a particular state, the estimates of the probability of triple ionization are quite different owing to the small probability of triple ionization. However, all of the estimates are larger than the value reported in Ref. [6] using an alternative method.

The results shown in Table III illustrate the difficulty in estimating the probability of multiple ionization using Eq. (9) when the probability of multiple ionization is small. In order to achieve an accuracy of 5% in the triple to double ratio shown in Table III one would have to be able to calculate the probability of a doubly charged ion being left in the principal excited states, $2s$ and $3s$ to an accuracy of 2×10^5. Clearly, none of the three calculations are this accurate. The same considerations appear to apply to the result of Ref. [6] where the probability of bound-state excitation is calculated and the probability of triple ionization is obtained by subtraction.

Clearly more calculations are needed in order to obtain definitive ratios for lithium. For the triple to double ratio, such calculations provide a severe test of the accuracy of ground-state wave functions since the wave function must be accurate near the origin as well as at distances, which are important for the calculation of the probability of being left

in low-lying excited states. Additional calculations using highly accurate ground-state wave functions of neutral lithium [6,14,20] would be useful. For the multiple to single ratio, one needs accurate wave functions for both the ground state and the singly excited S states of Li$^+$. The only calculation at present beyond the Hartree-Fock level is that of Ref.

[6]. Additional calculations here would be useful to access the accuracy of their result.

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