Electron-impact double ionization of Li^+

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Electron-impact direct double ionization (DDI) of the ground-state Li^+ ion is investigated using an approach which takes into account contribution from ionization-ionization, ionization-excitation-ionization, and excitation-ionization-ionization processes. Reasonable agreement with the experimental data is obtained when bound electrons of the Li^+ ion are considered as residing on the opposite sides of the nucleus. It is shown that distribution of the excess energy between the scattered and the ejected electrons, which participate in the next step of ionization, has a significant effect on the DDI cross sections. Better agreement with the experiment is obtained when electrons share the excess energy. The DDI study reveals the dominant role of the ionization-ionization process for the Li^+ ion.

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I. INTRODUCTION

Electron-impact single and multiple ionizations of atoms and ions are some of the most fundamental atomic processes that provide knowledge about the structure and dynamics of atomic systems. The ionization cross sections are needed for modeling spectra from high-temperature plasmas. Such studies are of great importance in astrophysics and controlled nuclear fusion research. Among multiple ionization processes, double ionization has a major impact on the ionization state distribution of ions in the plasma and environments with an abundance of energetic electrons.

Double ionization can be described by direct and indirect processes. The indirect process is determined by removal of an inner-shell electron and subsequent autoionization. The direct process occurs when two electrons of the target are simultaneously ejected to continuum. Only the direct process takes place in two-electron systems because the indirect process includes autoionization which requires two electrons after the first ionization.

During the direct double-ionization (DDI) process, simultaneous emission of the two target electrons is stimulated by the incident electron. Here one has to deal with a four-body Coulomb breakup problem. Currently, only the time-dependent close-coupling (TDCC) method provides good agreement with absolute experimental measurements of total cross sections for double ionization of light atoms and ions [1–5]. However, investigation of the electron-impact double ionization of atoms and ions using the TDCC approach is a challenging computational task, therefore this method is ineffective for more complex systems.

From the classical point of view, the DDI mechanisms have been determined by Gryziński [6]. Successive collisions of the ionizing incident particle with two electrons of the system and collision between the electron being ejected and one of the remaining target electrons have been considered to be the causes of the formation of a doubly ionized atomic system. However, this simplified approach failed to provide good agreement with experiment in many cases for various reasons [7–11].

Recently it was suggested that disagreement between experimental results and theoretical cross sections calculated using a few-step approach arises from the omitted population of states produced by the first interaction of the incident electron which leads to excitation or ionization of the atomic system [12]. Furthermore, excitation-ionization-ionization (EII) and ionization-excitation-ionization (IEI) processes, which were not taken into account in the previous investigations, have to be considered in addition to ionization-ionization (II). This approach was successfully employed to study DDI cross sections for the light ions: O^{1+}, O^{2+}, O^{3+}, C^{1+}, and Ar^{2+} [12]. However, two-electron ions are investigated here.

The aim of this paper is to study the electron-impact double ionization of the Li^+ ion using the two- and three-step approaches, i.e., by analyzing the II, EII, and IEI processes. From the theoretical point of view, it is important to estimate the limits of this approach because electrons in the two-electron system cannot be described as equally distributed in the cloud of electrons due to strong correlation effects. Therefore, the question whether a few-step approach is valid for such systems still needs to be answered. Furthermore, the large contributions from the EII and IEI processes for the light ions [12] contradict the initial idea of Gryziński [6] where results for the two-electron system were presented. Good agreement with experiment for He [6] suggested that the role of these two processes is very small. Finally, it was previously demonstrated that one of the electrons tends to take all the excess energy after the first ionization at the lower energies of the incident electron while they share the excess energy at the higher energies [12]. However, the reasons for these effects are still unclear.

The remainder of this paper is organized as follows. Section II gives an overview of the theoretical method, the obtained double-ionization cross sections for Li^+ are compared with crossed-beam measurements in Sec. III, and Sec. IV provides some final conclusions and directions for future work.

II. THEORETICAL APPROACH

The two- and three-step approaches proposed previously [12] are applied to study the electron-impact double-ionization cross sections for the Li^+ ion. These approaches deal with an

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ensemble of ions or atoms that undergo collisions with the electrons resulting in excitation of some ions to the higher-energy levels and ionization of the others. DDI is described by the ionization-ionization, ionization-excitation-ionization, and excitation-ionization-ionization processes. Population of the ions in the various energy levels after the first collision with the incident electron is taken into account since the strengths of the further processes that result in the double ionization depend on the populations of the levels from which these processes start.

The DDI process corresponding to ionization from level i to level f through the II path can be expressed by the equation,

$$\sigma_{if}^{\mathrm{DDI-II}}(\varepsilon_0) = \sum_j \sigma_{ij}^{CI}(\varepsilon_0) p_j(\varepsilon_0) \frac{\sigma_{jf}^{CI}(\varepsilon_1) N_{nl}^{2/3}}{4\pi \bar{R}_{nl}^2}. \quad (1)$$

Here $p_j(\varepsilon_0)$ is the population of level j from which the further ionization process starts

$$p_j(\varepsilon_0) = \frac{\sigma_{ij}^{CI}(\varepsilon_0)}{\sum_k \sigma_{ik}^{CI}(\varepsilon_0) + \sum_m \sigma_{im}^{CE}(\varepsilon_0)}.$$

$\sigma_{ij}^{CI}(\varepsilon_0)$ is the cross section of the first ionization process from level i to level j by an incident electron with energy ε_0; $\sigma_{im}^{CE}(\varepsilon_0)$ is the electron-impact excitation cross section from the initial level i to level m; $\frac{\sigma_{jf}^{CI}(\varepsilon_1) N_{nl}^{2/3}}{4\pi \bar{R}_{nl}^2}$ is the probability of removing the additional electron from the nl shell by the scattered or ejected electron having energy ε_1 when the atomic system undergoes a transition from level j to level f assuming that the density of the electrons in the shell is uniform (i.e., $\bar{R}_{nl} \approx \bar{r}_{nl} N_{nl}^{1/3}$, where $\bar{R}_{nl}$ is the mean distance of the electrons from the nucleus, $\bar{r}_{nl}$ is the average distance among the electrons in the nl shell, and N_{nl} is the number of the electrons in the nl shell). To obtain the total DDI cross sections, the summation over all final levels f has to be performed.

The equation for DDI through the EII path can be written as

$$\sigma_{if}^{\mathrm{DDI-EII}}(\varepsilon_0) = \sum_{kj} \sigma_{ik}^{CE}(\varepsilon_0) p_k(\varepsilon_0) \frac{\sigma_{kj}^{CI}(\varepsilon_1) N_{nl}^{2/3}}{4\pi \bar{R}_{nl}^2} \times p_j(\varepsilon_1) \frac{\sigma_{jf}^{CI}(\varepsilon_2) N_{n'l'}^{2/3}}{4\pi \bar{R}_{n'l'}^2}. \quad (2)$$

Here $p_k(\varepsilon_0)$ is the population of the excited level k from which the further ionization-ionization process starts; $\varepsilon_1 = \varepsilon_0 - \Delta E_{ik}$, ΔE_{ik} is a transition energy, and ε_2 is the energy of the scattered or ejected electron. The population of levels $p_j(\varepsilon_1)$ obtained after the second step is taken as 1 in order to simplify calculations. In any case, as we will see below, the contribution from the three-step processes is very small. During the first ionization process the electron is removed from the nl shell, whereas the next electron is taken from the $n'l'$ shell. Both electrons can be removed from the same shell as well, i.e., $nl = n'l'$.

Similarly, the cross section for the DDI process through the IEI path can be written as

$$\sigma_{\mathrm{if}}^{\mathrm{DDI-IEI}}(\varepsilon_0) = \sum_{kj} \sigma_{ik}^{CI}(\varepsilon_0) p_k(\varepsilon_0) \frac{\sigma_{kj}^{CE}(\varepsilon_1) N_{nl}^{2/3}}{4\pi \bar{R}_{nl}^2} \times p_j(\varepsilon_1) \frac{\sigma_{jf}^{CI}(\varepsilon_2) N_{n'l'}^{2/3}}{4\pi \bar{R}_{n'l'}^2}. \quad (3)$$

Here $\frac{\sigma_{kj}^{CE}(\varepsilon_1) N_{nl}^{2/3}}{4\pi \bar{R}_{nl}^2}$ is the probability to excite an electron from the nl shell of level k to level j by the scattered or ejected electron having energy ε_1. Again, the population of levels $p_j(\varepsilon_1)$ obtained after the second step is taken as 1 in order to simplify calculations.

It has to be noted that electron-impact excitation (σ^{CE}) and ionization (σ^{CI}) cross sections can be obtained using any available approximation. The distorted-wave (DW), binary-encounter dipole (BED), and Coulomb-Born (CB) approximations have been applied in this paper for single-ionization studies. The DW approximation is used to obtain electron-impact excitation cross sections.

Energy levels, autoionization transition probabilities, electron-impact excitation, and single-ionization cross sections have been calculated using the Flexible atomic code [13], which implements the Dirac-Fock-Slater approach. Continuum orbitals of incident and scattered electrons are evaluated in the potential of the ionizing ion since this approach provides a reasonable agreement with experimental measurements for the single-ionization cross sections obtained in the distorted-wave approximation for the Li^+ ions. An alternative approach (i.e., evaluation of the orbitals in the potential of the ionized ion) underestimates the experimental single-ionization cross sections for the Li^+ ion [14] by approximately 30% at the peak value and by approximately 50% at the larger energies of the incident electron.

III. RESULTS

Our study includes energy levels of the $1s^2$ and $1snl$ configurations ($0 < n \leqslant 4, l < n$) for the Li^+ ion and the $n'l'$ ($n' \leqslant 4$, $l' < n'$) configurations for Li^{2+}. Electron-impact ionization and excitation cross sections among the all considered levels are investigated. In addition, the populations of the levels for the Li^+ and Li^{2+} ions determined by the first interaction of the incident electron with the system are calculated for the studied energies. The theoretical single- and double-ionization thresholds for the Li^+ ion (74.45, 196.91 eV) are in close agreement with values provided by NIST (75.64, 198.09 eV) [15].

Electron-impact single ionization from the ground states of the Li^+ and Li^{2+} ions are studied using the DW, BED, and CB approximations. This study is performed in order to estimate which one gives the better agreement with available experimental data.

For the single ionization of the Li^+ and Li^{2+} ions, all approximations provide similar results at the energies near threshold (Figs. 1 and 2). At the peak, all calculations overestimate the experimental single-ionization cross sections for the Li^+ ion [14] and underestimate them at the higher energies

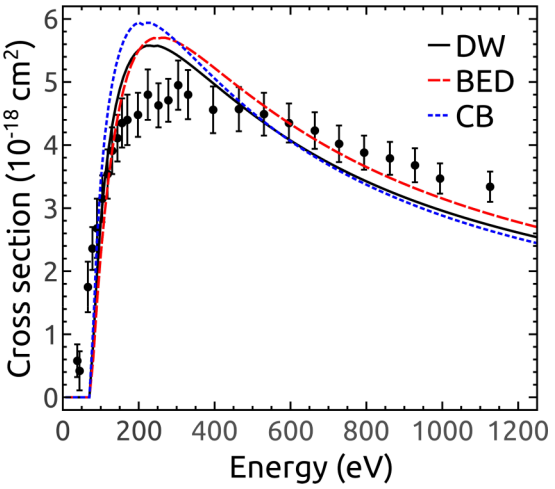

FIG. 1. Electron-impact single-ionization cross sections for Li^+. DW, cross sections obtained using the distorted-wave approximation; BED, cross sections obtained using the binary-encounter-dipole approximation; CB, cross sections obtained using the Coulomb-Born approximation. Experiment: solid circles [14].

of the incident electron (Fig. 1). The largest discrepancies are observed for the CB approximation.

For the Li^{2+} ion, all approximations overestimate the experimental cross sections [16] at the energies close to peak (Fig. 2). This is especially the case for the BED data, which overestimate the experimental cross sections not only at the peak, but also slightly at the higher energies where good agreement is seen for the DW and CB values.

Since the DW approximation provides reasonably good agreement with the experimental data for single-ionization cross sections of the Li^+ and Li^{2+} ions, it is applied for the calculations of the DDI cross sections presented further in this paper.

Two limiting cases of the energy distribution of the scattered and ejected electrons after the first ionization process are

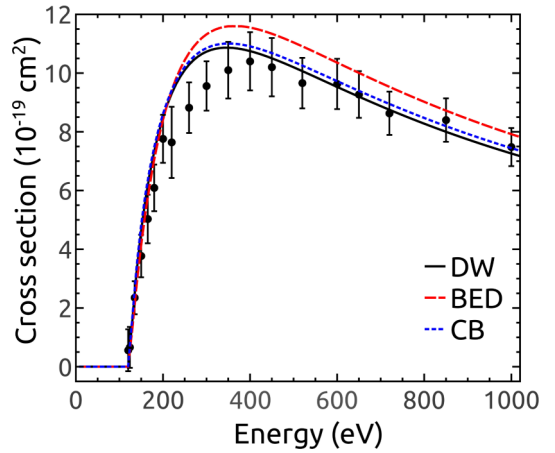

FIG. 2. Electron-impact single-ionization cross sections for Li^{2+}. DW, cross sections obtained using the distorted-wave approximation; BED, cross sections obtained using the binary-encounter-dipole approximation; CB, cross sections obtained using the Coulomb-Born approximation. Experiment: solid circles [16].

investigated. As was mentioned above, in one case, the excess energy is taken by one of the electrons participating in the collision, whereas in the other case, the ejected and scattered electrons equally share the excess energy. In the first case, only one electron participates in the further process and, on its way out, removes the second target electron, whereas in the second case, one of two available electrons can collide with any remaining target electron and remove it from the system. It was demonstrated previously for the O^{1+}, O^{2+}, O^{3+}, C^{1+}, and Ar^{2+} ions [12] that the better agreement with the experiment for the higher energies of the incident electron was obtained when it was assumed that the scattered and ejected electrons share the excess energy. On the other hand, mainly one of the electrons takes all the excess energy and participates in the further processes at the lower energies of the incident electron.

Unfortunately, the electron-impact DDI cross sections for the ground state of the Li^+ ion obtained using the two- and three-step approaches strongly overestimate the values from the crossed-beam measurements [17] if assumed that the density of electrons in the shell is uniform. The experimental cross sections reach a maximum value of about 1.0×10^{-20} cm^2 at 600 eV electron energy, whereas theoretical calculations show that peak corresponds to 8.7×10^{-20} cm^2 in a case when electrons equally share the excess energy.

One of the reasons for disagreement of theoretical cross sections with the experimental measurements [17] can be related to the fact that an assumption of uniform distribution of electrons is not valid for the two-electron system. Furthermore, only one bound electron is left after the first ionization process in such a system, and its position can be strongly affected by the other electrons. Therefore, it is suggested that for the two-electron system we have to consider the bound electrons positioned on the opposite sides of the nucleus. In this case, the average distance between the two bound electrons is $\bar{r}_{nl} \approx 2\bar{R}_{nl}$.

The electron-impact DDI cross sections from the ground level of the Li^+ ion obtained using the two- and three-step approaches with an assumption that bound electrons reside on the opposite sides of the nucleus are compared with the experimental values from the crossed-beam measurements [17] in Fig. 3. Surprisingly, much better agreement among the theoretical and the experimental values is obtained in this case. Two limiting cases of the energy distribution of the scattered and ejected electrons are presented: scattered and ejected electrons share the excess energy (DDI^1), and one of the electrons takes all the available energy (DDI^2). On the other hand, large discrepancies between experiment and calculations [7,8] based on the modification of Gryzinski's model are observed. This shows that the previously used analytic expressions do not correctly reproduce the single-ionization cross sections for the Li^+ and Li^{2+} ions. Furthermore, populations of levels are omitted in the previous studies [7,8].

It has to be noted that the largest contribution to DDI comes from the II process. The role of the IEI and EII processes is relatively insignificant. These findings are consistent with study of Gryziński [6]. The II process provided quite good agreement with experiment for He and, therefore, three-step processes have not been investigated [6].

The study of the population of levels reveals that electron-impact ionization from the ground level of the Li^+ ion mainly

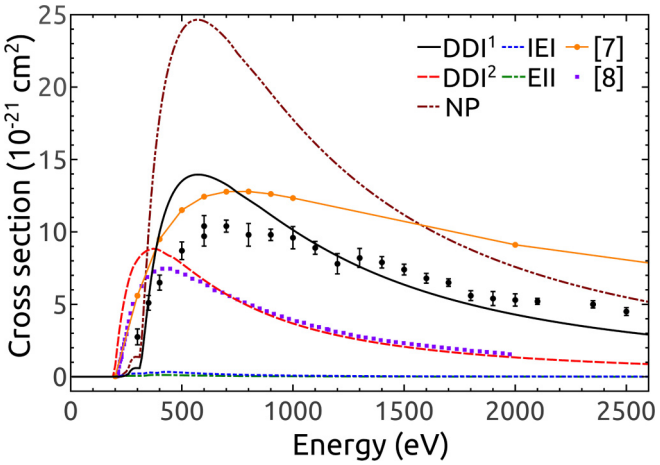

FIG. 3. Electron-impact DDI cross sections for Li^+, assuming that bound-state electrons reside on the opposite sides of the nucleus. DDI^1, cross sections when scattered and ejected electrons share the excess energy; DDI^2, one of the electrons takes all the available energy after ionization; NP, no populations of levels included in the DDI^1 calculations. See explanations in the text for the IEI and EII processes. Previous calculations based on the modification of Gryzinski's model: Tripathi and Rai [7], Roy and Rai [8]. Experiment: solid circles [17].

competes with excitations to the $1s2s, 1s2p, 1s3p$, and $1s4p$ configurations at the first step of the interaction. At the higher energies of the incident electron, the single-ionization cross sections are about of the same magnitude as the total excitation cross section to the levels of the Li^+ ion. The four highest relative populations of the excited levels amount to 29.9% ($1s2p\ ^1P_1$), 6.4% ($1s3p\ ^1P_1$), 3.1% ($1s2s\ ^1S_0$), and 2.4% ($1s4p\ ^1P_1$) whereas the ionization leads to 57.0% ($1s\ ^2S_{0.5}$) for 600 eV. On the other hand, it can be easily shown that the probability [Eq. (2)] to remove an electron from the excited configuration is less than 0.1 due to very low single-ionization cross sections compared to the square mean distance of electrons from the nucleus (Tables I and II). The same tendency is observed for the excitation probability from the $1s$ configuration of the Li^{2+} ion [Eq. (3)]. This explains the small contribution to DDI from the IEI and EII processes. It has to be noted that the DDI cross sections are about 60% higher if the populations of levels are not considered in the study for Li^+ (Fig. 3).

At low and high energies of the incident electron, the better agreement with the measurements is provided by the case when the ejected and scattered electrons equally share the excess energy. This result contradicts the previous findings for the light ions as one of the electrons tended to take all the excess energy after the first ionization process at the low energies of the incident electron [12]. This can be related to the complicated structure of the studied systems compared to the two-electron ion.

The maximum value of the theoretical cross sections is found to be higher than the maximum value of the crossed-beam experiment [17]. The theoretical cross sections reach a value of 1.4×10^{-20} cm^2 at the peak (Fig. 3). It is overestimated by approximately 30% when compared with the experimental results. At the high energies of the incident

TABLE I. DW electron-impact single-ionization cross sections (10^{-20} cm^2) for the $1s$ configuration for some levels of the Li^+ ion as a function of the total energy. Energies presented for the total energy of scattered and ejected electrons. The second row shows ionization energies in eV.

Energy (eV)	$1s^2\ ^1S_0$	$1s2s\ ^1S_0$	$1s2p\ ^1P_1$	$1s3p\ ^1P_1$	$1s4p\ ^1P_1$
	74.45	13.99	12.64	5.79	3.40
0.1	1.7	110.1	238.1	1481.3	1361.1
1.0	17.0	1045.5	2128.5	18084.0	75759.0
3.0	48.5	2719.7	5088.8	43285.0	158790.0
10.0	139.1	5333.6	9041.7	44517.0	101530.0
50.0	410.0	4396.6	7269.9	11906.0	18233.0
100.0	529.6	2986.3	4882.1	6103.3	9012.8
200.0	552.0	1856.3	2951.6	3277.3	4840.4
300.0	508.7	1370.8	2133.0	2318.1	3444.1
500.0	417.3	919.2	1388.3	1512.4	2266.6
700.0	349.7	700.7	1037.3	1144.0	1723.9
800.0	323.4	628.3	922.7	1024.0	1546.3
1000.0	281.2	522.6	757.5	850.8	1288.9
3000.0	126.4	206.1	281.2	338.0	519.1
7000.0	63.2	98.3	129.0	163.2	252.5
10000.0	46.7	71.7	92.6	119.5	185.4

electron, the experimental DDI cross sections are underestimated in both cases of energy distribution between the ejected and the scattered electrons. The obtained differences between the theoretical and the experimental values can be explained by the similar discrepancies observed in the above presented calculations of single-ionization cross sections for the Li^+ and Li^{2+} ions (Figs. 1 and 2). Therefore, more accurate methods have to be used to calculate single-ionization cross sections in order to remove the obtained differences. Moreover, the crossed-beam experiment [17] dates back to the 1960s, and no experiments have been performed since that date for the Li^+ ion. It is interesting that Müller notes that the double-ionization cross-sectional maximum for the Li^+ ion is about 1.5×10^{-20} cm^2 [18]. This value is in better agreement with our calculations.

Finally, it has to be noted that the peak position of the theoretical cross sections is in a fairly good agreement with experiment when the ejected and scattered electrons equally share the excess energy (Fig. 3). Our findings would seem

TABLE II. The mean distance (a.u.) of the electrons from the nucleus in the nl shells for the Li^+ and Li^{2+} ions.

nl	Li^+	Li^{2+}
$1s$	0.572	0.500
$2s$	2.631	2.000
$2p$	2.444	1.667
$3s$	6.191	4.499
$3p$	6.166	4.167
$3d$	5.247	3.500
$4s$	11.251	8.000
$4p$	11.387	7.666
$4d$	10.496	7.000
$4f$	8.999	5.999

to demonstrate that the current approach, which analyzes sequential ionization of the Li^+ ion, successfully describes physical processes occurring during kickoff of two electrons from the system. On the other hand, the DDI study for levels of the excited long-lived $1s2s$ configuration shows peaks that are shifted to the low-energy side. Furthermore, the cross sections are about four times smaller at the higher energies of the incident electron than the ones obtained for the ground level.

IV. CONCLUSIONS

As stated in the Introduction, our main aim was to investigate electron-impact DDI cross sections for the Li^+ ion by applying a few-step approach. Therefore, the II, IEI, and EII processes have been studied. However, this approach fails to provide a good agreement with the experiment under the assumption that the density of electrons in the shell is uniform. Therefore, it has been suggested that bound electrons have to be considered as residing on the opposite sides of the nucleus. This assumption yields much better agreement with the experimental measurements. The obtained results demonstrate that a few-step approach can be successfully applied in the analysis of this strongly correlated system. It was found that the contribution from the II process dominates over the contribution from IEI and EII. In addition, good agreement with experiment for Li^+ shows that the contribution from the shake-off process is negligible even for the large energies of the incident electron.

Two limiting cases of energy distribution of scattered and ejected electrons have been studied. In one case, the excess energy is taken by one of the electrons participating in the collision. In the other case, the excess energy is equally shared between these electrons. The better agreement with the experiment at low and high energies of the incident electron is obtained when the electrons share the excess energy. However, the maximum value of theoretical cross sections is found to be higher than the maximum value of the crossed-beam experiment. On the other hand, the theoretical study underestimates the cross sections compared to the experiment at the higher energies. The obtained differences can be explained by the similar discrepancies observed in calculations of the single-ionization cross sections for the Li^+ and Li^{2+} ions. More accurate experimental measurements may also contribute to removing the differences between the theoretical and the experimental values. Furthermore, the theoretical studies using other more sophisticated approaches may also help to bring clarity to a situation which occurs in the Li^+ ion during DDI.

Finally, in this paper, we presented an *ab initio* study that provided such good agreement with the experimental cross sections for the Li^+ ion.

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