

Photoionization of the Li atom: Convergent-close-coupling calculations with a focus on two-electron removal

Alfred Müller ^{*}

I. Physikalisches Institut, Justus-Liebig-Universität Gießen, 35392 Giessen, Germany

Anatoli S. Kheifets 

Research School of Physics, The Australian National University, Canberra, ACT 2601, Australia

Igor Bray  and Dmitry V. Fursa 

Department of Physics and Astronomy, Curtin University, Perth, WA 6102, Australia



(Received 17 December 2025; accepted 17 February 2026; published 9 March 2026)

In a combined experimental and theoretical study, Müller *et al.* [[Phys. Rev. A **111**, 053108 \(2025\)](#)] revealed highly detailed resonant structure in ionization with excitation and in double ionization of the Li-like B^{2+} ion. That work demonstrated the strong predictive power of the convergent-close-coupling (CCC) method when enhanced by modern supercomputing technology. In the present work, we apply CCC to analogous ionization processes in the Li atom. Again, we find K -shell ionization accompanied by K -shell excitation to contribute relatively strongly to the double photoionization of three-electron Li. Comprehensive detailed comparisons with the existing experimental data are presented and discussed.

DOI: [10.1103/PhysRevA.113.033105](https://doi.org/10.1103/PhysRevA.113.033105)

I. INTRODUCTION

The breakup of few-electron systems induced by particle impact or photoabsorption is an ideal testing ground for our understanding of basic atomic interactions and fundamental atomic structure. For that reason, photoprocesses of the neutral He atom have received a great deal of attention from both experiment and theory. In recent publications on single and double photoionization of He-like B^{3+} ions [1,2], an overview of the associated literature has been provided.

Next in complexity are the Li atom and Li-like ions for which also an impressive body of literature on photon-induced processes has been accumulated over five decades, almost exclusively restricted to neutral Li [3]. One of the most intriguing aspects in the ionization of Li-like atoms and ions is the production of autoionizing excited states with empty K shells which are often called hollow states. Such hollow, or triply excited, states particularly of the neutral Li atom have stimulated exceptionally strong interest both in experiment and theory [4–38].

Experiments aiming at absolute cross sections for single and multiple photoionization of the Li atom are relatively scarce in spite of the outstanding importance of this prototypical three-electron system. Photoabsorption spectra in the energy range 50 to 70 eV involving excitation of $1sn\ell n'\ell'$ au-

toionizing states in Li were first observed by Ederer *et al.* [39]. Absolute cross sections for photoabsorption were measured by Mehlman *et al.* [40–42] covering the same single- K -shell-excitation resonances and extending the photon-energy range up to 107 eV. High-resolution photoion yield measurements on single photoionization were performed by Kiernan *et al.* [43] in the 60–75-eV energy range, i.e., in the region around the K edge.

The first observation of triply excited Li($2s^2 2p^2 P$) produced by the absorption of a single photon was reported by Kiernan *et al.* [7]. The investigated photon-energy range 140.5 to 143.5 eV was extended by the same group in a similar, subsequent photoion-yield measurement at a resolution $\Delta E_{\text{ph}}/E_{\text{ph}} = 1/7000$ [8]. A lower-resolution ($\Delta E_{\text{ph}} = 0.1$ eV) photoion yield spectrum, almost identical to the Li^+ yield function, was presented by Azuma *et al.* [9].

Absolute cross sections for single, double, and triple photoionization of the Li atom over extended photon-energy ranges have been determined in experiments by Wehlitz and collaborators:

- (1) σ_{01} for single ionization [44,45],
- (2) σ_{02} for double ionization [36,44,46,47], and
- (3) σ_{03} for triple ionization [48].

Few additional experiments covering very narrow energy ranges around specific resonance features were performed to determine the role of triply excited states [9,16,20]. In all cases, cross sections σ_{02} were inferred on the basis of measurements of cross-section ratios $r = \sigma_{02}/\sigma_{01}$ and by multiplying r with the experimentally determined cross sections σ_{01} which, in turn, were derived from the absolute photoionization measurements of Mehlman *et al.* [42].

Theoretical calculations of cross sections for photon-interaction processes of the lithium atom have been restricted

^{*}Contact author: Alfred.Mueller@physik.jlug.de

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](#) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

mainly to direct single photoionization and selected excitation channels contributing to σ_{01} and in a few cases also to σ_{02} . Since the focus has often been on resonances, the cross-section functions were calculated in such studies only in limited photon-energy ranges. To the best of our knowledge, only one attempt has been published in which the cross sections σ_{01} and σ_{02} were separately calculated in the energy range 136 to 151 eV by employing an *R*-matrix approach [19]. Mixed agreement with the experiment of Wehlitz and Juranic [36] was found.

In the present study, the convergent-close-coupling (CCC) approach to the calculation of cross sections σ_{01} and σ_{02} for neutral Li was employed. CCC has been applied previously [49–51] to the identical problem of photoionization; however, the calculations had to be limited in the size of the basis set and in the density of the photon-energy grid to keep the calculations tractable. Similar limitations were present in previous calculations of double photoionization of Li using the time-dependent close-coupling method [52–54] and the *R*-matrix with pseudostates approach [54].

Given the progress in the availability of computational resources, the present CCC model goes far beyond the work that had been possible in these previous attempts including the *R*-matrix calculations of Berrington and Nakazaki [19]. We investigate photoionization of neutral Li($1s^2 2s^2 S$) in its ground level with a focus on the cross section σ_{02} for net double ionization by a single photon—similar to the preceding study on B^{2+} ions [3]. Accordingly, the photon-energy region of interest for the present study starts at the threshold (81.032 eV [55]) for double ionization of the neutral Li atom.

II. THEORY

A. The convergent-close-coupling approach

The general application of the CCC method to photoionization problems has been described previously [56–59]. In the present context, the photoionization dynamics of atomic lithium is treated using the CCC method, which provides a fully nonperturbative description of electron correlation in both the initially bound and the final excited and ionized states. The CCC formalism was originally developed for electron-atom scattering and has subsequently been extended to photon-induced single and multiple ionization processes in few-electron atomic and molecular systems. In the present work, CCC is applied to photoionization of neutral lithium, where electron correlation governs both the magnitude and energy dependence of single- and double-ionization cross sections.

The CCC approach to two-electron ionization of Li has been described in detail in earlier publications [49–51]. Here we recap the key elements of the CCC theory without necessitating the reader to consult the previous works.

1. Physical picture and separation of ionization stages

Within the CCC framework, single-photon two-electron ionization is formulated as a two-stage process. In the first stage, one atomic electron absorbs the photon and is promoted to the continuum. In the second stage, the primary photoelectron undergoes inelastic scattering from the

residual ionic core, which may lead to excitation or ionization of the remaining bound electron. This formulation establishes a direct correspondence between photoionization and electron-impact ionization and allows well-developed inelastic-scattering techniques to be employed.

In the case of lithium, photon absorption is dominated by ionization of a $1s$ electron. This dominance arises from the proximity of the core electron to the nucleus, which must absorb the recoil momentum of the photon. Ionization of the valence $2s$ electron is comparatively suppressed. Following photoionization of a $1s$ electron, the remaining two electrons form a heliumlike Li^+ ion, and the subsequent dynamics are governed by electron scattering from this ionic core.

2. Channel expansion of the final state

The final scattering state is expanded over a complete set of channel functions constructed as products of Li^+ target states and distorted waves of the outgoing electron:

$$|\Psi^{(-)}\rangle = \sum_{\alpha\ell} |\Phi_{\alpha}^{Li^+}\rangle |k\ell\rangle C_{\alpha\ell}(k), \quad (1)$$

where $\alpha \equiv (NLS)$ labels the discrete and pseudostate spectrum of the Li^+ ion with total orbital angular momentum L and spin S . The photoelectron is characterized by its linear momentum k and orbital angular momentum ℓ . The expansion coefficients $C_{\alpha\ell}(k)$ encode the full electron-electron correlation dynamics of the problem.

The completeness of the channel expansion is ensured by the inclusion of both negative-energy bound states and positive-energy pseudostates of the Li^+ ion. The latter provide a discretized representation of the continuum and enable excitation and ionization channels to be treated within the same formalism.

3. Construction of Li^+ target states

The Li^+ target states $\Phi_{\alpha}^{Li^+}$ are obtained by diagonalizing the two-electron Hamiltonian of the ion,

$$H_{Li^+} = \sum_{i=1}^2 \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2)$$

with $Z = 3$, in a basis of antisymmetrized two-electron configurations.

One-electron orbitals are generated using Laguerre functions of the form

$$\langle r|n\ell\rangle = N_{n\ell} r^{\ell+1} e^{-\lambda_{\ell} r/2} L_{n-1}^{2\ell+2}(\lambda_{\ell} r), \quad (3)$$

where $L_{n-1}^{2\ell+2}$ are associated Laguerre polynomials, λ_{ℓ} are exponential falloff parameters, and $N_{n\ell}$ are normalization constants. For each angular momentum ℓ , a finite number N_{ℓ} of Laguerre orbitals is retained. The key feature of the CCC method is that with increasing size of the Laguerre basis completeness of the expansions is approached, and hence convergence is achieved.

Two-electron configurations are constructed as antisymmetrized products of these orbitals and coupled to definite total orbital angular momentum L and spin S . Diagonalization of H_{Li^+} in this basis yields a finite spectrum of target states $\Phi_{\alpha}^{Li^+}$ with eigenenergies E_{α} . States with $E_{\alpha} < 0$ represent

physical bound states of Li^+ , whereas states with $E_\alpha > 0$ form a pseudostate representation of the continuum.

4. Dipole interaction and reduced matrix elements

Photoionization amplitudes are constructed from matrix elements of the dipole operator between the initial ground state of lithium and the final multichannel state. After separation of angular variables, the reduced dipole matrix element for photoionization into a channel (α, ℓ) takes the form

$$D_{\alpha\ell}(k) = d_{\alpha\ell}(k) + \sum_{\beta\ell'} \int d\varepsilon_{k'} \frac{\langle \alpha\ell k \| T \| \beta\ell' k' \rangle d_{\beta\ell'}(k')}{E - \varepsilon_{k'} - E_\beta + i0}. \quad (4)$$

Here $d_{\alpha\ell}(k)$ is the bare dipole matrix element and T is the electron- Li^+ scattering T matrix. The integration over the intermediate electron states of energy $\varepsilon_{k'}$ includes summation over the discrete negative-energy states. The total energy of the scattering system is $E = k^2/2 + E_\alpha$.

The T matrix is obtained by solving a set of coupled Lippmann-Schwinger equations:

$$T = V + VG_0T, \quad (5)$$

where V is the electron-electron interaction and G_0 is the free Green's function. These equations sum the Coulomb interaction to all orders and ensure a fully nonperturbative treatment of correlation effects.

5. Initial-state wave function

The ground state of neutral lithium is represented by a multiconfiguration Hartree-Fock (MCHF) expansion:

$$\Psi_0(1, 2, 3) = \sum_{n\ell} C_{n\ell} |n\ell\rangle |n\ell\rangle |2s\rangle, \quad (6)$$

which accounts for dominant pair correlations between the core electrons. Configurations involving simultaneous excitation of all three electrons were tested and found to have a negligible effect on photoionization observables. We used a nine-term MCHF expansion, which includes $n\ell^2$ configurations with $\ell \leq 3$ and $n \leq 4$, thus recovering 92% of the correlation energy. The usage of this MCHF ground state leads to the velocity gauge yielding the most accurate results.

6. Double photoionization amplitudes

The reduced dipole matrix elements are used to construct double photoionization amplitudes describing emission of two electrons with momenta $(\mathbf{k}_1, \mathbf{k}_2)$ and angular momenta (ℓ_1, ℓ_2) :

$$D_{\ell_1\ell_2}^S(k_1, k_2) = (-i)^{\ell_1+\ell_2} e^{i[\sigma_{\ell_1}(\zeta=2)+\sigma_{\ell_2}(\zeta=1)]} \times D_{\alpha\ell_2}(k_2) \langle \ell_1 k_1, 1s \| \alpha \rangle, \quad (7)$$

where $\sigma_\ell(\zeta)$ are Coulomb phase shifts for asymptotic charges $\zeta = 2$ and 1, respectively. The index S denotes the spin of the intermediate Li^+ state.

For equal energy sharing, the amplitudes are recoupled with respect to the spin of the photoelectron pair:

$$F_{\ell_1\ell_2}^S(k_1, k_2) = \sum_{S'} [(-1)^{S'} D_{\ell_1\ell_2}^{S'}(k_1, k_2) + D_{\ell_2\ell_1}^{S'}(k_1, k_2)] \gamma_{SS'}, \quad (8)$$

where $\gamma_{SS'}$ are spin-recoupling coefficients expressed in terms of $6j$ symbols. These amplitudes possess the correct exchange symmetry under permutation of the two outgoing electrons.

7. Differential cross sections

The triply differential cross section is expressed as a partial-wave expansion:

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_2} = C \sum_S \left| \sum_{\ell_1\ell_2} \mathbf{e} \cdot \mathbf{Y}_1^{\ell_1\ell_2}(\hat{k}_1, \hat{k}_2) F_{\ell_1\ell_2}^S(k_1, k_2) \right|^2, \quad (9)$$

where $\mathbf{e}$ is the photon polarization vector and $\mathbf{Y}_1^{\ell_1\ell_2}$ are bipolar harmonics of rank 1. Integration over angles and energies yields total and partial cross sections for single and double photoionization.

8. Convergence in the final state

We require the final-state wave function of electron scattering on the He-like ion Li^+ . For this purpose we use the CCC theory developed for two-electron targets [60,61]. The first step is to obtain a set of Laguerre one-electron basis functions by taking $N_\ell = 30 - \ell$ for $\ell \leq 3$ with exponential falloff $\lambda_\ell = 3$, and diagonalize the one-electron Hamiltonian of Li^{2+} for each ℓ . This results in one-electron Li^{2+} wave functions. We then use the lowest-energy $25 - \ell$ functions to generate two-electron configurations for diagonalizing Eq. (2), the two-electron Hamiltonian of Li^+ . To ensure a sufficiently accurate ground state, and to allow for autoionization processes, we include $1s$, $2s$, and $2p$ orbitals for the inner electron, and all possible combinations for the outer electron. Diagonalization of the Li^+ Hamiltonian results in a total of 829 two-electron states. These states include one- and two-electron excitation as well as ionization. All of these states are then included in the CCC calculations of the required electron- Li^+ wave function on a fine energy mesh of incident electron energies. This is a substantial computational task, made easier by requiring just one partial wave of total orbital angular momentum.

Convergence was verified with respect to the size of the Laguerre basis, the maximum orbital angular momentum included in the channel expansion, and the density of the photon-energy grid. All parameters were systematically increased until stable results were obtained.

9. Computational implementation and accuracy

The CCC computational code has evolved from the late 1980s, and is presently written in a mix of FORTRAN77 and FORTRAN90. It has three levels of parallelism: message passing interface, which enables the separation of the calculation to an arbitrary number of nodes; OpenMP, which allows multithreading to utilize all available cores; and GPU acceleration if available. A typical single node used in the present calculations had 48 cores and no GPUs. Owing to the efficiency of memory transfer it is best to subdivide each physical node into four virtual nodes of 12 cores each. For each incident energy we take four physical nodes, and hence have a total of 16 virtual nodes of 12 cores each. Such a configuration leads to around 10-min execution time per energy, roughly split evenly

between calculating matrix elements and solving the resultant linear equations.

In the presented cross sections around 2200 energies have been calculated to attempt to map out the resonant structures with sufficient resolution to perform convolution with the experimental resolution. The choice of Laguerre bases discussed above ensures that the accuracy at each calculated energy is of order 1%. There may also be systematic inaccuracy due to gauge dependence, but we expect this to be no more than 5%.

B. Knockout PDI model

Direct, or nonsequential, photo double ionization (PDI) energies not too far above the threshold is facilitated by two main mechanisms. The first mechanism is a knockout collision of the primary photoelectron with the residual ion. The second, the shakeoff process, is relaxation of the ion with the release of a secondary photoelectron. While the sudden shakeoff mechanism is most efficient at large photon energies, the knockout process is largely responsible for PDI near the threshold. The complete CCC theory treats both the knockout and shakeoff processes on the same footing. A simplified knockout model [62] ignores the shakeoff contribution to PDI. Nor does it take into account the two-electron ionization-excitation (IE) processes. In such a simplified treatment, the primary photoelectron undergoes an ionizing ($e, 2e$) collision with the ion and the whole of its energy is shared between the two secondary photoelectrons. The application of such a model was found successful in direct double ionization of the $\text{Ar}^+(3p^{-1})$ ion [63]. It was also useful in estimating partial contribution of various PDI channels and evaluating the role of L -shell single and double core-hole production and decay in m -fold ($1 \leq m \leq 6$) photoionization of the Ar^+ ion [64].

III. RESULTS AND DISCUSSION

We present theoretical results for net single and double photoionization separately. While the main focus of the present study is on two-electron removal, also the cross section σ_{01} for single photoionization has been calculated to facilitate critical comparisons of the present theoretical calculations with available experimental data. An overview of our theoretical results is presented in Fig. 1. The curves labeled σ_{01} and σ_{02} are the results of the present CCC calculations (see Sec. II A) while the lines labeled σ_{KL} and σ_{KK} were obtained from the PDI model (see Sec. II B). They describe the direct-ionization contributions to σ_{02} .

Several individual reaction channels lead to the final production of Li^+ and Li^{2+} ions, respectively. The cross sections σ_{01} (σ_{02}) comprise the partial cross sections of all individual reaction channels contributing to the net production of Li^+ (Li^{2+}) ions. In the following, we compare the present calculations with measured cross sections σ_{01} and σ_{02} . Where available, experimental partial cross sections are also compared with the corresponding CCC results.

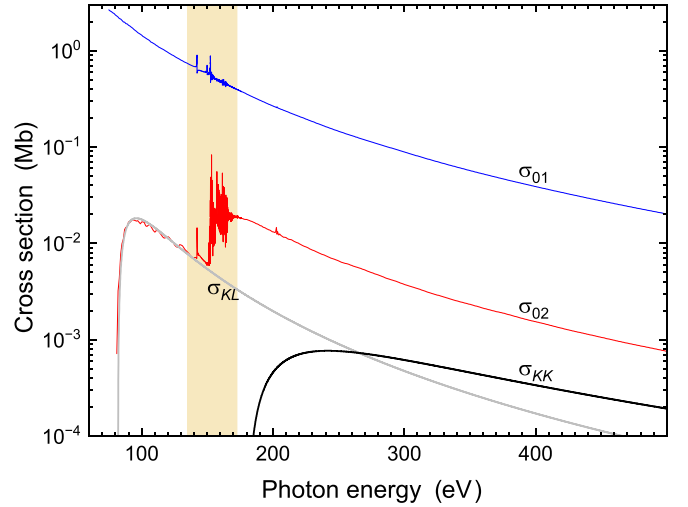
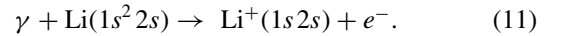
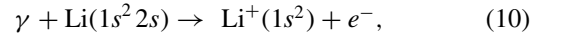


FIG. 1. Theoretical cross sections for the single and double photoionization of ground-level $\text{Li}(1s^2 2s^2 S_{1/2})$ atoms. The upper blue solid line represents σ_{01} obtained from the present CCC model. The lower red solid line is the CCC result for σ_{02} . The solid gray line labeled σ_{KL} was obtained from the present PDI model. It represents the cross section for direct double photoionization involving the L -shell electron and one of the K -shell electrons. Accordingly, the thick black solid line labeled σ_{KK} also results from the PDI model and represents the cross section for direct removal of both K -shell electrons by a single photon. The photon-energy range of triply excited intermediate states is highlighted by light-brown shading.

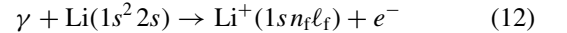
A. Net single ionization of $\text{Li}(1s^2 2s)$

The most obvious contributions to net single photoionization of the neutral Li atom in its $1s^2 2s^2 S_{1/2}$ ground level comprise direct removal of an L -shell or a K -shell electron:



Here, γ represents the incoming photon with energy E_{ph} . The associated cross sections are $\sigma_{2s}^{\text{dir ion}}$ and $\sigma_{1s}^{\text{dir ion}}$, respectively.

Ionization of the K shell may be accompanied by excitation of the valence electron:

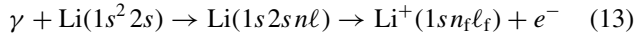


with principal quantum numbers $n_f \geq 2$ and angular momentum quantum numbers $0 \leq \ell_f \leq n_f - 1$. In the present context, the associated IE cross sections are termed $\sigma_{\text{IE}}^{n_f \ell_f}$. All the above processes lead to net single ionization of Li. Our CCC calculations show that the cross-section sum $\sum_{n_f \ell_f} \sigma_{\text{IE}}^{n_f \ell_f}$ for direct K -shell ionization accompanied by L -shell excitation to any $n_f \geq 3$ makes up for about one fourth of the total direct single-ionization cross section $\sigma_{1s}^{\text{dir}} = \sigma_{1s}^{\text{dir ion}} + \sum_{n_f \ell_f} \sigma_{\text{IE}}^{n_f \ell_f}$.

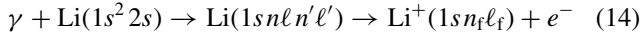
When K -shell single ionization is accompanied by the excitation of the second K -shell electron, an autoionizing state is produced. This reaction path may also contribute to σ_{01} if the intermediate doubly excited $\text{Li}^+(2s n \ell)$ stabilizes by photoemission. Along with ionization of one K -shell electron, also the excitation of both the K and the L shell may occur populating intermediate doubly excited $\text{Li}^+(n \ell n' \ell')$ states with

both remaining electrons in excited subshells. Again, such states may stabilize by photoemission and thus contribute to σ_{01} . However, it is much more likely that they decay by autoionization and thus add to σ_{02} (see below).

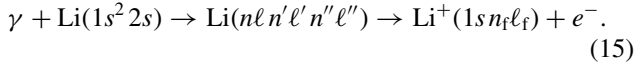
Clearly, also the formation of resonances in the Li atom is an important photoabsorption mechanism and can contribute to net single photoionization via one-electron excitation from the K shell



or via two-electron excitation from the K and the L shell



or via three-electron excitation processes



All quantum numbers $n_f \geq 1$ and $0 \leq \ell_f \leq n_f - 1$ are possible. Some of the most important partial cross sections $\sigma(1s n_f \ell_f)$ summing up the single-ionization channels described by Eqs. (12)–(15) are available in the literature [11,13–15].

The processes listed above are not independent of one another. The quantum-mechanical amplitudes of different reaction channels may interfere with each other. Therefore, in principle, a unified theoretical approach like the present CCC theory treating the reaction channels all at once on the same footing is necessary for producing reliable results. However, to some limited extent, the different contributing channels may be regarded as independent processes to simplify the discussion.

Cross sections σ_{2s}^{dir} and σ_{1s}^{dir} [see Eqs. (10) and (11), respectively] have been calculated using a variety of theoretical approaches [49,65–67]. As already discussed in preceding publications [1–3], direct photoionization at least from the K and L shells can be assumed to be fairly well understood. Different theoretical results show a relatively consistent picture (see Fig. 2) with maximum deviations between calculated cross sections of $\pm 10\%$ at most. Figure 2 shows theoretical and experimental results for nonresonant single photoionization of the Li atom at energies above 70 eV. Experimental data displayed in the figure comprise measurements by Mehlman *et al.* [42] of absolute cross sections σ_{abs} for total photoabsorption and measurements by Huang *et al.* [44] of relative single photoionization cross sections σ_{01} [44] normalized by employing the results of Mehlman *et al.* [42]. Such normalization and the present comparison are justified by the fact that outside the energy ranges where resonances occur, σ_{2s}^{dir} and σ_{1s}^{dir} by far dominate the cross section σ_{01} for net single ionization of the Li atom and, hence, also σ_{abs} for total photoabsorption by Li. In the present photon-energy range, even the contribution σ_{2s}^{dir} of valence-shell photoionization is negligibly small and makes up for not much more than 1% of σ_{01} (see Fig. 2).

Apart from experimental cross sections, Fig. 2 displays theoretical results (I) for nonresonant photoabsorption calculated by Reilman and Manson [65]; (II) for the total direct photoionization where the contributions of the $1s$ and $2s$ subshells, σ_{1s}^{dir} and σ_{2s}^{dir} , have been separately calculated by Yeh and Lindau [66]; (III) for the same contribution obtained

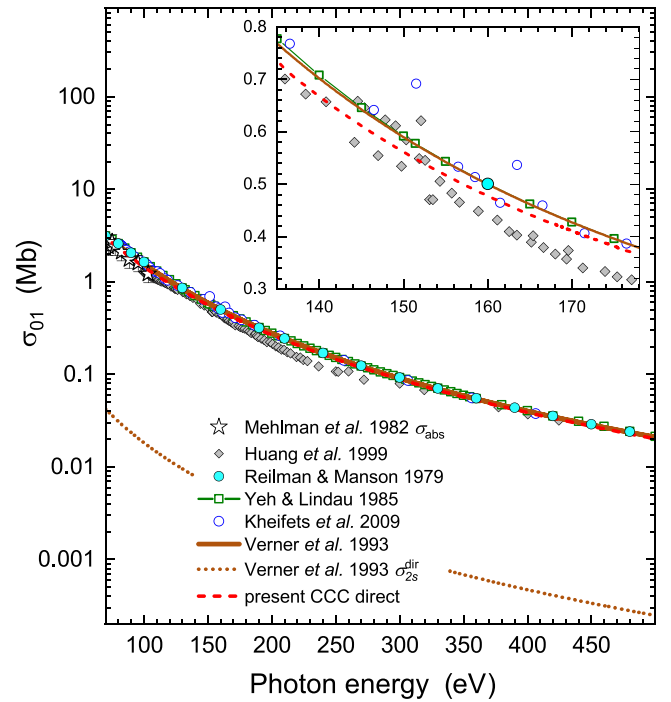


FIG. 2. Cross sections for the photoionization of ground-level Li($1s^2 2s \ ^2S_{1/2}$) atoms. Experimental data are the open stars [42] and the gray-shaded diamonds [44]. Theoretical results are represented by (I) cyan-shaded circles [65], (II) green open squares [66], (III) the thick brown line [67], (IV) the blue open circles [49], and (V) the red dashed line showing the present nonresonant CCC cross section (where the resonance contributions have been artificially removed). Inset: The photon-energy region between 135 and 178 eV where triply excited resonances contribute. The brown dotted line shows σ_{2s}^{dir} [67].

in a different approach by Verner *et al.* [67]; (IV) for net single photoionization (σ_{01}) previously calculated by Kheifets *et al.* [49] by employing a CCC model; and (V) for direct single photoionization derived from the present CCC calculations by fitting a smooth function to the original CCC curve outside regions where resonances occur.

The theoretical results for direct single ionization all agree closely with one another, confirming the expectations. The inset of Fig. 2 zooms into the energy region of triply excited levels. The previous CCC calculations [49] for the total net single photoionization include resonance contributions and, therefore, show some scatter particularly at energies between 150 and 170 eV. Similarly, the cross sections σ_{01} determined by Huang *et al.* [44] show excursions in that same energy range which have to be attributed to the presence of triply excited resonances. In the energy range between 150 and 330 eV, the normalized results of Huang *et al.* [44] exhibit a systematic deviation from the well-based theoretical single-ionization cross sections. The maximum difference is approximately 40% at 250 eV. This is much more than the quoted uncertainty of $\pm 20\%$ of the experimental cross sections. Apparently, the experimental error bars were underestimated here.

High-resolution relative measurements of photoion yields were reported by Kiernan *et al.* [8] covering the photon-energy region of the dominant triply excited resonances. These data

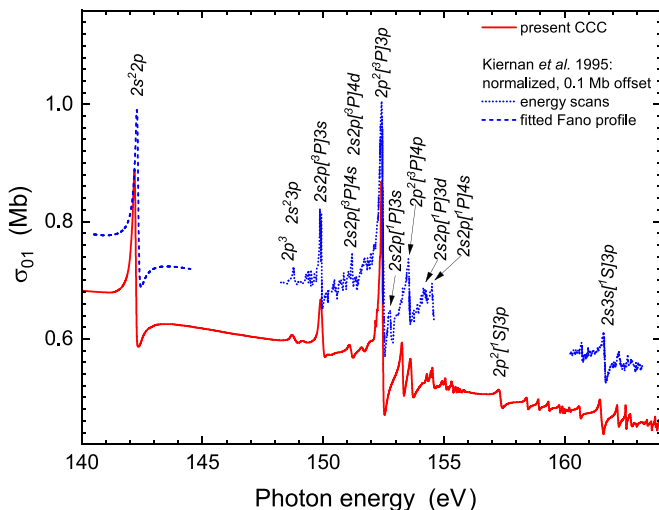


FIG. 3. Cross sections for the single photoionization of ground-level $\text{Li}(1s^2 2s \ ^2S_{1/2})$ atoms in the region of triply excited hollow-lithium resonances. The red solid line is the present CCC result. The blue dashed line is the Fano profile calculated from the resonance parameters experimentally determined by Kiernan *et al.* [8]. The blue dotted lines are the scan data of these same authors. All relative yields measured by Kiernan *et al.* were multiplied by a suitable factor to approximately match the present CCC cross sections and an offset of 0.1 Mb was then added to avoid cluttering of the theoretical and experimental data. The tentative assignments of resonance features suggested by Kiernan *et al.* on the basis of calculations with the Cowan code [68] are indicated. All levels are associated with dipole-allowed ^2P terms.

can be compared with the present CCC results by applying a constant factor that brings the Kiernan *et al.* data close to the present CCC σ_{01} cross-section function. This factor was appropriately chosen but an additional offset of 0.1 Mb was added for better visibility of the two different datasets (see Fig. 3 where also the tentative assignments provided by Kiernan *et al.* for resonance features are shown). The energy spread of the experimental yields is approximately 21 meV, very much smaller than the natural widths of the dominating triply excited resonances. Convolution of the CCC spectrum with a Gaussian function of 21-meV full width at half maximum (FWHM) produces a result that cannot be distinguished from the original theoretical spectrum at the level of detail visualized by Fig. 3. The statistical quality of the experimental result for the $2s^2 2p^2 P$ resonance is so good that it is represented here as the Fano profile calculated by using the resonance parameters that were determined by Kiernan *et al.*

The overall agreement of calculated and measured features is very good. In the details, there are differences. For example, the present theoretical $2s^2 2p\ ^2P$ resonance energy is $E_{\text{res}} = 142.22$ eV as compared to the experiment with 142.32(3) eV where the number in parentheses indicates the quoted uncertainty of the last digit. The difference is within the expected uncertainty of the theoretical level energies. The natural width obtained from the CCC calculation is $\Gamma = 0.126$ eV in agreement with the experimental $\Gamma = 0.14(2)$ eV. The Fano parameter $q = -1.86$ agrees with the experimental value $-2.0(3)$. In this context, it is worth

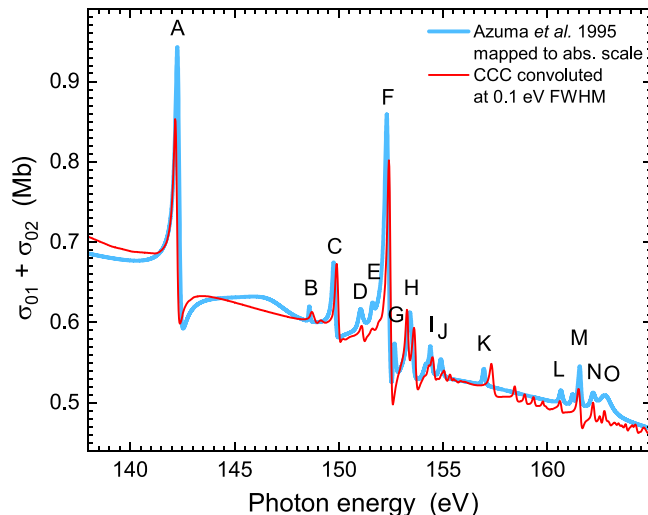


FIG. 4. Cross sections for the total photoionization of ground-level Li($1s^2 2s \ ^2S_{1/2}$) atoms in the region of triply excited hollow-lithium resonances. The red solid line is the present CCC result for $\sigma_{01} + \sigma_{02}$. The light-blue thick solid line represents the measurement of relative photoion yields by Azuma *et al.* [9] mapped to the present theory by a linear transformation (see main text). The capital letters are directly associated with the peak assignments provided by Azuma *et al.* on the basis of multiconfiguration Dirac-Fock calculations.

mentioning a later precision experiment by Diehl *et al.* [13] delivering $E_{\text{res}} = 142.28(3)$ eV and $\Gamma = 0.118(3)$ eV with both parameters closer to the present CCC results.

A comprehensive compilation of resonance energies, natural widths, and Fano parameters found by theory and experiment for the $2s^2 2p\ ^2P$ resonance has been provided by Chung [35]. Fang and Chung used a combination of the saddle-point method with the L^2 K -matrix method to calculate total and partial photoionization cross sections in the vicinity of the $\text{Li}(2s^2 2p\ ^2P)$ resonance [69]. Given their quoted uncertainty margins, they probably provided the most accurate resonance energy and width available to date for $\text{Li}(2s^2 2p\ ^2P)$. Their results are $E_{\text{res}} = 142.254(1)$ eV, $\Gamma = 0.116(1)$ eV, and $q = -2.11(3)$.

A Li photoionization experiment in the energy range 140–163 eV (see Fig. 4) was reported by Azuma *et al.* [9] only a few weeks after the publication by Kiernan *et al.* [8]. Relative total yields of photoions in the energy region of triply excited levels of the Li atom were measured at an energy resolution of ≈ 0.1 eV. The resulting data correspond to the sum $\sigma_{01} + \sigma_{02}$ of net single and double ionization. For the $2s^2 2p\ ^2P$ resonance, additional measurements were carried out using a time-of-flight technique to identify the final ion charge state. Thus, Li^+ and Li^{2+} photoion yields could be determined separately. However, the relative measurement of single-ionization yields for the $2s^2 2p\ ^2P$ resonance cannot compete in quality with the results of Kiernan *et al.* either in energy resolution or in statistical significance. The same is true for the measured yield of Li^{2+} product ions when compared to the detailed experiment of Wehlitz *et al.* [20], who presented cross sections σ_{01} and σ_{02} with good statistics at an energy resolution of 39 meV in the close vicinity of

the $2s^2 2p^2 P$ resonance. The latter results are discussed in Sec. III B, where the focus is on double photoionization.

Azuma *et al.* subtracted a slope from their yield spectrum for better visualization of the resonance features. For a critical comparison of their measurements with the results of the present CCC calculations, the data shown in Fig. 1 of their publication [9] were first digitized, then fitted by employing 19 Fano profiles convoluted with a Gaussian of 0.1-eV FWHM, and then mapped to the present theory by multiplication of a constant factor and adding a constant offset, thus imitating the data transformation applied by Azuma *et al.* The cross-section structures obtained by theory and experiment are in agreement with one another.

The resonance assignments of Azuma *et al.* provide the percentages of the leading configurations in the multiconfiguration Dirac-Fock (MCDHF) representation. For example, resonance A involves contributions of 74% $2s^2 2p$, 12% $2p^3$, and 8% $2s 2p 3s$ configurations. This cumbersome characterization of a given resonance level in the MCDHF representation is suggestive for a more appropriate classification of triply excited states. Such a classification was suggested by Morishita and Lin [33].

In a series of photoelectron-spectroscopy experiments with Li atoms exposed to narrow-bandwidth synchrotron radiation, partial cross sections and relative yields $\sigma(1sn_f\ell_f)$ summing up the single-ionization channels described by Eqs. (12)–(15) were measured [11,13–15]. The experiments were accompanied by *R*-matrix calculations which typically agree quite well with the experimental data. The present CCC approach also permits the calculation of partial cross sections $\sigma(1sn_f\ell_f)$. Comparisons of the CCC results with the available experiments are shown in Figs. 5–7.

The prime purpose of the experiments was a thorough investigation of triply excited resonances and their decay properties. Resonance contributions to $\sigma(1sn_f\ell_f)$ are accompanied by nonresonant direct-ionization channels and interference of associated amplitudes may occur. In principle, the present CCC calculations include all that. However, one has to keep in mind that only a finite basis of states can be used to represent the real physical states involved in the photoionization processes. Contributions of the basis states to a certain reaction channel can be projected out. Such projections can be immediately interpreted as partial cross sections in cases where the basis states make up for a dominating contribution to the wave functions of real states. In order to judge this, the weights w_{BS} of the $1sn_f\ell_f$ basis states in the multiconfiguration representation of real physical states are important to know. Therefore, the w_{BS} parameters resulting from the present CCC calculations are provided for each comparison with experimental data.

Figure 5 displays comparisons of experimental and theoretical partial cross sections $\sigma(1sn_f\ell_f)$ in the vicinity of the $2s^2 2p$ resonance at 142.254 eV. The experimental data were obtained by Journal *et al.* [11] [Figs. 5(a) and 5(b)] and Diehl *et al.* [13] [Fig. 5(c)]. Relative measurements were normalized by these authors to the absolute photoabsorption cross section of Mehlman *et al.* [42] at $E_{ph} = 110$ eV. The estimated total uncertainties of the resulting cross sections are $\pm 27\%$. For the comparison with our CCC calculations, the experimental cross sections were additionally scaled up by

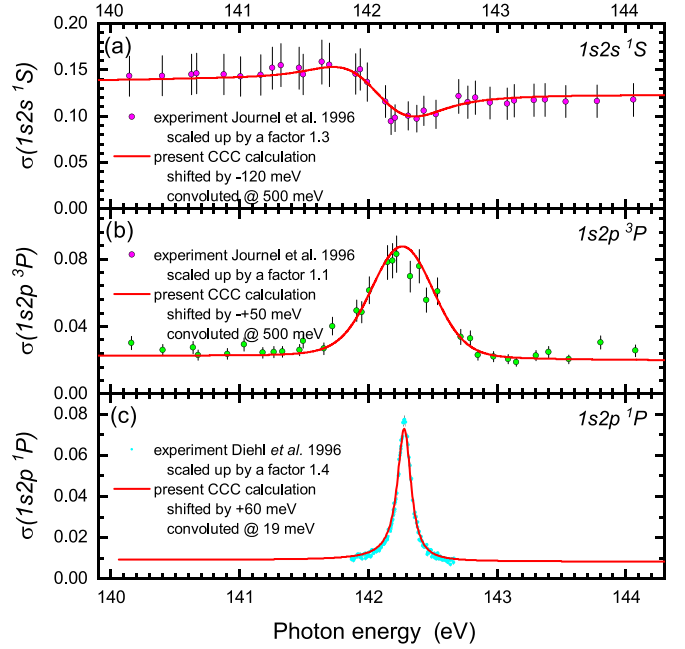


FIG. 5. Partial cross sections $\sigma(1sn_f\ell_f)$ for populating excited singlet or triplet terms in two-electron Li^+ by photoionization of neutral Li in the energy region of the $2s^2 2p$ resonance. The investigated intermediate terms are $1s2s^1S$ (a), $1s2p^3P$ (b), and $1s2p^1P$ (c). The red solid lines represent the present CCC calculations shifted in energy to match the experimental resonance positions and convoluted by Gaussians to simulate the experimental energy spread. The experimental data [11,13] were scaled by constant factors to match the theoretical cross sections. The relevant parameters are provided in each panel individually. All cross sections are given in Mb.

factors 1.3 for $\sigma(1s2s^1S)$ [Fig. 5(a)], 1.1 for $\sigma(1s2p^3P)$ [Fig. 5(b)], and 1.4 for $\sigma(1s2p^1P)$ [Fig. 5(c)]. These factors are compatible with the quoted uncertainties of the experimental data.

The measurements were taken at different bandwidths of the synchrotron radiation: 500 meV [Figs. 5(a) and 5(b)] and only 19 meV [Fig. 5(c)]. The CCC results were convoluted with Gaussians of appropriate FWHM to simulate the experimental energy spread. According to the CCC calculations, the basis state termed $1s2s^1S$ makes up for 99.96% ($w_{BS} = 0.9996$) of the associated physical state, i.e., it provides an excellent representation of the real $1s2s^1S$ state. The other two weight factors for intermediate excited states addressed in Figs. 5(b) and 5(c) are $w_{BS} = 0.9995$ and 0.9997 , respectively.

For easier comparison, the energy scales of the theoretical cross sections are shifted to the experimental resonance positions. The shifts are -120 meV [Fig. 5(a)], $+50$ meV [Fig. 5(b)], and $+60$ meV [Fig. 5(c)]. Such shifts can be rationalized with the uncertainties expected for the calculations but partly also reflect the experimental uncertainties of the photon-energy scale. Overall, the agreement between theory and experiment is quite satisfying. Similar agreement was found for the *R*-matrix calculations accompanying the cited experiments.

Partial cross sections $\sigma(1sn_f\ell_f)$ were also measured [13,14] in the photon-energy range 149.3–154.5 eV

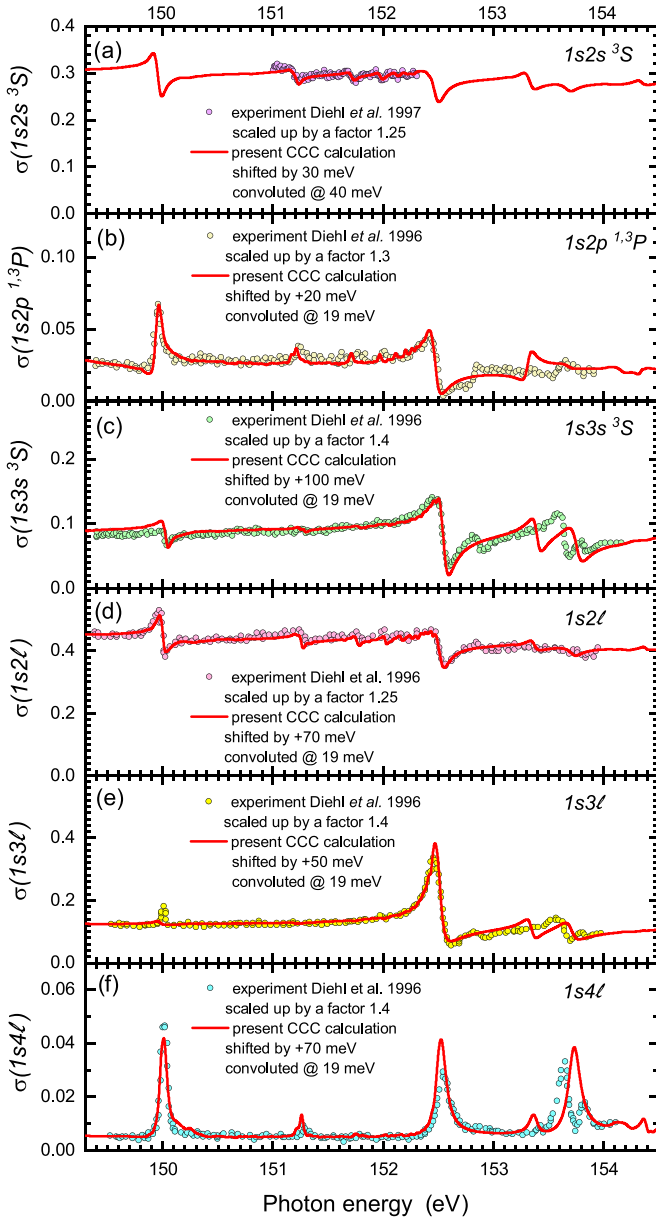


FIG. 6. Partial cross sections for populating excited intermediate singlet or triplet states in two-electron Li^+ by photoionization of neutral Li in the energy region 149.3–154.5 eV. The investigated cross sections are $\sigma(1s2s\ ^3S)$ (a), $\sigma(1s2p\ ^{1,3}P)$ (b), $\sigma(1s3s\ ^3S)$ (c), $\sigma(1s2\ell)$ (d), $\sigma(1s3\ell)$ (e), and $\sigma(1s4\ell)$ (f). The experimentally derived cross sections [13,14] are multiplied with constant factors between 1.25 and 1.4 to match the theoretical results. The red solid lines represent the present CCC calculations shifted in energy by 20 to 100 meV to match the experimental resonance positions and convoluted by Gaussians to simulate the experimental energy spread. The transformation parameters are provided in each panel individually. All cross sections are given in Mb.

(see Fig. 6). The dominant triply excited resonances expected in that energy range are identified in Fig. 3 with the strongest feature at about 152.5 eV associated with the term $2p^2[{}^3P]3s\ ^2P$. Except for $\sigma(1s2s\ ^3S)$ [Fig. 6(a)] which was measured at a photon-energy bandwidth of 40 meV, the other partial cross sections were obtained with a resolution of 19 meV. While Figs. 6(a) and 6(c) show partial cross

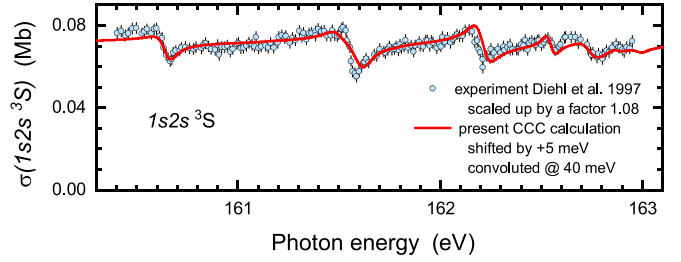


FIG. 7. The partial cross section $\sigma(1s2s\ ^3S)$ for populating the excited intermediate triplet state $1s2s\ ^3S$ in the two-electron Li^+ ion by photoionization of neutral Li in the energy region 160.3–163.1 eV. The experimentally derived cross-section function [15] is multiplied with a constant factor 1.08 to match the theoretical result. The red solid line represents the present CCC calculation shifted in energy by 5 meV to match the experimental resonance positions and convoluted by a 40-meV FWHM Gaussian to simulate the experimental energy spread.

sections for single intermediate terms, all other panels in Fig. 6 display partial cross sections summed over several terms.

In particular, the results presented in Fig. 6 are $\sigma(1s2s\ ^3S)$ in Fig. 6(a); $\sigma(1s2p\ ^1P) + \sigma(1s2p\ ^3P)$ in Fig. 6(b); $\sigma(1s3s\ ^3S)$ in Fig. 6(c); $\sigma(1s2\ell)$ comprising all singlet and triplet terms possible within the configurations $1s2s$ and $1s2p$ in Fig. 6(d); $\sigma(1s3\ell)$ comprising all singlet and triplet terms possible within the configurations $1s3s$, $1s3p$, and $1s3d$ in Fig. 6(e); and $\sigma(1s4\ell)$ comprising all singlet and triplet terms possible within the configurations $1s4s$, $1s4p$, $1s4d$, and $1s4f$ in Fig. 6(f).

All CCC weight factors w_{BS} for the states addressed in Fig. 6 are greater than 0.9995. The experimental cross-section functions were multiplied by constant factors between 1.25 and 1.4 to match the present CCC results which, in turn, were shifted by energies between 20 and 100 meV to (approximately) match the experimental resonance energies. The calculated cross sections were convoluted with Gaussians of an appropriate FWHM of 40 meV for Fig. 6(a) and 19 meV in all other cases. The theoretical and experimental cross sections are in agreement again. Notable differences occur at energies greater than 153 eV showing limitations of the present CCC approach.

All partial cross sections discussed so far contribute to net single photoionization. One last example in this series is $\sigma(1s2s\ ^3S)$ in the photon-energy range 160.3–163.1 eV. The experimental results of Diehl *et al.* [15] obtained with a photon-energy spread of 40 meV are compared with the present CCC calculations in Fig. 7. For the comparison, the experimental cross sections were multiplied with a constant factor 1.08 to match the CCC calculation which is shifted by +5 meV and convoluted with a Gaussian of 40-meV FWHM. The energy shift and correction factor are relatively small. The agreement of theory and experiment is very good.

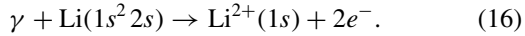
B. Net double ionization of $\text{Li}(1s^22s)$

The primary goal of the present investigation is the understanding of net double photoionization of the neutral three-electron Li atom and a high-quality calculation of the

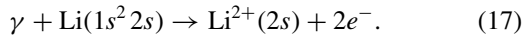
cross section σ_{02} . As in the preceding study on photoionization of the lithiumlike B^{2+} ion [3], this cross section is strongly influenced by IE processes including resonances with double K -shell vacancies. The same intermediate resonant states that are seen in net single ionization of Li also play a strong role in double photoionization.

Similar to the case of net single photoionization, several individual channels contribute to σ_{02} . Without regard of the probabilities of possible single-photon double-ionization processes to happen, they can be listed as follows.

(i) Direct nonsequential removal of the L -shell electron and one of the two K -shell electrons:

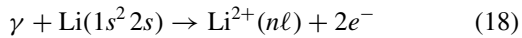


(ii) Direct nonsequential removal of both K -shell electrons:



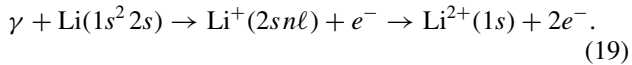
In the present context, we call these direct processes PDI in contrast to double photoionization, which includes direct and indirect processes leading to the net production of Li^{2+} ions.

(iii) The PDI processes may be accompanied by excitation of the remaining electron:



with principal quantum numbers $n \geq 2$ and orbital momentum quantum numbers $0 \leq \ell \leq n-1$. The excited Li^{2+} states produced in each of the listed processes (ii) and (iii) can only stabilize by radiative transitions so that the final charge state of the Li atom does not change further.

(iv) Ionization of a K -shell electron and excitation of the second K -shell electron to subshell $n\ell$ with subsequent autoionization of the intermediate doubly excited Li^+ ion:



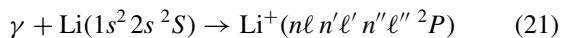
Excitation of the L -shell instead of the second K -shell electron together with single K -shell ionization produces a nonautoionizing excited state which remains in charge state Li^+ [see Eq. (12)].

(v) Again, together with single K -shell ionization, also the $2s$ electron can be excited in addition to a $1s$ electron:



with $n, n' \geq 2$ and $0 \leq \ell, \ell' \leq n-1, n'-1$, respectively. The intermediate doubly excited state autoionizes with high probability so that the final product is practically always a Li^{2+} ion the charge state of which cannot change further in a possible additional stabilization cascade.

(vi) Finally, direct K -shell double excitation with or without additional excitation of the L shell produces triply excited states that can decay by the emission of two electrons (emission of only one electron naturally contributes to net single ionization):



with $n, n', n'' \geq 2$ and all ℓ that are allowed for an electric dipole transition (other multipole transitions, although possible, are very unlikely and need not be considered here). Two classes of such highly excited states contributing to the final production of Li^{2+} have to be distinguished.

(vi a) The excitation energy of the resonant state is sufficient for the emission of two electrons only by (nonsequential) double-Auger decay. This is the case, for example, for the most prominent triply excited $2s^2 2p^2 P$ resonance for which a single-Auger process exclusively leads to a nonautoionizing Li^+ state. Ejection of two electrons to form Li^{2+} and thus contributing to σ_{02} is then only possible by a double-Auger decay.

(vi b) The excitation energy $E_{n\ell n'\ell' n''\ell''}$ of the resonant state relative to the $\text{Li}(1s^2 2s^2 S)$ ground level is greater than the threshold energy for the process described by Eq. (19) with $n\ell = 2s$, that is, $E_{n\ell n'\ell' n''\ell''} > (E_{2s^2}^{\text{tot}} - E_{1s^2 2s}^{\text{tot}})$ where $E_{2s^2}^{\text{tot}}$ and $E_{1s^2 2s}^{\text{tot}}$ are the total energies of the levels $2s^2^1 S$ and $1s^2 2s^2 S$ of Li^+ and neutral Li, respectively. In this case, two sequential single-Auger decays proceeding via an intermediate autoionizing Li^+ state can lead to the final production of Li^{2+} . When net double ionization by such a two-step Auger cascade is energetically allowed, the sequential emission of two electrons is typically more probable than a double-Auger process.

The threshold energy for populating the energetically lowest autoionizing two-electron level $\text{Li}^+(2s^2^1 S)$ from the ground state of neutral Li was found to be 151.65(3) eV in a precision Auger-spectroscopy experiment [70]. We note that a later experiment provided a threshold energy of 151.51(3) eV [71] which is outside the mutual quoted uncertainties by almost 3 times the estimated error bars. The existing theoretical predictions show similar differences [72]. Chung and Lin predicted an excitation energy $E_{2s^2} = 146.2366$ eV above the $1s^2$ ground level of Li^+ [73]. Together with the precisely known ionization potential 5.391 714 996(22) eV [74] of the Li atom, a threshold energy of 151.6283 eV results for the transition $\text{Li}(1s^2 2s^2 S_{1/2}) \rightarrow \text{Li}^+(2s^2^1 S_0)$. This may be the most accurate number available to date for the minimum energy above which IE processes can contribute to σ_{02} and above which triply excited resonances can decay in two sequential Auger processes leading to an enhancement of resonance features in the double-ionization cross-section function.

The PDI cross section σ_{KL} for direct removal of a K -shell and a L -shell electron [see Eq. (16)] with its onset at 81.0318 eV [74,75] is shown as the gray solid line in Fig. 1. It results from the present PDI model calculations. In the energy range from the threshold to ≈ 151 eV and apart from any resonance contribution, σ_{KL} is practically identical with the cross section σ_{02} obtained from our CCC calculations. The PDI cross section σ_{KK} for direct removal of both K -shell electrons [see Eq. (17)] has an onset of 172.8714 eV, a quantity which results from a combination of the results from a high-accuracy measurement [74] and high-precision calculations [75,76]. The cross section σ_{KK} was calculated using the present PDI model and is shown as the black thick solid line in Fig. 1. Its contribution to σ_{02} is only about 25% at $E_{\text{ph}} = 500$ eV and rapidly decreases towards lower energies. Processes (iii) described by Eq. (18) have a minimum onset energy of 172.8714 eV and thus cannot explain the strong increase of σ_{02} above ≈ 151 eV. What remains to fill in the gap between σ_{02} and the direct-ionization cross sections $\sigma_{KL} + \sigma_{KK}$ are the IE processes and associated resonances described

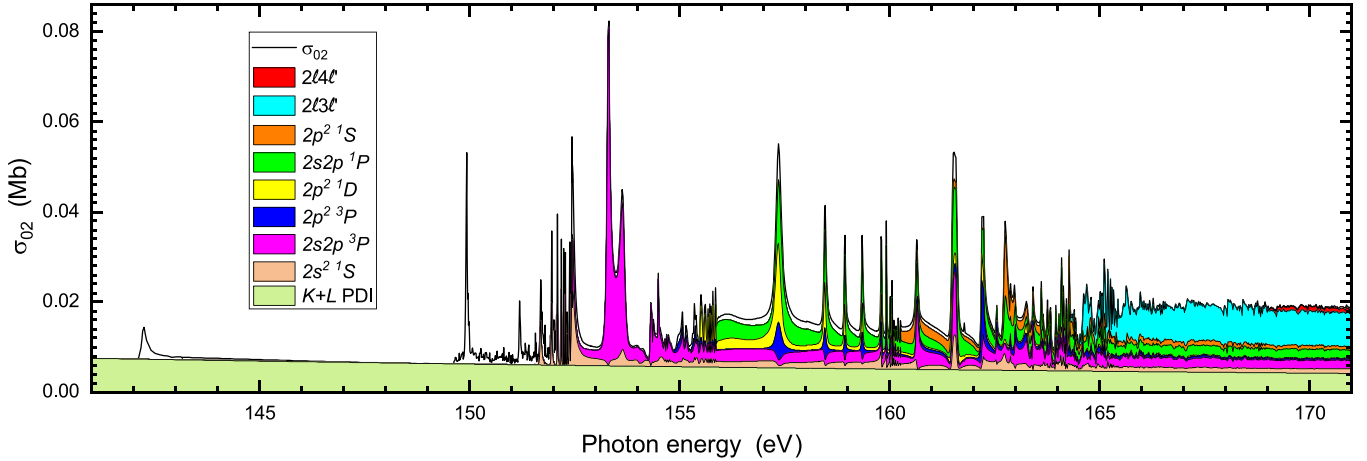


FIG. 8. Calculated contributions to the cross section σ_{02} for double photoionization of ground-level $\text{Li}(1s^2 2s^2 S_{1/2})$ atoms. The top black solid line represents σ_{02} obtained from the present CCC model. The light-green-shaded area at the bottom marks the contribution of $K + L$ PDI. The other color-shaded areas indicate the IE contributions from all possible individual terms in the $2\ell 2\ell'$ manifold and from the sums of all terms in the $2\ell 3\ell'$ (cyan shaded) and $2\ell 4\ell'$ (red-shaded) configurations.

by Eqs. (19) [process (iv)], (20) [process (v)], and (21) [process (vi)].

Figure 8 shows the dominant contributions of different mechanisms to the total cross section σ_{02} for the double photoionization of the neutral Li atom at energies below 171 eV. At the lower energies, the dominant contribution is direct non-sequential removal of one K -shell plus the L -shell electron. The cross section for this PDI process has been introduced as σ_{KL} and was calculated separately in the frame of the present PDI model. Close inspection shows that the model cross section is slightly lower than the CCC result in the region of the IE threshold. For the extrapolation of σ_{KL} towards higher energies we chose, therefore, to derive it from a fit to the CCC double-ionization cross section at energies below 151 eV. A suitable shape function for describing double photoionization cross sections was developed by Pattard [77]. It was used in the fit and the resulting extrapolated contribution to σ_{02} is represented by the light-green-shaded area at the bottom of the figure.

Plotted on top of σ_{KL} is the IE cross section $\sigma(2s^2 1S)$. This contribution is marked by light-brown shading. A strong contribution with a slightly higher onset energy follows. It is the partial cross section $\sigma(2s 2p^3 P)$ marked by magenta shading. The blue, yellow, green, and orange shadings belong to the IE cross sections $\sigma(2p^2 3P)$, $\sigma(2p^2 1D)$, $\sigma(2s 2p^1 P)$, and $\sigma(2s 2p^1 S)$, respectively. The contribution of all terms within the manifold of $2\ell 3\ell'$ configurations is represented by the cyan-shaded area in the stacked plot. A much smaller contribution of all terms within $2\ell 4\ell'$ configurations is visible as the red-shaded narrow area starting at an energy of approximately 169 eV.

The white area below the total double-ionization cross section σ_{02} cannot be assigned to individual contributions from different basis states but results from the whole set of 829 basis states used in the present CCC model. This is particularly obvious for the resonance features at energies below the IE threshold at about 151 eV.

Several of the calculated cross sections for direct and resonant IE processes can be compared to existing experi-

mental data obtained by Diehl *et al.* [14,15]. Partial cross sections $\sigma(n\ell n'\ell')$ and relative yields for the photoproduction of intermediate $\text{Li}^+(n\ell n'\ell')$ states from ground-level Li have been measured by detecting Auger electrons from the intermediate autoionizing levels and by determining their yields as a function of the photon energy. Comparisons of the present CCC results with experimentally derived partial cross sections are presented and discussed below.

Figure 9 shows partial IE cross sections $\sigma(2s^2 1S)$ for K -shell ionization plus K -shell excitation of the neutral Li atom. In the investigated photon-energy range, the Rydberg series of $2s 2p [^3P]ns^2 P$ resonances dominates the cross section for $n \geq 5$, that is, when the resonance energies exceed the threshold for the population of the $2s^2 1S$ level and thus permit sequential single-Auger decay for producing the final Li^{2+} ion.

The experimentally derived cross sections [14] are based on yield measurements of the Auger electrons emitted by autoionization of the intermediate $\text{Li}^+(2s^2 1S)$ ions. The yields were normalized to the photoabsorption cross sections of

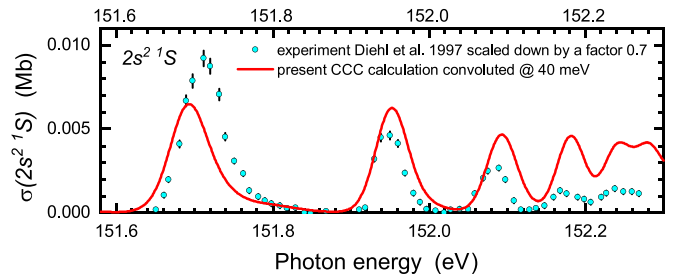


FIG. 9. Partial cross section for the photoproduction of intermediate $\text{Li}^+(2s^2 1S)$ from $\text{Li}(1s^2 2s^2 S)$. The cyan-shaded circles are the experimental results [14] scaled down by a factor 0.7 together with their statistical uncertainties. Measured yields were originally normalized to the photoabsorption cross sections of Mehlman *et al.* [42]. The solid red line is the result of the present CCC calculations convoluted with a 40-meV FWHM Gaussian. The basis-state weight factor in the CCC calculation is $w_{BS} = 0.7147$.

Mehlman *et al.* [42]. The uncertainty of that normalization is expected to be higher than the quoted $\pm 25\%$. As in the examples for nonautoionizing intermediate excited two-electron states, the published experimental partial cross sections were multiplied by a constant (energy-independent) factor to match the size of the CCC cross sections and to thereby facilitate a better comparison of theory and experiment. In the case of the $2s^2\ ^1S$ level, the constant factor 0.7 was chosen. The theoretical energy scale was left unchanged. For simulating the experimental energy spread of 40 meV, the calculated cross section was convoluted with a Gaussian of 40-meV FWHM.

Different from the IE cross sections for the production of intermediate singly excited $1snl$ states of the Li^+ ion, there are more obvious discrepancies between theory and experiment. This can be partly attributed to uncertainties in the experimental normalization procedure. But there are also differences in the relative sizes of peak features and different energy spacings between resonances that cannot be simply removed by a constant scaling factor or a fixed shift of the energy axis. We rationalize these discrepancies with the fact that the solid line only represents the contribution of one basis state with a weight factor $w_{\text{BS}} = 0.7147$. Consideration of the remaining 28% from admixtures of other configurations would probably fix most of the observed differences between theory and experiment.

We point out that the remaining $1-w_{\text{BS}}$ fraction of basis states that contribute to the representation of the true physical state $2s^2\ ^1S$ are dispersed among the 829 basis states considered in the present CCC model. All of these basis states contribute to the total single and double photoionization cross sections shown in Fig. 1 while their individual contributions to, e.g., the population of intermediate $2s^2\ ^1S$ cannot be sorted out.

Figure 10 displays the partial IE cross sections $\sigma(2p^2\ ^1D)$ and $\sigma(2s2p\ ^1P)$ at energies between 155.8 and 159.8 eV. In this range, a series of triply excited resonances is visible similar to the IE cross-section results shown in Fig. 9. Triply excited levels $2p^2\ [^1P]np\ ^2P$ of the Li atom with $n \geq 3$ decaying either to $2p^2\ ^1D$ [Fig. 10(a)] or $2s2p\ ^1P$ [Fig. 10(b)] are responsible for the observed Rydberg series.

The yellow-shaded and green-shaded circles represent the experimental data obtained by Diehl *et al.* [14] multiplied here by energy-independent factors 0.8 and 0.5, respectively. The latter factor is unusually different from 1. It was chosen to match the nonresonant “background” contribution of direct IE to the cross section $\sigma(2s2p\ ^1P)$ obtained from the present CCC calculations. However, as a consequence, the resonance contributions are then considerably smaller than the prediction of the CCC model. This discrepancy, like in the context of $\sigma(2s^2\ ^1S)$, is partly attributed to the nonunity weight factor $w_{\text{BS}} = 0.9010$ of the basis state assumed to represent the real physical state behind $2s2p\ ^1P$. As before, the theoretical results were convoluted with appropriate 40-meV FWHM Gaussians to simulate the experimental energy spread. In addition, the theory curves were shifted down by 40 meV to better match the experimental resonance positions.

Relative yields of Auger electrons from intermediate $\text{Li}^+(2s^2\ ^1S)$, $\text{Li}^+(2s2p\ ^3P)$, and $\text{Li}^+(2s2p\ ^1P)$ formed by the absorption of a single photon by neutral Li were measured by

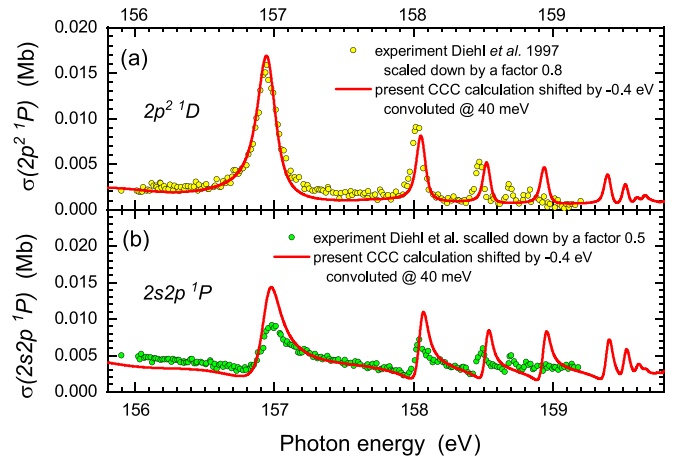


FIG. 10. IE cross sections for the photoproduction of intermediate $\text{Li}^+(2p^2\ ^1D)$ (a) and $\text{Li}^+(2s2p\ ^1P)$ (b) from ground-level $\text{Li}(1s^2\ 2s\ ^2S_{1/2})$ atoms. The experimental data [14] are represented by shaded circles. They were multiplied by factors 0.8 (a) and 0.5 (b). The red solid lines represent the contributions of the two most important basis states considered in the present CCC model for the representation of the real intermediate autoionizing states. Their weight factors within the presently employed set of basis states are $w_{\text{BS}} = 0.9542$ and 0.9010 , respectively. The theory curves were convoluted with Gaussians of 40-meV FWHM and shifted by -40 meV.

Diehl *et al.* [15] in the photon-energy range 160.0 to 163.6 eV. The bandwidth of the employed synchrotron radiation was determined to be 110 meV. The results of the experiments are shown by the shaded circles in Figs. 11(a)–11(c). Diehl *et al.* normalized their yields to match the direct-IE background with the predictions of their accompanying *R*-matrix calculations. The quoted uncertainty of the photon-energy scale is only ± 10 meV which is probably somewhat overoptimistic. The present CCC cross sections were shifted by -40 meV, a correction that is expected given the uncertainties of experimental and theoretical resonance energies. For the comparison with the experimental data, the theoretical cross sections $\sigma(2s^2\ ^1S)$, $\sigma(2s2p\ ^3P)$, and $\sigma(2s2p\ ^1P)$ were convoluted with a Gaussian of 110-meV FWHM.

There is mixed agreement between theoretical and experimental results. In particular, the resonance feature at about 161.5 eV is overestimated in Figs. 11(a) and 11(b). It is underestimated in Fig. 11(c). This resonance has been associated with the term $2s3s[^1S]3p\ ^2P$ by Kiernan *et al.* [8] (see Fig. 3). Azuma *et al.* assigned capital letter M to that resonance [9] (see Fig. 4) and specified resonance M to be represented by the leading configuration admixtures of 35% $2p3p^2$, 33% $2p3s^2$, and 23% $2s3s3p$ with an unknown 9% admixture of additional configurations. Yet another assignment, namely $2s2p[^1P]3s\ ^2P$, has been provided by Vo Ky *et al.* [17]. According to the present CCC calculations, this triply excited state of the Li atom can decay by a single-Auger process to $\text{Li}^+(2s^2\ ^1S)$, $\text{Li}^+(2s2p\ ^3P)$, or $\text{Li}^+(2s2p\ ^1P)$ with different decay probabilities and thus contributes to $\sigma(2s^2\ ^1S)$, $\sigma(2s2p\ ^3P)$, and $\sigma(2s2p\ ^1P)$.

The comparisons in Fig. 11 suggest that the decay rates to $\text{Li}^+(2s^2\ ^1S)$ and $\text{Li}^+(2s2p\ ^3P)$ are overestimated and that

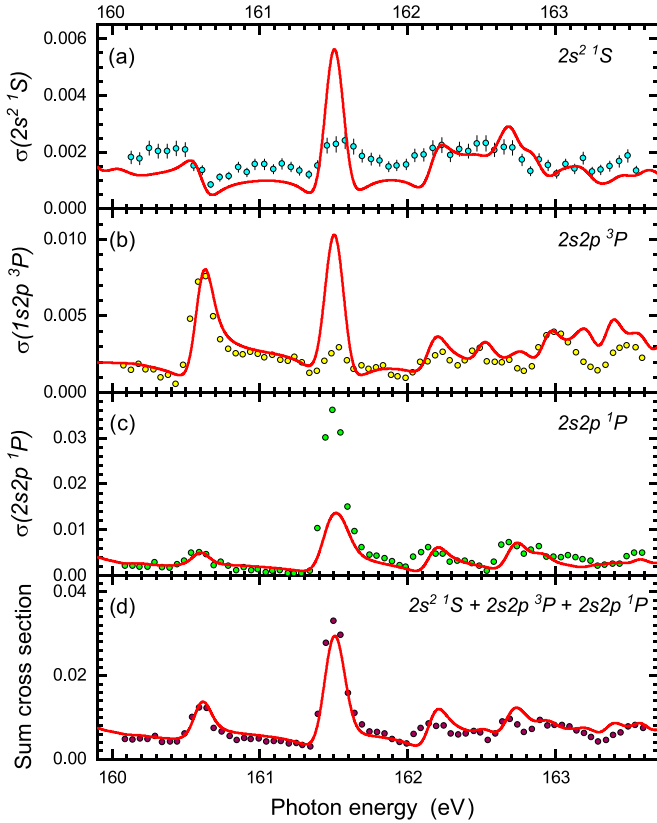


FIG. 11. Normalized yields of Auger electrons representing IE cross sections $\sigma(2s^2 \ ^1S)$, $\sigma(2s2p \ ^3P)$, and $\sigma(2s2p \ ^1P)$ of neutral Li describing the production of intermediate doubly excited levels in Li^+ . The experimental data were obtained by Diehl *et al.* [15]. (d) The sum of these cross sections scaled down by a factor 0.8. The present CCC results were convoluted with Gaussians of 110-meV FWHM and shifted to lower photon energies by -40 meV. All cross sections are given in Mb. For the basis-state weight factors see Figs. 9 and 10. For $2s2p \ ^3P$ the CCC model gives $w_{\text{BS}} = 0.9695$.

the probability for decay to $\text{Li}^+(2s2p \ ^1P)$ is underestimated. However, the total decay rate of resonance M is calculated fairly correctly in the present CCC model as indicated by the comparison shown in Fig. 11(d). The experimental yields of all Auger electrons arising from $\text{Li}^+(2s^2 \ ^1S)$, $\text{Li}^+(2s2p \ ^3P)$, and $\text{Li}^+(2s2p \ ^1P)$ were summed and recorded as a function of the photon energy. Accordingly, the theoretical convoluted cross sections $\sigma(2s^2 \ ^1S)$, $\sigma(2s2p \ ^3P)$, and $\sigma(2s2p \ ^1P)$ were summed and the result is shown by the red solid line in Fig. 11(d). With the experiment scaled down by a constant factor 0.8 there is agreement between theory and experiment. In this comparison, one still has to keep in mind that the intermediate doubly excited states of the Li^+ ion are represented by a single configuration each. These are 71.47% $2s^2$, 96.95% $2s2p \ ^3P$, and 90.1% $2s2p \ ^1P$, i.e., certain contributions are missing in the IE cross sections which are there in the 829-state representation of the present CCC model and the sum of which appears in the total single- and double-ionization cross sections.

The total double-photoionization cross section σ_{02} obtained from the present CCC calculations is compared with experimental data in Fig. 12. The bulk of measured cross sec-

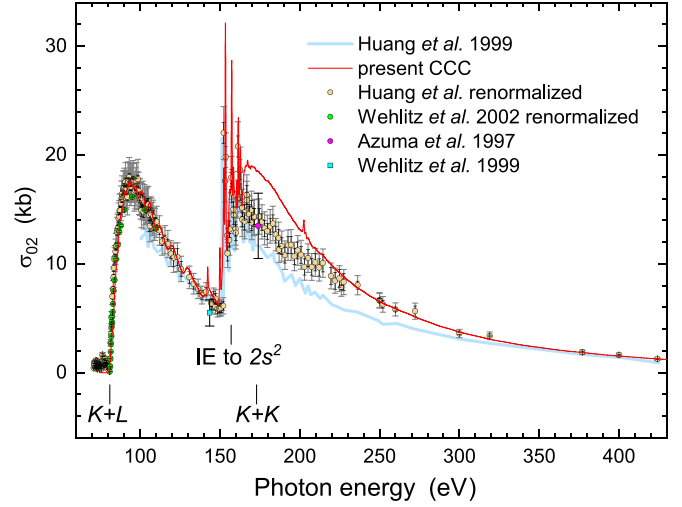


FIG. 12. Cross sections for the double photoionization of ground-level $\text{Li}(1s^2 2s \ ^2S_{1/2})$ atoms. Experimentally derived data are represented by yellow-shaded circles [44], green-shaded circles [46], the cyan-shaded square [20], and the magenta-shaded circle [16]. The original cross sections determined by Huang *et al.* [44] are shown as a light-blue solid line. The present CCC result is shown as the red solid line. Thresholds for $K+L$ and $K+K$ PDI are indicated as well as the onset of IE processes that contribute to double ionization.

tions is from a publication by Huang *et al.* [44]. The light-blue solid line in Fig. 12 represents the absolute cross sections as determined by Huang *et al.*, who essentially measured cross-section ratios $r = \sigma_{02}/\sigma_{01}$ and derived the individual cross sections σ_{01} and σ_{02} by normalization to the photoabsorption cross section of Mehlman *et al.* [42] near 110 eV. The quoted uncertainty of that procedure is between 22 and 25%.

The cross-section function σ_{01} thus obtained by Huang *et al.* [44] is represented in Fig. 2 by the gray-shaded diamonds. It obviously deviates from all other expectations with a maximum difference of almost 50% at 235 eV relative to the direct-ionization cross section calculated by Verner *et al.* [67]. Similar deviations have to be expected for σ_{02} and are visible in Fig. 12. We have decided therefore to renormalize the data of Huang *et al.* [44] by using their measured cross-section ratios r and determining the cross section σ_{02} by multiplication of r with what we think is a better representation of σ_{01} . As discussed in the connection with Fig. 2, the cross section $\sigma_{1s}^{\text{dir}} + \sigma_{2s}^{\text{dir}}$ calculated by Verner *et al.* [67] has a much reduced systematic uncertainty of (probably less than) $\pm 10\%$. The open circles in Fig. 12 are the result of our renormalization. They are shown with their error bars Δr determined by Huang *et al.* [44] for the ratios r and the total uncertainties resulting from the combination of Δr with the estimated uncertainty of 10% of the normalization.

Figure 12 also shows two isolated cross-section points obtained by Azuma *et al.* [16] at 174 eV and Wehlitz *et al.* [20] at 143.5 eV. The experiment by Azuma *et al.* [16] determined the absolute cross section σ_{02} in the close vicinity of the $3s^2 3p$ resonance with empty K and L shells. This resonance is not included in the present CCC model and cannot be compared with theory therefore. However, the nonresonant background of σ_{02} should be described well by the CCC calculations.

Instead, the nonresonant background cross section determined by Azuma *et al.* at 174 eV perfectly fits the renormalized cross-section function of Huang *et al.* [44] which deviates from the CCC result in this energy region. The quoted uncertainty of Azuma *et al.*'s [16] experimental cross section is quite large, though.

The additional measurement at 143.5 eV by Wehlitz *et al.* [20] is shown in Fig. 12 without additional renormalization. It is part of an experiment scrutinizing the role of the $2s^2 2p\ ^2P$ resonance in the double ionization of Li. The selected data point is fully consistent with the measurements of Huang *et al.* [44]. A more detailed comparison with the present CCC calculations is discussed below.

The CCC cross section σ_{02} represented by the red solid line in Fig. 12 was convoluted with a Gaussian with FWHM = 500 meV in order to simulate the experimental energy resolution of the Huang *et al.* data [44]. Very remarkable overall agreement of theory and experiment is found, except for the energy range between approximately 170 and 220 eV. Given the uncertainties of the experimental cross sections as they were originally published, one may argue that an inappropriate normalization of the experiment might have produced the observed deviation. However, all cross sections obtained by Huang *et al.* have been renormalized, which only partly removed the existing discrepancy.

The isolated data point at 174 eV determined by Azuma *et al.* [16] was also originally obtained by normalization of measured yields to the photoabsorption cross section of Mehlman *et al.* [42], which suggests that also that point should be corrected by a factor of approximately 1.2. Such renormalization would bring up the cross section to 16.2 Mb, which is still within the error bars shown in Fig. 12. Its total error bar would extend beyond the red solid line. We also mention that a similar deviation measured from calculated cross sections was not observed in the preceding study on double photoionization of Li-like B^{2+} ions. There, a CCC model similar to the present one was applied. After all, it is not clear whether the observed discrepancy between theory and experiment at energies from 170 to 220 eV can be attributed solely to either one of them.

Wehlitz and Juranić [36] made a strong attempt to find resonance contributions in the total double-photoionization cross section σ_{02} of the Li atom. For this purpose, they scanned the yields of Li^+ and Li^{2+} product ions and determined ratios $r = \sigma_{02}/\sigma_{01}$ as before. Compared to their preceding experiments [44] they improved the photon-energy resolution from 500 to 110 meV and greatly reduced statistical uncertainties. Different from their normalization to the measured photoabsorption cross section of Mehlman *et al.* [42] we normalized their ratios to the nonresonant direct-ionization cross section of Verner *et al.* [67]. The resulting σ_{02} data are shown as blue full circles in Fig. 13. The red solid line is the cross section obtained from the present CCC calculations convoluted with a 110-meV FWHM Gaussian.

The experimental and theoretical cross-section baselines between the resonances are in very satisfying agreement with one another. The dominant resonance features observed and identified in the experiments of Azuma *et al.* [9] were found again in σ_{02} by Wehlitz and Juranić [36]. They are reproduced by the present calculations though with energies slightly shifted and strengths not always identical. This is particularly

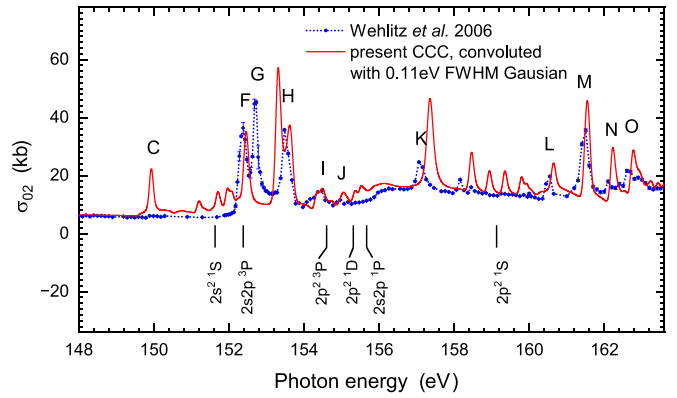


FIG. 13. Cross sections for the double photoionization of ground-level $Li(1s^2 2s^2 S_{1/2})$ atoms in the region of triply excited hollow Li states. The data were obtained at a resolution of 110 meV [36]. The present CCC result for σ_{02} has been convoluted with a 110-meV FWHM Gaussian to simulate the experimental conditions. The thresholds of IE cross sections $\sigma(2l 2l')$ for all possible terms are given by vertical bars. The resonances are identified by the capital letters introduced by Azuma *et al.* [9] (see Fig. 4).

true for the Rydberg series found by theory in the 157- to 160-eV energy range. The series was experimentally observed in the partial cross sections $\sigma(2p^2\ ^1D)$ and $\sigma(2s2p\ ^1P)$ (see Fig. 10) but is barely seen in the experimental σ_{02} . A similar rather striking example is the resonance at about 150 eV. It is quite strong in the theoretical cross section and practically invisible in the measured data. This is surprising since the resonance does show up in the total photoionization cross section displayed in Fig. 4 as well as in the single-ionization yield measurement presented in Fig. 3. It is resonance C in Azuma *et al.*'s [9] assignment while Kiernan *et al.* [8] identified it to be associated with the level $2s2p[^3P]3s\ ^2P$. This resonance has to decay by a double-Auger process in order to contribute to σ_{02} .

Wehlitz *et al.* [20] have investigated the possibility to observe double-Auger decay of the lowest-energy triply excited $2s^2 2p\ ^2P$ level in neutral Li (termed resonance A by Azuma *et al.* [9]). The experimental results of Wehlitz *et al.* [20] for the cross sections σ_{01} and σ_{02} are displayed in Fig. 14. The ratio of resonance peak heights above the nonresonant background cross section is one possible measure for the detectability of the double-Auger decay channel. In the example of Fig. 14, the ratio is approximately 3.5%. The peak height of resonance C in single ionization is approximately 75 kb. If the double-to-single-Auger decay ratio is the same as that of resonance A one can expect the contribution of resonance C to σ_{02} to be more than 2.5 kb. Observing this should have been possible by the experiment of Wehlitz *et al.* shown in Fig. 13.

The experimental cross sections σ_{01} and σ_{02} in the close vicinity of resonance A shown in Fig. 14 were renormalized to the direct nonresonant cross section of Verner *et al.* [67] as discussed several times already in this article. The cross section of Verner *et al.* is shown as a brown dotted line. The results of the present CCC calculation are the red solid lines which were convoluted with a 39-meV FWHM Gaussian to simulate the experimental energy resolution. Also shown in Fig. 14 is the cross section σ_{01} obtained by Fang and Chung [69]. Their result reproduces the experiment slightly

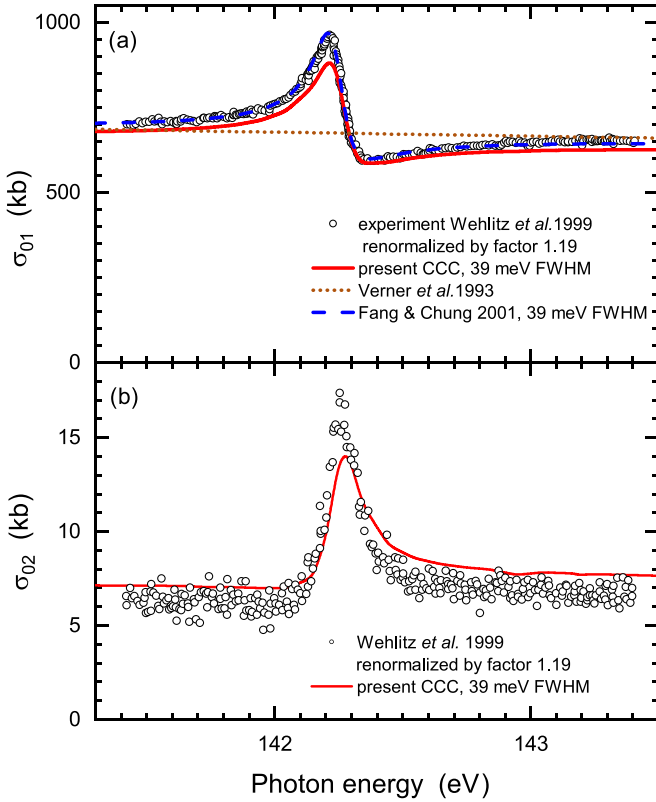


FIG. 14. Cross sections σ_{01} and σ_{02} for the double photoionization of ground-level $\text{Li}(1s^2 2s \ ^2S_{1/2})$ atoms in the vicinity of the $2s^2 2p \ ^2P$ resonance. The data published by Wehlitz *et al.* [20] were renormalized by a factor of 1.19. This factor was chosen such that the direct-ionization background of the measured resonance cross section matches the calculation of Verner *et al.* [67] which is shown in panel (a) as the brown dotted line. The renormalized experimental data are shown by open circles. The red solid lines are the present CCC results convoluted with a Gaussian of 110-meV FWHM. The blue dashed line in panel (a) is the result of Fang and Chung [69] for σ_{01} . The resonance positions were shifted to 42.254 eV as calculated by Fang and Chung with a quoted uncertainty of only ± 1 meV.

better than the present CCC calculation. However, different from the present work, the cross section σ_{02} could not be calculated by Fang and Chung while the present CCC calculations produced a cross section σ_{02} that matches the measurement quite well.

IV. SUMMARY AND OUTLOOK

For the neutral Li atom, the most fundamental three-electron system, we present comprehensive calculations of single- and double-photoionization cross sections, σ_{01} and σ_{02} , respectively, based on a large-scale convergent-close-coupling model. Direct nonsequential two-electron ionization channels are considered as well as numerous channels of ionization of the K shell with excitation of the second K -shell electron which are especially important in the double photoionization of the Li atom and Li-like ions. The CCC approach is a unified theory and considers interference of quantum-mechanical amplitudes of different reaction pathways. This manifests itself by the asymmetric Fano profiles

of resonance contributions to σ_{02} . All pathways to double photoionization of the Li atom are included in the calculations. Partial cross sections for individual ionization-excitation channels are among the byproducts of our theoretical approach.

Different from a limited attempt by Berrington and Nakazaki [19] to calculate σ_{02} in the region of triply excited resonances, the present theoretical approach produced good-quality results for the double-photoionization cross section from its threshold to the region far beyond all resonances and beyond the onset of direct nonsequential double ionization of the K shell. The overall agreement with the available experimental data is remarkably good. However, there are discrepancies in some details and, in particular, there are deviations between calculated and measured resonance features, mostly in their level energies and strengths. Given the difficulty to put the experimental cross sections for vaporized Li on an absolute scale, it remains unclear whether the observed differences have their origin in deficiencies of the experiments or the theoretical approach. Further measurements of double photoionization of other Li-like systems are desirable. There is already a set of experimental results available for the three-electron B^{2+} ion [3]; however, in that experiment only limited information on the contributions of triply excited resonances to the double-photoionization cross section could be obtained. In future measurements, emphasis should be put on the clear observation of resonance structures to provide benchmarks for improvements of theoretical models for double photoionization.

A good candidate for further measurements would be Li-like $\text{C}^{3+}(1s^2 2s)$ ions in their ground level. They can be relatively easily produced in an electron-cyclotron resonance ion source and the application of a merged-beams photon-ion arrangement like the one that was used for the B^{2+} photoionization experiments would facilitate the collection of the C^{5+} double-photoionization products. Preliminary CCC calculations show that, by concentrating on the resonance features in the cross section, high-resolution results can be obtained with good statistical accuracy.

ACKNOWLEDGMENTS

This work was supported by the Australian Research Council. High-performance computing resources were provided by the Pawsey Supercomputing Research Centre with funding from the Australian Government and the Government of Western Australia, the Australian National Computational Infrastructure, and the Texas Advanced Computing Center at the University of Texas at Austin. We cordially thank Dr. Ralf Wehlitz from the University of Wisconsin for providing experimental results in numerical form.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

- [1] A. Müller, P.-M. Hillenbrand, S.-X. Wang, S. Schippers, E. Lindroth, F. Trinter, J. Seltmann, S. Reinwardt, M. Martins, A. S. Kheifets, and I. Bray, Double- K -hole resonances in single photoionization of He-like B^{3+} ions, *Phys. Rev. A* **110**, 062802 (2024).
- [2] A. Müller, P.-M. Hillenbrand, S.-X. Wang, S. Schippers, I. Bray, A. S. Kheifets, E. Lindroth, S. Reinwardt, M. Martins, J. Seltmann, and F. Trinter, Direct double ionization of the He-like B^{3+} ion by a single photon, *Phys. Rev. A* **111**, 023115 (2025).
- [3] A. Müller, P.-M. Hillenbrand, S.-X. Wang, S. Schippers, S. Reinwardt, M. Martins, J. Seltmann, F. Trinter, I. Bray, D. V. Fursa, and A. S. Kheifets, Single and double photoionization of the Li-like B^{2+} ion: Unexpectedly strong ionization-excitation contributions, *Phys. Rev. A* **111**, 053108 (2025).
- [4] R. Bruch, G. Paul, J. Andrä, and L. Lipsky, Autoionization of foil-excited states in Li I and Li II, *Phys. Rev. A* **12**, 1808 (1975).
- [5] M. Rødbro, R. Bruch, and P. Bisgaard, High-resolution projectile Auger spectroscopy for Li, Be, B and C excited in single gas collisions I. Line energies for prompt decay, *J. Phys. B* **12**, 2413 (1979).
- [6] A. Müller, G. Hofmann, B. Weissbecker, M. Stenke, K. Tinschert, M. Wagner, and E. Salzborn, Correlated two-electron transitions in electron-impact ionization of Li^+ ions, *Phys. Rev. Lett.* **63**, 758 (1989).
- [7] L. M. Kiernan, E. T. Kennedy, J.-P. Mosnier, J. T. Costello, and B. F. Sonntag, First observation of a photon-induced triply excited state in atomic lithium, *Phys. Rev. Lett.* **72**, 2359 (1994).
- [8] L. M. Kiernan, M.-K. Lee, B. F. Sonntag, P. Sladeczek, P. Zimmermann, E. T. Kennedy, J.-P. Mosnier, and J. T. Costello, High-resolution photoion yield measurements of "hollow" atomic lithium, *J. Phys. B* **28**, L161 (1995).
- [9] Y. Azuma, S. Hasegawa, F. Koike, G. Kutluk, T. Nagata, E. Shigemasa, A. Yagishita, and I. A. Sellin, New photon-induced triply excited hollow atom states of lithium, *Phys. Rev. Lett.* **74**, 3768 (1995).
- [10] D. Cubaynes, S. Diehl, L. Journal, B. Rouvellou, J.-M. Bizau, S. Al Moussalami, F. J. Wullemier, N. Berrah, L. Vo Ky, P. Faucher, A. Hibbert, C. Blancard, E. Kennedy, T. J. Morgan, J. Bozek, and A. S. Schlachter, First photoexcitation measurements and R -matrix calculations of even-parity hollow states in laser-excited lithium atoms, *Phys. Rev. Lett.* **77**, 2194 (1996).
- [11] L. Journal, D. Cubaynes, J.-M. Bizau, S. Al Moussalami, B. Rouvellou, F. J. Wullemier, L. Vo Ky, P. Faucher, and A. Hibbert, First experimental determination and theoretical calculation of partial photoionization cross sections of lithium over the energy region of hollow atomic states, *Phys. Rev. Lett.* **76**, 30 (1996).
- [12] X. Yang, C. G. Bao, and C. D. Lin, Analysis of triply excited states of atoms in hyperspherical coordinates, *Phys. Rev. Lett.* **76**, 3096 (1996).
- [13] S. Diehl, D. Cubaynes, J.-M. Bizau, L. Journal, B. Rouvellou, S. Al Moussalami, F. J. Wullemier, E. T. Kennedy, N. Berrah, C. Blancard, T. J. Morgan, J. Bozek, A. S. Schlachter, L. Vo Ky, P. Faucher, and A. Hibbert, High resolution measurements of partial photoionization cross sections in hollow lithium: A critical comparison with advanced many-body calculations, *Phys. Rev. Lett.* **76**, 3915 (1996).
- [14] S. Diehl, D. Cubaynes, F. J. Wullemier, J.-M. Bizau, L. Journal, E. T. Kennedy, C. Blancard, L. Vo Ky, P. Faucher, A. Hibbert, N. Berrah, T. J. Morgan, J. Bozek, and A. S. Schlachter, Experimental observation and theoretical calculations of Rydberg series in hollow lithium atomic states, *Phys. Rev. Lett.* **79**, 1241 (1997).
- [15] S. Diehl, D. Cubaynes, E. T. Kennedy, F. J. Wullemier, J.-M. Bizau, L. Journal, L. Vo Ky, P. Faucher, A. Hibbert, C. Blancard, N. Berrah, T. J. Morgan, J. Bozek, and A. S. Schlachter, Hollow-atom-hollow-ion decay routes of triply excited lithium: First Auger results and a comparison with R -matrix calculations, *J. Phys. B* **30**, L595 (1997).
- [16] Y. Azuma, F. Koike, J. W. Cooper, T. Nagata, G. Kutluk, E. Shigemasa, R. Wehlitz, and I. A. Sellin, Photoexcitation of hollow lithium with completely empty K and L shells, *Phys. Rev. Lett.* **79**, 2419 (1997).
- [17] L. Vo Ky, P. Faucher, H. L. Zhou, A. Hibbert, Y.-Z. Qu, J.-M. Li, and F. Bely-Dubau, Inner-shell photoionization of ground-state lithium: Theoretical calculation in the photon energy region of hollow atomic states, *Phys. Rev. A* **58**, 3688 (1998).
- [18] Y. Zhang and K. T. Chung, Even-parity triply excited states of lithium, *Phys. Rev. A* **58**, 1098 (1998).
- [19] K. Berrington and S. Nakazaki, Direct and indirect ionization processes near the Li "hollow-atom" threshold, *J. Phys. B* **31**, 313 (1998).
- [20] R. Wehlitz, M.-T. Huang, K. A. Berrington, S. Nakazaki, and Y. Azuma, One-step double autoionization into the double-photoionization continuum, *Phys. Rev. A* **60**, R17(R) (1999).
- [21] F. W. King, High-precision calculations for the ground and excited states of the lithium atom, *Adv. At. Mol. Opt. Phys.* **40**, 57 (1999).
- [22] H. L. Zhou, S. T. Manson, L. Vo Ky, P. Faucher, F. Bely-Dubau, A. Hibbert, S. Diehl, D. Cubaynes, J.-M. Bizau, L. Journal, and F. J. Wullemier, Inner-shell photoionization of excited lithium, *Phys. Rev. A* **59**, 462 (1999).
- [23] H. L. Zhou, S. T. Manson, P. Faucher, and L. Vo Ky, Analysis of $2\ell 2\ell' n'' \ell''$ resonances in the photoionization of $1s^2 2p$ excited lithium, *Phys. Rev. A* **62**, 012707 (2000).
- [24] L. B. Madsen, P. Schlagheck, and P. Lambropoulos, Laser-induced transitions between triply excited hollow states, *Phys. Rev. A* **62**, 062719 (2000).
- [25] S. Diehl, D. Cubaynes, H. L. Zhou, L. Vo Ky, F. J. Wullemier, E. T. Kennedy, J. M. Bizau, S. T. Manson, T. J. Morgan, C. Blancard, N. Berrah, and J. Bozek, Angle-resolved photoelectron spectrometry studies of the autoionization of the $2s^2 2p^2 P$ triply excited state of atomic lithium: Experimental results and R -matrix calculations, *Phys. Rev. Lett.* **84**, 1677 (2000).
- [26] S. Diehl, D. Cubaynes, H. S. Zhou, L. Vo Ky, F. J. Wullemier, E. T. Kennedy, J. M. Bizau, S. T. Manson, C. Blancard, N. Berrah, and J. Bozek, The $2p^3$ triply excited hollow resonance of lithium: measurement and calculation of partial cross sections and angular behaviour, *J. Phys. B* **33**, L487 (2000).
- [27] G. Verbockhaven and J. E. Hansen, Autoionization of triply excited Rydberg series, *Phys. Rev. Lett.* **84**, 2810 (2000).
- [28] L. B. Madsen and K. Mølmer, Correlated electrons in lithium-like hollow atoms, *Phys. Rev. Lett.* **87**, 133002 (2001).
- [29] F. J. Wullemier, From doubly excited states of helium to triply excited states of lithium, *Phys. Essays* **13**, 230 (2000).
- [30] E. T. Kennedy, Photogeneration of hollow atoms: Recent developments, *Phys. Scr.* **2001**, 32 (2001).

- [31] M. J. Conneely and L. Lipsky, Energy levels and classifications of triply excited states of Li, Be⁺, B²⁺, and C³⁺, *At. Data Nucl. Data Tables* **82**, 115 (2002).
- [32] L. B. Madsen, Triply excited states: electron-electron correlations in lithium, *J. Phys. B* **36**, R223 (2003).
- [33] T. Morishita and C. D. Lin, Radial and angular correlations and the classification of intershell $2\ell 2\ell' 3\ell''$ triply excited states of atoms, *Phys. Rev. A* **67**, 022511 (2003).
- [34] A. K. Roy, Studies on the hollow states of atomic lithium using a density functional approach, *J. Phys. B* **37**, 4369 (2004).
- [35] K. T. Chung, Resonances in atomic photoionization, *Radiat. Phys. Chem.* **70**, 83 (2004).
- [36] R. Wehlitz and P. N. Juranić, Resonant double photoionization of lithium studied with medium energy resolution, *Phys. Rev. A* **74**, 042721 (2006).
- [37] R. Wehlitz, Simultaneous emission of multiple electrons from atoms and molecules using synchrotron radiation, *Adv. At. Mol. Opt. Phys.* **58**, 1 (2010).
- [38] A. Müller, A. Borovik, Jr., K. Huber, S. Schippers, D. V. Fursa, and I. Bray, Indirect contributions to electron-impact ionization of Li⁺($1s2s^3S_1$) ions: Role of intermediate double-*K*-vacancy states, *Phys. Rev. A* **97**, 022709 (2018).
- [39] D. L. Ederer, T. Lucatorto, and R. P. Madden, Autoionization spectra of lithium, *Phys. Rev. Lett.* **25**, 1537 (1970).
- [40] G. Mehlman, D. L. Ederer, E. B. Saloman, and J. W. Cooper, The *K*-edge photoabsorption cross section of lithium vapour, *J. Phys. B* **11**, L689 (1978).
- [41] G. Mehlman, D. L. Ederer, E. B. Saloman, and J. W. Cooper, Absolute photoabsorption cross section of core excited electrons in lithium vapor, *Jpn. J. Appl. Phys.* **17**, 167 (1978).
- [42] G. Mehlman, J. W. Cooper, and E. B. Saloman, Absolute photoabsorption cross section of the *K* shell of atomic lithium, *Phys. Rev. A* **25**, 2113 (1982).
- [43] L. M. Kiernan, M.-K. Lee, B. F. Sonntag, P. Zimmermann, J. T. Costello, E. T. Kennedy, A. Gray, and L. Vo Ky, Resonant photoionization of atomic lithium in the region of the first and second inner-shell thresholds, *J. Phys. B* **29**, L181 (1996).
- [44] M.-T. Huang, R. Wehlitz, Y. Azuma, L. Pibida, I. A. Sellin, J. W. Cooper, M. Koide, H. Ishijima, and T. Nagata, Single and double photoionization of lithium, *Phys. Rev. A* **59**, 3397 (1999).
- [45] D. Lukić, S. B. Whitfield, and R. Wehlitz, Lithium inner-shell resonances in the 70–77 eV photon energy region, *J. Phys. B* **42**, 085004 (2009).
- [46] R. Wehlitz, J. B. Bluett, and S. B. Whitfield, Comparison of the double- to single-photoionization ratio of Li with He, *Phys. Rev. A* **66**, 012701 (2002).
- [47] R. Wehlitz, M. M. Martinez, J. B. Bluett, D. Lukić, and S. B. Whitfield, Double-to-single photoionization ratio of lithium at medium energies, *Phys. Rev. A* **69**, 062709 (2004).
- [48] R. Wehlitz, M.-T. Huang, B. D. DePaola, J. C. Levin, I. A. Sellin, T. Nagata, J. W. Cooper, and Y. Azuma, Triple photoionization of lithium, *Phys. Rev. Lett.* **81**, 1813 (1998).
- [49] A. S. Kheifets, D. V. Fursa, and I. Bray, Two-electron photoionization of ground-state lithium, *Phys. Rev. A* **80**, 063413 (2009).
- [50] A. S. Kheifets, D. V. Fursa, C. W. Hines, I. Bray, J. Colgan, and M. S. Pindzola, Spin effects in double photoionization of lithium, *Phys. Rev. A* **81**, 023418 (2010).
- [51] A. S. Kheifets, D. V. Fursa, I. Bray, J. Colgan, and M. S. Pindzola, Differential cross sections of double photoionization of lithium, *Phys. Rev. A* **82**, 023403 (2010).
- [52] J. Colgan, M. S. Pindzola, and F. Robicheaux, Lattice calculations of the photoionization of Li, *Phys. Rev. Lett.* **93**, 053201 (2004).
- [53] J. Colgan, M. S. Pindzola, and F. Robicheaux, Double and triple photoionization of Li and Be, *Phys. Rev. A* **72**, 022727 (2005).
- [54] J. Colgan, D. C. Griffin, C. P. Ballance, and M. S. Pindzola, Total cross sections for the double photoionization of Li from the ground and excited states, *Phys. Rev. A* **80**, 063414 (2009).
- [55] A. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (version 5.12), National Institute of Standards and Technology, Gaithersburg, MD, 2024, <http://physics.nist.gov/asd> 10.18434/T4W30F.
- [56] A. S. Kheifets and I. Bray, Calculation of double photoionization of helium using the convergent close-coupling method, *Phys. Rev. A* **54**, R995(R) (1996).
- [57] A. S. Kheifets and I. Bray, Photoionization with excitation and double photoionization of the helium isoelectronic sequence, *Phys. Rev. A* **58**, 4501 (1998).
- [58] I. Bray, D. V. Fursa, A. S. Kheifets, and A. T. Stelbovics, Electrons and photons colliding with atoms: Development and application of the convergent close-coupling method, *J. Phys. B* **35**, R117 (2002).
- [59] A. W. Bray, A. S. Kheifets, and I. Bray, Calculation of atomic photoionization using the nonsingular convergent close-coupling method, *Phys. Rev. A* **95**, 053405 (2017).
- [60] D. V. Fursa and I. Bray, Calculation of electron-helium scattering, *Phys. Rev. A* **52**, 1279 (1995).
- [61] D. V. Fursa and I. Bray, Convergent close-coupling calculations of electron scattering on helium-like atoms and ions: Electron-beryllium scattering, *J. Phys. B* **30**, 5895 (1997).
- [62] A. S. Kheifets, Dynamic scaling of photo-double-ionization to electron impact, *Phys. Rev. A* **101**, 032701 (2020).
- [63] A. Müller, A. L. D. Kilcoyne, R. A. Phaneuf, K. Holste, S. Schippers, and A. S. Kheifets, Direct double ionization of the Ar⁺*M* shell by a single photon, *Phys. Rev. A* **103**, L031101 (2021).
- [64] A. Müller, M. Martins, A. Borovik, Jr., T. Buhr, A. Perry-Sassmannshausen, S. Reinwardt, F. Trinter, S. Schippers, S. Fritzsche, and A. S. Kheifets, Role of *L*-shell single and double core-hole production and decay in *m*-fold ($1 \leq m \leq 6$) photoionization of the Ar⁺ ion, *Phys. Rev. A* **104**, 033105 (2021).
- [65] R. F. Reilman and S. T. Manson, Photoabsorption cross sections for positive atomic ions with $Z \leq 30$, *Astrophys. J. Suppl. Ser.* **40**, 815 (1979).
- [66] J. J. Yeh and I. Lindau, Atomic subshell photoionization cross sections and asymmetry parameters: $1 \leq Z \leq 103$, *At. Data Nucl. Data Tables* **32**, 1 (1985).
- [67] D. A. Verner, D. G. Yakovlev, I. M. Band, and M. B. Trzhaskovskaya, Subshell photoionization cross sections and ionization energies of atoms and ions from He to Zn, *At. Data Nucl. Data Tables* **55**, 233 (1993).
- [68] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California, Berkeley, 1981).

- [69] T. K. Fang and K. T. Chung, L^2K -matrix method for triply excited lithium, *Phys. Rev. A* **63**, 020702(R) (2001).
- [70] P. Ziem, R. Bruch, and N. Stolterfoht, Autoionization spectra of Li I and Li II excited by H^+ and He^+ impact, *J. Phys. B* **8**, L480 (1975).
- [71] S. Diehl, D. Cubaynes, J.-M. Bizau, F. J. Wuilleumier, E. T. Kennedy, J.-P. Mosnier, and T. J. Morgan, New high-resolution measurements of doubly excited states of Li^+ , *J. Phys. B* **32**, 4193 (1999).
- [72] M. A. Albert, S. Laulan, and S. Barmaki, Calculation of doubly excited $^1S^e$ states of Li^+ using a B-spline based spectral approach of configuration type combined with the complex rotation method, *Radiat. Phys. Chem.* **158**, 83 (2019).
- [73] K. T. Chung and C. D. Lin, Doubly excited states of Li^+ below the $N = 2$ and $N = 3$ thresholds of Li^{2+} , *At. Data Nucl. Data Tables* **69**, 101 (1998).
- [74] B. A. Bushaw, W. Nörtershäuser, G. W. F. Drake, and H.-J. Kluge, Ionization energy of $^6,7Li$ determined by triple-resonance laser spectroscopy, *Phys. Rev. A* **75**, 052503 (2007).
- [75] G. W. F. Drake, Theoretical energies for the $n = 1$ and $n = 2$ states of the helium isoelectronic sequence up to $Z = 100$, *Can. J. Phys.* **66**, 586 (1988).
- [76] V. A. Yerokhin and V. M. Shabaev, Lamb shift of $n = 1$ and $n = 2$ states of hydrogen-like atoms, $1 \leq Z \leq 110$, *J. Phys. Chem. Ref. Data* **44**, 033103 (2015).
- [77] T. Pattard, A shape function for single-photon multiple ionization cross sections, *J. Phys. B* **35**, L207 (2002).