

Double autoionization of hollow-atom states

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A time-dependent close-coupling method for three-electron atomic systems is formulated to calculate the double autoionization of hollow-atom states. Initial excited states are obtained by relaxation of the Schrödinger equation in imaginary time, while autoionization rates are obtained by propagation in real time. A 12-coupled-channels nonperturbative calculation on a three-dimensional radial lattice yields a double-autoionization rate for the $\text{Li}(2s^22p) \rightarrow \text{Li}^{2+}(1s) + 2e^-$ transition that is somewhat smaller than earlier many-body perturbation theory calculations and in reasonable agreement with rates extracted from resonance profiles found in more recent γ -Li experiments.

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I. INTRODUCTION

The double-autoionization process in atoms is a three-electron process in which one electron becomes more tightly bound and the other two electrons move off in the long-range Coulomb field of the resulting ion. The lowest-order contribution in perturbation theory to the double-autoionization process is found in second-order correlation diagrams [1]. In the electron-impact ionization of atoms, triply excited states may be formed that only contribute to ionization by double autoionization [2], a so-called resonant-excitation auto-double-ionization (READI) process. The READI process was first observed in the electron-impact ionization of Li-like ions [3,4], where the resonant features are in reasonable agreement with both perturbative [5] and nonperturbative [6–10] calculations. To be specific, the calculated resonance-energy positions and total-autoionization widths are in reasonable agreement with experiment, while the absolute ionization strengths, which are directly related to the double-autoionization rates, are much more difficult to predict.

The double-autoionization process has also been observed for triply excited states of atoms with no additional inner electrons, so-called hollow-atom states. The READI process was first observed for hollow-atom states in the electron-impact ionization of Li^+ [11] and subsequently compared with perturbative [12] and nonperturbative [13,14] calculations. In the photon-impact ionization of atoms, triply excited states may be formed that only contribute to double ionization by double autoionization. This READI process was first observed in the photon-impact double ionization of Li [15], and then further experiments were compared with nonperturbative calculations [16]. Again, good agreement is found between experiment and theory for resonance-energy positions and total-autoionization widths, while the absolute double-ionization strengths, which are related to the double-autoionization rate, differ by a factor of 2. Recently, the READI process has been observed in the photon-impact double ionization of He^- [17], another example of the double autoionization of triply excited hollow-atom states.

In this paper a time-dependent close-coupling (TDCC) method for three-electron atomic systems, which has been

successfully applied to calculate photon-impact triple photoionization of Li [18] and electron-impact double ionization of He [19], is formulated to calculate the double autoionization of hollow-atom states. The three electrons in the atom are described by a nine-dimensional wave function, with the three radial dimensions represented on a numerical lattice and the six angular dimensions represented by a coupled-channels expansion. In this way, correlation effects among three electrons moving in the Coulomb field of the nucleus are taken into account—i.e., a numerical solution of the four-body Coulomb problem. Initial excited states are obtained by relaxation of the Schrödinger equation in imaginary time [20,21], while autoionization rates are obtained by projection onto final states during propagation in real time. Our first case nonperturbative results for $\text{Li}(2s^22p)$, which include resonance energies, total-autoionization rates, and double-autoionization rates, are compared with many-body perturbation theory (MBPT) calculations [1], nonperturbative calculations [13,14,16], and photoionization experiments [16]. Section II reviews the TDCC method for double autoionization, Sec. III presents results for $\text{Li}(2s^22p)$, and a brief summary is found in Sec. IV. Unless otherwise stated, we will use atomic units.

II. THEORY

For a three-electron atom the nonrelativistic Hamiltonian is given by

$$H = \sum_{i=1}^3 \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j=1}^3 \frac{1}{|\vec{r}_i - \vec{r}_j|}, \quad (1)$$

where \vec{r}_i are electron coordinates and Z is the atomic number. The total electronic wave function for a given total angular momentum \mathcal{L} may be expanded in coupled spherical harmonics:

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, t) = \sum_{l_1, l_2, L, l_3} \frac{P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t)}{r_1 r_2 r_3} W(((l_1, l_2) L, l_3) \mathcal{L}), \quad (2)$$

where l_i are electron angular momenta. The angular reduction of the time-dependent Schrödinger equation for the three-electron wave function of Eq. (2) yields a set of time-dependent close-coupled partial differential equations for each \mathcal{L} symmetry:

$$\begin{aligned} i \frac{\partial P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t)}{\partial t} &= T_{l_1 l_2 l_3}(r_1, r_2, r_3) P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) \\ &+ \sum_{l'_1, l'_2, l'_3} \sum_{i < j}^3 V_{l_1 l_2 L l_3, l'_1 l'_2 l'_3}^{\mathcal{L}}(r_i, r_j) \\ &\times P_{l'_1 l'_2 l'_3}^{\mathcal{L}}(r_1, r_2, r_3, t), \end{aligned} \quad (3)$$

where

$$T_{l_1 l_2 l_3}(r_1, r_2, r_3) = \sum_i^3 \left(-\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{l_i(l_i + 1)}{2r_i^2} - \frac{Z}{r_i} \right) \quad (4)$$

and the coupling operators are given in terms of standard $3j$ and $6j$ symbols; see the electron-impact double ionization of

the He paper of Pindzola *et al.* [19] [Eqs. (3)–(5)].

The initial condition for the solution of the time-dependent close-coupled equations of Eq. (3) in real time t is given by

$$P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t=0) = \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, \tau \rightarrow \infty), \quad (5)$$

where the radial wave functions for the resonance excited state, $\bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, \tau \rightarrow \infty)$, are obtained by relaxation of the close-coupled equations of Eq. (3) in imaginary time, $\tau = it$ [20,21]. As an example, the radial wave functions at $\tau = 0$ for Li($2s^2 2p$) are given by

$$\begin{aligned} \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, \tau = 0) &= P_{2s}(r_1) P_{2s}(r_2) P_{2p}(r_3) \delta_{l_1,0} \delta_{l_2,0} \delta_{L,0} \delta_{l_3,1} \\ &+ P_{2s}(r_1) P_{2p}(r_2) P_{2s}(r_3) \delta_{l_1,0} \delta_{l_2,1} \delta_{L,1} \delta_{l_3,0} \\ &+ P_{2p}(r_1) P_{2s}(r_2) P_{2s}(r_3) \delta_{l_1,1} \delta_{l_2,0} \delta_{L,1} \delta_{l_3,0}, \end{aligned} \quad (6)$$

where $P_{nl}(r)$ are bound single-particle orbitals and $\mathcal{L}=1$. To guard against relaxation to any state involving $1s$ character, the Schmidt orthogonalization

$$\begin{aligned} \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, \tau) &= \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, \tau) - \int_0^\infty P_{1s}(r'_1) \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r'_1, r_2, r_3, \tau) dr'_1 P_{1s}(r_1) \delta_{l_1,0} \\ &- \int_0^\infty P_{1s}(r'_2) \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r'_2, r_3, \tau) dr'_2 P_{1s}(r_2) \delta_{l_2,0} - \int_0^\infty P_{1s}(r'_3) \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r'_3, \tau) dr'_3 P_{1s}(r_3) \delta_{l_3,0} \\ &+ \int_0^\infty \int_0^\infty P_{1s}(r'_1) P_{1s}(r'_2) \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r'_1, r'_2, r_3, \tau) dr'_1 dr'_2 P_{1s}(r_1) P_{1s}(r_2) \delta_{l_1,0} \delta_{l_2,0} \\ &+ \int_0^\infty \int_0^\infty P_{1s}(r'_1) P_{1s}(r'_3) \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r'_1, r_2, r'_3, \tau) dr'_1 dr'_3 P_{1s}(r_1) P_{1s}(r_3) \delta_{l_1,0} \delta_{l_3,0} \\ &+ \int_0^\infty \int_0^\infty P_{1s}(r'_2) P_{1s}(r'_3) \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r'_2, r'_3, \tau) dr'_2 dr'_3 P_{1s}(r_2) P_{1s}(r_3) \delta_{l_2,0} \delta_{l_3,0} \end{aligned} \quad (7)$$

is carried out at each imaginary time step. For the $(ss)Sp$ channel, the first projection eliminates the $1sns2p$ states, the second projection eliminates the $ns1s2p$ states, and the fourth projection restores the $1s1s2p$ state that was double counted. The elimination of any $1s$ character in the relaxation procedure is equivalent to a Feshbach projection [20], yielding a fully correlated nine-dimensional $Q\Psi$ wave function representing the autoionizing excited state.

The time-dependent close-coupled equations of Eq. (3) are solved, in both real and imaginary time, using standard numerical methods [18,19] to obtain a discrete representation of the radial wave functions and all operators on a three-dimensional lattice. Our specific implementation on massively parallel computers is to partition all the radial coordinates over the many processors, so-called domain decomposition. At each time step of the solution only those parts of the radial wave functions needed to calculate the

second derivatives found in Eq. (4) are passed between the processors.

Specific double-autoionization rates are obtained by projection onto fully antisymmetric determinantal wave functions during the propagation of Schrödinger's equation in real time. For example, the double-autoionization rate for the $\text{Li}(2s^2p) \rightarrow \text{Li}^{2+}(1s) + 2e^-$ transition is obtained from periodic calculation of the probability

$$\mathcal{P}(t) = \sum_{l_1, l_2, L, S, l_3} \mathcal{P}_{l_1 l_2 L S l_3}(t), \quad (8)$$

where the individual spins s_i are assumed to be $\frac{1}{2}$, S is the intermediate total spin, and the number of distinct $l_1 l_2 L S l_3$ determinantal wave functions is quite different from the number of $l_1 l_2 L l_3$ coupled channels. The determinantal projection probability is given by

$$\begin{aligned} \mathcal{P}_{l_1 l_2 L S l_3}(t) = & \sum_{k_2} \sum_{k_3} \left| \sum_{L'} \delta_{L, L'} Q_a R(123, t) - \sum_{L'} (-1)^{l_2 + l_3 + L + L'} \sqrt{(2L+1)(2L'+1)} \begin{Bmatrix} l_2 & l_1 & L \\ l_3 & \mathcal{L} & L' \end{Bmatrix} Q_b R(132, t) \right. \\ & - \sum_{L'} (-1)^{l_1 + l_2 - L'} \delta_{L, L'} Q_c R(213, t) + \sum_{L'} (-1)^{l_1 + l_2 + L} \sqrt{(2L+1)(2L'+1)} \begin{Bmatrix} l_2 & l_1 & L \\ l_3 & \mathcal{L} & L' \end{Bmatrix} Q_c R(312, t) \\ & \left. + \sum_{L'} (-1)^{l_2 + l_3 + L'} \sqrt{(2L+1)(2L'+1)} \begin{Bmatrix} l_1 & l_2 & L \\ l_3 & \mathcal{L} & L' \end{Bmatrix} Q_b R(231, t) - \sum_{L'} \sqrt{(2L+1)(2L'+1)} \begin{Bmatrix} l_1 & l_2 & L \\ l_3 & \mathcal{L} & L' \end{Bmatrix} Q_a R(321, t) \right|^2, \end{aligned} \quad (9)$$

where

$$\begin{aligned} R(ijk, t) = & \int_0^\infty \int_0^\infty \int_0^\infty P_{1s}(r_i) P_{k_2 l_2}(r_j) \\ & \times P_{k_3 l_3}(r_k) P_{l_1 l_2 L' l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) dr_1 dr_2 dr_3 \end{aligned} \quad (10)$$

and

$$\begin{aligned} Q_a = & \sqrt{\frac{1}{2}} \delta_{S,0} - \sqrt{\frac{1}{6}} \delta_{S,1}, \\ Q_b = & \sqrt{\frac{2}{3}} \delta_{S,1}, \\ Q_c = & -\sqrt{\frac{1}{2}} \delta_{S,0} - \sqrt{\frac{1}{6}} \delta_{S,1}. \end{aligned} \quad (11)$$

Care must be taken in the sums over the electron momenta k_2 and k_3 found in the collision probability of Eq. (9). When the associated angular momenta are equal—for example, $l_2 = l_3$ —the sums must be restricted to avoid doubling counting of distinct continuum states. To avoid contamination

from the continuum piece of the two-electron bound-state wave functions, we restrict the sums over the electron momenta k_2 and k_3 to those approximately satisfying the conservation of energy [18,19]:

$$E_{atom} = E_{ion} + \frac{k_2^2}{2} + \frac{k_3^2}{2}. \quad (12)$$

We note that the total-autoionization rate for $\text{Li}(2s^2p)$ may be obtained from periodic calculation of the probability

$$\mathcal{P}(t) = 1.0 - \sum_{l_1, l_2, L, l_3} \mathcal{P}_{l_1 l_2 L l_3}(t), \quad (13)$$

where the sum is now over $l_1 l_2 L l_3$ coupled channels. The coupled-channels probability is given by either

$$\begin{aligned} \mathcal{P}_{l_1 l_2 L l_3}(t) = & \left| \int_0^\infty \int_0^\infty \int_0^\infty \bar{P}_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, \tau \rightarrow \infty) \right. \\ & \left. \times P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) dr_1 dr_2 dr_3 \right|^2 \end{aligned} \quad (14)$$

or

$$\begin{aligned} \mathcal{P}_{l_1 l_2 L l_3}(t) = & \left| \int_0^\infty \int_0^\infty \int_0^\infty P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) dr_1 dr_2 dr_3 \right|^2 - \int_0^\infty \int_0^\infty \left| \int_0^\infty P_{1s}(r_1) P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) dr_1 \right|^2 dr_2 dr_3 \delta_{l_1,0} \\ & - \int_0^\infty \int_0^\infty \left| \int_0^\infty P_{1s}(r_2) P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) dr_2 \right|^2 dr_1 dr_3 \delta_{l_2,0} - \int_0^\infty \int_0^\infty \left| \int_0^\infty P_{1s}(r_3) P_{l_1 l_2 L l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) dr_3 \right|^2 dr_1 dr_2 \delta_{l_3,0}. \end{aligned} \quad (15)$$

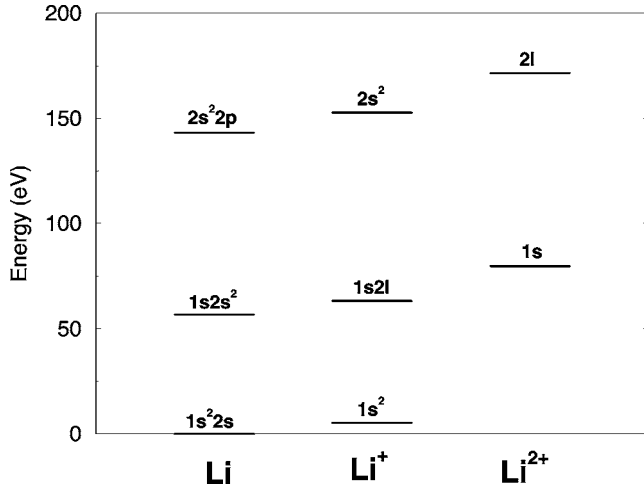


FIG. 1. Energy levels for selected states in the Li isonuclear sequence

The double- and total-autoionization rates are obtained by plotting the probabilities of Eqs. (8) and (13) versus time and extracting the slopes.

III. RESULTS

Energy levels for selected states in the Li isonuclear sequence are shown in Fig. 1. A single-configuration Hartree-Fock method [22] is used to calculate the approximate energy positions for the Li and Li⁺ states. The Li($2s^22p$) triply excited hollow-atom state has a strong single-autoionization rate to the Li⁺($1s2l$) excited states and a much weaker correlated single-autoionization rate to the Li⁺($1s^2$) ground state [23]. We note that double autoionization of Li($2s^22p$) may only occur to the Li²⁺($1s$) ground state.

The time-dependent close-coupling calculations for the Li($2s^22p$) triply excited hollow-atom state employed a $(192)^3$ lattice with each radial direction from $0.0 \rightarrow 19.2$ spanned by a uniform mesh spacing $\Delta r_i = 0.10$. Relaxation of the coupled equations in imaginary time used 18 000 time steps of $\Delta \tau = 0.01$ to achieve full convergence. Propagation of the coupled equations in real time used 5000 time steps of $\Delta t = 0.002$. A mask function was employed at the lattice boundary to prevent reflection of the large fast-moving part of the wave function due to autoionization.

Li($2s^22p$) hollow-atom state energies, total-autoionization rates, and double-autoionization rates are presented in Table I. The first TDCC calculation used three coupled channels [$(ss)Sp$, $(sp)Ps$, and $(ps)Ps$] and two determinantal projection functions [$(ss)^1Sp$ and $(ss)^3Sp$]. The second TDCC calculation used six coupled channels and eight determinantal projection functions. To take into account initial-state angular correlation, the second TDCC calculation added three coupled channels [$(pp)Sp$, $(pp)Pp$, and $(pp)Dp$] and six determinantal projection functions [$(pp)^1Sp$, $(pp)^3Sp$, $(pp)^1Pp$, $(pp)^3Pp$, $(pp)^1Dp$, and $(pp)^3Dp$]. The third TDCC calculation used 12 coupled channels and 10 determinantal projection functions. To take into account final-state angular correlation, the third TDCC calculation added six coupled channels [$(sp)Pd$, $(ps)Pd$, $(sd)Dp$, $(ds)Dp$, $(pd)Ps$, and $(dp)Ps$] and two determinantal projection functions [$(sp)^1Pd$ and $(sp)^3Pd$]. The total TDCC autoionization rates obtained using either Eq. (14) or (15) are in excellent agreement. The largest 12-channel TDCC calculation has a hollow-atom state energy that is 0.2% lower than MBPT calculations [1] and 0.2% higher than experiment [16]. The 12-channel TDCC calculation has a total-autoionization rate that is in excellent agreement with MBPT calculations [1], 8% higher than R -matrix pseudostates calculations [13,16], 14% higher than saddle-point complex rotation calculations [14], and 7% higher than experiment [16]. Finally, the 12-channel TDCC calculation has a double-autoionization rate that is 45% lower than MBPT calculations [1] and 20% higher than experiment [16]. The TDCC ratio of double-autoionization rate to the total-autoionization rate is found to be 3.7%, in comparison with the experimental value of 3.3% [16].

IV. SUMMARY

In conclusion, we find that a time-dependent close-coupling method for three-electron atomic systems may be formulated and used to calculate accurate double-autoionization rates of hollow-atom states. Our first case nonperturbative results for Li($2s^22p$) are found to be in reasonable agreement with energies and rates found in previous γ +Li experiments [16]. The fact that our time-dependent close-coupling method includes Coulomb four-body breakup in a nonperturbative manner gives it a powerful advantage over all many-body perturbation theory

TABLE I. Energies and autoionization rates for the Li($2s^22p$) hollow-atom state (1.0 a.u. of energy = 27.212 eV, 1.0 a.u. of frequency = 4.13×10^{16} Hz).

Method	Energy	Total-autoionization rate	Double-autoionization rate
TDCC (3 channels)	-2.1747	0.0033	0.00010
TDCC (6 channels)	-2.2200	0.0044	0.00014
TDCC (12 channels)	-2.2402	0.0049	0.00018
MBPT [1]	-2.2354	0.0049	0.00033
Experiment [16]	-2.2453	0.0046	0.00015

methods. With steady growth in computational power, we look forward to refining the accuracy of the present results for Li and to the study of other hollow-atom states found in three-electron atomic ions.

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