Benchmark Nonperturbative Calculations for the Electron-Impact Ionization of Li(2*s*) and Li(2*p*)

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Three independent nonperturbative calculations are reported for the electron-impact ionization of both the ground and first excited states of the neutral lithium atom. The time-dependent close-coupling, the *R* matrix with pseudostates, and the converged close-coupling methods yield total integral cross sections that are in very good agreement with each other, while perturbative distorted-wave calculations yield cross sections that are substantially higher. These nonperturbative calculations provide a benchmark for the continued development of electron-atom experimental methods designed to measure both ground and excited state ionization.

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A key production process for many astrophysical and laboratory plasmas is the electron-impact ionization of the atomic and molecular constituents. Accurate collisional-radiative modeling [1] of plasmas far from equilibrium requires a knowledge of electron ionization rates from both the ground state and the metastable excited states of atoms, molecules, and their ions [2]. To date, experiments have concentrated almost exclusively on measurements of electron-impact ionization from the ground state of atomic and molecular systems [3]. However, novel experimental techniques using magneto-optical traps [4] and crossed electron, atom, and laser beams [5] have recently been developed which provide measurements of electron-impact ionization of alkali atoms in excited levels.

Until eight years ago, the most accurate theoretical calculations for the electron-impact direct ionization of atoms and their ions were based on quantal perturbative methods [6]. The perturbative methods were known to be of limited accuracy, especially for neutral atoms, due to their incomplete treatment of long-range Coulomb three-body interactions. Since 1993, a number of quantal nonperturbative methods have been developed which provide benchmark accuracy for the electron-impact excitation and ionization of simple atoms and their ions. For the electron-impact ionization of hydrogen, the convergent close-coupling [7], the hyperspherical close-coupling [8], the *R* matrix with pseudostates [9], the time-dependent close-coupling [10], and the exterior complex scaling [11] methods yield results over a wide range of incident energies that are all within the error bars of the total cross section measurements of Shah *et al.* [12]. The convergent close-coupling (CCC), the *R* matrix with pseudostates (RMPS), and the time-dependent close-coupling (TDCC) methods have been successfully used to calculate electron-impact direct ionization cross sections for other atoms and their ions. For example, all three methods were found to predict [13] peak ionization cross sections for Al^{2+} that were substantially higher (40%) than previous crossed-beam experimental measurements [14]. Subsequent new experimental measurements for Al^{2+} [15] were found to be in much better agreement with the predictions of the nonperturbative methods.

In this Letter we report on three independent nonperturbative calculations for the electron-impact ionization of both the ground and first excited states of the neutral lithium atom. For ionization of Li(2*s*) the new RMPS calculations are found to be in very good agreement with previous CCC [16] and TDCC [17] nonperturbative calculations of total integral cross sections. Because of the doubling of total *LS* symmetries, and subsequent tripling of the number of sets of close-coupled channels, the ionization of Li(2*p*) is computationally much more demanding than the ionization of Li(2*s*) for all three nonperturbative methods. For ionization of Li(2*p*) the new TDCC and RMPS calculations are found to be in very good agreement with previous CCC [18] nonperturbative calculations of total integral cross sections. In addition, for ionization of both Li(2*s*) and Li(2*p*) the TDCC and CCC calculations of ejected-energy differential cross sections are found to be in very good agreement. Thus, the combined theoretical results provide individual absolute total integral and ejected-energy differential cross sections, as well as Li(2*p*)/Li(2*s*) cross section ratios, that can serve as benchmarks for future experimental efforts to measure electron-impact ionization of atoms in excited states. In the following paragraphs, we first discuss the application

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of the nonperturbative methods to the ionization of lithium, then present total integral and ejected-energy differential cross section results, and finally compare the nonperturbative results with perturbative distorted-wave calculations and existing experimental measurements.

In all three nonperturbative methods, the $1s^2$ core of the neutral lithium atom remains inactive or frozen. All three methods make use of a basis set of bound and continuum radial orbitals for the active outer electron of the lithium atom. In the TDCC method, the one-electron target basis is obtained by direct lattice diagonalization of the radial Hamiltonian given by

$$h(r) = -\frac{1}{2}\frac{d^2}{dr} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_D(r) + V_X(r), \tag{1}$$

where $Z = 3$, $V_D(r)$ is the direct Hartree potential for the $1s^2$ core, and $V_X(r)$ is a local exchange potential. To eliminate unphysical excitation of the core, the $l = 0$ bound and continuum radial orbitals are generated using a pseudopotential. In the RMPS method, the $2l$, $3l$, and $4l$ bound radial orbitals are obtained by solution of the radial frozen-core Hartree-Fock equation; i.e., the $V_X(r)$ of Eq. (1) becomes a nonlocal operator. In our version of the RMPS method (see [13] for details) the remaining bound and continuum radial orbitals begin as a set of nonorthogonal Laguerre orbitals of the form

$$P_{nl}(r) = N_{nl}(\lambda_l r)^{l+1} e^{-\lambda_l/2} L_{n+l}^{2l+1}(\lambda_l r), \tag{2}$$

which are subsequently orthogonalized to the Hartree-Fock orbitals and each other in the process of diagonalizing the target Hamiltonian. The screening parameters, λ_l, are adjusted so that the ionization limit for lithium is roughly midway between two term energies of the same symmetry. In the CCC method, all bound radial orbitals begin as a set of orthogonal Laguerre orbitals similar to those of Eq. (2). The screening parameters, λ_l, are adjusted so that diagonalization of the target Hamiltonian yields accurate low-lying eigenvalues and a reasonable spread of continuum eigenvalues in the energy range of interest for ionization.

With a description of the N-electron target atom now in hand, the three nonperturbative methods solve the $(N+1)$-electron scattering problem in quite different manners. For more details, we refer the reader to the original TDCC [10], RMPS [13], and CCC [7] papers that addressed very similar problems in the electron ionization of atoms.

In the TDCC method, the time-dependent Schrödinger equation takes the form

$$i\frac{\partial P_{l_1 l_2}^{LS}(r_1, r_2, t)}{\partial t} = T_{l_1 l_2}(r_1, r_2) P_{l_1, l_2}^{LS}(r_1, r_2, t) + \sum_{l_1', l_2'} U_{l_1 l_2, l_1' l_2'}^{L}(r_1, r_2) P_{l_1' l_2'}^{LS}(r_1, r_2, t), \tag{3}$$

where $T_{l_1 l_2}(r_1, r_2)$ contains kinetic energy, centrifugal barrier, nuclear, direct Hartree and local exchange operators, and $U_{l_1 l_2, l_1' l_2'}^{L}(r_1, r_2)$ couples the various $(l_1 l_2)$ scattering channels. At a time $t = 0$ before the collision, the two-electron radial wave functions, $P_{l_1 l_2}^{LS}(r_1, r_2, t = 0)$, are given by spatial products of the $P_{2s}(r)$ or $P_{2p}(r)$ orbitals and an incoming radial wave packet. At a sufficient time $t = T$ following the collision, the radial wave functions, $P_{l_1 l_2}^{LS}(r_1, r_2, t = T)$, are projected onto products of bound and continuum radial orbitals to obtain probabilities and collision cross sections for both excitation and ionization. The TDCC equations were solved for all partial waves from $L = 0$ to 6 and these results were topped up for partial waves from $L = 7$ to 50 using an extrapolation method based on perturbative distorted-wave calculations.

In the RMPS method, the time-independent $(N+1)$-electron Hamiltonian is diagonalized in a basis of antisymmetrized products of N-electron target states and a complete set of bound and continuum radial orbitals whose derivatives vanish at the surface of an internal region box. By matching this solution with the solution in the external region a K matrix may be extracted which yields excitation cross sections to positive-energy pseudostates that may be interpreted as ionization of the target. The pseudostate expansion used is very similar to that employed in [13] where more details can be found. Just below the ionization limit, the negative-energy pseudostates contain some continuum character, and just above the ionization limit, the positive-energy pseudostates contain some bound character. Thus, to calculate a more accurate total cross section, we determine the sum of partial cross sections to those pseudostates just below the ionization limit plus all pseudostates above the ionization limit, while projecting out the contributions from the bound portions of these pseudostates [see Eq. (1) of [13]]. Here the equations in the asymptotic region were solved using the unpublished program STGF, originally written by Seaton [19] for ions and modified by Badnell [20] for neutral atoms; it uses perturbation theory to treat the direct multipole coupling terms. We employed the R-matrix method with exchange for all partial waves from $L = 0$ to 12 and the R-matrix method without exchange for partial waves from $L = 12$ to 20; we then topped up the partial-wave sum using the method described in Badnell *et al.* [13].

In the CCC method, the time-independent $(N+1)$-electron Lippman-Schwinger equation for the K matrix is solved directly in momentum space. The resulting K matrix again yields excitation cross sections to positive-energy pseudostates that may be interpreted as ionization of the target. The quality of this pseudostate representation of a true continuum state may be measured by the overlap of the two states. This has been checked to tend to infinity with increasing basis size. We note also that these pseudostates are very similar to those used in the RMPS method, with the main difference being that, in the RMPS case the Laguerre orbitals are orthogonalized to Hartree-Fock orbitals and themselves, where in the CCC case an orthogonal Laguerre basis is used for all radial

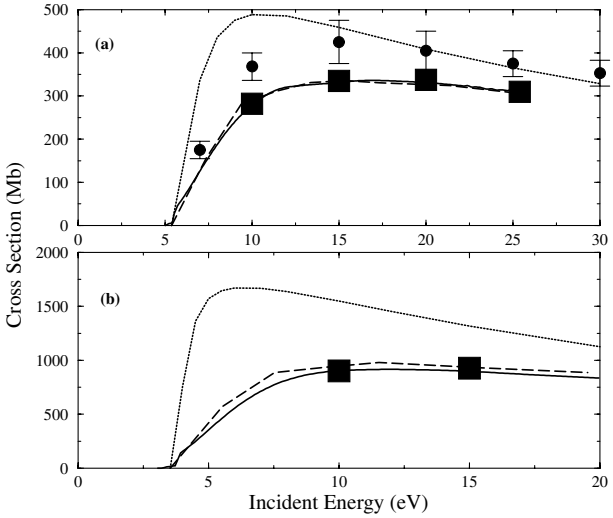

FIG. 1. Total integral cross section for electron-impact ionization of (a) Li($2s$) and (b) Li($2p$). Solid squares: time-dependent close-coupling method, solid line: R matrix with pseudostates method: long dashed line: converged close-coupling method; short dashed line: distorted-wave method; solid circles: experiment [22]. (1.0 Mb $= 1.0 \times 10^{-18}$ cm^{-2}.)

target-space orbitals. The equations may be solved for every partial wave treated, with the higher partial waves requiring the least computational effort. Exchange is incorporated in the potential matrix elements and dies off gradually with increasing angular momentum. The number of partial waves treated increases with the incident electron energy, and enough are taken to ensure convergence. In the present case $L = 0$ to 20 proved to be sufficient.

A perturbative distorted-wave (DW) method [21] is also employed to calculate electron-impact ionization cross sections for the neutral lithium atom. The $2s$ and $2p$ bound orbitals are obtained by solution of the $1s^2$ frozen-core Hartree-Fock equation. The continuum radial orbitals for the ejected electron are calculated in the V^{N-1} potential for the $Li^+ 1s^2$ core, while the orbitals for the incident and scattered electrons are calculated in the V^N potential for Li $1s^2 2s$ or $1s^2 2p$. The first-order scattering amplitude obtained using a mixed basis of V^N and V^{N-1} continuum orbitals yields partial-wave cross sections that match the nonperturbative calculations at sufficiently high total angular momentum. Alternative choices for the continuum orbital potentials may be made, yielding a variety of perturbative distorted-wave methods whose cross section predictions may vary by 50% and more for neutral-atom ionization.

Total integral cross sections for the electron-impact ionization of Li($2s$) are presented in Fig. 1(a). The three independent nonperturbative calculations are in very good agreement with each other. A perturbative DW calculation yields a peak cross section at 10 eV that is 50% higher than the nonperturbative cross section peak near 15 eV. The only experimental measurements [22] in this lower energy region also peak near 15 eV but are 40% higher than the nonperturbative cross section peak. The apparent agreement between experiment and the perturbative distorted-wave calculation is, in our opinion, fortuitous. At higher energies this experimental cross section is larger than the cross section determined from a more recent experiment [23], which, as discussed in [16], is in good agreement with the cross section determined from CCC calculations in this energy range. There is also evidence to indicate that the measurements of [22] suffered from experimental difficulties [23].

Total integral cross sections for the electron-impact ionization of Li($2p$) are presented in Fig. 1(b). Again the

TABLE I. Spin-resolved partial wave total integral cross sections for Li($2p$) at an incident energy of 10 eV. TDCC denotes time-dependent close-coupling method, CCC denotes convergent close-coupling method, RMPS denotes R-matrix pseudostates method, and DW denotes distorted-wave method. The superscript of the angular momentum channel L denotes the parity of the state, and cross sections are given in Mb (1.0 Mb $= 1.0 \times 10^{-18}$ cm^2).

	Singlet				Triplet			
L	TDCC	CCC	RMPS	DW	TDCC	CCC	RMPS	DW
0^e	5.32	5.66	5.44	23.56	1.88	2.12	1.43	5.63
1°	20.19	20.36	19.94	37.05	21.62	22.30	22.47	19.99
1^e	1.57	1.79	1.27	2.29	36.18	36.60	42.08	45.27
2^e	33.52	33.96	39.14	85.62	30.56	32.98	42.90	69.17
2°	2.39	2.60	2.33	2.67	38.70	40.00	44.72	39.01
3°	34.14	40.78	39.35	113.95	27.56	28.00	29.57	144.70
3^e	3.87	4.14	3.89	4.09	41.58	42.64	46.32	31.01
4^e	53.27	53.12	54.09	100.73	35.22	37.60	33.88	158.88
4°	5.22	5.51	5.64	3.73	32.10	33.90	37.12	21.78
5°	47.78	49.59	47.82	79.37	50.06	52.58	50.04	130.02
5^e	5.40	5.34	5.16	2.94	25.47	24.22	23.55	14.53
6^e	35.68	37.44	32.76	55.72	54.07	58.23	55.01	88.89
6°	3.91	4.28	3.56	2.14	15.10	16.48	13.95	9.39
0−6	252.26	264.57	260.40	513.86	410.10	427.65	443.04	778.27
Total	(Singlet	plus	Triplet)					
plus top-up	903.52	980.06	887.60	1551.99				

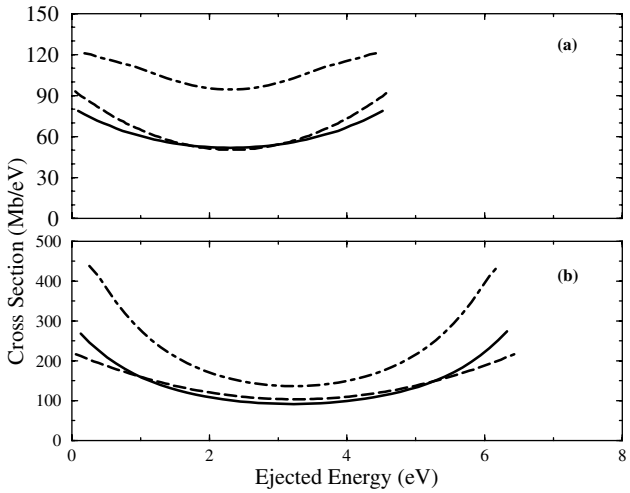

FIG. 2. Ejected-energy differential cross sections for electron-impact ionization of Li at an incident energy of 10 eV, (a) Li($2s$), (b) Li($2p$). Solid line: time-dependent close-coupling method; long dashed line: converged close-coupling method; chain dashed line: distorted-wave method. (1.0 Mb = 1.0×10^{-18} cm^2.)

three independent nonperturbative calculations are in very good agreement with each other. A perturbative DW calculation yields a peak cross section at 6 eV that is 90% higher than the nonperturbative cross section peak near 12 eV. We also note that the Li($2p$) ionization cross section is almost 3 times larger than the Li($2s$) ionization cross section.

The very good agreement among the nonperturbative methods for total integral cross sections also extends to spin-resolved partial wave cross sections. As an example, we present results for Li($2p$) ionization at an incident energy of 10 eV in Table I. For low angular momenta the perturbative distorted-wave calculations may differ by up to a factor of 4 from the consensus nonperturbative result.

As a further challenge to experiment, we present in Fig. 2 ejected-energy differential cross sections for the electron-impact ionization of Li($2s$) and Li($2p$) at an incident energy of 10 eV. The range of ejected energies for the $2s$ and $2p$ cross sections is different because of the difference in ionization potentials ($I_{2s} = 5.39$ eV and $I_{2p} = 3.54$ eV). The time-dependent close-coupling and the converged close-coupling methods are in very good agreement with each other. The largest differences in the nonperturbative results are found at the smallest ejected energies, being at most 15%. On the other hand, the perturbative DW calculations for Li($2s$) are almost uniformly a factor of 2 higher than the nonperturbative cross sections at all ejected energies. The perturbative DW calculations for Li($2p$) are about 30% higher than the nonperturbative cross sections at equal energy sharing, growing to almost a factor of 2 at the smallest ejected energies.

In summary, three independent nonperturbative calculations are reported for the electon-impact ionization of both the ground $2s$ and excited $2p$ states of the neutral lithium atom. The Li($2p$) ionization calculations are found to be much more computationally demanding than the Li($2s$) ionization calculations due to a threefold increase in the number of sets of coupled channels. The TDCC, RMPS, and CCC nonperturbative calculations for Li($2s$) and Li($2p$) are found to yield ionization cross sections that are substantially lower than the predictions of a perturbative DW method based on a mixed basis of V^N and V^{N-1} scattering potentials. We hope that these nonperturbative cross section results will serve as benchmarks for the continued development of electron-atom experiments designed to measure both ground and excited state ionization. Excited state ionization from metastable levels in more complex atoms and ions is a key process in the accurate collisional-radiative modeling of rapidly evolving astrophysical and laboratory plasmas.

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