Electron-impact ionization of the metastable excited states of Li⁺

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Abstract
Electron-impact ionization cross sections for the 1s2s 1S and 1s2s 3S metastable states of Li⁺ are calculated using both perturbative distorted-wave and non-perturbative R-matrix with pseudo-states and time-dependent close-coupling methods. Term-resolved distorted-wave calculations are found to be approximately 15% above term-resolved R-matrix with pseudostates calculations. On the other hand, configuration-average time-dependent close-coupling calculations are found to be in excellent agreement with the configuration-average R-matrix with pseudostates calculations. The non-perturbative R-matrix and close-coupling calculations provide a benchmark for experimental studies of electron-impact ionization of metastable states along the He isoelectronic sequence.

1. Introduction
Electron-impact ionization of low-charged ions is an important component of many processes in astrophysics and controlled fusion plasmas. This topic has therefore generated considerable interest, both experimental and theoretical. Previous studies of ground-state He (Pindzola and Robicheaux 1998, Pindzola et al 2004), as well as He–like Li (Pindzola et al 2000) and Be (Colgan et al 2003), have shown that both the R-matrix with pseudo-states (RMPS) method (Bartschat 1998) and time-dependent close-coupling (TDCC) methods (Pindzola and Schultz 1996, Pindzola and Robicheaux 1996) give cross sections that are in very good agreement with experiment.

Far less work has been done on the electron-impact ionization cross section of metastable ions. One important example is excited He (1s2s 3S), which has been studied both in experiment and theory. The experiment, performed by Dixon et al (1976), is in reasonable agreement at high energies with Bethe–Born calculations that pre-date the experiment (Briggs and Kim 1971), and is in good agreement with first-order plane-wave Born results generated shortly afterwards (Ton-That et al 1977). More recently, however, several non-perturbative calculations have shown a large discrepancy with experiment (Colgan and Pindzola 2002, Bartschat 2002, Fursa and Bray 2003). These papers used TDCC, convergent close-coupling,
and R-matrix with pseudostates (RMPS) methods. All of these calculations are in agreement, and all differ from the Dixon experiment by a factor of 2, even at high energies. The helium discrepancy motivates us to see whether the situation improves with metastable He-like Li; this paper presents the results of our theoretical calculations in anticipation of experiments.

Further motivation comes from plasma modelling. It has been previously shown that ionization from the metastable Li+ can dominate the effective ionization rate coefficient even at relatively low electron densities \(10^{10}\ \text{cm}^{-3}\) (Loch et al 2004). However, all existing data on the excited states of Li+ are based on distorted-wave calculations, which can get progressively worse as the term energy gets higher; this was demonstrated in H-like ions, including Li2+ (see Griffin et al 2005). Thus it is important to test the accuracy of the ionization data from excited states and to determine the effect that such data have on plasma modelling.

In this paper we build upon a previous study of the Li+ ground state (Pindzola et al 2000) to examine the electron-impact ionization cross section of metastable 1s2s 1S and 1s2s 3S Li+. We compare the perturbative distorted-wave method with the non-perturbative RMPS and TDCC methods. The cross sections calculated using the non-perturbative methods converge to the same value in Li+, while the distorted-wave method gives results that are significantly higher. This study provides a benchmark for future experimental studies of electron-impact ionization from metastable states along the He isoelectronic sequence. In the following section we discuss the various methods we have used to calculate electron-impact ionization cross sections of metastable Li+.

The results of these calculations are presented and compared in section 3.

2. **Theory**

2.1. Distorted-wave method

The distorted-wave (DW) cross sections are calculated from a triple partial-wave expansion of the first-order perturbation theory scattering amplitude. Both direct and exchange components of the scattering amplitude are included. The incoming and outgoing electrons are calculated in a \(V_N\) potential, while the ejected electron is calculated in a \(V_{N-1}\) potential, where \(N\) is the number of electrons in the target ion (Younger 1985). The DW potential for all continuum electrons is made up of a configuration-average Hartree potential for the direct interaction, and a local semiclassical approximation for the exchange interaction.

For the term-resolved distorted-wave calculations, the bound orbitals are calculated using Fischer’s multi-configuration Hartree–Fock code (Froese Fischer et al 1997). A double configuration (1s2 and 1s2s) calculation for the 1s2s 1S term yields an energy of \(-5.036\ \text{au}\) and an ionization potential of 14.59 eV, in good agreement with the experimental value of 14.86 eV (National Institute of Standards and Technology 2006). A single configuration (1s2s) calculation for the 1s2s 3S term yields an energy of \(-5.109\ \text{au}\) and an ionization potential of 16.58 eV, in very good agreement with the experimental value of 16.60 (National Institute of Standards and Technology 2006).

For the configuration-average DW calculations, the bound orbitals are calculated using Cowan’s (1981) Hartree–Fock code. Calculation for the 1s2s configuration yields an energy of 16.07 eV, in good agreement with the experimental value of 16.16 eV.

2.2. R-matrix with pseudostates method

The codes used in this work are based on the serial codes published by Berrington et al (1995), with modifications for the addition of pseudostates (see, e.g. Gorczyca and Badnell 1997), and
Table 1. Partial wave contributions to the configuration-averaged ionization cross sections for several incident electron energies, \( E \). The RMPS calculation was topped-up using the methods described by Burgess et al (1970) from \( L = 14 \), while the TDCC calculation was topped up with DW from \( L = 7 \). The relative magnitude of the top up becomes larger as \( E \) increases because higher partial waves become significant (1 Mb = 10\(^{-18}\) cm\(^2\)).

| \( E \) (eV) | \( L = 0 \rightarrow 13 \) | \( L = 14 \rightarrow 50 \) | \( L = 0 \rightarrow 6 \) | \( L = 7 \rightarrow 25 \) |
|------------|-----------------|-----------------|-----------------|-----------------|
| 30         | 38.02           | 0.01            | 31.43           | 5.56            |
| 40         | 43.18           | 0.16            | 32.50           | 10.08           |
| 50         | 43.28           | 0.50            | 30.04           | 13.70           |
| 100        | 33.48           | 3.42            | —               | —               |

parallelization described in Mitnik et al (1999), Mitnik et al (2003) and Ballance and Griffin (2004). In this method, the high Rydberg states and the target continuum are represented by a set of orthogonalized Laguerre radial wavefunctions: the so-called pseudostates. The ionization cross sections are determined by summing over excitations above the ionization threshold, including all single-electron excitations to the pseudostates as well as doubly excited states.

Our RMPS basis used spectroscopic orbitals up to \( n = 3 \) and pseudostates from \( n = 4 \) to \( n = 14 \), with a maximum orbital angular momentum of \( l = 4 \), though omitting \( g \) orbitals when the principal quantum number exceeded 10. \( LS \Pi \) partial waves from \( L = 0 \) to 13 were calculated using the RMPS method which includes exchange. Higher angular momentum contributions to the ionization cross section, commonly referred to as ‘top-up’, were accounted for by employing methods originally described by Burgess et al (1970) (see also Burgess1974). The magnitude of the top-up is shown for several incoming-electron energies in table 1. The contribution of these higher partial waves only becomes significant at higher energies (past the peak of the cross section), but these contributions are well treated by the perturbative methods used.

2.3. Time-dependent close-coupling method

We use the ‘frozen core’ approximation that was previously used in electron-ionization from metastable helium, where we freeze the 1s electron (see Colgan and Pindzola (2002) and references therein). The frozen 1s orbital is the ground state of the hydrogenic Li\(^{2+}\) ion. A complete set of orbitals are then obtained by diagonalization of the single-particle Hamiltonian, including the direct term of the Hartree potential, and a local approximation to the exchange interaction. The local exchange potential was scaled to give single-particle energies close to experiment.

The initial two-electron wavefunction, \( P^{LS}_{l_1l_2}(r_1, r_2, t = 0) \), is an antisymmetrized product of a radial wavepacket and the target 2s radial orbital, with a particular \( LS \) symmetry. The propagation in time is governed by the Schrödinger equation, which we write as a set of time-dependent close-coupled partial differential equations

\[
\frac{\partial P^{LS}_{l_1l_2}(r_1, r_2, t)}{\partial t} = T_{l_1l_2}(r_1, r_2) P^{LS}_{l_1l_2}(r_1, r_2, t) + \sum_{l_1', l_2'} U^{L}_{l_1l_2, l_1'l_2'}(r_1, r_2) P^{LS}_{l_1'l_2'}(r_1, r_2, t),
\]

where \( T_{l_1l_2}(r_1, r_2) \) is the single particle Hamiltonian, which includes kinetic energy, nuclear, direct and local exchange operators, while \( U^{L}_{l_1l_2, l_1'l_2'}(r_1, r_2) \) couples the \((l_1l_2)\) scattering channels.

Some time after the collision, the two-electron radial wavefunctions are projected onto products of the single-particle orbitals to calculate the probability of excitation. The ionization
probabilities, and hence the ionization cross sections, are found by subtracting the probability of any electrons being bound from unity.

The TDCC calculations are topped up from $L = 7$ to 25 with distorted-wave calculations (see table 1 for the magnitude of the top-up). At the energies considered, DW agrees with TDCC at higher partial waves: the discrepancy is only for low angular momenta. Because we have not gone to very high energy in our TDCC calculations, the contribution of $L > 25$ partial waves is negligible.

3. Results

The term-resolved DW and RMPS results are shown in figure 1. We see that for both methods the cross sections are larger for the $1s2s \, 1S$ than the $1s2s \, 3S$ across the entire energy range. Furthermore, the DW results are approximately 15% higher than the fitted RMPS results. The data fits were made using the formula of Younger (1981):

$$\sigma_{\text{ionization}} = \frac{1}{IE} \left( A(1 - 1/u) + B(1 - 1/u)^2 + C \ln(u) + D \ln(u)/u \right)$$  \hspace{1cm} (2)

where $I$ is the ionization energy, $E$ is the incident electron energy and $u = E/I$. The coefficients $A$, $B$, $C$ and $D$ are determined from a least-squares fit to the calculated cross section (fitting parameters are available from the authors upon request). Note that the coefficient $C$ can be independently determined from the photoionization cross section, but we have left it as a free parameter.

While the DW and RMPS calculations are term resolved, and thus return both $1s2s \, 1S$ and $1s2s \, 3S$ cross sections, the TDCC calculation is configuration averaged and only gives a single cross section for the $1s2s$ configuration. In order to compare the various theoretical calculations we show all of the configuration-averaged results in figure 2. The RMPS $1S$ and $3S$ results have been converted to a configuration-average cross section by averaging the fits of (2). The DW cross section in this graph was calculated using the configuration-average approximation (see section 2.1). We also took an average of the term-resolved DW
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Figure 2. Configuration-averaged electron-impact ionization cross sections, $\sigma_{\text{ionization}}$, against incident electron energy, $E$. The distorted-wave calculation (dashed line) gives a cross section around 15% larger than the non-perturbative RMPS calculation (solid line). Three TDCC points are also shown (squares), and these are in good agreement with the RMPS calculation ($1\text{Mb} = 10^{-18}\text{ cm}^2$).

It is interesting that the perturbative DW method produces cross sections that are in good agreement with TDCC and RMPS for the ground state ($1s^2 1S$) ionization (Pindzola et al 2000) and overestimates the metastable cross section. This is not unexpected for such a near-neutral system, since DW does not include higher-order coupling between the outgoing electrons. This ‘three-body’ effect is more important when the ionization limit is lower, as it is in the case of metastable Li$^+$. This trend is similar to that found by Griffin et al (2005) for hydrogenic systems, including Li$^{2+}$. The discrepancy between the perturbative distorted-wave method and the non-perturbative RMPS and TDCC methods is therefore larger for ionization from excited states than for ground states.

One would also expect the effect to be more important when the effective ion charge (the charge that the escaping electrons see) is smaller. In fact, this trend can be seen when one compares the metastable He ionization cross sections of Colgan and Pindzola (2002) with the He-like Li results of this paper. As mentioned in the introduction, the DW and perturbative methods differ by a factor of 2 for metastable He. Furthermore, this trend can be observed by comparing ionization from H to ionization from Li$^{2+}$ (Griffin et al 2005).

4. Conclusion

We present results of three different calculations of the electron-impact cross section of metastable $1s2s \, \, 1S$ and $1s2s \, \, 3S$ Li$^+$: distorted-wave, $R$-matrix with pseudostates, and time-dependent close-coupling. We find that the non-perturbative methods, $R$-matrix and time-dependent close-coupling, are in excellent agreement. The perturbative distorted-wave method, however, gives cross sections that are somewhat larger than those given by the non-perturbative methods. The non-perturbative $R$-matrix and close-coupling calculations provide...
a benchmark for future experimental determination of absolute ionization cross sections from metastable states along the He isoelectronic sequence.

The fact that the DW and TDCC methods are actually in agreement for ionization cross section from the Li$^+$ ground state (Pindzola et al 2000) has previously been taken as a sign that DW is fairly dependable for this species. However, higher-order coupling between the outgoing electrons is not taken into account in the DW calculations. Although these correlations become smaller as the nuclear charge $Z$ increases, they become larger for excited-state ionization. Thus the non-perturbative methods are more appropriate for excited-state ionization. All existing electron-impact ionization data for Li$^+$ excited states come from distorted-wave calculations (Loch et al 2006). In the light of the results presented in this paper, however, these data will need significant revision.

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References

Ballance C P and Griffin D C 2004 J. Phys. B: At. Mol. Opt. Phys. 37 2943
Bartschat K 1998 Comput. Phys. Commun. 114 168
Bartschat K 2002 J. Phys. B: At. Mol. Opt. Phys. 35 L527–9
Berrington K A, Eissner W B and Norrington P H 1995 Comput. Phys. Commun. 92 290–420
Briggs J S and Kim Y K 1971 Phys. Rev. A 3 1342
Burgess A 1974 J. Phys. B: At. Mol. Phys. 7 L364
Burgess A, Hummer D G and Tully J A 1970 Phil. Trans. R. Soc. A 266 225
Colgan J, Loch S D, Pindzola M S, Ballance C P and Griffin D C 2003 Phys. Rev. A 68 032712
Colgan J and Pindzola M S 2002 Phys. Rev. A 66 062707
Cowan R D 1981 The Theory of Atomic Structure and Spectra (Berkeley, CA: University of California Press)
Dixon A J, Harrison M F A and Smith A C H 1976 J. Phys. B: At. Mol. Phys. 9 2617–31
Fursa D V and Bray I 2003 J. Phys. B: At. Mol. Opt. Phys. 36 1663–71
Gorczyca T W and Badnell N R 1997 J. Phys. B: At. Mol. Opt. Phys. 30 3897
Griffin D C, Ballance C P, Pindzola M S, Robicheaux F, Loch S D, Ludlow J A, Witthoeft M C, Colgan J, Fontes C J and Schultz D R 2005 J. Phys. B: At. Mol. Opt. Phys. 38 L199–206
Froese Fischer C, Jonsson P and Brage T 1997 Computational Atomic Structure (Bristol: Institute of Physics)
Loch S, Colgan J, Witthoeft M, Pindzola M, Ballance C, Mitnik D, Griffin D, O’Mullane M, Badnell N and Summers H 2006 At. Data Nucl. Data Tables 92 813
Loch S D, Fontes C J, Colgan J, Pindzola M S, Ballance C P, Griffin D C, O’Mullane M G and Summers H P 2004 Phys. Rev. E 69 066405
National Institute of Standards and Technology 2006 ‘Atomic spectra database’
Mitnik D M, Griffin D C, Ballance C P and Badnell N R 2003 J. Phys. B: At. Mol. Opt. Phys. 36 717
Mitnik D M, Pindzola M S, Griffin D C and Badnell N R 1999 J. Phys. B: At. Mol. Opt. Phys. 32 L479
Pindzola M S, Mitnik D M, Colgan J and Griffin D C 2000 Phys. Rev. A 61 052712
Pindzola M S and Robicheaux F 1996 Phys. Rev. A 54 2142–5
Pindzola M S and Robicheaux F 1998 Phys. Rev. A 57 318–24
Pindzola M S, Robicheaux F, Colgan J P, Witthoeft M C and Ludlow J A 2004 Phys. Rev. A 70 032705
Pindzola M S and Schultz D R 1996 Phys. Rev. A 53 1525–36
Ton-That D, Flannery M R and Manson S T 1977 J. Phys. B: At. Mol. Phys. 10 621–35
Younger S M 1981 Phys. Rev. A 24 1272–7
Younger S M 1985 Electron Impact Ionization (Berlin: Springer)