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Scattering of low-energy electrons by neutral lithium atoms: five-state close-coupling calculations

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Abstract. Results of five-state (2s-2p-3s-3p-3d) close-coupling calculations, using the published program IMPACT, of the scattering of 2-10 eV electrons by neutral lithium atoms are reported. Cross sections for all upward transitions between these five states are given. For the 2s-2p transition, the excitation cross section, the singlet-triplet asymmetry factor and the polarisation of the line radiation are compared with available experimental data and with previous two-state close-coupling calculations.

1. Introduction

In this paper we present the results of a five-state (2s-2p-3s-3p-3d) close-coupling calculation of cross sections for scattering of slow (2-10 eV) electrons by neutral lithium atoms. The coupled integro-differential equations were solved with the aid of the published computer program IMPACT (Crees *et al* 1978). Numerical wavefunctions for the target lithium atom were obtained by the method described by Mendoza (1981). In this method the $1s^2$ core wavefunctions are first obtained from a single-configuration Thomas-Fermi statistical model calculation for Li^+. The valence electron (2s, 2p, 3s, 3p, 3d) wavefunctions are then obtained from a $Li^+ + e^-$ calculation, with IMPACT, in a one-closed-channel approximation in which an empirical core polarisation potential is added. A free parameter in this potential is adjusted to give calculated quantum defects in agreement with experimental ones, thereby ensuring that in the $Li + e^-$ problem the excitation thresholds will occur at exactly the correct energies. In order to test the wavefunctions used, a five-state calculation for $Li + e^-$ was carried out for the ^1S intermediate state with all channels closed, in order to determine a value for the electron affinity of Li^-. A value of 0.0458 Ryd was obtained with agrees very well with the experimental value of 0.0454 Ryd (with an estimated accuracy of less than 1%) quoted by Smirnov (1982) and the value of 0.0452 Ryd calculated by Weiss (1971).

2. Calculations and results

The total cross section for the transition $nl \rightarrow n'l'$ in Li is given by

$$Q(nl \rightarrow n'l') = \frac{\pi a_0^2}{4k_{nl}^2} \sum_{\substack{l_2, l_2' \\ S, L}} (2L+1)(2S+1) \left| T^{S,L}_{nll_2, n'l'l_2'} \right|^2 . \tag{1}$$

In order to ensure convergence of this expansion, it is often necessary to include a large number of values of the total angular momentum L, especially for transitions between excited states. For large L, although IMPACT does not give numerically accurate solutions, simpler approximations may be used for the T-matrix elements. Thus, five-state calculations were performed for values of $L(S=0$ and $S=1)$ up to some maximum value L_1. For $L > L_1$, the off-diagonal elements of the reactance matrix **K** were calculated from the Bethe formula

$$K_{ij} = -\tfrac{1}{2}\pi \int_0^\infty J_{l_{2_i}+1/2}(k_i r)\, U_{ij}(r) J_{l_{2_j}+1/2}(k_j r) r \, \mathrm{d}r \tag{2}$$

where l_{2_i} is the angular momentum quantum number of the scattered electron in channel i, k_i^2 is the channel energy in rydbergs and $U_{ij}(r)$ is the asymptotic form of the potential $V_{ij}(r)$ coupling channels i and j. $U_{ij}(r)$ is of the form

$$U_{ij}(r) = \sum_\lambda \frac{a_{ij\lambda}}{r^{\lambda+1}} \tag{3}$$

where $\lambda \geqslant 1$ and $a_{ij\lambda}$ are numerical coefficients. Using (3) in (2) the integral may be evaluated analytically. The Bethe approximation (2) does not give accurate values for the diagonal elements K_{ii}, so for $L > L_1$ they were obtained by extrapolation in a geometric progression. The partial wave sums were truncated at $L = L_2$. Values of L_1 and L_2 are given in table 1. For all transitions except $3p \rightarrow 3d$ the sum was judged to have converged at $L = L_2$.

Table 1. Values of L_1 and L_2. Parity π_i refers to the coupled channels (2s, L), (2p, $L \pm 1$), (3s, L), (3p, $L \pm 1$), (3d, L), (3d, $L \pm 2$) and parity π_2 to the channels (2p, L), (3p, L), (3d, $L \pm 1$).

	π_1		π_2	
k_1^2 (Ryd)	L_1	L_2	L_1	L_2
0.15			9	9
0.175			14	14
0.2			11	11
0.225	13	74	11	11
0.265	10	74	16	16
0.3	15	74	17	17
0.3675	18	74	21	74
$\geqslant$0.45	22	74	21	74

The extrapolation of K_{ii} in a geometric progression for $L > L_1$ is not rigorously justifiable, but in the present case we justify it empirically by the following. The extrapolation was commenced at $L = L_1 - 5$ or so and the results compared with close-coupling results for $L < L_1$ and with the other extrapolation for $L > L_1$. Similar results were obtained. Previous experience with Na and K has shown that extrapolation in geometric progression gives good agreement with full Born calculations (using equation (2) with the short-range part of the potential added).

In all cases where (2) was used, extensive checks were made against close-coupling calculations to ensure that no extensive error was being made and that, at the change-over, close-coupling and Bethe calculations were given the same results to within a few per cent for the dominant K-matrix elements.

Cross sections for transitions from $nl = 2s$, $nl = 2p$, $nl = 3s$ and $nl = 3p$, 3d are given in tables 2 to 4. For $2s \rightarrow 2p$ excitation we define the cross section $Q_{S,M}(2s \rightarrow 2p)$ for singlet ($S = 0$) or triplet ($S = 1$) excitation of the substate with magnetic quantum $M (M = 0, |M| = 1)$ by

$$Q_{S,M}(2s \rightarrow 2p) = \frac{\pi a_0^2}{k_{2p}^2} \sum_{\substack{l_2' = L \pm 1 \\ L}} |(2L+1)^{1/2} i^{L-l_2'} C^{1 l_2' L}_{M-M0} T^{S,L}_{2sL,2pl_2'}|^2 \tag{4}$$

where $C^{abc}_{\alpha\beta\gamma}$ is a vector-coupling coefficient. The cross section for a fixed total spin is

Table 2. Transitions $2s \rightarrow nl$ in lithium. Total cross sections in πa_0^2.

	nl				
k_1^2 (Ryd)	2s	2p	3s	3p	3d
0.15	133.8	13.7			
0.175	115.8	22.3			
0.2	102.4	31.5			
0.225	90.9	37.3			
0.265	75.7	39.0	2.7		
0.3	65.8	40.9	1.9	1.4	1.9
0.3675	53.8	41.1	2.5	2.0	4.5
0.45	43.6	42.4	2.7	2.6	5.8
0.5	38.2	43.5	2.7	2.5	5.9
0.55	34.6	44.7	2.4	2.5	6.0
0.6	31.9	45.3	2.4	2.3	5.6
0.65	28.6	45.8	2.3	2.1	5.3
0.7	26.0	46.0	2.4	2.0	5.2
0.75	24.9	46.0	2.1	2.0	4.7

Table 3. Transitions $2p \rightarrow nl$ in lithium. Total cross sections in πa_0^2.

	nl			
k_1^2 (Ryd)	2p	3s	3p	3d
0.15	232			
0.175	187			
0.2	166			
0.225	154			
0.265	134	10.0		
0.3	108	6.2	6.6	11.2
0.3675	85	7.1	11.4	22.7
0.45	64	6.5	12.4	29.7
0.5	55	6.1	12.0	30.8
0.55	50	5.9	11.7	30.9
0.6	44	5.7	11.2	30.6
0.65	40	5.6	10.7	30.0
0.7	38	5.7	10.8	30.6
0.75	34	5.6	9.7	29.1

Table 4. Total cross sections in πa_0^2. Numbers in brackets denote multiplication by powers of 10.

k_1^2 (Ryd)	3s→3s	3s→3p	3s→3d	3p→3p	3p→3d	3d→3d
0.265	2201					
0.3	1072	86	195	4.4 (+3)	1.6 (+4)	7.6 (+3)
0.3675	663	201	259	1.3 (+3)	4.3 (+3)	1.3 (+3)
0.45	484	375	202	7.3 (+2)	2.2 (+3)	8.1 (+2)
0.5	415	413	176	5.8 (+2)	1.6 (+3)	5.0 (+2)
0.55	356	440	163	4.9 (+2)	1.3 (+3)	4.2 (+2)
0.6	319	419	139	4.1 (+2)	1.1 (+3)	3.6 (+2)
0.65	282	406	125	3.6 (+2)	9.5 (+2)	3.2 (+2)
0.7	246	392	123	3.2 (+2)	8.3 (+2)	2.8 (+2)
0.75	230	371	103	2.9 (+2)	7.4 (+2)	2.5 (+2)

given by

$$Q^S(2s\rightarrow 2p)=\sum_M Q_{S,M}(2s\rightarrow 2p)=\frac{\pi a_0^2}{k_{2p}^2}\sum_{L,l_2'}(2L+1)\left|T^{S,L}_{2sL,2pl_2'}\right|^2. \tag{5}$$

The total cross section is then just

$$Q(2s\rightarrow 2p)=\tfrac{1}{4}\sum_{S=0,1}(2S+1)Q^S(2s\rightarrow 2p). \tag{6}$$

Values of $Q_{S,M}$ are given in table 5, together with the asymmetry parameter defined by

$$A=(Q^0-Q^1)/Q. \tag{7}$$

One may also define cross sections for excitation of the magnetic sublevels by averaging (4) over spins:

$$Q_M(2s\rightarrow 2p)=\tfrac{1}{4}\sum_{S=0,1}(2S+1)Q_{S,M}(2s\rightarrow 2p). \tag{8}$$

The polarisation of the 2s-2p doublet radiation that would be emitted at 90° to an

Table 5. 2s→2p excitation of lithium. Partial cross sections in πa_0^2, asymmetry factor and polarisation of line radiation.

k_1^2 (Ryd)	$Q_{0,0}$	$Q_{1,0}$	$Q_{0,1}$	$Q_{1,1}$	A	P_7 (%)	P_6 (%)
0.15	41.6	1.1	4.0	0.3	0.873	16.2	28.8
0.175	44.9	8.2	3.7	2.1	0.448	14.8	26.5
0.2	43.6	16.7	4.9	3.8	0.232	13.7	24.6
0.225	43.4	21.3	6.2	4.9	0.166	13.0	23.5
0.265	35.9	21.9	9.5	5.9	0.136	10.8	19.5
0.3	32.3	22.4	9.8	7.5	0.089	9.3	18.6
0.3675	25.9	21.2	10.7	8.9	0.050	7.2	13.2
0.45	22.4	20.6	11.3	10.5	0.021	5.6	10.3
0.5	21.9	20.3	12.0	11.2	0.019	4.9	9.1
0.55	22.0	20.4	12.8	11.7	0.022	4.5	8.4
0.6	21.8	19.6	13.7	12.2	0.028	3.9	7.1
0.65	21.5	19.1	14.3	12.6	0.032	3.4	6.2
0.7	20.8	18.6	15.0	12.9	0.034	2.7	5.1
0.75	20.3	18.2	15.3	13.1	0.036	2.6	4.7

incident electron beam is then (Percival and Seaton 1958)

$$P = \frac{300x}{12Q_0 + 24Q_1 + x} \tag{9}$$

where $x = (9\alpha - 2)(Q_0 - Q_1)$ and $\alpha = 0.416$ for the isotope Li^6 and 0.326 for Li^7. Values of the polarisation (P_7 for Li^7, P_6 for Li^6) are also given in table 5.

3. Discussion of results for 2s–2p excitation

Two-state (2s-2p) close-coupling calculations of this cross section have been carried out by Karule and Peterkop (1965) and by Burke and Taylor (1969a). Both sets of authors used Hartree-Fock target functions, but Burke and Taylor included exchange with the core. Norcross (1974a) has calculated the same cross section using target functions generated from the model potential of Moores and Norcross (1974). When the Karule and Peterkop results are corrected for high L by adding the contribution from Norcross' calculations, and if the Burke and Taylor results are recalculated from their own published K matrices (Burke and Taylor 1969b) using (1) the three calculations are in good mutual agreement. It is possible that the Burke and Taylor (1969a) results were incorrectly plotted†.

In figure 1 the two-state results are compared with the present five-state results and with the experimental data of Leep and Gallagher (1974). Below the 3s excitation

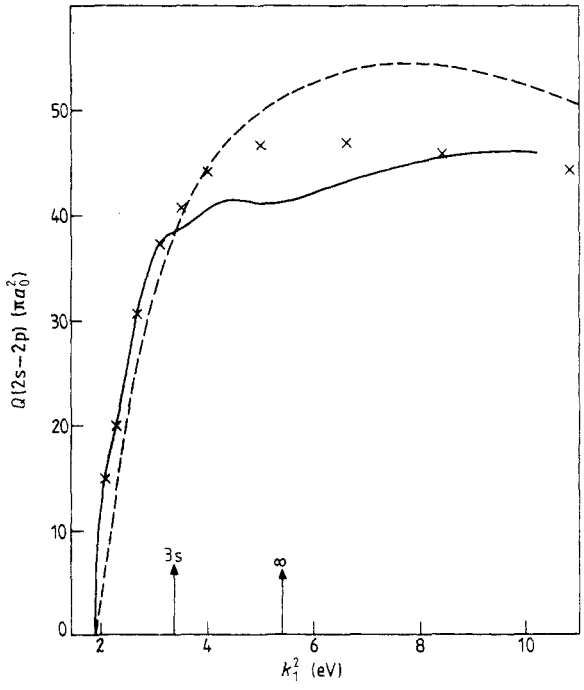

Figure 1. 2s-2p excitation cross section of lithium in πa_0^2 plotted against incident electron energy in eV. ——, present five-state calculation; - - -, two-state calculation (Norcross 1974); ×, experimental results of Leep and Gallagher (1974).

† The author is indebted to Dr D W Norcross (1974b) for the information given in this paragraph.

threshold at 3.38 eV the five-state results are in perfect agreement with experiment, with the two-state results somewhat lower. Above this energy, the two-state results rise higher than experiment, but the five-state and experimental results also part company, appearing to re-unite above 8 eV. The maximum discrepancy occurs at about 5 eV, but even here it is only about 10%.

There are two possible explanations for the differences between 3 and 8 eV; this is the energy region where higher states, neglected in the five-state calculation, occur (the ionisation energy is 5.39 eV) and this neglect might be expected to affect the calculations in this region. At the same time, it is also the case that above the 3s threshold it was necessary for Leep and Gallagher to correct their measured cross sections for cascade. This was done using the experimental cross sections for excitation of higher levels obtained by Aleksakhin and Zapesochnyi (1966a, b). However, there is evidence that these cross sections may be too low. The present calculated values of the 3s and 3d excitation cross sections (table 2) are a factor of about 5 larger than the values quoted by Aleksakhin and Zapesochnyi, while the 3p cross section is three orders of magnitude greater than the experimental one. Also, Leep and Gallagher point out that the 2s–2p excitation cross section of Aleksakhin and Zapesochnyi is considerably smaller than theirs, the ratio being 0.55 at the peak. Use of the present calculated cross sections to estimate cascade would reduce the discrepancy between theory and experiment below 7 eV, but would then give experimental results 20% below theory at 10 eV. This need not necessarily be significant since the neglect of coupling to higher states in the theory could still account for the difference from experiment.

The rather numerous other theoretical estimates of this cross section are discussed in Leep and Gallagher's paper. Most of them are in poor agreement with experiment.

The asymmetry factor for 2s–2p excitation defined by equation (7) is shown in figure 2, in which two-state and five-state calculations are compared with the experimental data of Schröder (1982). The two-state results appear to be in closer agreement with experiment. However, if one compares the results of a different measurement by the same group in which the differential asymmetry parameter for 2s–2p excitation is

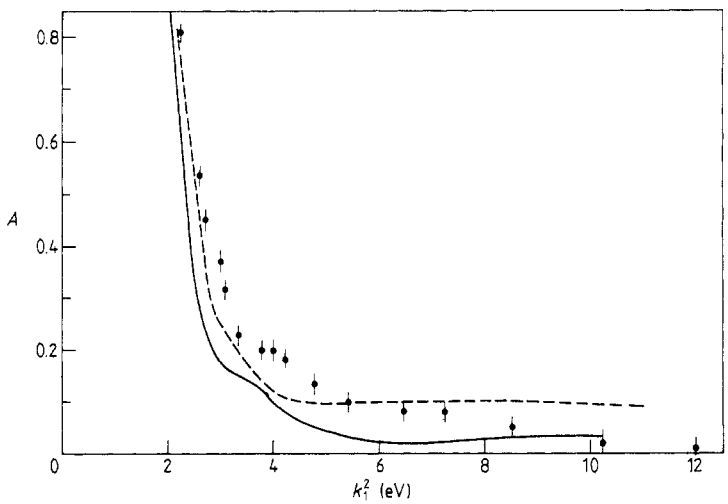

Figure 2. Asymmetry parameter for 2s–2p excitation of lithium. ——, present five-state calculation; - - -, two-state calculation (Burke and Taylor 1969); ●, Schröder (1982).

obtained as a function of electron energy at a fixed angle of scattering (107.5°; Baum *et al* 1985), the five-state results are in much better agreement with experiment. The calculations of Kennedy *et al* (1977) disagree considerably with experiment.

In figure 3 are shown the values obtained for the polarisation of the 2s–2p line radiation excited by electron impact for the isotope ^{6}Li. At threshold, since $Q_1/Q_0 = 0$, the polarisation as given by (9) is constrained to go to a value independent of cross sections and therefore of the approximation used in a theoretical determination (Flower and Seaton 1967). For ^{6}Li this is 37.5%. Also shown are the results of Burke and Taylor and the experimental results of Leep and Gallagher, and Hafner and Kleinpoppen (1967). The experimental results are not corrected for cascade. If allowance is made for the experimental energy distribution, the present results appear to be in very good agreement with Leep and Gallagher, with some discrepancy in the 3–5 V region, where the states neglected in the calculations have their maximum effect and where cascade contributions start to take effect.

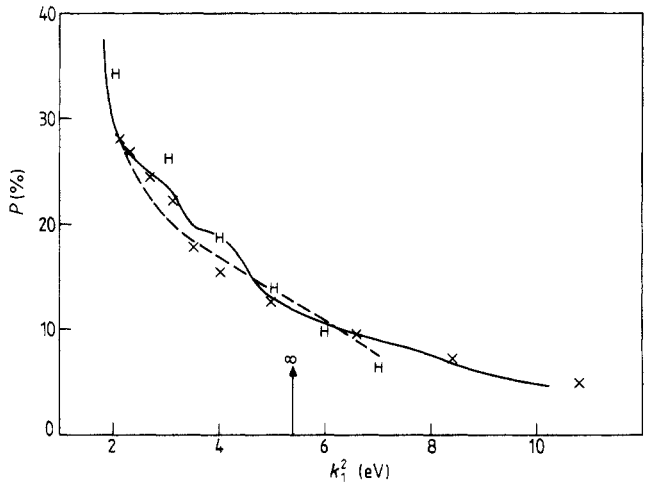

Figure 3. Polarisation of 2s–2p line radiation, ^{6}Li. ——, present five-state results; - - -, two-state calculation (Burke and Taylor 1969); H, experiment of Hafner and Kleinpoppen (1967); ×, experiment of Leep and Gallagher (1974).

Jaduszliwer *et al* (1981) have measured the absolute total cross sections for scattering of electrons between 2 and 20 eV by neutral lithium atoms by an atomic recoil technique. The results are shown in figure 4, together with several theoretical estimates. The present calculations include contributions from 2s → 2s, 2p, 3s, 3p and 3d whereas the other theories only include 2s and 2p. The hybrid theoretical result which combines the modified polarised-orbital elastic cross section of Bhatia *et al* (1978) with the 2s–2p excitation cross section of Burke and Taylor seems to give the best overall agreement with experiment. The five-state calculations are in better agreement at the upper end of the energy range, owing no doubt to the $n = 3$ contribution, since the other calculations fall below experiment. Substitution of the $n = 3$ contribution obtained by Aleksakhin and Zapesochnyi would give a lower cross section but would still not explain the main difference between theory and experiment which arises from the 2s–2s and 2s–2p contributions.

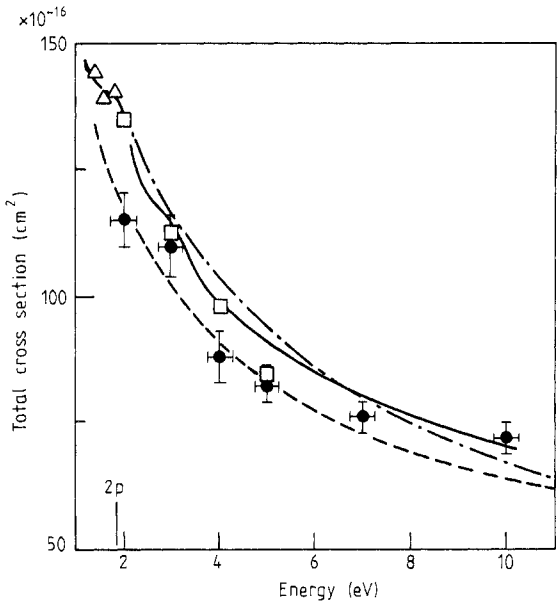

Figure 4. Total cross section for electron-lithium scattering. ●, Jaduszliwer *et al* (1981); △, Karule (1965); □, Karule and Peterkop (1965); — · —, Burke and Taylor (1969); - - -, sum of elastic cross section of Bhatia *et al* (1978) and 2s-2p excitation cross section of Burke and Taylor; ——, present five-state results.

The remaining results in the tables are for transitions between excited states. In the absence of the inclusion of states higher than $n = 3$ in the calculation, their accuracy must remain uncertain. The partial-wave expansion of the cross section for 3p-3d excitation has not converged at $L_2 = 74$ but in view of the other uncertainties in the calculation it was not considered worthwhile to obtain a converged value, and it has been included merely for completeness. Rough estimates indicated that this cross section should be increased by about 25% to allow for the partial waves omitted.

In addition to the results published in this paper, amplitudes for elastic scattering and 2s-2p excitation have been computed and, together with the T matrices, stored on private magnetic disc. These data are available from the author on request.

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