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Atomic orbital expansion study of electron capture in $H^+ + Li$ and $He^{2+} + Li$ collisions

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Abstract. A modified two-centre atomic orbital expansion is used in an investigation of electron capture in collisions of H^+ and He^{2+} ions with Li atoms. The calculated total and partial transfer cross sections constitute the first published origin-independent results in the energy range 0.5–20 keV for $H^+ + Li$ and in the range 0.1–2.0 keV amu^{-1} for $He^{2+} + Li$ collisions. Total capture cross sections are found to agree well with experimental data wherever the measurements have led to a consistent picture among themselves. For $He^{2+} + Li$ collisions, low-energy capture cross sections are predicted to be much larger than is indicated by results from two-state molecular orbital calculations without translational factors.

1. Introduction

Electron capture in ion–atom collisions has been investigated theoretically with a large variety of methods in the past (Taulbjerg 1983), with the region of applicability for each method determined by the charge asymmetry and the adiabaticity ratio . Within the semiclassical close-coupling method, expansions of the time-dependent electronic wavefunction in molecular orbitals (MO) of the system have been widely used for low-energy collisions. For higher energies, expansions in atomic orbitals (AO) have been employed. Only recently has it been realised (Fritsch and Lin 1982a) that suitably modified AO expansion schemes are capable of describing the electronic system in slow collisions, as well. In investigations of one-electron systems like $H^+ + H$ and $He^+ + H^+$, it has been demonstrated (Fritsch and Lin 1982a, b) that model sensitive partial cross sections and impact-parameter-dependent transition probabilities from such AO expansion calculations agree well with the results from MO calculations. For more asymmetric collision systems like $Li^{3+} + H$ where molecular effects are less prominent, even conventional AO expansion schemes have been successfully applied (Bransden and Noble 1982, Fritsch and Lin 1982c).

In this communication we present and discuss electron transfer cross sections calculated for the processes

$$H^+ + Li(2s) \rightarrow H(nl) + Li^+ \tag{1}$$

and

$$He^{2+} + Li(2s) \rightarrow He^+(nl) + Li^+ \tag{2}$$

in the impact energy region from 0.4 up to 20 keV amu^{-1}. The calculations are based

on the two-centre AO expansion method with orbitals of the separated atoms (SA: H or He^+, Li) *and of the united atom* (UA: Be^+ or B^{2+}), the latter chosen such that account is taken of the molecular binding effect in slow collisions (Fritsch and Lin 1982a). While this 'AO+' method has been applied to various one-electron systems before (Fritsch and Lin 1983) it is the primary purpose of the present investigation to establish it as an effective and convenient alternative to the MO expansion method in *dynamical* studies of slow collisions between *complex* atoms and ions. The collision systems (1) and (2) are, moreover, interesting in themselves, mainly because (for system (1)) very little theoretical information is available and (for system (2)) conflicting theoretical and experimental data have been reported in the literature, see below. It is noted that process (2) has attracted much attention recently due to its proposed use in the diagnostics of fusion plasmas (Post *et al* 1979).

2. Theory

The close-coupling method with AO basis sets has been repeatedly described in the literature (e.g. McDowell and Coleman 1970). Here we will summarise only some features of the calculations as they differ from our earlier communications (Fritsch and Lin 1982a).

Both processes (1) and (2) are described in a one-electron potential model. The effective two-centre Hamiltonian H_{el} is taken as the sum of the Coulombic potential of the projectile, V_1, and that of the target Li, V_2,

$$H_{el} = T + V_1 + V_2. \tag{3}$$

V_2 is taken to be of the form used in the recent MO study for $H^+ + Li$ by Allan *et al* (1983), i.e. (in atomic units),

$$V_2(r_2) = -1/r_2 - (2/r_2)(1+\alpha r_2)\exp(-2\alpha r_2) \tag{4}$$

where r_2 is the radial electronic coordinate from centre 2, and $\alpha = 1.655$. Calculations have been done with various basis sets. Orbitals at the Li centre have been calculated by diagonalising the Li Hamiltonian $T + V_2$ in a space of simple Slater-type or hydrogenic states, cf table 1, separately for process (1) and (2). As is seen from table 1, these two sets of 20 (21) states for process (1) ((2)) allow for a fair representation of the lowest Li *and* UA orbitals, and they are still not prohibitively much larger than basis sets needed for purely one-electron systems of similar complexity. It is noted that the $n = 2$, 3 Li energies from the reference MO calculation are very close to experimental separation energies (Allan *et al* 1983). On the other hand, the UA Hamiltonian as given by equation (3) at vanishing internuclear separation R is *not* optimised for representing ground-state Be^+ or B^{2+} ions. If, for small energies or close collisions, the 'frozen potential' approximation to the Hamiltonian, equation (3), becomes insufficient and relaxation in a true dynamical molecular Hamiltonian becomes important, calculations with the present Hamiltonian, employing either MO or AO+ basis sets, are expected to become less valid. From the MO work by Allan *et al* (1983), however, there is no evidence for a need to improve on H_{el} in the energy range under consideration.

Starting from AO+ basis sets, consisting of the Li-centred orbitals of table 1 and projectile-centred orbitals (cf below), and with plane-wave translational factors, the coupled differential equations have been set up and solved numerically. Exchange

Table 1. Basis states at Li centre and atomic energies as used in calculations for processes (1) and (2). The entry (S) indicates that the decay constant is in Slater-type orbitals, all other constants are effective charges in hydrogenic orbitals. All *nlm* basis states of a given *nl* type are included in the calculations.

	Decay constants					Li energies (keV)			UA energies (keV)			
Type	(1) and (2)			(1)	(2)	(1)	(2)	MO[a]	(1)	Exact[b]	(2)	Exact[b]
1s	0.630	1.200	2.000			−1.876	−1.932	−1.932				
2s	1.259				2.800 (S)	−0.1972	−0.1982	−0.1982	−0.710	−0.717	-1.546	−1.546
2p	1.019			2.125	3.800	−0.1297	−0.1299	−0.1298	−0.555	−0.564	-1.345	−1.352
3s	0.352 (S)					−0.0738	−0.0741	−0.0743	−0.277	−0.279	−0.607	−0.608
3p	0.352 (S)					−0.0562	−0.0562	−0.0572	−0.240	−0.241	−0.534	−0.557
3d	0.352 (S)	1.248 (S)		2.000	2.800	−0.0555	−0.0555	−0.0553	−0.223	−0.223	−0.506	−0.506

[a] From Allan *et al* (1983).

[b] From diagonalisation of UA Hamiltonian, equation (3), at $R = 0$ in large basis.

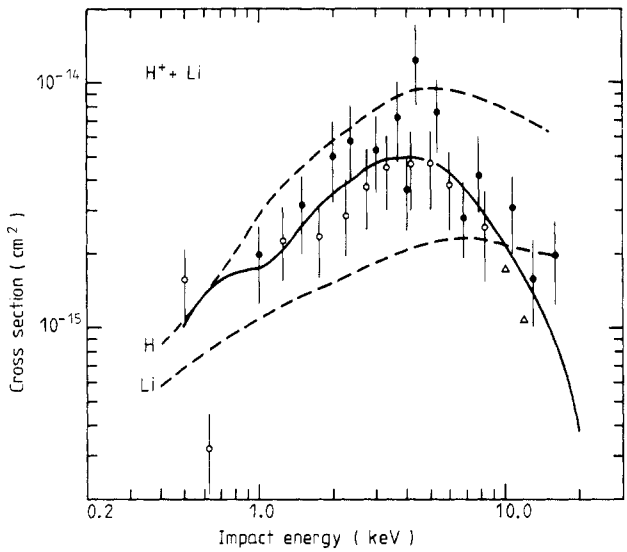

Figure 1. Cross sections for total electron capture in $H^+ + Li$ collisions. Theory: ——, AO+ calculation (this work); – – –, MO calculation (Allan *et al* 1983) with two choices of origin (H, Li). Experiment: ● and ○, Grüebler *et al* (1970) with, respectively, H^+ and D^+ incident ions (D^+ ions at half their energies); △, Il'in *et al* (1965).

coupling matrix elements have been calculated by performing the two-dimensional integration in prolate spheroidal coordinates numerically. This procedure turned out to be hardly more time consuming than the well known procedure used in problems with purely Coulombic potentials (McCarroll 1961). Straight-line trajectories are assumed for the atomic centres. As an initial condition, the electron is put into the Li 2s orbital.

3. Results

Figure 1 shows total capture cross sections for $H^+ + Li$ collisions over the (laboratory) impact energy, calculated with a 36 AO+ expansion consisting of 20 orbitals at the Li centre (cf table 1) and the 10 $n = 1$–3 H orbitals as well as six other hydrogenic orbitals of 2s, 2p and 3d type at the H centre, the latter optimised for the representation of $n = 2$, 3 UA orbitals at that centre. The calculated cross sections are seen to agree well with the experimental data of Grüebler *et al* (1970) and Il'in *et al* (1965, 1967) over the whole energy range. Also shown are the two curves calculated by Allan *et al* (1983) with two choices of origin (H, Li), starting from equation (3) with an expansion into six (non-travelling) MO. At the low-energy end ($E \leq 1$ keV), the cross sections from the AO+ expansion display a small shoulder. There, the cross sections are dominated by small impact parameter collisions ($b \leq 4$ au). Since the Hamiltonian, equation (3), is not well suited for describing slow close collisions, it is not clear whether this shoulder is real. At the high-energy end of figure 1, additional bound as well as continuum H orbitals in the AO+ expansion may be needed in order to arrive at convergent results.

Table 2 lists calculated total transfer cross sections as well as partial cross sections for transfer into individual *nl* subshells at selected impact energies. Partial transfer

Table 2. Cross sections (in 10^{-15} cm^2) for electron transfer into H subshells (σ_n) and into all bound states (σ_{bound}) in $H^+ + Li$ collisions. For each n, P_l denotes the normalised l shell contribution.

E (keV)	n	σ_n	P_0	P_1	P_2	σ_{bound}
0.5	2	0.98	0.15	0.85		1.00
	3	0.03	0.07	0.30	0.63	
0.7	2	1.51	0.25	0.75		1.60
	3	0.07	0.19	0.24	0.57	
1.2	2	1.75	0.41	0.59		1.96
	3	0.21	0.26	0.14	0.60	
2.0	2	3.36	0.44	0.56		3.52
	3	0.16	0.21	0.38	0.41	
3.0	2	4.46	0.42	0.58		4.79
	3	0.31	0.22	0.35	0.43	
4.0	2	4.47	0.38	0.62		4.90
	3	0.42	0.16	0.41	0.43	
6.0	1	0.03				4.25
	2	3.67	0.36	0.64		
	3	0.50	0.26	0.40	0.34	
10.0	1	0.06				2.29
	2	1.70	0.37	0.63		
	3	0.43	0.40	0.43	0.13	
15.0	1	0.04				0.97
	2	0.53	0.44	0.56		
	3	0.30	0.44	0.46	0.10	
20.0	1	0.05				0.39
	2	0.17	0.49	0.51		
	3	0.12	0.49	0.38	0.13	

cross sections for $H^+ + Li$ collisions have not been reported in the literature before. Their variation as a function of energy in table 2 clearly reflects the transfer mechanism as briefly discussed by Allan *et al* (1983). At low energies, the 2s Li electron moves on the adiabatic 3σ orbital which is very close to the 1π orbital below the internuclear separation $R = 3.5$ au. After coupling between these orbitals, the electron may move out on the 1π orbital and may couple with 4σ–6σ and 2π orbitals at $R \geqslant 8$ au, which all correlate to 2p Li and 2s, 2p H orbitals. In slow collisions, therefore, the transfer into 2p H is strongest, and the most important impact parameter range is below 4 au. Actually, for decreasing velocities, the transfer mechanism is expected to approach a two-step mechanism with essentially the $2p\sigma$–$2p\pi$ coupling effective at small R. For higher energies, direct coupling of the 3σ MO with the higher orbitals at large R becomes increasingly important so that population of 2p H becomes less dominant and, eventually, orbitals with $n \geqslant 3$ become important. In the impact parameter b dependence of transfer probabilities, this change in transfer mechanism is reflected in an increased importance of higher impact parameters, up to $b = 14$ au.

For $He^{2+} + Li$ collisions, calculations have been performed with a 40 AO+ expansion consisting of all 19 $n = 2, 3, 4$ He^+ orbitals at the He centre and the 21 Li-centred

orbitals of table 1. Since the 2s Li energy (cf table 1) is very close to the $n = 3$ He^+ energies it is obvious that these He^+ orbitals are the most important ones in slow collisions. In fact, the one-electron correlation diagram for this system is distinguished by a well developed band of closely lying 5σ–8σ and 3π–4π orbitals at $R \geq 15$ au, all of them strongly coupling with each other and eventually correlating to 2s Li and $n = 3$ He^+ orbitals. As further features of the correlation diagram it is noted here only that, for $R \leq 8$ au, it indicates some weak coupling to MO correlating to $n = 2$ He^+ orbitals and, for $R \leq 10$ au, strong coupling to MO correlating to $n = 4$ He^+ orbitals.

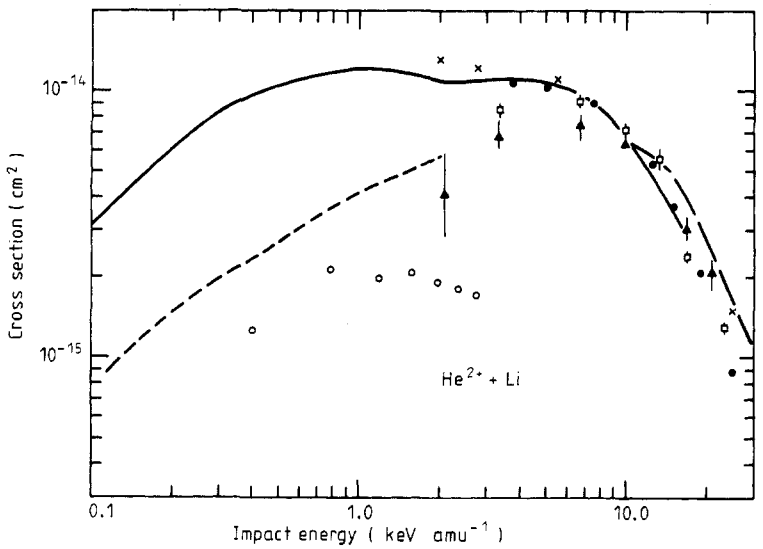

Figure 2. Cross sections for total electron capture in He^{2+} + Li collisions. Theory: ——, 40 AO+ calculation (this work); – – –, MO calculation (Shipsey *et al* 1978); — —, classical-trajectory Monte-Carlo calculation (Shipsey *et al* 1978); ×, sum over two-centre AO calculations (Bransden and Ermolaev 1981). Experiment: □, McCullough *et al* (1982); ▲, Murray *et al* (1982); ●, Kadota *et al* (1982); ○, Barrett and Leventhal (1981).

In figure 2, total capture cross sections for He^{2+} + Li collisions from the 40 AO+ calculations are displayed and compared with results from other calculations and from experiments. For impact energies above 3 keV amu^{-1}, the cross sections from the AO+ calculations are very close to the results from recent optical measurements by Kadota *et al* (1982) and, for higher energies, to experimental data obtained by McCullough *et al* (1982) and by Murray *et al* (1982) with charge state analysis. At their low-energy end, however, the latter two sets of experimental data seem to approach the results of the optical measurements of Barrett and Leventhal (1981) which, in turn, at about 3 keV amu^{-1}, are about a factor of five lower than those by Kadota *et al*, i.e. about twice as much as would be consistent with the assessed experimental accuracy (Kadota *et al* 1982).

On the theoretical side, the total capture cross sections reported here are close to those of Bransden and Ermolaev (1981) which are arrived at by summing over results from two-centre AO coupled-state calculations. The procedure of summing individually determined two-centre AO cross sections constitutes an approximation to the simultaneous solution of the full set of coupled channels as undertaken here. It involves some violation of unitarity which, in the energy region of large transition

probabilities, should lead to an overestimation of the total capture cross sections. An effect like this is actually observed in figure 2 around 2–3 keV amu^{-1}. This effect is, however, partly counteracted by the lack of including couplings to 2p Li orbitals in the two-centre AO calculations, so that the overestimation of capture cross sections by the two-centre AO calculations is in fact the net result of two approximations with opposite actions. At the high-energy end in figure 2, the classical-trajectory Monte-Carlo calculation of Shipsey *et al* (1978) lies above our results. Here, AO calculations involving He^+ orbitals with $n \geq 5$ would result in somewhat larger cross sections as well.

A serious discrepancy exists between the low-energy total capture cross sections from the AO+ calculations and those from the MO calculations of Shipsey *et al* (1978). In the MO work, the accuracy of total capture cross sections is assessed as about 50%, due to the lack of translational factors and the uncertainties of potential energies. In the present work, translational factors are taken into account. In test calculations at 1.0 keV amu^{-1}, varying the 2s Li energy by 2% through changing the Li potential in equation (3) has altered the capture cross sections by roughly 10%. Two more points, however, are worth mentioning here. Firstly, it should be pointed out that capture cross sections at low energy are dominated by *large* impact parameter contributions (e.g., at 1 keV amu^{-1}, more than 70% of the cross section is accumulated between $b = 10$ and 20 au) due to the quasi-resonant situation between the initial and transfer channels. Therefore, an AO expansion is very appropriate here since the sets of MO and of (SA) AO at large internuclear separations are equivalent (LCAO method). Moreover, the employment of an unrelaxed Hamiltonian, equation (3), seems to be not unreasonable in these distant collisions, in contrast to the relaxed Hartree–Fock Hamiltonian used by Shipsey *et al.* Secondly, in the MO work of Shipsey *et al* (1978), couplings between only one diabatic Σ and one Π orbital are retained. In our opinion and from our experience†, however, it is very hard to assess the importance of couplings in a dynamical calculation without actually solving the coupled equations at least in an exploratory way. For example, leaving out couplings to 3d($m = 2$) orbitals in AO+ test calculations at 0.5 keV amu^{-1} reduces total capture by some 15% while the corresponding couplings to δ MO have not even been considered in the work of Shipsey *et al.* We, therefore, have reasons to believe that the AO+ capture cross sections in figure 2 are fairly reliable. More experimental information on low-energy $He^{2+} + Li$ collisions certainly is needed for a further exploration of this point. It is interesting to note that measurements currently being undertaken by Cocke and Waggoner indicate (Cocke 1982) $He^{2+} + Li$ capture cross sections significantly in excess of the MO results.

In table 3, total and partial transfer cross sections in $He^{2+} + Li$ collisions are given at selected impact energies. At low energies, capture to $n = 3$ He^+ orbitals is dominant in agreement with the predictions of Shipsey *et al* (1978). Strong couplings between the $n = 3$ subshells at large internuclear separation lead to population of all these subshells even at the lowest energies considered. Above 3.75 keV amu^{-1}, the partial cross sections follow the trend of the experimental data of Kadota *et al* (1982) with deviations, however, of up to 50% in absolute numbers. Partial cross sections from experiment are typically larger than the results in table 3 for $n = 4$ orbitals and smaller for $n = 3$ orbitals. Transitions into $n \geq 5$ He^+ orbitals are observed in experiment as well. For a theoretical estimate on these high-n partial cross sections, close-coupling

† The present situation is reminiscent of that encountered in the course of studies for $Li^{3+} + H$ collisions, see the discussion by Fritsch and Lin (1982c) and the improved, large-scale MO calculations of Salin (1982).

Table 3. Cross sections (in 10^{-15} cm^2) for electron transfer into He^+ subshells (σ_n) and into all $n \leq 4$ states (σ^4_{bound}) in He^{2+} + Li collisions. For each n, P_l denotes the normalised l shell contribution.

E (keV amu^{-1})	n	σ_n	P_0	P_1	P_2	P_3	σ^4_{bound}
0.1	3	2.76	0.21	0.42	0.37		3.11
	4	0.35	0.25	0.38	0.18	0.20	
0.2	3	5.34	0.18	0.43	0.39		5.92
	4	0.58	0.21	0.32	0.16	0.31	
0.5	2	0.03	0.36	0.64			10.65
	3	10.53	0.14	0.42	0.44		
	4	0.10	0.07	0.24	0.44	0.26	
1.0	2	0.08	0.52	0.48			12.41
	3	11.60	0.16	0.36	0.48		
	4	0.73	0.13	0.29	0.39	0.19	
2.0	2	0.11	0.23	0.77			10.89
	3	9.70	0.08	0.31	0.61		
	4	1.07	0.11	0.26	0.30	0.33	
3.0	2	0.12	0.18	0.82			10.98
	3	9.50	0.07	0.29	0.64		
	4	1.35	0.08	0.19	0.37	0.36	
6.0	2	0.17	0.32	0.68			10.11
	3	7.92	0.06	0.22	0.72		
	4	2.02	0.06	0.18	0.37	0.39	
	5	0.72					
	6	0.22					
8.0	2	0.21	0.30	0.70			8.64
	3	6.38	0.06	0.22	0.72		
	4	2.05	0.08	0.23	0.41	0.28	
	5	0.90					
	6	0.34					
11.0	2	0.25	0.27	0.73			5.70
	3	3.76	0.07	0.27	0.66		
	4	1.68	0.09	0.32	0.40	0.19	
	5	1.00					
	6	0.46					
16.0	2	0.22	0.25	0.75			2.72
	3	1.35	0.07	0.34	0.59		
	4	1.14	0.12	0.39	0.35	0.14	
	5	0.71					
	6	0.45					

calculations have been performed separately for $n = 5$ and $n = 6$, with basis sets consisting of the He^+ n-shell orbitals and the Li 2s and 2p orbitals. The resulting partial cross sections are included in table 3. Their sum agrees with the measured transfer cross sections into $n \geq 5$ orbitals (Kadota *et al* 1982) within some 20%. Experimental information on partial cross sections at low energies is not available.

4. Conclusions

In conclusion, total and partial transfer cross sections have been calculated for $H^+ + Li$ and for $He^{2+} + Li$ collisions with modified atomic orbital expansions. In the case of $H^+ + Li$ the present calculated total capture cross sections agree well with experiment and with the available MO results between 0.5 and 20 keV. For $He^{2+} + Li$ collisions, the present calculated low-energy capture cross sections are far larger than those predicted in a MO study. Further experimental and theoretical work is needed to clarify this point. Such work might, in particular, shed light on the problem of choosing appropriate effective one-electron Hamiltonians for multielectron systems and/or on the accuracy of few-channel approximations to multichannel situations. The calculated partial cross sections display the expected qualitative behaviour as a function of energy. At higher energies, comparison with experiment indicates the need of including higher-n orbitals for an improved convergence of the results. This inclusion of high-n orbitals may conveniently be done in a perturbative manner.

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