

LETTER TO THE EDITOR

**Electron transfer in  $\text{Li}^{3+} + \text{H}$  collisions at low and intermediate energies**

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**Abstract.** A modified two-centre atomic orbital expansion is employed in a study of charge transfer in  $\text{Li}^{3+} + \text{H}$  collisions at  ${}^7\text{Li}$  impact energies  $E = 1.4\text{--}140$  keV. Cross sections are calculated for transitions into individual  $\text{Li}^{2+}$  orbitals as well as into all bound orbitals. The calculated total transfer cross sections are in excellent agreement with existing experimental data but differ significantly from those of other model descriptions.

In recent years, considerable attention has been directed towards an understanding of inelastic processes in collisions of highly charged light projectiles with hydrogen. A particularly intricate problem is that of describing charge transfer in the intermediate- and low-velocity regions where molecular binding effects are of some consequence if not of decisive importance. A description of charge transfer processes within the molecular orbital (MO) picture becomes increasingly cumbersome with increasing projectile charge due to the large number of orbitals involved. The situation worsens more seriously when the collision velocity  $v$  increases such that it cannot be regarded as small compared with the mean electronic orbital velocity  $v_e$ . For the intermediate-energy region, a perturbation approach has been presented recently (Ryufuku and Watanabe 1978, 1979). This method, however, has been questioned (Bransden *et al* 1980, Eichler 1981) on theoretical grounds and, furthermore, the calculated transfer cross sections show poor agreement with experimental data for impact energies below  $2 \text{ keV amu}^{-1}$  (Ryufuku and Watanabe 1979).

In this communication, we present and discuss charge transfer cross sections calculated for the process



in the  ${}^7\text{Li}$  impact energy region  $E = 1.4\text{--}140$  keV. The calculations are based on a modified two-centre atomic orbital expansion as proposed recently (Fritsch *et al* 1981, Fritsch and Lin 1982) for a proper representation of the time-dependent electronic wavefunction at low and intermediate collision velocities $\S$ ,

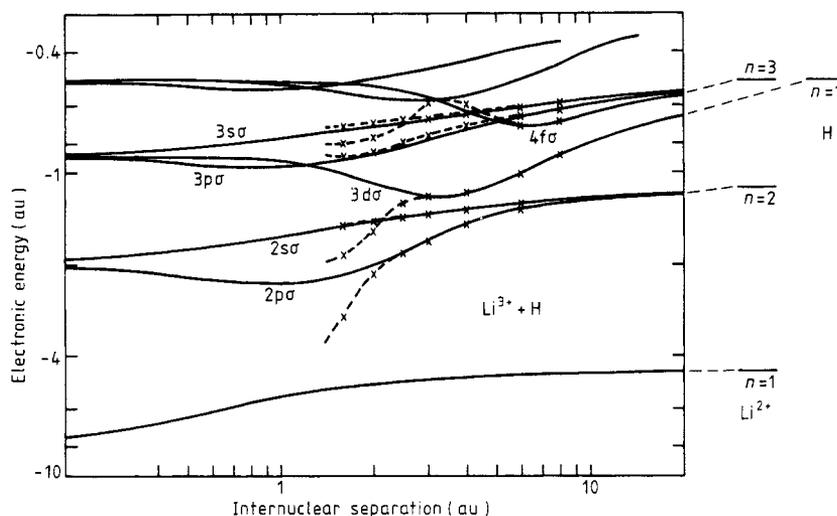
$$\Psi(\mathbf{r}, t) = \sum_j a_j^{\hat{A}}(t) \phi_j^{\hat{A}}(\mathbf{r}_A) \exp[-i(-\frac{1}{2}\mathbf{v} \cdot \mathbf{r} + \frac{1}{8}v^2 t + \varepsilon_j^{\hat{A}} t)] + \sum_k a_k^{\hat{B}}(t) \phi_k^{\hat{B}}(\mathbf{r}_B) \exp[-i(\frac{1}{2}\mathbf{v} \cdot \mathbf{r} + \frac{1}{8}v^2 t + \varepsilon_k^{\hat{B}} t)]. \quad (2)$$

$\S$  In the discussion of this paper, the term 'low velocity' is used for collision velocities associated with the MO model, i.e.  $v/v_e \leq 0.3$ , while 'intermediate velocities' are those with  $0.3 \leq v/v_e \leq 1$ . The calculations reported in this paper cover adiabaticity ratios  $0.09 \leq v/v_e(\text{H}) \leq 0.9$ .

In equation (2), the customary notation is adopted, i.e.  $r$ ,  $r_A$  and  $r_B$  denote the electronic coordinate referred to, respectively, the midpoint between the atomic centres and the atomic centres A and B,  $v$  is the constant collision velocity on a classical straight-line internuclear trajectory,  $\phi_n^C(r_C)$  with  $C = A$  and B are some atomic basis states attached to either collision centre, the energies  $\varepsilon_n^C$  are the expectation values of the atomic Hamiltonians  $H_C$  between the basis states, and  $a_n^C(t)$  denote the time-dependent occupation amplitudes of travelling states  $\phi_n^C(r_C)$ , to be determined by solving the standard set of coupled differential equations.

As basis states  $\phi_n^C(r_C)$  in equation (2) we take some separated-atom (SA) orbitals as well as united-atom (UA) orbitals. Pseudostate expansions using SA and UA atomic orbitals, henceforth denoted as AO+ expansions, have been used already (Fritsch and Lin 1982) in a study of charge transfer processes in  $H^+ + H$  and  $He^+ + H^+$  collisions, and details of the discussion in that paper will not be repeated here. We note, however, that the inclusion of UA orbitals in expansion (2) is shown to be essential for representing the molecular binding effect in slow collisions. Cross sections calculated with appropriate AO+ expansions are shown to agree well with the results of MO calculations at low velocities. At higher velocities, AO+ expansions appear to provide a better representation of the time evolution of the electronic system than do even extended MO expansions. It is the aim of the present paper to establish AO+ expansions as an effective and practical means to investigate quantitatively low-energy transfer processes for rather asymmetric collision systems such as the one in equation (1) and to assess the role of molecular binding effects for those systems.

The most important electronic transfer mechanisms in low-energy  $Li^{3+} + H$  collisions are easily identified by a glance at the correlation diagram of the system, figure 1. The  $\pi$  and  $\delta$  orbitals of the system, not shown in figure 1, simply correlate each  $n$  shell of  $Li^{2+}$  to the corresponding  $n$  shell of the united atom (Helfrich and Hartmann 1970). From the correlation diagram, it is clear that transitions into the  $n = 2, 3$  orbitals of  $Li^{2+}$  should be dominant at least for low collision velocities, and that they



**Figure 1.** Correlation diagram for the system  $(Li+H)^{3+}$ . Shown are the energies of the lowest  $\sigma$  orbitals only. —, exact MO energies; — $\times$ —, energies from diagonalising the Hamiltonian within a 10 AO space, see text.

**Table 1.** Basis states  $\phi_n^C$  used in expansion (2) of the electronic wavefunction.

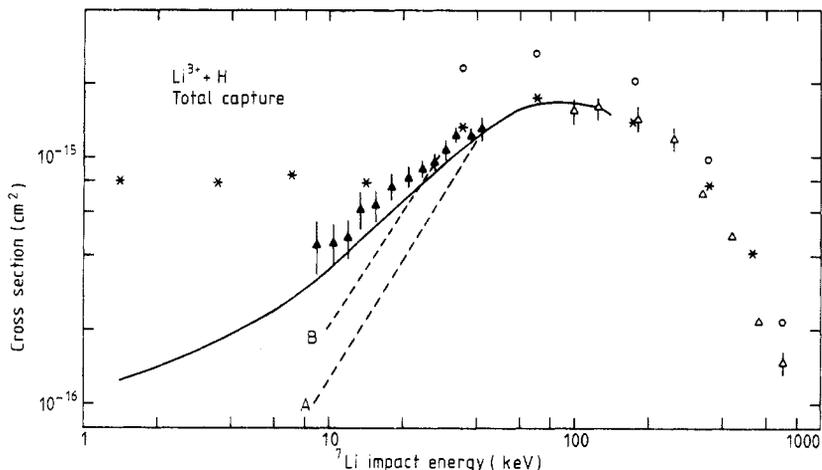
Expansion	Li centre		H centre	
	Li <sup>2+</sup> orbitals	Be <sup>3+</sup> orbitals	H orbitals	Be <sup>3+</sup> orbitals
24 AO+	2s2p3s3p3d	2s2p3s3d	1s	2s2p3s3d
32 AO+	2s2p3s3p3d	2s2p3s3d4f	1s	2s2p3s3d4f
34 AO+	2s2p3s3p3d4s4p4d4f	2s2p3s3d	1s2s2p	2s3d
10 AO	2s2p3s3p3d	—	1s	—

are produced by couplings of the  $3d\sigma$  MO to a multitude of  $2/\Omega$  and  $3/\Omega$  orbitals ( $l, \Omega = 0, 1, 2$ ) and possibly to the  $4f\sigma$  orbital.

The correlation diagram, figure 1, provides guidance as well for the definition of the AO+ basis sets  $\{\phi_n^C\}$  appropriate for the system under consideration. The basis sets used in the present investigation are listed in table 1. Most of the calculations were performed with a 24 AO+ set comprising the 1s H and the  $n = 2, 3$  Li<sup>2+</sup> SA orbitals as well as the 2s, 2p, 3s and 3d UA (Be<sup>3+</sup>) orbitals at both atomic centres. Of those UA orbitals to which the SA orbitals correlate in the UA limit, the 3p and 4f UA orbitals were left out from this basis set for reasons of computing efficiency. The convergence of calculations with the 24 AO+ basis set was checked by comparison with results from a 32 AO+ and a 34 AO+ expansion. The former consists of the 24 AO+ set augmented by the 4f UA orbitals at both centres and is meant to test the importance of an improved representation of the  $4f\sigma$  orbital in slow collisions. For the 34 AO+ set, the  $n = 4$  Li<sup>2+</sup> and  $n = 2$  H orbitals are added to the 24 AO+ set but a few UA orbitals are left out. Calculations with this set are aimed at assessing the role of transfer into higher ( $n = 4$ ) Li<sup>2+</sup> orbitals and of excitation of H in intermediate-energy collisions. Finally, a few runs were made with a 10 AO basis set which is a conventional AO expansion set consisting of the SA orbitals of the 24 AO+ expansion.

Molecular eigenenergies have been calculated by diagonalising the two-centre Hamiltonian within the space of the 24 AO+ set and that of the 10 AO set. With the 24 AO+ set, the exact energies of the MO correlating to the  $n = 2, 3$  states of Li<sup>2+</sup> and to the 1s H state are closely reproduced. Only the  $4f\sigma$  energies are slightly altered from the exact ones in the molecular region of internuclear separations  $R \leq 6$  au. With the 10 AO set, the Stark splitting of MO energies at large internuclear separations is still well reproduced. In the molecular region for  $R$ , however, large deviations from the exact MO energies are observed and correlations are altered; see the broken curves in figure 1. It seems, therefore, obvious that the 10 AO expansion cannot realistically describe any transient molecular structure of the electronic wavefunction or any feature of the cross sections which depends greatly on that structure, such as for example, partial cross sections for transfer into individual  $nlm$  orbitals.

In figure 2, the calculated and measured total capture cross sections in Li<sup>3+</sup> + H collisions are displayed over a range of <sup>7</sup>Li impact energy. The transfer cross sections calculated with the 24 AO+ basis set are seen to agree well with the experimental data of Seim *et al* (1981), given their systematic error of 15%, and they join smoothly with the lowest energy data of Shah *et al* (1978). The cross sections calculated by Ryufuku and Watanabe (1979) follow the trend of both the experimental data and the present results for impact energies above 14 keV ( $2 \text{ keV amu}^{-1}$ ) but overestimate both curves below that energy, i.e. in the low-velocity region ( $v/v_e \leq 0.3$ ). The total



**Figure 2.** Total transfer cross sections in  $\text{Li}^{3+} + \text{H}$  collisions. Theory: —, 24  $\text{AO}+$ , this work; ---, 5  $\text{MO}$  (Casaubon *et al* 1981) with origin on the proton (A) and on the centre of charge (B);  $\star$ , Ryufuku and Watanabe (1979);  $\circ$ , sum over 2  $\text{AO}$  expansion cross sections (Bransden *et al* 1980). Experiments:  $\blacktriangle$ , Seim *et al* (1981);  $\triangle$ , Shah *et al* (1978).

transfer cross sections calculated by summing over individually calculated two-state  $\text{AO}$  expansion cross sections for transitions into substates (Bransden *et al* 1980) largely overestimate the present results and the experimental data. This seems to be hardly surprising since each individual 2  $\text{AO}$  expansion calculation conserves unitarity but not so the sum over all substates, so that double counting occurs to a large degree in that calculation. Finally, the cross sections from the  $\text{MO}$  calculation of Casaubon *et al* (1981) seem to fall off too sharply for decreasing energy. These calculations are done without a translational factor and are, therefore, not meant to provide quantitative predictions of cross sections. Furthermore, the five  $\text{MO}$  included by Casaubon *et al* ( $2p\sigma$ ,  $2p\pi$ ,  $3d\sigma$ ,  $3d\pi$ ,  $4f\sigma$ ) do not allow for a consistent rotational coupling process within the  $3dm$  ( $m = \sigma, \pi, \delta$ ) orbitals at small internuclear separations. In the present calculations, however, the impact parameter dependent transition probabilities indicate that this process governs the population of  $n = 3$   $\text{Li}^{2+}$  orbitals at small velocities (cf below). It seems, therefore, natural that the 5  $\text{MO}$  calculation should underestimate the full transfer process in the low-velocity region.

Table 2 shows partial transfer cross sections for transitions into  $nl$  subshells from 24  $\text{AO}+$  expansion calculations as well as total transfer cross sections from calculations with this and other basis sets of table 1 $\dagger$ . The close agreement between total cross sections from the 24  $\text{AO}+$  and the 32  $\text{AO}+$  expansion calculations at 3 keV demonstrates the high degree of convergence of the 24  $\text{AO}+$  calculations below the energy region where experiments are available. On the high-energy side, a comparison of total transfer cross sections from 24  $\text{AO}+$  and 34  $\text{AO}+$  expansion calculations shows slowly growing deviations with increasing energy (up to 8% for  $E = 100$  keV). These are due to the onset of transitions into  $n = 4$   $\text{Li}^{2+}$  orbitals in the 34  $\text{AO}+$  expansion calculation. We note that deviations between partial cross sections from  $N$   $\text{AO}+$  expansion calculations,  $N = 24, 32$  and  $34$ , are larger than those between total transfer

$\dagger$  The total transfer cross sections contain small contributions from transitions into the bound-state components of the pseudostates. The total transfer cross sections from the 24  $\text{AO}+$  expansion calculation are, therefore, slightly larger than the sum of partial cross sections in table 2.

**Table 2.** Partial and total electron transfer cross sections (in  $10^{-17} \text{ cm}^2$ ) for  $\text{Li}^{3+} + \text{H}$  collisions, calculated with various basis sets.

$E$ (keV)	24 AO+					$\sigma_{\text{total}}$	$\sigma_{\text{total}}$		
	2s	2p	3s	3p	3d		32 AO+	34 AO+	10 AO
3	0.19	0.34	0.28	3.32	12.7	16.9	16.2		
5	0.91	1.25	1.37	5.73	12.1	21.4			
7	2.46	2.76	2.08	8.37	10.5	26.4			
10	4.98	5.40	4.40	11.3	8.52	35.0			38.1
15	9.77	10.6	3.18	14.9	12.2	51.5			
20	14.6	16.1	4.12	13.9	15.4	65.0			
35	23.2	28.1	8.13	19.4	26.1	107			101
50	23.7	37.3	10.9	26.0	41.2	142		146	
70	20.1	45.9	7.20	26.4	60.6	163		169	157
100	16.2	52.7	4.81	26.1	65.3	166		179	160

cross sections, but that they are generally still smaller than 10% for each subshell, indicating a comparatively high degree of convergence even for the partial cross sections shown in table 2. On the other hand, low-energy partial cross sections from the 10 AO expansion calculations are rather different from those of the 24 AO+ expansion calculation. In the latter case the  $n = 2$   $\text{Li}^{2+}$  orbitals are populated almost exclusively (cf a similar trend observed by Bransden *et al* 1980), in agreement with the unrealistic correlation diagram from the 10 AO expansion, see figure 1. Still, the total transfer cross sections from the 10 AO expansion calculation agree amazingly well with the converged ones. The 10 AO expansion seems to offer an extremely efficient way to calculate total transfer cross sections. In practical applications, however, this efficiency is reduced by the need to check the convergence with larger expansions and by the need to use a particular fine mesh of impact parameters since the transition probabilities from calculations with AO expansions fluctuate much more than the converged probabilities.

The low-energy behaviour of the partial cross sections in table 2 is qualitatively understood by simple considerations based on the MO model. In that model, the electronic wavefunction is expected to develop along the adiabatic  $3d\sigma$  orbital on the incoming path, and to couple rotationally to the  $3d\pi$  orbital near the distance of closest approach. The  $3d\pi$  components of the electronic wavefunction are expected to couple further with the  $3d\delta$  orbital, with the  $3d\pi$  and  $3d\delta$  components eventually ending up in the  $n = 3$  orbitals of  $\text{Li}^{2+}$ . Further population of  $n = 3$   $\text{Li}^{2+}$  orbitals is possible via  $3d\sigma$ - $3p\pi$  rotational coupling at finite internuclear separations, but to a lesser degree since the corresponding rotational matrix element vanishes in the united-atom limit<sup>†</sup>. At the lowest energies in table 2,  $n = 2$  orbitals in  $\text{Li}^{2+}$  are barely populated at all since the radial couplings of the relevant MO ( $2p\sigma$ ,  $2s\sigma$ ) to the initial  $3d\sigma$  orbital are less effective than the rotational couplings. These considerations are supported by the behaviour of the impact parameter ( $b$ ) dependent excitation probabilities to  $\text{Li}^{2+}$  ( $nlm$ ) orbitals. At low energies, the  $n = 2$  probabilities oscillate strongly for  $b \leq 4$  au and decay exponentially beyond that impact parameter, as is characteristic for the two-passage situation involving radial couplings. The  $n = 3$

<sup>†</sup> At 3 keV, the ratios of the cross sections  $\sigma(n||m)$  for the combined population of  $\text{Li}^{2+}(nlm)$  and  $\text{Li}^{2+}(nl-m)$  orbitals are  $\sigma(3p1):\sigma(3p0) = 11:1$  and  $\sigma(3d2):\sigma(3d1):\sigma(3d0) = 2.2:3.3:1$ .

probabilities are far less structured and already decay for  $b \geq 2$  au. A quantitative understanding of all these features requires, of course, a more detailed discussion of the couplings and correlations and will not be undertaken here.

At higher velocities, direct transition processes become significant. Their onset is indicated by the more even distribution of the partial cross sections over all the  $\text{Li}^{2+}$  ( $n = 2, 3$ ) orbitals at higher energies and increasing contributions from large impact parameter collisions. Even more significantly, the partial cross sections from the 10 AO expansion approach those of the 24 AO+ expansion for increasing velocities (e.g. to up to 15% at 70 keV), i.e. binding effects become less important as the adiabatic ratio increases. In this connection, it is interesting to note that the cross section weighted mean principal quantum number

$$\bar{n} = \left( \sum_n n \sum_{lm} \sigma(nlm) \right) \left( \sum_{nlm} \sigma(nlm) \right)^{-1} \quad (3)$$

from the 24 AO+ calculation already reaches an almost constant value at  $E = 50$  keV ( $\bar{n} = 2.56$ – $2.59$  for  $E = 50$ – $100$  keV). These values for  $\bar{n}$  are not far from the one which is obtained from the results of the classical-trajectory Monte-Carlo method (Olson 1981) at  $E = 350$  keV ( $\bar{n} = 2.5$ , from figure 3 of Olson 1981, sum over  $n = 2, 3$  only). The  $n$  distribution of capture cross sections at high energies is interpreted by Olson as a tendency of the captured electron to preserve both its original orbital energy and spatial dimensions, i.e. it reflects the (classical) direct character of the transfer process. A further slow decrease of the mean principal quantum number  $\bar{n}$  (sum over  $n = 2, 3$  only) is expected within first-order theories for even higher energies (McDowell and Coleman 1970 give as the high-energy limit  $\bar{n} (E \rightarrow \infty) = 2.23$ ).

In conclusion, modified atomic orbital expansions have been demonstrated to be a powerful tool in the investigation of electron transfer in  $\text{Li}^{3+} + \text{H}$  collisions at low and intermediate collision energies. While a conventional atomic orbital expansion is found to be sufficient for the determination of total transfer cross sections in the present case, the representation of molecular binding effects by united-atom pseudo-states is required for an understanding of details of the transfer process, such as the partial cross sections for transfer into individual subshells or impact parameter dependent transition probabilities. An investigation of transfer processes for a number of more asymmetric collision systems is being undertaken.

After completion of this manuscript, it came to our notice that further theoretical work on the  $\text{Li}^{3+} + \text{H}$  system is in progress (H J Lüdde 1982), involving a decomposition of the time-dependent electronic wavefunction in terms of Hylleraas basis functions (Lüdde and Dreizler 1981). The calculated total transfer cross sections in the intermediate-energy range,  $E \geq 14$  keV, appear to be very close to the ones presented here.

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