Theoretical study of population sharing between $n = 2$ levels in the $\text{Li}^+ + \text{He}$ collision

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Abstract. This paper presents a theoretical study of the relative populations of Σ and Π states associated with $\text{Li}^*(n=2) + \text{He}^+$ and $\text{Li}^+ + \text{He}^*(n=2)$ products that are formed in $\text{Li}^+ + \text{He}$ collisions at keV energies. A half-collision model is considered where the $(1s\sigma^2 2p\sigma 2p\pi) \ ^1\Pi$ molecular state is assumed to be prepared initially (as a result of a primary $2p\sigma - 2p\pi$ rotational coupling step) and the population-sharing processes occur as the collisional system breaks apart. The corresponding calculations involve six-state and twelve-state atomic-like diabatic representations and are carried out using the impact parameter method. The differential electron capture probability and the Stokes' parameters for $\text{Li}^*(2^2\text{P})$ and $\text{He}^*(2^1\text{P})$ excitations are determined. The calculated alignment angles $\gamma(\text{Li}, \text{He})$ and shape parameters are found to be slowly oscillating functions of the collision energy. The differences between the results for Li and He are discussed in terms of the various electron transition mechanisms. Qualitative agreement between theory and experiment is found for $\gamma(\text{Li})$ but the comparison for $\gamma(\text{He})$ is disappointing.

1. Introduction

The $\text{Li}^+ + \text{He}$ collisional system has previously been investigated as a prototype of asymmetric systems involving the interaction of two closed K shells (Lorents and Conklin 1972, Francois *et al* 1972, McCarroll and Piacentini 1972, Lesech *et al* 1973, Junker and Browne 1974, Sidis *et al* 1977). The previous theoretical studies have focused particularly on the primary transitions of one and two electrons at small ion-atom distances ($R < 1 a_0$), and rough estimates of the secondary population sharings at large R were obtained from the Demkov (1964)-Meyerhof (1973) model. A renewed interest in this collisional system has appeared recently, following the experiment of Andersen *et al* (1985). This enabled the extraction, from coherence and correlation analyses of the $\text{Li}^*(2^2\text{P})$ and $\text{He}^*(2^1\text{P})$ photon emissions from the $\text{Li}^+ + \text{He}$ collision, of the alignment angles $\gamma(\text{Li})$ and $\gamma(\text{He})$ of the corresponding 2p electron clouds. The experiment of Andersen *et al* (1985) shows that, for laboratory collision energies $E > 5 \text{ keV}$, the alignment angles are $\gamma(\text{Li}) > \theta_c + \frac{1}{2}\pi$ and $\gamma(\text{He}) < \theta_c + \frac{1}{2}\pi$ (where θ_c is the scattering angle in the centre-of-mass frame).

Considering the electron transition mechanism in the $\text{Li}^+ + \text{He}$ system, if the $2p\sigma - 2p\pi$ rotational coupling ($R < 1 a_0$) were the *exclusive* excitation process, then, since

the $2p\pi$ MO correlates with the $\pi 2p_{\text{Li}}$ AO, the $2p$ electron cloud should be formed on Li perpendicular to the asymptotic direction of the internuclear axis, i.e. $\gamma(\text{Li}) = \theta_c + \frac{1}{2}\pi$; consideration of the $\pi 2p_{\text{Li}} - \pi 2p_{\text{He}}$ electron transfer would only add $\gamma(\text{He}) = \theta_c + \frac{1}{2}\pi$ to the latter prediction. The result of Andersen *et al* (1985) thereby implies that $\pi - \sigma$ population sharings ought to occur between outgoing channels that are associated with the $\text{Li}^*(n=2) + \text{He}^+$ and $\text{Li}^+ + \text{He}^*(n=2)$ states. Inspection of the corresponding diagram of energy levels (figure 1) shows great similarities between the present collisional system and those investigated previously (Sidis *et al* 1981):

Figure 1. (a) Diagram of the adiabatic potential energy curves correlated with $\text{Li}^*(n=2) + \text{He}^+$ and $\text{Li}^+ + \text{He}^*(n=2)$ states. These curves are obtained after diagonalisation of the $\langle \Phi_i | H_{\text{el}} | \Phi_j \rangle$ matrix discussed in § 2.1 and are referred to the average energy level associated with $\pi 2p_{\text{Li}}$ and $\pi 2p_{\text{He}}$ (see also figures 2 and 3). (b) Expanded view of the energy curves at large R .

This similarity suggests that the population-sharing processes that are responsible for the departure of the alignment angles $\gamma(\text{Li}, \text{He})$ from $\theta_c + \frac{1}{2}\pi$ take place at *large* R (typically $R > 4 a_0$) as results of the following elementary interactions (figure 1):

- (i) orbital *unlocking* due to long-range $\sigma 2p$ - $\pi 2p$ rotational coupling (see, for example, Grosser 1981);
- (ii) $\sigma 2s$ - $\sigma 2p$ transitions due to the *Stark effect* which is induced by the ion on the $n = 2$ excited state of the relevant atom ($\text{Li}^+ + \text{He}^*(n = 2)$ and $\text{Li}^*(n = 2) + \text{He}^+$); and
- (iii) $\pi_{\text{Li}}-\pi_{\text{He}}$ and $\sigma_{\text{Li}}-\sigma_{\text{He}}$ *near-resonant electron transfer*.

In this paper we undertake a theoretical study of the above population-sharing processes in $\text{Li}^+ + \text{He}$ collisions in the $0.5 < E_{\text{lab}} < 25$ keV energy range. Due to the prediction that the related transitions occur at large internuclear distances, we have chosen to treat the dynamics of the problem in an almost diabatic atomic-like representation (§ 2). The dynamical treatment (§ 3) itself consists of assuming that the system has been initially prepared in the $2p\pi$ adiabatic molecular state by a primary $2p\sigma$ - $2p\pi$ rotational-coupling step at $R < 1 a_0$ and we study its evolution as the system breaks apart using the impact parameter method (IPM).

2. Potential energy curves and coupling terms

2.1. Electronic wavefunctions

Since the studied processes are expected to take place at rather large internuclear distances the considered electronic states are described as valence-bond configuration states built from *orthonormalised* atomic orbitals (AO). Except when stated otherwise, we consider, throughout, singlet-excited electronic states of the $(\text{Li}-\text{He})^+$ system that are correlated with $\text{Li}^*(1s^2 nl) + \text{He}^+(1s)$ and $\text{Li}^+(1s^2) + \text{He}^*(1s nl)$; $n = 2, 3$. The general form of the corresponding wavefunctions is then

$$\Phi_{\lambda nl\nu} = 2^{-1/2} (|1s_{\text{Li}} \overline{1s_{\text{Li}}} \widetilde{1s_{\text{He}}} \overline{\psi_{\lambda nl\nu}}| - |1s_{\text{Li}} \overline{1s_{\text{Li}}} \widetilde{1s_{\text{He}}} \psi_{\lambda nl\nu}|) \quad nl\nu \neq 1s_{\text{Li}}, \widetilde{1s_{\text{He}}}. \quad (1)$$

n and l are the usual atomic quantum numbers, $\lambda = \sigma$ or π , and $\nu = \text{Li}$ or He . The above orbitals are obtained from a Schmidt orthogonalisation (and normalisation) of the following ordered set of AO

$$\sigma: 1s_{\text{Li}}, 1s_{\text{He}}, 2s_{\text{Li}}, 2s_{\text{He}}, 2p_{\text{Li}}, 2p_{\text{He}}, 3s_{\text{Li}}, 3s_{\text{He}}, 3p_{\text{Li}}, 3p_{\text{He}} \quad (2a)$$

$$\pi: 2p_{\text{Li}}, 2p_{\text{He}}, 3p_{\text{Li}}, 3p_{\text{He}}. \quad (2b)$$

It should be kept in mind throughout that the label π designates real orbitals perpendicular to the internuclear axis and symmetric in the collision plane. The atomic orbitals labelled Li in equations (2a) and (2b) are obtained as the occupied and virtual eigenvectors of an SCF (self-consistent field) calculation on the isolated Li^+ ion. The $1s_{\text{He}}$ orbital is obtained as the isolated $\text{He}(1s^2)$ ground-state SCF-AO. The nl_{He} ($n = 2, 3$) orbitals are *improved virtual orbitals* (IVO) that are determined as the lowest eigenvectors of the Fock-type operator:

$$f = -\frac{1}{2}\Delta - 2/r_{\text{He}} + J_{1s_{\text{He}}} + K_{1s_{\text{He}}} \quad (3)$$

in the space orthogonal to $1s_{\text{He}}$ (see Courbin-Gaussorgues *et al* 1983).

In equation (3) J and K are the Coulomb and exchange operators built using the neutral ground-state SCF-AO ($1s_{\text{He}}$). This AO generation scheme ensures that, as $R \rightarrow \infty$, all states having the form given in equation (1) have no interaction with each other or with the $\text{Li}^+ + \text{He}$ ground state. Moreover, the method provides a balanced

description of the ground and excited states and it is seen that the AO energies have a nice physical interpretation as the binding energies of an electron attached to a $\text{Li}^+ + \text{He}^+$ core (in singlet states).

The calculations have been carried out using the Li (6s3p) and the He (8s4p) CGTO (contracted Gaussian orbital) basis sets given in table 1. The separated-atom orbital energies are compared in table 2 with the corresponding experimental data (Moore 1949). It is seen that the locations and spacings of the energy levels are correctly reproduced except for a systematic shift of about 0.06 eV of the He^* manifold with respect to the Li^* manifold. Comparison of the theoretical and experimental energy levels of the $\text{Li}^* + \text{He}^+$ and the $\text{Li}^+ + \text{He}^*$ separated-atom states relative to the $\text{Li}^+ + \text{He}$ level shows a systematic 2% error that is due to the description of the 1s orbital of He^+ and He^* using the neutral $1s_{\text{He}}$ AO.

Using the above AO in the many-electron wavefunction given in equation (1) with the orthogonalisation order specified in equations (2a) and (2b) we have calculated

Table 1. The contracted Gaussian-type orbital (CGTO) basis sets used in the calculations: (6s3p) for Li and (8s4p) for He.

Lithium		Helium		Lithium		Helium	
γ_s	(6s)	γ_s	(8s)	γ_p	(3p)	γ_p	(4p)
921.3	0.001 367	272.64	0.006 735	1.488 00	0.038 77	1.000 00	1.000 000
138.7	0.010 425	40.986	0.051 155	0.266 70	0.236 26	0.200 00	1.000 000
31.94	0.049 859	9.385 92	0.245 311	0.072 01	0.830 45	0.050 00	1.000 000
9.353	0.160 701	2.693 58	0.776 024			0.010 00	1.000 000
				0.023 70	1.000 000		
3.158	0.344 604	0.898 64	1.000 000	0.010 00	1.000 000		
1.157	0.425 197						
0.500	1.000 000	0.500 00	1.000 000				
0.100	1.000 000	0.300 00	1.000 000				
0.050	1.000 000	0.100 00	1.000 000				
0.010	1.000 000	0.050 00	1.000 000				
		0.030 00	1.000 000				
		0.010 00	1.000 000				

Table 2. Comparison between experimental (Exp.) binding energies (Moore 1949) and those calculated here (Th.), in eV, for the relevant atomic levels of Li and He. Δ shows the difference between the two. These values represent the asymptotic energies of $\text{Li}^*(1s^2nl) + \text{He}^+$ and $\text{Li}^+ + \text{He}^*(1snl)$ levels with respect to the $\text{Li}^+ + \text{He}^+$ reference energy level. The calculated energy of the $\text{Li}^+ + \text{He}(1s^2)$ ground state with respect to this reference is in error by 0.39 eV.

$\text{Li}^*(1s^2nl)^2\text{L}$				$\text{He}^*(1snl)^1\text{L}$			
nl	Th.	Exp.	Δ	nl	Th.	Exp.	Δ
2s	5.3312	5.3914	0.0602	2s	3.3481	3.9715	0.1234
2p	3.4950	3.5437	0.0487	2p	3.2529	3.3692	0.1163
3s	1.9895	2.0185	0.0350	3s	1.5697	1.6670	0.0973
3p	1.5224	1.5574	0.0350	3p	1.4103	1.5004	0.0901

for $1 < R < 80 a_0$ the matrix elements

$$\langle \Phi_{\lambda n l_\nu} | H_{el} | \Phi_{\lambda n' l'_\nu} \rangle$$

of the $(\text{LiHe})^+$ electronic Hamiltonian. All the above calculations have been performed using the MOLECULE-ALCHEMY program[†]. The results are plotted in figures 2 and 3.

Figure 2. Diagram of the diabatic energy curves associated with the atomic-like states Φ_i of § 2.1. As in figure 1, the curves are referred to the average energy level, $\frac{1}{2}(H_{\pi 2p_{Li}} - \pi 2p_{Li} + H_{\pi 2p_{He}} - \pi 2p_{He})$.

In addition to H_{el} matrix elements, the coupling matrix involved in the (IPM) treatment of the collision (§ 3) contains

$$\langle \Phi_{\lambda n l_\nu} | d/dR |_C | \Phi_{\lambda n' l'_\nu} \rangle$$

and

$$\langle \Phi_{\lambda n l_\nu} | iLy |_C | \Phi_{(\lambda+1)n' l'_\nu} \rangle$$

matrix elements. The d/dR couplings are calculated using the overlap method of Halkjaer and Linderberg (1979) whereas the Ly couplings are calculated analytically[‡]. As is now well known, these couplings depend on the chosen electron coordinate origin C and generally have spurious long-range behaviours (see, for

[†] The joint MOLECULE-ALCHEMY program incorporates the MOLECULE integral program and the ALCHEMY SCF program. MOLECULE was written by D J Almlöf of the University of Uppsala, Sweden. The ALCHEMY SCF program was written by P S Bagus and B Liu of the IBM San Jose Research Laboratory. The interfacing of these programs was performed by U Wahlgren and P S Bagus at IBM.

[‡] Both calculations are performed using computer codes written by J Vaaben of the Ørsted Institute, University of Copenhagen, Denmark.

Figure 3. Off-diagonal matrix elements of the electronic Hamiltonian between the atomic-like Φ_i states.

example, Delos and Thorson 1978 and references therein). These drawbacks stem from the inability of 'clamped-nuclei' electronic basis sets to represent electron clouds that are travelling with the nuclei. We do not solve this problem here, but, as in the work by Sidis *et al* (1981) (see also Taubjerg and Briggs 1975), we admittedly circumvent it by choosing

$$C = \nu \quad \text{when } \nu = \nu' \quad (4a)$$

$$C = \text{centre of mass} \quad \text{when } \nu \neq \nu' \quad (4b)$$

The corresponding radial (d/dR) and rotational (iLy) coupling matrix elements are shown in figures 4 and 5.

2.2. Results and discussion

It may first be remarked that at large R (greater than $20 a_0$) the H_{ei} matrix elements involving $n = 2$ orbitals behave as

$$\langle \Phi_{\sigma 2s_\nu} | H_{ei} | \Phi_{\sigma 2s_\nu} \rangle = E_{2s_\nu}(R \rightarrow \infty) \quad (5a)$$

$$\langle \Phi_{\lambda 2p_\nu} | H_{ei} | \Phi_{\lambda 2p_\nu} \rangle = E_{2p_\nu}(R \rightarrow \infty) + \frac{1}{5}(3\lambda^2 - 2)Q_\nu/R^3 \quad (5b)$$

$$\langle \Phi_{\sigma 2s_\nu} | H_{ei} | \Phi_{\sigma 2p_\nu} \rangle = D_\nu/R^2 \quad (5c)$$

where $\nu = \text{Li or He}$ and

$$D_{\text{Li}} = 2.35 \text{ au} \quad D_{\text{He}} = 2.98 \text{ au}$$

$$Q_{\text{Li}} \approx 28 \text{ au} \quad Q_{\text{He}} \approx 34 \text{ au}$$

Figure 4. $\langle \Phi_i | d/dR |_C | \Phi_j \rangle$ radial-coupling matrix elements between the atomic-like states of § 2. ●, $C = \text{Li}$, ○, $C = \text{He}$; —, $C = \text{centre of mass of Li and He}$.

Figure 5. $\langle \Phi_i | iL_{ij} |_C | \Phi_j \rangle$ rotational-coupling matrix elements between the atomic-like states of § 2.1 (with the same labelling as in figure 4).

which are slightly different from the H^* ($n=2$) values ($D_H=3$ au and $Q_H=30$ au). Equation (5b), along with the actual values of Q_v , is quite interesting as it indicates that the long-range rotational coupling (process (i) in § 1) is almost the same for Li and He. Accordingly, if there were no competing transition path other than

the alignment angles γ (Li or He) would be almost identical (albeit different from $\theta_c + \frac{1}{2}\pi$) since γ depends only on the ratio of the Σ and Π transition amplitudes (see § 3 for further details). From the experimental data of Andersen *et al* (1985) it may thereby be inferred that other processes ought to occur in addition to those shown in equation (6).

Another noteworthy result is the smallness and smoothness of the d/dR coupling matrix elements for $R > 3a_0$ (figure 4). The moderate increase of the $\langle \sigma 2s_{He} | d/dR | \sigma 2p_{Li} \rangle$ and $\langle \sigma 2p_{Li} | d/dR | \sigma 2p_{He} \rangle$ matrix elements at smaller distance is caused by the orthogonality constraints (equation (2)). This overall behaviour of the d/dR radial couplings allows us to consider that the chosen atomic-like description (§ 2.1) actually provides an almost diabatic representation.

Considering the rotational-coupling matrix elements (figure 5), three features are worth pointing out. Firstly, both the $\langle \sigma 2p_{Li} | iLy | \pi 2p_{Li} \rangle$ and $\langle \sigma 2p_{He} | iLy | \pi 2p_{He} \rangle$ matrix elements remain close to 1 down to $R \approx 5 a_0$. Secondly, for $R < 3 a_0$ the nodal structures imposed by the orthogonality constraints (equations (2a) and (2b)) on the $\sigma 2p_{He}$ and $\pi 2p_{He}$ AO is such that these orbitals transform into $3d\sigma$ - and $3d\pi$ -type MO as attested by the value of approximately $3^{1/2}$ reached by the $\langle \sigma 2p_{He} | iLy | \pi 2p_{He} \rangle$ matrix element (figure 5). Thirdly, the orthogonalised $\sigma 2s_{He}$ orbital acquires a substantial $2p\pi$ component that is kept throughout the $1.5 < R < 7 a_0$ range as is attested by the value of the $\langle \sigma 2s_{He} | iLy | \pi 2p_{Li} \rangle$ matrix element (figure 5). A similar feature was noticed and discussed by Guberman and Goddard (1975) and Gauyacq (1976, 1977) in their studies of the isoelectronic homonuclear system He_2 . This feature (also touched on by Sidis *et al* (1977)) is thereby expected to play an important role in the π - σ population-sharing processes that determine the alignment angles γ (Li and He).

From the computed energy curves and coupling terms one may deduce, as we will now do, the most important transition regions for the sharing processes that involve the $n=2$ states of Li and He.

2.2.1. The charge exchange regions. From the Demkov (1964) model of near-resonant charge exchange the critical transition region is expected to lie around $R^{(E)}$ so that

$$H_{ij}(R^{(E)}) = \frac{1}{2} |H_{ii}(R^{(E)}) - H_{jj}(R^{(E)})|.$$

Accordingly, the $\pi 2p_{Li}-\pi 2p_{He}$ transition zone would lie around $R^{(E)} \approx 11 a_0$ whereas for $\sigma 2p_{Li}-\sigma 2p_{He}$ it would lie around $R^{(E)} \approx 16-17 a_0$. On the other hand, the $\sigma 2s_{Li}-\sigma 2s_{He}$ energy splitting and the corresponding coupling are such that $R^{(E)}$ cannot be defined, which thereby indicates a weak process. Still, using the above criterion, a $\sigma 2p_{Li}-\sigma 2s_{He}$ transition is likely to occur around $R^{(E)} \approx 15 a_0$. Moreover, the transition between the latter states may also occur in the range $4 < R < 6 a_0$ where their energy curves approach each other closely and even cross twice (figure 2).

2.2.2. *The Stark-effect regions.* The transition region for states having slowly varying or nearly parallel energy curves and interacting via an R^{-2} power law (see equations (5b) and 5(c)) is expected to lie around $R^{(S)}$ so that

$$H_{ij}(R^{(S)}) \approx \frac{1}{2}\alpha |H_{ii}(R^{(S)}) - H_{jj}(R^{(S)})|$$

with $3^{1/2} < \alpha < 3$. (This expression actually locates the maximum of the d/dR coupling associated with the two adiabatic states that arise from the diagonalisation of the H_{el} matrix corresponding to the relevant $\sigma 2s$ and $\sigma 2p$ states; see equation (5)).

Accordingly, the Stark region for He is located in the range $10 < R_{He}^{(S)} < 13 a_0$ whereas for Li it lies in the range $5 < R_{Li}^{(S)} < 7 a_0$. The difference between $R_{He}^{(S)}$ and $R_{Li}^{(S)}$ is readily understood as arising from the much larger $2s$ - $2p$ energy splitting in Li than in He (by a factor of about 3) for comparable coupling terms. This feature adds up to the aforementioned $\sigma 2p_{Li}$ - $\sigma 2s_{He}$ transition to make $\gamma(Li) \neq \gamma(He)$.

2.2.3. *The rotational coupling regions.* An obvious Σ - Π rotational-coupling process is that occurring between the asymptotically degenerate $\sigma 2p_v$ and $\pi 2p_v$ states the energy levels of which split at large (but finite) R , as expressed by equation (5b). The corresponding transition radius characterises a zone where the electronic angular momentum unlocks from the internuclear axis when the collisional system breaks apart. Grosser (1981) shows that, provided equation 5(b) is valid, this unlocking region lies around $R = R^{(R)}$ such that

$$R_v^{(R)} \approx (3Q_v/13v)^{1/2} \quad (7)$$

which implies the values $R_{He}^{(R)} \approx 10 a_0$ and $R_{Li}^{(R)} \approx 9 a_0$ for a collision velocity v of about 0.1 au. Although these values of $R_v^{(R)}$ fall below the range of validity of equation (5b), they may nevertheless be considered as characteristic of the $\sigma 2p_v$ - $\pi 2p_v$ transitions since they correspond to a range of R values where the related energy curves approach each other and even cross.

In addition to the above $\sigma 2p_v$ - $\pi 2p_v$ transitions, the aforementioned $\sigma 2s_{He}$ - $\pi 2p_{Li}$ rotational coupling (figure 5) and the large $\sigma 2s_{He}$ - $\sigma 2p_{Li}$ interaction (§ 2.2.1) are expected to have a combined effect in the range $2 < R < 7 a_0$.

Finally it may be noticed that $\sigma 2s_v$ - $\pi 2p_v$ transitions are unlikely owing to the smallness of the corresponding iLy matrix element (less than 0.1 au; see figure 5).

In closing this section, it may be remarked that the dominant transition processes that may share the initial $2p\pi$ population between the various $n = 2$ states of Li and He are likely to take place at rather large internuclear distances $R > 4 a_0$ which justifies *a posteriori* our choice of an atomic-like description of the problem considered.

3. Collision dynamics

3.1. The half-collision model

It should be remembered throughout that we consider *single-excitation processes* into $Li^*(2^2S, 2^2P) + He^+$ and $Li^+ + He^*(2^1S, 2^1P)$. The corresponding electron transition mechanism is viewed as occurring in two steps:

- (i) one-electron $2p\sigma$ - $2p\pi$ rotational coupling at small R ($< 1 a_0$);
- (ii) sharing of the subsequent $2p\pi$ population between the $n = 2$ states considered, as a result of the various couplings discussed in § 2.2.

Transitions of two electrons, via $2p\sigma^2-2p\sigma 2p\pi-2p\pi^2$ rotational coupling and subsequent sharings of the $2p\pi^2$ population, are neglected for the following two reasons.

(i) Photons of wavelength 6707 Å emitted from $\text{Li}^*(2^2\text{P}) + \text{He}^{+*}(n=2)$ or of wavelength 584 Å emitted from $\text{Li}^{+*}(n=2) + \text{He}^*(2^1\text{P})$, when not separated from emissions from the above singly excited channels (as is the case in the experiment of Andersen *et al* (1985)), should contribute to coherence loss which, in turn, should invalidate the experimental analysis that has triggered the present investigation.

(ii) Extra population of the singly excited channels at curve crossings with the doubly excited $2p\pi^2$ channels (see, for example, Sidis *et al* 1977) involve two-electron rearrangement processes; these processes are likely to be quite weak in the $1 < E < 25$ keV energy range investigated here.

Accordingly, we assume in our treatment that the *adiabatic* $2p\pi$ molecular orbital has already been populated by the primary electron transition mechanism at some $R < R_s$ and solve the IPM close-coupling equations (see, for example, Gaussorgues *et al* 1975) for the outward path of the collision starting at $R = R_s$ with initial probability amplitudes given by (see § 2.1 for definitions)

$$c_{\lambda n l_\nu}(z(R_s, b)) = \langle \psi_{\lambda n l_\nu} | 2p\pi \rangle |_{R=R_s} \quad (8a)$$

with

$$R^2 = z^2 + b^2 \quad z > 0 \quad (8b)$$

($b < R_s$ being the selected impact parameter).

Owing to both the long-range behaviour of the rotational coupling (which is proportional to R^{-2}) and the smallness of the $\sigma 2s_\nu - \pi 2p_\nu$ energy difference at large R , the IPM equations are integrated up to $z = z_{\text{max}}$ (such that $(z_{\text{max}}^2 + b^2)^{1/2} \gg R_\nu^{(R)}$; see equation (7)) where the final $\sigma 2p_\nu$ and $\pi 2p_\nu$ probability amplitudes are extracted using the transformation (Courbin-Gaussorgues 1979)

$$\begin{pmatrix} c_{\sigma 2p_\nu}(z \rightarrow \infty) \\ c_{\pi 2p_\nu}(z \rightarrow \infty) \end{pmatrix} = \begin{pmatrix} \cos \beta & -\sin \beta \\ \sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} c_{\sigma 2p_\nu}(z_{\text{max}}) \\ c_{\pi 2p_\nu}(z_{\text{max}}) \end{pmatrix} \quad (9a)$$

$$(9b)$$

where $\beta = b \langle \sigma 2p_\nu | iLy | \pi 2p_\nu \rangle / R(z_{\text{max}})$.

3.2. Technical

The reported calculations have been carried out for $0.5 < E_{\text{lab}} < 25$ keV in a six-state basis made of all of the $\Phi_{\lambda 2l}$ states of § 2.1. Calculations using a twelve-state basis also including $\Phi_{\lambda 3l}$ ($l=0, 1$) states have also been carried out to test the sensitivity of the results to the basis set size. In these calculations R_s has been chosen to be equal to $1.5 a_0$. This is so that the atomic-like basis (described in § 2) is still reliable†; it excludes the R range (less than $1 a_0$) where the $2p\sigma-2p\pi$ rotational coupling takes place (Sidis *et al* 1977). This choice was made after several tests in which R_s was varied between $1 a_0$ and $2 a_0$. The largest changes were observed for $R \approx 1 a_0$ at $E > 5$ keV; these results were rejected after consideration of (i) the inadequacy of the atomic-like basis at such small distances† and (ii) the spreading out of the $2p\sigma-2p\pi$ rotational-coupling zone with increasing energy (Taulbjerg *et al* 1976).

† By 'reliability of the basis' we mean the degree to which the innermost $\sigma 1s_L$ and $\sigma 1s_{\text{He}}$ orbitals are able to represent the actual $1s\sigma$ and $2p\sigma$ MO (as an example see Henri *et al* 1985).

Finally, the actual choice of $z_{\max}$ (in equation (9)) was $80 a_0$, where, as shown in figures 3, 4 and 5, all coupling-matrix elements except $\sigma_{2p}-\pi_{2p}$ have vanished, thereby indicating that the collision has 'ended' and that the resulting $2p$ orbital is viewed from the slowly rotating body-fixed frame (Courbin-Gaussorgues 1979, Grosser 1981).

3.3. The Stokes' parameters

For a general presentation and discussion of these parameters the reader is referred to the comprehensive studies by Hermann and Hertel (1982) and Andersen *et al* (1983, 1985). In this subsection we just summarise the relevant definitions.

At the end of the collision the $|2p_\nu\rangle$ wavefunction is formed as a superposition:

$$|2p_\nu\rangle = a_{\sigma 2p_\nu}|2p_{\nu z}\rangle - a_{\pi 2p_\nu}|2p_{\nu x}\rangle \quad (10)$$

where the indices z and x refer respectively to the directions, in the collision plane, parallel and perpendicular to the asymptotic R axis and

$$|2p_{\nu z}\rangle = |\sigma_{2p_\nu}(R \rightarrow \infty)\rangle \quad (11a)$$

$$|2p_{\nu x}\rangle = -|\pi_{2p_\nu}(R \rightarrow \infty)\rangle \quad (11b)$$

$$a_{\lambda n l_\nu} = c_{\lambda n l_\nu}(z \rightarrow +\infty).$$

With these conventions the λ and x parameters are defined as

$$\lambda_\nu = |a_{\sigma 2p_\nu}|^2 / (|a_{\sigma 2p_\nu}|^2 + |a_{\pi 2p_\nu}|^2) \quad (12a)$$

$$x_\nu = \arg(a_{\pi 2p_\nu} / a_{\sigma 2p_\nu}) \quad (12b)$$

in terms of which the Stokes' parameters are expressed

$$P_1^\nu = 2\lambda_\nu - 1 \quad (13a)$$

$$P_2^\nu = -2[\lambda_\nu(1 - x_\nu)]^{1/2} \cos x_\nu \quad (13b)$$

$$P_3^\nu = 2[\lambda_\nu(1 - \lambda_\nu)]^{1/2} \sin x_\nu \quad (13c)$$

and the 'pseudo' alignment angle $\Gamma(\nu)$

$$\Gamma(\nu) = \frac{1}{2}\pi + \frac{1}{2}\tan^{-1}(P_2^\nu / P_1^\nu) \quad (13d)$$

(with $-\frac{1}{2}\pi < \tan^{-1} x_\nu < \frac{1}{2}\pi$). It is seen that when $\lambda = 0$, $\Gamma(\nu) = \frac{1}{2}\pi$, i.e. the $2p_\nu$ orbital is aligned perpendicularly to the asymptotic direction of the internuclear axis. Alternatively, referring to the direction of the incident beam, the 'actual' alignment angle is then

$$\gamma(\nu) = \Gamma(\nu) + \theta_c \quad (13e)$$

where θ_c is the scattering angle in the centre-of-mass frame. For comparison with the data of Andersen *et al* (1985) we have assumed the same dependence of θ_c upon b as displayed by these authors in their table 1.

3.4. Results

3.4.1. Electron capture probability. In figure 6 the sharing probabilities for the $\pi 2p_\nu$ states as functions of the laboratory collision energy are shown. We point out, firstly,

that the total population of these states (P_π) is larger by far than that of the $\sigma 2l_\nu$ states ($P_\pi > 90\%$). Secondly, the sharing probabilities (figure 6) are found to agree only qualitatively with the previously used Demkov-Meyerhof model (Sidis *et al* 1977).

Consistently with our half-collision model, the impact parameter dependence of the single-electron capture process

may be obtained as

$$P_{\text{exch}}(b) = P_{2p\sigma-2p\pi}(b) |a_{\pi 2p_{\text{Li}}}|^2 \quad (14)$$

using the previously calculated $2p\sigma-2p\pi$ transition probabilities (see, for example, Sidis *et al* 1977) and the present $|a_{\pi 2p}|^2$ values for Li (figure 6). Owing to the dominance of the $\pi 2p_\nu$ channels, equation (14) actually provides the total charge exchange probability within a few per cent (approximately 5% for $E < 5$ keV).

Figure 7 shows a comparison between the experimental capture probability (Andersen *et al* 1985), and the result of equation (14) obtained for $E = 2$ keV. The capture probabilities are plotted as functions of the 'modified' reduced angle $E^{3/2}\theta$ (Park *et al* 1975). In this calculation the theoretical $\theta(b)$ relation was obtained as the classical deflection function for elastic scattering by the diabatic $1s\sigma^2 2p\sigma^2$ potential

Figure 6. Transition probabilities $|a_{\pi 2p}|^2$ for Li(●) and He(○) plotted against the Li^+ laboratory energy (keV) for impact parameters $b < R_s = 1.5 a_0$. Results of TPM calculations involving six coupled states (---) and twelve coupled states (—). The result of the Demkov (1964)–Meyerhof (1973) model as used previously by Sidis *et al* (1977) is shown for comparison (– · – · –).

Figure 7. Electron capture probabilities plotted against the reduced parameter $E^{3/2}\theta$ appropriate for $2p\sigma-2p\pi$ rotational coupling (Park *et al* 1975). Experimental data of Andersen *et al* (1985): ●, 1.5 keV; ▼, 2 keV; ▲, 3 keV; ○, 5 keV; ▽, 9 keV; and △, 13.5 keV. The theoretical result (—) is obtained for $E_{\text{lab}} = 2$ keV by multiplying the one-electron $P_{2p\sigma-2p\pi}$ transition probability of Sidis *et al* (1977) by the $|a_{\pi 2p}|^2$ result of figure 6 for Li.

of Sidis *et al* (1977). The comparison shows a good agreement between the theoretical result and the experimental data for low collision energies ($E < 3$ keV). On the other hand, deviations are seen between theory and experiment for $E > 5$ keV and $E^{3/2}\theta > 25$ keV $^{3/2}$ deg. The observed deviations are attributed unambiguously to contributions from two-electron excitation processes ($2p\sigma^2-2p\sigma 2p\pi-2p\pi^2$). Indeed, these contributions manifest themselves at smaller impact parameters (larger values of the product $E\theta$) than those characterising the one-electron $2p\sigma-2p\pi$ transition and require high collision energies (typically $E > 5$ keV) for a significant fraction ($>13\%$) of the $2p\pi^2$ population to show up as $\text{Li}^*(2^2\text{P}) + \text{He}^+(2^2\text{P})$ products (see Sidis *et al* 1977). Hence, from this result we conclude that for $E > 5$ keV and $E^{3/2}\theta > 25$ keV $^{3/2}$ deg (e.g. $E\theta > 11.2$ keV deg, $b < 0.57 a_0$ for $E = 10$ keV and $E\theta > 5$ keV deg, $b < 0.82 a_0$ for $E = 25$ keV) both one- and two-electron transition processes actually contribute to the experimental $\text{Li}^*(2^2\text{P})$ data of Andersen *et al* (1985), in good agreement with figure 6 of their paper.

3.4.2. Alignment and shape of the $2p_v$ electron clouds. As discussed in §§ 1 and 2 the alignment and shape of the $2p_v$ clouds are determined by the processes that share the initial $2p\pi$ population between the various $\lambda 2I_v$ channels at large R . Figure 8 shows the evolution at $E_{\text{lab}} = 2$ keV of the related transition probability as the collision partners separate, i.e. as functions of $z = (R^2 - 0.55^2)^{1/2}$. This figure illustrates well the predicted regions associated with the various transition mechanisms. There are clearly three zones:

Figure 8. Evolution of the transition probabilities $|c_{\sigma 2 l_\nu}(b, z)|^2$ along the outgoing part of the trajectory: $z = (R^2 - b^2)^{1/2} > 0$, for $b = 0.55 a_0$ and $E_{lab} = 2$ keV. —, Li; ---, He.

(i) in the range $3 < z < 7 a_0$ the $\sigma 2 s_{Li}$ and $\pi 2 p_{He}$ channels draw off flux from the dominant $\pi 2 p_{Li}$ channel;

(ii) in the range $7 < z < 20 a_0$ dramatic probability rearrangements occur between all channels;

(iii) in the range $z > 20 a_0$ the probabilities evolve somewhat smoothly and keep varying owing to the long-range couplings (proportional to R^{-2}) discussed in § 2.

We again stress that despite the observed important changes of the $\sigma 2 \lambda_\nu$ channel populations the related probabilities do not exceed a few per cent.

(a) *Li(2^2P) results.* In figure 9 we show the $\gamma(Li)$ alignment angle as a function of impact parameter for various collision energies. It is seen that, provided the impact parameter is not too small (i.e. $E^{3/2}\theta(b) < 25 \text{ keV}^{3/2} \text{ deg}$) and the collision energy is not too high ($E < 5$ keV), the theoretical results agree with the measurements of Andersen *et al* (1985) within the experimental uncertainties.

Figures 10(a), (b) and (c), display $\gamma(Li)$, P_1^{Li} and P_3^{Li} respectively for a fixed impact parameter, $b = 0.55 a_0$, as functions of the collision energy. The closeness to unity of the theoretical P_1^{Li} values clearly illustrates the weakness of the $\sigma 2 l_{Li}$ probabilities noticed already. This is not the case with the experimental data of Andersen *et al* (1985) which reflect larger values of λ_{Li} especially above $E \approx 5$ keV. Owing to the slow variation of the theoretical P_1^{Li} curve (figure 10(b)) the corresponding P_3^{Li} curve (in figure 10(c)) actually reflects, via its $\cos x_{Li}$ dependence (equation (13)), the evolution of the x_{Li} phase difference. The theoretical x_{Li} curve is thence seen to go through multiples of π at $E \approx 0.65$ and 1.3 keV and through odd multiples of $\frac{1}{2}\pi$ at $E \approx 0.85$ and 3.8 keV. Consistent with this finding, the calculated $\gamma(Li)$ curve of figure 10(a)

Figure 9. The $\gamma(\text{Li})$ alignment angle (in degrees) plotted against the impact parameter for various energies. The broken curve represents the direction perpendicular to the asymptotic internuclear axis ($\theta_c + \frac{1}{2}\pi$). $\triangle$, the present calculated values in the twelve-state basis. The experimental data points ($\bullet$) are from Andersen *et al* (1985). The shaded parts of the horizontal axes indicate the range of impact parameters b where two-electron excitation processes may contribute to the formation of $\text{Li}^*(2^2\text{P})$.

goes through $\theta_c + \frac{1}{2}\pi$ (see equation (13d)) when P_3^{Li} displays a minimum or a maximum and it exhibits a ventral segment when P_3^{Li} goes through a node. On the other hand, the $\gamma(\text{Li})$ curve drawn through the experimental data points undulates too much, about $\theta_c + \frac{1}{2}\pi$, in comparison with what may be expected from the corresponding P_3^{Li} data. This apparent inconsistency is not understood. Still, the experimental and theoretical alignment curves display the same qualitative behaviour if the 1.5 and 25 keV data points are discarded.

(b) *He(2¹P) results.* In figures 11(a), (b) and (c) the calculated $\gamma(\text{He})$, P_1^{He} and P_3^{He} functions are plotted against the collision energy for $b = 0.55 a_0$. The closeness to unity of the $-P_1^{\text{He}}$ curve (figure 11(b)) illustrates the weakness of the calculated $\sigma 2p_{\text{He}}$ probability compared with that of $\pi 2p_{\text{He}}$. Still a significant enhancement of the corresponding λ_{He} ratio is observed at high energy $E > 10$ keV. Here again, the nodes and antinodes seen in P_3^{He} reflect the passage of x_{He} through multiples of π and odd multiples of $\frac{1}{2}\pi$ respectively. As already discussed for Li, these features are also well reflected in the undulations of $\gamma(\text{He})$ about $\theta_c + \frac{1}{2}\pi$. For comparison with experiment we also plot in figure 11(d) the shape parameter $\hat{P}_1 = (1 - |P_3^{\text{He}}|^2)^{1/2}$; the minima and maxima in this curve are associated in a straightforward manner with the aforementioned characteristic values of x_{He} .

A glance at figures 11(a) and (d) reveals large discrepancies between theory and experiment for both $\hat{P}_1$ and $\gamma(\text{He})$. The experimental data points are not abundant enough to enable us to proceed unambiguously to consistency checks as we have done for $\gamma(\text{Li})$ and P_3^{Li} . The λ_{He} values that may be extracted from the experimental $\hat{P}_1$

Figure 10. Shape parameters for $\text{Li}^*(2^2\text{P})$ plotted against the laboratory collision energy at a fixed impact parameter ($b = 0.55 a_0$). (a) The alignment angle $\gamma(\text{Li})$: ●, measurements of Andersen *et al* (1985); △, present twelve-state calculation; ○, present six-state calculation. The curve $\theta_c + \frac{1}{2}\pi$ is shown for comparison. (b) P_1^{Li} : ●, Measurements of Andersen *et al*; —, present twelve-state calculation. (c) The circular polarisation P_3^{Li} : ●, measurements of Andersen *et al*; —, present twelve-state calculation.

Figure 11. Same as figure 10 for $\text{He}^*(2^1\text{P})$. (d) $\hat{P}_1$: ●, measurements of Andersen *et al*; —, present twelve-state calculation.

and $\gamma(\text{He})$ data lie in the range $0.10 < \lambda_{\text{He}} < 0.25$ whereas the present calculations give λ_{He} values that do not exceed 0.06. As shown in figures 10(a) and 11(a), the results of our calculations are essentially the same for the six-state basis restricted to $\lambda 2l_v$ states or the twelve-state basis involving λnl_v states with both $n = 2$ and 3. This result indicates that the observed discrepancy is not attributable to a problem caused by the size of the basis set. Moreover, it should be noted that the general trend of the calculated curves could not be brought into much better agreement with experiment by displacing the starting distance R_s of our half-collision model (§ 3.1) in the range 1–2 a_0 . Furthermore, at low keV energies $E < 5$ keV, and for $E\theta \approx 8$ keV deg (i.e.

$b \approx 0.55 a_0$) where discrepancies are also seen, one can hardly invoke the neglected $2p\pi^2\ ^1\Delta$, $\ ^1\Sigma$ states as extra feeding channels since their population is one order of magnitude smaller than that of the $2p\pi$ channel considered (Sidis *et al* 1977).

4. Conclusion

We have presented a detailed theoretical investigation of the electron transition mechanisms that share the initial population of the $(1s\sigma^2 2p\sigma 2p\pi)\ ^1\Pi$ molecular state between the six $\lambda 2I_\nu$ atomic-like (diabatic) states of the $\text{Li}^+ + \text{He}$ collisional system. The inspection of the various molecular interactions and the analysis of the evolution of the transition probabilities along the outgoing path of the collision clearly reveal three characteristic ranges of internuclear distances, namely $2 < R < 7 a_0$, $7 < R < 15 a_0$ and $R > 10 a_0$. In the first region the $\pi 2p_{\text{He}}$ and $\sigma 2s_{\text{He}}$ states initiate the sharing processes resulting from exchange interaction and rotational coupling respectively. In the second region, up to $R \approx 10 a_0$, while $\pi 2p_{\text{Li}} - \pi 2p_{\text{He}}$ transitions still proceed, dramatic $\sigma - \sigma$ rearrangements occur owing to exchange interactions and the Stark effect. The latter interaction extends into the third region, for He, and competes with long-range $\pi 2p_\nu - \sigma 2p_\nu$ ($\nu = \text{Li, He}$) rotational coupling.

From the $\pi 2p_{\text{He}} - \pi 2p_{\text{Li}}$ sharing probabilities provided by our half-collision model we have been able to calculate differential probabilities for electron capture. The results are found to agree with experiment in the range $E < 5 \text{ keV}$, $E^{3/2} \theta < 25 \text{ keV}^{3/2} \text{ deg}$. Beyond these boundaries, processes involving excitation of two $2p\pi$ electrons (not taken into account in our study) exist and contribute to the emission of the 6707 Å photon line from $\text{Li}^*(2^2\text{P})$.

From the calculated $\sigma 2p_\nu$ and $\pi 2p_\nu$ transition amplitudes we have derived the alignment angles and shape parameters for the $2p_\nu$ electron cloud as functions of the energy and impact parameter. Slow oscillations are found in the plots of $\gamma(\nu)$, P_3^ν and P_1^ν as functions of energy for a fixed impact parameter. We have shown that these oscillations are related to the passage of x_ν (the relative phase of the $\sigma 2p_\nu$ and $\pi 2p_\nu$ amplitudes) through multiples of $\frac{1}{2}\pi$. From this finding we conclude that the experimental $\gamma(\text{Li})$ curve of Andersen *et al* (1985) displays too many oscillations compared with what is expected from the measured P_3^{Li} . As in the work of Andersen *et al* (1985) we do find that, above $E \approx 5 \text{ keV}$, $\gamma(\text{Li}) > \theta_c + \frac{1}{2}\pi$ whereas $\gamma(\text{He}) < \theta_c + \frac{1}{2}\pi$. The different behaviour of $\gamma(\text{Li})$ and $\gamma(\text{He})$ is attributed to

- (i) different $2s_\nu - 2p_\nu$ energy differences for quite similar coupling strengths; and
- (ii) the specific role played by the $\sigma 2s_{\text{He}}$ intermediate state at moderate and large R .

For $\text{Li}^*(2^2\text{P})$ the $\gamma(\text{Li})$ curves calculated in the present work are found to agree qualitatively with the experimental data whereas for $\text{He}^*(2^1\text{P})$ there is almost no agreement. There are at present no clear indications to advocate that this disagreement is attributable to the neglect of the $(2p\pi^2)\ ^1\Delta$, $\ ^1\Sigma$ initial channels or to effects of the electron translation factors that we have disregarded so far.

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