SHARING PROCESSES IN Li^+ + He COLLISION

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ABSTRACT

The aim of this work is to study theoretically the dominant mechanism in the population distribution between n=2 of Li and He levels. To be able to account for the experimental findups, 'ab-initio' calculations have been performed. These calculations take into account both the rotational and radial couplings.

INTRODUCTION

The collisional system Li^+-He has been studied since 1972, from the experimental (ref.1) and theoretical (ref.2) points of view. The main reason is that such a system provides a typical example of K-K closed shells interations. There has been several reports on electronic excitations of $He^*(1s\ nl)$ and on charge transfer processes $Li^*(1s^2nl)$ with or without electronic excitation of He^+.

Active electrons in the collisional process are those from He since the electron from Li^+ are more strongly bound and no significant Li^+ excitation is observed in the low-medium energy range (1-50 kev).

Preceeding work (ref.2) has shown that the main excitation mechanism is the rotational coupling between the $2p\sigma$ and $2p\pi$ orbitals at short internuclear distances ($R < 1a_0$), then when the lowest π orbital is populated, there is a sharing process at larger distances which populates all the outgoing channels. Recent experimental measurements (ref.1) on coherence and polarization of light emitted by Li ($1s^22p\ ^2P$) and He ($1s2p\ ^1P$) states, show surprisingly different evolution with energy for the angular charge distribution shape in the two atoms. The purpose of this work is to perform the theoretical study of the population sharing between the n=2 levels of the He (direct excitation) and Li (excitation with charge transfer) atoms:

$$
\begin{aligned}
Li^+ + He \quad &\rightarrow Li^* \ (^2P) + He^+(^2S) \\
&\rightarrow Li^+ \ (^1S) + He^*(^1P, \ ^1S) \\
&\rightarrow Li^* \ (^2P) + He^{+*}(^2S, ^2P) \\
&\rightarrow Li^+ \ (^1S) + He^{**}(^1S, ^1P, ^1D)
\end{aligned}
$$

THEORETICAL METHOD

Due to the small energy difference between the n=2 energy levels in this system, the population sharing processes are expected to occur at large internuclear distances. For this reason we do the hypothesis that this long range process can be treated independently from the primary (short range) excitation transition.

Looking at the qualitative diabatic molecular orbitals (MO) diagram (see Fig. 1), one can choose the mono and diexcited states that would play a role in the collisional process. In a first step we have studied the states which correspond to mono-excitation from the ground state since there is strong experimental evidence that (ref.3) double excitation processes are only important in the high energy range. For these large internuclear distances the states are described as single configuration wave functions built from frozen atomic orbitals (using the Projected Valence Bond method (ref.4)).

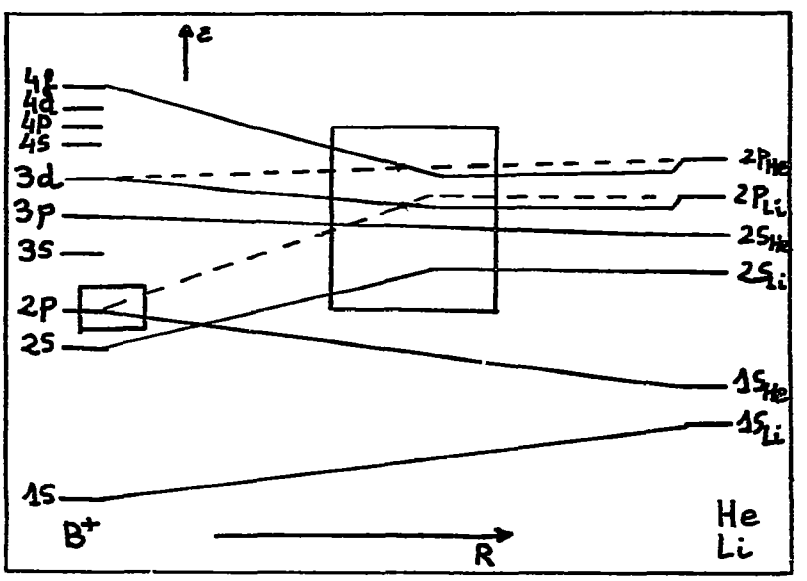

Fig. 1. Schematic MO correlation diagram for the Li^+- He system.

We used an "ad hoc" C.G.T.O. basis set (Table 1) to achieve a balanced description of ground state energy and virtual orbitals.

The frozen atomic orbitals are orthogonalized by the Schimdt method in the following order = $1s_{Li}$, $1s_{He}$, $2s_{Li}$, $2s_{He}$, $2p_{Li}$, $2p_{He}$, $3s_{Li}$, $3s_{He}$, $3p_{Li}$, $3p_{He}$.

TABLE 1

The C.G.T.O. basis set: (6s 3p) for Li, (8s4p) for He.

	Li (6s) (3p)		He (8s) (4p)	
	α_i	C_i	α_i	C_i
S	921.3	.001367	272.64	.006735
	138.7	.010425	40.986	.051155
	31.94	.049859	9.38592	.245311
	9.353	.160701	2.69358	.776024
	3.158	.344604	.89864	1.0
	1.157	.425197		
	.5	1.0	.5	1.0
	.1	1.0	.3	1.0
	.05	1.0	.1	1.0
	.01	1.0	.05	1.0
			.03	1.0
			.01	1.0
P	1.488	.038770	1.0	1.0
	.2667	.236257		
	.07201	.830448	.2	1.0
	.02370	1.0	.05	1.0
	.01	1.0	.01	1.0

The excited atomic orbitals are obtained by a technical procedure optimizing the virtual orbitals (ref.5). The following single configurations,mono-excited molecular states have been used:

1 $^1\Sigma^+$ $(\sigma 1s_{Li})^2$ $\sigma 1s_{He}^2$

2 $^1\Sigma^+$ ------ $\sigma 1s_{He}$ $\sigma 2s_{Li}$

3 $^1\Sigma^+$------- ----- $\sigma 2s_{He}$

4	$^1\Sigma^+$	------	-----	$\sigma 2p_{Li}$
5	$^1\Sigma^+$	------	-----	$\sigma 2p_{He}$
6	$^1\Pi$	------	-----	$\pi 2p_{Li}$
7	$^1\Pi$	------	-----	$\pi 2p_{He}$

Fig. 2 shows the results obtained for energies and off diagonal matrix element of the electronic Hamiltonian H_{el}.

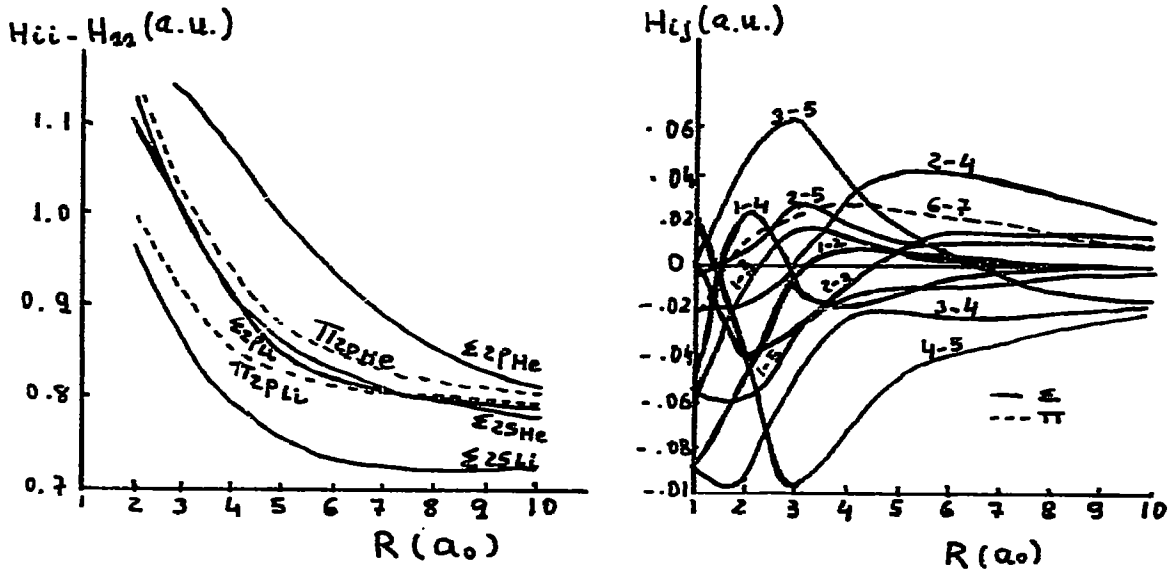

Fig. 2. Potential energies and H_{ij} off-diagonal matrix elements from FAO calculations.

Since the above methods not yield fully diabatic states in the Smith sense (ref.6) the radial coupling <d/dR> have been evaluated, by using a Taylor series expansion (ref.7) with respect to the internuclear distance. The rotational couplings between $^1\Sigma$ and $^1\Pi$ states have been also calculated. As the dynamical couplings are origin dependent (due to the "electronic transfer factor", ETF, which are not taken into account here) and can affect the collisional results (ref.8), four kinds of calculation have been performed with different coordinate origin (see Fig. 3).

For the scattering problem we consider the 7 states (5Σ states and 2Π states) presented above. The corresponding first order coupled differential equations of the impact parameter method are solved for various impact parameters and energies ($0.5\ a_o < \rho \leq 1.2\ a_o$, $1\ \text{kev} \leq E_{lab} \leq 25\ \text{kev}$).

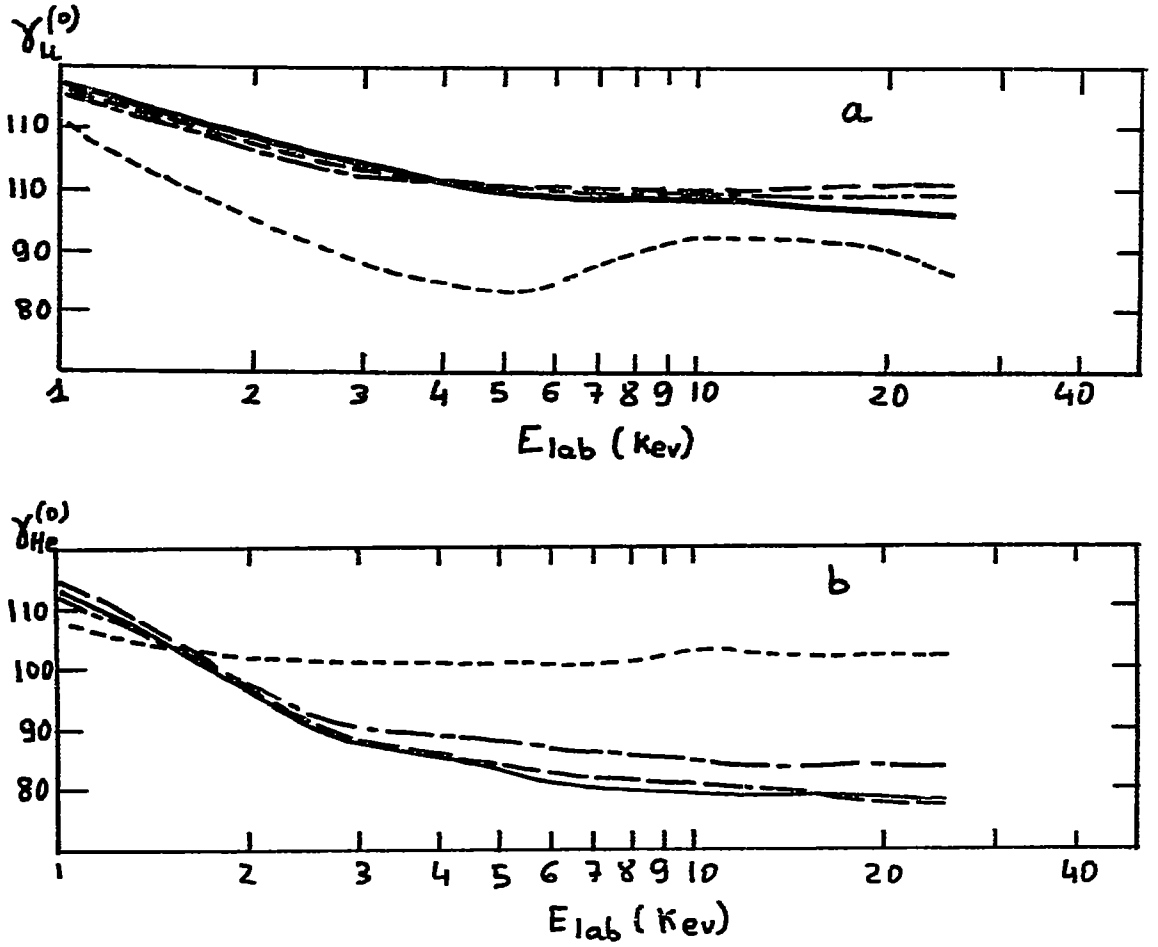

Fig. 3. The sensitivity of the parameter γ to the coordinate origin versus the collision energy E_{lab}, for the impact parameter b = 0.55 a_o (a) results for γ_{Li}: origin at, —— CM, --- Li center, ... He center, -.-.-. mixed calculation where the origin is Li if the dynamical coupling are between Li orbitals, He if they are between He orbitals and CM if they are between Li and He orbitals. (b) results for γ_{He} with the same convention.

As shown above, the population sharing is expected to occur at large distances and the population of the 2pΠ state is known(ref.2) to be finished at $R = 2a_o$. In this case, it is a good approximation to solve the coupled equations for a half collision by giving the initial conditions (obtained from the primary mechanism) on the sphere $R = 2a_o$. The transition probabilities for the different levels n=2 and the polarization are calculated for the energy range above mentionned. We present on Fig. 4 the comparison between the

preliminary theoretical and experimental values of the parameters γ defined as: $\tan 2\gamma = P2/P1$, where :

$$P_1 = 2\lambda - 1, \qquad P_2 = -2(\lambda(1-\lambda))^{1/2}\cos\chi, \qquad \lambda = a_\Sigma^2/(a_\Sigma^2 + a_\Pi^2),$$

a_Σ and a_Π being the respective amplitude for the Li (2^2P) and He (2^1P) levels, and $\chi = \arg(a_\Pi/a_\Sigma)$.

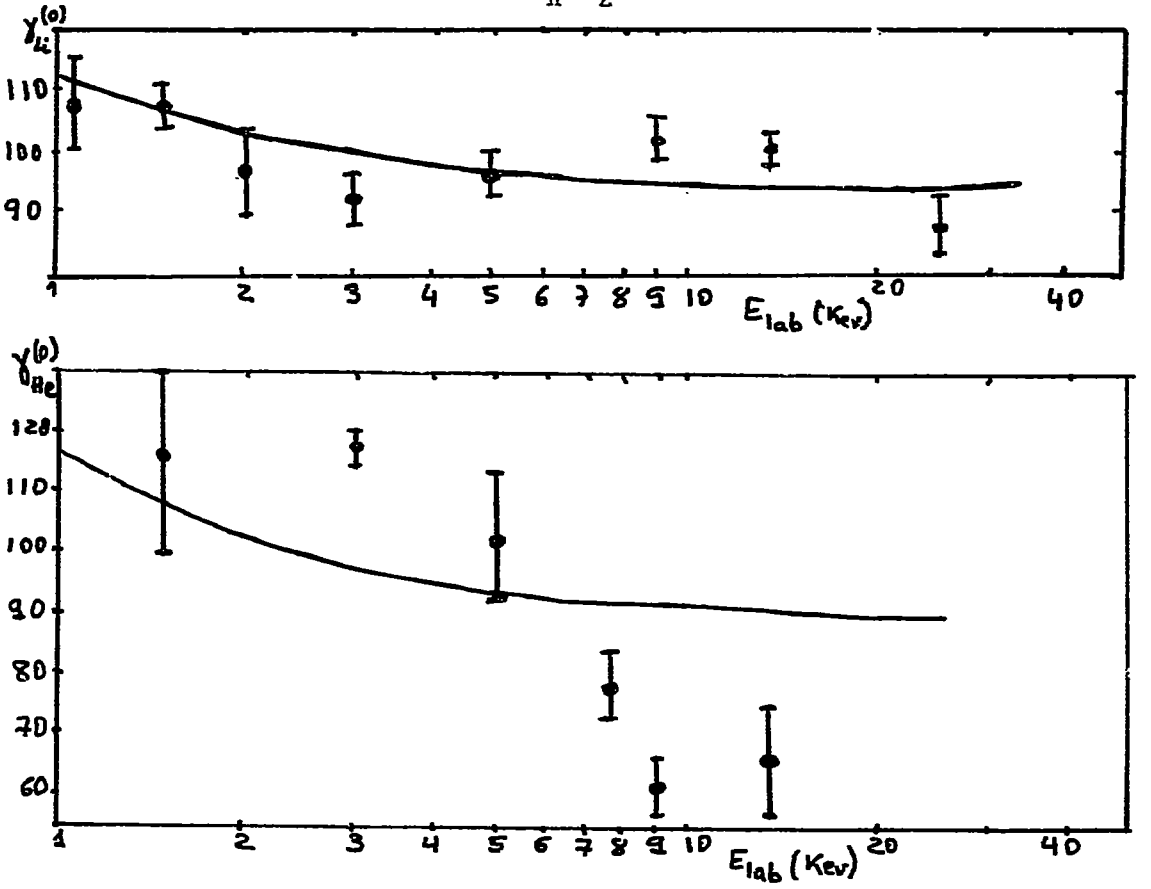

Fig. 4. Comparison of the theoretical γ_{Li}, γ_{He} (mixed calculation) at $b = 0.5\ a_o$ with the experimental value.

REFERENCES

1 T. Andersen and H.P.Neitzke, XIII ICPEAC, Invited Papers, Berlin 1983.
2 V. Sidis, N. Stolterfoht and M. Barat, J. Phys. B 14 (1977) 2815
3 N. Andersen, 1984 private communication.
4 V. Sidis, C. Kubach and J. Pommier, Phys. Rev. A, 23 (1981) 119.
5 C. Courbin-Gaussorgus, V. Sidis and J. Vaaben, J. Phys. B, 16 (1983) 2817.
6 F.T. Smith, Phys. Rev. 179 (1969) 111.
7 O. Halkajaer and J. Linderberg, Int. J. Quantum Chem. Sym., 10 (1979) 475-84.
8 J. Vaaben and K. Taulbjerg, J. Phys. B 14 (1981) 1815.