

Electron capture and excitation in alkali ion-atom collisions using an atomic eigenfunction expansion^{*,†}

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Previous calculations of (Li^+, Li) scattering utilizing an expansion in traveling atomic orbitals have been extended to the collisions (Na^+, Na) , (Li^+, Na) , and (Na^+, Li) . While the over-all trends of the experimental energy dependences of the cross sections are reproduced by the theory, the detailed structure in the data is very poorly represented by our calculations. Since this structure is due to collisions at small impact parameter (less than $\sim 5 a_0$) it appears that a variational technique is required to allow the atomic orbitals to contract at small separations. Unless this is done, the atomic expansion method fails badly at small impact parameter. We believe the calculations are reasonable at large impact parameters, however.

I. INTRODUCTION

The study of excitation and electron capture processes in ion-atom collisions has been carried out using two main approaches.¹ Within the framework of a constant velocity, straight line path impact parameter method, the total wavefunction can be expanded in terms of either atomic or molecular orbitals. The original calculations generally were limited in either case to two states, and did not adequately account for the change in electron momentum when the electron jumped to the other nucleus. In 1958, Bates and McCarroll² published a landmark paper in which they showed that the past calculations suffered from a basic imperfection in that the expansion functions were not solutions of the asymptotic Schrödinger equation. They showed that by introducing so-called traveling wave terms into the expansion functions, the asymptotic Schrödinger equation would be satisfied. Riley and Green³ (and references therein) discuss various approaches for using traveling wave terms in the molecular expansion method. In both the atomic and molecular methods, it is conceptually necessary to use the traveling wave terms at all velocities. However, from a computational point of view, certain integrals which appear in both methods can be replaced by simpler integrals with the traveling wave terms omitted, provided the velocity is low enough.

Following the work of Bates and McCarroll,² McCarroll⁴ demonstrated the quantitative effect of the traveling wave terms on the two-state atomic treatment of (H^+, H) collisions. More comprehensive atomic calculations were performed on (H^+, H) by Lovell and McElroy,⁵ Wilets and Gallagher⁶ and other workers.^{7,8} Other systems such as $(\text{He}^{++}, \text{H})$ and (Li^+, Li) have also recently^{9,10} been studied. It appears from this work that the atomic-type calculation is fairly rapidly conver-

gent, but suffers at small separations from an inadequate representation of the transient molecular ion during the middle of the collision. Attempts to deal with smaller separations by using Sturmian atomic functions¹¹ and pseudostates⁷ have been somewhat artificial. Perhaps the best hope for representing close-in collisions in the atomic method lies in the proposal of Cheshire¹² for variationally adjusting the parameters in the atomic wavefunctions so as to better represent the configurations at small internuclear separations. We have recently extended this procedure.¹³ In general, the method of atomic orbitals appears to be a reasonable approach which works best for large impact parameters, but which can lead to considerable error¹⁰ at distances where molecular bonding is strong, unless sufficient flexibility is provided in the wavefunction to account for bonding effects.

Most applications of the molecular expansion have been made in the two-state approximation, with traveling wave terms omitted. Approximate treatments of (H^+, H) using multistate traveling wave molecular expansions are incomplete.^{14,15,16} A number of investigators have recently applied the molecular expansion method with traveling waves omitted for treating alkali-ion-alkali-atom collisions. Part of the inspiration for doing this was the variety of structure found in experimental cross sections^{17,18} versus energy. Two-state molecular calculations were done for the collisions (Li^+, Li) and (Na^+, Na) , without traveling wave terms using the best available potential curves.¹⁹ McMillan²⁰ made a similar treatment of (Li^+, Li) , but also took into account the lowest π state as well as the ground σ_u and σ_g states, although it is difficult to understand how he did this. Bottcher and Oppenheimer²¹ extended the calculations of Ref. 19 to the asymmetric processes (Li^+, Na) and (Na^+, Li) ,

but with rather crude approximations. Most recently, Melius and Goddard²² have done two-state calculations on (Li^+, Li) and (Na^+, Na) and multi-state calculations on the asymmetric processes (Li^+, Na) and (Na^+, Li) . They find good agreement in the oscillatory structure with experiment for the asymmetric processes.

Despite all these calculations, there remain fundamental unanswered questions. The relation between atomic and molecular calculations remains unclear. The effect of traveling wave terms on molecular calculations is bound to be important at higher velocities, but is difficult to evaluate explicitly.

In the present work, we shall give the results of calculations for the collisions (Na^+, Na) , (Na^+, Li) , and (Li^+, Na) using the atomic method with traveling wave terms included. This is essentially a simple extension of previous work¹⁰ on (Li^+, Li) . Upon comparison with molecular calculations²² on the asymmetric processes and experimental data,¹⁷ it appears that the atomic method is not adequately describing the system for internuclear separations less than $\sim 6a_0$, although it is probably giving a reasonable description at larger distances. Since it is easier to apply the traveling wave terms in the atomic method, we believe this procedure is still a useful approach, but more adequate treatment^{12,13} of the effect of molecular bonding on the atomic orbitals while in close is called for in future calculations.

II. CALCULATIONAL METHOD

In a previous paper¹⁰ we used the method of expansion in atomic orbitals to calculate cross sections for excitation and electron capture in (Li^+, Li) collisions. The atomic orbitals were chosen as one-electron functions which are essentially exact solutions of a Schrödinger equation with a model pseudopotential.²³ Calculations were performed with one, three, four, or six states on each moving center. For purposes of calculating the total exchange cross section, it was found that inclusion of the $2p$ states was very important, as these are strongly coupled to the $2s$ states and have only a 1.9 eV energy gap. This is in contrast to (H^+, H) collisions,⁸ where the 10.2 eV gap between $n=1$ and $n=2$ states results in the excited states playing a relatively minor role in determining the total capture cross section. It was found that the oscillatory structure obtained in the calculated total capture cross section versus energy for (Li^+, Li) collisions with only the $2s$ state included on each center was strongly damped out when excited states were added to the expansion. Although the general magnitude and over-all energy dependence was in good agreement with experiment,¹⁷ the detailed

structure predicted by our theory was in poor agreement with experiment and with other calculations. It appears that the atomic method, in this case, leads to good probabilities at large impact parameters, but not at the small impact parameters which determine the structure in the total exchange cross section versus energy curve.

In the present work, we report the results of extension of our previous calculations for (Li^+, Li) collisions to (Na^+, Na) , (Li^+, Na) , and (Na^+, Li) collisions. The sodium wavefunctions were taken from Ref. 23(b). The calculational procedures used here are essentially the same as those used in Ref. 10, except that for asymmetric collisions, we could not use expansion functions with definite parity. On the basis of our past experience with (Li^+, Li) collisions,¹⁰ it was decided that the calculation would be reasonably converged if we included only three states on each moving center.

III. RESULTS

When only one state ($2s$ on Li or $3s$ on Na) is included on each moving center, the calculated cross sections for electron capture are as given in Table I. In this "one-state" approximation, the exchange cross sections are the same for (Li^+, Na) and (Na^+, Li) collisions. When the $2p$ states are added on Li and the $3p$ states on Na, the cross sections calculated for direct and exchange transitions are given in Tables II-IV. All calculated cross sections suffer from some lack of precision due to the use of a finite number (about 40) of impact parameters at each energy. The ground state exchange processes have probabilities which oscillate rapidly with impact parameter at low ion velocities, and the resultant cross sections obtained by integration may be in error by about $\pm 0.2 \text{ \AA}^2$. For direct and exchange excitation of the p states, we estimate our cross sections represent the integration of $P(b)2\pi b db$ to about $\pm 0.1 \text{ \AA}^2$. Clearly, at low velocities where our calculated cross sections are small, they are calculationally quite inaccurate. The cross sections for total exchange are given in Figs. 1-3, where we compare the calculated cross sections with one state on each center, and with three states on each center, with the experimental data. Aside from disagreement in the oscillatory structure, the general magnitudes and over-all trends of variation of calculated cross sections with energy is in conformity with experiment. The oscillations predicted in the theoretical curves are not in agreement with those found theoretically. The general shapes of these cross section curves, except for detailed structure, is in rough conformity with the simple theory of Rapp and Francis.²⁴ The symmetrical processes have cross sections which rise as the ion velocity is

TABLE I. Calculated cross sections (10^{-16} cm 2) for electron capture with one wavefunction on each moving center. E_{Li} is the energy a Li atom would have in 10^3 electron volts at velocity v .

v (10^7 cm/sec)	Na $^+$, Na	Li $^+$, Na	Li $^+$, Li	E_{Li}
1.393	101.6	44.6	93.9	0.7
1.489	106.1	50.8	94.2	0.8
1.579	105.2	54.4	97.4	0.9
1.665	100.2	53.5	98.2	1.0
1.824	90.5	59.7	91.4	1.2
1.970	88.8	65.1	83.7	1.4
2.106	91.0	62.7	81.5	1.6
2.234	94.0	61.0	82.8	1.8
2.355	94.7	62.8	85.1	2.0
2.632	89.3	67.6	86.4	2.5
2.884	80.5	63.4	80.6	3.0
3.330	68.8	61.7	67.2	4.0
3.723	68.0	67.9	61.5	5.0
4.078	71.2	67.9	61.6	6.0
4.995	74.0	52.8	66.8	9.0
5.767	67.6	49.1	65.7	12.0
6.448	58.8	51.1	60.1	15.0
7.446	55.3	51.8	48.6	20.0
9.119	26.8	41.7	30.3	30.0
10.530		29.9	19.2	40.0
12.897	7.1	14.9	8.6	60.0
14.892	3.4	7.8		80.0
16.649	1.8	4.3	2.3	100.0
23.546	0.13	0.32		200.0
28.838	0.02	0.03	0.02	300.0
33.299	0.003			400.0

reduced, and the asymmetrical processes have maximum cross sections at a velocity near 2×10^7 cm/sec which is characteristic of the difference in ionization potentials of Li and Na of ~ 0.25 eV.

In the symmetrical collisions [(Li $^+$, Li) and (Na $^+$, Na)] the effect of adding the p states in our atomic calculations is to increase the calculated cross sections and to damp out the oscillations. In the case of asymmetric collisions [(Li $^+$, Na) and (Na $^+$,

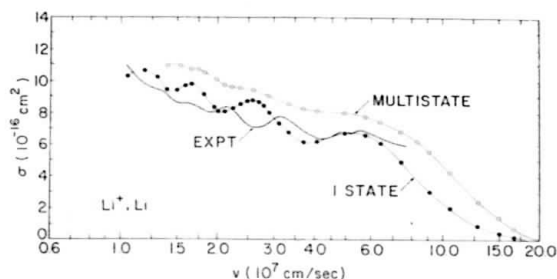


FIG. 1. Cross section for total electron capture into all states on the incident ion in (Li $^+$, Li) collisions. The curve marked multistate refers to the calculation with three states on each center, and the experimental data are from Ref. 17.

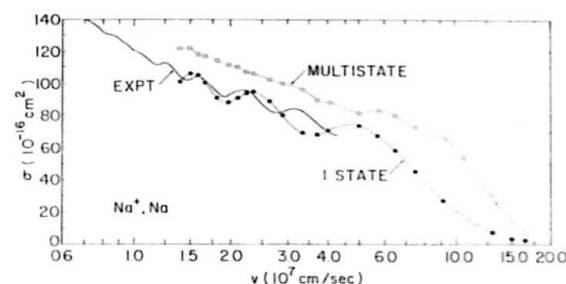


FIG. 2. Cross section for total electron capture into all states on the incident ion in (Na $^+$, Na) collisions. The curve marked "multistate" refers to the calculation with three states on each center, and the experimental data are from Ref. 17.

Li)] the effect of the p states is to increase the amplitude and wavelength of the oscillations. In all cases, the general shapes and magnitudes of the exchange cross sections are in agreement with experiment,¹² but the oscillatory structure disagrees substantially with experiment. Since the oscillatory structure depends primarily on impact parameters from about $0-5a_0$, and the over-all magnitude of the cross section depends primarily on impact parameters greater than $5a_0$, it appears that this calculation which uses an expansion in atomic orbitals, cannot adequately account for collisions at small impact parameter.

The cross sections for direct excitation of the target to the lowest p states are given in Fig. 4. It can be seen that at high velocities, all the systems behave in a similar way. At low velocities, the cross sections differ somewhat. Plots of the cross sections for electron capture into the lowest p states are given in Fig. 5. There is a considerable divergence between the velocity dependences of the various processes. We believe that the behavior of the p -state cross sections reflects two different processes which will be discussed in detail in the next section. At high velocities, jumping between potential curves is of importance, whereas, in those cases where the cross sections approach relatively constant values at low velocities, the mechanism is probably due to a crossing of potential curves of σ and π states. A limited amount of data is available at low ion velocities for comparison.²⁵ In the range 1×10^7 cm/sec $\leq v \leq 2 \times 10^7$ cm/sec, it is found experimentally that the cross section for direct excitation of Na by Na $^+$ impact is $\sim 7 \text{ \AA}^2$, and by Li $^+$ impact is $\sim 1.5 \text{ \AA}^2$. While these values are somewhat higher than we obtain, our calculations do predict that Na $^+$ impact will be much more effective than Li $^+$ impact. The experimental results for electron capture into the $2p$ state by Li $^+$ impact on Na lie around 0.08 \AA^2 , which is considerably smaller than that predicted

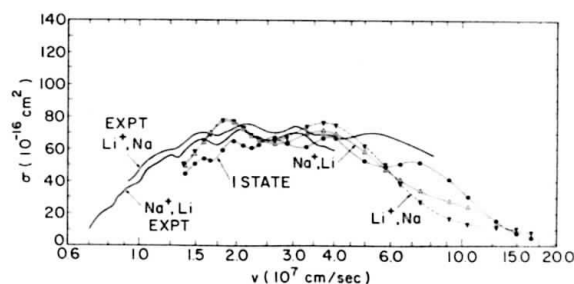


FIG. 3. Cross sections for total electron capture into all states on the incident ion in (Li^+, Na) and (Na^+, Li) collisions. The curves marked Li^+, Na and Na^+, Li refer to calculations with three states on each center, and the data are from Ref. 17.

by theory. The experimental result is hard to believe²² because the potential curve asymptotic to $\text{Li}(2p)$ lies lower than that asymptotic to $\text{Na}(3p)$, and one must expect that capture into p states will be at least as important as direct excitation in (Li^+, Na) collisions. It is interesting that the molecular calculations⁸ lead to cross sections forming p states at low velocities which are essentially ten times greater than we predict.

IV. DISCUSSION

It is not obvious whether the concept of potential curves has great significance in a multistate cal-

TABLE II. Calculated cross sections (10^{-16} cm^2) for producing various final states in Na^+ , Na collisions with three states included on each moving center. E_{Li} is the energy a Li atom would have at velocity v .

v (10^7 cm/sec)	Direct			Exchange			Total	E_{Li}
	$3p_0$	$3p_1$	$3s$	$3p_0$	$3p_1$	$3s$		
1.393	1.4	1.0	120.0	1.3	1.1	122.4	0.7	
1.489	1.4	1.1	119.5	1.4	1.1	121.5	0.8	
1.579	1.3	1.1	115.8	1.2	1.1	118.1	0.9	
1.665	1.6	1.1	114.6	1.5	1.2	117.4	1.0	
1.824	1.4	1.4	112.0	1.4	1.2	114.7	1.2	
1.970	1.3	1.3	109.1	1.2	1.4	111.7	1.4	
2.106	1.4	1.3	107.4	1.4	1.5	110.3	1.6	
2.234	1.2	1.4	103.9	1.3	1.5	106.7	1.8	
2.355	1.3	1.6	103.6	1.2	1.6	106.4	2.0	
2.632	1.1	1.9	99.7	1.2	1.6	102.6	2.5	
2.884	1.5	2.0	97.0	1.2	2.0	100.2	3.0	
3.330	1.9	1.9	92.2	1.7	2.6	96.5	4.0	
3.723	2.5	2.3	84.6*	2.1	2.5	89.3	5.0	
4.078	2.5	3.0	84.4	1.8	2.4	88.7	6.0	
4.995	1.9	4.2	74.4	3.9	3.4	81.5	9.0	
5.767	2.5	4.1	72.7	5.0	5.7	83.3	12.0	
6.448	3.4	4.2	66.6	6.1	7.6	80.3	15.0	
7.446	7.2	4.5	57.3	7.4	8.2	72.9	20.0	
9.119	9.7	8.0	48.3	11.0	7.1	66.5	30.0	
10.530	11.6	14.6	36.1	12.8	5.3	54.2	40.0	
12.897	20.0	26.7	18.0	9.7	2.3	30.1	60.0	
14.892	26.7	33.3	7.3	5.7	1.1	14.1	80.0	
16.649	27.7	36.3	3.2	3.3	0.60	7.1	100.0	
23.546	21.1	34.4	0.18	0.3	0.04	0.54	200.0	
28.838	15.4	29.0	0.024	0.04	0.008	0.08	300.0	
33.299	12.5	25.2	0.006	0.008	0.002	0.02	400.0	

TABLE III. Calculated cross sections (10^{-16} cm^2) for producing final states in Na^+ , Li collisions with three states on each center. E_{Li} is the energy a Li atom would have at velocity v .

v (10^7 cm/sec)	Direct			Exchange			Total	E_{Li}
	$2p_0$	$2p_1$	$3s$	$3p_0$	$3p_1$	$3s$		
1.393	0.2	0.1	49.4	0.03	0.02	49.5	0.7	
1.489	0.2	0.2	57.0	0.03	0.02	57.0	0.8	
1.579	0.2	0.2	64.4	0.04	0.02	64.4	0.9	
1.665	0.2	0.2	70.4	0.06	0.01	70.5	1.0	
1.824	0.3	0.3	77.0	0.06	0.01	77.1	1.2	
1.970	0.4	0.3	76.4	0.05	0.02	77.1	1.4	
2.106	0.5	0.3	72.2	0.09	0.03	72.3	1.6	
2.234	0.7	0.4	68.5	0.1	0.05	68.6	1.8	
2.355	0.6	0.3	65.2	0.1	0.09	65.4	2.0	
2.632	0.6	0.3	62.7	0.1	0.1	62.9	2.5	
2.884	1.2	0.5	64.5	0.1	0.1	64.7	3.0	
3.330	2.3	1.0	69.2	0.63	0.1	69.9	4.0	
3.723	2.8	1.7	70.4	1.0	0.3	71.7	5.0	
4.078	3.2	2.6	68.4	1.1	0.47	70.0	6.0	
4.995	6.8	6.7	54.6	2.9	0.95	58.5	9.0	
5.767	11.2	10.9	40.5	5.3	1.9	47.6	12.0	
6.448	15.3	14.5	29.7	7.7	2.8	40.1	15.0	
7.446	20.1	19.0	19.0	10.4	4.8	34.2	20.0	
9.119	26.2	24.9	10.4	10.6	6.8	27.7	30.0	
10.530	27.8	27.4	7.0	10.1	7.3	24.4	40.0	
12.897	28.2	33.8	5.3	5.2	4.5	15.0	60.0	
14.892	27.3	38.5	4.1	2.8	2.0	9.0	80.0	
16.649	25.7	40.3	3.0	1.5	0.96	5.4	100.0	
23.546	18.1	35.5	0.36	0.09	0.032	0.48	200.0	
28.838	13.9	29.4	0.06	0.018	0.005	0.09	300.0	
33.299	11.2	25.0	0.02	0.007	0.003	0.03	400.0	

culation employing an expansion in traveling wave atomic orbitals. Nevertheless, it is interesting to examine our results to see if an interpretation in terms of potential curves is plausible. We would like to hypothesize that at low velocities, the results of an atomic calculation do contain patterns which can be interpreted as implying specific potential curves. It is then of interest to compare these effective potential curves with those used in molecular calculations,²² and to examine where divergences from experiment originate.

It was demonstrated some time ago¹⁸ that in the molecular treatment of symmetric resonant charge exchange with only two states included, the behavior of the energy difference $\Delta E = (E_u - E_g)/2$ vs R determines the shape of the cross section for exchange versus ion velocity. Here, E_u and E_g are the molecular electronic energies of the ungerade and gerade states, and R is the internuclear distance. Since the probability of exchange in any encounter is $\sin^2\{\Delta E dt\}$, it follows that if ΔE monotonically increases as R is reduced, the cross section will increase monotonically as the ion velocity is reduced. On the other hand, if $\Delta E(R)$ passes through a maximum, oscillations are to be expected in σ as v is varied, even though the overall secular trend is such that σ will increase as v is reduced. If the ungerade and gerade curves actually cross at a moderate internuclear separa-

TABLE IV. Calculated cross sections (10^{-16} cm²) for producing final states in Li⁺, Na collisions with three states on each center. E_{Li} is the energy a Li atom would have at velocity v .

v (10^7 cm/sec)	Direct			Exchange			Total	E_{Li}
	$3p_0$	$3p_1$	$2s$	$2p_0$	$2p_1$			
1.393	0.2	0.05	50.5	0.1	0.3		50.9	0.7
1.489	0.2	0.05	57.4	0.1	0.3		57.8	0.8
1.579	0.2	0.03	64.6	0.2	0.3		64.9	0.9
1.665	0.2	0.01	69.1	0.2	0.3		69.6	1.0
1.824	0.2	0.02	77.7	0.3	0.3		78.3	1.2
1.970	0.2	0.03	76.4	0.4	0.4		77.2	1.4
2.106	0.2	0.07	72.2	0.7	0.4		73.3	1.6
2.234	0.3	0.1	68.4	0.9	0.4		69.7	1.8
2.355	0.4	0.2	65.2	1.3	0.5		67.0	2.0
2.632	0.4	0.3	62.6	2.0	0.8		65.4	2.5
2.884	0.4	0.4	64.6	2.3	1.1		68.0	3.0
3.330	1.1	0.4	68.9	3.5	1.8		74.2	4.0
3.723	1.6	0.3	70.6	3.6	2.4		76.6	5.0
4.078	1.7	0.37	68.6	3.9	2.8		75.3	6.0
4.995	3.6	0.75	54.7	4.6	4.0		63.3	9.0
5.767	5.8	1.5	40.5	5.2	4.8		50.4	12.0
6.448	8.3	2.8	29.7	4.6	5.3		39.6	15.0
7.446	11.9	5.2	19.0	3.6	5.2		27.8	20.0
9.119	16.0	11.7	10.2	2.6	4.9		17.7	30.0
10.530	19.8	18.5	7.0	2.9	3.9		13.8	40.0
12.897	25.5	31.8	5.2	3.9	2.5		11.6	60.0
14.892	28.0	38.0	4.1	4.3	1.9		10.0	80.0
16.649	28.0	38.4	3.0	4.5	1.2		8.6	100.0
23.546	19.9	31.9	0.36	1.3	0.10		1.8	200.0
28.838	14.5	26.3	0.06	0.29	0.02		0.35	300.0

tion it is to be expected that the oscillations in the $\sigma(v)$ curve will be of larger amplitude and low frequency.

An examination of our calculated results in Figs. 1 and 2 with one state on each center leads to the conclusion that the effective $\Delta E(R)$ for these calculations passes through a maximum in these symmetrical cases. Closer examination of the probability versus impact parameter curves [$P(b)$] leads to the conclusion that the maximum is

reached at an internuclear separation of about $\sim 4a_0$. When the p states are included on each center, it appears that the σ -molecular states become polarized, and the resulting effective molecular curves pull apart incorrectly, reducing (or eliminating) the maximum in $\Delta E(R)$. This essentially removes the oscillatory structure in our calculated $\sigma(v)$ curve and gives poor agreement with experiment. Further evidence of this interpretation is afforded by examining the plots of bP vs b for direct excitation of the $2p$ state given in Fig. 4. At low velocity, the bP curves have a rapidly oscillating structure with a sharp cutoff near $\sim 6a_0$. We interpret this process, which leads to a cross section at low velocity that varies slowly as due to a curve crossing of a $2p\pi$ state with the $2s\sigma_u$ state at $\sim 6a_0$. The process which comes in at larger impact parameters at higher velocities is interpreted as curve jumping between the $2s\sigma_u$ and a $2p\pi$ state, which can take place over a wide range of internuclear separations.

It appears that in the case of the asymmetric LiNa⁺ system our results are very different. With only one state on each center, we obtain the oscillating curve shown in Fig. 3. When the p states are added to the expansion, it is found that the oscillations in $\sigma(v)$ increase in amplitude and wavelength, implying that in our calculation the Li($2s\sigma$) curve incorrectly crosses the Na($3s\sigma$) potential curve at moderate R . Further evidence for this is provided in Fig. 6 in which we show the bP vs b curve for electron capture by Li⁺ into the $2s$ state in collision with Na. It can be seen that for $b > 4.5a_0$, the curve is a "normal" oscillatory bP vs b curve, but for $b < 4.5a_0$, there is considerable structure which we interpret as due to a crossing of the Li($2s\sigma$) curve with the Na($3s\sigma$) curve. We believe that the effective Na($3s\sigma$) curve in our calculation incorrectly lies lower

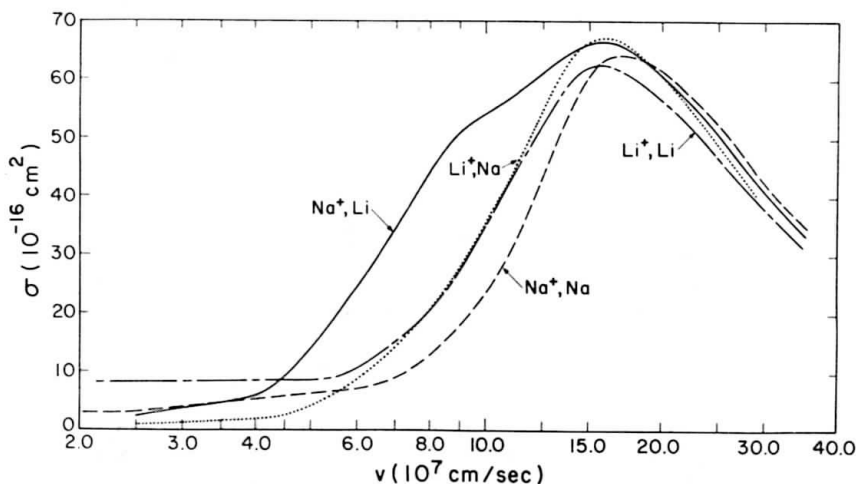


FIG. 4. Calculated cross sections for direct excitation of p states in alkali ion-atom collisions versus ion velocity. Calculations were done with $2s$ and $2p$ states on Li and $3s$ and $3p$ states of Na. Cross sections are for excitation of $2p$ states of Li targets and $3p$ states of Na targets.

than the relatively accurate curves given by Melius and Goddard.²² Thus, we do not get a crossing of the $\text{Na}(3s\sigma)$ curve with the $\text{Li}(2p\pi)$ curve, and our cross sections for p state excitation in asymmetric collisions do not display the relatively large, velocity independent behavior that characterizes the crossing in symmetric processes.

Melius and Goddard²² discuss the asymmetric collisions (Li^+, Na) and (Na^+, Li) in some detail from the molecular point of view with the traveling wave terms omitted from their wave functions. They find excellent agreement between theory and experiment for the structure in the $\sigma(v)$ curve for total capture. They invoke a crossing between their $\text{Li}(2p\pi)$ and $\text{Na}(3s\sigma)$ potential curves to explain the difference between (Li^+, Na) and (Na^+, Li) exchange cross sections. It is surprising to us that their theory²² works as well as it does. From the agreement between the molecular theory²² and experiment,¹⁷ it appears that Melius and Goddard are providing a good description of the potential curves and molecular electronic wavefunctions even for R down to $\sim 2a_0$. One disturbing thing is that we find it very difficult to estimate how accurate the potential curves of Melius and Goddard²² are. They do miss the energy difference at ∞ by ~ 0.1 eV, which is larger than our error in the $\text{Li}-\text{Na}$ atomic energy levels. As a corollary, we would have to conclude that the expansion in one-electron atomic states is giving an incorrect description for $R \gtrsim 6a_0$. We do believe that our description of the alkali molecular ions in terms of atomic states should work well at large R , and therefore we are calculating the correct over-all magnitude of the exchange cross sections, even though we cannot predict the structure in $\sigma(v)$. For p state excitation at high velocities, where the main contribution to the cross sections is from potential curve jumping at large R , we believe our calculations should be fairly good.

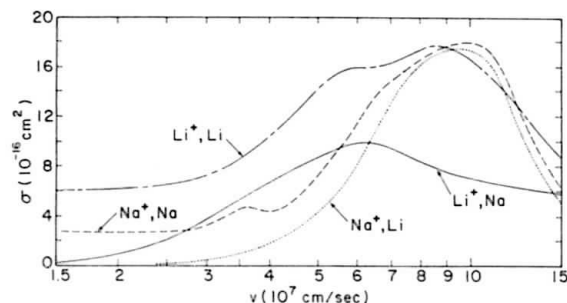


FIG. 5. Calculated cross sections for electron capture into p states on the incident ion in alkali ion-atom collisions versus ion velocity. Cross sections are for capture into $2p$ states in Li^+ collisions and $3p$ states in Na^+ collisions.

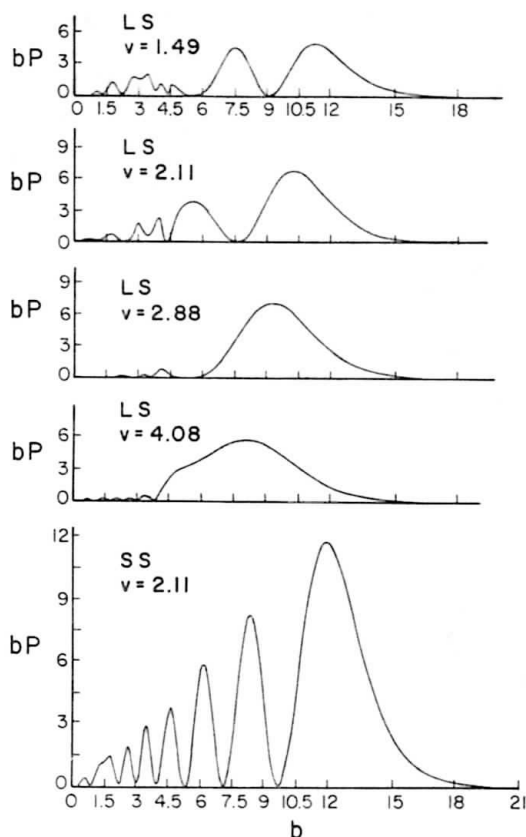


FIG. 6. Impact parameter \times probability versus impact parameter (a. u.) for ground state electron capture. SS refers to (Na^+, Na) and LS to (Li^+, Na) collisions with three states on each center. The velocities are in 10^7 cm/sec.

In order to improve our calculations, it is probably necessary to allow for the effects of molecular bonding on the atomic orbitals when the nuclei are separated by distances less than $\sim 6a_0$. One way to do this would be to use effective nuclear charges for the atomic orbitals, which would allow the orbitals to contract when in the presence of the other nucleus. We are now testing various ways of doing this.¹³

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