

THEORETICAL STUDY OF  $\text{Na}^*(3p)$  CHARGE CLOUD ORIENTATION IN  $\text{Na} + \text{He}$  COLLISIONS.

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SUMMARY

The Projected Valence Bond potential energies of Na-He system calculated by Courbin-Gaussorgues and Sidis are used in an 8-state model to study the direct excitation, deexcitation probabilities and the orientation of the charge cloud of  $\text{Na}^*(3p)$ . The corresponding calculation are carried out using the impact parameter method in the  $0.5 \text{ Kev} < E_{\text{CM}} < 100 \text{ Kev}$  energy range. A comparison with the theoretical prediction of a 3-state model of Andersen and Nielsen is made and discrepancies are discussed.

INTRODUCTION

Atomic collision experiments have progressed recently by the analysis of the polarization of the light emitted by the excited atom in the differential cross section measurements. The analysis of the coherence and correlation of the light gives the alignment angle and orientation parameter of the electronic cloud of the excited atom(ref.1).

A new class of collision experiments in which the entrance - channel is a selectively excited state is at present being undertaken at Kev energies and is the motive for this theoretical investigation.

The prototype system for this study is the case of Na-He. The knowledge of the excitation mechanism is deduced from differential and total cross section measurements(ref.2) and from theoretical calculations(ref.3): the mechanism is well understood as a direct excitation of the valence electron at  $R \approx 3a_0$  with a maximum at Kev energies.

To study deexcitation probabilities of  $\text{Na}^*(3p)$  by He Andersen and Nielsen (ref.4) have used a simple "propensity rule" which - predicts that the reaction probability is very sensitive to the - polarization of the Na initial state near the excitation maximum: for sodium in an initial state  $\text{Na}(3p_{-1})$  the deexcitation probabi-

lity should be large whereas it should be small for initial state  $\text{Na}(3p_1)$ .

As these rules have been deduced from an atomic 3-state calculation using simple model potentials, we propose to revisit these predictions by using an 8-state basis built with the Frozen Atomic Orbitals which have been used to study the direct excitation(ref.3)

#### THE PROJECTED VALENCE BOND (PVB) 8-STATE METHOD

##### Potential and coupling calculations

As the direct excitation mechanism from  $3s_{\text{Na}}$  to  $3p_{\text{Na}}$  occurs at intermediate distances of approach  $2 < R < 6 a_0$  (ref.3) a perturbed atomic basis is thought to be the most adequate way of explaining excitation and deexcitation processes. The frozen atomic orbitals (FAO) are taken to be SCF orbitals at  $R = 20 a_0$  of the  $(\text{NaHe})^+ \Sigma^+$  state. This orbital set gives a correct description of the  $3s_{\text{Na}}$  and  $3p_{\text{Na}}$  orbitals. The FAO are orthonormalised to each other by the Schmidt method in the following order :

$1s_{\text{Na}}, 2s_{\text{Na}}, 1s_{\text{He}}, 3s_{\text{Na}}, 3p_{\text{Na}}, 2s_{\text{He}}, 2p_{\text{He}}, 3d_{\text{Na}}$  for  $\sigma$  orbitals and  $3p_{\text{Na}}, 2p_{\text{He}}, 3d_{\text{Na}}$ , for  $\pi$  orbitals.

Single Configuration State Functions are built from the orthogonalised FAO. These states correspond to

${}^2\Sigma_{3s_{\text{Na}}}, {}^2\Sigma_{3p_{\text{Na}}}, {}^2\Sigma_{3d_{\text{Na}}}$  and  
 ${}^2\Pi_{3p_{\text{Na}}}, {}^2\Pi_{3d_{\text{Na}}}$

as ground and excited Na states and

${}^2\Sigma_{2s_{\text{He}}}, {}^2\Sigma_{2p_{\text{He}}}, {}^2\Pi_{2p_{\text{He}}}$

as charge exchange states.

The set of orbitals must be flexible enough to allow the outer electron to fill a Rydberg orbital. The inclusion of these "pseudostates" of  $\text{He}^-$  permits to avoid the use of a large basis set for Na diffuse orbitals. These  $\text{He}^-$  states are not stable and dissociate to the ionisation channel  $\text{Na}^+ + \text{He} + e$ .

The diabatic energy curves are plotted in Fig.1. The electronic coupling terms  $\langle {}^2\Sigma^+ | \text{He} | {}^2\Sigma^+ \rangle$  and  $\langle {}^2\Pi^+ | \text{He} | {}^2\Pi^+ \rangle$  are taken into account for the eight states. Since the above methods do not yield fully diabatic states in the Smith sense(ref.5) the remaining dynamical couplings  $\langle \phi_{\lambda 1 n \nu} | d/dR | \phi_{\lambda n' 1' \nu'} \rangle$  and  $\langle \phi_{\lambda 1 n \nu} | iL_y | \phi_{(\lambda+1)n' 1' \nu'} \rangle$  are included.

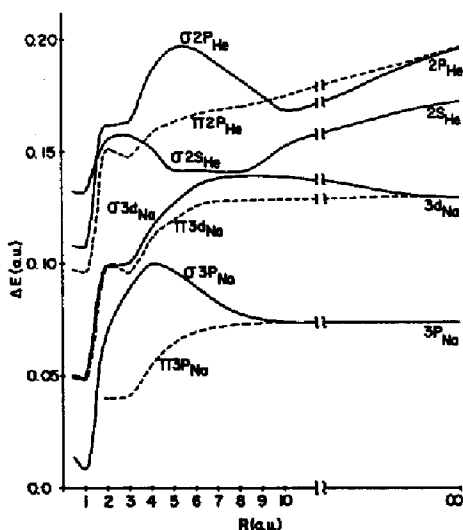


Fig.1. Diabatic potential energy curves of the first monoexcited states of NaHe referred to the  $\Sigma_{3s}$  ground state.

As is well known the dynamical matrix elements depend on the choice of the coordinate center. We avoid this problem as proposed by Taulbjerg and Briggs (ref.6) by choosing  $C=V$  when  $v=v'$  and  $C=$  center of mass when  $v \neq v'$ .

Fig.2 shows those coupling matrix elements which are most important:

- 1)  $\langle \Sigma_{3s} | \text{HeI} | \Sigma_{3p} \rangle$  its maximum stands at  $R \approx 3 a_0$  so the direct transition will take place in this region.
- 2)  $\langle \Sigma_{2s} | \text{HeI} | \Sigma_{3p} \rangle$  has a maximum at about  $3-4 a_0$  in the same region where the energy curves are split by lev only. It is the most important charge exchange process. The dynamical matrix elements  $d/dR$  have to be multiplied by  $v$ , so they are small but not negligible and we included them in our calculations.

#### TRANSITION PROBABILITIES AND ORIENTATION

All dynamical calculations are made by the Impact Parameter Method. The eight coupled first order differential equations are solved for various kinetic energies ( $0.5 < E_{CM} < 100$  Kev) and impact parameters ( $1 a_0 < b < 15 a_0$ ) along the incident direction.

The transformation matrix from molecular to natural frames where the quantization axis is perpendicular to the collision plane is :

$$\begin{pmatrix} |n,1,0\rangle_v \\ |n,1,+\rangle_v \\ |n,1,-\rangle_v \end{pmatrix} = 1/\sqrt{2} \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & -1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} |n,1,y\rangle_v \\ |n,1,z\rangle_v \\ |n,1,x\rangle_v \end{pmatrix}$$

Excitation of the  $|n,1,0\rangle$  state is forbidden owing to the reflection symmetry property of this state in the collision plane (ref.4).

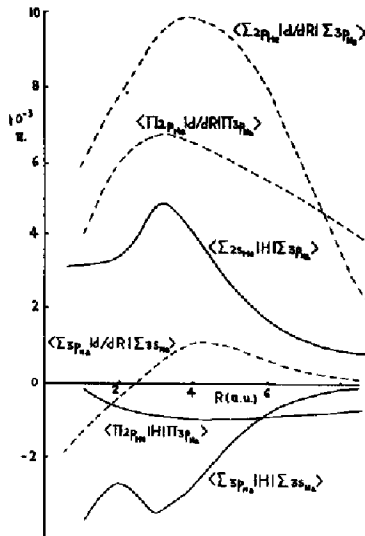


Fig.2. Matrix elements: — off diagonal coupling terms of HeI and - - - radial coupling terms between the atomic-like states.

The probability amplitudes are calculated for the following initial conditions:

$$a_{3s}(-\infty) = 1, \quad a_{3p+1}(-\infty) = 1 \quad \text{and} \quad a_{3p-1}(-\infty) = 1$$

and the orientation  $\langle L_L \rangle$  of the  $\text{Na}(3p)$  state is calculated as :

$$\langle L_L \rangle = ((a_{3p+1}(\infty))^2 - (a_{3p-1}(\infty))^2) / ((a_{3p+1}(\infty))^2 + (a_{3p-1}(\infty))^2)$$

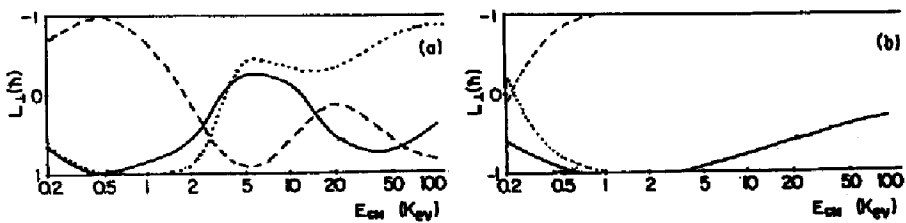


Fig.3. Orientation of the  $\text{Na}^*(3p)$  : a) present result , b) Andersen and Nielsen result (ref.4), for initial conditions:  $|s=1\rangle$  : — ,  $|p+1=1\rangle$  : - - - , and  $|p-1=1\rangle$  : .....

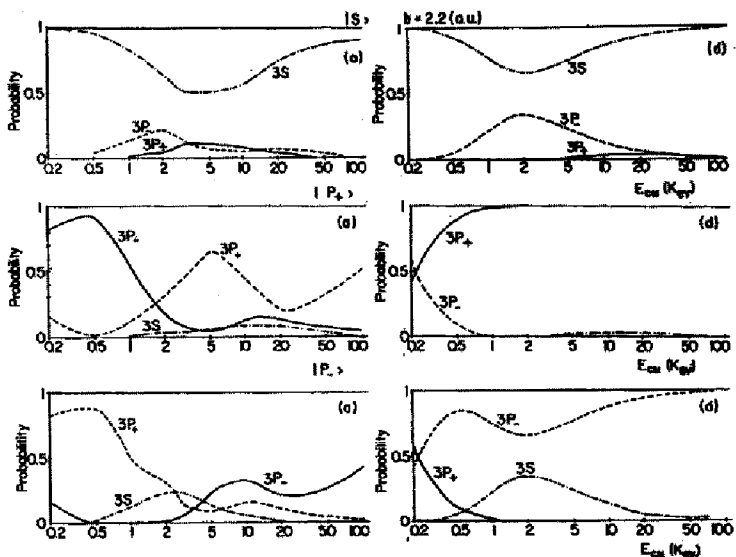


Fig.4. Probabilities versus the kinetic energy for  $b=2.2 a_0$ , and the initial condition  $a_{3S}^0=1$ ,  $a_{3P}^0=1$ ,  $a_{3P-1}^0=1$ , a) present results and d) Andersen and Nielsen (ref.4) results.

The PVB 8-state model calculations show that the orientation of the  $Na^*(3p)$  charge cloud is very different from the 3-state model (see Fig.3) at  $b=2.2 a_0$  and 2 keV - 50KeV  $E_{CM}$ . They also show that, in the deexcitation process (see Fig.4), the sharing between  $3_{p+1}$  and  $3_{p-1}$  sublevels is different from the 3-state model prediction. Only the deexcitation to 3s state has the same energy dependence in the two models. The  $2s_{He}$  - pseudo-state plays an important role via a kind of charge exchange process and the role of the  $3d_{Na}$  states is negligible. The present work modifies the 3-state model result and as a consequence the propensity rule which was in agreement with a 3-state model is no longer verified in a 8-state model.

The limits of the present calculations suggest the following improvements are necessary:

- 1) treatment by an adiabatic basis set to clarify the role of the ionic configurations.
- 2) The Electronic Translation Factor must be introduced for this type of direct excitation occurring at intermediate internuclear distances and its role must be clarified.

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