I. INTRODUCTION

Mutual Neutralization (MN) is a process where positive and negative ions collide, resulting in charge transfer and the formation of neutral atoms. When the MN reaction rate is very large, Whitten et al concluded that it can be an important escape channel for the formation of the excimer species [1]. When a helium cation and a hydrogen anion collide, the process is

\[ \text{He}^- + \text{H}^+ \rightarrow \text{He} + \text{H}. \]  

(1)

The process is of interests in many fields of research, such as the chemistry of the interstellar medium [2] and the gas evolution of the early universe [3, 4]. Helium and hydrogen ions played a crucial role in the formation of important species like HeH, H2, H3, and H2+. At the diatomic-reactor section, like ITER [5], ions of helium and hydrogen are proposed to be present [6–8]. Thus it is of importance to study all the possible reactions, involving the ions, that may take place, including MN. With the advent of cold ion storage rings, like Desiree [9] and merged beam facilities, the MN reaction can be studied experimentally.

This MN reaction is good enough for testing theory, due to the size of the species involved. A fully quantum study for this reaction has been recently reported [10], where eleven \( 2\Sigma^+ \) states were included in modelling the nuclear dynamics using the log-derivative method. In this study autoionization amongst the coupled electronic states was also studied. However, autoionization was found to have a very low contribution to the MN total cross section, for energies below 10 eV. The results showed a large cross section, comparable with previous results [12–15]. The current study includes ten adiabatic states and the aim is to test the reliability of the Landau-Zener model for the HeH system, since it is not computationally demanding as the log-derivative method.

In Section III of this paper, details on the computations of the tranformation matrix and diabatic potential energy curves are discussed. The results and conclusion are given in section IV and section V respectively.

II. COMPUTATIONS

The MN reaction can be theoretically studied by viewing the ionic and covalent interaction of the potential energy surfaces. In the adiabatic picture [18], the potential energy curves for a diatomic system do not cross [18, 19]. Such curves, however, do not preserve the ionic/covalent character of the states. Thus a potential energy curve may exhibit an ion-pair state character at short internuclear distances and a covalent state character at large distances. On the other hand, if the potential energy curves are transformed to a diabatic representation, the character can be preserved. Such potential energy curves, though, will cross each other, even for a diatomic system.

The Landau-Zener model assumes only two states are interacting at an avoided crossing. The adiabatic potential energy curves obtained by some of us previously [10], are used in this study. The adiabatic-to-diabatic transformation matrix, \( \mathbf{T} \) is of the form

\[
\mathbf{T} = \begin{pmatrix}
\cos[\gamma(R)] & \sin[\gamma(R)] \\
-\sin[\gamma(R)] & \cos[\gamma(R)]
\end{pmatrix}.
\]  

(2)

The rotational angle, \( \gamma(R) \) is obtained from integrating the first derivative coupling element [18] obtained by Larson et al [10],

\[
\gamma(R) = \int_R^\infty F_{ij}(R')dR',
\]  

(3)

where \( F_{ij}(R) \) is the first derivative non-adiabatic coupling element between states \( i \) and \( j \). The couplings are at large internuclear distances and are known to drive the MN reaction in many systems [19, 22]. The coupling elements are peaked at the avoided crossing. Thus the rotational angle exhibit a drop by a factor of \( \frac{1}{\pi} \) at the avoided crossing. This drop has been observed previously for other systems [21, 22]. The rotational angles for the HeH system are shown in fig. 1. The diabatic potential
energy curves (shown in fig. 2) are assumed to vary linearly with the internuclear distance \( R \) in the vicinity of the crossing \( R_x \), i.e.

\[
V_1(R) - V_2(R) = cR,
\]

where \( V_1(R) \) and \( V_2(R) \) are the diabatic potential energy curves for the two states and \( c \) is a constant. The probability \( p_\ell \) for remain in a diabatic curve is given by [16, 17]

\[
p_\ell = \exp \left( \frac{\eta}{V_x} \right),
\]

where \( \eta = \frac{2\pi H_1^2}{c} \) and \( H_{12} \) is the electronic coupling element. \( V_x \) is the radial velocity at the curve crossing. As pointed out previously [20, 22], the electronic couplings play a crucial role on the quality of the results one may obtain by using the Landau-Zener method. Here we are using electronic coupling elements obtained from taking the values of the diabatic potentials at the curve crossings.

In the HeH system, the ion-pair state crosses nine covalent states. The probability for ending in the highest covalent state (here the covalent states are numbered 1-9, starting from the highest in energy, refer to fig. 2) is given by

\[
\varphi(ion, 1) = \begin{cases} 
2p_{\ell_{ion}}p_{\ell_5}p_{\ell_6}p_{\ell_7}p_{\ell_8}p_{\ell_9}(1 - p_{\ell_1}), & \text{if } \ell < \ell_1; \\
0, & \text{otherwise},
\end{cases}
\]

The Landau-Zener probability for a transition from the ion-pair state to a covalent state is

\[
\varphi(ion, n) = \left\{ \begin{array}{ll}
\prod_{i=1}^{n-1} (1 - p_{\ell_i}) + p_{\ell_{ion}} \times (1 - p_{\ell_n}), & \text{if } \ell_{n-1} < \ell < \ell_n \\
\prod_{i=1}^{n-1} (1 - p_{\ell_i}) \times (1 - p_{\ell_n}), & \text{if } \ell_{n-2} < \ell < \ell_{n-1} \\
\vdots \\
\end{array} \right.
\]

Here \( \ell_n \) denotes the maximum rotational quantum number (\( \ell_{max} \)) attainable before \( R_x \) is reached for state \( n \);

\[
\ell_{max} = 2R_x \sqrt{\mu(E + \Delta E)},
\]

where \( E + \Delta E \) is the total energy of the system, without including the centrifugal barrier term, and \( \mu \) is the reduced mass for the species.

The values where the ion-pair curve crosses the covalent states, \( R_x \), are displayed in table I. The electronic couplings are obtained using the ATD method reported in ref. [22]. The total cross section formula, for state \( n \) is given by

\[
\sigma_n(E) = \frac{\pi}{\hbar_n} \sum_{\ell=0}^{\ell_{max}} (2\ell + 1)\varphi(ion, n),
\]

\begin{table}
| \( R_x (a_0) \) | \( H_{12} (eV) \) |
|-----------------|-----------------|
| 1               | 7.74 1.2817×10^{-2} |
| 2               | 9.28 3.7956×10^{-3} |
| 3               | 10.38 6.3394×10^{-3} |
| 4               | 11.51 7.8453×10^{-4} |
| 5               | 23.89 6.9397×10^{-4} |
| 6               | 28.88 1.9948×10^{-4} |
| 7               | 32.15 2.4096×10^{-4} |
| 8               | 35.39 1.5679×10^{-4} |
| 9               | 36.52 1.5246×10^{-4} |
\end{table}
where \( E \) is the collision energy, if we assume the threshold energy to be zero. \( k_n \) is the asymptotic wave number of the incoming channel,

\[
k_n = \sqrt{2\mu(E - E_{n}^{th})}, \tag{10}
\]

and \( E_{n}^{th} \) is the asymptotic energy of state \( n \).

### III. RESULTS

The total MN cross section for collisions of \( ^4\text{He}^+ + \text{H}^- \) is computed using eq. (10) for each of the nine states. The total cross section is then computed using

\[
\sigma_{total}(E) = \sum_{n=1}^{9} \sigma_n(E). \tag{11}
\]

![Graph showing cross section vs collision energy](image)

**FIG. 3.** Total cross section for MN of \( ^4\text{He}^+ + \text{H}^- \) compared with other results [10, 12, 13].

The MN total cross section results are shown in fig. 3. Results from the current calculations are labelled “LZ model”. Here, they are compared with results from a fully quantum model [21] and some experimental results by Peart et al [13] and Olamba et al [12]. The cross section from the Landau-Zener model is comparable with the fully quantum model at low collision energies. For energies above 1 eV, the total cross section from the current model is larger. This is a phenomenon previously observed in other systems [20, 21].

### IV. CONCLUSION

The MN reaction total cross section computed from the Landau-Zener model is comparable with other results for the \( ^4\text{He}^+ + \text{H}^- \) reaction. At low collision energies the cross section follows the Wigner threshold law [23]. The MN reaction is driven by non-adiabatic couplings at large internuclear distances.

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