Theoretical studies of charged particle collisions

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Abstract. Results from quantum mechanical ab initio studies on mutual neutralization in collision of H⁺ with H⁻ and H₂⁺ with H⁻ are reported. The theoretical studies require computations of the potentials as well as the non-adiabatic interactions among highly excited electronic states. The electronic states are transformed to a diabatic representation and the coupled radial Schrödinger equation is solved using a logarithmic derivative method. For H₂⁺ collisions with H⁻, the process is studied using reduced dimensionality. Calculated cross sections and final state distributions are compared with measurements.

1. Introduction

In mutual neutralization oppositely charged ions collide, an electron is transferred and neutral atoms or molecules are formed. The reaction is by necessity a non-adiabatic process since there is a transition from an ion-pair state to a covalent state. Due to the long-range attraction of the ion-pair state potential there are in general avoided crossings at large internuclear distances (≈ 10 – 40 a₀) where the electron transfer will most probably take place. Here we will report from theoretical studies on the following mutual neutralization collisions:

\[ \text{H}^+ + \text{H}^- \rightarrow \text{H} + \text{H}, \]  

(1)

and

\[ \text{H}_2^+ + \text{H}^- \rightarrow \left\{ \begin{array}{l} \text{H}_2 + \text{H} \\ \text{H} + \text{H} + \text{H} \end{array} \right\}, \]  

(2)

where either the atomic or molecular fragments can be excited. The H⁺+H⁻ mutual neutralization reaction is important for understanding the formation of H₂ and the resulting cooling of the gas in the early universe [1]. The processes (1) and (2) are fundamental since the smallest of all atomic and/or molecular ions are involved. Still, these mutual neutralization reactions are non-trivial to study at low collision energies both theoretically and experimentally. Experimental studies of mutual neutralization at low collision energies (or low temperatures) can be performed using e.g. the flowing afterglow Langmuir-probe technique [2], single-pass merged beam measurements [3] or using the double electrostatic storage ring DESIREE [4] at Stockholm University.
2. Structure calculations on H₂

We have previously performed series of theoretical studies [5, 6] on mutual neutralization in H⁺+H⁻ collisions by considering 1Σ⁺g and 1Σ⁺u electronic states of H₂ associated with the H(n ≤ 3)+H covalent limits as well as the ion-pair states. All non-adiabatic radial couplings among these states were included and the coupled Schrödinger equation for the radial wave function was solved in a strictly diabatic representation using a logarithmic derivative method [7]. In the theoretical model, the symmetry requirement due to the presence of identical nuclei was considered. The total and differential cross sections for mutual neutralization were calculated for energies between 0.001 and 100 eV. Reasonable agreement with previous calculated cross sections as well as with the measured cross sections above a few eV was obtained. Also the calculated final state distributions were compared with experimental results and satisfactory agreement was found. In the collision process between H⁺ and H⁻ both electrons can be transferred. This double charge transfer process has also been studied [8], however, for this reaction the calculated cross section was found to be an order of magnitude larger than the measured cross sections for collision energies below 100 eV. This is not yet understood.

In order to test the approximations applied in the theoretical model and perform detailed comparisons with experiments, we have now returned to the system to improve the model and include effects previously neglected. New extensive structure calculations on the H₂ system have been performed in order to obtain consistent molecular data of all electronic states with asymptotic limits below the ion-pair H⁺+H⁻ threshold. These are the covalent states associated with the H(n ≤ 4)+H limits. The calculations were carried out using the DALTON program [9, 10]. The adiabatic potential energy curves for states of all symmetries as well as the radial non-adiabatic coupling elements, ⟨i|∂R|j⟩, and rotational coupling elements, ⟨i|Lµ|j⟩, were computed using the full configuration interaction method with a hydrogen basis set composed of (1s,8p,7d,6f) primitive functions contracted to (9s,8p,7d,6f). A basis set similar to the one used in our previous study [5] was used, however, with more diffuse basis functions added where the exponents of these functions were optimized in order to obtain correct asymptotic energies of covalent states and correct positions of the large distance avoided crossings due to the interaction between the ion-pair and the covalent states. An accurate description of these avoided crossings at large distances is a necessity in order to compute reliable cross sections for the mutual neutralization reaction. The calculated adiabatic potential energy curves are displayed with red lines in Fig. 1 and compared with previously calculated potential energy curves [11, 12, 13].

Mutual neutralization processes like (1) and (2) are in general driven by the non-adiabatic interactions between the ion-pair and covalent states occurring at large internuclear distances. Other types of interactions have in general been neglected. Rotational couplings originating from the matrix elements of the angular part of the nuclear kinetic energy operator have the form ⟨i|Lµ|j⟩ J(J+1)/[2μR²] and these will couple states with ∆Λ = ±1. Bardsley pointed out [14] that even though these couplings are localized at small internuclear distances, the large angular momentum contributing in these types of processes, could make the rotational couplings important to consider for mutual neutralization reactions. We have here calculated these rotational couplings between all the 1Σ⁺g and 1Πg as well as the 1Σ⁺u and 1Πu set of states. Some of the rotational coupling elements of the lower lying electronic states have previously been calculated by Wolniewicz and Dressler [13] and they are found to be in reasonable agreement with our data.

3. H⁺-H⁻ mutual neutralization

The cross section for mutual neutralization in H⁺ + H⁻ collisions was calculated by considering the 11 electronic states of 1Σ⁺g symmetry and the 10 states of 1Σ⁺u symmetry, all with threshold energies below the ion-pair limit. The radial non-adiabatic couplings among these states were
Figure 1. Calculated adiabatic potential energy curves (red lines) of H₂ in 1Σ⁺, 1Σ⁺, 1Π⁺, and 1Π⁺ symmetries are compared with results obtained by Detmer et al. (blue crosses) [11] and Dressler and Wolniewicz (black stars) [12, 13]. The potential associated with the ground state fragments is not displayed.

considered, but the rotational couplings to the Πg/u states have not yet been included in the model. The electronic states were diabatized and the coupled Schrödinger equation was solved using similar numerical parameters as in [5, 6]. The calculated total mutual neutralization cross section is displayed in Fig. 2 a) and compared with our previous calculation [5, 6] as well as with other calculated cross sections [15] and measurements [16, 17]. The electronic states associated with the H(n = 4)+H limit do not significantly change the total neutralization cross section as can be seen by comparing the black and blue curves in the figure. There is a small increase of the cross section (by approximately 1% at 30 eV) when the n = 4 states are included. There is a reasonable comparison of the cross section computed here with the one computed by Fussen and Kubach [15] (red dashed curve) using an one-electron quantum approach. The calculated cross section agrees with measured ones (at higher collision energies, but not with the one measured by Moseley et al. [16] at low energies. Considering the small effect on the total neutralization cross section, it is interesting to note that by analyzing the final state contribution [see Fig. 2 b]), the H(n = 4)+H fragments are formed with a ratio of about 10% at collision energies above 10 eV. At low collision energies, the H(n = 3)+H fragments are mainly formed as the mutual neutralization reaction is driven by non-adiabatic interactions due to the avoided crossings between ionic and covalent states around 35 a₀. At larger energies, the n = 2 channels start to contribute when the avoided crossings around 10 a₀ start to become important.
Figure 2. In a) the calculated cross section for $H^+ + H^-$ mutual neutralization cross section (blue line) is compared with previously calculated cross sections [5, 6, 15] and measurements [16, 17]. In b), the calculated final state distributions are displayed.

4. Structure calculations on $H_3$
Performing an ab initio quantum mechanical study on the mutual neutralization reaction when $H_3^+$ collides with $H^-$ as in reaction (2) is demanding. The potential energy surfaces and the non-adiabatic coupling elements have to be computed as functions of the three vibrational coordinates. The $H_3$ system with only three electrons allows for structure calculations using the full configuration interaction method and a hydrogen basis set of (11s,5p,1d) contracted to (6s,5p,1d) was used. Fig. 3 shows the calculated potential energy surfaces of $H_3$ in $^2A^\prime$ symmetry where the H-H Jacobi coordinate is frozen at $r = 1.99$ a$_0$ and $\theta = 89.9^\circ$. (This angle is chosen rather than 90$^\circ$ in order to run the calculations in $C_s$ symmetry and avoid $C_{2v}$.) As can be seen there are avoided crossings at large internuclear distances (20-30 a$_0$) when the attractive ion-pair state crosses the covalent state potentials. There are additionally higher lying states with a long-range attractive Coulomb potential. These states have configurations mimicking continuum states of $H_2^- + H^+$. The electronic states involved in the long range avoided crossings that are believed to play an important role in the $H_2^+ + H^-$ mutual neutralization reaction are identified [red curves in Fig. 3 a)] and the non-adiabatic coupling elements among these states are computed. The structure calculations of the potential energy surfaces and non-adiabatic coupling elements are repeated for different values of the $r$ and $\theta$ Jacobi coordinates.
Figure 3. a) shows the potential energy surfaces of H$_3$ in $^2A'$ symmetry for fixed Jacobi coordinates $r = 1.99$ a$_0$ and $\theta = 89.9^\circ$. The electronic states that are believed to play an important role in the mutual neutralization reaction are shown with red curves and among these states the non-adiabatic coupling elements have been computed. In b), the calculated cross section for mutual neutralization in H$_2^+$+H$^-$ collisions is displayed (with the red curve) and compared with previous Landau-Zener calculations [20, 21] and measured cross sections [18, 19].

5. H$_2^+$-H$^-$ mutual neutralization
An estimation of the mutual neutralization cross section was obtained by describing the H$_2^+$-H$^-$ system as an one-dimensional system where the Jacobi ($r, \theta$) coordinates are assumed to be frozen during the collision. The one-dimensional slices of the H$_3$ potential energy surfaces are diabatized and the coupled Schrödinger equation was solved using the same logarithmic derivative method as for the diatomic collision complexes. The cross section for mutual neutralization was then estimated by keeping $\theta = 89.9^\circ$ frozen and from a weighted sum of the cross sections computed at the different values of the Jacobi coordinate $r$. The weights were given by the probability distribution obtained from the H$_2^+ (v = 0)$ vibrational wavefunction. The resulting cross section is displayed with the red curve in Fig. 3 b). When the radial coordinate $r$ changes, the neutralization cross section was changing which can be understood since the avoided crossings between the ionic and covalent states occur at other distances. The H$_2^+$+H$^-$ mutual neutralization cross section has previously been measured at collision energies above a few eV [18, 19]. The cross section has also been computed using multi-state semi-classical Landau-Zener calculations [20, 21]. In [20] the interactions to covalent states associated with H$_2^+$+H limit were considered, where the excited H$_2$ was assumed to be in an excited electronic state of gerade symmetry. In [21] only covalent states associated with H$_2$ in the electronic ground state and excited H-atoms were considered. Present $ab$ initio calculation includes both types of states. By analyzing the partial cross sections it is found that mainly states associated with H$_2^+$+H are formed and the agreement between the present result with that of [20] is better than the agreement with [21].
6. Discussion and conclusion

The results presented here for processes (1) and (2) are preliminary. In the case of H^+ + H^−, the next step is to include the computed rotational couplings in the model. Some of the calculated non-adiabatic coupling elements between the covalent states are not completely zero asymptotically. This is a well-known problem that have been discussed and been analyzed in the case of inelastic atomic collisions [22]. We believe, the influence of the electron translation is not as dramatic in mutual neutralization reactions compared to other charge-transfer collisions due to the relatively small non-adiabatic couplings between ionic and covalent states in the asymptotic region. However, we would like to apply the correct asymptotic boundary condition in the logarithmic derivative code considering that asymptotically some of the electronic states are coupled. In the ab initio studies on H^+ + H^− performed so far, only bound electronic states have been considered. These bound states are known to interact with electronic resonant states imbedded in the ionization continuum of H_2^+. By connecting the bound states with the electronic resonant states, autoionization could be included in the model and processes such as associative ionization or penning ionization could be studied.

The next step in the H_2^+ + H^− calculations is to perform an averaging of the calculated cross section over the angle θ. We are also running new structure calculations on the H_3 system using the full configuration interaction method and with a larger basis set in order to obtain more of the covalent states that possess avoided crossings with the ion-pair state at large distances. The plan is to perform the scattering calculations in reduced dimensionality to determine what states of H_2^+ + H that are populated and then in the subsequent step follow the fate of the H_2 fragments to determine whether two fragments or three fragments are formed in the reaction. Studying the collision in full dimensionality is the ultimate goal. This, however, is a non-trivial task.

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