RESONANCES IN COLLINEAR He + H\textsubscript{2}\textsuperscript{+} COLLISIONS

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Reactive and non-reactive transition probabilities are reported for the collinear He + H\textsubscript{2}\textsuperscript{+} collisions in the energy range 0.955-1.5 eV. An interesting mirror-image relation between states of the same symmetry is pointed out. The scattering resonances are interpreted qualitatively in terms of the bound states supported by the vibrational adiabatic potential in hyperspherical coordinates.

1. Introduction

There has been a lot of interest in resonances [1] in reactive collisions as they can provide valuable information on the interaction potential. Theoretically, resonances in collinear reactive collisions have been identified in a variety of systems. A summary of the means of characterising a resonance and its interpretation may be found elsewhere [2]. Experimentally, the search for reactive scattering resonances (RSR) has been on for some time. Only for the reaction

\[ \text{He} + \text{H}_2 \rightarrow \text{HeH}^+ + \text{H} \]  \hspace{1cm} (I)

there is some indication that some aspect of the product angular distribution may be due to an RSR [3].

The reaction

\[ \text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H} \]  \hspace{1cm} (II)

has been of interest as a potential candidate for an experimental study of RSR [4]. Kouri and Baer [5] found that the collinear reaction probability \( P_{\nu}^R \) for different vibrational states \( \nu = 0-5 \) showed significant oscillations as a function of the total energy \( E \) in the range 0.93-1.4 eV. Their finding was reiterated by Adams [6] by a detailed investigation of \( P_{\nu}^R(E) \), using a finer mesh of \( E \) values. Subsequently, Chapman and Hayes [7] pointed out that the vibrational inelastic transition probability \( P_{\nu \rightarrow 1}^R(E) \) for He-H\textsubscript{2}\textsuperscript{+} collisions in the energy range 0.4-0.65 eV (well below the reaction threshold) also showed several oscillations. They characterised one of the oscillations to be a shape (open) resonance and the others as Feshbach (compound) resonances. A similar analysis of the \( P_{\nu}^R(E) \) has not been carried out till now. Also, all the above studies were carried out on an approximate potential-energy surface (PES) [8]. Recently, we reported [9] the \( P_{\nu}^R \) values for the collinear reaction (II) for \( \nu = 0-4 \) of H\textsubscript{2}\textsuperscript{+} over a range of 0.955 \( \leq E \leq \) 1.44 eV, obtained using an
R-matrix approach [10] on an accurate ab initio PES [11]. In this paper we report some additional $P_v^R$ values up to $E = 1.5$ eV and also the non-reactive transition probabilities $P_v^{NR}$ in the range $0.955 \leq E \leq 1.20$ eV. We characterise most of the oscillations to be Feshbach resonances by identifying them with the bound states supported by the vibrational adiabatic potential in hyperspherical coordinates [12,13]. Further, we point out a mirror-image symmetry relation between $P_v^R$ for $v = 0$ and 2 and also for $v = 1$ and 3 and explain it in terms of coupling between channels.

2. Results and discussion

A comprehensive plot of $P_v^R$ versus $E$ for $v = 0$–5 in the range of $0.955 \leq E \leq 1.50$ eV is presented in fig. 1. Two aspects of the results are striking: (i) the $P_v^R(E)$ is oscillatory, (ii) there is a mirror-image symmetry relation between $P_v^R$ for $v = 0$ and 2 and also for $v = 1$ and 3 and explain it in terms of coupling between channels.

![Fig. 1. $P_v^R$ as a function of $E$. The arrows along the abscissa indicate the thresholds for $v = 4, 5$ and $v' = 1$ channels. The dashed line emphasizes that at lower $E$, only $v' = 0$ is open, and that the mirror image relation between $P_0^R$ and $P_2^R$ and $P_1^R$ and $P_3^R$ can be noted.](image)

2.1. Oscillations in $P_v^R(E)$

In order to characterise the oscillations in $P_v^R(E)$ as reactive scattering resonances, the Argand diagram of the $S$-matrix element $S_{00}^R$ is shown in fig. 2. It is clear that the $S$-matrix element changes rapidly in the (real, imaginary) space. Normally, it is expected [2] that points in the Argand diagram move counter-clockwise with respect to energy changes wherever there is a strong resonance. Also, typically, the circling is about a point away from the origin. Such a behavior is evident at the lowest energy range $0.955–0.965$ eV. At the higher $E$, we do not see such a behavior possibly because the resolution in $E$ is not adequate. For example, corresponding to the resonance at 1.08 eV, we see a concave curvature in the Argand diagram between $E = 1.07$ and 1.08 eV suggesting that a finer mesh of $E$ may show the typical counter-clockwise movement. For
Im $S^R_{00'}$

Fig. 2. Argand diagram for the S-matrix element $S^R_{00'}$ in the $0.955 \leq E \leq 1.20$ eV range.

the sake of clarity we provide results only up to $E = 1.20$ eV. Plots for $S^R_{10'}$, $S^R_{20'}$, and $S^R_{30'}$ appear very similar and therefore are not included.

Another indicator of a resonance is the phase ($\phi$) of the S-matrix element. Its variation with $E$ for the $0 \rightarrow 0'$ transition is illustrated in fig. 3. The rapid variation in $\phi$ at certain $E$ values is clearly an indication of resonances. Unfortunately, it does not predict the location of resonances in a quantitative manner. Plots of $\phi$ for $S^R_{10'}$, $S^R_{20'}$, and $S^R_{30'}$, are similar in shape and do not provide any additional insight into the location of the resonances. Hence, they are not shown here.

We present in figs. 4–6 the $P^\text{NR}_{v_1v_2}$ for the different $v_1$, $v_2$ states in the $E$ range 0.95–1.20 eV. Particularly striking is the elastic $P^\text{NR}_{00}$ curve which shows three major maxima with values up to 0.5. The Argand diagram of the $S^R_{00'}$ matrix element, shown in fig. 7, exhibits the characteristics normally expected of resonances: movement in the counter-clockwise direction with respect to increase in $E$ and circles centered away from the origin. It is also clear that for the major resonances the circles have large radii. A plot of the corresponding phase $\phi_{00}$, shown in fig. 8, reinforces the observations in fig. 7.

An interesting aspect of the dynamics is revealed by a plot of state-to-state reactive transition probabilities $P^R_{vv'}$, shown in fig. 9 for the higher $E$ range. (It should be noted that for the

Fig. 3. Phase $\phi$ of $S^R_{00'}$ in the $0.955 \leq E \leq 1.20$ eV range.
Fig. 4. Non-reactive transition probabilities $P_{00}^{NR}$, $P_{01}^{NR}$, $P_{02}^{NR}$ and $P_{03}^{NR}$ as a function of $E$.

Fig. 5. Same as fig. 4 for $P_{11}^{NR}$, $P_{12}^{NR}$, $P_{13}^{NR}$. Note that $P_{10}^{NR} = P_{01}^{NR}$ by the principle of microscopic reversibility and it is included in fig. 4.

Fig. 6. Same as fig. 4 for $P_{22}^{NR}$, $P_{23}^{NR}$ and $P_{33}^{NR}$. By the principle of microscopic reversibility $P_{22}^{NR}$, $P_{23}^{NR}$, $P_{33}^{NR}$, $P_{31}^{NR}$ and $P_{22}^{NR}$ are included in figs. 4 and 5.

Fig. 7. Same as fig. 2 for $S_{00}^{NR}$.
lower $E$ range such a plot is already included in fig. 1, as only one product channel, $v' = 0$, is open at $E < 1.32$ eV. Only for $v = 0$, both $v' = 0'$ and $1'$ channels contribute to the total $P^R_0$ in a comparable way. For all other initial $v$ states, only one product channel dominates. For $v = 1$ and 2, the products are predominantly in the $v' = 0'$ channel, while for $v = 3, 4, 5$ the products are predominantly in the $v' = 1'$ channel. It must be noted that, like in many other studies, the $P^R_{00'}$ and $P^R_{11'}$ are similar in shape, although there is a substantial difference in their absolute magnitudes.

The mirror-image relation between the $v$ states of the same symmetry (even or odd) can be understood to some extent by examining the $P^R_v(E)$ for the reverse reaction

$$\text{HeH}^+(v') + \text{H} \rightarrow \text{He} + \text{H}_2^+(v).$$

By the principle of microscopic reversibility, the values we have presented for $E < 1.32$ eV can also be interpreted as the detailed state-to-state transition probabilities for the reaction (III), starting from $v' = 0'$, with $v = 0−4$ being open. Over the range of $0.955 \leq E \leq 1.31$ eV, the overall reaction probability $P^R = \sum_v P^R_v$ is nearly unity, as illustrated in fig. 10. Values of $(P^R_{00'} + P^R_{01'})$ and $(P^R_{00'} + P^R_{02'})$, plotted in fig. 10, show that they are comparable in magnitude. (For simplicity, we have neglected the results for $v = 4$, as it contributes very little in this $E$ range.) This means, any coupling between the even and odd $v$ states is very small, while, within the same symmetry group, the coupling between two $v$ states (for example, $v = 0$ and 2) is large.

2.2. Characterisation of resonances using Delves' coordinates

The basic philosophy of the different methods [1,2] that are available in the literature in characterising resonances is to interpret them as quasi-
Perhaps the most powerful approach developed in recent times is to identify them as the bound states supported by vibrational adiabatic potential in Delves' coordinates [12,13]. We have followed the same approach in identifying the resonances in collinear He + H₂⁺ collisions. Since the methodology is described in detail in the recent literature [12-15], we only identify the radial coordinate as \( p \) and the polar angle as \( \theta \).

For a mass combination of 4.003(He) + 1.00797(H)-1.00797(H) amu the \( \theta \) would vary from 0 to 50.8°. For \( p = 15 \) msb (mass-scaled bohr) the variation of the potential along \( \theta \) and the bound states of \( H_2 \) and HeH⁺ are shown in fig. 11. The potential along \( \theta \) for different \( p \) values for a collinear geometry is shown in fig. 12. It is important to note that the maximum in each of the curves occurs at the same \( \theta \), and this corresponds to a value of 0.75 for the \( B \) factor.
used in the reactive infinite order sudden scattering (RIOS) theory [16]. The change in the potential at the maximum with $\rho$ is shown as a dashed line in fig. 13. This line is helpful in identifying which of the vibrational adiabatic potential curves interact most [17].

The eigenvalues for the potential along $\theta$ were computed by dividing the $\theta$ range into 300 equal intervals and using a three-point finite difference for the laplacian in $\theta$. The $\rho$ dependence of the eigenvalues was computed for $\rho = 3.0(0.05)9.3$ msb. The results in fig. 13 show that the vibrational adiabatic potentials have wells which are deep enough to support several bound states. The bound states of the vibrational adiabatic potential were also computed using a three-point finite difference approximation for the laplacian in $\rho$.

Since there are several bound states supported by each of the vibrational adiabatic potentials, one should observe several scattering resonances: non-reactive, below the reaction threshold, and reactive, above. Since we have considered only $0.955 \leq E \leq 1.5$ eV, we analyze only the bound states in this energy range. A comparison of the oscillations in fig. 1 with the bound states of the vibrational adiabatic potentials in fig. 13 shows that the hyperspherical approach is successful in predicting the resonances. However, a quantitative one-to-one matching is lacking.

The reason is that the above interpretation is valid only to a zero-order approximation. In the diagonally corrected vibrational adiabatic hyperspherical (DIVAH) model [12], the resonances are to be viewed as the bound states of an effective potential

$$U_j(\rho) = \epsilon_j(\rho) - \frac{\hbar^2}{8\mu\rho^2} - \frac{\hbar^2}{2\mu} Q_{jj}(\rho),$$

where $\mu$ is the effective mass $= \frac{m_A m_B m_C}{(m_A + m_B + m_C)^{1/2}}$ for an $A + BC$ collision; the term

$$Q_{jj}(\rho) = \left\langle \phi_j(\rho; \theta) \left| \frac{\partial^2 \phi_j(\rho; \theta)}{\partial \rho^2} \right. \right\rangle$$

is evaluated as $-\left(2/\Delta \rho^2\right)(1 - \left\langle \phi_j(\rho + \Delta \rho) | \phi_j(\rho) \right\rangle)$ and the justification for the same is given elsewhere [12]; $\phi_j(\rho, \theta)$ is the eigenfunction with an eigenvalue $\epsilon_j$ corresponding to the $j$th vibrational adiabatic potential at $\rho$; $\Delta \rho$ is the increment along $\rho$. $\langle \rangle$ indicates the integral over $\theta$. The resulting effective vibrational adiabatic potentials

$$U_j(\rho) = \epsilon_j(\rho) - \frac{\hbar^2}{8\mu\rho^2}$$

$$+ \frac{\hbar^2}{\mu \Delta \rho^2} (1 - \left\langle \phi_j(\rho + \Delta \rho) | \phi_j(\rho) \right\rangle)$$

for different $j$ states are shown in fig. 14.

A superposition of figs. 14 and 13 would reveal that the DIVAH curves are shifted upwards when compared to the uncorrected analogs in the interaction region, as has been observed in other systems [12,13]. In order to bring out the correlation between the resonances in fig. 1 and the bound states supported by the DIVAH curves, we have reproduced the $P^{R}_v(E)$ on the left-hand side of fig. 14. To avoid overcrowding, we have not included the other $P^R_v$ results. It is clear that while there is a good correlation between some of the reso-
nances and the bound states in the DIVAH model, a quantitative agreement between the two is lacking. This implies that the inclusion of the diagonal corrections is not sufficient; the off-diagonal elements are not negligible and their inclusion would be tantamount to doing an exact calculation. In that case the resonances would be recovered quantitatively. But then the computational advantage of the DIVAH model would be lost. The reason for the lack of quantitative success of the DIVAH model is obvious from fig. 14. The different adiabatic curves interact strongly, particularly along the dashed line – the potential ridge [17]. It is possible that in such situations, a vibrational variational hyperspherical approach [18] may prove to be better.

The diabatic curves for \( v' = 0', 1' \) and \( 2' \) show some interesting features of the He–H\(_2^+\) collisions. Because of the avoided crossing of the adiabatic curves for \( v = 3 \) and \( v' = 0' \), the 0' diabatic curve can be thought of as getting as low as 0.44 eV – very close to the asymptotic \( v = 1 \) state. This implies that \( v = 0 \rightarrow 1 \) transitions would show resonances due to the \( v' = 0' \) closed channel. Normally, one would assume that for energies well below the reaction threshold the inclusion of the product states is not necessary. In HeH\(_2^+\) it would be necessary. To some extent this is reflected in the classical trajectories. The PES for HeH\(_2^+\) is such that often the trajectories go into the product channel before returning into the reactant channel. Similarly, the diabatic curve for \( v' = 1' \) goes as low as 0.76 eV, implying that even near the reaction threshold (0.955 eV) one should expect resonances arising from the closed \( v' = 1' \) channel. This is depicted in fig. 1. The diabatic curve for \( v' = 2' \) gets as low as 1.06 eV. It is clear from the figure that it interacts not only with the \( v = 6 \) curve, but also with the \( v = 5 \) curve to such an extent that the adiabatic curves for \( v = 5 \) and 6 cross each other.

The fact that the adiabatic curves for \( v = 3 \) and \( v' = 0 \) show an avoided crossing at large \( \rho \) suggests that there is a strong correlation between the two states. The reactants "readily" go over to the products. This tendency is reflected in the substantial \( P_v^R \) at the threshold.

On the whole it is clear that the collinear He–H\(_2^+\) collisions are rich in resonances and that the different vibrational channels are strongly coupled. This was becoming clear during the dynamical calculations. We had to include as many as 17 channels while there are only 6 reagent channels and 2 product channels open in the energy range investigated. It is also clear that while the zeroeth-order adiabatic potential in hyperspherical coordinates is able to predict qualitatively the presence of reactive scattering resonances in He + H\(_2^+\) collisions, inclusion of the adiabatic correction is not sufficient for a quantitative prediction. It nevertheless serves the purpose of emphasizing the strength of the non-adiabatic interactions in the system. Thus the collinear reaction (II) would serve as a stringent testing ground for (new) theories in predicting RSR.

2.3. Resonances in 3D collisions

It would be worthwhile if we could predict whether any of the resonances would survive in the three-dimensional (3D) world. In principle, we could do this by examining the shape of the adiabatic potential-energy curves in hyperspherical coordinates for the full 3D collision [19]. In practice, however, as a first step, we have chosen to investigate the problem in restricted geometries in the RIOS framework [16]. The definition of the coordinates \((\rho, \theta)\) for different angular \((\gamma)\) approaches of He to the center-of-mass of H\(_2^+\) is given in the appendix. Cuts of the PES along \( \theta \) for different \( \rho \), obtained using \( B = 0.75 \) (vide supra), for different \( \gamma \) values are shown in fig. 15.

It is clear that the reactant and product channels become less and less interacting with an increase in \( \gamma \). This is reflected in the (zeroeth-order) vibrational adiabatic potentials shown in fig. 16. It is clear that the wells become shallower with increasing \( \gamma \). Therefore one expects that the collinear resonances would not survive \( \gamma \) averaging. Similarly, we have examined the shape of the vibrational adiabatic potentials for the orbital angular momentum quantum number \( l = 20 \) and 40 in the RIOS framework. (The results in fig. 1 would correspond to \( l = 0 \).) Once again, it becomes clear that the collinear resonances would not survive \( l \)-averaging. However, it is possible
that a reaction attribute like product angular distribution in the backward direction, which is dominated by collinear collisions at zero $l$, would carry the signature of the collinear reactive scattering resonance in He + H$_2^+$ collisions.

3. Conclusions

We have reported reactive and non-reactive transition probabilities for the collinear reaction (II) over the energy range 0.955–1.5 eV on an
accurate ab initio potential-energy surface. There are several oscillations in the $P_j^R(E)$ curves and they are identified as resonances. Qualitatively, we have been able to interpret them as the bound states supported by the vibrational adiabatic potentials in Delves’ coordinates. Diagonally corrected vibrational adiabatic model is not adequate in quantitatively predicting the resonances, indicating the strength of (vibrational) non-adiabatic interaction in HeH$_2^+$ collisions. This system should serve as a stringent testing ground for (new) theories developed to predict reactive scattering resonances. It would be interesting to see if the resonant periodic orbit approach [20] would be successful in predicting the collinear HeH$_2^+$ reactive scattering resonances. Such a study is in progress.

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Appendix

For a chosen channel-matching parameter $B$ in the RIOS theory [16], the bending angle $\gamma_i$ in the entry channel is related to $\gamma_f$ in the exit channel through

$$\cos \gamma_f = -\frac{\cos \gamma_i - (1 - B^2) \tan \alpha_i \cot \beta}{B [1 + (1 - B^2) \tan^2 \alpha_i]^{1/2}},$$

where

$$\tan \alpha_i = \frac{\sin \beta}{B^2 - \cos^2 \beta} \left\{ -\cos \beta \cos \gamma_i + \left( B^2 - \sin^2 \gamma_i \cos^2 \beta \right)^{1/2} \right\}$$

and $\beta$ is the skew angle defined by

$$\beta = \tan^{-1}\left[ m_B (m_A + m_B + m_C) / m_A m_C \right]^{1/2},$$

with $m_A = m_{He}$, $m_B = m_C = m_H$ in the present case. For a fixed $\gamma_i$ (and the corresponding $\gamma_f$), $\rho$ and $\theta$ are related to the channel coordinates $(x_i, y_i)$ and $(x_f, y_f)$ through

$$x_i = \rho \cos \theta, \quad x_f = \rho \cos(\theta - \beta),$$

$$y_i = \rho \sin \theta, \quad y_f = \rho \sin(\theta - \beta),$$

where

$$x_i = \left[ \mu_{A,BC}/\mu \right]^{1/2} R_{A,BC},$$

$$x_f = \left[ \mu_{AB,C}/\mu \right]^{1/2} R_{AB,C},$$

$$y_i = \left[ \mu_{BC}/\mu \right]^{1/2} r_{BC},$$

$$y_f = \left[ \mu_{AB}/\mu \right]^{1/2} r_{AB},$$

with $\mu = [m_A m_B m_C / (m_A + m_B + m_C)]^{1/2}$. $R_{A,BC}$ and $R_{AB,C}$ are the center-of-mass separations between the atom and the diatom in the entry and the exit channels, respectively; $r_{BC}$ and $r_{AB}$ are the corresponding diatomic bond distances. The entry and exit channels correspond to $0 \leq \theta \leq \alpha_i$ and $\alpha_i < \theta < \beta$, respectively.

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