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Shape resonances in ion–molecule reaction

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Abstract
A simple analytical formula for the probability of reaction in low-energy ion–molecule collisions is given by Wentzel–Kramers–Brillouin and uniform approximations. By using this formula, one can deal with any type of shape resonances regardless of whether the collision energy is below or above a potential barrier. The reaction probability is completely determined by three parameters: the high-energy limit \( P_0 \) of the reaction probability obtained at a collision energy much above the potential barrier, a universal measure \( \alpha \) of the difference between the collision energy and the barrier top, and a scattering phase shift \( \theta \) due to short-range reactive interaction. It is very useful to draw a topographical map of the reaction probability by assuming that \( P_0 \) is given as a constant and that \( (\alpha, \theta) \) are independent variables. The energy dependence of the reaction probability in a collision process is represented by the section view along a route actually allowed on this topographical map. A resonance structure appears when the actual route crosses a prominent mountain ridge. It is shown that the reaction probability can be unity at a resonance energy even if the probabilities at off-resonance energies are very small. No sharp tunnelling resonance would be expected in the collision system having \( P_0 > 2(\sqrt{2} - 1) = 0.828 \).

Keywords: ion–molecule reaction, shape resonance, WKB approximation
(Some figures may appear in colour only in the online journal)

1. Introduction

In low-energy reactive collisions between an ion and a molecule, the long-range part of the effective potential which is the sum of centrifugal and interaction potentials plays an important role. The effective potential typically has a structure of a deep well and a barrier, as seen in figure 1. The potential barrier top \( E_{BT} \) is regarded as a classical threshold of reactive (e.g., rearrangement) channels. The presence of the potential barrier can induce the quantum-mechanical (QM) phenomenon of resonance in the collisions. This type of phenomenon is called specifically a shape (or potential) resonance.

Let \( A \) be the range of interaction which causes reactive processes (figure 1). Here, the reaction range \( A \) is assumed to be much smaller than the position of the barrier top \( R_{BT} \). If the ion–molecule reaction is exoergic, and has no other activation energy, the low-energy reaction cross section except for resonances may be written as

\[
\sigma = \kappa \sigma_{cap},
\]

where \( \sigma_{cap} \) is the cross section for the capture of the ion by the molecule. The reactivity \( \kappa \) of the collision system can be defined as the ratio of \( \sigma \) to \( \sigma_{cap} \) (i.e., \( 0 \leq \kappa \leq 1 \)), and can be frequently assumed to be mostly independent of the collision energy \( E \). In the classical picture, the capture cross section is calculated by \( \sigma_{cap} = \pi b_0^2 \), with \( b_0 \) being the impact parameter at which the barrier top \( E_{BT} \) coincides with \( E \). If the long-range potential is dominated by an asymptotic polarization form, \( \sigma_{cap} \) is given by the well-known Langevin cross section \( \sigma_L = \pi (2a/E)^{1/2} \), where \( a \) is the polarizability of the molecule. (Here and in the following, atomic units are used unless otherwise stated.) The quantal version of the Langevin cross section was discussed recently, and was shown to have somewhat complicated energy dependence at very-low collision energies [1].

Since resonance phenomena can significantly enhance reaction cross sections, it is usually expected that the effect of the shape resonance is more pronounced in the collision system having very small reactivity \( (\kappa \ll 1) \). If the reactivity is large \( (\kappa \sim 1) \), it seems that a quasi-stationary wave cannot
classical turning points are indicated by $R$, and their location is $E < E_{\text{BT}}$. The effective potential shows a barrier structure for low orbital energies. The reaction rates are generally localized at small distances $R < A$. The centrifugal and non-reactive (long-range) interaction potentials contribute to barrier resonances. As a prototypical and instructive example let us consider the reactive collision system as illustrated in figure 1. The relative distance between an ion and a molecule is denoted by $R$. Any form of reactive interaction is permissible except that it has only a short range $A \ll R_{\text{BT}}$. The interaction at $R > A$ is assumed to be given by only a spherically symmetric local potential $V(R)$. In the region $R > A$, hence the problem is reduced to one-dimensional radial motion. The scattering radial wave function $F(R)$ at $R > A$ is given by solving the following Schrödinger equation:

$$\frac{d^2}{dr^2} + k^2(R) F(R) = 0,$$

(2)

with

$$k^2(R) = \frac{2m}{\hbar^2} \left( E - \frac{J(J+1)}{2mR^2} - V(R) \right),$$

(3)

where $m$ is the reduced mass of the collision system, and $J$ is the orbital angular momentum of the relative motion. In the present study, the WKB method is employed, and accordingly the term $(J+1/2)^2$ is replaced with $(J+1/2)^2$. To take the effects of the potential barrier properly into account, one must connect the WKB solutions at $R \ll R_{\text{BT}}$ and at $R \gg R_{\text{BT}}$. For this purpose, the connection formula using parabolic cylinder functions [2] is appropriate [3, 4].

In the present paper, a comprehensive study is made on the relation between the reactivity and the shape resonance. For this purpose, the Wentzel–Kramers–Brillouin (WKB) approximation and connection formulae based on the uniform approximation are employed [3, 4]. The present method covers not only under-barrier (tunnelling) resonances but also over-barrier resonances. As a prototypical and instructive example of ion–molecule reaction, the formation of antiprotonic hydrogen ($\bar{\text{p}}\text{p}$) in collisions between an antiproton ($\bar{\text{p}}$) and a hydrogen atom, i.e., $\bar{\text{p}} + \text{H} \rightarrow \bar{\text{p}}\text{p} + \text{e}$, is discussed.

### 2. WKB connection formulae

Let us consider the reactive collision system as illustrated in figure 1. The relative distance between an ion and a molecule is denoted by $R$. Any form of reactive interaction is permissible except that it has only a short range $A \ll R_{\text{BT}}$. The interaction at $R > A$ is assumed to be given by only a spherically symmetric local potential $V(R)$. In the region $R > A$, hence the problem is reduced to one-dimensional radial motion. The scattering radial wave function $F(R)$ at $R > A$ is given by solving the following Schrödinger equation:

$$\frac{d^2}{dr^2} + k^2(R) F(R) = 0,$$

(2)

where $R_{1,2}$ are roots of $k(R) = 0$. If the energy is $E < E_{\text{BT}}$, the roots $R_{1,2}$ are the classical turning points. If $E > E_{\text{BT}}$, the local potential might not be well defined everywhere inside the barrier. Is the presence of the well-defined local potential at all the distances an absolutely necessary condition for the occurrence of the shape resonance? If not, does there exist any other physical factor that dominates the shape resonance?

In the present paper, a comprehensive study is made on the relation between the reactivity and the shape resonance. For this purpose, the Wentzel–Kramers–Brillouin (WKB) approximation and connection formulae based on the uniform approximation are employed [3, 4]. The present method covers not only under-barrier (tunnelling) resonances but also over-barrier resonances. As a prototypical and instructive example of ion–molecule reaction, the formation of antiprotonic hydrogen ($\bar{\text{p}}\text{p}$) in collisions between an antiproton ($\bar{\text{p}}$) and a hydrogen atom, i.e., $\bar{\text{p}} + \text{H} \rightarrow \bar{\text{p}}\text{p} + \text{e}$, is discussed.
The variable $R$ is transformed to the argument $x$ of the parabolic cylinder functions $y(x)$ by the relation

$$\int_{\sqrt{2x}}^{x} \left( \frac{x^2}{4} - \alpha \right)^{1/2} \, dx' = \int_{R_\eta}^{R} k(R') \, dR', \quad (9)$$

or equivalently

$$\int_{\sqrt{2x}}^{x} \left( \frac{x^2}{4} - \alpha \right)^{1/2} \, dx' = \int_{R}^{R_\eta} k(R') \, dR', \quad (10)$$

where the constant $\alpha$ is expressed in terms of the action integral across the potential barrier $[3, 4]$, i.e.,

$$\int_{R_\eta}^{R} k(R) \, dR = \int_{-\sqrt{2\alpha}}^{\sqrt{2\alpha}} \left( \frac{x^2}{4} - \alpha \right)^{1/2} \, dx = i\pi \alpha, \quad (11)$$

and is a monotonically decreasing function of $E$ ($\alpha > 0$ if $E < E_{BT}$ and $\alpha < 0$ if $E > E_{BT}$). Using equations (A.6) and (A.8), the wave function (6) in the region $A < R \ll R_{BT}$ can be expressed in terms of $\gamma_1(x)$ and $\gamma_2(x)$ as

$$F(R) = \left[ \frac{\pi}{2} \right]^{-1/2} e^{i\pi/2} \left\{ \left( (\beta^2 - 1) + (\beta^2 + 1) e^{i\phi} \right) \gamma_1(x) + \left( (\beta^2 + 1) - (\beta^2 - 1) e^{i\phi} \right) \gamma_2(x) \right\}, \quad (12)$$

where $\beta$ and $\phi$ are defined by equations (A.3) and (A.11), respectively. What is important is that this form is valid even at $x \to \infty$ (i.e., $R \gg R_{BT}$). In this limit, with use of the asymptotic forms (A.3) and (A.7), the wave function $F(R)$ at $R \to \infty$ can be written in the form satisfying the scattering boundary condition:

$$F(R) \to \frac{N}{\pi^{1/2} \sqrt{E}} \left[ e^{-i\Phi_s(x)} - S e^{i\Phi_s(x)} \right] \quad (13)$$

where the scattering $S$ matrix (without an unimportant factor $e^{i\phi}$) is explicitly given by

$$S = \delta + \frac{1}{1 + e^{2\pi\alpha \phi}} \quad (14)$$

Since the reaction is expressed as the flux loss in the elastic channel, the reaction probability is given by $P = 1 - |S|^2$. Using (7) for $\chi$, one can finally show

$$P = \frac{1 - e^{-2\eta}}{1 + e^{2\pi\alpha} \left[ 1 + e^{2\pi\eta} - 2 \sqrt{1 + e^{2\pi\eta}} \cos \theta \right]} \quad (15)$$

where $\theta = \phi + \delta$. The reaction probability has a peak at $\theta = 2\pi n$, with $n$ being an integer. The peak occurs regardless of whether $E < E_{BT}$ or $E > E_{BT}$, and is considered to be due to a shape resonance. Any type of shape (under- or over-barrier) resonance can be explained by the formula (15) in terms of the three parameters $\eta$, $\alpha$, and $\theta$. As seen below in a specific example (cf. figure 6), the parameter $\eta$ can be practically assumed to be independent of energy at least at energies around the barrier top. Then, the important energy-dependent parameters in (15) are $\alpha$ and $\theta$. The parameter $\alpha$ measures the difference between the collision energy and the potential barrier top in terms of the action integral (cf., $\alpha = 0$ at $E = E_{BT}$), and the parameter $\theta$ (or $\delta$) is the (scattering) phase shift due to the reactive interaction (as can be seen later, $\theta \approx \delta$).

Jachymski et al [8] derived an expression for the scattering length including the effect of the flux loss due to the reaction by using the QDT method. However, they disregarded the phase factor $\delta$ of $\chi$, and instead unspecified QDT parameters were inevitably introduced in their expression. As seen later, the phase $\delta$ is an important factor dominating the resonance condition. Furthermore, by using the WKB method consistently for the description of the motion across the potential barrier, all the parameters related to the shape resonance can be incorporated explicitly in the expression (14) or (15).

### 3. Some properties of reaction probabilities

#### 3.1. Low energies $E \ll E_{BT}$

If the collision energy is far below the barrier top (i.e., $\alpha \to \infty$), the centrifugal potential dominates the motion. In this limit, equations (14) and (15) become

$$S = 1, \quad (16)$$

$$P = 0. \quad (17)$$

The reference functions $e^{i\phi(x)}$ in equation (13) contain the phase $\phi/2$. This phase also becomes zero as $\alpha \to \infty$.

#### 3.2. High energies $E \gg E_{BT}$

If the energy is far above the barrier top (i.e., $\alpha \to -\infty$), one has

$$S = -e^{i\phi} \chi, \quad (18)$$

$$P = P_0 = 1 - e^{-2\eta}. \quad (19)$$

The high-energy limit of the reaction probability becomes the reactivity $P_0$. If the energy dependence of $\eta$ (i.e., of $|\chi|$) is negligible, then the constant parameter $\eta$ can be directly estimated from the high-energy limit. If $P_0$ is further independent of $J$, it is natural to presume $\kappa = P_0$. The loose $E$- or $J$-dependence of $|\chi|$ was utilized by Jachymski et al [8] also in the QDT formulation.

#### 3.3. Perfect absorption $\chi = 0$

For the perfect absorption, one can assume $\chi = 0$ (i.e., $\eta \to \infty$ or $P_0 = 1$). In this case,

$$S = -\frac{1}{\sqrt{1 + e^{2\pi\alpha}}} \quad (20)$$

$$P = \frac{1}{1 + e^{2\pi\alpha}}. \quad (21)$$

The latter is a monotonic function of $E$, and is just the transmission coefficient derived primarily by Miller and Good [3]. This result also indicates that no resonance structure can be seen if the system has high reactivity $P_0 \approx 1$ (or $\eta \to \infty$). The WKB version of the capture cross section may be given by

$$\sigma_{\text{cap}}^{\text{WKB}} = \frac{\pi}{2mE} \sum_{J} P(J, \chi = 0). \quad (22)$$

As shown by Gao [1] for the quantal version, this capture cross section, unlike the Langevin cross section $\sigma_{L}$, is not a monotonic function of $E$, and exhibits an undulation structure irrelevant to resonances.
3.4. No reaction \( \eta = 0 \)

If no reactive channel exists (i.e., \( \eta = 0 \)), the short-range \( S \) matrix \( \chi = e^{i\alpha} \) is unitary. Then,

\[
S = \frac{e^{i\alpha} - \sqrt{1 + e^{2i\alpha}} e^{i\varphi}}{\sqrt{1 + e^{2i\alpha}}}
\]

(23)

which is the same as derived in [9, 10]. From (23), one can easily verify that \( S^* = S^{-1} \), i.e., \( |S|^2 = 1 \). In the case of no reaction, it may be expected that a local potential \( V(R) \) is valid even for the motion at \( R < A \). Then, the wave function \( F(R) \) at \( R \ll R_B \) is also given in a familiar form

\[
F(R) = \frac{C}{\sqrt{K(R)}} \sin \left[ \int_{R_0}^R k(R') \, dR' + \frac{\pi}{2} \right],
\]

(24)

with \( R_0 (\ll A) \) being the inner classical turning point, and one can easily show

\[
\delta = 2 \int_{R_0}^{R_1} k(R) \, dR + \pi.
\]

(25)

By using equations (23) and (25), Krstić et al [10] analysed in detail the resonances for elastic collisions in \( H^+ + H \) at both \( E < E_B \) and \( E \approx E_B \): the poles of the \( S \) matrix in the complex \( E \) plane are roots of the denominator of (23). Equations (23) and (25) may be still usable if \( \pi \) is finite but sufficiently small. In this case, the condition of the peak position in the reaction probability, \( \theta = \phi + \delta = 2n\pi \), becomes

\[
\int_{R_0}^{R_1} k(R) \, dR + \frac{\phi}{2} = \left( n + \frac{1}{2} \right) \pi.
\]

(26)

When \( E < E_B \), this is the Bohr–Sommerfeld quantization condition for a quasi-bound state.

4. Mathematical properties of the function form \( P(\alpha, \theta) \)

In this section, the reactivity \( P_0 = 1 - e^{-2\eta} \) is assumed to be independent of \( E \), and to be given as a constant value. Then, equation (15) for the reaction probability \( P \) contains only two parameters \( \alpha \) and \( \theta \), which are essentially functions of \( E \). Let us assume however that \( (\alpha, \theta) \) are independent variables, and investigate the mathematical property of the function \( P(\alpha, \theta) \). As will be seen later, it is very helpful to do this for gaining a more complete understanding of resonances and for predicting all the possible patterns of resonance profiles in any collision system.

In figures 2–4, the function values \( P(\alpha, \theta)/P_0 \) are plotted as a topographical contour map on the \( \alpha-\theta \) plane, for the reactivities \( P_0 = 0.9, 0.2 \) and 0.02 respectively. It is seen that the topography undergoes a great change for these values of \( P_0 \). If the reactivity \( P_0 \) is large (figure 2), there is a steep cliff rising on the line of \( \alpha \sim 0 \). With decreasing \( P_0 \), the slope of the cliff becomes gentle. Unless \( P_0 = 1 \), a probability ridge is always present on the line of \( \theta = 0 \), and the topography is symmetrical about this ridge line. It should be noted that the topographical map is universal irrespective of collision systems except that \( P_0 \) is given.

![Figure 2](image-url)  
**Figure 2.** A contour plot of \( P/P_0 \) for the reactivity \( P_0 = 0.9 \). The \( x \) axis is \( \alpha \) in au, and the \( y \) axis is \( \theta/\pi \). The highest summit is located at \( (\alpha, \theta) = (-0.350 \text{ au}, 0) \), and its value is \( 1/P_0 = 1.11 \). Bold lines are the plot of \( \theta(E)/\pi \) against \( \alpha(E) \) for \( \tilde{p} + H \) collisions: (a) the angular momentum \( J = 16 \), (b) \( J = 15 \) and (c) \( J = 14 \).

![Figure 3](image-url)  
**Figure 3.** A contour plot of \( P/P_0 \) for the reactivity \( P_0 = 0.2 \). The \( x \) axis is \( \alpha \) in au, and the \( y \) axis is \( \theta/\pi \). The highest summit is located at \( (\alpha, \theta) = (0.221 \text{ au}, 0) \), and its value is \( 1/P_0 = 5 \). Bold lines are the plot of \( \theta(E)/\pi \) against \( \alpha(E) \) for a model study of optical potential (see text): (a) the angular momentum \( J = 16 \) and (b) \( J = 14 \).

4.1. Resonance appearance on the topographical map of \( P(\alpha, \theta) \)

It is evident that the presence of the ridge is closely related to the resonance. The ridge on the \( \alpha > 0 \) side corresponds to the
tunnelling resonance, and the $\alpha < 0$ side corresponds to the over-barrier resonance. If the ridge has a narrow \textit{(knife edge)} structure along the $\theta$ direction, the resonance is expected to appear remarkable. It can be seen that the ridge is narrower as $P_0$ becomes larger. Furthermore, when the reaction probability takes a value much greater than $P_0$, this occurrence is also considered to be due to a resonance. Therefore, an area having $P/P_0 > 1$ on the topographical map is important as an indication of the resonance effect.

\subsection*{4.2. The structure of the ridge line $P(\alpha, \theta = 0)$}

It is interesting to investigate the function form on the ridge line, i.e., $P(\alpha, \theta = 0)$. The structure of the ridge line is shown in figure 5 for various $P_0$. At $\alpha = \alpha_{WP} = (2\pi)^{-1}\ln[(1 - P_0)/P_0]$, the function $P(\alpha, \theta = 0)$ becomes the maximum (the crest of the ridge), and its value is always $P = 1$ (or $P/P_0 = 1/P_0 \geq 1$). This maximum peak is also the highest summit on the topographical map. The position $\alpha_{WP}$ becomes $\sim \infty$ (or $\infty$) for $P_0 = 1$ (or 0), and $\alpha_{WP} < 0$ (or $\geq 0$) for $P_0 > 0.5$ (or $< 0.5$). For very large $P_0$, the maximum peak forms a \textit{low mountain} (or a \textit{hill}) on the cliff top. As $P_0$ becomes small, the maximum peak rises more sharply as a \textit{lonely mountain}.

As seen in the topographical map for $P_0 = 0.9$ (figure 2), although the effect of the tunnelling ($\alpha > 0$) resonance is no longer noticeable, the over-barrier ($\alpha < 0$) resonance still remains observable. In figure 5, one can see that the over-barrier resonance can occur for any value of $P_0 < 1$ since the situation $P/P_0 \geq 1$ arises as long as $\alpha < 0$. However, this is not the case for the tunnelling resonance. It can be easily shown that $P(\theta = 0, \alpha = 0) = P_0$, when $P_0 = 2(\sqrt{2} - 1) = 0.828$. This means that the inequality $P/P_0 < 1$ is always satisfied at $\alpha > 0$ when $P_0 > 0.828$. Furthermore, as seen in figure 2, the slopes on both ($\theta > 0$ and $< 0$) sides of the ridge are gentle for large $P_0$. Therefore, it may be concluded that the tunnelling resonance is significant only for $P_0 < 0.828$.

\subsection*{4.3. Possible routes on the topographical map, allowed for an actual collision system}

In reality, the two variables ($\alpha, \theta$) are not independent, and are functions of the energy $E$: the point ($\alpha, \theta$) on the map, with varying $E$, form a line route. The bold lines indicated by (a), (b) and (c) in the figures 2–4 are such examples of the route. The energy dependence of the reaction probability is represented by a height topography obtained by tracing the route that is allowed for a specific system.

When the route crosses the ridge line ($\theta = 0$), one can actually observe a resonance phenomenon, which always appears as a peak structure. As the ridge on the route is more salient, the resonance becomes more remarkable. Furthermore, only when the route happens to include the point $\alpha \simeq \alpha_{WP}$ on the ridge, the reaction probability becomes $P \simeq 1$. This is the most significant case of the resonance effect. The maximum probability $P = 1$ at a resonance energy can happen even if the system has very small reactivity ($P_0 \sim 0$). In the limit as $P_0 \to 0$ (accordingly $\alpha_{WP} \to \infty$), however the highest summit ($P = 1$) is a lonely mountain localized only in a very narrow area ($\Delta \alpha \sim 1$) located at very large $\alpha$: in such a case, the possibility that an actual collision satisfies
\( (\alpha, \theta) \approx (\alpha_{TP}, 0) \) would be unlikely. In this way, one can imagine all the possible aspects of resonances. Drawing the \( (\alpha, \theta) \) topographical map and the allowed route on the map is very useful for understanding the appearance of resonances.

### 5. Specific examples

#### 5.1. Antiprotonic hydrogen formation

As a specific example, the ion–molecule reaction \( \bar{p} + H \rightarrow \bar{p}p + e \) [11] is investigated. The antiproton \( \bar{p} \) is a negatively charged heavy particle, and the formation of antiprotonic hydrogen \( \bar{p}p \) has exoergic channels in the \( \bar{p} + H \) collisions. Although particle–antiparticle annihilation occurs in the exotic system \( \bar{p} + H \), this channel is important only for \( s (J = 0) \) wave scattering [12]. If the annihilation is negligible, the \( \bar{p}p \) formation bears a close similarity to an atomic process of associative detachment such as \( H^+ + H \rightarrow H_2 + e \) [11]. The fact that the \( \bar{p} + H \) system consists of only three bodies makes it possible to carry out an accurate and detailed QM calculation for the reactive process. Such studies, including also a negative muon \( \mu^- \) instead of \( \bar{p} \), were recently progressed by the present author [12, 13] for low-energy collisions \( (E \leq 0.1 \text{ eV}) \). The reactive interaction and the long-range part of the effective potential has exactly the same feature as shown in figure 1. In the QM study of \( \bar{p} + H \) [12], the dynamical problem was solved by means of an \( R \)-matrix (RM) method [14], in which the whole configuration space was partitioned into several domains. The boundary of a domain was set at \( R = 2.7 \text{ au} \).

In the inner domain \((R < 2.7 \text{ au})\), the problem was solved by the diagonalization of a proper Hamiltonian for the three-body system. In the outer domain \((R \geq 2.7 \text{ au})\), where the reactive interaction is negligible, the adiabatic (Born–Oppenheimer) approximation is fairly accurate for the \( \bar{p} + H \) collisions, and hence \( V(R) \) in (3) is exactly given by the adiabatic potential \( V_{ad}(R) \) [12, 15, 16]. The scattering wave functions of the \( \bar{p} + H \) channel at \( R \geq 2.7 \text{ au} \) were numerically calculated by the backward propagation of the proper asymptotic forms valid at \( R = 150–1000 \text{ au} \). Then, the wave functions in the two domains were matched on the boundary \( R = 2.7 \text{ au} \), and thus the scattering \( S \) matrix was obtained.

In applying the present WKB method to the \( \bar{p} + H \) system, it is reasonable to choose \( A = 2.7 \text{ au} \) (the condition \( A \ll R_{BT} \) is also satisfied). Thus, the short-range \( S \) matrix \( \chi \) can be calculated straightforwardly from the RM calculation by assuming the form (6) on the boundary \((R = 2.7 \text{ au})\). For the calculation of the complex-valued roots \( R_{1,2} \) at \( E > E_{BT} \), the adiabatic potential at \( R > 3 \text{ au} \) was assumed to be the analytical form

\[
V_{ad}(R) = \frac{c_4}{R^4} + \frac{c_5}{R^5} + \frac{c_6}{R^6}, \tag{27}
\]

where \( a = -2c_4 = 4.5 \text{ au} \) is the polarization of the hydrogen atom [17], and the other coefficients are adjusted as fitting parameters \((c_5 = -1.118 86 \text{ au} \text{ and } c_6 = 6.517 51 \text{ au})\). For real-valued calculations, the spline fitting was used for \( V_{ad}(R) \).

Figure 6 shows the energy dependence of \( P_0 = 1 - |\chi|^2 \) for some partial waves \( J \), obtained by the present RM calculation. The reactivity \( P_0 \) is found to be only slightly dependent on \( E \) and also on \( J \) at least at energies around the barrier top, and to be close to unity \((\sim 0.9)\) in the \( \bar{p} + H \) system. The phases \( \delta \) and \( \theta = \phi + \delta \) are shown for the angular momentum \( J = 16, 15, 14, \) and \( 8 \) plotted against the collision energy \( E \). The arrows indicate the potential barrier top \( E_{BT} \) \((E_{BT} = 4.59 \times 10^{-3} \text{ eV} \text{ for } J = 8)\).

![Figure 6. Reactivity](image-url)

Figure 6. Reactivity \( P_0 = 1 - |\chi|^2 \) of \( \bar{p} + H \rightarrow \bar{p}p + e \) for \( J = 16, 15, 14, \) and \( 8 \) plotted against the collision energy \( E \). The arrows indicate the potential barrier top \( E_{BT} \) \((E_{BT} = 4.59 \times 10^{-3} \text{ eV} \text{ for } J = 8)\).

\( E \) (and also on \( J \)) at least at energies around the barrier top, and to be close to unity \((\sim 0.9)\) in the \( \bar{p} + H \) system. The phases \( \delta \) and \( \theta = \phi + \delta \) are shown for the angular momentum \( J = 16, 15, 14, \) and \( 12 \), respectively in figures 7–9. It can be seen that \( \theta \) is almost equal to \( \delta \). (The phase \( \phi \) always satisfies \(|\phi| \lesssim 0.15 \), and the maximum occurs at \( \alpha \sim \pm 0.2 \).) This indicates that the phase factor \( \delta \) of the short-range \( S \) matrix \( \chi \) predominantly determines the resonance condition. If the adiabatic potential \( V_{ad}(R) \) were valid even for the short-range part of the interaction, then \( \delta \) could be calculated by (25) with \( V(R) = V_{ad}(R) \). In the \( \bar{p} + H \) system, actually the adiabatic potential \( V_{ad}(R) \) becomes absolutely invalid when the distance \( R \) is less than the so-called Fermi–Teller critical value \( R_{FT} = 0.639 \text{ au} \) [15]: no electronic bound state exists at \( R \leq R_{FT} \). Nevertheless, let us assume here that the potential \( V(R) \) is given by \(-1/R + I \) at \( R \leq R_{FT} \), with \( I \) being the ionization energy of the hydrogen atom. This assumption, which makes \( V(R) \) smoothly connected at \( R = R_{FT} \), was introduced in a semiclassical study of \( \bar{p} + H \) [18]. As shown in the figures, the phase \( \theta_{ad} \) obtained by using this potential \( V'(R) \) is qualitatively similar to, but significantly different in the magnitude from the correct phase \( \theta \). Unfortunately, the calculation of the phase using the local potential \( V(R) \) is found to be less useful for understanding an accurate profile of the resonance in the \( \bar{p} + H \) system. It should be remembered that the \( \bar{p} + H \) system has the high reactivity \( P_0 \sim 0.9 \). One cannot always expect that the local potential is of practical use in the reaction zone.

The reaction probabilities obtained by the present WKB method (15) are shown in figures 7–9, and are compared with the results of the full QM calculation [12]. The difference in theory between the present WKB and the previous QM
$\theta = \phi + \delta$

methods is only the way that the effect of the potential barrier is handled. First of all, fairly good agreement is always obtained between the WKB and QM results regardless of the collision energy (below/above or even near the barrier top), and also regardless of the presence or absence of resonance. In the case of $J = 16$ (figure 7), a peak is present at an energy (corresponding to $\theta = 2\pi$) above the potential barrier top $E_{BT}$ (i.e., $\alpha < 0$); it is identified as an over-barrier resonance. In the case of $J = 14$ (figure 9), no resonance appears although the condition $\theta = 0$ is achieved at an energy below $E_{BT}$. (The same situation at $E < E_{BT}$ is observed also for $J = 16$.) For $J = 15$ (figure 8), a shoulder structure can be seen at energies $E \simeq E_{BT}$. In this case, $\theta = 2\pi$ is realized nearly at $E = E_{BT}$, and the structure is considered to be due to an orbiting resonance [9, 10, 19, 20]. As pointed out in previous studies [10, 13, 19, 20], the above-barrier and orbiting resonances have broad widths, and hence look less pronounced.

It is very interesting to trace the routes $(\alpha, \theta)$ corresponding to figures 7–9 on the topographical map. These are shown as the bold lines (a), (b) and (c) on the map for $P_0 = 0.9$ (figure 2). The route (a) of $J = 16$ passes nearby the highest summit (hump) located at $(\alpha, \theta) = (-0.350\text{ au}, 0)$; therefore, the peak profile in figure 7 is nearly the most prominent one allowed in the case of $P_0 \sim 0.9$, and the reaction probability becomes very close to unity at the resonance energy. The route (b) of $J = 15$ passes through the place near $(\alpha, \theta) = (0, 0)$ which is a promontory jutting out from the cliff on the line of $\alpha \sim 0$: the shoulder structure in figure 8 is associated with this promontory. The route (c) of $J = 14$ crosses the $\theta = 0$ line at $\alpha = 0.86$ au; however, the ridge structure practically disappears there, and hence it produces little effect of resonance (figure 9). Since $P_0 \sim 0.9 > 2(\sqrt{2} - 1)$, no sharp tunnelling resonance can be expected in the $\bar{p} + H$ system.

5.2. Model study

In a previous study [18], the $\bar{p}p$ formation in $\bar{p} + H$ was investigated also by using an optical potential:

\[ V_{\text{opt}}(R) = V_{\text{ad}}(R) - \frac{i}{2} \Gamma(R) \quad R \geq R_{FT} \]  
\[ = I - \frac{1}{R} - \frac{i}{2} \Gamma(R) \quad R < R_{FT}. \]
\[ \theta = \phi + \delta \]

Figure 9. Reaction probabilities \( P \) and phases \( (\theta \text{ and } \delta) \) of \( \bar{p} + H \rightarrow \bar{p}p + e \) for \( J = 14 \) as a function of the collision energy \( E \) (or \( \alpha \)). The barrier top (\( \alpha = 0 \)) is indicated by the vertical dashed line. The probabilities are obtained by the QM [12] and the present WKB calculations. The phase \( \theta_{\text{ad}} \) is obtained by assuming that \( \delta \) is calculated by (25) with the adiabatic potential (see text). The horizontal line indicates \( \theta = 0 \).

where
\[ \frac{1}{2} \Gamma(R) = \frac{2.2}{87.5 + R} \exp[-3.13(R - 0.394)^4] \quad (30) \]
practically vanishes at \( R > 2 \) au. In the present study, for the purpose of examining various cases of system reactivity, this form of optical potential was adopted as a model case, and the imaginary part was altered as
\[ \text{Im} V_{\text{opt}}(R) = -\frac{1}{2} \gamma \Gamma(R), \quad (31) \]
where \( \gamma \) is a scaling factor. In the present study, a single-channel QM calculation using the optical potential was performed in the region of \( R \leq 3 \) au, and the short-range \( S \) matrix \( \chi \) was obtained at \( R = 3 \) au for the application of the WKB formula (15). The WKB reaction probabilities \( P \) obtained by taking \( \gamma = 10, 1, 0.1, 0.01 \) and 0.001 are shown for \( J = 16 \) and 14, respectively in figures 10 and 11. The reaction probabilities become constant at high energies, and this reflects the fact that the \( E \) dependence of \( P_0 \) (i.e., \( \eta \)) is negligible. For comparison, a full single-channel QM calculation [18] using the optical potentials with \( \gamma = 1 \) and 0.1 was carried out, and these QM results are plotted in the same figures. Also for the optical potential model, agreement between the QM and WKB results is satisfactory.
In the present optical potential model, if the scaling factor is large (i.e., \( \gamma = 10 \)), the reactivity \( P_0 \) is practically unity, and the reaction probability becomes identical to (21). When the perfect absorption occurs, no resonance structure can be observed. For other cases (\( \gamma = 0.1, 0.01 \) and 0.001), the peak due to the over-barrier (\( \alpha < 0 \)) resonance remains for \( J = 16 \) (figure 10). The significance of the over-barrier resonance increases with decreasing \( \gamma \) (i.e., \( P_0 \)). When \( J = 14 \) (figure 11), although no resonance is intrinsically observed for \( \gamma = 1 \) (in this case \( P_0 = 0.91 > 2(\sqrt{2} - 1) \)), the tunnelling (\( \alpha > 0 \)) resonance appears as \( \gamma \) becomes small. For \( \gamma \leq 0.01 \) (\( P_0 \leq 0.024 \)), the peak position of the tunnelling resonance can be predicted by (26). For \( \gamma = 0.1 \), however the reactivity is not necessarily very small (\( P_0 = 0.22 \)), and accordingly the peak position slightly differs from the one predicted by (26). As expected, the tunnelling resonance becomes less significant as \( P_0 \) increases.

In the case of \( \gamma = 0.1 \) (\( P_0 \sim 0.2 \)), the routes on the topographical map for \( J = 16 \) and 14 are drawn in figure 3: the route (a) of \( J = 16 \) crosses the ridge (\( \theta = 0 \)) line at \( \alpha < 0 \) (over-barrier resonance), while the route (b) of \( J = 14 \) crosses it at \( \alpha > 0 \) (tunnelling resonance). In case of \( \gamma = 0.01 \) (\( P_0 \sim 0.02 \)), the routes of \( J = 16 \) and 14 are drawn in figure 4: the tunnelling resonance is very narrow since the ridge for very small \( P_0 \) is a knife edge. It is seen that the route in figure 3 (\( P_0 = 0.2 \)) and the one of the same \( J \) in figure 4 (\( P_0 = 0.02 \)) are very similar. This is because the phase shift \( \theta \) (or \( \delta \)) is mainly determined by the real part of the optical potential \( V_{opt}(R) \). Accordingly, the type of the resonance remains the same even if the imaginary part of \( V_{opt}(R) \) is largely changed (figures 10 and 11).

6. Summary

The shape resonance occurring due to the potential barrier has been investigated for ion–molecule reactive collisions. By using the WKB and uniform approximations, the general formula (15) which can describe any type of shape resonance remains for \( J = 16 \) (figure 10). The shape resonance occurring due to the potential barrier is universal, and is very useful for predicting what a profile the reaction probability becomes at energies much above the potential barrier. The parameter \( \alpha \) is associated with an action integral along the potential barrier, and gives a universal measure of the difference between the collision energy and the potential barrier top. The parameter \( \theta \) is almost equal to \( \delta \), which is a scattering phase shift due to the dynamical process in the reactive region.

The reactivity \( P_0 \) undergoes only a little change at energies around the barrier top. If \( P_0 \) is given as a constant, the topographical map of the reaction probability drawn on the \( \alpha-\theta \) plane by assuming that \( (\alpha, \theta) \) are independent variables is universal, and is very useful for predicting what a profile the resonance can have in conceivable reactive collisions. In an actual case, \( (\alpha, \theta) \) are not independent, and only a specific route corresponding to real collisions is allowed on the topographical map. By viewing this route, one can evaluate the significance of the resonance effect in an individual reactive process. The resonance structure appears when the route crosses a prominent mountain ridge. The tunnelling resonance would become less noticeable for \( P_0 > 2(\sqrt{2} - 1) \), while the over-barrier resonance can occur for any case of \( P_0 < 1 \). If the resonance peak occurs at an energy corresponding to \( \alpha \approx (2\pi)^{-1}\ln[(1 - P_0)/P_0] \), the peak height of the reaction probability is \( P \approx 1 \). For the appearance of shape resonances, it turns out that the presence of a well-defined local potential in the reactive region is not an absolutely necessary condition. As in the \( \tilde{p} + H \) system, the shape resonance can be observed even if the local potential becomes meaningless at small distances.

The present study aims at investigating ion–molecule reactive collisions. However, the present result (15) is evidently applicable to any other systems whenever a potential barrier plays an important role: e.g., reactions between neutral atoms in which van der Waals interaction is important at large distances \([8, 21, 22]\), ionization of atoms in an external electric field \([23–25]\), nuclear reactions in which the potential barrier exists owing to Coulomb repulsion \([26]\), etc.

Appendix. Parabolic cylinder functions

The parabolic cylinder functions \( y(x) \) are solutions of the differential equation

\[
\frac{d^2}{dx^2} y(x) + \frac{x^2}{4} - \alpha y(x) = 0, \quad (A.1)
\]

where \( \alpha \) is a real-valued constant. Here, the notation of Abramowitz and Stegun [2] is used. Two linearly independent complex-valued solutions \( y_1(x) \) and \( y_2(x) \) appropriate for the present purpose are given by equations (19.17.6) and (19.17.7) in [2], i.e.,

\[
y_1(x) = E(\alpha, x) = \beta^{-1/2} W(\alpha, x) + i \beta^{1/2} W(\alpha, -x), \quad (A.2)
y_2(x) = E^*(\alpha, x) = \beta^{-1/2} W(\alpha, x) - i \beta^{1/2} W(\alpha, -x), \quad (A.3)
\]

where the real-valued function \( W(\alpha, x) \) is defined by equation (19.17.1) in [2], and

\[
\beta = \sqrt{1 + e^{2\pi_a} - e^{2\pi_a}} \quad 1/\beta = \sqrt{1 + e^{2\pi_a} + e^{2\pi_a}}. \quad (A.4)
\]

The functions \( y_1(x) \) and \( y_2(x) \) have the following asymptotic forms,

\[
y_1(x) \xrightarrow{x \to \pm \infty} \sqrt{\frac{2}{\pi}} \frac{e^{i\Phi_+(x)}}{\sqrt{x}}, \quad (A.5)
y_2(x) \xrightarrow{x \to \pm \infty} -i \sqrt{\frac{2}{\pi}} \frac{e^{-i\Phi_-(x)}}{\sqrt{x}}, \quad (A.6)
\]

\[
y_1(x) \xrightarrow{x \to \pm \infty} \sqrt{\frac{2}{\pi}} \frac{e^{i\Phi_+(x)}}{\sqrt{x}}, \quad (A.7)
y_2(x) \xrightarrow{x \to \pm \infty} -i \sqrt{\frac{2}{\pi}} \frac{e^{-i\Phi_-(x)}}{\sqrt{x}}, \quad (A.8)
\]

where

\[
\Phi_+(x) = \text{Re} \int_{\sqrt{2}x^{1/2}}^{x} \left( \frac{x^2}{4} - \alpha \right)^{1/2} \text{d}x' + \frac{\pi}{4} + \phi, \quad (A.9)
\]
\[ \Phi_-(x) = \Phi_+(x) = \text{Re} \int_x^{\infty} e^{-t^2} \left( \frac{t^2}{4} - \alpha \right)^{1/2} \log t \, dt + \frac{\pi}{4} + \frac{\phi}{2}, \]  
\begin{align}
\phi &= \arg \Gamma \left( \frac{1}{2} + i \alpha \right) + \alpha (1 - \ln |\alpha|). 
(A.11)
\end{align}

References