Threshold resonance effects in reactive processes

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We investigate the effect of near threshold resonances in reactive scattering at low energy. We find a general type of anomalous behavior of the cross sections, and illustrate it with a real system (H2 + Cl). For inelastic processes, the anomalous energy dependence of the total cross sections is given by $\sigma \sim e^{-1/2}$. The standard threshold behavior given by Wigner’s law ($\sigma \sim e^{-1/2}$) is eventually recovered at vanishing energies, but its validity is now limited to a much narrower range of energies. The universal anomalous behavior leads to reaction rate coefficients behaving as $K \sim 1/T$ at low temperatures, instead of the expected constant rate of the Wigner regime. We also provide analytical expressions for s-wave cross sections, and discuss the implication in ultracold physics and chemistry.

In recent years, the level of control over the interaction in ultracold gases, e.g., by using magnetically tuned Feshbach resonances [1] or by orienting ultracold molecules [2–3], has allowed the investigation of various phenomena in degenerate quantum gases (e.g., BEC-BCS cross-over, solitons, multi-component condensates, etc.) [4–5], as well as of exotic three-body Efimov states [6]. The advances in the formation of cold molecules [7–9] are paving the way to the study [2, 10] and [11] in chemistry of low temperature systems.

In this Letter, we explore the effect of near threshold resonances (NTR) in the entrance channel of a reactive scattering system. In the absence of NTR, it is well known that scattering cross sections behave at ultralow energy $\varepsilon$ according to Wigner’s threshold law [16]; namely, the elastic cross section tends to a constant, while the inelastic cross sections behave as $e^{-1/2}$, when $\varepsilon \to 0$. However, Wigner cautioned that, when resonance poles are present near channel thresholds, renewed attention should be paid to the low energy behavior of cross sections [16–17]. Indeed, resonances in low energy collisions, originally analyzed by Bethe [18] for collisions between neutrons and nuclei, and by Fano in atomic collisions [19], may affect the threshold behavior.

For our study, we selected a barrier-dominated reaction containing a large number of channels, namely H2 + Cl → H + HCl. In particular, for H2 in the initial ro-vibrational level ($v=1, j=0$), the shallow potential well of the Cl···H2 van der Waals complex supports quasibound states, which can lead to resonances in the entrance arrangement (see Fig. 1) [20]; note that there are no nearby closed channels that could give Feshbach resonances. This system was recently investigated at ultralow temperatures by Balakrishnan [21]. To explore the effect of near threshold resonances (NTR) on reactive scattering, we vary the mass of H, as was done in [22], so that the channel thresholds in both arrangements H2−Cl and H−HCl shift at different rate, an approach similar to modifying the potential surface itself [23]. The scattering cross section from an initial internal state $i$ to a final state $f$ is given by [24]

$$\sigma_{i \rightarrow f}(\varepsilon_i) = \frac{\pi}{k_i} \sum_{j=0}^{\infty} \frac{2j+1}{2j+1} \sum_{\ell} |\delta_{ij} - S_{ij}|^2,$$

where $\ell = |J - j|, \ldots, J + j$ and $\ell' = |J - j'|, \ldots, J + j'$; $J = J + \ell = J + \ell'$ is the total angular momentum, with molecular rotational momentum $j$ and orbital angular $\ell$ in the entrance channel $i$, and corresponding quantum numbers $J$, $j$, and $\ell$ (the primes indicate the exit channel $f$). Here, $\varepsilon_i = \hbar^2 k_i^2/2\mu$ is the kinetic energy with respect to the entrance channel threshold, $k_i$ the wave number, and $\mu^{-1} = m_{H_2}^{-1} + m_{Cl}^{-1}$ the reduced mass in the entrance arrangement. We are focusing on the effect of resonances at ultralow temperatures, and thus consider only s-wave scattering with $\ell = 0$, which requires $J = j$ and thus $(2J+1)/(2j+1) = 1$. In addition, we limit ourselves to

![FIG. 1. Rovibrational energy levels for H2 and HCl. For H2 we show the rotational series for $v = 0$ (dashed blue) and $v = 1$ (solid black). Similarly for HCl, we have $v = 0$ (dashed green), $v = 1$ (solid red) and $v = 2$ (dot-dashed cyan). The inset shows the diagonal matrix elements of the potential energy surface for the rovibrational channels that are near the entrance channel; the dashed line represents a weakly quasi-bound level for the van der Waals complex Cl···H2 in the entrance channel H2(1,0).]
molecules initially in their rotational ground state with \( j = 0 \), so that \( J = 0 \), and thus \( \ell' = f' \). This simplifies Eq. (1) to

\[
\sigma_{i \rightarrow f}(\varepsilon_i) = \frac{\pi}{k_i^2} |\delta_{if} - S_{if}^{J=0}(k_i)|^2.
\]

We note that with \( \ell' = j' \), the centrifugal term in the exit channels becomes large for high rotational diatomic levels and makes the van der Waals potential well disappear (see Fig. 1). For the sake of clarity, we omit the subscript \( i \) in \( \varepsilon_i \) and \( k_i \), and \( f \) in \( S_{if}^{J=0} \), in the rest of this Letter.

In the zero-energy limit, the elastic and total inelastic cross sections are described in terms of the complex scattering length \( \alpha \) for a given entrance channel \( i \),

\[
\sigma^{\text{in}}(\varepsilon) = \sum_{f \neq i} \sigma_{i \rightarrow f}(\varepsilon_i) \rightarrow 4\pi |\beta|^2,
\]

\[
\sigma^{\text{el}}(\varepsilon) = \sum_{i} \sigma_{i \rightarrow i}(\varepsilon) \rightarrow 4\pi(\alpha^2 + \beta^2).
\]

Although these limits remain valid in the presence of NTR, their applicability will be limited to a much narrower domain of energies. For the remainder of the low energy regime, a new behavior emerges, as we now show.

The results we present here were obtained using the ABC reactive scattering code of Manolopoulos and coworkers \(^{26} \), which we have optimized for ultralow energies. We used the potential energy surface developed by Bain and Werner \(^{27} \).

Fig. 2 shows the variation of the real and imaginary parts of the scattering length for the entrance channel \( \text{H}_2(\nu = 1, j = 0) + \text{Cl} \), as we scan the mass \( m \) of \( \text{H} \). The open circles indicate the true masses of \( \text{H} \) and \( \text{D} \); \( \text{H} \) lies on the wing of a resonance in the entrance channel, which gives a sharp increase for \( \beta \). In Fig. 3 we show the total inelastic cross section (including both quenching and reaction) as a function of \( m \) for a few energies (in Kelvin). From Eq. (3), we expect \( \sigma^{\text{in}} \) to simply scale as \( e^{-1/2} \), i.e., showing as equidistant curves for the energies chosen in the logarithmic scale; this is indeed the case, except in the vicinity of the resonances. In the inset, we zoom on the resonance, with three masses \( m \) of increasing values being singled out (dashed vertical lines) corresponding to \( 1.0078 \text{u} = m_{\text{H}} \) (true mass), \( 1.038 \text{u} \), and \( 1.042 \text{u} \), respectively; the inset indicates that the energy dependence follows Wigner’s threshold law only for \( m_{\text{H}} \), and departs from it as \( m \) approaches the resonance. Thus, we focus our attention on these three masses, and we analyze in detail the energy dependence of the cross sections.

In Fig. 3(a), we show the low energy behavior of \( \sigma^{\text{in}} \) for the three masses selected above. When \( \varepsilon \rightarrow 0 \), \( \sigma^{\text{in}} \) reaches the Wigner’s regime, scaling as \( e^{-1/2} \) for all three masses. However, for masses closer to the resonance shown in Fig. 3, the scaling changes to \( e^{-3/2} \). In addition, the behavior appears to be universal, i.e., as \( m \) nears the resonance, \( \sigma^{\text{in}} \) has the same value until it deviates from the universal NTR \( e^{-3/2} \) scaling to join the Wigner \( e^{-1/2} \) scaling at lower collision energies. For completeness sake, we also show the elastic cross sections \( \sigma^{\text{el}} \) for the same masses in Fig. 3(b); the Wigner regime’s constant cross section as \( \varepsilon \rightarrow 0 \) changes to the expected \( e^{-1} \) scaling for \( m \) near a resonance. Finally, Figs. 3(c) and (d) depict the corresponding rate coefficients \( K^{\text{in}}(T) \) and \( K^{\text{el}}(T) \) obtained from thermal averaging with a Maxwell distribution of relative velocity \( v_{\text{rel}} \) characterized by the temperature \( T \), i.e., \( K(T) = \langle v_{\text{rel}} \sigma \rangle_T \). Again for \( m \) close to the resonance, there is a significant enhancement of \( K^{\text{in}} \) scaling as \( T^{-1} \) until \( T \) is small enough that the Wigner regime is reached and \( K^{\text{m}} \) becomes constant. The corresponding scaling for \( K^{\text{el}} \) changes from \( T^{-1/2} \) for NTR to \( T^{1/2} \) for Wigner’s regime. This change in behavior is due to the fact that, for \( m = 1.042 \text{u} \), the potential well of the \( \text{Cl} + \text{H}_2 \) van der Waals complex is acquiring a new \( s \)-wave bound state; this so-called zero energy bound state is responsible for the large increase of the probability.
Specifically, if \( \delta \) and assuming that \( |\tilde{\delta}| \), we focus our attention on the S-matrix. Recalling that the energy decreases) is due to the presence of a resonance pole near the threshold of the entrance channel. To understand it, we focus our attention on the S-matrix. Recalling that \( \Sigma_j |S_j|^2 = |S_0|^2 + \Sigma_{j \neq 0} |S_j|^2 = 1 \), and using Eq. (2), we rewrite the cross sections in Eq. (3) in terms of the diagonal element \( S_0(k) \):

\[
\sigma_{\text{el}}(\epsilon) = \frac{\pi}{k^2} (1 - |S_0(k)|^2),
\]

\[
\sigma_{\text{in}}(\epsilon) = \frac{\pi}{k^2} |1 - S_0(k)|^2.
\]

The analytical properties of the S-matrix for single-channel s-wave scattering follow from those of the Jost function \( J(k) \):

\[
S(k) = \frac{J(k)}{J(-k)}.
\]

Specifically, if \( k = z \) is a zero of the Jost function (and of the S-matrix), then \( k = \bar{z} \) is a pole of the of the S-matrix. Hence, given a resonance in the entrance channel \( \ell \), we rewrite the diagonal S-matrix element as a product of a resonant part (due to a zero of \( S \) located at \( k = z \)) and a non-resonant part \( \tilde{S}_0(k) \):

\[
S_0(k) = \frac{z - k}{z + k} \tilde{S}_0(k).
\]

The background contribution \( \tilde{S}_0(k) \) is assumed to be a slowly varying function of \( k \), and can be described as \( \tilde{S}_0(k) = e^{2i\tilde{\delta}} \), where the background phaseshift \( \tilde{\delta} \) is implicitly for the \( \ell = 0 \) partial wave. Here, we are interested in the case when \( |z| \) is very small, such that the energy associated with the pole, \( |E_z| = \hbar^2 |z|^2 / 2\mu \), is within (or near) the ultrasoft core.

Writing the background scattering length as \( \tilde{a}_0 = \tilde{a}_0 - i\tilde{\beta} \), and assuming that \( \tilde{\delta} \approx -k\tilde{a}_0 \), as \( k \to 0 \), we get

\[
\tilde{S}_0(k) = e^{-2ik\tilde{a}_0} = e^{-2ik\tilde{a}_0} e^{-2ik\tilde{\beta}},
\]

so that \( |\tilde{S}_0(k)|^2 = e^{-4ik\tilde{\beta}} \). Expressing the zero in the complex plane as \( z = z' - i\epsilon' \), then \( |\tilde{S}_0(k)|^2 = e^{-4ik\tilde{\beta} |z| / |z| + k} \) in Eq. (4) leads to

\[
\sigma_{\text{in}}^{\text{el}} = \frac{\pi}{k^2} \left( \frac{2(|z|^2 + 2k\tilde{\beta})}{|z| + k} \right) + 4k\epsilon' \cosh(2k\tilde{\beta}) \right),
\]

where we omitted the channel subscript. As \( k \to 0 \), we recover the two different behaviors shown in Eq. (4). Namely, depending on the relative values of \( k \) and \( z \), we have:

- Wigner regime \( (k \ll |z|) \)

\[
\sigma_{\text{in}}^{\text{el}} \approx \frac{4\pi}{k} e^{-2ik\tilde{\beta}} \left( \frac{z'}{|z|^2} + \tilde{\beta} \right) \xrightarrow{k \to 0} \frac{4\pi}{k} \tilde{\beta}.
\]

- NTR regime \( (|z| \ll k) \)

\[
\sigma_{\text{in}}^{\text{el}} \approx 4\pi e^{-2ik\tilde{\beta}} \frac{z'}{k^3} \xrightarrow{k \to 0} \frac{4\pi}{k} \tilde{z'}.
\]

In Eq. (10), the imaginary component of the background scattering length, \( \tilde{\beta} \), is augmented by a contribution from the resonance at \( k = -z \). This is also true for the real component; writing \( \tilde{S}_0 = e^{2i\tilde{\delta}} \) with \( \tilde{\delta} \approx -k\tilde{a} \) as \( k \to 0 \), and expanding (7) to the leading order in \( k \), so that \( 1 - 2i\tilde{a} \approx 1 - 2i\tilde{a}(\tilde{a} - \frac{1}{2}) \), we identify \( a = \tilde{a} - \frac{1}{2} \). Separating the real and imaginary components, we have

\[
\alpha = \tilde{\alpha} + \frac{z''}{|z|^2},
\]

\[
\beta = \tilde{\beta} + \frac{z'}{|z|^2}.
\]

If \( z \) is very close to zero, the effect on the Wigner’s regime can be significant, with large increases of the cross sections from their background values.

Fig. 5 shows the inelastic probability \( 1 - |S_0|^2 \) for various masses ranging from the true mass of hydrogen \( (m = m_H) \) to \( m = 1.042 \) u. The linear scale accentuates the asymmetrical profile of the inelastic probability near threshold, and the good agreement between the numerical results and the analytical expression (9). The values of \( \tilde{\beta} \) and \( z \) can be obtained by fitting the calculated \( \sigma_{\text{in}}^{\text{el}} \) to Eq. (9). The inset shows the results for \( m = 1.042 \) u on a log-log scale, together with the maximum possible value of unity (corresponding to the unitarity limit, when \( S_0 = 0 \)). It reveals the simplicity of the low energy behavior in the presence of NTR; the Wigner power-law scaling for \( k \ll |z| \), a different power-law for \( k \gg |z| \), and the transition between the two regimes taking place near \( k \approx |z| \).

The inset also illustrates the deviation of the analytical expression from numerical results at larger \( k \), where \( \delta \approx -ka \) ceases to be valid. Finally, the state-to-state results for all final channels are also shown, exhibiting the same resonant behavior. It also emphasizes that although Eq. (9) is rather simple, the coupled channel computations are quite complex, involving several hundreds of channels (open and closed).
the zero \((k = z)\) and the pole \((k = -z)\) are the identical;
\[
E_k = \frac{\hbar^2 (z^2 + z'^2)}{2\mu} \equiv \varepsilon_k - i\hbar \frac{\Gamma}{2},
\]
with \(\varepsilon_k = \frac{k}{a} (z^2 - z'^2)\) and \(\Gamma = \frac{2\hbar}{a} \frac{\varepsilon'}{2} \) remaining unchanged for \(\pm z\). As shown in Eq. (11), we must have \(\varepsilon' > 0\) for a physical cross section, and thus the decay rate \(\Gamma\) of the vdW-complex is positive (physical) in the quasi-bound case \((z'' > 0)\), and negative (unphysical) in the anti-bound case \((z'' < 0)\). For an \(s\)-wave NTR, inelastic scattering alone cannot distinguish between shallow bound and anti-bound (virtual) states, since \(\sigma^{m}(k)\) depends on \((z'')^2\) (see Eq. (9)).

In conclusion, we found that a near threshold resonance (NTR) splits the \(s\)-wave low energy domain in two distinct regimes, with the total inelastic cross section gradually transitioning from the well known \(k^{-1}\) Wigner regime into the \(k^{-3}\) NTR regime. We derived simple analytical expressions for both elastic and total inelastic cross sections as a function of the position of the zero/pole of the \(S\)-matrix, and found very good agreement with values obtained numerically. This \(s\)-wave \(k^{-3}\) NTR behavior is a general feature, but its presence can be masked by higher partial wave contributions. Although previous work hinted at such effect using mass-scaling \([23, 28]\) or external fields \([29]\), the new universal NTR \(k^{-3}\) behavior shown in Eq. (9) remained elusive until now. We revealed the effect of NTR in a benchmark atom-diatom reactive scattering by mass-scaling, but it should appear in any system with a zero-energy resonance, such as in photoassociation \([30, 31]\), collision \([52]\), or spin-relaxation in ultracold atomic samples \([33]\). The modified \(k^{-3}\) inelastic cross section will impact not only the interpretation of experiments such as \([12]\), but also theories developed to account for resonances in ultracold molecular systems \([13]\).

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