Particle scattering and resonances involving avoided crossing

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Abstract

In molecules, the nonadiabatic couplings between two adiabatic potentials build the avoided crossing (AC) region. The rovibronic resonances in the AC region of two-coupled potentials are very special, since they are not in the bound state region of the adiabatic potentials, and they usually do not play important roles on the scatterings and are less discussed. Exemplified in particle scattering, resonances in the AC region are comprehensively investigated. The effects of resonances in the AC region on the scattering cross sections strongly depend on the nonadiabatic couplings of the system, it can be very significant as sharp peaks, or inconspicuous buried in the background. More importantly, it shows a simple quantity proposed by Zhu and Nakamura (1992 J. Chem. Phys. 97 8497) to classify the coupling strength of nonadiabatic interactions, can be well applied to quantitatively estimate the importance of resonances in the AC region. Example applications of the quantity for real molecules (MgH, CO and OH) can well explain the evolutions of cross sections in the AC region published in the literatures. This work provides a simple and practical way to determine the candidate molecules when studying the resonances in the AC region.

1. Introduction

Different from bound and continuum states, a resonance is known as a discrete quantum state embedded in and coupled to a continuum [1–5]. It occurs as a short-lived decaying state of the scattering system. Mathematically, resonance can be defined as the pole of $S$-matrix in the fourth quadrant of the complex energy plane as $\varepsilon_s = \varepsilon_{sr} - \frac{i}{2} \Gamma_{si}$ [6], where $\varepsilon_{sr}$ and $\Gamma_{si}$ are the resonance position and width, respectively. The larger of width $\Gamma_{si}$, the shorter of resonance lifetime. Physically, the unique existence of resonance is interpreted by Ugo Fano as the results of interference between bound and continuum channels, exemplified with the doubly excited state He (2s2p) [7]. Resonances are very important in many areas related to physics and chemistry [8–11]. They generally appear in quantum scattering and its subsequent dynamic processes, manifested as abrupt changes in the cross sections of the (electron/photon/ion) energy spectra [6, 12, 13], including nuclear collisions [14], electron scatterings [9], photon absorption [7, 15], heavy ion collisions [16], ultracold atom and molecule physics [17], chemical reaction dynamics [10] and so on.

Generally, resonances are classified as shape and Feshbach resonances from the aspect of the interaction-potentials [3, 5]. Taking the particle-collision system as an example, figure 1 shows the typical interaction potential energy curves. The involved energy space can be clearly divided into four regions by the two adiabatic potential energy curves (APECs) $V_A^{11}$ and $V_A^{22}$. If the nonadiabatic electronic couplings between the two APECs can be ignored, regions I and III can be considered as the bound and continuum regions of potential $V_A^{11}$, respectively. And in region IV, both the continuum states of potential $V_A^{11}$ and the bound states of potential $V_A^{22}$ sit independently. However in region II, quasi-bound states could be
temporally built by the potential barrier, these quasi-bound states will decay into continuums through tunneling and are known as the shape resonances.

Alternatively, for the system with important nonadiabatic electronic couplings, obviously, region I is still the bound state region mainly pertaining to potential $V_{a1}^1$, and the quasi-bound states in region II would be altered by the electronic couplings. However in region IV, the bound states of potential $V_{d2}^2$ can not be sustained any more, due to the electronic couplings, they would leak or decay into potential $V_{a1}^1$ as continuum states, these states are known as the Feshbach resonances, or Fano resonances, interpreted as the results of interactions between bound and continuum channels. The left region III, or the avoided crossing (AC) region, becomes into a quite special region by the nonadiabatic interactions. Besides particle scattering, the avoided crossing of potentials is also important to a large number of optical spectra and dynamical processes [16, 18, 19]. Among these phenomena are the spectroscopic anomalies [20], predissociation [21], quenching [22], energy transfer processes [23], ion pair formation or recombination [24], chemi-ionization [25], collisional excitation [26], and the harpooning mechanism of chemical reactions [27].

Interestingly, there could be resonances in the AC region due to the electronic couplings between the potentials. However, the formation of these resonances are quite complex, since no adiabatic potentials can sustain the ‘bound’ states following the picture of Fano (see figure 1). An complementary way is to transform the system into the diabatic representation, then the bound and continuum states of the crossing diabatic potential energy curves (DPECs) $V_{d1}^1$ and $V_{d2}^2$ in the AC region could be roughly treated as bound and continuum channels for these resonances, respectively. The issues of representations are broadly and necessarily discussed for dynamics as heavy ion collisions and predissociation, due to the driving of nonadiabatic electronic couplings [16], and also molecular electronic structure calculations to go beyond the Born–Oppenheimer approximation. Many documentations on adiabatic and diabatic representations can be achieved [16, 28–30], here we only briefly summarized the framework for the two-level coupled system.

Generally, the total wavefunction of the system could be well built as the product basis set of electronic and nuclear functions, then the electronic levels are represented by the potential energy curves, and the nucleus evolve on these potential energy curves. In the adiabatic representation, the nuclear kinetic energy operator is nondiagonal and the potential energy operator is diagonal, while in the diabatic representation, the nuclear kinetic energy operator is diagonal and potential energy operator is nondiagonal [28]. Explicitly, in the diabatic representation, the total Hamiltonian may be written as

\[
H^d = \begin{pmatrix}
T(R) & 0 \\
0 & T(R)
\end{pmatrix} + \begin{pmatrix}
V_{d11}^d(R) & V_{d12}^d(R) \\
V_{d21}^d(R) & V_{d22}^d(R)
\end{pmatrix},
\]

where the kinetic $T(R) = -\frac{\hbar^2}{2\mu} \left[ \frac{d^2}{dR^2} - \mu \left( \frac{1}{R^2} \right) \right]$, $\mu$ is the reduced mass of the system, $R$ is the internuclear distance, $J$ is the rotational quantum number, $V_{a\text{ref}}^n(n = 1, 2)$ are the DPECs, and the off-diagonal potential energy curves $V_{d12}^d = V_{d21}^d$. In contrast, the total Hamiltonian in the adiabatic representation may be written as
\[ \mathbf{H} = \begin{pmatrix} T_{11}(R) & T_{12}(R) \\ T_{21}(R) & T_{22}(R) \end{pmatrix} + \begin{pmatrix} V_{11}^d(R) & 0 \\ 0 & V_{22}^d(R) \end{pmatrix}, \]  

where the diagonal kinetic matrix elements \( T_{\text{nn}}(R) = T(R) - \frac{d^2}{dR^2} B_{\text{nn}}(R) \) and its off-diagonal terms \( T_{\text{nl}}(R) = -\frac{d}{dR} \left( A_{\text{nl}}(R) \frac{d}{dR} + 2 B_{\text{nl}}(R) \right) \), with the radial coupling matrix elements defined as \( A_{\text{nl}}(R) = \langle \varphi_n^a | \frac{d}{dR} | \varphi_l^b \rangle \), and \( B_{\text{nl}}(R) = \langle \varphi_n^a | \frac{d^2}{dR^2} | \varphi_l^b \rangle \). Subscript \( \tau \) indicates the integration over the electronic coordinates between different adiabatic electronic states \( |\varphi_{\text{nn}}^a\rangle, |\varphi_{\text{nl}}^a\rangle \) is satisfied with a complete basis set, and \( V_{\text{nn}}^d(R) \) are the APECs. More details of the transformations between adiabatic and diabatic representations will be introduced in section 2.

Such a diabatic picture for resonances in AC region could also be applied to the existence of resonances in regions II and IV, i.e., the bound and continuum channels of resonances could be roughly ‘interpreted’ pertaining to either APECs or DPECs. However, it should be noted that the bound levels of APECs and DPECs differ from each other (especially the ones close to the AC region), and the resonance positions \((\varepsilon_n, \gamma)\) also differ from these bound levels [31, 32]. Resonances in regions II and IV could exhibit as sharp peaks in the scattering cross sections, and resonances in the AC region generally do not contribute much on the scattering cross sections can be roughly estimated by escaping doing scattering calculations [16, 35–38] or complex scaled structure calculations [39–41], and it would become practical to determine the candidate molecules when using resonances in the AC region for molecular manipulations [42–45].

All the issues of resonances are more or less related to the nonadiabatic electronic couplings, which couple or combine the independent electronic states (potentials) into a unified one. For such a coupled system, it can be equivalently described both in the adiabatic representation and the diabatic representation, which will be exemplified with the two-level system in section 2. Another issue of broad and long interest in the same coupled system is the nonadiabatic electronic transition (NET) [46–49], studying the nuclear motions on multiple potential energy curves. The Landau–Zener formula [47, 48] can well estimate the nonadiabatic transition probability for scatterings. Obviously, the issues of resonances and NET are intrinsically correlated by the nonadiabatic electronic couplings. So one possible way to promote the present investigations of resonances in the AC region could learn from the well-founded theories of NET. Further studies reveal that, a simple quantity proposed by Zhu and Nakamura [46, 50–52] to classify the coupling strength of nonadiabatic interactions, can be well applied to quantitatively estimate the importance of resonances in the AC region, and the relevant applications and results will be presented in section 3.

2. Transformations between adiabatic and diabatic representations

The Hamiltonians \( \mathbf{H}^\text{d} \) and \( \mathbf{H}^\text{f} \) can be unitarily transformed as \( \mathbf{H}^\text{d} = \mathbf{C}^\dagger \mathbf{H}^\text{f} \mathbf{C} \), where \( \mathbf{C}(R) \) is the transformation matrix created so that in the diabatic representation, its transformed radial coupling matrix \( \mathbf{A}^\text{d} = \mathbf{C}^\dagger \mathbf{A} \mathbf{C} + \mathbf{C}^\dagger \frac{d}{dR} \mathbf{C} \) is zero and in the limit of \( \mathbf{C}(R \to \infty) \to \mathbf{I} \), or as,

\[ \mathbf{A}(R)\mathbf{C}(R) + \frac{\partial}{\partial R} \mathbf{C}(R) = 0. \]

The relevant nuclear wave vectors of equations (1) and (2) satisfy \( \psi^\text{d} = \mathbf{C}^\dagger \psi^\text{a} \). For the present two level-system, the unitary matrix can be explicitly solved as

\[ \mathbf{C}(R) = \begin{pmatrix} \cos \eta(R) & \sin \eta(R) \\ -\sin \eta(R) & \cos \eta(R) \end{pmatrix}, \]

with the diabatic angle defined as \( \eta(R) = \int_R^{\infty} A_{12}(R')dR' = \frac{1}{2} \arctan \frac{2V_{12}^d(R)}{V_{11}^d(R)-V_{22}^d(R)} \). And the potential energy curves satisfy the relations

\[ V_{11,22}^d = \frac{1}{2} \left[ V_{11}^d + V_{22}^d \pm \sqrt{(V_{11}^d-V_{22}^d)^2+4(V_{12}^d)^2} \right]. \]

Note that in structure calculations, the potential energy curves and radial coupling matrix elements are generally and firstly calculated in the adiabatic representation within the Born–Oppenheimer approximation; after solving the transformation matrix from equation (3), the diabatic potential energy
curves and other parameters such as (transition) dipole moments can be achieved by unitary transformation from the adiabatic representation. Generally, if the nonadiabatic coupling is weak, or the curves and other parameters such as (transition) dipole moments can be achieved by unitary from the DPECs, with (DPECs could be roughly achieved by interchanging the APECs (see figure1) that Fj finally, we realize that the simplicity of the coupling strength is quite impressive, since a^2 can well indicate the situations that when the adiabatic representation or the diabatic representation could be employed efficiently. Explicitly, when a^2 ≪ 1, the system is weakly coupled, all the ‘bound’ and ‘continuum’ states of the system could be well estimated from the APECs, and the weak nonadiabatic coupling (a^2) slightly alters these states; while when a^2 ≫ 1, everything is reversed, the system is strongly coupled, all the ‘bound’ and ‘continuum’ states of the system could be well estimated from the DPECs, and the weak diabatic coupling (V^d_j) slightly alters these states; when a^2 ≃ 1, there would be no priority to employ either representation. Finally, we realize that the simple quantity a^2 is of crucial importance for the present interest of resonances in the AC region, since a^2 can efficiently and properly suggest us the ‘bound’ channels of resonances, and the ‘bound’ channels are quite important to build resonances following the picture of Fano. Our further investigations for different systems approve that a^2 can be well applied to quantitatively estimate the importance of resonances in the AC region, as revealed in the next section, for system with a^2 ≈ 1 (a^2 ≪ 1), resonance in the AC would abruptly (invisibly) change the particle scattering cross sections, and its contribution is unobtrusive when a^2 ≃ 1.

The next section presents the applications and discussions. Further theories involved in the present studies are quantum-mechanical molecular orbital close-coupling method (QMOCC) [16, 35–38] for ion scattering cross sections, and contour deformation method (CDM) [55] for resonance parameters. All these methods have been well documented in the literatures provided and will not be repeated here any more.

3. Results and discussion

A typical model system of the Mulliken C^+ type [56] is firstly investigated, to comprehensively represent all the properties of resonances in the particle scattering. The Child–Lefebvre model [57] is of this type and slightly modified as

\[
\begin{align*}
V^d_1(R) &= D_1 e^{-\alpha(R–R_e)} + D_2 \\
V^d_2(R) &= D_2 \left[1 - e^{-\beta(R–R_e)} \right]^2 \\
V^d_2(R) &= \beta_2 \left[1 + \frac{1}{e^{-(R-4.98821)}} \right]^{-1}
\end{align*}
\]

(7)

In the studies, the diabatic coupling (V^d_2) will be altered by changing \( \beta_2 \) to represent cases with different coupling strength (a^2), while the DPECs (V^d_1 and V^d_2) do not change. All the relevant parameters of the
Table 1. Parameters for the potential energy curves of modified Child-Lefebvre model [57].

| Parameter | Value       | Parameter | Value       | Parameter | Value       |
|-----------|-------------|-----------|-------------|-----------|-------------|
| $D_1$     | 18154.95 cm$^{-1}$ | $D_2$     | −8000 cm$^{-1}$ | $D_3$     | 15000 cm$^{-1}$ |
| $\alpha$  | 2.2039 Å$^{-1}$   | $\beta$  | 1.9685 Å$^{-1}$ | $R_e$     | 2.48 Å       |
| $R_c$     | 2.48 Å      |           |             |           |              |

 potentials are listed in table 1 with reduced mass $\mu = 8$ AMU, and the DPECs and APECs (transformed with equation (5)) are shown in figure 2 for different coupling cases. As clearly shown in figure 2, the upper APEC ($V_{a22}$) is a bound one and the lower APEC ($V_{a11}$) has a substantial barrier; with the increasing of $\beta$, the AC region becomes broader and the energy gap between the APECs becomes larger, corresponding to the decreasing of nonadiabatic couplings between the APECs. In this model, the DPECs are fixed, $F_j$ does not change; the diabatic coupling $V_X$ and parameter $a_2$ change with the variations of $\beta$; which is adjusted so that $a_2 = 10, 1.0, 0.1$ and 0.01, corresponding to values of $\beta$ being 575, 1238, 2670 and 5750 cm$^{-1}$, respectively.

With the full potential energy curves of figure 2 and supposing the lower state being the initial projecting channel, the elastic particle scattering cross sections are calculated by the advanced QMOCC method [16, 35–38]. To highlight the resonance effect in the AC region, the typical s-wave Feshbach resonances and elastic cross sections (ECS) are investigated as showcases, unless stated explicitly. Note that higher partial-waves can be studied in the same way without changes of the theory. The calculations have performed with full coupled channels (equation (1) or equation (2), FC – model), and only one channel of $V_{a11}$ (OC – model) to explore the coupling effects from the upper channel $V_{a22}$ and lower channel $V_{a11}$. Similar as in figures 1 and 3 shows the potentials (b) and QMOCC results (a) for the case of $\beta = 2670$ cm$^{-1}$ ($a^2 = 0.1$) as an example around the AC region. As is shows, the variations of ECS and resonance peaks depend strongly on the scattering energies, and the quite different structures of ECS in the AC region are surely related to the couplings. Furthermore, the sharp horizontal black lines (resonance peaks) in the cross sections do not precisely coincide with neither the bound levels of $V_{d22}$ nor the shape resonances of $V_{a11}$ and bound levels of $V_{a22}$. Detailed analysis are presented pertaining to figure 4.

Other relevant s-wave ECS around the energy region of AC are detailly presented in figure 4 for different cases of couplings ($\beta$). As revealed in figure 4, the ECS are dominated by the background modulations with the increasing of the scattering energy, resulting from the constructive and destructive interferences between the incoming and outgoing waves that their phases (or the scattering phase shift) differ by exactly...
Figure 3. Local s-wave Elastic scattering cross sections and potential energy curves of modified Child–Lefebvre model \([57]\) for the case of \(\beta_e = 2670 \text{ cm}^{-1}\). Red-bold line in panel (a) is ECS in the AC region. Purple-dash lines are bound states of DPEC \(V_{d22}\) shown in panel (b), the black-dotted and green-dotted lines are shape resonances of APEC \(V_{a11}\) and bound states of APEC \(V_{a22}\), respectively. This figure is a further extension of figure 1 with cross sections.

\((n + 1/2)\pi\) and \(n\pi\), respectively [6, 12]. Sharp structures on top of the background modulations are contributed by resonances, and some resonances can greatly destroy the background modulations and even contribute inverted window structures. Note that the phase shift would increase sharply by about \(\pi\) when the scattering energy passes the resonance, and generally decreases with the increasing of scattering energy [6, 12], so there would be always the cases that the phase shift could be \((n + 1/2)\pi\) or \(n\pi\), and the background modulations generally would appear accompanying with the resonances.

As also shown in figure 4, for the results between FC- and OC- models, when the scattering energy is below the potential barrier of \(V_{a11}\) (left side of AC region), both models produce quite similar ECS and resonance structures except in the energy region close to AC region, but such differences become smaller and smaller with the increasing of \(\beta_e\) or the decreasing of \(a^2\). While when the scattering energy is over the potential barrier of \(V_{a11}\), besides the significant differences between the background ECS of the two models, the FC-model is still featured by the resonance structures, while no remarkable resonance peaks exist in the OC-model; with the increasing of \(\beta_e\) or the decreasing of \(a^2\), the background modulations of FC-model gradually fade out, and both models produce almost the same ECS except the sharp resonance structures. All these features of similarities and differences of the ECS are directly related to the coupling strength of the system.

When \(a^2\) is far less than 1 \((a^2 = 0.01\) or \(\beta_e = 5750 \text{ cm}^{-1}\), figure 4(d)), the upper channel \((V_{a22})\) is weakly coupled to the lower one \((V_{a11})\), and the upper channel can hardly affect the elastic scatterings, then the FC- and OC- model would surely produce very similar results in the whole energy region, including the Shape resonances; Feshbach resonances exist once the system is coupled (FC-model) and their positions will move close to the bound states (vertical green-dotted line) of APEC \(V_{a22}\), but no resonance peaks can be observed in the AC region. While when \(a^2\) is much larger than 1 \((a^2 = 10\) or \(\beta_e = 575 \text{ cm}^{-1}\), figure 4(a)), the projecting channel \((V_{a11})\) is strongly coupled to the upper one \((V_{a22})\), so the differences of the ECS between the two models are quite large above the potential barrier of \(V_{a11}\), due to the contributions from the upper channel; the scattering and resonances are also strongly affected by the coupling even below the potential barrier around the AC region, such effects become tiny once the scattering energy is far below the potential barrier; all the resonance positions move to the bound states (vertical purple dash line) of diabatic potential \(V_{d22}\), indicating the efficiency and suitability to describe the strongly coupled system in the diabatic representation. In such a strongly coupled system, resonances in the AC region exhibit as sharp peaks (see the peak at \(\nu_{V_{d22}} = 18\) in figure 4(a)).
Figure 4. Elastic scattering cross sections (s-wave) of the modified Child–Lefebvre model shown in figure 2, the results of FC- and OC-model are presented in black-solid and blue-dash lines, respectively, red-bold lines are in the AC region, its left side is below the potential barrier of $V_{11}$. The vertical purple-dash and green-dotted lines are the positions of the bound states of DPEC $V_{22}$ and APEC $V_{11}$, respectively.

When $a^2$ is about 1 ($a^2 = 1$ or $\beta_e = 1238 \text{ cm}^{-1}$ (see figure 4(b)), both channels are coupled intermediately, the evolutions of ECS do not show much differences from that of strongly coupled case, however, Shape resonances below the potential barrier of $V_{11}$ have moved away from the bound states of diabatic potential $V_{22}$, and resonances in the AC region is not so sharp or significant any more. Such variations are more significant when $a^2 = 0.1$ or $\beta_e = 2670 \text{ cm}^{-1}$ (see figure 4(c)), where all the resonances have moved away from the bound states of $V_{22}$ and become close to the quasi-bound states of $V_{11}$ and bound states of $V_{22}$, and resonances in the AC region are buried in the background and become totally invisible.

In a short summary, resonances depend strongly on the electronic couplings and play important roles on the scatterings. For the weakly coupled system ($a^2 \ll 1$), resonances sit around the (quasi-) bound states of APECs, no resonances can be observed in the AC region; while resonances will move close to the bound states of DPECs when the system is strongly coupled ($a^2 \gg 1$), and resonances in the AC region exhibit significantly in the scattering; for the intermediately coupled system ($a^2 \simeq 1$), resonances will be around both the bound states of APECs and DPECs, and the tiny roles of resonances in the AC region could also been recorded in the scattering. Surprisingly, all these features agree quite well with the classifications of coupling strength with the dimensionless parameter $a^2$ suggested by Zhu and Nakamura [51]. One can conclude that the exhibition of resonances in the AC region is directly related to the coupling strength or parameter $a^2$, that for system with $a^2 \gg 1$ ($a^2 \ll 1$), resonances in the AC would abruptly (invisibly) change the cross sections, and its contribution is unobtrusive when $a^2 \simeq 1$.

As a first application of these results to real molecules, the coupled predissociation system of MgH [58, 59] is investigated. The potentials are described as

\[
\begin{align*}
V_{11}(R) &= M_1 e^{-b_1 R} + M_2 \\
V_{22}(R) &= M_3 \left(1 - e^{-b_2 (R - \alpha)}\right)^2 + M_4 \\
V_{12}(R) &= A_{\text{int}} e^{-\left(\frac{R - c_1}{c_2}\right)^2}
\end{align*}
\]

with the reduced mass $\mu = 0.9672 \text{ AMU}$ and other parameters listed in table 2. Resonances of this system have been extensively studied [58–62], here we focus on the ion scattering cross sections around the AC region. Figures 5(a) and (b) show the relevant results for the case of $A_{\text{int}} = 0.015 \text{ a.u.}$, broadly studied in previous literatures [58–62]. Further calculation shows $a^2 = 0.018$, much smaller than 1, indicating this
Table 2. Parameters for the potential energy curves of MgH predissociation system [58, 59].

| Parameter | Value          | Parameter | Value          | Parameter | Value          |
|-----------|----------------|-----------|----------------|-----------|----------------|
| $M_1$     | 95817.22 cm$^{-1}$ | $M_2$     | 5859.824 cm$^{-1}$ | $M_3$     | 38339.19 cm$^{-1}$ |
| $M_4$     | $-100.2809$ cm$^{-1}$ | $b_1$     | 0.7872477 Å$^{-1}$ | $b_2$     | 0.9766027 Å$^{-1}$ |
| $c_1$     | 1.736154 Å      | $c_2$     | 2.284 Å         | $c_3$     | 1.0 Å           |

Figure 5. Upper panels (a), (c) and (e) are the resonance parameters of MgH predissociation system for $a^2(A_{int}$ a.u.$) = 0.018 (0.015), 1.0 (0.00393) and 10 (0.001828), respectively, by CSM [58–60] (triangle) and present CDM (square). The corresponding s-wave elastic particle scattering cross sections are shown in the lower panels (b), (d) and (f), the red-bold lines are in the AC region.

predissociation system of MgH being a weakly coupled one. With the estimations from the previous model system, resonances in the AC region of this system should bury in the background modulations, which totally agrees with the ECS shown in figure 5(b) that only the background modulations are observed in the AC region. Resonance parameters from the present CDM [55] and previous CSM methods [58–60] are also shown in figure 5(a). Both methods produce the same resonance widths, however, the resonance parameters in the AC region can not be calculated due to its quite broad decay width. It turns invisible to read the broad resonance structures on the ECS (figure 5(a)), the width of such broad resonance should bury in the ECS modulation background, we would expect the lower limit of the broad resonance width to be $\sim 10^3$ cm$^{-1}$.

We also reduce the parameter $A_{int}$ to make artificial systems with stronger nonadiabatic couplings. Figures 5(c) and (d) and figures 5(e) and (f) show the relevant results for the cases with $a^2 = 1$ and $a^2 = 10$, respectively. As the figures show, resonances in the AC region exhibit significantly when $a^2 = 1$ (figure 5(d)), and appear as sharp peaks when $a^2 = 10$ (figure 5(f)), totally consistent with the estimations of the model system; resonance parameters in the AC region can be calculated, and their widths become smaller with the increasing of coupling strength. Note that the scattering cross sections are proportional to $|I - S(\varepsilon)|^2$, and resonances are the poles of $S$-matrix in the fourth quadrant of the complex energy plane as $\varepsilon_s = \varepsilon_{sr} - \frac{i}{2} \Gamma_{sr}$ [6], so when the scattering energy $\varepsilon$ passes over the pole or resonance through $\varepsilon_{sr}$, a peak structure would appear in the cross sections. Such a structure would be very sharp if $\Gamma_{sr}$ is small or the pole is close to the real energy axis; while this structure could never be observed if the resonance width is broad or the pole is far away from the real energy axis. So the exhibitions of resonances in the AC region are essentially related to their widths, and it looks that their widths would be small for strongly coupled system ($a^2 \gg 1$), and quite broad for weakly coupled one ($a^2 \ll 1$) in the AC regions. Note that the well-isolated resonance peaks can also be indicated by the Fano $q$-factor [5, 7], in figure 5 (b) the sharp peak in the lower
energy region is $q \approx -0.465$, and the two sharp peaks in the higher energy region are $q \approx 3.537$ and 1.439, respectively; besides, the well-formed resonance peak in AC region of figure 5(f) is $q \approx -0.551$.

The coupled $B^1\Sigma^+ \rightarrow D^1\Sigma^+$ states of CO are also illustrated, with all the potentials and parameters from reference [64], and $a^2 = 0.158$ is far less than 1. Figure 6 shows the resonance parameters and the s-wave ECS from the lower state $B^1\Sigma^+$ around the AC region. As shown in figure 6(a), both theoretical methods (the present CDM and CSM in the literature [63]) can produce the same resonance parameters, and many resonances are quite broad. The s-wave ECS are dominated by the background modulations (figure 6(b)), no resonances in the AC region can be observed in the cross sections, consistent with the estimations from the value of $a^2$. Note that four sharp resonance peaks can be observed away from the AC region, corresponding to the narrow resonances ($\Gamma_{\alpha} < 90$ cm$^{-1}$); other resonances (including the ones in the AC region) are quite broad ($\Gamma_{\alpha} > 600$ cm$^{-1}$) and play invisible roles on the cross sections. Figures 5(b) and 6(b) also show that the background modulations are more pronounced in the AC region in CO than in MgH, it could be related to the fact that CO is about 7 times heavier than MgH. CO will experience much more rapid changes of wave numbers and phases than MgH in the AC energy region of $\sim 6 \times 10^3$ cm$^{-1}$ (see figures 5(b) and 6(b)), and more modulation structures are expected.

Extended applications to the existing results from the literatures also approve the present studies. Taking the OH molecule as an example, figure 7 of reference [32] shows its APECs are sharply avoided, $a^2 \approx 14.5 \gg 1$ can be easily obtained. We will estimate that the resonances in the AC region should play very important roles in such a strongly coupled system. As shown in figures 6(b) and 8 of reference [32], the photodissociation cross sections surely exhibit a very sharp peak in the AC region (at about 10 eV), totally consistent with the determinations from $a^2$. The generality and applicability of the present conclusions would be expected.

4. Conclusions

Resonances in the AC region on particle scattering are comprehensively investigated. The contributions of resonances in the AC region to the cross sections depend strongly on the coupling strength of the system, and the simple quantity $a^2$ proposed by Zhu and Nakamura can be well applied to quantitatively estimate the importance of resonances in the AC region. For the strongly (weakly) coupled system with $a^2 \gg 1$ ($a^2 \ll 1$), resonances in the AC region would abruptly (invisibly) change the cross sections, and their contributions are unobtrusive when $a^2 \approx 1$. Example applications of the quantity $a^2$ for different system can well explain the evolutions of cross sections in the AC region. Further analysis shows that the present conclusions are essentially related to the resonance widths, that narrow resonances could exhibit strongly as sharp peaks, and broad ones would bury in the background. Practically, this work provides an easy way to determine the candidate molecules when studying the resonances in the AC region.
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