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Exponential bound of the width of molecular predissociation resonances

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1 Introduction

The main purpose of this article is to announce the results of [1] on the Molecular predissociation resonances below an energy level crossing. We determine the precise positions of resonances for a system of Schrödinger equations. In particular the imaginary parts (widths) of the resonances are exponentially small and the indices are determined by the Agmon distance of the minimum of potentials.

Before we consider the molecular predissociation resonances, it is instructive to recall the relation of spectrum and resonance to classical trajectories. We consider the Hamiltonian $H = -h^2\Delta + V$ with a potential V and the solution $(x(t), \xi(t))$ of the Hamilton's equation of its symbol $H(x,\xi) = \xi^2 + V(x)$. If a potential $V \in C^1(\mathbb{R}^n)$ satisfies $V(x) \to +\infty$ as $|x| \to +\infty$, $x(t)$ of any solution $(x(t), \xi(t))$ of the Hamilton's equation is bounded and H has purely discrete spectrum (see, e.g., [13, Theorem XIII.16]). The corresponding eigenfunctions do not change as time passes except for multiplication by complex numbers with modulus 1. On the other hand, if $V(x) \in C^1(\mathbb{R}^n)$ satisfies $\partial^\alpha V(x) = \langle x\rangle^{-\rho-|\alpha|}$, $|\alpha| \leq 1$, there are unbounded trajectories for energies $E > 0$ and $(0,\infty)$ is continuous spectrum. The functions corresponding to the continuous spectrum scatters as time passes.

Resonances appear if for an interval of energy there are both bounded and unbounded trajectries. Resonances are complex eigenvalues of the formal eigenfunctions of the Hamiltonian which are not in $L^2(\mathbb{R}^n)$ because of the growth as $|x| \to \infty$. A formal eigenfunction u corresponding to a resonance E is outgoing, that is, in one dimensional space if $\limsup_{x\to+\infty} V(x) < \operatorname{Re} E$ then

$$u \sim (E-V)^{1/4} e^{i\int_a^x (E-V(t))^{1/2}dt/h} \text{ as } x \to +\infty,$$

and if $\limsup_{x\to-\infty} V(x) < \operatorname{Re} E$ then

$$u \sim (E-V)^{1/4} e^{-i\int_a^x (E-V(t))^{1/2}dt/h} \text{ as } x \to -\infty,$$

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where $a \in \mathbb{R}$ is a constant. Note that u decays exponentially on $\mathbb{R}_\theta := e^{i\theta}\mathbb{R}$ where $\theta > 0$ is large enough compared to $\operatorname{Im} E$. We use this property to define resonances later.

Let E be a resonance and u the corresponding eigenfunction and assume that the region $\{x : V(x) < \operatorname{Re} E\}$ is divided into a bounded region Ω and an unbounded region If χ is a cutoff function on a region Ω' including Ω, the part of $e^{-itH}\chi u$ inside Ω' decays as $e^{-\operatorname{Im} Et}$ (see Skibsted [14, 15]). Thus if the imaginary part (width) of the resonance is small, the square integrable approximation of the resonance function stays in Ω for a long period.

In the theory of shape resonances of Schrödinger operators it is known that widths of the resonances have exponential bounds as $C_\epsilon e^{-2(1-\epsilon)S/h}$ where ϵ can be taken arbitrarily small, h is the semiclassical parameter and S is the Agmon distance between the bounded and unbounded regions where the potential is below the real part of the resonance (see, e.g., [3, 6, 7]).

In this article we determine positions of resonances of operators related to molecular predissociation. In particular we find that widths of the resonances have exponential bounds as above with the Agmon distance of the minimum of the potentials.

2 The model for molecular predissociation

The study of Schrödinger equation of systems of nuclei and electrons is reduced to that of matrices of pseudodifferential operators as follows:

$$P := \operatorname{diag}(P_1, \dots, P_m) + hR(x, hD_x),$$

where $R(x, hD_x)$ is a symmetric $m \times m$ matrix of pseudodifferential operators of order less than one, $P_j := -h^2\Delta + V_j(x)$ and V_j are potentials corresponding to electronic energy levels. This reduction scheme is called the Born–Oppenheimer approximation and justified in both the eigenvalue problem (see Klein-Martinez-Seiler-Wang [9]) and the study of the time-dependent Schrödinger equations (see Martinez-Sordoni [11]).

In Martinez [10], Nakamura [12], Baklouti [2] and Grigis-Martinez [5], they study resonances for two electronic levels with potentials that do not intersect and obtain exponential bound on their widths. Klein [8] studies the case of more than two intersecting potentials some of them forming wells to confine nuclei and the others being non-trapping. In this case, it is shown that the widths of the resonances with real parts converging to the bottom of the potential well have the exponential bound as in the case of usual Schrödinger operators with Agmon distance for $V_{\min} = \min_{1 \le j \le m} V_j$.

In Fujiié-Martinez-Watanabe [4] they considered the following operator.

$$P = \begin{pmatrix} P_1 & hW \\ hW^* & P_2 \end{pmatrix}, \tag{1}$$

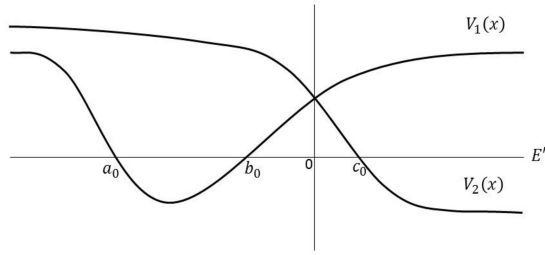

Fig. 1: The graph of the two potentials on the real axis

where $P_j = -h^2\Delta + V_j(x), j = 1, 2\ x \in \mathbb{R}$, $W = r_0(x) + hr_1(x)\partial_x$ and W^* is the formal adjoint of W. They studied the resonances with real parts in the distance of order $h^{2/3}$ from a crossing of two potentials. Under a condition of ellipticity on the interaction they obtain the exact order $h^{5/3}$ of the widths of the resonances.

3 Assumptions and the main result

We assume $V_1(x)$ in (1) has a well and $V_2(x)$ is lower than the energy considered for x large enough. We also assume that V_1 and V_2 cross transversally (see Fig. 1). The components governed by P_1 and P_2 interact due to the off-diagonal elements hW and hW^*. More precisely, we suppose the following conditions on $V_1(x)$, $V_2(x)$ and $r_0(x)$, $r_1(x)$.

Assumption (A1) $V_1(x)$ and $V_2(x)$ are real-valued analytic functions on $\mathbb{R}$ and extend to holomorphic functions in the complex domain,

$$\Gamma = \{x \in \mathbb{C}; |\mathrm{Im}\, x| < \delta_0\langle \mathrm{Re}\, x\rangle\},$$

where $\delta_0 > 0$ is a constant and $\langle t\rangle := (1 + |t|^2)^{1/2}$.

Assumption (A2) For $j = 1, 2$, V_j admits limits as $\mathrm{Re}\, x \to \pm\infty$ in Γ and there exists a real number E' such that

$$\lim_{\substack{\mathrm{Re}\, x\to-\infty \\ x\in\Gamma}} V_1(x) > E'; \quad \lim_{\substack{\mathrm{Re}\, x\to-\infty \\ x\in\Gamma}} V_2(x) > E';$$
$$\lim_{\substack{\mathrm{Re}\, x\to+\infty \\ x\in\Gamma}} V_1(x) > E'; \quad \lim_{\substack{\mathrm{Re}\, x\to+\infty \\ x\in\Gamma}} V_2(x) < E'.$$

Assumption (A3) There exist real numbers $a_0 < b_0 < 0 < c_0$ such that

- $V_1 > E'$ and $V_2 > E'$ on $(-\infty, a_0)$;
- $V_1 < E' < V_2$ on (a_0, b_0);

- $E' < V_1 < V_2$ on $(b_0, 0)$;
- $E' < V_2 < V_1$ on $(0, c_0)$;
- $V_2 < E' < V_1$ on $(c_0, +\infty)$,

Moreover, one has

$$V_1'(a_0) < 0,\ V_1'(b_0) > 0,\ V_2'(c_0) < 0,\ V_1'(0) > V_2'(0).$$

Assumption (A4) r_0 and r_1 are bounded analytic functions on Γ, and $r_0(x)$ and $r_1(x)$ are real when x is real. The resonances of P can be defined as eigenvalues of the operator P acting on $L^2(\mathbb{R}_\theta) \oplus L^2(\mathbb{R}_\theta)$ where $\mathbb{R}_\theta$ is a complex distortion of $\mathbb{R}$ that coincides with $e^{i\theta}\mathbb{R}$ for $x \gg 1$. We denote by $\mathrm{Res}(P)$ the set of the resonances of P.

The examples of the potentials satisfying the assumptions are $-\frac{2}{x^2+1} = i\left(\frac{1}{x-i} - \frac{1}{x+i}\right)$ and $\tanh(-x) = \frac{e^{-x}-e^{x}}{e^{-x}+e^{x}}$ translated appropriately.

We consider the resonances with real parts close to E' above and imaginary parts of order $\mathcal{O}(h)$. For $d > 0$ small enough, we set $I := [E' - d, E' + d]$. We fix C_0 arbitrarily large, and we study the resonances of P lying in the set

$$\mathcal{D}_I := \{E \in \mathbb{C}; \mathrm{Re}\, E \in I,\ -C_0 h < \mathrm{Im}\, E < 0\}.$$

For $E \in \mathcal{D}_I$, $V_1(x) = E$ has only two solutions and we denote the solution with the smaller real part and the larger one by $a = a(E)$ and $b = b(E)$ respectively. We also denote the unique solution of $V_2(x) = E$ for $E \in \mathcal{D}_I$ by $c = c(E)$. For $E \in \mathcal{D}_I$ we define the action,

$$\mathcal{A}(E) := \int_{a(E)}^{b(E)} \sqrt{E - V_1(t)}dt.$$

Then our result is the following.

Theorem 3.1 *Under Assumptions (A1)-(A4), for $h > 0$ small enough, one has,*

$$\mathrm{Res}(P) \cap \mathcal{D}_I = \{E_k(h); k \in \mathbb{Z}\} \cap \mathcal{D}_I$$

where $E_k(h)$'s are complex numbers that satisfy,

$$\mathrm{Re}\, E_k(h) = e_k(h) + \mathcal{O}(h^{3/2})$$

$$\mathrm{Im}\, E_k(h) = -\frac{h^2\pi}{4}\mathcal{A}'(e_k(h))^{-1}e^{-2S(e_k)/h}(V_1(0) - e_k(h))^{-1/2}(V_1'(0) - V_2'(0))^{-1}$$
$$\cdot (r_0(0) + r_1(0)\sqrt{V_1(0) - e_k(h)})^2 + \mathcal{O}(h^{5/2}e^{-2S(e_k)/h}),$$

uniformly as $h \to 0_+$ where

$$e_k = e_k(h) := \mathcal{A}^{-1}((k + \frac{1}{2})\pi h),$$

$$S(e_k) = \int_{b(e_k)}^{0} \sqrt{V_1(t) - e_k}dt + \int_{0}^{c(e_k)} \sqrt{V_2(t) - e_k}dt.$$

4 Outline of the proof of the main theorem

The proof of the theorem is based on the construction of the solutions to the system as in Fujiie-Martinez-Watanabe [4]. We introduce a function $f \in C^\infty(\mathbb{R}_+, \mathbb{R}_+)$ such that $f(x) = x$ for x large enough and $f(x) = 0$ for $x \in [0, x_\infty]$ for $x_\infty > 0$ large enough. In the sequel we will use the following notation:

$$I_b := [b, 0] \ ; \ I_c := [0, c];$$
$$I_L := (-\infty, b] \ ; \ I_R^\theta := F_\theta([c, +\infty)),$$

for real b and c where $F_\theta(x) := x + i\theta f(x)$. For complex b and c, we denote by the same notation appropriate curves in the complex plane connecting the end points.

The procedure of the proof is as follows. First, for $E \in D_I$ we construct the solutions to the system on I_b, I_c, I_L and I_R^θ using the solutions to $(P_j - E)u = 0, \ j = 1, 2$ constructed by Yafaev's construction. Next we consider the connection of the solutions at 0 and change the basis of the solutions so that the transition matrix at 0 will be simple. We also consider the connection of the solutions at b and c. Finally, we obtain the condition on E that the decaying solutions on I_L and I_R^θ are linearly dependent. We call this condition the quantization condition.

4.1 Construction of the solutions

Let x_0 be a point between a and b. By Yafaev's construction (see Yafaev [16] and appendix in Fujiie-Martinez-Watanabe [4]) we obtain the solutions $u_{1,R}^\pm(x)$ and $u_{1,L}^\pm(x)$ to $(P_1 - E)u = 0$ on the right and left of x_0 such that

$$u_{1,R}^\pm(x) \sim (1 + \mathcal{O}(h))\frac{h^{1/6}}{\sqrt{\pi}}(V_1(x) - E)^{-1/4} e^{\pm \int_{b(E)}^x \sqrt{V_1(t) - E}dt/h}, \ (x \to +\infty),$$

and

$$u_{1,L}^\pm(x) \sim (1 + \mathcal{O}(h))\frac{h^{1/6}}{\sqrt{\pi}}(V_1(x) - E)^{-1/4} e^{\mp \int_{a(E)}^x \sqrt{V_1(t) - E}dt/h}, \ (x \to -\infty).$$

We also obtain the solutions $u_{2,L}^\pm(x)$ to $(P_2 - E)u = 0$ such that

$$u_{2,L}^\pm(x) \sim (1 + \mathcal{O}(h))\frac{h^{1/6}}{\sqrt{\pi}}(V_2(x) - E)^{-1/4} e^{\mp \int_{c(E)}^x \sqrt{V_2(t) - E}dt/h}, \ (x \to -\infty);$$
$$e^{\mp i\frac{\pi}{4}}\left(\frac{1}{2}a_2^- u_{2,L}^- \pm i a_2^+ u_{2,L}^+(x)\right)$$
$$\sim (1 + \mathcal{O}(h))\frac{h^{1/6}}{\sqrt{\pi}}(E - V_2(x))^{-1/4} e^{\mp i \int_{c(E)}^x \sqrt{E - V_2(t)}dt/h}, \ (x \to +\infty).$$

We define $u^{\pm}_{2,R}$ as

$$u^{\pm}_{2,R} := e^{\mp i\frac{\pi}{4}}(\frac{1}{2}a^{-}_{2}u^{-}_{2,L} \pm ia^{+}_{2}u^{+}_{2,L}).$$

To see the growth and decay from the points b and c, we define the solutions $u^{\pm}_{j,b}$ on I_L, $u^{\pm}_{j,c}$ on I^{θ}_{R}, $v^{\pm}_{j,b}$ on I_b and $v^{\pm}_{j,c}$ on I_c as follows:

$$\begin{aligned}
u^{\pm}_{1,b} &:= u^{\pm}_{1,L},\ u^{+}_{2,b} := e^{-S_2/h}u^{+}_{2,L},\ u^{-}_{2,b} := e^{S_2/h}u^{-}_{2,L},\\
u^{\pm}_{2,c} &:= u^{\pm}_{2,R},\ u^{+}_{1,c} := e^{-S_1/h}u^{+}_{1,R},\ u^{-}_{1,c} := e^{S_1/h}u^{-}_{1,R},\\
v^{\pm}_{1,b} &:= u^{\pm}_{1,R},\ v^{+}_{2,b} := e^{S_2/h}u^{-}_{2,L},\ v^{-}_{2,b} := e^{-S_2/h}u^{+}_{2,L},\\
v^{\pm}_{2,c} &:= u^{\pm}_{2,L},\ v^{+}_{1,c} := e^{S_1/h}u^{-}_{1,R},\ v^{-}_{1,c} := e^{-S_1/h}u^{+}_{1,R},
\end{aligned}$$

where $S_1 := \int_b^c \sqrt{V_1(t)-E}dt$, $S_2 := \int_b^c \sqrt{V_2(t)-E}dt$.

For $E \in D_I$ we can define a fundamental solutions,

$$K_{1,b}C(I_b) \to C^2(I_b)$$

of $P_1 - E$ and

$$K_{2,b} : C(I_b) \to C^2(I_b)$$

of $P_2 - E$ on I_b by setting for $v \in C(I_b)$,

$$\begin{aligned}
K_{1,b}[v](x) &:= \frac{1}{h^2\mathcal{W}[v^{-}_{1,b}, v^{+}_{1,b}]}\left(v^{-}_{1,b}(x)\int_b^x v^{+}_{1,b}(t)v(t)dt + v^{+}_{1,b}(x)\int_x^0 v^{-}_{1,b}(t)v(t)dt\right),\\
K_{2,b}[v](x) &:= \frac{1}{h^2\mathcal{W}[v^{-}_{2,b}, v^{+}_{2,b}]}\left(v^{-}_{2,b}(x)\int_b^x v^{+}_{2,b}(t)v(t)dt + v^{+}_{2,b}(x)\int_x^0 v^{-}_{2,b}(t)v(t)dt\right),
\end{aligned}$$

where $\mathcal{W}[v^{-}_{1,b}, v^{+}_{1,b}]$ is the Wronskian of $v^{-}_{1,b}$ and $v^{+}_{1,b}$ and so on. Then we have $(P_1-E)K_{1,b} = \mathbf{1}$ and $(P_2 - E)K_{2,b} = \mathbf{1}$. Even if we replace the first term and the second one in the parenthesis on the right-hand side by $-v^{-}_{1,b}(x)\int_x^0 v^{+}_{1,b}(t)v(t)dt$ and $-v^{+}_{1,b}(x)\int_b^x v^{-}_{1,b}(t)v(t)dt$ respectively, the operator is still a fundamental solution. We denote them by $K''_{1,b}$ and $K'_{1,b}$ respectively.

Noting

$$Pu = Eu \Leftrightarrow \begin{cases}(P_1 - E)u_1 = -hWu_2\\ (P_2 - E)u_2 = -hW^*u_1\end{cases},$$

we set $u_2 = -hK_{2,b}W^*u_1$,. Then we have

$$(P_1 - E)u_1 = h^2WK_{2,b}W^*u_1,$$

and solutions are given by

$$u_1 = v^{\pm}_{1,b} + h^2K_{1,b}WK_{2,b}W^*u_1.$$

Thus by the successive approximation we obtain solutions

$$w^{\pm}_{1,b} := \begin{pmatrix} v^{\pm}_{1,b} + hK_{1,b}W\sum_{j\geq 0} M_b^j(hK_{2,b}W^*v^{\pm}_{1,b}) \\ -\sum_{j\geq 0} M_b^j(hK_{2,b}W^*v^{\pm}_{1,b}) \end{pmatrix},$$

on I_b where $M_b := h^2K_{2,b}W^*K_{1,b}W$. We can see by some estimates for fundamental solutions that the series in the solutions converge. We can see also that the leading term is ${}^t(v^{\pm}_{1,b}, 0)$ and the order of the remaining terms with respect to h are that of $v^{\pm}_{1,b}$ times $h^{1/2}$. We can construct solutions $w^{\pm}_{2,b}$ in the similar way, but we need to use the fundamental solutions $K'_{1,b}$ and $K''_{1,b}$ instead of $K_{1,b}$ so that the leading terms will be ${}^t(0, v^{\pm}_{2,b})$.

In the same way we can construct solutions $w^{\pm}_{j,c}$ on I_c with leading terms ${}^t(v^{\pm}_{1,c}, 0)$ and ${}^t(0, v^{\pm}_{2,c})$. On the intervals I_L and I^{θ}_R we consider only decaying solutions. In the similar way as on I_b and I_c we construct solutions $w_{1,L}$, $w_{2,L}$, $w_{1,R}$ and $w_{2,R}$ with leading terms ${}^t(u^-_{1,b}, 0)$, ${}^t(0, u^-_{2,b})$, ${}^t(u^-_{1,c}, 0)$ and ${}^t(0, u^-_{2,c})$ respectively. Then the solutions $w_{j,L}$ and $w_{j,R}$ satisfy,

$$w_{j,L} \in L^2(I_L) \oplus L^2(I_L)\ ;\ w_{j,R} \in L^2(I^{\theta}_R) \oplus L^2(I^{\theta}_R).$$

4.2 Connection of the solutions

To calculate the condition that the decaying solutions on the left and right intervals are linearly dependent, we need to consider the connection at 0, b and c. As for the connection at 0, we define the 4×4 transition matrix T as follows:

$$\begin{pmatrix} w^+_{1,b} \\ w^-_{1,b} \\ w^+_{2,b} \\ w^-_{2,b} \end{pmatrix} = T \begin{pmatrix} w^+_{1,c} \\ w^-_{1,c} \\ w^+_{2,c} \\ w^-_{2,c} \end{pmatrix}.$$

For the calculation of the quantization condition, we replace the basis $w^{\pm}_{j,b}$ and $w^{\pm}_{j,c}$ with the new ones $\tilde{w}^{\pm}_{j,b}$ and $\tilde{w}^{\pm}_{j,c}$ so that the matrix $\tilde{T}$ defined by

$$\begin{pmatrix} \tilde{w}^+_{1,b} \\ \tilde{w}^-_{1,b} \\ \tilde{w}^+_{2,b} \\ \tilde{w}^-_{2,b} \end{pmatrix} = \tilde{T} \begin{pmatrix} \tilde{w}^+_{1,c} \\ \tilde{w}^-_{1,c} \\ \tilde{w}^+_{2,c} \\ \tilde{w}^-_{2,c} \end{pmatrix},$$

will have the following form;

$$\tilde{T} = \begin{pmatrix} 0 & \tilde{t}_{12} & 0 & \tilde{t}_{14} \\ \tilde{t}_{21} & 0 & \tilde{t}_{23} & 0 \\ 0 & \tilde{t}_{32} & 0 & \tilde{t}_{34} \\ \tilde{t}_{41} & 0 & \tilde{t}_{43} & 0 \end{pmatrix}. \tag{2}$$

The asymptotic behavior of $\tilde{w}^{\pm}_{j,b}$ and $\tilde{w}^{\pm}_{j,c}$ are same as those of $w^{\pm}_{j,b}$ and $w^{\pm}_{j,c}$ respectively.

Next, we calculate the coefficients of $\tilde{w}^{\pm}_{j,b}$ (resp., $\tilde{w}^{\pm}_{j,c}$) in the representation of $w_{1,L}$ and $w_{2,L}$ (resp., $w_{1,R}$ and $w_{2,R}$) as linear conbinations of $\tilde{w}^{\pm}_{j,b}$ (resp., $\tilde{w}^{\pm}_{j,c}$). We can write as folows:

$$\begin{aligned}
w_{1,L} &= D_L^{-1}(a_1^+\tilde{w}^+_{1,b} + a_1^-\tilde{w}^-_{1,b} + a_2^+\tilde{w}^+_{2,b} + a_2^-\tilde{w}^-_{2,b}),\\
w_{2,L} &= D_L^{-1}(b_1^+\tilde{w}^+_{1,b} + b_1^-\tilde{w}^-_{1,b} + b_2^+\tilde{w}^+_{2,b} + b_2^-\tilde{w}^-_{2,b}),\\
w_{1,R} &= D_R^{-1}(c_1^+\tilde{w}^+_{1,c} + c_1^-\tilde{w}^-_{1,c} + c_2^+\tilde{w}^+_{2,c} + c_2^-\tilde{w}^-_{2,c}),\\
w_{2,R} &= D_R^{-1}(d_1^+\tilde{w}^+_{1,c} + d_1^-\tilde{w}^-_{1,c} + d_2^+\tilde{w}^+_{2,c} + d_2^-\tilde{w}^-_{2,c}),
\end{aligned} \tag{3}$$

where D_L and D_R are Wronskians

$$\begin{aligned}
D_L &= \mathcal{W}[\tilde{w}^+_{1,b}, \tilde{w}^-_{1,b}, \tilde{w}^+_{2,b}, \tilde{w}^-_{2,b}],\\
D_R &= \mathcal{W}[\tilde{w}^+_{1,c}, \tilde{w}^-_{1,c}, \tilde{w}^+_{2,c}, \tilde{w}^-_{2,c}].
\end{aligned}$$

4.3 Quantization condition

The condition for $E \in D_I$ to be a resonance is that the some linear combination of the decaying solutions $w_{1,L}$ and $w_{2,L}$ and that of $w_{1,R}$ and $w_{2,R}$ are linearly dependent, that is, $w_{1,L}$, $w_{2,L}$, $w_{1,R}$ and $w_{2,R}$ are linearly dependent. This condition can be written as,

$$\mathcal{W}_0(E) = \mathcal{W}[w_{1,L}, w_{2,L}, w_{1,R}, w_{2,R}] = 0. \tag{4}$$

We substitute the right-hand side of (3) for $w_{j,L}, w_{j,R}$ in (4) and develop the Wronskian as a sum of terms of the form $C(h)\mathcal{W}[w_1, w_2, w_3, w_4]$ where $C(h)$ is a constant, w_1, w_2 and w_3, w_4 are chosen from $w^{\pm}_{j,b}$, $(j = 1, 2)$ and $w^{\pm}_{j,c}$, $(j = 1, 2)$ respectively. Then the leading term is $(a_1^+b_2^+ - b_1^+a_2^+)(c_1^+d_2^+ - d_1^+c_2^+)\mathcal{W}[\tilde{w}^+_{1,b}, \tilde{w}^+_{2,b}, \tilde{w}^+_{1,c}, \tilde{w}^+_{2,c}]$. Moreover, if only one of the w_j, $(j = 1, \ldots, 4)$ is chosen from $w^-_{j,b}$ or $w^-_{j,c}$, then by the form of $\tilde{T}$ in (2) we can see that $\mathcal{W}[w_1, w_2, w_3, w_4] = 0$. Thus we have.

$$\begin{aligned}
D_L^2D_R^2\mathcal{W}_0(E) =&(a_1^+b_2^+ - b_1^+a_2^+)(c_1^+d_2^+ - d_1^+c_2^+)\mathcal{W}[\tilde{w}^+_{1,b}, \tilde{w}^+_{2,b}, \tilde{w}^+_{1,c}, \tilde{w}^+_{2,c}]\\
&+ (a_1^-b_2^+ - b_1^-a_2^+)(c_1^+d_2^- - d_1^+c_2^-)\mathcal{W}[\tilde{w}^-_{1,b}, \tilde{w}^+_{2,b}, \tilde{w}^+_{1,c}, \tilde{w}^-_{2,c}]\\
&+ \mathcal{O}(e^{\max\{A_1-B_1-A_2+B_2,\ -A_1+B_1+A_2-B_2\}}),
\end{aligned} \tag{5}$$

where

$$\begin{aligned}
A_1 &:= \int_b^0 \sqrt{V_1(t) - E}dt/h,\ B_1 = \int_0^c \sqrt{V_1(t) - E}dt/h,\\
A_2 &:= \int_0^c \sqrt{V_2(t) - E}dt/h,\ B_2 = \int_b^0 \sqrt{V_2(t) - E}dt/h.
\end{aligned}$$

Since we can calculate the coefficients and Wronskians in (5), we can rewrite (5) as,

$$\cos\frac{\mathcal{A}(E)}{h} + f(E,h) = hF(E,h). \tag{6}$$

where $f(E,h)$ and $F(E,h)$ are analytic for $E \in \mathcal{D}_I$, $f(E,h)$ is real for real E and

$$\begin{aligned} f(E,h) =& \mathcal{O}(h^{1/2}), \\ F(E,h) =& -\frac{\pi}{4i}\left(\sin\frac{\mathcal{A}(E)}{h}\right) e^{-2A_1-2A_2}(V_1(0)-E)^{-1/2} \\ & \cdot (V_1'(0)-V_2'(0))^{-1}(r_0(0)+r_1(0)\sqrt{V_1(0)-E})^2 + \mathcal{O}(h^{1/2}e^{-2A_1-2A_2}). \end{aligned}$$

Using the Rouché's theorem we can see that for sufficiently large $C_0' > 0$ and sufficiently small $h > 0$, $\cos\mathcal{A}(z)/h + f(z,h) = 0$ has a unique solution $\tilde{e}_k(h)$ in $B(e_k; C_0'h^{3/2})$ for $e_k \in \tilde{I}$ and conversely, all the roots in $\mathcal{D}_I$ are of this type. Considering the variation of $\cos\mathcal{A}(z)/h$, we can also see that $\tilde{e}_k(h) \in \mathbb{R}$. Applying the Rouché's theorem again, we conclude that for sufficiently large $C_0'' > 0$ and sufficiently small $h > 0$, (6) has a unique solution $E_k(h)$ in

$$B(\tilde{e}_k; C_0''h^2e^{-2A_1-2A_2}),$$

Substituting E_k into (6) by an easy calculation we obtain the explicit expression of $\operatorname{Im} E_k$ as in Theorem 3.1.

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References

[1] S. Ashida, Molecular predissociation resonances below an energy level crossing. in preparation.

[2] H. Baklouti, Asymptotique des largeurs de résonances pour un modéle d'effet tunnel microlocal, *Ann. Inst. H. Poincaré Phys. Theor.* **68** (1998), 179-228

[3] J. M. Combes, P. Duclos, M. Klein, R. Seiler, The shape resonance, *Commun. Math. Phys.* **110** (1987), 215-236

[4] S. Fujiié, A. Martinez, T. Watanabe, Molecular predissociation resonances near an energy-level crossing I: Elliptic interaction, *J. Differential Equations* **260** (2016), 4051-4085

[5] A. Grigis, A. Martinez, Resonance widths in a case of multidimensional phase space tunneling, *Asymptotic Anal.* **391** (2015), 33-90

[6] B. Helffer, J. Sjöstrand, Résonances en limite semi-classique, *Mém. Soc. Math. France* **24-25** (1986), 1-228

[7] P. D. Hislop, I. M. Sigal, Introduction to spectral theory: with applications to Schrödinger operators, Appl. Math. Sci., vol. 113. Springer-Verlag. New York, (1996)

[8] M. Klein, On the mathematical theory of predissociation, *Ann. Physics* **178** (1987), 48-73

[9] M. Klein, A. Martinez, R. Seiler, X. P. Wang, On the Born–Oppenheimer expansions for polyatomic molecules, *Commun. Math. Phys.* **143** (1992), 607-639

[10] A. Martinez, Estimates on complex interactions in phase space, *Math. Nachr.* **167** (1994), 203-254

[11] A. Martinez, V. Sordoni, Twisted pseudodifferential calculus and application to the quantum evolution of molecules, *Memoirs of the AMS.* **936** (2009)

[12] S. Nakamura, On an example of phase-space tunneling, *Ann. Inst. H. Poincaré Phys. Theor.* **63** (1995), 221-229

[13] M. Reed, B. Simon, Methods of modern mathematical physics. I-IV. (Academic Press, New York, 1972, 1975, 1979, 1978)

[14] E. Skibsted, Truncated Gamow functions, α-decay and the exponential law, *Commun. Math. Phys.* **104** (1986), 591-604

[15] E. Skibsted, On the evolution of resonance states, *J. Math. Anal. Appl.* **141** (1989), 27-48

[16] D. R. Yafaev, The semiclassical limit of eigenfunctions of the Schrödinger equation and the Bohr-Sommerfeld quantization condition, revisited, *Algebra i Analiz* **22** (6) (2010), 270-291; translation in *St. Petersburg Math. J.* **22** (2011), 1051-1067