Resonances of metastable molecular systems

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Quantum resonances and related topics: Conference in honor of André Martinez 60th birthday

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Metastable states

A Characterization of a state of a given quantum system with initial condition $\psi_0 \in \mathcal{H}$ ($\|\psi_0\| = 1$) is given by the so called the *survival probability* (*persistence probability*):

$$\mathcal{P}_{\psi_0}(t) := |a_{\psi_0}(t)|^2; \; a_{\psi_0}(t) = \big(\psi(t), \psi_0\big)$$

where, $\psi(t) = U(t)\psi_0 =$ and $U(.)$ is the propagator associated to the Hamiltonian H of the system.

Here we consider H independent of time so $U(t) = \exp(-itH)$

Metastable states

Then ψ_0 is a metastable state if *the survival amplitude*

$$a_{\psi_0}(t) \to 0 \text{ when } t \to \infty.$$

Note that

$$a_{\psi_0}(t) = \big(\exp(-itH)\psi_0, \psi_0\big) = \int \exp(-it\lambda) d(E_\lambda \psi_0, \psi_0)$$

If $\psi_0 \in \mathcal{H}_{ac}$ then $a_{\psi_0}(t) \to 0$ as $t \to \infty$ (Riemann-Lebesgue)

Fock-Krylov theory *JETP (1947)*

$\rightarrow$ Main question is the deviation of $a_{\psi_0}(.)$ w.r.t. an exponential law

Metastable states

L.A. Khalfin *JETP (1957)* $\rightarrow$

Suppose that $H \geq E_0 > -\infty$ then

$$|a_{\psi_0}(t)| \geq A\exp(-bt^q), \text{as } t \to \infty$$

for any $A, b > 0$ and $1 > q > 0$

In fact by using standard measure theory arguments we can prove that there are no $A > 0$ and $b > 0$ s.t. $|a_{\psi_0}(t)| \leq A\exp(-bt)$ for any $t > 0$ see e.g. B.Simon *Int. J of quant. chem. (1978)*

Metastable states

The Stark effect, I. Herbst *CMP (1980)* :

Let $H = H_0 + Fx_1$, $H_0 = -\Delta + V$ on $\mathcal{H} = L^2(\mathbb{R}^3)$, V is translational analytic in the strip $\{|\Im z| \leq \alpha\}$ then for any $\alpha > 0$ and some $\psi_0 \in \mathcal{H}$

$$a_{\psi_0}(t) = \sum_{\Im \rho_j \leq \alpha} C_j \exp(-it\rho_j) + r_\alpha(t, \psi, F), \ t \geq 0$$

Where $\{\rho_j, j \in \mathbb{N}\}$ are identified with the stark resonances and $\{C_j, j \in \mathbb{N}\}$are computed in terms of projections of resonance eigenfunctions. Moreover

$$|r_\alpha(t, \psi, F)| = O(\exp(-\frac{\alpha}{2} t))$$

From now we only consider bounded below Hamiltonian

Metastable states

The Strategy from W. Hunziker *CMP(1990)* .

Let $H_\kappa = H_0 + \kappa V$ suppose that the dilated family $\{H_{\kappa,\theta}, \theta \in \mathbb{R}\}$ extend to an analytic family of operators in $|\Im\theta| < \beta, \beta > 0$.

If λ_0 an simple eigenvalue of H_0 and $\psi_0, \|\psi_0\| = 1$ the associated eigenvector. Let $g \in C_0^\infty(\mathbb{R})$ supported in some interval containing λ_0 and $g = 1$ near λ_0. Then denote

$$\mathcal{A}_{\psi_0}(t) := \big(\exp(-itH_\kappa)g(H_\kappa)\psi_0, \psi_0\big)$$

Metastable states

Theorem : *Suppose κ small enough, then for any $m > 0$*

$$\mathcal{A}_{\psi_0}(t) = b(\kappa)\exp(-it\lambda_\kappa) + r(t, \psi_0), t \geq 0$$

Here λ_κ is the eigenvalue of $H_\theta, \Im\theta \neq 0$ near λ_0 and

$$r(t, \psi) = O_m(\frac{\kappa^2}{t^m}), \quad b(\kappa) = 1 + O(\kappa^2)$$

Metastable states

Remarks: - If λ_0 is a discret eigenvalue of H_0 then for κ small enough, λ_κ is a real discret eigenvalue of H : there is no exponential decay.
-If λ_0 is eigenvalue of H_0 embedded in the continuous spectrum, if since $\Im\lambda_\kappa < 0$, $g^{1/2}(H_\kappa)\psi_0$ is a "metastable state"
-Removing the energy cut off we can see readily that

$$a_{\psi_0}(t) = \big(\exp(-itH)\psi_0, \psi_0\big) = b(\kappa)\exp(-it\lambda_\kappa) + O(\kappa^2)$$

-Determination of the critical time t_c : for all $t > t_c$ the rest becomes dominant, here $t_c \geq 2\frac{|\ln(\kappa)|}{|\Im\lambda_\kappa|}$

Metastable states

L.Cattaneo, G.M., Graff, W. Hunziker A.H.P. (2006) $\rightarrow$ In the same condition as before, let Δ be an interval $\lambda_0 \in \Delta$.

Theorem : *Suppose that there exits a conjugate operator A s.t. $e^{isA}D(H) \subset D(H)$ and the following Mourre's estimate holds,*

$$P_\Delta [H_0, A] P_\Delta \geq c P_\Delta + K;$$

for some $c > 0$ and a compact operator K. Moreover we suppose that $ad_A^k(H_0)$ are H-bounded for $k = 1...n$, $n > 0$. Then

$$\mathcal{A}_{\psi_0}(t) = b(\kappa) \exp(-it\lambda_\kappa) + r(t, \psi_0), t \geq 0$$

$$r(t, \psi) = O(\kappa^2 |\ln \kappa| t^{-m}), m + 5 \leq n, \quad b(\kappa) = 1 + O(\kappa^2)$$

$$\lambda_\kappa = \lambda_0 + \kappa (V\psi_0, \psi_0) + \kappa^2 F(\lambda_0 + i0, 0) + o(\kappa^2)$$

Metastable states

Here

$$F(z,\kappa) = (\psi_0, VQ(QHQ - z)^{-1} QV\psi_0)$$

In that case, If $\Im F(\lambda_0 + i0, 0) < 0$ (Fermi-Golden rule), we define λ_κ as a resonance for the pair $\{H_0, H_\kappa\}$

Metastable states

Further references :

- M. Klein, J.Rama, R.Wust : Asymptotics Analysis (2007), (2014)
- E. Skibsted : CMP (1986)
- V. Dinu, A. Jensen, G. Nenciu Rev. Math Phys (1991)
- B. Simon, I.Sigal, A. Soffer, M.I. Weinstein, G. Hagedorn, A. Joye ....
- S. Nakamura, P Stephanov, M. Zworski, B. Helffer, J. Sjöstrand....
- K. Urbanowski Eur. Phys. J (2017), K. Raczynska, K. Urbanowski (arXiv-2018), C. Anastopoulos (arXiv-2018) (and references therein)......

Diatomic molecular systems

In the usual Born Oppenheimer framework, we consider the situation of two electronic levels V_1, V_2. Denoting by h the "small parameter". The hamiltonian is

$$H = H_0 + h\mathcal{W}(x, hD_x) \quad \text{on} \quad \mathcal{H} = \mathrm{L}^2(\mathbb{R}^{\mathrm{n}}) \oplus \mathrm{L}^2(\mathbb{R}^{\mathrm{n}})$$

$$H_0 = \begin{pmatrix} P_1 & 0 \\ 0 & P_2 \end{pmatrix} \tag{1}$$

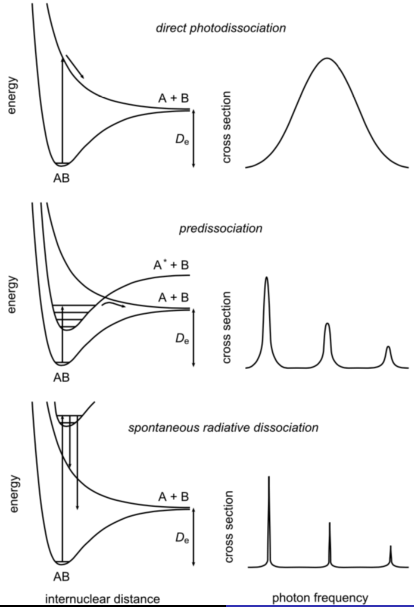
where $P_j := -h^2\Delta + V_j(x), \quad j = 1, 2$ and the level coupling

$$\mathcal{W}(x, hD_x) = \begin{pmatrix} 0 & W \\ W^* & 0 \end{pmatrix}$$

$W = w(x, hD_x)$ first-order semiclassical pseudo-differential operators.

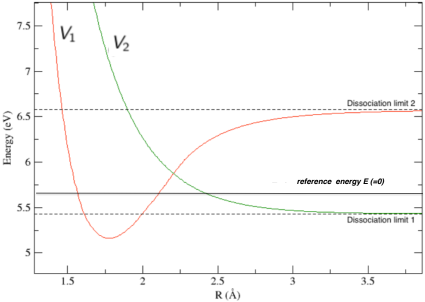
See: M.Klein, A. Martinez, R.Seiler, X.P.Wang, *C.M.P. (1992)*, M.Klein *Anal. of Physics (1987)* A. Martinez, Sordoni. V. J.M.P. (2015)

Diatomic molecular systems



Diatomic molecular systems

Remarks -Photodissociation involves a Born-Oppenheimer approximation but a time dependent theory.
-In this work we study the predissociation phenomena:



Potential curves for V_1 (red) and V_2 (green) states of sulfur monoxide.

Diatomic molecular systems

h 1 *The potentials* $V_1, V_2 \in C_b^\infty(\mathbb{R}^n)$ and satisfy

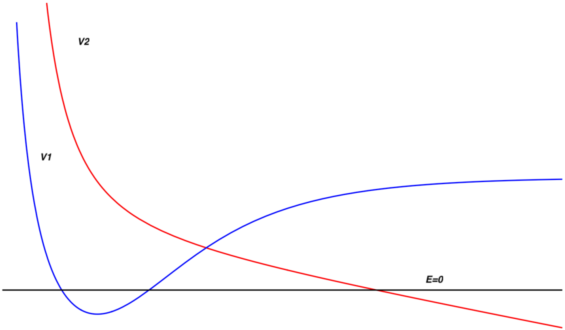
$$U = \{x \in \mathbb{R}^n / V_1 \leq 0\} \textit{is bounded}, \ \liminf_{|x|\to\infty} V_1 > 0;$$

$$V_2 > 0 \textit{ on } U \textit{ and } \lim_{|x|\to\infty} V_2 = -\Gamma < 0$$

h 2 *The potentials* V_1 *and* V_2 *extend to bounded holomorphic in* $\mathcal{S}_{R_0,\delta} = \{z \in \mathbb{C}^n \, ; \, |\Re z| \geq R_0 \, , \, |\Im z| \leq \delta |\Re z|\}$,
for some $R_0, \delta > 0$.
Moreover in $\mathcal{S}_{R_0,\delta}$, V_2 *tends to its limit at* ∞ *and* $|\Re V_1| > 0$.

Diatomic molecular systems

A typical situation in one direction:



Diatomic molecular systems

W has he following form: $\forall \varphi \in C_0^\infty(\mathbb{R}^n)$

$$(W\varphi)(x) = \frac{1}{(2\pi h)^n} \int e^{i(x-y)\frac{\xi}{h}} w(x,\xi)\varphi(y)dyd\xi$$

where

h 3 *The symbol $w(x,\xi)$ extends to a holomorphic functions in,*

$$\widetilde{\mathcal{S}}_{R_0,\delta} := \mathcal{S}_{R_0,\delta} \times \{x \in \mathbb{C}^n \,;\, |\Im x| \leq \delta |\Re x|\},$$

and, for real x, w is a smooth function of x with values in the set of holomorphic functions in ξ near $\{|\Im \xi| \leq \delta\}$.
Moreover, we assume that, for any $\alpha \in \mathbb{N}^{2n}$, it satisfies

$$\partial^\alpha w(x,\xi) = \mathcal{O}(|\Re \xi|) \text{ uniformly on } \widetilde{\mathcal{S}}_{R_0,\delta} \cup (\mathbb{R}^n \times \{|\Im \xi| \leq \delta\})$$

see A. Martinez, A. Grigis *Anal. PDE (2014)*

hNT *E=0 is a non trapping energy for V_2 i.e. the following Virial condition is satisfied on* $\{V_2 < 0\}$

$$2V_2(x) + x.\nabla V_2 \leq const. < 0$$

Remark: We can impose a weaker NT condition by using B.Helffer, J. Sjöstrand *M. S. M. (1986)* and A. Martinez *A.H.P (2002)*,

Resonances

Introduce the following distortion J. Aguilar, J.M. Combes, *C.M.P (1971)*, W.Hunziker *A.I.H.P. (1986)*.
Let $f \in C^\infty(\mathbb{R}^n)$ such that $f(x) = x$ if $|x|$ is large enough. Let $\theta \in \mathbb{R}$, $|\theta|$ small and for $\varphi \in C_0^\infty(\mathbb{R}^n)$

$$(U_\theta \varphi)(x) = det(1 + \theta f')^{1/2} \varphi(x + \theta f(x))$$

Denote by $H_\theta = U_\theta H U_\theta^{-1}$, then this family has an extension as an analytic family in the sens of Kato in $\theta \in \mathbb{C}$, $|\theta|$ small A. Martinez, A. Grigis *Anal. PDE (2014)*
In the following we choose $\theta = i\beta, \beta > 0$.

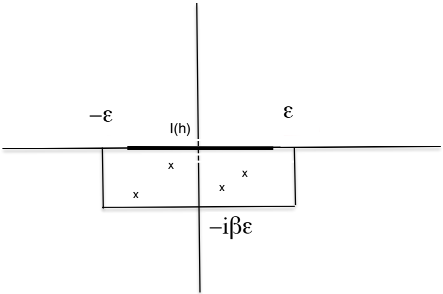
Resonances

We have A. Martinez, A. Grigis *Anal. PDE (2014)*, M.Klein *Ann. Phys. (1987)*

Theorem (definition of resonances): *Under the conditions stated above, then there exits $\varepsilon > 0$ s.t. for h and β small enough H_θ has purely discrete spectrum in $\{z \in \mathbb{C}, \Re z \in (-\varepsilon, \varepsilon), \Im z \geq -\beta\varepsilon\}$. The eigenvalues of H_θ are the resonances of H*

Resonances

Figure: The eigenvalues of H_θ coincide with the poles of the meromorphic extension of $z \to ((H - z)^{-1}\varphi, \varphi)$ for φ in a dense subset of $\mathcal{H}$ see e.g. W.Hunziker *A.I.H.P. (1986)* or B. Helffer , A. Martinez *Helv. Phys. Acta (1987)*



Resonances

We need the following more precise result (in a simplified version):

Let $I(h) \subset [-\varepsilon, \varepsilon]$ be an open interval s.t. there exists $a(h) > 0$ and $h^2/a(h) \to 0$ as $h \to 0$ and

$$\sigma(P_1) \cap (I(h) + [-3a(h), 3a(h)]) \setminus I(h) = \emptyset.$$

Theorem (existence and localisation of resonances)
For h small enough $\exists\ \varepsilon_1 > 0$ *s.t. for each eigenvalue* $\lambda_0(h), \ldots, \lambda_m(h)$ *of* P_1 *in* $I(h)$*, there exists a resonance for* H *:* $\rho_0(h), \ldots, \rho_m(h) \in \Omega(h)$ *with*

$$\Omega(h) = I(h) + [-a(h), a(h)] + i[0, -\varepsilon_1]$$

s.t. $\rho_j(h) = \lambda_j(h) + O(h^2)$*. Moreover* $\Im \rho_j(h) = O(e^{-\frac{c_j}{h}})$.

Results

A. Martinez, P.B. *J.S.T (2017)* $\rightarrow$

- Let $u_0, \ldots, u_m$ orthonormal basis of eigenspace of P_1 corresponding to the eigenvalues of P_1, $\lambda_0, \ldots, \lambda_m$ in $I(h)$;
- Denote: $U_j := \begin{pmatrix} u_j \\ 0 \end{pmatrix}$, $j = 0, \ldots, m$;

-Introduce the energy cut off: $g \in C_0^n(\mathbb{R})$, s.t.

g is supported in $I(h) + [-2a, 2a]$ and $g = 1$ in $I(h) + [-a, a]$

and for $k = 0, \ldots, n$, $g^{(k)} = O(a^{-k})$,

Results

Theorem *Let h small enough, for* $\varphi = \sum_j \alpha_j U_j$, $\|\varphi\| = 1$, *one has*

$$\mathcal{A}_\varphi(t) = \sum_{j=0}^{m} e^{-it\rho_j} b_j(\varphi, h) + r(t, \varphi, h),\ t \geq 0$$

where $\rho_0, \dots, \rho_m$ *are the resonances of* H *in* $\Omega(h)$ *s.t.* $\rho_j = \lambda_j + O(h^2)$. *The rest satisfies*

$$r(t, \varphi, h) = O\left(\frac{h^2}{a(h)} \min_{0 \leq k \leq n} \{a(h)^{-k}(1+t)^{-k}\}\right)$$

and $b_j(\varphi; h)$ *satisfy*

$$\sum_{j=0}^{m} b_j(\varphi, h) = 1 + O\left(h^2 + (\frac{h^2}{a(h)})^2\right)$$

Results

Corollary: *The survival amplitude satisfies,*

$$a_\varphi(t) = \sum_{j=0}^{m} e^{-it\rho_j} b_j(\varphi, h) + O\left(h^2 + \frac{h^2}{a}\right), t \geq 0$$

then $t_c > \frac{|\ln(a/h^2|)}{\eta}$ with $\eta = \min\{|\Im\rho_j|\}$ so that $t_c \to \infty$ as $h \to 0$.

The rest goes to 0 when $t \to \infty$?

Results

Remarks:

-If $g \in C_0^\infty$ then $r(t,\varphi,h) = h^2/a(h) O\left(a(h)t)^{-\infty}\right)$

-Suppose that $\lambda_1, \dots, \lambda_m$ are discrete simple eigenvalues s.t. $\tilde{a}(h) = \min_{i \neq j} |\lambda_i - \lambda_j|$ satisfies $h^2/\tilde{a}(h) \to 0$ as $h \to 0$ then

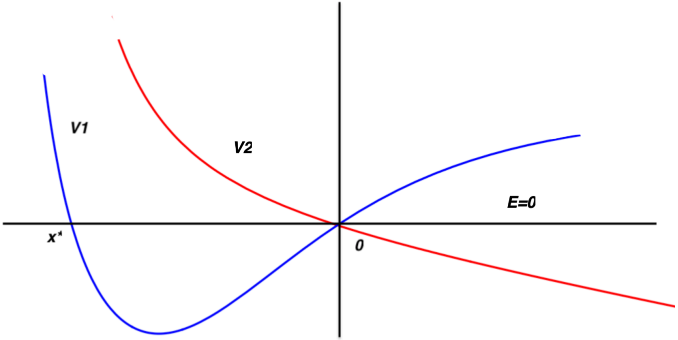
$$b_j(\varphi,h) = |(\varphi,U_j)|^2 + \mathcal{O}\left((h^2 + h^4(a\tilde{a})^{-1})\right)$$

-If H has only one resonance in $\Omega(h)$, let $\varphi = U_0$ then $b_0 = 1 + O\left(h^2 + \frac{h^4}{a^2}\right)$ and

$$\mathcal{A}_\varphi(t) = b_0 e^{-it\rho_0} + h^2/a(h) O\left(a(h)t\right)^{-\infty}\right)$$

energy level crossing case

S. Fujiié, A. Martinez, T. Watanabe *J. Diff. Equat. (2016)*, *J. Diff. Equat. (2017)*, *ArXiv (2019)* $\rightarrow$



Energy level crossing case

Let

$$H = H_0 + h\mathcal{W}(x, hD_x) \quad \text{on} \quad \mathcal{H} = \mathrm{L}^2(\mathbb{R}) \oplus \mathrm{L}^2(\mathbb{R})$$

with

$$W(x, hD_x) = r_0(x) + ir_1(x)hD_x,$$

where $r_0(x)$ and $r_1(x)$ and V_1, V_2 have an analytic extension (and bounded) in $\mathcal{S}_{0,\delta}$, in the complex domain $\mathcal{S}_{0,\delta}$ for some $\delta > 0$.

and

Energy level crossing case

Suppose also For $j = 1, 2$, V_j admits limits as $\Re x \to \pm\infty$ in Γ, and they satisfy,

$$\lim_{\substack{\Re x \to -\infty \\ x \in \Gamma}} V_1(x) > 0\,; \lim_{\substack{\Re x \to -\infty \\ x \in \Gamma}} V_2(x) > 0\,;$$
$$\lim_{\substack{\Re x \to +\infty \\ x \in \Gamma}} V_1(x) > 0\,; \lim_{\substack{\Re x \to +\infty \\ x \in \Gamma}} V_2(x) < 0.$$

There exists a negative number $x^* < 0$ such that,

$$V_1 > 0,\ V_2 > 0 \ on\ (-\infty, x^*);$$
$$V_1 < 0 < V_2 \ on\ (x^*, 0);$$
$$V_2 < 0 < V_1 \ on\ (0, +\infty),$$

$\exists x* > 0$ s.t. $V_1'(x*) := -1$, $V_1'(0) := 1$ and $V_2'(0) := -1$.

Energy level crossing case

Theorem: *For h small enough, the resonances of H in*

$$\Omega(h) = [-C_0 h^{2/3}, C_0 h^{2/3}] - i[0, C_0 h], \; C_0 > 0$$

are of the form :

$$\rho_k(h) = \lambda_k(h) + 0(h^{\frac{4}{3}}) \quad ; \quad \Im \rho_k(h) = O(h^{\frac{5}{3}})$$

where $\lambda_k(h) \in \mathbb{R}$ corresponds to an eigenvalue $e_k(h)$ of P_1 s.t. $\lambda_k(h) = e_k(h) - O(h^2)$,

Remark: This covers the case of avoiding-crossing with gap having a length of $O(h^\alpha), \alpha \geq 1 \rightarrow$ to a slight modification of the coefficient r_0 introducing a perturbation of the same order.

Energy level crossing case

A. Martinez, P.B. *arXiv:1812.08724 math-ph (2018)* and *JDE (2019)* $\rightarrow$

Let h small enough, fix an resonance $\rho_0(h)$ of H corresponding to an eigenvalue $e_0(h)$ of $P_1 \in [-C_0 h^{2/3}, C_0 h^{2/3}]$ s.t.

$$\rho_0(h) = e_0(h) + O(h^{\frac{4}{3}})$$

Denote by u_0 the normalized eigenfunction of P_1 associated with e_0 and $\varphi = (u_0, 0)$.

We choose an energy cut off $g \in C_0^\infty(\mathbb{R})$

Energy level crossing case

Theorem : For h small enough then

$$\mathcal{A}_\varphi(t) = b(h)e^{-it\rho_0} + h^{\frac{2}{3}} q_0(t,h) + \mathcal{O}(h(ht)^{-\infty}), \ t \geq 0$$

uniformly for $h > 0$ small enough and $t \in \mathbb{R}$, with,

$$b(h) = 1 + \mathcal{O}(h^{1/3});$$

$$q_0(t,h) = 4r_0(0)^2 c_0^2 e^{-ite_0} \left[A_0(e_0 h^{-\frac{2}{3}})\right]^2 F(ht),$$

where F is an analytic function s.t. $F(\lambda) = O(|\lambda|^{-\infty})$ and A_0 is the function,

$$A_0(s) := 2^{-\frac{1}{3}} Ai\left(-2^{\frac{2}{3}} s\right).$$

Strategy of proof

From Stone's formula,

$$\mathcal{A}_\varphi(t) = \lim_{\varepsilon \to 0_+} \frac{1}{2i\pi} \int_{\mathbb{R}} e^{-it\lambda} g(\lambda)((R(\lambda + i\varepsilon) - R(\lambda - i\varepsilon))\varphi, \varphi) d\lambda =$$

$$= \frac{1}{2i\pi} \int_\gamma e^{-itz} (R_\theta(z)\varphi_\theta, \varphi_{-\theta}) dz + \frac{1}{2i\pi} \int_{\gamma_-} e^{-itz} g(\Re z) T_\theta(z) dz,$$

where γ is a certain contour around $I(h)$, $\gamma_- \subset \{Imz \leq 0\}$ and

$$T_\theta(z) := (R_\theta(z)\varphi_\theta, \varphi_{-\theta}) - (R_{-\theta}(z)\varphi_{-\theta}, \varphi_\theta)$$

Strategy of proof

By the Cauchy formula,

$$\mathcal{A}_\varphi(t) = \sum_{j=1}^{m} e^{-it\rho_j} b_j(\varphi, h) + r(t, \varphi, h),$$

where b_j is the residue of $z \to (R_\theta(z)\varphi_\theta, \varphi_{-\theta})$ at $z = \rho_j$ and

$$r(t, \varphi, h) := \frac{1}{2i\pi} \int_{\gamma_-} e^{-itz} g(\Re z) T_\theta(z) dz.$$

Strategy of proof

Estimates on the coefficients b_j:
By using a reduction process (Feshbach method) we get that

$$b_j = Residue_{z=\rho_j}(E_+(z)(E_{-+}(z))^{-1}E_-(z)\varphi_\theta, \varphi_{-\theta})$$

where $E_+(z), E_-(z)$ are analytic operators in $\Omega(h)$ and

$$E_{-+}(z) = z\mathbb{I}_m - \Lambda + h^2 F(z)$$

with $\Lambda = diag(\lambda_0, ..., \lambda_m)$ and $F(z)$ is the meromorphic extension in $\Omega(h)$ of $(m+1) \times (m+1)$ matrix:

$$F_{k,l}(z) = (\mathcal{W}Q(QHQ - z)^{-1}Q\mathcal{W}\phi_k, \phi_l)$$

This gives $\sum_{j=0}^m b_j = \frac{1}{2i\pi}\int_\gamma (E_{-+}(z))^{-1}\alpha_\varphi, \alpha_\varphi)$, $\alpha_\varphi = (\alpha_0, ..., \alpha_m)$
The result follows by using accurate semiclassical estimates.

Strategy of proof

Estimate on the rest term follows from usual estimates on the dilated resolvent + Agmon estimate + integration by parts

Thanks for your attention