THE STARK EFFECT ON $H_2^+$-LIKE MOLECULES

V. GRECCHI, H. KOVAŘÍK, A. MARTINEZ, A. SACCHETTI, AND V. SORDONI

Abstract. We consider the vibrational energy levels of the first two electronic states of the molecule ion $H_2^+$. The Born-Oppenheimer method applied to the case of the Stark effect on a $H_2^+$-like molecule gives existence of sharp resonances localized in the same interval of energy of the vibrational levels.

In Memory of Pierre Duclos

1. Introduction

We consider the Stark effect on a diatomic ionized molecule of the type of $H_2^+$ due to an external field.

Up to now, this problem has been treated by many authors in a heuristic way in the coaxial case where the external field and the nuclear axis of the molecule have same direction [Ca, Hi, MPS]. This attitude is justified since, in such a case, the effect of the external field on the diatomic molecule is the strongest one.

Our problem consists of a non isolated three-body system, where one of the masses is much smaller than the other ones, under the effect of a coaxial and locally uniform external electric field. Under some reasonable assumptions on the problem, we prove (see Theorem [7.1]) the existence of resonances with the associated metastable states at mean energy, in certain bands that contain the energy levels of the isolated molecule, too. Resonances are defined as complex eigenvalues of a distorted Hamiltonian; it is worth pointing out that our definition of resonances includes, as a special case, the notion of embedded eigenvalues where the imaginary part is exactly zero. In fact we prove that the imaginary part of the resonances is non positive and, in absolute value, smaller than $Ch$, where $C$ is a given positive constant and $h$ is the semiclassical parameter defined below. Our result does not exclude the case of resonances with imaginary part exactly zero (in fact, embedded eigenvalues). Finally, our result still holds true even in absence of the external field; in such a case we don’t need to define the distorted Hamiltonian and we simply have discrete eigenvalues instead of resonances.

Because of the heavy mass of the nuclei (denoted by $h^{-2}$ in the text, with $0 < h \ll 1$), at a first stage it is possible to consider the position of the nuclei as fixed, in order to determine the electronic states. This approach is known as the Born-Oppenheimer’s one [KMSW]. Following Woolley, [Wo], we can say that the assumption of an almost fixed structure of the molecule is more appropriate for metastable states, which is our case, than in the case of definitely stationary states.

The first two levels of the electron, $E_1(R)$ of the state $1\sigma_g$ and $E_2(R)$ of the state $1\sigma_u$, as functions of the nuclear distance $R$, contribute to the effective potentials.

Date: September 24, 2010.

1991 Mathematics Subject Classification. Primary 35Q40; Secondary 81Q20.

H.K. was supported by the German Research Foundation (DFG) under Grant KO 3636/1-1.
used for the determination of the nuclear dynamics. Such behavior of the electronic levels are well known by the explicit asymptotic expansions for large $R$ \cite{CI} and their distributional Borel sums \cite{CGM,GG}. It is a reasonable hypothesis that each effective potential function, $W_j(R) = (1/R) + E_j(R)$, $j = 1, 2$, has only one minimum point where a certain number of nucleonic states are trapped, identified with the first vibrational energy levels of the molecule. Such levels have been experimentally observed \cite{Ca}. In the case of the coaxial Stark effect we have different behaviors of the electronic level functions $W_j(R)$, see Fig. 2 of \cite{Ca}. The perturbation effect is an $R$ dependent splitting of the asymptotically degenerated levels, or shortly, an avoided crossing. The picture of the behavior of such effective potentials changes at large distances, giving a maximum of the first one $W_1(R)$. As a consequence, we have metastability of the vibrational states of the molecule. Since we expect exponentially large mean life of the metastable states, we use a small complex distortion on the nuclear relative position variable \cite{Hu}. We also use the theory of the twisted pseudodifferential operators introduced in \cite{MaSo}. The theory of pseudodifferential operators goes back to the quantization rule of Hermann Weyl and is now well established \cite{Ma1}. The recent theory of twisted pseudodifferential operators \cite{MaSo} is a formalization and extension of the method of regularization going back to Hunziker \cite{Hu,KMSW}. This theory is able to regularize the Coulomb singularity of the nuclei-electrons potentials of the interaction. The Grushin-Feshbach method is now a standard method for defining and computing a finite number of expected eigenvalues \cite{KMSW}.

The Hamiltonian operator is the following:

$$H = -\hbar^2 \Delta_R + \frac{1}{R} + H_e$$  \hspace{1cm} (1)

where $\hbar^2 \ll 1$ is the inverse of the nuclei mass (where we fix, for the sake of definiteness, the unit of mass such that the electron mass is equal to 1), and $H_e$ is the \textit{electronic Hamiltonian}, formally defined on $L^2(\mathbb{R}^3)$ as

$$H_e := H_e(R) = -\Delta_r - \frac{1}{|r - \frac{1}{2} R|} - \frac{1}{|r + \frac{1}{2} R|} + V,$$  \hspace{1cm} (2)

where $V$ is the external potential.

The three-body operator (1) acts on the Hilbert space of square integrable sections in the trivial fiber bundle

$$\mathcal{K} = L^2(\mathbb{R}^3; L^2(\mathbb{R}^3)).$$

In this picture the operator $H$ decomposes into two terms. The first one, the nuclear kinetic energy, acts on the base space. The second one operates on the fiber only,

$$\tilde{H}_e = \int^\oplus H_e(R)dR,$$

where $H_e(R)$ is the electronic Hamiltonian for fixed nuclei. The small parameter $\hbar$ allows the use of semiclassical approximation. For our purposes, the second order is enough.

Since $H_e$ is not simply a multiplication operator, we use the pseudodifferential calculus with operator valued symbols. For that, it is useful to translate the eigenvalue problem for $H$ by the Grushin method into the problem of inverting a
2 × 2 matrix operator. Moreover we define the spectral projector \( \Pi_e(R) \) of \( H_e(R) \) up to a fixed value of the energy, so that,

\[
\Pi = \int \Pi_e(R) dR,
\]

is a projector on the molecular space \( K \). The lower part of the spectrum of the compressed operator \( \Pi H \Pi \) is expected near of part of the spectrum of \( H \). The eigenvalues are given by the generalized eigenvalues, \( Q(E)\psi = E\psi \), where \( Q(E) \) is the Feshbach operator,

\[
Q(E) = \Pi H \Pi - \Pi H (\Pi (H - E)^{-1}) \Pi H \Pi.
\]

Furthermore, a smooth relationship, with respect to \( R \), is requested between the first eigenvectors of \( H_e(R) \) and the corresponding final generalized eigenvectors of the Feshbach operator.

The paper is organized as follows.

In Section 2 we introduce the model and we state our main assumptions. In particular we discuss the \( H^+_2 \) molecule under the effect of a Stark effect and we show that this physical problem substantially fits with our model.

In Section 3 we consider the analytic distortion and regularization of the operator. Analytic distortion is a standard way to define resonances \([\text{BCD}]\). Because of the singularity of the Coulomb potential we have to regularize our effective Hamiltonian. If we denote by \( \tilde{H}_\mu \) (\( \mu \) is the complex distortion constant) the regularized operator then we see (see Theorem 3.8) that part of its spectrum coincides with the spectrum of a reduced problem denoted by \( \tilde{P}_\mu \). The reduced problem consists of two coupled Schrödinger operator.

In Section 4 we study the spectrum of the reduced problem denoted by \( \tilde{P}_\mu^\sharp \), which coincides with \( \tilde{P}_\mu \) up to a bounded operator with norm less that \( C h^2 \) for some \( C > 0 \). We separately consider the spectrum associated to first level alone, and the part of the spectrum located in the bottom of the second level.

In Section 5 we compare the spectrum of the two operators \( P_\mu^\sharp \) and \( \tilde{H}_\mu^0 \), where \( \tilde{H}_\mu^0 \) is the restriction of the regularized and distorted operator on the eigenspace of the vibrational spectrum.

In Section 6 we compare the spectrum of the two operators \( \tilde{H}_\mu^0 \) and \( \tilde{H}_\mu^0 \), where \( \tilde{H}_\mu^0 \) is the restriction of the distorted operator on the eigenspace of the vibrational spectrum.

In Section 7 we finally state our main results.

1.1. Notations. Here we list the main notations, meaning \( j \in \{1, 2\} \):

- \( H \) denotes the Hamiltonian operator \([1]\);
- \( H_e \) denotes the electronic Hamiltonian operator \([2]\) with eigenvalues \( E_j(R) \) depending on \( R \);
- \( H_0 = \text{Ker}(L_R + L_r) \) where \( L_R \) and \( L_r \) respectively denote the angular momentum with respect to the variables \( R \) and \( r \);
- \( W_j(R) = \frac{1}{2} + E_j(R) \) denotes the effective potential;
- \( m_1 \) and \( m_2 \) respectively are the non degenerate minima of \( W_1(R) \) and \( W_2(R) \) at \( R_{1,m} \) and \( R_{2,m} \), \( M_1 \) is the non degenerate maximum of \( W_1(R) \) at \( R_{1,M} \) (see Remark \([2, 3]\);
- $P_j$ is the operator formally defined by
  \[-\hbar^2 \frac{d^2}{dR^2} + W_j(R)\]
on $L^2(\mathbb{R}, dR)$ with Dirichlet boundary conditions at $R = 0$;
- $\tilde{S}_\mu$ denotes the analytic distortion operator \([16]\);
- $H_\mu$ and $H_{\mu,e}$ denote the distorted operators
  \[H_\mu = \tilde{S}_\mu H \tilde{S}_\mu^{-1} \quad \text{and} \quad H_{\mu,e} = \tilde{S}_\mu H_e \tilde{S}_\mu^{-1};\]
- $\tilde{H}_{\mu,e}$ is the regularization of $H_{\mu,e}$ as defined in Proposition \([34]\);
- $\tilde{H}_\mu$ is the regularization of $H_\mu$ as defined in Definition \([35]\);
- $\tilde{P}_\mu$ and $\tilde{P}_{\mu,e}$ respectively are the restriction of $H_\mu$ and $\tilde{H}_\mu$ to the invariant subspace $Ker(L_R + L_r)$;
- $\tilde{W}_j$ is the reduced problem defined by equation \((32)\) on the Hilbert space
  \[H^2 = L^2((0, +\infty), dR) \oplus L^2((0, +\infty), dR)\]
with Dirichlet boundary conditions at $R = 0$;
- $\tilde{P}_{j,\mu}$ is the operator formally defined by
  \[\hbar^2 \tilde{S}_\mu D_R^2 \tilde{S}_\mu^{-1} + W_{j,\mu}(R)\]
on $L^2(\mathbb{R}, dR)$ with Dirichlet boundary conditions at $R = 0$, where $D_R$ and $W_{j,\mu}$ are defined at the beginning of \S4;
- $P_D^2$ is the Dirichlet realization of $P_0^2$ on the interval $[0, R_1,M]$;
- $P_\mu^2$ and $P_j$ are respectively obtained by $P_\mu^2$ and $P_j$ by substituting $\tilde{W}_j$ to $W_j$; that is $\text{"fill the well"}$;
- $\tilde{P}_\mu^0(z)$ is the restriction of $\tilde{P}_\mu^0(z)$, defined by equation \((23)\), to $Ker(L_R)$;
- when this fact does not cause misunderstanding $\| \cdot \|$ denotes the usual norm on the Hilbert space $L^2$ or the norm of linear operators defined on the Hilbert space $L^2$.

2. The model

2.1. The three-body problem. The analysis of the three-body problem \([1]\) is a very difficult task and we have to introduce here some suitable assumptions.

**Hypothesis 1.** We assume that the potential $V$ only depends on the component of the vector $r$ along the direction $R$; that is
\[V(R, r) = \chi \left( \frac{R}{R, r} \right), \quad R = |R|, \quad (3)\]
where $\chi$ is a real-valued function bounded from below. The function $\chi$ admits an analytic extension in a complex strip containing the real axis.

**Remark 2.1.** Given a rotation $O$ in $\mathbb{R}^3$, let us consider the unitary operators $S_O$ and $T_O$ on $L^2(\mathbb{R}^3_\mathbb{R})$ and $L^2(\mathbb{R}^3_\mathbb{R}) \otimes L^2(\mathbb{R}^3_\mathbb{R})$ respectively, given by,
\[S_O\phi(R) = \phi(OR), \quad \forall \phi \in L^2(\mathbb{R}^3_\mathbb{R})\]
\[T_O := S_O \otimes S_O, \quad T_O\psi(R, r) = \psi(OR, Or), \quad \forall \psi \in L^2(\mathbb{R}^3_\mathbb{R}) \otimes L^2(\mathbb{R}^3_\mathbb{R})\]
Then $H$ commutes with $T_O$, i.e. $T_O H = H T_O$ and therefore, the spectrum of the electronic Hamiltonian operator $H_e(R)$ depends only on $R := |R|$,.
Remark 2.2. Now, let us denote by $\mathbf{L}_R$ and $\mathbf{L}_r$ the angular momentum with respect to the variables $\mathbf{R}$ and $\mathbf{r}$ respectively. By the previous remark, we see that we have,

$$[H, \mathbf{L}_R + \mathbf{L}_r] = 0. \quad (4)$$

In the sequel, we will be particularly interested on the eigenvalues and resonances of the restriction of $H$ to the invariant subspace

$$\mathcal{H}_0 := \text{Ker}(\mathbf{L}_R + \mathbf{L}_r).$$

This somehow corresponds to fix to 0 the rotational energy of the molecule. As we will see, after the Born-Oppenheimer reduction to an effective Hamiltonian $P = P(\mathbf{R}, \hbar D_R)$, this is equivalent to study the restriction of $P$ to $\text{Ker}(\mathbf{L}_R)$. Therefore, this will also permit us to reduce the study to a one-dimensional operator.

2.2. Effective Potential. For any fixed $\mathbf{R} \in \mathbb{R}^3$, we denote by $\text{Sp}(H_e(\mathbf{R}))$ the spectrum of the electronic Hamiltonian operator $H_e(\mathbf{R})$ defined on the Hilbert space $L^2(\mathbb{R}^3)$. This spectrum actually depends on $\mathbf{R}$ (see Remark 2.1) and we assume that

**Hypothesis 2.** The discrete spectrum of the electronic Hamiltonian operator $H_e(\mathbf{R})$ contains at least two eigenvalues, and the first two eigenvalues $E_1(\mathbf{R})$ and $E_2(\mathbf{R})$ are non degenerate, extend holomorphically to complex values of $\mathbf{R}$ in a domain of the form $\Gamma_\delta := \{\mathbf{R} \in \mathbb{C} ; \text{Re} \mathbf{R} \geq \delta^{-1}, |\text{Im} \mathbf{R}| < \delta \text{Re} \mathbf{R}\}$ with $\delta > 0$ constant, and are such that,

$$\lim_{|\mathbf{R}| \to +\infty, \mathbf{R} \in \Gamma_\delta} E_j(\mathbf{R}) = E_j^\infty, \quad (5)$$

where,

$$E_1^\infty < E_2^\infty. \quad (6)$$

Furthermore, there is a gap between $E_j(\mathbf{R})$, $j = 1, 2$, and the remainder of the spectrum:

$$\min_{R > 0} \text{dist} \{\{E_1(\mathbf{R}), E_2(\mathbf{R})\}, E_3(\mathbf{R})\} \geq C$$

for some positive constant $C > 0$, where

$$E_3(\mathbf{R}) = \{\text{Sp}(H_e(\mathbf{R})) - \{E_1(\mathbf{R}), E_2(\mathbf{R})\}\},.$$

We observe that, for any rotation $O$ in $\mathbb{R}^3$, one has (with obvious notations),

$$H_e(OR, Or, O^{-1}D_r) = H_e(\mathbf{R}, \mathbf{r}, D_\mathbf{r}), \quad D_\mathbf{r} = -i \nabla_\mathbf{r}.$$

As a consequence, the first two normalized eigenfunctions

$$H_e(\mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}) = E_j(\mathbf{R}) \psi_j(\mathbf{r}, \mathbf{R}), \quad j = 1, 2. \quad (7)$$

can be taken real-valued and verify $\psi_j(OR, Or) = \psi_j(\mathbf{R}, \mathbf{r})$, and thus

$$(\mathbf{L}_R + \mathbf{L}_r) \psi_j = 0. \quad (8)$$

We also denote by,

$$W_j(\mathbf{R}) = \frac{1}{R} + E_j(\mathbf{R}), \quad j = 1, 2,$$

the effective potential associated with the $j$-th eigenvalue.

By Hypothesis 2 we observe that the effective potential satisfies to the following properties
(1) The effective potentials \( W_j(R) \), \( j = 1, 2 \), are analytic functions;

(2) There exists a positive constant \( C > 0 \) such that
\[
\min_{R>0} [W_3(R) - W_2(R)] \geq C
\]
where \( W_3 = \frac{1}{R^2} + \inf [E_3(R)] \).

(3) The following limits hold true
\[
\lim_{R \to 0^+} W_j(R) = +\infty, \quad j = 1, 2.
\]

Here, we introduce the following assumptions on the effective potentials \( W_1(R) \) and \( W_2(R) \).

**Hypothesis 3.** The effective potential \( W_1 \) has a single well shape, with local non-degenerate minimum value \( m_1 \) at some point \( R_{1,m} \), with a barrier with local non-degenerate maximum value \( M_1 \) at some point \( R_{1,M} \); beside, \( W_1 \) does not admit other critical points in the domain \( W_1^{-1}([m_1, M_1]) \). The effective potential \( W_2 \) has a single well shape, with local minimum value \( m_2 \) at some point \( R_{2,m} > R(1,m) \).

**Remark 2.3.** In absence of the external field the local maximum value \( M_1 \) disappears and we only have two local minimum values [C], in such a case \( E_1^\infty = E_2^\infty \) and we could treat the spectral problem for eigenvalues belonging to the interval \([m_1, M_1]\), for any \( M_1 < E_1^\infty \). If the external field is small enough, but not zero, then we expect to observe a local maximum value such that \( m_1 < m_2 < M_1 \) and \( R_{1,m} < R_{2,m} < R_{1,M} \) as in Fig. 1. For increasing external field, as considered by [MuSh], can happen to have \( m_1 < M_1 < m_2 \).

### 2.3. Spectrum of the reduced operator.

In polar coordinates, Hamiltonian (1) takes the form,
\[
H = -\hbar^2 \left[ \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right] - \hbar^2 \frac{1}{R^2} \Lambda^2 + \frac{1}{R} + H_e(R)
\]  
(9)

where \( \Lambda^2 \) is the Legendrian operator,
\[
\Lambda^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}.
\]

The operator \( -\hbar^2 \frac{1}{R^2} \Lambda^2 \) has eigenvalues \( \hbar^2 \frac{1}{R^2} \ell (\ell + 1) \), \( \ell \in \{0, 1, 2, \ldots\} \). As a consequence, using Remark 2.2 a suitable choice of the rotation \( O \) makes the operator \( H \) take the form,
\[
H = -\hbar^2 \left[ \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right] + \hbar^2 \ell (\ell + 1) \frac{1}{R^2} + \frac{1}{R} + H_e(R)
\]
on \( L^2(\mathbb{R}_+, R^2 dR; L^2(\mathbb{R}^3_+)) \). Finally, by taking \( \ell = 0 \), that is, by considering the restriction of \( H \) on \( \text{Ker}(L_R) \) (still denoted by \( H \)), and by performing the change \( \psi(R, r) \to R \psi(R, r) \), the Hamiltonian \( H \) takes the form,
\[
H_0 = -\hbar^2 \frac{\partial^2}{\partial R^2} + \frac{1}{R} + H_e(R)
\]
on \( L^2(\mathbb{R}_+, dR; L^2(\mathbb{R}^3_+)) \) with Dirichlet boundary condition at \( R = 0 \).

Let \( P_j \), \( j = 1, 2 \), be the reduced operator formally defined by
\[
P_j = -\hbar^2 \frac{d^2}{dR^2} + W_j(R), \quad W_j(R) = \frac{1}{R} + E_j(R),
\]  
(10)
THE STARK EFFECT ON $H^+_2$-LIKE MOLECULES

Figure 1. Graph of the effective potentials $W_1(R)$ and $W_2(R)$ with single well shapes. The effective potential $W_1(R)$ has a barrier and it does not admit other critical points in the domain $W_1^{-1}([m_1, M_1])$; where $m_1$ and $M_1$ are the values of the local maximum and minimum point of $W_1$.

on the Hilbert space $L^2(\mathbb{R}^+, dR)$ with Dirichlet boundary condition at $R = 0$.

Then, it follows that for $h$ small enough and for small external field, the discrete spectra of $P_j$ in the interval $[m_j, E^\infty_j]$, $j = 1, 2$, is not empty (see, e.g., [La] in the case without the external field), and we denote it by

$$\text{Sp}_d(P_j) = \{e^j_k, k \geq 1\}, \quad j = 1, 2.$$ 

In particular, in the case of non degenerate minima points $m_1$ and $m_2$, combining results from [HeRo] and [HeSj1], we know that the gap $e^j_{k+1} - e^j_k$ between two consecutive eigenvalues of $P_j$ ($j = 1, 2$) is of order $h$ as $h \to 0^+$, in the sense that $c_jh \leq e^j_{k+1} - e^j_k \leq C_jh$ with $c_j, C_j > 0$ independent of $h$ and $k = O(h^{-1})$.

2.4. Physical motivation. It is well known [Ca] that the dynamics of the three particle system called molecule-ion $H^+_2$, referred to its center of mass, and under the effect of an external homogeneous field, is described by a Hamiltonian operator of the form,

$$H = -\hbar^2\Delta_R + \frac{Z^2}{R} + H_e$$  \hspace{1cm} (11)

where $\hbar \ll 1$ is the effective semiclassical parameter given by the square root of the ratio between the light mass of the electron $e$ and the heavy mass (when compared with the electron mass) of the hydrogen nuclei. Moreover,

$$R = x\hat{x} + y\hat{y} + z\hat{z}$$
is the relative position of the two hydrogen nuclei of \( H_2^+ \), and \( Z \) is the electron charge (hereafter, for the sake of definiteness we assume that the units are such that, \( Z = 1 \)). The electronic Hamiltonian \( \hat{H} \) describes the relative motion of the electron \( e \) referred to the fixed nuclei, and it actually depends on the nuclear distance \( R \), where \( V \) is the potential of the external force.

Now we consider the isolated molecule. The asymptotic behavior for large \( R \) of the functions \( W_j(R) \) is dominated by the Van der Waals force given by,

\[
W_j(R) = -\frac{c_4}{R^4} + O(R^{-6}), \quad W_j'(R) = 4\frac{c_4}{R^6} + O(R^{-7}),
\]

for a constant \( c_4 > 0 \) (see the constant \( E^{(4)} \) of \([C^4]\)). The energy binding of the molecule, \( \mathcal{E}_\infty^1 - m_1 > 0 \) is much smaller than the separation distance of the fundamental level of the atom \( \mathcal{E}_\infty^3 - \mathcal{E}_\infty^1 > 0 \).

Following \([Hi, MuSh]\), we consider the case where the external field is a Stark-like field directed along the axes of the two nuclei, in agreement with Hyp. 1, with potential

\[
V(R, r) = -\chi \left( \frac{R}{R'} r \right), \quad R = |R|,
\]

where \( \chi \) is a real-valued function bounded from below. In such a case, the Hamiltonian \( \hat{H} \) commutes with the angular momentum \( \hat{L}_R + \hat{L}_r \). In fact, the effective potentials \( W_1(R) \) and \( W_2(R) \) show a shape as in Fig. 1 (see, e.g., \([MuSh]\), and Fig. 2 of \([Ca]\)).

The function \( \chi \) admits an analytic extension to a complex strip containing the real axis. More precisely, we assume,

\[
\chi(x) = \chi_d(x) = \nu \frac{x}{\sqrt{1 + (x/d)^2}} = \frac{d\nu}{\sqrt{1 + (d/x)^2}} = d\nu (1 - \frac{d^2}{2x^2} + \frac{3d^4}{8x^4} + O(\frac{d^6}{x^6})),
\]

for \( x^2 > d^2 \), where \( d > 0 \) is a parameter much larger than the molecular size.

For

\[
\Delta \mathcal{E}(R) = \mathcal{E}_2(R) - \mathcal{E}_1(R),
\]

small enough for \( R^2 >> d^2 \), we can approximate with a degenerate perturbation with effective Stark potential for the nucleons given by the matrix element of the potential on the two electronic states \( \psi_{j,R} = \psi_{j,R}(r) \),

\[
V_S(R) = | < \psi_{1,R}, V(R,)\psi_{2,R} > | = C \chi(R) = \delta (1 - \frac{d^2}{2R^2} + \frac{3d^4}{8R^4} + O(\frac{d^6}{R^6})),
\]

where \( \delta = Cd\nu > 0 \). Thus, for large \( R \), the two nuclear potentials are bounded and behaves as in Fig. 1,

\[
W_1(R) = \mathcal{E}_\infty^1 - \delta (1 - \frac{d^2}{2R^2}) - (c_4 + \delta \frac{3d^4}{8}) \frac{1}{R^4} + O(1/R^6),
\]

\[
W_2(R) = \mathcal{E}_\infty^1 + \delta (1 - \frac{d^2}{2R^2}) - (c_4 - \delta \frac{3d^4}{8}) \frac{1}{R^4} + O(1/R^6).
\]

If we admit derivation of the asymptotic series, we have a maximum \( R_{1,M} \) of \( W_1(R) \) diverging as \( \delta \to 0 \),

\[
R_{1,M}^2 \sim \frac{4c_4}{\delta d^2} + \frac{3d^2}{2}.
\]
3. Analytic distortion and regularization of the operator

3.1. Analytic distortion. Let \( s \in C^\infty(\mathbb{R}) \), \( 0 \leq s \leq 1 \) with \( s(x) = 0 \) in an arbitrarily large compact set containing 0, and \( s(x) = 1 \) if \(|x|\) is large enough. For \( \mu \) real small enough, we set,

\[
I_\mu : \mathbb{R}^3 \to \mathbb{R}^3, \quad I_\mu(R) = R(1 + \mu s(R))
\]

and we define the analytic distortion on the test function \( \psi \), by the formula,

\[
(S_\mu \psi)(\mathbf{r}) = |J(\mathbf{R}, \mathbf{r})|^{1/2} \psi(I_\mu(\mathbf{R}), J_\mu(\mathbf{R}, \mathbf{r}))
\]

where we have set \( R = |\mathbf{R}| \), and \( J(\mathbf{R}, \mathbf{r}) \) is the Jacobian of the transformation \( F_\mu \) given by,

\[
F_\mu : \mathbb{R}^6 \to \mathbb{R}^6, \quad F_\mu(\mathbf{R}, \mathbf{r}) = (I_\mu(\mathbf{R}), J_\mu(\mathbf{R}, \mathbf{r})).
\]

We also set

\[
\phi_\mu : \mathbb{R}^+ \to \mathbb{R}^+ , \phi_\mu(\mu) = R(1 + \mu s(R)).
\]

Then, the analytic distortion applied to the operator \( \mathcal{I} \) defined on the Hilbert space \( \mathcal{K} \) takes the form,

\[
H_\mu = S_\mu HS_\mu^{-1} = -\hbar^2 S_\mu \Delta R S_\mu^{-1} + \frac{1}{\phi_\mu(R)} + H_{\mu,c}(\mathbf{R}),
\]

with \( H_{\mu,c}(\mathbf{R}) \) given by,

\[
H_{\mu,c}(\mathbf{R}) = -S_\mu \Delta R S_\mu^{-1} - \frac{1}{|J_\mu(\mathbf{R}, \mathbf{r}) - \frac{1}{2} I_\mu(\mathbf{R})|} - \frac{1}{|J_\mu(\mathbf{R}, \mathbf{r}) + \frac{1}{2} I_\mu(\mathbf{R})|} + V_\mu(n)
\]

where the distorted external potential is given by,

\[
V_\mu(\mathbf{R}, \mathbf{r}) = V \left[ \left( \frac{\mathbf{R}}{\mathbf{R}} , \mathbf{r} \right) \left( 1 + \mu s \left( \frac{\mathbf{R}}{\mathbf{R}} , \mathbf{r} \right) \right) \right].
\]

Thus, \( H_{\mu,c}(\mathbf{R}) \) can be extended to small enough complex values of \( \mu \) as an analytic family of type A.

Remark 3.1. We also observe that, if \( O \) is a rotation in \( \mathbb{R}^3 \), then,

\[
I_\mu(OR) = OI_\mu(\mathbf{R}) \quad ; \quad J_\mu(OR, Or) = OJ_\mu(\mathbf{R}, \mathbf{r}).
\]

As a consequence,

\[
[S_\mu, \mathbf{L}_R + \mathbf{L}_r] = 0,
\]

and,

\[
H_{\mu,c}(OR, Or, O^{-1}D_\mathbf{r}) = H_{\mu,c}(\mathbf{R}, \mathbf{r}, D_\mathbf{r}).
\]

We denote by \( H_{\mu,0} \) the restriction of \( H_{\mu,c}(\mathbf{R}, \mathbf{r}, D_\mathbf{r}) \) to the invariant subspace \( \text{Ker}(\mathbf{L}_R + \mathbf{L}_r) \).
3.2. Regularization of $H_\mu$. In this section, we want to regularize the operator $H_\mu$ with respect to the $R$-variable. Having in mind the representation (6) of the Laplacian in polar coordinates, we denote

$$\Omega(1/M) := \left\{ R \in \mathbb{R}^3 : R > \frac{1}{M} \right\}, \quad \Omega_0(1/M) := \left\{ R \in \mathbb{R}^3 : R < \frac{1}{M} \right\},$$

and $S^2$ is the unit sphere in $\mathbb{R}^3$, and

$$L_0 := -\Delta_R + C_0$$

with $C_0, M > 0$ large enough. We have the following preliminary technical lemma:

**Lemma 3.2.** Under the previous assumptions, there exists a finite family of conical open sets $(\Omega_\ell)_{\ell=1}^m$ in $\mathbb{R}^3$, of the form $\Omega_\ell = \left[ \frac{1}{M_\ell}, +\infty \right) \times \omega_\ell$ with $\omega_\ell$ bounded open set of $S^2$, and a corresponding family of unitary operators $U_\ell(R)$ ($\ell = 1, \ldots, m, R \in \Omega_\ell$) on $L^2(\mathbb{R}^3)$, such that (denoting by $U_\ell$ the unitary operator on $L^2(\Omega_\ell)$) $L^2(\Omega_\ell) \otimes L^2(\mathbb{R}^3)$ induced by the action of $U_\ell(R)$ on $L^2(\mathbb{R}^3)$, one has,

1. $\Omega(1/M) = \bigcup_{\ell=1}^m \Omega_\ell$;
2. For all $\ell = 1, \ldots, m$ and $R \in \Omega_\ell$, $U_\ell(R)$ leaves $H^2(\mathbb{R}^3)$ invariant;
3. For all $\ell$, the operator $U_\ell(\tau h^2 S_\mu \Delta_R S_\mu^{-1}) U_\ell^{-1}$ is a semiclassical differential operator with operator-valued symbols, of the form,

$$-h^2 S_\mu \Delta_R S_\mu^{-1} + h^2 \sum_{|\beta|=1} \omega_{\beta,\ell}(R)(h D_R)^{\beta} + h^2 \omega_0,\ell(R), \quad D_R = -i\nabla_R$$

where $\omega_{\beta,\ell}(\Pi) = \omega_{\beta,\ell}(R) = C^\infty(\Omega_\ell L^2(\mathbb{R}^3))$, and, for any $\gamma \in \mathbb{N}^3$, the quantity $||\partial_\gamma^2 \omega_{\beta,\ell}(x)L_0^{(\Pi)} ||_{L^2(\mathbb{R}^3)}$ is bounded uniformly with respect to $h$ small enough and locally uniformly with respect to $x \in \Omega_\ell$;
4. For all $\ell$, the operators $U_\ell H_\mu U_\ell^{-1}$ are in $C^\infty(\Omega_\ell L^2(\mathbb{R}^3), L^2(\mathbb{R}^3))$.

**Proof.** At first, let us make a change of variables as in [MaMe], that localizes into a compact set the $R$- dependent singularities appearing into the interaction potential. Let $\chi \in C^\infty(\mathbb{R}^+)$ satisfying $0 \leq \chi \leq 1, \chi' \leq 0$, such that,

$$\chi(s) = 1, \quad \text{if } 0 \leq s \leq 1, \quad \chi(s) = 0, \quad \text{if } s \geq 2$$

For $\tau > 1/2M$ and $\tau > 0$, we consider the function,

$$\rho(\tau,t) = \frac{t}{\tau} \chi \left( \frac{t}{\tau} \right) + 2Mt \left( 1 - \chi \left( \frac{t}{\tau} \right) \right).$$

Then, it is easy to check that

$$\frac{\partial \rho}{\partial t} > 0 \quad \text{on} \quad \left[ \frac{1}{2M}, +\infty \right) \times \mathbb{R}^+, \quad \rho \quad \text{is surjective onto} \quad \mathbb{R}^+, \quad \frac{\partial^k \rho}{\partial t^k} \quad \text{is uniformly bounded on} \quad \left[ \frac{1}{2M}, +\infty \right) \times \mathbb{R}^+, \forall k \geq 1.$$

Therefore we can define $\alpha_\tau$ as the inverse diffeomorphism on $\mathbb{R}^+$ of the function $t \rightarrow \rho(\tau,t)$. In particular, by construction we have,

$$\alpha_\tau(t) = \frac{t}{2M} \quad \text{if} \quad t \geq 4M\tau, \quad \alpha_\tau(t) = \tau t \quad \text{if} \quad t \leq 1.$$
Now, for \( \mathbf{R} \in \Omega(1/M) \), we define
\[
\theta(\mathbf{R}, \cdot) : \mathbb{R}^3 \to \mathbb{R}^3, \quad \theta(\mathbf{R}, \mathbf{r}) = \alpha_{R/2}(|\mathbf{r}|) \frac{\mathbf{r}}{|\mathbf{r}|}.
\]
Then, for any \( \mathbf{R} \in \Omega(1/M) \), the function \( \theta(\mathbf{R}, \cdot) \) is a diffeomorphism of \( \mathbb{R}^3 \), it depends smoothly on \( \mathbf{R} \), and is such that \( \partial^2_{\mathbf{R}} \theta(\mathbf{R}, \mathbf{r}) \) is uniformly bounded on \( \Omega(1/2M) \times \mathbb{R}^3 \), for any \( \alpha \in \mathbb{N}^3 \setminus \{0\} \) (see [MaMe], Lemma 3.1). Moreover
\[
\theta \left( \mathbf{R}, \frac{\mathbf{r}}{R} \right) = \frac{\mathbf{r}}{2}, \quad \theta(\mathbf{R}, \mathbf{r}) = \frac{\mathbf{r}}{2M} \quad \text{for} \ |\mathbf{r}| \geq 2MR,
\]
\[
\theta(\mathbf{R}, \mathbf{r}) = \frac{\mathbf{R}}{2r} \quad \text{for} \ |\mathbf{r}| \leq 1.
\]
For \( R > \frac{1}{M} \), we consider the unitary transformation on \( L^2(\mathbb{R}^3) \), given by,
\[
(U(\mathbf{R})\phi)(\mathbf{r}) = \phi(\theta(\mathbf{R}, \mathbf{r}))|\partial_\mathbf{r}\theta(\mathbf{R}, \mathbf{r})|^{1/2}.
\]
The advantage of performing this change of variables is that the \( \mathbf{R} \)-depending singularities of the potential are now localized in some compact subset of \( \mathbb{R}^3 \). Now, following the arguments of [KMSW] and with the help of the previous change of variables, let us show that, by a patch and cut procedure, one can localize the singularities of the potential at some fixed (\( \mathbf{R} \)-independent) points.

For any fixed \( z_0 \in S^2 \) (the unit sphere in \( \mathbb{R}^3 \)), we choose a functions \( f_{z_0} \in C_0^\infty(\mathbb{R}^3; \mathbb{R}) \), such that,
\[
f_{z_0}(z_0) = 1, \quad f_{z_0}(-z_0) = 0
\]
and, for \( z \) close enough to \( z_0 \) and \( s \in \mathbb{R}^3 \), we define
\[
F_{z_0}(z, s) := s + (z - z_0)(f_{z_0}(s) - f_{z_0}(-s)) \in \mathbb{R}^3.
\]
For \( z \) in a smooth neighborhood \( \omega_z \) of \( z_0 \), the application \( s \mapsto F_{z_0}(z, s) \) is a diffeomorphism of \( \mathbb{R}^3 \), and we have,
\[
F_{z_0}(z, z_0) = z, \quad F_{z_0}(z, -z_0) = -z.
\]
Moreover, for any \( \alpha \in \mathbb{R}^3 \), there exists \( C_\alpha > 0 \) such that, for any \( z \in \omega_z \), for any \( s, s' \in \mathbb{R}^3 \)
\[
\frac{1}{C_0}|s - s'| \leq |F_{z_0}(z, s) - F_{z_0}(z, s')| \leq C_0|s - s'|
\]
\[
|\partial_\mathbf{s}^2 F_{z_0}(z, s) - \partial_\mathbf{s}^2 F_{z_0}(z, s')| \leq C_0|s - s'|
\]
\[
|\partial_\mathbf{s}^2 F_{z_0}(z, s)| \leq C_0, \quad |\alpha| \geq 1
\]
If \( (\omega_\ell)^m_{\ell=1} := (\omega_{\ell_1})^{m_{\ell_1}}_{\ell_1=1} \) is a family of such open sets that covers \( S^2 \), we set \( F_\ell(z, \cdot) := F_{\ell_1}(z, \cdot), \) and we define,
\[
\Omega_\ell := \left\{ \frac{1}{M}, +\infty \right\} \times \omega_\ell.
\]
For \( \mathbf{R} \in \Omega_\ell \), we also set,
\[
(U_\ell(\mathbf{R})\phi)(\mathbf{r}) = \left| \det(\partial_\mathbf{r}F_\ell) \left( \frac{\mathbf{R}}{R}, \mathbf{r} \right) \right|^{1/2} \phi \left( F_\ell \left( \frac{\mathbf{R}}{R}, \mathbf{r} \right) \right),
\]
and,
\[
U_\ell(\mathbf{R}) := \overline{U_\ell(\mathbf{R})} U(\mathbf{R});
\]
\[(\mathcal{U}_\ell(R)\phi)(r) = \phi(\gamma_\ell(R, r))| \det(\partial_r \gamma_\ell)(R, r)|,\]

where
\[\gamma_\ell(R, r) = \theta \left( R, F_\ell \left( \frac{R}{r}, r \right) \right).\]

Then, it is easy to check (see [MaMe]) that $\mathcal{U}_\ell$ satisfy (1), (2), (3), and (4). This completes the proof of the lemma. □

Now, let us consider the spectral projection $\Pi_0(R)$ associated to $\{E_1(R), E_2(R)\}$ of $H_\ell(R)$, where $E_1(R)$ and $E_2(R)$ are the first two (simple) eigenvalues of $H_\ell(R)$. If one denote by $\gamma(R)$ a continuous simple loop in $\mathbb{C}$ enclosing $\{E_1(R), E_2(R)\}$ and having the rest of $\text{Sp}(H_\ell(R))$ in its exterior, one can write $\Pi_0(R)$ as,
\[\Pi_0(R) = \frac{1}{2\pi i} \int_{\gamma(R)} (H_\ell(R) - z)^{-1} \, dz.\]

Moreover, for $\mu$ complex small enough, one can define the projector,
\[\Pi_{\mu,0}(R) = \frac{1}{2\pi i} \int_{\gamma(R)} (H_{\mu,e}(R) - z)^{-1} \, dz\]
satisfying $(\Pi_{\mu,0})^* = \Pi_{\bar{\mu},0}$. We have the following

**Lemma 3.3.** There exist two functions,
\[w_1^\mu(R, r), w_2^\mu(R, r) \in C^0(\mathbb{R}^3_{\mu}; H^2(\mathbb{R}^3_{\mu}))\]
depending analytically on $\mu$, and real-valued for $\mu$ real, such that,

i. $\langle w_1^\mu(R, r), w_1^\mu(R, r) \rangle_{L^2(\mathbb{R}^3_{\mu})} = \delta_{k,l}, \quad k, l = 1, 2$;

ii. $w_j^\mu \in C^\infty(\Omega(2/M); H^2(\mathbb{R}^3_{\mu}))$, $j = 1, 2$, and, for $R \in \Omega(3/M)$, $w_1^\mu(R, r)$ and $w_2^\mu(R, r)$ form a basis of Ran$\Pi_0^\mu$;

iii. For $R \in \Omega(3/M)$, $w_1^\mu(R, r)$ and $w_2^\mu(R, r)$ are eigenfunctions of $H_{\mu,e}(R)$ associated to $E_1(\phi_\mu(R))$ and $E_2(\phi_\mu(R))$ respectively;

iv. For all $\ell = 1, \ldots, m$, one has $\mathcal{U}_\ell(R)w_j^\mu(R, r) \in C^\infty(\Omega_\ell(M), H^2(\mathbb{R}^3_\mu))$, $j = 1, 2$.

v. $w_1^\mu$ and $w_2^\mu$ can be chosen in such a way that,
\[(L_R + \mathcal{L}_r)w_1^\mu = (L_R + \mathcal{L}_r)w_2^\mu = 0.\]

**Proof.** Taking into account that (see [19]),
\[\lim_{R \to +\infty} \mathcal{E}_1(R) \neq \lim_{R \to +\infty} \mathcal{E}_2(R),\]

the points (i)-(iv) follow from Lemma 3.1 of [MaSo] and from the arguments of Proposition 5.1 in [MaMe]. Moreover, since $\mathcal{E}_1(R)$ and $\mathcal{E}_2(R)$ are non degenerate, the last point (v) follows from [KMSW], Theorem 2.1, and from [19]. □

Thanks to the previous lemma, we see that the family $(U_{\ell}, \Omega_\ell)_{\ell=0,m}$ (with $\Omega_0 = \Omega(2/M), U_0 = 1$ and $\Omega_\ell, U_\ell$ defined in Lemma 3.2 and Lemma 3.3), is a regular unitary covering of $L^2(\mathbb{R}^3_R; L^2(\mathbb{R}^3_{\mu}))$ in the sense of [MaSo], Definition 4.1.

We set,
\[\bar{\Pi}_{\mu,0}(R) = \langle \cdot, w_1^\mu(R) \rangle_{L^2(\mathbb{R}^3_{\mu})}w_1^\mu(R) + \langle \cdot, w_2^\mu(R) \rangle_{L^2(\mathbb{R}^3_{\mu})}w_2^\mu(R)\]
so that $\bar{\Pi}_{\mu,0}(R)$ coincides with $\Pi_{\mu,0}(R)$ for $R \in \Omega(3/M)$, and verify,
\[\mathcal{U}_\ell(R)\bar{\Pi}_{\mu,0}(R)\mathcal{U}_\ell(R)^{-1} \in C^\infty(\Omega_\ell, \mathcal{L}(L^2(\mathbb{R}^3_{\mu}))).\]
for all $\ell = 0, \ldots, m$. Also observe that, for any rotation $O$,
\[ T_O \tilde{\Pi}_{\mu,0}(R) = \tilde{\Pi}_{\mu,0}(R)T_O \]
or, equivalently, $[\Pi_{\mu,0}(R), L_R + L_r] = 0$.
We also denote by $\tilde{\Pi}_0(R)$ the value of $\tilde{\Pi}_{\mu,0}(R)$ for $\mu = 0$.
Now, with the help of $\tilde{\Pi}_{\mu,0}(R)$, we modify $H_{\mu,e}(R)$ outside a neighborhood of
$\Omega(5/M)$ as follows (see Proposition 3.2 in $\text{MaSo}$).

**Proposition 3.4.** We choose a function $\zeta \in C^\infty(\mathbb{R}^3; [0, 1])$, such that $\zeta = 1$
for $R \geq 3/M$ and $\text{supp} \zeta \subseteq [2/M, +\infty[$. Then, for all $R \in \mathbb{R}^3$, and $\mu$
complex small enough, there exists an operator $\tilde{H}_{\mu,e}(R)$ on $L^2(\mathbb{R}^3)$, with domain $H^2(\mathbb{R}^3)$,
depending analytically on $\mu$, such that,
\[ \tilde{H}_{\mu,e}(R) = H_{\mu,e}(R) \quad \text{if } R \in \Omega(4/M); \]
\[ [\tilde{H}_{\mu,e}(R), \tilde{\Pi}_{\mu,0}(R)] = 0 \quad \text{for all } R \in \mathbb{R}^3, \]
and the application $R \mapsto \mathcal{U}_t(R)\tilde{H}_{\mu,e}(R)\mathcal{U}_t(R)^{-1}$ is in $C^\infty(\Omega_t; \mathcal{L}(H^2(\mathbb{R}^3), L^2(\mathbb{R}^3)))$
for all $\ell = 0, \ldots, m$. Moreover, $\tilde{H}_{\mu,e}(R)$ commutes with $L_R + L_r$, in the sense that, for
any $\varphi \in C^\infty_0(\mathbb{R}^6)$, one has,
\[ (L_R + L_r)\tilde{H}_{\mu,e}(R)\varphi = \tilde{H}_{\mu,e}(R)(L_R + L_r)\varphi. \]
Hence, the spectrum of $\tilde{H}_{\mu,e}(R)$ actually depends only on $R \in \mathbb{R}_+$. Moreover, for
$\mu$ real, $\tilde{H}_{\mu,e}(R)$ is selfadjoint, uniformly semibounded from below, and the bottom
of its spectrum consists in two eigenvalues,
\[ \bar{\mathcal{E}}^{\mu}_j(R) = \mathcal{E}_j(\phi_\mu(R)), \ j = 1, 2, \]
where
\[ \mathcal{E}_j(R) = \zeta(R)\mathcal{E}_j(R). \]
Furthermore, $\tilde{H}_{\mu,e}(R)$ admits a global gap in its spectrum, in the sense that,
\[ \inf_{R \in \mathbb{R}_+} \text{dist}(\{\bar{\mathcal{E}}^{\mu}_1(R), \bar{\mathcal{E}}^{\mu}_2(R)\}, \bar{\mathcal{E}}^{\mu}_3(R)) > 0. \]
where we set
\[ \bar{\mathcal{E}}^{\mu}_3(R) = \text{Sp}(\tilde{H}_{\mu,e}(R)) \setminus \{\bar{\mathcal{E}}^{\mu}_1(R), \bar{\mathcal{E}}^{\mu}_2(R)\} \]

**Proof.** The proof is similar to that of Proposition 3.2 in $\text{MaSo}$, and we write it for
$\mu = 0$ only (the general case is obtained by just substituting $H_{\mu,e}$ to $H_e$ and $\tilde{\Pi}_{\mu,0}$
to $\tilde{\Pi}_0$). We set $\tilde{\Pi}_{\mu}^\perp(R) = 1 - \tilde{\Pi}_{\mu}(R)$ and
\[ \tilde{H}_e(R) = \zeta(R)H_e(R) + (1 - \zeta(R))\tilde{\Pi}_{\mu}^\perp(R)(-\Delta_r + C_0)\tilde{\Pi}_{\mu}^\perp(R), \]
with $C_0 > 0$ large enough and such that $C_0 > \bar{\mathcal{E}}_3$, where
\[ \bar{\mathcal{E}}_3 := \inf_R \mathcal{E}_3(R). \]
Since $\tilde{\Pi}_0(R) = \Pi_0(R)$ on Supp$\zeta$, we see that $\tilde{\Pi}_0(R)$ commutes with $\tilde{H}_e(R)$, and it
is also clear that $\tilde{H}_e(R)$ is selfadjoint with domain $H^2(\mathbb{R}^3)$. Moreover,
\[ \tilde{\Pi}_0(R)H_e(R)\tilde{\Pi}_0(R) = \zeta(R)\Pi_0(R)H_e(R)\Pi_0(R), \]
and,
\[ \tilde{\Pi}_0(R)\tilde{H}_e(R)\tilde{\Pi}_0(R) \geq (\zeta(R)\mathcal{E}_3(R) + (1 - \zeta(R))C_0) \tilde{\Pi}_0(R) \geq \bar{\mathcal{E}}_3\tilde{\Pi}_0(R). \]
In particular, the bottom of the spectrum of $\tilde{H}_\mu(R)$ consists in two eigenvalues $\tilde{E}_j(R) = \zeta(R)\tilde{E}_j(R)$ with associated eigenvectors $\tilde{\Pi}_0(R)\psi_j$, $j = 1, 2$, where $\tilde{E}_j$ and $\psi_j$ are the first two eigenvalues and eigenvectors of \eqref{6}. Furthermore, one has
\[
\inf_{R > 2/M} \text{dist}(\tilde{E}_3(R), \{\tilde{E}_1(R), \tilde{E}_2(R)\}) \geq \inf_{R > 2/M} (\zeta(R)(\inf_{R > 2/M} |\tilde{E}_3(R)| - \tilde{E}_2(R)) + (1 - \zeta(R))C_0) > 0,
\]
and
\[
\inf_{R > 2/M} \text{dist}(\tilde{E}_3(R), \{\tilde{E}_1(R), \tilde{E}_2(R)\}) \geq C_0.
\]
In particular, $\tilde{H}_\mu(R)$ admits a fix global gap in its spectrum as stated in the proposition. Finally, we see that $\tilde{H}_\mu(R)$ commutes with $L_R + L_r$, and $U_\mu H_\mu(R)U_\mu^{-1}$ depends smoothly on $R$ in $\Omega_\ell$ for all $\ell = 0, \ldots, m$. \hfill \Box

3.3. Regularization of the operator.

**Definition 3.5** (Regularization of $H_\mu$). Let $S_\mu$ be the analytic distortion defined in \cite{MaSo} for $\mu$ in some small complex neighborhood of zero, and let $H_{\mu,e}(R)$ and $\zeta(R)$ be defined as in Proposition 3.4. Then, we define the regularization of $H_\mu$ as,
\[
\tilde{H}_\mu = -h^2 S_\mu \Delta R S_\mu^{-1} + \tilde{H}_{\mu,e}(R) + \frac{\zeta(R)}{\phi_\mu(R)} + \frac{M}{3}(1 - \zeta(R)).
\]

Taking into account Definition 4.4 in \cite{MaSo}, we see that Lemma 3.2, Proposition 3.4 and \eqref{14} imply,

**Lemma 3.6.** The operator $\tilde{H}_\mu$ is a twisted PDO (of degree 2) on $L^2(\mathbb{R}_R^3, L^2(\mathbb{R}_R^3))$ (in the sense of Definition 5.1 in \cite{MaSo}), associated with the regular unitary covering ($U_\ell, \Omega_\ell$)$_{\ell=0, \ldots, m}$. Moreover, it commutes with $L_R + L_r$.

Now, we define
\[
Z_\mu^+ : L^2(\mathbb{R}_R^6) \rightarrow L^2(\mathbb{R}_R^3) \oplus L^2(\mathbb{R}_R^3)
\]
by the formula,
\[
(Z_\mu^+ \psi)(R) = \langle \psi(R, \cdot), w_1^R(R, \cdot) \rangle_{L^2(\mathbb{R}_R^3)} \oplus \langle \psi(R, \cdot), w_2^R(R, \cdot) \rangle_{L^2(\mathbb{R}_R^3)},
\]
and,
\[
Z_\mu^- = (Z_\mu^+)^* : L^2(\mathbb{R}_R^3) \oplus L^2(\mathbb{R}_R^3) \rightarrow L^2(\mathbb{R}_R^6),
\]
by
\[
(Z_\mu^- (u_1 \oplus u_2))(R, r) = u_1(R)w_1^R(R, r) + u_2(R)w_2^R(R, r).
\]
Following \cite{MaMe}, we consider the Grushin problem,
\[
\tilde{G}_\mu(z) = \begin{pmatrix} \tilde{H}_\mu - z & Z_\mu^- \\ Z_\mu^+ & 0 \end{pmatrix},
\]
that sends $H^2(\mathbb{R}_R^6) \oplus (L^2(\mathbb{R}_R^3) \oplus L^2(\mathbb{R}_R^3))$ into $L^2(\mathbb{R}_R^6) \oplus (H^2(\mathbb{R}_R^3) \oplus H^2(\mathbb{R}_R^3))$.

Thanks to Lemma 3.4 and Lemma 3.5, we see that $\tilde{G}_\mu(z)$ is a twisted PDO (of degree 2) on $L^2(\mathbb{R}_R^3, L^2(\mathbb{R}_R^3) \oplus C \oplus C)$, associated with the regular unitary covering ($V_\ell, \Omega_\ell$)$_{\ell=0, \ldots, m}$, where we have set
\[
V_\ell := \begin{pmatrix} U_\ell & 0 \\ 0 & 1_2 \end{pmatrix}.
\]
We also have,

**Lemma 3.7.** For all \( \mu \in \mathbb{C} \) small enough and \( z \in \mathbb{C} \), the operator \( \tilde{G}_\mu(z) \) commutes with \( L := \begin{pmatrix} L_R + L_r & 0 \\ 0 & L_R \end{pmatrix} \).

**Proof.** By Lemma 3.6 we only need to study the commutation rules between \( Z_\mu^+ \) and the operators \( L_R \) and \( L_r \). But, using Lemma 3.3 v., plus the fact that the formal adjoint of \( L_r \) is \( -L_r \), we immediately obtain,

\[
(L_R + L_r)Z_\mu^- = Z_\mu^- L_R \\
L_R Z_\mu^+ = Z_\mu^+(L_R + L_r),
\]

and the result follows. \( \square \)

Moreover, we see as in [MaMe], Section 5, that, for \( z \in \mathbb{C} \) with \( \text{Re} z < \inf_{R>0} \tilde{E}_j(R) \) and \( \text{Im} z \) sufficiently small, the operator \( \tilde{G}_\mu(z) \) is invertible, and its inverse \( \tilde{G}_\mu(z)^{-1} \) is such that the operators,

\[
\left( \begin{array}{cc} 1 & 0 \\ 0 & (-\Delta_R)^{-1} \end{array} \right) \tilde{G}_\mu(z)^{-1} \quad \tilde{G}_\mu(z)^{-1} \left( \begin{array}{cc} 1 & 0 \\ 0 & (-\Delta_R)^{-1} \end{array} \right)
\]

are twisted (bounded) \( h \)-admissible operators associated with the regular unitary covering \((\mathcal{U}_\ell, \Omega_\ell)_{\ell=0,\ldots,m} \). As a consequence, \( \tilde{G}_\mu(z)^{-1} \) can be written as,

\[
\tilde{G}_\mu(z)^{-1} = \begin{pmatrix} E_\mu^+(z) & E_\mu^-(z) \\ E_\mu^-(z) & z - \bar{P}_\mu(z) \end{pmatrix},
\]

where \( \bar{P}_\mu(z) \) is an unbounded \( h \)-admissible operator on \( L^2(\mathbb{R}^3) \oplus L^2(\mathbb{R}^3) \) with domain \( H^2(\mathbb{R}^3) \oplus H^2(\mathbb{R}^3) \), and \( E_\mu(z), E_\mu^\pm(z) \) are (bounded) twisted \( h \)-admissible operators (all depending in a holomorphic way on \( z \)).

More precisely, it results from [MaMe], formula (2.11), that the operator \( \bar{P}_\mu(z) \) is given by the formula,

\[
\bar{P}_\mu(z) = Z_\mu^+ \tilde{H}_\mu Z_\mu^- - Z_\mu^+ [h^2 S_\mu \Delta_R S^-_\mu, \tilde{\Pi}_{\mu,0}] (\tilde{H}_\mu' - z)^{-1} [\tilde{\Pi}_{\mu,0}, h^2 S_\mu \Delta_R S^-_\mu] Z_\mu^- \quad (24)
\]

where \( \tilde{\Pi}_{\mu,0} \) stands for the projection on \( L^2(\mathbb{R}^6) \) induced by the action of \( \tilde{\Pi}_{\mu,0}(R) \) on \( L^2(\mathbb{R}^3) \), and \( \tilde{H}_\mu' \) is the restriction of \( (1 - \tilde{\Pi}_{\mu,0}) \tilde{H}_\mu(1 - \tilde{\Pi}_{\mu,0}) \) to the range of \( 1 - \tilde{\Pi}_{\mu,0} \). In particular, \( \tilde{H}_\mu' - z \) is invertible in virtue of (22), and \( \tilde{\Pi}_{\mu,0} \) is a twisted \( h \)-admissible operator on \( L^2(\mathbb{R}^3, L^2(\mathbb{R}^3)) \) (in the sense of Definition 4.4 in [MaSo]), associated with the regular unitary covering \((\mathcal{U}_\ell, \Omega_\ell)_{\ell=0,\ldots,m} \).

By Lemma 3.7 we also know that \( \bar{P}_\mu(z) \) commutes with \( L_R \), and thus, gathering all the previous information on \( \bar{P}_\mu(z) \), we finally obtain that it can be written as,

\[
\bar{P}_\mu(z) = -h^2 S_\mu \Delta_R S^-_\mu + \mathcal{M}_\mu(R) + h A_\mu(R, hD_R) + h^2 B_\mu(R, hD_R; z, h) \quad (25)
\]

where, for any \( R > \frac{3}{R} \), \( \mathcal{M}_\mu \) is given by,

\[
\mathcal{M}_\mu(R) = \begin{pmatrix} W_1(\phi_\mu(R)) & 0 \\ 0 & W_2(\phi_\mu(R)) \end{pmatrix}, \quad W_j(R) = \mathcal{E}_j(R) + \frac{1}{R} \quad (26)
\]

and, for \( R \leq \frac{3}{R} \) and \( \mu \) sufficiently small, it satisfies,

\[
\text{Re} \mathcal{M}_\mu(R) \geq \frac{M}{4} + \text{inf}_{R} \mathcal{E}_1(R). \quad (27)
\]
Moreover, for some smooth bounded (together with its derivatives) function $a_\mu(R)$ independent of $z$. Finally, $B_\mu(R, hD_R; z, h)$ is an $h$-admissible pseudodifferential operator depending analytically on $z$, with Weyl symbol $b_\mu(R, R^*; z, h)$ holomorphic with respect to $R^*$ in a complex strip of the form $\{|\Im R^*| < \delta\}$ (with $\delta > 0$ independent of $z$ and $\mu$), such that, for any multi-index $\alpha$,

$$\partial^\alpha b_\mu(R, R^*; z, h) = O(1)$$

uniformly with respect to $(R, R^*) \in \mathbb{R}^3 \times \mathbb{R}^3$, $h > 0$ small enough, and $z$ close enough to some fix $\lambda_0 \in \mathbb{C}$ such that $\Re \lambda_0 < \inf_R \tilde{E}_3(R)$ and $\Im \lambda_0$ sufficiently small.

Finally, the operators $A_\mu$ and $B_\mu(R, hD_R; z, h)$ commute with $L_R$, and one has the Feshbach identities,

$$\begin{align*}
(H_\mu - z)^{-1} &= E_\mu^+(z) + E_\mu^-(z)(\tilde{P}_\mu^r(z) - z)^{-1}E^r_\mu^-(z), \\
(\tilde{P}_\mu^r(z) - z)^{-1} &= Z^*_\mu(\tilde{H}_\mu - z)^{-1}Z^r_\mu.
\end{align*}$$

Summing up, we have proved,

**Theorem 3.8.** Let $\tilde{E}_3(R)$ be defined as in Proposition 3.4 and let $\lambda_0 \in \mathbb{C}$ with $\Re(\lambda_0) < \inf_R \tilde{E}_3(R)$ and $\Im(\lambda_0)$ sufficiently small. Under the previous assumptions, there exists a complex neighborhood $D_{\lambda_0}$ of $\lambda_0$ such that, for any $z \in D_{\lambda_0}$, one has the equivalence,

$$z \in \text{Sp}(\tilde{H}_\mu) \iff z \in \text{Sp}(\tilde{P}_\mu(z)),$$

where $\tilde{P}_\mu(z)$ is as in (25) with (20)-(29).

Now, taking advantage of Lemma 3.7, we can consider the restriction of the Grushin problem $\mathcal{G}_\mu(z)$ on $\text{Ker}(L_R + L^r) \oplus \text{Ker}(L_R) \oplus \text{Ker}(L^r)$, and we also immediately obtain,

**Corollary 3.9.** Denote by $\tilde{H}_\mu^0$ the restriction of $\tilde{H}_\mu$ on the invariant subspace $\text{Ker}(L_R + L^r)$, and by $\tilde{P}_\mu^0(z)$ the restriction of $\tilde{P}_\mu(z)$ on the invariant subspace $\text{Ker}(L^r)$. Then, for any $\lambda_0 \in \mathbb{C}$ with $\Re(\lambda_0) < \inf_R \tilde{E}_3(R)$ and $\Im(\lambda_0)$ sufficiently small, there exists a complex neighborhood $D_{\lambda_0}$ of $\lambda_0$ such that, for any $z \in D_{\lambda_0}$, one has the equivalence,

$$z \in \text{Sp}(\tilde{H}_\mu^0) \iff z \in \text{Sp}(\tilde{P}_\mu^0(z)).$$

In the sequel, we also denote by $H_\mu^0$ the restriction of $H_\mu$ on the invariant subspace $\text{Ker}(L_R + L^r)$. 

Here, $M$ is the same as in Proposition 3.4 and Definition 3.5 and it can be chosen arbitrarily large.
4. Reduced problem

Let us introduce the following shortcut notation,
\[ D = hD_R, \quad D_R = -i \frac{d}{dR}. \]

For all \( R > 0 \), we define,
\[ W_{j,\mu}(R) := \zeta(R)W_j(\phi_\mu(R)) + \frac{M}{3}(1 - \zeta(R)), \]
where \( \zeta \) is as in Proposition 3.3 and \( M \) is taken large enough. In particular, \( W_{j,\mu} \) is bounded and depends analytically on \( \mu \).

Then, we set,
\[ A^0_{\mu}(R, hD_R) := \left( \begin{array}{cc} 0 & 0 \\ hD_R \cdot a^0_\mu(R) & 0 \end{array} \right), \]
where the function \( a^0_\mu \) is smooth and bounded together with all its derivatives on \((0, +\infty)\).

In this section, we look for the solutions to the eigenvalue equation,
\[ P^\#_{\mu}\varphi = \lambda \varphi, \quad \lambda \in \mathbb{C}, \quad \varphi = \left( \begin{array}{c} \varphi_1 \\ \varphi_2 \end{array} \right), \]
where \( P^\#_{\mu} \) is the differential operator formally defined as,
\[ P^\#_{\mu} = h^2S_\mu D^2R S^{-1}_\mu + M^0_{\mu}(R) + hA^0_{\mu}(R, hD_R) \]
acting on the Hilbert space,
\[ \mathcal{H}^2 = L^2([0, +\infty), dR) \oplus L^2([0, +\infty), dR), \]
with zero Dirichlet boundary condition at \( R = 0 \), and where now, with abuse of notation, we denote,
\[ (S_\mu \varphi)(R) = |I'(R)|^{1/2}\varphi |I(R)|, \quad I(R) = R[1 + \mu s(R)]. \]

If we set,
\[ P_{j,\mu} = h^2S_\mu D^2R S^{-1}_\mu + W_{j,\mu}(R), \]
then equation (31) turns into
\[ (P_{1,\mu} - \lambda) \varphi_1 = -hA^0_{\mu}\varphi_2; \quad (P_{2,\mu} - \lambda) \varphi_2 = -hA^0_{\mu}^*\varphi_1, \]
where
\[ A^0_{\mu} = ha^0_\mu(R)D_R. \]

Let us also observe that, by the Weyl theorem, the essential spectrum of \( P^\#_{\mu} \) is given by,
\[ \text{Sp}_{\text{ess}}(P^\#_{\mu}) = \mathcal{E}^\infty_1 + (1 + \mu)^{-2}[0, +\infty). \]
As before, \( m_j \) is the local minima of \( W_j \) and \( M^1 \) is the local maximum of \( W^1 \), as defined in Remark 2.3. Now, for the sake of definiteness, we consider the case where

\[
E^\infty_1 < m_1 < m_2 < M_1
\]

(37)

In the case where \( E^\infty_1 < m_1 < M_1 < m_2 \) then we can apply the same argument to the interval \([m_1, M_1]\).

Remark 4.1. By construction, we have \( \text{Sp}(H_{\mu,e}(\mathbb{R})) = \text{Sp}(H_e(I_{\mu}(\mathbb{R}))). \) Therefore, if the function \( s(x) \) used in the distortion vanishes in a sufficiently compact set (and since \( W_{j,\mu} \) and \( W_j \) coincide on this set), a continuity argument shows that, for \( \mu \in \mathbb{C} \) small enough, the critical points of \( \text{Re} W_{j,\mu} \) and \( W_j \) coincide and remain non-degenerate.

As a consequence, for any \( \lambda \in [m_1, m_2 + \alpha] \) (with \( \alpha > 0 \) small enough), the function \( W_1(R) - \lambda \) presents the shape of a well in an island in the sense of \([\text{HeS}]^2\). Moreover, since we are in dimension one, the complementary of the island (that is, the non compact component of \( \{W_1 \leq \lambda\} \)) is automatically non-trapping, and we can adopt the general strategy used in \([\text{Ma2}]\) (see also \([\text{CMR, FLM}]\)), that consists in taking \( \mu = 2i h \ln \frac{1}{\lambda} \) in the definition of the analytic distortion. The function \( s(x) \) used in \([\text{I}-\text{E}]\) can also be assumed to be 0 on a neighborhood of the “greatest” island, defined by \( \{ R > 0 ; W_1(R) \geq m_1 \} \). Then, following \([\text{FLM}]\), Theorem 2.2 (see also \([\text{HeS}]^2\), Proposition 9.6), we first show that the eigenvalues of \( P^\mu_{\Delta} \) with their real part in \([m_1, m_2 + \alpha]\), coincide, up to an exponentially small error term, with eigenvalues of the Dirichlet realization \( P^\mu_D \) of \( P^\mu_{\Delta} \) on the interval \([0, R_1,M]\).

Proposition 4.2. Let \( \alpha > 0 \) small enough, and let \( \mathcal{J} \subset (0,1] \), with \( 0 \in \mathcal{J} \), such that there exists a function \( a(h) > 0 \) defined for \( h \in \mathcal{J} \) and verifying,

\[
\text{For all } \varepsilon > 0, a(h) \geq \frac{1}{C_\varepsilon} e^{-\varepsilon/h} \text{ for } h \in \mathcal{J} \text{ small enough; (38)}
\]

\[
\text{Sp}(P^\mu_D) \cap [m_2 + \alpha - 2a(h), m_2 + \alpha + 2a(h)] = \emptyset. \quad (39)
\]

Set,

\[
\Omega(h) := \{ z \in \mathbb{C} ; \text{dist}(\text{Re} z, [m_1, m_2 + \alpha]) < a(h), | \text{Im} z | < C^{-1} h \ln \frac{1}{R} \},
\]

with \( C > 0 \) a large enough constant. Then, there exists \( \delta_0 > 0 \) and a bijection,

\[
b : \text{Sp}(P^\mu_D) \cap [m_1, m_2 + \alpha] \to \text{Sp}(P^\mu_{\Delta}) \cap \Omega(h),
\]

such that,

\[
b(\lambda) - \lambda = \mathcal{O}(e^{-\delta_0/h}),
\]

uniformly for \( h \in \mathcal{J} \).

Remark 4.3. In our situation, it is well known (see, e.g., \([\text{HeRo}]\)) that the distance between two consecutive eigenvalues of the Dirichlet realizations of \( P_1 \) and \( P_2 \) on \((0, R_{1,M})\), behaves like \( h \) as \( h \to 0_+ \). Then, by slightly moving the parameter \( \alpha \), it is not difficult to deduce that the previous proposition actually gives a complete description of the spectrum of \( P^\mu_{\Delta} \) in a neighborhood of \([m_1, m_2 + \alpha]\), for all sufficiently small values of \( h > 0 \).
Proof. At first, we fix a function $F = F(R) \in C^\infty_0((0, R_{1,M}); \mathbb{R}_+)$, such that,

$$\inf_{(0,R_{1,M})} (W_1 + F) > m_2 + \alpha,$$

and we denote by $p_{j,x} = p_{j,x}(R, R^*)$ the principal symbol of the operator $P_{j,x}$. We also denote by $\tilde{p}_{j,x}$ an almost analytic extension of $p_{j,x}$ (see, e.g., [CMR] Section 7). If $\alpha$ and, by means of a density argument, we can extend such an estimate to any $\{F(R) + \text{Re } p_{1,\mu}(R, R^*)\in [m_1 - \delta, m_2 + \alpha + \delta]\}$ (with $\delta > 0$ small enough), one has,

$$- \Im \tilde{p}_{1,\mu} \left( R - h \ln \frac{1}{h} (\partial R_{f_0} + i \partial R_{f_0}), R^* - h \ln \frac{1}{h} (\partial R_{v_0} - i \partial R_{f_0}) \right) \geq \delta h \ln \frac{1}{h}.$$

As a consequence (see, e.g., [CMR] Section 7), if $z \in \mathbb{C}$ is such that $\text{dist}(z, [m_1, m_2 + \alpha]) << h \ln(1/h)$, then, the operator $P_{1,\mu} + F - z$ is invertible on $L^2(\mathbb{R}_+)$, and its inverse satisfies,

$$\|h^{-f_0} T(P_{1,\mu} + F - z)^{-1} u\|_{L^2(\mathbb{R})} \leq C |h \ln h|^{-1} \|h^{-f_0} T u\|_{L^2(\mathbb{R})},$$

(40)

where $C > 0$ is a constant, and $T : L^2(\mathbb{R}_+) \to L^2(\mathbb{R}^2)$ is the Bargmann transform, defined by,

$$Tu(R, R^*) := \frac{1}{2\pi h} \int_{R^2 > 0} e^{i(R - R')R^*/h - (R - R')^2/2h} u(R') dR'.$$

Indeed, for any $u \in C^\infty_0(\mathbb{R}_+)$ we have,

$$\|h^{-f_0} T e\|_{L^2(\mathbb{R})} \leq \frac{C}{|h \ln h|} \|h^{-f_0} T(P_{1,\mu} + F - z)v\|_{L^2(\mathbb{R})},$$

(41)

and, by means of a density argument, we can extend such an estimate to any $u \in H^2 \cap H^1_0(\mathbb{R}_+)$. Then, inequality (40) holds true for the function $u = (P_{1,\mu} + F - z)v$, which belongs to the space $L^2(\mathbb{R}_+)$ and satisfies the Dirichlet condition at $R = 0$. This means that the operator $(P_{1,\mu} + F - z)^{-1}$ has a norm $O(|h \ln h|^{-1})$ if we consider it as acting on the space $\mathcal{H} = L^2(\mathbb{R}_+)$ endowed with the norm given by: $\|u\|_{\mathcal{H}} := \|h^{-f_0} T u\|_{L^2(\mathbb{R})}$. On the other hand, by construction, the operator $P_{2,\mu} + F$ has a real part larger than $m_2 + \alpha$, and thus, if $\Re z \leq m_2 + \alpha$, we also see that the operator $(P_{2,\mu} + F - z)^{-1}$ has a uniformly bounded norm when acting on $\mathcal{H}$. Then, proceeding as in [HeS2], Section 9 (see also [FLM], Section 2), we pick up two functions $\chi_1, \chi_2 \in C^\infty_0((0, R_{1,M}); [0, 1])$, such that $\chi_1 = 1$ in a neighborhood of $\text{Supp } \chi_2$, and $\chi_2 = 1$ in a neighborhood of $\text{Supp } F$. Setting,

$$Q^D_\mu := P^D_\mu + F ; R^D_\mu(z) := \chi_1 (P^D_\mu - z)^{-1} \chi_2 + (Q^D_\mu - z)^{-1} (1 - \chi_2),$$

(42)

we see that, if $\text{dist}(z, \text{Sp}(P^D_\mu)) \geq \alpha(h)$, then (HeS2, Formula (9.39) and Proposition 9.8),

$$(P^D_{\mu} - z)R^D_{\mu}(z) = I + K^\mu_{\mu}(z) \text{ with } \|K^\mu_{\mu}(z)\|_{\mathcal{L}(\mathcal{H})} = O(e^{-2\delta/h}),$$
where $\delta > 0$ is some constant. Therefore, for such values of $z$ and for $h$ small enough, we have,

$$
(P^\sharp_\mu - z)^{-1} = R^\sharp_\mu(z) \sum_{j \geq 0} (-K_\mu(z))^j,
$$

and since $\|R^\sharp_\mu(z)\|_\mathcal{H} = \mathcal{O}(h^{-C})$ for some constant $C > 0$, we deduce that, if $\gamma$ is a simple oriented loop around $\text{Sp}(P^\sharp_D) \cap [m_1, m_2 + \alpha]$, such that $\text{dist}(\gamma, \text{Sp}(P^\sharp_D)) \geq a(h)$ and $\text{dist}(\gamma, [m_1, m_2 + \alpha]) << |h \ln h|$, then,

$$
\Pi^\sharp_\mu := \frac{1}{2i\pi} \int_\gamma (z - P^\sharp_\mu)^{-1} \, dz = -\frac{1}{2i\pi} \int_\gamma R^\sharp_\mu(z) + \mathcal{O}(e^{-\delta/h})
$$

$$
= \frac{1}{2i\pi} \int_\gamma \chi_1(z - P^\sharp_D)^{-1} \chi_2 \, dz + \mathcal{O}(e^{-\delta/h}).
$$

Here, we have also used the fact that $z \mapsto (Q^\sharp_\mu - z)^{-1}$ is holomorphic in the interior of $\gamma$, that can be taken equal to $\Omega(h)$.

Now, since $\Pi^\sharp_\mu$ is the spectral projector of $P^\sharp_\mu$ associated with $\Omega(h)$, the corresponding resonances of $P^\sharp$ are nothing but the eigenvalues of $P^\sharp_\mu \Pi^\sharp_\mu$, restricted to the range of $\Pi^\sharp_\mu$. Moreover, if we set $\{\mu_1, \ldots, \mu_m\} := \text{Sp}(P^\sharp_\mu) \cap [m_1, m_2 + \alpha]$, and if we denote by $\phi_1, \ldots, \phi_m$ an orthonormal basis of $\bigoplus_{j=1}^m \ker(P^\sharp_D - \mu_j)$, then, by Agmon estimates, we see on $\{44\}$ (see also $[\text{HeS}2]$, Theorem 9.9 and Corollary 9.10) that the functions $\Pi^\sharp_\mu \phi_j$ form a basis of $\text{ran} \Pi^\sharp_\mu$, and the matrix of $P^\sharp_\mu |_{\text{ran} \Pi^\sharp_\mu}$ in this basis, is of the form $\text{diag}(\mu_1, \ldots, \mu_m) + \mathcal{O}(e^{-\delta/h})$. Then, the result follows from standard arguments on the eigenvalues of finite matrices (plus the fact that $m = \mathcal{O}(h^{-N_0})$ for some $N_0 \geq 1$ constant).

Now, exploiting the fact that both $W_1(R_1, M)$ and $W_2(R_1, M)$ are (strictly) greater than $m_2$, we consider two functions $W_j \in C^\infty(\mathbb{R}^+; \mathbb{R})$ ($j = 1, 2$), such that,

$$
\tilde{W}_j = W_j \text{ on } [0, R_1, M]; \tilde{W}_j \text{ is constant on } [2R_1, +\infty]; \inf_{[R_1, M, +\infty]} \tilde{W}_j > m_2,
$$

and we set,

$$
\tilde{\mathcal{M}}_0(R) := \begin{pmatrix}
\tilde{W}_1(R) & 0 \\
0 & \tilde{W}_2(R)
\end{pmatrix},
$$

$$
\tilde{P}^\sharp := h^2D^2_R + \tilde{\mathcal{M}}_0(R) + hA_0(R, hD_R),
$$

acting on the space $\mathcal{H}^\sharp$. That is, $\tilde{P}^\sharp$ is obtained form $P^\sharp$ by substituting $\tilde{W}_1, \tilde{W}_2$ to $W_1, W_2$. Then, the same arguments used in Proposition L2 (and actually simpler, since both operators are self-adjoints) show that, under the same conditions, the spectrum of $P^\sharp_D$ and the spectrum of $\tilde{P}^\sharp$ coincide in $[m_1, m_1 + \alpha + a(h)]$, up to some exponentially small error-terms. Therefore, in order to know the resonances of $P^\sharp$ in $\Omega(h)$ (up to those exponentially small error-terms), it is sufficient to study the eigenvalues $\lambda$ of the self-adjoint $\tilde{P}^\sharp$ in $[m_1, m_1 + \alpha + a(h)]$.

For $j = 1, 2$, we set,

$$
\tilde{P}_j := h^2D^2_R + \tilde{W}_j,
$$

acting on $L^2(\mathbb{R}^+; dR)$ with Dirichlet condition at $R = 0$, and we consider separately two different cases.
4.1. **Case 1**: $\lambda \leq (m_2 - \alpha)$. In that case, the operator $\tilde{P}_2 - \lambda$ is invertible, with a uniformly bounded inverse, and the equation,

$$\tilde{P}_2 \varphi = \lambda \varphi, \quad \varphi = \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix},$$  \hspace{1cm} (45)

can be re-written as,

$$\varphi_2 = - h (\tilde{P}_2 - \lambda)^{-1} A_0^* \varphi_1;$$
$$[\tilde{P}_1 - h^2 A_0 (\tilde{P}_2 - \lambda)^{-1} A_0^*] \varphi_1 = \lambda \varphi_1.$$  

Thus, the eigenvalues $\lambda$ are given by the equation,

$$\lambda = \tilde{f}_k(\lambda),$$  \hspace{1cm} (46)

where the $\tilde{f}_k(\lambda)$’s are the eigenvalues of $\hat{P}_1(\lambda) := \tilde{P}_1 - h^2 A_0 (\tilde{P}_2 - \lambda)^{-1} A_0^*$.

Writing,

$$\hat{P}_1(\lambda) - z = (1 - h^2 A_0 (\tilde{P}_2 - \lambda)^{-1} A_0^* (\tilde{P}_1 - z)^{-1}) (\tilde{P}_1 - z),$$

and observing that, for $z \notin \text{Sp}(\tilde{P}_1)$, $A_0^* (\tilde{P}_1 - z)^{-1}$ is bounded and has a norm $O(\text{dist} (z, \text{Sp}(\tilde{P}_1))^{-1})$, we conclude that, if $\text{dist} (z, \text{Sp}(\tilde{P}_1)) \gg h^2$, then $\hat{P}_1(\lambda) - z$ is invertible, and its inverse satisfies,

$$(\hat{P}_1(\lambda) - z)^{-1} = (\tilde{P}_1 - z)^{-1} (1 + O(h^2/\text{dist} (z, \text{Sp}(\tilde{P}_1)))).$$  

Differentiating with respect to $\lambda$, we also obtain,

$$\frac{d}{d\lambda} (\hat{P}_1(\lambda) - z)^{-1} = (\tilde{P}_1 - z)^{-1} O(h^2/\text{dist} (z, \text{Sp}(\tilde{P}_1))) = O(h^2/\text{dist} (z, \text{Sp}(\tilde{P}_1))^2).$$

Then, using the fact that, under the non degenerate condition discussed in Remark 411, the eigenvalues $E_{1,k}$ ($k \geq 1$) of $\hat{P}_1$ are distant at least of order $h$ between each other, for each of them we can define the projection,

$$\hat{\Pi}_1(\lambda) := \frac{1}{2i\pi} \int_{\gamma_k} (z - \hat{P}_1(\lambda))^{-1} dz,$$

where $\gamma_k$ is a complex oriented simple circle centered at $E_{1,k}$ of radius $\delta h$ with $\delta > 0$ small enough. Applying standard regular perturbation theory, we easily conclude that the $k$-th eigenvalue of $f_k(\lambda)$ of $\hat{P}_1(\lambda)$ satisfies,

$$f_k(\lambda) = E_{1,k} + O(h^2); \quad \frac{df_k}{d\lambda}(\lambda) = O(h),$$  \hspace{1cm} (47)

uniformly with respect to $h$ small enough, $k \geq 1$ such that $E_{1,k}^2 \leq m_2 - \frac{1}{2}\alpha$, and $\lambda \leq m_2 - \alpha$.

By the implicit function theorem, it follows that the $k$-th eigenvalue $\lambda_k$ of $\tilde{P}_2$ satisfies,

$$\lambda_k = E_{1,k} + O(h^2),$$

uniformly with respect to $h > 0$ small enough and to $k = O(h^{-1})$, such that $E_{1,k} \leq m_2 - \frac{1}{2}\alpha$. 

THE STARK EFFECT ON $h_2^*-LIKE$ MOLECULES 21
4.2. Case 2: $\lambda \in [m_2 - \alpha, m_2 + \alpha]$ with $\alpha > 0$ small enough. We denote by $\phi_1, \ldots, \phi_n$ an orthonormal family of eigenfunctions of $\tilde{P}_1$ with eigenvalues in the interval $[m_2 - 2\alpha, m_2 + 2\alpha]$ and by $\psi_1, \ldots, \psi_m$ an orthonormal family of eigenfunctions of $\tilde{P}_2$ with eigenvalues in the interval $[m_2, m_2 + 2\alpha]$ (in particular, we have $n, m = O(h^{-1})$).

For $\alpha + \beta \in \mathbb{C}^n + \mathbb{C}^m$, we set,
\[
R_{-}(\alpha + \beta) := \alpha \cdot \phi + \beta \cdot \psi \in \mathcal{H}^2,
\]
where we have used the notation,
\[
\alpha \cdot \phi := \sum_{k=1}^{n} \alpha_k \phi_k ; \quad \beta \cdot \psi := \sum_{\ell=1}^{m} \beta_\ell \psi_\ell.
\]

We also denote by $R_+$ the adjoint of $R_-$, given by,
\[
R_{+}(u + v) = ((u, \phi_k))_{1 \leq k \leq n} + ((v, \psi_\ell))_{1 \leq \ell \leq m}.
\]

Then, we consider the operator valued matrix,
\[
G(\lambda) = \begin{pmatrix}
\tilde{P}_2^* - \lambda & R_- \\
R_+ & 0
\end{pmatrix},
\]
on
\[
\mathcal{H}^2 \oplus \mathbb{C}^n \oplus \mathbb{C}^m,
\]
with domain $(H^2 \cap H^1_0)(\mathbb{R}_+) \oplus (H^2 \cap H^1_0)(\mathbb{R}_+) \oplus \mathbb{C}^n \oplus \mathbb{C}^m$, and we want to know whether $G(\lambda)$ is invertible.

We denote by $\Pi_1$ and $\Pi_2$ the orthogonal projections on the subspaces $S_n$ and $S_m$ of $L^2(\mathbb{R}_+)$ spanned by the eigenfunctions $\phi_1, \ldots, \phi_n$ and $\psi_1, \ldots, \psi_m$ respectively, and we set,
\[
\Pi := \begin{pmatrix}
\Pi_1 & 0 \\
0 & \Pi_2
\end{pmatrix} ; \quad \Pi^\perp := \begin{pmatrix}
\Pi^\perp_1 & 0 \\
0 & \Pi^\perp_2
\end{pmatrix} := \begin{pmatrix}
1 - \Pi_1 & 0 \\
0 & 1 - \Pi_2
\end{pmatrix}.
\]

We first prove,

**Lemma 4.4.** For $\lambda \in [m_2 - \alpha, m_2 + \alpha]$, the operator $\Pi_1 \tilde{P}_2^* \Pi_1^\perp - \lambda =: \tilde{P}_1^\perp - \lambda$ is invertible on the range $\text{Ran} \, \Pi_1^\perp$ of $\Pi_1^\perp$, and its inverse $(\tilde{P}_1^\perp - \lambda)^{-1}$ is uniformly bounded.

**Proof.** We have,
\[
\Pi_1^\perp (\tilde{P}_2^* - \lambda) \Pi_1^\perp = \begin{pmatrix}
\Pi_1^\perp (\tilde{P}_1^\perp - \lambda) \Pi_1^\perp & h \Pi_1^\perp A_0 \Pi_2^\perp \\
h \Pi_2^\perp A_0^\perp \Pi_1^\perp & \Pi_2^\perp (\tilde{P}_2^* - \lambda) \Pi_2^\perp
\end{pmatrix},
\]
and, denoting by $\tilde{P}^\perp_j$ the restriction of $\tilde{P}_j$ to $\text{Ran} \, \Pi_1^\perp$, we know that $\tilde{P}^\perp_j - \lambda$ is invertible, and it is standard to show that its inverse is uniformly bounded from $\text{Ran} \, \Pi_1^\perp$ to $\text{Ran} \, \Pi_2^\perp \cap (H^2 \cap H^1_0)(\mathbb{R}_+)$, if one takes the $h$-dependent norm on $H^2(\mathbb{R}_+)$ defined by: $\|u\|_{H^2}^2 := h^2 \|\Delta u\|_{L_2}^2 + \|u\|_{L_2}^2$. As a consequence, $A_0 \Pi_2^\perp (\tilde{P}_2^* - \lambda)^{-1} \Pi_2^\perp$ and $A_0 \Pi_1^\perp (\tilde{P}_2^* - \lambda)^{-1} \Pi_1^\perp$ are uniformly bounded on $L^2(\mathbb{R}_+)$ (together with their adjoint), and we find,
\[
\Pi_1^\perp (\tilde{P}_2^* - \lambda) \Pi_1^\perp = \Pi_1^\perp (1 + O(h)) \Pi_1^\perp;
\]
Moreover, using that \( \| \) to see that both \( A_1 \Pi \) and \( \Pi \) therefore, in order to complete the proof of Proposition 4.5, it is enough to show, and, since \( \Pi \) j \( Q \) in particular, \( \psi \) where \( E \) \( \perp \) thus, the result follows by taking the restriction to \( \text{Ran} \ \Pi \) , and by using the Neumann series in order to inverse \( \Pi (1+O(h)) \Pi \big|_{\text{Ran} \ \Pi} = (1+\Pi O(h)) \big|_{\text{Ran} \ \Pi} \). Using the previous lemma, it is easy to show that \( G(\lambda) \) is invertible, and to check that its inverse is given by, \[
G(\lambda)^{-1} = \begin{pmatrix}
\Pi (\tilde{P}_+^\perp - \lambda)^{-1} 
\Pi (\tilde{P}_-^\perp - \lambda)^{-1}
\end{pmatrix}
\begin{pmatrix}
1 - \Pi (\tilde{P}_+^\perp - \lambda)^{-1} \Pi (\tilde{P}_-^\perp - \lambda)^{-1} \Pi \lambda - Q(\lambda)
R_+(1 - \tilde{P}_+^\perp \Pi \tilde{P}_-^\perp - \lambda)^{-1} \Pi \lambda - Q(\lambda)
\end{pmatrix}
\] with, \[
Q(\lambda) := R_+ \tilde{P}_+^\perp (1 - \Pi (\tilde{P}_+^\perp - \lambda)^{-1} \Pi (\tilde{P}_-^\perp - \lambda)^{-1} \Pi \lambda - Q(\lambda)) \big|_{\text{Ran} \ \Pi}.
\] (48)
In particular, \( Q(\lambda) \) is an \((n+m) \times (n+m)\) matrix with \( n, m = O(h^{-1}) \).

**Proposition 4.5.** The matrix \( Q(\lambda) \) satisfies, \[
Q(\lambda) = \text{diag} (E_{1,1}, \ldots, E_{1,n}, E_{2,1}, \ldots, E_{2,m}) + S(\lambda),
\] where \( E_{1,j}, E_{2,k} \in [m_2 - 2\alpha, m_2 + 2\alpha] \) are the eigenvalues associated with \( \phi_j \) and \( \psi_k \), respectively, and with, \[
\| S(\lambda) \| + \| \frac{d}{d\lambda} S(\lambda) \| = O(h^2),
\] in the sense of the norm of operators on \( \mathbb{C}^{n+m} \), and uniformly with respect to \( h > 0 \) small enough and \( n, m = O(h^{-1}) \).

**Proof.** Since \( R_+ \Pi = 0 \) and \( \Pi \Pi R_- = 0 \), by (48), we have, \[
Q(\lambda) = R_+ \tilde{P}_+^\perp R_- + R_+ \Pi \tilde{P}_+^\perp \Pi (\tilde{P}_+^\perp - \lambda)^{-1} \Pi (\tilde{P}_-^\perp - \lambda)^{-1} \Pi \lambda - Q(\lambda) \big|_{\text{Ran} \ \Pi},
\] (49)
\[
\frac{d}{d\lambda} Q(\lambda) = R_+ \Pi \tilde{P}_+^\perp R_- + R_+ \Pi \tilde{P}_+^\perp \Pi (\tilde{P}_+^\perp - \lambda)^{-2} \Pi \tilde{P}_+^\perp \Pi \lambda - Q(\lambda) \big|_{\text{Ran} \ \Pi},
\] (50)
and, since \( \Pi_+ \tilde{P}_j \Pi_+^\perp = 0 \) \((j = 1, 2)\), \[
\Pi \tilde{P}_+^\perp \Pi_+^\perp = \begin{pmatrix}
0 
\hbar \Pi_1 A_0 \Pi_2^\perp 
\hbar \Pi_1 A_0 \Pi_2^\perp 
0
\end{pmatrix}
\] (51)
Moreover, using that \( \| \tilde{P}_j \|_{L^2(\mathcal{D})} \leq |m_2| + 2\alpha \) and the ellipticity of \( \tilde{P}_j \), it is easy to see that both \( A_0^* \Pi_1 \) and \( A_0^* \Pi_2 \) are uniformly bounded, thus so are their adjoints \( \Pi_1 A_0 \) and \( \Pi_2 A_0 \), and we deduce from (49)-(51) (plus the fact that \( R \leq 1 \)), \[
Q(\lambda) = R_+ \tilde{P}_+^\perp R_- + O(h^2) \big|_{\text{Ran} \ \Pi}, \quad \frac{d}{d\lambda} Q(\lambda) = O(h^2).
\] (52)
Therefore, in order to complete the proof of Proposition 4.5, it is enough to show,

**Lemma 4.6.** For all \( N \geq 0 \), there exists a constant \( C_N > 0 \) such that, for all \( j \in \{1, \ldots, n\} \) and \( k \in \{1, \ldots, m\} \), one has, \[
|\langle A_0 \phi_j, \psi_k \rangle| + |\langle A_0 \psi_k, \phi_j \rangle| \leq C_N h^N.
\]
Proof. We use the equations, 
\[ (\tilde{P}_1 - E_{1,j})\phi_j = 0 \quad ; \quad (\tilde{P}_2 - E_{2,k})\psi_k = 0. \] (53)
At first, we observe that, for \( R \) close enough to 0 (say, \( 0 < R < r_0 \)), and \( R \) large enough (say, \( R > R_0 \)), both \( W_1(R) - E_{1,j} \) and \( W_2(R) - E_{2,k} \) remain greater than some fix constant \( C > 0 \). Therefore, by standard Agmon estimates (see, e.g., [Ma1], Chapter 3, exercise 8), it is easy to show that, for \( h \) small enough, 
\[ \|\phi_j\|_{H^r((0,r_0)\cup(R_0,\infty))} + \|\psi_k\|_{H^r((0,r_0)\cup(R_0,\infty))} \leq e^{-c_0/h}, \] (54)
where the positive constant \( c_0 \) does not depend on \( j,k \) and \( s \geq 0 \) is arbitrary.

For \( \ell = 1,2 \), we set,
\[ \Sigma_\ell := \{(R,R^*) \in \mathbb{R}_+ \times \mathbb{R}; \tilde{p}_\ell(R,R^*) \in [m_2 - 2\alpha, m_2 + 2\alpha]\} \]
(whose we have used the notation \( \tilde{p}_\ell(R,R^*) := (R^*)^2 + \tilde{W}_\ell(R) \), and chose \( \chi_\ell \in C_0^\infty((\frac{1}{2}r_0,2R_0) \times \mathbb{R}) \), supported near \( \Sigma_\ell \), such that \( \chi_\ell = 1 \) in a neighborhood of \( \Sigma_\ell \). We also fix \( \chi_0 = \chi_0(R) \in C_0^\infty((\frac{1}{2}r_0,2R_0) \times \mathbb{R}) \), such that \( \chi_0 = 1 \) near \([r_0,R_0] \).

Then, using standard pseudodifferential calculus, for any \( E \in [m_2 - 2\alpha, m_2 + 2\alpha] \) one can construct a symbol \( q(E) = q_\ell(E,R,R^*;h) \in S((R^*)^{-2}) \), supported in \((\frac{1}{2}r_0,2R_0) \times \mathbb{R} \) and depending smoothly on \( E \), such that,
\[ q_\ell(E)\#(\tilde{p}_\ell - E)(R,R^*) \sim \chi_0(R)(1 - \chi_\ell(R,R^*)). \] (55)
Here, \( \# \) stands for the Weyl-composition of symbols, and the asymptotic equivalence holds in \( S(1) \), uniformly with respect to \( E \in [m_2 - 2\alpha, m_2 + 2\alpha] \) (see, e.g., [Ma1]). Then, first multiplying \( \chi_0(R) \) by \( \chi_0 \), then, commuting \( \chi_0 \) and \( \tilde{P}_j \), and finally applying the usual Weyl-quantization of \( q_\ell(E) \) (with \( E = E_{1,j}, E_{2,k} \), respectively), we deduce from \( \chi_0(R) \), \( \chi_\ell(R) \) and \( \chi_\ell(R) \),
\[ \|(1 - \chi_1(R,hD_R))\chi_0\phi_j\|_{H^*} = O(h^\infty); \] (56)
\[ \|(1 - \chi_2(R,hD_R))\chi_0\psi_k\|_{H^*} = O(h^\infty) \] (57)
uniformly with respect to \( j,k \) (here, \( \chi_\ell(R,hD_R) \) stands for the Weyl-quantization of \( \chi_\ell \)).

Now, if \( \alpha \) is taken sufficiently small, the sets \( \Sigma_1 \) and \( \Sigma_2 \) are disjoints, and thus the supports of \( \chi_1 \) and \( \chi_2 \) can be taken disjoints, too. Since they are also disjoints from \( \text{Supp} \ (1 - \chi_0) \), one can find \( \chi_3 \in C^\infty(\mathbb{R}_+ \times \mathbb{R}; [0,1]) \), supported in \((\frac{1}{2}r_0,2R_0) \times \mathbb{R} \), such that the family \( \{\chi_1,\chi_2,\chi_3\} \) forms a partition of unity on \( \text{Supp} \ \chi_0 \times \mathbb{R} \). In particular, on \( L^2(\mathbb{R}_+) \), one has,
\[ 1 - \chi_0(R) + \sum_{\ell=1}^3 \chi_\ell(R,hD_R)\chi_0(R) = I, \]
and now, it is clear that, inserting this microlocal partition of unity in the products \( \langle A_0\phi_j,\psi_k \rangle \) and \( \langle A_0\psi_k,\phi_j \rangle \), the estimates \( \chi_0 \), \( \chi_\ell \) and \( \chi_\ell \) give the required result. \( \square \)

Remark 4.7. Actually, following more precisely the construction of \( \tilde{H}_\ell^p \) made in Section 4, one can prove that the functions \( \tilde{W}_j \) (\( j = 1,2 \)) and \( a_0 \) depend in an analytic way of \( R \) in a neighborhood of the relevant classically allowed region \( \{\tilde{W}_1(R) \leq m_2 + 2\alpha\} \). As a consequence, one can use the standard microlocal
analytic techniques in this region (see, e.g., \cite{Ma}), and obtain the existence of a constant \( c_0 > 0 \) (independent of \( j, k \)), such that,
\[
|\langle A_0 \phi_j, \psi_k \rangle| + |\langle A_0 \psi_k, \phi_j \rangle| \leq e^{-c_0/h}.
\]

**Completion of the proof of the proposition:** Since the matrix,
\[
R_+ \tilde{P}^t R_- - \text{diag} \left( E_{1,1}, \ldots, E_{2,m} \right) = \begin{pmatrix}
0 & \langle A_0 \psi_k, \phi_j \rangle \\
\langle A_0 \psi_k, \phi_j \rangle & 0
\end{pmatrix}
\]
is of size \( O(h^{-1}) \), Lemma \ref{lem:high} implies that it has a norm \( O(h^\infty) \) on \( \mathbb{C}^{n+m} \), uniformly with respect to \( n, m \). Thus, Proposition \ref{prop:existence} is a consequence of \( \ref{prop:high} \).

By the Min-Max principle, it results from Proposition \ref{prop:convergence} that, for \( \lambda \in [m_2 - \alpha, m_2 + \alpha] \), the eigenvalues \( g_1(\lambda), \ldots, g_{m+n}(\lambda) \) of \( Q(\lambda) \) satisfy,
\[
\{ g_1(\lambda), \ldots, g_{m+n}(\lambda) \} = \{ E_{1,1}, \ldots, E_{1,n}, E_{2,1}, \ldots, E_{2,m} \} + O(h^2);
\]
\( \lambda \to g_\ell(\lambda) \) is Lipschitz continuous \( (\ell = 1, \ldots, n + m) \);
\[
\left| \frac{dg_\ell}{d\lambda} \right| = O(h^2) \text{ a.e. (} k = 1, \ldots, n + m \text{).} (58)
\]

Note that the values \( E_{1,1}, \ldots, E_{1,n} \) are at a distance of order \( h \) from each other, and the same is true for the values \( E_{2,1}, \ldots, E_{2,m} \). So the only problem that may appear in the computation of \( g_\ell(\lambda) \) is when, along some sequence \( h = h_j \to 0_+ \), two values \( E_{1,j} \) and \( E_{2,k} \) become closer than \( O(h^2) \). But, in that case, the two corresponding values of \( g_\ell(\lambda) \) are given by,
\[
g_\ell(\lambda) = \frac{1}{2} \left( E_{1,j} + E_{2,k} + h^2 r_1 \pm \sqrt{(E_{1,j} - E_{2,k} + h^2 r_2)^2 + h^4 r_3^2} \right), \quad (59)
\]
with \( r_1 = r_1(\lambda) \) smooth, \( r_t = O(1) \), \( dr_t/d\lambda = O(1) \) \( (t = 1, 2, 3) \). Thus, actually, a correct \( (h\text{-depending}) \) indexing of the \( g_\ell \)'s make them smooth functions of \( \lambda \), and then \( \ref{prop:existence} \) becomes true everywhere.

Anyway, \( \ref{prop:existence} \) is enough to insure that all the values of \( \lambda \in [m_2 - \alpha, m_2 + \alpha] \) such that \( \lambda \in \text{Sp } Q(\lambda) \) verify,
\[
\text{dist} (\lambda, \{ E_{1,1}, \ldots, E_{1,n}, E_{2,1}, \ldots, E_{2,m} \}) = O(h^2),
\]
and, conversely, at any \( E \in \{ E_{1,1}, \ldots, E_{1,n}, E_{2,1}, \ldots, E_{2,m} \} \cap [m_2 - \alpha + Ch^2, m_2 + \alpha - Ch^2] \) \( (C > 0 \text{ large enough}) \), can be associated a unique \( \lambda \in [m_2 - \alpha, m_2 + \alpha] \) such that \( \lambda \in \text{Sp } Q(\lambda) \).

Finally, using the fact that, by construction, the eigenvalues of \( \tilde{P}^t \) that lie in \( [m_2 - \alpha, m_2 + \alpha] \) coincide with the solutions there of \( \lambda \in \text{Sp } Q(\lambda) \), and summing up with the results of Subsection \ref{subsec:diagonals} and Proposition \ref{prop:convergence}, we finally obtain,

**Theorem 4.8.** For \( h > 0 \) small enough the resonances of \( P^t \) with real part in \( [m_1, m_2 + \alpha] \) and with imaginary part \( \ll |h \ln h| \), coincide, up to \( O(h^2) \) error-terms, with eigenvalues of the Dirichlet realizations of \( P_1 \) and \( P_2 \) on \( (0,R_{1,M}) \), where \( R_{1,M} > 0 \) is the point where \( W_1 \) admits a local maximum with value greater than \( m_2 \).
5. Comparison between the spectrum of the operators $P_\mu^\#$ and $\tilde{H}_\mu^0$

Here we prove,

**Proposition 5.1.** Let $\alpha > 0$ fixed small enough, and let $J \subset (0,1]$, with $0 \in \overline{J}$, such that there exists $\delta > 0$ such that,

$$\text{Sp}(P_\mu^\#) \cap [m_2 + \alpha - 2\delta h, m_2 + \alpha + 2\delta h] = \emptyset.$$  

(60)

Set,

$$\Omega(h) := \{ z \in \mathbb{C} : \text{dist}(\text{Re} z, [m_1, m_2 + \alpha]) < \delta h, |\text{Im} z| < C^{-1} h \ln \frac{1}{h} \},$$

with $C > 0$ a large enough constant. Then, there exists a bijection,

$$b : \text{Sp}(P_\mu^\#) \cap \Omega(h) \to \text{Sp}(\tilde{H}_\mu^0) \cap \Omega(h),$$

such that,

$$b(\lambda) - \lambda = \mathcal{O}(h^2),$$

uniformly for $h \in J$.

**Remark 5.2.** As before, by slightly moving the parameter $\alpha$, one can actually reach all the values of $h > 0$ small enough.

**Proof.** By Corollary 3.9, it is enough to prove that, for any $z \in \Omega(h)$, there exists a bijection

$$b_z : \text{Sp}(P_\mu^\#) \cap \Omega(h) \to \text{Sp}(\tilde{P}_\mu^0(z)) \cap \Omega(h),$$

such that,

$$b_z(\lambda) - \lambda = \mathcal{O}(h^2),$$

uniformly for $h \in J$ and $z \in \Omega(h)$.

By (25) we have,

$$\tilde{P}_\mu^0(z) = Q_\mu^0 + h^2 B_\mu^0,$$  

(61)

where $B_\mu^0$ stands for the restriction of $B_\mu(R, hD_R; z, h)$ to $\text{Ker}(L_R)$, and where we have set,

$$Q_\mu^0 := Q_\mu \big|_{\text{Ker}(L_R)},$$

$$Q_\mu := -h^2 S_\mu \Delta_R S_\mu^{-1} + M_\mu(R) + h A_\mu(R, hD_R).$$

By passing in polar coordinates, and by conjugating $Q_\mu$ with the transform

$$L^2(\mathbb{R}_+; R^2dR) \otimes L^2(S^2) \ni \psi \mapsto R\psi \in L^2(\mathbb{R}_+; dR) \otimes L^2(S^2),$$

we see that $Q_\mu^0$ is unitarily equivalent to,

$$\tilde{Q}_\mu^0 := h^2 S_\mu D_R^2 S_\mu^{-1} + M_\mu(R) + h A_\mu^0(R, hD_R)$$

on $L^2(\mathbb{R}_+; dR)$ with Dirichlet boundary condition at $R = 0$ (the notations are those of the previous section, in particular (31)).

We first have,

**Lemma 5.3.** There exist $\delta_0 > 0$ and a bijection,

$$b_0 : \text{Sp}(P_\mu^\#) \cap \Omega(h) \to \text{Sp}(Q_\mu^0) \cap \Omega(h),$$

such that,

$$b_0(\lambda) - \lambda = \mathcal{O}(e^{-\delta_0/h}),$$

uniformly for $h \in J$. 


Proof: This is just a slight modification of the proof of Proposition 4.2. Indeed, using (27), we see that the proof can be repeated exactly in the same way by substituting \( \tilde{Q}_\mu^0 \) to \( P_\mu^2 \). Thus, both the spectra of \( \tilde{Q}_\mu^0 \) and \( P_\mu^2 \) are close to that of \( P_\mu^2_D \) up to exponentially small error terms, and since \( \tilde{Q}_\mu^0 \) and \( Q_\mu^0 \) have the same spectrum, the result follows. \( \square \)

Therefore, it only remains to compare the spectra of \( \tilde{P}_\mu^0(z) \) and \( Q_\mu^0 \).

For any fixed integer \( k \geq 1 \), let us denote by \( E_k = E_k(h) \) the \( k \)-th eigenvalue of \( P_2 \). By the previous lemma and Remark 4.3, we see that, if we fix \( \delta > 0 \) sufficiently small, then, the disc \( \{ \lambda \in \mathbb{C}; |\lambda - E_k(h)| \leq \delta h \} \) contains at most two eigenvalues of \( Q_\mu^0 \) (for \( h > 0 \) small enough) and, on the set \( J_k \) of those values of \( h \) for which it contains two eigenvalues, the domain \( \{ \lambda \in \mathbb{C}; \delta h < |\lambda - E_k(h)| \leq 2\delta h \} \) does not meet \( \text{Sp}(Q_\mu^0) \).

Then, for \( k \geq 1 \) we define,

\[
\gamma_k(h) = \begin{cases} \{ \lambda \in \mathbb{C}; |\lambda - E_k(h)| = 3\delta h/2 \} & \text{if } h \in J_k; \\ \{ \lambda \in \mathbb{C}; |\lambda - E_k(h)| = \delta h/2 \} & \text{if } h \in J \setminus J_k. \end{cases} \tag{62}
\]

In the same way, the set \( \{ \lambda \in \mathbb{C}; |\lambda - m_2| \leq \delta h \} \) contains at most one eigenvalue of \( Q_\mu^0 \), and on the set \( J_0 \) of those values of \( h \) for which it contains one eigenvalue, the domain \( \{ \lambda \in \mathbb{C}; \delta h < |\lambda - m_2| \leq 2\delta h \} \) does not meet \( \text{Sp}(Q_\mu^0) \). Then, we set,

\[
\gamma_0(h) = \begin{cases} \{ \lambda \in \mathbb{C}; \text{dist}(\lambda, \{m_1, m_2\}) = 3\delta h/2 \} & \text{if } h \in J_0; \\ \{ \lambda \in \mathbb{C}; \text{dist}(\lambda, \{m_1, m_2\}) = \delta h/2 \} & \text{if } h \in J \setminus J_0. \end{cases}
\]

When \( \lambda \in \gamma_k(h) \ (k \geq 0) \), we see as in the proof of Proposition 4.2 (see (43)) that the inverse of \( \tilde{Q}_\mu^0 - \lambda \) can be written as,

\[
(\tilde{Q}_\mu^0 - \lambda)^{-1} = \chi_1(\tilde{Q}_D - \lambda)^{-1}\chi_2 + R(\lambda),
\]

where \( \tilde{Q}_D \) is the Dirichlet realization of \( \tilde{Q}_\mu^0 \) on \([0, R_{1,M}]\), \( \chi_1, \chi_2 \) are as in (42), and \( R(\lambda) \) satisfies,

\[
\|R(\lambda)\|_{\mathcal{L}^2(\mathcal{H})} = \mathcal{O}(|h \ln h|^{-1})
\]

as in (41). Here, \( \mathcal{H} \) is the space introduced in the proof of Proposition 4.2. In particular, we obtain,

\[
\|(\tilde{Q}_\mu^0 - \lambda)^{-1}\|_{\mathcal{L}^2(\mathcal{H})} = \mathcal{O}(h^{-1}),
\]

and thus, if we denote by \( \mathcal{K}_0 \) the space \( \text{Ker}(L_{\mathcal{R}}) \) endowed with the norm

\[
\|\psi\|_{\mathcal{K}_0} := \|R\psi(R\omega)\|_{\mathcal{H} \otimes L^2(S^2)},
\]

we have,

\[
\|(Q_\mu^0 - \lambda)^{-1}\|_{\mathcal{L}(\mathcal{K}_0)} = \mathcal{O}(h^{-1}). \tag{63}
\]

On the other hand, thanks to (29), and by using the Calderon-Vaillancourt theorem (see, e.g., [Ma1]), it is not difficult to show that the operator \( B_\mu^0 \) is uniformly bounded on \( \mathcal{K}_0 \) (for instance, one can start by working on \( C_0^\infty(\mathbb{R}^3; 0) \) with the so-called right-quantization, in order to be able to pass in polar coordinates without problem, and then use a density argument and the fact that the polynomial weight used in the definition of \( \mathcal{H} \) becomes trivial near \( R = 0 \)).
Therefore, we see on (61) that, for \( h > 0 \) small enough and \( \lambda \in \cup_{k \geq 0} \gamma_k(h) \), the operator \( \tilde{P}_\mu^0(z) - \lambda \) is invertible, and its inverse can be written as,

\[
(\tilde{P}_\mu^0(z) - \lambda)^{-1} = (Q_\mu^0 - \lambda)^{-1} \left( I - h^2 R_\mu^0 (Q_\mu^0 - \lambda)^{-1} + \mathcal{O}(h^2) \right),
\]

in \( L(K_0) \).

For \( k \geq 0 \), we set,

\[
\Pi_{P,k}(h) := \frac{1}{2i\pi} \oint_{\gamma_k(h)} (\lambda - \tilde{P}_\mu^0(z))^{-1} d\lambda;
\]

\[
\Pi_{Q,k}(h) := \frac{1}{2i\pi} \oint_{\gamma_k(h)} (\lambda - Q_\mu^0)^{-1} d\lambda.
\]

In particular, for \( k \geq 1 \), the rank of \( \Pi_{Q,k}(h) \) is 1 or 2, depending if \( h \in J_k \) or not. In both cases, \( \Pi_{P,k}(h) \) and \( \Pi_{Q,k}(h) \) are identical, and that the eigenvalues of \( \tilde{P}_\mu^0(z) \) inside \( \gamma_k(h) \) coincide to those of \( Q_\mu^0 \) up to \( \mathcal{O}(h^2) \) (the computation is similar to that of (63)).

For \( k = 0 \), the situation is even simpler, because we know that the eigenvalues of \( Q_\mu^0 \) that lie inside \( \gamma_0(h) \) are simple and separated by a distance of order \( h \), and the same result holds.

Finally, for \( \lambda \in \Omega(h) \) in the exterior of all the \( \gamma_k(h) \)'s, the estimate (63) is still valid, and thus so is (63). Therefore, the spectral projector of \( \tilde{P}_\mu^0(z) \) on \( \Omega(h) \) can be split into a finite sum of the \( \Pi_{P,k}(h) \) (with a number of \( k \)'s that is \( \mathcal{O}(h^{-1}) \)), and the previous arguments show that the eigenvalues of \( \tilde{P}_\mu^0(z) \) in \( \Omega(h) \) coincide with those of \( Q_\mu^0 \) up to \( \mathcal{O}(h^2) \).

\[\square\]

6. Comparison between the spectrum of the operators \( \tilde{H}_\mu^0 \) and \( H_\mu^0 \)

We have,

**Proposition 6.1.** Let \( \alpha > 0 \) fixed small enough, and let \( J \subset (0,1] \), with \( 0 \in J \), such that there exists \( \delta > 0 \) such that,

\[
\operatorname{Sp}(P_D^\perp) \cap [m_2 + \alpha - 2\delta h, m_2 + \alpha + 2\delta h] = \emptyset. \tag{65}
\]

Set,

\[
\Omega(h) := \{ z \in \mathbb{C} ; \text{dist}(\text{Re } z, [m_1, m_2 + \alpha]) < \delta h, |\text{Im } z| < C^{-1} h \ln \frac{1}{h} \},
\]

with \( C > 0 \) a large enough constant. Then, there exists \( \delta_0 > 0 \) and a bijection,

\[
b : \operatorname{Sp}(\tilde{H}_\mu^0) \cap \Omega(h) \to \operatorname{Sp}(H_\mu^0) \cap \Omega(h),
\]

such that,

\[
b(\lambda) - \lambda = \mathcal{O}(e^{-\delta_0/h}),
\]

uniformly for \( h \in J \).

**Proof.** To prove this result, we use the arguments of Proposition 6.1 in [MaMe]. In particular we have to check that condition (6.6) in [MaMe] holds true. We consider the oriented loop,

\[
\gamma(h) := \{ z \in \mathbb{C} ; \text{dist}(z, [m_1, m_2 + \alpha]) = \delta h/2 \}.
\]
By [30] and the results of the previous section (in particular (63)-(64)), we already know that there exists some constant $C > 0$ such that,

$$\sup_{z \in \gamma(h)} \| (z - \tilde{H}_\mu^0)^{-1} \|_{L(Ker(L_R + L_\tau))} = O(h^{-C}).$$

We set,

$$\tilde{\Pi}_\mu := \frac{1}{2i\pi} \oint_{\gamma(h)} (z - \tilde{H}_\mu^0)^{-1} dz,$$

and we denote by $F = F(R) \in C^\infty_0((\frac{4}{M}, R_1, M); \mathbb{R}^+)$ a function that ‘fills the wells’, in the same sense as in the proof of Proposition 4.2, that is,

$$\inf_{(0, R_1, M)} (W_1 + F) > m_2 + \alpha. \quad (66)$$

Then, we set,

$$\hat{H}_\mu^0 = H_\mu^0 + F(R), \quad (67)$$

and we first prove,

**Lemma 6.2.** Let $\Gamma(h)$ be the closure of the complex domain surrounded by $\gamma(h)$. Then, there exists a constant $C > 0$ such that, for all $z \in \Gamma(h)$, one has,

$$\left\| (\hat{H}_\mu^0 - z)^{-1} \right\|_{L(Ker(L_R + L_\tau))} = O(h^{-C}),$$

uniformly for $h > 0$ small enough.

**Proof.** We use a standard method of localization that consists in decoupling the effects of the barrier from those of the remaining part of the operator (see, e.g., [BCD]).

We fix $a, b > 0$ such that $\frac{3}{M} < a < b < \frac{4}{M}$, and we denote by $J_I, J_E \in C^\infty((\mathbb{R}_+; [0, 1])$ two functions satisfying,

$$\text{Supp} \ J_I \subset [0, b); \text{Supp} \ J_E \subset (a, +\infty); \quad (68)$$

$$J_I = 1 \text{ on } [0, a]; \quad J_E = 1 \text{ on } [b, +\infty); \quad (69)$$

$$J_I^2 + J_E^2 = 1. \quad (70)$$

Next we denote by $\mathcal{H}_I$ the space $\{ u |_{|R| \leq b} : u \in Ker(L_R + L_\tau) \}$ endowed with the standard $L^2$-norm, and $\mathcal{H}_E$ the space $Ker(L_R + L_\tau)$ endowed with the norm,

$$\| u \|_{\mathcal{H}_E} := \| Ru(R_\omega, r) \|_{H \otimes L^2(S^2) \otimes L^2(\mathbb{R}^2)}. \quad (71)$$

We also define $\tilde{\mathcal{H}}$ as the space $Ker(L_R + L_\tau)$ endowed with the norm,

$$\| u \|_{\tilde{\mathcal{H}}} := \left( \| J_I u \|_{L^2}^2 + \| J_E u \|_{\mathcal{H}_E}^2 \right)^{\frac{1}{2}}. \quad (72)$$

All these norms are clearly equivalent to the standard $L^2$-norms, with constants of equivalence of order $h^{\pm C}$ with $C > 0$ constant, that is

$$h^C \| u \|_{L^2} \leq \| u \|_{\mathcal{H}_E} \leq h^{-C} \| u \|_{L^2}. \quad (73)$$

In particular, it is enough to prove the result with $Ker(L_R + L_\tau)$ substituted by $\tilde{\mathcal{H}}$. 
Moreover, we have the so-called identifying operators,
\[ J : \mathcal{H}_I \oplus \mathcal{H}_E \rightarrow \mathcal{H}, \]
\[ u \oplus v \mapsto J_I u + J_E v \]
\[ \mathcal{J} : \mathcal{H} \rightarrow \mathcal{H}_I \oplus \mathcal{H}_E, \]
\[ w \mapsto J_I w + J_E w \]
that satisfy \( J \mathcal{J} = 1, \| J \| = 1 \) (actually, \( \mathcal{J} \) is an isometry, and is nothing but the adjoint of \( J \) for the standard \( L^2 \)-scalar product). By standard estimates on the transform \( T \) (see, e.g., [Ma1]), one can also easily see that \( \| J \| = \mathcal{O}(1) \) uniformly as \( h \rightarrow 0 \).

Observing that the operator \( \tilde{H}_\mu^0 \) is differential with respect to \( R \) (with operator-valued coefficients acting on \( L^2(\mathbb{R}^3) \)), we can consider the zero Dirichlet boundary condition at \( |R| = b \) realizations \( H_I \) of \( \tilde{H}_\mu^0 \) on \( \mathcal{H}_I \) (note that it is nothing else but the restriction to \( \text{Ker}(L_R + \mathbf{L}_r) \) of the Dirichlet realizations of \( H_\mu + F \) on \( L^2(|R| < b) \)). Finally, we set
\[ H_E := \tilde{H}_\mu^0 + F, \]
acting on \( \mathcal{H}_E \), and we define,
\[ H_A := H_I \oplus H_E, \]
as an operator acting on \( \mathcal{H}_I \oplus \mathcal{H}_E \). Then, setting,
\[ \Theta := \tilde{H}_\mu^0 J - J H_A, \]
it is elementary to check the identity,
\[ (\tilde{H}_\mu^0 - z)^{-1} = J(H_A - z)^{-1} \mathcal{J} - (\tilde{H}_\mu^0 - z)^{-1} \Theta (H_A - z)^{-1} \mathcal{J}. \]  
\[ \tag{71} \]
Using (80) and proceeding as in the proof of Proposition 4.2 and in Section 5, we immediately obtain,
\[ \| (H_E - z)^{-1} \|_{\mathcal{L}(\mathcal{H}_E)} = \mathcal{O}(|h \ln h|^{-1}). \]  
\[ \tag{72} \]
On the other hand, since \( b < 4/M \), by (26)-(27) we have,
\[ \text{Re} H_I \geq \frac{M}{4} + \inf_{R} E_1(R) \geq m_2 + \alpha + 1, \]
if \( M \geq 1 \) has been chosen sufficiently large. As a consequence, for \( z \in \Gamma(h) \), we have,
\[ \| (H_I - z)^{-1} \|_{\mathcal{L}(\mathcal{H}_I)} = \mathcal{O}(1), \]  
\[ \tag{73} \]
uniformly. From (72)-(73), we deduce,
\[ \| (H_A - z)^{-1} \|_{\mathcal{L}(\mathcal{H}_I \oplus \mathcal{H}_E)} = \mathcal{O}(|h \ln h|^{-1}), \]
and thus also, by standard estimates on the Laplacian,
\[ \| (h \nabla_R (H_A - z)^{-1}) \|_{\mathcal{L}(\mathcal{H}_I \oplus \mathcal{H}_E)} = \mathcal{O}(|h \ln h|^{-1}). \]  
\[ \tag{74} \]
Now, we compute,
\[ \Theta(u \oplus v) = -h^2[\Delta_R, J_I]u - h^2[\Delta_R, J_E]v \]
\[ = -h^2(2(\nabla_R J_I)\nabla_R + (\Delta_R J_I))u - h^2(2(\nabla_R J_E)\nabla_R + (\Delta_R J_E))v. \]
Therefore, we deduce from (74) that we have,
\[ \| \Theta(H_A - z)^{-1} \mathcal{J} \|_{\mathcal{L}(\mathcal{H})} = \mathcal{O}(|h \ln h|^{-1}). \]
In particular, for $h$ small enough we obtain $\|\Theta(H_A - z)^{-1}\vec{J}\|_{L(\tilde{\nu})} \leq 1/2$, and then, by using (71) and, again, (74), we finally deduce,

$$\|(\hat{H}_1^0 - z)^{-1}\|_{L(\tilde{\nu})} = O(|h \ln h|^{-1}),$$

and the result follows.

Now, let (see Fig. 2)

$$R_1 := \min\{R > 0 ; W_1(R) = m_2 + \alpha, W_1'(R) > 0\};$$

$$R_2 := \min\{R > R_1 ; W_1(R) = m_2 + \alpha, W_1'(R) < 0\}.$$ 

Let also $\chi_1(R), \chi_2(R) \in C_0^\infty([0, R_2])$, and $R_3 \in (R_1, R_2)$, such that,

$$\chi_1 = \chi_2 = 1 \text{ near } [0, R_1]; \supp \chi_2 \subset [0, R_3] \subset \{\chi_1 = 1\}.$$ 

We can also assume that the function $F(R)$ used in (66) is such that $\chi_1 = \chi_2 = 1$ in a neighborhood of $\text{Supp} F$, too.
Then, following [HeSj2], we set,
\[ R_1(z) = \chi_1(H_D - z)^{-1} + (\hat{H}_\mu^0 - z)^{-1}(1 - \chi_2), \]
where \( H_D \) is the Dirichlet realization of \( H_\mu^0 \) on \( L^2(\{|R| \leq R_3\} \times \mathbb{R}^3) \). Actually, \( H_D \) does not depend on \( \mu \) since \( S_\mu \equiv 1 \) for \( |R| < R_3 \). Since \( \chi_1 \chi_2 = \chi_2 \), it follows from this definition (recalling that \( H_\mu^0 = \hat{H}_\mu^0 - F(R) \)), that we have,
\[ (H_\mu^0 - z)R_1(z) = [h^2D_{R, \chi_1}^2](H_D - z)^{-1}\chi_2 + \chi_2 + (H_\mu^0 - z)(\hat{H}_\mu^0 - z)^{-1}(1 - \chi_2) \]
\[ = [h^2D_{R, \chi_1}^2](H_D - z)^{-1}\chi_2 + 1 - F(R)(\hat{H}_\mu^0 - z)^{-1}(1 - \chi_2) \]
\[ = 1 + K_1(z) + K_2(z), \]
where we have set,
\[ K_1(z) := [h^2D_{R, \chi_1}^2](H_D - z)^{-1}\chi_2 \]
\[ K_2(z) := -F(R)(\hat{H}_\mu^0 - z)^{-1}(1 - \chi_2). \]

Here, we observe that,
\[ \text{Supp}(D_{R\chi_1}) \cap \text{Supp}(\chi_2) = \emptyset = \text{Supp} F \cap \text{Supp}(1 - \chi_2). \]

Moreover, introducing the notations,
\[ H_D = -h^2\Delta_R + P(R); \]
\[ \hat{H}_\mu^0 = -h^2S_\mu\Delta_RS_\mu^{-1} + Q(R) \]
(where the two \( R \)-dependent operators \( P(R) \) and \( Q(R) \) act on the electronic variables only), we also have,
\[ \text{Supp}(D_{R\chi_1}) \subset \{ P(R) > m_2 + \alpha \} ; \quad \text{Supp} F \subset \{ \text{Re} Q(R) > m_2 + \alpha \}. \]

Therefore, proceeding as in [HeSj2], Section 9 (see also [HeSj1]), by performing Agmon estimates, we deduce the existence of some constant \( \delta > 0 \), such that,
\[ \|K_1(z)\| + \|K_2(z)\| = \mathcal{O}(e^{-\delta/h}), \]
uniformly for \( z \in \gamma(h) \) and \( h > 0 \) small enough.

In the same way, setting,
\[ R_2(z) = \chi_2(H_D - z)^{-1}\chi_1 + (1 - \chi_2)(\hat{H}_\mu^0 - z)^{-1}, \]
we also have,
\[ R_2(z)(H_\mu^0 - z) = 1 + \mathcal{O}(e^{-\delta'/h}), \]
with \( \delta' > 0 \) constant. As a consequence, we deduce that \( H_\mu^0 - z \) is invertible, and its inverse is given by,
\[ (H_\mu^0 - z)^{-1} = R_1(z)(1 + K_1 + K_2)^{-1}. \]

In particular, using Lemma 6.2 and the fact that \( H_D \) is selfadjoint, and defining \( \gamma_k(h) \) as in (62), we conclude that, for all \( z \in \gamma_k(h) \), we have,
\[ \| (H_\mu^0 - z)^{-1} \| = \mathcal{O}(h^{-C}) \]
where \( C > 0 \) is a constant.
Now, we set,
\[ \Pi_{\mu,k} := \frac{1}{2i\pi} \oint_{\gamma_k(h)} (H^0_{\mu} - z)^{-1} dz; \]
\[ A_k := \frac{1}{2i\pi} \chi_1 \oint_{\gamma_k(h)} (H_D - z)^{-1} \chi_2 dz. \]

(Note that, by construction, \( \|A_k\| = \mathcal{O}(h^{-1}) \) and \( A_k \) is of rank at most 2.)

From (75)-(76) and Lemma 6.2 (plus the fact that \( (\tilde{H}^0_{\mu} - z)^{-1} \) is holomorphic inside \( \gamma(h) \)), we obtain,
\[ \Pi_{\mu,k} = A_k + \mathcal{O}(e^{-\delta/h}). \quad (78) \]

In particular, since \( \Pi^2_{\mu,k} = \Pi_{\mu,k} \) and \( \|\Pi_{\mu,k}\| = \mathcal{O}(h^{-C}) \), we deduce,
\[ A_k^2 = A_k + \mathcal{O}(e^{-\delta/2h}), \quad (79) \]

and thus, for any \( \zeta \in \mathbb{C} \),
\[ (A_k - \zeta)(A_k + \zeta - 1) = -\zeta(\zeta - 1) + R_k; \|R_k\| = \mathcal{O}(e^{-\delta/2h}). \quad (80) \]

As a consequence, if \( \zeta \neq 0, 1 \) is fixed, then \( (A_k - \zeta) \) is invertible, and we can consider the projection,
\[ \Pi_{A_k} := \frac{1}{2i\pi} \oint_{|\zeta - 1| = 1/2} (\zeta - A_k)^{-1} d\zeta. \]

Then, we prove,

**Lemma 6.3.** One has,
\[ \|A_k - \Pi_{A_k}\| = \mathcal{O}(e^{-\delta/4h}). \]

uniformly for \( h > 0 \) small enough.

**Proof.** We write,
\[ \Pi_{A_k} - A_k = \frac{1}{2\pi i} \oint_{|\zeta - 1| = 1/2} [((\zeta - A_k)^{-1} - (\zeta - 1)^{-1} A_k)] d\zeta \]

and,
\[ (\zeta - A_k)^{-1} - (\zeta - 1)^{-1} A_k = (\zeta - A_k)^{-1} (1 - A_k + (\zeta - 1)^{-1}(A_k - A_k^2)). \]

Moreover, by (80), we also have,
\[ (A_k - \zeta)^{-1} = (A_k + \zeta - 1) [\zeta(1 - \zeta) + R_k]^{-1} \]

In particular, \( \|(A_k - \zeta)^{-1}\| = \mathcal{O}(h^{-1}) \) uniformly on \( \{|\zeta - 1| = 1/2\} \), and thus, using (79), we obtain,
\[ \Pi_{A_k} - A_k = \Pi_{A_k}(1 - A_k) + \mathcal{O}(e^{-\delta/3h}). \quad (82) \]
On the other hand, using (81) (and the fact that \( R_k = A_k^2 - A_k \) commutes with \( A_k \)), we have,

\[
\Pi A_k (1 - A_k) = 1 - \frac{1}{2i\pi} \oint_{|\zeta - 1| = 1/2} (\zeta - 1)^{-1} (\zeta - 1) d\zeta
\]

\[
= 1 - \frac{1}{2i\pi} \oint_{|\zeta - 1| = 1/2} (\zeta - 1)(A_k + \zeta - 1) [\zeta(1 - \zeta) + R_k]^{-1} d\zeta
\]

\[
= 1 - \frac{1}{2i\pi} \oint_{|\zeta - 1| = 1/2} \left( \zeta - 1 - \frac{1}{\zeta} R_k \right) (\zeta(1 - \zeta) + R_k)^{-1} (A_k + \zeta - 1) d\zeta
\]

\[
+ 1 - \frac{1}{2i\pi} \oint_{|\zeta - 1| = 1/2} \zeta R_k \left( \zeta(1 - \zeta) + R_k \right)^{-1} (A_k + \zeta - 1) d\zeta
\]

\[
= 1 - \frac{1}{2i\pi} \oint_{|\zeta - 1| = 1/2} \zeta^{-1} R_k \left( \zeta(1 - \zeta) + R_k \right)^{-1} (A_k + \zeta - 1) d\zeta
\]

\[
= O(e^{-\delta/4h}),
\]

where we have used the fact that,

\[
\oint_{|\zeta - 1| = 1/2} \left( \zeta - 1 - \frac{1}{\zeta} R_k \right) (\zeta(1 - \zeta) + R_k)^{-1} (A_k + \zeta - 1) d\zeta
\]

\[
= \oint_{|\zeta - 1| = 1/2} -\zeta^{-1} (A_k + \zeta - 1) d\zeta = 0,
\]

because the function inside the integral is analytic in the disc \(|\zeta - 1| \leq 1/2\). □

We deduce from Lemma 6.3 and (78) that we have,

\[
\Pi_{\mu, k} = \Pi A_k + O(e^{-\delta/4h}).
\]

(83)

Moreover, still by Lemma 6.3, we see that the restriction,

\[
A_k \big|_{\operatorname{Im}(\Pi A_k)} : \operatorname{Im}(\Pi A_k) \to \operatorname{Im}(\Pi A_k)
\]

is invertible, and thus, since the rank of \( A_k \) is at most 2, we deduce,

\[
\operatorname{Rank}(\Pi A_k) \leq 2.
\]

As a consequence, by (83), we obtain,

\[
\operatorname{Rank}(\Pi_{\mu, k}) \leq 2.
\]

Then, we are exactly in the situation of [MaMe] Proposition 6.1, (i)-(ii), and, setting,

\[
\widetilde{\Pi}_{\mu, k} := 1 - \frac{1}{2i\pi} \oint_{\gamma_k(h)} (z - \tilde{H}_\mu^0)^{-1} dz,
\]

we conclude that we have,

\[
||\Pi_{\mu, k} - \widetilde{\Pi}_{\mu, k}|| = O(e^{-\delta''/h}),
\]

(84)

with \( \delta'' > 0 \) constant. As before, the result on the interior of \( \gamma_k(h) \) \((k \geq 1)\) follows in a standard way, and one obtains the required comparison of the spectra of \( H_\mu^0 \) and \( \tilde{H}_\mu^0 \) on

\[
B = \{ \operatorname{Re} z \in [m_2, m_2 + \alpha], |\operatorname{Im} z| < C^{-1}|h \ln h| \}.
THE STARK EFFECT ON $H^2_\mu$-LIKE MOLECULES

As before, the same arguments can be performed on \( \{ \text{Re} z \in [m_1, m_2], \ | \text{Im} z \| < C^{-1} |h \ln h| \} \) (in a simpler way, since the eigenvalues of \( H_D \) are separated by a distance of order \( \sim h \)), and Proposition 6.1 follows.

\[ \square \]

Remark 6.4. The same argument, using (77), also show that the spectrum of \( H^0_\mu \) and \( H_D \) on \( B \) coincides up to an exponentially small term. In particular, the eigenvalues of \( H_D \) are real and then the resonances of \( H^0_\mu \) have exponentially small part.

7. MAIN RESULT

Here, by collecting the Propositions 5.1 and 6.1, and Theorem 4.8 it turns out our main result.

**Theorem 7.1.** Let \( \alpha > 0 \) fixed small enough, and let \( J \subset (0, 1] \), with \( 0 \in J \), such that there exists \( \delta > 0 \) such that,

\[
\text{Sp}(P^1_D) \cap [m_2 + \alpha - 2\delta h, m_2 + \alpha + 2\delta h] = \emptyset.
\]

Set,

\[
\Omega(h) := \{ z \in \mathbb{C}; \ \text{dist}(\text{Re} z, [m_1, m_2 + \alpha]) < \delta h, \ | \text{Im} z| < C^{-1} h \ln \frac{1}{h} \},
\]

with \( C > 0 \) a large enough constant. For \( h > 0 \) small enough then the resonances of \( H^0_\mu \) in \( \Omega(h) \) coincide up to \( O(h^2) \) error-terms, with eigenvalues of the Dirichlet realizations of \( P_1 \) and \( P_2 \) on \( (0, R_{1, M}) \), where \( R_{1, M} > 0 \) is the point where \( W_1 \) admits a local maximum with value greater than \( m_2 \).

**Remark 7.2.** As done in §5, by slightly moving the parameter \( \alpha \) one can actually reach all the values of \( h > 0 \) small enough.

**Remark 7.3.** We would point out that this result still holds true even in absence of the external field; in such a case we don’t have resonances for \( H^0_\mu \), but real eigenvalues.

References

[BCD] Briet, P., Combes, J.-M., Duclos, P., On the location of resonances for Schrödinger operators in the semiclassical limit II, Comm. Part. Diff. Eq., 12(2) (1987), 201–222.

[CGM] Caliceti, E., Grecchi, V., Maioli, M., Double Wells: Nevanlinna Analyticity, Distributional Borel Sum and Asymptotics, Commun. Math. Phys. 176 (1996), 1–22.

[Ca] Carrington, A., McNab, I. R., and Montgomery, C. A., Spectroscopy of the hydrogen molecular ion, J. Phys. B 22 (1989), 3551–3586.

[Cl] Cizek, J., et al, 1/R expansion for $H^1_\mu$: Calculation of exponentially small terms and asymptotics, Phys. Rev. A 33 (1986), 12–54.

[CMR] Cancelier, C., Martinez, A., Ramond, T., Quantum resonances without analyticity, Asymptot. Anal. 44 (2005), 47–74.

[FLM] Fujie, S., Lahmar-Benbernou, A., Martinez, A., Width of shape resonances for non globally analytic potentials, Preprint arXiv: 0811.0734 (2008).

[GG] Giachetti, R., Grecchi, V., Perturbation theory for metastable states of the Dirac equation with quadratic vector interaction, Phys. Rev. A 80 (2009), 032107.

[HeRo] Helffer, B., Robert, D., Puits de potentiel généralisés et asymptotique semi-classique, Ann. Inst. Henri Poincaré, section Physique Théorique, 41(3) (1984), 291–331.

[HeSj1] Helffer, B., Sjöstrand, J., Puits Multiple wells in the semiclassical limit I, Commun. Part. Diff. Eq. 9(4) (1984), 337–408.

[HeSj2] Helffer, B., Sjöstrand, J., Resonances en limite semi-classique, Bull. Soc. Math. France, Mémoire 24/25, (1986).
[Hi] Hiskes, J.R., Dissociation of molecular ions by electric and magnetic fields, Phys. Rev. 122 (1961), 1207–1217.

[MPS] Mulyukov Z., Pont M. and Shakeshaft R., Ionization, dissociation, and level shifts of $H_2^+$ in a strong dc or low frequency ac field Phys. Rev. A, 54, (1996) 4299–4308.

[Hu] Hunziker, W., Distortion analyticity and molecular resonance curve, Ann. Inst. H. Poincaré 45 (1986), 339-358

[KMSW] M. Klein, A. Martinez, R. Seiler, X.P. Wang, On the Born-Oppenheimer Expansion for Polyatomic Molecules, Commun. Math. Phys. 143(3) (1992), 607–639.

[La] Lifshitz, E.M., Landau, L.D., Quantum Mechanics: Non-Relativistic Theory, (Butterworth-Heinemann) (1981).

[Ma1] Martinez, A., An Introduction to Semiclassical and Microlocal Analysis, Springer-Verlag New-York, UTX Series, ISBN: 0-387-95344-2 (2002).

[Ma2] Martinez, A., Resonance Free Domains for Non Globally Analytic Potentials, Ann. Henri Poincaré 4 (2002), 739–756 [Erratum: Ann. Henri Poincaré 8 (2007), 1425–1431]

[MaMe] Martinez, A., Messerdi, B., Resonances of diatomic molecules in the Born-Oppenheimer approximation, Comm. Part. Diff. Eq. 19 (1994), 1139–1162.

[MaSo] Martinez, A., Sordoni, V., Twisted pseudodifferential calculus and application to the quantum evolution of molecules, Memoirs of the American Mathematical Society 200(936) (2009).

[MeSj] Melin, A., Sjöstrand, J., Fourier integral operators with complex valued phase functions, Springer Lecture Notes in Math. 459 (1974), 120–223.

[MuSh] Mulyukov, Z., Shakeshaft, R., Breakup of $H_2^+$ by one photon in the presence of a strong dc field, Phys. Rev. A 63 (2001), 053404:1-10.

[Sj] Sjöstrand, J., Singularités analytiques microlocales, Soc. Math. France, Astérisque 95 (1982), 1–166.

[Wo] Woolley R. G., Quantum theory of molecular structure, Advances in Physics 1 (1976), 27–52.

Vincenzo Grecchi, Dipartimento di Matematica, Università degli Studi di Bologna, Piazza di Porta San Donato 5, Bologna 40126, Italy
E-mail address: grecchi@dm.unibo.it

Hynek Kovařík, Dipartimento di Matematica, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy
E-mail address: hynek.kovarik@polito.it

André Martinez, Dipartimento di Matematica, Università degli Studi di Bologna, Piazza di Porta San Donato 5, Bologna 40126, Italy
E-mail address: martinez@dm.unibo.it

Andrea Sacchetti, Dipartimento di Matematica Pura ed Applicata, Università degli studi di Modena e Reggio Emilia, Via Campi 213/B, Modena 41100, Italy
E-mail address: andrea.sacchetti@unimore.it

Vania Sordoni, Dipartimento di Matematica, Università degli Studi di Bologna, Piazza di Porta San Donato 5, Bologna 40126, Italy
E-mail address: sordoni@dm.unibo.it