Landau-Zener Transitions for Eigenvalue Avoided Crossings in the Adiabatic and Born-Oppenheimer Approximations

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Abstract

[1] [2] In the Born-Oppenheimer approximation context, we study the propagation of Gaussian wave packets through the simplest type of eigenvalue avoided crossings of an electronic Hamiltonian $\mathcal{C}^4$ in the nuclear position variable. It yields a two-parameter problem: the mass ratio ε^4 between electrons and nuclei and the minimum gap δ between the two eigenvalues. We prove that, up to first order, the Landau-Zener formula correctly predicts the transition probability from a level to another when the wave packet propagates through the avoided crossing in the two different regimes: δ being either asymptotically smaller or greater than ε when both go to 0.

1 Introduction

The Hamiltonian for a molecular system with K nuclei and $N-K$ electrons has the form

$$H(\varepsilon) = -\sum_{j=1}^{K} \frac{\varepsilon^4}{2M_j}\Delta_{x_j} - \sum_{j=K+1}^{N} \frac{1}{2m_j}\Delta_{x_j} + \sum_{i<j} V_{ij}(x_i - x_j) \tag{1}$$

where $x_j \in \mathbb{R}^l$ denotes the position of the j^{th} particle, the mass of the j^{th} nucleus is $\varepsilon^{-4}M_j$ (for $1 \le j \le K$), the mass of the j^{th} electron is m_j (for $K+1 \le j \le N$), and V_{ij} is the potential between particles i and j. The role of the parameter ε is to make the

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reduced mass M_j of each nucleus be of a comparable order of magnitude with the mass m_j of any electron. For convenience we assume $M_j = 1$ for $1 \leq j \leq K$. Set $d = Kl$ and let $x = (x_1, \ldots, x_d) \in \mathbb{R}^d$ denote the nuclear configuration vector. We decompose $H(\varepsilon)$ as

$$H(\varepsilon) = -\frac{\varepsilon^4}{2}\Delta_x + h(x) \ . \tag{2}$$

This defines the electronic Hamiltonian $h(x)$ that depends parametrically on x. The time-dependent Schrödinger equation that we study is

$$i\varepsilon^2 \frac{\partial \psi}{\partial t} = H(\varepsilon)\psi \ , \tag{3}$$

for t in a fixed interval. The factor ε^2 on the left-hand side of this equation indicates a particular choice of time scaling. Other choices could be made, but this choice is the "distinguished limit" [1] that produces the most interesting leading order solutions as all terms in the equation play significant roles.

Nowhere in this paper do we require the Hamiltonian to have the particular form (1). We only require the Hamiltonian to be of the form (2). The mechanism behind the Born-Oppenheimer approximation is the following :

- the electrons remain approximately in a quantum mechanical bound state depending on the position of the nuclei which move relatively slowly because of their large masses,
- the electronic energy level plays the role of an effective potential for the semi-classical dynamics of the nuclei.

Approximations of solutions of (3) with errors of order n in ε can be found in [6] and [7] for hamiltonians of regularity $\mathcal{C}^{n+2}$. When $h(x)$ is analytic, exponentially precise results have been obtained in [13]. However, the validity of these approximations is dependent upon the assumption that the electron energy level of interest is well isolated from the rest of the spectrum of the electronic Hamiltonian.

In the case of the propagation of wave packets through generic crossings of two different electron energy levels, [9] is a good reference. In the $\mathcal{C}^\infty$ case, similar results has been recently obtained in a microlocal context in [2] and from a Wigner measure point of view in [4] (and references therein).

In some realistic systems, $h(x)$ may have two electron energy levels that approach one another with a minimum gap of size δ that is of a comparable order of magnitude with the relevant value of ε but without actual crossing. For this reason, we generalize the form (2) to allow the electronic Hamiltonian to depend on δ as well as x. We study solutions to equation

$$i\varepsilon^2 \frac{\partial \psi}{\partial t} = H(\delta, \varepsilon)\psi \ , \tag{4}$$

with Hamiltonians of the form

$$H(\delta, \varepsilon) = -\frac{\varepsilon^4}{2}\Delta_x + h(x, \delta) \ \text{on} \ L^2(\mathbb{R}^d; \mathcal{H}) \ ,$$

where $\mathcal{H}$ is a separable Hilbert space and with the assumption that $h(x,\delta)$ has an avoided crossing according to the following definition with an extra generic condition (see type I below).

Definition 1 *$h(x,\delta)$ is a family of self-adjoint operators with fixed domain $\mathcal{D}$ in any separable Hilbert space $\mathcal{H}$, uniformly bounded from below and whose resolvent is strongly $\mathcal{C}^4$ for $(x,\delta) \in \Omega\times]-2\delta_0, 2\delta_0[$ where Ω is an open subset of $\mathbb{R}^d$. Suppose $h(x,\delta)$ has two eigenvalues $E_{\mathcal{A}}(x,\delta)$ and $E_{\mathcal{B}}(x,\delta)$ that depend continuously on (x,δ) and are uniformly isolated from the rest of the spectrum of $h(x,\delta)$. Moreover, assume the set $\Gamma := \{x \in \Omega / E_{\mathcal{A}}(x,0) = E_{\mathcal{B}}(x,0)\}$ is either a single point or a non-empty connected proper submanifold of Ω but that for all $x \in \Omega$, $E_{\mathcal{A}}(x,\delta) \neq E_{\mathcal{B}}(x,\delta)$ when $\delta \neq 0$. In such a situation, we say that $h(x,\delta)$ has an avoided crossing on Γ.*

Remarks

1. Realistic molecules have Coulomb potentials which give rise to electronic Hamiltonians that do not satisfy the smoothness assumptions of this definition. However, one should be able to accomodate Coulomb potentials by using the regularization techniques of [7] and [17].

2. $H(\delta,\varepsilon)$ is naturally defined on the domain $D := \mathcal{C}^2_c(\Omega;\mathcal{H}) \cap \mathcal{F}(\Omega;\mathcal{D})$ of functions $\mathcal{C}^2$ on Ω with compact support and values in $\mathcal{D}$, $h(x,\delta)$ acting on each fiber. If $h(x,\delta)$ is supposed to be uniformly bounded from below, $H(\delta,\varepsilon)$ becomes a symmetric operator, bounded from below, then Friedrichs extension theorem (cf [16]) gives us the existence of a self-adjoint extension to $H(\delta,\varepsilon)$ because D is dense in the Hilbert space $L^2(\Omega;\mathcal{H})$. In what follows, we work with any self-adjoint extension also denoted by $H(\delta,\varepsilon)$.

3. In our case, the set Ω in the definition plays no interesting role, so we henceforth assume $\Omega = \mathbb{R}^d$ and drop any further reference to it. The wave packets we construct are supported on sets in which the nuclear coordinates are restricted to a neighbourhood of a compact classical nuclear orbit. Our techniques apply to any Ω and any classical path, provided the time interval is restricted to keep the nuclei inside Ω. In realistic systems, Ω may be a proper subset of $\mathbb{R}^d$, since electron energy levels may cross one another or be absorbed into the continuous spectrum as the nuclei move.

Let $P(x,\delta)$ be the spectral projector of $h(x,\delta)$ associated with $E_{\mathcal{A}}(x,\delta)$ and $E_{\mathcal{B}}(x,\delta)$, and denote $h_{||}(x,\delta) = h(x,\delta)P(x,\delta)$.

In type I avoided crossing (cf [11] for a classification of non-degenerate minimal multiplicity avoided crossings), Γ is of codimension 1 and both eigenvalues are simple. After a convenient change of variables and a reduction process (mentioned in [12] and described in section 8.1 for the adiabatic similar case), we know that there exists an orthonormal basis $\{\psi_1(x,\delta), \psi_2(x,\delta)\}$ of $P(x,\delta)\mathcal{H}$, $\mathcal{C}^3$ on $\mathbb{R}^d\times]-2\delta_0, 2\delta_0[$ in which the restriction of $h_{||}(x,\delta)$ to $P(x,\delta)\mathcal{H}$ takes the following form

$$\begin{aligned} h_{||}(x,\delta) &= h_1(x,\delta) + E(x,\delta) \\ &= \begin{pmatrix} b(x,\delta) & c(x,\delta)+id(x,\delta) \\ c(x,\delta)-id(x,\delta) & -b(x,\delta) \end{pmatrix} + E(x,\delta) \; . \end{aligned} \tag{5}$$

Here $E(x,\delta)=\frac{1}{2}\mathrm{Tr}(h_{||}(x,\delta))$, $b(x,\delta)$, $c(x,\delta)$ and $d(x,\delta)$ are real-valued functions, $\mathcal{C}^3$ on $\mathbb{R}^d\times]-2\delta_0,2\delta_0[$, with asymptotics

$$\left\{\begin{array}{rcl} b(x,\delta) &=& rx_1+O(\|x\|^2+\delta^2)\\ c(x,\delta) &=& r\delta+O(\|x\|^2+\delta^2)\\ d(x,\delta) &=& O(\|x\|^2+\delta^2)\\ E(x,\delta) &=& O(1)\end{array}\right. \tag{6}$$

where $r>0$ and the O are to be understood in the limit $\|x\|$ and δ going to 0.

In practice, type I avoided crossings occur for diatomic molecules, where the electron energy levels depend only on the distance between the nuclei because of rotational symmetry.

Our main result is the determination of what happens when a standard time-dependent Born-Oppenheimer molecular wave packet propagates through those avoided crossing if the gap size δ is either asymptotically smaller or greater than ε. Our analysis, together with the results of [12] where the critical case $\delta=\varepsilon$ is considered, allow to get a complete picture of the dynamics through those avoided crossings for all ranges of $(\delta,\varepsilon)\to 0$ with a regularity of order $\mathcal{C}^4$ only on the electronic Hamiltonian $h(x,\delta)$. Using matched asymptotic expansions already used in [12], we compute approximate solutions to the molecular Schrödinger equation. We observe that, to leading order in δ and ε, the Landau-Zener formula (see [15]) correctly describes the probabilities for the system to remain in the original electronic level or to make a transition to the other electronic level involved in the avoided crossing (Theorem 1 in Section 7). To apply the Landau-Zener formula in this case, one treats the nuclei as classical point particles to obtain a time-dependent Hamiltonian for the electrons. More precisely, suppose there is a generic type I avoided crossing at nuclear configuration $x=0$. In an appropriate coordinate system, the gap between the electron energy levels is

$$2r\sqrt{x_1^2+\delta^2}+O(\|x\|^2+\delta^2)\ ,$$

with $r>0$. Suppose that a semi-classical nuclear wave packet passes through the avoided crossing with velocity μ, whose first component is $\mu_1\neq 0$. Then the Landau-Zener formula predicts that the probability of remaining in the same electronic state is $1-e^{-\pi r\delta^2/(\mu_1\varepsilon^2)}$, and the probability of making a transition to the other electronic level involved in the avoided crossing is $e^{-\pi r\delta^2/(\mu_1\varepsilon^2)}$. This formula yields a transition probability, at leading order, 1 (respectively 0) when $\delta/\varepsilon\to 0$ (respectively $+\infty$). Mimicking our analysis in the Born-Oppenheimer context, we also get results for the following simpler problem in the adiabatic context: we want to solve the time-dependent Schrödinger equation

$$i\varepsilon^2\frac{\partial}{\partial t}\psi=H(t,\delta)\psi \tag{7}$$

where $H(t,\delta)$ is a family of self-adjoint operators with fixed domain $\mathcal{D}$ (in any separable Hilbert space $\mathcal{H}$) and whose resolvent is strongly $\mathcal{C}^4$ in $(t,\delta)\in]t_0-2T+t_0+2T[\times]-2\delta_0,2\delta_0[$. We assume that $H(t,\delta)$ displays the simplest case of avoided crossing at t_0 (see section 8.1 for details) and establish the validity of the Landau-Zener formula to leading order for the two same regimes δ either asymptotically smaller or greater than ε (the critical case where $\delta=\varepsilon$ can be found in [8] for $H(t,\delta)$ real symmetric). The result is stated in Theorem 2 of Section 8.

In a $\mathcal{C}^\infty$ context, similar microlocal results based on pseudodifferential techniques can be found in [3].

The organization of the paper is as follows. Section 2 gives usual tools for constructing the leading order Born-Oppenheimer approximation with δ fixed (the eigenvalues do not cross, are simple and isolated). Section 3 deals with the asymptotics of the classical quantities of the problem. Sections 4 and 5 give the different Ansätze used respectively far from and close to the crossing surface Γ. Section 6 makes the matching of those different Ansätze in an overlapping region, and Section 7 states the main result. Finally, Section 8 deals with avoided crossings in the adiabatic context.

2 Coherent States and Classical Dynamics

We recall the definition of the coherent states $\varphi_l(A,B,\hbar,a,\eta,x)$ that are described in detail in [10]. A more explicit, but more complicated definition is given in [5].

We adopt the standard multi-index notation. A multi-index $l=(l_1,\ldots,l_d)$ is a d-tuple of non-negative integers. We define $|l|=\sum_{k=1}^d l_k$, $x^l=x_1^{l_1}\ldots x_d^{l_d}$, $l!=(l_1!)\ldots(l_d!)$, and $D^l=\frac{\partial^{|l|}}{(\partial x_1)^{l_1}\ldots(\partial x_d)^{l_d}}$.

Throughout the paper we assume $a\in\mathbb{R}^d$, $\eta\in\mathbb{R}^d$ and $\hbar>0$. We also assume that A and B are $d\times d$ complex invertible matrices that satisfy

$$\begin{array}{rcl} A^tB-B^tA &=& 0\ ,\\ A^*B+B^*A &=& 2I\ . \end{array} \tag{8}$$

These conditions guarantee that both the real and imaginary parts of BA^{-1} are symmetric. Furthermore, the real part of BA^{-1} is strictly positive definite and has inverse AA^*.

Our definition of $\varphi_l(A,B,\hbar,a,\eta,x)$ is based on the following raising operators defined for $j=1,\ldots,d$ by

$$\mathcal{A}_j(A,B,\hbar,a,\eta)^*=\frac{1}{\sqrt{2\hbar}}\left[\sum_{k=1}^d\overline{B_{kj}}(x_k-a_k)-i\sum_{k=1}^d\overline{A_{kj}}\left(-i\hbar\frac{\partial}{\partial x_j}-\eta_j\right)\right]\ .$$

The corresponding lowering operators $\mathcal{A}_j(A,B,\hbar,a,\eta)$ are their formal adjoints.

These operators satisfy the following useful commutation relations : the raising operators $\mathcal{A}_j(A,B,\hbar,a,\eta)^*$ for $j=1,\ldots,d$ commute with one another, the lowering operators $\mathcal{A}_j(A,B,\hbar,a,\eta)$ commute with one another, however, for $j,k=1,\ldots,d$

$$\mathcal{A}_j(A,B,\hbar,a,\eta)\mathcal{A}_k(A,B,\hbar,a,\eta)^*-\mathcal{A}_k(A,B,\hbar,a,\eta)^*\mathcal{A}_j(A,B,\hbar,a,\eta)=\delta_{jk}\ .$$

For the multi-index $l=0$, we define the normalized complex Gaussian wave packet (modulo the sign of a square root) by

$$\varphi_0(A,B,\hbar,a,\eta,x)=(\pi\hbar)^{-d/4}(\det A)^{-1/2}\exp\left(-\frac{\langle x-a,BA^{-1}(x-a)\rangle}{2\hbar}+i\frac{\langle\eta,x-a\rangle}{\hbar}\right)\ .$$

Then, for any non-zero multi-index l, we define

$$\varphi_l(A,B,\hbar,a,\eta,\cdot) = \frac{1}{\sqrt{l!}}\mathcal{A}_1(A,B,\hbar,a,\eta)^{*l_1}\dots\mathcal{A}_d(A,B,\hbar,a,\eta)^{*l_d}\varphi_0(A,B,\hbar,a,\eta,\cdot)\ ,$$

$$\phi_l(A,B,y) = \varphi_l(A,B,1,0,0,y)\ .$$

We have the following properties

1. For $A=B=I$, $\hbar=1$ and $a=\eta=0$, the $\varphi_l(A,B,\hbar,a,\eta,\cdot)$ are just the standard harmonic oscillator eigenstates with energies $|l|+d/2$.

2. For each admissible A, B, $\hbar$, a and η, the set $(\varphi_l(A,B,\hbar,a,\eta,\cdot))_{l\in\mathbb{N}^d}$ is an orthonormal basis for $L^2(\mathbb{R}^d;\mathbb{C})$.

3. In [5], the state $\varphi_l(A,B,\hbar,a,\eta,x)$ is defined as a normalization factor times

   $$H_l(A;\hbar^{-1/2}|A|^{-1}(x-a))\varphi_0(A,B,\hbar,a,\eta,x)\ .$$

   Here $H_l(A;y)$ is a recursively defined $|l|^{th}$ order polynomial in y that depends on A only through U_A, where $A=|A|U_A$ is the polar decomposition of A.

4. When the dimension d is 1, the position and momentum uncertainties of the $\varphi_l(A,B,\hbar,a,\eta,\cdot)$ are $\sqrt{(l+1/2)\hbar}|A|$ and $\sqrt{(l+1/2)\hbar}|B|$, respectively. In higher dimensions, they are bounded by $\sqrt{(|l|+d/2)\hbar}\|A\|$ and $\sqrt{(|l|+d/2)\hbar}\|B\|$, respectively.

5. When we approximately solve the Schrödinger equation, the choice of the sign of the square root in the definition of $\varphi_0(A,B,\hbar,a,\eta,\cdot)$ is determined by continuity in time after an arbitrary initial choice.

6. The behaviour of $\varphi_l(A,B,\hbar,a,\eta,\cdot)$ through small perturbations of parameters A, B and a is the following

   $$\begin{aligned}&\|\varphi_l(A,B,\hbar,a,\eta,\cdot)-\varphi_l(A_0,B_0,\hbar,a_0,\eta,\cdot)\|_{L^2}\\ &\quad\le C_l(A_0,B_0,a_0)\left[\|A-A_0\|+\|B-B_0\|+\frac{\|a-a_0\|}{\sqrt{\hbar}}\right]\ ,\end{aligned}$$

   for (A,B) in a neighbourhood of (A_0,B_0). This estimation is already mentioned in [12], but the proof needs some modification (we cannot treat each matrix variable separately) : generalize the one-dimensional formulae of propositions 4 and 7 of [14] and give asymptotics when A_2-A_1 and B_2-B_1 are small.

7. If we fix a cutoff function $F\in\mathcal{C}^\infty(\mathbb{R}_+;[0,1])$ (with $F(x)=1$ for $x\leqslant 1$ and $F(x)=0$ for $x\geqslant 2$), we have the following estimates

   $$\begin{aligned}&\|(1-F)^{(n)}(\gamma^2\|y\|^2)\phi_l(A,B,y)\|_{L^2(\mathbb{R}^d;\mathbb{C})}\\ &\quad\le C_{l,n}\left[1+(\|A\|\gamma)^{|l|}\right](\|A\|\gamma)^{d/2}\,e^{-d\|A\|^{-2}\gamma^{-2}}\ ,\end{aligned}\qquad(9)$$

$$
\begin{aligned}
&\|(1-F)^{(n)}(\gamma^2\|y\|^2)y.\nabla_y\phi_l(A,B,y)\| \\
&\quad \leq C'_{l,n}\|A\|.\|B\| \left[1+(\|A\|\gamma)^{|l|+2}\right](\|A\|\gamma)^{d/2}\, e^{-d\|A\|^{-2}\gamma^{-2}}
\end{aligned} \tag{10}
$$

for $n \geqslant 0$ and $l \in \mathbb{N}^d$ when γ tends to 0.

In the Born-Oppenheimer approximation, the semi-classical dynamics of the nuclei is generated by an effective potential given by a chosen isolated electronic eigenvalue $E(x,\delta_0)$ of the electronic Hamiltonian $h(x,\delta_0)$, $x \in \mathbb{R}^d$ (we keep δ fixed). For a given effective potential $E(x,\delta_0)$ we describe the semi-classical dynamics of the nuclei by means of the time dependent basis constructed as follows. Associated to $E(x,\delta_0)$, we have the following classical equations of motion

$$
\begin{array}{rcl}
\dot{a}(t) & = & \eta(t)\ , \\
\dot{\eta}(t) & = & -\nabla_x E(a(t),\delta_0), \\
\dot{A}(t) & = & iB(t)\ , \\
\dot{B}(t) & = & i\mathrm{Hess}_x E(a(t),\delta_0)A(t)\ , \\
\dot{S}(t) & = & \frac{1}{2}\|\eta(t)\|^2 - E(a(t),\delta_0)\ .
\end{array} \tag{11}
$$

We always assume the initial condition $(A(0),B(0))$ satisfies (8).

The matrices $A(t)$ and $B(t)$ are related to the linearization of the classical flow through the following identities

$$
\begin{array}{rcl}
A(t) & = & \dfrac{\partial a(t)}{\partial a(0)}A(0) + i\dfrac{\partial a(t)}{\partial \eta(0)}B(0)\ , \\
B(t) & = & \dfrac{\partial \eta(t)}{\partial \eta(0)}B(0) - i\dfrac{\partial \eta(t)}{\partial a(0)}A(0)\ .
\end{array}
$$

Furthermore, it is not difficult to prove that conditions (8) are preserved by the flow.

The usefulness of those wave packets stems from the following important property. If we decompose the potential as

$$
E(x,\delta_0) = W_a(x,\delta_0) + [E(x,\delta_0) - W_a(x,\delta_0)]
$$

where $W_a(x,\delta_0)$ denotes the second order Taylor expansion

$$
W_a(x,\delta_0) = E(a,\delta_0) + \nabla_x E(a,\delta_0)(x-a) + \langle x-a, \frac{\mathrm{Hess}_x E(a,\delta_0)}{2}(x-a)\rangle
$$

then for all multi-indices l,

$$
\begin{aligned}
&i\hbar\frac{\partial}{\partial t}\left[e^{iS(t)/\hbar}\varphi_l(A(t),B(t),\hbar,a(t),\eta(t),x)\right] \\
&\quad = \left(-\frac{\hbar^2}{2}\Delta_x + W_{a(t)}(x,\delta_0)\right)\left[e^{iS(t)/\hbar}\varphi_l(A(t),B(t),\hbar,a(t),\eta(t),x)\right]
\end{aligned}
$$

if $a(t)$, $\eta(t)$, $A(t)$, $B(t)$ and $S(t)$ satisfy (11). In other words, those semi-classical wave packets φ_l exactly take into account the kinetic energy and quadratic part $W_{a(t)}(x,\delta_0)$

of the potential when propagated by means of the classical flow and its linearization around the classical trajectory selected by the initial conditions.

Then, the leading order Born-Oppenheimer approximation for (4) is

$$\psi(t,x,\delta_0) = e^{\frac{i}{\hbar}S(t)}\varphi_l(A(t),B(t),\hbar,a(t),\eta(t),x)\Phi_E(x,\delta_0) \tag{12}$$

where $\Phi_E(x,\delta_0)$ denotes a particular smooth normalized eigenvector associated to the eigenvalue $E(x,\delta_0)$ (see [6]).

3 Asymptotics of Classical Quantities

In our case, we have a supplementary parameter δ and we deal with two eigenvalues isolated from the rest of the spectrum but that do approach one another. This leads to two different classical dynamics (one for each eigenvalue). Close to the crossing surface, those two dynamics almost reduce to the one corresponding to the mean of those two. For each of those three, we will now give their asymptotics in a neighbourhood of the crossing surface Γ.

We define

$$\rho(x,\delta) = \sqrt{b(x,\delta)^2 + c(x,\delta)^2 + d(x,\delta)^2}\ ,$$
$$E_{\mathcal{C}}(x,\delta) := E(x,\delta) + \nu^{\mathcal{C}}\rho(x,\delta)$$

where $\nu^{\mathcal{A}} = 1$, $\nu^{\mathcal{B}} = -1$ and we choose $\eta^0, \eta^{0^{\mathcal{C}}} \in \mathcal{C}^0([-\delta_0,\delta_0];\mathbb{R}^d)$ with $\eta^0(\delta) = \eta^0 + O(\delta)$ and $\eta^{0^{\mathcal{C}}}(\delta) = \eta^0 + O(\delta)$ where the first component of the vector η^0 satisfies $\eta^0_1 > 0$.

We solve the following systems with the corresponding initial conditions

$$\left\{\begin{array}{rcl} \dot a(t,\delta) & = & \eta(t,\delta) \\ \dot\eta(t,\delta) & = & -\nabla_x E(a(t,\delta),\delta) \\ \dot A(t,\delta) & = & iB(t,\delta) \\ \dot B(t,\delta) & = & i\mathrm{Hess}_x E(a(t,\delta),\delta)A(t,\delta) \\ \dot S(t,\delta) & = & \frac{1}{2}\|\eta(t,\delta)\|^2 - E(a(t,\delta),\delta) \end{array}\right. , \quad \left\{\begin{array}{rcl} a(0,\delta) & = & 0 \\ \eta(0,\delta) & = & \eta^0(\delta) \\ A(0,\delta) & = & A_0 \\ B(0,\delta) & = & B_0 \\ S(0,\delta) & = & 0 \end{array}\right. , \tag{13}$$

$$\left\{\begin{array}{rcl} \dot a^{\mathcal{C}}(t,\delta) & = & \eta^{\mathcal{C}}(t,\delta) \\ \dot\eta^{\mathcal{C}}(t,\delta) & = & -\nabla_x E_{\mathcal{C}}(a^{\mathcal{C}}(t,\delta),\delta) \\ \dot A^{\mathcal{C}}(t,\delta) & = & iB^{\mathcal{C}}(t,\delta) \\ \dot B^{\mathcal{C}}(t,\delta) & = & i\mathrm{Hess}_x E_{\mathcal{C}}(a^{\mathcal{C}}(t,\delta),\delta)A^{\mathcal{C}}(t,\delta) \\ \dot S^{\mathcal{C}}(t,\delta) & = & \frac{1}{2}\|\eta^{\mathcal{C}}(t,\delta)\|^2 - E_{\mathcal{C}}(a^{\mathcal{C}}(t,\delta),\delta) \end{array}\right. , \quad \left\{\begin{array}{rcl} a^{\mathcal{C}}(0,\delta) & = & 0 \\ \eta^{\mathcal{C}}(0,\delta) & = & \eta^{0^{\mathcal{C}}}(\delta) \\ A^{\mathcal{C}}(0,\delta) & = & A_0 \\ B^{\mathcal{C}}(0,\delta) & = & B_0 \\ S^{\mathcal{C}}(0,\delta) & = & 0 \end{array}\right. . \tag{14}$$

We note that the initial momenta can differ by a term of order $O(\delta)$; we will explain why in section 6.1.

As in [12], Picard fixed point theorem techniques yield

Proposition 1 *The solutions of differential systems (13) and (14) have the following asymptotics when t and δ tend to* 0

$$\begin{aligned} a(t,\delta) &= \eta^0(\delta)t - \nabla_x E(0,\delta)\frac{t^2}{2} + O(t^3) \ , \\ \eta(t,\delta) &= \eta^0(\delta) - \nabla_x E(0,\delta)t + O(t^2) \end{aligned}$$

(those two are uniform in δ) ;

$$\begin{aligned} a^{\mathcal{C}}(t,\delta) &= \eta^{0^{\mathcal{C}}}(\delta)t - \nabla_x E(0,\delta)\frac{t^2}{2} + O(|t|^3 + \delta t^2) - \nu^{\mathcal{C}} \frac{r}{2\eta_1^{0^{\mathcal{C}}}(\delta)} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\ &\quad \times \left[t\sqrt{(\eta_1^{0^{\mathcal{C}}}(\delta)t)^2 + \delta^2} + \frac{\delta^2}{\eta_1^{0^{\mathcal{C}}}(\delta)} \ln\left(\frac{\eta_1^{0^{\mathcal{C}}}(\delta)t + \sqrt{(\eta_1^{0^{\mathcal{C}}}(\delta)t)^2 + \delta^2}}{\delta} \right) - 2\delta t \right] \ , \\ \eta^{\mathcal{C}}(t,\delta) &= \eta^{0^{\mathcal{C}}}(\delta) - \nabla_x E(0,\delta)t + O(t^2 + \delta|t|) \\ &\quad - \nu^{\mathcal{C}} \frac{r}{\eta_1^{0^{\mathcal{C}}}(\delta)} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \left[\sqrt{(\eta_1^{0^{\mathcal{C}}}(\delta)t)^2 + \delta^2} - \delta \right] \ ; \end{aligned}$$

$$\begin{aligned} S(t,\delta) &= \left(\frac{1}{2}\|\eta^0(\delta)\|^2 - E(0,\delta) \right) t - \eta^0(\delta).\nabla_x E(0,\delta)t^2 + O(t^3) \ , \\ S^{\mathcal{C}}(t,\delta) &= \left(\frac{1}{2}\|\eta^{0^{\mathcal{C}}}(\delta)\|^2 - E(0,\delta) \right) t - \eta^{0^{\mathcal{C}}}(\delta).\nabla_x E(0,\delta)t^2 + \nu^{\mathcal{C}} r\delta t + O(t^3 + \delta^2 t) \\ &\quad - \nu^{\mathcal{C}} r \left[t\sqrt{(\eta_1^{0^{\mathcal{C}}}(\delta)t)^2 + \delta^2} + \frac{\delta^2}{\eta_1^{0^{\mathcal{C}}}(\delta)} \ln\left(\frac{\eta_1^{0^{\mathcal{C}}}(\delta)t + \sqrt{(\eta_1^{0^{\mathcal{C}}}(\delta)t)^2 + \delta^2}}{\delta} \right) \right] \ ; \end{aligned}$$

$$\begin{aligned} A^{\mathcal{C}}(t,\delta) &= A_0 + O(t) \ , \\ B^{\mathcal{C}}(t,\delta) &= B_0 + \nu^{\mathcal{C}} ir \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & 0 \end{pmatrix} A_0 \frac{t}{\sqrt{(\eta_1^{0^{\mathcal{C}}}(\delta)t)^2 + \delta^2}} + O(|t| + \delta) \ . \end{aligned}$$

Throughout the rest of this paper, we will drop the δ-dependence of those quantities (in the notation only).

4 Away from the Crossing

We fix a cutoff function $F \in \mathcal{C}^\infty(\mathbb{R}_+; [0,1])$ with $F(x) = 1$ for $x \leqslant 1$ and $F(x) = 0$ for $x \geqslant 2$.

4.1 Crossing Surface vs Cutoff Zone

We introduce the following sets that are suggested in figure 1.

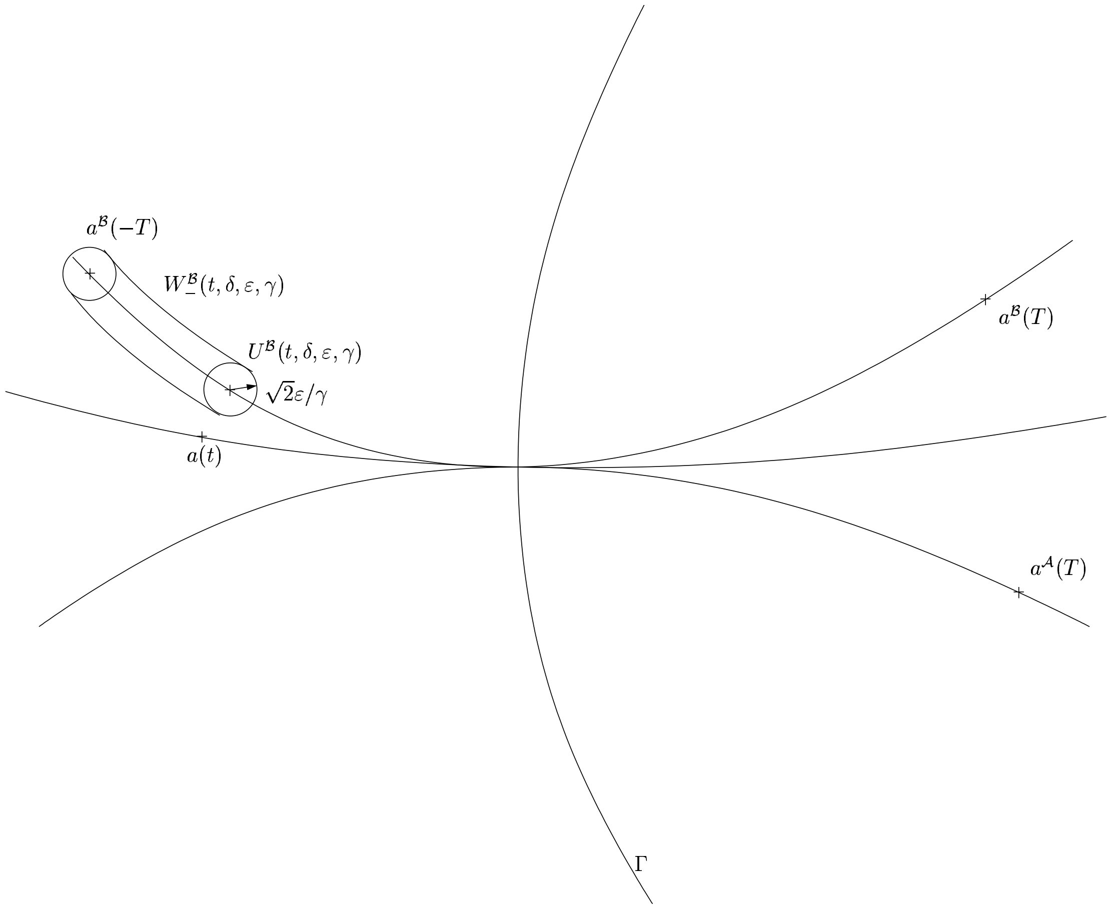

Figure 1: Classical propagation of the nuclei through the crossing surface

For $\delta \in]-2\delta_0, 2\delta_0[$, we define

$$Z_-(\delta) = \left\{ x \in \mathbb{R}^d / b(x,\delta) < \frac{1}{2}\rho(x,\delta) \right\} \ , \ Z_+(\delta) = \left\{ x \in \mathbb{R}^d / b(x,\delta) > -\frac{1}{2}\rho(x,\delta) \right\}$$

the two overlapping zones where $h_1(x,\delta)$ avoids some diagonal form,

$$J(\delta) = \left\{ x \in \mathbb{R}^d / \rho(x,\delta) > \frac{r}{2}\sqrt{x_1^2 + \delta^2} \right\}$$

the zone where the gap is well bounded from below,

$$U^{\mathcal{C}}(t,\delta,\varepsilon,\gamma) = \left\{ x \in \mathbb{R}^d / \|x - a^{\mathcal{C}}(t,\delta)\|_\infty \leqslant \sqrt{2}\frac{\varepsilon}{\gamma} \right\}$$

for $t \in [-T,T]$ the cutoff zone at time t, and finally

$$W_-^{\mathcal{C}}(t,\delta,\varepsilon,\gamma) = \bigcup_{\tau \in [-T,t]} U^{\mathcal{C}}(\tau,\delta,\varepsilon,\gamma) \ , \ W_+^{\mathcal{C}}(t,\delta,\varepsilon,\gamma) = \bigcup_{\tau \in [t,T]} U^{\mathcal{C}}(\tau,\delta,\varepsilon,\gamma)$$

the two disjoint cutoff zones in the incoming and outgoing time intervals.

Anticipating estimates required for the proof of Proposition 2, we give a precise statement of how close to the crossing surface we can approach if we want to control

- the gap between the two eigenvalues $E^{\mathcal{A}}(x,\delta)$ and $E^{\mathcal{B}}(x,\delta)$,
- the deformation of the eigenvectors $\Phi^*_{\mathcal{C}}(x,\delta)$ defined in section 4.2 for $\mathcal{C}=\mathcal{A},\mathcal{B}$ and $*=+,-$.

Lemma 1 *If δ_0 and T are small enough, then for all δ in $]0,\delta_0]$, ε and γ in $]0,1]$, and t in $]0,T]$ such that*

$$\frac{\varepsilon}{\gamma}\leqslant\frac{\eta_1^0}{8\sqrt{2}}t\ ,$$

we have $W_-^{\mathcal{C}}(-t,\delta,\varepsilon,\gamma)\subseteq(Z_-(\delta)\cap J(\delta))$ and $W_+^{\mathcal{C}}(t,\delta,\varepsilon,\gamma)\subseteq(Z_+(\delta)\cap J(\delta))$.

Proof We prove only the first part, the other is analogous. We denote by C_a, C_η, C_b, C_c, C_d and C_ρ strictly positive constants such that for every $(t,x,\delta)\in[-T,T]\times\overline{B}(0,\kappa)\times[0,\delta_0]$, we have

$$\|a^{\mathcal{C}}(t,\delta)-\eta^{0^{\mathcal{C}}}(\delta)t\|_\infty\leqslant C_a t^2\ ,\ \|\eta^{0^{\mathcal{C}}}(\delta)-\eta^0\|\leqslant C_\eta\delta\ ,$$

$$|b(x,\delta)-rx_1|\leqslant C_b(\|x\|_\infty^2+\delta^2)\ ,\ |\rho(x,\delta)^2-r^2(x_1^2+\delta^2)|\leqslant C_\rho(\|x\|_\infty^2+\delta^2)^{3/2}\ .$$

If $x\in W_-^{\mathcal{C}}(t,\delta,\varepsilon,\gamma)$, we have

$$x_1=\eta_1^0t+\left(x_1-a_1^{\mathcal{C}}(t,\delta)\right)+\left(a_1^{\mathcal{C}}(t,\delta)-\eta_1^{0^{\mathcal{C}}}(\delta)t\right)+\left(\eta_1^{0^{\mathcal{C}}}(\delta)t-\eta_1^0t\right)\ ,$$

but

$$|x_1-a_1^{\mathcal{C}}(t,\delta)|\leqslant\sqrt{2}\frac{\varepsilon}{\gamma}\ ,\ |a_1^{\mathcal{C}}(t,\delta)-\eta_1^{0^{\mathcal{C}}}(\delta)t|\leqslant C_at^2\ ,\ |\eta_1^{0^{\mathcal{C}}}(\delta)-\eta_1^0|\leqslant C_\eta\delta\ ,$$

hence, if $\varepsilon/\gamma\leqslant\eta_1^0|t|/(8\sqrt{2})$, $|t|\leqslant\eta_1^0/(8C_a)$ and $\delta\leqslant\eta_1^0/(2C_\eta)$,

$$x_1\leqslant\eta_1^0t-\frac{\eta_1^0}{8}t-\frac{\eta_1^0}{8}t-\frac{\eta_1^0}{2}t=\frac{\eta_1^0}{4}t<0\ .$$

Moreover,

$$x=\eta^0t+\left(x-a^{\mathcal{C}}(t,\delta)\right)+\left(a^{\mathcal{C}}(t,\delta)-\eta^{0^{\mathcal{C}}}(\delta)t\right)+\left(\eta^{0^{\mathcal{C}}}(\delta)t-\eta^0t\right)\ ,$$

hence

$$\|x\|_\infty\leqslant\|\eta^0\|_\infty|t|+\sqrt{2}\frac{\varepsilon}{\gamma}+C_at^2+C_\eta\delta|t|\leqslant(\|\eta^0\|_\infty+\frac{3\eta_1^0}{4})|t|=D_t|t|\ .$$

Let us show first condition $W_-^{\mathcal{C}}(t,\delta,\varepsilon,\gamma)\subseteq J(\delta)$: from above, we have

$$\frac{\rho(x,\delta)^2}{r^2(x_1^2+\delta^2)}\geqslant1-\frac{C_\rho}{r^2}\frac{(\|x\|_\infty^2+\delta^2)^{3/2}}{(x_1^2+\delta^2)}\geqslant1-\frac{C_\rho}{r^2}\frac{(D_t^2t^2+\delta^2)^{3/2}}{\frac{\eta_1^{0^2}}{16}t^2+\delta^2}$$

hence, if $t^2+\delta^2 \leqslant (r^4\min(1,{\eta_1^0}^4/256))/(4C_\rho^2\max(1,D_t^6))$,

$$\rho(x,\delta)^2 \geqslant \frac{r^2}{2}(x_1^2+\delta^2)\ .$$

Let us show now condition $W_-^{\mathcal{C}}(t,\delta,\varepsilon,\gamma)\subseteq Z_-(\delta)$:

$$b(x,\delta)=rx_1+(b(x,\delta)-rx_1)<C_b(\|x\|_\infty^2+\delta^2)\leqslant C_b\max\left(1,\frac{16D_t^2}{{\eta_1^0}^2}\right)(x_1^2+\delta^2)$$

$$\leqslant \rho(x,\delta)\frac{2C_b}{r}\max\left(1,\frac{16D_t^2}{{\eta_1^0}^2}\right)\sqrt{\frac{{\eta_1^0}^2}{16}t^2+\delta^2}$$

hence, if $\frac{{\eta_1^0}^2}{16}t^2+\delta^2\leqslant r/(4C_b\max(1,16D_t^2/{\eta_1^0}^2))$, $b(x,\delta)<\frac{1}{2}\rho(x,\delta)$.

Finally by diminishing T and δ_0, the only remaining constraint is $\varepsilon/\gamma\leqslant\eta_1^0|t|/(8\sqrt{2})$, as expected. □

Remark By the way, we note that $\rho(x,\delta)>\frac{r}{2}\sqrt{\frac{{\eta_1^0}^2}{16}t^2+\delta^2}\geqslant R(|t|+\delta)$ for every x in $U^{\mathcal{C}}(t,\delta,\varepsilon,\gamma)$ and that $a^{\mathcal{C}}([-T,T],\delta)\subseteq J(\delta)$.

4.2 Construction and Asymptotics of Selected Eigenvectors

For $(x,\delta)\in\mathbb{R}^d\times]0,2\delta_0[$, we define

$$B(x,\delta)=\frac{b(x,\delta)}{\rho(x,\delta)}\ ,\ C(x,\delta)=\frac{c(x,\delta)}{\rho(x,\delta)}\ ,\ D(x,\delta)=\frac{d(x,\delta)}{\rho(x,\delta)}\ ,$$

$$f^-(x,\delta)=\sqrt{\frac{1-B(x,\delta)}{2}}\ ,\ g^-(x,\delta)=\frac{C(x,\delta)+iD(x,\delta)}{\sqrt{2(1-B(x,\delta))}}$$

when $B(x,\delta)<1$, and

$$f^+(x,\delta)=\sqrt{\frac{1+B(x,\delta)}{2}}\ ,\ g^+(x,\delta)=\frac{C(x,\delta)+iD(x,\delta)}{\sqrt{2(1+B(x,\delta))}}$$

when $B(x,\delta)>-1$.

We define static eigenvectors by

$$\begin{aligned}\Phi_{\mathcal{A}}^-(x,\delta) &= g^-(x,\delta)\psi_1(x,\delta)+f^-(x,\delta)\psi_2(x,\delta)\ ,\\ \Phi_{\mathcal{B}}^-(x,\delta) &= -f^-(x,\delta)\psi_1(x,\delta)+\overline{g^-(x,\delta)}\psi_2(x,\delta)\end{aligned}$$

when $B(x,\delta)<1$, and

$$\begin{aligned}\Phi_{\mathcal{A}}^+(x,\delta) &= f^+(x,\delta)\psi_1(x,\delta)+\overline{g^+(x,\delta)}\psi_2(x,\delta)\ ,\\ \Phi_{\mathcal{B}}^+(x,\delta) &= -g^+(x,\delta)\psi_1(x,\delta)+f^+(x,\delta)\psi_2(x,\delta)\end{aligned}$$

when $B(x,\delta)>-1$.

We now turn to the asymptotics of those static eigenvectors around $(x,\delta)=(0,0)$. First in the same asymptotic time regime as in [12], we have

Lemma 2 *When δ, ε and t tend to 0, we have, uniformly in $\gamma \leqslant 1$, $|\varepsilon/(\gamma t)| \leqslant M$ and $|\delta/t| \leqslant M'$, for $t < 0$,*

$$\begin{aligned}
\left\| F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{A}}(t)\|^2) \left[\Phi_{\mathcal{A}}^-(x,\delta) - \psi_2(x,\delta)\right] \right\|_{L^\infty} &= O\left(|t| + \left|\frac{\delta}{t}\right|\right) , \\
\left\| F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{B}}(t)\|^2) \left[\Phi_{\mathcal{B}}^-(x,\delta) + \psi_1(x,\delta)\right] \right\|_{L^\infty} &= O\left(|t| + \left|\frac{\delta}{t}\right|\right) ,
\end{aligned}$$

and for $t > 0$,

$$\begin{aligned}
\left\| F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{A}}(t)\|^2) \left[\Phi_{\mathcal{A}}^+(x,\delta) - \psi_1(x,\delta)\right] \right\|_{L^\infty} &= O\left(|t| + \left|\frac{\delta}{t}\right|\right) , \\
\left\| F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{B}}(t)\|^2) \left[\Phi_{\mathcal{B}}^+(x,\delta) - \psi_2(x,\delta)\right] \right\|_{L^\infty} &= O\left(|t| + \left|\frac{\delta}{t}\right|\right) .
\end{aligned}$$

Proof If $x_1 \neq 0$,

$$|\rho(x,\delta) - r|x_1|| \leqslant \frac{r^2\delta^2 + C_\rho(\|x\|_\infty^2 + \delta^2)^{3/2}}{r|x_1|} .$$

Thus, for $x \in W_*^{\mathcal{C}}(t,\delta,\varepsilon,\gamma)$ with $* = +, -$,

$$\begin{aligned}
|B(x,\delta) - \mathrm{sgn}(t)| &= \left| \frac{\mathrm{sgn}(t) b(x,\delta) - \rho(x,\delta)}{\rho(x,\delta)} \right| \\
&\leqslant \frac{|b(x,\delta) - r x_1| + |\rho(x,\delta) - r|x_1||}{\frac{r}{2}|x_1|} \\
&\leqslant 2\frac{r C_b |x_1|(\|x\|_\infty^2 + \delta^2) + r^2\delta^2 + C_\rho(\|x\|_\infty^2 + \delta^2)^{3/2}}{r^2 x_1^2} ,
\end{aligned}$$

hence

$$B(x,\delta) - \mathrm{sgn}(t) = O\left(|t| + \frac{\delta^2}{t^2}\right) .$$

Moreover, similar calculations yield

$$C(x,\delta) + iD(x,\delta) = O\left(|t| + \left|\frac{\delta}{t}\right|\right)$$

which leads to the result. □

By similar considerations, we get also in the opposite asymptotic case

Lemma 3 *When δ, ε and t tend to 0, we have, uniformly in $\gamma \leqslant 1$, $|\varepsilon/(\gamma t)| \leqslant M$ and $|t/\delta| \leqslant M'$, for $t < 0$,*

$$\begin{aligned}
\left\| F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{A}}(t)\|^2) \left[\Phi_{\mathcal{A}}^-(x,\delta) - \frac{\sqrt{2}}{2}(\psi_1(x,\delta) + \psi_2(x,\delta))\right] \right\|_{L^\infty} &= O\left(\delta + \left|\frac{t}{\delta}\right|\right) , \\
\left\| F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{B}}(t)\|^2) \left[\Phi_{\mathcal{B}}^-(x,\delta) - \frac{\sqrt{2}}{2}(-\psi_1(x,\delta) + \psi_2(x,\delta))\right] \right\|_{L^\infty} &= O\left(\delta + \left|\frac{t}{\delta}\right|\right) ,
\end{aligned}$$

and for $t>0$,

$$\left\|F(\varepsilon^{-2}\gamma^2\|x-a^{\mathcal{A}}(t)\|^2)\left[\Phi^+_{\mathcal{A}}(x,\delta)-\frac{\sqrt{2}}{2}(\psi_1(x,\delta)+\psi_2(x,\delta))\right]\right\|_{L^\infty} = O\left(\delta+\left|\frac{t}{\delta}\right|\right) ,$$

$$\left\|F(\varepsilon^{-2}\gamma^2\|x-a^{\mathcal{B}}(t)\|^2)\left[\Phi^+_{\mathcal{B}}(x,\delta)-\frac{\sqrt{2}}{2}(-\psi_1(x,\delta)+\psi_2(x,\delta))\right]\right\|_{L^\infty} = O\left(\delta+\left|\frac{t}{\delta}\right|\right) .$$

We introduce now dynamical eigenvectors

$$\Phi^*_{\mathcal{C}}(t,x,\delta)=e^{i\omega^*_{\mathcal{C}}(t,x,\delta)}\Phi^*_{\mathcal{C}}(x,\delta)$$

for $\mathcal{C}=\mathcal{A},\mathcal{B}$ and $*=+,-$ in order to fulfill the orthogonality condition

$$\langle\Phi^*_{\mathcal{C}}(t,x,\delta),\left(\frac{\partial}{\partial t}+\eta^{\mathcal{C}}(t).\nabla_x\right)\Phi^*_{\mathcal{C}}(t,x,\delta)\rangle=0 .$$

Introducing the new variables $s=t$, $z=x-a^{\mathcal{C}}(t)$, we have the sufficient condition

$$\frac{\partial}{\partial s}\tilde{\omega}^*_{\mathcal{C}}(s,z,\delta)=i\langle\Phi^*_{\mathcal{C}}(a^{\mathcal{C}}(s)+z,\delta),\eta^{\mathcal{C}}(s).\nabla_x\Phi^*_{\mathcal{C}}(a^{\mathcal{C}}(s)+z,\delta)\rangle \tag{15}$$

where $\tilde{\omega}^*_{\mathcal{C}}(s,z,\delta)=\omega^*_{\mathcal{C}}(s,a^{\mathcal{C}}(s)+z,\delta)$. If we suppose $\omega^-_{\mathcal{C}}(-T,x,\delta)=\omega^+_{\mathcal{C}}(T,x,\delta)=0$, we have the following result

Lemma 4 *When δ, ε and t tend to 0, we have, for $\mathcal{C}=\mathcal{A},\mathcal{B}$ and $*=+,-$,*

$$\left\|F(\varepsilon^{-2}\gamma^2\|x-a^{\mathcal{C}}(t)\|^2)\left[\Phi^*_{\mathcal{C}}(t,x,\delta)-e^{i\omega^*_{\mathcal{C}}(t,a^{\mathcal{C}}(t),\delta)}\Phi^*_{\mathcal{C}}(x,\delta)\right]\right\|_{L^\infty(\mathbb{R}^d;\mathcal{H})}=O\left(\frac{\varepsilon}{\gamma}\ln\frac{1}{|t|+\delta}\right)$$

uniformly in $\gamma\leqslant 1$ and $|\varepsilon/(\gamma t)|\leqslant M$.

Proof Because of (15), we try to compare with the situation at $z=0$. We treat only the case $(\mathcal{C},*)=(\mathcal{B},-)$, others are analogous. Dropping the parameters t, x and δ, we get

$$\begin{aligned}&\langle\Phi^-_{\mathcal{B}}(x,\delta),\eta^{\mathcal{B}}(t).\nabla_x\Phi^-_{\mathcal{B}}(x,\delta)\rangle\\ &\quad=\eta^{\mathcal{B}}.(f^-\nabla_x f^-+g^-\nabla_x\overline{g^-})+{f^-}^2\lambda_{11}|g^-|^2\lambda_{22}-f^-\overline{g^-}\lambda_{12}-f^-g^-\lambda_{21}\end{aligned}$$

where $\lambda_{ij}(t,x,\delta)=\langle\psi_i(x,\delta),\eta^{\mathcal{B}}(t).\nabla_x\psi_j(x,\delta)\rangle$.

Short calculations show that we have to estimate the difference between $L(x,\delta)$ and $L(a^{\mathcal{B}}(t),\delta)$ for $x\in U^{\mathcal{B}}(t,\delta,\varepsilon,\gamma)$ where L is one of the following quantities : ρ, B, C, D, $\nabla_x c$, $\nabla_x d$ and λ_{ij}. Set $[L]^x_t=L(x,\delta)-L(a^{\mathcal{B}}(t),\delta)$. Further computations show that, for $x\in U^{\mathcal{B}}(t,\delta,\varepsilon,\gamma)$:

1. $[\rho]^x_t=O\left(\frac{\varepsilon|t|}{\gamma(|t|+\delta)}+\frac{\varepsilon}{\gamma}(|t|+\delta)\right)$;

2. $[B]^x_t=O\left(\frac{\varepsilon}{\gamma(|t|+\delta)}\right)$;

3. $[C]_t^x = O\left(\frac{\varepsilon}{\gamma} + \frac{\varepsilon|t|}{\gamma(|t|+\delta)^2}\right)$ with same estimate for D ;

4. $[L]_t^x = O(\frac{\varepsilon}{\gamma})$ for $\nabla_x c$, $\nabla_x d$ and λ_{ij} ;

5. $[f^-\nabla_x f^- + g^-\nabla_x \overline{g^-}]_t^x = O\left(\frac{\varepsilon}{\gamma(|t|+\delta)}\right)$.

Finally

$$\langle \Phi_{\mathcal{B}}^- | \eta^{\mathcal{B}}.\nabla_x \Phi_{\mathcal{B}}^- \rangle = O\left(\frac{\varepsilon}{\gamma(|t|+\delta)}\right)$$

and the claim is obtained by integration on $[-T, t]$. □

Now we have constructed those dynamical eigenvectors $\Phi_{\mathcal{C}}^*(t, x, \delta)$ and given the classical dynamics of (14), we want to use the approximation (12) and to estimate how good it is. We just recall the following abstract lemma of [10]

Lemma 5 *Suppose $H(\hbar)$ is a family of self-adjoint operators in any separable Hilbert space $\mathcal{H}$ for $\hbar > 0$ and let ν be a strictly positive real number. Suppose $\psi(r, \hbar)$ belongs to the domain of $H(\hbar)$, is continuously differentiable in r, and approximately solves the Schrödinger equation*

$$i\hbar^\nu \frac{\partial \psi}{\partial r} = H(\hbar)\psi \ , \tag{16}$$

in the sense that

$$i\hbar^\nu \frac{\partial \psi}{\partial r}(r, \hbar) = H(\hbar)\psi(r, \hbar) + \zeta(r, \hbar)$$

where $\zeta(r, \hbar)$ satisfies

$$\|\zeta(r, \hbar)\| \leqslant \mu(r, \hbar) \ .$$

If $\Psi(r, \hbar)$ denotes the solution of the Schrödinger equation (16) with initial condition $\Psi(r_0, \hbar) = \psi(r_0, \hbar)$, then

$$\|\Psi(r, \hbar) - \psi(r, \hbar)\| \leqslant \hbar^{-\nu} \left| \int_{r_0}^{r} \mu(\rho, \hbar) d\rho \right| \ .$$

4.3 Outer Ansatz

Carefully analyzing the time when the usual Born-Oppenheimer approximation (12) actually breaks down and setting for $\mathcal{C} = \mathcal{A}, \mathcal{B}$ and $l \in \mathbb{N}^n$

$$\varphi_l^{\mathcal{C}}(t, y, \varepsilon) = \exp\left(i\frac{S^{\mathcal{C}}(t)}{\varepsilon^2} + i\frac{\eta^{\mathcal{C}}(t).y}{\varepsilon}\right) \phi_l(A^{\mathcal{C}}(t), B^{\mathcal{C}}(t), y) \ ,$$

we get the following result

Proposition 2 *In the incoming outer region $-T \leqslant t \leqslant -t_o(\delta, \varepsilon) < 0$, if*

$$\psi_{IO}(t, x, \delta, \varepsilon) = \sum_{\mathcal{C}=\mathcal{A},\mathcal{B}} \Lambda_{\mathcal{C}}^-(\delta, \varepsilon) F(\varepsilon^{-2}\gamma^2 \|x - a^{\mathcal{C}}(t)\|^2) \varphi_l^{\mathcal{C}}\left(t, \frac{x - a^{\mathcal{C}}(t)}{\varepsilon}, \varepsilon\right) \Phi_{\mathcal{C}}^-(t, x, \delta) \tag{17}$$

where $\Lambda_{\mathcal{C}}^-(\delta,\varepsilon) = O(1)$ *and if* $\psi(\cdot,\delta,\varepsilon)$ *denotes the solution of (4) with initial condition* $\psi(-T,\cdot,\delta,\varepsilon) = \psi_{IO}(-T,\cdot,\delta,\varepsilon)$*, we have*

$$\sup_{t\in[-T,-t_o]} \|\psi(t,x,\delta,\varepsilon) - \psi_{IO}(t,x,\delta,\varepsilon)\|_{L^2(\mathbb{R}^d;\mathcal{H})} = O\left(\varepsilon \ln \frac{1}{t_o+\delta} + \frac{\varepsilon^2}{(t_o+\delta)^2} + \frac{\varepsilon^4}{(t_o+\delta)^3}\right)$$

when δ *and* ε *tend to* 0 *and where* $\gamma(\delta,\varepsilon)$ *and* $t_o(\delta,\varepsilon)$ *are chosen to tend to* 0 *with* $\varepsilon/(\gamma(\delta,\varepsilon)t_o(\delta,\varepsilon))$ *bounded.*

Remarks

1. If we fix $\delta > 0$, we recover the usual Born-Oppenheimer approximation with an error of order $O(\varepsilon)$.
2. There is a similar result in the outgoing outer region $0 < t_o(\delta,\varepsilon) \leqslant t \leqslant T$ substituting $\psi_{IO}(t,x,\delta,\varepsilon)$, $\Phi_{\mathcal{C}}^-(t,x,\delta)$ and $\Lambda_{\mathcal{C}}^-(\delta,\varepsilon)$ by $\psi_{OO}(t,x,\delta,\varepsilon)$, $\Phi_{\mathcal{C}}^+(t,x,\delta)$ and $\Lambda_{\mathcal{C}}^+(\delta,\varepsilon)$ respectively.
3. When stating this proposition, the cutoff function F can not be removed because a priori $\Phi_{\mathcal{C}}^-(t,x,\delta)$ is not well defined near the crossing surface Γ.
4. T has to be chosen small enough such that $a^{\mathcal{C}}(t)$ is close to Γ only when t goes to 0, but if we take it as an additional hypothesis, the usual Born-Oppenheimer approximation gives estimates for the error between any finite time $-\tilde{T}$ and time $-T$ mentioned above.

We introduce the multiple scale notation often used in such a situation: $y = \frac{x-a(t)}{\varepsilon}$. In term of variables t,x,y (thought of as independent), the Schrödinger equation (4) reads

$$i\varepsilon^2 \frac{\partial}{\partial t}\Psi = H(t,\delta,\varepsilon)\Psi \tag{18}$$

where $H(t,\delta,\varepsilon) = -\frac{\varepsilon^4}{2}\Delta_x - \varepsilon^3\nabla_y.\nabla_x - \frac{\varepsilon^2}{2}\Delta_y + i\varepsilon\eta(t).\nabla_y + E(a(t)+\varepsilon y,\delta) + h_E(x,\delta)$ with $h_E(x,\delta) = h(x,\delta) - E(x,\delta)$. We immediately check that if $\Psi(t,x,y,\varepsilon)$ satisfies equation (18) then $\psi(t,x,\varepsilon) = \Psi\left(t,x,\frac{x-a(t)}{\varepsilon},\varepsilon\right)$ satisfies equation (3).

Let us now give a sketch of the proof in the case where $\Lambda_{\mathcal{A}}^-(\delta,\varepsilon) = 0$ and $\Lambda_{\mathcal{B}}^-(\delta,\varepsilon) = 1$. The multiple scale second order Ansatz established in [6] in absence of crossing is:

$$\begin{aligned}\Psi(t,x,y,\delta,\varepsilon) = {} & F\left(\varepsilon^{-2}\gamma^2\left\|x-a^{\mathcal{B}}(t)\right\|^2\right)\varphi_l^{\mathcal{B}}(t,y,\varepsilon)\\ & \left[\Phi_{\mathcal{B}}^- + i\varepsilon^2\left(\frac{1}{E_{\mathcal{A}}-E_{\mathcal{B}}}|\Phi_{\mathcal{A}}^-\rangle\langle\Phi_{\mathcal{A}}^-| + r_{\mathcal{B}}(x,\delta)P^\perp(x,\delta)\right)\left(\frac{\partial}{\partial t} + \eta^{\mathcal{B}}(t).\nabla_x\right)\Phi_{\mathcal{B}}^-\right]\end{aligned} \tag{19}$$

where $P^\perp(x,\delta) = 1 - P(x,\delta)$ is the spectral projector on the orthogonal of the eigenspaces associated to eigenvalues $E_{\mathcal{A}}(x,\delta)$ and $E_{\mathcal{B}}(x,\delta)$, $r_{\mathcal{B}}(x,\delta)$ is the restriction to $P^\perp(x,\delta)\mathcal{H}$ of the resolvent of $h(x,\delta)$ taken in $E_{\mathcal{B}}(x,\delta)$ and we have dropped the variables in the dynamical eigenvectors $\Phi_{\mathcal{C}}^-(t,x,\delta)$ and in the eigenvalues $E_{\mathcal{C}}(x,\delta)$ for $\mathcal{C} = \mathcal{A},\mathcal{B}$. Terms that involve derivatives of the cutoff function turn out to be exponentially small and we can neglect them comparing with others. Thus we only treat the remaining terms following the same method as on pages 108-110 of [9].

The quantity $\exp\left(-\frac{i}{\varepsilon^2}S^{\mathcal{B}}(t)-\frac{i}{\varepsilon}\eta^{\mathcal{B}}(t).y\right)\left[i\varepsilon^2\frac{\partial}{\partial t}-H(t,\delta,\varepsilon)\right]\Psi(t,x,y,\delta,\varepsilon)$ is the sum of 35 product terms. Performing brute force estimates on each product with the L^2-norm for y-dependent factors and the L^∞-norm for x-dependent ones, we need the following estimates of the singular terms on the support of F :

- successive derivatives of the gap between eigenvalues

$$\frac{1}{E_{\mathcal{A}}(x,\delta)-E_{\mathcal{B}}(x,\delta)}=O\left(\frac{1}{|t|+\delta}\right)\ ,\ \nabla_x\left(\frac{1}{E_{\mathcal{A}}-E_{\mathcal{B}}}\right)=O\left(\frac{1}{(|t|+\delta)^2}\right)\ ,$$

$$\Delta_x\left(\frac{1}{E_{\mathcal{A}}-E_{\mathcal{B}}}\right)=O\left(\frac{1}{(|t|+\delta)^3}\right)\ ,$$

- successive derivatives of the dynamic eigenvectors

$$\nabla_x\Phi_{\mathcal{C}}^-(t,x,\delta)=O\left(\frac{1}{|t|+\delta}\right)\ ,\ \left(\frac{\partial}{\partial t}+\eta^{\mathcal{B}}.\nabla_x\right)\Phi_{\mathcal{A}}^-=O\left(\frac{1}{|t|+\delta}\right)\ ,$$

$$\left(\frac{\partial}{\partial t}+\eta^{\mathcal{C}}.\nabla_x\right)\Phi_{\mathcal{C}}^-=O\left(\frac{1}{|t|+\delta}\right)\ ,\ \Delta_x\Phi_{\mathcal{C}}^-=O\left(\frac{1}{(|t|+\delta)^2}\right)\ ,$$

$$\left(\frac{\partial}{\partial t}+\eta^{\mathcal{C}}.\nabla_x\right)^2\Phi_{\mathcal{C}}^-=O\left(\frac{1}{(|t|+\delta)^2}\right)\ ,\ \nabla_x\left(\frac{\partial}{\partial t}+\eta^{\mathcal{C}}.\nabla_x\right)\Phi_{\mathcal{C}}^-=O\left(\frac{1}{(|t|+\delta)^2}\right)\ ,$$

$$\Delta_x\left(\frac{\partial}{\partial t}+\eta^{\mathcal{C}}.\nabla_x\right)\Phi_{\mathcal{C}}^-=O\left(\frac{1}{(|t|+\delta)^3}\right)\ ,$$

Finally $\left\|\left[i\varepsilon^2\frac{\partial}{\partial t}-H(\delta,\varepsilon)\right]\Psi\left(t,x,\frac{x-a^{\mathcal{B}}(t)}{\varepsilon},\delta,\varepsilon\right)\right\|_{L^2(x)}$ is bounded by a constant times

$$\left(1+\frac{\varepsilon^2}{(|t|+\delta)^2}\right)\left[\frac{\varepsilon^4}{(|t|+\delta)^3}\|\phi_l\|_{L^2(y)}+\frac{\varepsilon^3}{|t|+\delta}\|\nabla_y\phi_l\|_{L^2(y)}+\varepsilon^3\left\|\|y\|^3\phi_l\right\|_{L^2(y)}\right]\ . \qquad (20)$$

To conclude, we apply lemma 5 with estimate (20) and note that the ε^2-term of (19) is of order $O\left(\frac{\varepsilon^2}{(|t|+\delta)^2}\right)$.

5 Near the Crossing

We now need an Ansatz around the crossing time (when the semi-classical dynamics of the nuclei reach the crossing surface Γ) where the eigenvectors are not well defined, so we make this Ansatz essentially live in the two-dimensional eigenspace $P(x,\delta)\mathcal{H}$ of the two eigenvalues.

Proposition 3 *In the inner region $|t| \leqslant t_i(\delta,\varepsilon)$, we set*

$$\psi_I(t,x,\delta,\varepsilon) = \exp\left(i\frac{S(t)+\eta(t).(x-a(t))}{\varepsilon^2}\right)\sum_{k=1,2} f_k\left(\frac{t}{\varepsilon},\frac{x-a(t)}{\varepsilon},\delta,\varepsilon\right)\psi_k(x,\delta) \quad (21)$$

with

$$\begin{pmatrix} f_1(s,y,\delta,\varepsilon) \\ f_2(s,y,\delta,\varepsilon)\end{pmatrix} = \begin{cases} \begin{pmatrix} g_1(y,\delta,\varepsilon)e^{-ir(\eta_1^0\frac{s^2}{2}+sy_1)} \\ g_2(y,\delta,\varepsilon)e^{ir(\eta_1^0\frac{s^2}{2}+sy_1)}\end{pmatrix} & \text{if } \delta/\varepsilon \to 0 \\ \begin{pmatrix} g_1(y,\delta,\varepsilon)e^{-ir\frac{\delta}{\varepsilon}s} - g_2(y,\delta,\varepsilon)e^{ir\frac{\delta}{\varepsilon}s} \\ g_1(y,\delta,\varepsilon)e^{-ir\frac{\delta}{\varepsilon}s} + g_2(y,\delta,\varepsilon)e^{ir\frac{\delta}{\varepsilon}s}\end{pmatrix} & \text{if } \delta/\varepsilon \to +\infty \end{cases}$$

where $g_k(y,\delta,\varepsilon)$ satisfy

- $g_k \in H^2(\mathbb{R}^d) \cap (1+\|y\|^2)^{-1}L^2(\mathbb{R}^d)$ *if* $\delta/\varepsilon \to 0$,
- $g_k \in H^2(\mathbb{R}^d) \cap (1+\|y\|^2)^{-3/2}L^2(\mathbb{R}^d)$ *and* $\nabla_y g_k, \Delta_y g_k \in (1+\|y\|^2)^{-1/2}L^2(\mathbb{R}^d)$ *if* $\delta/\varepsilon \to +\infty$,

and $(1-F(\gamma^2\|y\|^2)g_k(y,\delta,\varepsilon)$ with their spatial derivatives up to second order are exponentially small in γ.

If $\psi(t,\cdot,\delta,\varepsilon)$ denotes the solution of (4) with initial condition at $t=0$, $\psi_I(0,\cdot,\delta,\varepsilon)$, then the quantity

$$\sup_{t\in[-t_i,t_i]} \|\psi(t,x,\delta,\varepsilon)-\psi_I(t,x,\delta,\varepsilon)\|_{L^2(\mathbb{R}^d;\mathcal{H})}$$

is bounded by a constant times

- $t_i + \frac{t_i^3}{\varepsilon^2} + \frac{t_i\delta}{\varepsilon^2} + \frac{t_i^2}{\varepsilon}$ *if* $\delta/\varepsilon \to 0$,
- $\frac{t_i\delta^2}{\varepsilon^2} + \frac{t_i^2\delta}{\varepsilon^2} + \frac{t_i}{\delta} + \frac{t_i^2}{\delta\varepsilon} + \frac{t_i^3}{\delta\varepsilon^2} + \frac{t_i^4}{\delta\varepsilon^2} + \frac{\varepsilon}{\delta}$ *if* $\delta/\varepsilon \to +\infty$

when δ and ε tend to 0.

Remarks

1. In the expression of the Ansatz (21), the cutoff function does not appear as the vectors $\psi_k(x,\delta)$ are defined everywhere. But without extra knowledge about the growth at infinity of some spatial derivatives of those vectors, we have to introduce it in the proof or to impose some extra conditions on functions $g_k(y,\delta,\varepsilon)$ that balance this growth.

2. Note that in the proof below (equations (24) and (25)) and in section 6.1 (equations (27) and (28)), we mention corrections for the $f_k(s,y,\delta,\varepsilon)$ that lead to a more precise result.

Proof After rescaling time by ε $(s = t/\varepsilon)$, equation (4) becomes

$$i\varepsilon \frac{\partial}{\partial s}\hat{\psi} = H(\delta,\varepsilon)\hat{\psi}$$

where $\hat{\psi}(s,x,\delta,\varepsilon) = \psi(\varepsilon s,x,\delta,\varepsilon)$. Then, we substitute the Ansatz

$$\begin{aligned}\hat{\psi}_I(s,x,\delta,\varepsilon) &= F(\varepsilon^{-2}\gamma^2\|x-a(\varepsilon s)\|^2)\exp\left(i\frac{S(\varepsilon s)+\eta(\varepsilon s).(x-a(\varepsilon s))}{\varepsilon^2}\right)\\ &\quad\times\sum_{k=1,2} f_k\left(s,\frac{x-a(\varepsilon s)}{\varepsilon},\delta,\varepsilon\right)\psi_k(x,\delta)\ ,\end{aligned}$$

in this equation. The error term $\exp\left(-i\frac{S(\varepsilon s)}{\varepsilon^2} - i\frac{\eta(\varepsilon s).y}{\varepsilon}\right)\left[i\varepsilon\frac{\partial}{\partial s} - H(s,\delta,\varepsilon)\right]\hat{\psi}_I(s,x,\delta,\varepsilon)$ is, removing the contribution of the cutoff function and its derivatives (which turns out to be exponentially small),

$$\begin{aligned}&\sum_{k=1,2}\left(i\varepsilon\frac{\partial f_k}{\partial s}(s,y,\delta,\varepsilon)\psi_k(x,\delta) - f_k(s,y,\delta,\varepsilon)h_1(x,\delta)\psi_k(x,\delta)\right)\\ &-[E(\varepsilon y,\delta)-E(a(\varepsilon s),\delta)-\varepsilon y.\nabla_x E(a(\varepsilon s),\delta)]\sum_{k=1,2} f_k(s,y,\delta,\varepsilon)\psi_k(x,\delta)\\ &+\frac{\varepsilon^2}{2}\sum_{k=1,2}\Delta_y f_k(s,y,\delta,\varepsilon)\psi_k(x,\delta) + i\varepsilon^2\sum_{k=1,2} f_k(s,y,\delta,\varepsilon)\eta(\varepsilon s).\nabla_x\psi_k(x,\delta) \qquad (22)\\ &+\varepsilon^3\sum_{k=1,2}\nabla_y f_k(s,y,\delta,\varepsilon).\nabla_x\psi_k(x,\delta) + \frac{\varepsilon^4}{2}\sum_{k=1,2} f_k(s,y,\delta,\varepsilon)\Delta_x\psi_k(x,\delta)\end{aligned}$$

where $h_1(x,\delta)$ is given in (5).

To reduce the error, the first term is already to be removed by a suitable choice of the f_k, i.e., we approximately solve

$$i\varepsilon\frac{\partial}{\partial s}\begin{pmatrix} f_1\\ f_2\end{pmatrix} = \begin{pmatrix} b(a(\varepsilon s)+\varepsilon y,\delta) & (c+id)(a(\varepsilon s)+\varepsilon y,\delta)\\ (c-id)(a(\varepsilon s)+\varepsilon y,\delta) & -b(a(\varepsilon s)+\varepsilon y,\delta)\end{pmatrix}\begin{pmatrix} f_1\\ f_2\end{pmatrix}.$$

Ignoring the five remaining terms in (22) leads to an error of order

$$O\left(\varepsilon^2(1+\|y\|^2)|f_k| + \varepsilon^3|\nabla_y f_k| + \varepsilon^2|\Delta_y f_k|\right)\ .$$

From (6) and asymptotics of proposition 1, we approximate this system by

$$i\varepsilon\frac{\partial}{\partial s}\begin{pmatrix} f_1\\ f_2\end{pmatrix} = r\begin{pmatrix} \eta_1^0\varepsilon s+\varepsilon y_1 & \delta\\ \delta & -(\eta_1^0\varepsilon s+\varepsilon y_1)\end{pmatrix}\begin{pmatrix} f_1\\ f_2\end{pmatrix}. \qquad (23)$$

Doing so leads to an error term of order $O\left((\varepsilon^2 s^2 + \varepsilon^2\|y\|^2 + \delta^2)|f_k|\right)$.

We now deal with two situations :

1. $\delta/\varepsilon \to 0$ and the system is almost

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix} = r\begin{pmatrix} \eta_1^0 s + y_1 & 0 \\ 0 & -(\eta_1^0 s + y_1) \end{pmatrix}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix},$$

with solution

$$\begin{aligned} f_1(s,y,\delta,\varepsilon) &= g_1(y,\delta,\varepsilon)e^{-ir(\eta_1^0\frac{s^2}{2}+sy_1)} \\ f_2(s,y,\delta,\varepsilon) &= g_2(y,\delta,\varepsilon)e^{ir(\eta_1^0\frac{s^2}{2}+sy_1)} \end{aligned}$$

which leads to an extra error term of order $O(\delta|f_k|)$;

2. $\delta/\varepsilon \to +\infty$ and the system is almost

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix} = r\begin{pmatrix} 0 & \frac{\delta}{\varepsilon} \\ \frac{\delta}{\varepsilon} & 0 \end{pmatrix}\begin{pmatrix} f_1 \\ f_2 \end{pmatrix},$$

with solution

$$\begin{aligned} f_1(s,y,\delta,\varepsilon) &= g_1(y,\delta,\varepsilon)e^{-ir\frac{\delta}{\varepsilon}s} - g_2(y,\delta,\varepsilon)e^{ir\frac{\delta}{\varepsilon}s} \\ f_2(s,y,\delta,\varepsilon) &= g_1(y,\delta,\varepsilon)e^{-ir\frac{\delta}{\varepsilon}s} + g_2(y,\delta,\varepsilon)e^{ir\frac{\delta}{\varepsilon}s} . \end{aligned}$$

Unfortunately, if g_1 and g_2 are chosen uniformly bounded in (δ,ε) for the L^2-norm, this approximation yields an error of order $O\left(\frac{|t|}{\varepsilon} + \frac{t^2}{\varepsilon^2}\right)$ and we have shown in section 4.1 that the outer Ansatz imposes the condition $\varepsilon/(\gamma t)$ bounded with γ tending to 0. We go further in solving system (23) substituting a formal expansion in ε/δ

$$f_k(s,y,\delta,\varepsilon) = f_k^0(s,y,\delta,\varepsilon) + \frac{\varepsilon}{\delta}f_k^1(s,y,\delta,\varepsilon) + \cdots$$

for f_k. We solve successively

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_1^0 \\ f_2^0 \end{pmatrix} = r\begin{pmatrix} 0 & \frac{\delta}{\varepsilon} \\ \frac{\delta}{\varepsilon} & 0 \end{pmatrix}\begin{pmatrix} f_1^0 \\ f_2^0 \end{pmatrix}$$

and

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_1^1 \\ f_2^1 \end{pmatrix} = r\begin{pmatrix} 0 & \frac{\delta}{\varepsilon} \\ \frac{\delta}{\varepsilon} & 0 \end{pmatrix}\begin{pmatrix} f_1^1 \\ f_2^1 \end{pmatrix} + r\frac{\delta}{\varepsilon}\begin{pmatrix} \eta_1^0 s + y_1 & 0 \\ 0 & -(\eta_1^0 s + y_1) \end{pmatrix}\begin{pmatrix} f_1^0 \\ f_2^0 \end{pmatrix}.$$

Hence the solutions

$$\begin{aligned} \left[f_1^0 + f_2^0\right](s,y,\delta,\varepsilon) &= g_1(y,\delta,\varepsilon)e^{-ir\frac{\delta}{\varepsilon}s} \\ \left[-f_1^0 + f_2^0\right](s,y,\delta,\varepsilon) &= g_2(y,\delta,\varepsilon)e^{ir\frac{\delta}{\varepsilon}s} \\ \left[f_1^1 + f_2^1\right](s,y,\delta,\varepsilon) &= h_1(y,\delta,\varepsilon)e^{-ir\frac{\delta}{\varepsilon}s} - g_2(y,\delta,\varepsilon) \\ &\quad \times \left[\frac{\eta_1^0}{2}se^{ir\frac{\delta}{\varepsilon}s} - \left(\frac{\eta_1^0}{2}\frac{\varepsilon}{\delta} - iy_1\right)\sin\left(r\frac{\delta}{\varepsilon}s\right)\right] \qquad (24) \\ \left[-f_1^1 + f_2^1\right](s,y,\delta,\varepsilon) &= h_2(y,\delta,\varepsilon)e^{ir\frac{\delta}{\varepsilon}s} + g_1(y,\delta,\varepsilon) \\ &\quad \times \left[\frac{\eta_1^0}{2}se^{-ir\frac{\delta}{\varepsilon}s} - \left(\frac{\eta_1^0}{2}\frac{\varepsilon}{\delta} + iy_1\right)\sin\left(r\frac{\delta}{\varepsilon}s\right)\right] . \qquad (25) \end{aligned}$$

We choose $h_1 = h_2 = 0$ and stop to first order. We obtain an extra error term of order $O\left(\frac{\varepsilon^2}{\delta}(|s| + \|y\|)|f_k^1|\right)$.

For each case, we have

1.

$$f_k = O(g_k),$$
$$\nabla_y f_k = O(|\nabla_y g_k| + |s|.|g_k|) \ ,$$
$$\Delta_y f_k = O(|\Delta_y g_k| + |s|.|\nabla_y g_k| + s^2|g_k|) \ ;$$

2.

$$f_k^0 = O\left(|g_1| + |g_2|\right) \ ,$$
$$\nabla_y f_k^0 = O\left(|\nabla_y g_1| + |\nabla_y g_2|\right) \ ,$$
$$\Delta_y f_k^0 = O\left(|\Delta_y g_1| + |\Delta_y g_2|\right) \ ,$$
$$f_k^1 = O\left(\left(|s| + \frac{\varepsilon}{\delta} + \|y\|\right)\left(|g_1| + |g_2|\right)\right) \ ,$$
$$\nabla_y f_k^1 = O\left(\left(|s| + \frac{\varepsilon}{\delta} + \|y\|\right)\left(|\nabla_y g_1| + |\nabla_y g_2|\right) + \left(|g_1| + |g_2|\right)\right) \ ,$$
$$\Delta_y f_k^1 = O\left(\left(|s| + \frac{\varepsilon}{\delta} + \|y\|\right)\left(|\Delta_y g_1| + |\Delta_y g_2|\right) + \left(|\nabla_y g_1| + |\nabla_y g_2|\right)\right) \ .$$

Thus, with the conditions of the theorem, the error term is bounded by a constant times

$$\begin{cases} \varepsilon^2(1+s+s^2)+\delta & \text{if } \delta/\varepsilon \to 0 \\ \left(\varepsilon^2 s^2 + \delta^2\right)\left(1 + \frac{\varepsilon}{\delta}s\right) + \frac{\varepsilon^2}{\delta}(1+s+s^2) & \text{if } \delta/\varepsilon \to +\infty \end{cases}$$

To conclude in the $\delta/\varepsilon \to +\infty$ case, we just drop the terms $\frac{\varepsilon}{\delta} f_k^1(s, y, \delta, \varepsilon)$ but add an error of order $O\left(\frac{\varepsilon}{\delta} + \frac{t_i}{\delta}\right)$. $\square$

6 Matching Procedure

We now try to match the outer and inner Ansätze. We begin with the incoming outer Ansatz (17) where $\Lambda_{\mathcal{A}}^-(\delta, \varepsilon) = 0$ and $\Lambda_{\mathcal{B}}^-(\delta, \varepsilon) = 1$ and we ask how to choose $\Lambda_{\mathcal{C}}^+(\delta, \varepsilon)$ in the outgoing outer Ansatz. In each matching (incoming outer with inner Ansätze and inner with outgoing outer Ansätze), we make use of the equality between the first terms in the asymptotic expansion of each Ansatz in the overlapping region where both exist.

Rigorous statement of the procedure is

Lemma 6 *Suppose $H(\delta, \varepsilon)$ is a family of self-adjoint operators in any separable Hilbert space $\mathcal{H}$. We choose three times $t_l(\delta, \varepsilon) < t_m(\delta, \varepsilon) < t_r(\delta, \varepsilon)$ and two initial conditions $\alpha_l(\delta, \varepsilon)$ and $\alpha_r(\delta, \varepsilon)$ of order $O(1)$ in the domain of $H(\delta, \varepsilon)$ when δ and ε tend to 0. Let $\psi_*(t, \delta, \varepsilon)$ denote the solution of (4) with initial condition $\alpha_*(\delta, \varepsilon)$ at $t_*(\delta, \varepsilon)$ for $* = l$, r and we suppose that*

$$\|\psi_l(t_m(\delta, \varepsilon), \delta, \varepsilon) - \psi_r(t_m(\delta, \varepsilon), \delta, \varepsilon)\| = o(1)$$

when δ and ε tend to 0.

Then there exists a function $\beta(\delta,\varepsilon) = o(1)$ in the domain of $H(\delta,\varepsilon)$ such that, if $\tilde{\psi}(t,\delta,\varepsilon)$ denotes the solution of (4) with initial condition $\alpha_r(\delta,\varepsilon)+\beta(\delta,\varepsilon)$ in $t_r(\delta,\varepsilon)$, we have $\psi_l(t,\delta,\varepsilon) = \tilde{\psi}_r(t,\delta,\varepsilon)$ for every t in the interval $[t_l(\delta,\varepsilon), t_r(\delta,\varepsilon)]$.

Remark This lemma remains true if we substitute $O(\lambda(\delta,\varepsilon))$ for $o(1)$ where λ is any function tending to 0 when δ and ε tend to 0.

Proof Self-adjointness of $H(\delta,\varepsilon)$ gives us the existence of a unitary propagator $U(t,t',\delta,\varepsilon)$ associated to the Schrödinger equation (4) (see [18]). Thus left and right solutions are given by

$$\begin{aligned}
\psi_l(t,\delta,\varepsilon) &= U(t,t_l(\delta,\varepsilon),\delta,\varepsilon)\alpha_l(\delta,\varepsilon)\\
\psi_r(t,\delta,\varepsilon) &= U(t,t_r(\delta,\varepsilon),\delta,\varepsilon)\alpha_r(\delta,\varepsilon)\\
\tilde{\psi}_r(t,\delta,\varepsilon) &= \psi_r(t,\delta,\varepsilon)+U(t,t_r(\delta,\varepsilon),\delta,\varepsilon)\beta(\delta,\varepsilon).
\end{aligned}$$

Then $\beta(\delta,\varepsilon) = U(t_r(\delta,\varepsilon),t_m(\delta,\varepsilon),\delta,\varepsilon)[\psi_l(t_m(\delta,\varepsilon),\delta,\varepsilon) - \psi_r(t_m(\delta,\varepsilon),\delta,\varepsilon)]$ makes the lemma true. □

6.1 Narrow Avoided Crossing ($\delta/\varepsilon \to 0$): we use the $|t|/\delta \to +\infty$ regime.

First, by proposition 1, we have the following asymptotics

$$\begin{aligned}
S^{\mathcal{C}}(t) - S(t) &= \left(\eta^{0^{\mathcal{C}}}(\delta) - \eta^0(\delta)\right).\eta^0 t + O\left(|t|^3 + \frac{\delta^4}{t^2}\right)\\
&\quad -r\nu^{\mathcal{C}}\left[\operatorname{sgn}(t)\left(\eta_1^0 t^2 + \frac{\delta^2}{2\eta_1^0} + \frac{\delta^2}{\eta_1^{0^{\mathcal{C}}}(\delta)}\ln\left(\frac{2\eta_1^{0^{\mathcal{C}}}(\delta)|t|}{\delta}\right)\right) - \delta t\right],
\end{aligned}$$

$$\begin{aligned}
a^{\mathcal{C}}(t) - a(t) &= \left(\eta^{0^{\mathcal{C}}}(\delta) - \eta^0(\delta)\right) t + O\left(|t|^3 + \frac{\delta^4}{t^2}\right) - r\nu^{\mathcal{C}}\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix}\\
&\quad\times\left[\frac{\operatorname{sgn}(t)}{2}\left(t^2 + \frac{\delta^2}{2\eta_1^{0^2}} + \frac{\delta^2}{\eta_1^{0^{\mathcal{C}}}(\delta)^2}\ln\left(\frac{2\eta_1^{0^{\mathcal{C}}}(\delta)|t|}{\delta}\right)\right) - \delta t\right],
\end{aligned}$$

$$\eta^{\mathcal{C}}(t) - \eta(t) = \eta^{0^{\mathcal{C}}}(\delta) - \eta^0(\delta) - \frac{r\nu^{\mathcal{C}}}{\eta_1^0}\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix}(\eta_1^0|t| - \delta) + O\left(t^2 + \frac{\delta^2}{|t|}\right),$$

$$\begin{aligned}
\eta^{\mathcal{C}}(t).(a(t) - a^{\mathcal{C}}(t)) &= \left(\eta^0(\delta) - \eta^{0^{\mathcal{C}}}(\delta)\right).\eta^0 t + O\left(|t|^3 + \frac{\delta^4}{t^2}\right)\\
&\quad + r\nu^{\mathcal{C}}\left[\frac{\operatorname{sgn}(t)}{2}\left(\eta_1^0 t^2 + \frac{\delta^2}{2\eta_1^0} + \frac{\delta^2}{\eta_1^{0^{\mathcal{C}}}(\delta)}\ln\left(\frac{2\eta_1^{0^{\mathcal{C}}}(\delta)|t|}{\delta}\right)\right) - \delta t\right],
\end{aligned}$$

$$\begin{aligned}
&\left[S^{\mathcal{C}}(t)+\eta^{\mathcal{C}}(t).(x-a^{\mathcal{C}}(t))\right]-\left[S(t)+\eta(t).(x-a(t))\right]\\
&\quad=\left(S^{\mathcal{C}}(t)-S(t)\right)+\eta^{\mathcal{C}}(t).\left(a(t)-a^{\mathcal{C}}(t)\right)+\left(\eta^{\mathcal{C}}(t)-\eta(t)\right).\varepsilon y\\
&\quad=-\frac{r\nu^{\mathcal{C}}\mathrm{sgn}(t)}{2}\left(\eta_1^0t^2+\frac{\delta^2}{2\eta_1^0}+\frac{\delta^2}{\eta_1^{0^{\mathcal{C}}}(\delta)}\ln\left(\frac{2\eta_1^{0^{\mathcal{C}}}(\delta)|t|}{\delta}\right)\right) \qquad (26)\\
&\quad\quad+O\left(|t|^3+\frac{\delta^4}{t^2}+\left(t^2+\frac{\delta^2}{|t|}\right)\varepsilon\|y\|\right)+\left(\eta^{0^{\mathcal{C}}}(\delta)-\eta^0(\delta)\right).\varepsilon y+r\nu^{\mathcal{C}}\varepsilon y_1\left(\frac{\delta}{\eta_1^0}-|t|\right)\ ,
\end{aligned}$$

$$\begin{aligned}
A^{\mathcal{C}}(t)&=A_0+O(t)\ ,\\
B^{\mathcal{C}}(t)&=B_0+\frac{ir\nu^{\mathcal{C}}\mathrm{sgn}(t)}{\eta_1^0}PA_0+O\left(|t|+\frac{\delta^2}{t^2}\right)\\
&=B_0^{\mathcal{C}}(\mathrm{sgn}(t))+O\left(|t|+\frac{\delta^2}{t^2}\right)\ .
\end{aligned}$$

We note that $(A_0,B_0^{\mathcal{C}}(\pm1))$ satisfies conditions (8), if (A_0,B_0) does. Moreover, we have that

$$\left\|\phi_l\left(A^{\mathcal{C}}(t),B^{\mathcal{C}}(t),y+\frac{a(t)-a^{\mathcal{C}}(t)}{\varepsilon}\right)-\phi_l(A_0,B_0^{\mathcal{C}}(\mathrm{sgn}(t)),y)\right\|_{L^2}$$

is bounded by a constant times $|t|+\frac{\delta^2}{t^2}+\frac{t^2}{\varepsilon}+\frac{\delta^2}{\varepsilon}\ln\left|\frac{t}{\delta}\right|$.

Incoming Outer Asymptotics.

$$\begin{aligned}
\psi_{IO}(t,x,\delta,\varepsilon)&=F\left(\gamma^2\frac{\|x-a^{\mathcal{B}}(t)\|^2}{\varepsilon^2}\right)\varphi_l^{\mathcal{B}}\left(t,\frac{x-a^{\mathcal{B}}(t)}{\varepsilon},\varepsilon\right)\Phi_{\mathcal{B}}^-(t,x,\delta)\\
&=-e^{\frac{i}{\varepsilon^2}(S(t)+\eta(t).(x-a(t)))}e^{-ir(\eta_1^0\frac{t^2}{2\varepsilon^2}+\frac{t}{\varepsilon}y_1)}e^{i\omega_{\mathcal{B}}^-(t,a^{\mathcal{B}}(t),\delta)}\\
&\quad\times\phi_l\left(A_0,B_0^{\mathcal{B}}(-1),\frac{x-a(t)}{\varepsilon}\right)\psi_1(x,\delta)\\
&\quad\times\left[1+O\left(e_\varphi(t,\delta,\varepsilon,\gamma)+e_\phi(t,\delta,\varepsilon)+e_\Phi(t,\delta)+e_O(t,\varepsilon)+e_\omega(t,\delta,\varepsilon,\gamma)\right)\right]
\end{aligned}$$

where

$$e_\varphi(t,\delta,\varepsilon,\gamma)=\frac{|t|^3}{\varepsilon^2}+\frac{t^2}{\varepsilon\gamma}+\frac{\delta^2}{\varepsilon^2}\ln\left|\frac{t}{\delta}\right|+\frac{\delta}{\varepsilon\gamma}\ ,\ e_\phi(t,\delta,\varepsilon)=|t|+\frac{\delta^2}{t^2}+\frac{t^2}{\varepsilon}+\frac{\delta^2}{\varepsilon}\ln\left|\frac{t}{\delta}\right|\ ,$$

$$e_\Phi(t,\delta)=|t|+\frac{\delta}{|t|}\ ,\ e_O(t,\varepsilon)=\varepsilon\ln\left|\frac{1}{t}\right|+\frac{\varepsilon^2}{t^2}+\frac{\varepsilon^4}{|t|^3}\ ,\ e_\omega(t,\delta,\varepsilon,\gamma)=\frac{\delta\varepsilon}{\gamma|t|}+\frac{\varepsilon}{\gamma}\ln\left|\frac{1}{t}\right|$$

are errors due respectively to the phase $S(t)+\eta(t).(x-a(t))$ (cf (26)), the Gaussian wave packet ϕ_l (see the end of the preceding paragraph), the eigenvector $\Phi_{\mathcal{B}}^-(x,\delta)$ (cf lemma 2), the incoming outer Ansatz (cf proposition 2) and the corrected phase $\omega_{\mathcal{B}}^-(t,x,\delta)$ (cf lemma 4).

Inner Asymptotics.

$$\begin{aligned}\hat{\psi}_I(s,y,\delta,\varepsilon) &= e^{\frac{i}{\varepsilon^2}(S(\varepsilon s)+\varepsilon\eta(\varepsilon s).y)} \sum_{k=1,2} g_k(y,\delta,\varepsilon) e^{(-1)^k ir(\eta_1^0 \frac{s^2}{2}+sy_1)} \psi_k(a(\varepsilon s)+\varepsilon y,\delta) \\ &\quad \times \left[1+O\left(e_I(\varepsilon s,\delta,\varepsilon)\right)\right]\end{aligned}$$

where $e_I(t,\delta,\varepsilon) = |t| + \frac{|t|^3}{\varepsilon^2} + \frac{|t|\delta}{\varepsilon^2} + \frac{t^2}{\varepsilon}$ is the error term given by proposition 3.

Matching for $t<0$. We can match those two Ansätze with an error of order

$$O\left(e_\varphi(t,\delta,\varepsilon,\gamma) + e_\phi(t,\delta,\varepsilon) + e_\Phi(t,\delta) + e_E(t,\varepsilon) + e_\omega(t,\delta,\varepsilon,\gamma) + e_I(t,\delta,\varepsilon)\right)$$

by choosing

$$\begin{aligned} g_1(y,\delta,\varepsilon) &= -\phi_l(A_0, B_0^{\mathcal{B}}(-1), y) e^{i\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon), a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta)} \\ g_2(y,\delta,\varepsilon) &= 0\ . \end{aligned}$$

Outgoing Outer Asymptotics.

$$\begin{aligned}&\psi_{OO}(t,x,\delta,\varepsilon) = \\ &\quad e^{\frac{i}{\varepsilon^2}(S(t)+\eta(t).(x-a(t)))} \sum_{(\mathcal{C},k)=(\mathcal{A},1),(\mathcal{B},2)} \Lambda_{\mathcal{C}}^+(\delta,\varepsilon) e^{(-1)^k ir(\eta_1^0 \frac{t^2}{2\varepsilon^2}+\frac{t}{\varepsilon}y_1)} e^{i\omega_{\mathcal{C}}^+(t,a^{\mathcal{C}}(t),\delta)} \\ &\quad \times \phi_l\left(A_0, B_0^{\mathcal{C}}(+1), \frac{x-a(t)}{\varepsilon}\right)\psi_k(x,\delta) \\ &\quad \times \left[1+O\left(e_\varphi(t,\delta,\varepsilon,\gamma)+e_\phi(t,\delta,\varepsilon)+e_\Phi(t,\delta)+e_O(t,\varepsilon)+e_\omega(t,\delta,\varepsilon,\gamma)\right)\right]\ .\end{aligned}$$

Matching for $t>0$. We can match the two preceding Ansätze with an error of same order as for $t<0$ by choosing

$$\begin{aligned} \Lambda_{\mathcal{A}}^+(\delta,\varepsilon) &= e^{i[\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta) - \omega_{\mathcal{A}}^+(t_m(\delta,\varepsilon),a^{\mathcal{A}}(t_m(\delta,\varepsilon)),\delta)]} \\ \Lambda_{\mathcal{B}}^+(\delta,\varepsilon) &= 0. \end{aligned}$$

Then, the error term is of order $o(1)$ if we choose $t = t_m(\delta,\varepsilon) \in [t_o(\delta,\varepsilon), t_i(\delta,\varepsilon)]$ and $\gamma = \gamma(\delta,\varepsilon)$ tending to 0 with

$$\max\left(\delta, \frac{\varepsilon}{\gamma}\right) \ll t \ll \min\left(\varepsilon^{2/3}, \sqrt{\varepsilon\gamma}, \frac{\varepsilon^2}{\delta}\right) \text{ and } \max\left(\varepsilon^{1/3}, \frac{\delta}{\varepsilon}\right) \ll \gamma \ll 1$$

(which is a non-empty zone).

First Order Matching. By choosing $\eta^{0^{\mathcal{C}}}(\delta) = \eta^0(\delta) - \frac{r\nu^{\mathcal{C}}}{\eta_1^0}\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix}\delta$, we substitute the error term of order $\frac{\delta}{\varepsilon\gamma}$ in $e_\varphi(t,\delta,\varepsilon,\gamma)$ by $\frac{\delta^2}{\varepsilon\gamma|t|}$ (by the way, total energy conservation at 0, $\left[\frac{\|\eta^{0^{\mathcal{A}}}(\delta)\|^2}{2} - E_{\mathcal{A}}(0,\delta)\right] - \left[\frac{\|\eta^{0^{\mathcal{B}}}(\delta)\|^2}{2} - E_{\mathcal{B}}(0,\delta)\right] = O(\delta^2)$, is now fulfilled up to first order) ; we go further in solving (23) by taking

$$f_1(s,y,\delta,\varepsilon) = e^{-ir(\eta_1^0\frac{s^2}{2}+sy_1)} \times \left[g_1(y,\delta,\varepsilon) + \frac{\delta}{\varepsilon}\left(h_1(y,\delta,\varepsilon) - irg_2(y,\delta,\varepsilon)\int_{-\infty}^{s} e^{ir(\eta_1^0\sigma^2+2\sigma y_1)}d\sigma\right)\right] \quad (27)$$

$$f_2(s,y,\delta,\varepsilon) = e^{ir(\eta_1^0\frac{s^2}{2}+sy_1)} \times \left[g_2(y,\delta,\varepsilon) + \frac{\delta}{\varepsilon}\left(h_2(y,\delta,\varepsilon) + irg_1(y,\delta,\varepsilon)\int_{-\infty}^{s} e^{-ir(\eta_1^0\sigma^2+2\sigma y_1)}d\sigma\right)\right] \quad (28)$$

with $g_k, h_k \in H^2(\mathbb{R}^d) \cap (1+\|y\|^2)^{-1}L^2(\mathbb{R}^d)$, thus we substitute the error term of order $\frac{|t|\delta}{\varepsilon^2}$ in $e_I(t,\delta,\varepsilon)$ by $\frac{\delta^2}{\varepsilon}$; matching for $t<0$ can be performed by choosing

$$\begin{aligned}
g_1(y,\delta,\varepsilon) &= -\phi_l(A_0, B_0^{\mathcal{B}}(-1), y)e^{i\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta)} \\
g_2(y,\delta,\varepsilon) &= 0 \\
h_1(y,\delta,\varepsilon) &= 0 \\
h_2(y,\delta,\varepsilon) &= 0\ ;
\end{aligned}$$

matching for $t>0$ can be performed too (we use the identity $\phi_l(A_0, B_0^{\mathcal{B}}(-1), y) = \exp(-i\frac{r}{\eta_1^0}y_1^2)\phi_l(A_0, B_0^{\mathcal{B}}(+1), y))$ by choosing

$$\begin{aligned}
\Lambda_{\mathcal{A}}^+(\delta,\varepsilon) &= e^{i[\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta)-\omega_{\mathcal{A}}^+(t_m(\delta,\varepsilon),a^{\mathcal{A}}(t_m(\delta,\varepsilon)),\delta)]}\sqrt{1-|\Lambda_{\mathcal{B}}^+(\delta,\varepsilon)|^2} \\
\Lambda_{\mathcal{B}}^+(\delta,\varepsilon) &= -\frac{\delta}{\varepsilon}\sqrt{\frac{\pi r}{\eta_1^0}}e^{i\frac{\pi}{4}}e^{i[\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta)-\omega_{\mathcal{B}}^+(t_m(\delta,\varepsilon),a^{\mathcal{B}}(t_m(\delta,\varepsilon)),\delta)]}\ ;
\end{aligned}$$

thus global error is of order $o(\frac{\delta}{\varepsilon})$ if we can choose $t = t_m(\delta,\varepsilon)$ and $\gamma = \gamma(\delta,\varepsilon)$ tending to 0 with

$$\max\left(\delta, \frac{\varepsilon}{\gamma}, \frac{\varepsilon^4}{\delta}, \frac{\varepsilon^{3/2}}{\delta^{1/2}}, \frac{\varepsilon^{5/3}}{\delta^{1/3}}\right) \ll t \ll \min\left(\delta^{1/3}\varepsilon^{1/3}, \sqrt{\delta\gamma}, \frac{\delta}{\varepsilon}\right)$$

and

$$\max\left(\frac{\varepsilon^{2/3}}{\delta^{1/3}}, \frac{\varepsilon^{10/3}}{\delta^{5/3}}, \frac{\varepsilon^3}{\delta^2}, \frac{\varepsilon^8}{\delta^3}, \frac{\varepsilon^2}{\delta}, \delta\right) \ll \gamma \ll 1$$

which is a non-empty zone with the extra condition $\delta/\varepsilon^{7/5} \to +\infty$ (a natural condition would be $\delta/\varepsilon^2 \to +\infty$: the predicted first order term is of order $O\left(\frac{\delta}{\varepsilon}\right)$ and the general Born-Oppenheimer error is of order $O(\varepsilon)$; the technical condition follows from unknown second order terms of the operator $h_1(x,\delta)$ and from the choice of the phase in (21): with more regularity on $h(x,\delta)$, one can improve this technical condition but the choice of the phase seems to be the limiting factor of improvement).

6.2 Wide Avoided Crossing ($\delta/\varepsilon \to +\infty$): we use the $t/\delta \to 0$ regime.

Similar calculations lead to estimates

$$\begin{aligned}
&\left[S^{\mathcal{C}}(t) + \eta^{\mathcal{C}}(t).(x - a^{\mathcal{C}}(t))\right] - \left[S(t) + \eta(t).(x - a(t))\right] = \\
&\quad -r\nu^{\mathcal{C}}\left[\delta t + \frac{{\eta_1^0}^2 t^3}{6\delta} + \frac{\eta_1^0 t^2 \varepsilon}{2\delta} y_1\right] + O\left(\delta^2 |t| + \frac{t^4}{\delta^2} + \left(\frac{t^4}{\delta^3} + \delta |t|\right)\varepsilon \|y\|\right) \\
&\quad + \left(\eta^{0^{\mathcal{C}}}(\delta) - \eta^0(\delta)\right).\varepsilon y \ ,
\end{aligned}$$

we remove the last term which would lead to an error of order $O(\frac{\delta}{\varepsilon\gamma})$ by choosing $\eta^{0^{\mathcal{C}}}(\delta) = \eta^0(\delta)$ (an extra choice compared to the narrow avoided crossing case) ; and

$$\left\| \phi_l\left(A^{\mathcal{C}}(t), B^{\mathcal{C}}(t), y + \frac{a(t) - a^{\mathcal{C}}(t)}{\varepsilon}\right) - \phi_l(A_0, B_0, y)\right\|_{L^2}$$

is bounded by a constant times $|t| + \delta + \frac{|t|}{\delta} + \frac{\delta^2 |t|}{\varepsilon} + \frac{|t|^3}{\delta\varepsilon}$.

Incoming Outer Asymptotics.

$$\begin{aligned}
\psi_{IO}(t, x, \delta, \varepsilon) &= e^{\frac{i}{\varepsilon^2}(S(t) + \eta(t).(x - a(t)))} e^{ir\frac{\delta}{\varepsilon}\frac{t}{\varepsilon}} e^{i\omega_{\mathcal{B}}^-(t, a^{\mathcal{B}}(t), \delta)} \\
&\times \phi_l\left(A_0, B_0, \frac{x - a(t)}{\varepsilon}\right) \frac{\sqrt{2}}{2}\left[-\psi_1(x, \delta) + \psi_2(x, \delta)\right] \\
&\times \left[1 + O\left(e_\varphi(t, \delta, \varepsilon, \gamma) + e_\phi(t, \varepsilon, \gamma) + e_\Phi(t, \delta) + e_O(t, \varepsilon) + e_\omega(t, \delta, \varepsilon, \gamma)\right)\right]
\end{aligned}$$

where

$$e_\phi(t, \delta, \varepsilon) = |t| + \delta + \frac{|t|}{\delta} + \frac{\delta^2 |t|}{\varepsilon} + \frac{|t|^3}{\delta\varepsilon} \ , \ e_\omega(t, \delta, \varepsilon, \gamma) = \frac{\delta\varepsilon}{\gamma |t|} + \frac{\varepsilon}{\gamma}\ln\frac{1}{\delta} \ ,$$

$$e_\varphi(t, \delta, \varepsilon, \gamma) = \frac{\delta^2 |t|}{\varepsilon^2} + \frac{|t|^3}{\delta\varepsilon^2} + \frac{t^2}{\delta\varepsilon\gamma} + \frac{\delta |t|}{\varepsilon\gamma} \ , \ e_\Phi(t, \delta) = \delta + \frac{|t|}{\delta} \ ,$$

$$e_O(t, \varepsilon) = \varepsilon \ln\frac{1}{\delta} + \frac{\varepsilon^2}{\delta^2}$$

are error terms analogous to the narrow avoided crossing case.

Inner Asymptotics.

$$\begin{aligned}
\hat{\psi}_I(s, y, \delta, \varepsilon) &= e^{\frac{i}{\varepsilon^2}S(\varepsilon s) + \frac{i}{\varepsilon}\eta(\varepsilon s).y} \\
&\times \left[g_1(y, \delta, \varepsilon) e^{-ir\frac{\delta}{\varepsilon}s}(\psi_1 + \psi_2) + g_2(y, \delta, \varepsilon) e^{ir\frac{\delta}{\varepsilon}s}(-\psi_1 + \psi_2)\right](a(\varepsilon s) + \varepsilon y, \delta) \\
&\times \left[1 + O\left(e_I(\varepsilon s, \delta, \varepsilon)\right)\right]
\end{aligned}$$

where $e_I(t, \delta, \varepsilon) = \frac{\delta^2 |t|}{\varepsilon^2} + \frac{|t|}{\delta} + \frac{t^2}{\delta\varepsilon} + \frac{|t|^3}{\delta\varepsilon^2}$ is the error term given by proposition 3.

Matching for $t < 0$. We can match those two Ansätze with an error of order

$$O\left(e_\varphi(t,\delta,\varepsilon,\gamma) + e_\phi(t,\delta,\varepsilon) + e_\Phi(t,\delta) + e_E(t,\varepsilon) + e_\omega(t,\delta,\varepsilon,\gamma) + e_I(t,\delta,\varepsilon)\right)$$

by choosing

$$\begin{aligned} g_1(y,\delta,\varepsilon) &= 0 \\ g_2(y,\delta,\varepsilon) &= \frac{\sqrt{2}}{2}\phi_l(A_0,B_0,y)e^{i\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta)} . \end{aligned}$$

Outgoing Outer Asymptotics.

$$\begin{aligned} \psi_{OO}(t,x,\delta,\varepsilon) &= e^{\frac{i}{\varepsilon^2}(S(t)+\eta(t).(x-a(t)))}\phi_l\left(A_0,B_0,\frac{x-a(t)}{\varepsilon}\right) \\ &\times \sum_{(\mathcal{C},k)=(\mathcal{A},1),(\mathcal{B},2)} \Lambda_{\mathcal{C}}^+(\delta,\varepsilon)e^{(-1)^k ir\frac{\delta}{\varepsilon}\frac{t}{\varepsilon}}e^{i\omega_{\mathcal{C}}^+(t,a^{\mathcal{C}}(t),\delta)}\frac{\sqrt{2}}{2}\left((-1)^{k-1}\psi_1(x,\delta)+\psi_2(x,\delta)\right) \\ &\times \left[1+O\left(e_\varphi(t,\delta,\varepsilon,\gamma)+e_\phi(t,\delta,\varepsilon)+e_\Phi(t,\delta)+e_O(t,\varepsilon)+e_\omega(t,\delta,\varepsilon,\gamma)\right)\right] . \end{aligned}$$

Matching for $t > 0$. We can match the two preceding Ansätze with an error of the same order as for $t < 0$ by choosing

$$\begin{aligned} \Lambda_{\mathcal{A}}^+(\delta,\varepsilon) &= 0 \\ \Lambda_{\mathcal{B}}^+(\delta,\varepsilon) &= e^{i\left[\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),a^{\mathcal{B}}(-t_m(\delta,\varepsilon)),\delta)-\omega_{\mathcal{B}}^+(t_m(\delta,\varepsilon),a^{\mathcal{B}}(t_m(\delta,\varepsilon)),\delta)\right]} . \end{aligned}$$

Then, the error term is of order $o(1)$ if we choose $t = t_m(\delta,\varepsilon) \in [t_o(\delta,\varepsilon), t_i(\delta,\varepsilon)]$ and $\gamma = \gamma(\delta,\varepsilon)$ tending to 0 with

$$\frac{\varepsilon}{\gamma} \ll t \ll \min\left(\delta, \sqrt{\delta\varepsilon\gamma}, \frac{\varepsilon\gamma}{\delta}, \delta^{1/3}\varepsilon^{2/3}, \frac{\varepsilon}{\sqrt{\delta}}\right) \text{ and } \max\left(\frac{\varepsilon^{1/3}}{\delta^{1/3}}, \sqrt{\delta}\right) \ll \gamma \ll 1$$

(which is a non-empty zone). Note that a first order result in this regime can not be expected with this method, again because of the choice of the phase in (21).

7 Main Result

With the preceding notations, we have

Theorem 1 *Let $h(x,\delta)$ be a Hamiltonian that satisfies the hypothesis above, and let $\psi(t,x,\delta,\varepsilon)$ denote the solution of (4) with initial condition at $t = -T$*

$$\sum_{\mathcal{C}=\mathcal{A},\mathcal{B}} \Lambda_{\mathcal{C}}^-(\delta,\varepsilon)F\left(\gamma^2\frac{\|x-a^{\mathcal{C}}(-T)\|^2}{\varepsilon^2}\right)\varphi_l^{\mathcal{C}}\left(-T,\frac{x-a^{\mathcal{C}}(-T)}{\varepsilon},\varepsilon\right)\Phi_{\mathcal{C}}^-(-T,x,\delta)$$

with $|\Lambda^-_{\mathcal{A}}(\delta,\varepsilon)|^2+|\Lambda^-_{\mathcal{B}}(\delta,\varepsilon)|^2=1$, *then we have, in the limit* δ *and* ε *tending to* 0,

$$\left\|\psi(T,x,\delta,\varepsilon)-\sum_{\mathcal{C}=\mathcal{A},\mathcal{B}}\Lambda^+_{\mathcal{C}}(\delta,\varepsilon)\varphi^{\mathcal{C}}_l\left(T,\frac{x-a^{\mathcal{C}}(T)}{\varepsilon},\varepsilon\right)\Phi^+_{\mathcal{C}}(T,x,\delta)\right\|_{L^2(\mathbb{R}^d;\mathcal{H})}=o(1) \qquad (29)$$

where

$$\begin{pmatrix}\Lambda^+_{\mathcal{A}}(\delta,\varepsilon)\\ \Lambda^+_{\mathcal{B}}(\delta,\varepsilon)\end{pmatrix}=S(\delta,\varepsilon)\begin{pmatrix}\Lambda^-_{\mathcal{A}}(\delta,\varepsilon)\\ \Lambda^-_{\mathcal{B}}(\delta,\varepsilon)\end{pmatrix},$$

with,

- *if* $\delta/\varepsilon\to 0$,
$$S(\delta,\varepsilon)=\begin{pmatrix}0 & e^{i\omega_{\mathcal{AB}}(\delta,\varepsilon)}\\ e^{i\omega_{\mathcal{BA}}(\delta,\varepsilon)} & 0\end{pmatrix},$$
- *if* $\delta/\varepsilon\to+\infty$,
$$S(\delta,\varepsilon)=\begin{pmatrix}e^{i\omega_{\mathcal{A}}(\delta,\varepsilon)} & 0\\ 0 & e^{i\omega_{\mathcal{B}}(\delta,\varepsilon)}\end{pmatrix}$$

where each phase only depends on the choice of an initial phase for dynamic eigenvectors $\Phi^*_{\mathcal{C}}(t,x,\delta)$ *(the matrix* $S(\delta,\varepsilon)$ *is unitary).*

Moreover, in the case $\delta/\varepsilon\to 0$, *with the extra condition* $\delta/\varepsilon^{7/5}\to+\infty$, *(29) holds with* $o\left(\frac{\delta}{\varepsilon}\right)$ *on the right-hand side and*

$$S(\delta,\varepsilon)=\begin{pmatrix}\frac{\delta}{\varepsilon}\sqrt{\frac{\pi r}{\eta^0_1}}e^{i\omega_{\mathcal{A}}(\delta,\varepsilon)} & \sqrt{1-\frac{\pi r\delta^2}{\eta^0_1\varepsilon^2}}e^{i\omega_{\mathcal{AB}}(\delta,\varepsilon)}\\ \sqrt{1-\frac{\pi r\delta^2}{\eta^0_1\varepsilon^2}}e^{i\omega_{\mathcal{BA}}(\delta,\varepsilon)} & \frac{\delta}{\varepsilon}\sqrt{\frac{\pi r}{\eta^0_1}}e^{i\omega_{\mathcal{B}}(\delta,\varepsilon)}\end{pmatrix}.$$

8 Landau-Zener Transitions for Eigenvalue Avoided Crossings in an Adiabatic Limit

In the Born-Oppenheimer approximation, we saw that the x-variable was relevant only around the semi-classical position $a(t,\delta)$ so that the molecular Hamiltonian essentially behaved like

$$\frac{1}{2}\|\eta(t,\delta)\|^2+h(a(t,\delta),\delta)$$

and equation (4) essentially turned to equation (7) with this time-dependent Hamiltonian. This time-dependent reduced situation leads to a purely adiabatic problem (we have dropped the semi-classical approximation for the nuclei by saying that they exactly follow their classical trajectory) with an avoided crossing for the two eigenvalues

$$\frac{1}{2}\|\eta(t,\delta)\|^2+E(a(t,\delta),\delta)\pm\rho(a(t,\delta),\delta)$$

at $t=0$. Let us now treat a case of a general purely adiabatic problem for equation (7) with an avoided crossing of variable width δ.

8.1 Avoided Crossings and Normal Form for the Generic Case

Definition 2 *Suppose $H(t,\delta)$ is a family of self-adjoint operators with fixed domain $\mathcal{D}$ (in any separable Hilbert space $\mathcal{H}$) for $]t_0-2T, t_0+2T[\times]-2\delta_0, 2\delta_0[$. Assume that for every $\delta>0$, $H(t,\delta)$ has two distinct eigenvalues $E_{\mathcal{A}}(t,\delta)$ and $E_{\mathcal{B}}(t,\delta)$ uniformly isolated from the rest of the spectrum with $E_{\mathcal{A}}(t,\delta)<E_{\mathcal{B}}(t,\delta)$ and that $E_{\mathcal{A}}(t_0,0)=E_{\mathcal{B}}(t_0,0)$. In such a situation, we say that $H(t,\delta)$ has an avoided crossing at t_0.*

From now on, we suppose both eigenvalues have multiplicity one and we reproduce the reduction process presented in [8].

Let $P(t,\delta)$ be the spectral projector associated to the two eigenvalues $E_{\mathcal{A}}(t,\delta)$ and $E_{\mathcal{B}}(t,\delta)$. We set successively $H_{||}(t,\delta)=H(t,\delta)P(t,\delta)$, $E(t,\delta)=\frac{1}{2}\mathrm{Tr}H_{||}(t,\delta)$ and $H_1(t,\delta)=H(t,\delta)-E(t,\delta)I$. Let $\{\psi_1,\psi_2\}$ be an orthonormal basis for $P(t_0,0)\mathcal{H}$, for (t,δ) around $(t_0,0)$. We set

$$\psi_1(t,\delta)=\frac{P(t,\delta)\psi_1}{\langle\psi_1|P(t,\delta)\psi_1\rangle}\ ,$$

$$\psi_2(t,\delta)=\frac{P(t,\delta)\psi_2-\langle\psi_1(t,\delta)|P(t,\delta)\psi_2\rangle\psi_1(t,\delta)}{\|P(t,\delta)\psi_2-\langle\psi_1(t,\delta)|P(t,\delta)\psi_2\rangle\psi_1(t,\delta)\|}\ .$$

In such an orthonormal basis the restriction of $H_1(t,\delta)$ to $P(t,\delta)\mathcal{H}$ has the form

$$A(t-t_0)+B\delta+M(t,\delta)$$

where M is a $\mathcal{C}^3$ matrix-valued function with $M(t,\delta)$ self-adjoint and of trace zero, $M(t_0,0)=0$, $\frac{\partial M}{\partial t}(t_0,0)=0$ and $\frac{\partial M}{\partial\delta}(t_0,0)=0$.

Definition 3 *We say that $H(t,\delta)$ has a non-degenerate, multiplicity one avoided crossing at t_0 if $\{A,B\}$ is a set of independent self-adjoint matrices with trace zero.*

Then, by a (t,δ)-independent successive rotation of the basis and rotation of the second vector of the basis, we can assume that A is diagonal and that both non-diagonal coefficients of B are equal to a same strictly positive real number, thus

$$A=\begin{pmatrix} a & 0\\ 0 & -a\end{pmatrix}\ ,\ B=\begin{pmatrix} b & c\\ c & -b\end{pmatrix}$$

where a, c are strictly positive real numbers and b is real. We introduce the new variables

$$\underline{t}=t-t_0+\frac{b}{a}\delta,\ \underline{\delta}=\frac{c}{a}\delta$$

so that the restriction of $H_{||}(t,\delta)$ to $P(t,\delta)\mathcal{H}$ takes the form, in a $\mathcal{C}^3$ orthonormal basis,

$$H_{||}(t,\delta)=\begin{pmatrix} b(\underline{t},\underline{\delta}) & c(\underline{t},\underline{\delta})+id(\underline{t},\underline{\delta})\\ c(\underline{t},\underline{\delta})-id(\underline{t},\underline{\delta}) & -b(\underline{t},\underline{\delta})\end{pmatrix}+E(\underline{t},\underline{\delta})I$$

where b, c, d and E are $\mathcal{C}^3$ real-valued functions and satisfy

$$\left\{\begin{array}{rcl} b(\underline{t},\underline{\delta}) & = & r\underline{t} + O(\underline{t}^2+\underline{\delta}^2) \\ c(\underline{t},\underline{\delta}) & = & r\underline{\delta} + O(\underline{t}^2+\underline{\delta}^2) \\ d(\underline{t},\underline{\delta}) & = & O(\underline{t}^2+\underline{\delta}^2) \\ E(\underline{t},\underline{\delta}) & = & O(1) \end{array}\right.$$

with $r > 0$.

In what follows, we forget the underlined notation for those variables. Finally, we set $\rho(t,\delta) = \sqrt{b(t,\delta)^2 + c(t,\delta)^2 + d(t,\delta)^2}$ and $E_{\mathcal{C}}(t,\delta) = E(t,\delta) + \nu^{\mathcal{C}}\rho(t,\delta)$ where $\nu^{\mathcal{A}} = 1$ and $\nu^{\mathcal{B}} = -1$.

8.2 Away from the Crossing

Let

$$Z_-(\delta) = \{t \in I / b(t,\delta) < \frac{1}{2}\rho(t,\delta)\}\ ,\ Z_+(\delta) = \{t \in I / b(t,\delta) > -\frac{1}{2}\rho(t,\delta)\}\ ,$$

$$J(\delta) = \{t \in I / \rho(t,\delta) > \frac{r}{2}\sqrt{t^2+\delta^2}\}\ .$$

Mimicking section 4.1, we get that if T and δ_0 are chosen small enough, for every $\delta \in [0,\delta_0]$, $[-T,0] \subseteq (Z_-(\delta) \cap J(\delta))$ and $[0,T] \subseteq (Z_+(\delta) \cap J(\delta))$.

The definition of normalized eigenvectors is similar to section 4.2 substituting t for x. Then we have the same asymptotics as in lemmas 2 and 3 dropping the cutoff function and substituting t for x.

We still transform the eigenvectors with $\underline{\Phi}^*_{\mathcal{C}}(t,\delta) := e^{i\omega^*_{\mathcal{C}}(t,\delta)}\Phi^*_{\mathcal{C}}(t,\delta)$ for $\mathcal{C} = \mathcal{A},\mathcal{B}$ and $* = +,-$ in order to fulfill the orthogonality condition $< \underline{\Phi}^*_{\mathcal{C}}(t,\delta) | \frac{\partial}{\partial t}\underline{\Phi}^*_{\mathcal{C}}(t,\delta) >= 0$ and we choose initial conditions $\omega^-_{\mathcal{C}}(-T,\delta) = 0$ and $\omega^+_{\mathcal{C}}(T,\delta) = 0$.

By analogy with proposition 2, we can prove

Proposition 4 *In the incoming outer region $-T \leqslant t \leqslant -t_o(\delta,\varepsilon) < 0$, if*

$$\psi_{IO}(t,\delta,\varepsilon) = \sum_{\mathcal{C}=\mathcal{A},\mathcal{B}} \Lambda^-_{\mathcal{C}}(\delta,\varepsilon)\exp\Big(-\frac{i}{\varepsilon^2}\int_0^t E_{\mathcal{C}}(\tau,\delta)d\tau\Big)\underline{\Phi}^-_{\mathcal{C}}(t,\delta)$$

where $\Lambda^-_{\mathcal{C}}(\delta,\varepsilon)$ are chosen with order $O(1)$ and if $\psi(t,\delta,\varepsilon)$ denotes the solution of (7) with initial condition $\psi(-T,\delta,\varepsilon) = \psi_{IO}(-T,\delta,\varepsilon)$, then there exists a strictly positive constant C, such that

$$\sup_{t\in[-T,-t_o]} \|\psi(t,\delta,\varepsilon) - \psi_{IO}(t,\delta,\varepsilon)\| \leqslant C\frac{\varepsilon^2}{t_o^2+\delta^2}\ .$$

Remarks

1. If we fix $\delta > 0$, we recover the classical adiabatic theorem with an error of order $O(\varepsilon^2)$.

2. There is a similar result in the outgoing outer region $0 < t_o(\delta,\varepsilon) \leqslant t \leqslant T$ substituting $\psi_{OO}(t,\delta,\varepsilon)$, $\Lambda^+_{\mathcal{C}}(\delta,\varepsilon)$ and $\underline{\Phi}^+_{\mathcal{C}}(t,\delta)$ for $\psi_{IO}(t,\delta,\varepsilon)$, $\Lambda^-_{\mathcal{C}}(\delta,\varepsilon)$ and $\underline{\Phi}^-_{\mathcal{C}}(t,\delta)$ respectively.

8.3 Near the Crossing

Once again, we have an analog of proposition 3

Proposition 5 *In the inner region $|t| \leqslant t_i(\delta,\varepsilon)$, if*

$$\psi_I(t,\delta,\varepsilon) = \exp\left(-\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right)\sum_{k=1,2} f_k\left(\frac{t}{\varepsilon},\delta,\varepsilon\right)\psi_k(t,\delta) \tag{30}$$

with

$$\begin{pmatrix} f_1(s,\delta,\varepsilon) \\ f_2(s,\delta,\varepsilon)\end{pmatrix} = \begin{cases} \begin{pmatrix} C_1(\delta,\varepsilon)e^{-irs^2/2} \\ C_2(\delta,\varepsilon)e^{irs^2/2}\end{pmatrix} \ if\ \delta/\varepsilon \to 0 \\ \begin{pmatrix} C_1(\varepsilon)D_{-\frac{ir}{2}} + C_2(\varepsilon)\frac{1-i}{2}\sqrt{r}D_{\frac{ir}{2}-1} \\ -C_1(\varepsilon)\frac{1+i}{2}\sqrt{r}D_{-\frac{ir}{2}-1} + C_2(\varepsilon)D_{\frac{ir}{2}}\end{pmatrix}(-(1+i)\sqrt{r}s) \ \ if\ \delta=\varepsilon \\ \begin{pmatrix} C_1(\delta,\varepsilon)e^{-ir\delta s/\varepsilon} - C_2(\delta,\varepsilon)e^{ir\delta s/\varepsilon} \\ C_1(\delta,\varepsilon)e^{-ir\delta s/\varepsilon} + C_2(\delta,\varepsilon)e^{ir\delta s/\varepsilon}\end{pmatrix} \ if\ \delta/\varepsilon \to +\infty \end{cases}$$

where $C_k(\delta,\varepsilon)$ are chosen with order $O(1)$ and if $\psi(t,\delta,\varepsilon)$ denotes the solution of (7) with initial condition $\psi(0,\delta,\varepsilon) = \psi_I(0,\delta,\varepsilon)$, then there exists a strictly positive constant C such that

$$\sup_{t\in[-t_i,t_i]} \|\psi(t,\delta,\varepsilon) - \psi_I(t,\delta,\varepsilon)\| \leqslant \begin{cases} C\left(t_i + \frac{t_i^3}{\varepsilon^2} + \frac{t_i\delta}{\varepsilon^2}\right) \ if\ \delta/\varepsilon \to 0 \\ C\left(t_i + \frac{t_i^3}{\varepsilon^2}\right) \ if\ \delta = \varepsilon \\ C\left(\frac{t_i^2}{\varepsilon^2} + \frac{t_i\delta^2}{\varepsilon^2}\right) \ if\ \delta/\varepsilon \to +\infty\ . \end{cases}$$

The case $\delta = \varepsilon$ for $H_{||}(t,\delta)$ real symmetric is treated in [8].

8.4 Matching

8.4.1 Narrow Avoided Crossing ($\delta/\varepsilon \to 0$): we use the $|t|/\delta \to +\infty$ regime.

We have

$$\int_0^t \rho(\tau,\delta)d\tau = \mathrm{sgn}(t)r\left(\frac{t^2}{2} + \frac{\delta^2}{2}\ln\left|\frac{t}{\delta}\right|\right) + O(|t|^3+\delta^2)\ ,$$

$$\begin{aligned}\psi_{IO}(t,\delta,\varepsilon) = &-\exp\left(-\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right) \\ &\times \exp\left(-i\frac{rt^2}{2\varepsilon^2}\right)\exp(i\omega_{\mathcal{B}}^-(t,\delta))\psi_1(t,\delta)\left[1+O(e_O(t,\delta,\varepsilon))\right]\ , \\ \psi_I(t,\delta,\varepsilon) = &\exp\left(-\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right) \\ &\times\sum_{k=1,2} C_k(\delta,\varepsilon)\exp\left((-1)^k i\frac{rt^2}{2\varepsilon^2}\right)\psi_k(t,\delta)\left[1+O(e_I(t,\delta,\varepsilon))\right]\ ,\end{aligned}$$

$$\psi_{OO}(t,\delta,\varepsilon) = \exp\left(-\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right)$$
$$\times \sum_{(\mathcal{C},k)=(\mathcal{A},1),(\mathcal{B},2)} \Lambda_{\mathcal{C}}^{+}(\delta,\varepsilon)\exp\left((-1)^k i\frac{rt^2}{2\varepsilon^2}\right)\exp(i\omega_{\mathcal{C}}^{+}(t,\delta))\psi_k(t,\delta)\left[1+O(e_O(t,\delta,\varepsilon))\right]$$

with $e_O(t,\delta,\varepsilon) = \frac{\delta^2}{\varepsilon^2}\ln\left|\frac{t}{\delta}\right| + \frac{|t|^3}{\varepsilon^2} + \frac{\delta^2}{\varepsilon^2} + |t| + \left|\frac{\delta}{t}\right| + \frac{\varepsilon^2}{t^2}$ and $e_I(t,\delta,\varepsilon) = |t| + \frac{|t|^3}{\varepsilon^2} + \frac{|t|\delta}{\varepsilon^2}$.

Matchings with an error of order $O\left(e_O(t,\delta,\varepsilon) + e_I(t,\delta,\varepsilon)\right)$ can be performed by choosing successively

$$\begin{aligned} C_1(\delta,\varepsilon) &= -e^{i\omega_{\mathcal{B}}^{-}(-t_m(\delta,\varepsilon),\delta)} , \\ C_2(\delta,\varepsilon) &= 0 \end{aligned}$$

and

$$\begin{aligned} \Lambda_{\mathcal{A}}^{+}(\delta,\varepsilon) &= -e^{i[\omega_{\mathcal{B}}^{-}(-t_m(\delta,\varepsilon),\delta)-\omega_{\mathcal{A}}^{+}(t_m(\delta,\varepsilon),\delta)]} , \\ \Lambda_{\mathcal{B}}^{+}(\delta,\varepsilon) &= 0 . \end{aligned}$$

The global error is now of order $o(1)$ if $t = t_m(\delta,\varepsilon)$ tends to 0 with $\varepsilon \ll t \ll \min(\varepsilon^{2/3}, \frac{\varepsilon^2}{\delta})$.

To make a first order matching, we choose

$$\begin{aligned} f_1(s,\delta,\varepsilon) &= e^{-i\frac{rs^2}{2}}\left[C_1(\delta,\varepsilon) + \frac{\delta}{\varepsilon}\left(D_1(\delta,\varepsilon) - irC_2(\delta,\varepsilon)\int_{-\infty}^{s} e^{ir\sigma^2}d\sigma\right)\right] , \\ f_2(s,\delta,\varepsilon) &= e^{i\frac{rs^2}{2}}\left[C_2(\delta,\varepsilon) + \frac{\delta}{\varepsilon}\left(D_2(\delta,\varepsilon) + irC_1(\delta,\varepsilon)\int_{-\infty}^{s} e^{-ir\sigma^2}d\sigma\right)\right] \end{aligned}$$

with $C_k(\delta,\varepsilon)$ and $D_k(\delta,\varepsilon)$ of order $O(1)$ in (30). The error term of order $O\left(\frac{|t|\delta}{\varepsilon^2}\right)$ in $e_I(t,\delta,\varepsilon)$ now turns out to be $O\left(\frac{|t|\delta^2}{\varepsilon^3}\right)$. We obtain

$$\begin{aligned} \Lambda_{\mathcal{A}}^{+}(\delta,\varepsilon) &= -e^{i[\omega_{\mathcal{B}}^{-}(-t_m(\delta,\varepsilon),\delta)-\omega_{\mathcal{A}}^{+}(t_m(\delta,\varepsilon),\delta)]}\sqrt{1-|\Lambda_{\mathcal{B}}^{+}(\delta,\varepsilon)|^2} , \\ \Lambda_{\mathcal{B}}^{+}(\delta,\varepsilon) &= -\frac{\delta}{\varepsilon}\sqrt{\pi r}e^{i\frac{\pi}{4}}e^{i[\omega_{\mathcal{B}}^{-}(-t_m(\delta,\varepsilon),\delta)-\omega_{\mathcal{B}}^{+}(t_m(\delta,\varepsilon),\delta)]} \end{aligned}$$

with an error of order $o\left(\frac{\delta}{\varepsilon}\right)$ if $t = t_m(\delta,\varepsilon)$ tends to 0 with

$$\max\left(\frac{\varepsilon^{3/2}}{\delta^{1/2}},\varepsilon\right) \ll t \ll \min\left((\delta\varepsilon)^{1/3},\frac{\delta}{\varepsilon},\frac{\varepsilon^2}{\delta}\right)$$

which implies the extra technical condition $\delta/\varepsilon^{7/5} \to +\infty$ (the expected condition is $\delta/\varepsilon^3 \to +\infty$, the technical condition can be improved by introducing more terms in the asymptotics but the calculations are lengthy).

8.4.2 Critical Avoided Crossing ($\delta = \varepsilon$): we use the $|t|/\varepsilon \to +\infty$ regime.

The computations for $H_{||}(t,\delta)$ real symmetric are made in [8], we only add that the error is of order $O(\varepsilon^{1/4})$ if we choose $t_m(\varepsilon) = \varepsilon^{3/4}$.

8.4.3 Wide Avoided Crossing ($\delta/\varepsilon \to +\infty$): we use the $|t|/\delta \to 0$ regime.

We have

$$\int_0^t \rho(\tau,\delta)d\tau = rt\delta + O\left(\frac{t^4}{\delta^2}\right) ,$$

$$\begin{aligned}
\psi_{IO}(t,\delta,\varepsilon) &= \exp\left(\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right) \\
&\times e^{irt\delta/\varepsilon^2}\exp(i\omega_{\mathcal{B}}^-(t,\delta))\frac{\sqrt{2}}{2}[-\psi_1(t,\delta)+\psi_2(t,\delta)]\,[1+O(e_O(t,\delta,\varepsilon))] , \\
\psi_I(t,\delta,\varepsilon) &= \exp\left(\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right)[1+O(e_I(t,\delta,\varepsilon))] \\
&\times \left[C_1(\delta,\varepsilon)e^{-ir\delta t/\varepsilon^2}\left(\psi_1(t,\delta)+\psi_2(t,\delta)\right)+C_2(\delta,\varepsilon)e^{ir\delta t/\varepsilon^2}\left(-\psi_1(t,\delta)+\psi_2(t,\delta)\right)\right] , \\
\psi_{OO}(t,\delta,\varepsilon) &= \exp\left(\frac{i}{\varepsilon^2}\int_0^t E(\tau,\delta)d\tau\right)[1+O(e_O(t,\delta,\varepsilon))] \\
&\times \sum_{(\mathcal{C},k)=(\mathcal{A},1),(\mathcal{B},2)} \Lambda_{\mathcal{C}}^+(\delta,\varepsilon)e^{(-1)^k irt\delta/\varepsilon^2}\exp(i\omega_{\mathcal{C}}^+(t,\delta))\frac{\sqrt{2}}{2}\left((-1)^{k-1}\psi_1(t,\delta)+\psi_2(t,\delta)\right)
\end{aligned}$$

with $e_O(t,\delta,\varepsilon) = \frac{t^4}{\delta^2\varepsilon^2}+\delta+\left|\frac{t}{\delta}\right|+\frac{\varepsilon^2}{\delta^2}$ and $e_I(t,\delta,\varepsilon) = \frac{t^2}{\varepsilon^2}+\frac{|t|\delta^2}{\varepsilon^2}$.

Matchings with an error of order $O\left(e_O(t,\delta,\varepsilon)+e_I(t,\delta,\varepsilon)\right)$ can be performed by choosing successively

$$\begin{aligned}
C_1(\delta,\varepsilon) &= 0 , \\
C_2(\delta,\varepsilon) &= \frac{\sqrt{2}}{2}e^{i\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),\delta)}
\end{aligned}$$

and

$$\begin{aligned}
\Lambda_{\mathcal{A}}^+(\delta,\varepsilon) &= 0 , \\
\Lambda_{\mathcal{B}}^+(\delta,\varepsilon) &= e^{i[\omega_{\mathcal{B}}^-(-t_m(\delta,\varepsilon),\delta)-\omega_{\mathcal{B}}^+(t_m(\delta,\varepsilon),\delta)]} .
\end{aligned}$$

The global error is now of order $o(1)$ if $t = t_m(\delta,\varepsilon)$ tends to 0 with $t \ll \min\left(\varepsilon, \frac{\varepsilon^2}{\delta^2}\right)$.

First order matching can be performed without extra calculations if the technical condition $\delta/\varepsilon^{1/2} \to 0$ is satisfied. As expected, no extra term (of order $\frac{\varepsilon}{\delta}$) appears.

8.5 Main Result

Theorem 2 *Let $H(t,\delta)$ be a Hamiltonian that satisfies the hypothesis above, and let $\psi(t,\delta,\varepsilon)$ denote the solution of (7) with initial condition*

$$\psi(-T,\delta,\varepsilon) = \sum_{\mathcal{C}=\mathcal{A},\mathcal{B}} \Lambda_{\mathcal{C}}^-(\delta,\varepsilon)\exp\left(-\frac{i}{\varepsilon^2}\int_0^{-T} E_{\mathcal{C}}(\tau,\delta)d\tau\right)\underline{\Phi_{\mathcal{C}}^-}(-T,\delta)$$

where $|\Lambda^-_{\mathcal{A}}(\delta,\varepsilon)|^2+|\Lambda^-_{\mathcal{B}}(\delta,\varepsilon)|^2=1$*, then we have*

$$\left\|\psi(T,\delta,\varepsilon)-\sum_{\mathcal{C}=\mathcal{A},\mathcal{B}}\Lambda^+_{\mathcal{C}}(\delta,\varepsilon)\exp\left(-\frac{i}{\varepsilon^2}\int_0^T E_{\mathcal{C}}(\tau,\delta)d\tau\right)\underline{\Phi}^+_{\mathcal{C}}(T,\delta)\right\|=o(1) \tag{31}$$

where

$$\begin{pmatrix}\Lambda^+_{\mathcal{A}}(\delta,\varepsilon)\\ \Lambda^+_{\mathcal{B}}(\delta,\varepsilon)\end{pmatrix}=S(\delta,\varepsilon)\begin{pmatrix}\Lambda^-_{\mathcal{A}}(\delta,\varepsilon)\\ \Lambda^-_{\mathcal{B}}(\delta,\varepsilon)\end{pmatrix},$$

with,

- *if* $\delta/\varepsilon\to 0$,

$$S(\delta,\varepsilon)=\begin{pmatrix}0 & e^{i\omega_{\mathcal{AB}}(\delta,\varepsilon)}\\ e^{i\omega_{\mathcal{BA}}(\delta,\varepsilon)} & 0\end{pmatrix},$$

- *if* $\delta=\varepsilon$,

$$S(\delta=\varepsilon,\varepsilon)=\begin{pmatrix}e^{-\frac{\pi r}{4}}\frac{\sqrt{\pi r}}{\Gamma(1-\frac{ir}{2})}e^{i\omega_{\mathcal{A}}(\varepsilon)} & e^{-\frac{\pi r}{2}}e^{i\omega_{\mathcal{AB}}(\varepsilon)}\\ e^{-\frac{\pi r}{2}}e^{i\omega_{\mathcal{BA}}(\varepsilon)} & e^{-\frac{\pi r}{4}}\frac{\sqrt{\pi r}}{\Gamma(1+\frac{ir}{2})}e^{i\omega_{\mathcal{B}}(\varepsilon)}\end{pmatrix},$$

- *if* $\delta/\varepsilon\to+\infty$,

$$S(\delta,\varepsilon)=\begin{pmatrix}e^{i\omega_{\mathcal{A}}(\delta,\varepsilon)} & 0\\ 0 & e^{i\omega_{\mathcal{B}}(\delta,\varepsilon)}\end{pmatrix},$$

where each phase only depends on the choice of an initial phase for eigenvectors $\underline{\Phi}^*_{\mathcal{C}}(t,\delta)$ *(the matrix* $S(\delta,\varepsilon)$ *is unitary).*

Moreover,

- *if* $\delta/\varepsilon\to 0$ *and* $\delta/\varepsilon^{7/5}\to+\infty$*, (31) holds with* $o\left(\frac{\delta}{\varepsilon}\right)$ *on the right-hand side and*

$$S(\delta,\varepsilon)=\begin{pmatrix}\frac{\delta}{\varepsilon}\sqrt{\pi r}e^{i\omega_{\mathcal{A}}(\delta,\varepsilon)} & \sqrt{1-\pi r\frac{\delta^2}{\varepsilon^2}}e^{i\omega_{\mathcal{AB}}(\delta,\varepsilon)}\\ \sqrt{1-\pi r\frac{\delta^2}{\varepsilon^2}}e^{i\omega_{\mathcal{BA}}(\delta,\varepsilon)} & \frac{\delta}{\varepsilon}\sqrt{\pi r}e^{i\omega_{\mathcal{B}}(\delta,\varepsilon)}\end{pmatrix},$$

- *if* $\delta/\varepsilon\to+\infty$ *and* $\delta/\varepsilon^{1/2}\to 0$*, (31) holds with* $o\left(\frac{\varepsilon}{\delta}\right)$ *on the right-hand side with the same* $S(\delta,\varepsilon)$*.*

References

[1] J. D. Cole, Perturbation Methods in Applied Mathematics, Waltham, Mass., Toronto, London : Blaisdell 1968.

[2] Y. Colin de Verdière, The Level Crossing Problem in Semi-Classical Analysis I. The Symmetric Case, *to appear in the Proccedings of Frédéric Pham's Congress* (2002).

[3] Y. Colin de Verdière, J. Pollet, M. Lombardi, The Microlocal Landau-Zener Formula, *Ann. Inst. H. Poincaré* (1999), **71**, p 95.

[4] C. Fermanian Kammerer, Wigner Measures and Molecular Propagation through Generic Energy Level Crossings, *Prépublication de l'Université de Cergy Pontoise* (2002).

[5] G. A. Hagedorn, Semi-Classical Quantum Mechanics IV : Large Order Asymptotics and More General States in More than One Dimension, *Ann. Inst. H. Poincaré Sect. A* (1985), **42**, p 363.

[6] G. A. Hagedorn, High Order Corrections to the Time-Dependent Born-Oppenheimer Approximation I : Smooth Potentials, *Ann. Math.* (1986), **124**, p 571. Erratum (1987), **126**, p 219.

[7] G. A. Hagedorn, High Order Corrections to the Time-Dependent Born-Oppenheimer Approximation II : Diatomic Coulomb Systems, *Commun. Math. Phys.* (1988), **117**, p 387.

[8] G. A. Hagedorn, Proof of the Landau-Zener Formula in an Adiabatic Limit with Small Eigenvalue Gaps, *Commun. Math. Phys.* (1991), **136**, p 433.

[9] G. A. Hagedorn, Molecular Propagation Through Electron Energy Level Crossings, *Memoirs Amer. Math. Soc.* (1994), **111**, No. 536.

[10] G. A. Hagedorn, Raising and Lowering Operators for Semi-Classical Wave Packets, *Ann. Phys.* (1998), **269**, p 77.

[11] G. A. Hagedorn, Classification and Normal Forms for Avoided Crossings, *J. Phys. A* (1998), **31**, p 369.

[12] G. A. Hagedorn, A. Joye, Landau-Zener Transitions Through Small Electronic Eigenvalue Gaps in the Born-Oppenheimer Approximation, *Ann. Inst. H. Poincaré Sect. A* (1998), **68**, p 85.

[13] G. A. Hagedorn, A. Joye, A Time-Dependent Born-Oppenheimer Approximation with Exponentially Small Error Estimates, *Commun. Math. Phys.* (2001), **223**, p 583.

[14] G. A. Hagedorn, S. L. Robinson, Bohr-Sommerfeld Quantization Rules in the Semi-Classical Limit, *J. Phys. A* (1998), **31**, No. 50, p 10113.

[15] A. Joye, Proof of the Landau-Zener Formula, *Asympt. Anal.* (1994), **9**, p 209.

[16] T. Kato, Perturbation Theory of Linear Operators, Springer Verlag 1976.

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

[18] M. Reed, B. Simon, Methods of Modern Mathematical Physics, Vol II. Fourier Analysis, Self-adjointness. New York : Academic Press 1975.