Conical Intersections and Avoided Crossings of Electronic Energy Levels

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ABSTRACT

We study the unique phenomena which occur in certain systems characterized by the crossing or avoided crossing of two electronic eigenvalues. First, an example problem will be investigated for a given Hamiltonian resulting in a codimension 1 crossing by implementing results by Hagedorn from 1994. Then we perturb the Hamiltonian to study the system for the corresponding avoided crossing by implementing results by Hagedorn and Joye from 1998. The results from these demonstrate the behavior which occurs at a codimension 1 crossing and avoided crossing and illustrates the differences. These solutions may also be used in further studies with Herman-Kluk propagation and more.

Secondly, we study codimension 2 crossings by considering a more general type of wave packet. We focus on the case of Schrödinger equation but our methods are general enough to be adapted to other systems with the geometric conditions therein. The motivation comes from the construction of surface hopping algorithms giving an approximation of the solution of a system of Schrödinger equations coupled by a potential admitting a conical intersection, in the spirit of Herman-Kluk approximation (in close relation with frozen/thawed approximations). Our main Theorem gives explicit transition formulas for the profiles when passing

through a conical crossing point, including precise computation of the transformation of the phase and its proof is based on a normal form approach.

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GENERAL AUDIENCE ABSTRACT

We study energies of molecular systems in which special circumstances occur. In particular, when these energies intersect, or come close to intersecting. These phenomena give rise to unique physics which allows special reactions to occur and are thus of interest to study. We study one example of a more specific type of energy level crossing and avoided crossing, and then consider another type of crossing in a more general setting. We find solutions for these systems to draw our results from.

Dedication

For Nick

and my parents, George and Angie Gamble

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Contents

Chapter 1

Introduction

Let us begin by considering the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\psi \;=\; H(x)\psi.$$

Consider a molecular system consisting of K nuclei and $N-K$ electrons, $x \in \mathbb{R}^{Nl}$ where $x_i \in \mathbb{R}^l$ denotes the position of the i^{th} particle, the Hamiltonian has the form

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

where M_j, for $1 \le j \le K$ is the mass of the j^{th} nucleus, and m_j for $K+1 \le j \le N$ is the mass of the j^{th} electron. V_{ij} are the potential energies. This can be extended to more generalized systems as well, including other particles and other forms of potentials.

This equation is often difficult to solve, and it is common practice to use a standard Born-Oppenheimer approximation which separates the electronic and nuclear parts of the Hamiltonian. It implements a parameter ϵ, where ϵ^4 is the ratio of the mass of an electron to the average mass of the nuclei. (Note, sometimes $\varepsilon = \epsilon^2$ is used instead.) After scaling of the variables, we write the Schrödinger equation as

$$i\epsilon^2 \frac{\partial}{\partial t}\psi \;=\; \left[-\frac{\epsilon^4}{2}\Delta_x + h(x)\right]\psi.$$

Here, $h(x)$ is called the electronic Hamiltonian. The energies of the system are given by the eigenvalues of $H(x)$.

We wish to study the interesting phenomena which occur in certain systems which are characterized by the crossing or avoided crossing of two electronic eigenvalues. The solutions given by the standard Born-Oppenheimer approximation depend on the assumption that the electronic eigenvalues are isolated away from each other, and thus breaks down at the crossings. This allows for unique physics to occur in these systems.

In the first part of this dissertation, given in Chapter 3, we will consider an example of a certain type of crossing. The crossings are classified in part based on the dimension of the crossing in the space. In particular, we study a particular codimension 1, Type C crossing. The main results are obtained by implementing results given in [34] to construct the solutions for the crossing system, in terms of Gaussian wave packets, or Hagedorn wave packets [28, 29, 54, 35]. Recently, results on codimension 1 crossings in relatively general situations have been obtained [21], [22]. For the avoided crossing case of the same type of system, we implement the results of [39] to obtain solutions in terms of the same wave packets.

With the solutions to both of these system, we demonstrate how one uses the theorems of

[34, 39], and are able to investigate the differences between the solutions of these two cases, and the difference in the probability of an electronic energy level transition. A motivation for obtaining these results is so it may be possible that the solutions for other general systems with codimension 1 crossing or avoided crossing may be found from these or by using a perturbation or variation. It is also motivating that one could develop a Herman Kluk algorithm for both the crossing and avoided crossing [22]. This has been considered previously for the scalar case [47].

In the second part of the dissertation, given in Chapter 4, we consider any general codimension 2 crossing and analyze the propagation of a wave packet through the intersection. This question has been addressed for Gaussian wave packets in [34] and we consider here more general ones. We focus on the case of Schrödinger equation but our methods are general enough to be adapted to other systems as those of [13, 14] with the geometric conditions therein.

The motivation comes from the construction of algorithms giving an approximation of the solution of a system of Schrödinger equations coupled by a potential admitting a conical intersection, in the spirit of [55, 57, 47] and generalizing [19, 20]. Our main Theorem gives explicit transition formulas for the profile when passing through a conical crossing point, including precise computation of the transformation of the phase and its proof is based on a normal form approach.

Chapter 2

Background

2.1 Semiclassical Wave Packets

2.1.1 Hagedorn Wave Packets

Before we consider solving the approximate solutions for the system, let us introduce the structure of the semiclassical wave packets which will be used to construct our solutions. We will use these to study the approximation for the nuclear motion. First we will identify some of the notation that will be used. We let n be the dimension of the nuclear configuration space. Let the multi-index $l = (l_1,\ l_2,\ ...,\ l_n)$ be an ordered n-tuple of non-negative integers. We define the order of l as $|l| = \sum_{j=1}^{n} l_j$, and define the factorial of l as $l! = (l_1!)(l_2!)...(l_n!)$. Let D^l denote the differential operator $D^l = \dfrac{\partial^{|l|}}{(\partial x_1)^{l_1}(\partial x_2)^{l_2}...(\partial x_n)^{l_n}}$. Let x^l be the monomial

$x^l = x_1^{l_1} x_2^{l_2} ... x_n^{l_n}$. The notation $f^{(1)}$ indicates the gradient of the function f and $f^{(2)}$ is the matrix of second partial derivatives of f. Considering $\mathbb{R}$ as a subset of $\mathbb{C}$, we denote the i^{th} standard basis vector in $\mathbb{R}^n$ or $\mathbb{C}^n$ by e_i. The inner product on $\mathbb{R}^n$ or $\mathbb{C}^n$ is denoted by $\langle v,\ w \rangle = \sum_{j=1}^{n} \overline{v_j} w_j$.

The wave packets use complex Gaussian functions and Hermite polynomials. For $x \in \mathbb{C}$, these are defined by

$$\mathcal{H}_0(x) = 1$$

$$\mathcal{H}_1(x) = 2x$$

$$\mathcal{H}_2(x) = 4x^2 - 2$$

$$...$$

and in general, for integer k,

$$\mathcal{H}_k(x) = (-1)^k e^{x^2} \frac{d^k}{dx^k} e^{-x^2}.$$

In the more general setting where $x \in \mathbb{C}^n$, the Hermite polynomials are given by

$$\widetilde{\mathcal{H}}_0(x) = 1$$

$$\widetilde{\mathcal{H}}_1(x) = 2\langle v,\ x \rangle$$

where v is an arbitrary non-zero vector in $\mathbb{C}^n$. Then for any integer $k \geq 2$, the Hermite polynomials are defined recursively by

$$\widetilde{\mathcal{H}}_k(v_1,\ v_2,\ ...,\ v_k;\ x) = 2\langle v_k,\ x \rangle \widetilde{\mathcal{H}}_{k-1}(v_1,\ v_2,\ ...,\ v_{k-1};\ x)$$

$$-2\sum_{i=1}^{k-1}\langle v_k,\ \overline{v_i}\rangle\widetilde{\mathcal{H}}_{k-2}(v_1,\ ...,\ v_{i-1},\ v_{i+1},\ ...,v_{k-1};\ x)$$

These functions do not depend on the order of the vectors $v_1,\ v_2,\ ...,\ v_k$. Actually if $n=1$ and we let $v_1,\ v_2,\ ...,\ v_k=1\in\mathbb{C}^1$, then the generalized Hermite polynomials are equal to the usual ones, i.e. $\widetilde{\mathcal{H}}_k(v_1,\ v_2,\ ...,\ v_k;\ x)=\mathcal{H}_k(x)$.

For a complex $n\times n$ matrix A, we define $|A|$ by $|A|=[AA^*]^{1/2}$, where A^* is the adjoint of A. There is a unique unitary matrix U_A such that we can decompose $A=|A|U_A$. For a multi-index l, we define the polynomial

$$\mathcal{H}_l(A;\ x)=\widetilde{\mathcal{H}}_{|l|}(\underbrace{U_Ae_1,\ ...,\ U_Ae_1}_{l_1\ entries},\ \underbrace{U_Ae_2,\ ...,\ U_Ae_2}_{l_2\ entries},\ ...,\ \underbrace{U_Ae_n,\ ...,\ U_Ae_n}_{l_n\ entries};\ x)$$

Now we can define the semiclassical wave packets $\phi_l(A,B,\hbar,a,\eta,x)$. Note that in the Born-Oppenheimer approximation we replace $\hbar$ by ϵ^2.

Definition [28]: "For $n\times n$ matrices A and B satisfying

$$A \text{ and } B \text{ are invertible,} \tag{2.1}$$

$$BA^{-1} \text{ is symmetric ([real symmetric] +i[real symmetric]),} \tag{2.2}$$

$$\mathrm{Re}(BA^{-1})\ =\ \frac{1}{2}[(BA^{-1})+(BA^{-1})^*] \text{ is strictly positive definite,} \tag{2.3}$$

$$[\mathrm{Re}(BA^{-1})]^{-1}=AA^*, \tag{2.4}$$

and let $a\in\mathbb{R}^n,\ \eta\in\mathbb{R}^n$, and $\hbar>0$, then for each multi-index l, we define the wave packet

$$\phi_l(A,B,\hbar,a,\eta,x)\ =2^{-|l|/2}(l!)^{-1/2}\pi^{-n/4}\hbar^{-n/4}[\det\ A]^{1/2}$$

$$\cdot\,\mathcal{H}_l(A;\hbar^{-1/2}|A|^{-1}(x-a))$$

$$\cdot \exp\left\{-\frac{\langle (x-a),\ BA^{-1}(x-a)\rangle}{2\hbar} + i\frac{\langle \eta,\ (x-a)\rangle}{\hbar}\right\}."$$

The choice of $[\det\ A]^{1/2}$ here depends on the context of the problem and is determined by the initial conditions and continuity in time.

There are some things to note when using this definition. First, these wave packets are only used when the conditions (2.1)-(2.4) are satisfied for the matrices A and B. We can also notice that condition 4 is equivalent to

$$A^*B + B^*A \ = \ 2I$$

where I is the $n \times n$ identity matrix. Given $A,\ B,\ \hbar,\ a$, and η, the functions $\phi_l(A, B, \hbar, a, \eta, x)$ are an orthonormal basis of $L^2(\mathbb{R}^n)$.

U_A and U_B are complex unitary matrices, and A and B are Hermitian matrices. In the case where all of these are real matrices, the functions $\phi_l(A, B, \hbar, a, \eta, x)$ are just rotated and dilated eignenfunctions of the harmonic oscillator in n dimensions.

$\phi_l(A, B, \hbar, a, \eta, x)$ are very useful due to their behavior under Fourier transforms. For the scaled Fourier transform defined as

$$[\mathcal{F}_\hbar \Psi](\xi) \ = \ (2\pi\hbar)^{-n/2} \int_{\mathbb{R}^n} \Psi(x)^{-i\langle \xi,\ x\rangle/\hbar}\, dx,$$

we have

$$[\mathcal{F}_\hbar \phi_l(A, B, \hbar, a, \eta, \cdot)](\xi) \ = \ (-i)^{|l|} e^{-i\langle \eta,\ a\rangle/\hbar} \phi_l(B, A, \hbar, \eta, -a, \xi).$$

The functions $\phi_l(A, B, \hbar, a, \eta, x)$ also separate the uncertainties of position and momentum. For a given l, the uncertainty of the position only depends on $|A|$, and the uncertainty of the momentum only depends on $|B|$. In one dimension, $n = 1$, the uncertainties of $\phi_l(A, B, \hbar, a, \eta, x)$ are given by

$$\left[\left(l + \frac{1}{2}\right)\hbar\right]^{1/2} |A|$$

for the uncertainty of position, and

$$\left[\left(l + \frac{1}{2}\right)\hbar\right]^{1/2} |B|$$

for the uncertainty of momentum.

Note that B only appears in the exponent of $\phi_l(A, B, \hbar, a, \eta, x)$. A only appears in the exponent of the Fourier Transform of $\phi_l(A, B, \hbar, a, \eta, x)$. These are important for some of the properties discussed above.

Under reasonable assumptions (such as $V \in C^3$ and bounded), the Schödinger equation

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

has the approximated solution

$$\psi(x, t) = e^{iS(t)/\hbar}\phi_l(A(t), B(t), \hbar, a(t), \eta(t), x) + O(\hbar^{1/2})$$

where in this setting, $O(\hbar^{1/2})$ means the error of the approximation has a norm bounded by an l-dependent constant times $\hbar$ for $t \in [-T, T]$ for a fixed number T.

The vectors $a(t)$ and $\eta(t)$, the classical position and momentum, satisfy

$$\frac{\partial a}{\partial t}(t) = \eta(t) \tag{2.5}$$

$$\frac{\partial \eta}{\partial t} = -V^{(1)}(a(t)). \tag{2.6}$$

$S(t)$, the classical action integral associated with the classical path, satisfies

$$S(t) = \int_{-T}^{t} \left(\frac{(\eta(s))^2}{2} - V(a(s)) \right) \, ds. \tag{2.7}$$

The matrices $A(t)$ and $B(t)$ satisfy

$$\frac{\partial A}{\partial t} \;=\; iB(t), \tag{2.8}$$

$$\frac{\partial B}{\partial t} \;=\; iV^{(2)}(a(t))A(t). \tag{2.9}$$

If $A(-T)$ and $B(-T)$ satisfy the conditions (2.1)-(2.4), then so do $A(t)$ and $B(t)$ for all $t \in [-T, T]$. The solutions $A(t)$ and $B(t)$ to the differential equations above can be obtained from the derivative of the classical phase flow variable, with respect to the phase space variables,

$$\begin{aligned} A(t) &= \frac{\partial a(t)}{\partial a(-T)} A(-T) + i \frac{\partial a(t)}{\partial \eta(-T)} B(-T) \\ B(t) &= \frac{\partial \eta(t)}{\partial \eta(-T)} B(-T) - i \frac{\partial \eta(t)}{\partial a(-T)} A(-T). \end{aligned}$$

Using the wave packets $\phi_l(A, B, \hbar, a, \eta, x)$. we can study higher order semiclassical approximations. The Schrödinger equation can be solved up to errors of order $O(\hbar^{m/2})$ for any m in terms of finite linear combinations of $\phi_l(A, B, \hbar, a, \eta, x)$.

2.1.2 Raising and Lowering Operators

In this section we will discuss a more natural way of constructing the Hagedorn wave packets. Proof of the theorems and lemmas from this section can be found in [35]. Starting with just one-dimension, we will go through the construction of the wave packets, asymptotic expansions of the solutions to the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} \;=\; -\frac{\hbar^2}{2}\Delta\psi + V(x)\psi.$$

We will then continue to the general n-dimension case, as we are interested in a two-dimensional problem.

We let $a \in \mathbb{R},\ \eta \in \mathbb{R},\ \hbar > 0,\ A \in \mathbb{C}$, and $B \in \mathbb{C}$. We also assume the normalizing condition $\overline{A}B + \overline{B}A = 2$. The momentum operator, p, is given by $p \;=\; -i\hbar\frac{\partial}{\partial x}$. Then we can define the raising and lowering operators $\mathcal{A}^*$ and $\mathcal{A}$, operators from the Schwartz space $\mathcal{S}$ to itself. Note, a Schwartz space is the space of functions $f \in \mathbb{C}^\infty(\mathbb{R}^n)$ such that f and all derivatives of f decay to 0 faster than any inverse power of x as $|x| \to \infty$.

$$\mathcal{A}(A,B,\hbar,a,\eta)^* \;=\; \frac{1}{\sqrt{2\hbar}}\left[\overline{B}(x-a) - i\overline{A}(p-\eta)\right],$$

and

$$\mathcal{A}(A,B,\hbar,a,\eta) = \frac{1}{\sqrt{2\hbar}}\left[B(x-a) + iA(p-\eta)\right].$$

The normalizing condition implies the following.

$$\mathcal{A}(A,B,\hbar,a,\eta)\mathcal{A}(A,B,\hbar,a,\eta)^* - \mathcal{A}(A,B,\hbar,a,\eta)^*\mathcal{A}(A,B,\hbar,a,\eta) = I$$

By solving $\mathcal{A}(A,B,\hbar,a,\eta)\phi_0(A,B,\hbar,a,\eta,\cdot) \;=\; 0$, we see that 0 is a non-degenerate eigenvalue of $\mathcal{A}(A,B,\hbar,a,\eta)$. We will fix the phase, modulo a plus or minus sign depending on the context, and normalize the eigenvector $\phi_0(A,B,\hbar,a,\eta,\cdot)$ by

$$\phi_0(A,B,\hbar,a,\eta,x) \;=\; \pi^{-1/4}\hbar^{-1/4}A^{-1/2}\exp\left\{\frac{-BA^{-1}(x-a)^2}{2\hbar} + \frac{i\eta(x-a)}{\hbar}\right\}.$$

Recursively, we then define $\phi_k(A, B, \hbar, a, \eta, \cdot)$ by

$$\phi_{k+1}(A, B, \hbar, a, \eta, \cdot) \;=\; \frac{1}{\sqrt{k+1}}\mathcal{A}(A, B, \hbar, a, \eta)^* \phi_k(A, B, \hbar, a, \eta, \cdot).$$

From this formula, we note $\phi_k(A, B, \hbar, a, \eta, x)$ is a kth degree polynomial in $\frac{x-a}{\sqrt{\hbar}}$ times $\phi_0(A, B, \hbar, a, \eta, x)$. Then for $k = 0, 1, 2...$, we find the following.

Theorem 2.1.1. *[Theorem 2.3 of [35]] "The functions $\phi_k(A, B, \hbar, a, \eta, \cdot)$ form an orthonormal basis of $L^2(\mathbb{R})$ and satisfy the following.*

$$\mathcal{A}(A, B, \hbar, a, \eta)\phi_k(A, B, \hbar, a, \eta, \cdot) \;=\; \sqrt{k}\phi_{k-1}(A, B, \hbar, a, \eta, \cdot),$$

$$\mathcal{A}(A, B, \hbar, a, \eta)^*\phi_k(A, B, \hbar, a, \eta, \cdot) \;=\; \sqrt{k+1}\phi_{k+1}(A, B, \hbar, a, \eta, \cdot),$$

$$\mathcal{A}(A, B, \hbar, a, \eta)^*\mathcal{A}(A, B, \hbar, a, \eta)\phi_k(A, B, \hbar, a, \eta, \cdot) \;=\; k\phi_k(A, B, \hbar, a, \eta, \cdot),$$

$$\mathcal{A}(A, B, \hbar, a, \eta)\mathcal{A}(A, B, \hbar, a, \eta)^*\phi_k(A, B, \hbar, a, \eta, \cdot) \;=\; (k+1)\phi_k(A, B, \hbar, a, \eta, \cdot)."$$

This allows us to diagonalize any quantum Hamiltonian of the form

$$H \;=\; \frac{1}{2}\left(\alpha p^2 + \beta(xp + px) + \gamma x^2\right)$$

where $\omega^2 \;=\; (\alpha\gamma - \beta^2) > 0$. This allows us to write H as

$$H \;=\; \frac{\hbar\omega}{2}(\mathcal{A}^*\mathcal{A} + \mathcal{A}\mathcal{A}^*) \tag{2.10}$$

for the chosen values of $a = 0$, $\eta = 0$, $A = \sqrt{\frac{\alpha}{\omega}}e^{i\theta}$, and $B = \sqrt{\frac{\gamma}{\omega}}e^{-i\theta}$, where $\theta = \frac{1}{2}\sin^{-1}\left(\frac{\beta}{\sqrt{\alpha\gamma}}\right)$.

The eigenvalues and corresponding eigenvectors of H are $(k+\frac{1}{2})\hbar\omega$ and $\phi_k(A, B, \hbar, a, \eta, \cdot)$ for $k = 0, 1, 2....$

The wave functions can be transformed from position space to momentum space with a Fourier Transform.

$$(\mathcal{F}_\hbar \psi)(\xi) \;=\; (2\pi\hbar)^{-1/2} \int_{\mathbb{R}} \psi(x) e^{-i\xi x/\hbar}\, dx$$

This gives us the following,

$$\mathcal{F}_\hbar \mathcal{A}(A,B,\hbar,a,\eta) {\mathcal{F}_\hbar}^{-1} \;=\; i\mathcal{A}(B,A,\hbar,\eta,-a)$$

and

$${\mathcal{F}_\hbar}^{-1} \mathcal{A}(A,B,\hbar,a,\eta) \mathcal{F}_\hbar \;=\; -i\mathcal{A}(B,A,\hbar,\eta,-a)^*.$$

Then we can show that

$$(\mathcal{F}_\hbar \mathcal{A}(A,B,\hbar,a,\eta,\cdot))(\xi) \;=\; -e^{ia\eta/\hbar} \phi_0(B,A,\hbar,\eta,-a,\xi),$$

and then

$$(\mathcal{F}_\hbar \phi_k(A,B,\hbar,a,\eta,\cdot))(\xi) \;=\; (-i)^k e^{-ia\eta/\hbar} \phi_k(B,A,\hbar,\eta,-a,\xi).$$

The wave packets $\phi_k(A,B,\hbar,a,\eta,\cdot)$ are convenient for studying the propagation of a wave function generated by time-dependent Hamiltonians which is quadratic in position and momentum.

Let $\alpha(\cdot)$, $\beta(\cdot)$, $\gamma(\cdot)$, $\delta(\cdot)$, $\epsilon(\cdot)$, and $\zeta(\cdot)$ be continuous, real valued functions. We consider the classical Hamiltonian given by

$$H(x,p,t) \;=\; \frac{1}{2}\alpha(t)p^2 + \beta(t)xp + \frac{1}{2}\gamma(t)x^2 + \delta(t)p + \epsilon(t)x + \zeta(t).$$

Given the initial conditions, $(A(0),B(0),a(0),\eta(0),S(0))$, there is a unique solution

$(A(t), B(t), a(t), \eta(t), S(t))$ to the system

$$\begin{aligned}
\dot{a}(t) &= \beta(t)a(t) + \alpha(t)\eta(t) + \delta(t) \\
\dot{\eta}(t) &= -\gamma(t)a(t) - \beta(t)\eta(t) - \epsilon(t) \\
\dot{A}(t) &= \beta(t)A(t) + i\alpha(t)B(t) \\
\dot{B}(t) &= i\gamma(t)A(t) - \beta(t)B(t) \\
\dot{S}(t) &= \alpha(t)\frac{\eta(t)^2}{2} - \gamma(t)\frac{a(t)^2}{2} - \epsilon(t)a(t) - \zeta(t)
\end{aligned}$$

Assuming that $A(0)$ and $B(0)$ satisfy the normalization condition, $\overline{A}B + A\overline{B} = 2$, then so will $A(t)$ and $B(t)$. We can write $A(t)$ and $B(t)$ in terms of derivatives of the phase space flow associated with $a(t)$ and $\eta(t)$.

$$\begin{aligned}
A(t) &= \frac{\partial a(t)}{\partial a(0)}A(0) + i\frac{\partial a(t)}{\partial \eta(0)}B(0) \\
B(t) &= \frac{\partial \eta(t)}{\partial \eta(0)}B(0) - i\frac{\partial \eta(t)}{\partial a(0)}A(0)
\end{aligned}$$

These are true since each side of the equations satisfy the differential equations in the system and same initial conditions.

Theorem 2.1.2. *[Theorem 2.5 of [35]] "For every k,*

$$\psi(\hbar, t) = e^{iS(t)/\hbar}\phi_k(A(t), B(t), \hbar, a(t), \eta(t), \cdot)$$

satisfies the time-dependent Schrödinger equation

$$i\hbar\frac{\partial \psi}{\partial t} = H(t)\psi$$

for the time-dependent quantum Hamiltonian

$$H(t) = -\frac{\alpha(t)\hbar^2}{2}\frac{\partial^2}{\partial x^2} - i\frac{\beta(t)\hbar}{2}\left(x\frac{\partial}{\partial x} + \frac{\partial}{\partial x}x\right) + \frac{\gamma(t)}{2}x^2 - i\hbar\delta(t)\frac{\partial}{\partial x} + \epsilon(t)x + \zeta(t).''$$

Corollary 2.1.3. *[Corollary 2.6 of [35]] "There is a unique unitary propagator $U_\hbar(t,s)$ for the time-dependent quantum Hamiltonian satisfying*

$$U(t,s) \ : \ \mathcal{S} \to \mathcal{S}$$

and

$$U_\hbar(t,s)e^{iS(s)/\hbar}\phi_k(A(s),B(s),\hbar,a(s),\eta(s),\cdot) \ = \ e^{iS(t)/\hbar}\phi_k(A(t),B(t),\hbar,a(t),\eta(t),\cdot),$$

for all k and all solutions $(A(t),B(t),a(t),\eta(t),S(t))$ to solve the system."

Note that on $\mathcal{S}$, we can write

$$x - a \ = \ \sqrt{\frac{\hbar}{2}}\left(A\mathcal{A}(A,B,\hbar,a,\eta)^* + \overline{A}\mathcal{A}(A,B,\hbar,a,\eta)\right)$$

and

$$p - \eta \ = \ i\sqrt{\frac{\hbar}{2}}\left(B\mathcal{A}(A,B,\hbar,a,\eta)^* - \overline{B}\mathcal{A}(A,B,\hbar,a,\eta)\right).$$

Using these and equations from Theorem (2.1.1), we can calculate the following norms,

$$||(x-a)\phi_k(A,B,\hbar,a,\eta,\cdot)|| \ = \ \left(\frac{\hbar}{2}\right)^{1/2}|A|\sqrt{2k+1}$$

$$||(x-a)^2\phi_k(A,B,\hbar,a,\eta,\cdot)|| \ = \ \left(\frac{\hbar}{2}\right)|A|^2\sqrt{6k^2+6k+3}$$

$$||(x-a)^3\phi_k(A,B,\hbar,a,\eta,\cdot)|| \ = \ \left(\frac{\hbar}{2}\right)^{3/2}|A|^3\sqrt{20k^3+30k^2+40k+15}$$

For a general m,

$$||(x-a)^m\phi_k(A,B,\hbar,a,\eta,\cdot)|| \ = = \left(\frac{\hbar}{2}\right)^{m/2}|A|^m\sqrt{Q_m(k)}$$

where Q_m is an mth degree polynomial with integer coefficients. Specifically,

$$Q_m(k) \;=\; 1\cdot 3\cdot 5\cdots(2m-1)\sum_{p=0}^{\min\{m,k\}} 2^p \begin{pmatrix} m \\ p \end{pmatrix}\begin{pmatrix} k \\ p \end{pmatrix}$$

Also,

$$\begin{aligned}
||(p-\eta)\phi_k(A,B,\hbar,a,\eta,\cdot)|| &= \left(\frac{\hbar}{2}\right)^{1/2}|B|\sqrt{2k+1}\\
||(p-\eta)^2\phi_k(A,B,\hbar,a,\eta,\cdot)|| &= \left(\frac{\hbar}{2}\right)|B|^2\sqrt{6k^2+6k+3}\\
||(p-\eta)^3\phi_k(A,B,\hbar,a,\eta,\cdot)|| &= \left(\frac{\hbar}{2}\right)^{3/2}|B|^3\sqrt{20k^3+30k^2+40k+15}
\end{aligned}$$

and

$$||(p-\eta)^m\phi_k(A,B,\hbar,a,\eta,\cdot)|| \;==\; \left(\frac{\hbar}{2}\right)^{m/2}|B|^m\sqrt{Q_m(k)}.$$

We can then extend these results for quadratic Hamiltonians to more general Hamiltonians. The construction of these wave packets is indeed equivalent to the following more recognized formula, for $k=0,1,2,...$

$$\begin{aligned}
\phi_k(A,B,\hbar,a,\eta,x) \;&=\; 2^{-k/2}(k!)^{-1/2}\pi^{-1/4}\hbar^{-1/4}A^{-(k+1)/2}(\overline{A})^{k/2}\\
&\times\mathcal{H}_k\left(\hbar^{-1/2}|A|^{-1}(x-a)\right) exp\left\{\frac{-BA^{-1}(x-a)^2}{2\hbar}+\frac{i\eta(x-a)}{\hbar}\right\}
\end{aligned}$$

where $\mathcal{H}_k$ is the kth Hermite polynomial. The choice of the sign of the square roots of A and $\overline{A}$ depends on the context.

Now we will consider the multi-dimensional case. We will now let $a\in\mathbb{R}^n,\ \eta\in\mathbb{R}$, and $\hbar>0$. Let A and B be $n\times n$ complex matrices which satisfy the following

$$A^tB-B^tA=0$$

$$A^*B + B^*A = 2I.$$

This implies that A and B are invertible, also that BA^{-1} is symmetric ([real symmetric$+i$ real symmetric]). Furthermore, $(\mathrm{Re}BA^{-1})^{-1} = AA*$, and $\mathrm{Re}BA^{-1}$ must be strictly positive definite.

The momentum operator p is defined by $p = -i\hbar\nabla_x$. For any $v \in \mathbb{C}^n$, we define the raising and lowering operators by

$$\mathcal{A}(A, B, \hbar, a, \eta, v)^* = \frac{1}{\sqrt{2\hbar}} \left[\langle B\overline{v},\ (x-a)\rangle - i\langle A\overline{v},\ (p-\eta)\rangle\right]$$

$$= \frac{1}{\sqrt{2\hbar}} \left[\sum_{j,k=1}^{n} \overline{B}_{j,k} v_k (x_j - a_j) + i \sum_{j,k=1}^{n} \overline{A}_{j,k} v_k \left(-i\hbar\frac{\partial}{\partial x_j} - \eta_j\right)\right]$$

and

$$\mathcal{A}(A, B, \hbar, a, \eta, v) = \frac{1}{\sqrt{2\hbar}} \left[\langle \overline{B}v,\ (x-a)\rangle - i\langle \overline{A}v,\ (p-\eta)\rangle\right]$$

$$= \frac{1}{\sqrt{2\hbar}} \left[\sum_{j,k=1}^{n} B_{j,k} \overline{v}_k (x_j - a_j) + i \sum_{j,k=1}^{n} A_{j,k} \overline{v}_k \left(-i\hbar\frac{\partial}{\partial x_j} - \eta_j\right)\right].$$

From this we can see the following properties.

$$''\mathcal{A}(A, B, \hbar, a, \eta, v)\mathcal{A}(A, B, \hbar, a, \eta, w) - \mathcal{A}(A, B, \hbar, a, \eta, w)\mathcal{A}(A, B, \hbar, a, \eta, v) = 0$$

$$\mathcal{A}(A, B, \hbar, a, \eta, v)^*\mathcal{A}(A, B, \hbar, a, \eta, w)^* - \mathcal{A}(A, B, \hbar, a, \eta, w)^*\mathcal{A}(A, B, \hbar, a, \eta, v)^* = 0$$

$$\mathcal{A}(A, B, \hbar, a, \eta, v)\mathcal{A}(A, B, \hbar, a, \eta, w)^* - \mathcal{A}(A, B, \hbar, a, \eta, w)^*\mathcal{A}(A, B, \hbar, a, \eta, v) = \langle v,\ w\rangle''$$

We will choose to use the standard orthonormal basis, e_j, of $\mathbb{R}^n$. Define

$$''\mathcal{A}_j(A, B, \hbar, a, \eta)^* = \mathcal{A}(A, B, \hbar, a, \eta, e_j)^*$$

$$\mathcal{A}_j(A, B, \hbar, a, \eta) = \mathcal{A}(A, B, \hbar, a, \eta, e_j).''$$

Then $\mathcal{A}(A, B, \hbar, a, \eta)^*$ and $\mathcal{A}(A, B, \hbar, a, \eta)$ are the vectors whose components are the n raising and lowering operators, specifically,

$$\mathcal{A}(A, B, \hbar, a, \eta)^* = \frac{1}{\sqrt{2\hbar}}[B^*(x-a) - iA^*(p-\eta)]$$
$$\mathcal{A}(A, B, \hbar, a, \eta) = \frac{1}{\sqrt{2\hbar}}[B^t(x-a) + iA^t(p-\eta)].$$

It will be convenient for us to use a multi-index $k = (k_1, k_2, ..., k_n)$, an n-tuple of non-negative integers. The order of k will be defined as $|k| = \sum_{j=1}^{n} k_j$, and the factorial of k as $k! = (k_1!)(k_2!)...(k_n!)$. We also define $D^k = \dfrac{\partial^{|}k|}{(\partial x_1)^{k_1}(\partial x_2)^{k_2}...(\partial x_n)^{k_n}}$, and $x^k = x_1^{k_1} x_2^{k_2} ... x_n^{k_n}$.

We can solve the equation

$$\mathcal{A}(A, B, \hbar, a, \eta)\phi_0(A, B, \hbar, a, \eta, \cdot) \;=\; 0.$$

In n dimensions, this gives us that the intersection of the kernels of the lowering operators $\mathcal{A}_j$ is a one-dimensional subspace. We can fix the phase, modulo a plus or minus sign, and normalize the solution.

$$\phi_0(A, B, \hbar, a, \eta, x) \;=\;$$
$$\pi^{-n/4}\hbar^{-n/4}(\det(A))^{-1/2} \exp\left\{ -\frac{\langle (x-a),\; BA^{-1}(x-a)\rangle}{2\hbar} + i\frac{\langle \eta,\; (x-a)\rangle}{\hbar} \right\}$$

Then we can define for any multi-index k,

$$\phi_k(A, B, \hbar, a, \eta, \cdot) \;=\;$$
$$\frac{1}{\sqrt{k!}}(\mathcal{A}_1(A, B, \hbar, a, \eta)^*)^{k_1}(\mathcal{A}_2(A, B, \hbar, a, \eta)^*)^{k_2}...(\mathcal{A}_n(A, B, \hbar, a, \eta)^*)^{k_n}\phi_0(A, B, \hbar, a, \eta, \cdot)$$

From this we can see that $\phi_k(A, B, \hbar, a, \eta, x)$ is a $|k|^{th}$ degree polynomial in $\frac{x-a}{\hbar}$ times $\phi_0(A, B, \hbar, a, \eta, x)$.

Theorem 2.1.4. *[Theorem 3.3 of [35]] "The functions $\phi_k(A, B, \hbar, a, \eta, \cdot)$ form an orthonormal basis of $L^2(\mathbb{R}^n)$ and satisfy the following properties,*

$$\mathcal{A}_j(A, B, \hbar, a, \eta)\phi_k(A, B, \hbar, a, \eta, \cdot) \ = \sqrt{k_j}\phi_{k'}(A, B, \hbar, a, \eta, \cdot),$$

where $k' = (k_1,\ k_2,\ ...,\ k_{j-1},\ k_j - 1,\ k_{j+1},\ ...,\ k_n)$,

$$\mathcal{A}_j(A, B, \hbar, a, \eta)^*\phi_k(A, B, \hbar, a, \eta, \cdot) \ = \sqrt{k_j + 1}\phi_{k''}(A, B, \hbar, a, \eta, \cdot),$$

where $k'' = (k_1,\ k_2,\ ...,\ k_{j-1},\ k_j + 1,\ k_{j+1},\ ...,\ k_n)$,

$$\mathcal{A}_j(A, B, \hbar, a, \eta)^*\mathcal{A}_j(A, B, \hbar, a, \eta)\phi_k(A, B, \hbar, a, \eta, \cdot) \ = \ k_j\phi_k(A, B, \hbar, a, \eta, \cdot),$$

$$\mathcal{A}_j(A, B, \hbar, a, \eta)\mathcal{A}_j(A, B, \hbar, a, \eta)^*\phi_k(A, B, \hbar, a, \eta, \cdot) \ = \ (k_j + 1)\phi_k(A, B, \hbar, a, \eta, \cdot).$$

Using the scaled Fourier transform

$$(\mathcal{F}_\hbar\psi)(\xi) \ = \ (2\pi\hbar)^{-n/2}\int_{\mathbb{R}^n} \psi(x)e^{-i\xi x/\hbar}\ dx,$$

each $\mathcal{A}_j$ and A_j^* satisfy analogous properties to those of the one-dimensional case. Specifically, for any multi-index k,

$$(\mathcal{F}_\hbar\phi_k(A, B, \hbar, a, \eta, \cdot))(\xi) \ = \ (-i)^{|k|}e^{-i\langle a,\eta\rangle/\hbar}\phi_k(B, A, \hbar, \eta, -a, \xi)"$$

Continuing the analogous results for the time-dependent quadratic Hamiltonian, we consider the classical Hamiltonian

$$H(x, p, t) \ = \ \frac{1}{2}\begin{pmatrix} p \\ x \end{pmatrix} \cdot \begin{pmatrix} \alpha(t) & \beta(t) \\ \beta^t(t) & \gamma(t) \end{pmatrix}\begin{pmatrix} p \\ x \end{pmatrix} + \langle\delta(t),\ p\rangle + \langle\epsilon(t),\ x\rangle + \zeta(t),$$

where we suppose $\alpha(\cdot)$, $\beta(\cdot)$ and $\gamma(\cdot)$ are continuous, real, $n \times n$ matrix-valued functions. $\delta(\cdot)$ and $\epsilon(\cdot)$ are continuous $\mathbb{R}^n$-valued functions, and $\zeta(\cdot)$ is a continuous real valued function. Assume $\alpha(t)$ and $\gamma(t)$ are symmetric for any t, and $\beta^t(t)$ is the transpose of $\beta(t)$.

Given the initial conditions $(A(0), B(0), a(0), \eta(0), S(0))$, there is a unique solution $(A(t), B(t), a(t), \eta(t), S(t))$ to the system

$$\begin{aligned}
\dot{a}(t) &= \beta(t)a(t) + \alpha(t)\eta(t) + \delta(t) \\
\dot{\eta}(t) &= -\gamma(t)a(t) - \beta^t(t)\eta(t) - \epsilon(t) \\
\dot{A}(t) &= \beta(t)A(t) + i\alpha(t)B(t) \\
\dot{B}(t) &= i\gamma(t)A(t) - \beta^t(t)B(t) \\
\dot{S}(t) &= \alpha(t)\frac{\eta(t)^2}{2} - \gamma(t)\frac{a(t)^2}{2} - \epsilon(t)a(t) - \zeta(t)
\end{aligned}$$

As in the one-dimensional case, we can write A and B in terms of the derivative of the phase space flow associated with a and η. Specifically,

$$\begin{aligned}
A(t) &= \frac{\partial a(t)}{\partial a(0)}A(0) + i\frac{\partial a(t)}{\partial \eta(0)}B(0) \\
B(t) &= \frac{\partial \eta(t)}{\partial \eta(0)}B(0) - i\frac{\partial \eta(t)}{\partial a(0)}A(0)
\end{aligned}$$

Theorem 2.1.5. *[Theorem 3.4 of [35]] "For the system of equations (2.5)-(2.9), for every k,*

$$\psi(\hbar, t) = e^{iS(t)/\hbar}\phi_k(A(t), B(t), \hbar, a(t), \eta(t), \cdot)$$

satisfies the Schrödinger equation

$$i\hbar\frac{\partial \psi}{\partial t} = H(t)\psi$$

for the time-dependent quantum Hamiltonian

$$H(t) \;=\; -\frac{\hbar^2}{2}\sum_{i,j}\alpha_{i,j}(t)\frac{\partial^2}{\partial x_i\partial x_j} - \frac{i\hbar}{2}\sum_{i,j}\left(x_j\frac{\partial}{\partial x_i} + \frac{\partial}{\partial x_i}x_j\right)$$

$$+\frac{1}{2}\sum_{i,j}\gamma_{i,j}(t)x_ix_j - i\hbar\sum_i\delta_i(t)\frac{\partial}{\partial x_i} + \sum_i\epsilon_i(t)x_i + \zeta(t).$$

"

Since BA^{-1} is symmetric and $(ReBA^{-1})^{-1} = AA^*$, it follows that AA^* is a real symmetric matrix. Hence,

$$AA^* \;=\; (AA^*)^t \;=\; \overline{A}A^t.$$

Also recalling that $A^tB - B^tA = 0$ and $A^*B + B^*A = 2I$,

$$AB^* + \overline{A}B^t \;=\; 2I.$$

Similarly,

$$BB^* \;=\; (BB^*)^t \;=\; \overline{B}B^t$$

and

$$\overline{B}A^t + BA^* \;=\; 2I.$$

Therefore, as operators on $\mathcal{S}$,

$$x - a \;=\; \sqrt{\frac{\hbar}{2}}(A\mathcal{A}(A,B,\hbar,a,\eta)^* + \overline{A}\mathcal{A}(A,B,\hbar,a,\eta)),$$

and

$$p - \eta \;=\; i\sqrt{\frac{\hbar}{2}}(B\mathcal{A}(A,B,\hbar,a,\eta)^* - \overline{B}\mathcal{A}(A,B,\hbar,a,\eta)).$$

We get the result analogous to the one-dimensional case, for any multi-index k,

$$||(x_j - a_j)\phi_k(A, B, \hbar, a, \eta, \cdot)|| = \left(\frac{\hbar}{2}\right)^{1/2} \left(\sum_{l=1}^{n} |A_{j,l}|^2 * 2k_l + 1)\right)^{1/2},$$

and for any multi-indices m and k,

$$||(x - a)^m \phi_k(A, B, \hbar, a, \eta, \cdot)|| = O(\hbar^{|m|/2}).$$

2.1.3 Pseudo-Differential Operators

We introduce semi-classical pseudo-differential operators for use as tools in the analysis of solutions to Schrödiner operators We consider matrix-valued functions $a \in \mathcal{C}^\infty(\mathbb{R}^{2d}, \mathcal{C}^{2,2})$ which are bounded together with their derivatives. Then, one defines the Weyl semi-classical pseudo-differential operator of symbol a as

$$\mathrm{op}_\varepsilon\ (a)f(x) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \mathrm{e}^{\frac{i}{\varepsilon}\xi\cdot(x-y)} a\left(\frac{x+y}{2}, \xi\right) f(y)dy\, d\xi, \quad \forall f \in \mathcal{S}(\mathbb{R}^d, \mathcal{C}^2). \tag{2.11}$$

The reader may find proofs of the results presented here in [9, 62, 24], for instance. We note that $\mathrm{op}_\varepsilon\ (a)$ maps $\mathcal{S}(\mathbb{R})$ onto itself.

The Calderón-Vaillancourt theorem [3] ensures the existence of a constant $C_d > 0$ such that for every $a \in \mathcal{C}^\infty(\mathbb{R}^d, \mathcal{C}^{2,2})$ one has

$$\|\ \mathrm{op}_\varepsilon\ (a)\|_{\mathcal{L}(L^2(\mathbb{R}^d, \mathcal{C}^2))} \le C_d\, N_d^\varepsilon(a), \tag{2.12}$$

where

$$N_d^\varepsilon(a) := \sum_{\alpha \in \mathbb{N}^{2d}, |\alpha| \le d+2} \varepsilon^{|\alpha|} \sup_{\mathbb{R}^d \times \mathbb{R}^d} |\partial_{x,\xi}^\alpha a|.$$

The calculus extends to functions a that are polynomial functions in ξ with coefficients depending smoothly on x. We assume that there exists $N \in \mathbb{N}$, such that

$$\forall \alpha \in \mathbb{N}^{2d}, \;\; \exists C_\alpha, \;\; |\partial_z^\alpha a(z)| \leq C_\alpha \langle z \rangle^{N-|\alpha|}. \tag{2.13}$$

Then, the operator $\mathrm{op}_\varepsilon(a)$ maps Σ_ε^{N+k} into Σ_ε^{N}.

Matrix-valued pseudodifferential operators enjoy a symbolic calculus:

Proposition 2.1.6. *Let $a, b \in \mathcal{C}_0^\infty(\mathbb{R}^d)$, then*

$$\mathrm{op}_\varepsilon\,(a)\;\mathrm{op}_\varepsilon\,(b) = \mathrm{op}_\varepsilon\,(ab) + \frac{\varepsilon}{2i}\;\mathrm{op}_\varepsilon\,(\{a,b\}) + \varepsilon^2 R_\varepsilon^{(1)},$$

with $\{a,b\} = \sum_{j=1}^d \partial_{\xi_j} a\, \partial_{x_j} b - \partial_{x_j} a\, \partial_{\xi_j} b$ and

$$[\mathrm{op}_\varepsilon\,(a), \mathrm{op}_\varepsilon\,(b)] = \mathrm{op}_\varepsilon\,([a,b]) + \frac{\varepsilon}{2i}(\mathrm{op}_\varepsilon\,(\{a,b\}) - \mathrm{op}_\varepsilon\,(\{b,a\})) + \varepsilon^2 R_\varepsilon^{(2)},$$

$$\|R_\varepsilon^{(j)}\|_{\mathcal{L}(L^2(\mathbb{R}^d,\mathcal{C}^2))} \leq C \sup_{|\alpha|+|\beta|=2} N_d^\varepsilon(\partial_\xi^\alpha \partial_x^\beta a) N_d^\varepsilon(\partial_\xi^\beta \partial_x^\alpha b), \quad j \in \{1,2\},$$

for some constant $C > 0$ independent of a, b and ε.

Similar results hold for symbols satisfying (A.4) in the adequate functional spaces.

Remark: The term of order ε^2 above has symmetries so that if $[a,b] = 0$,

$$[\mathrm{op}_\varepsilon\,(a), \mathrm{op}_\varepsilon\,(b)] = \frac{\varepsilon}{i}\;\mathrm{op}_\varepsilon\,(\{a,b\}) + O(\varepsilon^3).$$

Besides it has a particularly simple expression when the function b does not depend on x. The following hold in $\mathcal{L}(L^2(\mathbb{R}^d, \mathcal{C}^2))$:

$$\mathrm{op}_\varepsilon\,(b)\;\mathrm{op}_\varepsilon\,(a) = \mathrm{op}_\varepsilon\,(ba) + \frac{\varepsilon}{2i}\sum_{j=1}^d \mathrm{op}_\varepsilon\,(\partial_{\xi_j} b\, \partial_{x_j} a) + \frac{\varepsilon^2}{8}\sum_{1\leq \ell,p\leq d} \mathrm{op}_\varepsilon\,(\partial^2_{\xi_\ell \xi_p} b\, \partial^2_{x_\ell x_p} a) + O(\varepsilon^3),$$

$$\mathrm{op}_\varepsilon\,(a)\;\mathrm{op}_\varepsilon\,(b) = \mathrm{op}_\varepsilon\,(ab) - \frac{\varepsilon}{2i}\sum_{j=1}^d \mathrm{op}_\varepsilon\,(\partial_{x_j} a\, \partial_{\xi_j} b) + \frac{\varepsilon^2}{8}\sum_{1\leq \ell,p\leq d} \mathrm{op}_\varepsilon\,(\partial^2_{x_\ell x_p} a\, \partial^2_{\xi_\ell \xi_p} b) + O(\varepsilon^3).$$

2.2 Electron Energy Level Crossings

2.2.1 Introduction to Energy Level Crossings

When assuming that the electron energy levels are discrete, the standard Born-Oppenheimer approach is typically used to approximate a solution to the time dependent Schrödinger equation. Now we minimally break that assumption by instead assuming that there are two energy levels which intersect. We let $E_A(X)$ and $E_B(X)$ be two discrete electronic levels isolated away from the rest of the electronic spectrum of $h(X)$ for all X in some region of interest. Let $E_A(X) \neq E_B(X)$ except for $X \in \Gamma$ where Γ is some proper manifold of the space of nuclear configurations. To simplify some, we will assume $E_A(X)$ and $E_B(X)$ have the minimal degeneracy allowed by the symmetric group of the electronic Hamilitonian, and also that the electronic Hamiltonian satisfies a generality condition near the crossing manifold Γ.

The codimension of the crossing manifold Γ will serve to classify these types of level crossings. The codimension of the crossing is the number of nuclear configuration parameters which must be adjusted in order to arrive at the crossing submanifold. Typically Γ has codimension 1, 2, 3, or 5, and there are 11 distinct types of crossing for these generic, minimal multiplicity level crossings. (Seven of the types of crossings have codimension 1.)

Suppose we have a molecular system consisting of K nuclei and $N - K$ electrons. The

Hamiltonian is given by

$$H(\epsilon) = \sum_{j=1}^{K} -\frac{\epsilon^4}{2M_j}\Delta_{X_j} - \sum_{j=K+1}^{N} \frac{1}{2m_j}\Delta_{X_j} + \sum_{i<j} V_{ij}(X_i - X_j) \tag{2.14}$$

where $X_j \in \mathbb{R}^l$ is the position of the jth particle, M_j is the mass of the jth nucleus (particle $1 \leq j \leq K$), m_j is the mass of an electron (mass of particle $K+1 \leq j \leq N$), and V_{ij} is the potential between particles i and j.

If we let $M_j = 1$ for $1 \leq j \leq K$, set $n = lK$, and define the nuclear configuration vector $X + (X_1,\ X_2,\ ...,\ X_K)$, we can express the Hamiltonian as

$$H(\epsilon) = -\frac{\epsilon^4}{2}\Delta_X + h(X) \tag{2.15}$$

where $h(X)$ is the electronic Hamiltonian which depends parametrically on X.

The eigenvalues of $h(X)$, $E(X)$, are the discrete electron energy levels. We will assume that $h(X)$ satisfies that $(h(X) - i)^{-1}$ is a C^k operator of X for various values of $k \geq 2$. This guarantees that the electron energy levels are C^k away from the crossing or absorbed into the continuous spectrum. (Note that not all electron Hamiltonians with Coulomb potentials satisfy these assumptions. However, they can be accommodated by using regularization techniques.)

We want to study the time-dependent Schrödinger equation, given by

$$i\epsilon^2 \frac{\partial \psi}{\partial t} = H(\epsilon)\psi \tag{2.16}$$

for t in a fixed interval.Here ϵ^2 indicates the choice of time scaling we have made which gives the solutions of interest. Using this choice of scaling, all terms have significance at leading order. We also note that the limit of the nuclear motion is non-trivial and the average initial nuclear energy is constant as ϵ goes to 0.

2.2.2 Classifying Eigenvalue Crossings

As given in [34], we classify the normal forms for the types of generic crossings of eigenvalues of minimal degeneracy for quantum mechanical systems. In each situation, we will assume the dimension n is sufficiently large so that the crossings do occur. As stated before, we will assume that $h(X)$ is C^k for some $k \geq 2$ in the sense that the resolvent $(z - h(X))^{-1}$ is C^k in X for $x \notin \mathbb{R}$. As in [36] let G be the symmetry group for $h(X)$. Then "G is the group of all unitary and antiunitary operators which are independent of X in some representation of the electronic Hilbert space and which commute with $h(X)$ for all X in some open set of interest. Let H be the subgroup of unitary operators in G. The elements of G which are not in H are sometimes called time reversing symmetry operators.

The product of two antiunitary operators is unitary, so either $G = H$ or H is a subgroup of G of index 2." If $G = H$, each distinct eigenvalue of $h(X)$ is associated with a unique representation of G in standard group representation theory. These are 1-dimensional representations due to the assumed minimal multiplicity of eigenvalues. If two simple eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ cross, then there are two cases, which we will call Type A and Type B. The definitions of all of the following crossing types are defined as below in [34].

"Type A Crossings: The two irreducible representations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are not unitarily equivalent to each other.

Type B Crossings: The two irreducible representations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are unitarily equivalent to each other."

If H is a subgroup of index 2, rather than using standard group representations, we must look at corepresentations. Corepresentations can be decomposed as a direct some of irreducible corepresentations, and there are three distinct types of irreducible corepresentations: Types I, II, and III.

Note that $G = H \cup \mathcal{K}H$ where $\mathcal{K}$ is an arbitrary, fixed, antiunitary operator in G. If U is an irreducible corepresentation of G, let U_H be the restriction of U to H. Then we can describe the three types of irreducible corepresentations in this situation by the following:

"Type I Corepresentations: U_H is an irreducible representation

Type II Corepresentations: U_H decomposes into a direct sum of two equivalent irreducible representations, $U_H = D \oplus D$. $U(h) = \begin{pmatrix} D(h) & 0 \\ 0 & D(h) \end{pmatrix}$, $U(\mathcal{K}) = \begin{pmatrix} 0 & -K \\ K & 0 \end{pmatrix}$, and $U(\mathcal{K}h) = U(\mathcal{K})U(h)$, for all $h \in H$ and K is an antiunitary operator satisfying $K^2 = -D(\mathcal{K}^2)$ and $KD(\mathcal{K}^{-1}h\mathcal{K})K^{-1} = D(h)$ for all $h \in H$.

Type III Corepresentations: U_H decomposes into a sum of two inequivalent irreducible representations, $U_H = D \oplus C$. $U(h) = \begin{pmatrix} D(h) & 0 \\ 0 & C(h) \end{pmatrix}$, $U(a) = \begin{pmatrix} 0 & D(\mathcal{K}^2)K^{-1} \\ K & 0 \end{pmatrix}$, and $U(\mathcal{K}h) = U(\mathcal{K})U(h)$ for all $h \in H$ and $K : \mathcal{H}_D \to \mathcal{H}_C$ is an antiunitary operator satisfying $KD(\mathcal{K}^{-1}h\mathcal{K})D^{-1} = C(h)$ for all $h \in H$."

Then when $G \neq H$, if the eigenvalues are of minimal multiplicity and associated Type I corepresentations, then they have multiplicity 1. Minimal multiplicity eigenvalues associated with Type II or III corepresentations have multiplicity 2. In Type II corepresentations, the antiunitary operator K map a one dimensional space to itself and $K^2 = 1$. Then K is a conjugation and $D(\mathcal{K}^2) = -1$.

From this, we get that there are nine different types of eigenvalue crossings when $G \neq H$.

"Type C Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both Type I, but are not unitarily equivalent to each other. Hence both eigenvalues have multiplicity 1 away from the crossing.

Type D Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both Type II, but are not unitarily equivalent to each other. Hence both eigenvalues have multiplicity 2 away from the crossing.

Type E Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both Type III, but are not unitarily equivalent to each other. Hence both eigenvalues have multiplicity 2 away from the crossing.

Type F Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are Type I and Type II. Hence the eigenvalue associated with the Type I corepresentation has multiplicity 1 away from the crossing, and the eigenvalue associated with the Type II corepresentation has multiplicity 2.

Type G Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are Type I and Type III. Hence the eigenvalue associated with the Type I corepresentation has multiplicity 1 away from the crossing, and the eigenvalue associated with the Type II corepresentation has multiplicity 2.

Type H Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are Type II and Type III. Hence both eigenvalues have multiplicity 2 away from the crossing.

Type I Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both Type I, and are unitarily equivalent to each other. Hence both eigenvalues have multiplicity 1 away from the crossing.

Type J Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both Type II, and are unitarily equivalent to each other. Hence both eigenvalues have multiplicity 2 away from the crossing.

Type K Crossings: The two irreducible corepresentations of G that correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are both Type III, and are unitarily equivalent to each other. Hence both eigenvalues have multiplicity 2 away from the crossing."

Crossings of types A, C, D, E, F, G, and H all generally occur on submanifolds with codimension 1. Type I crossings generally occur on submanifolds with codimension 2. Types B and K generally occur on codimension 3 submanifolds, and Type J on codimension 5 submanifolds.

2.2.3 Structure of Crossings

We will investigate the structure of the types of crossing which are of interest to us for our topics. Thus we will focus on Type C crossings and Type I crossings.

Type A and C Crossings

Types A and C begin with the same structure. Supposing we have a system with two eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ of a C^k electron Hamiltonian $h(X)$. We suppose these two eigenvalues cross at $X = 0$ with a crossing of either Type A or C, meaning the crossing is of codimension 1 and the eigenvalues both have multiplicity 1 away from the crossing. We label the irreducible representation (for Type A) or corepresentation (for Type C) of G for all X corresponding to $E_{\mathcal{A}}(X)$ as U_1 and the one corresponding to $E_{\mathcal{B}}(X)$ as U_2. Let P_1 and P_2 be the orthogonal projection onto the mutually orthogonal carrier subspaces associated with U_1 and U_2 respectively. Since $h(X)$ commutes with the action of G, it also commutes with P_1 and P_2.

For X in a neighborhood of the origin, we write the spectral projection, $P(X)$, for $h(X)$ as

$$P(X) \;=\; \frac{1}{2\pi i}\int_C (z - h(X))^{-1}\, dz$$

where C is a contour that encloses both eigenvalues, $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ but no other parts of the spectrum of $h(X)$. Then $P(X)$ is a C^k, rank 2 operator valued function of X near $X = 0$. It also commutes with P_1 and P_2.

Then we have the projections $P_{\mathcal{A}}(X) = P_1 P(X)$ and $P_{\mathcal{B}}(X)$. Due to U_1 and U_2 being inequivalent, these are C^k, rank 1 orthogonal projections which project onto mutually orthogonal subspaces.

For a Type A crossing, we choose $\Phi_{\mathcal{A}}(0)$ and $\Phi_{\mathcal{B}}(0)$ to be arbitrary unit vectors in the ranges of $P_{\mathcal{A}}(0)$ and $P_{\mathcal{B}}(0)$ respectively. Then we define

$$\Phi_{\mathcal{A}}(X) = \frac{P_{\mathcal{A}}(X)\Phi_{\mathcal{A}}(0)}{\sqrt{\langle \Phi_{\mathcal{A}}(0),\ P_{\mathcal{A}}(X)\Phi_{\mathcal{A}}(0)\rangle}}$$

and

$$\Phi_{\mathcal{B}}(X) = \frac{P_{\mathcal{B}}(X)\Phi_{\mathcal{B}}(0)}{\sqrt{\langle \Phi_{\mathcal{B}}(0),\ P_{\mathcal{B}}(X)\Phi_{\mathcal{B}}(0)\rangle}}.$$

These are C^k unit-vector valued functions near the origin. The vectors $\Phi_{\mathcal{A}}(X)$ and $\Phi_{\mathcal{B}}(X)$ are in the ranges of $P_{\mathcal{A}}(X)$ and $P_{\mathcal{B}}(X)$ respectively, for each X. It follows that $\Phi_{\mathcal{A}}(X)$ and $\Phi_{\mathcal{B}}(X)$ are eigenvectors of $h(X)$ which correspond to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$, respectively.

For a Type C crossing, the construction is the same, but with an imposed constraint. Since we can decompose $G = \mathcal{K}H$, where $\mathcal{K}$ is a specially chosen antiunitary element of G. We can choose the phases of $\Phi_{\mathcal{A}}(0)$ and $\Phi_{\mathcal{B}}(0)$ so that $\mathcal{K}\Phi_{\mathcal{A}}(0) = \Phi_{\mathcal{A}}(0)$ and $\mathcal{K}\Phi_{\mathcal{B}}(0) = \Phi_{\mathcal{B}}(0)$. By making these choices, we obtain vectors $\Phi_{\mathcal{A}}(X)$ and $\Phi_{\mathcal{B}}(X)$ which satisfy $\mathcal{K}\Phi_{\mathcal{A}}(X) = \Phi_{\mathcal{A}}(X)$ and $\mathcal{K}\Phi_{\mathcal{B}}(X) = \Phi_{\mathcal{B}}(X)$. This actually trivializes the adiabatic connections on the vector bundles of eigenvectors for the two eigenvalues.

Let $h^{\perp}(X)$ be the restriction of $h(X)$ to the subspace orthonormal to the range of $P(X)$, of which we use the basis $\Phi_{\mathcal{A}}(X)$ and $\Phi_{\mathcal{B}}(X)$. Then $\mathcal{H} \cong \mathbb{C} \oplus \mathbb{C} \oplus \mathrm{Ran}(1 - P(X))$, and we can locally represent $h(X)$ by the following matrix.

$$\tilde{h}(X) \ = \begin{pmatrix} E_{\mathcal{A}}(X) & 0 & 0 \\ 0 & E_{\mathcal{B}}(X) & 0 \\ 0 & 0 & h^{\perp}(X) \end{pmatrix}$$

Type I Crossings

Now we will investigate the structure of a Type I crossing. Suppose we have a C^k electron Hamiltonian function $h(X)$ which has a Type I crossing of two simple eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$. Without loss of generality, we can assume this crossing occurs at $X = 0$. For X in a neighborhood of the origin, we write the spectral projection $P(X)$ for $h(X)$ associated with $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ as an integral of the resolvent of $h(X)$. Therefore, $P(X)$ is is a C^k operator valued function with rank 2 near $X = 0$. Further, $E_{\mathcal{A}}(X) + E_{\mathcal{B}}(X) = \text{trace}(h(X)P(X))$ is also a C^k function of X.

$$h_1(X) = h(X) - \frac{1}{2}(E_{\mathcal{A}}(X) + E_{\mathcal{B}}(X))$$

is a C^k operator valued function which is traceless when restricted to the range of $P(X)$.

Let $\{\psi_1, \psi_2\}$ be "a basis for the range of $P(0)$. We may alter the phases of these vectors to allow $\mathcal{K}\psi_1 = \psi_1$ and $\mathcal{K}\psi_2 = \psi_2$, where $\mathcal{K}$ is the antiunitary operator chosen for the decomposition $G = H \cup \mathcal{K}H$. We define

$$\psi_1(X) \;=\; \frac{P(X)\psi_1}{\sqrt{\langle \psi_1, P(X)\psi_1 \rangle}}.$$

This is well defined since $P(X)$ is C^k and commutes with the action of G. $\psi_1(X)$ is also C^k in a neighborhood of the origin and satisfies $\psi_1(X) = \mathcal{K}\psi_1(X)$. Let $P_1(X)$ be the projection onto the subspace spanned by $\psi_1(X)$, hence a C^k operator valued function in a neighborhood of X that commutes with $P(X)$ and with the action of G. Then define

$$\psi_2(X) \;=\; \frac{P(X)(1 - P_1(X))\psi_2}{\sqrt{\langle \psi_2, P(X)(1 - P_1(X))\psi_2 \rangle}}.$$

This is also a C^k vector valued function with $\psi_2(X) = \mathcal{K}\psi_2(X)$. Hence $\{\psi_1(X), \psi_2(X)\}$ is an orthonormal basis for the range of $P(X)$ for X in a neighborhood of the origin.

In the basis $\{\psi_1(X), \psi_2(X)\}$, $h_1(X)$ restricted to the range of $P(X)$ is represented by a real symmetric, traceless, 2×2 matrix valued function $M_1(X)$ whose entries are C^k functions which all vanish at $X = 0$.

$$M_1(X) = \begin{pmatrix} \beta(X) & \gamma(X) \\ \gamma(X) & -\beta(X) \end{pmatrix},$$

where β and γ are real valued C^k functions." $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ cross at the points in X where $\beta(X) = \gamma(X) = 0$. Generally this defines a codimension 2 manifold Γ for a Type I crossing. Also, the difference between $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ is the same as the difference between the eigenvalues of $M_1(X)$. The eigenvalues of $M_1(X)$ are $\pm\sqrt{\beta(X)^2 + \gamma(X)^2}$. These are continuous, but not differentiable near Γ. The eigenvectors are not continuous near Γ.

Using Taylor series, $M_1(X)$ can be written as $M_1(X) = N(X) + O(\|X\|^2)$, where

$$N(X) = \begin{pmatrix} b \cdot X & c \cdot X \\ c \cdot X & -b \cdot X \end{pmatrix},$$

for some vectors b and c, which are generally linearly independent. We may rotate the coordinate system so that only the first two components of b and c are non-zero.

For a generic nuclear momentum vector $\eta(0)$, we can rotate the first two coordinate axis so that the projection of $\eta(0)$ onto the two dimensional subspace spanned by b and c lies along the positive X_1 axis. From here, the X_j coordinates, $j > 2$, do not play any role in the structure of $N(X)$. Also, the form of $N(X)$ is not changed by any X-independent orthogonal transformations of the two dimensional space spanned by the basic electronic wave functions $\psi_1(X)$ and $\psi_2(X)$. We can make the following replacements.

$$\psi_1(X) \to \cos(\theta)\psi_1(X) + \sin(\theta)\psi_2(X)$$

$$\psi_2(X) \to -\sin(\theta)\psi_1(X) + \cos(\theta)\psi_2(X)$$

We can choose θ so that the X_1 component of c is 0. Then we can ensure the X_1 component of b and the X_2 component of c are both positive by doing any necessary interchanging of $\psi_1(X)$ and $\psi_2(X)$ and multiplication by -1. Then we can assume $N(X)$ can be written as

$$N(X) = \begin{pmatrix} b_1X_1 + b_2X_2 & c_2X_2 \\ c_2X_2 & -b_1X_1 - c_2X_2 \end{pmatrix}.$$

Identifying $\mathcal{H} \cong \mathbb{C} \oplus \mathbb{C} \oplus$ Ran$(1 - P(X))$, we can locally approximate $h_1(X)$ by

$$\tilde{h}_1(X) = \begin{pmatrix} \beta(X) & \gamma(X) & 0 \\ \gamma(X) & -\beta(X) & 0 \\ 0 & 0 & h_1^{\perp}(X) \end{pmatrix},$$

where $\beta(X) = b_1X_1 + b_2X_2 + O(X^2)$ and $\gamma(X) = c_2X_2 + O(X^2)$ with $b_1 > 0,\ c_2 > 0$, and $b_2 \neq 0$.

2.2.4 Adiabatic Electronic States

In a molecular system, electrons move much more quickly than the nuclei due to the large difference in the masses. This allows us to approximate the solutions, to the leading order in ϵ, of the electronic wave functions at each instance of time as though the nuclei were stationary. The electrons adjust their motion based on the positions of the nuclei rapidly compared to nuclear motion. This is the basis of what is called the adiabatic approximation for the electrons. If the electrons are in an initial state where there is an isolated quantum energy level, then we can apply this approximation as the electrons remain in that state as the nuclei move. However, this approximation breaks down at an energy level crossing since the level is no longer isolated.

The phase of electronic eigenstates must be determined for each time and nuclear position. The proper choice of eigenstate must also be made in any cases of degeneracy, which are determined by the adiabatic connection on the vector bundle of eigenfunctions of the particular energy level.

For an adiabatic electron state of multiplicity 1, the following proposition applies.

Proposition 2.2.1. *[Proposition 3.1 [34]] "Suppose $h(\cdot)$ is a C^k electron Hamiltonian operator on some open set $U \in \mathbb{R}^n$. Assume either that $h(X)$ has a discrete, multiplicity one eigenvalue $E(X)$ for all $X \in U$ that depends continuously on X, or that $E(X)$ has a generic crossing of type A, C, F, or G with some other eigenvalue of $h(X)$ in U. Suppose $a(t)$ and $\eta(t)$ are solutions to the classical motion equations,*

$$\begin{aligned} \frac{\partial a}{\partial t}(t) &= \eta(t) \\ \frac{\partial \eta}{\partial t}(t) &= -V^{(1)}(a(t)), \end{aligned}$$

with $V(X) = E(X)$, such that $a(t) \in U$ for $t \in [-T, t]$. Choose $\delta > 0$, such that $U_2(t) =$

$\{x \;:\; |x-a(t)| \leq 2\delta\} \subset U$ for all $t \in [-T,T]$. Then, for any C^k choice of initial normalized electron eigenfunction $\Phi(X,-T)$ corresponding to $E(X)$ for $X \in U_2(-T)$, there exists a unique C^k function $\Phi(X,t)$ on the set $\{(X,t) \;:\; X \in U_2(t),\; t \in [-T,T]\}$, such that $\Phi(X,t)$ is a normalized eigenfunction corresponding to $E(X)$ and

$$\langle \Phi(X,t), (i\frac{\partial}{\partial t} + i\eta(t)\cdot\nabla_X)\Phi(X,t)\rangle \;=\; 0,$$

for all $X \in U_2(t)$ and $t \in [-T,T]$. Moreover, if the symmetry group of $h(X)$ contains an antiunitary operator $\mathcal{K}$, and if $a(t)$ remains in a simply connected subset of U, then for appropriate initial conditions, a special choice can be made. There exist time independent choices $\Phi(X,t)$, unique up to a factor of ±1, that satisfy $\mathcal{K}\Phi(X,t) = \Phi(X,t)$; any such choice automatically satisfies the condition given by the equation above."

The following lemma provides error estimates for the approximations discussed. Formal calculations should be done to produce a candidate ψ for an approximate solution. After substituting ψ into each side of the Schrödinger equation, we take the resulting expression from each side and subtract the expressions to obtain an error term ζ. The lemma states that ζ provides bounds on how much ψ differs from the exact solution Ψ to the Schrödinger equation. Here, the variable r is a scaled time $r = e^{-b}t$ with $b \geq 0$ and $a = 2-b$.

Lemma 2.2.2. *[Lemma 3.3 of [34]] (The Magic Lemma) "Suppose $H(\epsilon)$ is a family of self-adjoint operators for $\epsilon > 0$. Suppose $\psi(r,\epsilon)$ belongs to the domain of $H(\epsilon)$, is continuously differentiable in r, and approximately solves the Schrödinger equation in the sense that*

$$i\epsilon^a \frac{\partial \psi}{\partial r}(r,\epsilon) \;=\; H(\epsilon)\psi(r,\epsilon) + \zeta(r,\epsilon),$$

where $\zeta(r,\epsilon)$ *satisfies*

$$||\zeta(r,\epsilon)|| \ \leq \ \mu(r,\epsilon)$$

for $T_1(\epsilon) \leq r \leq T_2(\epsilon)$*. Suppose* $\Phi(r,\epsilon)$ *is the exact solution to the equation*

$$i\epsilon^a \frac{\partial \Psi}{\partial r}(r,\epsilon)$$

with initial condition $\Psi(r_0,\epsilon) = \psi(r_0,\epsilon)$ *with* $T_1(\epsilon) \leq r_0 \leq T_2(\epsilon)$*. Then, for* $T_1(\epsilon) \leq t \leq T_2(\epsilon)$*, the following estimate holds:*

$$||\Psi(r,\epsilon) - \psi(r,\epsilon)|| \ \leq \ e^{-a} \int_{T_1(\epsilon)}^{T_2(\epsilon)} \mu(r,\epsilon) \ dr.\text{”}$$

2.2.5 Born-Oppenheimer Propagation Away From Crossings

We wish to study the time-dependent Born-Oppenheimer approximation to the solution to the Schrödinger equation when the nuclei are localized away from the electron eigenvalue crossing. We will restrict to the zeroth and first order approximations for a crossing with multiplicity 1. Higher order approximations are not necessary for understanding the general behavior in the system we wish to study.

The Multiplicity 1 Case

We suppose that the hypothesis of Proposition 2.2.1 are satisfied. Explicitly, suppose $h(\cdot)$ is a C^k electron Hamiltonian and that there exists an open set $U \in \mathbb{R}^n$ such that $h(X)$ has a discrete, multiplicity one eigenvalue $E(X)$ for $X \in U$ that depends continuously on X.

Assume $a(t)$ and $\eta(t)$ satisfy the equations of classical motion with $V(X) = E(X)$. Assume that $a(t) \in U$ for $t \in [-T, T]$. Then we can choose $\delta > 0$ such that $\{x \,:\, |x - a(t)| \leq 2\delta\} \subset U$ for all $t \in [-T, T]$. We define $U_1(t) = \{x \,:\, |x - a(t) \leq \delta\}$ and $U_2(t) = \{x \,:\, |x - a(t)| \leq 2\delta\}$. Now we choose a C^∞ function $F : \mathbb{R}^n \to [0, 1]$, such that $F(X) = 0$ for $|X| \geq 2\delta$ and $F(X) = 1$ for $X \leq \delta$.

Let $\Phi(X, -T)$ be a C^k choice of initial normalized electron eigenfunction corresponding to $E(X)$ for $X \in U_2(-T)$, and let $\Phi(X, t)$ be the corresponding normalized adiabatic electronic eigenfunction constructed as in Proposition 2.2.1 for all $X \in U_2(t)$ and $t \in [-T, T]$.

We will use this to construct formal approximate solutions to the Schrödinger equation

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} \;=\; -\frac{\epsilon^4}{2} \Delta_X \Psi + h(x)\Psi$$

with approximate solutions of the form

$$\Psi(X, t) \;=\; \sum_{j=0}^{J} \epsilon^j \Psi_j(X, t).$$

We will apply the method of multiple scales to calculate $\Psi_j(X, t)$. The electronic wave function is sensitive to X, the nuclear configuration, on a length scale of order 1. The quantum mechanical fluctuations of the nuclei around the classical configuration $a(t)$ are on a length scale order of ϵ. As ϵ approaches 0, from above, the two quantities which are physcially important are $x = X$ and $y = \frac{X - a(t)}{\epsilon}$, which approximately behave independently. Then we will actually solve for the functions $\widehat{\Psi}_j(x, y, t)$ which we can find $\Psi_j(X, t)$ by the relation

$$\Psi_j(X, t) \;=\; \widehat{\Psi}_j(X, \frac{X - a(t)}{\epsilon}, t). \tag{2.17}$$

However, since $x = X$ and $y = \frac{X-a(t)}{\epsilon}$ are not actually independent, this does not completely determine $\widehat{\Psi}_j(x,y,t)$. Therefore to determine $\widehat{\Psi}_j(x,y,t)$, we choose

$$\Psi(x,y,t) = \sum_{j=0}^{J} \epsilon^j \widehat{\Psi}_j(x,y,t) \tag{2.18}$$

to satisfy

$$\begin{aligned} i\epsilon^2 \frac{\partial \widehat{\Psi}}{\partial t} &= \Big[-\frac{\epsilon^4}{2}\Delta_x - \epsilon^3 \nabla_x \cdot \nabla_y - \frac{\epsilon^3}{2}\Delta_y \\ &\quad + i\epsilon\eta(t)\cdot\nabla_y + E(a(t)-\epsilon y) + h(x) - E(x)\Big]\widehat{\Psi} \end{aligned} \tag{2.19}$$

We obtain this by replacing equation (2.17) above into the Schrödinger equation and adding $E(a(t)+\epsilon y) - E(x)$ which is 0 when $x = X$ and $y = \frac{X-a(t)}{\epsilon}$. Solutions to above provide a solution $\Psi(X,t) = \widehat{\Psi}(X, \frac{X-a(t)}{\epsilon}, t)$ to the Schrödinger equation.

To construct our approximate solutions, we make the ansatz that they are of the form

$$\widehat{\Psi}(x,y,t) \;=\; e^{iS(t)/\epsilon^2} e^{i\eta(t)\cdot y/\epsilon} F(x-a(t)) \times (\psi_0(x,y,t) + \epsilon\psi_1(x,y,t) + \ldots).$$

Plugging this solution into equation (2.19), many terms cancel, including all terms containing derivatives of F, which is supported within distance δ of $a(t)$. ψ_j are exponentially small in this region, so these terms to not contribute to the expansion in ϵ. Thus, we can neglect these terms. From this we find that if we consider

$$\chi(x,y,t) \;=\; (\psi_0(x,y,t) + \epsilon\psi_1(x,y,t) + \ldots),$$

it must satisfy

$$i\epsilon^2 \frac{\partial \chi}{\partial t} \;=\; \Big[-\frac{\epsilon^4}{2}\Delta_x - \epsilon^3 \nabla_x \cdot \nabla_y - \frac{\epsilon^2}{2}\Delta_y - i\epsilon^2 \eta(t)\cdot\nabla_x$$

$$+\Big[E(a(t)-\epsilon y)-E(a(t))-\epsilon E^{(1)}(a(t)\cdot y)\big]+[h(x)-E(x)]\Big]\chi.$$

Substituting the equation for $\chi(x,y,t)$ into this and then expanding $E(a(t)+\epsilon y)$ in its Taylor series in ϵ, we obtain a set of equations by equating the powers of ϵ from each side. The zero order equation we have to solve is

$$F(x-a(t))[h(x)-E(x)]\psi_0 \;=\; 0.$$

Then for $x\in U_2(t)$, we need

$$\psi_0(x,y,t) \;=\; g_0(x,y,t)\Phi(x,t)$$

where g_0 is a complex valued function that will need to be determined. For $x\notin U_2(t)$, we can just choose $\psi_0(x,y,t)=0$. In fact, for any ψ_j, if $x\notin U_2(t)$, we can let $\psi_j(x,y,t)=0$.

The first order equation to be solved is

$$F(x-a(t))[h(x)-E(x)]\psi_1 \;=\; 0$$

so as before, for $x\in U_2(t)$,

$$\psi_1(x,y,t) \;=\; g_1(x,y,t)\Phi(x,t)$$

where g_1 is another complex valued function that needs to be determined.

The second order equation is

$$\begin{aligned} iF(x-a(t))\dot{\psi}_0 = F(x-a(t))\Big[&-\frac{1}{2}\Delta_y\psi_0+E^{(2)}(a(t))\frac{y^2}{2}\psi_0 \\ &-i\eta(t)\cdot\nabla_x\psi_0+[h(x)-E(x)]\psi_2\Big], \end{aligned} \tag{2.20}$$

where $\dot{\psi}_0$ denotes the time derivative, and $E^{(2)}(a(t))\frac{y^2}{2}$ is shorthand notation

$$E^{(2)}(a(t))\frac{y^2}{2} = \frac{1}{2}\sum_{i,j}\frac{\partial^2 E}{\partial y_i \partial y_j}(a(t))y_i y_j.$$

To solve the equation for the second order terms, equation (2.20), we can separate the equation into two parts. The first part contains all terms that are x, y, and t dependent scalar multiples of $\Phi(x,t)$. For these, we can use the condition

$$\langle \Phi(X,t), (i\frac{\partial}{\partial t} + i\eta(t)\cdot\nabla_X)\Phi(X,t)\rangle \;=\; 0$$

to cancel some terms.

$$i\dot{g_0} \;= \frac{1}{2}\Delta_y g_0 + E^{(2)}(a(t))\frac{y^2}{2}g_0 - i\eta(t)\nabla_x g_0$$

The second part contains all components that are orthogonal to $\Phi(x,t)$ in $\mathcal{H}_{el}$.

$$[h(x) - E(x)]\psi_2 \;=\; ig_0\big[\eta(t)\cdot\nabla_x\Phi(x,t) + \dot{\Phi}(x,t)\big]$$

To solve the first part, it is beneficial to make the change of variables $w = x - a(t)$ and define $f_0(w,y,t) = g_0(w + a(t), y, t) = g_0(x,y,t)$. Then f_0 satisfies

$$i\dot{f_0} \;=\; -\frac{1}{2}\Delta_y f_0 + E^{(2)}(a(t))\frac{y^2}{2}f_0.$$

We can solve this in y and t for a fixed w where $|w| < 2\delta$. Then this is just the Schrödinger equation for a harmonic oscillator with time varying spring strength. The wave packets ϕ_l solve this equation. Since we can superimpose the solutions obtained, we choose a multi-index l and obtain

$$f_0(w,y,t) \;=\; \epsilon^{-n/2}\phi_l(A(t), B(t), 1, 0, 0, y).$$

We do not actually need to make the solution dependent on w, which reflects the non-uniqueness of the solutions found using multiple scales techniques. Then the solution to the first part of the separated equation is

$$g_0(x, y, t) \;=\; \epsilon^{-n/2}\phi_l(A(t), B(t), 1, 0, 0, y).$$

This is defined everywhere on the domain of $F(x - a(t))$.

Now we need to solve the second part. First, we note that $[h(x) - E(x)]$ has a bounded inverse when restricted to the orthogonal complement of multiples of $\Phi(x, t)$ in $\mathcal{H}_{el}$. We will call this inverse $r(x)$. Also, $\psi_2 = \psi_2^{\perp} + \psi_2^{\|}$, where

$$\psi_2^{\perp}(x, y, t) \;=\; i g_0(x, y, t) r(x)[\eta(t) \cdot \nabla_x \Phi(x, t) + \dot{\Phi}(x, t)]$$

and

$$\psi_2^{\|}(x, y, t) \;=\; g_2(x, y, t)\Phi(x, t)$$

and g_2 is some complex valued function which again needs to be determined. If only the first order terms are needed for the Born-Oppenheimer expansion, we can stop here and use the approximate solution

$$\begin{aligned} \widehat{\Psi}(x, y, t) \;&= e^{iS(t)/\epsilon^2} e^{i\eta(t)\cdot y/\epsilon} F(x - a(t)) \\ &\qquad \times \left(\psi_0(x, y, t) + \epsilon^2 \psi_2^{\perp}(x, y, t)\right). \end{aligned}$$

We can use this solution to find $\Psi(X, t)$, and to analyze the error,

$$\zeta(X, t) \;=\; i\epsilon^2 \frac{\partial \Psi}{\partial t}(X, t) - H(\epsilon)\Psi(X, t).$$

After canceling terms and bounding remaining terms by Taylor series expansions, we find that the norm of $\zeta(\cdot, t)$ is bounded by a constant times ϵ^3. Applying the Magic Lemma, Lemma (2.2.2), for $a = 2$, $T_1(\epsilon) = -T$, and $T_2(\epsilon) = T$, we see that this provides an approximate solution with error of $O(\epsilon)$. If a first order approximation is required, then we must continue calculations to the third order equation,

$$\begin{aligned} iF(x-a(t))\dot{\psi}_1 &= F(x-a(t))\Big[-\frac{1}{2}\Delta_y\psi_1 + E^{(2)}(a(t))\frac{y^2}{2}\psi_1 + E^{(3)}(a(t))\frac{y^3}{6}\psi_0 \\ &\quad - i\eta(t)\cdot\nabla_x\psi_1 - \nabla_x\cdot\nabla_y\psi_0 + [h(x)-E(x)]\psi_3\Big]. \end{aligned}$$

This again uses the same shorthand notation as before. As we did with the second order equation, we can split this equation into two parts as well. The terms which are multiples of $\Phi(x,t)$ produce the equation

$$\begin{aligned} iP_{\parallel}(x)\dot{\psi}_1 &= -\frac{1}{2}\Delta_y\psi_1 + E^{(2)}(a(t))\frac{y^2}{2}\psi_1 + E^{(3)}(a(t))\frac{y^3}{6}\psi_0 \\ &\quad - iP_{\parallel}(x)\eta(t)\cdot\nabla_x\psi_1 - P_{\parallel}(x)\nabla_x\cdot\nabla_y\psi_0 \end{aligned}$$

where $P_{\parallel}(x)$ is the projection onto x, y, and t dependent scalar multiples of $\Phi(x,t)$. The terms orthogonal to $\Phi(x,t)$ produce the second part of the equation

$$[h(x)-E(x)]\psi_3 = iP_{\perp}(x)\dot{\psi}_1 + iP_{\perp}(x)\eta(t)\cdot\nabla_x\psi_1 - P_{\perp}(x)\nabla_x\cdot\nabla_y\psi_0$$

where $P_{\perp}(x)$ is the projection onto the orthogonal complement of the scalar multiples of $\Phi(x,t)$ in $\mathcal{H}_{el}$. We follow the same process as we did with the second order terms, and let $w = x - a(t)$ and $f_1(w,y,t) = g_0(x,y,t)$. We find that f_1 must satisfy

$$i\dot{f}_1 = -\frac{1}{2}\Delta_y f_1 + E^{(2)}(a(t))\frac{y^2}{2}f_1 + E^{(3)}(a(t))\frac{y^3}{6}f_0$$

$$- \nabla_w \cdot \nabla_y f_0 - (\nabla_y f_0) \cdot \langle \Phi(w + a(t), t),\ \nabla \Phi(w + a(t), t) \rangle_{\mathcal{H}_{el}}.$$

Since f_0 does not depend on w, the $\nabla_w \cdot \nabla_y f_0$ is dropped. The nonhomogeneous terms can be expressed as functions of w and t times a linear combination of a finite number of wave packets, ϕ_m with $|m| \leq |l| + 3$. Then for a fixed w, following methods from [30, 33] to obtain the solution for g_1,

$$g_1(x, y, t) \;=\; \sum_{|m| \leq |l|+3} d_m(x - a(t), t) \epsilon^{-n/2} \phi_m(A(t), B(t), 1, 0, 0, y)$$

where $d_m(w, t)$ are determined by solving an initial value problem for a system of ordinary differential equations. Details of this can be found in [30, 33].

We define $\psi_3 = \psi_3^{\perp} + \psi_2^{\|}$ where

$$\psi_2^{\perp} \;=\; r(x) \Big(i g_1 \Big[\eta(t) \cdot \nabla_x \Phi(x, t) + \dot{\Phi}(x, t) \Big] + P_{\perp}(x)(\nabla_x \Phi(x, t) \Big)$$

and

$$\psi_3^{\|} \;=\; g_3(x, y, t) \Phi(x, t)$$

and g_3 is a function to be determined later by terms further in the expansion.

At this point, we have done all of the calculations need for the first order approximation.

$$\hat{\Psi}(x, y, t) \;= e^{iS(t)/\epsilon^2} e^{i\eta(t)\cdot y/\epsilon} F(x - a(t))$$
$$\Big(\psi_0(x, y, t) + \epsilon \psi_1(x, y, t) + \epsilon^2 \psi_2^{\perp}(x, y, t) + \epsilon^3 \psi_3^{\perp}(x, y, t) \Big)$$

Again, we use $\Psi_j(X, t) \;=\; \hat{\Psi}_j(X, \dfrac{X - a(t)}{\epsilon}, t)$ and $\Psi(X, t) \;=\; \sum_{j=0}^{J} \epsilon^j \Psi_j(X, t)$ to obtain the approximate solution to the Schrödinger equation. The Magic Lemma (2.2.2) shows that this solution has error with norm of $O(\epsilon^2)$.

2.2.6 Codimension 1 Crossings

For crossings which occur on a submanifold with codimension 1 (Type A, C, D, E, F, G, and H), we study the approximate solutions to the Schrödinger equation which agree up to order ϵ with the exact solution. Error for the approximate solutions should be $O(\epsilon^\alpha)$ for some $\alpha > 1$. The zeroth order terms of the solution are not affected by the presence of the crossing.

We will consider a system which has two eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ which are each of multiplicity 1 away from the crossing, i.e. a type A or C crossing. The following theorem from [34] provides the approximate solution to the Schrödinger equation.

Theorem 2.2.3. *[Theorem 5.1 of [34]] "If $h(X)$ has a crossing type A or C, then there is an approximate solution $\Psi(\epsilon, X, t)$ to the Schrödinger equation that satisfies*

$$\begin{aligned}\Psi(\epsilon, X, t) &= \Phi_{\mathcal{A}}(X,t) e^{iS^{\mathcal{A}}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2} \\ &\qquad \times \Big(\phi_l(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), X) \\ &\qquad\quad + \epsilon \sum_{|m|\le|l|+3} d_m(X + a^{\mathcal{A}}(t), t)\phi_m(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), X)\Big) \\ &\quad + O(\epsilon^2)\end{aligned}$$

for $t \in [-T, -T_1]$, for any fixed $T_1 > 0$. For $t \in [T_1, T]$, the solution satisfies

$$\begin{aligned}\Psi(\epsilon, X, t) &= \Phi_{\mathcal{A}}(X,t) e^{iS^{\mathcal{A}}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2} \\ &\qquad \times \Big(\phi_l(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), X) \\ &\qquad\quad + \epsilon \sum_{|m|\le|l|+3} d_m(X + a^{\mathcal{A}}(t), t)\phi_m(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), X)\Big)\end{aligned}$$

$$
\begin{aligned}
&- \epsilon(1+i)\pi^{1/2} \left(\langle (E_{\mathcal{A}}^{(1)} - E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle\right)^{-1/2} \\
&\qquad \times \langle \Phi_{\mathcal{B}}(0,0),\ \left(\left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}}(0)\cdot\nabla_X\right)\Phi_{\mathcal{A}}\right)(0,0)\rangle_{\mathscr{H}_{el}} \\
&\qquad \times \Phi_{\mathcal{B}}(X,t) e^{iS^{\mathcal{B}}(t)/\epsilon^2} e^{i\eta^{\mathcal{B}}(t)\cdot(x-a^{\mathcal{B}}(t))/\epsilon^2} \phi_l(A^{\mathcal{A}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), X) \\
&+ O(\epsilon^{\alpha})
\end{aligned}
$$

for some $\alpha > 1$. The coefficients $d_m \in \mathbb{C}$ are found by solving a system of ordinary differential equations, described below. Note that if $\langle (E_{\mathcal{A}}^{(1)} - E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle$ is positive, then we take the positive square root, and if it is negative, we take the positive imaginary square root. "

Lemma 2.2.4. *[Lemma 5.2 of [34]] "Under the hypothesis of the previous theorem, the approximate solution of the theorem agrees with an exact solution of the Schrödinger equation up to errors whose norms are of order $\epsilon^{2-\xi}$ for $t \in [-T, -\epsilon^{\xi}]$ for any $\xi \in (0,1)$."*

Lemma 2.2.5. *[Lemma 5.3 of [34]] "Under the hypothesis of Theorem (3.1.1), the approximate solution agrees with an exact solution of the Schrödinger equation up to errors whose norms are of order $\epsilon^{2\xi'}$ for $t \in [-\epsilon^{\xi'}, \epsilon^{\xi'}]$ for any $\xi' \in (\frac{1}{2}, 1)$."*

The lemma above is possible due to Lemma (2.2.2).

2.2.7 Codimension 2 Crossings

Similarly to the previous section, will discuss Born-Oppenheimer propagation through an electron eigenvalue crossing, but now considering a crossing with codimension 2. This means the crossing is assumed to be Type I. We wish to approximate the solutions to the Schrödiner equations which agree with the exact solutions up to errors of order $O(\epsilon^\alpha)$ for some $\alpha > 0$.

For a crossing of this type, the zeroth order approximation of the wave function splits into two components as it passes through the crossing. Assuming that the system is initially in a state associated with the $E_{\mathcal{A}}$ and passes through the crossing, the final state is a superposition of of an $O(1)$ component associated with $E_{\mathcal{A}}$ and another $O(1)$ component associated with $E_{\mathcal{B}}$. Hence, this type of crossing strongly couples the electronic states associated with the two levels $E_{\mathcal{A}}$ and $E_{\mathcal{B}}$.

Without loss of generality, assume the coordinate system is shifted so the origin is some point of the crossing set $\Gamma = \{X : \ E_{\mathcal{A}}(X) = E_{\mathcal{B}}(X)\}$. Then let $\Phi_{\mathcal{A}}(X)$ and $\Phi_{\mathcal{B}}(X)$ be the corresponding eigenvectors of the electronic Hamiltonian $h(X)$.

The details of the proofs for all lemmas and theorems from this section can be found in [34].

Lemma 2.2.6. *[Lemma 6.1 of [34]] "Assume V is any of the potentials $E_{\mathcal{A}},\ E_{\mathcal{B}}$, or $\tilde{V} = \frac{1}{2}(E_{\mathcal{A}} + E_{\mathcal{B}})$. Assume that a momentum vector $\eta_0 \neq 0$ is given that is not tangent to Γ at the origin, and let S_0 be arbitrary. Then for each choice of V, there exists a unique solution to the equations (2.5)-(2.9) that satisfies $a(0) = 0$, $\eta(0) = \eta_0$, and $S(0) = S_0$.*

In particular, if $V = \tilde{V}$, then

$$\begin{aligned} a(t) &= \eta_0 t - \nabla \tilde{V}(0)\frac{t^2}{2} + O(t^3) \\ \eta(t) &= \eta_0 - \nabla \tilde{V}(0)t + O(t^2) \\ S(t) &= S_0 + \frac{\eta_0^2}{2}t - \tilde{V}(0)t - \eta_0 \cdot \tilde{V}(0)t^2 + O(t^3), \end{aligned}$$

If $V = E_{\mathcal{A}}$ *and* $t < 0$ *or if* $V = E_{\mathcal{B}}$ *and* $t > 0$*, then*

$$\begin{aligned} a(t) &= \eta_0 t - \nabla\tilde{V}(0)\frac{t^2}{2} - \frac{b}{2}t^2 + O(t^3) \\ \eta(t) &= \eta_0 - \nabla\tilde{V}(0)t - bt + O(t^2) \\ S(t) &= S_0 + \frac{\eta_0^2}{2}t - \tilde{V}(0)t - \eta_0\cdot\tilde{V}(0)t^2 - b\eta_0 t^2 + O(t^3). \end{aligned}$$

If $V = E_{\mathcal{B}}$ *and* $t < 0$ *or if* $V = E_{\mathcal{A}}$ *and* $t > 0$*, then*

$$\begin{aligned} a(t) &= \eta_0 t - \nabla\tilde{V}(0)\frac{t^2}{2} + \frac{b}{2}t^2 + O(t^3) \\ \eta(t) &= \eta_0 - \nabla\tilde{V}(0)t + bt + O(t^2) \\ S(t) &= S_0 + \frac{\eta_0^2}{2}t - \tilde{V}(0)t - \eta_0\cdot\tilde{V}(0)t^2 + b\eta_0 t^2 + O(t^3).\text{"} \end{aligned}$$

Lemma 2.2.7. *[Lemma 6.2 of [34]] "Restrict* t *to be either positive or negative, and suppose* $V = E_{\mathcal{A}}$ *or* $V = E_{\mathcal{B}}$*. If* $t < 0$ *and* $V = E_{\mathcal{A}}$ *or* $t > 0$ *and* $V = E_{\mathcal{B}}$*, then let* M *be the matrix*

$$M_{\mathcal{A}}^{-} = M_{\mathcal{B}}^{+} = \begin{pmatrix} 0 & 0 & 0 & \cdots & 0 \\ 0 & \frac{c^2}{b_1\widetilde{\eta_0}} & 0 & \cdots & 0 \\ 0 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 0 \end{pmatrix},$$

where $\widetilde{\eta_0}$ *is the first component of* η_0*, ie* $\eta_0 = (\widetilde{\eta_0},\ \eta_{0,2},\ \ldots,\ \eta_{0,n})^t$.

If $t < 0$ and $V = E_{\mathcal{B}}$ or $t > 0$ and $V = E_{\mathcal{A}}$, then let M be the matrix

$$M_{\mathcal{A}}^{+} = M_{\mathcal{B}}^{-} = \begin{pmatrix} 0 & 0 & 0 & \cdots & 0 \\ 0 & -\frac{c^2}{b_1 \widetilde{\eta}_0} & 0 & \cdots & 0 \\ 0 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 0 \end{pmatrix}.$$

Suppose that $\begin{pmatrix} A(t) \\ B(t) \end{pmatrix}$ is any solution to (2.8)-(2.9) for $t \in (0, t_0)$ or $t \in (-t_0, 0)$ which satisfies conditions (2.1)-(2.4). Then there exist matrices A_0 and D_0 that satisfy (2.1)-(2.4) such that

$$\begin{aligned} A(t) &= A_0 + O(t \ln |t|) \\ B(t) &= D_0 + iMA_0 \ln |t| + O(t \ln |t|). \end{aligned}$$

Conversely, given any A_0 and D_0 which satisfy (2.1)-(2.4) and a sufficiently small positive t_0, there exists a unique solution $\begin{pmatrix} A(t) \\ B(t) \end{pmatrix}$ to (2.8)-(2.9) for $t \in (0, t_0)$ and $t \in (-t_0, 0)$ that satisfy (2.1)-(2.4) and have asymptotics given as above."

Suppose we have chosen to have a wave function associated with the lower level $E_{\mathcal{A}}$ for $t < 0$, and given some $A_0^{\mathcal{A},-}$ and $D_0^{\mathcal{A},-}$ satisfying (2.1)-(2.4). For the lower surface and positive times we choose $A^{\mathcal{A}}(\epsilon, t)$ and $B^{\mathcal{A}}(\epsilon, t)$ to be solutions to (2.8)-(2.9) such that A_0 and D_0 are given by

$$A_0^{\mathcal{A},+} = A_0^{\mathcal{A},-}$$

and

$$
\begin{aligned}
D_{0,\epsilon}^{\mathcal{A},+} =& D_0^{\mathcal{A},-} - \frac{2i}{b_1\widetilde{\eta_0}}|b\rangle\langle b|A_0^{\mathcal{A},+} \\
&+ i\ln(2b_1\widetilde{\eta_0})M_{\mathcal{A}}^{+}A_0^{\mathcal{A},+} - 2i(\ln\epsilon)M_{\mathcal{A}}^{+}A_0^{\mathcal{A},+}.
\end{aligned}
$$

For the upper surface $E_{\mathcal{B}}$ and positive times, we similarly find A_0 and D_0 given by

$$
A_0^{\mathcal{B},+} = \left(|A_0^{\mathcal{A},-}|^{-2} + \frac{\pi}{b_1\widetilde{\eta_0}}|c\rangle\langle c|\right)^{-1/2}
$$

and

$$
D_0^{\mathcal{B},+} = \left(D_0^{\mathcal{A},-}(A_0^{\mathcal{A},-})^{-1} + \frac{\pi}{b_1\widetilde{\eta_0}}|c\rangle\langle c|\right)A_0^{\mathcal{B},+}.
$$

It is easily checked that these choices for A_0 and D_0 satisfy the conditions (2.1)-(2.4), and thus implies that $A(t)$ and $B(t)$ satisfy those conditions as well.

We constructed a basis $\{\psi_1(X), \psi_2(X)\}$ of the spectral subspace corresponding to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$. Then the eigenvectors corresponding to $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are given by

$$
\begin{aligned}
\Phi_{\mathcal{A}}(X) &= -\sin(\theta(X)/2)\psi_1(X) + \cos(\theta(X)/2)\psi_2(X) \\
\Phi_{\mathcal{B}}(X) &= \cos(\theta(X)/2)\psi_1(X) + \sin(\theta(X)/2)\psi_2(X),
\end{aligned}
$$

where $\tan(\theta(X)) = \gamma(X)/\beta(X)$. These eigenvectors are not smooth near the origin, but we choose $\theta(X)$ such that $-\pi/2 \leq \theta(X) < 3\pi/2$ with the discontinuity supported on the hypersurface where $\gamma(X)$ is negative.

Then we can obtain the solutions we desired for a codimension 2 crossing, or Type I crossing.

Theorem 2.2.8. *[Theorem 6.3 of [34]] "If $h(X)$ has a crossing of Type I, then there is an approximate solution $\Psi(\epsilon, X, t)$ to the Schrödinger equation that satisfies*

$$\begin{aligned}\Psi(\epsilon, X, t) &= \Phi_{\mathcal{A}}(X) e^{iS^{\mathcal{A},-}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2} \\ &\quad \times \phi_l(A^{\mathcal{A},-}(t), B^{\mathcal{A},-}(t).\epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), X) \\ &+ O(\epsilon)\end{aligned} \tag{2.21}$$

for $t \in [-T, -T_1]$, for any $T_1 > 0$. For $t \in [T_1, T]$, the solution satisfies

$$\begin{aligned}\Psi(\epsilon, X, t) &= \Phi_{\mathcal{A}}(X) e^{iS^{\mathcal{A},+}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2} \\ &\quad \times \sum_m d_m^{\mathcal{A}} \phi_m(A^{\mathcal{A},+}(t), B^{\mathcal{A},+}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), X) \\ &+ \Phi_{\mathcal{B}}(X) e^{iS^{\mathcal{B},+}(t)/\epsilon^2} e^{i\eta^{\mathcal{B}}(t)\cdot(x-a^{\mathcal{B}}(t))/\epsilon^2} \\ &\quad \times \sum_{|m|\leq|l|+3} d_m^{\mathcal{B}} \phi_m(A^{\mathcal{B},+}(t), B^{\mathcal{B},+}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), X) \\ &+ O(\epsilon^\alpha),\end{aligned} \tag{2.22}$$

for some $\alpha > 0$."

2.3 Avoided Energy Level Crossings

2.3.1 Introduction to avoided crossings

We suppose that we are again interested in solving the time-dependent Schrödinger equation for a molecular system, with the same assumptions on the system as previously. In particular, we use the standard Born-Oppenheimer approximation and letting ϵ^4 be the ratio of the mass of an electron to the average masses of the nuclei.

$$i\epsilon^2 \frac{\partial \psi}{\partial t} = H(\epsilon)\psi$$

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

where $h(x)$ is the electronic Hamiltonian. Now we would like to study electronic transitions which are not associated with level crossings. We consider $h(x)$ which has two eigenvalues which approach each other with a minimal gap. The gap size then is of the appropriate order of magnitude as the specific value of ϵ. Following the method of [39], we assume the electronic Hamiltonian may be ϵ dependent so that there is a crossing when $\epsilon = 0$. Thus we study a Hamiltonian of the form

$$H(\epsilon) = -\frac{\epsilon^4}{2}\Delta_x + h(x, \epsilon)$$

assuming $h(x, \epsilon)$ has an avoided crossing, given the following definition of [39].

Definition: "Suppose $h(x, \epsilon)$ is a family of self-adjoint operators with a fixed domain $\mathcal{D}$ in a Hilbert space $\mathcal{H}$, for $x \in \Omega$ and $\epsilon \in [0, \alpha)$, where Ω is an open subset of $\mathbb{R}^n$. Suppose that the resolvent of $h(x, \epsilon)$ has two eigenvalues $E_A(x, \epsilon)$ and $E_B(x, \epsilon)$ that depend continuously on x and ϵ and are isolated from the rest of the spectrum of $h(x, \epsilon)$. Assume $\Gamma = \{x : E_{\mathcal{A}}(x, 0) = E_{\mathcal{B}}(x, 0)\}$ is a single point or non-empty connected proper submanifold of Γ, but that for all $x \in \Omega$, $E_{\mathcal{A}}(x, \epsilon) \neq E_{\mathcal{B}}(x, \epsilon)$ when $\epsilon > 0$. Then we say $h(x, \epsilon)$ has an **avoided crossing** on Γ."

2.3.2 Classification of Avoided Crossings

As given by [36], we can classify and study the local structure of "avoided crossings" of discrete eigenvalues of Hamiltonian operators. This refers to when two discrete eigenvalues $E_{\mathcal{A}}(x)$ and $E_{\mathcal{B}}(x)$ of $h(x)$ come very close to each other, but remain a small positive distance apart.

These types of system are of interest because avoided crossings significantly affect the physics of the situation. For the time-dependent Born-Oppenheimer approximation, the adiabatic approximation for the electrons can fail at an avoided crossing. This is a mechanism which allows certain chemical reactions to occur.

We will assume the Hamiltonian depends on the nuclear parameters $x \in \mathbb{R}^n$ and a "detuning" parameter ϵ, such that $h(x, 0)$ has a crossing but $h(x, \epsilon)$ does not, for small $\epsilon > 0$.

In the definition of an avoided crossing, it is possible that Γ is a manifold, which may arise in application due to symmetries in the system. For example, in the absence of external fields, electronic Hamiltonians for molecular systems undergo similarity transformations as nuclear configurations are translated or rotated. The eigenvalues are invariant under these transformations thus allowing these crossings to occur on a manifold of positive dimension.

To study the molecular propagation through the avoided crossing, we choose a direction of propagation of the nuclei. This direction in the nuclear configuration space has a non-trivial component in the hyperplane perpendicular to Γ at any particular point. Let us choose the x_1 coordinate direction to be aligned with that component. The normal forms of the solutions we find will depend on this.

We wish to classify the different types of avoided crossings, and it will depend on the codimension of Γ and symmetries of $h(x, \epsilon)$. The codimension of $\Gamma \subset \mathbb{R}^n$ is $n - m$ where m is the dimension of Γ. In other words, the codimension is the minimum number of parameters that must be altered to move a generic point of $\mathbb{R}^n$ near Γ onto Γ. As discussed earlier in the section on crossings, each Hamiltonian $h(x, \epsilon)$ has a symmetry group G, the set of all (x, ϵ)-independent unitary and anti-unitary operators that commute with $h(x, \epsilon)$.

For our purposes, we will only consider avoided crossings of two energy levels $E_{\mathcal{A}}(x, \epsilon)$ and $E_{\mathcal{B}}(x, \epsilon)$ which are generic and have minimal multiplicity allowed by the symmetry group. Using definitions from [39], n the case that G has no anti-unitary operators, "each energy level of $h(x, \epsilon)$ is associated with an irreducible representation of G, and the minimal multiplicity allowed is 1.

If G does contain anti-unitary operators, then each discrete energy level of $h(x, \epsilon)$ is associated with an irreducible corepresentation of G [60, 47]. In this case, the unitary elements of G form a subgroup H of index 2. Each irreducible corepresentation belongs to one of three types.

A corepresentation U of G is of *Type 1* if its restriction U_H to H is an irreducible representation of H. In this case, the energy levels of $h(x, \epsilon)$ also have minimal multiplicity 1.

A corepresentation U of G is of *Type 2* if its restriction U_H to H is a direct sum of two equivalent irreducible representations of H. This means $U_H = D \oplus D$. Also, for any antiunitary $\mathcal{K} \in G$, the corepresentation U can be expressed in the form

$$U(h) = \begin{pmatrix} D(h) & 0 \\ 0 & D(h) \end{pmatrix}, \; U(\mathcal{K}) = \begin{pmatrix} 0 & -K \\ K & 0 \end{pmatrix}, \text{ and } \; U(\mathcal{K}h) = U(\mathcal{K})U(h),$$

for all $h \in H$. Here K is an anti-unitary operator which satisfies $K^2 = -D(\mathcal{K})$ and $KD(\mathcal{K}^{-1}h\mathcal{K})K^{-1} = D(h)$ for all $h \in H$. For this case, the energy levels of $h(x, \epsilon)$ have minimal multiplicity 2.

A corepresentation U of G is of *Type III* if its restriction U_H to H is a direct sum of two inequivalent irreducible representations of H. This means $U_H = D \oplus C$. Also, for any antiunitary $\mathcal{K} \in G$, the corepresentation U can be expressed in the form

$$U(h) = \begin{pmatrix} D(h) & 0 \\ 0 & D = C(h) \end{pmatrix}, \; U(\mathcal{K}) = \begin{pmatrix} 0 & -K \\ D(\mathcal{K}^2)K^{-1} & 0 \end{pmatrix}, \text{ and } \; U(\mathcal{K}h) = U(\mathcal{K})U(h),$$

for all $h \in H$. Here $K : \mathcal{H}_D \to \mathcal{H}_C$ is an anti-unitary operator which satisfies $K^2 = -D(\mathcal{K})$ and $KD(\mathcal{K}^{-1}h\mathcal{K})K^{-1} = D(h)$ for all $h \in H$. For this case, the energy levels of $h(x, \epsilon)$ have minimal multiplicity 2.

Let us assume that two energy levels $E_{\mathcal{A}}(x, 0)$ and $E_{\mathcal{B}}(x, 0)$ have a crossing and are associated with inequivalent representations or corepresentations. Without loss of generality, we can assume this crossing occurs at $x = 0$. As discussed earlier while classifying the crossings,

$E_{\mathcal{A}}(x,0)$ and $E_{\mathcal{B}}(x,0)$ do not satisfy any special conditions, therefore $\nabla_x|_{(x,\epsilon)=(0,0)}(E_{\mathcal{A}}(x,\epsilon) - E_{\mathcal{B}}(x,\epsilon))$ is non-zero under generic conditions. Restricting x to any line $\mathcal{L}$ through the origin that is not perpendicular to this gradient, with the Implicit Function Theorem, we can conclude that for small ϵ, there is a unique $x(\delta)$ near the origin on $\mathcal{L}$ which satisfies

$$E_{\mathcal{A}}(x(\epsilon),\epsilon) - E_{\mathcal{B}}(x(\epsilon),\epsilon) \ = \ 0.$$

Therefore, for small ϵ, the perturbed energy levels $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ still cross and an avoided crossing cannot occur." From here, we will only consider situations where $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ correspond to equivalent representations and corepresentations.

"Type 1 Avoided Crossings: Γ has codimension 1 and $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ both have multiplicity 1, and the corepresentations are *Type I*.

Type 2 Avoided Crossings: Γ has codimension 1 and $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ both have multiplicity 2, and the corepresentations are either *Type II* or *Type III*.

Type 3 Avoided Crossings: Γ has codimension 2 and $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ both have multiplicity 1, and the corepresentations are *Type I*.

Type 4 Avoided Crossings: Γ has codimension 2 and $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ both have multiplicity 2, and the corepresentations are either *Type II* or *Type III*.

Type 5 Avoided Crossings: Γ has codimension 3 and $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ both have multiplicity 2, and the corepresentations are *Type II*.

Type 6 Avoided Crossings: Γ has codimension 4 and $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ both have multiplicity 2, and the corepresentations are *Type II*."

Note that when $\operatorname{codim}(\Gamma) \geq 3$, generic avoided crossings cannot arise unless G contains anti-unitary operators and the corepresentaition for the eigenvalues is of *Type II*. Therefore in these cases, we can only have an avoided crossing if the eighenvalues have minimal multiplicity 2. Avoided crossings cannot occur on any system where $\operatorname{codim}(\Gamma) \geq 5$. Hence we have classified all possible avoided crossings.

Type 1 Avoided Crossings

Consider the Schrödinger equation

$$i\epsilon^2 \frac{\partial}{\partial t}\phi(x,t) \;=\; -\frac{\epsilon^4}{2}\Delta\psi(x,t) + h(x,\epsilon)\psi(x,t). \tag{2.23}$$

Type 1 avoided crossings are the simplest type of avoided crossings. Since the two levels are isolated from the rest of the spectrum, we can write the rank 2 spectral projection onto the spectral subspace corresponding to the two eigenvalues with contour integration of the resolvent of $h(x, \epsilon)$.

$$P(x, \epsilon) \;=\; \frac{1}{2\pi i}\int_\gamma (z - h(x, \epsilon))^{-1} dz$$

where γ is a path surrounding the two eigenvalues.

Without loss of generality, we can assume $0 \in \Gamma \subset \mathbb{R}^n$. The resolvent of $h(x, \epsilon)$ is C^2, Γ has a well defined tangent plane at $x = 0$. We choose a coordinate system such that the x_2, x_3, ..., x_n axes are tangent to Γ at $x = 0$ and x_1 is perpendicular to Γ at $x = 0$.

Next we choose $\{\psi_1,\ \psi_2\}$ to be an orthonormal basis of the range of $P(0, 0)$. Let

$$\psi_1(x, \epsilon) \;=\; \frac{P(x, \epsilon)\psi_1}{\|P(x, \epsilon)\psi_1\|},$$

and let $P_1(x, \epsilon)$ be the orthogonal projection onto $\psi_1(x, \epsilon)$. Note that the projections $P(x, \epsilon)$ and $P_1(x, \epsilon)$ commute. Then, as in [39], let

$$''\psi_1(x, \epsilon) \;=\; \frac{(1 - P_1(x, \epsilon))P(x, \epsilon)\psi_2}{\|(1 - P_1(x, \epsilon))P(x, \epsilon)\psi_2\|}.$$

Then $\{\psi_1(x, \epsilon),\ \psi_2(s, \epsilon)\}$ is an orthonormal basis for the range of $P(x, \epsilon)$ for small $\|x\|$ and small ϵ.

The range of $P(x, \epsilon)$ is an invariant subspace for $h(x, \epsilon)$. In the basis of $\{\psi_1(x, \epsilon),\ \psi_2(s, \epsilon)\}$, the restriction of $h(x, \epsilon)$ to the range of $P(x, \epsilon)$ is given by a $2{\times}2$ matrix $h_1(x, \epsilon)$. Let us define

$$h_2(x, \epsilon) \;=\; h_1(x, \epsilon) - \frac{1}{2}(E_{\mathcal{A}}(x, \epsilon) + E_{\mathcal{B}}(x, \epsilon))I,$$

where I is the $2{\times}2$ identity matrix. $h_2(x, \epsilon)$ is a self-adjoint $2{\times}2$ matrix valued function with 0 trace. Since $E_{\mathcal{A}}(0, 0) = E_{\mathcal{B}}(0, 0)$, $h_2(0, 0) = 0_{2\times 2}$.

Since the resolvent of $h(x,\epsilon)$ is C^2, we know $h_2(x,\epsilon)$ is also C^2 in x and ϵ for small $\|x\|$ and ϵ. Hence for small $\|x\|$ and ϵ, with a first order Taylor series, we have

$$h_2(x,\epsilon) \;=\; Bx_1 + C\epsilon + O(x^2+\epsilon^2)$$

where B and C are 2×2 traceless self-adjoint matrices." We can make a change of basis independent of x and ϵ by the spectral theorem so that B is diagonal. Let us call the new basis $\{\phi_1(x,\epsilon),\ \phi_2(x,\epsilon)\}$. For a generic avoided crossing, we will assume B is not 0. In the new basis, $h_2(x,\epsilon)$ can be written in the form

$$h_3(x,\epsilon) \;=\; \begin{pmatrix} b_1 & 0 \\ 0 & -b_1 \end{pmatrix} x_1 + \begin{pmatrix} b_2 & c_2+id_2 \\ c_2-id_2 & -b_2 \end{pmatrix} \epsilon + O(x^2+\epsilon^2).$$

If we replace $\phi_2(x,\epsilon)$ with $e^{i\theta}\phi_2(x,\epsilon)$ for the appropriate θ, we can arrange the terms so that in this final basis, $h_2(x,\epsilon)$ is represented by

$$h_4(x,\epsilon) \;=\; \begin{pmatrix} b_1x_1+b_2\epsilon & \tilde{c_2}\epsilon \\ \tilde{c_2}\epsilon & -b_1x_1-b_2\epsilon \end{pmatrix} + O(x^2+\epsilon^2).$$

From this we find the following.

$$E_{\mathcal{A}}(x,\epsilon) - E_{\mathcal{B}}(x,\epsilon) \;=\; 2\sqrt{(b_1x_1+b_2\epsilon)^2+(\tilde{c_2}\epsilon)^2} + O(x^2+\epsilon^2),$$

and $h_1(x,\epsilon) - \frac{1}{2}\mathrm{tr}(h_1(x,\epsilon))$ is unitarily equivalent to the normal form of $h_4(x,\epsilon)$.

Note that the normal forms of the matrices are written as simply as possible. We cannot eliminate any other parameters by adjusting the bases. b_1 is the minimum eigenvalue gap divided by ϵ. b_2 is the scaling factor for the leading order dependence on ϵ of the location in

x of closest approach of the eigenvalues. $\tilde{c_2}$ is a scaling factor for the x_1 dependence of the eigenvalues.

For the purposes of our problem of interest, we will consider the case that the energy levels of the avoided crossing are of minimal mutliplicity and Γ has codimension 1. Without loss of generality, we may assume the crossing is at $x = 0$. We make the following decomposition, following the method of [39].

$$h(x, \epsilon) \;=\; h_{\|}(x, \epsilon) + h_{\perp}(x, \epsilon)$$

where

$$h_{\|}(x, \epsilon) \;=\; h(x, \epsilon)P(x, \epsilon)$$

and

$$h_{\perp}(x, \epsilon) \;=\; h(x, \epsilon)(I - P(x, \epsilon))$$

for $P(x, \epsilon)$ a spectral projector of $h(x, \epsilon)$ associated with $E_{\mathcal{A}}(x, \epsilon)$ and $E_{\mathcal{B}}(x, \epsilon)$. For a Type 1 avoided crossing where both eigenvalues have multiplicity 1, there is an orthonormal basis $\{\psi_1(x, \epsilon),\ \psi_2(x, \epsilon)\}$ of $P(x, \epsilon)\mathcal{H}$, which is regular in (x, ϵ) around the crossing set $(0, 0)$. In this basis, $h_{\|}(x, \epsilon)$ is written in the form

$$\begin{aligned} h_{\|}(x, \epsilon) &= h_1(x, \epsilon) + \tilde{V}(x, \epsilon) \qquad (2.24) \\ &= \begin{pmatrix} \beta(x, \epsilon) & \gamma(x, \epsilon) + i\delta(x, \epsilon) \\ \gamma(x, \epsilon) + i\delta(x, \epsilon) & -\beta(x, \epsilon) \end{pmatrix} + \tilde{V}(x, \epsilon). \end{aligned}$$

$\tilde{V}(x, \epsilon) =$trace$(h(x, \epsilon)P(x, \epsilon))$ is a regular function of (x, ϵ) around the origin and

$$\beta(x, \epsilon) \;=\; b_1 x_1 + b_2 \epsilon + O(2)$$

$$
\begin{aligned}
\gamma(x,\epsilon) &= c_2\epsilon + O(2) \\
\delta(x,\epsilon) &= O(2) \\
\tilde{V}(x,\epsilon) &= O(0),
\end{aligned}
$$

where $b_1 > 0,\ c_2 > 0,\ b_2 \in \mathbb{R}$, and $O(m) = O\left(\left(\sum_{j=0}^{n} x_j^2\right)^{m/2}\right)$ with $x_0 = \epsilon$.

It is convenient to make a change of variables to avoid the ϵ-dependence in the leading order of $\beta(x,\epsilon)$. Let us define the new variables $x',\ \epsilon'$, and t' as follows.

$$
\begin{aligned}
x' &= b_1 x + \begin{pmatrix} b_2\epsilon \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\
\epsilon' &= c_2\epsilon \\
t' &= \frac{b_1^2}{c_2^2} t
\end{aligned}
$$

Also let

$$
\phi(x',t') = \psi(x(x',\epsilon'), t(t')).
$$

The Schrödinger equation in terms of these new variables becomes

$$
i\epsilon'^2 \frac{\partial}{\partial t'}\phi(x',t') = -\frac{\epsilon'^4}{2}\Delta\phi(x',t') + \frac{c_2^4}{b_1^2} h(x(x',\epsilon'),\epsilon(\epsilon'))\phi(x',t')
$$

in the limit $\epsilon' \to 0$, and

$$
h_{\parallel}(x(x',\epsilon'),\epsilon(\epsilon')) = \begin{pmatrix} x_1' & \epsilon' \\ \epsilon' & -x_1' \end{pmatrix} + O(2) + \tilde{V}(x(x',\epsilon'),\epsilon(\epsilon'))
$$

where $\tilde{V}(x(x', \epsilon'), \epsilon(\epsilon')$ is also regular in (x', ϵ') around the origin and $O(2)$ refers to x' and ϵ'. We define the fixed parameter $r = \dfrac{c_2^4}{b_1^2} > 0$. From here we will drop the prime notation for the new variables. Then $h_1(x, \epsilon)$ has the same form as previously, but with

$$\begin{aligned} \beta(x, \epsilon) &= r x_1 + O(2) \\ \gamma(x, \epsilon) &= r\epsilon + O(2) \\ \delta(x, \epsilon) &= O(2) \\ \tilde{V}(x, \epsilon) &= O(0). \end{aligned} \tag{2.25}$$

2.3.3 Semiclassical Mechanics

We will use semiclassical wave packets as we did when studying the conical intersections. First, let us study the classical mechanics, classical action, and matricies A and B describing the uncertainties of position and momentum of the wave packets. We will study the small ϵ asymptotics of these quantities. The proofs of all of the lemmas and theorems can be found in [39]. Define

$$V^{\mathcal{A},\mathcal{B}}(x, \epsilon) = \tilde{V}(x, \epsilon) \pm \sqrt{\beta^2(x, \epsilon) + \gamma^2(x, \epsilon) + \delta^2(x, \epsilon)}.$$

Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions to the classical equations of motion for $\mathcal{C} = \mathcal{A}, \mathcal{B}$.

$$\frac{d}{dt} a^{\mathcal{C}}(t) = \eta^{\mathcal{C}}(t) \tag{2.26}$$

$$\frac{d}{dt} \eta^{\mathcal{C}}(t) = -\nabla V^{\mathcal{C}}(a^{\mathcal{C}}(t), \epsilon) \tag{2.27}$$

with initial conditions

$$a^{\mathcal{C}}(t) \;=\; 0$$

$$\eta^{\mathcal{C}}(t) \;=\; \widetilde{\eta_0}(\epsilon)$$

with $\widetilde{\eta_0}(\epsilon) = \widetilde{\eta_0} + O(\epsilon)$ and $\widetilde{\eta}_{01} > 0$. Note that the $O(\epsilon)$ term depends on whether $\mathcal{C} = \mathcal{A}$ or $\mathcal{B}$. Also note that $|\beta(x,\epsilon)|$, $|\gamma(x,\epsilon)|$, and $|\delta(x,\epsilon)|$ are $O(0)$, and using $\frac{\beta}{\sqrt{\beta^2+\gamma^2+\delta^2}} \leq 1$ we have

$$\|\nabla V^{\mathcal{C}}(x,\epsilon)\| \;=\; O(0).$$

Therefore the solutions for the classical motion equations, (2.26)-(2.27), exist and are unique. Due to two different time scales, we implement matched asymptotic expansions. For $|t| \gg \epsilon$, we use a formal perturbation expansion for which the unperturbed problem is the classical equations associated with $V^{\mathcal{C}}(x,0)$. This provides the "incoming outer solution" for $t < 0$ and the "outgoing outer solution" for $t > 0$. The outer solutions are only valid for times t when $|t| \gg \epsilon$.

When $|t| \ll \epsilon^{2/3}$, we use a different expansion to find the "inner solutions" using a rescaled time $s = t/\epsilon$.

For these approximations to be valid, there must be a region where the inner solutions and outer solutions agree to the appropriate order of ϵ. Specifically, this matching region is where $\epsilon \ll |t| \ll \epsilon^{2/3}$.

Inner Solutions

We will begin with studying the behavior of the solutions to (2.26)-(2.27) when $|t|$ and ϵ are small.

Lemma 2.3.1. *[Lemma 2.1 of [39]] "Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions to (2.26)-(2.27). If ϵ and $|t|$ are small enough, we have*

$$\begin{cases} a^{\mathcal{C}}(t) &= \eta_0(\epsilon)t + O(t^2) \\ \eta^{\mathcal{C}}(t) &= \eta_0(\epsilon) + O(t) \end{cases}$$

as $t \to 0$, uniformly in ϵ."

If we replace $V^{\mathcal{C}}(x,\epsilon)$ with $\tilde{V}(x,\epsilon)$, we can find higher order terms in the asymptotics.

Lemma 2.3.2. *[Lemma 2.2 of [39]] "Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions to (2.26)-(2.27) with $V^{\mathcal{C}}(x,\epsilon) = \tilde{V}(x,\epsilon)$. If ϵ and $|t|$ are small enough, we have*

$$\begin{cases} a^{\mathcal{C}}(t) &= \eta_0(\epsilon)t + \nabla\tilde{V}(0,\epsilon)\frac{t^2}{2} + O(t^3) \\ \eta^{\mathcal{C}}(t) &= \eta_0(\epsilon) + \nabla\tilde{V}(0,\epsilon)t + O(t^2) \end{cases}$$

as $t \to 0$, uniformly in ϵ."

To solve the inner solutions, we use rescaled variables s and $z^{C}(s)$,

$$\begin{aligned} t &= \epsilon s \\ a^{C}(t) &= \epsilon z^{\mathcal{C}}(s). \end{aligned}$$

With these new variables, the classical motion equations from (2.26)-(2.27) become

$$\frac{d^2}{ds^2}z^C(s) = -\epsilon\nabla V^C(\epsilon z^{\mathcal{C}}(s),\epsilon) \quad (2.28)$$

$$\frac{d}{ds}z^{\mathcal{C}}(0) = \widetilde{\eta}_0(\epsilon) \quad (2.29)$$

$$z^C(0) = 0. \quad (2.30)$$

We make the ansatz that $z^{\mathcal{C}}(s) = z_0^{\mathcal{C}}(s) + \epsilon z_0^{\epsilon}(s) + \epsilon^2 x_1^{\mathcal{C}}(s) + ...$ For the order of accuracy desired, it is sufficient to use just the first two terms. Then we have $a^{\mathcal{C}}(t) = \epsilon z_0^{\mathcal{C}}(t/\epsilon) + \epsilon^2 z_1^{\mathcal{C}}(t/\epsilon)$ as the inner solution.

Proposition 2.3.3. *[Proposition 2.1 [39]] "Let $z^{\mathcal{C}}(s)$ be the solution of (2.28)-(2.30). We have the following asymptotic behaviors for small values of ϵ and ϵs^3:*

$$\begin{aligned} z^{\mathcal{C}}(s) &= z_0^{\mathcal{C}}(0) + \epsilon z_1^{\mathcal{C}}(s) + O(\epsilon^2 s^3) \\ \frac{d}{ds}z^{\mathcal{C}}(s) &= \frac{d}{ds}z_0^{\mathcal{C}}(s) + \epsilon\frac{d}{ds}z_1^{\mathcal{C}}(s) + O(\epsilon^2 s^2), \end{aligned}$$

where

$$\begin{aligned} z_0^{\mathcal{A},\mathcal{B}}(s) &= \widetilde{\eta}_0(\epsilon)s \\ z_1^{\mathcal{A},\mathcal{B}}(s) &= -\nabla\tilde{V}(0,\epsilon)\epsilon\frac{s^2}{2} \pm \left[\frac{r}{\widetilde{\eta}_{01}(\epsilon)}s - \frac{r}{2\widetilde{\eta}_0(\epsilon)s}\sqrt{(\widetilde{\eta}_0(\epsilon)s)^2+1}\right. \\ &\quad \left. + \frac{r}{2\widetilde{\eta}_0(\epsilon)^2}\ln\left(\widetilde{\eta}_{01}(\epsilon)s + \sqrt{(\widetilde{\eta}_0(\epsilon)s)^2+1}\right)\right]\begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix}." \end{aligned}$$

Corollary 2.3.4. *[Corollary 2.1 of [39]] "Further expanding we get in the same regime in the limit* $|s| \to \infty$

$$
\begin{aligned}
z^{\mathcal{A},\mathcal{B}}(s) &= \widetilde{\eta_0}(\epsilon)s - \nabla\tilde{V}(0,\epsilon)\epsilon\frac{s^2}{2} \pm \frac{r}{\widetilde{\eta_0}(\epsilon)}\epsilon s \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\
&\mp r\,sign(s)\left[\epsilon\frac{s^2}{2} + \epsilon\frac{\ln|s|}{2\widetilde{\eta_{01}}^2(\epsilon)} + \frac{\epsilon}{4\widetilde{\eta_{01}}^2(\epsilon)} + \frac{\epsilon\ln(2\widetilde{\eta_{01}}(\epsilon))}{2\widetilde{\eta_{01}}^2(\epsilon)}\right]\begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\
&+ O(\epsilon/s^2) + O(\epsilon^2 s^3)
\end{aligned}
$$

The asymptotics for $\frac{d}{ds}z^{\mathcal{C}}(s)$ *in the same regime are obtained by termwise differentiation of the above formulae up to errors* $O(\epsilon/s^3) + O(\epsilon^2 s^2)$*."*

So that the remainder terms tend to zero, we consider the inner solutions only when $s \leq \epsilon^{-\xi}$, with $0 < \xi < 1/3$.

Outer Solutions

We now want to consider times when $|t|$ is large compared to ϵ to determine the outer solutions. We make the assumption that the solutions have expansions of the form

$$a^{\mathcal{C}}(t) \;=\; a_0^{\mathcal{C}}(t) + g_1(\epsilon)a_1^{\mathcal{C}}(t) + g_2(\epsilon)a_2^{\mathcal{C}}(t) + ...$$

The form ϵ dependence of $g_j(\epsilon)$ is determined by the computations of matching the inner solutions in the matching region. We must consider the cases of $t < 0$ and $t > 0$ separately. The constants of integration are determined by the matching conditions. In order to obtain the desired order of accuracy, we may truncate the expansions after terms of order ϵ^2.

Proposition 2.3.5. *[Proposition 2.2 of [39]] "Let $a^{\mathcal{C}}(t)$ be the solution of (2.28)-(2.30). In the regime $\epsilon \to 0,\ t \to 0,\ |t|/\epsilon \to \infty$, and $t^3/\epsilon^2 \to 0$, we have the asymptotics*

$$a^{\mathcal{A},\mathcal{B}}(t) \;=\; -\nabla\tilde{V}(0,\epsilon)\frac{t^2}{2} + \widetilde{\eta}_0(\epsilon)t \pm \frac{r}{\widetilde{\eta}_{01}(\epsilon)}\epsilon t \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$\mp\, sign(t)\left[r\frac{t^2}{2} + \frac{\epsilon^2 \ln|t|}{2(\widetilde{\eta}_{01}(\epsilon))^2} + \frac{\epsilon^2}{4(\widetilde{\eta}_{01}(\epsilon))^2}(1 + 2\ln(2\widetilde{\eta}_{01}(\epsilon))) - \frac{\epsilon^2 \ln\epsilon}{2(\widetilde{\eta}_{01}(\epsilon))^2}\right] \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$+\, O(t^3) + O(\epsilon^4/t^2)$$

The asymptotics for $\eta^{\mathcal{C}}(t)$ in the same regime is obtained by termwise differentiation of the above formulae up to errors $O(t^2) + O(\epsilon^4/t^3)$."

Classical Action Integrals

We will need to calculate the small $|t|$ asymptotics of the classical action integrals associated with the outer solutions in order to obtain the quantum mechanical wave functions used in the solutions to the Schrödinger equation.

$$\begin{aligned} S^{\mathcal{C}}(t) &= \int_0^t \left(\frac{\eta^{\mathcal{C}2}(t')}{2} - V^C(a^{\mathcal{C}}(t'), \epsilon) \right) dt' \\ &= \int_0^t \eta^{\mathcal{C}2}(t')dt' - \widetilde{\eta_0}^2(\epsilon)\frac{t}{2} - V^{\mathcal{C}}(a^{\mathcal{C}}(0), \epsilon)t \end{aligned}$$

and let $S(t)$ be the same for $V^{\mathcal{C}}(x, \epsilon) = \tilde{V}(x, \epsilon)$.

Lemma 2.3.6. *[Lemma 2.3 of [39]] "As $t \to 0$,*

$$S(t) = \widetilde{\eta_0}^2(\epsilon)\frac{t}{2} - \tilde{V}(0, \epsilon)t - \widetilde{\eta_0}(\epsilon)\nabla\tilde{V}(0, \epsilon)t^2 + O(t^3)$$

uniformly in ϵ."

From the previous proposition and $V^{\mathcal{A},\mathcal{B}}(0, \epsilon) = \tilde{V}(0, \epsilon) \pm \epsilon r + O(\epsilon^2)$, we have the following.

Lemma 2.3.7. *[Lemma 2.4 of [39]] "In the regime $\epsilon \to 0,\ t \to 0,\ |t|/\epsilon \to \infty$, and $t^3/\epsilon^3 \to 0$, we have the asymptotics*

$$\begin{aligned} S^{\mathcal{A},\mathcal{B}}(t) &= S_0^{\mathcal{A},\mathcal{B}}(\epsilon, sign(t)) - \tilde{V}(0, \epsilon)t + \widetilde{\eta_0}^2(\epsilon)\frac{t}{2} - \widetilde{\eta_0}(\epsilon)\nabla\tilde{V})0, \epsilon)t^2 \pm t\epsilon t \\ &\quad \mp sign(t)\left(r\widetilde{\eta}_{01}(\epsilon)t^2 + \frac{r}{\widetilde{\eta}_{01}(\epsilon)}\epsilon^2 \ln|t| \right) + O(t^3) + O(\epsilon^4/t^2) + O(\epsilon^3 \ln t)." \end{aligned}$$

Initial Momenta

To be used later, we will assume that the solution of $a(t)$ in (2.26)-(2.27) with $V^{\mathcal{C}}(x,\epsilon) = \tilde{V}(x,\epsilon)$ is subject to the initial conditions

$$\begin{aligned} a(0) &= 0 \\ \eta(0) &= \widetilde{\eta_0} \end{aligned}$$

while $a^{\mathcal{C}}(t)$ is subject to the initial conditions

$$\begin{aligned} a^{\mathcal{C}}(0) &= 0 \\ \eta^{\mathcal{C}}(0) &= \widetilde{\eta_0}(\epsilon) = \widetilde{\eta_0} + O(\epsilon) \end{aligned}$$

We must include the $O(\epsilon)$ term in the calculations because when the electrons transition from one energy level surface to another, the nuclei compensate by adjusting their kinetic energy so that the total energy of the system is conserved. We get the following corollaries.

Corollary 2.3.8. *[Corollary 2.2 of [39]] "When* $\epsilon \to 0,\ t \to 0,\ t^3/\epsilon^2$*, and* $|t|/\epsilon \to \infty$*, we have*

$$\begin{aligned} \eta^{\mathcal{A},\mathcal{B}}(t)(a(t) - a^{\mathcal{A},\mathcal{B}}(t)) &= \mp r\epsilon t - (\widetilde{\eta_0}(\epsilon) - \widetilde{\eta_0})\widetilde{\eta_0}(\epsilon)t \\ &\pm sign(t)\left[\frac{r\widetilde{\eta}_{01}(\epsilon)}{2}t^2 + \frac{r}{2\widetilde{\eta}_{01}(\epsilon)}(\epsilon^2 \ln|t| + \epsilon^2(\ln(2\widetilde{\eta}_{01}(\epsilon)) + \frac{1}{2}) - \epsilon^2 \ln\epsilon)\right] \\ &+ O(t^3) + O(\epsilon^4/t^2) + O(t\epsilon^2 \ln\epsilon)." \end{aligned}$$

Corollary 2.3.9. *[Corollary 2.3 of [39]] "When* $\epsilon \to 0,\ t \to 0,\ t^3/\epsilon^2$*, and* $|t|/\epsilon \to \infty$*, we have*

$$S^{\mathcal{A},\mathcal{B}}(t) = S_0^{\mathcal{A},\mathcal{B}}(\epsilon, sign(t)) + S(t) \pm r\epsilon t - (\widetilde{\eta_0}^2(\epsilon) - \widetilde{\eta_0})\frac{t}{2}$$

$$\mp\, sign(t)\left(\frac{r\widetilde{\eta}_{01}(\epsilon)}{2}t^2+\frac{r}{\widetilde{\eta}_{01}(\epsilon)}\epsilon^2\ln|t|\right)$$

$$+\,O(t^3)+O(\epsilon^4/t^2)+O(\epsilon^3\ln t).\text{''}$$

Uncertainty Matrices

We also need the formulas for matrices $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ for the semiclassical wave packets that will be used. Let $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ be the $n\times n$ matrix solutions to the following system.

$$\begin{aligned}\frac{d}{dt}A^{\mathcal{C}}(t) &= iB^{\mathcal{C}}(t)\\ \frac{d}{dt}B^{\mathcal{C}}(t) &= iV^{(2)}(a^{\mathcal{C}}(t),\epsilon)A^{\mathcal{C}}(t)\end{aligned}\tag{2.31}$$

subject to initial conditions

$$\begin{aligned}A^{\mathcal{C}}(0) &= A_0\\ B^{\mathcal{C}}(0) &= B_0\end{aligned}$$

where $a^{\mathcal{C}}(t)$ is the solution to (2.26)-(2.27) discussed previously.

We will determine the leading order behavior of $V^{(2)}(a^{\mathcal{C}}(t),\epsilon)$ for small $|t|$ and ϵ.

$$V^{(2)}(a^{\mathcal{C}}(t),\epsilon) \;=\; \left(\sqrt{\beta^2+\gamma^2+\delta^2}\right)^{(2)} \;=\; \frac{(\delta^2+\gamma^2)|\nabla\beta\rangle\langle\nabla\beta|+O(3)}{(\beta^2+\gamma^2+\delta^2)^{3/2}}.$$

Explicitly,

$$\left(\sqrt{\beta^2(x,\epsilon)+\gamma^2(x,\epsilon)+\delta^2(x,\epsilon)}\right)^{(2)} \;=\; \frac{r\epsilon^2P+O(3)}{(x_1^2+\epsilon^2+O(3))^{3/2}}$$

where

$$P = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & 0 \end{pmatrix}.$$

When we replace x with $a^{\mathcal{C}}(t) = \widetilde{\eta}_0(\epsilon)t + O(t^2)$, the error terms $O(3)$ become $O((|t| + \epsilon)^3)$. Using $|a^{\mathcal{C}}(t)| \geq c|t|$, we have

$$(a^{\mathcal{C}}(t)^2 + \epsilon^2 + O(3))^{3/2} = ((\widetilde{\eta}_{01}(\epsilon)t)^2 + \epsilon^2)^{3/2}(1 + O(|t| + \epsilon)).$$

Thus the leading order behavior of $V^{(2)}(a^{\mathcal{C}}(t), \epsilon)$ as $\epsilon \to 0$ and $t \to 0$ is

$$V^{(2)}(a^{\mathcal{A},\mathcal{B}}(t), \epsilon) = \pm \frac{r\epsilon}{((\widetilde{\eta}_{01}(\epsilon)t)^2 + \epsilon^2)^{3/2}} P + O(\epsilon^0 + t^0).$$

Therefore, $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ are regular as $t \to 0$ for any positive ϵ.

Proposition 2.3.10. *[Proposition 2.3 of [39]] "Let $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ be the solutions to (2.31). For t and ϵ small enough, we have*

$$A^{\mathcal{A},\mathcal{B}}(t) = A_0 + O(t)$$

$$B^{\mathcal{A},\mathcal{B}}(t) = B_0 \pm irPA_0 \frac{t}{\sqrt{(\widetilde{\eta}_{01}(\epsilon)t)^2 + \epsilon^2}} + O(t)$$

uniformly in ϵ."

Corollary 2.3.11. *[Corollary 2.4 of [39]] "In the regime $\epsilon \to 0$, $t \to 0$, and $|t|/\epsilon \to \infty$, we have*

$$B^{\mathcal{A},\mathcal{B}}(t) = B_0 \mp sign(t) \frac{ir}{\widetilde{\eta}_{01}(\epsilon)} PA_0 + O(t) + O(\epsilon^2/t^2)$$

$$= B^{\mathcal{A},\mathcal{B}}(sign(t)) + O(t) + O(\epsilon^2/t^2)."$$

2.3.4 Type 1 Avoided Crossings

We will use the same semiclassical wave packets as previously defined for the solutions to the Schrödinger equation as $\epsilon \to 0$.

$$\begin{aligned}\phi_l(A,B,\hbar,a,\eta,x) &= 2^{-|l|/2}(l!)^{-1/2}\pi^{-n/4}\hbar^{-n/4}[\det\ A]^{1/2} \\ &\quad \cdot \mathcal{H}_l(A;\hbar^{-1/2}|A|^{-1}(x-a)) \\ &\quad \cdot \exp\left\{-\frac{\langle (x-a),\ BA^{-1}(x-a)\rangle}{2\hbar} + i\frac{\langle \eta,\ (x-a)\rangle}{\hbar}\right\}.\end{aligned}$$

or alternatively,

$$\phi_{k+1}(A,B,\hbar,a,\eta,\cdot) = \frac{1}{\sqrt{k+1}}\mathcal{A}(A,B,\hbar,a,\eta)^*\phi_k(A,B,\hbar,a,\eta,\cdot).$$

with

$$\phi_0(A,B,\hbar,a,\eta,x) = \pi^{-1/4}\hbar^{-1/4}A^{-1/2}\exp\left\{\frac{-BA^{-1}(x-a)^2}{2\hbar} + \frac{i\eta(x-a)}{\hbar}\right\}.$$

See section 2.1 for details on these formulea.

Lemma 2.3.12. *[Lemma 3.1 of [39]] "We have, in the $L^2(\mathbb{R}^n)$ sense,*

$$\begin{aligned}\phi_l(A,B,\epsilon^2,a,0,x) &= \phi_l(A_0,B_0,\epsilon^2,a_0,0,x) \\ &\quad + O(\|A-A_0\| + \|B-B_0\| + \|a-a_0\|/\epsilon)."\end{aligned}$$

2.3.5 Choice of Eigenvectors

Now we will describe the process of choosing the electronic eigenvectors and their phases. The electronic Hamiltonian is time dependent, but to use specific time dependent eigenvectors, we will consider the time-dependent Schrödinger equation. The electrons react to the motion of the nuclei in an adiabatic manner, so the appropriate instantaneous electronic eigenvectors must satisfy a parallel transport condition. The classical trajectories become singular as the corresponding eigenvalues are degenerate (or almost degenerate) thus we will define them for t in the outer regime. We define the eigenvectors by $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$, where $\mathcal{C} = \mathcal{A}, \mathcal{B}$ and $\pm$ refers to $t > 0$ and $t < 0$.

Let $\eta^{\mathcal{C}}(t)$ be the solutions to the classical momentum equations found in the previous section. The normalized eigenvectors are the solutions of

$$\langle \Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon) | (\partial/\partial t + \eta^{\mathcal{C}}(t) \nabla) \Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon) \rangle \;=\; 0. \tag{2.32}$$

The eigenvalues $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ are non-degenerate for any time t small enough, therefore these eigenvectors exist and are unique up to a phase factor.

Let us define the angles $\varphi(x,\epsilon)$ and $\theta(x,\epsilon)$ by

$$\begin{aligned}
\beta(x,\epsilon) &= \sqrt{\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)}\,\cos(\theta(x,\epsilon)) \\
\gamma(x,\epsilon) &= \sqrt{\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)}\,\sin(\theta(x,\epsilon))\cos(\varphi(x,\epsilon)) \\
\delta(x,\epsilon) &= \sqrt{\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)}\,\sin(\theta(x,\epsilon))\sin(\varphi(x,\epsilon)).
\end{aligned}$$

Then the static eigenvectors of $h_1(x,\epsilon)$ for $\pi/2 < \theta(x,\epsilon) \leq \pi$ are given by

$$\begin{aligned}
\Phi^{-}_{\mathcal{A}}(x,\epsilon) &= e^{i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon) + \sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon) \\
\Phi^{-}_{\mathcal{B}}(x,\epsilon) &= e^{-i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_2(x,\epsilon) + \sin(\theta(x,\epsilon)/2)\psi_1(x,\epsilon).
\end{aligned}$$

For $0 \leq \theta(x,\epsilon) < \pi/2$, the eigenvectors are given by

$$\begin{aligned}\Phi^+_{\mathcal{A}}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon) + e^{-i\varphi(s,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon)\\ \Phi^+_{\mathcal{B}}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_2(x,\epsilon) - e^{i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_1(x,\epsilon).\end{aligned}$$

Therefore, the solutions to (2.32) are of the form

$$\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon) = \Phi^{\pm}_{\mathcal{C}}(x,\epsilon)e^{i\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon)}$$

where $\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon)$ is a real valued function which satisfies

$$i\frac{\partial}{\partial t}\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon) + i\eta^{\mathcal{C}}(t)\nabla\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon) + \langle\Phi_{\mathcal{C}}(x,\epsilon)|\eta^{\mathcal{C}}(t)\nabla\Phi_{\mathcal{C}}(x,\epsilon)\rangle = 0.$$

Lemma 2.3.13. *[Lemma 3.2 of [39]] "Let $\eta^{\mathcal{C}}(t)$ be the momentum solution of the classical equations of motion. There exist eigenvectors $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$, $\mathcal{C} = \mathcal{A},\mathcal{B}$, such that*

$$\langle\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)|(\partial/\partial t + \eta^{\mathcal{C}}(t)\nabla)\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)\rangle = 0.$$

If $\|x\| = O(\epsilon^{\kappa})$, $x_1 \gtrless 0$, with $2/3 < \kappa < 1$,

$$\left|\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon) - \Phi^{\pm}_{\mathcal{C}}(x,\epsilon)\right| = O(t/\epsilon^{1-\kappa})."$$

In the semiclassical regime, the nuclear wave function is localized around the classical trajectory. Since $\widetilde{\eta}_{01} > 0$, during the times of the outer regime, the major part of the nuclear wave function is supported away from the crossing set. Hence we define a cutoff function which does not significantly alter the solution and will force the support of the wave function away from the crossing set. Let F be a C^{∞} cutoff function

$$F : \mathbb{R}^+ \to \mathbb{R}$$

such that

$$\begin{cases} F(r) = 1 & 0 \le r \le 1 \\ F(r) = 0 & r \ge 2 \end{cases}$$

In the outer regime, we will multiply the wave functions by $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$ where $\delta' < \xi$.

If $\xi < 2/3 < \kappa < 1 - \xi$, the correction terms in Lemma (2.3.13) tend to zero and the set $\|x\| = O(\epsilon^{\kappa})$ includes the set $\|x - a^{\mathcal{C}}(t)\| = O(\epsilon^{1-\delta'})$. On the support of F,

$$x = \widetilde{\eta}_0(\epsilon)t + O(\epsilon^{1-\delta'} + t^2)$$

and since $\widetilde{\eta}_{01}(\epsilon) = \widetilde{\eta}_{01} + O(\epsilon)$, where $\widetilde{\eta}_{01} > 0$, we know that $|x_1| > c|t|$ uniformly in ϵ. Using this, we have the following.

Lemma 2.3.14. *[Lemma 3.3 of [39]] "For x in the support of $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, $\mathcal{C} = \mathcal{A}, \mathcal{B}$, we have for $t < 0$,*

$$\begin{aligned} \Phi^-_{\mathcal{A}}(x,\epsilon) &= \psi_2(x,\epsilon) + O(\epsilon/t^{1/2}) \\ \Phi^-_{\mathcal{B}}(x,\epsilon) &= -\psi_1(x,\epsilon) + O(\epsilon/t^{1/2}), \end{aligned}$$

and for $t > 0$,

$$\begin{aligned} \Phi^+_{\mathcal{A}}(x,\epsilon) &= \psi_1(x,\epsilon) + O(\epsilon/t^{1/2}) \\ \Phi^+_{\mathcal{B}}(x,\epsilon) &= \psi_2(x,\epsilon) + O(\epsilon/t^{1/2}).\text{"} \end{aligned}$$

2.3.6 The Incoming Outgoing Solution

Let us assume that at our initial time, $-T$, the wave function is given by

$$\psi(x,-T) = e^{iS^{\mathcal{B}}(-T)/\epsilon^2}\phi_l(A^{\mathcal{B}}(-T), B^{\mathcal{B}}(-T), \epsilon^2, a^{\mathcal{B}}(-T), \eta^{\mathcal{B}}(-T), x)\Phi_{\mathcal{B}}(x,\epsilon).$$

The associated classical quantities have the following initial conditions.

$$a^{\mathcal{B}}(0) = 0 \tag{2.33}$$

$$\eta^{\mathcal{B}}(0) = \widetilde{\eta_0} \tag{2.34}$$

$$A^{\mathcal{B}}(0) = A_0 \tag{2.35}$$

$$B^{\mathcal{B}}(0) = B_0 \tag{2.36}$$

$$S^{\mathcal{B}}(0) = 0 \tag{2.37}$$

and we assume that A_0 and B_0 satisfy the requirements in the definition of the wave packets ϕ_l. The standard time-dependent Born-Oppenheimer wave packets approximate the solution to the Schrödinger equation to an acceptable error when far from the avoided crossing of the electronic levels. However, these fail to sufficiently approximate the solution when close to the avoided crossing. The following lemma describes explicitly how close to the crossing the standard wave packets are an acceptable approximation.

Lemma 2.3.15. *[Lemma 3.4 of [39]] "In the incoming outer time regime, $-T \leq t \leq -\epsilon^{1-\xi}$, there is an approximation $\psi_{IO}(x,t)$ of a solution of the Schrödinger equation $\psi(x,t)$ of the form*

$$\psi_{IO}(x,t) = F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'}) \exp\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2} + i\frac{\eta^{\mathcal{B}}(t)(x, a^{\mathcal{B}}(t))}{\epsilon^2}\right)$$

$$\times\phi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), 0, x)\Phi^-_{\mathcal{B}}(x,t,\epsilon)$$

such that

$$\psi(x,t) = \psi_{IO}(x,t) + R(x,t,\epsilon)$$

where

$$R(x,t,\epsilon) = O(\epsilon^{\xi})$$

in the $L^2(\mathbb{R}^n)$ *sense, as* $\epsilon \to 0$*."*

2.3.7 The Inner Solutions

For the inner time regime, we construct the solution using the classical quantities associated with the potential $\tilde{V}(x,\epsilon)$. The initial conditions for these quantities are

$$\begin{aligned} a(0) &= 0 \\ \eta(0) &= \widetilde{\eta_0} \\ S(0) &= 0. \end{aligned}$$

We will use rescaled variable y and s defined by

$$\begin{cases} y = (x - a(t))/\epsilon \\ s = t/\epsilon \end{cases}$$

In these variables, the Schrödinger equation is given by

$$i\epsilon\frac{\partial}{\partial s}\psi - i\epsilon\eta(\epsilon s)\nabla_y\psi = -\frac{\epsilon^2}{2}\Delta_y\psi + h(a(\epsilon s) + \epsilon y, \epsilon)\psi.$$

We want to find solutions of the form

$$F(\|y\|\epsilon^{\delta'})\exp\left(i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{\eta(\epsilon s)y}{\epsilon}\right)\chi(y,s,\epsilon)$$

with

$$\chi(y,s,\epsilon) = \{f(y,s,\epsilon)\psi_1(a(\epsilon s)+\epsilon y,\epsilon) + g(y,s,\epsilon)\psi_2(a(\epsilon s)+\epsilon y,\epsilon) + \psi_\perp(a(\epsilon s)+\epsilon y,\epsilon)\},$$

where $\psi_\perp(x,\epsilon) \in (I - P(x,\epsilon))\mathcal{H}$, and f, g are scalar functions. Inserting this form into the Schrödinger equation, we have

$$\begin{aligned}
& i\epsilon\frac{\partial}{\partial s}f + i\epsilon\psi_2\frac{\partial}{\partial s}g + i\epsilon\frac{\partial}{\partial s}\psi_\perp + (\tilde{V}(a) + \epsilon y\nabla_x\tilde{V}(a))(f\psi_1 + g\psi_2 + \psi_\perp) \\
& + i\epsilon^2 f\eta\nabla_x\psi_1 + i\epsilon^2 g\eta\nabla_x\psi_2 + i\epsilon^2\eta\nabla_x\psi_\perp \\
= & -\epsilon^4\Delta_x\psi_\perp/2 - \epsilon^4 f\Delta_x\psi_1/2 - \epsilon^4 g\Delta_x\psi_2/2 - \epsilon^3\nabla_y f\nabla_x\psi_1 \\
& - \epsilon^3\nabla_y g\nabla_x\psi_2 - \epsilon^2\psi_1\Delta_y f - \epsilon^2\psi_2\Delta_y g + h_1(f\psi_1 + g\psi_2) \\
& + \tilde{V}(a + \epsilon y)(f\psi_1 + g\psi_2 + \psi_\perp).
\end{aligned}$$

We assume the functions have the following expansions.

$$\begin{aligned}
f(y,s,\epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)f_j(y,s), \\
g(y,s,\epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)g_j(y,s), \\
\psi_\perp(x,t,\epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)\psi_{\perp j}(x,t),
\end{aligned}$$

where the ϵ dependence of $\nu_j(\epsilon)$ depends on the matching conditions. With these expansions, the Schrödinger equation, after dropping higher order terms, becomes

$$\begin{aligned}
& i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0(y,s)\psi_1(a(\epsilon s) + \epsilon y, \epsilon) + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0(y,s)\psi_2(a(\epsilon s) + \epsilon y, \epsilon) \\
= & \; h_\perp(a(\epsilon s) + \epsilon y, \epsilon)\psi_\perp(a(\epsilon s) + \epsilon y, \epsilon) \\
& + \epsilon\nu_0(\epsilon)h_{11}(y,s)(f_0(y,s)\psi_1(a(\epsilon s) + \epsilon y, \epsilon) + g_0(y,s)\psi_2(a(\epsilon s) + \epsilon y, \epsilon))
\end{aligned}$$

on the support of F. Here $h_{11}(y,s)$ is the operator on the span of $\{\psi_1(a(\epsilon s)+\epsilon y,\epsilon),\psi_2(a(\epsilon s)+\epsilon y,\epsilon)\}$ whose matrix values in this basis are given by

$$r\begin{pmatrix}\widetilde{\eta}_{01}s+y_1 & 1\\ 1 & -\widetilde{\eta}_{01}s-y_1\end{pmatrix}.$$

In order to match the incoming outer solution, we have

$$\nu_j(\epsilon)h_\perp(a(\epsilon s)+\epsilon y,\epsilon)\psi_{\perp j}(a(\epsilon s)+\epsilon y,\epsilon) \;=\; 0$$

if $\nu_j(\epsilon)\ll\epsilon\nu_0(\epsilon)$, for $j=0,1,2,...,m-1$. Since the spectrum of $h_\perp(x,\epsilon)$ is bounded away from 0 in a neighborhood of $(0,0)$, we must have

$$\psi_{\perp j}(x,t) \;=\; 0, \quad j=0,1,2,...,m-1.$$

For the remaining order, with $\epsilon\nu_0=v_m$,

$$\begin{aligned}&i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0\psi_1+i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0\psi_2\\ &=\nu_m(\epsilon)h_\perp\psi_\perp+\epsilon\nu_0(\epsilon)h_{11}(f_0\psi_1+g_0\psi_2)\end{aligned}$$

becomes

$$i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0\psi_1+i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0\psi_2 \;=\; \epsilon\nu_0(\epsilon)h_{11}(f_0\psi_1+g_0\psi_2). \tag{2.38}$$

By projection with $P(x,\epsilon)$ and $(I-P(x,\epsilon))$,

$$\nu_m(\epsilon)h_\perp\psi_{\perp m}=0,$$

which implies $\psi_{\perp m}=0$.

(2.38) is equivalently,

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix} = r\begin{pmatrix} \widetilde{\eta}_{01}s + y_1 & 1 \\ 1 & -\widetilde{\eta}_{01}s - y_1 \end{pmatrix}\begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix}.$$

The solution of these equations can be found in terms of parabolic cylinder functions $D_\nu(\cdot)$ with methods from [27].

$$\begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix} = C_1(y)\begin{pmatrix} \frac{(1-i)}{2}\sqrt{\frac{r}{\widetilde{\eta}_{01}}}D_{\frac{ir}{2\widetilde{\eta}_{01}}-1}\left((-1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right) \\ D_{\frac{ir}{2\widetilde{\eta}_{01}}}\left((-1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right) \end{pmatrix}$$

$$+ C_2(y)\begin{pmatrix} D_{\frac{ir}{2\widetilde{\eta}_{01}}}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}sy_1)\right) \\ -\frac{(1+i)}{2}\sqrt{\frac{r}{\widetilde{\eta}_{01}}}D_{-\frac{ir}{2\widetilde{\eta}_{01}}-1}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right) \end{pmatrix}$$

We define the approximation of the inner solution by

$$\begin{aligned} \psi_1(y,s) &= F(\|y\|\epsilon^{\delta'})\exp\left(i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{\eta(\epsilon s)y}{\epsilon}\right) \\ &\quad \times [\nu_0(\epsilon)f_0(y,s)\psi_1(a(\epsilon s)+\epsilon y,\epsilon) + \nu_0(\epsilon)g_0(y,s)\psi_2(a(\epsilon s)+\epsilon y,\epsilon)]. \end{aligned}$$

To begin with a vector along the B level for $t < 0$, we need $g_0(y,s) \to 0$ as $s \to -\infty$.

We note that $\|y\|/s = O(\epsilon^{\xi-\delta'}) \to 0$. With the cutoff function,

$$D_{\frac{ir}{2\widetilde{\eta}_{01}}}\left((-1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right) = e^{i\lambda(y,s)}e^{\frac{\pi r}{8\widetilde{\eta}_{01}}}(1 + O(1/(s+\|y\|)^2))$$

as $s \to -\infty$, for $\lambda(y,s) \in \mathbb{R}$. Thus $C_1(y) = 0$.

Further,

$$D_{-\frac{ir}{2\widetilde{\eta}_{01}}}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right)$$

$$= \exp\left\{-\frac{ir}{2\widetilde{\eta}_{01}}((\widetilde{\eta}_{01}s)^2 + 2y_1\widetilde{\eta}_{01}s + y_1^2 + \ln|s| + \ln(2r\widetilde{\eta}_{01})/2)\right\}$$

$$\times e^{r\pi}2\widetilde{\eta}_{01}(1 + O(\|y\|/s) + O(1/s^2))$$

and

$$D_{-\frac{ir}{2\widetilde{\eta}_{01}}-1}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right) \;=\; O(1/(s + \|y\|))$$

as $s \to -\infty$.

In the matching region where $t = \epsilon s,\ s = -\epsilon^{-\xi},\ y = O(\epsilon^{-\delta'},\ x = O(\epsilon^{\kappa})$ with $0 < \delta' < \xi < 1/3,\ 2/3 < \kappa < 1 - \xi$, we match $\psi_I(y, s)$ with $\psi_{IO}(x, t)$.

We consider the incoming outer solution $\psi_{IO}(x, t)$ as $t, \epsilon \to 0$ and write the results in terms of the scaled variables (y, s). Noting that $(a^{\mathcal{B}}(t) - a(t))/\epsilon = O(t^2/\epsilon) = O(\epsilon s)$, we find the following.

$$F(\|y^{\mathcal{B}}\|\epsilon^{\delta'}) \;=\; F(\|y\|\epsilon^{\delta'} + O(\epsilon^{1+\delta'}s)) \;=\; F(\|y\|\epsilon^{\delta'}) + O(\epsilon^{1+\delta'}s)$$

Then applying Proposition (2.3.10) and it's Corollary (2.3.11), and Lemma (2.3.12), in the $L^2(\mathbb{R}^3)$ sense, we have

$$\phi_l(A^{\mathcal{B}}(t)), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), 0, x) = \epsilon^{-n/2}\phi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y) + O(\epsilon s) + O(1/s^2). \quad (2.39)$$

By using Corollary (2.3.9),

$$\exp\left\{i\frac{S^{\mathcal{B}}(\epsilon s)}{\epsilon^2}\right\} \;=\; \exp\left\{i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon, -)}{\epsilon^2} - irs - i\left(r\widetilde{\eta}_{01}s^2 + \frac{r}{\widetilde{\eta}_{01}}\ln(\epsilon|s|)\right)\right\}$$

$$\times\,(1 + O(\epsilon s^3) + O(1/s^2) + O(\epsilon\ln(\epsilon|s|))).$$

We also use Proposition (2.3.5) and Corollary (2.3.8) to approximate

$$\exp\left\{i\eta^{\mathcal{B}}(\epsilon s)\frac{x - a^{\mathcal{B}}(\epsilon s)}{\epsilon^2}\right\}$$

$$
\begin{aligned}
&= \exp\left\{ i\eta(\epsilon s)\frac{y}{\epsilon} + i(\eta^{\mathcal{B}}(\epsilon s) - \eta(\epsilon s))\frac{y}{\epsilon} + i\eta^{\mathcal{B}}(\epsilon s)\frac{a(\epsilon s) - a^{\mathcal{B}}(\epsilon s)}{\epsilon^2} \right\} \\
&= \exp\left\{ i\eta(\epsilon s)\frac{y}{\epsilon} - iy_1(r/\widetilde{\eta}_{01} + rs) \right\} \\
&\quad \times \exp\left\{ irs + i\frac{r\widetilde{\eta}_{01}}{2}s^2 + i\frac{r}{2\widetilde{\eta}_{01}}(\ln(\epsilon|s|) + \ln(2\widetilde{\eta}_{01}) + \frac{1}{2} - \ln\epsilon) \right\} \\
&\quad \times (1 + O(\epsilon s^3) + O(1/s^2) + O(\|y\|\epsilon s^2) + O(\|y\|/s) + O(\epsilon s \ln\epsilon))
\end{aligned}
$$

as $s \to -\infty$.

Lastly, using Lemma (2.3.13) and Lemma (2.3.14),

$$
\Phi_{\mathcal{B}}^{-}(x, \epsilon s, \epsilon) \; = \psi_1(x, \epsilon) + O(\epsilon^{1/2}/s^{1/2}) + O(s\epsilon^{\kappa}).
$$

Now we can perform the matching, assuming $\nu_0(\epsilon) = 1$ and

$$
\begin{aligned}
C_2(y) \;&=\; -\epsilon^{-n/2}\phi_l(A_0, B_0^B(-), 1, 0, 0, y)e^{-\frac{\pi r}{8\widetilde{\eta}_{01}}}\exp\left(\frac{ir}{2\widetilde{\eta}_{01}}(y_1^2 - 2y_1)\right) \\
&\quad \times \exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon, -)}{\epsilon^2} + \frac{ir}{4\widetilde{\eta}_{01}}(1 + 3\ln(2\widetilde{\eta}_{01}) + \ln r - 4\ln\epsilon)\right).
\end{aligned}
$$

Since $\phi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), 0, x)$ is normalized, we see that in the $L^2(\mathbb{R}^n)$ sense

$$
\psi_{IO}(a(\epsilon s) + \epsilon y, \epsilon s) \;=\; \psi_I(y, s) + O(\epsilon^p)
$$

for some positive number p.

To check the validity of the inner solution approximation, we return to the original variables (x, t) and set

$$
\Psi_I(x, t) \;=\; \psi_I\left(\frac{x - a(t)}{\epsilon}, \frac{t}{\epsilon}\right).
$$

Let us define $\zeta(x, t)$ by the following.

$$
i\epsilon^2\frac{\partial}{\partial t}\Psi_I(x, t) \;=\; -\frac{\epsilon^4}{2}\Delta\Psi_I(x, t) + h(x, \epsilon)\Psi_I(x, t) + \zeta(x, \epsilon)
$$

and obtain the follow results.

Proposition 2.3.16. *[Proposition 3.1 of [39]] "In the $L^2(\mathbb{R}^n)$ norm,*

$$\frac{1}{\epsilon^2}\int_{-\epsilon^{1-\xi}}^{\epsilon^{1-\xi}} \|\zeta(x,t)\| dt \;=\; O(\epsilon^{1-3\zeta})."$$

Thus we obtain the following lemma.

Lemma 2.3.17. *[Lemma 3.5 of [39]] "The function $\Psi_I(x,t)$ is an approximation of a solution $\psi(x,t)$ of the Schrödinger equation for $-\epsilon^{1-\xi} \le t \le \epsilon^{1-\xi}$, such that in the $L^2(\mathbb{R}^3)$ sense,*

$$\psi(x,t) - \Psi_I(x,t) \;=\; O(\epsilon^{1-3\xi}) \to 0,$$

as $\epsilon \to 0$."

2.3.8 The Outgoing Outer Solution

For times in the outer regime, we consider the classical quantities associated with the $\mathcal{A}$ level and satisfy the following initial conditions.

$$\begin{aligned} a^{\mathcal{A}}(0) &= 0 \\ \eta^{\mathcal{A}}(0) &= \widetilde{\eta}_0 - \epsilon \frac{2r}{\widetilde{\eta}_{01}} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\ A^{\mathcal{A}}(0) &= A_0 \end{aligned}$$

$$\begin{aligned} B^{\mathcal{A}}(0) &= B_0 \\ S^{\mathcal{A}}(0) &= 0. \end{aligned}$$

The reason for the difference in the initial condition for the classical momentum from the $\mathcal{B}$ level is due to the corresponding loss in kinetic energy equaling the gain in potential energy, to the leading order. In the time region where the outer solution is valid, $\epsilon^{1-\xi} \le t < T$, we wish to obtain an outgoing outer solution $\psi_{OO}(x,t)$ which is a linear combination of standard Born-Oppenheimer wave packets. The first wave packet is associated with the $\mathcal{A}$ level and initial conditions above, and the other is associated with the $\mathcal{B}$ level with the initial conditions (2.33)-(2.37). We must require that the outgoing outer solution matches the inner solutions on a matching region. Specifically,

$$t = \epsilon s, \;\; s = +\epsilon^{-\xi}, \;\; y = O(\epsilon^{-\delta'}), \;\; x = O(\epsilon^{\kappa}).$$

with $0 < \delta' < \xi < 1/3$ and $2/3 < \kappa < 1 - \xi$ as before. Proceeding as we did previously, we have

$$\begin{aligned} & D_{-\frac{ir}{2\widetilde{\eta}_{01}}}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right) \\ = \;& \exp\left\{-\frac{ir}{2\widetilde{\eta}_{00}}((\widetilde{\eta}_{01}s)^2 + 2y_1\widetilde{\eta}_{01}s + y_1^2 + \ln|s| + \ln(2r\widetilde{\eta}_{01})/2)\right\} \\ & \times e^{-\frac{3r\pi}{8\widetilde{\eta}_{01}}}(1 + O(\|y\|/s)) + O(1/s) \end{aligned}$$

and

$$D_{-\frac{ir}{2\widetilde{\eta}_{01}}-1}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta}_{01}}}(\widetilde{\eta}_{01}s + y_1)\right)$$

$$= \exp\left\{\frac{ir}{2\widetilde{\eta}_{00}}((\widetilde{\eta}_{01}s)^2 + 2y_1\widetilde{\eta}_{01}s + y_1^2 + \ln|s| + \ln(2r\widetilde{\eta}_{01})/2)\right\}$$
$$\times \frac{\sqrt{2\pi}}{\Gamma(1+\frac{ir}{2\widetilde{\eta}_{01}})} e^{-\frac{r\pi}{8\widetilde{\eta}_{01}}}(1+O(1/s)) + O(1/s)$$

as $s \to \infty$ and $\|y\|/s = O(\epsilon^{\xi-\delta'}) \to 0$. The equation below is also satisfied for level $\mathcal{A}$.

$$F(\|y^{\mathcal{A}}\|\epsilon^{\delta'}) = F(\|y\|\epsilon^{\delta'} + O(\epsilon^{1+\delta'}s)) = F(\|y\|\epsilon^{\delta'}) + O(\epsilon^{1+\delta'}s)$$

and since $B_0^{\mathcal{B}}(-) = B_0^{\mathcal{A}}(+)$,

$$\phi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y) = \phi_l(A_0, B_0^{\mathcal{A}}(+), 1, 0, 0, y).$$

We can also say

$$\phi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y)$$
$$= h(A_0, |A_0|^{-1}y)\exp\left\{-\frac{\langle y|B_0A_0^{-1}y\rangle}{2} - i\frac{\langle y|rPy\rangle}{2\widetilde{\eta}_{01}}\right\}$$
$$= \phi_l(A_0, B_0^{\mathcal{B}}(+), 1, 0, 0, y)e^{-iy_1^2 r/\widetilde{\eta}_{01}}.$$

Equation (2.39) also holds for level $\mathcal{A}$ for $s \to +\infty$, with the same error terms. For the phases,

$$\exp\left\{i\frac{S^{\mathcal{B}}(\epsilon s)}{\epsilon^2}\right\}$$
$$= \exp\left\{i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,+)}{\epsilon^2} - irs + i(r\widetilde{\eta}_{01}s^2 + \frac{r}{\widetilde{\eta}_{01}}\ln(\epsilon s))\right\}$$
$$\times (1 + O(\epsilon s^3) + O(1/s^2) + O(\epsilon\ln(\epsilon s)))$$

and

$$\exp\left\{i\frac{S^{\mathcal{A}}(\epsilon s)}{\epsilon^2}\right\}$$

$$= \exp\left\{ i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{S_0^{\mathcal{A}}(\epsilon,+)}{\epsilon^2} - irs - i(r\widetilde{\eta}_{01}s^2 + \frac{r}{\widetilde{\eta}_{01}}\ln(\epsilon|s|)) \right\}$$
$$\times (1 + O(\epsilon s^3) + O(1/s^2) + O(\epsilon \ln(\epsilon|s|))).$$

We also have

$$\exp\left\{ i\eta^{\mathcal{B}}(\epsilon s)\frac{x - a^{\mathcal{B}}(\epsilon\epsilon)}{\epsilon^2} \right\}$$
$$= \exp\left\{ i\eta(\epsilon s)\frac{y}{\epsilon} - iy(\frac{r}{\widetilde{\eta}_{01}} - rs) \right\}$$
$$\times \exp\left\{ irs - i\frac{r\widetilde{\eta}_{01}}{2}s^2 - i\frac{r}{2\widetilde{\eta}_{01}}(\ln(\epsilon s) + \ln(2\widetilde{\eta}_{01}) + \frac{1}{2} - \ln\epsilon) \right\}$$
$$\times (1 + O(\epsilon s^3) + O(1/s^2) + O(\|y\|\epsilon s^2) + O(\|y\|/s) + O(\epsilon s \ln\epsilon))$$

and

$$\exp\left\{ i\eta^{\mathcal{A}}(\epsilon s)\frac{x - a^{\mathcal{A}}(\epsilon\epsilon)}{\epsilon^2} \right\}$$
$$= \exp\left\{ i\eta(\epsilon s)\frac{y}{\epsilon} - iy(\frac{r}{\widetilde{\eta}_{01}} - rs) \right\}$$
$$\times \exp\left\{ irs + i\frac{r\widetilde{\eta}_{01}}{2}s^2 + i\frac{r}{2\widetilde{\eta}_{01}}(\ln(\epsilon s) + \ln(2\widetilde{\eta}_{01}) + \frac{1}{2} - \ln\epsilon) \right\}$$
$$\times (1 + O(\epsilon s^3) + O(1/s^2) + O(\|y\|\epsilon s^2) + O(\|y\|/s) + O(\epsilon s \ln\epsilon))$$

as $x \to +\infty$.

And lastly, by Lemma (2.3.13) and Lemma (2.3.14),

$$\Phi_{\mathcal{A}}^+(x, \epsilon s, \epsilon) = \psi_1(x,\epsilon) + O(\epsilon^{1/2}s^{1/2}) + O(s\epsilon^{\kappa})$$
$$\Phi_{\mathcal{B}}^+(x, \epsilon s, \epsilon) = \psi_2(x,\epsilon) + O(\epsilon^{1/2}s^{1/2}) + O(s\epsilon^{\kappa})$$

In the domain of the match region, $t = \epsilon s,\ s = +\epsilon^{-\xi},\ y = O(\epsilon^{-\delta'})$, and $x = O(\epsilon^{\kappa})$, we must match the inner solution and outgoing outer solution. Up to terms of order $O(\epsilon^p)$, in the

$L^2(\mathbb{R}^n)$ sense, we find

$$\begin{aligned}
\psi_{OO}(x,t) &= -e^{-\pi r/2\widetilde{\eta}_{01}} F(\|x-a^{\mathcal{A}}(t)\|/\epsilon^{1-\delta'}) e^{\left(i\frac{S^{\mathcal{A}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{A}}(t)(x-a^{\mathcal{A}}(t))}{\epsilon^2}\right)} \\
&\quad \times \phi_l(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), 0, x)\Phi^+_{\mathcal{A}}(x,t,\epsilon) \\
&\quad + e^{-\pi r/2\widetilde{\eta}_{01}} \sqrt{\frac{\pi r}{\widetilde{\eta}_{01}}} \frac{e^{i\lambda(\epsilon)}}{\Gamma(1+\frac{ir}{2\widetilde{\eta}_{01}})} \\
&\quad \times F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'}) e^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\
&\quad \times \phi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), 0, x)\Phi^+_{\mathcal{B}}(x,t,\epsilon),
\end{aligned}$$

where

$$\lambda(\epsilon) \;=\; \frac{\pi}{4} + \frac{S_0^{\mathcal{A}}(\epsilon,-)}{\epsilon^2} + \frac{r}{2\widetilde{\eta}_{01}}(1 + 3\ln(2\widetilde{\eta}_{01}) + \ln r - 4\ln\epsilon). \tag{2.40}$$

Thus we find the following result.

Lemma 2.3.18. *[Lemma 3.6 of [39]] "For any $\epsilon^{1-\xi} \le t \le T$, the function $\psi_{OO}(x,t)$ is an approximation of a solution of the Schrödinger equation $\psi(x,t)$, such that*

$$\psi(x,t) \;=\; \psi_{OO}(x,t) + R(x,t,\epsilon)$$

with

$$R(x,t\epsilon) \;=\; O(\epsilon^{\xi})$$

in the $L^2(\mathbb{R}^n)$ sense, as $\epsilon \to 0$."

Note that in the formulae in Lemmas (2.3.15), (2.3.17), and (2.3.18), the cutoff functions F can be dropped without altering the results. It is redundant when multiplied by the Gaussian functions which decay exponentially.

We can now gather all the results for the following theorem.

Theorem 2.3.19. *[Theorem 3.1 of [39]] "Let $h(x,\epsilon)$ be a hamiltonian such that $h_{\|}(x,\epsilon)$ is characterized by (2.24) and (2.25), and let $\psi(x,t)$ be a solution of the corresponding Schrödinger equation (2.23) such that*

$$\begin{aligned}\psi(x,-T) &= e^{\left(i\frac{S^{\mathcal{B}}(-T)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(-T)(x-a^{\mathcal{B}}(-T))}{\epsilon^2}\right)} \\ &\qquad \times \phi_l(A^{\mathcal{B}}(-T),B^{\mathcal{B}}(-T),\epsilon^2,a^{\mathcal{B}}(-T),0,x)\Phi^-_{\mathcal{B}}(x,-T,\epsilon)+O(\epsilon^q)\end{aligned}$$

for some positive q, in the $L^2(\mathbb{R}^n)$ sense. Then for any $0<\xi<1/3$, there exists a positive p such that in the limit $\epsilon\to 0$ we have for $-T\le t\le -e^{1-\xi}$:

$$\begin{aligned}\psi(x,t) &= e^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\ &\qquad \times \phi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),0,x)\Phi^-_{\mathcal{B}}(x,t,\epsilon)+O(\epsilon^p)\end{aligned}$$

and for $-\epsilon^{1-\xi}\le t\le \epsilon^{1-\xi}$:

$$\psi(x,t) = e^{\left(i\frac{S(t)}{\epsilon^2}+i\frac{\eta(t)(x-a(t))}{\epsilon^2}\right)}\left(f_0(y,s)\psi_1(x,\epsilon)+g_0(y,s)\psi_2(x,\epsilon)\right),$$

where f_0 and g_0 are defined by (2.38), with $y=(x-a(t))/\epsilon$, $s=t/\epsilon$, and finally for $\epsilon^{1-\xi}\le t\le T$:

$$\begin{aligned}\psi(x,t) &= -\,e^{-\pi r/2\widetilde{\eta}_{01}}e^{\left(i\frac{S^{\mathcal{A}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{A}}(t)(x-a^{\mathcal{A}}(t))}{\epsilon^2}\right)} \\ &\qquad \times \phi_l(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),0,x)\Phi^+_{\mathcal{A}}(x,t,\epsilon) \\ &\qquad + e^{-\pi r/4\widetilde{\eta}_{01}}\sqrt{\frac{\pi r}{\widetilde{\eta}_{01}}}\frac{e^{i\lambda(\epsilon)}}{\Gamma(1+\frac{ir}{2\widetilde{\eta}_{01}})} \\ &\qquad \times e^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\ &\qquad \times \phi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),0,x)\Phi^+_{\mathcal{B}}(x,t,\epsilon)+O(\epsilon^p)\end{aligned}$$

where $\lambda(\epsilon)$ is given in (2.40)."

We can also compute the transition probability $\mathcal{P}_{\mathcal{B}\to\mathcal{A}}$ from level $\mathcal{B}$ at $t=-T$ to level $\mathcal{A}$ at $t=+T$. For the limit $\epsilon \to 0$,

$$\mathcal{P}_{\mathcal{B}\to\mathcal{A}} \;=\; e^{-ir/\widetilde{\eta}_{01}} + O(\epsilon^p).$$

This coincides with the solution provided by the Landau-Zener formula where the gap is given by ϵ. Then the probability of remaining on the $\mathcal{B}$ level is

$$\begin{aligned} P_{\mathcal{B}\to\mathcal{B}} &= e^{-\pi r/2\widetilde{\eta}_{01}} \frac{\pi r}{\widetilde{\eta}_{01}\left|\Gamma(1+\frac{ir}{2\widetilde{\eta}_{01}})\right|^2} + O(\epsilon^p) \\ &= 1 - e^{-\pi r/\widetilde{\eta}_{01}} + O(\epsilon^p). \end{aligned}$$

Chapter 3

A codimension 1 conical intersection and avoided crossing

To study the behavior of a system as the energy levels approach a crossing or conical intersection, we will first investigate the case where we force the system to pass through the intersection. In this chapter we consider and example to apply some results obtained in [34] and [39], of which we discuss the proofs in a special case. Thus, we will study the solutions to the Schrödinger equation

$$i\epsilon^2 \frac{\partial \psi}{\partial t} = H(x)\psi \tag{3.1}$$

under general Born-Oppenheimer and adiabatic assumptions, for Hamiltonians which result in a codimension 1 crossing system or avoided crossing system.

Recently, results on codimension 1 crossings in relatively general situations have been obtained [21], [22].

3.1 Through the crossing

We will study the particular Hamiltonian operator $H(x)$ given below,

$$H(x) = -\frac{\epsilon^4}{2}\Delta - x\begin{pmatrix} \cos^2(x) & \cos(x)\sin(x) \\ \cos(x)\sin(x) & \sin^2(x) \end{pmatrix} \tag{3.2}$$

where $x \in \mathbb{R}$.

Then $h(x) = -x\begin{pmatrix} \cos^2(x) & \cos(x)\sin(x) \\ \cos(x)\sin(x) & \sin^2(x) \end{pmatrix}$

To find the eigenvalues of $h(x)$, we write it in terms of the Pauli spin matrices.

$$\begin{aligned} h(x) &= -x\left(\frac{1}{2}I_2 + \begin{pmatrix} \cos^2(x) - \frac{1}{2} & \cos(x)\sin(x) \\ \cos(x)\sin(x) & -(\cos^2(x) - \frac{1}{2}) \end{pmatrix}\right) \\ &= -x\left(\frac{1}{2}I_2 + (\cos^2(x) - \frac{1}{2})\sigma_z + \cos(x)\sin(x)\sigma_x\right) \end{aligned}$$

This is in the form $h(x) = qI_2 + \vec{r}\cdot\vec{\sigma}$ where $\vec{\sigma} = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}$. Hence

$$\vec{r} = -x\begin{pmatrix} \cos(x)\sin(x) \\ 0 \\ \cos^2(x) - \frac{1}{2} \end{pmatrix}.$$

Then the spectrum of $h(x)$ is given by

$$\sigma(h) = q + |\vec{r}| = -x\left(\frac{1}{2} \pm \sqrt{\cos^2(x)\sin^2(x) + \left(\cos^2(x) - \frac{1}{2}\right)^2}\right)$$

$$= -x\left(\frac{1}{2} \pm \sqrt{\cos^2(x)\sin^2(x) + \cos^4(x) - \cos^2(x) + \frac{1}{4}}\right)$$

$$= -x\left(\frac{1}{2} \pm \sqrt{\cos^4(x) + \cos^2(x)(\sin^2(x) - 1) + \frac{1}{4}}\right)$$

$$= -x\left(\frac{1}{2} \pm \sqrt{\frac{1}{4}}\right) = -x\left(\frac{1}{2} \pm \frac{1}{2}\right) = 0,\ -x$$

To find the eigenvectors for each of these eigenvalues, we solve $(h(x) - \sigma(h))v = 0$.

First we find the eigenvector for $\sigma(h) = 0$.

$$-x\begin{pmatrix} \cos^2(x) & \cos(x)\sin(x) \\ \cos(x)\sin(x) & \sin^2(x) \end{pmatrix}\begin{pmatrix} v_1^- \\ v_2^- \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$-x\begin{pmatrix} \cos^2(x)v_1^- + \cos(x)\sin(x)v_2^- \\ \cos(x)\sin(x)v_1^- + \sin^2(x)v_2^- \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$-x\begin{pmatrix} \cos(x)(\cos(x)v_1^- + \sin(x)v_2^-) \\ \sin(x)(\cos(x)v_1^- + \sin(x)v_2^-) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Then we get the normalized eigenvector $\begin{pmatrix} -\sin(x) \\ \cos(x) \end{pmatrix}$.

$|v^-| = \sqrt{\sin^2(x) + \cos^2(x)} = 1.$

Next we find the eigenvector for $\sigma(h) = -x$.

$$-x \begin{pmatrix} \cos^2(x) - 1 & \cos(x)\sin(x) \\ \cos(x)\sin(x) & \sin^2(x) - 1 \end{pmatrix} \begin{pmatrix} v_1^+ \\ v_2^+ \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$-x \begin{pmatrix} \sin^2(x) & \cos(x)\sin(x) \\ \cos(x)\sin(x) & -\cos^2(x) \end{pmatrix} \begin{pmatrix} v_1^+ \\ v_2^+ \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$-x \begin{pmatrix} -\sin^2(x)v_1^+ + \cos(x)\sin(x)v_2^+ \\ \cos(x)\sin(x)v_1^+ - \cos^2(x)v_2^+ \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$-x \begin{pmatrix} \sin(x)(-\sin(x)v_1^+ + \cos(x)v_2^+) \\ \cos(x)(\sin(x)v_1^+ - \cos(x)v_2^+) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Then we get the normalized eigenvector $\begin{pmatrix} \cos(x) \\ \sin(x) \end{pmatrix}$.

$|v^+| = \sqrt{\cos^2(x) + \sin^2(x)} = 1.$

$V(x)$ is given by eigenvalues of $h(x)$. We will use the following notation for the spectrum and eigenfunctions of $h(x)$.

$$E_{\mathcal{A}}(x) = 0$$
$$\Phi_{\mathcal{A}}(x) = \begin{pmatrix} -\sin(x) \\ \cos(x) \end{pmatrix}$$
$$E_{\mathcal{B}}(x) = -x$$
$$\Phi_{\mathcal{B}}(x) = \begin{pmatrix} \cos(x) \\ \sin(x) \end{pmatrix}$$

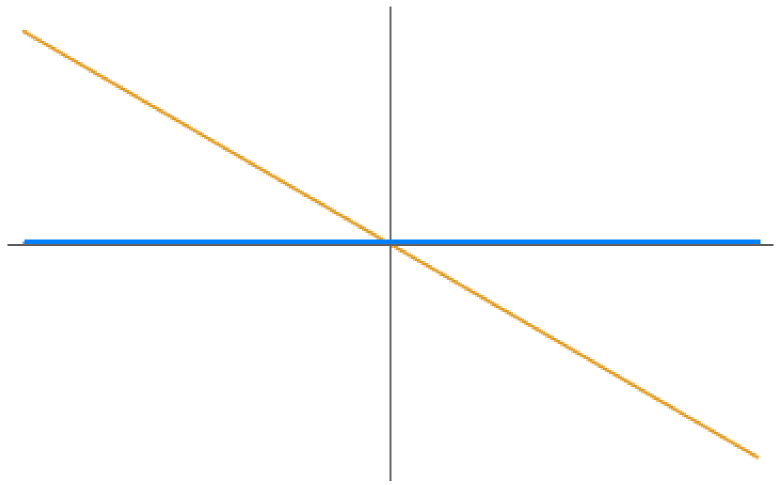

Figure 3.1: $E_{\mathcal{A}}(x)$ and $E_{\mathcal{B}}(x)$

These values coincide on a submanifold Γ, which in this case is a single point. In nuclear space for this system, Γ has codimension 1.

Let G be the symmetry group of $h(x)$, i.e. the group of all unitary and antiunitary operators that are independent of x in some representation of the electronic Hilbert space, and also commute with $h(x)$, for x in an open set of interest.

The irreducible corepresentations of G that correspond to these two eigenvalues are both Type I, and are not unitarily equivalent to each other. Both eigenvalues have multiplicity 1 away from the crossing, therefore this is either a Type A or Type C crossing, as classified in [34].

We may decompose $G = \mathcal{K}H$ with $\mathcal{K}$ being a special antiunitary element of G. Then we can choose the phases of the vectors $\Phi_{\mathcal{A}}(0)$ and $\Phi_{\mathcal{B}}(0)$ so that $\mathcal{K}\Phi_{\mathcal{A}}(0) = \Phi_{\mathcal{A}}(0)$ and $\mathcal{K}\Phi_{\mathcal{B}}(0) = \Phi_{\mathcal{B}}(0)$. This choice then gives us $\mathcal{K}\Phi_{\mathcal{A}}(x) = \Phi_{\mathcal{A}}(x)$ and $\mathcal{K}\Phi_{\mathcal{B}}(x) = \Phi_{\mathcal{B}}(x)$.

For our problem, choosing $\mathcal{K}$ to be the complex conjugation operator satisfies these conditions. (I.e. $\mathcal{K}z = \overline{z}$.) For any x, $\Phi_{\mathcal{A}}(x)$ and $\Phi_{\mathcal{B}}(x)$ are real, so $\mathcal{K}\Phi_{\mathcal{A}}(x) = \Phi_{\mathcal{A}}(x)$ and $\mathcal{K}\Phi_{B}(x) = \Phi_{B}(x)$. Also $\mathcal{K}^2 = Id$, and for any $z_1,\ z_2 \in \mathbb{C}^n$, $\langle \mathcal{K}z_1, \mathcal{K}z_2\rangle = \overline{\langle z_1, z_2\rangle}$. Therefore we know this choice of $\mathcal{K}$ is an antiunitary operator which preserves the eigenvectors.

This determines that the crossing of $E_{\mathcal{A}}(x)$ and $E_{\mathcal{B}}(x)$ is a Type C crossing.

To begin considering the solutions for this system, let us first define some important components which will allow us to find the solutions to the Schrödinger equation. Our solutions will be built of semi-classical wave packets in the sense that they depend on classical quantities. The relevant quantities are the classical position $a(t)$, the classical momentum $\eta(t)$, the classical action integral $S(t)$, and the uncertainty matrices for the classical position and momentum, $A(t)$ and $B(t)$ respectively. They are given by the unique solutions to the following system.

$$\begin{aligned}
\frac{\partial a}{\partial t}(t) &= \eta(t), && (3.3)\\
\frac{\partial \eta}{\partial t}(t) &= -V^{(1)}(a(t)), && (3.4)\\
\frac{\partial S}{\partial t}(t) &= \frac{1}{2}\eta(t)^2 - V(a(t)), && (3.5)\\
\frac{\partial A}{\partial t}(t) &= iB(t), && (3.6)\\
\frac{\partial B}{\partial t}(t) &= iV^{(2)}(a(t))A(t). && (3.7)
\end{aligned}$$

with initial conditions

$$\begin{aligned} a(0) &= 0 & (3.8) \\ \eta(0) &= \widetilde{\eta}_0 & (3.9) \\ S(0) &= S_0 & (3.10) \\ A(0) &= A_0 & (3.11) \\ B(0) &= D_0. & (3.12) \end{aligned}$$

Here $V(x)$ is the potential, given by the eigenvalues of $h(x)$, $E_-(x)$ and $E_+(x)$, or the average potential $\widetilde{V}(x) = \frac{1}{2}(E_-(x) + E_+(x))$. $V^{(1)}(x)$ denotes the first derivative of V with respect to x, and $V^{(2)}(x)$ denotes the second derivative. We assume A_0 and D_0 satisfy the four conditions (2.1)-(2.4). If $A(0) = A_0$ and $B(0) = D_0$ satisfy these conditions, then $A(t)$ and $B(t)$ satisfy them for all t.

For one dimension, we only need the normalization condition that $\overline{A}B + \overline{B}A = 2I$.

Let us define the semiclassical Hagedorn wave packets, ϕ_l for the multi-index l, which give us the base of our solutions, [28, 29, 35].

$$\phi_0(A, B, \hbar, a, \eta, x) \;=\; \pi^{-1/4}\hbar^{-1/4}A^{-1/2}\exp\left\{\frac{-BA^{-1}(x-a)^2}{2\hbar} + \frac{i\eta(x-a)}{\hbar}\right\} \qquad (3.13)$$

Recursively, we then define $\phi_k(A, B, \hbar, a, \eta, \cdot)$ by

$$\phi_{k+1}(A, B, \hbar, a, \eta, \cdot) \;=\; \frac{1}{\sqrt{k+1}}\mathcal{A}(A, B, \hbar, a, \eta)^*\phi_k(A, B, \hbar, a, \eta, \cdot). \qquad (3.14)$$

We can now express an approximate solution $\Psi(\epsilon, x, t)$, to the Schrödinger equation by implementing the following theorem from [34].

Theorem 3.1.1. *[Theorem 5.1 of [34]] "If $h(X)$ has a crossing of Type A or C, then there is an approximate solutions $\Psi(\epsilon, X, t)$ to the Schrödinger equation that satisfies*

$$\begin{aligned}\Psi(\epsilon,x,t) &= \Phi_{\mathcal{A}}(x,t)e^{iS^{\mathcal{A}}(t)/\epsilon^2}e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2}\\ &\qquad\times\Big(\phi_l(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\\ &\qquad\quad+\epsilon\sum_{|m|\le|l|+3}d_m(x-a^{\mathcal{A}}(t),t)\phi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\Big)\\ &\quad+O(\epsilon^2)\end{aligned}$$

for $t\in[-T,-T_1]$ for some fixed $T_1>0$. For $t\in[T_1,T]$, this solution satisfies

$$\begin{aligned}\Psi(\epsilon,x,t) &= \Phi_{\mathcal{A}}(x,t)e^{iS^{\mathcal{A}}(t)/\epsilon^2}e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2}\\ &\qquad\times\Big(\phi_l(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\\ &\qquad\quad+\epsilon\sum_{|m|\le|l|+3}d_m(x-a^{\mathcal{A}}(t),t)\phi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\Big)\\ &\quad-\epsilon(1+i)\pi^{1/2}\left(\langle(E_{\mathcal{A}}^{(1)}-E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle\right)^{-1/2}\\ &\qquad\times\langle\Phi_{\mathcal{B}}(0,0),\ \left(\left(\frac{\partial}{\partial t}+\eta^{\mathcal{A}}(0)\nabla_x\right)\Phi_{\mathcal{A}}\right)(0,0)\rangle_{\mathcal{H}_{el}}\\ &\qquad\times\Phi_{\mathcal{B}}(x,t)e^{iS^{\mathcal{B}}(t)/\epsilon^2}e^{i\eta^{\mathcal{A}}(t)\cdot(x-a^{\mathcal{A}}(t))/\epsilon^2}\phi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\\ &\quad+O(\epsilon^\alpha),\end{aligned}$$

for some $\alpha>1$. In this equation, if $\langle(E_{\mathcal{A}}^{(1)}-E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle$ is positive, we can just take the positive square root. If $\langle(E_{\mathcal{A}}^{(1)}-E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle$ is negative, we take the positive imaginary square root. The coefficients $d_m(w,t)$ are found by solving the initial value problem for a system of ordinary differential equations."

Applying the solutions found above, we start with an initial incoming wave packet of the form

$$\phi_l(A^{\mathcal{A}}(-T),\ B^{\mathcal{A}}(-T),\ \epsilon^2,\ a^{\mathcal{A}}(-T),\ \eta^{\mathcal{A}}(-T),\ x)\Phi_{\mathcal{A}}(x)$$

where

$$\phi_0(A, B, \hbar, a, \eta, x) \;=\; \pi^{-1/4}\hbar^{-1/4}A^{-1/2}\exp\left\{\frac{-BA^{-1}(x-a)^2}{2\hbar} + i\frac{\eta(x-a)}{\hbar}\right\},$$

and defined recursively,

$$\phi_{l+1}(A, B, \hbar, a, \eta, \cdot) \;=\; \frac{1}{\sqrt{l+1}}\mathscr{A}(A, B, \hbar, a, \eta)^*\phi_l(A, B, \hbar, a, \eta, \cdot).$$

Where $\mathscr{A}(A, B, \hbar, a, \eta)^*$ is the raising operator given by the following definition from [35].

Define raising and lowering operators by

$$\mathscr{A}(A, B, \hbar, a, \eta)^* \;=\; \frac{1}{\sqrt{2\hbar}}[\overline{B}(x-a) - i\overline{A}(p-\eta)],$$

and

$$\mathscr{A}(A, B, \hbar, a, \eta) \;=\; \frac{1}{\sqrt{2\hbar}}[B(x-a) + iA(p-\eta)],$$

where $p = -i\epsilon^2\frac{\partial}{\partial x}$ is the momentum operator.

The following lemma allows us to define the value of T_1 in the theorem which allows us to maintain an acceptable order of error as we approach the crossing at $t = 0$.

Lemma 3.1.2. *[Lemma 5.2 of [34]] "Under the hypothesis of the previous theorem, the approximate solution of the theorem agrees with an exact solution of the Schrödinger equation up to errors whose norms are of order $\epsilon^{2-\xi}$ for $t \in [-T, -\epsilon^{\xi}]$ for any $\xi \in (0,1)$."*

For times close to the crossing at $t = 0$, the solutions from Theorem (3.1.1) break down due to a boundary layer in the solutions around this point. We must separately consider the solutions when $t \in [-\epsilon^{\xi'}, \epsilon^{\xi'}]$, which we call the inner solutions. (For $|t| > \epsilon^{\xi}$, the solutions described in the Theorem are referred to as the outer solutions.) We rescale the following variables in the inner regime.

Let $s = t/\epsilon$, $y_A = (x - a^{\mathcal{A}}(t))/\epsilon$, and $y_B = (x - a^{B}(t))/\epsilon = y_{\mathcal{A}} + (a^{\mathcal{B}}(t) - a^{\mathcal{A}}(t))/\epsilon$. Then the inner solutions are given by the following lemma.

Lemma 3.1.3. *[Lemma 5.3 of [34]] "Under the hypothesis of the previous theorem, the approximate solution given below agrees with an exact solution of the Schrödinger equation up to errors whose norms are of order $\epsilon^{2\xi'}$ for $t \in [-\epsilon^{\xi'}, \epsilon^{\xi'}]$ for any $\xi' \in (\frac{1}{2}, 1)$.*

$$
\begin{aligned}
& e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \epsilon^{-n/2} \Phi_{\mathcal{A}}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s) \\
& \quad \times \left(\left(1 - i\epsilon s \left(-\frac{1}{2}\Delta_{y_{\mathcal{A}}} + E^{(2)}_{\mathcal{A}}(a^{\mathcal{A}}) \frac{y_{\mathcal{A}}^2}{2} \right) \right) \phi_l(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}}) \right. \\
& \quad \left. + \epsilon \sum_{|m| \le |l|+3} d_m(\epsilon y_{\mathcal{A}}, 0) \epsilon^{-n/2} \phi_m(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}}) \right) \\
& + \epsilon e^{iS^{\mathcal{B}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{B}}(\epsilon s)\cdot y_{\mathcal{B}}/\epsilon} g_1(y_{\mathcal{B}}, s) \Phi_{\mathcal{B}}(a^{\mathcal{B}}(\epsilon s) + \epsilon y_{\mathcal{B}}, \epsilon s) \\
& + \epsilon^2 e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \psi_j^{\perp}
\end{aligned}
$$

where $\psi_j^{\perp}$ is perpendicular to both $\Phi_{\mathcal{A}}(x,t)$ and $\Phi_{\mathcal{B}}(x,t)$, and

$$
\begin{aligned}
\frac{\partial}{\partial s} g_1(y_{\mathcal{B}}, s) \; &= \\
- e^{i(S^{\mathcal{B}} - S^{\mathcal{A}})/\epsilon^2} & e^{i\eta^{\mathcal{B}}\cdot y_{\mathcal{B}} - \eta^{\mathcal{A}}\cdot y_{\mathcal{A}})/\epsilon} \langle \Phi_{\mathcal{B}}, \left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}} \cdot \nabla_X \right) \Phi_{\mathcal{A}} \rangle \left(\epsilon^{-1/2} \phi_0(A_0, D_0^{\mathcal{A}}, 1, 0, 0, 0) \right) ."
\end{aligned}
$$

By implementing these results for our system of interest, we obtain the following main results, which will be proved over the course of this section.

Corollary 3.1.4. *For the system given by the Hamiltonian operator (3.2), the approximate solution to the Schrödinger equation for $t < 0$, for any $\xi \in (\frac{1}{2}, 1)$, up to order epsilon is given by*

$$\Psi(x,t,\epsilon) = \begin{pmatrix} -\sin x \\ \\ \cos x \end{pmatrix} e^{iS^{\mathcal{A}}(t)/\epsilon^2} \phi_0(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x) + \epsilon \left(\frac{-1}{\sqrt{2}A_0} \right) \phi_1(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x) \tag{3.15}$$

for $t > 0$, the solution is given by

$$\begin{aligned} \Psi(x,t,\epsilon) = {} & \begin{pmatrix} -\sin x \\ \\ \cos x \end{pmatrix} e^{iS^{\mathcal{A}}(t)/\epsilon^2} \phi_0(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x) \\ & + \epsilon \left(\frac{-1}{\sqrt{2}A_0} \right) \phi_1(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x) \\ & + \begin{pmatrix} \cos x \\ \\ \sin x \end{pmatrix} \left(\epsilon (1-i) \pi^{1/2} \widetilde{\eta_0}^{1/2} \right) e^{iS^{\mathcal{B}}(t)/\epsilon^2} \phi_0(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x) \end{aligned} \tag{3.16}$$

where $a^{\mathcal{C}}(t)$, $\eta^{\mathcal{C}}(t)$, $S^{\mathcal{C}}(t)$, $A^{\mathcal{C}}(t)$, and $B^{\mathcal{C}}(t)$, for $\mathcal{C} = \{\mathcal{A}, \mathcal{B}\}$, is given by equations (3.17)-(3.26) of Lemma (3.1.5).

3.1.1 Classical Quantities

The functions which will be used to construct the solutions of the Schrödinger equation will be semiclassical in the sense that they depend on classical quantities. The classical quantities relevant to the solutions are given by the unique solutions to the system (3.3)-(3.7), with the initial conditions (3.8)-(3.12). We also assume that the nuclear momentum vector $\eta^{\mathcal{A}}(0)$ is not tangent to Γ, which in this case is satisfied for any initial condition $\widetilde{\eta}_0$. We should assume that $\eta^{\mathcal{A}}(0)$ has a positive component in the x direction.

Lemma 3.1.5. *For the system with the Hamiltonian operator given by (3.2), the relevant classical quantities, which are the solutions to equations (3.3)-(3.7) for each level $E_{\mathcal{A}}(x) = 0$ and $E_{\mathcal{B}}(x) = -x$, are*

$$a^{\mathcal{A}}(t) = \widetilde{\eta}_0 t, \tag{3.17}$$

$$\eta^{\mathcal{A}}(t) = \widetilde{\eta}_0, \tag{3.18}$$

$$S^{\mathcal{A}}(t) = S_0 + \frac{1}{2}\widetilde{\eta}_0^2 t, \tag{3.19}$$

$$A^{\mathcal{A}}(t) = A_0 + itD_0^{\mathcal{A}}, \tag{3.20}$$

$$B^{\mathcal{A}}(t) = D_0^{\mathcal{A}}. \tag{3.21}$$

and

$$a^{\mathcal{B}}(t) = \widetilde{\eta}_0 t + \frac{t^2}{2}, \tag{3.22}$$

$$\eta^{\mathcal{B}}(t) = \widetilde{\eta}_0 + t, \tag{3.23}$$

$$S^{\mathcal{B}}(t) = S_0 + \frac{1}{2}\widetilde{\eta}_0^2 t - \widetilde{\eta}_0 t^2 - \frac{t^3}{3}, \tag{3.24}$$

$$A^{\mathcal{B}}(t) = A_0 + itD_0^{\mathcal{B}}, \tag{3.25}$$

$$B^{\mathcal{B}}(t) = D_0^{\mathcal{B}}. \tag{3.26}$$

for all times t. These solutions are exact.

Proof. $V(x)$ is given by the eigenvalues of $h(x)$. For the incoming wave packet we use $V(x) = E_{\mathcal{A}}(x) = 0$.

$$V^{(1)}(x) = \frac{dE_{\mathcal{A}}(x)}{dx} = 0$$
$$V^{(2)}(x) = \frac{d^2E_{\mathcal{A}}(x)}{dx^2} = 0$$

Then the system we need to solve for the incoming wave packet, $t \leq 0$, is

$$\begin{aligned}
\frac{\partial a}{\partial t}(t) &= \eta(t), \\
\frac{\partial \eta}{\partial t}(t) &= 0, \\
\frac{\partial S}{\partial t}(t) &= \frac{1}{2}\eta(t)^2, \\
\frac{\partial A}{\partial t}(t) &= iB(t), \\
\frac{\partial B}{\partial t}(t) &= 0.
\end{aligned}$$

with the initial conditions

$$a^{\mathcal{A}}(0) = 0,$$

$$\eta^{\mathcal{A}}(0) = \widetilde{\eta}_0,$$

$$S^{\mathcal{A}}(0) = S_0,$$

$$A^{\mathcal{A}}(0) = A_0.$$

This gives us the solutions

$$a^{\mathcal{A}}(t) = \widetilde{\eta}_0 t,$$

$$\eta^{\mathcal{A}}(t) = \widetilde{\eta}_0,$$

$$
\begin{aligned}
S^{\mathcal{A}}(t) &= S_0 + \frac{1}{2}\widetilde{\eta}_0^2 t, \\
A^{\mathcal{A}}(t) &= A_0 + itD_0^{\mathcal{A}}, \\
B^{\mathcal{A}}(t) &= D_0^{\mathcal{A}}.
\end{aligned}
$$

for $t \leq 0$.

$D_0^{\mathcal{A}}$ is the matrix such that $A^{\mathcal{A}}(-T)$ and $B^{\mathcal{A}}(-T)$ satisfy conditions (2.1)-(2.4).

For the outgoing wave packet, let $a^{\mathcal{A}}(t)$, $\eta^{\mathcal{A}}(t)$, $S^{\mathcal{A}}(t), A^{\mathcal{A}}(t)$, and $B^{\mathcal{A}}(t)$ be the unique solutions to the system of equations (3.3)-(3.7).

$V(x) = E_{\mathcal{B}}(x) = x$ for the outgoing wave packet, $t \geq 0$.

$$
V^{(1)}(x) = \frac{dE_{\mathcal{B}}(x)}{dx} = -1
$$

$$
V^{(2)}(x) = \frac{d^2E_{\mathcal{B}}(x)}{dx^2} = 0
$$

$$
\begin{aligned}
\frac{\partial a}{\partial t}(t) &= \eta(t), \\
\frac{\partial \eta}{\partial t}(t) &= 1, \\
\frac{\partial S}{\partial t}(t) &= \frac{1}{2}\eta(t)^2 - a(t), \\
\frac{\partial A}{\partial t}(t) &= iB(t), \\
\frac{\partial B}{\partial t}(t) &= 0.
\end{aligned}
$$

We require the same initial conditions so that

$$a^{\mathcal{B}}(0) = a^{\mathcal{A}}(0) = 0,$$

$$\eta^{\mathcal{B}}(0) = \eta^{\mathcal{A}}(0) = \widetilde{\eta}_0,$$

$$S^{\mathcal{B}}(0) = S^{\mathcal{A}}(0) = S_0,$$

$$A^{\mathcal{B}}(0) = A^{\mathcal{A}}(0) = A_0.$$

$$\begin{aligned} B^{\mathcal{B}}(0) &= B_0^{\mathcal{A}}(0) + i\frac{|(E_{\mathcal{B}}^{(1)}(0) - E_{\mathcal{A}}^{(1)}(0))\rangle\langle(E_{\mathcal{B}}^{(1)}(0) - E_{\mathcal{A}}^{(1)}(0))|}{\langle(E_{\mathcal{B}}^{(1)}(0) - E_{\mathcal{A}}^{(1)}(0)),\ \eta_{\mathcal{A}}(0)\rangle}A^{\mathcal{A}}(0) \\ &= D_0^{\mathcal{A}} - i\frac{1}{\widetilde{\eta}_0}A_0 \end{aligned}$$

Let us call $B^{\mathcal{B}}(0) = D_0^{\mathcal{A}} - i\frac{A_0}{\widetilde{\eta}_0} = D_0^{\mathcal{B}}$.

The unique solutions to this system are

$$\begin{aligned} a^{\mathcal{B}}(t) &= \widetilde{\eta}_0 t + \frac{t^2}{2}, \\ \eta^{\mathcal{B}}(t) &= \widetilde{\eta}_0 + t, \\ S^{\mathcal{B}}(t) &= S_0 + \frac{1}{2}\widetilde{\eta}_0^2 t - \widetilde{\eta}_0 t^2 - \frac{t^3}{3}, \\ A^{\mathcal{B}}(t) &= A_0 + itD_0^{\mathcal{B}}, \\ B^{\mathcal{B}}(t) &= D_0^{\mathcal{B}}. \end{aligned}$$

for $t \geq 0$. □

Below is a plot of the solutions of $a^{\mathcal{A}}(t)$ and $a^{\mathcal{B}}(t)$.

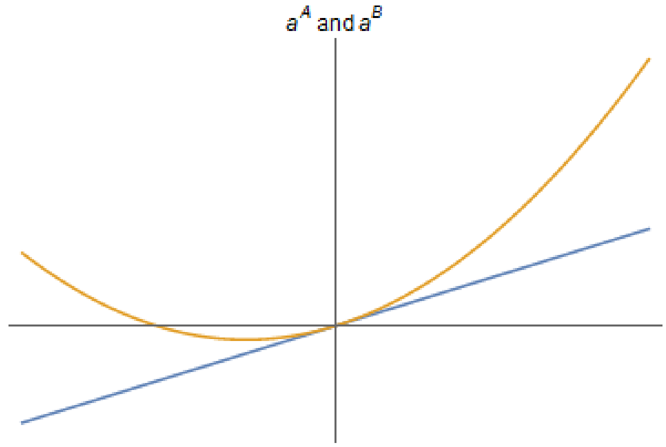

Figure 3.2: $a^{\mathcal{A}}(t)$ and $a^{\mathcal{B}}(t)$

3.1.2 Wave packets

We are most interested in the wave packet when $l = 0$. For $l = 0$, ϕ_l is a Gaussian function which are convenient functions to work with and are of particular interest to chemists and physicists.

For the solution to $a(t),\ \eta(t),\ A(t),\ B(t)$, and $S(t)$ previously found, for $t \le \epsilon^{\xi}$,

$$\begin{aligned}\phi_0(A^{\mathcal{A}}(t),&B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\\ &= \pi^{-1/4}\epsilon^{-1/2}(A_0^{\mathcal{A}}+itD_0^{\mathcal{A}})^{-1/2}\\ &\quad\times\exp\left\{\frac{-(D_0^{\mathcal{A}})(A_0^{\mathcal{A}}+itD_0^{\mathcal{A}})^{-1}(x-\widetilde{\eta}_0t)^2}{2\epsilon^2}+i\frac{\widetilde{\eta}_0(x-\widetilde{\eta}_0t)}{\epsilon^2}\right\}.\end{aligned}$$

For $t > 0$,

$$\begin{aligned}\phi_0(A^{\mathcal{B}}(t),&B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\\ &= \pi^{-1/4}\epsilon^{-1/2}(A_0^{\mathcal{B}}+itD_0^{\mathcal{B}})^{-1/2}\end{aligned}$$

$$\times \exp\left\{ \frac{-(D_0^{\mathcal{B}})(A_0^{\mathcal{B}} + itD_0^{\mathcal{B}})^{-1}(x - \widetilde{\eta}_0 t - \frac{t^2}{2})^2}{2\epsilon^2} + i\frac{(\widetilde{\eta}_0 + t)(x - \widetilde{\eta}_0 t - \frac{t^2}{2})}{\epsilon^2}. \right\}.$$

The plot for$|\phi_0^{\mathcal{A}}|$ is shown below in Figure 3.3, for $t \in (-30\epsilon, 30\epsilon)$.

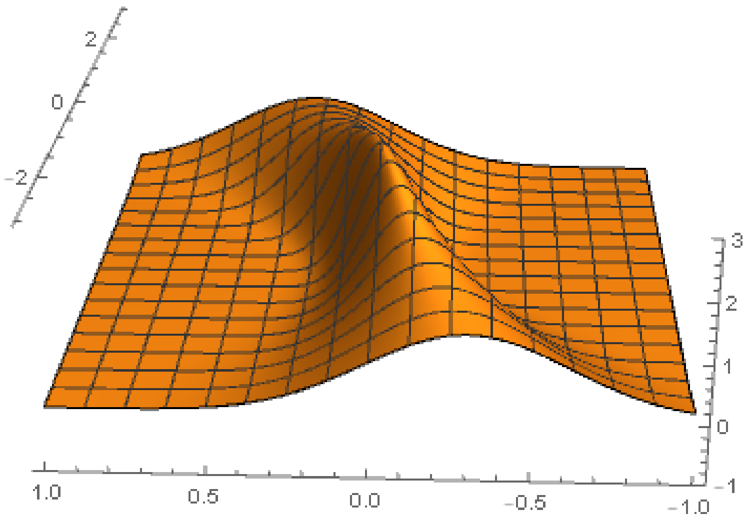

Figure 3.3: $|\phi_0^{\mathcal{A}}|$

Also, we should look at $|\phi_0^{\mathcal{A}}|$ at $t = 0$, and notice that it is a Gaussian in x at $t = 0$, shown in Figure 3.4.

Similarly, Firgure 3.5 shows $|\phi_0^{\mathcal{B}}|$, but for $t > 0$ only, and Figure 3.6 shows at $|\phi_0^{\mathcal{B}}|$ at $t = 0$.

3.1.3 Incoming Outer Solutions

We must calculate the coefficients $d_m(w,t)$, seen in the solutions given by Theorem (3.1.1), for the system of interest. Following the same methods of [34], we make the ansatz that far from the crossing, the solutions are of the form

$$\Psi(x,y,t) \;=\; e^{iS^{\mathcal{A}}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot y_{\mathcal{A}}/\epsilon} F\left(\frac{x - a^{\mathcal{A}}(t)}{\epsilon}\right)\left(\psi_0(x, y^{\mathcal{A}}, t) + \epsilon\psi_1(x, y^{\mathcal{A}}, t) + ...\right),$$

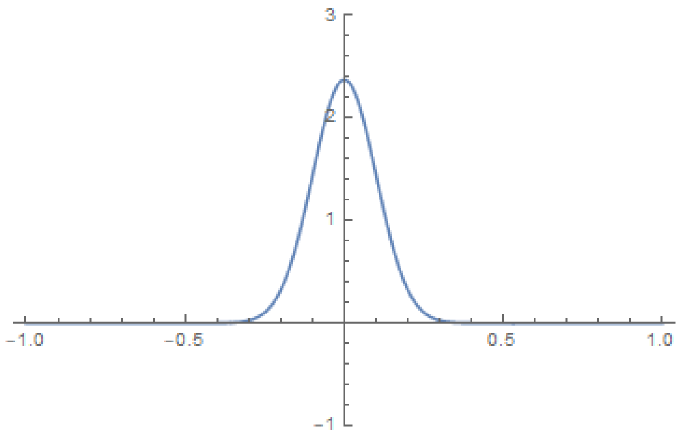

Figure 3.4: $|\phi_0^{\mathcal{A}}|$ for $t = 0$

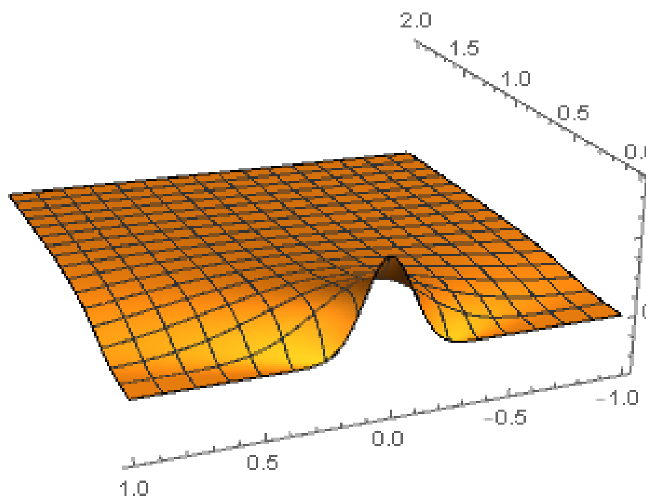

Figure 3.5: $|\phi_0^{\mathcal{B}}|$ for $t > 0$

where $y^{\mathcal{A}} = (x - a^{\mathcal{A}}(t))/\epsilon$ since $y^{\mathcal{A}}$ and x behave as though they were independent. Note that for this secion we will drop the $\mathcal{A}$ notation as everything will be in relation to this level. For our solutions, this corresponds to the outer solutions when $t \in [-T, -\epsilon^{\xi}]$. F is a cut off function where the derivatives of F are supported away from $a(t)$. We may cut the solutions after the ϵ order term, as we only require our approximation to be accurate up to errors of

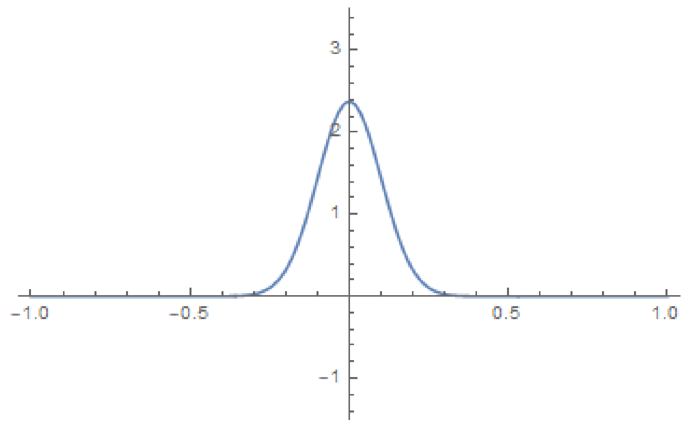

Figure 3.6: $|\phi_0^{\mathcal{B}}|$ for $t = 0$

order $O(\epsilon^2)$. Let

$$\chi(x, y, t) = F\left(\frac{x - a(t)}{\epsilon}\right)(\psi_0(x, y, t) + \epsilon\psi_1(x, y, t))$$

These are the terms which contribute to the error of the approximation,

$$\zeta(x, y, t) = \left[i\epsilon^2\frac{\partial}{\partial t} + \frac{\epsilon^4}{2}\Delta_x - h(x)\right]$$

or to include an expansion for the energy, we add $E(x) - E(a(t) + \epsilon y)$,

$$\zeta(x, y, t) = \left[i\epsilon^2\frac{\partial}{\partial t} + \frac{\epsilon^4}{2}\Delta_x - E(a(t) - \epsilon y) - h(x) + E(x)\right].$$

Then χ must satisfy,

$$\begin{aligned}\zeta(x, y, t) =& i\epsilon^2\frac{\partial \chi}{\partial t} - \Big[- \frac{\epsilon^4}{2}\Delta_x - \epsilon^3\nabla_x \cdot \nabla_y - \frac{\epsilon^2}{2}\Delta_y - i\epsilon^2\eta(t) \cdot \nabla)x \\ &+ \big(E(a(t) + \epsilon y) - E(a(t)) - \epsilon E^{(1)}(a(t)) \cdot y\big) + [h(x) - E(x)]\Big]\chi\end{aligned}$$

We must satisfy this for each order of epsilon. The terms of order ϵ^0 are

$$F\left(\frac{x - a(t)}{\epsilon}\right)[h(x) - E(x)]\psi_0 = 0.$$

In the domain of F, this means

$$\psi_0(x,y,t) \;=\; g_0(x,y,t)\Phi(x).$$

Recall that for a Type C crossing, the eigenvectors can be chosen to be independent of t. Similarly, the second order terms are

$$F\left(\frac{x-a(t)}{\epsilon}\right)[h(x)-E(x)]\psi_1 = 0,$$

and therefore

$$\psi_1(x,y,t) \;=\; g_1(x,y,t)\Phi(x).$$

The second order terms are

$$iF\left(\frac{x-a(t)}{\epsilon}\right)\frac{\partial}{\partial t}\psi_0 = F\left(\frac{x-a(t)}{\epsilon}\right)\left[-\frac{1}{2}\Delta_y\psi_0 + E^{(2)}(a(t))\frac{y^2}{2}\psi_0 - i\eta(t)\cdot\nabla_x\psi_0.\right]$$

To solve for $g_0(x,y,t)$, we project this into two parts, the part parallel to $\Phi(x)$ and the part perpendicular. Therefore we find the parallel and perpendicular parts are, respectively,

$$i g_0 = -\frac{1}{2}\Delta_y g_0 + E^{(2)}(a(t))\frac{y^2}{2}g_0 - i\eta(t)\cdot\nabla_x g_0$$

and

$$0 = i g_0\left(\eta(t)\cdot\nabla_x\Phi(x)\right).$$

If we replace x with $w = x - a(t)$ and define $f_0(w,y,t) = g_0(w+a(t),y,t) = g_0(x,y,t)$, then f_0 satisfies

$$i\frac{\partial}{\partial t}f_0 \;=\; -\frac{1}{2}\Delta_y f_0 + E^{(2)}(a(t))\frac{y^2}{2}f_0$$

This is the Schrödinger equation for a harmonic oscillator with time varying spring strength. Thus, utilizing the Hagedorn wave packets ϕ_l which were designed to solve these equations, we use the solution

$$f_0(w,y,t) \;=\; \epsilon^{-n/2}\phi_l(A(t),B(t),1,0,0,y).$$

However, for our system of interest, $E_{\mathcal{A}}(x)=0$, so $E^{(2)}(a(t))=0$, which helps to simplify this. Also note $n=1$ for our problem.

$$i\frac{\partial}{\partial t}f_0 \;=-\frac{1}{2}\Delta_y f_0$$

There is no need for any w dependence. We have chosen $l=0$ for our solutions which are of the most interest to us. Then we obtain

$$g_0 \;=\; \epsilon^{-1/2}\phi_0(A(t),B(t),1,0,0,y)=\phi_0(A(t),B(t),\epsilon^2,a(t),0,x).$$

The terms of order ϵ^3 in ζ are

$$\begin{aligned} iF\left(\frac{x-a(t)}{\epsilon}\right)\frac{\partial}{\partial t}\psi_1 =&F\left(\frac{x-a(t)}{\epsilon}\right)\Big[-\frac{1}{2}\Delta_y\psi_1+E^{(2)}(a(t))\frac{y^2}{2} \\ &+E^{(3)}(a(t))\psi_1\frac{y^3}{6}\psi_0-i\eta(t)\cdot\nabla_x\psi_1-\nabla_x\cdot\nabla_y\psi_0\Big] \end{aligned}$$

Splitting this into the components parallel and perpendicular to $\Phi_{\mathcal{A}}(x)$, we obtain the two equations

$$\begin{aligned} iP_{\parallel}(x)\frac{\partial}{\partial t}\psi_1 =&-\frac{1}{2}\Delta_y\psi_1+E^{(2)}(a(t))\frac{y^2}{2}\psi_1+E^{(3)}(a(t))\frac{y^3}{6}\psi_0 \\ &-iP_{\parallel}(x)\eta(t)\cdot\nabla_x\psi_1-P_{\parallel}(x)\nabla_x\cdot\nabla_y\psi_0 \end{aligned}$$

and

$$0=iP_{\perp}(x)\frac{\partial}{\partial t}\psi_1+iP_{\perp}(x)\eta(t)\cdot\nabla_x\psi_1-P_{\perp}(x)\nabla_x\cdot\nabla_y\psi_0.$$

Let us make a change of variables $w = x - a(t)$, and replace $f_1(w, y, t) = g_1(x, y, t)$.

$$
\begin{aligned}
i\frac{\partial}{\partial t} f_1 &= -\frac{1}{2}\Delta_y f_1 + E^{(2)}(a(t))\frac{y^2}{2} f_1 + E^{(3)}(a(t))\frac{y^3}{6} f_0 \\
&\quad - \nabla_w \cdot \nabla_y f_0 - (\nabla_y f_0) \cdot \langle \Phi(w + a(t), t),\ \nabla(\Phi(w + a(t), t)\rangle_{\mathcal{H}_{el}}
\end{aligned}
$$

and

$$
0 = \nabla_w f_1 - \nabla_x \cdot \nabla_y f_0.
$$

We search for solutions of the form

$$
g_1(x, y, t) \;=\; \sum_{|m| \le |l|+3} d_m(x - a(t), t)\epsilon^{-1/2}\phi_m(A(t), B(t), 1, 0, 0, y).
$$

For $x + a(t) = w$, we just have

$$
f_1(w, y, t) \;=\; \sum_{|m| \le |l|+3} d_m(w, t)\epsilon^{-1/2}\phi_m(A(t), B(t), 1, 0, 0, y).
$$

Then using the quantities from our problem, we can simplify these. Again, $E^{(2)}(a(t)) = 0$ and $E^{(3)}(a(t)) = 0$. Also, we can note that we chose $f_0(w, y, t)$ not to be dependent on w, so that eliminates the term with ∇_w. Lastly, using $\Phi_A(x, t) = \begin{pmatrix} -\sin(x) \\ \cos(x) \end{pmatrix}$,

$$
\langle \Phi(w + a(t), t),\ \nabla(\Phi(w + a(t), t)\rangle_{\mathcal{H}_{el}} = \left\langle \begin{pmatrix} -\sin(w + a(t)) \\ \cos(w + a(t)) \end{pmatrix}, \begin{pmatrix} -\cos(w + a(t)) \\ -\sin(w + a(t)) \end{pmatrix} \right\rangle = 0.
$$

We are just left with

$$
i\sum_{m \le 3}\left(\frac{\partial}{\partial t} d_m(w, t)\right)\phi_m(A, B, 1, 0, 0, y) = \sum_{m \le 3}\left(\nabla_x d_m(w, t)\right)\phi_m(A, B, 1, 0, 0, y)
$$

and

$$
\sum_{m \le 3} d_m(w, t)\phi_m(A, B, 1, 0, 0, y) = -BA^{-1}y\phi_0(A, B, 1, 0, 0, y)
$$

We focus first on the perpendicular part.

Refer to Appendix (D) for the calcuations of $\phi_m(A, B, \epsilon^2, a, 0, x)$ for $m = 0, 1, 2, 3$. The only terms matching the order of epsilon on the right hand side results in

$$\begin{aligned} d_1(w,t)\phi_1(A,B,1,0,0,y) =& d_1(w,t)\left(\frac{1}{\sqrt{2}}[(B+\overline{A}BA^{-1})]y\right)\phi_0(A,B,1,0,0,y) \\ =& -BA^{-1}y\phi_0(A,B,1,0,0,y). \end{aligned}$$

Then we find

$$d_1(w,t) = \frac{-\sqrt{2}BA^{-1}}{B+\overline{A}BA^{-1}}.$$

Since the dimension of our system is $n = 1$, these quantities all commute, so we can simplify this to

$$d_1(w,t) = \frac{-\sqrt{2}}{A+\overline{A}}.$$

Assuming the initial conditions A_0 and D_0^A are chosen to be real, this is

$$d_1(w,t) = \frac{-1}{\sqrt{2}A_0}.$$

Then we consider the parallel part, which is satisfied for $d_0 = 0$, $d_1 = \frac{-1}{\sqrt{2}A_0}$, $d_2 = 0$, and $d_3 = 0$.

These coefficients satisfy that all the remainder terms in $\zeta(x, y, t)$ are of order $O(\epsilon^4)$ and above. Then applying the following lemma from [34], with $a = 2$, we can see that this results in an approximate solution $\Psi(x, y, t)$ which is accurate up to errors of order $O(\epsilon^2)$ as desired.

Lemma 3.1.6 (Lemma 3.3 of [34]). *(The Magic Lemma) "Suppose $H(\epsilon)$ is a family of self-adjoint operators for $\epsilon > 0$. Suppose $\psi(r, \epsilon)$ belongs to the domain of $H(\epsilon)$, is continuously* *differentiable in* r*, and approximately solves the Schrödinger equation in the sense that*

$$i\epsilon^a \frac{\partial \psi}{\partial r}(r, \epsilon) \;=\; H(\epsilon)\psi(r, \epsilon) + \zeta(r, \epsilon),$$

where $\zeta(r, \epsilon)$ *satisfies*

$$||\zeta(r, \epsilon)|| \;\leq\; \mu(r, \epsilon)$$

for $T_1(\epsilon) \leq r \leq T_2(\epsilon)$*. Suppose* $\Phi(r, \epsilon)$ *is the exact solution to the equation*

$$i\epsilon^a \frac{\partial \Psi}{\partial r}(r, \epsilon)$$

with initial condition $\Psi(r_0, \epsilon) = \psi(r_0, \epsilon)$ *with* $T_1(\epsilon) \leq r_0 \leq T_2(\epsilon)$*. Then, for* $T_1(\epsilon) \leq t \leq T_2(\epsilon)$*, the following estimate holds:*

$$||\Psi(r, \epsilon) - \psi(r, \epsilon)|| \;\leq\; e^{-a} \int_{T_1(\epsilon)}^{T_2(\epsilon)} \mu(r, \epsilon)\; dr.\text{"}$$

3.1.4 Inner Solutions

For the situation we considered, i.e. we begin with a state following the lower energy level, $E_{\mathcal{A}}(x)$, and propagate through the crossing, we can take T to be as large as we wish, and take $T_1 = \epsilon^{\xi}$, by Lemma (3.1.2), for any $\xi \in (0, 1)$. Thus, the solution for the outer regime, $t < \epsilon^{\xi}$, given by (3.15) are accurate up to terms of order ϵ.

Since we were able to find uniform solutions to the classical quantities $a(t),\ \eta(t),\ S(t),\ A(t)$, and $B(t)$ exactly for all t, we do not have any further restrictions on the value of ξ required to have the desired order of accuracy for our solutions.

Now using the results of Lemma (3.1.3), we can find the solutions for $t \in [-\epsilon^{\xi'}, \epsilon^{\xi'}]$, for any $\xi' \in (\frac{1}{2}, 1)$, accurate up to errors of order $\epsilon^{\xi'}$.

For the inner solution, we will make the following replacements.

$$y_{\mathcal{A}} = \frac{x - a^{\mathcal{A}}(t)}{\epsilon}$$

$$y_{\mathcal{B}} = \frac{x - a^{\mathcal{B}}(t)}{\epsilon} = y_{\mathcal{A}} + \frac{a^{\mathcal{A}}(t) - a^{\mathcal{B}}(t)}{\epsilon}$$

$$s = \frac{t}{\epsilon}$$

We make the ansatz that the inner solution is of the form

$$\begin{aligned}\psi(y_{\mathcal{A}}, s) =& e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} f(y_{\mathcal{A}}, s)\Phi_{\mathcal{A}}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s)\\ &+ e^{iS^{\mathcal{B}}(\epsilon s/\epsilon^2} e^{i\eta^{\mathcal{B}}(\epsilon s)\cdot y_{\mathcal{B}}/\epsilon} g(y_{\mathcal{B}}, \epsilon s)\Phi_{\mathcal{B}}(a^{\mathcal{B}}(\epsilon s) + \epsilon y_{\mathcal{B}}, \epsilon s)\\ &+ e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \psi^{\perp}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s),\end{aligned}$$

where $\psi(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s)$ is orthogonal to both $\Phi_{\mathcal{A}}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}})$ and $\Phi_{\mathcal{B}}(a^{\mathcal{B}}(\epsilon s) + \epsilon y_{\mathcal{B}})$. However, we note

$$\Phi_{\mathcal{A}}(x) = \begin{pmatrix} -\sin(x) \\ \\ \cos(x) \end{pmatrix} \text{ and } \Phi_{\mathcal{B}}(x) = \begin{pmatrix} \cos(x) \\ \\ \sin(x) \end{pmatrix},$$

which span the whole space. Therefore, $\psi^{\perp}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s) = 0$. We assume f and g have asymptotic expansions of the forms

$$f(y_{\mathcal{A}}, s) = \sum_{j=0}^{\infty} \nu_j(\epsilon) f_j(y_{\mathcal{A}}, s)$$

and

$$g(y_{\mathcal{B}}, s) = \sum_{j=0}^{\infty} \nu_j(\epsilon) g_j(y_{\mathcal{B}}, s).$$

After plugging these into the Schrödinger equation and simplifying, we will investigate solutions by orders of epsilon. The terms of order $\nu_j(\epsilon)$ such that $\nu_j(\epsilon) = \epsilon\nu_j(\epsilon)$ are

$$
\begin{aligned}
& ie^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \frac{\partial f_0}{\partial s}(y_{\mathcal{A}}, s)\Phi_{\mathcal{A}}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s) \\
& + ie^{iS^{\mathcal{B}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{B}}(\epsilon s)\cdot y_{\mathcal{B}}/\epsilon} \frac{\partial g_0}{\partial s}\Phi_{\mathcal{B}}(a^{\mathcal{B}}(\epsilon s) + \epsilon y_{\mathcal{B}}) \\
& = 0.
\end{aligned}
$$

The two terms are orthogonal in the electronic Hilbert space, so we must have

$$
\frac{\partial f_0}{\partial s}(y_{\mathcal{A}}, s) \; = \; 0
$$

and

$$
\frac{\partial g_0}{\partial s}(y_{\mathcal{B}}, s) \; = \; 0.
$$

In order for the inner solutions to match the outer solutions, we choose $\nu_0(\epsilon) = 1$. Then we can let $\nu_1(\epsilon) = \epsilon$, and the solutions for these order terms are

$$
f_0(y_{\mathcal{A}}, s) \; = \; \epsilon^{-1/2}\phi_0(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}})
$$

and

$$
g_0(y_{\mathcal{B}}, s) \; = \; 0.
$$

Next we look at terms whose order is $\nu_2(\epsilon) = \epsilon^2$.

$$
\begin{aligned}
& ie^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \frac{\partial f_1}{\partial s}(y_{\mathcal{A}}, s)\Phi_{\mathcal{A}}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s) \\
& + ie^{iS^{\mathcal{B}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{B}}(\epsilon s)\cdot y_{\mathcal{B}}/\epsilon} \frac{\partial g_1}{\partial s}\Phi_{\mathcal{B}}(a^{\mathcal{B}}(\epsilon s) + \epsilon y_{\mathcal{B}}) \\
& + ie^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}} \cdot \nabla_x \right) \Phi_{\mathcal{A}}
\end{aligned}
$$

$$= -e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \frac{1}{2}(\Delta_{y_{\mathcal{A}}} f_0)\Phi_{\mathcal{A}}$$
$$+ e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{A}}(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} E^{(2)}_{\mathcal{A}}(a^{\mathcal{A}}) \frac{y^2_{\mathcal{A}}}{2} f_0 \Phi_{\mathcal{A}}$$

After separating the orthogonal directions, we have F

$$i\frac{\partial f_1}{\partial s} = -\frac{1}{2}\Delta_{y_{\mathcal{A}}} f_0 + E^{(2)}_{\mathcal{A}}(a^{\mathcal{A}})\frac{y^2_{\mathcal{A}}}{2} f_0$$

and

$$\frac{\partial g_1}{\partial s} = -e^{i(S^{\mathcal{B}}-S^{\mathcal{A}})/\epsilon^2} e^{i(\eta^{\mathcal{B}}\cdot y_{\mathcal{B}}-\eta^{\mathcal{A}}\cdot y_{\mathcal{A}})/\epsilon}\langle \Phi_{\mathcal{B}}, \left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}}\cdot\nabla_x\right)\Phi_{\mathcal{A}}\rangle f_0.$$

First we will solve f_1. We integrate and match to the outer solutions to obtain

$$f_1(y_{\mathcal{A}}, s) = -is\left(-\frac{1}{2}\Delta_{y_{\mathcal{A}}} f_0 + E^{(2)}_{\mathcal{A}}(a^{\mathcal{A}})\frac{y^2_{\mathcal{A}}}{2} f_0\right)$$
$$+ \sum_{|m|\le 3} d_m(\epsilon y_{\mathcal{A}}, 0)\epsilon^{-1/2}\phi_m(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}}).$$

Now, we can use the following.

$$E^{(2)}_{\mathcal{A}}(x) = 0$$

$$\Delta_{y_{\mathcal{A}}} f_0 = \epsilon^{-1/2}\left([-BA^{-1}]^2 y^2 + BA^{-1}\right)\phi_0(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}})$$

Thus we are looking for solutions of the form

$$f_1(y_{\mathcal{A}}, s) = is\left(\epsilon^{-1/2}\frac{1}{2}\left([BA^{-1}]^2 y^2 - BA^{-1}\right)\phi_0(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}})\right)$$
$$+ \sum_{|m|\le 3} d_m(\epsilon y_{\mathcal{A}}, 0)\epsilon^{-1/2}\phi_m(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}}).$$

which solves

$$\frac{\partial f_1}{\partial s} = i\epsilon^{-1/2}\frac{1}{8}[B^{\mathcal{A}} A^{\mathcal{A}^{-1}}]^2\phi_0(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}})$$

Next we move on to $g_1(y_{\mathcal{B}}, s)$ which is found by solving the complicated oscillatory integral

$$
\begin{aligned}
g_1(y_{\mathcal{B}}, s) &= g_1(y_{\mathcal{A}}, 0) \\
&\quad - \int_0^s e^{i(S^{\mathcal{B}}-S^{\mathcal{A}})/\epsilon^2} e^{i\eta^{\mathcal{B}}\cdot y_{\mathcal{B}} - \eta^{\mathcal{A}}\cdot y_{\mathcal{A}})/\epsilon} \langle \Phi_{\mathcal{B}}, \left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}} \cdot \nabla_X\right) \Phi_{\mathcal{A}} \rangle f_0 ds'
\end{aligned}
$$

with

$$
g_1(y_{\mathcal{B}}, 0) = -\frac{(1+i)\pi^{1/2}}{2b(0)^{1/2}} \Omega(0,0) e^{i\omega(c(\epsilon, y_{\mathcal{B}}), \epsilon y_{\mathcal{A}})/\epsilon^2} f_0(0,0).
$$

The functions b, c, and Ω will be defined later. We can also note that

$$
\langle \Phi_{\mathcal{B}}, \left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}} \cdot \nabla_X\right) \Phi_{\mathcal{A}} \rangle = \left\langle \begin{pmatrix} \cos(x) \\ \\ \sin(x) \end{pmatrix}, \begin{pmatrix} -\cos(x) \\ \\ -\sin(x) \end{pmatrix} \right\rangle = -1
$$

Since f_0 for our problem does not depend on s, or t. Thus we need to solve the integral

$$
\int_0^s e^{i\omega(\epsilon s', \epsilon y_{\mathcal{B}})/\epsilon^2} ds'
$$

where we define

$$
\begin{aligned}
\omega(t, \epsilon y_{\mathcal{B}}) &= (S^{\mathcal{B}}(t) - S^{\mathcal{A}}(t)) + \epsilon(\eta^{\mathcal{B}}(t) \cdot y_{\mathcal{B}} - \eta^{\mathcal{A}}(t) \cdot y_{\mathcal{A}}) \\
&= (S^{\mathcal{B}}(t) - S^{\mathcal{A}}(t)) + \eta^{\mathcal{A}}(t) \cdot (a^{\mathcal{B}}(t) - a^{\mathcal{A}}(t)) + (\eta^{\mathcal{B}}(t) - \eta^{\mathcal{A}}(t)) \cdot y_{\mathcal{B}} \\
&= -\frac{\widetilde{\eta_0}}{2} t^2 - \frac{1}{3} t^3 - t(\epsilon y_{\mathcal{B}}).
\end{aligned}
$$

Then we use a Taylor expansion to solve this integral up to acceptable errors.

$$
\begin{aligned}
e^{i\omega(t, \epsilon y_{\mathcal{B}})\epsilon^2} &= 1 - i\epsilon^{-2} \left(\frac{\widetilde{\eta_0}}{2} t^2 + \frac{1}{3} t^3 + t(\epsilon y_{\mathcal{B}}) \right) + \ldots \\
&= 1 - i \left(\frac{\widetilde{\eta_0}}{s}^2 + \epsilon \frac{1}{3} s^2 + s y_{\mathcal{B}} \right) + \ldots \\
&= 1 - i s y_{\mathcal{B}} + O(s^2)
\end{aligned}
$$

Then

$$\begin{aligned} g_1(y_{\mathcal{B}}, s) &= g_1(y_{\mathcal{B}}, 0) + \int_0^s 1 - isy_{\mathcal{B}} + O((s')^2) ds' f_0 \\ &= g_1(y_{\mathcal{B}}, 0) + s - i\frac{1}{2}s^2 y_{\mathcal{B}} + O(s^3). \end{aligned}$$

Then we solve for the initial condition for $g_1(y_{\mathcal{B}}, s)$,

$$g_1(y_{\mathcal{B}}, 0) = -\frac{(1+i)\pi^{1/2}}{2b(0)^{1/2}} \Omega(0,0) e^{i\omega(c(\epsilon, y_{\mathcal{B}}), \epsilon y_{\mathcal{B}})/\epsilon^2} f_0(0,0).$$

where the function $c(\epsilon y_{\mathcal{B}})$ satisfies

$$c(\epsilon y_{\mathcal{B}}) = \frac{(E_{\mathcal{A}}^{(1)}(0) - E_{\mathcal{B}}^{(1)}(0)) \cdot \epsilon y_{\mathcal{B}}}{(E_{\mathcal{A}}^{(1)}(0) - E_{\mathcal{B}}^{(1)}(0)) \cdot \widetilde{\eta}_0} + O(\epsilon^2 |y_{\mathcal{B}}|^2)$$

and

$$\begin{aligned} b(\epsilon y_{\mathcal{B}}) &= \frac{\partial^2 \omega}{\partial t^2}(c(\epsilon y_{\mathcal{B}}), \epsilon y_{\mathcal{B}}) \\ &= (E_{\mathcal{A}}^{(1)}(0) - E_{\mathcal{B}}^{(1)}(0)) \cdot \widetilde{\eta}_0 + O(\epsilon |y_{\mathcal{B}}|). \end{aligned}$$

Then we have

$$\omega(c(\epsilon y_{\mathcal{B}}), \epsilon y_{\mathcal{B}}) = -\frac{[(E_{\mathcal{A}}^{(1)}(0) - E_{\mathcal{B}}^{(1)}(0)) \cdot \epsilon y_{\mathcal{B}}]^2}{2(E_{\mathcal{A}}^{(1)}(0) - E_{\mathcal{B}}^{(1)}(0)) \cdot \widetilde{\eta}_0} + O(\epsilon^3 |y_{\mathcal{B}}|^3)$$

We use

$$\Omega(\epsilon y_{\mathcal{B}}) = \langle \Phi_{\mathcal{B}}(0,0), \left(\frac{\partial}{\partial t} - \eta^{\mathcal{A}} \nabla_x \right) \Phi_{\mathcal{A}}(0,0) \rangle f_0(0,0) + O(\epsilon |y_{\mathcal{B}}|).$$

For our problem, these function needed for $g_1(y_{\mathcal{B}}, s)$ are

$$\begin{aligned} c(\epsilon y_{\mathcal{B}}) &= \frac{\epsilon y_{\mathcal{B}}}{\widetilde{\eta}_0} + O(\epsilon^2 |y_{\mathcal{B}}|^2) \\ \omega(c(\epsilon y_{\mathcal{B}}), \epsilon y_{\mathcal{B}}) &= -\frac{\epsilon^2 y_{\mathcal{B}}^2}{2\widetilde{\eta}_0} + O(\epsilon^2 |y_{\mathcal{B}}|^3) \end{aligned}$$

$$b(\epsilon y_{\mathcal{B}}) = \widetilde{\eta}_0 + O(\epsilon |y_{\mathcal{B}}|)$$

$$\Omega(\epsilon y_{\mathcal{B}}, 0) = \eta^{\mathcal{A}}(t) f_0(0,0) + O(\epsilon |y_{\mathcal{B}}|) = \widetilde{\eta}_0 \epsilon^{-1} \pi^{-1/4} A_0^{-1/2} + O(\epsilon |y_{\mathcal{B}}|).$$

Therefore, we set

$$g_1(y_{\mathcal{B}}, 0) = -\frac{(1+i)}{2\widetilde{\eta}_0^{\,1/2}} \epsilon^{-2} A_0^{-1} e^{-iy_{\mathcal{B}}^2/2\widetilde{\eta}_0}$$

and

$$g_1(y_{\mathcal{B}}, s) = -\frac{(1+i)}{2\widetilde{\eta}_0^{\,1/2}} \epsilon^{-2} A_0^{-1} e^{-iy_{\mathcal{B}}^2/2\widetilde{\eta}_0} + s - i\frac{1}{2} s^2 y_{\mathcal{B}}.$$

Hence we obtain the inner solutions

$$\begin{aligned}
&e^{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2} e^{i\eta(\epsilon s)\cdot y_{\mathcal{A}}/\epsilon} \epsilon^{-1/2} \Phi_{\mathcal{A}}(a^{\mathcal{A}}(\epsilon s) + \epsilon y_{\mathcal{A}}, \epsilon s) \\
&\quad \times \left(\left(1 + \frac{1}{2} i\epsilon s \left([B^{\mathcal{A}}(\epsilon s) A^{\mathcal{A}}(\epsilon s)^{-1}]^2 y_{\mathcal{A}}^2 + B^{\mathcal{A}}(\epsilon s) A^{\mathcal{A}}(\epsilon s)^{-1} \right) \right) \phi_0(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}}) \right. \\
&\qquad \left. + \epsilon^{1/2} \left(\frac{1}{2} [B^{\mathcal{A}}(\epsilon s) A^{\mathcal{A}}(\epsilon s)^{-1}]^2 \right) \right) \phi_0(A^{\mathcal{A}}(0), B^{\mathcal{A}}(0), 1, 0, 0, y_{\mathcal{A}}) \Big) \\
&\quad + \epsilon e^{iS^{\mathcal{B}}(\epsilon s)/\epsilon^2} e^{i\eta^{\mathcal{B}}(\epsilon s)\cdot y_{\mathcal{B}}/\epsilon} \left(-\frac{(1+i)}{2\widetilde{\eta}_0^{\,1/2}} \epsilon^{-2} A_0^{-1} e^{-iy_{\mathcal{B}}^2/2\widetilde{\eta}_0} + s - i\frac{1}{2} s^2 y_{\mathcal{B}} \right) \Phi_{\mathcal{B}}(a^{\mathcal{B}}(\epsilon s) + \epsilon y_{\mathcal{B}}, \epsilon s).
\end{aligned}$$

3.1.5 Outgoing Outer solutions

Using the results from Theorem (3.1.1), the approximate solutions to the Schrödinger equation

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} \;=\; -\frac{\epsilon^4}{2} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

is given by

$$\Psi(\epsilon, x, t) \;= \Phi_{\mathcal{A}}(x,t) e^{iS^{\mathcal{A}}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot(x - a^{\mathcal{A}}(t))/\epsilon^2}$$

$$\times \Big(\phi_l(A(t), B(t), \epsilon^2, \eta(t), x)$$

$$+ \epsilon \sum_{|m| \le |l|+3} d_m(x - a^{\mathcal{A}}(t), t) \phi_m(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x)\Big)$$

$$+ O(\epsilon^2)$$

for $t \in [-T, -T_1]$, for any fixed $T_1 > 0$. Then for $t \in [T_1, T]$,

$$\begin{aligned}
\Psi(\epsilon, x, t) \ &= \Phi_{\mathcal{A}}(x, t) e^{iS^{\mathcal{A}}(t)/\epsilon^2} e^{i\eta^{\mathcal{A}}(t)\cdot(x - a^{\mathcal{A}}(t))/\epsilon^2} \\
&\qquad \times \Big(\phi_l(A(t), B(t), \epsilon^2, \eta(t), x) \\
&\qquad\quad + \epsilon \left(\frac{-1}{\sqrt{2}A_0}\right) \phi_1(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x)\Big) \\
&\quad - \epsilon(1+i)\pi^{1/2} \Big(\langle (E_{\mathcal{A}}^{(1)} - E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle\Big)^{-1/2} \\
&\qquad \times \langle \Phi_{\mathcal{A}}(0,0),\ \left(\left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}}(0)\cdot\nabla_x\right)\Phi_{\mathcal{A}}\right)(0,0)\rangle_{\mathcal{H}_{el}} \\
&\qquad \times \Phi_{\mathcal{B}}(x,t) e^{iS^{\mathcal{B}}(t)/\epsilon^2} e^{i\eta^{\mathcal{B}}(t)\cdot(x - a^{\mathcal{B}}(t))/\epsilon^2} \phi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x) \\
&\quad + O(\epsilon^{\alpha}),
\end{aligned}$$

for some $\alpha > 0$. Note that if $\langle (E_{\mathcal{A}}^{(1)} - E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle$ is positive, we take the positive square root in the equation above, and if it is negative, we take the positive imaginary square root.

Below are the calculations needed to find the solution:

$$\Big(\langle (E_{\mathcal{A}}^{(1)} - E_{\mathcal{B}}^{(1)}),\ \eta^{\mathcal{A}}(0)\rangle\Big)^{-1/2} = (\langle (0-1), \widetilde{\eta_0}\rangle)^{-1/2} = -i(\widetilde{\eta_0})^{-1/2}$$

Note that there is no t dependence in $\Phi_{\mathcal{A}}(x)$ and $\Phi_{\mathcal{B}}(x)$, so in the equation below, we only need to consider evaluating these at $x = 0$.

$$\langle \Phi_{\mathcal{B}}(0,0),\ \left(\left(\frac{\partial}{\partial t} + \eta^{\mathcal{A}}(0)\cdot\nabla_x\right)\Phi_{\mathcal{A}}\right)(0,0)\rangle_{\mathcal{H}_{el}}$$

$$= \left\langle \begin{pmatrix} \cos(0) \\ \\ \sin(0) \end{pmatrix}, \left(\widetilde{\eta}_0 \begin{pmatrix} -\cos(0) \\ \\ -\sin(0) \end{pmatrix} \right) \right\rangle_{\mathcal{H}_{el}} = \widetilde{\eta}_0 \left\langle \begin{pmatrix} 1 \\ \\ 0 \end{pmatrix}, \begin{pmatrix} -1 \\ \\ 0 \end{pmatrix} \right\rangle_{\mathcal{H}_{el}} = -\widetilde{\eta}_0$$

To find the solutions given by (3.15) and (3.16), we implement the main theorems and lemmas together: Theorem (3.1.1), Lemma (3.1.2), and Lemma (3.1.3). Thus proves the main results given by Corollary (3.1.4).

3.1.6 Numerical Example

With the solutions given by Corollary (3.1.4), we can find the solutions to any problem with a potential of this form. As an example, we will show the results for a system, with an initial wave packet at $t = -T$ associated with the electronic energy level $E_{\mathcal{A}}(x)$, the lower level for $t < 0$.

We can choose our starting time $t = -T$, with T being any arbitrary number as we do not need to worry about avoiding any other eigenvalue crossings or avoided crossing for this system in the case where we begin with a wave packet on the $E_{\mathcal{A}}(x)$ level with positive initial momentum. For this example I will choose $T = 30\epsilon$.

We will specify the value of ϵ, our Born-Oppenheimer averaged nuclear mass, using the mass of a C^{12} carbon nucleus. $\epsilon \approx .1$.

We let the classical initial conditions be given by

$$a^{\mathcal{A}}(0) \;=\; a_0 \;=\; 0$$

$$\eta^{\mathcal{A}}(0) = \widetilde{\eta}_0 = 1$$

$$S^{\mathcal{A}}(0) = S_0 = 0$$

$$A^{\mathcal{A}}(0) = A_0 = 1$$

$$B^{\mathcal{A}}(0) = D_0^{\mathcal{A}} = 1.$$

We can see the results graphed below in Figure (3.7).

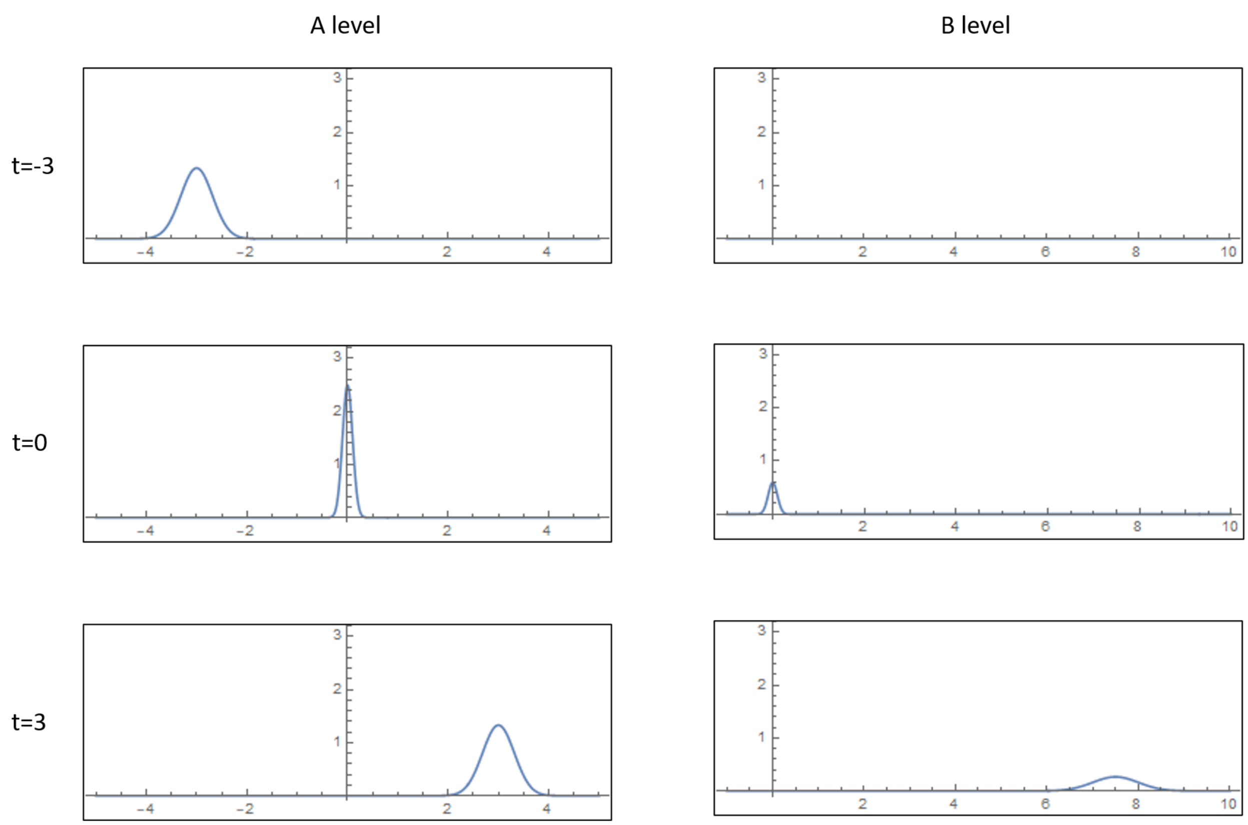

Figure 3.7: Propagation of a Gaussian wave packet through a codimension 1 crossing

3.2 Higher dimensions

To demonstrate that for this type of crossing it is sufficient to consider just one dimension, x, we will now consider $X \in \mathbb{R}^n$. Using the same Hamiltonian $H(x)$ as before, but in n dimensional space. We make the following adjustments to the equations to be solved.

$$H(x) \to H(X) = -\frac{\epsilon^4}{2}\Delta - X_1 \begin{pmatrix} \cos^2(X_1) & \cos(X_1)\sin(X_1) \\ \cos(X_1)\sin(X_1) & \sin^2(X_1) \end{pmatrix}$$

So we change $h(x)$ to $h(X_1)$. The choice of the first coordinate is arbitrary.

$a(t) \;\to\; \vec{a}(t)$

$\eta(t) \;\to\; \vec{\eta}(t)$

$A(t)$ and $B(t)$ are now $n \times n$ matrices with complex entries.

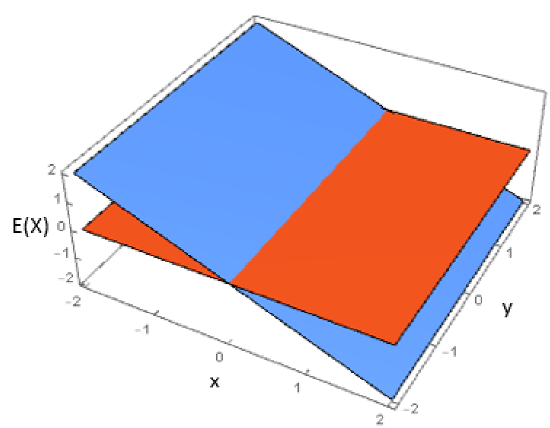

Figure 3.8: $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$, for $X = (x, y)^t \in \mathbb{R}^2$

$$\frac{\partial \vec{a}}{\partial t}(t) \;=\; \vec{\eta}(t), \tag{3.27}$$

$$\frac{\partial \vec{\eta}}{\partial t}(t) = -V^{(1)}(\vec{a}(t)), \tag{3.28}$$

$$\frac{\partial S}{\partial t}(t) = \frac{1}{2}\vec{\eta}(t)\cdot\vec{\eta}(t) - V(\vec{a}(t)), \tag{3.29}$$

$$\frac{\partial A}{\partial t}(t) = iB(t), \tag{3.30}$$

$$\frac{\partial B}{\partial t}(t) = iV^{(2)}(\vec{a}(t))A(t). \tag{3.31}$$

We assume $A^{\mathcal{A}}(-T)$ and $B^{\mathcal{A}}(-T)$ satisfy the four conditions (2.1)-(2.4). We also assume that the nuclear momentum vector $\vec{\eta}^{\mathcal{A}}(0)$ is not tangent to Γ, which in this case is satisfied for any initial condition $\widetilde{\eta}_0$. We should assume that $\vec{\eta}^{\mathcal{A}}(0)$ has a positive component in the X_1 direction.

$V(X)$ is given by the eigenvalues of $h(X)$. For the incoming wave packet we use $V(X) = E_{\mathcal{A}}(X) = 0$.

$$V^{(1)}(X) = \begin{pmatrix} \frac{dE_{\mathcal{A}}(X)}{dX_1} \\ \vdots \\ \frac{dE_{\mathcal{A}}(X)}{dX_n} \end{pmatrix} = \vec{0}$$

$$V^{(2)}(X) = \begin{pmatrix} \frac{d^2E_{\mathcal{A}}(X)}{dX_1^2} & \cdots & \frac{d^2E_{\mathcal{A}}(X)}{dX_1 dX_n} \\ \vdots & \ddots & \vdots \\ \frac{d^2E_{\mathcal{A}}(X)}{dX_n dX_1} & \cdots & \frac{d^2E_{\mathcal{A}}(X)}{dX_n^2} \end{pmatrix} = [0]_{n\times n}$$

Then the system we need to solve for the incoming wave packet, $t \le 0$, is

$$\frac{\partial \vec{a}}{\partial t}(t) = \vec{\eta}(t),$$

$$\frac{\partial \vec{\eta}}{\partial t}(t) = \vec{0},$$

$$\begin{aligned}
\frac{\partial S}{\partial t}(t) &= \frac{1}{2}\vec{\eta}(t)\cdot\vec{\eta}(t), \\
\frac{\partial A}{\partial t}(t) &= iB(t), \\
\frac{\partial B}{\partial t}(t) &= [0]_{n\times n}.
\end{aligned}$$

with the initial conditions

$$\vec{a}^{\mathcal{A}}(0) = \vec{0},$$

$$\vec{\eta}^{\mathcal{A}}(0) = \widetilde{\eta}_0$$

$$S^{\mathcal{A}}(0) = S_0,$$

$$A^{\mathcal{A}}(0) = A_0.$$

We require that $\widetilde{\eta}_{01} > 0$, but to keep generality, we will not restrict the other values for the initial momentum in other directions. We will find this will only affect our solutions for $S(t)$, thus only changing the phases compared to the previous case $x \in \mathbb{R}$.

This gives us the solutions

$$\begin{aligned}
\vec{a}^{\mathcal{A}}(t) &= \widetilde{\eta}_0 t, \\
\vec{\eta}^{\mathcal{A}}(t) &= \widetilde{\eta}_0, \\
S^{\mathcal{A}}(t) &= S_0 + \frac{1}{2}\widetilde{\eta}_0\cdot\widetilde{\eta}_0 t, \\
A^{\mathcal{A}}(t) &= A_0 + itD_0^{\mathcal{A}}, \\
B^{\mathcal{A}}(t) &= D_0^{\mathcal{A}}.
\end{aligned}$$

for $t \leq 0$.

$D_0^{\mathcal{A}}$ is the matrix such that $A^{\mathcal{A}}(-T)$ and $B^{\mathcal{A}}(-T)$ satisfy conditions (2.1)-(2.4).

For the outgoing wave packet, let $\vec{a}^{\mathcal{A}}(t)$, $\vec{\eta}^{\mathcal{A}}(t)$, $S^{\mathcal{A}}(t), A^{\mathcal{A}}(t)$, and $B^{\mathcal{A}}(t)$ be the unique solutions to the system of equations (3.3)-(3.7).

$V(X) = E_{\mathcal{B}}(X) = X_1$ for the outgoing wave packet, $t \geq 0$.

$$V^{(1)}(X) = \begin{pmatrix} \frac{dE_{\mathcal{B}}(X)}{dX_1} \\ \vdots \\ \frac{dE_{\mathcal{B}}(X)}{dX_n} \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$V^{(2)}(X) = \begin{pmatrix} \frac{d^2E_{\mathcal{B}}(X)}{dX_1^2} & \cdots & \frac{d^2E_{\mathcal{B}}(X)}{dX_1 dX_n} \\ \vdots & \ddots & \vdots \\ \frac{d^2E_{\mathcal{B}}(X)}{dX_n dX_1} & \cdots & \frac{d^2E_{\mathcal{B}}(X)}{dX_n^2} \end{pmatrix} = [0]_{n \times n}$$

Then the system we need to solve for $t > 0$ is

$$\begin{aligned} \frac{\partial \vec{a}}{\partial t}(t) &= \vec{\eta}(t), \\ \frac{\partial \vec{\eta}}{\partial t}(t) &= \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \\ \frac{\partial S}{\partial t}(t) &= \frac{1}{2}\vec{\eta}(t) \cdot \vec{\eta}(t) - \vec{a}(t), \\ \frac{\partial A}{\partial t}(t) &= iB(t), \\ \frac{\partial B}{\partial t}(t) &= [0]_{n \times n}. \end{aligned}$$

We require the same initial conditions so that

$$
\begin{aligned}
&\vec{a}_{\mathcal{B}}(0) = \vec{a}^{\mathcal{A}}(0) = \vec{0}, \\
&\vec{\eta}^{\mathcal{B}}(0) = \eta^{\mathcal{A}}(0) = \widetilde{\eta}_0, \\
&S^{\mathcal{B}}(0) = S^{\mathcal{A}}(0) = S_0, \\
&A^{\mathcal{B}}(0) = A^{\mathcal{A}}(0) = A_0, \\
&B^{\mathcal{B}}(0) = B_0^{\mathcal{A}}(0) + i\frac{|(E_{\mathcal{B}}^{(1)}(0) - E_{\mathcal{A}}^{(1)}(0))\rangle\langle(E_{\mathcal{B}}^{(1)}(0) - E_{\mathcal{A}}^{(1)}(0))|}{\langle(E_{\mathcal{B}}^{(1)}(0) - E_{\mathcal{A}}^{(1)}(0)),\ \vec{\eta}_{\mathcal{A}}(0)\rangle} A^{\mathcal{A}}(0) \\
&\qquad\quad = D_0^{\mathcal{A}} + i\frac{1}{\widetilde{\eta}_{0_1}} \begin{pmatrix} 1 & 0 & \cdots \\ 0 & \ddots & \vdots \\ \vdots & \cdots & 0 \end{pmatrix} A_0
\end{aligned}
$$

Let us call $B^{\mathcal{B}}(0) = D_0^{\mathcal{A}} + i\frac{1}{\widetilde{\eta}_{0_1}} \begin{pmatrix} 1 & 0 & \cdots \\ 0 & \ddots & \vdots \\ \vdots & \cdots & 0 \end{pmatrix} A_0 = D_0^{\mathcal{B}}$.

The unique solutions to this system are

$$
\begin{aligned}
\vec{a}^{\mathcal{B}}(t) &= \widetilde{\eta}_0 t + \begin{pmatrix} \frac{t^2}{2} \\ 0 \\ \vdots \end{pmatrix}, \\
\vec{\eta}^{\mathcal{B}}(t) &= \widetilde{\eta}_0 + \begin{pmatrix} t \\ 0 \\ \vdots \end{pmatrix}, \\
S^{\mathcal{B}}(t) &= S_0 + \frac{1}{2}\widetilde{\eta}_0 \cdot \widetilde{\eta}_0 t^2 - \frac{t^3}{3},
\end{aligned}
$$

$$A^{\mathcal{B}}(t) = A_0 + itD_0^{\mathcal{B}},$$

$$B^{\mathcal{B}}(t) = D_0^{\mathcal{B}},$$

for $t \geq 0$.

We can see that the first components of each solution have remained the same, with the exception of $S(t)$. If we projected this problem back into one dimension, the dimension of interest, X, we would see the same solutions as we found previously when considering just X alone. The only difference is that $S(t)$ depends on the positive constant chosen for the initial condition $\widetilde{\eta_0}$. This sufficiently shows that studying the behavior of system in just one space dimension is sufficient for studying the behavior in higher dimensions.

3.3 Avoiding the crossing

Let us begin by considering the time dependent Schrödinger equation

$$i\epsilon^2 \frac{\partial}{\partial t}\psi(x,t) = -\frac{\epsilon^4}{2}\Delta\psi(x,t) + h(x,\epsilon)\psi(x,t) \tag{3.32}$$

with the Hamiltonian operator $H(x)$ below, which results in a gapped system.

$$H(x) = -\frac{\epsilon^4}{2}\Delta + \begin{pmatrix} -x\cos^2(x) & -x\cos(x)\sin(x) + i\epsilon \\ -x\cos(x)\sin(x) - i\epsilon & -x\sin^2(x) \end{pmatrix} \tag{3.33}$$

where $x \in \mathbb{R}$.

Then $h(x,\epsilon) = \begin{pmatrix} -x\cos^2(x) & -x\cos(x)\sin(x) + i\epsilon \\ -x\cos(x)\sin(x) - i\epsilon & -x\sin^2(x) \end{pmatrix}$

$$= -\frac{x}{2} I_2 + \begin{pmatrix} -x(\cos^2(x) - \frac{1}{2}) & -x\cos(x)\sin(x) + i\epsilon \\ -x\cos(x)\sin(x) - i\epsilon & -x(\cos^2(x) - \frac{1}{2}) \end{pmatrix}$$

We wish to find the spectrum of $H(x)$, so we write $h(x,\epsilon)$ in terms of the Pauli spin matrices.

$$h(x,\epsilon) = -\frac{x}{2} I_2 + \left[-x\left(\cos^2(x) - \frac{1}{2}\right)\sigma_z - x\cos(x)\sin(x)\sigma_x + \epsilon\sigma_y \right]$$

This is in the form $h(x,\epsilon) = qI_2 + \vec{r}\cdot\vec{\sigma}$ where $\vec{\sigma} = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}$. Hence, for this system,

$\vec{r} = \begin{pmatrix} -x\cos(x)\sin(x) \\ \epsilon \\ -x(\cos^2(x) - \frac{1}{2}) \end{pmatrix}$.

Then the spectrum of $h(x,\epsilon)$ is given by

$$\sigma(h) = q + |\vec{r}| = -\frac{x}{2} \pm \sqrt{x^2(\cos^2(x) - \frac{1}{2})^2 + x^2\cos^2(x)\sin^2(x) + \epsilon^2}$$

$$= -\frac{1}{2}\left(x \pm \sqrt{x^2 + 4\epsilon^2}\right)$$

The eigenvalues of $h(x,\epsilon)$ are

$$E_-(x,\epsilon) = -\frac{1}{2}\left(x + \sqrt{x^2 + 4\epsilon^2}\right)$$

and

$$E_+(x,\epsilon) = -\frac{1}{2}\left(x - \sqrt{x^2 + 4\epsilon^2}\right)$$

To determine the eigenvectors of $h(x,\epsilon)$, we take each of the eigenvalues $E_-(x,\epsilon)$ and $E_+(x,\epsilon)$, and solve

$$[h(x,\epsilon) - E_j(x,\epsilon)I]\,\nu_j = 0$$

for $j = \{+,-\}$, to find the corresponding eigenvectors ν_- and ν_+. From this we find the following non-normalized eigenvectors.

$$\nu_-(x) = \begin{pmatrix} \frac{1}{2}x + \frac{1}{2}\sqrt{x^2+4\epsilon^2} - x\sin^2(x) \\ i\epsilon + x\cos(x)\sin(x) \end{pmatrix}$$

$$\nu_+(x) = \begin{pmatrix} \frac{1}{2}x - \frac{1}{2}\sqrt{x^2+4\epsilon^2} - x\sin^2(x) \\ i\epsilon + x\cos(x)\sin(x) \end{pmatrix}$$

The normalized eigenvectors are

$$\Phi_-(x) = \frac{1}{|\nu_-(x)|}\nu_-(x)$$

and

$$\Phi_+(x) = \frac{1}{|\nu_+(x)|}\nu_+(x).$$

For small epsilon, away from the gap, the system behaves like the previous case, where $E_-(x,\epsilon) \approx E_{\mathcal{A}}(x) = 0$ and $E_+(x,\epsilon) \approx E_{\mathcal{B}}(x) = -x$ for $x \ll 0$. Similarly, $E_-(x,\epsilon) \approx E_{\mathcal{B}}(x) = -x$ and $E_+(x,\epsilon) \approx E_{\mathcal{A}}(x) = 0$ for $x \gg 0$.

First let us define some important components which will allow us to find the solutions to the Schrödinger equation. Our solutions will be built of semi-classical wave packets in the sense

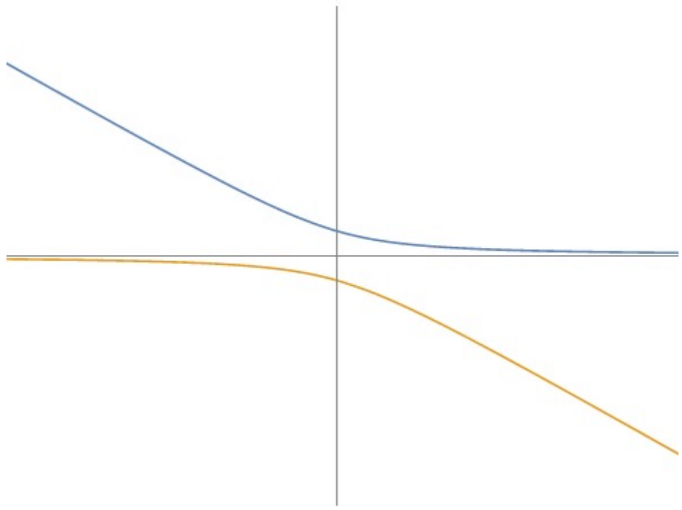

Figure 3.9: $E_-(x,\epsilon)$ and $E_+(x,\epsilon)$

that they depend on classical quantities. The relevant quantities are the classical position $a(t)$, the classical momentum $\eta(t)$, the classical action integral $S(t)$, and the uncertainty matrices for the classical position and momentum, $A(t)$ and $B(t)$ respectively. They are given by the unique solutions to the following system.

$$\frac{\partial a}{\partial t}(t) = \eta(t), \tag{3.34}$$

$$\frac{\partial \eta}{\partial t}(t) = -V^{(1)}(a(t)), \tag{3.35}$$

$$\frac{\partial S}{\partial t}(t) = \frac{1}{2}\eta(t)^2 - V(a(t)), \tag{3.36}$$

$$\frac{\partial A}{\partial t}(t) = iB(t), \tag{3.37}$$

$$\frac{\partial B}{\partial t}(t) = iV^{(2)}(a(t))A(t), \tag{3.38}$$

with initial conditions

$$a(0) = 0$$

$$\eta(0) = \widetilde{\eta}_0$$

$$S(0) = S_0$$

$$A(0) = A_0$$

$$B(0) = D_0.$$

Here $V(x)$ is the potential, given by the eigenvalues of $h(x,\epsilon)$, $E_-(x,\epsilon)$ and $E_+(x,\epsilon)$, or the average potential $\widetilde{V}(x) = \frac{1}{2}(E_-(x,\epsilon) + E_+(x,\epsilon))$. $V^{(1)}(x)$ denotes the first derivative of V with respect to x, and $V^{(2)}(x)$ denotes the second derivative. We assume A_0 and D_0 satisfy the conditions (2.1)-(2.4).

If $A(0) = A_0$ and $B(0) = D_0$ satisfy the conditions above, then $A(t)$ and $B(t)$ satisfy them for all t.

For one dimension, we only need the normalization condition that $\overline{A}B + \overline{B}A = 2I$ from above.

Let us define the semiclassical Hagedorn wave packets, ϕ_l for the multi-index l, which give us the base of our solutions.

$$\phi_0(A,B,\hbar,a,\eta,x) = \pi^{-1/4}\hbar^{-1/4}A^{-1/2}\exp\left\{\frac{-BA^{-1}(x-a)^2}{2\hbar} + \frac{i\eta(x-a)}{\hbar}\right\} \tag{3.39}$$

Recursively, we then define $\phi_k(A,B,\hbar,a,\eta,\cdot)$ by

$$\phi_{k+1}(A,B,\hbar,a,\eta,\cdot) = \frac{1}{\sqrt{k+1}}\mathcal{A}(A,B,\hbar,a,\eta)^*\phi_k(A,B,\hbar,a,\eta,\cdot). \tag{3.40}$$

The eigenvectors $\Phi_\pm(x,t,\epsilon)$ become singular as $(x,\epsilon)\to(0,0)$, therefore we must use some adjusted eigenvectors when we become close to the avoided crossing. We will define $\psi_1(x,\epsilon)$ and $\psi_2(x,\epsilon)$ for the eigenvectors of the inner solutions.

Let $P(x,\epsilon)$ be a spectral projector of $h(x,\epsilon)$.

$$P(x,\epsilon) \;=\; \frac{1}{2\pi i}\int_{\gamma}(z-h(x,\epsilon))^{-1}dz$$

for a path γ which encloses both eigenvalues $E_-(x,\epsilon)$ and $E_+(x,\epsilon)$. Define the functions $\psi_1(x,\epsilon)$ and $\psi_2(x,\epsilon)$ such that they form an orthonormal basis of $P(x,\epsilon)\mathcal{H}$ which is regular in (x,ϵ) around $(0,0)$. To construct, we choose ψ_1 and ψ_2 to be an orthonormal basis of the range of $P(0,0)$.

$$\psi_1(x,\epsilon) \;=\; \frac{P(x,\epsilon)\psi_1}{\|P(x,\epsilon)\psi_1\|} \tag{3.41}$$

Let $P_1(x,\epsilon)$ be the orthogonal projection onto $\psi_1(x,\epsilon)$. Then

$$\psi_2(x,\epsilon) \;=\; \frac{(1-P_1(x,\epsilon))P(x,\epsilon)\psi_2}{\|(1-P_1(x,\epsilon))P(x,\epsilon)\|}. \tag{3.42}$$

The following lemma simplifies these for us some.

Lemma 3.3.1. *[Lemma 3.3 of [39]] "For x in the support of $F(\|x-a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, $\mathcal{C}=\mathcal{A},\mathcal{B}$, we have for $t<0$,*

$$\Phi^-_{\mathcal{A}}(x,\epsilon) \;=\; \psi_2(x,\epsilon)+O(\epsilon/t^{1/2})$$

$$\Phi^-_{\mathcal{B}}(x,\epsilon) \;=\; -\psi_1(x,\epsilon)+O(\epsilon/t^{1/2}),$$

and for $t>0$,

$$\Phi^+_{\mathcal{A}}(x,\epsilon) \;=\; \psi_1(x,\epsilon)+O(\epsilon/t^{1/2})$$

$$\Phi^+_{\mathcal{B}}(x,\epsilon) \;=\; \psi_2(x,\epsilon)+O(\epsilon/t^{1/2})."$$

Let us assume that we are on the surface $E_-(x,\epsilon)$ for all at some initial time $-T$ far from the avoided crossing. At some time $t^\flat$ we reach the point of minimal gap from the crossing set $\Gamma = x = 0$. Without loss of generality, let us choose $t^\flat = 0$. The following theorem provides solutions to the Schrödinger equation accurate up to errors of order ϵ^p, for some positive p.

Theorem 3.3.2. *[Theorem 3.1 of [39]] "Let $h(x',\epsilon')$ be a Hamiltonian such that*

$$h(x,\epsilon) \;=\; h_\parallel(x,\epsilon) + h_\perp(x,\epsilon)$$

with

$$h_\parallel(x,\epsilon) \;=\; h(x,\epsilon)P(x,\epsilon)$$

and

$$h_\perp(x,\epsilon) \;=\; h(x,\epsilon)(I - P(x,\epsilon))$$

for $P(x,\epsilon)$ a spectral projector of $h(x,\epsilon)$ associated with $E_-(x,\epsilon)$ and $E_+(x,\epsilon)$, with

$$h_\parallel(x,\epsilon) \;=\; \begin{pmatrix} \beta(x,\epsilon) & \gamma(x,\epsilon) + i\delta(x,\epsilon) \\ \gamma(x,\epsilon) - i\delta(x,\epsilon) & -\beta(x,\epsilon) \end{pmatrix} + \widetilde{V}(x,\epsilon).$$

Let $\psi(x',t')$ be a solution of the corresponding Schrödinger equation (3.32) such that

$$\begin{aligned} \psi(x',-T') \;&=\; e^{\left(i\frac{S'^-(-T')}{\epsilon'^2} + i\frac{\eta'^-(-T')(x'-a'^{\mathcal{B}}(-T'))}{\epsilon'^2}\right)} \\ &\quad\times \phi_l(A'^-(-T'), B'^-(-T'), \epsilon'^2, a'^-(-T'), 0, x')\Phi_-^-(x',-T',\epsilon') + O(\epsilon'^q) \end{aligned}$$

for some positive q, in the $L^2(\mathbb{R}^n)$ sense. Then for any $0 < \xi < 1/3$, there exists a positive p such that in the limit $\epsilon' \to 0$ we have for $-T' \le t' \le -\epsilon'^{1-\xi}$:

$$\psi(x',t') \;=\; e^{\left(i\frac{S'^-(t')}{\epsilon'^2} + i\frac{\eta'^-(t')(x'-a'^-(t'))}{\epsilon'^2}\right)}$$

$$\times\, \phi_l(A'^{-}(t'), B'^{-}(t'), \epsilon'^2, a'^{-}(t'), 0, x')\Phi_-^-(x', t', \epsilon') + O(\epsilon'^p)$$

and for $-\epsilon'^{1-\xi} \le t' \le \epsilon'^{1-\xi}$*:*

$$\psi(x', t') \;=\; e^{\left(i\frac{S'^{\sim}(t')}{\epsilon'^2} + i\frac{\eta^{\sim}(t')(x'-a'^{\sim}(t'))}{\epsilon'^2}\right)} \left(f_0(y', s')\psi_1(x', \epsilon') + g_0(y', s')\psi_2(x', \epsilon')\right),$$

where f_0 *and* g_0 *are defined in (3.49), with* $y' = (x' - a'(t'))/\epsilon'$, $s' = t'/\epsilon'$, *and finally for* $\epsilon'^{1-\xi} \le t' \le T'$*:*

$$\begin{aligned}\psi(x', t') \;=\; & -e^{-\pi r/2\widetilde{\eta}_{01}'} e^{\left(i\frac{S'^{+}(t')}{\epsilon'^2} + i\frac{\eta'^{+}(t')(x'-a'^{+}(t'))}{\epsilon'^2}\right)} \\ & \times\, \phi_l(A'^{+}(t'), B'^{+}(t'), \epsilon'^2, a'^{+}(t'), 0, x')\Phi_+^+(x', t', \epsilon') \\ & + e^{-\pi r/4\widetilde{\eta}_{01}'} \sqrt{\frac{\pi r}{\widetilde{\eta}_{01}'}} \frac{e^{i\lambda(\epsilon')}}{\Gamma(1 + \frac{ir}{2\widetilde{\eta}_{01}'})} e^{\left(i\frac{S'^{-}(t')}{\epsilon'^2} + i\frac{\eta'^{-}(t')(x'-a'^{-}(t'))}{\epsilon'^2}\right)} \\ & \times\, \phi_l(A'^{-}(t'), B'^{-}(t'), \epsilon'^2, a'^{-}(t'), 0, x')\Phi_-^+(x', t', \epsilon') + O(\epsilon'^p)\end{aligned}$$

where $\lambda(\epsilon')$ *is given by*

$$\lambda(\epsilon') \;=\; \frac{\pi}{4} + \frac{S_0'(\epsilon', -)}{\epsilon'^2} + \frac{r}{2\widetilde{\eta}_{01}'}(1 + 3\ln(2\widetilde{\eta}_{01}') + \ln r - 4\ln\epsilon').\text{”}$$

Remark: The variables x and t in Theorem (3.3.2) are scaled from the variables in our problem. I have notated this with the prime notation, where x' and t' are the variables as stated in the theorem in [39], and x and t are the original variable that I will use for my problem. Thus we will make the following replacements:

$$x' = b_1 x + b_2\epsilon = \frac{1}{2}x \tag{3.43}$$

$$\epsilon' = c_2\epsilon = \epsilon \tag{3.44}$$

$$t' = \frac{b_1^2}{c_2^2} t = \frac{1}{4} t \tag{3.45}$$

$$r = \frac{c_2^4}{b_1^2} = 4 \tag{3.46}$$

$$a'(t') = b_1 a(t) + b_2 \epsilon = \frac{1}{2} a(t) \tag{3.47}$$

$$\eta'(t') = \frac{b_1}{c_2^2} = 2\eta(t) \tag{3.48}$$

Also note that $\widetilde{\eta_0}_1'$ is also scaled. $\widetilde{\eta_0}_1' = 2\widetilde{\eta_0}$. We do not need to specify the first component of $\widetilde{\eta_0}$ as our problem is only one-dimensional. $S'(t')$ must be scaled for each problem individually, as well as $A'(t')$ and $B'(t')$.

In the theorem, the functions $f_0(y', s')$ and $g_0(y', s')$, where $y' = (x' - a'(t'))/\epsilon'$, and $s' = t'/\epsilon'$, satisfy

$$i\epsilon' \frac{\partial}{\partial s'} f_0 \psi_1 + i\epsilon' \frac{\partial}{\partial s'} g_0 \psi_2 \ = \ \epsilon' h_{11}(f_0 \psi_1 + g_0 \psi_2). \tag{3.49}$$

or equivalently,

$$i \frac{\partial}{\partial s'} \begin{pmatrix} f_0(y', s') \\ g_0(y', s') \end{pmatrix} \ = \ r \begin{pmatrix} \widetilde{\eta_0}_1' s' + y_1' & 1 \\ 1 & -(\widetilde{\eta_0}_1' s' + y_1') \end{pmatrix} \begin{pmatrix} f_0(y', s') \\ g_0(y', s') \end{pmatrix}.$$

From this we obtain our main results as a corollary to the previous theorem and will be proved over the course of this section.

Corollary 3.3.3. *For the Hamiltonian given by (3.33), and assuming an initial wave packet of the form*

$$\begin{aligned} \psi(x, -T) \ &= e^{\left(i \frac{S^-(-T)}{\epsilon^2} + i \frac{\eta^-(-T)(x - a^{\mathcal{B}}(-T))}{\epsilon^2} \right)} \\ &\qquad \times \phi_0(A^-(-T), B^-(-T), \epsilon^2, a^-(-T), 0, x) \Phi_-(x, \epsilon), \end{aligned}$$

for any large $T > 0$, the solutions to the Schrödinger equation for $t < -\epsilon^{1-\xi}$ are given by

$$\begin{aligned}\psi(x,t) \ &= e^{\left(i\frac{S^-(t)}{\epsilon^2}+i\frac{\eta^-(t)(x-a^-(t))}{\epsilon^2}\right)} \\ &\qquad \times \phi_0(A^-(t),B^-(t),\epsilon^2,a^-(t),0,x)\Phi_-(x,\epsilon)+O(\epsilon^\xi)\end{aligned}$$

and for $t \in [-\epsilon^{1-\xi}, \epsilon^{1-\xi}]$,

$$\begin{aligned}\psi(x,t) \ &= e^{\left(i\frac{S^\sim(t)}{\epsilon^2}+i\frac{\eta^\sim(t)(x-a^\sim(t))}{\epsilon^2}\right)} C_2\left(\frac{x-a^\sim(t)}{\epsilon}\right) \\ &\times \left(D_{\frac{i}{\widetilde{\eta}_0}}\left(-(1+i)\sqrt{\frac{1}{2\widetilde{\eta}_0}}\left(\frac{\widetilde{\eta}_0 t}{\epsilon}+\frac{x-a^\sim(t)}{\epsilon}\right)\right)\psi_1(x,\epsilon)\right. \\ &\quad \left. -(1+i)\sqrt{\frac{1}{2\widetilde{\eta}_0}}D_{-\frac{i}{\widetilde{\eta}_0}-1}\left(-(1+i)\sqrt{\frac{1}{2\widetilde{\eta}_0}}\left(\frac{\widetilde{\eta}_0 t}{\epsilon}+\frac{x-a^\sim(t)}{\epsilon}\right)\right)\psi_2(x,\epsilon)\right) \\ &+O(\epsilon^{1-3\xi})\end{aligned}$$

with

$$\begin{aligned}C_2(y^\sim) \ &= \ -\epsilon^{-1/2}\phi_0(A_0,B_0,1,0,0,y^\sim)e^{-\frac{\pi}{4\widetilde{\eta}_0}}\exp\left(\frac{i}{4\widetilde{\eta}_0}(y^{\sim 2}-4y^\sim)\right) \\ &\qquad \times \exp\left(i\frac{S_0}{\epsilon^2}+\frac{i}{2\widetilde{\eta}_0}(1+3\ln(4\widetilde{\eta}_0)+\ln 4-4\ln\epsilon)\right).\end{aligned}$$

and for $t > \epsilon^{1-\xi}$,

$$\begin{aligned}\psi(x,t) \ &= \ -e^{-\pi/\widetilde{\eta}_0}e^{\left(i\frac{S^+(t)}{\epsilon^2}+i\frac{\eta^+(t)(x-a^+(t))}{\epsilon^2}\right)} \\ &\qquad \times \phi_0(A^+(t),B^+(t),\epsilon^2,a^+(t),0,x)\Phi_+(x,\epsilon) \\ &\qquad + e^{-\pi/2\widetilde{\eta}_0}\sqrt{\frac{2\pi}{\widetilde{\eta}_0}}\frac{e^{i\lambda(\epsilon)}}{\Gamma(1+\frac{i}{\widetilde{\eta}_0})}e^{\left(i\frac{S^-(t)}{\epsilon^2}+i\frac{\eta^-(t)(x-a^-(t))}{\epsilon^2}\right)} \\ &\qquad \times \phi_0(A^-(t),B^-(t),\epsilon^2,a^-(t),0,x)\Phi_-(x,\epsilon)+O(\epsilon^\xi)\end{aligned}$$

with

$$\lambda(\epsilon) \ = \ \frac{\pi}{4}+\frac{S_0}{\epsilon^2}+\frac{1}{\widetilde{\eta}_{01}}(1+3\ln(4\widetilde{\eta}_0)+\ln 4-4\ln\epsilon).$$

3.3.1 Classical Quantities

To construct the solutions to the Schrödinger equation for this system, we must investigate the solutions to the classical quantities given by the system of equations (3.34)-(3.38), supposing we are on the surface $E_-(x,\epsilon)$.

The quantities that are needed are the classical position $a(t)$, the classical momentum $\eta(t)$, the classical action integral $S(t)$, and the uncertainty matrices for the position and momentum $A(t)$ and $B(t)$ respectively.

Lemma 3.3.4. *Part A:*

The classical quantities associated with the solutions of the Schrödinger equation (3.32) and associated with the lower energy level $E_-(x,\epsilon)$, to each appropriate order of accuracy in epsilon, are given by

$$\begin{aligned}
a^-(t) &= \widetilde{\eta_0} t + \epsilon \frac{1}{\widetilde{\eta_0}} t, \\
\eta^-(t) &= \widetilde{\eta_0} + \epsilon \frac{1}{\widetilde{\eta_0}}, \\
S^-(t) &= S_0 + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon t \\
&\quad + \epsilon^2 \left(-\frac{1}{\widetilde{\eta_0}^3 t} + \frac{t}{2\widetilde{\eta_0}^2} - \frac{t}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}} \ln|t| + \frac{1}{2\widetilde{\eta_0}} t \ln|t| \right), \\
A^-(t) &= itD_0^- + A_0, \\
B^-(t) &= D_0^-
\end{aligned}$$

for $t < -\epsilon^{1-\xi}$,

$$
\begin{aligned}
a^-(s) &= \epsilon\widetilde{\eta_0}s, \\
\eta^-(s) &= \widetilde{\eta_0} + \epsilon\left(\frac{1}{2}s + \frac{\sqrt{(\widetilde{\eta_0}s)^2+4}}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\right), \\
S^-(s) &= S_0 + \frac{\epsilon}{2}\widetilde{\eta_0}^2 s + \epsilon^2\left(\frac{\widetilde{\eta_0}}{2}s^2 + \frac{1}{2}s\sqrt{(\widetilde{\eta_0}s)^2+4}\right), \\
A^-(s) &= A_0 + i\epsilon s D_0^-, \\
B^-(s) &= D_0^-,
\end{aligned}
$$

for $\epsilon s = t \in [-\epsilon^{1-\xi}, \epsilon^{1-\xi}]$, *and*

$$
\begin{aligned}
a^-(t) &= \frac{1}{2}t^2 + \widetilde{\eta_0}t + \epsilon\frac{1}{\widetilde{\eta_0}}t, \\
\eta^-(t) &= t + \widetilde{\eta_0} + \epsilon\frac{1}{\widetilde{\eta_0}}, \\
S^-(t) &= S_0 + \frac{1}{3}t^3 + \widetilde{\eta_0}t^2 + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon\left(t + \frac{1}{\widetilde{\eta_0}}t^2\right) \\
&\quad \epsilon^2\left(\frac{t}{\widetilde{\eta_0}^2} + \frac{2}{\widetilde{\eta_0}}\ln t + \frac{3}{2\widetilde{\eta_0}^2}t\ln t + \frac{3}{4\widetilde{\eta_0}^3}t^2\ln t\right. \\
&\quad \left.-\frac{3}{2\widetilde{\eta_0}^2}t\ln(2\widetilde{\eta_0}+t) - \frac{3}{4\widetilde{\eta_0}^3}t^2\ln(2\widetilde{\eta_0}+t) - \frac{2}{\widetilde{\eta_0}}\ln(2\widetilde{\eta_0}+t)\right), \\
A^-(t) &= itD_0^- + A_0, \\
B^-(t) &= D_0^-
\end{aligned}
$$

for $t > \epsilon^{1-\xi}$.

Part B:

The classical quantities associated with the upper energy level $E_+(x,\epsilon)$, to each appropriate order of accuracy, are given by

$$
\begin{aligned}
a^+(t) &= \frac{1}{2}t^2 + \widetilde{\eta}_0 t + \epsilon\frac{1}{\widetilde{\eta}_0}t,\\
\eta^+(t) &= t + \widetilde{\eta}_0 + \epsilon\frac{1}{\widetilde{\eta}_0},\\
S^+(t) &= S_0 + \frac{1}{2}\widetilde{\eta}_0{}^2 t + \epsilon t\\
&\quad + \epsilon^2\left(-\frac{1}{\widetilde{\eta}_0{}^3 t} + \frac{t}{2\widetilde{\eta}_0{}^2} - \frac{t}{2\widetilde{\eta}_0} - \frac{1}{\widetilde{\eta}_0}\ln|t| + \frac{1}{2\widetilde{\eta}_0}t\ln|t|\right),\\
A^+(t) &= itD_0^+ + A_0,\\
B^+(t) &= D_0^+,
\end{aligned}
$$

for $t \in [-2\widetilde{\eta}_0, -\epsilon^\xi]$,

$$
\begin{aligned}
a^+(s) &= \epsilon\widetilde{\eta}_0 s,\\
\eta^+(s) &= \widetilde{\eta}_0 + \epsilon\left(\frac{1}{2}s - \frac{\sqrt{(\widetilde{\eta}_0 s)^2+4}}{2\widetilde{\eta}_0} + \frac{1}{\widetilde{\eta}_0}\right),\\
S^+(s) &= S_0 + \frac{\epsilon}{2}\widetilde{\eta}_0{}^2 s + \epsilon^2\left(\frac{\widetilde{\eta}_0}{2}s^2 - \frac{1}{2}s\sqrt{(\widetilde{\eta}_0 s)^2+4}\right),\\
A^+(s) &= A_0 + i\epsilon s D_0^+,\\
B^+(s) &= D_0^+,
\end{aligned}
$$

for $\epsilon s = t \in [-\epsilon^\xi, \epsilon^\xi]$, and

$$
a^+(t) = \widetilde{\eta}_0 t + \epsilon\frac{1}{\widetilde{\eta}_0}t,
$$

$$
\begin{aligned}
\eta^+(t) &= \widetilde{\eta_0} + \epsilon \frac{1}{\widetilde{\eta_0}}, \\
S^+(t) &= S_0 + \frac{1}{3}t^3 + \widetilde{\eta_0}t^2 + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon\left(t + \frac{1}{2\widetilde{\eta_0}}t^2\right) \\
&\quad \epsilon^2 \left(\frac{t}{\widetilde{\eta_0}^2} + \frac{2}{\widetilde{\eta_0}}\ln t + \frac{3}{2\widetilde{\eta_0}^2} t \ln t + \frac{3}{4\widetilde{\eta_0}^3} t^2 \ln t \right. \\
&\quad \left. -\frac{3}{2\widetilde{\eta_0}^2} t \ln(2\widetilde{\eta_0} + t) - \frac{3}{4\widetilde{\eta_0}^3} t^2 \ln(2\widetilde{\eta_0} + t) - \frac{2}{\widetilde{\eta_0}} \ln(2\widetilde{\eta_0} + t)\right), \\
A^+(t) &= itD_0^+ + A_0, \\
B^+(t) &= D_0^+,
\end{aligned}
$$

for $t > \epsilon^{\xi}$.

Part C:

The classical quantities associated with average energy level, $\widetilde{V}(x) = \frac{1}{2}(E_-(x,\epsilon) + E_+(x,\epsilon))$,

for all t *are given, exactly, by*

$$
\begin{aligned}
a^{\sim}(t) &= \widetilde{\eta_0}t + \frac{1}{4}t^2, \\
\eta^{\sim}(t) &= \widetilde{\eta_0} + \frac{1}{2}t, \\
S^{\sim}(t) &= = \frac{1}{2}\widetilde{\eta_0}^2 t.
\end{aligned}
$$

Proof.

$$
\begin{aligned}
\frac{\partial a^-}{\partial t}(t) &= \eta^-(t), \\
\frac{\partial \eta^-}{\partial t}(t) &= -V^{(1)}(a^-(t)) = \frac{1}{2}\left(1 + \frac{a^-(t)}{\sqrt{a^-(t)^2 + 4\epsilon^2}}\right), \\
\frac{\partial S^-}{\partial t}(t) &= \frac{1}{2}\eta^-(t)^2 - V(a^-(t)) = \frac{1}{2}\eta^-(t)^2 + \frac{1}{2}\left(a^-(t) + \sqrt{a^-(t)^2 + 4\epsilon^2}\right),
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial A^-}{\partial t}(t) &= iB^-(t), \\
\frac{\partial B^-}{\partial t}(t) &= iV^{(2)}(a^-(t))A^-(t) = -i\frac{2\epsilon^2}{(a^-(t)^2 + 4\epsilon^2)^{3/2}} A^-(t),
\end{aligned}
$$

with initial conditions

$$
\begin{aligned}
a^-(0) &= 0 \\
\eta^-(0) &= \widetilde{\eta_0} \\
S^-(0) &= S_0 \\
A^-(0) &= A_0 \\
B^-(0) &= D_0^-
\end{aligned}
$$

where $\alpha > 0$ is of order 1, $\widetilde{\eta_0} > 0$, and A_0 and D_0 satisfy conditions (2.1)-(2.4).

$$
\begin{aligned}
V(x) &= E_-(x,\epsilon) = 0 \\
V^{(1)}(x) &= \frac{\partial E_-(x,\epsilon)}{\partial x} \\
&= -\frac{1}{2}\left(1 + \frac{x}{\sqrt{x^2 + 4\epsilon^2}}\right)
\end{aligned}
$$

$$
\begin{aligned}
V^{(2)}(x) &= \frac{\partial^2 E_-(x,\epsilon)}{\partial x^2} \\
&= \frac{-2\epsilon^2}{(x^2 + 4\epsilon^2)^{3/2}}
\end{aligned}
$$

Unfortunately, $V(a(t))$, $V^{(1)}(a(t))$, and $V^{(2)}(a(t))$ are not easily integrated. Even using mathematical software, the integrals do not have nice forms. Instead, we will use Taylor series of each of these, expanded in powers of ϵ, centered at 0.

Since we will not be finding the exact solutions to this system of equations, we must consider that there is a boundary layer in the solution around $t = 0$. We will first consider t close to 0, so we will let $t = \epsilon s$, where $|s| \leq \epsilon^{(1-\kappa)}$. I will solve the system (3.34)-(3.38) for this boundary layer, which I will call the Inner Solution. For t away from the avoided crossing, the solutions will be called the Outer Solution. In order for this method to be valid, there must be a region where both of these solutions are valid, called the Matching Region.

Inner Solution

The system (3.34)-(3.38) becomes the following for the variable s, since $\frac{dt}{ds} = \epsilon$,

$$\begin{aligned}
\frac{\partial a^-}{\partial s}(s) &= \epsilon \eta^-(s), \\
\frac{\partial \eta^-}{\partial s}(s) &= -\epsilon V^{(1)}(a^-(s)), \\
\frac{\partial S^-}{\partial s}(s) &= \epsilon \frac{1}{2}\eta^-(s)^2 - V(a^-(s)), \\
\frac{\partial A^-}{\partial s}(s) &= i\epsilon B^-(s), \\
\frac{\partial B^-}{\partial s}(s) &= i\epsilon V^{(2)}(a^-(s))A^-(s).
\end{aligned}$$

Applying our setting to this system,

$$\begin{aligned}
\frac{\partial a^-}{\partial s}(s) &= \epsilon \eta^-(s), \\
\frac{\partial \eta^-}{\partial s}(s) &= \frac{\epsilon}{2}\left(1 + \frac{a(s)}{\sqrt{a(s)^2 + 4\epsilon^2}}\right), \\
\frac{\partial S^-}{\partial s}(s) &= \epsilon \frac{1}{2}\eta^-(s)^2 + \frac{1}{2}\left(a(s) + \sqrt{a(s)^2 + 4\epsilon^2}\right), \\
\frac{\partial A^-}{\partial s}(s) &= i\epsilon B^-(s),
\end{aligned}$$

$$\frac{\partial B^-}{\partial s}(s) = -i\epsilon \frac{2\epsilon^2}{(a(s)^2+4\epsilon^2)^{3/2}} A^-(s).$$

In order for our solution $\Psi(\epsilon, x, t)$ to be correct up to terms of order ϵ, we must make sure it has the level of accuracy desired when t is near 0, i.e. close to the avoided crossing, was well as when far away from the crossing.

From here, I will drop the notation $a^-(t)$ to just $a(t)$, but still we are considering just the lower surface without loss of generality.

To solve these equations to each appropriate order of accuracy, we expand the solutions in orders of epsilon.

$$a(s) = a_0(s) + \epsilon a_1(s) + \epsilon^2 a_2(s) + ...$$

and similarly for $\eta(s)$, $A(s)$, $B(s)$, and $S(s)$.

$$\begin{aligned}
\frac{\partial a}{\partial s}(s) &= \epsilon\eta_0(s) + \epsilon^2\eta_1(s) + O(\epsilon^3), \\
\frac{\partial \eta}{\partial s}(s) &= \frac{1}{2}\left(\epsilon + \frac{\epsilon a_0(s) + \epsilon^2 a_1(s)}{\sqrt{(a_0(s)+\epsilon a_1(s)+...)^2+4\epsilon^2}}\right) + O(\epsilon^3), \\
\frac{\partial S}{\partial s}(s) &= \frac{1}{2}(\epsilon\eta_0(s)^2 + 2\epsilon^2\eta_0(s)\eta_1(s)) \\
&\quad + \frac{1}{2}\left(\epsilon a_0(s) + \epsilon^2 a_1(s)) + \epsilon\sqrt{(a_0(s)+\epsilon a_1(s)+...)^2+4\epsilon^2}\right) + O(\epsilon^3), \\
\frac{\partial A}{\partial s}(s) &= i\epsilon B_0(s) + i\epsilon^2 B_1(s) + O(\epsilon^3), \\
\frac{\partial B}{\partial s}(s) &= -i\frac{2\epsilon^3}{((a_0(s)+\epsilon a_1(s)+...)^2+4\epsilon^2)^{3/2}} A_0(s) + O(\epsilon^4) = 0 + O(\epsilon^3).
\end{aligned}$$

We solve by each order of epsilon.

First, the system for terms of order ϵ^0:

$$\begin{aligned}
\frac{\partial a_0}{\partial s}(s) &= 0, \\
\frac{\partial \eta_0}{\partial s}(s) &= 0, \\
\frac{\partial S_0}{\partial s}(s) &= 0, \\
\frac{\partial A_0}{\partial s}(s) &= 0, \\
\frac{\partial B_0}{\partial s}(s) &= 0.
\end{aligned}$$

To satisfy the initial conditions, the solutions for order ϵ^0 are

$$\begin{aligned}
a_0(s) &= 0 \\
\eta_0(s) &= \widetilde{\eta}_0 \\
S_0(s) &= S_0 \\
A_0(s) &= A_0 \\
B_0(s) &= D_0^-
\end{aligned}$$

Since $a_0(s) = 0$, we will adjust the differential equations for $\eta(s)$ and $S(s)$ to the following:

$$\begin{aligned}
\frac{\partial \eta}{\partial s}(s) &= \frac{\epsilon}{2}\left(1 + \frac{a_1(s)}{\sqrt{a_1(s)^2 + 4}}\right) + \frac{\epsilon^2}{2}\left(\frac{a_2(s)}{\sqrt{a_1(s)^2 + 4}}\right) \\
\frac{\partial S}{\partial s}(s) &= \frac{1}{2}(\epsilon \eta_0(s)^2 + 2\epsilon^2 \eta_0(s)\eta_1(s)) + \frac{1}{2}\left(\epsilon^2 a_1(s) + \epsilon^2 \sqrt{a_1(s)^2 + 4}\right) \\
&= \epsilon\left(\frac{1}{2}\eta_0(s)^2\right) + \epsilon^2\left(\eta_0(s)\eta_1(s) + \frac{1}{2}a_1(s) + \frac{1}{2}\sqrt{a_1(s)^2 + 4}\right).
\end{aligned}$$

Order ϵ^1 terms:

$$\frac{\partial a_1}{\partial s}(s) = \eta_0(s) = \widetilde{\eta}_0,$$

$$\begin{aligned}
\frac{\partial \eta_1}{\partial s}(s) &= \frac{1}{2}\left(1 + \frac{a_1(s)}{\sqrt{a_1(s)^2+4}}\right), \\
\frac{\partial S_1}{\partial s}(s) &= \frac{1}{2}\eta_0(s)^2 = \frac{1}{2}\widetilde{\eta_0}^2, \\
\frac{\partial A_1}{\partial s}(s) &= iB_0(s) = iD_0^-, \\
\frac{\partial B_1}{\partial s}(s) &= 0.
\end{aligned}$$

The initial conditions for the overall system are met by the terms of order ϵ^0, so for all further orders, we will use the initial conditions that $a_i(0) = 0$, $\eta_i(0) = 0$, and so on, for $i \geq 1$. We integrate to obtain the solutions for the first order terms.

$$\begin{aligned}
a_1(s) &= \widetilde{\eta_0} s, \\
\eta_1(s) &= \frac{1}{2}s + \frac{\sqrt{(\widetilde{\eta_0} s)^2 + 4}}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}, \\
S_1(s) &= \frac{1}{2}\widetilde{\eta_0}^2 s, \\
A_1(s) &= isD_0^-, \\
B_1(s) &= 0.
\end{aligned}$$

For the relevant times, we only need to know $A(\cdot)$ and $B(\cdot)$ up to $O(\epsilon^0)$ errors, so we do not need to continue computations for further order terms for $A(\cdot)$ or $B(\cdot)$. We need to know $a(\cdot)$ and $\eta(\cdot)$ to $O(\epsilon)$ errors, and $S(\cdot)$ to $O(\epsilon^2)$ errors. These error estimates must hold even in the matching region, where $s = \epsilon^{\kappa-1}$ is large and $t = \epsilon^{\kappa}$ is small.

Order ϵ^2 terms:

$$\frac{\partial a_2}{\partial s}(s) = \eta_1(s) = \frac{1}{2}s + \frac{\sqrt{(\widetilde{\eta_0} s)^2 + 4}}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}},$$

$$\begin{aligned}
\frac{\partial \eta_2}{\partial s}(s) &= \frac{1}{2}\left(\frac{a_2(s)}{\sqrt{(\widetilde{\eta_0}s)^2+4}}\right),\\
\frac{\partial S_2}{\partial s}(s) &= \eta_0(s)\eta_1(s) + \frac{1}{2}\left(a_1(s) + \sqrt{a_1(s)^2+4}\right)\\
&= \widetilde{\eta_0}\left(\frac{1}{2}s + \frac{\sqrt{(\widetilde{\eta_0}s)^2+4}}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\right) + \frac{1}{2}\widetilde{\eta_0}s + \sqrt{(\widetilde{\eta_0}s)^2+4}\\
&= \widetilde{\eta_0}s + \sqrt{(\widetilde{\eta_0}s)^2+4} - 1.
\end{aligned}$$

Solutions for this order are

$$\begin{aligned}
a_2(s) &= \frac{1}{4}s^2 + \frac{1}{4\widetilde{\eta_0}}s\sqrt{(\widetilde{\eta_0}s)^2+4} + \frac{1}{\widetilde{\eta_0}^2}\operatorname{arcsinh}\left(\frac{\widetilde{\eta_0}s}{2}\right) - \frac{1}{\widetilde{\eta_0}}s,\\
\eta_2(s) &= -\frac{1}{16\widetilde{\eta_0}}s^2 + \frac{8-\widetilde{\eta_0}s}{16\widetilde{\eta_0}^3}\sqrt{(\widetilde{\eta_0}s)^2+4} + \frac{1}{4\widetilde{\eta_0}^3}\operatorname{arcsinh}\left(\frac{\widetilde{\eta_0}s}{2}\right) - \frac{1}{4\widetilde{\eta_0}^3}\operatorname{arcsinh}\left(\frac{\widetilde{\eta_0}s}{2}\right)^2 - \frac{1}{\widetilde{\eta_0}^3},\\
S_2(s) &= \frac{\widetilde{\eta_0}}{2}s^2 + \frac{1}{2}s\sqrt{(\widetilde{\eta_0}s)^2+4} + \frac{2}{\widetilde{\eta_0}}\operatorname{arcsinh}\left(\frac{\widetilde{\eta_0}s}{2}\right) - s.
\end{aligned}$$

Since these solutions are valid for t close to 0, we will use the Taylor expansions of the arcsin$(\cdot)$ terms at $s = 0$.

$$\begin{aligned}
a_2(s) &\approx \frac{1}{4}s^2 + \frac{1}{4\widetilde{\eta_0}}s\sqrt{(\widetilde{\eta_0}s)^2+4} - \frac{1}{2\widetilde{\eta_0}}s,\\
\eta_2(s) &\approx -\frac{1}{8\widetilde{\eta_0}}s^2 + \frac{8-\widetilde{\eta_0}s}{16\widetilde{\eta_0}^3}\sqrt{(\widetilde{\eta_0}s)^2+4} - \frac{1}{8\widetilde{\eta_0}^2}s - \frac{1}{\widetilde{\eta_0}^3},\\
S_2(s) &\approx \frac{\widetilde{\eta_0}}{2}s^2 + \frac{1}{2}s\sqrt{(\widetilde{\eta_0}s)^2+4}.
\end{aligned}$$

We do not need to know further orders of $a(\cdot)$ or $\eta(\cdot)$, however, we do need to find the third order terms for $S(\cdot)$ for an error estimate.

Order ϵ^3 terms:

$$\frac{\partial S_3}{\partial s}(s) = \frac{1}{2}(2\eta_0(s)\eta_2(s) + \eta_1(s)^2)$$

$$= \widetilde{\eta_0}\left(-\frac{1}{8\widetilde{\eta_0}}s^2 + \frac{8-\widetilde{\eta_0}s}{16\widetilde{\eta_0}^3}\sqrt{(\widetilde{\eta_0}s)^2+4} - \frac{1}{8\widetilde{\eta_0}^2}s - \frac{1}{\widetilde{\eta_0}^3}\right) + \frac{1}{2}\left(\frac{1}{2}s + \frac{\sqrt{(\widetilde{\eta_0}s)^2+4}}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\right)^2$$

$$= -\frac{5}{8\widetilde{\eta_0}}s + \frac{1}{8}s^2 + \frac{3}{16\widetilde{\eta_0}}s\sqrt{(\widetilde{\eta_0}s)^2+4}.$$

Solutions for this order are

$$S_3(s) = -\frac{5}{16\widetilde{\eta_0}}s^2 + \frac{1}{24}s^3 + \frac{1}{16\widetilde{\eta_0}^3}\left((\widetilde{\eta_0}s)^2+4\right)^{3/2} - \frac{1}{2\widetilde{\eta_0}^3}.$$

We can note the following observations:

1. $a_2(s)$ grows like s^2, so we want $\epsilon^2\epsilon^{2(1-\kappa)} \ll \epsilon$. If we take $\kappa < \frac{1}{2}$, we can drop the $a_2(s)$ term from our inner solutions.

2. $\eta_2(s)$ grows like s^2, as well, so taking $\kappa < \frac{1}{2}$ allows us to also drop $\eta_2(s)$ from our inner solutions.

3. $S_3(s)$ grows like s^3, so we want $\epsilon^3\epsilon^{3(1-\kappa)} \ll \epsilon$. If we take $\kappa < \frac{2}{3}$, we can drop the $S_3(s)$ term from our inner solutions.

From this we determine that the inner solutions are valid for $|s| \le \epsilon^{1-\kappa}$ for $0 < \kappa < \frac{1}{3}$.

After dropping unnecessary higher order terms, we take our Inner Solutions to be

$$a_I^-(s) = \epsilon\widetilde{\eta_0}s,$$

$$\eta_I^-(s) = \widetilde{\eta_0} + \epsilon\left(\frac{1}{2}s + \frac{\sqrt{(\widetilde{\eta_0}s)^2+4}}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\right),$$

$$S_I^-(s) = S_0 + \frac{\epsilon}{2}\widetilde{\eta_0}^2 s + \epsilon^2\left(\frac{\widetilde{\eta_0}}{2}s^2 + \frac{1}{2}s\sqrt{(\widetilde{\eta_0}s)^2+4}\right),$$

$$A_I^-(s) = A_0 + i\epsilon s D_0^-,$$

$$B_I^-(s) = D_0^-.$$

Matching Region

Now that we have Inner Solutions for when t is close to 0, we need to ensure there is a region where both the Inner Solutions and Outer Solutions are valid. This will be for $t \in [\epsilon, -\epsilon^\kappa]$. We will find Matching Conditions to ensure these match in this region. We do so by taking s to be large in the Inner Solutions, dropping lower order terms, and replacing $s = t/\epsilon$. We need to include some of the higher order terms of $a_I(s)$, $\eta_I(s)$, and $S_I(s)$.

The Matching Conditions we obtain are

$$a_M^-(t) = \widetilde{\eta_0}t,$$

$$\eta_M^-(t) = \widetilde{\eta_0} + t - \epsilon\left(\frac{1}{\widetilde{\eta_0}}\right),$$

$$S_M^-(t) = S_0 + \frac{\widetilde{\eta_0}^2}{2}t + \widetilde{\eta_0}t^2,$$

$$A_M^-(t) = A_0 + itD_0^-,$$

$$B_M^-(t) = D_0^-.$$

Outer Solutions

For the Outer Solutions, which are valid for large t, we return to the system of differential equations (3.34)-(3.38). We will again expand the solutions in orders of epsilon. However, we may note that now for the Outer Solutions, we will not find $a_0(t) = 0$, which can be seen just from the Matching Conditions. Thus cannot drop that term where it appears in the denominator in these equations. To find the solutions to the appropriate orders, we will approximate the system by the following.

$$
\begin{aligned}
\frac{\partial a}{\partial t}(t) &= \eta_0(t) + \epsilon\eta_1(t) + \epsilon^2\eta_2(t) + O(\epsilon^3), \\
\frac{\partial \eta}{\partial t}(t) &= \frac{1}{2}\left(1 + \frac{a_0(t) + \epsilon a_1(t) + \epsilon^2 a_2(t)}{\sqrt{(a_0(t) + \epsilon a_1(t) + \epsilon^2 a_2(t) + 4\epsilon^2}}\right) + O(\epsilon^3) \\
&= \frac{1}{2}\left(1 + \operatorname{sign}(a_0(t))\right) - \frac{\operatorname{sign}(a_0(t))}{a_0(t)^2}\epsilon^2 + O(\epsilon^3), \\
\frac{\partial S}{\partial t}(t) &= \frac{1}{2}(\eta_0(t)^2 + 2\epsilon\eta_0(t)\eta_1(t) + \epsilon^2\eta_1(t)^2 + 2\epsilon^2\eta_0(t)\eta_2(t)) \\
&\quad + \frac{1}{2}\left(a_0(t) + \epsilon a_1(t) + \epsilon^2 a_2(t)) + \sqrt{(a_0(t) + \epsilon a_1(t) + \epsilon^2 a_2(t))^2 + 4\epsilon^2}\right) + O(\epsilon^3) \\
&= \frac{1}{2}(\eta_0(t)^2 + (1 + \operatorname{sign}(a_0(t))a_0(t))) + \epsilon\left(\eta_0(t)\eta_1(t) + \frac{1}{2}(1 + \operatorname{sign}(a_0(t)))a_1(t)\right) \\
&\quad + \epsilon^2\left(\frac{1}{2}\eta_1(t)^2 + \eta_0(t)\eta_2(t) + \frac{1}{2}a_2(t) + \operatorname{sign}(a_0(t))\frac{1}{a_0(t)}\right) + O(\epsilon^3) \\
\frac{\partial A}{\partial t}(t) &= iB_0(t) + i\epsilon B_1(t) + O(\epsilon^2), \\
\frac{\partial B}{\partial t}(t) &= i\frac{2\epsilon^2}{|a_0(t)|^3}A_0(t) + O(\epsilon^3) = 0 + O(\epsilon^2).
\end{aligned}
$$

We will use the Matching Conditions as the initial conditions for the system of differential equations for each order of epsilon.

Order ϵ^0 terms, to leading order:

$$\begin{aligned}
\frac{\partial a_0}{\partial t}(t) &= \eta_0(t), \\
\frac{\partial \eta_0}{\partial t}(t) &= \frac{1}{2}\left(1 + \mathrm{sign}(a_0(t))\right), \\
\frac{\partial S_0}{\partial t}(t) &= \frac{1}{2}(\eta_0(t)^2 + (1 + \mathrm{sign}(a_0(t)))a_0(t)), \\
\frac{\partial A_0}{\partial t}(t) &= iB_0(t), \\
\frac{\partial B_0}{\partial t}(t) &= 0.
\end{aligned}$$

Let us first focus on the solutions for $\eta_0(s)$ and $a_0(s)$. The solutions for the order ϵ^0 terms are

$$\begin{aligned}
a_0(t) &= \frac{1}{4}\left(1 + \mathrm{sign}(a_0(t))\right)t^2 + \widetilde{\eta_0}t, \\
\eta_0(t) &= \frac{1}{2}\left(1 + \mathrm{sign}(a_0(t))\right)t + \widetilde{\eta_0}.
\end{aligned}$$

In fact, we can note the following for the signs.

$$a_0(t) = \begin{cases} t^2 + \widetilde{\eta_0}t & \text{if } a_0(t) > 0 \\ \widetilde{\eta_0}t & \text{if } a_0(t) < 0 \end{cases}$$

We can note that if $a_0(t) > 0$, we must have $t > 0$. Requiring continuous solutions, for $t < 0$, we have that if $a_0(t) < 0$, then we let $t < 0$. Thus we can replace $\mathrm{sign}(a_0(t))$ with $\mathrm{sign}(t)$.

$$\begin{aligned}
a_0(t) &= \frac{1}{4}\left(1 + \mathrm{sign}(t)\right)t^2 + \widetilde{\eta_0}t \\
&= \begin{cases} \widetilde{\eta_0}t & \text{if } t < 0 \\ \frac{1}{2}t^2 + \widetilde{\eta_0}t & \text{if } t > 0 \end{cases},
\end{aligned}$$

$$\begin{aligned}\eta_0(t) &= \frac{1}{2}\left(1+\operatorname{sign}(t)\right)t+\widetilde{\eta_0} \\ &= \begin{cases} \widetilde{\eta_0} & \text{if } t<0 \\ t+\widetilde{\eta_0} & \text{if } t>0 \end{cases}.\end{aligned}$$

For the action,

$$\frac{\partial S_0}{\partial t}(t) = \begin{cases} \frac{1}{2}\widetilde{\eta_0}^2 & \text{if } t<0 \\ \frac{1}{2}(t+\widetilde{\eta_0})^2+\left(\frac{1}{2}t^2+\widetilde{\eta_0}t\right) & \text{if } t>0 \end{cases},$$

and we get the solutions

$$S_0(t) = \begin{cases} S_0+\frac{1}{2}\widetilde{\eta_0}^2 t & \text{if } t<0 \\ S_0+\frac{1}{3}t^3+\widetilde{\eta_0}t^2+\frac{1}{2}\widetilde{\eta_0}^2 t & \text{if } t>0 \end{cases}.$$

For the other quantities, we have, for all t,

$$\begin{aligned}A_0(t) &= itD_0^- + A_0, \\ B_0(t) &= D_0^-.\end{aligned}$$

Order ϵ^1 terms, to leading order:

$$\begin{aligned}\frac{\partial a_1}{\partial t}(t) &= \eta_1(t), \\ \frac{\partial \eta_1}{\partial t}(t) &= 0, \\ \frac{\partial S_1}{\partial t}(t) &= \eta_0(t)\eta_1(t)+\frac{1}{2}(1+\operatorname{sign}(t))a_1(t), \\ \frac{\partial A_1}{\partial t}(t) &= iB_1(t), \\ \frac{\partial B_1}{\partial t}(t) &= 0.\end{aligned}$$

The solutions for the order ϵ^1 terms are

$$\begin{aligned} a_1(t) &= \frac{1}{\widetilde{\eta_0}} t, \\ \eta_1(t) &= \frac{1}{\widetilde{\eta_0}}, \\ A_1(t) &= 0, \\ B_1(t) &= 0. \end{aligned}$$

For the action,

$$\frac{\partial S_1}{\partial t}(t) = \begin{cases} 1 & \text{if } t < 0 \\ 1 + \frac{2}{\widetilde{\eta_0}} t & \text{if } t > 0 \end{cases},$$

and we get the solutions

$$S_1(t) = \begin{cases} t & \text{if } t < 0 \\ t + \frac{1}{\widetilde{\eta_0}} t^2 & \text{if } t > 0 \end{cases}.$$

Note that we do not need any further higher order information about $A(t)$ and $B(t)$. We also have solved $a(t)$ and $\eta(t)$ to the desired order, but we need to calculate $S(t)$ to order ϵ^2 and thus will need to calculate higher order for all to find these.

Order ϵ^2 terms, to leading order:

$$\begin{aligned} \frac{\partial a_2}{\partial t}(t) &= \eta_2(t), \\ \frac{\partial \eta_2}{\partial t}(t) &= -\frac{\text{sign}(t)}{a_0(t)^2} = \begin{cases} \frac{1}{(\widetilde{\eta_0} t)^2} & \text{if } t < 0 \\ \frac{-1}{(\frac{1}{2}t^2 + \widetilde{\eta_0} t)^2} & \text{if } t > 0 \end{cases}, \\ \frac{\partial S_2}{\partial t}(t) &= \frac{1}{2}\eta_1(t)^2 + \eta_0(t)\eta_2(t) + \frac{1}{2}\text{sign}(t) a_2(t) + \text{sign}(t)\frac{1}{a_0(t)}. \end{aligned}$$

The solutions for the order ϵ^2 terms are

$$a_2(t) = \begin{cases} -\frac{1}{\widetilde{\eta_0}^2}\ln|t| & \text{if } t<0 \\ \frac{1}{\widetilde{\eta_0}^2}\ln t + \frac{1}{\widetilde{\eta_0}^3} t\ln t - \frac{1}{\widetilde{\eta_0}^2}\ln(2\widetilde{\eta_0}+t) - \frac{1}{\widetilde{\eta_0}^3} t\ln(2\widetilde{\eta_0}+t) & \text{if } t>0 \end{cases},$$

$$\eta_2(t) = \begin{cases} -\frac{1}{\widetilde{\eta_0}^2 t} & \text{if } t<0 \\ \frac{1}{\widetilde{\eta_0}(2\widetilde{\eta_0}+t)} + \frac{1}{\widetilde{\eta_0}^2 t} + \frac{1}{\widetilde{\eta_0}^3}\ln t - \frac{1}{\widetilde{\eta_0}^3}\ln(2\widetilde{\eta_0}+t) & \text{if } t>0 \end{cases},$$

$$S_2(t) = \begin{cases} -\frac{1}{\widetilde{\eta_0}^3 t} + \frac{t}{2\widetilde{\eta_0}^2} - \frac{t}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\ln|t| + \frac{1}{2\widetilde{\eta_0}} t\ln|t| & \text{if } t<0 \\ \frac{t}{\widetilde{\eta_0}^2} + \frac{2}{\widetilde{\eta_0}}\ln t + \frac{3}{2\widetilde{\eta_0}^2} t\ln t + \frac{3}{4\widetilde{\eta_0}^3} t^2\ln t - \frac{3}{2\widetilde{\eta_0}^2} t\ln(2\widetilde{\eta_0}+t) & \\ -\frac{3}{4\widetilde{\eta_0}^3} t^2\ln(2\widetilde{\eta_0}+t) - \frac{2}{\widetilde{\eta_0}}\ln(2\widetilde{\eta_0}+t) & \text{if } t>0 \end{cases}.$$

Thus, we have obtained the Outer Solutions, for the lower level $\{-\}$, below.

$$a_O^-(t) = \begin{cases} \widetilde{\eta_0} t + \epsilon\frac{1}{\widetilde{\eta_0}} t & \text{if } t<0 \\ \frac{1}{2}t^2 + \widetilde{\eta_0} t + \epsilon\frac{1}{\widetilde{\eta_0}} t & \text{if } t>0 \end{cases},$$

$$\eta_O^-(t) = \begin{cases} \widetilde{\eta_0} + \epsilon\frac{1}{\widetilde{\eta_0}} & \text{if } t<0 \\ t + \widetilde{\eta_0} + \epsilon\frac{1}{\widetilde{\eta_0}} & \text{if } t>0 \end{cases},$$

$$S_O^-(t) = \begin{cases} S_0 + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon t & \\ +\epsilon^2\left(-\frac{1}{\widetilde{\eta_0}^3 t} + \frac{t}{2\widetilde{\eta_0}^2} - \frac{t}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\ln|t| + \frac{1}{2\widetilde{\eta_0}} t\ln|t|\right) & \text{if } t<0 \\ S_0 + \frac{1}{3}t^3 + \widetilde{\eta_0} t^2 + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon\left(t + \frac{1}{\widetilde{\eta_0}} t^2\right) & \\ \epsilon^2\left(\frac{t}{\widetilde{\eta_0}^2} + \frac{2}{\widetilde{\eta_0}}\ln t + \frac{3}{2\widetilde{\eta_0}^2} t\ln t + \frac{3}{4\widetilde{\eta_0}^3} t^2\ln t\right. & \\ \left.-\frac{3}{2\widetilde{\eta_0}^2} t\ln(2\widetilde{\eta_0}+t) - \frac{3}{4\widetilde{\eta_0}^3} t^2\ln(2\widetilde{\eta_0}+t) - \frac{2}{\widetilde{\eta_0}}\ln(2\widetilde{\eta_0}+t)\right) & \text{if } t>0 \end{cases},$$

$$A_O^-(t) = itD_0^- + A_0,$$

$$B_O^-(t) = D_0^-.$$

Solutions for upper level

Once we have reached the crossing point at time $t^\flat = 0$, we will find a piece of the wave function follows a trajectory along the upper level $\{+\}$, thus we must also consider the solutions for the classical quantities for the level $E_+(x,\epsilon)$. We will only need the solutions for $t > 0$ for the case that we are considering.

For the upper level,

$$
\begin{aligned}
V^{(1)}(x) &= \frac{\partial E_+(x,\epsilon)}{\partial x} \\
&= -\frac{1}{2}\left(1 - \frac{x}{\sqrt{x^2+4\epsilon^2}}\right) \\
V^{(2)}(x) &= \frac{\partial^2 E_-(x,\epsilon)}{\partial x^2} \\
&= \frac{2\epsilon^2}{(x^2+4\epsilon^2)^{3/2}}
\end{aligned}
$$

We solve the following system exactly as we did for the lower level before.

$$
\begin{aligned}
\frac{\partial a^+}{\partial t}(t) &= \eta^+(t), \\
\frac{\partial \eta^+}{\partial t}(t) &= -V^{(1)}(a^+(t)) = \frac{1}{2}\left(1 - \frac{a^+(t)}{\sqrt{a^+(t)^2+4\epsilon^2}}\right), \\
\frac{\partial S^+}{\partial t}(t) &= \frac{1}{2}\eta^+(t)^2 - V(a^+(t)) = \frac{1}{2}\eta^+(t)^2 + \frac{1}{2}\left(a^+(t) - \sqrt{a^+(t)^2+4\epsilon^2}\right), \\
\frac{\partial A^+}{\partial t}(t) &= iB^+(t), \\
\frac{\partial B^+}{\partial t}(t) &= iV^{(2)}(a^+(t))A^+(t) = i\frac{2\epsilon^2}{(a^+(t)^2+4\epsilon^2)^{3/2}}A^+(t),
\end{aligned}
$$

with initial conditions

$$
a^+(0) = 0
$$

$$
\begin{aligned}
\eta^+(0) &= \widetilde{\eta}_0 \\
S^+(0) &= S_0 \\
A^+(0) &= A_0 \\
B^+(0) &= D_0^+ = B_0^-(0) + i\frac{|(E_-^{(1)}(0) - E_+^{(1)}(0))\rangle\langle(E_-^{(1)} - E_+^{(1)}(0))|}{\langle(E_-^{(1)}(0) - E_+^{(1)}(0)),\ \eta_+(0)\rangle} A^+(0) \\
&= D_0^- + i(0)A_0 = D_0^-
\end{aligned}
$$

We find the inner solutions are given by

$$
\begin{aligned}
a_I^+(s) &= \epsilon\widetilde{\eta}_0 s, \\
\eta_I^+(s) &= \widetilde{\eta}_0 + \epsilon\left(\frac{1}{2}s - \frac{\sqrt{(\widetilde{\eta}_0 s)^2 + 4}}{2\widetilde{\eta}_0} + \frac{1}{\widetilde{\eta}_0}\right), \\
S_I^+(s) &= S_0 + \frac{\epsilon}{2}\widetilde{\eta}_0^{\,2} s + \epsilon^2\left(\frac{\widetilde{\eta}_0}{2}s^2 - \frac{1}{2}s\sqrt{(\widetilde{\eta}_0 s)^2 + 4}\right), \\
A_I^+(s) &= A_0 + i\epsilon s D_0^+, \\
B_I^+(s) &= D_0^+.
\end{aligned}
$$

The matching conditions are

$$
\begin{aligned}
a_M^+(t) &= \widetilde{\eta}_0 t, \\
\eta_M^+(t) &= \widetilde{\eta}_0 + \epsilon\left(\frac{1}{\widetilde{\eta}_0}\right), \\
S_M^+(t) &= S_0 + \frac{\widetilde{\eta}_0^{\,2}}{2}t, \\
A_M^+(t) &= A_0 + itD_0^+, \\
B_M^+(t) &= D_0^+.
\end{aligned}
$$

Lastly, the outer solutions are

$$
\begin{aligned}
a_O^+(t) &= \begin{cases} \frac{1}{2}t^2 + \widetilde{\eta}_0 t + \epsilon \frac{1}{\widetilde{\eta}_0} t & \text{if } t < 0 \\ \widetilde{\eta}_0 t + \epsilon \frac{1}{\widetilde{\eta}_0} t & \text{if } t > 0 \end{cases}, \\
\eta_O^+(t) &= \begin{cases} t + \widetilde{\eta}_0 + \epsilon \frac{1}{\widetilde{\eta}_0} & \text{if } t < 0 \\ \widetilde{\eta}_0 + \epsilon \frac{1}{\widetilde{\eta}_0} & \text{if } t > 0 \end{cases}, \\
S_O^+(t) &= \begin{cases} S_0 + \frac{1}{2}\widetilde{\eta}_0^{\,2} t + \epsilon t & \\ +\epsilon^2 \left(-\frac{1}{\widetilde{\eta}_0^{\,3} t} + \frac{t}{2\widetilde{\eta}_0^{\,2}} - \frac{t}{2\widetilde{\eta}_0} - \frac{1}{\widetilde{\eta}_0} \ln|t| + \frac{1}{2\widetilde{\eta}_0} t \ln|t| \right) & \text{if } t < 0 \\ S_0 + \frac{1}{3}t^3 + \widetilde{\eta}_0 t^2 + \frac{1}{2}\widetilde{\eta}_0^{\,2} t + \epsilon \left(t + \frac{1}{2\widetilde{\eta}_0} t^2 \right) & \\ \epsilon^2 \left(\frac{t}{\widetilde{\eta}_0^{\,2}} + \frac{2}{\widetilde{\eta}_0} \ln t + \frac{3}{2\widetilde{\eta}_0^{\,2}} t \ln t + \frac{3}{4\widetilde{\eta}_0^{\,3}} t^2 \ln t \right. & \\ \left. -\frac{3}{2\widetilde{\eta}_0^{\,2}} t \ln(2\widetilde{\eta}_0 + t) - \frac{3}{4\widetilde{\eta}_0^{\,3}} t^2 \ln(2\widetilde{\eta}_0 + t) - \frac{2}{\widetilde{\eta}_0} \ln(2\widetilde{\eta}_0 + t) \right) & \text{if } t > 0 \end{cases}, \\
A_O^+(t) &= itD_0^+ + A_0, \\
B_O^+(t) &= D_0^+.
\end{aligned}
$$

Remark: For the upper $\{+\}$ level in the case we are considering (i.e. beginning on the lower level and going through the crossing at $t = 0$ with momentum $\widetilde{\eta}_0 > 0$), the solutions for $t < 0$ are only valid for $t \in (-2\widetilde{\eta}_0, 0)$. There is no solution for these for $t < -2\widetilde{\eta}_0$. This is due to the $|a_0(t)|$ terms in the differential equations, just as in the equations for the lower $\{-\}$ level. The solutions for $a_0^+(t)$ are

$$
a_0^+(t) = \begin{cases} \frac{t^2}{2} + \widetilde{\eta}_0 t & \text{if } a_0^+(t) < 0 \\ \widetilde{\eta}_0 t & \text{if } a_0^+(t) > 0 \end{cases}
$$

Uniform Solutions

As a Corollary to Lemma (3.3.4), we may combine these and the matching conditions to find the uniform solutions to the classical quantities, given by the inner solutions plus the outer solutions minus the matching conditions.

Corollary 3.3.5. *The uniform solutions for the classical quantities associated with the solutions of the Schrödinger equation (3.32) for the lower level $E_-(x,\epsilon)$ are given by*

$$a^-_{unif}(t) = \begin{cases} \widetilde{\eta_0}t + \epsilon\frac{1}{\widetilde{\eta_0}}t & \text{if } t<0 \\ \frac{1}{2}t^2 + \widetilde{\eta_0}t + \epsilon\frac{1}{\widetilde{\eta_0}}t & \text{if } t>0 \end{cases},$$

$$\eta^-_{unif}(t) = \begin{cases} \widetilde{\eta_0} - \frac{1}{2}t + \frac{\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2}}{2\widetilde{\eta_0}} + \epsilon\frac{1}{\widetilde{\eta_0}} & \text{if } t<0 \\ \widetilde{\eta_0} + \frac{1}{2}t + \frac{\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2}}{2\widetilde{\eta_0}} + \epsilon\frac{1}{\widetilde{\eta_0}} & \text{if } t>0 \end{cases},$$

$$S^-_{unif}(t) = \begin{cases} S_0 - \frac{1}{2}\widetilde{\eta_0}t^2 + \frac{1}{2}t\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2} + \frac{1}{2}\widetilde{\eta_0}^2t + \epsilon t & \\ +\epsilon^2\left(-\frac{1}{\widetilde{\eta_0}^3t} + \frac{t}{2\widetilde{\eta_0}^2} - \frac{t}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\ln|t| + \frac{1}{2\widetilde{\eta_0}}t\ln|t|\right) & \text{if } t<0 \\ S_0 + \frac{1}{2}t\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2} + \frac{1}{3}t^3 + \frac{1}{2}\widetilde{\eta_0}t^2 + \frac{1}{2}\widetilde{\eta_0}^2t + \epsilon\left(t + \frac{1}{\widetilde{\eta_0}}t^2\right) & \\ \epsilon^2\left(\frac{t}{\widetilde{\eta_0}^2} + \frac{2}{\widetilde{\eta_0}}\ln t + \frac{3}{2\widetilde{\eta_0}^2}t\ln t + \frac{3}{4\widetilde{\eta_0}^3}t^2\ln t\right. & \\ \left.-\frac{3}{2\widetilde{\eta_0}^2}t\ln(2\widetilde{\eta_0}+t) - \frac{3}{4\widetilde{\eta_0}^3}t^2\ln(2\widetilde{\eta_0}+t) - \frac{2}{\widetilde{\eta_0}}\ln(2\widetilde{\eta_0}+t)\right) & \text{if } t>0 \end{cases},$$

$$A^-_{unif}(t) = itD^-_0 + A_0,$$

$$B^-_{unif}(t) = D^-_0.$$

For the upper level $E_+(x,\epsilon)$,

$$a^+_{unif}(t) = \begin{cases} \frac{1}{2}t^2 + \widetilde{\eta_0}t + \epsilon\frac{1}{\widetilde{\eta_0}}t & \text{if } t<0 \\ \widetilde{\eta_0}t + \epsilon\frac{1}{\widetilde{\eta_0}}t & \text{if } t>0 \end{cases},$$

$$\eta^{+}_{unif}(t) = \begin{cases} \widetilde{\eta_0} + \frac{1}{2}t - \frac{\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2}}{2\widetilde{\eta_0}} + t + \epsilon\frac{1}{\widetilde{\eta_0}} & if\ t<0 \\ \widetilde{\eta_0} + \frac{1}{2}t - \frac{\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2}}{2\widetilde{\eta_0}} + \epsilon\frac{1}{\widetilde{\eta_0}} & if\ t>0 \end{cases},$$

$$S^{+}_{unif}(t) = \begin{cases} S_0 + \frac{1}{2}\widetilde{\eta_0}t^2 + \frac{1}{2}t\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2} + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon t & \\ +\epsilon^2\left(-\frac{1}{\widetilde{\eta_0}^3 t} + \frac{t}{2\widetilde{\eta_0}^2} - \frac{t}{2\widetilde{\eta_0}} - \frac{1}{\widetilde{\eta_0}}\ln|t| + \frac{1}{2\widetilde{\eta_0}}t\ln|t|\right) & if\ t<0 \\ S_0 + \frac{1}{2}t\sqrt{(\widetilde{\eta_0}t)^2+4\epsilon^2} + \frac{1}{3}t^3 + \frac{3}{2}\widetilde{\eta_0}t^2 + \frac{1}{2}\widetilde{\eta_0}^2 t + \epsilon\left(t + \frac{1}{2\widetilde{\eta_0}}t^2\right) & \\ \epsilon^2\left(\frac{t}{\widetilde{\eta_0}^2} + \frac{2}{\widetilde{\eta_0}}\ln t + \frac{3}{2\widetilde{\eta_0}^2}t\ln t + \frac{3}{4\widetilde{\eta_0}^3}t^2\ln t\right. & \\ \left.-\frac{3}{2\widetilde{\eta_0}^2}t\ln(2\widetilde{\eta_0}+t) - \frac{3}{4\widetilde{\eta_0}^3}t^2\ln(2\widetilde{\eta_0}+t) - \frac{2}{\widetilde{\eta_0}}\ln(2\widetilde{\eta_0}+t)\right) & if\ t>0 \end{cases},$$

$$A^{+}_{unif}(t) = itD^{+}_0 + A_0,$$

$$B^{+}_{unif}(t) = D^{+}_0.$$

Average Level

We must also find the solutions for the classical quantities corresponding to the potential given by $V(x) = \widetilde{V}(x)$.

$$\widetilde{V}(x) = \frac{1}{2}(E_-(x,\epsilon) + E_+(x,\epsilon)) = \frac{1}{2}\left(-\frac{1}{2}x - \frac{1}{2}\sqrt{x^2+4\epsilon^2} - \frac{1}{2}x + \frac{1}{2}\sqrt{x^2+4\epsilon^2}\right) = -\frac{1}{2}x$$

$$\widetilde{V}^{(1)}(x) = -\frac{1}{2}$$

$$\widetilde{V}^{(2)}(x) = 0$$

The system (3.34)-(3.38) for this potential is then

$$\frac{\partial a^{\sim}}{\partial t}(t) = \eta^{\sim}(t),$$
$$\frac{\partial \eta^{\sim}}{\partial t}(t) = \frac{1}{2},$$

$$\frac{\partial S^{\sim}}{\partial t}(t) \;=\; \frac{1}{2}\eta^{\sim}(t)^2 - a^{\sim}(t),$$

but for this region, we use the following initial conditions

$$\begin{aligned} a^{\sim}(0) &= 0, \\ \eta^{\sim}(0) &= \widetilde{\eta}_0, \\ S^{\sim}(0) &= 0. \end{aligned}$$

Note that the inner solutions of the Schrödinger equation do not depend on matrices $A(t)$ and $B(t)$.

This system can be solved exactly by simple integration, so there is no need for the expansions that were necessary for $V(x) = E_-(x, \epsilon)$ and $V(x) = E_+(x, \epsilon)$ before. Thus we obtain the solutions

$$\begin{aligned} a^{\sim}(t) &= \widetilde{\eta}_0 t + \frac{1}{4}t^2, \\ \eta^{\sim}(t) &= \widetilde{\eta}_0 + \frac{1}{2}t, \\ S^{\sim}(t) &= = \frac{1}{2}\widetilde{\eta}_0{}^2 t. \end{aligned}$$

□

3.3.2 Eigenvectors

Consider the eigenvectors that we found previously,

$$\nu_-(x, \epsilon) \;=\; \begin{pmatrix} \frac{1}{2}x + \frac{1}{2}\sqrt{x^2 + 4\epsilon^2} - x\sin^2(x) \\ \\ i\epsilon + x\cos(x)\sin(x) \end{pmatrix}$$

$$\nu_+(x,\epsilon) = \begin{pmatrix} \frac{1}{2}x - \frac{1}{2}\sqrt{x^2+4\epsilon^2} - x\sin^2(x) \\ i\epsilon + x\cos(x)\sin(x) \end{pmatrix}$$

and normalized eigenvectors

$$\Phi_-(x,\epsilon) = \frac{1}{|\nu_-(x,\epsilon)|}\nu_-(x,\epsilon)$$

$$= \frac{1}{(\frac{1}{2}x^2 + \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))^{1/2}} \begin{pmatrix} \frac{1}{2}x\cos(2x) + \frac{1}{2}\sqrt{x^2+4\epsilon^2} \\ i\epsilon + \frac{1}{2}x\sin(2x) \end{pmatrix}$$

and

$$\Phi_+(x,\epsilon) = \frac{1}{|\nu_+(x,\epsilon)|}\nu_+(x,\epsilon)$$

$$= \frac{1}{(\frac{1}{2}x^2 - \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))^{1/2}} \begin{pmatrix} \frac{1}{2}x\cos(2x) - \frac{1}{2}\sqrt{x^2+4\epsilon^2} \\ i\epsilon + \frac{1}{2}x\sin(2x) \end{pmatrix}.$$

Note as $\epsilon \to 0$, $\nu_- = (\frac{1}{2}(1+\text{sign}(x)) - \sin^2(x), \cos(x)\sin(x))$, $\nu_+ = (\frac{1}{2}(1-\text{sign}(x)) - \sin^2(x), \cos(x)\sin(x))$. For large negative x, or $t \to -\infty$, $\Phi_- \approx (-\sin x, \cos x)$, and $\Phi_+ \approx (\cos x, \sin x)$, but for large positive x, or $t \to +\infty$, $\Phi_- \approx (\cos x, \sin x)$, and $\Phi_+ \approx (-\sin x, \cos x)$. These are $\Phi_{\mathcal{A}}(x)$, and $\Phi_{\mathcal{B}}(x)$ from the crossing Hamiltonian.

Using the change of variables for the eigenvectors Φ_- and Φ_+, $x \to x' = \frac{1}{2}x$, $t' = \frac{1}{4}t$, and $\epsilon' = \epsilon$,

$$\Phi_-(x',\epsilon') = \frac{1}{(2x'^2 + 2x'\cos(4x')\sqrt{x'^2+\epsilon'^2} + 2ix'\epsilon'\sin(4x'))^{1/2}} \begin{pmatrix} x'\cos(4x') + \sqrt{x'^2+\epsilon'^2} \\ i\epsilon' + x'\sin(4x') \end{pmatrix}$$

and

$$\Phi_+(x',\epsilon') = \frac{1}{(2x'^2 - 2x'\cos(4x')\sqrt{x'^2+\epsilon^2} + 2ix'\epsilon\sin(4x'))^{1/2}} \begin{pmatrix} x'\cos(4x') - \sqrt{x'^2+\epsilon^2} \\ i\epsilon + x'\sin(4x') \end{pmatrix}.$$

First I will construct static eigenvectors. Define the angles $\varphi(x,\epsilon)$ and $\theta(x,\epsilon)$ by

$$\beta'(x',\epsilon') = \sqrt{\beta'(x',\epsilon')^2 + \gamma'(x',\epsilon')^2 + \delta'(x',\epsilon')^2}\cos(\theta(x',\epsilon'))$$

$$\gamma'(x',\epsilon') = \sqrt{\beta'(x',\epsilon')^2 + \gamma'(x',\epsilon')^2 + \delta'(x',\epsilon')^2}\sin(\theta(x',\epsilon'))\cos(\varphi(x',\epsilon'))$$

$$\delta'(x',\epsilon') = \sqrt{\beta'(x',\epsilon')^2 + \gamma'(x',\epsilon')^2 + \delta'(x',\epsilon')^2}\sin(\theta(x',\epsilon'))\sin(\varphi(x',\epsilon'))$$

Let $\cos(\theta) = x'/\sqrt{x'^2+\epsilon'^2}$, $\sin(\theta) = \epsilon'/\sqrt{x'^2+\epsilon'^2}$.

$\gamma'(x',\epsilon') = \epsilon'/\sqrt{x'^2+\epsilon'^2} = \sin(\theta)\cos(\varphi)$, so we let $\cos(\varphi) = 1$, and $\varphi(x',\epsilon') = 0$.

Then $\sin(\theta(x,\epsilon)) = \frac{x}{\sqrt{x^2+4\epsilon^2}}$ in terms of our original variables, and $\varphi(x,\epsilon) = 0$.

Define the static eigenvectors of $h_1(x,\epsilon)$. For $\pi/2 < \theta(x,\epsilon) < \pi$,

$$\Phi_+^m(x,\epsilon) = e^{i\varphi}\cos(\theta/2)\psi_1(x,\epsilon) + \sin(\theta/2)\psi_2(x,\epsilon)$$

$$\Phi_-^m(x,\epsilon) = e^{-i\varphi}\cos(\theta/2)\psi_2(x,\epsilon) - \sin(\theta/2)\psi_1(x,\epsilon)$$

and for $0 \le \theta(x,\epsilon) \le \pi/2$,

$$\Phi_+^p(x,\epsilon) = \cos(\theta/2)\psi_1(x,\epsilon) + e^{-i\varphi}\sin(\theta/2)\psi_2(x,\epsilon)$$

$$\Phi_-^p(x,\epsilon) = \cos(\theta/2)\psi_2(x,\epsilon) - e^{i\varphi}\sin(\theta/2)\psi_1(x,\epsilon).$$

Use Φ_- and Φ_+ found above, but replace $x = 2x'$. Solving these for $\psi_1,\ \psi_2$, note that for $\varphi(x,\epsilon) = 0$, therefore no need to differentiate $\{m,p\}$.

$$\psi_1(x,\epsilon) = \cos(\theta/2)\Phi_+(x,\epsilon) - \sin(\theta/2)\Phi_-(x,\epsilon)$$

$$\psi_2(x,\epsilon) = \sin(\theta/2)\Phi_+(x,\epsilon) + \cos(\theta/2)\Phi_-(x,\epsilon)$$

Since $0 \le \theta(x,\epsilon) \le \pi$, $0 \le \theta/2 \le \pi/2$, hence $\cos(\theta/2) > 0$ and $\sin(\theta/2) > 0$ and

$$\cos(\theta/2) = \sqrt{\frac{1+\cos(\theta)}{2}}, \qquad \sin(\theta/2) = \sqrt{\frac{1-\cos(\theta)}{2}}.$$

$$\psi_1(x,\epsilon) = \sqrt{\frac{1+\cos(\theta)}{2}}\Phi_+(x,\epsilon) - \sqrt{\frac{1-\cos(\theta)}{2}}\Phi_-(x,\epsilon)$$
$$\psi_2(x,\epsilon) = \sqrt{\frac{1-\cos(\theta)}{2}}\Phi_+(x,\epsilon) + \sqrt{\frac{1+\cos(\theta)}{2}}\Phi_-(x,\epsilon)$$

Find normalized eigenvectors $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$ which are the solutions of

$$\langle \Phi^{m,p}_{\pm}(x,t,\epsilon)|(\partial/\partial t + \eta^{\pm}(t)\nabla)\Phi^{m,p}_{\pm}(x,t,\epsilon)\rangle = 0$$

$$\Phi^{m,p}_{\pm}(x,t,\epsilon) = \Phi^{m,p}_{\pm}(x,\epsilon)e^{i\lambda^{m,p}_{\pm}(x,t,\epsilon)}$$

where $\{m,p\}$ now refers to $t<0$ (m) and $t>0$ (p). $\lambda^{m,p}_{\pm}(x,t,\epsilon)$ is a real valued function satisfying

$$i\frac{\partial}{\partial t}\lambda^{m,p}_{\pm}(x,t,\epsilon) + i\eta^{\pm}(t)\nabla\lambda^{m,p}_{\pm}(x,t,\epsilon) + \langle\Phi_{\pm}(x,\epsilon)|\eta^{\pm}(t)\nabla\Phi_{\pm}(x,\epsilon)\rangle = 0$$

From Lemma (3.3.4), we use the outer solutions for $\eta^{\pm}(t)$,

$$\begin{aligned}
\eta^-_m(t) &= \widetilde{\eta}_0 + \epsilon\frac{1}{\widetilde{\eta}_0}, \\
\eta^-_p(t) &= t + \widetilde{\eta}_0 + \epsilon\frac{1}{\widetilde{\eta}_0}, \\
\eta^+_m(t) &= t + \widetilde{\eta}_0 + \epsilon\frac{1}{\widetilde{\eta}_0}, \\
\eta^+_p(t) &= \widetilde{\eta}_0 + \epsilon\frac{1}{\widetilde{\eta}_0},
\end{aligned}$$

where m refers to $t < 0$ and p refers to $t > 0$.

First, for the lower energy level, calculate

$$\langle \Phi_-(x,\epsilon) | \eta^-(t) \nabla \Phi_-(x,\epsilon) \rangle =$$

$$\eta^-(t) \Big\langle \frac{1}{(\frac{1}{2}x^2 + \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))^{1/2}} \begin{pmatrix} \frac{1}{2}x\cos(2x) + \frac{1}{2}\sqrt{x^2+4\epsilon^2} \\ \\ i\epsilon + \frac{1}{2}x\sin(2x) \end{pmatrix},$$

$$\frac{1}{(\frac{1}{2}x^2 + \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))^{1/2}} \begin{pmatrix} -2x\sin(2x) + \cos(2x) + x(x^2+4\epsilon^2)^{-1/2} \\ \\ 2x\cos(2x) + \sin(2x) \end{pmatrix}$$

$$+ \frac{-2x + (2x\sin(2x) - \cos(2x))\sqrt{x^2+4\epsilon^2} - x^2\cos(2x)(x^2+4\epsilon^2)^{-1/2} - 2i\epsilon\sin(2x) - 4ix\epsilon\cos(x)}{2(\frac{1}{2}x + \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))^{3/2}}$$

$$\times \begin{pmatrix} \frac{1}{2}x\cos(2x) + \frac{1}{2}\sqrt{x^2+4\epsilon^2} \\ \\ i\epsilon + \frac{1}{2}x\sin(x) \end{pmatrix} \Big\rangle$$

$$= \eta^-(t) \Bigg(\frac{-2x + (2x\sin(2x) - \cos(2x))\sqrt{x^2+4\epsilon^2} - x^2\cos(2x)(x^2+4\epsilon^2)^{\frac{-1}{2}} - 2i\epsilon(\sin(2x) + 2x\cos(2x))}{2(\frac{1}{2}x + \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))}$$

$$+ \frac{x + \frac{1}{2}x^2\cos(2x)(x^2+4\epsilon^2)^{\frac{-1}{2}} + (-x\sin(2x) + \frac{1}{2}\cos(2x))\sqrt{x^2+4\epsilon^2} + (2x\cos(2x) + \sin(2x))i\epsilon}{(\frac{1}{2}x + \frac{1}{2}x\cos(2x)\sqrt{x^2+4\epsilon^2} + ix\epsilon\sin(2x))} \Bigg)$$

Everything cancels in the equations above and we find

$$\langle \Phi_-(x,\epsilon) | \eta^-(t) \nabla \Phi_-(x,\epsilon) \rangle = 0.$$

We find the same is true for the upper energy level as well,

$$\langle \Phi_+(x,\epsilon) | \eta^+(t) \nabla \Phi_+(x,\epsilon) \rangle = 0.$$

Now we solve for $\lambda_{\pm}^{m,p}(x,t,\epsilon)$ by solving

$$i\frac{\partial}{\partial t}\lambda_{\pm}^{m,p}(x,t,\epsilon) + i\eta^{\pm}(t)\nabla\lambda_{\pm}^{m,p}(x,t,\epsilon) = 0,$$

but this is solved by just letting $\lambda_{\pm}^{m,p}(x,t,\epsilon) = 0$. This satisfies the definition that our time dependent eigenvectors solve $\langle\Phi_{\pm}^{m,p}(x,t,\epsilon)|(\partial/\partial t + \eta^{\pm}(t)\nabla)\Phi_{\pm}^{m,p}(x,t,\epsilon)\rangle = 0$. Therefore we may drop the t dependence and use the static eigenvectors $\Phi_{\pm}(x,\epsilon)$ and $\Phi_{\pm}(x,\epsilon)$.

3.3.3 Incoming Outer Solutions

From the first part of Theorem (3.3.2), we should look for solutions to the Schrödinger equation of the form

$$\begin{aligned}\psi(x',t') &= e^{\left(i\frac{S'^{-}(t')}{\epsilon'^2} + i\frac{\eta'^{-}(t')(x'-a'^{-}(t'))}{\epsilon'^2}\right)} \\ &\quad \times \phi_l(A'^{-}(t'), B'^{-}(t'), \epsilon'^2, a'^{-}(t'), 0, x')\Phi_{-}^{-}(x',t',\epsilon') + O(\epsilon'^p)\end{aligned}$$

during the time $t' \in [-T', \epsilon'^{1-\xi}]$, given we start with a wavepacket of the form

$$\begin{aligned}\psi(x',-T') &= e^{\left(i\frac{S'^{-}(-T')}{\epsilon'^2} + i\frac{\eta'^{-}(-T')(x'-a'^{\mathcal{B}}(-T'))}{\epsilon'^2}\right)} \\ &\quad \times \phi_l(A'^{-}(-T'), B'^{-}(-T'), \epsilon'^2, a'^{-}(-T'), 0, x')\Phi_{-}(x',-T',\epsilon')\end{aligned}$$

at time $t = -T'$.

We are most interested in the wave packet when $l = 0$. For $l = 0$, ϕ_l is a Gaussian function which are convenient functions to work with and are of particular interest to chemists and physicists. We must adjust for the change of variables that was made for the theorem, as mentioned previously. We make the replacements as given in (3.43)-(3.48).

We make the assumption instead that our initial wave packet is of the form

$$\psi(x,-T) = e^{\left(i\frac{S^-(-T)}{\epsilon^2}+i\frac{\eta^-(-T)(x-a^{\mathcal{B}}(-T))}{\epsilon^2}\right)}$$

$$\times\, \phi_0(A^-(-T),B^-(-T),\epsilon^2,a^-(-T),0,x)\Phi_-(x,-T,\epsilon)+O(\epsilon^q).$$

Therefore, we will not need to worry with the change of variables for $S(t)$, $A(t)$, and $B(t)$ for our solutions.

T is chosen far from the avoided crossing, but small enough to stay away from any other crossings or avoided crossing of the eigenvalues of $h(x,\epsilon)$. Hence for this problem, we may take $T\to\infty$.

In this region, these solutions are accurate up to errors of order $O(\xi)$ as $\epsilon\to 0$. So that we may use the outer solutions of the classical quantities found previously, we let $\xi=\kappa\in(0,\frac{1}{3})$.

Hence with the definition of the wave packet ϕ_0, (3.39), and the solutions of the classical quantities given in Lemma (3.3.4), we have obtained the outer solutions for the incoming wave packet (i.e. for $t<-\epsilon^{1-\xi}$), up to error of order ϵ^{ξ}.

$$\psi_{IO}(x,t) = e^{\left(i\frac{S_O^-(t)}{\epsilon^2}+i\frac{\eta_O^-(t)(x-a_O^-(t))}{\epsilon^2}\right)}$$

$$\times\, \phi_0(A_O^-(t),B_O^-(t),\epsilon^2,a_O^-(t),0,x)\Phi_-(x,t,\epsilon)+O(\epsilon^{\xi})$$

3.3.4 Inner Solutions

Now we consider the inner time regime, when $t=\epsilon s\in[-\epsilon^{1-\xi},\epsilon^{1-\xi}]$. Let $s=t/\epsilon$ and $y^{\sim}=(x-a^{\sim}(t))/\epsilon$. From the second part of Theorem (3.3.2), we let the solutions be of the form

$$\psi(x',t') \; = \; e^{\left(i\frac{S'^{\sim}(t')}{\epsilon'^2}+i\frac{\eta'^{\sim}(t')(x'-a'^{\sim}(t'))}{\epsilon^2}\right)}\left(f_0(y',s')\psi_1(x',\epsilon')+g_0(y',s')\psi_2(x',\epsilon')\right),$$

where $\psi_1(x',\epsilon')$ is given by (3.41), $\psi_2(x',\epsilon')$ is given by (3.42), and f_0 and g_0 satisfy (3.49).

Adjusting for our change of variables, we will use the inner solutions

$$\psi(x,t) \; = \; e^{\left(i\frac{S^{\sim}(t)}{\epsilon^2}+i\frac{\eta^{\sim}(t)(x-a^{\sim}(t))}{\epsilon^2}\right)}\left(f_0\left(\frac{x-a^{\sim}(t)}{2\epsilon},\frac{1}{4\epsilon}t\right)\psi_1(x,\epsilon)+g_0\left(\frac{x-a^{\sim}(t)}{2\epsilon},\frac{1}{4\epsilon}t\right)\psi_2(x,\epsilon)\right),$$

After scaling the variables, we make the ansatz that the Inner Solutions to the Schrödinger equation are of the form

$$F(\|y\|\epsilon^{\xi'})\exp\left(i\frac{S'^{\sim}(\epsilon's')}{\epsilon'^2}+i\frac{\eta'^{\sim}(\epsilon's')y'^{\sim}}{\epsilon'}\right)\{f(y',s',\epsilon')\psi_1(a(\epsilon s)+\epsilon y,\epsilon)$$
$$+\,g(y',s',\epsilon')\psi_2(a(\epsilon s)+\epsilon y),\epsilon)+\psi_\perp(a(\epsilon s)+\epsilon y,\epsilon)\}$$

where $F(r)$ is a C^∞ cutoff function such that

$$\begin{cases} F(r)=1 & \text{for } 0\le r\le 1 \\ F(r)=0 & \text{for } r\ge 2 \end{cases}$$

First, we may note that $\psi_\perp(x,\epsilon)=0$ since $\{\psi_1(x,\epsilon),\psi_2(x,\epsilon)\}$ spans all of $\mathbb{R}^2$.

For the functions $f_0(y',s')$ and $g_0(y',s')$, the solutions to (3.49) can be found exactly in terms of parabolic cylinder functions. See [27] for details on these parabolic cylinder functions D_z.

$$\begin{pmatrix} f_0(y',s') \\ g_0(y',s') \end{pmatrix} \; = C_1(y')\begin{pmatrix} \frac{(1-i)}{2}\sqrt{\frac{r}{\widetilde{\eta_0}'_1}}D_{\frac{ir}{2\widetilde{\eta_0}'_1}-1}\left((-1+i)\sqrt{\frac{r}{\widetilde{\eta_0}'_1}}(\widetilde{\eta_0}'_1s'+y'_1)\right) \\ D_{\frac{ir}{2\widetilde{\eta_0}'_1}}\left((-1+i)\sqrt{\frac{r}{\widetilde{\eta_0}'_1}}(\widetilde{\eta_0}'_1s'+y'_1)\right) \end{pmatrix}$$

$$+ C_2(y') \begin{pmatrix} D_{\frac{ir}{2\widetilde{\eta_0}_1'}}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta_0}_1'}}(\widetilde{\eta_0}_1' s' y_1')\right) \\ -\frac{(1+i)}{2}\sqrt{\frac{r}{\widetilde{\eta_0}_1'}}\, D_{-\frac{ir}{2\widetilde{\eta_0}_1'}-1}\left(-(1+i)\sqrt{\frac{r}{\widetilde{\eta_0}_1'}}(\widetilde{\eta_0}_1' s' + y_1')\right) \end{pmatrix}$$

For Type 1 crossings, as is our problem, we can find

$$C_1(y') = 0$$

$$\begin{aligned} C_2(y') \;&=\; -\,\epsilon'^{-n/2}\phi_l(A_0', {D_0^-}', 1, 0, 0, y')e^{-\frac{\pi r}{8\widetilde{\eta_0}_1'}} \exp\left(\frac{ir}{2\widetilde{\eta_0}_1'}(y_1'^2 - 2y_1')\right) \\ &\times \exp\left(i\frac{S_0^-}{\epsilon'^2} + \frac{ir}{4\widetilde{\eta_0}_1'}(1 + 3\ln(2\widetilde{\eta_0}_1') + \ln r - 4\ln\epsilon')\right) \end{aligned}$$

Writing this for our problem, and adjusting for the scaling, we have

$$\begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix} \;=\; C_2(y) \begin{pmatrix} D_{\frac{i}{\widetilde{\eta_0}}}\left(-(1+i)\sqrt{\frac{1}{2\widetilde{\eta_0}}}(\widetilde{\eta_0}s + y)\right) \\ -(1+i)\sqrt{\frac{1}{2\widetilde{\eta_0}}}\, D_{-\frac{i}{\widetilde{\eta_0}}-1}\left(-(1+i)\sqrt{\frac{1}{2\widetilde{\eta_0}}}(\widetilde{\eta_0}s + y)\right) \end{pmatrix}$$

with

$$\begin{aligned} C_2(y) \;&=\; -\,\epsilon^{-1/2}\phi_0(A_0, D_0^-), 1, 0, 0, y)e^{-\frac{\pi}{4\widetilde{\eta_0}}} \exp\left(\frac{i}{4\widetilde{\eta_0}}(y^2 - 4y)\right) \\ &\times \exp\left(i\frac{S_0}{\epsilon^2} + \frac{i}{2\widetilde{\eta_0}}(1 + 3\ln(4\widetilde{\eta_0}) + \ln 4 - 4\ln\epsilon)\right). \end{aligned}$$

Putting all of this together, we have obtained the inner solutions to the Schrödinger equation, accurate up to errors of order $O(\epsilon^{1-3\xi}) \to 0$ as $\epsilon \to 0$.

3.3.5 Outgoing Outer Solutions

Following the last part of (3.3.2), when $e^{1-\xi} \le t \le T$, the outgoing outer solutions are given by

$$\psi(x', t') \;=\; -\,e^{-\pi r/2\widetilde{\eta_0}_1'} e^{\left(i\frac{S'^{+}(t')}{\epsilon'^2} + i\frac{\eta'^{+}(t')(x' - a'^{+}(t'))}{\epsilon'^2}\right)}$$

$$\times\, \phi_l(A'^{+}(t'), B'^{+}(t'), \epsilon'^2, a'^{+}(t'), 0, x')\Phi_+^{+}(x', t', \epsilon')$$

$$+\, e^{-\pi r/4\widetilde{\eta_0}_1'}\sqrt{\frac{\pi r}{\widetilde{\eta_0}_1'}}\frac{e^{i\lambda(\epsilon')}}{\Gamma(1+\frac{ir}{2\widetilde{\eta_0}_1'})}e^{\left(i\frac{S'^{-}(t')}{\epsilon'^2}+i\frac{\eta'^{-}(t')(x'-a'^{-}(t'))}{\epsilon'^2}\right)}$$

$$\times\, \phi_l(A'^{-}(t'), B'^{-}(t'), \epsilon'^2, a'^{-}(t'), 0, x')\Phi_-^{+}(x', t', \epsilon') + O(\epsilon'^p)$$

where $\lambda(\epsilon')$ is given by

$$\lambda(\epsilon') \;=\; \frac{\pi}{4} + \frac{S_0(\epsilon', -)}{\epsilon'^2} + \frac{r}{2\widetilde{\eta_0}_1'}(1 + 3\ln(2\widetilde{\eta_0}_1') + \ln r - 4\ln\epsilon').$$

In this time regime the outgoing outer solutions agrees with the exact solution to the Schrödinger equation up to error terms of order $O(\epsilon^\xi)$ as $\epsilon \to 0$.

Adjusting for the change of variables, and using the outer solutions for the classical quantities, the outgoing outer solutions for the Schrödinger equation are given by

$$\psi_{OO}(x,t) \;=\; -\, e^{-\pi/\widetilde{\eta_0}}e^{\left(i\frac{S_O^{+}(t)}{\epsilon^2}+i\frac{\eta_O^{+}(t)(x-a_O^{+}(t))}{\epsilon^2}\right)}$$

$$\times\, \phi_0(A_O^{+}(t), B_O^{+}(t), \epsilon^2, a_O^{+}(t), 0, x)\Phi_+(x,t,\epsilon)$$

$$+\, e^{-\pi/2\widetilde{\eta_0}}\sqrt{\frac{2\pi}{\widetilde{\eta_0}}}\frac{e^{i\lambda(\epsilon)}}{\Gamma(1+\frac{i}{\widetilde{\eta_0}})}e^{\left(i\frac{S_O^{-}(t)}{\epsilon^2}+i\frac{\eta_O^{-}(t)(x-a_O^{-}(t))}{\epsilon^2}\right)}$$

$$\times\, \phi_0(A_O^{-}(t), B_O^{-}(t), \epsilon^2, a_O^{-}(t), 0, x)\Phi_-(x,t,\epsilon) + O(\epsilon^\xi)$$

with

$$\lambda(\epsilon) \;=\; \frac{\pi}{4} + \frac{S_0}{\epsilon^2} + \frac{1}{\widetilde{\eta_0}_1}(1 + 3\ln(4\widetilde{\eta_0}) + \ln 4 - 4\ln\epsilon).$$

Hence we have found the results given by Corollary (3.3.3).

3.3.6 Transition Probabilities

Corollary 3.3.6. *Given an initial wave packet on the $E_-(x,\epsilon)$ level, the probability of transitioning to the upper electronic level, $E_+(x,\epsilon)$, is*

$$\mathcal{P}_{-\to+} \;=\; e^{-2\pi/\widetilde{\eta}_0} + O(\epsilon^{\xi}).$$

The probability of remaining on the lower electronic level is

$$\mathcal{P}_{-\to-} \;=\; 1 - e^{-2\pi/\widetilde{\eta}_0} + O(\epsilon^{\xi}).$$

Proof.

$$\mathcal{P}_{-\to\pm}(t) = \int_{-\infty}^{\infty} |\Pi_{\pm}\psi(x,t)|^2 dx$$

where $\Pi_{\pm}$ is the projector on the the eigenspace corresponding to $\Phi_+(x,\epsilon)$ or $\Phi_-(x,\epsilon)$ respectively.

The result can be seen from the coefficients on the wave packets in the outgoing outer solutions since the wave packets ϕ_l are normalized. Also noting that

$$e^{-\pi/\widetilde{\eta}_0}\frac{2\pi}{\widetilde{\eta}_0\left|\Gamma(1+\frac{i}{\widetilde{\eta}_0})\right|^2} \;=\; 1 - e^{-2\pi/\widetilde{\eta}_0}.$$

□

3.3.7 Numerical Example

As with the crossing example, we will provide a similar example for the avoided crossing. With the solutions given by Corollary (3.3.3), we can find the solutions to any problem with

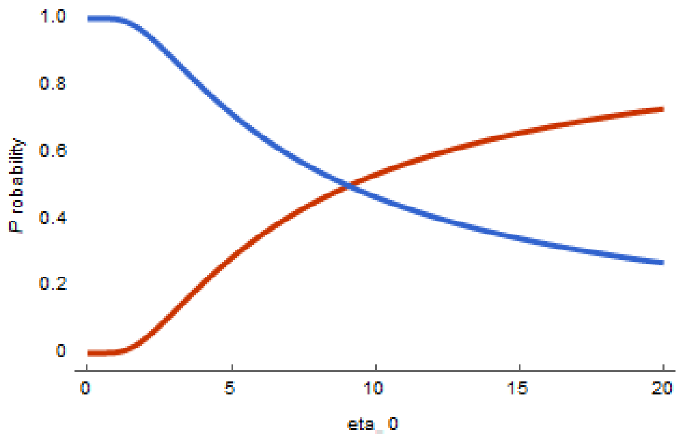

Figure 3.10: Transition Probabilities

a potential of this form. As an example, we will show the results for a system, with an initial wave packet at $t = -T$ associated with the electronic energy level $E_{-}(x)$, the lower level for $t < 0$.

We can choose our starting time $t = -T$, with T being any arbitrary number as we do not need to worry about avoiding any other eigenvalue crossings or avoided crossing for this system in the case where we begin with a wave packet on the $E_{-}(x)$ level with positive initial momentum. For this example I will choose $T = 30\epsilon$.

We will specify the value of ϵ, our Born-Oppenheimer averaged nuclear mass, using the mass of a C^{12} carbon nucleus. $\epsilon \approx .1$.

We let the classical initial conditions be given by

$$\begin{aligned} a^{-}(0) &= a_0 &= 0 \\ \eta^{-}(0) &= \widetilde{\eta_0} &= 1 \end{aligned}$$

$$S^-(0) = S_0 = 0$$

$$A^-(0) = A_0 = 1$$

$$B^-(0) = D_0^- = 1.$$

We can see the results graphed below in Figure (3.11).

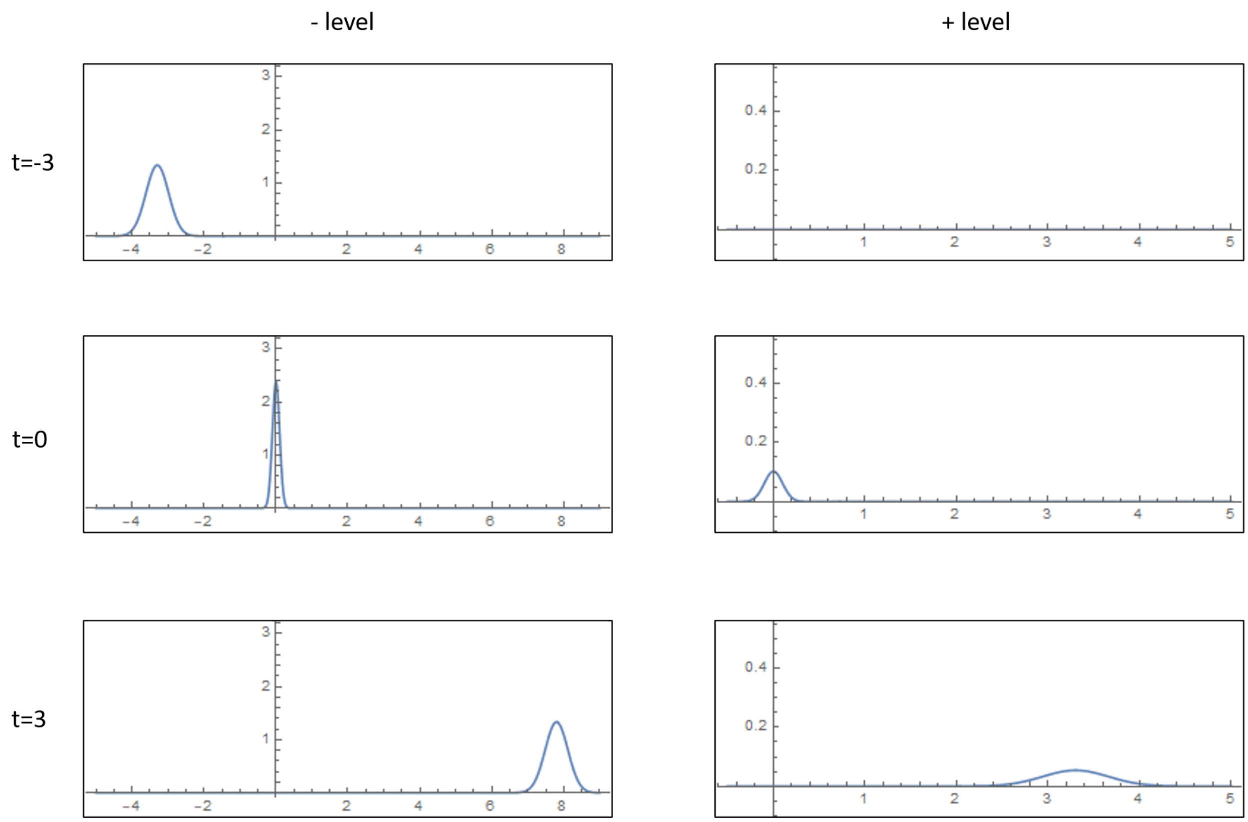

Figure 3.11: Propagation of a Gaussian wave packet through an avoided crossing

Chapter 4

Propagation of coherent states through conical intersections

4.1 Introduction

We consider a system of two Schrödinger equations coupled by a matrix-valued potential

$$i\varepsilon\partial_t\psi^\varepsilon = -\frac{\varepsilon^2}{2}\Delta\psi^\varepsilon + V(x)\psi^\varepsilon, \;\; \psi^\varepsilon_{|t=t_0} = \psi^\varepsilon_0 \tag{4.1}$$

where ψ^ε_0 is a bounded family in $L^2(\mathbb{R}^d, \mathcal{C}^2)$, and $V \in \mathcal{C}^\infty(\mathbb{R}^d, \mathcal{C}^{2,2})$ is a self-adjoint matrix that we assume to be bounded with bounded derivatives. These assumptions guarantee the existence of solutions to equation (4.1) in $L^2(\mathbb{R}^d, \mathcal{C}^2)$ or, more generally, in the functional spaces $\Sigma^k_\varepsilon := \Sigma^k_\varepsilon(\mathbb{R}^d, \mathcal{C}^2)$ defined for $k \in \mathbb{N}$ by

$$\Sigma^k_\varepsilon(\mathbb{R}^d, \mathcal{C}^2) = \{f \in L^2(\mathbb{R}^d, \mathcal{C}^2),\; \forall\alpha,\beta \in \mathbb{N}^d,\; |\alpha| + |\beta| \leq k,\; x^\alpha(\varepsilon\partial_x)^\beta f \in L^2(\mathbb{R}^d, \mathcal{C}^2)\}$$

and endowed with the norm

$$\|f\|_{\Sigma^k_\varepsilon} = \sup_{|\alpha|+|\beta|\leq k} \|x^\alpha (\varepsilon\partial_x)^\beta f\|_{L^2}.$$

For simplicity, we denote by Σ^k the sets Σ^k_ε corresponding to $\varepsilon = 1$. The Schwartz space $\mathcal{S}(\mathbb{R}^d)$ then satisfies $\cap_{k\in\mathbb{N}}\Sigma^k = \mathcal{S}(\mathbb{R}^d)$. We are interested in initial data that belong to these functional spaces as we shall see below, after describing the assumptions that we make on the eigenmodes of the potential.

We write

$$V(x) = v(x)\mathrm{Id} + \begin{pmatrix} w_1(x) & w_2(x) \\ w_2(x) & -w_1(x) \end{pmatrix}$$

and denote by λ_- and λ_+ the eigenvalues of V with $\lambda_- \leq \lambda_+$. We have

$$\lambda_\pm(x) = v(x) \pm |w(x)|, \quad |w(x)| = \sqrt{w_1(x)^2 + w_2(x)^2}$$

and we associate with these eigenvalues the scalar Hamiltonians

$$h_\pm(z) = \frac{|\xi|^2}{2} + \lambda_\pm(x), \quad z = (x, \xi).$$

Since V is smooth, its eigenvalues are smooth outside the set Υ of crossing points

$$\Upsilon = \{z = (x,\xi) \in \mathbb{R}^{2d}, \;\; h_+(z) = h_-(z)\} = \{w = 0\}.$$

Following [34], we work in the case of conical crossing points.

Assumption 4.1.1. *1. The crossing on Υ is a conical crossing of codimension 2: Υ is a manifold and*

$$\forall q^\flat \in \Upsilon, \;\; \mathrm{Rank}\, dw(q^\flat) = 2.$$

2. The conical crossing point $z^\flat = (q^\flat, p^\flat)$ is non-degenerate:

$$E(z^\flat) := (p^\flat \cdot \nabla w_1(q^\flat), p^\flat \cdot \nabla w_2(q^\flat)) = dw(q^\flat)p^\flat \neq 0_{\mathbb{R}^2}$$

In the notations above, we denote by $dw(q)$ the $2 \times d$ matrix

$$dw(q) = (\partial_{q_j} w_i)_{1 \leq i \leq 2,\, 1 \leq j \leq d},$$

meaning that, when applied to a vector $p \in \mathbb{R}^d$, one gets a vector $dw(q)p \in \mathbb{R}^2$. A crossing point satisfying (1) of Assumption 4.1.1 is said to be *conical* because the eigenvalues λ_+ and λ_- develop a conical singularity at that point. This singularity induces special behaviors of the solution of the equation (4.1) that has been already studied in the literature (see [34, 13] for example).

We also assume that the eigenvalues λ_+ and λ_- satisfy a polynomial gap condition at infinity, in the sense that there exist constants $c_0, n_0, r_0 > 0$ such that

$$|\lambda_+(x) - \lambda_-(x)| \geq c_0 \langle x \rangle^{-n_0} \text{ when } |w(x)| \geq r_0, \tag{4.2}$$

where we denote $\langle x \rangle = (1 + |x|^2)^{1/2}$. This gap condition at infinity (4.2) ensures, that the derivatives of the eigenprojectors $\Pi_\pm(x)$ grow at most polynomially, in the sense that for all $\beta \in \mathbb{N}^d$ there exists a constant $C_\beta > 0$ such that

$$\|\partial_x^\beta \Pi_\pm(x)\| \leq C_\beta \langle x \rangle^{|\beta|(1+n_0)} \text{ when } |w(x)| \geq r_0, \tag{4.3}$$

see [4, Lemma B.2] for a proof of this estimate.

We are interested in initial data that are coherent states as studied in [8]. This kind of initial data are highly localized in position and impulsion and are somehow more general that the Gaussian wave packets treated in [34], with whom they share lots of properties. Wave packets are associated with a profile $\varphi \in \mathcal{S}(\mathbb{R}^d)$ and a point $z = (q,p) \in \mathbb{R}^{2d}$ of the phase space according to

$$\mathrm{WP}^\varepsilon_z \varphi(x) = \varepsilon^{-d/4}\, \mathrm{e}^{\frac{i}{\varepsilon} p\cdot(x-q)} \varphi\Big(\frac{x-q}{\sqrt{\varepsilon}}\Big). \tag{4.4}$$

Such families are uniformly bounded in all the spaces Σ^k_ε for any $k \in \mathbb{N}$. With these notations, we shall make the following set of assumption on the initial data.

Assumption 4.1.2. *The initial data of the system* (4.1) *is given by*

$$\psi_0^\varepsilon(x) = \vec{V}_0\, \mathrm{WP}^\varepsilon_{z_0}\varphi(x),$$

where $\varphi \in \mathcal{S}(\mathbb{R}^d)$, $z_0 = (q_0, p_0) \in \mathbb{R}^{2d}$ is chosen far from the crossing set, and $\vec{V}_0 \in \mathbb{R}^2$ is a normalized eigenvector of the matrix V in q_0 for the minus mode:

$$V(q_0)\vec{V}_0 = \lambda_-(q_0)\vec{V}_0.$$

Note that since $\vec{V}_0$ is assumed to be a real-valued normalized eigenvector of $V(q_0)$ with $w(q_0) \neq 0$ and one can replace the pair $(\vec{V}_0, \varphi)$ by $(-\vec{V}_0, -\varphi)$.

Wave packets satisfy localization properties that are recalled in Appendix B. In particular, considering a function $\vec{V}_0 \in \mathcal{C}^\infty(\mathbb{R}^d, \mathbb{R}^2)$ such that $\vec{V}_0(x_0) = \vec{V}_0$, we have

$$\psi_0^\varepsilon(x) = \vec{V}_0(x)\mathrm{WP}^\varepsilon_{z_0}\varphi(x) + O_k(\sqrt{\varepsilon}) \tag{4.5}$$

in Σ^k_ε for all $k \in \mathbb{N}$. We can additionally assume without loss of generality that $\vec{V}_0(x)$ is an eigenvector of $V(x)$ for $\lambda_-(x)$ for all x in a neighborhood Ω of q_0. From now on, we shall make this assumption.

It is well-known (and we recall these elements more in details below) that, outside the crossing set, such a wave packet propagates along the classical trajectories associated with the mode $\lambda_-(x)$ (see [34] for Gaussian wave packets and [21] for a result for more general wave packets). Our aim here is to describe precisely what happens when a wave packet reaches the crossing set, and passes through it. We describe a picture similar to the one described for Gaussian wave packets in [34]: as long as the gap remains large enough on the trajectory, the solution can be approximated by a wave packet with a time dependent profile, an action $S_-(t,t_0,z_0)$ and a time dependent eigenvector of $V_-(t)$

$$\psi^\varepsilon(t) = \vec{V}_-(t) \mathrm{e}^{\frac{i}{\varepsilon} S_-(t,t_0,z_0)} \mathrm{WP}^\varepsilon_{\Phi_-^{t,t_0}}(u_-(t)) + o(1)$$

in Σ^k_ε; besides, when the gap shrinks, there happens transitions on the other mode that we carefully describe, leading to the birth of a quite similar wave packet on the other mode. We use the following ingredients:

1. The existence of generalized trajectories that exist despite the conical singularity (see [34, 13, 14]).
2. The definition of time-dependent eigenvectors by parallel transport as in [34, 21].
3. The introduction of a profile equation along a trajectory and the proof that when the trajectory reaches a crossing point, and precise estimates on its behavior close to the crossing time. This is done in Section 4.1.1 and uses ideas from [34, 16].
4. The definition of a thin layer close to the crossing point of the trajectory and the reduction to a model problem in this thin layer.

In the next Section 4.1.1, we introduce the main objects (classical trajectories, actions, time-dependent eigenvectors and profiles) that characterize the approximate solution and we state our result in Section 4.1.2.

We point out that this transfer has been precisely described in terms of Wigner measures by the results of [14] when one single wave packet reaches a crossing point. If two wave packets arrive simultaneously, the Wigner measure information is not enough and a phase information to describe the outgoing wave packets. One of our aim here is to get this phase information and get a more precise description than the one given by the analysis of Wigner measures in the special case of wave packets.

Even though our results are inspired by those of [34] for Gaussian wave packets, they differ on several aspects. First, the method we use here is different and easier to generalize to other Hamiltonians. Secondly, the results that we obtain are more general in terms of the data that are considered. Thirdly, the method we develop also allow to treat data that pass close to the crossing set and not exactly through it, as we will emphasize in the second part of this work [15], both situations being treated in a unified manner.

This latter point opens the way to develop and prove the convergence of numerical methods which mixed surface hopping approaches as in [17, 18, 19, 20, 48] and thawed or frozen Gaussian algorithms (also called Herman-Kluk approximation) as introduced in chemical literature in [41, 42, 43] and studied from mathematical point of view in [55, 57]. It is also possible to adapt the method to models issued from modeling of Graphene with Dirac points, with additional nonlinearity (work in progress [16]).

4.1.1 The parameters of the approximate solution

Our main result consists in a precise description of how one can approximate solutions of equation (4.1) in the frame of Assumptions 4.1.2 and 4.1.1. This result is presented in the next section and we begin here by introducing the parameters of the wave packets that are involved in the process. We describe their centers, profiles and phase factor, which are ε-independent and related with classical quantities.

Classical trajectories and actions

For $(t_0, z_0) \in \mathbb{R} \times (\mathbb{R}^{2d} \setminus \Upsilon)$ we consider the classical trajectory $(q_\pm(t), p_\pm(t))$ issued from $z_0 = (q_0, p_0)$ at time t_0, and defined by the ordinary differential equation

$$\dot{q}_\pm(t) = p_\pm(t), \quad \dot{p}_\pm(t) = -\nabla\lambda_\pm(q_\pm(t)).$$

The associated flow map is then denoted by $\Phi_\pm^{t,t_0}(z_0) = (q_\pm(t), p_\pm(t))$ and we have

$$\partial_t \Phi_\pm^{t,t_0} = J\nabla_z h_\pm \circ \Phi_\pm^{t,t_0}, \quad \Phi_\pm^{t_0,t_0} = \mathbf{1}_{\mathbb{R}^{2d}}, \tag{4.6}$$

where

$$J = \begin{pmatrix} 0 & \mathbf{1}_{\mathbb{R}^d} \\ -\mathbf{1}_{\mathbb{R}^d} & 0 \end{pmatrix}. \tag{4.7}$$

It will be convenient in the following to denote by $\{f, g\}$ the Poisson bracket of two smooth functions $f, g \in \mathcal{C}^\infty(\mathbb{R}^{2d})$, that might be scalar-, vector- or matrix-valued,

$$\{f, g\} := J\nabla f \cdot \nabla g = \sum_{j=1}^{d} \left(\partial_{\xi_j} f \partial_{x_j} g - \partial_{x_j} f \partial_{\xi_j} g\right).$$

Of course, if $w(q_0) \neq 0$, the existence of these Hamiltonian trajectories is guaranteed by Cauchy-Lipschitz theorem. Moreover, due to the genericity assumption performed on $dw(q^\flat)$ (point (2) of Assumption 4.1.1), one can prove that there exist trajectories passing through $z^\flat = (q^\flat, p^\flat) \in \Upsilon$ that are piecewise smooth, as soon as Assumptions 4.1.1 hold in $(q^\flat, p^\flat)$. We point out that we will make the convenient abuse of notation of saying indistinctly that $z = (q, p) \in \Upsilon$ or $q \in \Upsilon$.

Proposition 4.1.3. *[[14], Proposition 1] Let $z^\flat \in \Upsilon$ satisfying Assumptions 4.1.1, the notations of which we use. Let us write $E(z^\flat) = r\omega$ with $r > 0$ and $\omega \in \mathbb{S}^2$. Then, there exist two continuous maps*

$$t \mapsto \Phi_\pm^{t,t^\flat}(z^\flat) = (q_\pm(t), p_\pm(t))$$

defined in a neighborhood of $t^\flat$ and which satisfy (4.6) *for $t \neq t^\flat$ with $\Phi_\pm^{t^\flat,t^\flat}(z^\flat) = z^\flat$. Besides, we have*

$$w(q_\pm(t)) = (t - t^\flat) r\omega + O((t - t^\flat)^2). \tag{4.8}$$

We shall call generalized trajectories these continuous maps passing through points $z^\flat \in \Upsilon$ satisfying Assumptions 4.1.1. We associate with $\Phi_\pm^{t,t_0}(z_0) = (q_\pm(t), p_\pm(t))$ the action integral

$$S_\pm(t, t_0, z_0) = \int_{t_0}^{t} \left(p_\pm(s) \cdot \dot{q}_\pm(s) - h_\pm(z_\pm(s))\right) ds. \tag{4.9}$$

We analyze in Section 4.2.1 the behavior of these trajectories and of their actions close to a crossing point.

Time-dependent eigenvectors and parallel transport

Following [34, 5, 21], we associate with a given eigenvector associated with one of the ±-modes a family of time-dependent eigenvectors constructed along the classical trajectories. We set

$$B_\pm(x,\xi) = \pm\Pi_\mp(x)\xi\cdot\nabla_x\Pi_+(x)\,\Pi_\pm(x), \tag{4.10}$$

where $\xi\cdot\nabla_x = \sum_{1\le j\le d}\xi_j\partial_{x_j}$. These matrices are related by the relations

$$B_\pm^* = -B_\mp$$

and we also have the useful relation

$$B_\pm(x,\xi) = \mp\Pi_\mp(x)\xi\cdot\nabla_x\Pi_-(x)\,\Pi_\pm(x).$$

The time-dependent families of eigenvectors that we shall use depend on these matrices as stated below.

Proposition 4.1.4. *Let us consider a vector-valued function $\vec{V}_{0,\pm}(x)$ defined on $\mathbb{R}^d$, smooth and compactly supported in some open set $U'\subset\mathbb{R}^d\setminus\Upsilon$ and such that on an open set $U\subset U'$, $\vec{V}_{0,\pm}$ is an eigenvector for the mode ±*

$$\Pi_\pm(x)\vec{V}_{0,\pm}(x) = \vec{V}_{0,\pm}(x),\ \ \|\vec{V}_{0,\pm}(x)\|_{\mathbb{C}^2} = 1,\ \ \forall x\in U.$$

We assume that there exists $t_0, t^\flat \in \mathbb{R}$, $\tau, \delta > 0$ *such that*

$$\Phi^t_\pm(U' \times \mathbb{R}^d) \subset \{|w(x)| > \delta\}, \ \ \forall t \in [t_0, t^\flat - \tau].$$

Then, there exists a smooth map $(t,z) \mapsto \vec{V}_\pm(t,z)$ *defined on* $[t_0, t^\flat - \tau] \times \mathbb{R}^{2d}$ *such that for all* $t \in [t_0, t^\flat - \tau]$ *and* $z = (x,\xi) \in \Phi^{t,t_0}_\pm(U \times \mathbb{R}^d)$,

$$\Pi_\pm(x)\vec{V}_\pm(t,z) = \vec{V}_\pm(t,z), \ \ \|\vec{V}_\pm(t,z)\|_{\mathcal{C}^2} = 1,$$

and such that $\vec{V}_\pm(t,z)$ *satisfies the equation*

$$\partial_t \vec{V}_\pm + \left\{h_\pm(x,\xi), \vec{V}_\pm\right\} = \partial_t \vec{V}_\pm + \xi \cdot \nabla_x V_\pm - \nabla\lambda_\pm(x) \cdot \nabla_\xi = B_\pm(x,\xi)\vec{V}_\pm \tag{4.11}$$

subject to the initial condition $\vec{V}_\pm(t_0, x, \xi) = \vec{V}_{0,\pm}(x)$.

The proof of this proposition mimics the proofs of [34, 5, 21] and relies on the analysis, for fixed $z \in \mathbb{R}^{2d}$, of the function $\vec{V}_\pm(t, \Phi^{t,t_0}_\pm(z))$ which solves an ODE (see [21]).

We shall assume that Assumption 4.1.1 is satisfied in any of the points $\Phi^{t,t_0}(z)$ that are in Υ for $z \in U$ and $t > t_0$. Note that it is enough to guarantee this for some $z_0 \in U$ provided U and U' are small enough. We shall then say that the pair (U, U') is generic.

Proposition 4.1.5. *Assume the pair* (U,U') *is generic as stated above, and consider the notations and assumptions of Proposition 4.1.4. Then, for* $k \in \mathbb{N}^*$, *there exists* $C_k > 0$ *such that for all* $t \in [t_0, t^\flat - \tau]$ *and* $z \in U'$,

$$\left\|\partial_t^k \left(\vec{V}_\pm(t, \Phi^{t,t_0}_\pm(z))\right)\right\|_{\mathcal{C}^2} \le C_k \delta^{-k+1}. \tag{4.12}$$

Note that the first order derivative is bounded, which implies that, for $z \in \mathbb{R}^{2d}$ fixed, the map $t \mapsto \vec{V}_\pm(t, \Phi^{t,t_0}(z))$ has a limit on Υ that can be computed.

Proposition 4.1.6. *Assume the pair (U, U') is generic as stated above and consider the notations and assumptions of Proposition 4.1.4. There exists $(\vec{V}_\omega, \vec{V}_\omega^\perp)$ a direct orthogonal basis of normalized eigenvectors of $\begin{pmatrix} \omega_1 & \omega_2 \\ \omega_2 & -\omega_1 \end{pmatrix}$ for the eigenvalue $(+1, -1)$ respectively, such that we have*

$$\vec{V}_-(t, \Phi_-^{t,t_0}(z_0)) \underset{t \to (t^\flat)-}{\longrightarrow} \vec{V}_\omega, \quad \vec{V}_+(t, \Phi_-^{t,t_0}(z_0)) \underset{t \to (t^\flat)-}{\longrightarrow} \vec{V}_\omega^\perp. \tag{4.13}$$

Besides, there exists $\eta > 0$ such that one can define a map $t \mapsto V_\pm(t, \Phi^{t^\flat,t}(z_0))$ on $[t^\flat, t^\flat + \eta]$ satisfying (4.11) and such that

$$\vec{V}_-(t, \Phi^{t,t_0}(z_0)) \underset{t \to (t^\flat)+}{\longrightarrow} \vec{V}_\omega^\perp, \quad \vec{V}_+(t, \Phi^{t,t_0}(z_0)) \underset{t \to (t^\flat)+}{\longrightarrow} \vec{V}_\omega,$$

and the maps

$$\begin{cases} t \mapsto \vec{V}_\mp(t, \Phi_-^{t,t_0}(z_0)) \text{ for } t \in [t_0, t^\flat], \\ t \mapsto \vec{V}_\pm(t, \Phi_-^{t,t_0}(z_0)) \text{ for } t \in [t^\flat, t^\flat + \eta], \end{cases}$$

are continuous.

Note that we are left with families of time-dependent eigenvectors that pass continuously through the crossing, while changing of eigenspace.

Profile equations

The profiles of the approximate solutions are linked with the scalar Hamiltonians $h_\pm$ associated to the eigenvalues $\lambda_\pm$ and the trajectories. We consider a trajectory $\Phi_\pm^{t,t_0}(z_0)$ that does not meet Υ on some time interval I containing t_0 and associate with it the Schrödinger equations with time dependent harmonic potential

$$i\partial_t u_\pm = -\frac{1}{2}\Delta u_\pm + \frac{1}{2}\mathrm{Hess}\,\lambda_\pm(\Phi_\pm^{t,t_0}(z_0))y\cdot y\, u^\pm,\ \ u^\pm(t_0) = a_\pm \in \mathcal{S}(\mathbb{R}^d). \tag{4.14}$$

In view of [51], these equations have a solution in $\Sigma^k(\mathbb{R}^d)$ on the time interval I for nay $k\in\mathbb{N}^*$. Moreover, we have the following proposition for the generalized trajectories of the preceding section.

Proposition 4.1.7. *Let $(t_0, z_0) \in \mathbb{R}^{2d+1}$ be such that the trajectory $\Phi_\pm^{t,t_0}$ reaches Υ at time $t^\flat > t_0$ and point $z^\flat = \Phi_\pm^{t^\flat,t_0}(z_0)$ satisfying Assumption 4.1.1. Then, there exists a solution $u_\pm(t)$ of (4.14) on $[t_0, t^\flat)$ and for any $t\in[t_0,t^\flat)$, $\|u_\pm(t)\|_{L^2} = \|a_\pm\|_{L^2}$. Moreover, if $k\in\mathbb{N}^*$, $u_\pm(t)\in\Sigma^k$ and there exists a constant $C_k>0$ such that*

$$\sup_{t\in[t_0,t^\flat)} \|u_\pm(t)\|_{\Sigma^k} \le C_k|\log|t-t^\flat||. \tag{4.15}$$

The result of Proposition 4.1.7, implies that the time derivatives of the profile functions u_+ and u_- are integrable, up to a phase. With the notations of Assumptions 4.1.1, we consider the $d\times d$ matrix Γ_0 defined by

$$\Gamma_0 = r^{-1}\, {}^t dw(q^\flat)(\mathrm{Id}_{\mathbb{R}^2} - \omega\otimes\omega)dw(q^\flat) \tag{4.16}$$

where $\omega\otimes\omega$ is the 2 by 2 matrix $(\omega_i\omega_j)_{i,j}$ and dw is the $2\times d$ matrix $(\partial_{x_j} w_i)_{i,j}$. Note that $\mathrm{Id}_{\mathbb{R}^2} - \omega\otimes\omega$ is the orthogonal projector on $\mathbb{R}\,\omega^\perp$.

Corollary 4.1.8. *Under the assumptions of Proposition 4.1.7, there exists $u_\pm^{\mathrm{in}}\in\mathcal{S}(\mathbb{R}^d)$ such that*

$$\mathrm{Exp}(\mp\frac{i}{2}\Gamma_0 y\cdot y\,\ln|t-t^\flat|)u_\pm(t) \underset{t\to(t^\flat)^-}{\longrightarrow} u_\pm^{\mathrm{in}}. \tag{4.17}$$

Moreover, once given $u_\pm^{\rm out} \in \mathcal{S}(\mathbb{R}^d)$, *there exists a unique pair* $u_\pm(t)$ *for* $t > t^\flat$ *satisfying* (4.14) *and*

$$\mathrm{Exp}(\pm \frac{i}{2}\Gamma_0 y \cdot y \, \ln|t - t^\flat|) u_\pm(t) \underset{t \to (t^\flat)^+}{\longrightarrow} u_\pm^{\rm out}. \tag{4.18}$$

Let us consider an initial data as in (4.5) and assume that $\Phi_-^{t,t_0}(z_0)$ passes through Υ at time $t^\flat$ in a point $z^\flat$ that satisfies Assumption 4.1.1, then one can associate a profile $u_-(t)$ with the ingoing trajectory Φ_-^{t,t_0} for $t \in [t_0, t^\flat)$. This generates an ingoing profile $u_-^{\rm in} \in \mathcal{S}(\mathbb{R}^d)$. We shall see in the next section how to associate with $u_-^{\rm in}$ in an adequate manner two out-going profiles, $u_-^{\rm out}$ and $u_+^{\rm out}$, which generate when $t > t^\flat$ two profiles, one for each mode, and an approximate solution of the system (4.1).

4.1.2 Main results

Let us consider an initial data at time t_0 satisfying (4.5) and assume that the trajectory $\Phi_-^{t,t_0}(z_0)$ does not reach Υ on the interval $[t_0, t_0 + T]$ because $\Phi_-^{t,t_0}(z_0) \in \{|w(x)| \geq \delta\}$ for some $\delta > 0$. Then, there is adiabatic propagation of the wave packet in the sense that the solution remains at leading order in the same eigenspace and can be approximated by a wave packet the parameters of which are determined by the classical quantities associated with the related eigenvalue. This type of results are already present in the literature, see [2] for the case of wave packets and [50, 58] for more general results. Our contribution here is to emphasize the dependence of the approximation from the parameter δ which encodes the minimum gap along the trajectory, which is in a crucial ingredient of the proof of our next result.

Theorem 4.1.9. *Let $k \in \mathbb{N}$. Assume ψ_0^ε is chosen as in Assumption 4.1.2 and that the trajectory $\Phi_-^{t,t_0}(z_0)$ does not reach Υ. Let $\delta > 0$ such that $\Phi_-^{t,t_0}(z_0) \in \{|w(x)| \geq \delta\}$ for all $t \in [t_0, t_0 + T]$. Then, there exists $C_k > 0$ independent of δ such that*

$$\left\| \psi^\varepsilon(t) - \vec{V}_-(t, \Phi_-^{t,t^\flat}(z^\flat))\, \mathrm{e}^{\frac{i}{\varepsilon} S_-(t,t^\flat,z^\flat)} \mathrm{WP}_{\Phi_-^{t,t^\flat}(z^\flat)} u_-(t) \right\|_{\Sigma_\varepsilon^k} \leq C_k \left|\ln \delta\right| \left(\frac{\varepsilon^{3/2}}{\delta^4} + \sqrt{\varepsilon} \right).$$

Of course, this result easily extends to the case of data which have components on both modes with wave-packets structure. Theorem 4.1.9 only gives information when the gap along the trajectory is large enough.

Let us assume now that the trajectory $\Phi_-^{t,t_0}(z_0)$ pass close to Υ at time $t^\flat > t_0 + T$, $T > 0$. The description of Theorem 4.1.9 holds as long as the quantity $|w(\Phi_-^{t,t_0}(z_0))|$ remains much larger than $\delta_c = \sqrt{\varepsilon}$. We will now consider a trajectory which passes exactly through the crossing, and we postpone to the second part of this analysis (see [15]) the analysis of a trajectory for which the minimal value of $|w(\Phi_-^{t,t_0}(z_0))|$ is $\delta \leq \sqrt{\varepsilon}$. We now focus on the cas where this minimum is 0 and uses the classicla quantities introduced before.

- We consider the *trajectories* $\Phi_-^{t,t_0}(z_0)$ and assume $z^\flat = \Phi_-^{t^\flat,t_0}(z_0) \in \Upsilon$ for $t^\flat > t_0 + T$, $T > 0$. We assume that Assumption 4.1.1 is satisfied in $z^\flat$ and consider the trajectory $\Phi_+^{t,t^\flat}(z^\flat)$ constructed in Proposition 4.1.3.

- We consider the *time dependent eigenvectors* $\vec{V}_-(t)$ associated with $\vec{V}_0(x_0)$ by Proposition 4.1.4 for $t \in [t_0, t^\flat]$, and the time-dependent eigenvectors that we still denote by

$\vec{V}_-(t)$ on $[t^\flat, t_0+T]$ with data at time $t^\flat$

$$\vec{V}_-(t^\flat, z^\flat) = \vec{V}_\omega^\perp$$

together with the time-dependent eigenvectors $\vec{V}_+(t)$ defined on $[t^\flat, t_0+T]$ by Proposition 4.1.4 with data at time $t^\flat$

$$\vec{V}_+(t^\flat, z^\flat) = \vec{V}_\omega.$$

- We consider the *profiles* $u_-(t)$ constructed for $t \in [t_0, t^\flat)$ thanks to Proposition 4.1.7. Define u_-^{in} by Corollary 4.1.8, and associate with u_-^{in} the outgoing limiting profiles u_-^{out} and u_+^{out} given by the relations

$$\begin{pmatrix} u_+^{out} \\ \\ u_-^{out} \end{pmatrix} = \begin{pmatrix} a(\eta_2) & -\mathrm{e}^{i\theta_\varepsilon(\eta)}\bar{b}(\eta_2) \\ \\ \mathrm{e}^{-i\theta_\varepsilon(\eta)}b(\eta_2) & a(\eta_2) \end{pmatrix} \begin{pmatrix} 0 \\ \\ \mathrm{e}^{\frac{i}{\varepsilon}S_-^\flat}u_-^{in} \end{pmatrix}. \tag{4.19}$$

where, $S_-^\flat = S_-(t^\flat, t_0, z_0)$ and, with the notations of Assumption 4.1.1,

$$\eta = dw(q^\flat)y = (\eta_1, \eta_2), \tag{4.20}$$

$$a(\eta_2) = \mathrm{e}^{-\frac{\pi\eta_2^2}{2}},\ \ b(\eta_2) = \frac{2i}{\sqrt{\pi}\eta_2}2^{-i\eta_2^2/2}\mathrm{e}^{-\pi\eta_2^2/4}\,\Gamma\left(1+i\frac{\eta_2^2}{2}\right)\sinh\left(\frac{\pi\eta_2^2}{2}\right), \tag{4.21}$$

$$\theta_\varepsilon(\eta) = \frac{1}{2r}\eta_2^2\ln\left(\frac{r}{\varepsilon}\right) + \frac{1}{r}\eta_1^2 \tag{4.22}$$

Here we use the Gamma function and hyperbolic sine function given by

$$\Gamma(z) = \int_0^1 \left(\ln\frac{1}{t}\right)^{z-1} dt = \int_0^\infty t^{z-1}e^{-t}\,dt,\ \ \sinh(z) = \frac{e^z - e^{-z}}{2}.$$

We then have the following result.

Theorem 4.1.10. *Assume ψ_0^ε is chosen as in Assumption 4.1.2 and that the trajectory $\Phi_-^{t,t_0}(z_0)$ reaches Υ at some time $t^\flat$ and some point $z^\flat$ satisfying Assumption 4.1.1. Then, as ε goes to 0 , the solution of equation* (4.1) *with initial data ψ_0^ε satisfies in $L^2(\mathbb{R}^d)$: if $t \in [t_0, t^\flat)$*

$$\psi^\varepsilon(t) = \mathrm{e}^{\frac{i}{\varepsilon}S_-(t,t_0,z_0)}\vec{V}_-(t,\Phi_-^{t,t_0}(z_0))\mathrm{WP}_{\Phi_-^{t,t_0}(z_0)}u_-(t) + O(|\ln\varepsilon|\,\varepsilon^{\frac{1}{14}})$$

and if $t \in (t^\flat, t_0+T]$,

$$\begin{aligned}\psi^\varepsilon(t) = {} & \vec{V}_-(t,\Phi_-^{t,t^\flat}(z^\flat))\,\mathrm{e}^{\frac{i}{\varepsilon}S_-(t,t^\flat,z^\flat)}\mathrm{WP}_{\Phi_-^{t,t^\flat}(z^\flat)}u_-(t) \\ & + \vec{V}_+(t,\Phi_+^{t,t^\flat}(z^\flat))\,\mathrm{e}^{\frac{i}{\varepsilon}S_+(t,t^\flat,z^\flat)}\mathrm{WP}_{\Phi_+^{t,t^\flat}(z^\flat)}u_+(t) + O(|\ln\varepsilon|\,\varepsilon^{\frac{1}{14}}).\end{aligned} \tag{4.23}$$

The result extends by superposition to the case where two wave packets interact at a crossing point $z^\flat = \Phi_\pm^{t^\flat,t_0}(z_{0,\pm})$ with incoming profiles u_-^{in} and u_+^{in} on the modes $-$ and $+$ respectively. and incoming actions $S_\pm^\flat = S_\pm(t^\flat, t_0, z_{0,\pm})$ respectively. Then, setting

$$\begin{pmatrix} u_+^{out} \\ u_-^{out} \end{pmatrix} = \begin{pmatrix} a(\eta_2) & -\mathrm{e}^{i\theta_\varepsilon(\eta)}\bar{b}(\eta_2) \\ \mathrm{e}^{-i\theta_\varepsilon(\eta)}b(\eta_2) & a(\eta_2) \end{pmatrix} \begin{pmatrix} \mathrm{e}^{\frac{i}{\varepsilon}S_+^\flat}u_+^{in} \\ \mathrm{e}^{\frac{i}{\varepsilon}S_-^\flat}u_-^{in} \end{pmatrix}. \tag{4.24}$$

The outgoing wave packet (i.e. for $t > t^\flat$) then is

$$\begin{aligned}\psi^\varepsilon(t) = {} & \vec{V}_-(t,\Phi_-^{t,t^\flat}(z^\flat))\mathrm{e}^{\frac{i}{\varepsilon}S_-(t,t^\flat,z^\flat)}\mathrm{WP}_{\Phi_-^{t,t^\flat}(z^\flat)}u_-(t) \\ & + \vec{V}_+(t,\Phi_+^{t,t^\flat}(z^\flat))\mathrm{e}^{\frac{i}{\varepsilon}S_+(t,t^\flat,z^\flat)}\mathrm{WP}_{\Phi_+^{t,t^\flat}(z^\flat)}u_+(t) + O(|\ln\varepsilon|\,\varepsilon^{\frac{1}{14}})\end{aligned}$$

in $L^2(\mathbb{R}^d)$. We point out the special attention that has to be paid to the treatment of the action.

4.1.3 Ideas of the proof and organization of the paper

An important part of the proof consists in the construction of the approximate solutions and, in particular, in the resolution of equation (4.14) and the analysis of the properties of its solutions. This is done in Section 4.2, together with results on the classical quantities. Then the proof proceeds in two steps. We first show that the approximate solution fits outside Υ, which corresponds to times $t \notin (t^\flat - \delta, t^\flat + \delta)$ for some δ that will be chosen small. In this region which can be qualified as adiabatic, the solutions of (4.1) decouples on each of the modes. Using techniques arising from [2, 58] for example, as spelled out in [21], we analyze carefully the order of the approximation (which involves negative powers of δ combined with powers of ε) in Section 4.3. Then, in $(t^\flat - \delta, t^\flat + \delta)$, we reduce to a local model of Landau-Zener's type and exhibit in Section 4.4 the transitions relations (4.24) which allow to fix the ansatz for times $t > t^\flat + \delta$.

4.2 Analysis of classical quantities and construction of the approximate solution

In this section, we first focus on the properties of the classical trajectories and actions in the neighborhood of the crossing set. Then, in two next subsections, we construct the time-dependent eigenvectors satisfying (4.11) and the solutions of the profile equation (4.14), together with a careful analysis of their properties.

4.2.1 The classical trajectories and actions

It is interesting to compare a generalized classical trajectory $\Phi_{\pm}^{t,t_0}(z_0)$ reaching the crossing set Υ at time $t^\flat$ and point $z^\flat$ with the trajectory $\Phi_0^{t,t^\flat}(z^\flat)$ associated with the (smooth) Hamiltonian

$$h_0(z) = \frac{|\xi|^2}{2} + v(x). \tag{4.25}$$

A simple Taylor expansion close to $t = t^\flat$ gives the next lemma.

Lemma 4.2.1. *With the assumptions of Proposition 4.1.3, we have*

$$\begin{cases} q_\pm(t) &= q_0(t) \mp \frac{1}{2}\mathrm{sgn}(t-t^\flat)(t-t^\flat)^2\, {}^t dw(q^\flat)\omega + O((t-t^\flat)^3), \\ p_\pm(t) &= p_0(t) \mp |t-t^\flat|\, {}^t dw(q^\flat)\omega + O((t-t^\flat)^2). \end{cases}$$

The next lemma compare the action $S_\pm(t,t^\flat,z^\flat) = S_\pm(t,t_0,z_0) - S_\pm(t^\flat,t_0,z_0)$ associated with a generalized trajectory $\Phi_\pm^{t,t_0}(z_0)$ with the action

$$S_0(t,t^\flat,z^\flat) = \int_{t^\flat}^{t} \left(p_0(s)\cdot \dot q_0(s) - v(z_0(s))\right) ds \tag{4.26}$$

associated with the trajectory $\Phi_0^{t,t^\flat}(z^\flat)$.

Lemma 4.2.2. *With the notations of Proposition 4.1.3 we have the following asymptotics*

$$S_\pm(t,t^\flat,z^\flat) = S_0(t,t^\flat,z^\flat) \mp \mathrm{sgn}(t-t^\flat) r (t-t^\flat)^2 + O((t-t^\flat)^3),$$

and

$$S_0(t,t^\flat,z^\flat) = (t-t^\flat)\left(\frac{1}{2}|p^\flat|^2 - v(q^\flat)\right) - p^\flat\cdot\nabla v(q^\flat)(t-t^\flat)^2 + O((t-t^\flat)^3).$$

Proof of Lemma 4.2.2. We use that $h_\pm(z_\pm(t))$ is conserved along the trajectory and we write

$$\dot{S}_\pm(t,t_0,z_0) = p_\pm(t)\cdot \dot{q}_\pm(t) - h_\pm(z^\flat) = |p_\pm(t)|^2 - h_\pm(z^\flat).$$

Lemma 4.1.3 gives

$$\dot{S}_\pm(t,t_0,z_0) = |p^\flat|^2 - 2p^\flat\cdot\nabla v(q^\flat)(t-t^\flat) \mp 2\, dw(q^\flat)p^\flat\cdot\omega|t-t^\flat| - h_\pm(z^\flat) + O((t-t^\flat)^2).$$

Integrating between t and $t^\flat$ and using $|p^\flat|^2 - h_\pm(z^\flat) = \frac{1}{2}|p^\flat|^2 - v(q^\flat)$, we obtain

$$\begin{aligned} S_\pm(t,t_0,z_0) = S^\flat + (t-t^\flat)\left(\frac{1}{2}|p^\flat|^2 - v(q^\flat)\right) - p^\flat\cdot\nabla v(q^\flat)(t-t^\flat)^2 \\ \mp \operatorname{sgn}(t-t^\flat) dw(q^\flat)p^\flat\cdot\omega(t-t^\flat)^2 + O((t-t^\flat)^3) \end{aligned}$$

and we identify the terms $(t-t^\flat)\left(\frac{1}{2}|p^\flat|^2 - v(q^\flat)\right) - p^\flat\cdot\nabla v(q^\flat)(t-t^\flat)^2$ with the beginning of the Taylor expansion of $S_0(t,t^\flat,z^\flat)$ close to $t^\flat$. □

4.2.2 Parallel transport

We prove here Propositions 4.1.4, 4.1.5 and 4.1.6. These results crucially rely on the observation that for all $(x,\xi)\in(\mathbb{R}^d\setminus\Upsilon)\times\mathbb{R}^d$, the matrix $\xi\cdot\nabla\Pi_+(x)$ is off diagonal, that is

$$\Pi_\pm(x)\xi\cdot\nabla\Pi_+(x)\Pi_\pm(x) = 0$$

and that for $\alpha\in\mathbb{N}^d$, there exists constants $C_\alpha>0$, $n_\alpha\in\mathbb{N}$ such that

$$\|\partial_x^\alpha\Pi_\pm(x)\|_{\mathcal{C}^{2,2}} \le C_\alpha|w(x)|^{-|\alpha|}\langle x\rangle^{n_\alpha}, \tag{4.27}$$

which is obtained by combining the estimate (4.3) at infinity and the analysis of the singularity close to Υ. The proof Proposition 4.1.4, which states the existence of the function $\vec{V}_{\pm}(t)$ is done in Proposition 3.1 of [21]: one considers for $z \in \mathbb{R}^d$

$$Y_{\pm}(t,z) = \vec{V}_{\pm}(t, \Phi_{\pm}^{t,t_0}(z)),$$

which solves the equation

$$\partial_t Y_{\pm}(t,z) = B_{\pm}(\Phi_{\pm}^{t,t_0}(z))Y_{\pm}(t,z). \tag{4.28}$$

It is then enough to check (as done in [21]) that for $z \in U$, $\Pi_{\mp}(\Phi_{\pm}^{t,t_0}(z))Y_{\pm}(t,z) = 0$ and $|Y_{\pm}(t,z)|_{\mathcal{C}^N} = 1$.

We point out that $\vec{V}_{\pm}(t,z)$ is not in the range of $\Pi_{\pm}(x)$ for all $z = (x,\xi) \in U'$ and $t \in [t_0, t^\flat)$. Indeed, the construction described above requires to avoid the crossing set Υ where some of the involved quantities cease to exist. However, $\vec{V}_{\pm}(t,z)$ is in the range of $\Pi_{\pm}(x)$ above the points $z = \Phi_{\pm}^{t,t_0}(z_0)$ of a trajectory starting from $z_0 \in U \subset U'$. This is enough for our purpose. We now prove the properties of the functions $\vec{V}_{\pm}(t,z)$ stated in Proposition 4.1.5 and 4.1.6.

Proof of Proposition 4.1.5 and 4.1.6. We keep the notations of Propositions 4.1.4. Let us first focus on the estimates on the times derivatives of $\vec{Y}_{\pm}(t,z_0) = \vec{V}_{\pm}(t, \Phi_{\ell}^{t,t_0}(z_0))$ for $z_0 \in U$. The key observations are the following:

$$\Pi_-(\Phi_-^{t,t_0}(z_0)) \underset{t\to(t^\flat)^\mp}{\longrightarrow} V_\omega \otimes \overline{V}_\omega, \;\; \Pi_+(\Phi_+^{t,t_0}(z_0)) \underset{t\to(t^\flat)^\mp}{\longrightarrow} V_\omega^\perp \otimes \overline{V}_\omega^\perp, \tag{4.29}$$

$$\Pi_+(\Phi_+^{t,t_0}(z_0)) \underset{t\to(t^\flat)^\pm}{\longrightarrow} V_\omega \otimes \overline{V}_\omega, \;\; \Pi_-(\Phi_-^{t,t_0}(z_0)) \underset{t\to(t^\flat)^\pm}{\longrightarrow} V_\omega^\perp \otimes \overline{V}_\omega^\perp, \tag{4.30}$$

$$\forall t \in [t_0, t^\flat), \quad (\xi \cdot \nabla \Pi_\pm)(\Phi_\pm^{t,t_0}(z_0)) = O(1). \tag{4.31}$$

Let us first postpone the proof of these claims and see their consequences. We first deduce from (4.31) the boundedness of $\partial_t \vec{Y}_\pm(t, z_0)$ for $t \in [t_0, t^\flat)$, which yields the existence of a limit for $\vec{Y}_\pm(t, z_0)$ when t goes to $(t^\flat)^-$. Moreover, by construction, this limit is a normalized eigenvector of $V(\Phi_\pm^{t^\flat,t_0}(z_0))$. In view of (4.29) and (4.30), we obtain equation (4.13).

Let us now consider higher time derivatives. For $k \in \mathbb{N}$, the Faà di Bruno formula gives that $\partial_t^k \vec{Y}_\pm(t, z_0)$ is a linear combination of terms of the form

$$(\partial_t^1 \Phi_\pm^{t,t_0}(z_0))^{m_1} \cdots (\partial_t^n \Phi_\pm^{t_0,t}(z_0))^{m_n} \, \partial_z^\alpha B_\pm(\Phi_\pm^{t,t_0}(z_0)) \partial_t^p \vec{Y}_\pm(t, z_0)$$

with

$$m_1 + 2m_2 + 3m_3 + \cdots + nm_n = n, \quad |\alpha| = m_1 + m_2 + \cdots + m_n, \quad n + p = k - 1.$$

We observe that for $|t - t^\flat| > \tau$, then if $j \in \mathbb{N} \backslash \{0\}$, $\partial_t^j \Phi_\pm^{t,t_0}(z_0) = O(\tau^{-|j|+1})$ and $\partial_z^\alpha B_\pm(\Phi_\pm^{t,t_0}(z_0)) = O(\tau^{-|\alpha|})$. We perform the recursive assumption

$$\partial_t^\ell \vec{Y}_\pm(t, z_0) = O(\tau^{-\ell+1}) \;\text{ for }\; 1 \leq \ell \leq k-1.$$

Let us firs analyze the case corresponding to $p = 0$. Then $n = k-1$ and the corresponding term is of order $O(\tau^{-\beta})$ with

$$\beta = |\alpha| + \sum_{j=1}^n m_j(|j| - 1) = n = k - 1.$$

These terms are the worst ones since, those for which $p \geq 1$ are of order $O(\tau^\gamma)$ with

$$\gamma = p - 1 + |\alpha| + \sum_{j=1}^n m_j(|j| - 1) = p + n - 1 = k - 2.$$

Therefore, the recursive assumption implies

$$\partial_t^k \vec{Y}_\pm(t, z_0) = O(\delta^{-k+1}),$$

which concludes the proof.

It remains to prove the claims (4.29), (4.30) and (4.31). We perform the proofs for the +mode; the arguments are similar for the other mode. We recall

$$\Pi_+(x) = \frac{1}{2}\left(\mathrm{Id} + |w(x)|^{-1}\begin{pmatrix} w_1(x) & w_2(x) \\ w_2(x) & -w_1(x) \end{pmatrix}\right).$$

We use equation (4.8) setting $\omega = (\omega_1, \omega_2)^t$. We obtain

$$\Pi_+(\Phi_+^{t,t_0}(z_0)) = \frac{1}{2}\left(\mathrm{Id} + \mathrm{sgn}(t - t^\flat)\begin{pmatrix} \omega_1 & \omega_2 \\ \omega_2 & -\omega_1 \end{pmatrix}\right) + O(t - t^\flat).$$

Then

$$\Pi_+(\Phi_+^{t,t_0}(z_0)) \underset{t\to(t^\flat)^-}{\longrightarrow} \frac{1}{2}\left(\mathrm{Id} - \begin{pmatrix} \omega_1 & \omega_2 \\ \omega_2 & -\omega_1 \end{pmatrix}\right) = V_\omega^\perp \otimes \overline{V}_\omega^\perp,$$

$$\Pi_+(\Phi_+^{t,t_0}(z_0)) \underset{t\to(t^\flat)^+}{\longrightarrow} \frac{1}{2}\left(\mathrm{Id} + \begin{pmatrix} \omega_1 & \omega_2 \\ \omega_2 & -\omega_1 \end{pmatrix}\right) = V_\omega \otimes \overline{V}_\omega$$

and we have proved all the relations about $\Pi_+(\Phi_+^{t,t_0}(z_0))$ stated in (4.29), (4.30).

We now consider the limit of $B_+(\Phi_+^{t,t_0}(z_0))$ as t goes to $t^\flat$, as stated in (4.31). Using Lemma C.1.1, we obtain

$$B_+(x,\xi) = \frac{\xi \cdot \nabla w(x) \wedge w(x)}{2|w(x)|^3}\Pi_-(x)\begin{pmatrix} w_2(x) & -w_1(x) \\ -w_1(x) & -w_2(x) \end{pmatrix}\Pi_+(x) \tag{4.32}$$

We now specify this relation to $(x,\xi)=\Phi_+^{t,t_0}(z_0)$. By definition

$$p_+(t)\cdot\nabla_x w(q_+(t)) = r\omega + O(|t-t^\flat|),$$

and, using (4.8), we obtain

$$\left.\frac{\xi\cdot\nabla w(x)\wedge w(x)}{2|w(x)|^2}\right|_{(x,\xi)=\Phi_+^{t,t_0}(z_0)} = O(1)$$

and the singularity in $|t-t^\flat|^{-1}$ disappears in the expression of $B_+(\Phi_+^{t,t_0}(z_0))$. We obtain that $B_+(\Phi_+^{t,t_0}(z_0))$ is uniformly bounded in a neighborhood of $t^\flat$, whence (4.31).

Finally, the fact that $B_\pm(\Phi_\pm^{t,t^\flat}(z))Y_\pm(t)$ is bounded for $t\in[t^\flat,t^\flat+\eta]$, $\eta>0$, implies that one can solve the equation (4.28) with initial data at time $t^\flat$ by a fixed point argument on the map $Y\mapsto\Theta_+(Y)$ (resp. $\Theta_-(Y)$) defined on $\mathcal{C}^1([t^\flat,t^\flat+\eta])$

$$\Theta_+(Y)(t) = \vec{V}_\omega + \int_{t^\flat}^t B_+(\Phi_+^{s,t^\flat}(z))Y(s)ds$$

(resp. $\Theta_-(Y) = \vec{V}_\omega^\perp + \int_0^t B_-(\Phi_-^{s,t^\flat}(z))Y(s)ds$). □

4.2.3 Resolution of the profile equations

In this section, we discuss the properties of the solutions of equation (4.14) and prove Proposition 4.1.7 and Corollary 4.1.8. A crucial element of the proof is a good understanding of the singularity of the Hessian of the function $\lambda_\pm$ along the trajectories. We start by a technical Lemma that we shall use later.

Lemma 4.2.3. *There exist smooth matrices $M_\pm(t)$ defined on $[t_0, t^\flat]$ (resp. $[t^\flat, t^\flat+\tau]$) such that when t tends to $t^\flat$ with $t < t^\flat$ (resp. $t > t^\flat$),*

$$\operatorname{Hess}\lambda_\pm(q_\pm(t)) = M_\pm(t) \pm |t-t^\flat|^{-1}\Gamma_0 \tag{4.33}$$

with Γ_0 given by (4.16).

Proof. We have $\operatorname{Hess}\lambda_\pm = \operatorname{Hess} v \pm \operatorname{Hess}(|w|)$ and

$$\partial^2_{x_ix_j}(|w|) = \partial^2_{x_ix_j} w \cdot \frac{w}{|w|} + \frac{\partial_{x_i} w\cdot \partial_{x_j} w}{|w|} - \frac{(\partial_{x_i} w\cdot w)(\partial_{x_j} w\cdot w)}{|w|^3}.$$

We deduce from (4.8) that

$$\operatorname{Hess}\lambda_\pm(q_\pm(t)) = \pm\frac{1}{|t-t^\flat]}\Gamma_0 \pm \operatorname{sgn}(t-t^\flat)d^2w(z^\flat)\omega + \operatorname{Hess} v(q^\flat) + O(t-t^\flat)$$

with

$$\Gamma_0 = r^{-1}(\partial_{x_i} w\cdot\partial_{x_j} w - (\partial_{x_j} w\cdot\omega)(\partial_{x_i} w\cdot\omega))_{1\le i,j\le d},$$

whence (4.16) □

Proof of Proposition 4.1.7. Let us consider the operator

$$Q(t) = -\frac{1}{2}\Delta_y + \frac{1}{2}\operatorname{Hess}\lambda_\pm(q_\pm(t))y\cdot y. \tag{4.34}$$

This operator has a classical symbol $(y,\xi)\mapsto \frac{1}{2}|\xi|^2 + \lambda_\pm(\Phi_\pm^{t,t_0}(z_0))y\cdot y$ that satisfies sub-quadratic estimates in the interval $[t_0, t^\flat[$, which guarantees the existence of the solution (see [51]): the solution $u_-(t)$ exists for all $t\in[t_0,t^\flat[$ and is in all the spaces Σ^k for $k\in\mathbb{N}$. Since we know that the L^2-norms is conserved, we focus on $\|u_-(t)\|_{\Sigma^k}$ for $k\ge 1$. We set

$$U_1 = {}^t(yu_\pm, D_y u_\pm) = {}^t\widehat{z}u_\pm$$

and our aim is to prove that the norms $\|U_1\|_{\Sigma^k}$ are bounded for all $k \in \mathbb{N}$. Using

$$[Q(t), D_y] = i\text{Hess}\,\lambda_\pm(q_\pm(t))y \;\text{ and }\; [Q(t), y] = -\nabla_y = -iD_y, \tag{4.35}$$

we obtain

$$\begin{aligned}[Q(t), {}^t(y, D_y)]u_\pm &= {}^t(-iD_y u_\pm, i\text{Hess}\,\lambda_\pm(q_\pm(t))yu_\pm) \\ &= i\begin{pmatrix} 0 & -\text{Id} \\ \text{Hess}\,\lambda_\pm(q_\pm(t)) & 0 \end{pmatrix} {}^t(yu_\pm, D_y u_\pm)U_1.\end{aligned}$$

We deduce the equation

$$\begin{aligned} i\partial_t U_1 - Q(t)U_1 &= -\left[Q(t), \begin{pmatrix} y \\ D_y \end{pmatrix}\right] u \\ &= i\begin{pmatrix} 0 & -\text{Id} \\ \text{Hess}\,\lambda_\pm(q_\pm(t)) & 0 \end{pmatrix} U_1 \end{aligned}$$

This system is closed and the difficulty comes from the singularities of the matrix $\text{Hess}\,\lambda_\pm(q_\pm(t))$ that is described in Lemma 4.2.3. We work with the plus mode and $t < t^\flat$, the proofs for the minus mode or for $t > t^\flat$ are similar.

Lemma 4.2.4. *Let $k \in \mathbb{N}$ and $U \in \mathcal{C}^{2d}$ be a solution of a system of the form*

$$i\partial_t U - Q(t)\,U = (M(t) + i(t - t^\flat)^{-1}\Gamma)\,U$$

where $t \mapsto Q(t)$ is defined in (4.34), $t \mapsto M(t)$ depends smoothly on t for $t \in [t_0, t^\flat]$ (meaning that they have, and their derivatives too, limits when t goes to $t^\flat$ from below) and Γ_0 is a fixed matrix. We assume that there exists a projector $\mathbb{P}$ of rank d such that

$$(1 - \mathbb{P})\Gamma = 0 \;\text{ and }\; \mathbb{P}\Gamma = \mathbb{P}\Gamma(1 - \mathbb{P}).$$

Then, for all $k \in \mathbb{N}$, there exists $C_k > 0$ such that for all $t \in [t_0, t^\flat[$

$$\|U(t)\|_{\Sigma^k(\mathbb{R}^d, \mathcal{C}^{2d})} \leq C_k |\log|t - t^\flat||.$$

Lemma 4.2.4 allows to terminate the proof of Proposition 4.1.7. Indeed, we observe that $U_1(t)$ satisfies an equation of the form above with

$$\Gamma = \pm \operatorname{sgn}(t - t^\flat) \begin{pmatrix} 0 & 0 \\ \Gamma_0 & 0 \end{pmatrix}, \quad \mathbb{P} = \begin{pmatrix} 0 & 0 \\ 0 & \mathrm{Id} \end{pmatrix}.$$

□

Proof of Lemma 4.2.4. We begin with the case $k = 0$. We set $V = (1 - \mathbb{P})U$ and $W = \mathbb{P}U$. Then, because $(1 - \mathbb{P})\Gamma = 0$,

$$i\partial_t V - Q(t)V = (1 - \mathbb{P})M(t)(V + W)$$

and

$$i\partial_t W - Q(t)W = (t - t^\flat)^{-1}\mathbb{P}\Gamma V + \mathbb{P}M(t)(V + W).$$

We then introduce the variable

$$\tilde{V} = W - \log|t - t^\flat|\mathbb{P}\Gamma V$$

so that $\tilde{V}$ satisfies

$$\begin{aligned} i\partial_t \tilde{V} - Q(t)\tilde{V} &= \mathbb{P}M(t)(V + W) - \log|t - t^\flat|\mathbb{P}\Gamma(\partial_t V)i\partial_t V - Q(t)V) \\ &= \mathbb{P}M(t)(V + W) - \log|t - t^\flat|\mathbb{P}\Gamma(1 - \mathbb{P})M(t)(V + W) \end{aligned}$$

$$= (\mathbb{P} - \log|t - t^\flat|\mathbb{P}\Gamma)M(t)(V + \tilde{V} + \log|t - t^\flat|\mathbb{P}\Gamma V).$$

To conclude, V and $\tilde{V}$ satisfy the system

$$\begin{cases} i\partial_t V - Q(t)V &= A(t)V + B(t)\tilde{V} \\ i\partial_t \tilde{V} - Q(t)\tilde{V} &= \tilde{A}(t)V + \tilde{B}(t)\tilde{V}, \end{cases} \tag{4.36}$$

with $t \mapsto A(t), B(t), \tilde{A}(t), \tilde{B}(t)$ are integrable. We then conclude by an energy estimate and using that the functions of t which appear in the right-hand side are integrable. Note that Gronwall lemma applies of the integrability assumption of the functions involved. The change of unknown has contributed to improve the integrability of the functions of the right-hand side of the system. As a consequence, there exists a constant $C > 0$ such that

$$\forall t \in [t_0, t^\flat), \;\; \|V(t)\|_{L^2} + \|\tilde{V}(t)\|_{L^2} \leq C$$

which implies the existence of $C_1 > 0$ such that

$$\forall t \in [t_0, t^\flat), \;\; \|U(t)\|_{L^2} \leq C_1 \left|\log|t - t^\flat|\right|.$$

We now want to estimate $U_1(t)$ in Σ^k, or, equivalently, V and $\tilde{V}$ in Σ^k. We argue by a recursive argument and consider successive derivatives and momenta of V and $\tilde{V}$. We first examine the case $k = 1$. In view of the relations (4.35), for $1 \leq j \leq d$, the quantities

$$y_j V, \;\; y_j \tilde{V}, \;\; D_{y_j} V, \;\; D_{y_j} \tilde{V}$$

satisfy a closed system of equations of the form

$$i\partial_t(y_j V) - Q(t)(y_j V) = A(t)(y_j V) + B(t)(y_j \tilde{V}) + iD_{y_j}\tilde{V},$$

$$i\partial_t(y_j\tilde{V}) - Q(t)(y_j\tilde{V}) = \tilde{A}(t)(y_jV) + \tilde{B}(t)(y_j\tilde{V}) + iD_{y_j}\tilde{V},$$

$$i\partial_t(D_{y_j}V) - Q(t)(D_{y_j}V) = A(t)(D_{y_j}V) + B(t)(D_{y_j}\tilde{V}) + C(t)\cdot y\,V$$
$$+ i|t-t^\flat|^{-1}(e_j\cdot\Gamma_0 y)\,V,$$

$$i\partial_t(D_{y_j}\tilde{V}) - Q(t)(D_{y_j}\tilde{V}) = \tilde{A}(D_{y_j}V) + \tilde{B}(t)(D_{y_j}\tilde{V}) + \tilde{C}(t)\cdot y\tilde{V}$$
$$+ i|t-t^\flat|^{-1}(e_j\cdot\Gamma_0 y)\tilde{V}$$

with $A(t), \tilde{A}(t), B(t), \tilde{B}(t), C(t)$ and $\tilde{C}(t)$ smooth maps, and denoting by e_j the canonical basis of $\mathbb{R}^d$. This system presents again the non-integrable singularity $|t-t^\flat|^{-1}$ in the right-hand side that calls for a change of unknown, as we did previously. We set $V_1 = V \in \mathcal{C}^d$, $\tilde{V}_1 = \tilde{V} \in \mathcal{C}^d$ and consider the derivatives and momenta of V_1 and $\tilde{V}_1$. We set

$$V_2 = (y_1V, \cdots, y_dV, y_1\tilde{V}, \cdots, y_d\tilde{V})$$

and

$$\tilde{V}_2 = ((D_{y_j}V + \log|t-t^\flat|(e_j\cdot\Gamma_0 y)V)_{1\le j\le d}, (D_{y_j}\tilde{V} + \log|t-t^\flat|(e_j\cdot\Gamma_0 y))_{1\le j\le d}).$$

We have $V_2, \tilde{V}_2 \in \mathcal{C}^{2d^2}$ and the functions $t\mapsto V_2(t), \tilde{V}_2(t)$ satisfy a system of the form

$$\begin{cases} i\partial_t V_2 - Q(t)V_2 &= A_2(t)V_2 + B_2(t)\tilde{V}_2 + S_2(t) \\ i\partial_t \tilde{V}_2 - Q(t)\tilde{V}_2 &= \tilde{A}_2(t)V_2 + \tilde{B}_2(t)\tilde{V}_2 + \tilde{S}_2(t) \end{cases}$$

with $A_2(t), B_2(t), \tilde{A}_2(t), \tilde{B}_2(t)$ are integrable and with source terms $S_2(t)$ and $\tilde{S}_2(t)$ satisfying

$$\|S_2(t)\|_{L^2(\mathbb{R}^d,\mathcal{C}^{2d^2})} + \|\tilde{S}_2(t)\|_{L^2(\mathbb{R}^d,\mathcal{C}^{2d^2})} \le c_2|\log[t-t^\flat||$$

for some constant $c_2 > 0$. Arguing as above by use of energy estimate and Gromwall lemma, we obtain a control of the L^2 norm of $(V_2(t), \tilde{V}_2(t))$ of the form

$$\|V_2(t)\|_{L^2(\mathbb{R}^d, \mathcal{C}^{2d^2})} + \|\tilde{V}_2(t)\|_{L^2(\mathbb{R}^d, \mathcal{C}^{2d^2})} \leq C_2$$

whence

$$\|U(t)\|_{\Sigma^1} \leq C_2' |\log|t - t^\flat||.$$

All these considerations motivate to realize a recursive arguments by increasing successively the size of the momenta. At the $(\ell - 1)$-th step, we are left with a vector

$$(V_\ell(t), \tilde{V}_\ell(t)) \in \mathcal{C}^{(2d)^\ell}$$

satisfying a system of the form

$$\begin{cases} i\partial_t V_\ell - Q(t)V_\ell &= A_\ell(t)V_\ell + B_\ell(t)\tilde{V}_\ell + S_\ell(t) \\ i\partial_t \tilde{V}_\ell - Q(t)\tilde{V}_\ell &= \tilde{A}_\ell(t)V + \tilde{B}_\ell(t)\tilde{V}_\ell + \tilde{S}_\ell(t) \end{cases}$$

with $A_\ell(t), B_\ell(t), \tilde{A}_\ell(t), \tilde{B}_\ell(t)$ integrable and source terms $S_\ell(t)$ and $\tilde{S}_\ell(t)$ such that

$$\|S_\ell(t)\|_{L^2(\mathbb{R}^d, \mathcal{C}^{2d^2})} + \|\tilde{S}_\ell(t)\|_{L^2(\mathbb{R}^d, \mathcal{C}^{2d^2})} \leq c_\ell |\log|t - t^\flat||$$

for some constant $c_\ell > 0$. Moreover, the norm of U in $\Sigma^{\ell-1}$ is equivalent to the one of $(V_\ell, \tilde{V}_\ell)$ in L^2 up to a factor of the form $|\log|t - t^\flat||$, which holds by energy estimate and Gronwall lemma. We are then interested in the analysis of the derivatives and the momenta of V_ℓ and $\tilde{V}_\ell$. This leads to the construction of a vectors of $(2d)^\ell = d(2d)^{\ell-1} + d(2d)^{\ell-1}$ variables. Re-organizing the equation in order to suppress the singularity generated by the commutator $[D_y, Q(t)]$: we set

$$V_{\ell+1} = (y_1 V_\ell, \cdots, y_d V_\ell, y_1 \tilde{V}_\ell, \cdots, y_d \tilde{V}_\ell)$$

$$\text{and}\;\; \tilde V_{\ell+1} = ((D_{y_j} V + \log|t-t^\flat|(e_j\cdot\Gamma y)V)_{1\le j\le d},$$

$$(D_{y_j}\tilde V_\ell + \log|t-t^\flat|(e_j\cdot\Gamma y)\,\tilde V_\ell,\cdots, D_{y_d}\tilde V_\ell)_{1\le j\le d}.$$

It is then clear that one can proceed as before and that one obtains the boundedness of $(V_{\ell+1},\tilde V_{\ell+1})$ in L^2, whence an estimate of the form

$$\|(V_\ell,\tilde V_\ell)\|_{\Sigma^1} \le c_\ell \|(V_{\ell+1},\tilde V_{\ell+1})\|_{L^2} \le C_{\ell+1}|\log|t-t^\flat||$$

and

$$\|U\|_{\Sigma^\ell} \le C'_{\ell+1}|\log|t-t^\flat||.$$

□

At this stage of the proof, we have a precise information on the behavior of the Σ^k norms of the solutions of the system (4.14). This allows to characterize their limits on the crossing set and to solve the equation (4.14) in terms of this limit instead of some initial data. This is the subject of Corollary 4.1.8 that we prove now.

Proof of Corollary 4.1.8. Let us assume $t<t^\flat$ and set

$$v_\pm(t) = \text{Exp}(\mp i\Gamma_0 y\cdot y\;\ln|t-t^\flat|)u_\pm(t).$$

We have

$$i\partial_t v_\pm(t) = \text{Exp}(\pm i\Gamma_0 y\cdot y\;\ln|t-t^\flat|)$$
$$\times\left(\pm\frac{1}{t-t^\flat}\Gamma_0 y\cdot y\,u_\pm(t) - \frac12\Delta_y u_\pm(t) + \frac12(\text{Hess}\lambda_\pm(q_\pm(t))y\cdot y)u_\pm(t)\right)$$

$$= \mathrm{Exp}(\pm i\Gamma_0 y \cdot y \, \ln|t - t^\flat|) \left((-\frac{1}{2}\Delta_y + M_\pm(t) y \cdot y) u_\pm(t) \right)$$

where the matrix $M_\pm(t)$ is defined in Lemma 4.2.3 and is smooth on $[t_0, t^\flat]$ (the term $\pm(t - t^\flat)^{-1}\Gamma_0 y \cdot y$ compensates the singularity of the potential of the operator $Q(t)$ (see (4.34)). We now use Proposition 4.1.7. Therefore, for all $t \in [t_0, t^\flat)$, $\partial_t v_\pm(t) \in \Sigma^k$ for all $k \in \mathbb{N}$. Besides, for each $k \in \mathbb{N}$, there exists constants $C_k, \tilde{C}_k > 0$ and $N_k \in \mathbb{N}$ such that

$$\begin{aligned} \|\partial_t v_\pm(t)\|_{\Sigma^k} &\leq C_k \left| |t - t^\flat| \right|^{N_k} \|u_\pm(t)\|_{\Sigma^{k+3}} \\ &\leq \widetilde{C}_k \left| \log|t - t^\flat| \right|^{N_k} \|u_\pm(t_0)\|_{\Sigma^{k+3}}. \end{aligned}$$

We deduce that $\int_{t_0}^{t^\flat} \partial_t v_\pm(s) ds$ is well-defined as a function of Σ^k and we denote by $u_\pm^{\mathrm{in}}$ this function that satisfies (4.17).

We observe that the function $v_\pm(t)$ defined above solves an equation of the form

$$i\partial_t v_\pm(t) = \left(-\frac{1}{2}\Delta_y + \mathcal{V}(t, y) \right) v_\pm(t) \tag{4.37}$$

where $\mathcal{V}(t, y)$ is a quadratic potential $\mathcal{V}(t, y) = a(t)y^2 + b(t)y + c(t)$ with coefficients a, b, c that are functions bounded by powers of $\ln|t - t^\flat|$. We have the following facts:

1. It is equivalent to say that $u_\pm(t)$ solves (4.14) and to say that $v_\pm(t)$ solves (4.37).

2. There is conservation of the L^2-norm and

$$\|\|v_\pm(t)\|_{L^2} = \|v_\pm(t_0)\|_{L^2} = \|u_\pm(t_0)\|_{L^2}.$$

3. The two parameters propagator $\widetilde{\mathcal{U}}(t, s)$ associated with the equation (4.37) (see [51])

is defined for $t, s \in [t_0, t^\flat)$ and when t tends to $t^\flat$, $\widetilde{\mathcal{U}}(t,s)u_\pm(t_0)$ has a limit u^{in} with $\|u_\pm(t_0)\|_{L^2} = \|u_\pm^{\text{in}}\|_{L^2}$. We denote by $\widetilde{\mathcal{U}}(t^\flat, s)$ the operator mapping $u_\pm(t_0)$ on $u_\pm^{\text{in}}$.

4. For all $f \in \mathcal{S}(\mathbb{R}^d)$, $k \in \mathbb{N}$ there exists $C_k > 0$ such that

$$\forall f \in \mathcal{S}(\mathbb{R}^d), \;\; \|\widetilde{\mathcal{U}}(t^\flat, s)f\|_{\Sigma^k} \leq C_k \|f\|_{\Sigma^{k+3}}.$$

We claim that for $t, s \in [t_0, t^\flat)$ we have $\widetilde{\mathcal{U}}(s,t) = \widetilde{\mathcal{U}}(t,s)^*$, therefore we define the operator $\widetilde{\mathcal{U}}(s, t^\flat)$ by

$$\widetilde{\mathcal{U}}(s, t^\flat) := \widetilde{\mathcal{U}}(t^\flat, s)^*.$$

The claim comes from the definition of $\widetilde{\mathcal{U}}(t,s)$ as solving

$$i\partial_t \widetilde{\mathcal{U}}(t,s) = H(t)\widetilde{\mathcal{U}}(t,s), \;\; \widetilde{\mathcal{U}}(s,s) = \text{Id}. \tag{4.38}$$

In one hand, one deduces that

$$i\partial_t \widetilde{\mathcal{U}}(t,s)^* = -\widetilde{\mathcal{U}}(t,s)^* H(t), \;\; \widetilde{\mathcal{U}}(s,s) = \text{Id}.$$

On the other hand, differentiating in s the relation (4.38), we obtain that $V(t,s) = \partial_s \widetilde{\mathcal{U}}(t,s)$ satisfies

$$i\partial_t V(t,s) = H(t)V(t,s), \;\; V(s,s) = -\partial_t \widetilde{\mathcal{U}}(s,s) = iH(s).$$

Therefore, $V(t,s) = \widetilde{\mathcal{U}}(t,s)iH(s)$ which gives $i\partial_s \widetilde{\mathcal{U}}(t,s) = -\widetilde{\mathcal{U}}(t,s)H(s)$. Exchanging the roles of t and s we obtain that $\widetilde{\mathcal{U}}(s,t)$ solves the same equation than $\widetilde{\mathcal{U}}(t,s)^*$ with the same initial data and thus they are equal.

Therefore, we have proved that we can construct a function $u^\pm(t)$ solving (4.14) for $t \leq t^\flat$, starting from a data $u_\pm^{\text{in}}$ with enough regularity, in particular for $u_\pm^{\text{in}} \in \mathcal{S}(\mathbb{R}^d)$.

Arguing similarly in the zone $t > t^\flat$, we deduce that there exists a unique solution to (4.14) satisfying (4.18) for some given $u_\pm^{\text{out}} \in \mathcal{S}(\mathbb{R}^d)$. $\square$

4.3 Adiabatic transport outside the gap region

This section is inspired by [21] and discussions with Caroline Lasser and Didier Robert. We focus here on zones that are far enough from the gap region in the sense that $|w(x)| > \delta$ along the trajectories concerned by the process. In this adiabatic region, we prove the following result showing that one can approximate the solution of the system (4.1) by solutions of scalar type equations.

Proposition 4.3.1. *Let $k \in \mathbb{N}$ and $\delta \in (0,1)$ such that $\varepsilon\delta^{-2} \leq 1$. Consider $s_1, s_2 \in \mathbb{R}$, $s_1 < s_2$ and two classical trajectories $z_\pm(t))_{t\in[s_1,s_2]}$ that reach the crossing set Υ at time $t^\flat$ in a point where Assumptions 4.1.1 are satisfied. We assume $[s_1, s_2] \subset \{|t - t^\flat| > \delta\}$ and that at initial time s_1,*

$$\left\| \psi^\varepsilon(s_1) - \vec{Y}_+(s_1) v_+^\varepsilon(s_1) - \vec{Y}_-(s_1) v_-^\varepsilon(s_1) \right\|_{\Sigma_\varepsilon^k} \leq C\sqrt{\varepsilon},$$

$$v_\pm^\varepsilon(s_1) = \mathrm{WP}^\varepsilon_{z_\pm(s_1)}(u_\pm(s_1)), \;\; u_\pm(s_1) \in \mathcal{S}(\mathbb{R}^d), \;\; z_\pm(s_1) = (q_\pm(s_1), p_\pm(s_1)) \in \mathbb{R}^{2d},$$

and with $\Pi_\pm(q_\pm(s_1))\vec{Y}_\pm(s_1) = \vec{Y}_\pm(s_1)$. Then, for all $k \in \mathbb{N}$, one has

$$\sup_{t\in[s_1,s_2]} \left\| \Pi_\pm \psi^\varepsilon(t) - \vec{Y}_\pm(t) v_\pm^\varepsilon(t) \right\|_{\Sigma_\varepsilon^k} \leq C_k |\ln\delta| \left(\frac{\varepsilon^{3/2}}{\delta^4} + \frac{\sqrt{\varepsilon}}{\delta} \right),$$

where the constant C_k is uniform in δ and ε, and for $t \in [s_1, s_2]$

- *the functions* $v_\pm^\varepsilon(t)$ *are wave packets:*

$$v_\pm^\varepsilon(t) = \mathrm{e}^{\frac{i}{\varepsilon}S_\pm(t)}\mathrm{WP}^\varepsilon_{z_\pm(t)}\left(u_\pm(t)\right), \tag{4.39}$$

- *the trajectory* $z_\pm(t)$ *is the classical trajectory* $z_\pm(t) = \Phi_\pm^{t,s_1}(z_\pm(s_1))$ *and* $S_\pm(t) = S_\pm(t, s_1, z_\pm(s_1))$ *the related action (see* (4.9)*),*

- *the functions* $u_\pm(t)$ *satisfy* (4.14) *with data* $u_\pm(s_1)$ *at time* s_1 *and their norms in spaces* Σ^k *satisfy* (4.15)*,*

- *the vectors* $\vec{Y}_\pm(t)$ *are associated with* $\vec{Y}_\pm(s)$ *by Proposition 4.1.4 and satisfy* $\Pi_\pm(z_\pm(t))\vec{Y}_\pm(t) = \vec{Y}_\pm(t)$*, together with* $\partial_t\vec{Y}_\pm(t) = B_\pm(z_\pm(t))\vec{Y}_\pm(t)$ *with initial data* $\vec{Y}(s_1)$ *at time* $t = s_1$*.*

Note first that, by the results of Section 4.2, all the quantities involved in Proposition 4.3.1 are well defined for $t \in [s_1, s_2]$. Besides, the solution at time $t \in [s_1, s_2]$ on each mode only depends on the data on this mode at time s_1. It is in the sense that one can say that the approximation is of "scalar type" as mentioned above.

Note also that the assumptions of Proposition 4.3.1 implies that there exists $c > 0$ such that

$$\forall t \in [s_1, s_2], \quad |w(z_\pm(t))| > \delta.$$

In the proof of Theorem 4.1.10, we are going to use Proposition 4.3.1 twice: first between $s_1 = t_0$ and $s_2 = t^\flat - \delta$ with $u_+(t_0) = 0$ and $u_-(t_0) = a$, secondly, between $s_1 =: t^\flat + \delta$ and s_2 equal to some final time t with the profiles $u_\pm(t^\flat + \delta)$ arising from the process of passing through the crossing.

For proving Proposition 4.3.1, we use the semi-classical formalism of Appendix A and the pseudodifferential operators introduced therein: with $a \in \mathcal{C}^\infty(\mathbb{R}^{2d}, \mathcal{C}^N)$ $(N = 1$ or $2)$, we associate the operator $\mathrm{op}_\varepsilon(a)$ defined by (A.1). We shall also use the matrices $\mathbb{P}$, $\mathbb{P}_\pm^{(2)}$, Ω and $\Omega_\pm^{(2)}$ of Section C.2.

4.3.1 The adiabatic ansatz

For proving Proposition 4.3.1, we first study the properties of the ansatz

$$\psi^\varepsilon_{\pm,\mathrm{app}}(t) = \mathrm{op}_\varepsilon(\vec{V}_\pm(t)) v^\varepsilon_\pm(t), \tag{4.40}$$

where $\vec{V}_\pm(t,x)$ is a time dependent eigenvector constructed according to Proposition 4.1.4 and satisfying

$$\vec{V}_\pm(s_1, z_\pm(s_1)) = \vec{Y}_\pm(s_1).$$

We analyze the equations satisfied by $\psi^\varepsilon_{\pm,\mathrm{app}}$ and use the notations of Section C.2.

Lemma 4.3.2. *With the notations of Proposition 4.3.1 and equation* (4.40)*, there exists* $\delta_0 > 0$ *such that for* $\delta < \delta_0$*,* $k \in \mathbb{N}$ *and* $t \in [s_1, s_2]$*, we have*

$$\begin{aligned} i\varepsilon\partial_t \psi^\varepsilon_{\pm,\mathrm{app}} = & -\frac{\varepsilon^2}{2}\Delta\psi^\varepsilon_{\pm,\mathrm{app}} + \lambda_\pm(x)\psi^\varepsilon_{\pm,\mathrm{app}} + \varepsilon\,\mathrm{op}_\varepsilon(\Omega)\psi^\varepsilon_{\pm,\mathrm{app}} + \varepsilon^2\,\mathrm{op}_\varepsilon(\Omega^{(2)}_\pm)\psi^\varepsilon_{\pm,\mathrm{app}} \\ & + O\left(\varepsilon^{3/2}\delta^{-1}|\ln\delta|\right) + O\left(\varepsilon^{5/2}\delta^{-4}\,|\ln\delta|\right) \end{aligned}$$

in Σ^k_ε*, where* Ω *is the self-adjoint matrix*

$$\Omega = i(B_+ + B_-) = i(\Pi_-\xi\cdot\nabla\Pi_+\Pi_+ - \Pi_+\xi\cdot\nabla\Pi_+\Pi_-) \tag{4.41}$$

$$= -\frac{i}{2|w(x)|}\xi \cdot \nabla w(x) \wedge \frac{w(x)}{|w(x)|}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},$$

and $\Omega_\pm^{(2)}$ *is given in* (C.5).

We recall that the matrices $B_\pm$ are defined in (4.10) and we point out that Ω is self adjoint because

$$\Omega^* = -i(B_+^* + B_-^*) = i(B_+ + B_-) = \Omega.$$

Moreover, by (4.10) and (4.3), the operator $\mathrm{op}_\varepsilon(\Omega)$ is a differential operator of order 1 with matrix-valued coefficients that are growing polynomially at infinity. The different expressions of the matrix Ω are proved in Lemma C.1.1.

Remark 4.3.3. We shall use $\delta = \varepsilon^\alpha$ with $3/2 - 4\alpha > 0$, that is $\alpha \leq 3/8$. We shall see in the last section that the analysis requires $\delta^3\varepsilon^1 \ll 1$, which is possible since one has $1/3 < 3/8$. An optimal choice of δ consists in choosing $\delta = \varepsilon^{\frac{5}{14}}$, leading to $\varepsilon^{3/2}\delta^{-4} = \delta^3\varepsilon^{-1} = \delta^{\frac{1}{14}}$.

Proof. We begin by considering for $t \in [s_1, s_2]$ the family $(v_\pm^\varepsilon(t))$ defined in (4.39). It comes from a computation (see [8] for example) that $v^\varepsilon(t)$ solves in Σ^k,

$$i\varepsilon\partial_t v_\pm^\varepsilon(t) = -\frac{\varepsilon^2}{2}\Delta v_\pm(t) + \lambda_\pm(x)v_\pm^\varepsilon(t) + O(\varepsilon^{3/2}\|u_\pm(t)\|_{\Sigma^{k+3}}).$$

Since the profiles have been assumed to satisfy (4.15), we have

$$O(\varepsilon^{3/2}\|u_\pm\|_{\Sigma^{k+3}}) = O(\varepsilon^{3/2}|\ln\delta|).$$

We now consider $\psi_{\pm,\mathrm{app}}^\varepsilon$ and uses

$$\partial_t\vec{V}_\pm(t) = -\{h_\pm, \vec{V}_\pm\} + B_\pm\vec{V}_\pm(t) = -\{h_\pm, \vec{V}_\pm\} - i\Omega\vec{V}_\pm(t)$$

because of $\Pi_{\mp}\vec{V}_{\pm}(t) = 0$. Therefore, in Σ^k,

$$\begin{aligned} i\varepsilon\partial_t\psi^{\varepsilon}_{\pm,\mathrm{app}}(t) &= \varepsilon\,\mathrm{op}_\varepsilon(-i\{h_\pm,\vec{V}_\pm\} + \Omega\vec{V}_\pm(t))v^\varepsilon_\pm(t) \\ &\qquad + \mathrm{op}_\varepsilon(\vec{V}_\pm(t))\left(-\frac{\varepsilon^2}{2}\Delta + \lambda_\pm(x)\right)v^\varepsilon_\pm(t) + O(\varepsilon^{3/2}|\ln\delta|) \\ &= \left(-\frac{\varepsilon^2}{2}\Delta + \lambda_\pm(x) + \varepsilon\mathrm{op}_\varepsilon(\Omega)\right)\psi^\varepsilon_{\pm,\mathrm{app}}(t) + \varepsilon\,\left[\mathrm{op}_\varepsilon(\Omega),\mathrm{op}_\varepsilon(\vec{V}_\pm(t))\right]v^\varepsilon_\pm(t) \\ &\qquad + O(\varepsilon^{3/2}|\ln\delta|). \end{aligned}$$

We set

$$r^\varepsilon(t) = \left(\frac{1}{\varepsilon}\left[\mathrm{op}_\varepsilon(\Omega),\mathrm{op}_\varepsilon(\vec{V}_\pm(t))\right] - \mathrm{op}_\varepsilon(\Omega^{(2)}_\pm)\right)v^\varepsilon_\pm(t).$$

Note first that the operators $\mathrm{op}_\varepsilon(\Omega)$ and $\mathrm{op}_\varepsilon\left(\Omega^{(2)}_\pm\right)$ is well-defined: it is a differential operator with coefficients that have singularity on Υ. When acting on $v^\varepsilon_\pm(t)$, we use Lemma B.0.2 (1) to avoid the singularities. Let $\chi \in \mathcal{C}^\infty(\mathbb{R})$ a cut-off function such that $\chi(u) = 0$ for $|u| \leq 1$ and $\chi(u) = 1$ for $|u| > 1$, then for δ small enough,

$$\begin{aligned} r^\varepsilon(t) &= \left(\frac{1}{\varepsilon}\left[\mathrm{op}_\varepsilon(\chi_\delta\Omega),\mathrm{op}_\varepsilon(\vec{V}_\pm(t))\right] - \mathrm{op}_\varepsilon(\chi_\delta\Omega^{(2)}_\pm)\right)v^\varepsilon_\pm(t) + O(\sqrt{\varepsilon}\delta^{-1}|\ln\delta|) \\ &= \mathrm{op}_\varepsilon\left(-i\{\chi_\delta\Omega, V_\pm(t)\} + \chi_\delta\Omega^{(2)}_\pm\right)v^\varepsilon_\pm(t) + O(\sqrt{\varepsilon}\delta^{-1}|\ln\delta|), \end{aligned}$$

where we have used the estimates of Lemma C.2.1 and with $\chi_\delta(x) = \chi(|w(x)|\delta^{-1})$. We set

$$R = \chi_\delta(-i\{\Omega, V_\pm(t)\} + \Omega^{(2)}_\pm)$$

and, again by Lemma B.0.2 (1) and Lemma C.2.1, we have

$$r^\varepsilon(t) = R(z_\pm(t))v^\varepsilon_\pm(t) + O(\sqrt{\varepsilon}\delta^{-4}|\ln\delta|).$$

Since by Lemma C.2.3, $R(z_\pm(t)) = O(|t - t^\flat|^{-2}) = O(\delta^{-2})$, we are left with

$$r^\varepsilon(t) = O(\sqrt{\varepsilon}\delta^{-4}|\ln\delta|)$$

whence

$$i\varepsilon\partial_t \psi^\varepsilon_{\pm,\mathrm{app}}(t) = \left(-\frac{\varepsilon^2}{2}\Delta + \lambda_\pm(x) + \varepsilon\Omega + \varepsilon\Omega^{(2)}_\pm\right)\psi^\varepsilon_{\pm,\mathrm{app}}(t)$$
$$+ O(\varepsilon^{5/2}\delta^{-4}|\ln\delta|) + O(\varepsilon^{3/2}\delta^{-1}|\ln\delta|).$$

which terminates the proof. □

4.3.2 Superadiabatic correctors of the projectors

We use ideas issued from [58, 2, 52, 53, 50], aiming at ameliorating the projectors $\Pi_\pm(x)$ into operators called superadiabatic projectors that are pseudodifferential operators with symbols that are series in ε. For our purpose, we just need the first term of this series. We set

$$H(x,\xi) = \frac{|\xi|^2}{2} + V(x), \quad h_\pm(x,\xi) = \frac{|\xi|^2}{2} + \lambda_\pm(x),$$

and consider for $x \notin \Upsilon$, the matrices $\mathbb{P}$, $\mathbb{P}^{(2)}_\pm$, Ω and $\Omega^{(2)}_\pm$ of Section C.2, together with

$$\mathbb{P}(x,\xi) = \frac{i}{2|w(x)|}(\Pi_-(x)\xi\cdot\nabla\Pi_+(x) - \Pi_+(x)\xi\cdot\nabla\Pi_+(x)) \tag{4.42}$$
$$= \frac{-i}{4|w(x)|^2}\ \xi\cdot\nabla w \wedge \frac{w}{|w|}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

and

$$\Pi^\varepsilon_\pm(x,\xi) = \Pi_\pm(x) \pm \varepsilon\mathbb{P}(x,\xi) + \varepsilon^2\mathbb{P}^{(2)}_\pm(x,\xi).$$

These matrices are smooth outside Υ. From Lemma C.2.1, we have equation (C.1), i.e.

$$\Pi^{\varepsilon}_{\pm}\sharp_{\varepsilon}H = (h_{\pm} + \varepsilon\,\Omega^{(1)}_{\pm} + \varepsilon^2\,\Omega^{(2)}_{\pm})\sharp_{\varepsilon}\Pi^{\varepsilon}_{\pm} + \varepsilon^3 R^{\varepsilon}(x,\xi)$$

where for $(x,\xi) \in \mathbb{R}^{2d} \setminus \Upsilon$, for all $\alpha, \beta \in \mathbb{N}^d$, there exists constants $C_{\alpha,\beta},\ p_\alpha > 0$ such that

$$|\partial^{\alpha}_{x}\partial^{\beta}_{\xi} R^{\varepsilon}(x,\xi)| \leq C_{\alpha,\beta}\langle x\rangle^{(|\alpha|+3)(1+n_0)}|w(x)|^{-|\alpha|-5}.$$

Besides, equation (4.27) and Remark C.2.2 give precise estimates on these matrices at infinity and close toi Υ. Because these corrected projectors may grow in the variables x and ξ, we shall need to localize them by use of cut-off functions. It will also allow to restrict to the zone where they are smooth.

Let I be an interval containing $[s_1, s_2]$. We construct $\chi^{\delta}_{\pm}, \tilde{\chi}^{\delta}_{\pm} \in \mathcal{C}(I, \mathcal{C}^{\infty}_{0}(\mathbb{R}^{2d}))$, compactly supported in $\{|w(x)| > \delta\}$, equal to 1 close to the curve $(z_{\pm}(t))_{t\in[s_1,s_2]}$,

$$\partial_t \chi^{\delta}_{\pm} + \left\{\frac{|\xi|^2}{2} + \lambda_{\pm}, \chi^{\delta}_{\pm}\right\} = 0.$$

We choose $\tilde{\chi}^{\delta}_{\pm} \in \mathcal{C}^{\infty}_{0}(\mathbb{R}^{2d})$ such that for all $t \in [s_1, s_2]$, we have $\tilde{\chi}^{\delta}_{\pm}(t, x, \xi) = 1$ in a neighborhood of $z_{\pm}(t)$, the classical trajectory that we follow, and we assume that $\operatorname{supp}\tilde{\chi}^{\delta}_{\pm} \subset \{\chi^{\delta}_{\pm}(t) = 1\}$ and that for $\alpha \in \mathbb{N}^{2d}$, $\partial^{\alpha}\tilde{\chi}^{\delta}_{\pm} = O(\delta^{-|\alpha|})$.

Remark 4.3.4. Let s_1, s_2 as in Proposition 4.3.1. The functions $\chi^{\delta}_{\pm}$ can be taken for $t \in [s_1, s_2]$ as

$$\chi^{\delta}_{\pm}(t, x, \xi) = \chi\left(\frac{\Phi^{-t+s_2,0}_{\pm}(x,\xi) - z_{\pm}(s_2)}{\delta}\right)$$

where $0 \leq \chi \leq 1$ with $\chi = 1$ close to 0 and $\chi = 0$ far from 0, and $\tilde{\chi}^{\delta}_{\pm}$ similarly.

By construction, we have the following Lemma.

Lemma 4.3.5. *Let $k \in \mathbb{N}$, $\delta \in (0,1)$ such that $\varepsilon\delta^{-2} \leq 1$. Then, in $\mathcal{L}(L^2)$, we have*

$$\begin{aligned}\mathrm{op}_\varepsilon(\tilde{\chi}_\pm(t))\mathrm{op}_\varepsilon(\Pi^\varepsilon_\pm \chi^\delta_\pm(t)) \left(-\frac{\varepsilon^2}{2}\Delta + V(x)\right) \\ = \mathrm{op}_\varepsilon(\tilde{\chi}_\pm(t)) \left(-\frac{\varepsilon^2}{2}\Delta + \lambda_\pm(x) + \varepsilon\, \mathrm{op}_\varepsilon(\Omega) + \varepsilon^2 \mathrm{op}_\varepsilon(\Omega^{(2)}_\pm)\right) \mathrm{op}_\varepsilon(\Pi^\varepsilon_\pm \chi^\delta_\pm(t)) \\ + O(\varepsilon^3\delta^{-5}).\end{aligned}$$

Remark 4.3.6. Note that if $\delta = \varepsilon^\alpha$ with $\alpha \in (\frac{1}{3}, \frac{3}{8})$, as suggested in Remark 4.3.3, then $\varepsilon^2\delta^{-5} \ll \varepsilon^{3/2}\delta^{-4}$.

This lemma emphasizes the interest of these superadiabatic projectors, that allow to diagonalize the operator $\mathrm{op}_\varepsilon(H)$ up to a correction $\varepsilon\, \mathrm{op}_\varepsilon(\Omega)$ which is of lower order in ε (recall that $\Omega = i(B_+ + B_-)$ is self-adjoint).

Proof. The proof comes from the symbolic calculus of Proposition A.0.1 and Remark A.0.2, keeping in mind that we have $|w(x)| > \delta$ on the support of the cut-off functions. By (C.1), we obtain

$$\begin{aligned}\mathrm{op}_\varepsilon(\Pi^\varepsilon_\pm \chi^\delta_\pm(t))\mathrm{op}_\varepsilon(H) = \mathrm{op}_\varepsilon(h_\pm + \varepsilon\Omega + \varepsilon^2\Omega^{(2)}_\pm)\mathrm{op}_\varepsilon\left(\chi^\delta_\pm(t)\Pi^\varepsilon_\pm\right) \\ + \varepsilon^3 \mathrm{op}_\varepsilon(R^\varepsilon_\delta)\end{aligned}$$

with $R^\varepsilon_\delta(t)$ depending linearly on derivatives of $\partial_z \chi^\delta_\pm(t)$ and satisfying for $(x,\xi) \in \mathbb{R}^{2d}$ and $t \in [s_1, s_2]$,

$$|\partial^\alpha_x R_\delta(t,x,\xi)| = O(\delta^{-|\alpha|-5}).$$

The result then comes from the observation that because on the support of $\tilde{\chi}^{\delta}_{\pm}(t)$, the function $\partial_z \chi^{\delta}_{\pm}(t)$ is identically equal to 0 and thus, so it is for $R^{\varepsilon}_{\delta}(t) = 0$, the symbolic calculus implies that in Σ^k_{ε}

$$\mathrm{op}_{\varepsilon}(\tilde{\chi}^{\delta}_{\pm}(t))\mathrm{op}_{\varepsilon}(R^{\varepsilon}_{\delta}(t)) = O(\varepsilon^N \delta^{-2-N}).$$

One then concludes by choosing $N = 3$. □

Proof of Proposition 4.3.1

Proof. Without loss of generality, we can reduce to only one mode; the result then extends to the other mode and to the general case because of the linearity of the equation. It is also enough to prove

$$\left\| \Pi_{\pm}\psi^{\varepsilon}(s_2) - \psi^{\varepsilon}_{\pm,\mathrm{app}}(s_2) \right\|_{\Sigma^k_{\varepsilon}} \leq C_k |\ln \delta| \left(\frac{\varepsilon^{3/2}}{\delta^4} + \frac{\sqrt{\varepsilon}}{\delta} \right),$$

the same argument being valid for any $s^* \in [s_1, s_2]$, as long as the constant C_k depends on quantities that are continuous functions of x and ξ in $\{|w(x)| > \delta\}$. In the following, we assume $v^{\varepsilon}_{+}(s_1) = 0$.

We choose δ such that $\varepsilon\delta^{-2} \leq 1$ and consider $\chi^{\delta}_{\pm}(t)$ and $\tilde{\chi}^{\delta}_{\pm}(t)$ as in the preceding section (see Remark 4.3.4). We additionally requires

$$\partial_t \tilde{\chi}^{\delta}_{\pm}(t) = \{h_{\pm}, \tilde{\chi}^{\delta}_{\pm}(t)\}.$$

Both functions $\chi^{\delta}_{\pm}(s_2)$ localize close to the point $z_{-}(s_2)$ while for $t \in [s_1, s_2]$, $\chi^{\delta}_{\pm}(t)$ localizes on separated points, $\Phi^{t,s_2}_{\pm}(z_{-}(s_2))$. We set for $t \in [s_1, s_2]$

$$w^{\varepsilon}_{-}(t) = \mathrm{op}_{\varepsilon}(\tilde{\chi}^{\delta}_{-}(t)) \left(\mathrm{op}_{\varepsilon}(\chi^{\delta}_{-}(t)\Pi^{\varepsilon}_{-})\psi^{\varepsilon}(t) - \mathrm{op}_{\varepsilon}(\chi^{\delta}_{-}(t))\psi^{\varepsilon}_{-,\mathrm{app}}(t) \right)$$

and

$$w_+^\varepsilon(t) = \mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t),$$

with

$$\psi_{-,\mathrm{app}}^\varepsilon(t,x) = \mathrm{op}_\varepsilon(\vec{V}_-(t))v_-^\varepsilon(t).$$

The crucial point of the proof is to establish the equation satisfied by $w_\pm^\varepsilon(t)$.

Lemma 4.3.7. *Let $k \in \mathbb{N}$, $\delta \in (0,1)$ with $\varepsilon\delta^{-2} \leq 1$. For $t \in [s_1, s_2]$, we have in Σ_ε^k,*

$$\begin{aligned} i\varepsilon\partial_t w_+^\varepsilon &= -\frac{\varepsilon^2}{2}\Delta w_+^\varepsilon + \lambda_+ w_+^\varepsilon + \varepsilon\,\mathrm{op}_\varepsilon(\Omega + \varepsilon\Omega_+^{(2)})w_+^\varepsilon + O(\varepsilon^3\delta^{-5}) \\ i\varepsilon\partial_t w_-^\varepsilon &= -\frac{\varepsilon^2}{2}\Delta w_-^\varepsilon + \lambda_- w_-^\varepsilon + \varepsilon\,\mathrm{op}_\varepsilon(\Omega + \varepsilon\Omega_-^{(2)})w_-^\varepsilon + O(\varepsilon^3\delta^{-5}) \\ &\qquad + O((\varepsilon^{5/2}\delta^{-4} + \varepsilon^{3/2}\delta^{-1})|\ln\delta|) \end{aligned}$$

with initial data $w_\pm^\varepsilon(s_1) = O(\sqrt{\varepsilon})$.

Proof of Lemma 4.3.7. Let us begin with $w_+^\varepsilon(t)$. We have

$$\begin{aligned} i\varepsilon\partial_t w_+^\varepsilon(t) =& \mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\mathrm{op}_\varepsilon(H)\psi^\varepsilon(t) \\ &+ i\varepsilon\mathrm{op}_\varepsilon(\partial_t\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t) \\ &+ i\varepsilon\mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(\partial_t\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t). \end{aligned}$$

Using $\partial_t\chi_+^\delta(t) = \{\lambda_+, \chi_+^\delta(t)\}$ and the fact that $\partial_z\chi_+^\delta(t) = 0$ on the support of $\tilde{\chi}_+^\delta(t)$, we obtain

$$\mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(\partial_t\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t) = O(\varepsilon^N\delta^{-2-N}).$$

We choose as before $N = 3$. By Lemma 4.3.5, we are left with

$$i\varepsilon\partial_t w_+^\varepsilon(t) = \mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(h_+ + \varepsilon\Omega + \varepsilon^2\Omega_+^{(2)})\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t)$$

$$+ i\varepsilon \mathrm{op}_\varepsilon(\partial_t \tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t) + O(\varepsilon^3\delta^{-5}).$$

We now take advantage of

$$\left[\mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t)), \mathrm{op}_\varepsilon(h_+ + \varepsilon\Omega + \varepsilon^2\Omega_+^{(2)})\right] = - i\varepsilon\, \mathrm{op}_\varepsilon(\{h_+ + \varepsilon\Omega + \varepsilon^2\Omega_+^{(2)}, \tilde{\chi}_+^\delta(t)\}) + O(\varepsilon^3\delta^{-5}),$$

which implies

$$\begin{aligned}\mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(h_+ + \varepsilon\Omega + \varepsilon^2\Omega_+^{(2)}) =& \mathrm{op}_\varepsilon(h_+ + \varepsilon\Omega + \varepsilon^2\Omega_+^{(2)})\mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t)) \\ &- i\varepsilon\, \mathrm{op}_\varepsilon(\{h_+, \tilde{\chi}_+^\delta(t)\}) + O(\varepsilon^3\delta^{-5}).\end{aligned}$$

We deduce

$$\begin{aligned}\mathrm{op}_\varepsilon(\tilde{\chi}_+^\delta(t))\mathrm{op}_\varepsilon(h_+ + \varepsilon\Omega + \varepsilon^2\Omega_+^{(2)})\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t) =&\ \mathrm{op}_\varepsilon(h_+\varepsilon\Omega + \varepsilon^2\Omega_+^{(2)})w_+^\varepsilon \\ &- i\varepsilon\mathrm{op}_\varepsilon(\{h_+, \tilde{\chi}_+^\delta(t)\})\mathrm{op}_\varepsilon(\chi_+^\delta(t)\Pi_+^\varepsilon)\psi^\varepsilon(t) + O(\varepsilon^3\delta^{-5}).\end{aligned}$$

Combining the latter result with $\partial_t\tilde{\chi}_\pm^\delta(t) = \{h_\pm, \tilde{\chi}_\pm^\delta(t)\}$, we obtain

$$i\varepsilon\partial_t w_+^\varepsilon(t) = \mathrm{op}_\varepsilon(h_+ + \varepsilon\Omega)w_+^\varepsilon(t) + O(\varepsilon^3\delta^{-5})).$$

For $w_-^\varepsilon(t)$, the computation uses the same steps with the difference that there is an additional term for which we use Lemma 4.3.2, which generates an additional remainder in $O((\varepsilon^{5/2}\delta^{-4} + \varepsilon^{3/2}\delta^{-1})|\ln\delta|)$. □

We can now conclude the proof of Proposition 4.3.1. Using Lemma 4.3.7, and by the properties of the unitary propagator associated with the operator

$$-\frac{\varepsilon^2}{2}\Delta + \lambda_\pm + \varepsilon\mathrm{op}_\varepsilon(\Omega) + \varepsilon^2\mathrm{op}_\varepsilon(\Omega_\pm^2),$$

we obtain the existence of a constant C_k such that

$$\|w_+^\varepsilon(s_2)\|_{\Sigma_\varepsilon^k} + \|w_-^\varepsilon(s_2)\|_{\Sigma_\varepsilon^k} \leq C_k((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|). \tag{4.43}$$

Equivalently, using $\tilde{\chi}^\delta(s_2) = \tilde{\chi}^\delta(s_2)\chi^\delta(s_2)$ and the localisation properties of $\psi_{\rm app}^\varepsilon$ (see Lemma B.0.2), the latter relation writes

$$\mathrm{op}_\varepsilon(\tilde{\chi}^\delta(s_2))\psi^\varepsilon(s_2) = \psi_{-,\rm app}^\varepsilon(s_2) + O(\varepsilon\delta^{-3}) + O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|)$$

in Σ_ε^k. The argument could have been worked out between s_1 and any $s \in [s_1, s_2]$, therefore, at this stage of the proof, we have obtained that for any $t \in [s_1, s_2]$ and any cut-off function $\tilde{\chi}$ supported in $\{|w(x)| > \delta\}$, we have in Σ_ε^k,

$$\mathrm{op}_\varepsilon(\tilde{\chi}^\delta(t))\psi^\varepsilon(t) = \psi_{-,\rm app}^\varepsilon(t) + O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|).$$

We now want to extend this approximation to $\psi^\varepsilon(t)$ itself. For this, we consider two cut-off functions χ and θ as in Remark 4.3.4 (1) with $\theta = 1$ on the support of χ. We define $\chi_\pm^\delta$ and θ^δ and $\tilde{\theta}_\pm^\delta$ accordingly. We also ask that

$$\mathrm{supp}(\tilde{\theta}_-^\delta(t)) \subset \{\tilde{\chi}^\delta(t) = 1\}.$$

By the analysis performed above, we have in Σ_ε^k

$$\psi^\varepsilon(s_2) = \mathrm{op}_\varepsilon(1 - \tilde{\theta}_-^\delta(t))\psi^\varepsilon(s_2) + \psi_{-,\rm app}^\varepsilon(t) + O(\varepsilon\delta^{-3}) + O(\sqrt{\varepsilon}|\ln\delta|)$$

and for $t \in [s_1, s_2]$

$$\mathrm{op}_\varepsilon(\tilde{\chi}_-^\delta(t))\psi^\varepsilon(t) = \psi_{-,\rm app}^\varepsilon(t) + O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|).$$

We study

$$w^\varepsilon(t) = \mathrm{op}_\varepsilon(1 - \tilde\theta_-^\delta(t))\psi^\varepsilon(t).$$

By the hypothesis at time $t = s_1$, we have $w^\varepsilon(s_1) = O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|)$. Moreover, for $t \in [s_1, s_2]$,

$$i\varepsilon\partial_t w^\varepsilon = -\frac{\varepsilon^2}{2}\Delta w^\varepsilon(t) + V(x)w^\varepsilon(t) + \varepsilon\mathrm{op}_\varepsilon(q(t))\psi^\varepsilon(t)$$

with $q \in \mathcal{C}^\infty(\mathbb{R}^{2d+1})$ supported in $\{\tilde\chi^\delta(t) = 1\}$ with $\nabla_{x,\xi}q(t) = 0$ close to $\Phi^{t,s_2}(z_-(s_2))$ and $|\partial^\alpha q(t,x,\xi)| \leq C\delta^{-1-|\alpha|}$ for all $\alpha \in \mathbb{N}^{2d}$. We deduce that for $t \in [s_1, s_2]$ and in Σ_ε^k

$$\begin{aligned}
\mathrm{op}_\varepsilon(q(t))\psi^\varepsilon(t) &= \mathrm{op}_\varepsilon(q(t))\mathrm{op}_\varepsilon(\tilde\chi_-^\delta(t))\psi^\varepsilon(t) + O(\varepsilon\delta^{-3}) \\
&= \mathrm{op}_\varepsilon(q(t))\psi^\varepsilon_{-\mathrm{app}}(t) + O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|) \\
&= O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|)
\end{aligned}$$

Therefore, Duhamel formula gives

$$w^\varepsilon(s_2) = w^\varepsilon(s_1) + O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|)$$

and we deduce

$$\psi^\varepsilon(s_2) = \psi^\varepsilon_{-,\mathrm{app}}(s_2) + O((\varepsilon^{3/2}\delta^{-4} + \sqrt{\varepsilon}\delta^{-1})|\ln\delta|),$$

whence Proposition 4.3.1. □

4.4 Passing through the gap region

At this stage of the proof, we have obtained an approximation of the solution as long as it does not enter in the region $\{|w(q)| \leq \delta\}$, i.e. in a neighborhood of the crossing set Υ. We focus now on trajectories that reach their minimal gap inside this region and enter in the region at time $t^\flat - \delta$ and leaves it at time $t^\flat + \delta$.

The strategy is the following.

1. We first perform a change of time and unknown in order to reduce the system (4.1) into a Landau-Zener model in the region $\{|w(q)| \leq \delta\}$.

2. We identify the in-going wave-packet in the new coordinates, i.e. the function $\psi^\varepsilon(t^\flat - \delta)$ that satisfy in $L^2(\mathbb{R}^d)$,

$$\psi^\varepsilon(t^\flat - \delta) = \psi^\varepsilon_{\rm app}(t^\flat - \delta) + O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|).$$

3. We prove that we can use the resolution of the Landau Zener model to calculate the solution at time $t^\flat + \delta$.

4.4.1 Reduction to a Landau Zener model

For passing through the gap, following ideas of [34], we make a Taylor approximation along the trajectory $\Phi_0^{t,t^\flat}(z^\flat) = (q_0(t), p_0(t))$ introduced in Section 4.2.1. We make the time-scaling $t = t^\flat + s\sqrt{\varepsilon}$ and consider the new unknown $u^\varepsilon(s) \in L^2(\mathbb{R}^d, \mathcal{C}^2)$ defined by

$$\psi^\varepsilon(t) = {\rm e}^{\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)} {\rm WP}^\varepsilon_{\Phi_0^{t,t^\flat}(z^\flat)}(u^\varepsilon(s)), \quad t = t^\flat + s\sqrt{\varepsilon} \tag{4.44}$$

where the action $S_0(t, t^\flat, z^\flat)$ is associated with h_0 and $\Phi_0^{t,t^\flat}(z^\flat)$ as introduced in Lemma 4.2.2.

Note that when $t = t^\flat - \delta$, then $s = -s_0 := -\delta/\sqrt{\varepsilon}$ and when $t = t^\flat + \delta$, then $s = s_0 = \delta/\sqrt{\varepsilon}$. For $w \in \mathbb{R}^2$, we introduce the notation

$$A(w) = \begin{pmatrix} w_1 & w_2 \\ \\ w_2 & -w_1 \end{pmatrix}.$$

Lemma 4.4.1. *Let $k \in \mathbb{N}$. The family (u^ε) satisfies that for all $(s, y) \in \mathbb{R}^{2d+1}$*

$$i\partial_s u^\varepsilon = A\left(s\,E + dw(q^\flat)y\right)u^\varepsilon + \sqrt{\varepsilon}\left(\frac{1}{2}\Delta u^\varepsilon + B^\varepsilon(s,y)u^\varepsilon u^\varepsilon\right) \tag{4.45}$$

where there exists a constant $C > 0$ such that for all $s \in [-s_0, s_0]$ and $y \in \mathbb{R}^d$, the smooth hermitian matrix valued potential B^ε satisfies

$$|B^\varepsilon(s,y)| \leq C(\langle y\rangle^2 + s^2).$$

Remark 4.4.2. Recall that $E = r\omega = dw(q^\flat)p^\flat$ and that $q^\flat$ has been chosen as a point of minimal gap of the trajectory, which implies $dw(q^\flat)p^\flat \cdot w(q^\flat) = 0$.

We shall set in the following $\eta(y) := dw(q^\flat)y$ and compare u^ε with the solution u of the equation

$$i\partial_s u = A\left(\eta(y) + sr\omega\right)u.$$

Actually, the leading part $A\left(\eta(y) + sr\omega\right)$ of the system is close to the well-known Landau-Zener system (see references [44, 61] and equation (4.46) below), the analysis of which is well understood as explained in the next section. We shall use the initial data at times $s = -s_0$ with

$$s_0 = \delta/\sqrt{\varepsilon}.$$

The time $-s_0$ corresponds to $t = t^\flat - \delta$, i.e. to the ingoing solution, and we shall deduce the value of the outgoing solution at time $t = t^\flat + \delta$ or equivalently $s = +s_0$. This will be done assuming $\delta \gg \sqrt{\varepsilon}$ and thanks to the scattering result of the next section.

Proof. We use the formalism of Section 4.2.3, together with the observation of Appendix B. The first step consists in observing that

$$\left(i\varepsilon\partial_t + \frac{\varepsilon^2}{2}\Delta - v(x)\right)\psi^\varepsilon(t,x) = \mathrm{e}^{\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)}\mathrm{e}^{\frac{i}{\varepsilon}p_0(t)\cdot(\sqrt{\varepsilon}y)}\Big(i\sqrt{\varepsilon}\partial_s u^\varepsilon(s,y) + \frac{\varepsilon}{2}\Delta_y u^\varepsilon(s,y)$$
$$- \left(v(q_0(t)+\sqrt{\varepsilon}y) - v(q_0(t)) - y\sqrt{\varepsilon}dv(q_0(t))\right)u^\varepsilon(t,y)\Big)\Big|_{y=\frac{x-q_0(t)}{\sqrt{\varepsilon}}}$$
$$= \mathrm{e}^{\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)}\mathrm{e}^{\frac{i}{\varepsilon}p_0(t)\cdot(\sqrt{\varepsilon}y)}\left(i\sqrt{\varepsilon}\partial_s u^\varepsilon(s,y) + \frac{\varepsilon}{2}\Delta_y u^\varepsilon(s,y) + \varepsilon\mathcal{W}^\varepsilon(t,y)u^\varepsilon(s,y)\right)\Big|_{y=\frac{x-q_0(t)}{\sqrt{\varepsilon}}}$$

where $\mathcal{W}^\varepsilon(s,y)$ is a smooth potential such that $|\mathcal{W}^\varepsilon(s,y)| \lesssim |y|^2$ (we have used Lemma B.0.2 (1) and the definition of the action). Moreover,

$$A(w(x))\psi^\varepsilon(t,x) = \mathrm{e}^{\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)}\left(\mathrm{e}^{\frac{i}{\varepsilon}p_0(t)\cdot(\sqrt{\varepsilon}y)}A(w(q_0(t)+\sqrt{\varepsilon}y))u^\varepsilon(s,y)\right)\Big|_{y=\frac{x-q_0(t)}{\sqrt{\varepsilon}}}.$$

Therefore, the equation (4.1) becomes

$$i\sqrt{\varepsilon}\partial_s u^\varepsilon + \frac{\varepsilon}{2}\Delta u^\varepsilon + \varepsilon\mathcal{W}^\varepsilon(s,y)u^\varepsilon(s,y) = A(w(q_0(t)+\sqrt{\varepsilon}y))u^\varepsilon(s,y).$$

Writing $w(q_0(t)+\sqrt{\varepsilon}y) = w(q_0(t)) + \sqrt{\varepsilon}dw(q_0(t)y + O(\varepsilon|y|^2)$

$$i\sqrt{\varepsilon}\partial_s u^\varepsilon = A\left(w(q_0(t^\flat + s\sqrt{\varepsilon})) + \sqrt{\varepsilon}dw(q_0(t^\flat+s\sqrt{\varepsilon}))y\right)u^\varepsilon + O(\varepsilon y^2).$$

We conclude by performing a Taylor expansion in s, writing

$$q_0(t^\flat + s\sqrt{\varepsilon}) = q^\flat + \sqrt{\varepsilon}sp^\flat + O(\varepsilon s^2)$$

and $$w(q_0(t^\flat + s\sqrt{\varepsilon})) + \sqrt{\varepsilon} dw(q_0(t^\flat + s\sqrt{\varepsilon}))y$$

$$= \sqrt{\varepsilon} s dw(q^\flat)p^\flat + \sqrt{\varepsilon} dw(q^\flat)y + O(\varepsilon(s^2 + |y|^2)).$$

□

4.4.2 The Landau-Zener model and the structure of the solutions

The structure of the system (4.45) suggest to consider the model problem

$$\begin{cases} i\partial_s u = A(\eta + sr\omega)u, \\ u(0,\eta) = u_0(\eta) \in \mathcal{C}^2 \end{cases} \tag{4.46}$$

where $\eta \in \mathcal{C}^2$ is a parameter. As we shall see below, this problem can be turned by elementary computations into the Landau-Zener problem

$$\frac{1}{i}\partial_s u_{LZ}(s,z) = \begin{pmatrix} s + z_1 & z_2 \\ z_2 & -s - z_1 \end{pmatrix} u_{LZ}(s,z). \tag{4.47}$$

Therefore, one can deduce the behavior of its solutions from the asymptotics as $s \to \pm\infty$ of the solution of this Landau-Zener problem that are well-known. Besides the historical references [44, 61], the reader can refer to [13] where an analysis of the behavior of the solutions of the Landau Zener model is given with a stationary phase approach or to [34] where the proof is given in terms of parabolic-cylinder functions. We follow the results of the Appendix of [13] which are obtained for η taken in a fixed compact, while the analysis in terms of the size R of this compact is performed in [Appendix, [17]]: as $s \to \pm\infty$

$$u_{LZ}(s) = \mathrm{e}^{i\frac{(s+z_1)^2}{2}+i\frac{z_2^2}{2}\ln|s+z_1|}\begin{pmatrix} u_1^{\pm}(z_2) \\ \\ 0 \end{pmatrix} + \mathrm{e}^{-i\frac{(s+z_1)^2}{2}-i\frac{z_2^2}{2}\ln|s+z_1|}\begin{pmatrix} 0 \\ \\ u_2^{\pm}(z_2) \end{pmatrix} + O(R^2 s^{-1}), \quad (4.48)$$

with

$$u_1^+ = a(z_2)u_1^- - \bar{b}(z_2)u_2^-, \quad u_2^+ = b(z_2)u_1^- + a(z_2)u_2^-$$

where the coefficients a and b are given by (4.21). It is then possible to derive the next Proposition about solutions to (4.46) in which $(\vec{V}_\omega, \vec{V}_\omega^\perp)$ is a direct orthogonal basis of $\mathbb{R}^2$ consisting of normalized eigenvectors of $A(\omega)$ that satisfy

$$A(\omega)\vec{V}_\omega = \vec{V}_\omega \text{ and } A(\omega)\vec{V}_\omega^\perp = -\vec{V}_\omega^\perp.$$

Note that they are uniquely defined up to a phase. The next lemma gives the form of the asymptotics of $u(s,\eta)$ when $s \to \pm\infty$ in such a basis, together with scattering relations.

Lemma 4.4.3. *There exists $\alpha_1, \alpha_2, \omega_1, \omega_2 \in \mathcal{S}(\mathbb{R}^d)$ such that as s goes to $-\infty$ and for $|\eta| \leq R$,*

$$u(s,\eta) = \mathrm{e}^{i\Lambda(s,\eta)}\alpha_1(\eta)\vec{V}_\omega^\perp + \mathrm{e}^{-i\Lambda(s,\eta)}\alpha_2(\eta)\vec{V}_\omega + O(R^3|s|^{-1}),$$

and as s goes to $+\infty$ and $|\eta| \leq R$

$$u(s,\eta) = \mathrm{e}^{i\Lambda(s,\eta)}\omega_1(\eta)\vec{V}_\omega^\perp + \mathrm{e}^{-i\Lambda(s,\eta)}\omega_2(y)\vec{V}_\omega + O(R^3|s|^{-1}),$$

where

$$\Lambda(s,\eta) = \frac{1}{2r}|\omega\cdot\eta + rs|^2 + \frac{1}{2r}|\omega^\perp\cdot\eta|^2 \ln(\sqrt{r}|s|). \quad (4.49)$$

Besides

$$\begin{pmatrix} \omega_1 \\ \omega_2 \end{pmatrix} = S(r^{-1/2}\omega^{\perp} \cdot \eta) \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

with

$$S(\eta) = \begin{pmatrix} a(\eta) & -\bar{b}(\eta) \\ b(\eta) & a(\eta) \end{pmatrix},$$

where the coefficients a *and* b *are given by* (4.21).

Proof. For proving Lemma 4.4.3, we relate the solution u of the system (4.46) with u_{LZ} by use of change of variables and of the rotation matrix

$$\mathcal{R}(\theta) = \begin{pmatrix} \cos\frac{\theta}{2} & -\sin\frac{\theta}{2} \\ \sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix}, \quad \theta \in \mathbb{R}.$$

Indeed, one has for $\eta \in \mathbb{R}^2$,

$$\mathcal{R}(\theta)^{-1}A(\eta)\mathcal{R}(\theta) = \begin{pmatrix} \omega_\theta \cdot \eta & \omega_\theta \wedge \eta \\ \omega_\theta \wedge \eta & -\omega_\theta \cdot \eta \end{pmatrix} \tag{4.50}$$

with $\omega_\theta = (\cos\theta, \sin\theta)$. Therefore, choosing $\theta \in \mathbb{R}$ such that $\omega_\theta = -\omega$, we have

$$\mathcal{R}(\theta)^{-1}A(\eta + sr\omega)\mathcal{R}(\theta) = -\begin{pmatrix} \eta\cdot\omega + sr & \eta\cdot\omega^{\perp} \\ \eta\cdot\omega^{\perp} & -\eta\cdot\omega - sr \end{pmatrix}.$$

We then write

$$\begin{aligned} \frac{1}{i}\partial_s(\mathcal{R}(\theta)^{-1}u) &= \mathcal{R}(\theta)^{-1}A(-\eta - sr\omega)\mathcal{R}(\theta)\,(\mathcal{R}(\theta)^{-1}u) \\ &= \begin{pmatrix} \eta\cdot\omega + sr & \eta\cdot\omega^{\perp} \\ \eta\cdot\omega^{\perp} & -\eta\cdot\omega - sr \end{pmatrix}(\mathcal{R}(\theta)^{-1}u). \end{aligned}$$

and we deduce that

$$v(s,\eta) = \mathcal{R}(\theta)^{-1} u(sr^{-1/2}, r^{1/2}\eta)$$

solves

$$\frac{1}{i}\partial_s v(s,\eta) = \begin{pmatrix} \eta\cdot\omega + s & \eta\cdot\omega^\perp \\ \eta\cdot\omega^\perp & -\eta\cdot\omega - s \end{pmatrix} v(s,\eta),$$

i.e. the equation (4.47) for $z = (\eta\cdot\omega, \eta\cdot\omega^\perp)$ and we can write

$$u(s,\eta) = \mathcal{R}(\theta) u_{LZ}(sr^{1/2}, r^{-1/2}z).$$

Then, we observe

$$\begin{aligned}
\Lambda(s,\eta) &= \frac{1}{2}|sr^{1/2} + r^{-1/2}\eta\cdot\omega|^2 + \frac{1}{2}|r^{-1/2}\eta\cdot\omega^\perp|^2 \ln\left|sr^{1/2} + r^{-1/2}\eta\cdot\omega\right| \\
&= \frac{1}{2}|sr^{1/2} + r^{-1/2}\eta\cdot\omega|^2 + \frac{1}{2}|r^{-1/2}\eta\cdot\omega^\perp|^2 \left[\ln\left|sr^{1/2}\right| + \ln\left|1 + \frac{\eta\cdot\omega}{sr}\right|\right] \\
&= \frac{1}{2}|sr^{1/2} + r^{-1/2}\eta\cdot\omega|^2 + \frac{1}{2}|r^{-1/2}\eta\cdot\omega^\perp|^2 \ln\left|sr^{1/2}\right| + O(R^3|s|^{-1})
\end{aligned}$$

where we have performed a Taylor expansion of $\ln\left|1 + \frac{\eta\cdot\omega}{sr}\right|$ and used $|\eta| \le R$. We deduce that equation (4.48) yields that as $s \to \pm\infty$,

$$u(s,\eta) = \mathrm{e}^{i\Lambda(s,\eta)} u_1^\pm \mathcal{R}(\theta) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \mathrm{e}^{-i\Lambda(s,\eta)} u_2^\pm \mathcal{R}(\theta) \begin{pmatrix} 0 \\ 1 \end{pmatrix} + O(R^3|s|^{-1}).$$

In view of

$$\mathcal{R}(\theta)^{-1} A(\omega) \mathcal{R}(\theta) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

we deduce that we can choose

$$\vec{V}_\omega = \mathcal{R}(\theta) \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \vec{V}_\omega^\perp = \mathcal{R}(\theta) \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

as a basis of eigenvectors of $A(\omega)$. The result of Lemma 4.4.3 then follows with $\alpha_j = u_j^-$ and $\omega_j = u_j^+$, $j \in \{1, 2\}$. □

In the next sections, we will compare u^ε with a solution u of the Landau Zener model problem (4.46) with $\eta = \eta(y)$, and we will use Lemma 4.4.3 to deduce the behavior of u^ε at time $s_0 = t_0/\sqrt{\varepsilon}$ from what we know at time $-s_0 = -t_0/\sqrt{\varepsilon}$ (with $s_0 = \delta/\sqrt{\varepsilon}$). For that, we we need to identify entering profiles α_1 and α_2 associated with our entering data $u(-s_0) := u^\varepsilon(-s_0)$, $s_0 = \delta/\sqrt{\varepsilon} \gg 1$, what we will do in the next section after proving some properties of $u(s, y)$. Then, we will deduce the value of $u(s_0)$ and deduce the value of $u^\varepsilon(s_0)$.

Lemma 4.4.4. *Assume $u(-s_0) \in \Sigma^k(\mathbb{R}^d)$, $k \in \mathbb{N}$. Then, there exists a constant $C_k > 0$ such that for $s \in I_\delta$, we have*

$$\|u(s)\|_{\Sigma^k} \leq C_k \langle s \rangle^k.$$

Proof. One uses a recursive argument starting from the conservation of the L^2-norm. For passing from a control of the Σ^k norm to the control of the Σ^{k+1} norm, one observes that the momenta of length $k+1$ satisfy a closed system with source term which is bounded in L^2 by the recursive assumption at order k. Successive integration of an energy inequality generates the growth in s of the control. □

4.4.3 The in-going wave packet

We prove here the following proposition.

Proposition 4.4.5. *With the assumptions of Theorem 4.1.10, the solution of* (4.1) *satisfies* (4.44) *at time* $t = t^\flat - \delta$*, i.e.* $s = -s_0 = -\delta/\sqrt{\varepsilon}$ *with*

$$u^\varepsilon(-s_0, y) = \mathrm{e}^{-i\Lambda(-s_0,\eta)}\alpha_2(\eta\cdot\omega^\perp)\vec{V}_\omega + O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|) + O(\delta^3\varepsilon^{-1})$$

where $\Lambda(s,\eta)$ *is defined in* (4.49)*,* η *is given by* $\eta = dw(q^\flat)y$ *and we have*

$$\alpha_2(\eta) = \mathrm{Exp}\left(\frac{i}{\varepsilon}S_-^\flat + \frac{i}{4r}(\eta\cdot\omega^\perp)^2\ln(\frac{r}{\varepsilon}) + \frac{i}{2r}|\omega\cdot\eta|^2\right)u_-^{\mathrm{in}}(y), \tag{4.51}$$

Remark 4.4.6. Additionally to the constraints mentioned in Remark 4.3.3, this result suggests that δ has to be chosen so that $\delta^3 \ll \varepsilon$. Note that these constraints are compatible as soon as $\varepsilon^{1/2} \ll \delta \ll \varepsilon^{1/3}$ and that they are optimized with $\delta = \varepsilon^{2/5}$.

Proof. We start from the estimate obtained for $t \le t^\flat - \delta$, namely

$$\begin{aligned}\psi^\varepsilon(t,x) =& \varepsilon^{-d/4}\mathrm{e}^{\frac{i}{\varepsilon}S_-(t,t_0,z_0)+\frac{i}{\varepsilon}p_-(t)(x-q_-(t))}\vec{V}_-(t,\Phi_-^{t,t_0}(z_0))\\ &\times u_-\left(t,\frac{x-q_-(t)}{\sqrt{\varepsilon}}\right) + O((\sqrt{\varepsilon}\delta^{-1}+\varepsilon^{3/2}\delta^{-4})|\ln\delta|)\end{aligned}$$

in Σ_ε^k. We fix $k\in\mathbb{N}$ and make the estimates in this set.

We begin by considering the phase. The asymptotics of Lemma 4.2.1 and Lemma 4.2.2 implies that when $t = t^\flat + \sqrt{\varepsilon}s$ with $s<0$ and $x = q_0(t) + \sqrt{\varepsilon}y$, we have

$$\frac{i}{\varepsilon}S_-(t,t^\flat,z^\flat) = \frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat) - irs^2 + O(\sqrt{\varepsilon}s^3)$$

and

$$\frac{i}{\varepsilon}p_-(t)\cdot(x-q_-(t)) = \frac{i}{\varepsilon}\left(p_0(t) - \sqrt{\varepsilon}s\,{}^t dw(q^\flat)\omega + O(\varepsilon s^2)\right)$$

$$\cdot\Big(x-q_0(t)+\frac{\varepsilon}{2}s^{2\ t}dw(q^\flat)\omega+O(\varepsilon^{3/2}s^3)\Big)$$

$$=\frac{i}{\sqrt{\varepsilon}}p_0(t)\cdot y-is\omega\cdot dw(q^\flat)y+\frac{i}{2}s^2\omega\cdot dw(q^\flat)p_0(t)$$

$$+O(\sqrt{\varepsilon}s^2|y|)+O(\sqrt{\varepsilon}s^3).$$

We observe that

$$\omega\cdot dw(q^\flat)p_0(t)=\omega\cdot dw(q^\flat)p^\flat+O(s\sqrt{\varepsilon})=r+O(s\sqrt{\varepsilon}).$$

Therefore

$$\frac{i}{\varepsilon}S_\pm(t,t^\flat,z^\flat)+\frac{i}{\varepsilon}p_\pm(t)\cdot(x-q_\pm(t))=\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)+\frac{i}{\sqrt{\varepsilon}}y\cdot p_0(t)$$

$$-\frac{i}{2}rs^2-is\omega\cdot dw(q^\flat)y+O(\sqrt{\varepsilon}s^2|y|))+O(\sqrt{\varepsilon}s^3)$$

We now consider the profile and takes into account Corollary 4.1.8. We obtain

$$\psi^\varepsilon(t,x)=\varepsilon^{-d/4}\mathrm{Exp}\left(\frac{i}{\varepsilon}S_0(t^\flat-\sqrt{\varepsilon}s,t^\flat,z^\flat)+\frac{i}{\sqrt{\varepsilon}}p_0(t)\cdot y\right)$$

$$\times\vec{V}_\omega\,\mathrm{Exp}\left(-\frac{i}{2}\Gamma_0 y\cdot y\ln|s\sqrt{\varepsilon}|-\frac{i}{2}rs^2-is\,\omega\cdot dw(q^\flat)y+O(s^3\sqrt{\varepsilon})\right)$$

$$\times\,\mathrm{e}^{\frac{i}{\varepsilon}S^\flat_-}\,u_-^{\mathrm{in}}\left(y+O(s^2\sqrt{\varepsilon})+O(s^2|y|\sqrt{\varepsilon})\right)$$

$$+O((\sqrt{\varepsilon}\delta^{-1}+\varepsilon^{3/2}\delta^{-4})|\ln\delta|)+O(\delta)$$

where the $O(\delta)$ term comes from the approximation of $u_-(t)$ by u_-^{in} and of $\vec{V}_-(t,\Phi_-^{t,t_0}(z_0))$ by $\vec{V}_\omega$ for t close to $t^\flat$ ($|t-t^\flat|\sim\delta$). We deduce

$$u^\varepsilon(-s_0,y)=\vec{V}_\omega\,\mathrm{e}^{\frac{i}{\varepsilon}S^\flat}\,\mathrm{Exp}\left(-\frac{i}{2}\Gamma_0 y\cdot y\ln|s\sqrt{\varepsilon}|-\frac{i}{2}rs^2-is\,\omega\cdot dw(q^\flat)y\right)u_-^{\mathrm{in}}(y)$$

$$+O((\sqrt{\varepsilon}\delta^{-1}+\varepsilon^{3/2}\delta^{-4})|\ln\delta|)+O(\delta)+O(\delta^3\varepsilon^{-1}).$$

Given the definition of $\Lambda(s,\eta)$ in (4.49) with $\eta = dw(q^\flat)y$, we observe

$$\Lambda(s,\eta) = \frac{1}{2r}|\omega\cdot\eta + rs|^2 + \frac{1}{2r}|\omega^\perp\cdot\eta|^2\ln(\sqrt{r}|s|),$$

and since

$$\omega\cdot\eta = dw(q^\flat)p^\flat\cdot\big(dw(q^\flat)y\big) = \omega\cdot dw(q^\flat)y,$$

we obtain

$$\Lambda(s,\eta) = \frac{r}{2}s^2 + s\omega\cdot dw(q^\flat)y + \frac{1}{2r}|\omega\cdot\eta|^2 + \frac{1}{2r}|\omega^\perp\cdot\eta|^2\ln(\sqrt{r}|s|).$$

Moreover

$$\Gamma_0 y\cdot y = r^{-1}\left((\mathrm{Id}_{\mathbb{R}^2} - \omega\otimes\omega)dw(q^\flat)y\right)\cdot\left(dw(q^\flat)y\right) = r^{-1}(dw(q^\flat)y\cdot\omega^\perp)^2.$$

Therefore,

$$\begin{aligned} u^\varepsilon(-s_0,y) = \vec{V}_\omega\,\mathrm{Exp}\,(-i\Lambda(s,y)) \\ \times\,\mathrm{Exp}\left(\frac{i}{\varepsilon}S^\flat_- + \frac{i}{4r}(\eta\cdot\omega^\perp)^2\ln(\frac{r}{\varepsilon}) + \frac{i}{2r}|\omega\cdot\eta|^2\right)u^{\mathrm{in}}_-(y) \\ O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|) + O(\delta) + O(\delta^3\varepsilon^{-1}), \end{aligned}$$

whence the value of $\alpha_2(\eta)$. □

4.4.4 The outgoing solution

We now compare $u^\varepsilon(s)$ with a solution $u_R(s)$ of the Landau-Zener model problem. We consider $\chi_0 \in \mathcal{C}_0^\infty(\mathbb{R}^d)$ and the data at time $s = -s_0$

$$u_R(-s_0) = \mathrm{e}^{i\Lambda(-s_0,\eta)}\alpha_1(\eta)\chi_0(y/R)\vec{V}_\omega \tag{4.52}$$

where $\alpha_1(\eta)$ is given by (4.51), $R > 0$, $\eta = \eta(y)$ and χ_0 is chosen so that $|\eta(y)| \leq R$ when $y/R \in \text{supp}\chi_0$.

Lemma 4.4.7. *Let $u_R(s)$ be the solution of the Landau-Zener model problem* (4.46) *with data $u_R(-s_0)$ given by* (4.52)*, and $u^\varepsilon(s)$ be the solution of* (4.45)*. Let $k \in \mathbb{N}$, then for all $N_0 \in \mathbb{N}$ and for all $s \in [-s_0, s_0]$, in $L^2(\mathbb{R}^d)$*

$$u^\varepsilon(s) - u_R(s) = O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|) + O(\delta) + O(\delta^3\varepsilon^{-1}) + O(R^{-N_0})$$

Proof. Let us first observe that using that $u_-^{\text{in}} \in \mathcal{S}(\mathbb{R}^d)$ (see Proposition 4.4.5), we deduce that we have in Σ_1^k and for any $N_0 \in \mathbb{N}$,

$$u^\varepsilon(-s_0) - u_R(-s_0) = O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|) + O(\delta) + O(\delta^3\varepsilon^{-1}) + O(R^{-N_0}).$$

Therefore, it is enough to prove that u^ε can be approximated by the solution $u(s)$ of (4.46) with data $u^\varepsilon(-s_0)$. We set $u^\varepsilon(s) - u(s) = \sqrt{\varepsilon}u_1^\varepsilon(s)$ and we observe that u_1^ε satisfies $u_1^\varepsilon(-s_0) = 0$ and

$$i\partial_s u_1^\varepsilon - \frac{\sqrt{\varepsilon}}{2}\Delta u_1^\varepsilon(s) - A(sE + dw(q^\flat)y)u_1^\varepsilon - \sqrt{\varepsilon}B^\varepsilon(s,y)u_1^\varepsilon(s) = \frac{\sqrt{\varepsilon}}{2}\Delta u(s) + \sqrt{\varepsilon}B^\varepsilon(s,y)u(s).$$

An energy estimate gives

$$\|u_1^\varepsilon(s)\|_{L^2} \leq C\sqrt{\varepsilon}\int_{-s_0}^{s} \|u(s')\|_{\Sigma^2} ds' \leq C\delta^3\varepsilon^{-1},$$

where we have used Lemma 4.4.4. $\square$

4.5 Proof of the main results

4.5.1 Proof of Theorem 4.1.9

When the trajectory $\Phi_-^{t,t_0}(z_0)$ stays in the domain $\{|w(q)| > \delta\}$, the results of Proposition 4.3.1 apply and implies Theorem 4.1.9.

4.5.2 Proof of Theorem 4.1.10

Inside the gap region, for $t \in [t^\flat - \delta, t^\flat + \delta]$, we apply Lemma 4.3 to pass through. Then over the time $[t^\flat + \delta, t_0 + T]$ we again use Proposition 3.1 to propagate further, with initial data found from the resulting solution $\psi^\epsilon(t^\flat + \delta)$ from Lemma 4.3 in the gap region. Then, we optimize the δ to get the best approximation in terms of ε.

Away from the gap region

Given the initial assumptions of the theorem, we start at time t_0 far from the crossing point with initial data ψ_0^ε satisfying (4.5). We consider the trajectory $\Phi_-^{t,t_0}(z_0)$ and the classical quantities that are associated with it. Applying Proposition 3.1 during the time $[t_0, t^\flat - \delta]$ with $u_+(t_0) = 0$ and $u_-(t_0) = a$, we propagate the solution up to the gap region: at $t = t^\flat - s_0\sqrt{\varepsilon} = t^\flat - \delta$, we have

$$\begin{aligned}\psi^\varepsilon(t,x) =& \varepsilon^{-d/4} e^{\frac{i}{\varepsilon}S_-(t,t_0,z_0)+\frac{i}{\varepsilon}p_-(t)(x-q_-(t))}\vec{V}_-(t,\Phi_-^{t,t_0}(z_0)) \\ & \times u_-\left(t, \frac{x-q_-(t)}{\sqrt{\varepsilon}}\right) + O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|).\end{aligned}$$

Using the minimal gap of the avoided crossing, $\delta_c \gg \sqrt{\varepsilon}$, we are left with error terms $o(1)$.

Passing through the gap region

In this section, we compute an approximation of $\psi^\varepsilon(t^\flat + \delta)$, thanks to the representation of ψ^ε as (4.44) which reduces the analysis to this of function $u^\varepsilon(s)$ satisfying (4.45). Then, by Lemma 4.4.7, it is possible to use Lemma 4.4.3 for linking $u^\varepsilon(+s_0)$ and $u^\varepsilon(-s_0)$. Proposition 4.4.5 allow to identify the entering data at time $s = -s_0$ that we use in Lemma 4.4.3 : $\alpha_1 = 0$ and α_2 satisfying (4.51). We define (ω_1, ω_2) as

$$\begin{aligned} \omega_1(\eta) &= -\overline{b}(r^{-1/2}\eta \cdot \omega^\perp)\alpha_2(\eta) \\ \omega_2(\eta) &= a(r^{-1/2}\eta \cdot \omega^\perp)\alpha_2(\eta). \end{aligned} \tag{4.53}$$

This follows from the formula giving $\begin{pmatrix} \omega_1 \\ \omega_2 \end{pmatrix}$ in Lemma 4.4.3. Besides, we know that when $t = t^\flat + \delta = t^\flat + s_0\sqrt{\varepsilon}$, $\psi^\varepsilon(t)$ satisfies (4.44) with

$$\begin{aligned} u^\varepsilon(s_0, y) = \mathrm{e}^{i\Lambda(s,\eta)}\omega_1(\eta)\vec{V}_\omega^\perp + \mathrm{e}^{-i\Lambda(s,\eta)}\omega_2(y)\vec{V}_\omega \\ + O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|) + O(\delta) + O(\delta^3\varepsilon^{-1}). \end{aligned}$$

This implies that for $t = t^\flat + \delta = t^\flat + \sqrt{\varepsilon}s_0$,

$$\psi^\varepsilon(t,x) = \psi^\varepsilon_+(t,x) + \psi^\varepsilon_-(t,x) + O((\sqrt{\varepsilon}\delta^{-1} + \varepsilon^{3/2}\delta^{-4})|\ln\delta|) + O(\delta) + O(\delta^3\varepsilon^{-1})$$

with

$$\psi^\varepsilon_+(t,x) = \mathrm{e}^{\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat) + \frac{i}{\varepsilon}(x-q_0(t))\cdot p_0(t)} \left(\mathrm{e}^{-i\Lambda(s_0,\eta(y))}\omega_2(\eta)\right)\Big|_{y=\frac{x-q_0(t)}{\sqrt{\varepsilon}}} \vec{V}_\omega, \tag{4.54}$$

$$\psi_-^\varepsilon(t,x) = \mathrm{e}^{\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)+\frac{i}{\varepsilon}(x-q_0(t))\cdot p_0(t)}\left(\mathrm{e}^{+i\Lambda(s_0,\eta(y))}\omega_1(\eta)\right)\Big|_{y=\frac{x-q_0(t)}{\sqrt{\varepsilon}}}\vec{V}_\omega^\perp. \tag{4.55}$$

It remains to see why the functions $\psi_\pm^\varepsilon(t,x)$ can be approximated by wave packets associated with the curves $\Phi_\pm^{t,t^\flat}(z^\flat)$ respectively. For this, we study the asymptotics of the phase and of the profiles for $t > t^\flat$, as we did in Section 4.4.3 for times $t < t^\flat$.

Let us begin with the phases. We then observe that the asymptotics of Lemma 4.2.1 and Lemma 4.2.2 implies that when $t = t^\flat + \sqrt{\varepsilon}s$ with $s > 0$ and $x = q_0(t) + \sqrt{\varepsilon}y$, we have

$$\frac{i}{\varepsilon}S_\pm(t,t^\flat,z^\flat) = \frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat) \mp irs^2 + O(\sqrt{\varepsilon}s^3)$$

and

$$\begin{aligned}\frac{i}{\varepsilon}p_\pm(t)\cdot(x-q_\pm(t)) =& \frac{i}{\varepsilon}\left(p_0(t) \mp \sqrt{\varepsilon}s^t dw(q^\flat)\omega + O(\varepsilon s^2)\right) \\ &\cdot\left(x - q_0(t) \pm \frac{\varepsilon}{2}s^{2\,t}dw(q^\flat)\omega + O(\varepsilon^{3/2}s^3)\right) \\ =& \frac{i}{\sqrt{\varepsilon}}p_0(t)\cdot y \mp is\omega\cdot dw(q^\flat)y + O(\sqrt{\varepsilon}s^2|y|) \\ &\pm \frac{i}{2}s^2\omega\cdot dw(q^\flat)p_0(t) + O(\sqrt{\varepsilon}s^3) + O(\varepsilon s^3)\end{aligned}$$

We observe that

$$\omega\cdot dw(q^\flat)p_0(t) = \omega\cdot dw(q^\flat)p^\flat + O(s\sqrt{\varepsilon}) = r + O(s\sqrt{\varepsilon}).$$

Therefore

$$\frac{i}{\varepsilon}p_\pm(t)\cdot(x-q_\pm(t)) = \frac{i}{\sqrt{\varepsilon}}y\cdot p_0(t) \mp is\omega\cdot dw(q^\flat)y \pm \frac{i}{2}rs^2 + O(\sqrt{\varepsilon}s^2|y|)) + O(\sqrt{\varepsilon}s^3).$$

Then,

$$\frac{i}{\varepsilon}S_\pm(t,t^\flat,z^\flat)+\frac{i}{\varepsilon}p_\pm(t)\cdot(x-q_\pm(t))=\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)+\frac{i}{\sqrt{\varepsilon}}y\cdot p_0(t)$$
$$\mp\frac{i}{2}rs^2\mp is\omega\cdot dw(q^\flat)y+O(\sqrt{\varepsilon}s^2|y|))+O(\sqrt{\varepsilon}s^3)$$

Given the definition of $\Lambda(s,\eta)$, (4.49),

$$i\Lambda(s,\eta)=\frac{i}{2r}|\omega\cdot\eta+rs|^2+\frac{i}{4r}|\omega^\perp\cdot\eta|^2\ln(rs^2),$$

and since

$$\omega\cdot\eta=dw(q^\flat)p^\flat\cdot\left(\frac{w(q^\flat)}{\sqrt{\varepsilon}}+dw(q^\flat)y\right)=\omega\cdot dw(q^\flat)y,$$

we obtain

$$i\Lambda(s,\eta)=\frac{i}{2r}\left(|\omega\cdot\eta|^2+2rs\omega\cdot dw(q^\flat)y+r^2s^2\right)+\frac{i}{4r}|\omega^\perp\cdot\eta|^2\ln(rs^2)$$
$$=\frac{i}{2r}|\omega\cdot\eta|^2+is\omega\cdot dw(q^\flat)y+\frac{i}{2}rs^2+\frac{i}{4r}|\omega^\perp\cdot\eta|^2\ln(rs^2)$$

Using all of these together, we have

$$\frac{i}{\varepsilon}S_\pm(t,t^\flat,z^\flat)+\frac{i}{\varepsilon}p_\pm(t)\cdot(x-q_\pm(t))=\frac{i}{\varepsilon}S_0(t,t^\flat,z^\flat)$$
$$+\frac{i}{\sqrt{\varepsilon}}y\cdot p_0(t)\mp i\Lambda(s,\eta)\pm\frac{i}{2r}|\omega\cdot\eta|^2\pm\frac{i}{2r}|\omega^\perp\cdot\eta|^2\left(\ln(\sqrt{r}s)\right)$$
$$+O(\sqrt{\varepsilon}s^2|y|))+O(\sqrt{\varepsilon}s^3)$$

At this stage of the proof, we are able to see the wave packet structure of the functions $\psi^\varepsilon_\pm(t^\flat+\delta)$ defined in (4.54) and (4.55). Let us study precisely $\psi^\varepsilon_-(t,x)$, the computation for the other mode being similar. In view of the relations stated above, we have obtained

$$\psi^\varepsilon_-(t,x)=\mathrm{e}^{\frac{i}{\varepsilon}S_-(t,t^\flat,z^\flat)+\frac{i}{\varepsilon}(x-q_-(t))\cdot p_-(t)+\frac{i}{2r}|\omega\cdot\eta|^2+\frac{i}{2r}|\omega^\perp\cdot\eta|^2\ln(\sqrt{r}s)}\omega_1(\eta)\vec{V}^\perp_\omega$$

$$+O(\sqrt{\varepsilon}s^2|y|)+O(\sqrt{\varepsilon}s^3).$$

Here again

$$\frac{1}{r}(\omega^\perp\cdot\eta(y))^2\ln(s\sqrt{r})=\Gamma_0 y\cdot y\ln(s\sqrt{r})=\Gamma_0 y\cdot y\ln(s\sqrt{\varepsilon})+\frac{1}{2r}(\omega^\perp\cdot\eta(y))^2\ln(\frac{r}{\varepsilon}).$$

and we obtain for $t=t^\flat+\delta=t^\flat+s_0\sqrt{\varepsilon}$

$$\psi_-^\varepsilon(t,x)=V_\omega^\perp\,\mathrm{Exp}\left(\frac{i}{\varepsilon}S_-(t,t^\flat,z^\flat)+\frac{i}{\varepsilon}(x-q_-(t))\cdot p_-(t)\right)$$
$$\times\left(\mathrm{Exp}\left(\frac{i}{2}\Gamma_0 y\cdot y\ln s\right)\mathrm{Exp}\left(\frac{i}{4r}(\omega^\perp\cdot\eta(y))^2\ln(r/\varepsilon)+\frac{i}{2r}(\omega\cdot\eta)^2\right)\omega_1(\eta)\right)\Big|_{y=\frac{x-q_0(t)}{\sqrt{\varepsilon}}}$$
$$+O(\sqrt{\varepsilon}s^2|y|)+O(\sqrt{\varepsilon}s^3).$$

Using that $\omega_1\left(\frac{x-q_0(t)}{\sqrt{\varepsilon}}\right)=\omega_1\left(\frac{x-q_-(t)}{\sqrt{\varepsilon}}\right)+O(\sqrt{\varepsilon}s^2)$ with $O(\sqrt{\varepsilon}s^2)=O(\delta^2\varepsilon^{-1/2})$, we identify a wave packet

$$\psi_-^\varepsilon(t,x)=\mathrm{e}^{\frac{i}{\varepsilon}S_-(t,t^\flat,z^\flat)}\mathrm{WP}^\varepsilon_{\Phi_-^{t,t^\flat}(z^\flat)}\left(\mathrm{e}^{\frac{i}{2}\Gamma_0 y\cdot y\ln(s)}\mathrm{e}^{\frac{i}{4r}(\omega^\perp\cdot\eta(y))^2\ln(r/\varepsilon)+\frac{i}{2r}(\omega\cdot\eta)^2}\omega_1(\eta)\right)V_\omega^\perp$$
$$+O(\sqrt{\varepsilon}s^2(1+|y|))+O(\sqrt{\varepsilon}s^3).$$

For $t\in[t^\flat-\delta,t^\flat+\delta]$, $O(\sqrt{\varepsilon}s^2(1+|y|))+O(\sqrt{\varepsilon}s^3)=O(\sqrt{\varepsilon}\delta^2(1+|y|))+O(\sqrt{\varepsilon}\delta^3)$. Using the minimal gap found $\delta_c=\sqrt{\epsilon}$ and $y=\frac{x-q(t)}{\sqrt{\varepsilon}}$ for this region, we are left with the error terms $O(\delta^3\varepsilon^{-1})$. In view of (4.18), this suggests to set

$$u_-^{\mathrm{out}}(y)=\mathrm{Exp}\left(\frac{i}{4r}(\omega^\perp\cdot\eta(y))^2\ln(r/\varepsilon)+\frac{i}{2r}|\omega\cdot\eta|^2\right)\omega_1(\eta)$$
$$=-\mathrm{Exp}\left(\frac{i}{4r}(\omega^\perp\cdot\eta(y))^2\ln(r/\varepsilon)+\frac{i}{2r}|\omega\cdot\eta|^2\right)\bar{b}(r^{-1/2}\eta\cdot\omega^\perp)\alpha_2(\eta)$$

A similar computation for the plus mode gives

$$u_+^{\mathrm{out}}(y)=\mathrm{Exp}\left(-\frac{i}{4r}(\omega^\perp\cdot\eta(y))^2\ln(r/\varepsilon)-\frac{i}{2r}|\omega\cdot\eta|^2\right)\omega_2(\eta),$$

$$= \mathrm{Exp}\left(-\frac{i}{4r}(\omega^{\perp}\cdot\eta(y))^2\ln(r/\varepsilon) - \frac{i}{2r}|\omega\cdot\eta|^2\right) a(r^{-1/2}\eta\cdot\omega^{\perp})\alpha_2(\eta).$$

In view of (4.51), we deduce

$$u_+^{\mathrm{out}}(y) = \mathrm{e}^{\frac{i}{\varepsilon}S_-^{\flat}} a(r^{-1/2}\eta\cdot\omega^{\perp})u_-^{\mathrm{in}}(y),$$
$$u_-^{\mathrm{out}}(y) = -\mathrm{e}^{\frac{i}{\varepsilon}S_-^{\flat}}\mathrm{Exp}\left(\frac{i}{2r}(\omega^{\perp}\cdot\eta(y))^2\ln(r/\varepsilon) + \frac{i}{r}|\omega\cdot\eta|^2\right)\overline{b}(r^{-1/2}\eta\cdot\omega^{\perp})u_-^{\mathrm{in}}(y).$$

which is equivalent to (4.19).

Leaving the gap region

We define $u_{\pm}(t,y)$ for $t \geq t^{\flat}+\delta$ as the solution of (4.14) satisfying (4.18). Then, we have (4.23) when $t = t^{\flat}+\delta$ and the result for $[t \in t^{\flat}+\delta, T]$ comes by applying Proposition 4.3.1.

Chapter 5

Conclusion

In conclusion, we have gained important information about the behavior of a system as it passes through a conical intersection, or an avoided crossing. In the first part, we investigated a specific codimension 1 problem. For the system passing through the crossing, we found the approximate solutions to the Schrödinger equation given by Corollary (3.3.3). Then for the system with the avoided crossing, we found the approximate solutions given by Corollary (3.1.4). We also found the transition probabilities for each case, thus indicating that it is more likely to transition from the lower to the upper energy level in the crossing case. The probability of transitioning to the upper level depends on the momentum at the point of minimal gap for the avoided crossing. A greater initial momentum provides a higher probability of transitioning.

In the second part, we constructed a new form of solutions to the Schrödinger equation given by Theorem (4.1.10), for a general codimension 2 crossing. We gave explicit transition formulas for the profile when passing through a conical crossing point, including precise computation of the transformation of the phase, which provided solutions that are able to be adapted to more general types of system that previous results.

There are a few interesting observations we may make from the results found. For both the codimension 1 crossings and avoided crossing, we see that when we send in a Gaussian wave packet, we still get a Gaussian wave packet out. Comparing to the codimension 2 case, we see that is not true, a Gaussian wave packet is not preserved after passing through the crossing. This can be seen from the results in Chapter 4, as well as [34]. In the solutions found in Chapter 4, there is a Gamma function which is dependent on the space variable, and therefore the wave packet is no longer Gaussian after passing through the crossing.

Future work on these topics can also be done. With the solutions found for the codimension 1 systems, since Gaussian functions are preserved when propagating though the crossing and avoided crossing, we can use these to find Herman-Kluk approximations, or frozen and thawed Gaussian approximation. We may also continue work on the codimension 2 problem, where we also consider the corresponding avoided crossing in the same setting. Results for a codimension 2 avoided crossing are in progress, [15].

Appendix A

Semi-classical pseudo-differential calculus

We recall here results about semi-classical pseudo-differential operators. We consider matrix-valued functions $a \in \mathcal{C}^\infty(\mathbb{R}^{2d}, \mathcal{C}^{2,2})$ which are bounded together with their derivatives. Then, one defines the Weyl semi-classical pseudo-differential operator of symbol a as

$$\mathrm{op}_\varepsilon\,(a)f(x) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \mathrm{e}^{\frac{i}{\varepsilon}\xi\cdot(x-y)} a\left(\frac{x+y}{2}, \xi\right) f(y)dy\, d\xi, \quad \forall f \in \mathcal{S}(\mathbb{R}^d, \mathcal{C}^2). \tag{A.1}$$

The reader may found proofs of the results presented here in [9, 62, 24], for instance. In the following, we denote by $z = (x, \xi) \in \mathbb{R}^{2d}$ the variable of the functions $a \in \mathcal{C}^\infty(\mathbb{R}^{2d}, \mathcal{C}^{2,2})$.

The Calderón-Vaillancourt theorem [3] ensures the existence of constants $C_d, n_d > 0$ such that for every $a \in \mathcal{C}^\infty(\mathbb{R}^d, \mathcal{C}^{2,2})$, bounded with bounded derivatives, one has

$$\|\,\mathrm{op}_\varepsilon\,(a)\|_{\mathcal{L}(L^2(\mathbb{R}^d,\mathcal{C}^2))} \leq C_d\, N_d^\varepsilon(a), \tag{A.2}$$

where

$$N_d^{\varepsilon}(a) := \sum_{\alpha\in\mathbb{N}^{2d}, |\alpha|\leq n_d} \varepsilon^{|\alpha|} \sup_{\mathbb{R}^d\times\mathbb{R}^d} |\partial_{x,\xi}^{\alpha} a|.$$

Since we are going to deal with symbols that are singular in x, we shall also use the estimate

$$\|\mathrm{op}_{\varepsilon}\,(a)\|_{\mathcal{L}(L^2(\mathbb{R}^d))} \leq c \sup_{\substack{\beta\in\mathbb{N}^d \\ |\beta|\leq d+1}} \sup_{x,\xi\in\mathbb{R}^d} \left|(1+|\xi|)^{-d-1}\partial_{\xi}^{\beta} a(x,\xi)\right|. \tag{A.3}$$

for some constant c independent of a and ε. The proof of this estimate can be found in [1] (chapter 2) for example.

The calculus extends to functions a that are polynomial functions in ξ with coefficients depending smoothly on x. We assume that there exists $N\in\mathbb{N}$, such that

$$\forall\alpha\in\mathbb{N}^{2d},\ \ \exists C_{\alpha},\ \ |\partial_z^{\alpha} a(z)| \leq C_{\alpha}\langle z\rangle^{N-|\alpha|}. \tag{A.4}$$

Then, the operator $\mathrm{op}_{\varepsilon}(a)$ maps $\Sigma_{\varepsilon}^{N+k}$ into Σ_{ε}^{N}.

Matrix-valued pseudodifferential operators enjoy a symbolic calculus:

Proposition A.0.1. *Let $a,b\in\mathcal{C}_0^{\infty}(\mathbb{R}^d,\mathcal{C}^{2,2})$, then*

$$\mathrm{op}_{\varepsilon}\,(a)\ \mathrm{op}_{\varepsilon}\,(b) = \mathrm{op}_{\varepsilon}\,(ab) + \frac{\varepsilon}{2i}\ \mathrm{op}_{\varepsilon}\,(\{a,b\}) + \varepsilon^2 R_{\varepsilon}^{(1)},$$

with $\{a,b\} = \sum_{j=1}^d \partial_{\xi_j} a\,\partial_{x_j} b - \partial_{x_j} a\,\partial_{\xi_j} b$ and

$$[\mathrm{op}_{\varepsilon}\,(a), \mathrm{op}_{\varepsilon}\,(b)] = \mathrm{op}_{\varepsilon}\,([a,b]) + \frac{\varepsilon}{2i}(\mathrm{op}_{\varepsilon}\,(\{a,b\}) - \mathrm{op}_{\varepsilon}\,(\{b,a\})) + \varepsilon^2 R_{\varepsilon}^{(2)},$$

$$\|R_{\varepsilon}^{(j)}\|_{\mathcal{L}(L^2(\mathbb{R}^d,\mathcal{C}^2))} \leq C \sup_{|\alpha|+|\beta|=2} N_d^{\varepsilon}(\partial_{\xi}^{\alpha}\partial_x^{\beta} a) N_d^{\varepsilon}(\partial_{\xi}^{\beta}\partial_x^{\alpha} b), \quad j\in\{1,2\},$$

for some constant $C>0$ independent of a, b and ε.

Similar results hold for symbols satisfying (A.4) in the adequate functional spaces.

Remark A.0.2. The term of order ε^2 above has symmetries so that if a and b are scalar valued and $[a,b]=0$,

$$[\mathrm{op}_\varepsilon\,(a), \mathrm{op}_\varepsilon\,(b)] = \frac{\varepsilon}{i}\,\mathrm{op}_\varepsilon\,(\{a,b\}) + O(\varepsilon^3).$$

Besides it has a particularly simple expression when the function b does not depend on x. The following hold in $\mathcal{L}(L^2(\mathbb{R}^d, \mathcal{C}^2))$:

$$\begin{aligned}
\mathrm{op}_\varepsilon\,(b)\,\mathrm{op}_\varepsilon\,(a) =& \mathrm{op}_\varepsilon\,(ba) + \frac{\varepsilon}{2i}\sum_{j=1}^{d}\mathrm{op}_\varepsilon\,(\partial_{\xi_j} b\,\partial_{x_j} a) + \frac{\varepsilon^2}{8}\sum_{1\le \ell,p\le d}\mathrm{op}_\varepsilon\,(\partial^2_{\xi_\ell \xi_p} b\,\partial^2_{x_\ell x_p} a) + O(\varepsilon^3),\\
\mathrm{op}_\varepsilon\,(a)\,\mathrm{op}_\varepsilon\,(b) =& \mathrm{op}_\varepsilon\,(ab) - \frac{\varepsilon}{2i}\sum_{j=1}^{d}\mathrm{op}_\varepsilon\,(\partial_{x_j} a\,\partial_{\xi_j} b) + \frac{\varepsilon^2}{8}\sum_{1\le \ell,p\le d}\mathrm{op}_\varepsilon\,(\partial^2_{x_\ell x_p} a\,\partial^2_{\xi_\ell \xi_p} b) + O(\varepsilon^3).
\end{aligned}$$

Appendix B

Localization of wave packets

The wave packets enjoy localization properties. We use here the notations introduced in Appendix A and we use the notations $\widehat{a}$ for denoting (non semiclassical) pseudodifferential operators, $\widehat{a} = \mathrm{op}_1(a)$.

Lemma B.0.1. *Let* $z_0 = (q,p) \in \mathbb{R}^{2d}$, $\varphi \in \mathcal{S}(\mathbb{R}^d)$ *and* $a \in \mathcal{C}^\infty(\mathbb{R}^{2d})$ *satisfying* (A.4) *for some* $N \in \mathbb{N}$. *Then,*

$$\mathrm{op}_\varepsilon(a)\,\mathrm{WP}^\varepsilon_{z_0}(\varphi) = \mathrm{WP}^\varepsilon_{z_0}\left(\widehat{a(z_0 + \sqrt{\varepsilon} z)}\,\varphi\right).$$

Proof. We have

$$\mathrm{op}_\varepsilon(a)\,\mathrm{WP}^\varepsilon_{z_0}(\varphi)(x) = (2\pi\varepsilon)^{-d}\varepsilon^{-d/4}\int_{\mathbb{R}^{2d}} \mathrm{e}^{\frac{i}{\varepsilon}\xi\cdot(x-y)} a\left(\frac{x+y}{2},\xi\right)\mathrm{e}^{\frac{i}{\varepsilon}p\cdot(y-q)}\varphi\left(\frac{y-q}{\sqrt{\varepsilon}}\right)dyd\xi$$

We make the changes of variables $\tilde{y} = \frac{y-q}{\sqrt{\varepsilon}}$, $\tilde{x} = \frac{x-q}{\sqrt{\varepsilon}}$, and $\tilde{\xi} = \frac{\xi-p}{\sqrt{\varepsilon}}$ and we obtain

$\mathrm{op}_\varepsilon(a)\,\mathrm{WP}^\varepsilon_{z_0}(\varphi)(x)$

$$= (2\pi)^{-d}\varepsilon^{-d/4}\int_{\mathbb{R}^{2d}} \mathrm{e}^{\frac{i}{\varepsilon}(\tilde{\xi}\sqrt{\varepsilon}+p)\cdot(\sqrt{\varepsilon}\tilde{x}-\sqrt{\varepsilon}\tilde{y})} a\left(\frac{\tilde{x}+\tilde{y}}{2}\sqrt{\varepsilon}+q, \tilde{\xi}\sqrt{\varepsilon}+p\right) e^{\frac{i}{\varepsilon}p\cdot(\sqrt{\varepsilon}\tilde{y})}\varphi(\tilde{y})\, d\tilde{y}d\tilde{\xi}$$
$$= (2\pi)^{-d}\varepsilon^{-d/4}e^{\frac{i}{\sqrt{\varepsilon}}p\cdot\tilde{x}}\int_{\mathbb{R}^{2d}} \mathrm{e}^{i\tilde{\xi}\cdot(\tilde{x}-\tilde{y})} a\left(\frac{\tilde{x}+\tilde{y}}{2}\sqrt{\varepsilon}+q, \tilde{\xi}\sqrt{\varepsilon}+p\right)\varphi(\tilde{y})\, d\tilde{y}d\tilde{\xi}$$

Then we can define the following,

$$\Phi(y) = (2\pi)^{-d}\int_{\mathbb{R}^{2d}} \mathrm{e}^{i\tilde{\xi}\cdot(y-\tilde{y})} a\left(\frac{y+\tilde{y}}{2}\sqrt{\varepsilon}+q, p+\sqrt{\varepsilon}\tilde{\xi}\right)\varphi(\tilde{y})\, d\tilde{y}d\tilde{\xi}.$$

By the definition of pseudos

$$\Phi(x) = \mathrm{op}_1(a(q+\sqrt{\varepsilon}x, p+\sqrt{\varepsilon}\xi))\varphi(x)$$

and by the calculus we have performed,

$$\mathrm{op}_\varepsilon(a)\,\mathrm{WP}^\varepsilon_{z_0}(\varphi)(q+\sqrt{\varepsilon}\tilde{x}) = \varepsilon^{-d/4}\mathrm{e}^{\frac{i}{\sqrt{\varepsilon}}p\cdot\tilde{x}}\Phi(\tilde{x}).$$

Doing back the change $x = q+\sqrt{\varepsilon}\tilde{x}$, we obtain

$$\mathrm{op}_\varepsilon(a)\,\mathrm{WP}^\varepsilon_{z_0}(\varphi)(x) = \varepsilon^{-d/4}\mathrm{e}^{\frac{i}{\varepsilon}p\cdot(x-q)}\Phi((x-q)/\sqrt{\varepsilon}).$$

Which means

$$\mathrm{op}_\varepsilon(a)\,\mathrm{WP}^\varepsilon_{z_0}(\varphi) = \mathrm{WP}^\varepsilon_{z_0}(\Phi).$$

□

This Lemma has several important consequences.

Lemma B.0.2. *Let* $z_0 = (q,p) \in \mathbb{R}^{2d}$*,* $\varphi \in \mathcal{S}(\mathbb{R}^d)$ *and* $a \in \mathcal{C}^\infty(\mathbb{R}^{2d})$ *satisfying* (A.4) *for some* $N \in \mathbb{N}$*. Then, we have the following properties:*

1. For all $n_0, k \in \mathbb{N}$, there exists a constant C_k such that

$$\left\| \operatorname{op}_\varepsilon(a)\, \mathrm{WP}^\varepsilon_{z_0}(\varphi) - \mathrm{WP}^\varepsilon_{z_0}\left(\widehat{P_a^{(n_0)}(z\sqrt{\varepsilon})\varphi} \right) \right\|_{\Sigma_\varepsilon^{k+N}} \leq C_k\, \varepsilon^{\frac{n_0+1}{2}} \, \|\varphi\|_{\Sigma^{k+n_0+1}}$$

where $P_a^{(n_0)}(z)$ is the Taylor polynomial at order n_0 of a in z_0:

$$P_a^{(n_0)}(h) = a(z_0) + \nabla a(z_0) \cdot H + \frac{1}{2} \nabla^2 a(z_0) h \cdot h + ... + \frac{1}{(n_0)!} d^{n_0} a(z_0)[h]^{n_0}.$$

2. Assume moreover that $a(z) = 1$ for $|z - z_0| \leq 1$ and $a(z) = 0$ if $|z - z_0| > 2$. Then, for any $n \in \mathbb{N}$, there exists a constant $C'_{k,n}$ such that

$$\|\mathrm{WP}^\varepsilon_{z_0}(\varphi) - \operatorname{op}(a)\, \mathrm{WP}^\varepsilon_{z}(\varphi)\|_{\Sigma_\varepsilon^k} \leq C'_k \varepsilon^{n/2} \|\varphi\|_{\Sigma^{k+n}}.$$

Proof. Let us prove Point (1). Applying previous lemma,

$$\begin{aligned} &\|\operatorname{op}_\varepsilon(a)\, \mathrm{WP}^\varepsilon_{z_0}(\varphi) - \mathrm{WP}^\varepsilon_{z_0}(\widehat{P_a^{(n_0)}(z\sqrt{\varepsilon})}\varphi)\|_{\Sigma_\varepsilon^k} \\ &\qquad = \|\mathrm{WP}^\varepsilon_{z_0}(\widehat{a(z_0 + \sqrt{\varepsilon} z)}\, \varphi) - \mathrm{WP}^\varepsilon_{z_0}(\widehat{P_a^{(n_0)}(z\sqrt{\varepsilon})}\varphi)\|_{\Sigma_\varepsilon^k} \\ &\qquad = \|\mathrm{WP}^\varepsilon_{z_0}((\widehat{a(z_0 + \sqrt{\varepsilon} z)}\ - \widehat{P_a^{(n_0)}(z\sqrt{\varepsilon})})\varphi)\|_{\Sigma_\varepsilon^k}. \end{aligned}$$

There exists a constant C'_k such that for all profiles $\varphi \in \mathcal{S}(\mathbb{R}^d)$,

$$\|\mathrm{WP}^\varepsilon_{z_0}(\varphi)\|_{\Sigma_\varepsilon^k} \leq C'_k \|\varphi\|_{\Sigma^k}$$

hence

$$\|\mathrm{WP}^\varepsilon_{z_0}((\widehat{a(z_0 + \sqrt{\varepsilon} z)}\ - \widehat{P_a^{(n_0)}(z\sqrt{\varepsilon})})\varphi)\|_{\Sigma_\varepsilon^k} \leq C'_k \|(\widehat{a(z_0 + \sqrt{\varepsilon} z)} - \widehat{P_a^{(n_0)}(z\sqrt{\varepsilon})})\varphi\|_{\Sigma^k}.$$

We have

$$a(z_0 + \sqrt{\varepsilon} z) - P_a^{(n_0)}(z\sqrt{\varepsilon}) = \varepsilon^{\frac{n_0+1}{2}} r(\sqrt{\varepsilon} z)[z]^{n_0+1}$$

where $r \in \mathcal{C}^\infty(\mathbb{R}^{2d})$ is a tensor of order $n+1$, bounded together with its derivatives.

$$r(z) = \frac{1}{n_0!} \int_0^1 d^{(n_0+1)} a(z_0 + sz)(1-s)^{n_0} ds$$

We observe that $z \mapsto r(\sqrt{\varepsilon} z)[z]^{n_0+1}$ satisfies (A.4), therefore there exists a constant $C > 0$ such that

$$\|\widehat{r(\sqrt{\varepsilon}z)[z]}^{n_0+1} \varphi\|_{\Sigma^k} \leq C \, \|\varphi\|_{\Sigma^{k+n_0+1}},$$

which concludes the proof.

For Point (2), we just need to observe that since a is identically equal to 1 close to z_0, all its Taylor polynomial $P_a^{(n)}(z)$ are equal to 1 for all $n \in \mathbb{N}$. We then apply Point (1) with $n_0 = n-1$.

$\square$

Appendix C

Matricial relations

Setting for $w = (w_1, w_2) \in \mathbb{R}^2$

$$A(w) = \begin{pmatrix} w_1 & w_2 \\ w_2 & -w_1 \end{pmatrix},$$

we have for $w, u \in \mathbb{R}^2$

$$A(w)A(u) = \begin{pmatrix} w \cdot u & w \wedge u \\ -w \wedge u & w \cdot u \end{pmatrix}$$

where $w \wedge u = w_1 u_2 - w_2 u_1$.

C.1 The $B_\pm$ matrices

We prove here results about the matrices $B_\pm$ introduced in (4.10). We recall that for $\xi \in \mathbb{R}^d$, $\xi \cdot \nabla$ denotes the (scalar) operator

$$\xi \cdot \nabla = \sum_{j=1}^{d} \xi_j \partial_{\xi_j}.$$

Lemma C.1.1. *For $\xi \in \mathbb{R}^d$ and $w \in \mathcal{C}^\infty(\mathbb{R}^d, \mathbb{R}^2)$,*

$$\xi \cdot \nabla \Pi_+ = -\frac{\xi \cdot \nabla w(x) \wedge w(x)}{2|w(x)|^3} A(w^\perp(x)), \quad w^\perp = (-w_2, w_1).$$

Therefore,

$$\Pi_-(x)\xi \cdot \nabla \Pi_+(x) - \Pi_+(x)\xi \cdot \nabla \Pi_+(x) = -\frac{\xi \cdot \nabla w(x) \wedge w(x)}{2|w(x)|^2} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$

Proof. Since $\Pi_+(x) = \frac{1}{2}(\mathrm{Id} + A\left(\frac{w(x)}{|w(x)|}\right)$, a straightforward computation gives

$$\begin{aligned} \xi \cdot \nabla \Pi_+(x) =& \frac{1}{2|w(x)|}\left(A(\xi \cdot \nabla w(x)) - \frac{w(x) \cdot (\xi \cdot \nabla w(x))}{|w(x)|^2} A(w(x))\right. \\ =& \frac{1}{2|w(x)|^3}(w_2\, \xi \cdot \nabla w_1 - w_1\, \xi \cdot \nabla w_2) A(w_2, -w_1) \end{aligned}$$

whence the first formula. Then, we write

$$\begin{aligned} \Pi_-(x)\xi \cdot \nabla \Pi_+(x) - &\Pi_+(x)\xi \cdot \nabla \Pi_+(x) \\ &= -\frac{\xi \cdot \nabla w(x) \wedge w(x)}{2|w(x)|^3}\big(\Pi_-(x)A(w^\perp(x)) - \Pi_+(x)A(w^\perp(x))\big) \\ &= -\frac{\xi \cdot \nabla w(x) \wedge w(x)}{2|w(x)|^4} A(w(x))A(w^\perp(x)) \\ &= -\frac{\xi \cdot \nabla w(x) \wedge w(x)}{2|w(x)|^2} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \end{aligned}$$

□

C.2 Superadiabatic projectors

In this section we denote by $a\sharp_\varepsilon b$ the symbol of the operator $\mathrm{op}_\varepsilon(a)\circ\mathrm{op}_\varepsilon(b)$ as described in Appendix A.

Lemma C.2.1. *There exists $\mathbb{P}_\pm^{(1)}$, $\mathbb{P}_\pm^{(2)}$, $\Omega_\pm^{(1)}$ and $\Omega_\pm^{(2)}$ such that if*

$$\Pi_\pm^\varepsilon(x,\xi)=\Pi_\pm(x)+\varepsilon\mathbb{P}_\pm^{(1)}(x,\xi)+\varepsilon^2\mathbb{P}_\pm^{(2)}(x,\xi),$$

we have

$$\Pi_\pm^\varepsilon\sharp_\varepsilon H=(h_\pm+\varepsilon\,\Omega_\pm^{(1)}+\varepsilon^2\,\Omega_\pm^{(2)})\sharp_\varepsilon\Pi_\pm^\varepsilon+\varepsilon^3R^\varepsilon(x,\xi) \tag{C.1}$$

where for $(x,\xi)\in\mathbb{R}^{2d}\setminus\Upsilon$, for all $\alpha,\beta\in\mathbb{N}^d$, there exists constants $C_{\alpha,\beta},\ p_\alpha>0$ such that

$$|\partial_x^\alpha\partial_\xi^\beta R^\varepsilon(x,\xi)|\le C_{\alpha,\beta}\langle x\rangle^{(|\alpha|+3)(1+n_0)}|w(x)|^{-|\alpha|-5}.$$

Moreover, one has the following propertoes

1. *One has*

$$\mathbb{P}_\pm^{(1)}(x,\xi)=\pm\mathbb{P}(x,\xi),\ \ \Omega_\pm^{(1)}(x,\xi)=\Omega(x,\xi)$$

where $\mathbb{P}$ and Ω are the linear functions in ξ defined respectively in (4.42) and (4.41). They are homogeneous functions in w of degree -1 and -2 respectively.

2. *The matrices $\mathbb{P}_\pm^{(2)}$ and $\Omega_\pm^{(2)}$ are polynomial functions of order 2 of the variable ξ and for $(x,\xi)\in\mathbb{R}^{2d}\setminus\Upsilon$, for all $\alpha,\beta\in\mathbb{N}^d$, there exists $C_{\alpha,\beta}>0$ such that*

$$|\partial_x^\alpha\partial_\xi^\beta\mathbb{P}_\pm^{(2)}(x,\xi)|\le C_{\alpha,\beta}\langle\xi\rangle^2\langle x\rangle^{(|\alpha|+2)(1+n_0)}|w(x)|^{-|\alpha|-4},$$

$$|\partial_x^\alpha\partial_\xi^\beta\Omega_\pm^{(2)}(x,\xi)|\le C_{\alpha,\beta}\langle\xi\rangle^2\langle x\rangle^{(|\alpha|+2)(1+n_0)}|w(x)|^{-|\alpha|-3}.$$

Proof. We use the calculus of $a\sharp_\varepsilon b$ detailed in Proposition A.0.1 and the observations of Remark A.0.2. We have

$$\Pi^\varepsilon_\pm \sharp_\varepsilon H = \Pi_\pm H + \varepsilon(\mathbb{P}^{(1)}_\pm H + \frac{1}{2i}\{\Pi_\pm, H\}) + \varepsilon^2(\mathbb{P}^{(2)}_\pm H + \frac{1}{2i}\{\mathbb{P}^{(1)}_\pm, H\} + d_\pm) + \varepsilon^3 r^1,$$

$$\begin{aligned}(h_\pm + \varepsilon\,\Omega^{(1)}_\pm + \varepsilon^2\,\Omega^{(2)}_\pm)\sharp_\varepsilon \Pi^\varepsilon_\pm = h_\pm \Pi_\pm \\ &+ \varepsilon(h_\pm \mathbb{P}^{(1)}_\pm + \frac{1}{2i}\{h_\pm, \Pi_\pm\} + \Omega^{(1)}_\pm \Pi_\pm) \\ &+ \varepsilon^2(h_\pm \mathbb{P}^{(2)}_\pm + \frac{1}{2i}\{h_\pm, \mathbb{P}^{(1)}_\pm\} + \frac{1}{2i}\{\Omega^{(1)}_\pm, \Pi_\pm\} + \Omega^{(1)}_\pm \mathbb{P}^{(1)}_\pm + \Omega^{(2)}_\pm \Pi_\pm + d_\pm)\end{aligned}$$

where r^1 and r^2 involves derivatives of order 3 of $\Pi_\pm$, 2 of $\mathbb{P}^{(1)}_\pm$ and 1 of $\mathbb{P}^{(2)}_\pm$ and $d_\pm$ comes from the computations

$$\frac{|\xi|^2}{2}\sharp_\varepsilon \Pi_\pm = \frac{|\xi|^2}{2}\Pi_\pm + \frac{\varepsilon}{2i}\left\{\frac{|\xi|^2}{2}, \Pi_\pm\right\} + \varepsilon^2 d_\pm, \quad \Pi_\pm \sharp_\varepsilon \frac{|\xi|^2}{2} = \frac{|\xi|^2}{2}\Pi_\pm - \frac{\varepsilon}{2i}\left\{\frac{|\xi|^2}{2}, \Pi_\pm\right\} + \varepsilon^2 d_\pm.$$

We deduce that in order to realize equation (C.1), we need to equalize the terms of order ε and ε^2 on both side of the equality (indeed $\Pi_\pm H = h_\pm \Pi_\pm$). we obtain two equations that it is convenient to put on the form

$$[\mathbb{P}^{(1)}_\pm, H] - (h_\pm - H)\mathbb{P}^{(1)}_\pm - \Omega^{(1)}_\pm \Pi_\pm = \mp i\xi \cdot \nabla \Pi_\pm, \tag{C.2}$$

$$[\mathbb{P}^{(2)}_\pm, H] - (h_\pm - H)\mathbb{P}^{(2)}_\pm - \Omega^{(2)}_\pm \Pi_\pm = F_\pm \tag{C.3}$$

where $F_\pm$ depends on $\mathbb{P}^{(1)}$ and $\Omega^{(1)}_\pm$

$$F_\pm = \frac{1}{2i}\{h_\pm, \mathbb{P}^{(1)}_\pm\} + \frac{1}{2i}\{\Omega^{(1)}_\pm, \Pi_\pm\} + \Omega^{(1)}_\pm \mathbb{P}^{(1)}_\pm - \frac{1}{2i}\{\mathbb{P}^{(1)}_\pm, H\}.$$

For solving these equations, we multiply them on both sides by Π_+ or Π_-, which gives four relations each time.

Let us do the computation for the + mode. Multiplying (C.2) on the right by Π_+ and on the left successively by Π_+ and Π_-ht, we obtain two relations

$$\Pi_+\Omega_+^{(1)}\Pi_+ = 0, \quad \Pi_-\Omega_+^{(1)}\Pi_+ = i\Pi_-\xi \cdot \nabla\Pi_+\Pi_+.$$

Using that we want to find $\Omega_+^{(1)}$ self adjoint, we deduce that we can choose

$$\Omega_+^{(1)} = i\Pi_-\xi \cdot \nabla\Pi_+\Pi_+ - i\Pi_+\xi \cdot \nabla\Pi_+\Pi_- = \Omega.$$

Similarly, for the minus mode

$$\Omega_-^{(1)} = -i\Pi_+\xi \cdot \nabla\Pi_+\Pi_- + i\Pi_-\xi \cdot \nabla\Pi_+\Pi_+ = \Omega.$$

Multiplying (C.2) on the left by Π_+ and on the right by Π_- gives

$$(h_+ - h_-)\mathbb{P}_+^{(1)} = i\Pi_+\xi \cdot \nabla\Pi_+\Pi_-.$$

Choosing $\mathbb{P}_+^{(1)}$ self-adjoint, we obtain

$$\mathbb{P}_+^{(1)} = \frac{i}{2|w(x)|}(\Pi_+\xi \cdot \nabla\Pi_+\Pi_- - \Pi_-\xi \cdot \nabla\Pi_+\Pi_+) = \mathbb{P}.$$

We argue similarly for the mode $-$ and find

$$\mathbb{P}_-^{(1)} = -\frac{i}{2|w(x)|}(\Pi_-\xi \cdot \nabla\Pi_+\Pi_+ - \Pi_+\xi \cdot \nabla\Pi_+\Pi_-) = \mathbb{P}.$$

Let us now determine $\mathbb{P}_+^{(2)}$ and $\Omega_+^{(2)}$. We first decompose F_+ as the sum of a self-adjoint matrix and a skew-symmetric one: $F_+ = F_{+,\mathrm{aa}} + F_{+,\mathrm{ss}}$ with

$$F_{+,\mathrm{aa}} = \frac{1}{2}(F_+ + F_+^*), \qquad F_{+,\mathrm{ss}} = -\frac{1}{2i}(F_+ - F_+^*)$$

$$F_+^* = -\frac{1}{2i}\{h_+, \mathbb{P}\} + \frac{1}{2i}\{\Pi_+, \Omega\} + \Omega\mathbb{P} - \frac{1}{2i}\{H, \mathbb{P}\}.$$

We have used $\{M, N\}^* = -\{N, M\}$ for smooth matrix-valued function M and N. We also obtain

$$\Pi_\pm F_{+,\mathrm{ss}} \Pi_\pm = 0, \tag{C.4}$$

which is required from (C.3) (when multiplied on both side by $\Pi_\pm$). These relations come from $\mathbb{P}\Omega = \Omega\mathbb{P}$,

$$\Pi_\pm \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \Pi_\pm = 0_{\mathcal{C}^{2,2}},$$

and

$$A(u) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} A(u) = 0, \quad \forall u \in \mathbb{R}^2.$$

Then,multiplying (C.3) by Π_+ on the right, we deduce

$$\Omega^{(2)} \Pi_+ = -F_+ \Pi_+.$$

One then chooses

$$\Omega_\pm^{(2)} = -\Pi_+ F_{+,\mathrm{aa}} \Pi_+ - \Pi_- F_+ \Pi_+ - \Pi_+ F_+^* \Pi_-. \tag{C.5}$$

For determining $\mathbb{P}_+^{(2)}$, we multiply (C.3) by Π_- on the right

$$(h_+ - h_-)\mathbb{P}_+^{(2)} \Pi_- = -F_+ \Pi_-,$$

and we obtain

$$\mathbb{P}_+^{(2)} = -\frac{1}{2|w(x)|}(\Pi_+ F_+ \Pi_- + \Pi_- F_+^* \Pi_+ + \Pi_- F_{+,\mathrm{aa}} \Pi_-). \tag{C.6}$$

The polynomial features of these matrices in the variable ξ and their properties as functions of w come from their explicit formula. This latter aspects determine their behavior at ∞ and close to Υ. □

Remark C.2.2. As already observed in the literature ([2, 50, 52, 53, 58], it is develop to push these asymptotics at any order by constructing a sequence of matrices $(\Omega_{\pm}^{(j)}, \mathbb{P}_{\pm}^{(j)})_{j\in\mathbb{N}}$ that will satisfy controls of the form

$$|\partial_x^\alpha \partial_\xi^\beta \mathbb{P}_{\pm}^{(j)}(x,\xi)| \leq C_{\alpha,\beta} \langle \xi \rangle^j \langle x \rangle^{(|\alpha|+j)(1+n_0)} |w(x)|^{-|\alpha|-2j},$$

$$|\partial_x^\alpha \partial_\xi^\beta \Omega_{\pm}^{(j)}(x,\xi)| \leq C_{\alpha,\beta} \langle \xi \rangle^j \langle x \rangle^{(|\alpha|+j)(1+n_0)} |w(x)|^{-|\alpha|-2j+1}.$$

As a consequence of the calculations above, we have the following result.

Lemma C.2.3. *Let $\Phi_{\pm}^{t^\flat,t}(z^\flat)$ be a trajectory reaching the point $z^\flat \in \Upsilon$ at time $t^\flat$ with the conditions of* (4.1.1)*. Then, we have for t close to $t^\flat$,*

$$\Omega_{\pm}^{(1)}(\Phi_{\pm}^{t^\flat,t}(z^\flat)) = O(1), \quad \mathbb{P}_{\pm}^{(1)}(\Phi_{\pm}^{t^\flat,t}(z^\flat)) = O(|t-t^\flat|),$$

$$\Omega_{\pm}^{(2)}(\Phi_{\pm}^{t^\flat,t}(z^\flat)) = O(|t-t^\flat|^2), \quad \mathbb{P}_{\pm}^{(2)}(\Phi_{\pm}^{t^\flat,t}(z^\flat)) = O(|t-t^\flat|^3).$$

Appendix D

Semiclassical wave packets

Here I do the calculations for $\phi_m(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), 0, x)$ for $m = 0, 1, 2, 3$, corresponding to (3.2). I drop the $\mathcal{A}$ notation in this section as everything here will refer to the $\mathcal{A}$ level.

From the definitions given in [35],

$$\phi_0(A, B, \epsilon^2, a, 0, x) = \pi^{-1/4}\epsilon^{-1/2}A^{-1/2}\exp\left\{\frac{-1}{2\epsilon^2}BA^{-1}(x-a)^2\right\}$$

Using the raising operator $\mathscr{A}*$, given by

$$\mathscr{A}^*(A, B, \epsilon^2, a, 0) = \frac{1}{\epsilon\sqrt{2}}[\overline{B}(x-a) - i\overline{A}p]$$

where p is the momentum operator, $p = -i\epsilon\frac{\partial}{\partial x}$. Also note $\overline{B} = B$ for our assumption that $D_0^{\mathcal{A}}$ is real.

Note that

$$\frac{\partial}{\partial x}\phi_0 = \left(-\frac{1}{\epsilon^2}BA^{-1}(x-a)\right)\phi_0$$

We find

$$\begin{aligned}
\phi_1 &= \mathscr{A}^*\phi_0 \\
&= \frac{1}{\epsilon\sqrt{2}}\left[B(x-a) - \epsilon^2\overline{A}\frac{\partial}{\partial x}\right]\phi_0 \\
&= \frac{1}{\epsilon\sqrt{2}}\left[B + \overline{A}BA^{-1}\right](x-a)\phi_0
\end{aligned}$$

Then to calculate ϕ_2, we note

$$\begin{aligned}
\frac{\partial}{\partial x}\phi_1 &= \frac{1}{\epsilon\sqrt{2}}[B + \overline{A}BA^{-1}]\left(1 + (x-a)\left(-\frac{1}{\epsilon^2}BA^{-1}(x-a)\right)\right)\phi_0 \\
&= \left(\frac{1}{x-a} - \frac{1}{\epsilon^2}BA^{-1}(x-a)\right)\phi_1
\end{aligned}$$

Hence,

$$\begin{aligned}
\phi_2 =& \frac{1}{\sqrt{2}}\frac{1}{\epsilon\sqrt{2}}\left[B(x-a) - \epsilon^2\overline{A}\frac{\partial}{\partial x}\right]\phi_1 \\
=& \frac{1}{2\epsilon}\left([B + \overline{A}BA^{-1}](x-a) - \epsilon^2\overline{A}\frac{1}{x-a}\right)\phi_1 \\
=& \frac{1}{2\sqrt{2}\epsilon}\left([B + \overline{A}BA^{-1}]^2(x-a)^2 - \epsilon^2\overline{A}[B + \overline{A}BA^{-1}\right)\phi_0
\end{aligned}$$

To calculate ϕ_3, note

$$\begin{aligned}
\frac{\partial}{\partial x}\phi_2 =& \frac{1}{2\epsilon}\Bigg([B + \overline{A}BA^{-1}] + \epsilon^2\overline{A}\frac{1}{(x-a)^2} \\
&+ \left([B + \overline{A}BA^{-1}](x-a) - \epsilon^2\overline{A}\frac{1}{x-a}\right)\left(\frac{1}{x-a} - \frac{1}{\epsilon^2}BA^{-1}(x-a)^2\right)\Bigg)\phi_1
\end{aligned}$$

$$
\begin{aligned}
=&\frac{1}{2\epsilon^2}\left(2B+3\overline{A}BA^{-1}-\frac{1}{\epsilon^2}[B+\overline{A}BA^{-1}]BA^{-1}(x-a)^2\right)\phi_1\\
=&\frac{1}{2\sqrt{2}\epsilon^3}\left(2B+3\overline{A}BA^{-1}-\frac{1}{\epsilon^2}[B+\overline{A}BA^{-1}]BA^{-1}(x-a)^2\right)[B+\overline{A}BA^{-1}](x-a)\phi_0
\end{aligned}
$$

Hence,

$$
\begin{aligned}
\phi_3 =&\frac{1}{\sqrt{3}}\left[B(x-a)-\epsilon^2\overline{A}\frac{\partial}{\partial x}\right]\phi_2\\
=&\frac{1}{2\sqrt{6}\epsilon^2}\left([B+\overline{A}BA^{-1}]^2(x-a)^2-3\epsilon^2\overline{A}[B+\overline{A}BA^{-1}]\right)\phi_1\\
=&\frac{1}{4\sqrt{3}\epsilon^3}\left([B+\overline{A}BA^{-1}]^3(x-a)^3-3\epsilon^2\overline{A}[B+\overline{A}BA^{-1}]^2(x-a)\right)\phi_0
\end{aligned}
$$

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