Landau-Zener Transitions Through Small Electronic Eigenvalue Gaps in the Born-Oppenheimer Approximation

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Abstract

We study the propagation of molecular wave packets through the simplest two types of avoided crossings of electronic energy levels in a limit where the gap between the eigenvalues shrinks as the nuclear masses are increased. For these types of avoided crossings, the electron energy levels essentially depend on only one of the nuclear configuration parameters, as is the case for all diatomic molecules. We find that the transition probabilities are of order 1 and are determined by the Landau–Zener formula.

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1 Introduction

Because it is not practical to solve the time–dependent Schrödinger equation directly, the time–dependent Born–Oppenheimer approximation is a principal tool for studying molecular dynamics. This approximation makes use of the smallness of the parameter ϵ, where ϵ^4 is the ratio of the mass of an electron to the average of the masses of the nuclei.

In the standard time–dependent Born–Oppenheimer approximation, the electrons and nuclei are treated separately, but their motions are coupled. The electrons move much faster than the nuclei, and they quickly adjust their motion in response to the relatively slow nuclear motion. The electrons remain approximately in a quantum mechanical bound state as though the nuclei were at fixed classical positions. This is the *adiabatic approximation* for the electrons. The motion of the nuclei is accurately described by the *semiclassical approximation* because the nuclei have large masses. The electronic and nuclear motions are coupled because the energy level of the electronic bound state depends on the position of the nuclei and the electronic energy level plays the role of an effective potential for the semiclassical dynamics of the nuclei.

This physical intuition is the basis for rigorous asymptotic expansions of solutions to the molecular time–dependent Schrödinger equation [6, 8, 11, 15, 16]. However, the validity of the approximation is dependent upon the assumption that the electron energy level of interest is well isolated from the rest of the spectrum of the electronic Hamiltonian.

There is relatively little mathematical literature concerning the validity of Born–Oppenheimer approximations. Interested readers should consult references [2, 3, 4, 6, 8, 9, 10, 11, 12, 13, 15, 16, 17, 20, 32, 34, 35, 36, 38, 39, 40, 41].

The assumption that the electron energy level of interest is isolated from the rest of the spectrum can break down in various ways. For example, two electron energy levels may cross one another for some nuclear configurations. The effects of such crossings on molecular propagation have been recently studied in generic minimal multiplicity situations [13, 17, 16]. Another situation where the standard approximation breaks down is an "avoided crossing," where two electron energy levels approach close to one another, but do not actually cross. Generic avoided crossings of energy levels that have the minimal multiplicity allowed by the symmetry group have been classified, and normal forms for the electron Hamiltonian near these avoided crossings have been determined [18]. In [18] it is shown that there are six distinct types of these avoided crossings.

The purpose of this paper is to study molecular propagation through the simplest two types of avoided crossings described in [18]. In these types of crossings, the electron energy levels essentially depend on only one parameter in the nuclear configuration space. In practice, this occurs for diatomic molecules, where the electron energy levels depend only on the distance between the nuclei because of rotational symmetry. There are two types of such avoided crossings because of the possible presence of time reversing operators in the symmetry group of the electron Hamiltonian. The details of the situation dictate whether minimal multiplicity energy levels are of multiplicity 1 (Type 1 Avoided Crossings) or multiplicity 2 (Type 2 Avoided Crossings).

Our main result is the determination of what happens when a standard time–dependent Born–Oppenheimer molecular wave packet propagates through one of these avoided crossings if the gap size is on the order of ϵ. Using matched asymptotic expansions we explicitly compute approximate solutions to the molecular Schrödinger equation. We observe that to leading order in ϵ, the Landau–Zener formula correctly describes the probabilities for the system to remain in the original electronic level or to make a transition to the other electronic level involved in the avoided crossing. To apply the Landau–Zener formula in this case, one treats the nuclei as classical point particles to obtain a time–dependent Hamiltonian for the electrons. This leads to the study of the adiabatic limit of an effective time–dependent system with two levels isolated in its spectrum. The transition probabilty between the levels of such systems in the adiabatic limit is known for a variety of situations [24, 26, 25, 28, 29, 21, 30, 31]. In particular, when the levels display an avoided crossing, the Landau-Zener formula is valid [14, 27, 22, 37, 23]. In our case, we can apply the Landau–Zener formula to the resulting time–dependent Schrödinger equation for the electrons alone.

More precisely, suppose there is a generic Type 1 or Type 2 avoided crossing at nuclear configuration $x = 0$. In an appropriate coordinate system, the gap between the electron energy levels is

$$2\sqrt{(b_1x_1 + b_2\epsilon)^2 \,+\, (c_2\epsilon)^2} \;+\; O(x^2 + \epsilon^2), \tag{1.1}$$

with b_1 and c_2 non-zero. Suppose that a semiclassical nuclear wave packet passes through the avoided crossing with velocity μ, whose first component is $\mu_1 \neq 0$. Then the probability of remaining in the same electronic state is

$$1 \;-\; e^{-\pi c_2^2/(b_1\mu_1)} \;+\; O(\epsilon^p), \tag{1.2}$$

for some $p > 0$, and the probability of making a transition to the other electronic level involved in the avoided crossing is

$$e^{-\pi c_2^2/(b_1\mu_1)} \;+\; O(\epsilon^p). \tag{1.3}$$

This result is completely different from what one obtains for the four other types of avoided crossings, where the corresponding probabilities depend on the particular nuclear wave packet involved [19]. The reason is that in Type 1 and Type 2 avoided crossings, every part of the nuclear wave packet passes through the same size minimum gap between the eigenvalues. In Types 3, 4, 5, and 6 avoided crossings, different parts of the nuclear wave packet feel different size gaps as they pass through the avoided crossing.

Our results are also completely different from those obtained in the case of true level crossings [16]. For codimension 1 crossings, transition amplitudes produced by crossings are of order ϵ, not order 1 as in the present paper. Furthermore, the dependence of transition amplitudes on the nuclear velocity μ is exponential as opposed to algebraic in the crossing case. Also, although the problem we study in this paper is somewhat less singular than the case of true crossings, the technical details are more difficult. This stems largely from the complicated ϵ dependence of the classical mechanics in our problem. In [16], the classical mechanics had no ϵ dependence.

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

$$H(\epsilon) \;=\; \sum_{j=1}^{K} \,-\, \frac{\epsilon^4}{2M_j}\,\Delta_{x_j} \;-\; \sum_{j=K+1}^{N} \frac{1}{2m_j}\,\Delta_{x_j} \;+\; \sum_{i<j} V_{ij}(x_i - x_j). \tag{1.4}$$

Here $x_j \in I\!\!R^l$ denotes the position of the $j^{\rm th}$ particle, the mass of the $j^{\rm th}$ nucleus is M_j (for $1 \le j \le K$), the mass of the $j^{\rm th}$ electron is m_j (for $K+1 \le j \le N$), and V_{ij} is the potential between particles i and j. For convenience we assume $M_j = 1$ for $1 \le j \le K$. We set $n = Kl$ and let $x = (x_1, x_2, \ldots, x_{Kl}) \in I\!\!R^n$ denote the nuclear configuration vector. We decompose $H(\epsilon)$ as

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_x \,+\, h(x). \tag{1.5}$$

This defines the electronic Hamiltonian $h(x)$ that depends parametrically on x.

The time–dependent Schrödinger equation that we study is

$$i\,\epsilon^2\,\frac{\partial\psi}{\partial t} \;=\; H(\epsilon)\,\psi, \tag{1.6}$$

for t in a fixed interval. The factor of ϵ^2 on the left hand side of this equation indicates a particular choice of time scaling. Other choices could be made, but this choice is the "distinguished limit" [1] that produces the most interesting leading order solutions. With this scaling, all terms in the equation play significant roles at leading order, and the nuclear motion has a non-trivial classical limit. This is also the scaling for which the mean initial nuclear kinetic energy is held constant as ϵ tends to zero.

Nowhere in this paper do we require the Hamiltonian to have the particular form (1.4). We only require the Hamiltonian to be of the form (1.5). In some realistic systems, $h(x)$ may have two eigenvalues that approach one another with a minimum gap size that is of the same order of magnitude as the relevant value of ϵ. For this reason, we generalize the form (1.5) to allow the electron Hamiltonian to depend on ϵ as well as x. Thus, we allow Hamiltonians to have the form

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_x \,+\, h(x,\,\epsilon), \tag{1.7}$$

with the assumption that $h(x,\,\epsilon)$ has an Avoided Crossing according to the following definition:

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 $I\!\!R^n$. Suppose that the resolvent of $h(x,\,\epsilon)$ is a C^4 function of x and ϵ as an operator from $\mathcal{H}$ to $\mathcal{D}$. Suppose $h(x,\,\epsilon)$ has two eigenvalues $E_{\mathcal{A}}(x,\,\epsilon)$ and $E_{\mathcal{B}}(x,\,\epsilon)$ 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 Ω, but that for all $x \in \Omega$, $E_{\mathcal{A}}(x,\,\epsilon) \ne E_{\mathcal{B}}(x,\,\epsilon)$ when $\epsilon > 0$. Then we say $h(x,\,\epsilon)$ has an* **Avoided Crossing** *on Γ.*

Remark: Realistic molecules have Coulomb potentials which give rise to electron Hamiltonians that do not satisfy the smoothness assumptions of this definition. However, one should be able to accommodate Coulomb potentials by using the regularization techniques of [10, 11, 35].

Avoided Crossings of minimal multiplicity energy levels are classified in [18], and normal forms for the electron Hamiltonian near Γ are derived. When Γ has codimension 1, there are two types. To describe these, we need some notation. Assume without loss of generality that 0 is a generic point of Γ, and decompose

$$h(x,\epsilon) = h_{\|}(x,\epsilon) + h_{\perp}(x,\epsilon) \tag{1.8}$$

with

$$h_{\|}(x,\epsilon) = h(x,\epsilon) P(x,\epsilon) \tag{1.9}$$

and

$$h_{\perp}(x,\epsilon) = h(x,\epsilon)(I\!I - P(x,\epsilon)) \tag{1.10}$$

where $P(x,\epsilon)$ is a spectral projector of $h(x,\epsilon)$ associated with $E_{\mathcal{A}}(x,\,\epsilon)$ and $E_{\mathcal{B}}(x,\,\epsilon)$. In a Type 1 Avoided Crossing, Γ has codimension 1 and the two eigenvalues each have multiplicity 1. There exists [18] an orthonormal basis $\{\psi_1(x,\epsilon), \psi_2(x,\epsilon)\}$ of $P(x,\epsilon)\mathcal{H}$, which is regular in (x,ϵ) around $(0,0)$. In this basis, $h_{\|}(x,\epsilon)$ has the form

$$\begin{aligned} h_{\|}(x,\epsilon) &= h_1(x,\epsilon) + \widetilde{V}(x,\epsilon) \\ &= \begin{pmatrix} \beta(x,\epsilon) & \gamma(x,\epsilon) + i\delta(x,\epsilon) \\ \gamma(x,\epsilon) - i\delta(x,\epsilon) & -\beta(x,\epsilon) \end{pmatrix} + \widetilde{V}(x,\epsilon) \end{aligned} \tag{1.11}$$

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

$$\begin{aligned} \beta(x,\epsilon) &= b_1 x_1 + b_2\epsilon + \mathcal{O}(2) \\ \gamma(x,\epsilon) &= c_2\epsilon + \mathcal{O}(2) \\ \delta(x,\epsilon) &= \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0) \end{aligned} \tag{1.12}$$

where $b_1 > 0, c_2 > 0, b_2 \in I\!R$ and

$$\mathcal{O}(m) = \mathcal{O}\left(\left(\sum_{j=0}^{n} x_j^2 \right)^{m/2} \right) \;, \quad x_0 = \epsilon. \tag{1.13}$$

Type 2 Avoided Crossings are similar, except that the minimal multiplicity of eigenvalues allowed by the symmetry group is 2. Near one of these avoided crossings, one can choose an orthonormal basis $\{\psi_1(x,\epsilon), \psi_2(x,\epsilon), \psi_3(x,\epsilon), \psi_4(x,\epsilon),\}$ of $P(x,\epsilon)\mathcal{H}$, which is regular in (x,ϵ) around $(0,0)$. In this basis, $h_{\|}(x,\epsilon)$ has the form

$$\begin{aligned} h_{\|}(x,\epsilon) &= h_1(x,\epsilon) + \widetilde{V}(x,\epsilon) \\ &= \begin{pmatrix} \beta(x,\epsilon) & \gamma(x,\epsilon) + i\delta(x,\epsilon) & 0 & 0 \\ \gamma(x,\epsilon) - i\delta(x,\epsilon) & -\beta(x,\epsilon) & 0 & 0 \\ 0 & 0 & \beta(x,\epsilon) & \gamma(x,\epsilon) + i\delta(x,\epsilon) \\ 0 & 0 & \gamma(x,\epsilon) - i\delta(x,\epsilon) & -\beta(x,\epsilon) \end{pmatrix} \\ &\quad + \widetilde{V}(x,\epsilon), \end{aligned} \tag{1.14}$$

where β, γ, δ, and $\widetilde{V}$ are as above [18].

Throughout the paper we assume that the nuclei move transversally through Γ at the point 0. This means the classical momentum associated with their semiclassical wave packets has a non-trivial component in the x_1 direction when their classical position is passing through $0 \in \Gamma$.

Precise statements of our results require a considerable amount of notation and are presented in Theorems 3.1 and 4.1 for Type 1 and Type 2 Avoided Crossings, respectively. We have stated these theorems with the incoming state associated with the lower of the two relevant levels. The analogous results with the incoming state associated with the upper level are also true and proved in the same way, with the obvious changes. Immediate corollaries of the two theorems are that the Landau–Zener formula described above gives the correct transition probabilities in each case. The main technique we use is matched asymptotic expansions. We use the standard time–dependent Born–Oppenheimer approximate solutions to the Schrödinger equation when the nuclei are far enough away from Γ. We match these to "inner" solutions when the system is near Γ and the standard approximation breaks down.

The paper is organized as follows: In Section 2 we discuss the ordinary differential equations whose solutions will be used to describe the semiclassical motion of the nuclei. In Section 3 we discuss semiclassical nuclear wave packets and adiabatic motion of the electrons. We then prove our main result for Type 1 Avoided Crossings, Theorem 3.1 by using matched asymptotic expansions. In Section 4 we state our main result, Theorem 4.1, for Type 2 Avoided Crossings and describe the modifications of Section 3 that are required to prove this result.

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1.1 A Convenient Change of Variables

We consider the Schrödinger equation

$$i\epsilon^2 \frac{\partial}{\partial t}\psi(x,t) = -\frac{\epsilon^4}{2}\Delta\psi(x,t) + h(x,\epsilon)\psi(x,t) \tag{1.15}$$

In order to get rid of ϵ-dependence in the leading order of $\beta(x,\epsilon)$ in (1.11), we introduce the new variables

$$x' = b_1 x + \begin{pmatrix} b_2\epsilon \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \ \epsilon' = c_2\epsilon \ , \ t' = b_1^2/c_2^2 t. \tag{1.16}$$

In terms of these new variables, the Schrödinger equation (1.15) for

$$\phi(x',t') = \psi(x(x',\epsilon'), t(t')) \tag{1.17}$$

becomes

$$i\epsilon'^2 \frac{\partial}{\partial t'}\phi(x',t') = -\frac{\epsilon'^4}{2}\Delta\phi(x',t') + \frac{c_2^4}{b_1^2} h(x(x',\epsilon'),\epsilon(\epsilon'))\phi(x',t') \tag{1.18}$$

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

$$h_{\|}(x(x',\epsilon'),\epsilon(\epsilon')) = \begin{pmatrix} x'_1 & \epsilon' \\ \epsilon' & -x'_1 \end{pmatrix} + \mathcal{O}(2) + \widetilde{V}(x(x',\epsilon'),\epsilon(\epsilon')) \tag{1.19}$$

where $\widetilde{V}(x(x',\epsilon'),\epsilon(\epsilon'))$ is regular in (x',ϵ') around $(0,0)$ and $\mathcal{O}(2)$ refers to x' and ϵ'. We introduce the fixed parameter $r = c_2^4/b_1^2 > 0$ and *henceforth drop the primes on the new variables.* We assume that $h_1(x,\epsilon)$ has the form (1.11) with the following local behavior around $x = 0$ and $\epsilon = 0$:

$$\begin{aligned} \beta(x,\epsilon) &= rx_1 + \mathcal{O}(2) \\ \gamma(x,\epsilon) &= r\epsilon + \mathcal{O}(2) \\ \delta(x,\epsilon) &= \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0) \end{aligned} \tag{1.20}$$

with $r > 0$.

2 Ordinary Differential Equations of Semiclassical Mechanics

In Section 3.1 we introduce semiclassical wave packets for the nuclei. The leading order semiclassical motion for these wave packets is determined by the solutions to certain systems of ordinary differential equations. These involve classical mechanics, the classical action associated with a classical trajectory, and the dynamics of certain matrices that describe the position and momentum uncertainties of the wave packets. The goal of this section is to study the small t and ϵ behavior that we need for the asymptotic matching procedure that we use in Section 3 to prove our main results.

We define

$$V^{\mathcal{A}}_{\mathcal{B}}(x,\epsilon) = \widetilde{V}(x,\epsilon) \pm \sqrt{\beta^2(x,\epsilon)+\gamma^2(x,\epsilon)+\delta^2(x,\epsilon)} \tag{2.1}$$

where $x \in I\!R^n$, $\epsilon > 0$. Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions of the classical equations of motion

$$\begin{aligned} \frac{d}{dt}a^{\mathcal{C}}(t) &= \eta^{\mathcal{C}}(t) \\ \frac{d}{dt}\eta^{\mathcal{C}}(t) &= -\nabla V^{\mathcal{C}}(a^{\mathcal{C}}(t),\epsilon), \qquad \mathcal{C} = \mathcal{A},\ \mathcal{B}. \end{aligned} \tag{2.2}$$

with initial conditions

$$\begin{aligned} a^{\mathcal{C}}(0) &= 0 \\ \eta^{\mathcal{C}}(0) &= \eta^0(\epsilon), \qquad \text{with} \\ \eta^0(\epsilon) &= \eta^0 + \mathcal{O}(\epsilon)\ , \qquad \text{and } \eta^0_1 > 0, \end{aligned} \tag{2.3}$$

where the $\mathcal{O}(\epsilon)$ term depends on whether $\mathcal{C}$ is $\mathcal{A}$ or $\mathcal{B}$. Noticing that it follows from (1.20) that $|\beta(x,\epsilon)|$, $|\gamma(x,\epsilon)|$ and $|\delta(x,\epsilon)|$ are $\mathcal{O}(0)$, and using estimates of the type $\beta/\sqrt{\beta^2+\gamma^2+\delta^2} \leq 1$, we see that

$$\|\nabla V^{\mathcal{C}}(x,\epsilon)\| = \mathcal{O}(0). \tag{2.4}$$

This last condition implies the existence and uniqueness of the solutions of (2.2) for small but finite times, at least.

2.1 Small t Asymptotics

We want to compute the asymptotics of the solution of (2.2), (2.3) when both t and ϵ tend to zero. In order to get started, we need the following

Lemma 2.1 *Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions of (2.2) and (2.3). If ϵ and t are small enough, we have*

$$\begin{cases} a^{\mathcal{C}}(t) = \eta^0(\epsilon)t + \mathcal{O}(t^2) \\ \eta^{\mathcal{C}}(t) = \eta^0(\epsilon) + \mathcal{O}(t) \end{cases}$$

as $t \to 0$, uniformly in ϵ.

Proof:
We mimic the proof of [16], p.82. Let us drop the index $\mathcal{C}$ in the notation. We want to show that there exists $T > 0$, such that

$$\begin{aligned} a(t) &= \eta^0(\epsilon)t + u(t,\epsilon) \\ b(t) &= \eta^0(\epsilon) + v(t,\epsilon) \end{aligned} \tag{2.5}$$

where $u(t,\epsilon)/t^2$ and $v(t,\epsilon)/t$ are uniformly bounded if $\epsilon^2 + t^2 < T^2$, *i.e.*, if $(t,\epsilon) \in B_T$. We let Y_T be the Banach space of pairs of bounded, continuous in t, vector valued functions for $(t,\epsilon) \in B_T$, with the norm

$$\left\| \begin{pmatrix} u \\ v \end{pmatrix} \right\|_{Y_T} = \sup_{(t,\epsilon)\in B_T} \|u(t,\epsilon)/t^2\| + \sup_{(t,\epsilon)\in B_T} \|v(t,\epsilon)/t\|. \tag{2.6}$$

For $\begin{pmatrix} u \\ v \end{pmatrix} \in Y_T$, we define

$$\mathcal{F}\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} \int_0^t v(s,\epsilon)ds \\ -\int_0^t \nabla V(\eta^0(\epsilon)s + u(s,\epsilon),\epsilon)ds \end{pmatrix}. \tag{2.7}$$

Due to the estimate (2.4), $\mathcal{F}$ maps Y_T into Y_T, and furthermore, any fixed point of $\mathcal{F}$ gives rise to a solution of (2.2), (2.3) by way of (2.5). If we show that $\mathcal{F}$ is a strict contraction, it follows from the contraction mapping principle that the solution of (2.2), (2.3) exists, is unique and satisfies the assertion of the lemma. We show that this is the case for T small enough. Let $\begin{pmatrix} u_1 \\ v_1 \end{pmatrix}, \begin{pmatrix} u_2 \\ v_2 \end{pmatrix} \in Y_T$ and let us estimate the norm of $\begin{pmatrix} u_3 \\ v_3 \end{pmatrix} = \mathcal{F}\begin{pmatrix} u_1 \\ v_1 \end{pmatrix} - \mathcal{F}\begin{pmatrix} u_2 \\ v_2 \end{pmatrix}$.

$$\|u_3(t,\epsilon)/t^2\| = \frac{1}{t^2}\left\| \int_0^t v_1(s,\epsilon) - v_2(s,\epsilon)ds \right\| \tag{2.8}$$

$$\leq \frac{1}{t^2}\int_0^{|t|} |s| \sup_{(t,\epsilon)\in B_T} \|v_1(t,\epsilon) - v_2(t,\epsilon)\|\, ds$$

$$\leq \frac{1}{2}\left\| \begin{pmatrix} u_1 \\ v_1 \end{pmatrix} - \begin{pmatrix} u_2 \\ v_2 \end{pmatrix} \right\|_{Y_T}. \tag{2.9}$$

For the other component we use the mean value theorem

$$\nabla V(\eta^0(\epsilon)s + u_1(s,\epsilon),\epsilon) - \nabla V(\eta^0(\epsilon)s + u_2(s,\epsilon),\epsilon) \tag{2.10}$$
$$= V^{(2)}(\zeta(s,\epsilon),\epsilon)(u_1(s,\epsilon) - u_2(s,\epsilon))$$

where $V^{(2)}$ stands for the Hessian of V and

$$\zeta(s,\epsilon) = \eta^0(\epsilon)s + u_1(s,\epsilon) + \theta(s,\epsilon)(u_2(s,\epsilon) - u_1(s,\epsilon)) \tag{2.11}$$

with $\theta(s,\epsilon) \in]0,1[$. There will appear several constants, independent of ϵ in the sequel which we shall denote generically by c. By hypothesis, $u_j(s,\epsilon) \leq cs^2$, $j = 1,2$, uniformly in ϵ and $\eta_1^0(\epsilon) = \eta_1^0 + \mathcal{O}(\epsilon)$ with $\eta_1^0 > 0$. Consequently, there exists a constant c, independent of ϵ, such that

$$|\zeta_1(s,\epsilon)| \geq c|s|. \tag{2.12}$$

By explicit computation we get, (omitting the arguments (x,ϵ))

$$\begin{aligned} V^{(2)} = \quad & \widetilde{V}^{(2)} \pm \left(|\nabla\beta\rangle\langle\nabla\beta| + |\nabla\gamma\rangle\langle\nabla\gamma| + |\nabla\delta\rangle\langle\nabla\delta|\right)(\beta^2+\gamma^2+\delta^2)^{-1/2} \\ & + (\beta\beta^{(2)} + \gamma\gamma^{(2)} + \delta\delta^{(2)})(\beta^2+\gamma^2+\delta^2)^{-1/2} \\ & - |\beta\nabla\beta + \gamma\nabla\gamma + \delta\nabla\delta\rangle\langle\beta\nabla\beta + \gamma\nabla\gamma + \delta\nabla\delta|(\beta^2+\gamma^2+\delta^2)^{-3/2}. \end{aligned} \tag{2.13}$$

Using the behaviors (1.20) again and estimates of the type $\beta\gamma/(\beta^2+\gamma^2+\delta^2) \leq 1$, we get

$$\|V^{(2)}(x,\epsilon)\| \leq \frac{c}{\sqrt{\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)}} \tag{2.14}$$

where c is independent of (x,ϵ). Then,

$$\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon) = r^2({x_1}^2 + \epsilon^2) + \mathcal{O}(3), \tag{2.15}$$

with $\|\zeta(s,\epsilon)\| = \mathcal{O}(s)$ and (2.12) we get

$$\begin{aligned} \beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)|_{x=\zeta(s,\epsilon)} &= r^2\left({\zeta_1}^2(s,\epsilon) + \epsilon^2\right) + \mathcal{O}(s^3 + \epsilon^3) \\ &\geq c\left({\zeta_1}^2(s,\epsilon) + \epsilon^2\right) \\ &\geq cs^2 \end{aligned} \tag{2.16}$$

if s is small enough. Hence

$$\begin{aligned} \|V^{(2)}(\zeta(s,\epsilon),\epsilon)(u_2(s,\epsilon) - u_1(s,\epsilon))\| &\leq c\|u_2(s,\epsilon) - u_1(s,\epsilon)\|/|s| \\ &\leq c|s|\left\|\begin{pmatrix} u_1 \\ v_1 \end{pmatrix} - \begin{pmatrix} u_2 \\ v_2 \end{pmatrix}\right\|_{Y_T}, \end{aligned} \tag{2.17}$$

for some c independent of ϵ. Thus

$$\begin{aligned} \|v_3(t,\epsilon)\|/|t| &\leq c\frac{1}{|t|}\int_0^{|t|} |s|\left\|\begin{pmatrix} u_1 \\ v_1 \end{pmatrix} - \begin{pmatrix} u_2 \\ v_2 \end{pmatrix}\right\|_{Y_T} \\ &\leq c\frac{|t|}{2}\left\|\begin{pmatrix} u_1 \\ v_1 \end{pmatrix} - \begin{pmatrix} u_2 \\ v_2 \end{pmatrix}\right\|_{Y_T}. \end{aligned} \tag{2.18}$$

Choosing T small enough so that $c|t|/2 \leq 1/2$, we get the result. □

If we replace the potential $V^{\mathcal{C}}(x,\epsilon)$ by $\widetilde{V}(x,\epsilon)$ which is regular as x and $\epsilon \to 0$, we can go further in the asymptotics, as is easily checked.

Lemma 2.2 *Let $a(t)$ and $\eta(t)$ be the solutions of (2.2) and (2.3) with $V^{\mathcal{C}}(x,\epsilon) \equiv \widetilde{V}(x,\epsilon)$. If ϵ and t are small enough, we have*

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

as $t \to 0$, uniformly in ϵ.

2.2 Asymptotics for Inner Solution

We compute here the asymptotics of the classical motion in the inner temporal region. Let us define this inner regime by introducing the rescaled quantities s and $z^{\mathcal{C}}(s)$ by

$$t = \epsilon s \tag{2.19}$$

$$a^{\mathcal{C}}(t) = \epsilon z^{\mathcal{C}}(s) \tag{2.20}$$

which we study in the limits

$$\begin{cases} \epsilon \to 0 \\ \epsilon s^3 \to 0 \\ |s| \to \infty. \end{cases} \tag{2.21}$$

In terms of these new variables, equations (2.2) and (2.3) become

$$\begin{aligned} &\frac{d^2}{ds^2} z^{\mathcal{C}}(s) = -\epsilon \nabla V^{\mathcal{C}}(\epsilon z^{\mathcal{C}}(s), \epsilon) \\ &\frac{d}{ds} z^{\mathcal{C}}(0) = \eta^0(\epsilon) \\ &z^{\mathcal{C}}(0) = 0. \end{aligned} \tag{2.22}$$

Let us show the following

Proposition 2.1 *Let $z^{\mathcal{C}}(s)$ be the solution of (2.22). We have the following asymptotic behaviors as $\epsilon \to 0$, $s \to \pm\infty$ and $\epsilon s^3 \to 0$:*

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

where

$$\begin{aligned} z_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = \quad & \eta^0(\epsilon)s, \\ z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = \quad & -\nabla\widetilde{V}(0,\epsilon)\frac{s^2}{2} \pm \left[\frac{r}{\eta_1^0(\epsilon)} s - \frac{r}{2\eta_1^0(\epsilon)} s\sqrt{(\eta_1^0(\epsilon)s)^2 + 1} \right. \\ & \left. + \frac{r}{2\eta_1^0(\epsilon)^2} \ln\left(\eta_1^0(\epsilon)s + \sqrt{(\eta_1^0(\epsilon)s)^2+1} \right) \right] \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \end{aligned}$$

Proof:
The idea is to expand the potential $V^{\mathcal{C}}(\epsilon z^{\mathcal{C}}(s),\epsilon)$ around the origin in $I\!R^{n+1}$ and to insert an *a priori* expansion of the type

$$z^{\mathcal{C}}(s) = z_0^{\mathcal{C}}(s) + \epsilon z_1^{\mathcal{C}}(s) + \epsilon^2 z_2^{\mathcal{C}}(s) + \cdots \tag{2.23}$$

in (2.22). Then we solve the resulting equations order by order in ϵ, using $\eta^0(\epsilon) = \mathcal{O}(\epsilon^0)$ and lemma 2.1. We let $w_1^{\mathcal{C}}(s)$ denote the first component of $z^{\mathcal{C}}(s)$ and write

$$\begin{aligned} -\nabla V^{\overset{\mathcal{A}}{\mathcal{B}}}(\epsilon z^{\mathcal{C}}(s),\epsilon) = & - \nabla \widetilde{V}(0,\epsilon) \\ & \mp \left[r \begin{pmatrix} \epsilon w_1^{\overset{\mathcal{A}}{\mathcal{B}}}(s) \\ 0 \\ \vdots \\ 0 \end{pmatrix} + \mathcal{O}(2) \right] \left\{ \epsilon^2 w_1^{\overset{\mathcal{A}}{\mathcal{B}}\,2}(s) + \epsilon^2 + \mathcal{O}(3) \right\}^{-1/2} + \mathcal{O}(1), \end{aligned} \tag{2.24}$$

where $\mathcal{O}(n)$ is to be understood with ϵz in place of x. Since by lemma 2.1,

$$z^{\mathcal{C}}(s) = \eta^0(\epsilon)s + \mathcal{O}(\epsilon s^2), \tag{2.25}$$

where ϵs^2 is assumed to be small, we have $\mathcal{O}(n) = \mathcal{O}(\epsilon^n s^n)$, and the equation reads

$$\begin{aligned} \frac{d^2}{ds^2} z^{\overset{\mathcal{A}}{\mathcal{B}}}(s) = \quad & -\epsilon \nabla \widetilde{V}(0,\epsilon) + \mathcal{O}(\epsilon^2 s) \\ & \mp \left[r\epsilon \begin{pmatrix} w_1^{\overset{\mathcal{A}}{\mathcal{B}}}(s) \\ 0 \\ \vdots \\ 0 \end{pmatrix} + \mathcal{O}(\epsilon^2 s^2) \right] \left\{ w_1^{\overset{\mathcal{A}}{\mathcal{B}}\,2}(s) + 1 + \mathcal{O}(\epsilon s^3) \right\}^{-1/2} \end{aligned} \tag{2.26}$$

as $\epsilon s^3 \to 0$, $s \to \infty$ and $\epsilon \to 0$. Thus the leading order of the equation for the lowest term in ϵ of the expansion (2.23) becomes

$$\frac{d^2}{ds^2} z_0^{\mathcal{C}}(s) = 0 \tag{2.27}$$

so that, with the initial conditions $z_0^{\mathcal{C}}(0) = 0$ and $\frac{d}{ds} z_0^{\mathcal{C}}(0) = \eta^0(\epsilon)$, see (2.22), we get, as expected,

$$z_0^{\mathcal{C}}(s) = \eta^0(\epsilon)s. \tag{2.28}$$

Then the leading order of the equation for the next term in the expansion (2.23) yields

$$\frac{d^2}{ds^2} z_1^{\overset{\mathcal{A}}{\mathcal{B}}}(s) = -\nabla \widetilde{V}(0,\epsilon) \mp r \frac{\eta_1^0(\epsilon)s}{\sqrt{(\eta_1^0(\epsilon)s)^2 + 1}} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \tag{2.29}$$

The initial conditions are now $z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(0)=0$ and $\frac{d}{ds}z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(0)=0$, which gives

$$z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = -\nabla\widetilde{V}(0,\epsilon)\frac{s^2}{2} \pm \left[\frac{r}{\eta_1^0(\epsilon)}s - \frac{r}{2\eta_1^0(\epsilon)}s\sqrt{(\eta_1^0(\epsilon)s)^2+1}\right. \tag{2.30}$$
$$\left. + \frac{r}{2\eta_1^0(\epsilon)^2}\ln\left(\eta_1^0(\epsilon)s+\sqrt{(\eta_1^0(\epsilon)s)^2+1}\right)\right]\begin{pmatrix}1\\0\\ \vdots\\0\end{pmatrix}.$$

Let us estimate the difference between the actual solution of (2.22) and the formal approximation just constructed. We compute

$$\frac{d^2}{ds^2}\left(z^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - z_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - \epsilon z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s)\right) \tag{2.31}$$
$$= \mp\epsilon r\begin{pmatrix}1\\0\\ \vdots\\0\end{pmatrix}\left[\frac{w_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s)}{\sqrt{w_1^{\substack{\mathcal{A}\\ \mathcal{B}}\,2}(s)+1+\mathcal{O}(\epsilon s^3)}} - \frac{\eta_1^0(\epsilon)s}{\sqrt{(\eta_1^0(\epsilon)s)^2+1}}\right]$$
$$+ \frac{\mathcal{O}(\epsilon^2 s^2)}{\sqrt{w_1^{\substack{\mathcal{A}\\ \mathcal{B}}\,2}(s)+1+\mathcal{O}(\epsilon s^3)}}.$$

¿From lemma (2.1) we also have $w_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s)\geq cs$ for some c independent of ϵ, so that

$$\left(w_1^{\substack{\mathcal{A}\\ \mathcal{B}}\,2}(s)+1+\mathcal{O}(\epsilon s^3)\right)^{-1/2} = \left(((\eta_1^0(\epsilon)s)^2+1)(1+\mathcal{O}(\epsilon s^3))\right)^{-1/2} \tag{2.32}$$
$$= \left((\eta_1^0(\epsilon)s)^2+1\right)^{-1/2}+\mathcal{O}(\epsilon),$$

and finally

$$\frac{d^2}{ds^2}\left(z^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - z_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - \epsilon z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s)\right) = \mathcal{O}(\epsilon^2 s). \tag{2.33}$$

By integration, and taking the initial conditions into account, we get

$$\frac{d}{ds}\left(z^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - z_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - \epsilon z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s)\right) = \mathcal{O}(\epsilon^2 s^2), \tag{2.34}$$
$$z^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - z_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) - \epsilon z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = \mathcal{O}(\epsilon^2 s^3). \tag{2.35}$$

□

Corollary 2.1 *Further expanding we get in the same regime*

$$z^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = \eta^0(\epsilon)s - \nabla\widetilde{V}(0,\epsilon)\epsilon\frac{s^2}{2} \pm \frac{r}{\eta_1^0(\epsilon)}\epsilon s\begin{pmatrix}1\\0\\ \vdots\\0\end{pmatrix}$$
$$\mp r\,sign(s)\left[\epsilon\frac{s^2}{2}+\epsilon\frac{\ln|s|}{2\eta_1^{0\,2}(\epsilon)}+\frac{\epsilon}{4\eta_1^{0\,2}(\epsilon)}+\frac{\epsilon\ln(2\eta_1^0(\epsilon))}{2\eta_1^{0\,2}(\epsilon)}\right]\begin{pmatrix}1\\0\\0\end{pmatrix}$$
$$+\mathcal{O}(\epsilon/s^2)+\mathcal{O}(\epsilon^2 s^3). \tag{2.36}$$

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 $\mathcal{O}(\epsilon/s^3) + \mathcal{O}(\epsilon^2 s^2)$.

Remark: The remainders in these formulae tend to zero in the inner regime, since we assume $\epsilon s^3 \to 0$. So, we only make use of the inner solution when

$$s \le \epsilon^{-\xi}, \text{ with } 0 < \xi < 1/3. \tag{2.37}$$

2.3 Asymptotics for Outer Solution

The outer solution is characterized by the regime

$$\begin{cases} \epsilon \to 0 \\ t \to 0 \\ |t|/\epsilon \to \infty. \end{cases} \tag{2.38}$$

To get the asymptotics of the solution of (2.2) and (2.3) in this regime, we assume an expansion of the form

$$a^{\mathcal{C}}(t) = a_0^{\mathcal{C}}(t) + g_1(\epsilon)a_1^{\mathcal{C}}(t) + g_2(\epsilon)a_2^{\mathcal{C}}(t) + \cdots \tag{2.39}$$

and substitute it into the equation. We expand $\nabla V^{\mathcal{C}}(a^{\mathcal{C}}(t), \epsilon)$ accordingly, using the condition $\epsilon/t \to 0$ and lemma 2.1 again, and solve the resulting equations for $a_j^{\mathcal{C}}(t)$, order by order, the dependence in ϵ of the $g_j(\epsilon)$ being determined in the course of the computation by matching the inner solution. We have to deal with the two cases $t \gtrless 0$ separately. The constants of integration are determined by matching with the asymptotics obtained for the inner solution.

Proposition 2.2 *Let $a^{\mathcal{C}}(t)$ be the solution of (2.2) and (2.3). In the regime $\epsilon \to 0$, $t \to 0$, $|t|/\epsilon \to \infty$ and $t^3/\epsilon^2 \to 0$ we have the asymptotics*

$$\begin{aligned} a^{\mathcal{A}}_{\mathcal{B}}(t) = & - \nabla\widetilde{V}(0,\epsilon)\frac{t^2}{2} + \eta^0(\epsilon)t \pm \frac{r}{\eta_1^0(\epsilon)}\epsilon t \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\ & \mp \; sign(t)\left[r\frac{t^2}{2} + \frac{\epsilon^2 \ln|t|}{2(\eta_1^0(\epsilon))^2} + \frac{\epsilon^2}{4(\eta_1^0(\epsilon))^2}(1 + 2\ln(2\eta_1^0(\epsilon))) - \frac{\epsilon^2\ln\epsilon}{2(\eta_1^0(\epsilon))^2}\right]\begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\ & + \; \mathcal{O}(t^3) + \mathcal{O}(\epsilon^4/t^2) \end{aligned}$$

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

Proof:
For convenience, we drop the ϵ-dependence of η^0 in the notation. We have

$$\begin{aligned} \nabla V^{\mathcal{A}}_{\mathcal{B}}(a^{\mathcal{C}}(t),\epsilon) = & \; \nabla \;\; \widetilde{V}(0,\epsilon) + \mathcal{O}(1) \\ & \pm \left[r\begin{pmatrix} a_1^{\mathcal{C}}(t) \\ 0 \\ \vdots \\ 0 \end{pmatrix} + \mathcal{O}(2)\right]\left(|a_1^{\mathcal{C}}(t)|\sqrt{1 + (\epsilon/a_1^{\mathcal{C}}(t))^2 + \mathcal{O}(3)/(a_1^{\mathcal{C}}(t))^2}\right)^{-1} \end{aligned} \tag{2.40}$$

where $\mathcal{O}(n)$ with $a^{\mathcal{C}}(t) = \mathcal{O}(t)$ in place of x and $\epsilon/t \to 0$ gives

$$\mathcal{O}(n) = \mathcal{O}(t^n). \tag{2.41}$$

With the property

$$|a_1^{\mathcal{C}}(t)| \geq c|t| \tag{2.42}$$

for a constant c uniform in ϵ, we get for the leading order

$$\frac{d^2}{dt^2} a_0^{\overset{\mathcal{A}}{\mathcal{B}}}(t) = -\nabla \widetilde{V}(0,\epsilon) \mp \operatorname{sign}(t) \begin{pmatrix} r \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \tag{2.43}$$

By integration

$$a_0^{\overset{\mathcal{A}}{\mathcal{B}}}(t) = -\nabla \widetilde{V}(0,\epsilon)\frac{t^2}{2} \mp \operatorname{sign}(t) \begin{pmatrix} r \\ 0 \\ \vdots \\ 0 \end{pmatrix} \frac{t^2}{2} + C_0(\epsilon)t + C_1(\epsilon) \tag{2.44}$$

where C_0 and C_1 are time independent vectors. Comparing with the expansion of the inner solution in corollary 2.1 we deduce

$$C_0(\epsilon) = \eta^0(\epsilon) \pm \frac{\epsilon r}{\eta_1^0(\epsilon)} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{2.45}$$

$$C_1(\epsilon) = 0. \tag{2.46}$$

Note that the ϵ-dependence of the $a_j^{\overset{\mathcal{A}}{\mathcal{B}}}(t)$ will cause no problem, see below. Let us determine the next order. Using (2.41) and (2.42), we further expand

$$\begin{aligned} &\left(1 + (\epsilon/a_1^{\mathcal{C}}(t))^2 + \mathcal{O}(3)/(a_1^{\mathcal{C}}(t))^2\right)^{-1/2} \\ &= 1 - \frac{\epsilon^2}{2a_1^{\mathcal{C}\,2}(t)} + \mathcal{O}(t) + \mathcal{O}(\epsilon^4/t^4) \end{aligned} \tag{2.47}$$

to get the equation

$$\begin{aligned} &\frac{d^2}{dt^2}(a_0^{\overset{\mathcal{A}}{\mathcal{B}}}(t) + g_1(\epsilon)a_1^{\overset{\mathcal{A}}{\mathcal{B}}}(t) + \cdots) \\ = \;& -\nabla \widetilde{V}(0,\epsilon) \mp \operatorname{sign}(t) r \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\ &\pm \operatorname{sign}(t) \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \frac{\epsilon^2 r}{2} \frac{1}{(a_0^{\overset{\mathcal{A}}{\mathcal{B}}}{}_1(t) + g_1(\epsilon)a_1^{\overset{\mathcal{A}}{\mathcal{B}}}{}_1(t) + \cdots)^2} + \mathcal{O}(|t|) + \mathcal{O}(\epsilon^4/t^4). \end{aligned} \tag{2.48}$$

Thus, it follows from (2.43) and (2.44) that the next order must satisfy

$$g_1(\epsilon)\frac{d^2}{dt^2}a_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(t) = \pm\mathrm{sign}(t)\begin{pmatrix}1\\0\\ \vdots\\0\end{pmatrix}\frac{\epsilon^2 r}{2(\eta_1^0 t)^2}. \tag{2.49}$$

Comparison with the asymptotics of the inner solution shows that we must choose $g_1(\epsilon) = \epsilon^2$ and integration yields

$$a_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(t) = \mp\mathrm{sign}(t)\begin{pmatrix}r\\0\\ \vdots\\0\end{pmatrix}\frac{r}{2{\eta_1^0}^2}\ln|t| + D_0(\epsilon)t + D_1(\epsilon) \tag{2.50}$$

where $D_0(\epsilon)$ and $D_1(\epsilon)$ are constant vectors in $I\!R^n$. By matching with corollary 2.1, we get

$$\begin{aligned} D_0(\epsilon) &= 0 &(2.51)\\ D_1(\epsilon) &= \mp\mathrm{sign}(t)\begin{pmatrix}1\\0\\ \vdots\\0\end{pmatrix}\left[\frac{r}{2{\eta_1^0}^2}\left(1/2+\ln(2\eta_1^0)\right) - \frac{r\ln\epsilon}{2{\eta_1^0}^2}\right]. \end{aligned}$$

We now have to show that equations (2.44) and (2.50) correctly give the asymptotic behavior of $a^{\mathcal{C}}(t)$ in the chosen regime. We compute

$$\begin{aligned} &\frac{d^2}{dt^2}(a^{\substack{\mathcal{A}\\ \mathcal{B}}}(t) - a_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(t) - \epsilon^2 a_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(t)) &(2.52)\\ = \;& -\nabla\widetilde{V}(a^{\substack{\mathcal{A}\\ \mathcal{B}}}(t),\epsilon) + \nabla\widetilde{V}(0,\epsilon)\\ &\mp\begin{pmatrix}r\\0\\ \vdots\\0\end{pmatrix}\left[\frac{1}{\sqrt{1+(\epsilon/a_1^{\mathcal{C}}(t))^2+\mathcal{O}(t)}} - 1 + \frac{\epsilon^2}{2(\eta_1^0 t)^2}\right]\\ &+\mathcal{O}(t)/\sqrt{1+\mathcal{O}(\epsilon^2/t^2)+\mathcal{O}(t)}. \end{aligned}$$

Using lemma 2.1 again we have

$$\begin{aligned} \left(1+\frac{\epsilon^2}{{a_1^{\mathcal{C}}}^2(t)}+\mathcal{O}(t)\right)^{-1/2} &= 1 - \frac{\epsilon^2}{2{a_1^{\mathcal{C}}}^2(t)} + \mathcal{O}(t) + \mathcal{O}(\epsilon^4/t^4) &(2.53)\\ &= 1 - \frac{\epsilon^2}{2(\eta_1^0 t)^2} + \mathcal{O}(\epsilon^2/t) + \mathcal{O}(t) + \mathcal{O}(\epsilon^4/t^4) \end{aligned}$$

where $\epsilon^2/t = \mathcal{O}(t)$. Finally

$$\frac{d^2}{dt^2}(a^{\substack{\mathcal{A}\\ \mathcal{B}}}(t) - a_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(t) - \epsilon^2 a_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(t)) = \mathcal{O}(t) + \mathcal{O}(\epsilon^4/t^4) \tag{2.54}$$

from which the result follows. □

2.4 Classical Action Integrals

We give here the asymptotics in the outer regime of some classical quantities which will give rise to phases when we turn to the construction of the quantum mechanical wave functions. Let

$$
\begin{aligned}
S^{\mathcal{C}}(t) &= \int_0^t \left(\frac{\eta^{\mathcal{C}2}(t')}{2} - V^{\mathcal{C}}(a^{\mathcal{C}}(t'), \epsilon) \right) dt' &(2.55)\\
&= \int_0^t \eta^{\mathcal{C}2}(t')dt' - \eta^{02}(\epsilon)\frac{t}{2} - V^{\mathcal{C}}(a^{\mathcal{C}}(0), \epsilon)t, &(2.56)
\end{aligned}
$$

and let $S(t)$ be the same quantity for $V^{\mathcal{C}}(x,\epsilon) \equiv \widetilde{V}(x,\epsilon)$. ¿From lemma 2.2 we easily deduce

Lemma 2.3 *As $t \to 0$,*

$$
S(t) = \eta^{02}(\epsilon)\frac{t}{2} - \widetilde{V}(0,\epsilon)t - \eta^0(\epsilon)\nabla\widetilde{V}(0,\epsilon)t^2 + \mathcal{O}(t^3), \tag{2.57}
$$

uniformly in ϵ.

¿From proposition 2.2, and the formula

$$
V^{\mathcal{A}}_{\mathcal{B}}(0,\epsilon) = \widetilde{V}(0,\epsilon) \pm \epsilon r + \mathcal{O}(\epsilon^2) \tag{2.58}
$$

Lemma 2.4 *In the regime $\epsilon \to 0$, $t \to 0$, $|t|/\epsilon \to \infty$ and $t^3/\epsilon^2 \to 0$ we have the asymptotics*

$$
\begin{aligned}
S^{\mathcal{A}}_{\mathcal{B}}(t) = \quad & S_0{}^{\mathcal{A}}_{\mathcal{B}}(\epsilon, sign(t)) - \widetilde{V}(0,\epsilon)t + \eta^{02}(\epsilon)\frac{t}{2} - \eta^0(\epsilon)\nabla\widetilde{V}(0,\epsilon)t^2 \pm r\epsilon t \\
& \mp sign(t)\left(r\eta_1^0(\epsilon)t^2 + \frac{r}{\eta_1^0(\epsilon)}\epsilon^2 \ln|t| \right) + \mathcal{O}(t^3) + \mathcal{O}(\epsilon^4/t^2) + \mathcal{O}(\epsilon^3 \ln t).
\end{aligned}
$$

2.5 Different Initial Momenta

For later purposes, we assume from now on that the solution $a(t)$ of (2.2) with $V^{\mathcal{C}}(x,\epsilon) \equiv \widetilde{V}(x,\epsilon)$ is subject to the initial conditions

$$
\begin{aligned}
a(0) &= 0 \\
\eta(0) &= \eta^0
\end{aligned} \tag{2.59}
$$

whereas the solutions $a^{\mathcal{C}}(t)$ satisfy

$$
\begin{aligned}
a^{\mathcal{C}}(0) &= 0 \\
\eta^{\mathcal{C}}(0) &= \eta^0(\epsilon) = \eta^0 + \mathcal{O}(\epsilon).
\end{aligned} \tag{2.60}
$$

The $\mathcal{O}(\epsilon)$ term must be included in our calculations because when the electrons makes a transition from one energy level surface to another, the nuclei must compensate by making a change in their kinetic energy in order to conserve the total energy of the whole system.

We easily get the estimates

Corollary 2.2 *When $\epsilon \to 0$, $t \to 0$, $t^3/\epsilon^2 \to 0$ and $|t|/\epsilon \to \infty$ we have*

$$\begin{aligned}
& \eta^{\mathcal{A}}_{\mathcal{B}}(t)(a(t) - a^{\mathcal{A}}_{\mathcal{B}}(t)) \\
= & \mp r\epsilon t - (\eta^0(\epsilon) - \eta^0)\eta^0(\epsilon)t \\
& \pm sign(t)\left[\frac{r\eta_1^0(\epsilon)}{2}t^2 + \frac{r}{2\eta_1^0(\epsilon)}\left(\epsilon^2 \ln|t| + \epsilon^2(\ln(2\eta_1^0(\epsilon)) + 1/2) - \epsilon^2 \ln\epsilon\right)\right] \\
& +\mathcal{O}(t^3) + \mathcal{O}(\epsilon^4/t^2) + \mathcal{O}(t\epsilon^2 \ln\epsilon)
\end{aligned}$$

and

Corollary 2.3 *When $\epsilon \to 0$, $t \to 0$, $t^3/\epsilon^2 \to 0$ and $|t|/\epsilon \to \infty$ we have*

$$\begin{aligned}
S^{\mathcal{A}}_{\mathcal{B}}(t) &= S^{\mathcal{A}}_{\mathcal{B}}(\epsilon, sign(t))_0 + S(t) + ({\eta^0}^2(\epsilon) - {\eta^0}^2)\frac{t}{2} \pm r\epsilon t \\
& \mp sign(t)\left(r\eta_1^0(\epsilon)t^2 + \frac{r}{\eta_1^0(\epsilon)}\epsilon^2 \ln|t|\right) \\
& +\mathcal{O}(t^3) + \mathcal{O}(\epsilon^4/t^2) + \mathcal{O}(\epsilon^3 \ln t).
\end{aligned}$$

2.6 Matrices $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$

The construction of the semiclassical wave packets that describe the nuclei requires the computation of matrices which are defined by means of classical quantities. Let $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ be the matrix solutions of the linear system

$$\begin{aligned}
\frac{d}{dt}A^{\mathcal{C}}(t) &= iB^{\mathcal{C}}(t) \\
\frac{d}{dt}B^{\mathcal{C}}(t) &= iV^{(2)}(a^{\mathcal{C}}(t), \epsilon)A^{\mathcal{C}}(t)
\end{aligned} \tag{2.61}$$

where $a^{\mathcal{C}}(t)$ is the solution of (2.2) and (2.3), with initial conditions

$$\begin{aligned}
A^{\mathcal{C}}(0) &= A_0 \\
B^{\mathcal{C}}(0) &= B_0.
\end{aligned} \tag{2.62}$$

Let us determine the leading order of $V^{(2)}(a^{\mathcal{C}}(t), \epsilon)$. ¿From (2.13) and (1.20) it is easily seen that the Hessian matrix

$$\left(\sqrt{\beta^2 + \gamma^2 + \delta^2}\right)^{(2)} = \frac{(\delta^2 + \gamma^2)|\nabla\beta\rangle\langle\nabla\beta| + \mathcal{O}(3)}{(\beta^2 + \gamma^2 + \delta^2)^{3/2}}, \tag{2.63}$$

with the notation used above. Explicitly

$$\left(\sqrt{\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)}\right)^{(2)} = \frac{r\epsilon^2 P + \mathcal{O}(3)}{\left({x_1}^2 + \epsilon^2 + \mathcal{O}(3)\right)^{3/2}} \tag{2.64}$$

where

$$P = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & 0 \end{pmatrix}. \tag{2.65}$$

When x is replaced by $a^{\mathcal{C}}(t) = \eta^0(\epsilon)t + \mathcal{O}(t^2)$, the error terms $\mathcal{O}(3)$ become $\mathcal{O}((|t|+\epsilon)^3)$ and using $|a_1^{\mathcal{C}}(t)| \geq c|t|$, we get

$$\left(a_1^{\mathcal{C}}(t)^2 + \epsilon^2 + \mathcal{O}(3)\right)^{3/2} = \left((\eta^0(\epsilon)_1 t)^2 + \epsilon^2\right)^{3/2} (1 + \mathcal{O}(|t|+\epsilon)). \tag{2.66}$$

This last estimate allows us to get the leading order behavior of $V^{(2)}(a^{\mathcal{C}}(t),\epsilon)$ as $\epsilon \to 0$ and $t \to 0$:

$$V^{(2)}(a^{\mathcal{A}}_{\mathcal{B}}(t),\epsilon) = \pm \frac{r\epsilon^2}{((\eta_1^0(\epsilon)t)^2 + \epsilon^2)^{3/2}} P + \mathcal{O}(\epsilon^0 + t^0). \tag{2.67}$$

Consequently, for any positive ϵ, the equation defining $A^{\mathcal{C}}$ and $B^{\mathcal{C}}$ is regular as $t \to 0$. Moreover,

Proposition 2.3 *Let $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ be the solutions of (2.61) and (2.62). For t and ϵ small enough, we have*

$$\begin{aligned} A^{\mathcal{A}}_{\mathcal{B}}(t) &= A_0 + \mathcal{O}(t) \\ B^{\mathcal{A}}_{\mathcal{B}}(t) &= B_0 \pm irPA_0 \frac{t}{\sqrt{(\eta_1^0(\epsilon)t)^2 + \epsilon^2}} + \mathcal{O}(t), \end{aligned}$$

uniformly in ϵ.

Corollary 2.4 *In the regime $\epsilon \to 0$, $t \to 0$ and $|t|/\epsilon \to \infty$ we have*

$$\begin{aligned} B^{\mathcal{A}}_{\mathcal{B}}(t) &= B_0 \mp sign(t) \frac{ir}{\eta_1^0(\epsilon)} PA_0 + \mathcal{O}(t) + \mathcal{O}(\epsilon^2/t^2) \\ &\equiv B_0^{\mathcal{A}}{}_{\mathcal{B}}(sign(t)) + \mathcal{O}(t) + \mathcal{O}(\epsilon^2/t^2). \end{aligned}$$

Proof:
Equations (2.61) and (2.62) are equivalent to the linear system

$$\frac{d}{dt}\begin{pmatrix} A^{\mathcal{C}}(t) \\ B^{\mathcal{C}}(t) \end{pmatrix} = i \begin{pmatrix} \mathbb{O} & \mathbb{I} \\ V^{(2)}(a^{\mathcal{C}}(t),\epsilon) & \mathbb{O} \end{pmatrix} \begin{pmatrix} A^{\mathcal{C}}(t) \\ B^{\mathcal{C}}(t) \end{pmatrix}, \qquad \begin{pmatrix} A^{\mathcal{C}}(0) \\ B^{\mathcal{C}}(0) \end{pmatrix} = \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}, \tag{2.68}$$

where $\mathbb{O}$ and $\mathbb{I}$ are the $n \times n$ zero and unity matrices. Moreover, the generator is continuous and uniformly bounded for all t small enough, so that the solution exists, is unique, and satisfies the integral equation

$$\begin{pmatrix} A^{\mathcal{C}}(t) \\ B^{\mathcal{C}}(t) \end{pmatrix} = \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} + i \int_0^t \begin{pmatrix} B^{\mathcal{C}}(t') \\ V^{(2)}(a^{\mathcal{C}}(t'),\epsilon) A^{\mathcal{C}}(t') \end{pmatrix} dt'. \tag{2.69}$$

Introducing the norm

$$\|D\|_\infty = \sup_{(t,\epsilon)\in B_T} \|D(t,\epsilon)\| \tag{2.70}$$

on the set of matrices depending on t and ϵ, we get

$$\left\| \int_0^t B^{\mathcal{C}}(t')dt' \right\| \leq \|B^{\mathcal{C}}\|_\infty \, t, \tag{2.71}$$

$$\left\| \int_0^t V^{(2)}(a^{\mathcal{C}}(t'),\epsilon) A^{\mathcal{C}}(t') dt' \right\| \leq \|A^{\mathcal{C}}\|_\infty \int_0^t \|V^{(2)}(a^{\mathcal{C}}(t'),\epsilon)\| dt', \tag{2.72}$$

where, by virtue of (2.67),

$$\begin{aligned}\int_0^t \|V^{(2)}(a^{\mathcal{C}}(t'),\epsilon)\|dt' &\leq c\int_0^t \left(\frac{\epsilon^2}{\left(t'^2+\epsilon^2\right)^{3/2}}+1\right)dt' \\ &= c\frac{t}{\sqrt{t^2+\epsilon^2}}+ct \leq c(1+T)\equiv C \end{aligned} \tag{2.73}$$

uniformly in ϵ. Consequently, we get the estimates

$$\|A^{\mathcal{C}}-A_0\|_\infty \leq t\|B^{\mathcal{C}}-B_0\|_\infty + t\|B_0\| \tag{2.74}$$

$$\|B^{\mathcal{C}}-B_0\|_\infty \leq C\|A^{\mathcal{C}}-A_0\|_\infty + C\|A_0\| \tag{2.75}$$

which imply

$$\|A^{\mathcal{C}}-A_0\|_\infty \leq Ct\|A^{\mathcal{C}}-A_0\|_\infty + t\left(C\|A_0\|+\|B_0\|\right). \tag{2.76}$$

Hence, if t is so small that $1-Ct\geq 1/2$,

$$\|A^{\mathcal{C}}-A_0\|_\infty \leq 2t\left(C\|A_0\|+\|B_0\|\right) \tag{2.77}$$

and

$$A^{\mathcal{C}}(t)=A_0+\mathcal{O}(t) \tag{2.78}$$

uniformly in ϵ. The use of this estimate and (2.67) in (2.69) yields

$$\begin{aligned} B^{\mathcal{A}}_{\mathcal{B}}(t) &= B_0 \pm i\epsilon^2 rPA_0\int_0^t \frac{dt'}{\left((\eta_1^0t')^2+\epsilon^2\right)^{3/2}}+\mathcal{O}(t) \\ &\quad +\mathcal{O}\left(\int_0^t \frac{\epsilon^2 t'dt'}{\left((\eta_1^0t')^2+\epsilon^2\right)^{3/2}}\right) \\ &= B_0 \pm irPA_0\frac{t}{\sqrt{(\eta_1^0t)^2+\epsilon^2}}+\mathcal{O}(t)+\mathcal{O}\left(\frac{\epsilon t}{\sqrt{(\eta_1^0t)^2+\epsilon^2}}\right) \\ &= B_0 \pm irPA_0\frac{t}{\sqrt{(\eta_1^0t)^2+\epsilon^2}}+\mathcal{O}(t). \end{aligned} \tag{2.79}$$

□

3 Type 1 Avoided Crossings

We now have all the ingredients required to construct an asymptotic solution to the equation

$$i\epsilon^2\frac{\partial}{\partial t}\psi(x,t) = -\frac{\epsilon^4}{2}\Delta\psi(x,t)+h(x,\epsilon)\psi(x,t) \tag{3.1}$$

as $\epsilon\to 0$. Let us describe the building blocks and give their main properties.

3.1 Semiclassical Nuclear Wave Packets

The semiclassical motion of the nuclei is described by means of wave packets to be thought of as centered in phase space on the classical trajectory, and of width $\mathcal{O}(\epsilon)$. These are the same wave packets that are used in [7, 16].

Let n denote the dimension of the space of nuclear configurations. A multi-index $l = (l_1, l_2, \ldots, l_n)$ is an ordered n-tuple of non–negative integers. The order of l is defined to be $|l| = \sum_{j=1}^{n} l_j$, and the factorial of l is defined to be $l! = (l_1!)(l_2!)\cdots(l_n!)$. The symbol D^l denotes the differential operator $D^l = \frac{\partial^{|l|}}{(\partial x_1)^{l_1}(\partial x_2)^{l_2}\cdots(\partial x_n)^{l_n}}$, and the symbol x^l denotes the monomial $x^l = x_1^{l_1} x_2^{l_2}\cdots x_n^{l_n}$. We denote the gradient of a function f by $f^{(1)}$ and the matrix of second partial derivatives by $f^{(2)}$. We view $I\!R^n$ as a subset of $\mathbb{C}^n$, and let e_i denote the $i^{\rm th}$ standard basis vector in $I\!R^n$ or $\mathbb{C}^n$. The inner product on $I\!R^n$ or $\mathbb{C}^n$ is $\langle\, v,\, w\,\rangle = \sum_{j=1}^{n} \overline{v_j} w_j$.

The semiclassical wave packets we use are products of complex Gaussians and generalizations of Hermite polynomials. The generalizations of the zeroth and first order Hermite polynomials are

$$\widetilde{\mathcal{H}}_0(x) \;=\; 1 \qquad (3.2)$$

and

$$\widetilde{\mathcal{H}}_1(x) \;=\; 2\,\langle\, v,\, x\,\rangle, \qquad (3.3)$$

where v is an arbitrary non–zero vector in $\mathbb{C}^n$. The generalizations of the higher order Hermite polynomials are defined recursively as follows: Let $v_1, v_2, \ldots, v_m$ be m arbitrary non–zero vectors in $\mathbb{C}^n$. Then

$$\begin{aligned}\widetilde{\mathcal{H}}_m(v_1,\, v_2,\, \ldots,\, v_m;\, x) \;=\;& 2\,\langle\, v_m,\, x\,\rangle\, \widetilde{\mathcal{H}}_{m-1}(v_1,\, v_2,\, \ldots,\, v_{m-1};\, x) \\ &-\; 2\sum_{i=1}^{m-1} \langle\, v_m,\, \overline{v_i}\,\rangle\, \widetilde{\mathcal{H}}_{m-2}(v_1,\, \ldots,\, v_{i-1},\, v_{i+1},\, \ldots,\, v_{m-1};\, x).\end{aligned}$$

One can prove [7] that these functions do not depend on the ordering of the vectors $v_1, v_2, \ldots, v_m$. Furthermore, if the space dimension is $n = 1$ and the vectors $v_1, v_2, \ldots, v_m$ are all equal to $1 \in \mathbb{C}^1$, then $\widetilde{\mathcal{H}}_m(v_1, v_2, \ldots, v_m; x)$ is equal to the usual Hermite polynomial $H_m(x)$.

Now suppose A is a complex invertible $n \times n$ matrix. We define $|A| = [AA^*]^{1/2}$, where A^* denotes the adjoint of A. By the polar decomposition theorem, there exists a unique unitary matrix U_A, such that $A = |A|\,U_A$. Given a multi-index l, we define the polynomial

$$\mathcal{H}_l(A;\, x) \;=\; \widetilde{\mathcal{H}}_{|l|}(\underbrace{U_Ae_1, \ldots, U_Ae_1}_{l_1 \textit{ entries}}, \underbrace{U_Ae_2, \ldots, U_Ae_2}_{l_2 \textit{ entries}}, \ldots, \underbrace{U_Ae_n, \ldots, U_Ae_n}_{l_n \textit{ entries}};\, x) \qquad (3.4)$$

We can now define the semiclassical wave packets $\varphi_l(A, B, \hbar, a, \eta, x)$. In the Born–Oppenheimer approximation, the role of $\hbar$ is played by ϵ^2.

Definition. *Let A and B be complex $n \times n$ matrices with the following properties:*

A and B are invertible; (3.5)

BA^{-1} is symmetric ([real symmetric]$+\,i$[real symmetric]); (3.6)

$$\textit{Re } BA^{-1} \;=\; \frac{1}{2}[(BA^{-1}) + (BA^{-1})^*] \textit{ is strictly positive definite;} \qquad (3.7)$$

$$(\textit{Re } BA^{-1})^{-1} \;=\; AA^*. \qquad (3.8)$$

Let $a \in I\!R^n$, $\eta \in I\!R^n$, and $\hbar > 0$. Then for each multi-index l we define

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

The choice of the branch of the square root of $[\det\,A]^{-1}$ in this definition depends on the context, and is determined by initial conditions and continuity in time.

Remarks. 1. We never use the functions $\varphi_l(A,B,\hbar,a,\eta,x)$ unless conditions (3.5)–(3.8) are satisfied.
2. Condition (3.8) is equivalent to the more symmetrical condition

$$A^*B\;+\;B^*A\;=\;2I\!I, \tag{3.9}$$

3. For fixed A, B, $\hbar$, a, and η, the functions $\varphi_l(A,B,\hbar,a,\eta,x)$ form an orthonormal basis of $L^2(I\!R^n)$. The proof can be found in [7].
4. Generically U_A and U_B are complex unitary matrices, and A and B are Hermitian. In the special cases when they all happen to be real, the functions $\varphi_l(A,B,\hbar,a,\eta,x)$ are simply rotated and dilated eigenfunctions of the n dimensional harmonic oscillator.
5. The utility of the functions $\varphi_l(A,B,\hbar,a,\eta,x)$ stems from their remarkably beautiful behavior under Fourier transforms. If we define the scaled Fourier transform to be

$$[\,\mathcal{F}_\hbar\Psi\,](\xi)\;=\;(2\pi\hbar)^{-n/2}\int_{I\!R^n}\Psi(x)\,e^{-i\langle\,\xi,\,x\,\rangle/\hbar}\,dx, \tag{3.10}$$

then

$$[\,\mathcal{F}_\hbar\,\varphi_l(A,B,\hbar,a,\eta,\,\cdot\,)\,](\xi)\;=\;(-i)^{|l|}\,e^{-i\langle\,\eta,\,a\,\rangle/\hbar}\,\varphi_l(B,A,\hbar,\eta,-a,\xi). \tag{3.11}$$

The only proof we know of this formula involves a messy induction on $|l|$. The details may be found in [7].
6. The functions $\varphi_l(A,B,\hbar,a,\eta,x)$ separate the position and momentum uncertainties from one another. For any given l, the position uncertainty depends only on $|A|$ and the momentum uncertainty depends only on $|B|$. For example, when the space dimension is $n=1$, the position and momentum uncertainites of $\varphi_l(A,B,\hbar,a,\eta,x)$ are given by $[(l+\frac{1}{2})\hbar]^{1/2}|A|$ and $[(l+\frac{1}{2})\hbar]^{1/2}|B|$, respectively.
7. For technical reasons related to Remark 6, it is crucial that the matrix B only appear in the exponent in the definition of $\varphi_l(A,B,\hbar,a,\eta,x)$, and not in the polynomial. By Remark 5, the matrix A only occurs in the exponent of the Fourier transform. This turns out to be technically crucial, also. The fulfillment of these technical requirements makes the Fourier transform formula in Remark 5 all the more amazing.

The formulas for the functions $\varphi_l(A,B,\hbar,a,\eta,x)$ are rather complicated, but the leading order semiclassical propagation of these wave packets is very simple. Under mild hypotheses (*e.g.*, $V \in C^3$ and bounded below), the Schrödinger equation

$$i\,\hbar\,\frac{\partial\Psi}{\partial t}\;=\;-\,\frac{\hbar^2}{2}\,\frac{\partial^2\Psi}{\partial x^2}\;+\;V(x)\,\Psi \tag{3.12}$$

has an approximate solution of the form

$$e^{iS(t)/\hbar}\,\varphi_l(A(t),B(t),\hbar,a(t),\eta(t),x)\;+\;O(\hbar^{1/2}). \tag{3.13}$$

Here $O(\hbar^{1/2})$ means that the exact solution and the approximate solution agree up to an error whose norm is bounded by an l–dependent constant times $\hbar^{1/2}$ for t in a fixed bounded interval $[-T,\,T]$. The vectors $a(t)$ and $\eta(t)$ satisfy the classical equations of motion

$$\frac{\partial a}{\partial t}(t) \;=\; \eta(t), \tag{3.14}$$

$$\frac{\partial \eta}{\partial t}(t) \;=\; -V^{(1)}(a(t)). \tag{3.15}$$

The function $S(t)$ is the classical action integral associated with the classical path,

$$S(t) \;=\; \int_{-T}^{t}\left(\frac{(\eta(s))^2}{2}\;-\;V(a(s))\right)\,ds. \tag{3.16}$$

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

$$\frac{\partial A}{\partial t}(t) \;=\; iB(t), \tag{3.17}$$

$$\frac{\partial B}{\partial t}(t) \;=\; iV^{(2)}(a(t))\,A(t). \tag{3.18}$$

If $A(-T)$ and $B(-T)$ satisfy conditions (3.5)–(3.8), then so do $A(t)$ and $B(t)$ for each t. The proofs of the claims we have made about the $\varphi_l(A,B,\hbar,a,\eta,x)$ and other properties of the quantities introduced can be found in [7].

Consider φ_l defined in (3.9). Since the vectors and matrices a,η,A and B will be replaced in these functions by $a^{\mathcal{C}}(t),\eta^{\mathcal{C}}(t),A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ solutions of (2.2) and (2.61), we need to control the changes of φ_l induced by changes in a,η,A and B.

Lemma 3.1 *We have, in the $L^2(I\!\!R^n)$ sense,*

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

Proof:
Let us introduce the temporary notation

$$\psi(A,B,y) = \varphi_l(A,B,1,0,0,y) \tag{3.19}$$

so that

$$\varphi_l(A,B,\epsilon^2,0,a,x) = \epsilon^{-n/2}\psi(A,B,(x-a)/\epsilon). \tag{3.20}$$

Consider

$$\begin{aligned}&\psi(A+A',B+B',(x-a-a')/\epsilon)-\psi(A,B,(x-a)/\epsilon)\\ &=\psi(A+A',B+B',(x-a-a')/\epsilon)-\psi(A+A',B,(x-a-a')/\epsilon)\\ &\quad+\psi(A+A',B,(x-a-a')/\epsilon)-\psi(A,B,(x-a-a')/\epsilon)\\ &\quad+\psi(A,B,(x-a-a')/\epsilon)-\psi(A,B,(x-a)/\epsilon).\end{aligned} \tag{3.21}$$

We separately estimate each of the three differences on the right hand side of this equation.

We compute the Fréchet differential,

$$D_B\psi(A,B,y)(B') = -\frac{1}{2}\psi(A,B,y)\langle y|B'A^{-1}y\rangle, \tag{3.22}$$

so that by the mean value theorem,

$$\begin{aligned}
&|\psi(A+A',B+B',(x-a-a')/\epsilon) - \psi(A+A',B,(x-a-a')/\epsilon)| \\
&\leq \sup_{t\in[0,1]} |\psi(A+A',B+tB',(x-a-a')/\epsilon)|\frac{|x-a-a'|^2}{\epsilon^2}\|(A+A')^{-1}\|\|B'\|.
\end{aligned} \tag{3.23}$$

But, since by assumption $\operatorname{Re} BA^{-1}$ is strictly positive definite, and

$$h(A,|A|^{-1}y) = \frac{1}{2^{|l|/2}l!^{1/2}\pi^{n/4}(\det A)^{1/2}}\mathcal{H}_l(A,|A|^{-1}y) \tag{3.24}$$

is a polynomial of degree $|l|$ in its second variable, we have, for $\|A'\|$, $\|B'\|$ small enough, and for any positive p,

$$\begin{aligned}
&\epsilon^{-n}\int_{I\!R^n}\left|\exp\left(-\langle(x-a-a')|(B+B')(A+A')^{-1}(x-a-a')\rangle/(2\epsilon^2)\right)\right|^2 \times \\
&\qquad\qquad \times\ |(x-a-a')/\epsilon|^p\,dx \\
&= \int_{I\!R^n}\left|\exp\left(-\langle y|(B+B')(A+A')^{-1}y\rangle/2\right)\right|^2|y|^p\,dy \\
&\leq n_p(A,B),
\end{aligned} \tag{3.25}$$

uniformly in A', B', a and a'. Thus, for some constant depending only on A and B,

$$\begin{aligned}
&\epsilon^{-n/2}\|\psi(A+A',B+B',(\cdot-a-a')/\epsilon) - \\
&\qquad \psi(A+A',B,(\cdot-a-a')/\epsilon)\|_{L^2(I\!R^n)} \\
&\leq C(A,B)\|B'\|.
\end{aligned} \tag{3.26}$$

This estimate together with the Plancherel identity and (3.10) yield

$$\begin{aligned}
&\epsilon^{-n/2}\|\psi(A+A',B,(\cdot-a-a')/\epsilon) - \psi(A,B,(\cdot-a-a')/\epsilon)\|_{L^2(I\!R^n)} \\
&\leq \epsilon^{-n/2}\|[\,\mathcal{F}_\hbar\Psi\,](A+A',B,(\cdot-a-a')/\epsilon) - [\,\mathcal{F}_\hbar\Psi\,](A,B,(\cdot-a-a')/\epsilon)\|_{L^2(I\!R^n)} \\
&= \epsilon^{-n/2}\|\psi(B,A+A',(\cdot+a+a')/\epsilon) - \psi(B,A,(\cdot+a+a')/\epsilon)\|_{L^2(I\!R^n)} \\
&\leq C(B,A)\|A'\|.
\end{aligned} \tag{3.27}$$

Finally, using the notation given in (3.24),

$$|\psi(A,B,y) - \psi(A,B,y+y')| \leq \sup_{t\in[0,1]}|D_y\psi(A,B,y+ty')(y')| \tag{3.28}$$

where

$$\begin{aligned}
D_y\psi(A,B,y)(y') =\ &-\ \frac{1}{2}\psi(A,B,y)(\langle y|BA^{-1}y'\rangle + \langle y'|BA^{-1}y\rangle) \\
&+\ \exp\left(-\langle y|BA^{-1}y\rangle/2\right)D_2h(A,|A|^{-1}y)(|A|^{-1}y').
\end{aligned} \tag{3.29}$$

Thus we can write

$$
\begin{aligned}
&\epsilon^{-n/2}|\psi(A,B,(x-a-a')/\epsilon)-\psi(A,B,(x-a)/\epsilon)| \\
&\leq \epsilon^{-n/2}\sup_{t\in[0,1]}\Big|\exp\Big(-\langle (x-a-ta')/\epsilon|BA^{-1}(x-a-ta')/\epsilon\rangle/2\Big) \\
&\qquad\qquad \times P(A,|A|^{-1}(x-a-ta')/\epsilon)\Big|\,\|a'\|/\epsilon \\
&= \epsilon^{-n/2}\Big|\exp\Big(-\langle (x-a-t_0a')/\epsilon|BA^{-1}(x-a-t_0a')/\epsilon\rangle/2\Big) \\
&\qquad\qquad \times P(A,|A|^{-1}(x-a-t_0a')/\epsilon)\Big|\,\|a'\|/\epsilon
\end{aligned}
\tag{3.30}
$$

where $P(A,y)$ is a polynomial of order $|l|$ in y and $[0,1]\ni t_0=t_0(A,B,a,a',\epsilon)$ is the point where the supremum is reached. Hence, using (3.25) again, we deduce

$$
\epsilon^{-n/2}\|\psi(A,B,(x-a-a')/\epsilon)-\psi(A,B,(x-a)/\epsilon)\|_{L^2(\mathbb{R}^n)}\leq C'(A,B)\|a'\|/\epsilon \tag{3.31}
$$

for some constant $C'(A,B)$ uniform in a, a' and t_0. □

3.2 Choice of Eigenvectors

In this section we present a procedure for choosing the electronic eigenvectors and their phases. Although the electronic hamiltonian is independent of time, it is convenient, since we deal with the time dependent Schrödinger equation, to choose specific time dependent electronic eigenvectors. Indeed, the electrons follow the motion of the nuclei in an adiabatic way, so the suitable instantaneous electronic eigenvectors must satisfy some parallel transport condition to take into account the geometric phases arising in this situation. These eigenvectors thus depend on the classical trajectories. Since they may become singular when the corresponding eigenvalues are degenerate, or almost degenerate, we shall define them for t in the outer regime. We shall have two sets of eigenvectors, denoted by $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$, where the label $\pm$, refers to positive and negative times.

Let $\eta^{\mathcal{C}}(t)$ be the solution of the classical equations of motion (2.2) and (2.3). The normalized eigenvectors $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$ are the solutions of

$$
\langle \Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)|\left(\partial/\partial t+\eta^{\mathcal{C}}(t)\nabla\right)\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)\rangle\equiv 0 \tag{3.32}
$$

for $\mathcal{C}=\mathcal{A},\mathcal{B}$ and $t\gtrless 0$. Since the eigenvalues $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ are non-degenerate for any time t, t small enough, such vectors exist, are unique up to an overall time independent phase factors and are eigenvectors of $h_1(x,\epsilon)$ associated with $E_{\mathcal{C}}(x,\epsilon)$ for any time, see [16]. Let us make the construction of these eigenvectors more specific and give their small t and small ϵ asymptotics. We define the angles $\varphi(x,\epsilon)$ and $\theta(x,\epsilon)$ by

$$
\begin{aligned}
\beta(x,\epsilon) &= \sqrt{\beta^2(x,\epsilon)+\gamma^2(x,\epsilon)+\delta^2(x,\epsilon)}\cos(\theta(x,\epsilon)) && (3.33)\\
\gamma(x,\epsilon) &= \sqrt{\beta^2(x,\epsilon)+\gamma^2(x,\epsilon)+\delta^2(x,\epsilon)}\sin(\theta(x,\epsilon))\cos(\varphi(x,\epsilon)) && (3.34)\\
\delta(x,\epsilon) &= \sqrt{\beta^2(x,\epsilon)+\gamma^2(x,\epsilon)+\delta^2(x,\epsilon)}\sin(\theta(x,\epsilon))\sin(\varphi(x,\epsilon)). && (3.35)
\end{aligned}
$$

and construct static eigenvectors. Let

$$
\begin{aligned}
\Phi^{-}_{\mathcal{A}}(x,\epsilon) &= \mathrm{e}^{i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon)+\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon) && (3.36)\\
\Phi^{-}_{\mathcal{B}}(x,\epsilon) &= \mathrm{e}^{-i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_2(x,\epsilon)-\sin(\theta(x,\epsilon)/2)\psi_1(x,\epsilon) && (3.37)
\end{aligned}
$$

be the eigenvectors of $h_1(x,\epsilon)$ associated with $E_{\mathcal{C}}(x,\epsilon)$, $\mathcal{C}=\mathcal{A},\mathcal{B}$ for $\pi/2<\theta(x,\epsilon)\leq\pi$ and

$$\begin{aligned}\Phi^+_{\mathcal{A}}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon)+\mathrm{e}^{-i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon) && (3.38)\\ \Phi^+_{\mathcal{B}}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_2(x,\epsilon)-\mathrm{e}^{i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_1(x,\epsilon) && (3.39)\end{aligned}$$

be the eigenvectors of $h_1(x,\epsilon)$ for $0\leq\theta(x,\epsilon)<\pi/2$. The solutions of (3.32) are of the form

$$\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)=\Phi^{\pm}_{\mathcal{C}}(x,\epsilon)\mathrm{e}^{i\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon)},\qquad \begin{cases}t>0\\ t<0\end{cases}, \tag{3.40}$$

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

$$i\frac{\partial}{\partial t}\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon)+i\eta^{\mathcal{C}}(t)\nabla\lambda^{\pm}_{\mathcal{C}}(x,t,\epsilon)+\langle\Phi_{\mathcal{C}}(x,\epsilon)|\eta^{\mathcal{C}}(t)\nabla\Phi_{\mathcal{C}}(x,\epsilon)\rangle=0. \tag{3.41}$$

Lemma 3.2 *Let $\eta^{\mathcal{C}}(t)$ be the solution of the classical equations of motion (2.2) and (2.3). There exist eigenvectors $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$, $\mathcal{C}=\mathcal{A},\mathcal{B}$, such that*

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

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

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

Proof:
We give a proof for $\Phi^+_{\mathcal{A}}(x,t,\epsilon)$ only; the other cases are similar. In order to simplify the notation, we drop the indices $\mathcal{A}$ and $+$. Thus we need determine $\lambda(x,t,\epsilon)$ such that

$$\Phi(x,t,\epsilon)=\mathrm{e}^{i\lambda(x,t,\epsilon)}\Phi(x,\epsilon), \tag{3.42}$$

where

$$\Phi(x,\epsilon)=\cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon)+\mathrm{e}^{-i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon). \tag{3.43}$$

Also, let $a(t)\equiv a^{\mathcal{A}}(t)$ and $\eta(t)\equiv\eta^{\mathcal{A}}(t)$ for $t>0$. We introduce the new variable

$$\omega\equiv x-a(t) \tag{3.44}$$

and the notation

$$\begin{aligned}\widetilde{\lambda}(\omega,t,\epsilon) &\equiv \lambda(\omega+a(t),t,\epsilon), && (3.45)\\ \widetilde{\Phi}(\omega,t,\epsilon) &\equiv \Phi(\omega+a(t),\epsilon). && (3.46)\end{aligned}$$

In terms of these new variables, equation (3.41) for $\widetilde{\lambda}$ reads

$$i\frac{\partial}{\partial t}\widetilde{\lambda}(\omega,t,\epsilon)=-\langle\widetilde{\Phi}(\omega,t,\epsilon)|\frac{\partial}{\partial t}\widetilde{\Phi}(\omega,t,\epsilon)\rangle \tag{3.47}$$

with

$$\frac{\partial}{\partial t}\widetilde{\Phi}(\omega,t,\epsilon)=\eta(t)\nabla\Phi(\omega+a(t),\epsilon). \tag{3.48}$$

We compute, dropping the arguments,

$$\begin{aligned}\nabla\Phi = \quad & \left(-\sin(\theta/2)\psi_1 + \mathrm{e}^{-i\varphi}\cos(\theta/2)\psi_2\right)\nabla\theta/2 \\ & +\cos(\theta/2)\nabla\psi_1 + \mathrm{e}^{-i\varphi}\sin(\theta/2)\nabla\psi_2 \\ & -i\nabla\varphi\mathrm{e}^{-i\varphi}\sin(\theta/2)\psi_2. \end{aligned} \tag{3.49}$$

Since the ψ_j, $j = 1, 2$, are orthonormal, we get

$$\begin{aligned}\langle\widetilde{\Phi}|\frac{\partial}{\partial t}\widetilde{\Phi}\rangle = \; & - \; i\eta\nabla\varphi\sin^2(\theta/2) + \cos^2(\theta/2)\langle\psi_1|\eta\nabla\psi_1\rangle + \sin^2(\theta/2)\langle\psi_2|\eta\nabla\psi_2\rangle \\ & + \; \sin(\theta/2)\cos(\theta/2)\left(\mathrm{e}^{-i\varphi}\langle\psi_1|\eta\nabla\psi_2\rangle + \mathrm{e}^{i\varphi}\langle\psi_2|\eta\nabla\psi_1\rangle\right). \end{aligned} \tag{3.50}$$

As $\eta, \psi_j, \nabla\psi_j$ are all $\mathcal{O}(0)$, we can write

$$\widetilde{\lambda}(\omega, t, \epsilon) = \int^t \left(\eta(t')\nabla\varphi\sin^2(\theta(\omega + a(t'), \epsilon)/2) + \mathcal{O}(0)\right)dt' + \widetilde{\lambda}_0(\omega). \tag{3.51}$$

It remains to estimate $\nabla\varphi$.

$$\varphi(x, \epsilon) = \mathrm{atan}\,(\delta(x, \epsilon)/\gamma(x, \epsilon)) \tag{3.52}$$

provided $\gamma(x, \epsilon)$ is different from zero. Hence, using (1.20) we get

$$\begin{aligned}\nabla\varphi(x, \epsilon) \; &= \; \frac{\gamma(x, \epsilon)\nabla\delta(x, \epsilon) - \delta(x, \epsilon)\nabla\gamma(x, \epsilon)}{\gamma^2(x, \epsilon) + \delta^2(x, \epsilon)} = \frac{\epsilon\mathcal{O}(1) + \mathcal{O}(2)\mathcal{O}(1)}{r^2\epsilon^2 + \mathcal{O}(3)} \\ &= \; \frac{\mathcal{O}(1)/\epsilon + \mathcal{O}(3)/\epsilon^2}{1 + \mathcal{O}(3)/\epsilon^2}. \end{aligned} \tag{3.53}$$

The above computations are legitimate for

$$\|x\| = \mathcal{O}(\epsilon^\kappa), \qquad 2/3 < \kappa < 1, \tag{3.54}$$

which implies

$$\begin{aligned}\gamma(x, \epsilon) \; &= \; r\epsilon + \mathcal{O}(2) \\ &= \; r\epsilon(1 + \mathcal{O}(\epsilon + \|x\| + \|x\|^2/\epsilon)) \\ &= \; r\epsilon(1 + \mathcal{O}(\epsilon^{2\kappa-1})) \\ &\geq \; c\epsilon, \end{aligned} \tag{3.55}$$

for some uniform constant c, and

$$\begin{aligned}\mathcal{O}(1)/\epsilon \; &= \; \mathcal{O}(1 + \|x\|/\epsilon) \\ &= \; \mathcal{O}(1/\epsilon^{1-\kappa}), \end{aligned} \tag{3.56}$$

$$\begin{aligned}\mathcal{O}(3)/\epsilon^2 \; &= \; \mathcal{O}(\epsilon + \|x\| + \|x\|^2/\epsilon + \|x\|^3/\epsilon^2) \\ &\to \; 0 \end{aligned} \tag{3.57}$$

as $\epsilon \to 0$. Hence, if $\|\omega + a(t)\| = \mathcal{O}(\epsilon^\kappa)$,

$$\widetilde{\lambda}(\omega, t, \epsilon) = \widetilde{\lambda}_0(\omega) + \mathcal{O}(t/\epsilon^{1-\kappa}), \tag{3.58}$$

uniformly in t and ω. Taking the integration constant $\widetilde{\lambda}_0(\omega) \equiv 0$, we obtain

$$\lambda(x,t,\epsilon) = \mathcal{O}(t/\epsilon^{1-\kappa}). \tag{3.59}$$

We get the desired result by means of (3.42) and the fact that $\Phi(x,\epsilon) = \mathcal{O}(0)$. $\square$

The nuclear wave function is localized around the classical trajectory in the semiclassical regime. Thus, because of the genericity condition $\eta_1^0 > 0$, the major part of the nuclear wave function will be supported away from the neighbourhood where the levels almost cross in the outer temporal region. Hence we can introduce a cutoff function which does not significantly alter the solution and forces the support of the wave function to be away from this neighborhood. In particular, the support of the cutoff will be chosen so that the above lemma applies. Let F be a C^∞ cutoff function

$$F : I\!R^+ \mapsto I\!R, \tag{3.60}$$

such that

$$\begin{cases} F(r) = 1 & 0 \leq r \leq 1 \\ F(r) = 0 & r \geq 2 \end{cases} \tag{3.61}$$

The wave functions we construct below in the outer regime will be multiplied by the regulating factor

$$F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'}) \tag{3.62}$$

where $\delta' < \xi$, for $\mathcal{C} = \mathcal{A}, \mathcal{B}$ (see below).

Remark: If $\xi < 2/3 < \kappa < 1-\xi$, the correction terms in the above lemma tend to zero and the set $\|x\| = \mathcal{O}(\epsilon^\kappa)$ includes the set $\|x - a^{\mathcal{C}}(t)\| = \mathcal{O}(\epsilon^{1-\delta'})$.

On the support of F,

$$x = \eta^0(\epsilon)t + \mathcal{O}(\epsilon^{1-\delta'} + t^2) \tag{3.63}$$

and since $\eta_1^0(\epsilon) = \eta_1^0 + \mathcal{O}(\epsilon)$, where $\eta_1^0 > 0$, we deduce

$$|x_1| > c|t| \tag{3.64}$$

uniformly in ϵ. Using this property we have

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

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

and for $t > 0$,

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

Proof:
It follows from (1.20), (3.63) and (3.64) that for $t \gtrless 0$,

$$\begin{aligned}
\cos(\theta(x,\epsilon)) &= \frac{x_1 + \mathcal{O}(2)}{\sqrt{{x_1}^2 + \epsilon^2 + \mathcal{O}(3)}} = \frac{\pm 1 + \mathcal{O}(t)}{(1 + \mathcal{O}(\epsilon^2/t^2) + \mathcal{O}(t))^{1/2}} \\
&= \pm 1 + \mathcal{O}(\epsilon^2/t).
\end{aligned} \tag{3.65}$$

Similarly,

$$\tan(\varphi(x,\epsilon)) = \frac{\mathcal{O}(2)}{\epsilon(1 + \mathcal{O}(2))} = \frac{\mathcal{O}(t^2/\epsilon)}{1 + \mathcal{O}(t^2/\epsilon)} = \mathcal{O}(t^2/\epsilon), \tag{3.66}$$

hence

$$\varphi(x,\epsilon) = \mathcal{O}(t^2/\epsilon). \tag{3.67}$$

The result then follows from the identity

$$\sin^2(\theta(x,\epsilon)/2) = \frac{1 - \cos(\theta(x,\epsilon))}{2} = \frac{1 \pm 1}{2} + \mathcal{O}(t^2/\epsilon) \tag{3.68}$$

and $\|\psi_j\| = 1$, $j = 1, 2$. □

We can describe the solution of the Schrödinger equation in the different regimes introduced.

3.3 Incoming Outer Solution

We assume that at the initial time $-T$, the wave function is given by a semiclassical nuclear wave packet times an electronic function associated with the $\mathcal{B}$ level. We consider the associated classical quantities determined by the following initial conditions at $t = 0$:

$$\begin{aligned}
a^{\mathcal{B}}(0) &= 0 \\
\eta^{\mathcal{B}}(0) &= \eta^0 \\
A^{\mathcal{B}}(0) &= A_0 \\
B^{\mathcal{B}}(0) &= B_0 \\
S^{\mathcal{B}}(0) &= 0,
\end{aligned} \tag{3.69}$$

where A_0 and B_0 satisfy the hypotheses in the definition of the functions φ_l. Away from the avoided crossing of the electronic levels, the solution of the Schrödinger equation is well approximated by standard time–dependent Born–Oppenheimer wave packets. Close to the avoided crossing these standard wave packets fail to approximate the solution. The next lemma tells us how close to the avoided crossing time these standard wave packets can be used as approximations.

Lemma 3.4 *For any $-T \leq t \leq -\epsilon^{1-\xi}$, there is an approximation $\psi_{OI}(x,t)$ of a solution of the Schrödinger equation $\psi(x,t)$ of the form*

$$\begin{aligned}\psi_{OI}(x,t) &= F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'})\exp\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)\\ &\quad\times\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\Phi_{\mathcal{B}}^-(x,t,\epsilon)\end{aligned}\tag{3.70}$$

such that

$$\psi(x,t)=\psi_{OI}(x,t)+R(x,t,\epsilon)\tag{3.71}$$

where

$$R(x,t,\epsilon)=\mathcal{O}(\epsilon^{\xi})\tag{3.72}$$

in the $L^2(I\!R^n)$ sense, as $\epsilon\to 0$.

Proof:
The proof of this Lemma is very similar to that of Lemma 6.4 of [16]. For $-T\leq t\leq -\epsilon^{1-\xi}$ and x in the support of the cut off function $F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'})$, $\frac{1}{E_{\mathcal{A}}(x)-E_{\mathcal{B}}(x)}$ is bounded by a multiple of $\epsilon^{-1+\xi}$. Furthermore, for such x and t, a rather tedious calculation shows that $\left(\frac{\partial}{\partial t}+\eta^{\mathcal{B}}\cdot\nabla_x\right)\Phi_{\mathcal{B}}^-(x,t,\epsilon)$ is bounded by a multiple of $\epsilon^{-1+\xi}$. Thus, up to errors on the order of $\epsilon^{2\xi}$, $\psi_{OI}(x,t)$ is equal to

$$\begin{aligned}\Psi(x,t) &= F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'})\exp\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)\\ &\quad\times\left(\Psi_0(x,t)+\epsilon^2\Psi_2^{\perp}(x,\,t)\right)\end{aligned}\tag{3.73}$$

where

$$\Psi_0(x,t)=\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\Phi_{\mathcal{B}}^-(x,t,\epsilon)\tag{3.74}$$

and

$$\begin{aligned}\Psi_2^{\perp}(x,t) &= i\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\\ &\quad\times\Bigg(\Phi_{\mathcal{A}}^-(x,t,\epsilon)\,\frac{1}{E_{\mathcal{A}}(x)-E_{\mathcal{B}}(x)}\langle\,\Phi_{\mathcal{A}}^-(x,t,\epsilon),\,\left(\frac{\partial}{\partial t}+\eta^{\mathcal{B}}\cdot\nabla_x\right)\Phi_{\mathcal{B}}^-(x,t,\epsilon)\,\rangle\\ &\qquad+r_{\mathcal{BA}}(x,\epsilon)P_{\perp}^{\mathcal{AB}}(x,\epsilon)\left(\frac{\partial}{\partial t}+\eta^{\mathcal{B}}\cdot\nabla_x\right)\Phi_{\mathcal{B}}^-(x,t,\epsilon)\Bigg),\end{aligned}\tag{3.75}$$

where $r_{\mathcal{BA}}(x,\epsilon)$ is the restriction of $(h(x,\epsilon)-E_{\mathcal{B}}(x,\epsilon)^{-1}$ to the range of $P_{\perp}^{\mathcal{AB}}(x)$.

The expression (3.73) is a standard leading order Born-Oppenheimer wave packet, and it suffices to show that it agrees with a solution of the Schrödinger equation up to errors on the order of ϵ^{ξ}. To prove this, we explicitly compute

$$\zeta(x,t,\epsilon)=i\epsilon^2\frac{\partial\Psi}{\partial t}-H(\epsilon)\Psi.\tag{3.76}$$

For $-T \leq t \leq -\epsilon^{1-\xi}$, terms in $\zeta(x,t,\epsilon)$ that contain derivatives of F are easily seen to have norms that grow at worst like powers of $1/|t|$ times factors that are exponentially small in ϵ. Most of the remaining terms in $\zeta(x,t,\epsilon)$ are formally given on pages 105–108 of [16], with $\left(\frac{\partial}{\partial t} + \eta^{\mathcal{B}} \cdot \nabla_x\right)$ in place of $\eta^{\mathcal{B}} \cdot \nabla_x$ in many expressions. A few other terms arise from the $i\epsilon^2 \frac{\partial}{\partial t}$ acting on the electronic eigenfunctions in (3.73). Our error term $\zeta(x,t,\epsilon)$ differs formally from that of Section 6 of [16] because our eigenfunctions have time dependence and the ones in Section 6 of [16] do not.

After noting that numerous terms in $\zeta(x,t,\epsilon)$ cancel with one another, we estimate the remaining terms individually. This process is very similar to that described on pages 108–110 of [16], except that there are a few extra terms that contain time derivatives of the electronic eigenfunctions. To estimate these terms we use arguments similar to those used in the proof of lemma 3.2. Our avoided crossing problem is slightly less singular than the crossing problem treated in [16]. So, it is not surprising that our error term satisfies the same estimate

$$\|\zeta(\cdot,t,\epsilon)\| \leq C\,\epsilon^3 |t|^{-2} \tag{3.77}$$

as the corresponding error term in Section 6 of [16].

We obtain the desired estimate by using the estimate (3.77) and lemma 3.3 of [16]. $\square$

3.4 Inner Solution

For times very close to zero, we look for an approximation constructed by means of the classical quantities associated with the potential $\widetilde{V}(x,\epsilon)$. Let $a(t)$ and $S(t)$ be the corresponding classical quantities satisfying the initial conditions

$$\begin{array}{l} a(0) = 0 \\ \eta(0) = \eta^0 \\ S(0) = 0. \end{array} \tag{3.78}$$

In the rescaled variables

$$\left\{ \begin{array}{c} y = (x - a(t))/\epsilon, \\ s = t/\epsilon \end{array} \right. , \tag{3.79}$$

the Schrödinger equation reads

$$i\epsilon \frac{\partial}{\partial s}\psi - i\epsilon\eta(\epsilon s)\nabla_y \psi = -\frac{\epsilon^2}{2}\triangle_y \psi + h(a(\epsilon s) + \epsilon y, \epsilon)\psi. \tag{3.80}$$

We look for an approximate solution of the form

$$F(\|y\|\epsilon^{\delta'})\exp\left(i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{\eta(\epsilon s)y}{\epsilon}\right)\chi(y,s,\epsilon), \tag{3.81}$$

with

$$\begin{aligned} \chi(y,s,\epsilon) = \quad & \{f(y,s,\epsilon)\psi_1(a(\epsilon s) + \epsilon y, \epsilon) + g(y,s,\epsilon)\psi_2(a(\epsilon s) + \epsilon y, \epsilon) \\ & + \psi_\perp(a(\epsilon s) + \epsilon y, \epsilon)\}, \end{aligned} \tag{3.82}$$

where $\psi_\perp(x,\epsilon) \in (I\!I - P(x,\epsilon))\mathcal{H}$ and f, g are scalar functions. Anticipating exponential fall off of the solution, we insert (3.81) in (3.80) and neglect the derivatives of F. Making use of the decomposition (1.11) and eliminating the overall "classical phase" and cut-off F, we get (dropping the arguments)

$$\begin{aligned}
& i\epsilon\psi_1\frac{\partial}{\partial s}f + i\epsilon\psi_2\frac{\partial}{\partial s}g + i\epsilon\frac{\partial}{\partial s}\psi_\perp + (\widetilde{V}(a) + \epsilon y\nabla_x\widetilde{V}(a))(f\psi_1 + g\psi_2 + \psi_\perp) \\
& + i\epsilon^2 f\eta\nabla_x\psi_1 + i\epsilon^2 g\eta\nabla_x\psi_2 + i\epsilon^2\eta\nabla_x\psi_\perp \\
= \quad & -\epsilon^4\triangle_x\psi_\perp/2 - \epsilon^4 f\triangle_x\psi_1/2 - \epsilon^4 g\triangle_x\psi_2/2 - \epsilon^3\nabla_y f\nabla_x\psi_1 \\
& -\epsilon^3\nabla_y g\nabla_x\psi_2 - \epsilon^2\psi_1\triangle_y f - \epsilon^2\psi_2\triangle_y g + h^\perp\psi_\perp + h_1(f\psi_1 + g\psi_2) \\
& +\widetilde{V}(a+\epsilon y)(f\psi_1 + g\psi_2 + \psi_\perp).
\end{aligned} \tag{3.83}$$

We assume the solutions have expansions of the form

$$\begin{aligned}
f(y,s,\epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)f_j(y,s), \\
g(y,s,\epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)g_j(y,s), \\
\psi_\perp(x,t,\epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)\psi_{\perp j}(x,t),
\end{aligned} \tag{3.84}$$

with asymptotic scales $\nu_j(\epsilon)$ to be determined by matching. We insert these expansions in (3.83). Using the behaviors (1.20) and lemma 2.2 we verify that the lowest order terms yield

$$\begin{aligned}
& i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0(y,s)\psi_1(a(\epsilon s)+\epsilon y,\epsilon) + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0(y,s)\psi_2(a(\epsilon s)+\epsilon y,\epsilon) \\
= \quad & h_\perp(a(\epsilon s)+\epsilon y,\epsilon)\psi_\perp(a(\epsilon s)+\epsilon y,\epsilon s,\epsilon) \\
& +\epsilon\nu_0(\epsilon)h_{11}(y,s)(f_0(y,s)\psi_1(a(\epsilon s)+\epsilon y,\epsilon) + g_0(y,s)\psi_2(a(\epsilon s)+\epsilon y,\epsilon))
\end{aligned} \tag{3.85}$$

on the support of F, where $h_{11}(y,s)$ 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 in the basis $\{\,\psi_1(a(\epsilon s)+\epsilon y,\epsilon),\ \psi_2(a(\epsilon s)+\epsilon y,\epsilon)\,\}$ is given by

$$r\begin{pmatrix} \eta_1^0 s + y_1 & 1 \\ 1 & -\eta_1^0 s - y_1 \end{pmatrix}. \tag{3.86}$$

By matching the incoming outer solution, we obtain

$$\nu_j(\epsilon)h_\perp(a(\epsilon s)+\epsilon y,\epsilon)\psi_{\perp j}(a(\epsilon s)+\epsilon y,\epsilon s) = 0 \tag{3.87}$$

if $\nu_j(\epsilon) << \epsilon\nu_0(\epsilon)$, $\ j=0,1,\cdots,m-1$. The spectrum of $h_\perp(x,\epsilon)$ is bounded away from 0 in a neighborhood of $(0,0)$. This implies

$$\psi_{\perp j}(x,t) = 0, \quad j=0,1,\cdots,m-1. \tag{3.88}$$

We split the remaining equation for the order $\epsilon\nu_0(\epsilon) = \nu_m(\epsilon)$ (without arguments)

$$\begin{aligned}
& i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0\psi_1 + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0\psi_2 \\
= \quad & \nu_m(\epsilon)h_\perp\psi_\perp + \epsilon\nu_0(\epsilon)h_{11}(f_0\psi_1 + g_0\psi_2)
\end{aligned} \tag{3.89}$$

into

$$\begin{aligned} i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0\psi_1 + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0\psi_2 &= \epsilon\nu_0(\epsilon)h_{11}(f_0\psi_1+g_0\psi_2), \\ \nu_m(\epsilon)h_\perp\psi_{\perp m} &= 0 \end{aligned} \tag{3.90}$$

by projection with $P(x,\epsilon)$ and $(\mathbb{I}-P(x,\epsilon))$. The second equation gives $\psi_{\perp m}=0$. The first one is equivalent to

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_0(y,s) \\ g_0(y,s)\end{pmatrix} = r\begin{pmatrix} \eta_1^0 s+y_1 & 1 \\ 1 & -(\eta_1^0 s+y_1)\end{pmatrix}\begin{pmatrix} f_0(y,s) \\ g_0(y,s)\end{pmatrix}. \tag{3.91}$$

The general solution of this equation can be found exactly in terms of parabolic cylinder functions [5].

$$\begin{aligned} \begin{pmatrix} f_0(y,s) \\ g_0(y,s)\end{pmatrix} = \quad & C_1(y)\begin{pmatrix} \frac{(1-i)}{2}\sqrt{\frac{r}{\eta_1^0}}D_{\frac{ir}{2\eta_1^0}-1}\left((-1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right) \\ D_{\frac{ir}{2\eta_1^0}}\left((-1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right)\end{pmatrix} \\ & + C_2(y)\begin{pmatrix} D_{-\frac{ir}{2\eta_1^0}}\left(-(1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right) \\ -\frac{(1+i)}{2}\sqrt{\frac{r}{\eta_1^0}}D_{-\frac{ir}{2\eta_1^0}-1}\left(-(1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right)\end{pmatrix}. \end{aligned} \tag{3.92}$$

We define our inner approximation by taking

$$\begin{aligned} \psi_I(y,s) = \quad & F \quad (\|y\|\epsilon^{\delta'})\exp\left(i\frac{S(\epsilon s)}{\epsilon^2}+i\frac{\eta(\epsilon s)y}{\epsilon}\right) \\ \times \quad & \left[\nu_0(\epsilon)f_0(y,s)\psi_1(a(\epsilon s)+\epsilon y,\epsilon)+\nu_0(\epsilon)g_0(y,s)\psi_2(a(\epsilon s)+\epsilon y,\epsilon)\right], \end{aligned} \tag{3.93}$$

with f_0 and g_0 as above. To get a vector along the $\mathcal{B}$ level as $t<0$, we need to impose

$$g_0(y,s)\to 0, \ \text{as } s\to -\infty. \tag{3.94}$$

Using the asymptotic formulae in [5] with $\|y\|/s = \mathcal{O}(\epsilon^{\xi-\delta'})\to 0$, due to the cutoff, we have that

$$D_{\frac{ir}{2\eta_1^0}}\left((-1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right) = \mathrm{e}^{i\lambda(y,s)}\mathrm{e}^{\frac{\pi r}{8\eta_1^0}}(1+\mathcal{O}(1/(s+\|y\|)^2)) \tag{3.95}$$

as $s\to-\infty$, where $\lambda(y,s)\in\mathbb{R}$, so that

$$C_1(y)\equiv 0. \tag{3.96}$$

We further compute [5]

$$\begin{aligned} & D_{-\frac{ir}{2\eta_1^0}}\left(-(1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right) \\ = \quad & \exp\left\{-\frac{ir}{2\eta_1^0}\left({\eta_1^0}^2 s^2+2y_1\eta_1^0 s+{y_1}^2+\ln|s|+\ln(2r\eta_1^0)/2\right)\right\} \\ & \quad \times\mathrm{e}^{\frac{r\pi}{8\eta_1^0}}\left(1+\mathcal{O}(\|y\|/s)+\mathcal{O}(1/s^2)\right), \qquad \text{and} \\ & D_{-\frac{ir}{2\eta_1^0}-1}\left(-(1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s+y_1)\right) = \mathcal{O}(1/(s+\|y\|)) \end{aligned} \tag{3.97}$$

as $s \to -\infty$ under the same conditions. We match $\psi_I(y,s)$ with $\psi_{OI}(x,t)$, the incoming outer solution of lemma 3.4, in the regime characterized by

$$t = \epsilon s, \;\; s = -\epsilon^{-\xi}, \;\; y = \mathcal{O}(\epsilon^{-\delta'}), \;\; x = \mathcal{O}(\epsilon^{\kappa}) \tag{3.98}$$

with

$$0 < \delta' < \xi < 1/3, \;\; 2/3 < \kappa < 1 - \xi. \tag{3.99}$$

Let us consider $\psi_{OI}(x,t)$ as $t, \epsilon \to 0$ and express the result in terms of the new variables (y,s). ¿From $(a^{\mathcal{B}}(t) - a(t))/\epsilon = \mathcal{O}(t^2/\epsilon) = \mathcal{O}(\epsilon s)$, we deduce that

$$F(\|y^{\mathcal{B}}\|\epsilon^{\delta'}) = F(\|y\|\epsilon^{\delta'} + \mathcal{O}(\epsilon^{1+\delta'}s)) = F(\|y\|\epsilon^{\delta'}) + \mathcal{O}(\epsilon^{1+\delta'}s) \tag{3.100}$$

and from proposition 2.3, its corollary and lemma 3.1, we get, in the $L^2(I\!R^3)$ sense,

$$\begin{aligned} \varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, 0, a^{\mathcal{B}}(t), x) = \quad & \epsilon^{-n/2}\varphi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y) \\ & + \mathcal{O}(\epsilon s) + \mathcal{O}(1/s^2). \end{aligned} \tag{3.101}$$

We control the phases by means of the previous results on the asymptotic behaviors of the corresponding classical quantities. We use corollary 2.3 to see that

$$\begin{aligned} & \exp\left\{iS^{\mathcal{B}}(\epsilon s)/\epsilon^2\right\} \\ = \quad & \exp\left\{iS(\epsilon s)/\epsilon^2 + iS_0^{\mathcal{B}}(\epsilon, -)/\epsilon^2 - irs - i\left(r\eta_1^0 s^2 + \frac{r}{\eta_1^0}\ln(\epsilon|s|)\right)\right\} \\ & \quad \times \left(1 + \mathcal{O}(\epsilon s^3) + \mathcal{O}(1/s^2) + \mathcal{O}(\epsilon\ln(\epsilon|s|))\right), \end{aligned} \tag{3.102}$$

We use proposition 2.2 and corollary 2.2 to estimate

$$\begin{aligned} & \exp\left\{i\eta^{\mathcal{B}}(\epsilon s)(x - a^{\mathcal{B}}(\epsilon s))/\epsilon^2\right\} \\ = \quad & \exp\left\{i\eta(\epsilon s)y/\epsilon + i(\eta^{\mathcal{B}}(\epsilon s) - \eta(\epsilon s))y/\epsilon + i\eta^{\mathcal{B}}(\epsilon s)(a(\epsilon s) - a^{\mathcal{B}}(\epsilon s))/\epsilon^2\right\} \\ = \quad & \exp\left\{i\eta(\epsilon s)y/\epsilon - iy_1(r/\eta_1^0 + rs)\right\} \\ & \quad \times \exp\left\{irs + i\frac{r\eta_1^0}{2}s^2 + i\frac{r}{2\eta_1^0}\left(\ln(\epsilon|s|) + \ln(2\eta_1^0) + 1/2 - \ln\epsilon\right)\right\} \\ & \quad \times \left(1 + \mathcal{O}(\epsilon s^3) + \mathcal{O}(1/s^2) + \mathcal{O}(\|y\|\epsilon s^2) + \mathcal{O}(\|y\|/s) + \mathcal{O}(\epsilon s\ln\epsilon)\right) \end{aligned} \tag{3.103}$$

as $s \to -\infty$. Finally, by lemmas 3.2 and 3.3,

$$\Phi_{\mathcal{B}}^-(x, \epsilon s, \epsilon) = -\psi_1(x, \epsilon) + \mathcal{O}(\epsilon^{1/2}/s^{1/2}) + \mathcal{O}(s\epsilon^{\kappa}) \tag{3.104}$$

so that we can do the matching provided $\nu_0(\epsilon) = 1$ and

$$\begin{aligned} C_2(y) = \quad - \quad & \epsilon^{-n/2}\varphi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y)\mathrm{e}^{-\frac{\pi r}{8\eta_1^0}}\exp\left(\frac{ir}{2\eta_1^0}({y_1}^2 - 2y_1)\right) \\ \times \quad & \exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon, -)}{\epsilon^2} + \frac{ir}{4\eta_1^0}(1 + 3\ln(2\eta_1^0) + \ln r - 4\ln\epsilon)\right). \end{aligned} \tag{3.105}$$

Using the fact that $\varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, 0, a^{\mathcal{B}}(t), x)$ is normalized, we see that the difference between these expressions in the regime defined by (3.99) is, in the $L^2(I\!R^n)$ sense,

$$\psi_{OI}(\epsilon y + a(\epsilon s), \epsilon s) = \psi_I(y, s) + \mathcal{O}(\epsilon^p) \tag{3.106}$$

for some positive p.

We need to check the validity of this inner approximation. We return to the initial variables and set

$$\Psi_I(x, t) = \psi_I((x - a(t))/\epsilon, t/\epsilon). \tag{3.107}$$

If we define $\zeta(x, t)$ by

$$i\epsilon^2 \frac{\partial}{\partial t} \Psi_I(x, t) = -\frac{\epsilon^4}{2} \Delta \Psi_I(x, t) + h(x, \epsilon) \Psi_I(x, t) + \zeta(x, \epsilon), \tag{3.108}$$

then we have

Proposition 3.1 *In the $L^2(I\!R^n)$ norm*

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

Thus, by virtue of lemma 3.3 in [16], we have,

Lemma 3.5 *The function $\Psi_I(x, t)$ is an approximation of a solution $\psi(x, t)$ of the Schrödinger equation for $-\epsilon^{1-\xi} \leq t \leq \epsilon^{1-\xi}$, such that in the $L^2(I\!R^3)$ sense,*

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

as $\epsilon \to 0$.

Proof:
To compute $\zeta(x, t)$ we set

$$A(y, s) = F(\|y\| \epsilon^{\delta'}) \left[f_0(y, s) \psi_1(a(\epsilon s) + \epsilon y, \epsilon) + g_0(y, s) \psi_2(a(\epsilon s) + \epsilon y, \epsilon) \right], \tag{3.109}$$

and define

$$\widetilde{\zeta}(y, s) = i\epsilon \frac{\partial}{\partial s} A(y, s) - H(y, s) A(y, s), \tag{3.110}$$

where formally

$$\begin{aligned} H(y, s) = & - \frac{\epsilon^2}{2} \triangle_y + h_1(a(\epsilon s) + \epsilon y, \epsilon) \\ & + \left(\widetilde{V}(a(\epsilon s) + \epsilon y, \epsilon) - \widetilde{V}(a(\epsilon s), \epsilon) - \epsilon y \triangle_x \widetilde{V}(a(\epsilon s), \epsilon) \right). \end{aligned} \tag{3.111}$$

It is readily checked that

$$\zeta(x, t) = \exp\left(i \frac{S(t)}{\epsilon^2} + i \frac{\eta(t)(x - a(t))}{\epsilon^2} \right) \widetilde{\zeta}((x - a(t))/\epsilon, t/\epsilon). \tag{3.112}$$

Then, making use of

$$\begin{aligned}\nabla_y F(\|y\|\epsilon^{\delta'}) &= \epsilon^{\delta'} F'(\|y\|\epsilon^{\delta'}) y/\|y\| \\ \triangle_y F(\|y\|\epsilon^{\delta'}) &= \epsilon^{2\delta'} F''(\|y\|\epsilon^{\delta'}),\end{aligned} \tag{3.113}$$

the cancellations due to our choice of f_0 and g_0, and the mean value theorem, we get (dropping the arguments)

$$\begin{aligned}\widetilde{\zeta}(y,s) = & \ \tfrac{1}{2} \ \epsilon^{2\delta'+2} F''(f_0\psi_1 + g_0\psi_2) \\ & + \ \epsilon^{\delta'} F' \frac{y}{\|y\|} \left(\epsilon^2 \psi_1 \nabla_y f_0 + \epsilon^2 \psi_2 \nabla_y g_0 + \epsilon^3 f_0 \nabla_x \psi_1 + \epsilon^3 g_0 \nabla_x \psi_2\right) \\ & + \ F \Big(i\epsilon^2 f_0 \eta \nabla_x \psi_1 + i\epsilon^2 g_0 \eta \nabla_x \psi_2 + \epsilon^3 \nabla_y f_0 \nabla_x \psi_1 + \epsilon^3 \nabla_y g_0 \nabla_x \psi_2 \\ & + \ \frac{\epsilon^2}{2} \psi_1 \triangle_y f_0 + \epsilon^2/2 \psi_2 \triangle_y g_0 + \epsilon^4/2 f_0 \triangle_y \psi_1 + \epsilon^4/2 g_0 \triangle_y \psi_2\Big) \\ & - \ F \ (\psi_1, \ \psi_2) \begin{pmatrix} \beta - \epsilon r(\eta_1^0 s + y_1) & \gamma + i\delta - r\epsilon \\ \gamma - i\delta - r\epsilon & -\beta + \epsilon r(\eta_1^0 s + y_1) \end{pmatrix} \begin{pmatrix} f_0 \\ g_0 \end{pmatrix} \\ & + \ \frac{1}{2} \epsilon^2 y^2 F \widetilde{V}^{(2)}(a(\epsilon s) + \theta \epsilon y, \epsilon)(f_0\psi_1 + g_0\psi_2),\end{aligned} \tag{3.114}$$

where $\theta \in]0,1[$. Then we use the facts that in the equation above we have

- $\|y\| = \mathcal{O}(\epsilon^{-\delta'})$, $s = \mathcal{O}(\epsilon^{-\xi})$, with $\xi > \delta'$, $t = \mathcal{O}(\epsilon^{1-\xi})$, $x = \epsilon y + a(t) = \mathcal{O}(\epsilon^{1-\xi})$,
- $F(\|y\|\epsilon^{\delta'}), F'(\|y\|\epsilon^{\delta'})$ and $F''(\|y\|\epsilon^{\delta'})$ are uniformly bounded in (y,ϵ),
- $\psi_j(x,\epsilon), \nabla_x \psi_j(x,\epsilon), \triangle_x \psi_j(x,\epsilon)$ and $\widetilde{V}^{(2)}(x,\epsilon)$ are uniformly bounded as (x,ϵ) goes to $(0,0)$,
- $\eta(t)$ is uniformly bounded,
- $\beta - \epsilon r(\eta_1^0 s + y_1)$ and $\gamma - i\delta - r\epsilon$ are $\mathcal{O}(\epsilon^{2(1-\xi)})$,

to get the estimate, for y in the support of F,

$$\begin{aligned}|\widetilde{\zeta}(y,s)| = \ \mathcal{O} \ & \Big(\epsilon^{2(1-\xi)}(f_0(y,s) + g_0(y,s)) \\ & + \ \epsilon^{2+\delta'}(\nabla_y f_0(y,s) + \nabla_y g_0(y,s)) + \epsilon^2(\triangle_y f_0(y,s) + \triangle_y g_0(y,s))\Big).\end{aligned} \tag{3.115}$$

We can write

$$\begin{aligned}& \int_{-\epsilon^{1-\xi}}^{\epsilon^{1-\xi}} \|\zeta(\cdot,t)\|_{L^2(\mathbb{R}^n)} \, dt \\ = & \int_{-\epsilon^{1-\xi}}^{\epsilon^{1-\xi}} \left\{\int_{\mathbb{R}^n} |\widetilde{\zeta}((x-a(t))/\epsilon, t/\epsilon)|^2 dx\right\}^{1/2} dt \\ = & \int_{-\epsilon^{-\xi}}^{\epsilon^{-\xi}} \epsilon^{n/2} \epsilon \left\|\widetilde{\zeta}(\cdot,s)\right\|_{L^2(\mathbb{R}^n)} ds \\ \leq & \ 2 \sup_{s\in[-\epsilon^{-\xi},\epsilon^{-\xi}]} \epsilon^{n/2} \left\|\widetilde{\zeta}(\cdot,s)\right\|_{L^2(\mathbb{R}^n)} \epsilon^{1-\xi}.\end{aligned} \tag{3.116}$$

Now f_0, g_0 are given by a gaussian times a polynomial in y times a parabolic cylinder function. Asymptotically, these parabolic cylinder functions, their first and second derivatives are of order $\mathcal{O}((s+\|y\|)^0)$, $\mathcal{O}((s+\|y\|))$ and $\mathcal{O}((s+\|y\|)^2)$, respectively, where $s = \mathcal{O}(\epsilon^{-\xi})$. Since the factor $\epsilon^{-n/2}$ in $C_2(y)$ takes care of the Jacobian, this yields the result. □

3.5 Outgoing Outer Solution

Consider the classical quantities associated with the $\mathcal{A}$ level that satisfy the following initial conditions at $t = 0$:

$$
\begin{aligned}
a^{\mathcal{A}}(0) &= 0 && (3.117)\\
\eta^{\mathcal{A}}(0) &= \eta^0 - \epsilon \frac{2r}{\eta_1^0} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\
A^{\mathcal{A}}(0) &= A_0 \\
B^{\mathcal{A}}(0) &= B_0 \\
S^{\mathcal{A}}(0) &= 0. && (3.118)
\end{aligned}
$$

Note the difference in initial momentum with the classical quantities associated with the $\mathcal{B}$ level, (3.69). As explained earlier, the corresponding loss in kinetic energy equals the gain in potential energy, to leading order. We look for an outgoing outer solution $\psi_{OO}(x,t)$ valid in the temporal region $\epsilon^{1-\xi} \le t < T$ as a linear combination of standard Born–Oppenheimer wave packets. The first one is associated with the $\mathcal{A}$ level and initial conditions (3.117), the other one is associated with the $\mathcal{B}$ level and initial conditions (3.69). This function $\psi_{OO}(x,t)$ should match $\psi_I(y,s)$ in the temporal layer

$$
t = \epsilon s, \ s = +\epsilon^{-\xi}, \ y = \mathcal{O}(\epsilon^{-\delta'}), \ x = \mathcal{O}(\epsilon^{\kappa}) \tag{3.119}
$$

with (3.99). We proceed as above. We have [5]

$$
\begin{aligned}
& D_{-\frac{ir}{2\eta_1^0}}\left(-(1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s + y_1)\right) \\
= \quad & \exp\left\{-\frac{ir}{2\eta_1^0}\left({\eta_1^0}^2 s^2 + 2y_1\eta_1^0 s + {y_1}^2 + \ln|s| + \ln(2r\eta_1^0)/2\right)\right\} \\
& \times \mathrm{e}^{-\frac{3r\pi}{8\eta_1^0}}\left(1 + \mathcal{O}(\|y\|/s)\right) + \mathcal{O}(1/s), \\
& D_{-\frac{ir}{2\eta_1^0}-1}\left(-(1+i)\sqrt{\frac{r}{\eta_1^0}}(\eta_1^0 s + y_1)\right) \\
= \quad & \exp\left\{+\frac{ir}{2\eta_1^0}\left({\eta_1^0}^2 s^2 + 2y_1\eta_1^0 s + {y_1}^2 + \ln|s| + \ln(2r\eta_1^0)/2\right)\right\} \\
& \times \frac{\sqrt{2\pi}}{\Gamma\left(1 + \frac{ir}{2\eta_1^0}\right)} \mathrm{e}^{-\frac{r\pi}{8\eta_1^0}}\left(1 + \mathcal{O}(1/s^2)\right) + \mathcal{O}(1/s),
\end{aligned} \tag{3.120}
$$

as $s \to +\infty$ and $\|y\|/s = \mathcal{O}(\epsilon^{\xi-\delta'}) \to 0$. Equation (3.100) is also true if we replace the index $\mathcal{B}$ by $\mathcal{A}$ and since $B_0^{\mathcal{B}}(-) \equiv B_0^{\mathcal{A}}(+)$ (see corollary 2.4), we have

$$
\varphi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y) \equiv \varphi_l(A_0, B_0^{\mathcal{A}}(+), 1, 0, 0, y). \tag{3.121}
$$

On the other hand, using the notation (3.24), we can write

$$\begin{aligned}
& \varphi_l(A_0, B_0^{\mathcal{B}}(-), 1, 0, 0, y) \\
= \quad & h(A_0, |A_0|^{-1}y) \exp\left\{-\frac{\langle y|B_0A_0^{-1}y\rangle}{2} - i\frac{\langle y|rPy\rangle}{2\eta_1^0}\right\} \\
= \quad & \varphi_l(A_0, B_0^{\mathcal{B}}(+), 1, 0, 0, y)\mathrm{e}^{-iy_1{}^2 r/\eta_1^0}. \qquad (3.122)
\end{aligned}$$

The equivalent of equation (3.101) for $s \to +\infty$ and indices $\mathcal{A}$ and $\mathcal{B}$ is true with the same error terms. For the phases we have by corollary 2.3,

$$\begin{aligned}
& \exp\left\{iS^{\mathcal{B}}(\epsilon s)/\epsilon^2\right\} \\
= \quad & \exp\left\{iS(\epsilon s)/\epsilon^2 + iS_0^{\mathcal{B}}(\epsilon,+)/\epsilon^2 - irs + i\left(r\eta_1^0 s^2 + \frac{r}{\eta_1^0}\ln(\epsilon s)\right)\right\} \\
& \quad \times\left(1 + \mathcal{O}(\epsilon s^3) + \mathcal{O}(1/s^2) + \mathcal{O}(\epsilon\ln(\epsilon s))\right), \qquad (3.123)
\end{aligned}$$

and

$$\begin{aligned}
& \exp\left\{iS^{\mathcal{A}}(\epsilon s)/\epsilon^2\right\} \\
= \quad & \exp\left\{iS(\epsilon s)/\epsilon^2 + iS_0^{\mathcal{A}}(\epsilon,+)/\epsilon^2 - irs - i\left(r\eta_1^0 s^2 + \frac{r}{\eta_1^0}\ln(\epsilon|s|)\right)\right\} \\
& \quad \times\left(1 + \mathcal{O}(\epsilon s^3) + \mathcal{O}(1/s^2) + \mathcal{O}(\epsilon\ln(\epsilon|s|))\right). \qquad (3.124)
\end{aligned}$$

By proposition 2.2 and corollary 2.2,

$$\begin{aligned}
& \exp\left\{i\eta^{\mathcal{B}}(\epsilon s)(x - a^{\mathcal{B}}(\epsilon s))/\epsilon^2\right\} \\
= \quad & \exp\left\{i\eta(\epsilon s)y/\epsilon - iy_1(r/\eta_1^0 - rs)\right\} \\
& \times\exp\left\{irs - i\frac{r\eta_1^0}{2}s^2 - i\frac{r}{2\eta_1^0}\left(\ln(\epsilon s) + \ln(2\eta_1^0) + 1/2 - \ln\epsilon\right)\right\} \\
& \times\left(1 + \mathcal{O}(\epsilon s^3) + \mathcal{O}(1/s^2) + \mathcal{O}(\|y\|\epsilon s^2) + \mathcal{O}(\|y\|/s) + \mathcal{O}(\epsilon s\ln\epsilon)\right) \qquad (3.125)
\end{aligned}$$

and

$$\begin{aligned}
& \exp\left\{i\eta^{\mathcal{A}}(\epsilon s)(x - a^{\mathcal{A}}(\epsilon s))/\epsilon^2\right\} \\
= \quad & \exp\left\{i\eta(\epsilon s)y/\epsilon - iy_1(r/\eta_1^0 + rs)\right\} \\
& \times\exp\left\{irs + i\frac{r\eta_1^0}{2}s^2 + i\frac{r}{2\eta_1^0}\left(\ln(\epsilon s) + \ln(2\eta_1^0) + 1/2 - \ln\epsilon\right)\right\} \\
& \times\left(1 + \mathcal{O}(\epsilon s^3) + \mathcal{O}(1/s^2) + \mathcal{O}(\|y\|\epsilon s^2) + \mathcal{O}(\|y\|/s) + \mathcal{O}(\epsilon s\ln\epsilon)\right) \qquad (3.126)
\end{aligned}$$

as $s \to +\infty$. Then, by lemmas 3.2 and 3.3

$$\begin{aligned}
\Phi_{\mathcal{A}}^+(x, \epsilon s, \epsilon) &= \psi_1(x, \epsilon) + \mathcal{O}(\epsilon^{1/2}/s^{1/2}) + \mathcal{O}(s\epsilon^\kappa), \\
\Phi_{\mathcal{B}}^+(x, \epsilon s, \epsilon) &= \psi_2(x, \epsilon) + \mathcal{O}(\epsilon^{1/2}/s^{1/2}) + \mathcal{O}(s\epsilon^\kappa). \qquad (3.127)
\end{aligned}$$

By matching ψ_I and ψ_{OO} in the domain defined by (3.119) we get up to terms of order $\mathcal{O}(\epsilon^p)$ in the $L^2(I\!\!R^n)$ sense

$$\begin{aligned}
\psi_{OO}(x,t) = \quad & -\mathrm{e}^{-\pi r/2\eta_1^0} F(\|x-a^{\mathcal{A}}(t)\|/\epsilon^{1-\delta'})\mathrm{e}^{\left(i\frac{S^{\mathcal{A}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{A}}(t)(x-a^{\mathcal{A}}(t))}{\epsilon^2}\right)} \\
& \quad \times\varphi_l(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,0,a^{\mathcal{A}}(t),x)\Phi^+_{\mathcal{A}}(x,t,\epsilon) \\
& +\mathrm{e}^{-\pi r/4\eta_1^0}\sqrt{\frac{\pi r}{\eta_1^0}}\frac{\mathrm{e}^{i\lambda(\epsilon)}}{\Gamma\left(1+\frac{ir}{2\eta_1^0}\right)} \\
& \quad \times F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'})\mathrm{e}^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\
& \quad \times\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\Phi^+_{\mathcal{B}}(x,t,\epsilon), \qquad (3.128)
\end{aligned}$$

where

$$\lambda(\epsilon) = \pi/4 + S_0^{\mathcal{A}}(-,\epsilon)/\epsilon^2 + \frac{r}{2\eta_1^0}(1+3\ln(2\eta_1^0)+\ln r - 4\ln\epsilon). \qquad (3.129)$$

We show as above that this function is an approximate solution of the Schrödinger equation.

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

$$\psi(x,t) = \psi_{OO}(x,t) + R(x,t,\epsilon) \qquad (3.130)$$

with

$$R(x,t,\epsilon) = \mathcal{O}(\epsilon^{\xi}) \qquad (3.131)$$

in the $L^2(I\!\!R^n)$ sense, as $\epsilon \to 0$.

Proof:
This lemma is proved by the same techniques used to prove lemma 3.4. □

Remark: In lemmas 3.4, 3.5 and 3.6, the cut-off functions F appearing in the approximations can be dropped without altering the estimates because of the exponential decay of the gaussians they multiply.

Gathering the results of this last section and using the fact that the evolution operator is unitary, we obtain our main theorem:

Theorem 3.1 *Let $h(x,\epsilon)$ be a hamiltonian such that $h_{\|}(x,\epsilon)$ is characterized by (1.11) and (1.20), and let $\psi(x,t)$ be a solution of the corresponding Schrödinger equation (1.15) such that*

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

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

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

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

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

where f_0 and g_0 are defined in (3.92), (3.96) and (3.105) with $y=(x-a(t))/\epsilon, s=t/\epsilon$, and finally for $\epsilon^{1-\xi} \leq t \leq T$:

$$\begin{aligned}\psi(x,t) = \quad & -e^{-\pi r/2\eta_1^0}e^{\left(i\frac{S^{\mathcal{A}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{A}}(t)(x-a^{\mathcal{A}}(t))}{\epsilon^2}\right)} \\ &\times\varphi_l(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,0,a^{\mathcal{A}}(t),x)\Phi^+_{\mathcal{A}}(x,t,\epsilon) \\ &+e^{-\pi r/4\eta_1^0}\sqrt{\frac{\pi r}{\eta_1^0}}\frac{e^{i\lambda(\epsilon)}}{\Gamma\left(1+\frac{ir}{2\eta_1^0}\right)} \\ &\times e^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\ &\times\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\Phi^+_{\mathcal{B}}(x,t,\epsilon)+\mathcal{O}(\epsilon^p),\end{aligned}$$

where $\lambda(\epsilon)$ is given in (3.129).

As a direct corollary, we compute that the transition probability $\mathcal{P}_{\mathcal{B}\to\mathcal{A}}$ from the level $\mathcal{B}$ at $t=-T$ to the level $\mathcal{A}$ at $t=+T$ is given in the limit $\epsilon \to 0$ by

$$\mathcal{P}_{\mathcal{B}\to\mathcal{A}} = \mathrm{e}^{-\pi r/\eta_1^0}+\mathcal{O}(\epsilon^p). \tag{3.132}$$

As explained above, $\mathcal{P}_{\mathcal{B}\to\mathcal{A}}$ coincides with the answer provided by the Landau-Zener formula where the gap is given by ϵ. Of course, the probability to remain on the $\mathcal{B}$ level satisfies

$$\begin{aligned}\mathcal{P}_{\mathcal{B}\to\mathcal{B}} &= \mathrm{e}^{-\pi r/2\eta_1^0}\frac{\pi r}{\eta_1^0\left|\Gamma\left(1+\frac{ir}{2\eta_1^0}\right)\right|^2}+\mathcal{O}(\epsilon^p) \\ &= 1-\mathrm{e}^{-\pi r/\eta_1^0}+\mathcal{O}(\epsilon^p).\end{aligned} \tag{3.133}$$

Remark: The above formulae coincide with (1.2) and (1.3) when one takes into account the change of variables performed at the end of the first section. Indeed, it is not difficult to verify that in terms of the initial variables $(x,t) \in I\!R^{n+1}$ the classical position $f(t)$ and momentum $\mu(t)$ are related to the classical position $a(t')$ and momentum $\eta(t')$ associated with the new variables $(x',t') \in I\!R^{n+1}$ (1.16) by

$$\begin{aligned}f(t) &= a(t')/b_1 - \begin{pmatrix} b_2\epsilon/b_1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \\ \mu(t) &= \eta(t')b_1/c_2^2,\end{aligned} \tag{3.134}$$

which yields the result.

4 Type 2 Avoided Crossings

In this section we make a precise statement of our result for Type 2 Avoided Crossings and describe how to alter the arguments of Section 3 to produce a proof. The theorem is proved by the same arguments as Theorem 3.1 except for the adiabatic motion of the degenerate electronic states.

We choose electronic eigenvectors by mimicking Section 3.2. We let $\eta^{\mathcal{C}}(t)$ be the solution of the classical equations of motion (2.2) and (2.3). The normalized eigenvectors, $\Phi^{\pm}_{\mathcal{C},1}(x,t,\epsilon)$ and $\Phi^{\pm}_{\mathcal{C},2}(x,t,\epsilon)$, we wish to construct are the orthonormal solutions of

$$\langle \Phi^{\pm}_{\mathcal{C},j}(x,t,\epsilon)|\left(\partial/\partial t + \eta^{\mathcal{C}}(t)\nabla\right)\Phi^{\pm}_{\mathcal{C},k}(x,t,\epsilon)\rangle \equiv 0 \tag{4.1}$$

for $\mathcal{C}=\mathcal{A},\mathcal{B}$, $j=1,2$, $k=1,2$, and $t \gtrless 0$. Since the eigenvalues $E_{\mathcal{A}}(x,\epsilon)$ and $E_{\mathcal{B}}(x,\epsilon)$ are multiplicity 2 for any time t, t small enough, such vectors exist, are unique up to an overall time unitary transformation, and are eigenvectors of $h_1(x,\epsilon)$ associated with $E_{\mathcal{C}}(x,\epsilon)$ for any time, see [16]. Let us make the construction of these eigenvectors more specific and give their small t and small ϵ asymptotics.

As in Section 3.2, we define $\varphi(x,\epsilon)$ and $\theta(x,\epsilon)$ by equations (3.33)–(3.35), and construct the following static eigenvectors:

$$\begin{aligned}
\Phi^{-}_{\mathcal{A},1}(x,\epsilon) &= \mathrm{e}^{i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon)+\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon), &(4.2)\\
\Phi^{-}_{\mathcal{B},1}(x,\epsilon) &= \mathrm{e}^{-i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_2(x,\epsilon)-\sin(\theta(x,\epsilon)/2)\psi_1(x,\epsilon), &(4.3)\\
\Phi^{-}_{\mathcal{A},2}(x,\epsilon) &= \mathrm{e}^{i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_3(x,\epsilon)+\sin(\theta(x,\epsilon)/2)\psi_4(x,\epsilon), &(4.4)\\
\Phi^{-}_{\mathcal{B},2}(x,\epsilon) &= \mathrm{e}^{-i\varphi(x,\epsilon)}\cos(\theta(x,\epsilon)/2)\psi_4(x,\epsilon)-\sin(\theta(x,\epsilon)/2)\psi_3(x,\epsilon), &(4.5)
\end{aligned}$$

associated with $E_{\mathcal{C}}(x,\epsilon)$, $\mathcal{C}=\mathcal{A},\mathcal{B}$, for $\pi/2<\theta(x,\epsilon)\le\pi$, and

$$\begin{aligned}
\Phi^{+}_{\mathcal{A},1}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon)+\mathrm{e}^{-i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon), &(4.6)\\
\Phi^{+}_{\mathcal{B},1}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_2(x,\epsilon)-\mathrm{e}^{i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_1(x,\epsilon), &(4.7)\\
\Phi^{+}_{\mathcal{A},2}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_3(x,\epsilon)+\mathrm{e}^{-i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_4(x,\epsilon), &(4.8)\\
\Phi^{+}_{\mathcal{B},2}(x,\epsilon) &= \cos(\theta(x,\epsilon)/2)\psi_4(x,\epsilon)-\mathrm{e}^{i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_3(x,\epsilon), &(4.9)
\end{aligned}$$

for $0\le\theta(x,\epsilon)<\pi/2$. We then construct solutions of (4.1) by using

$$\begin{pmatrix}\Phi^{\pm}_{\mathcal{C},1}(x,t,\epsilon)\\ \Phi^{\pm}_{\mathcal{C},2}(x,t,\epsilon)\end{pmatrix} = U^{\pm}_{\mathcal{C}}(x,t,\epsilon)\begin{pmatrix}\Phi_{\mathcal{C},1}(x,\epsilon)\\ \Phi_{\mathcal{C},2}(x,\epsilon)\end{pmatrix}, \quad \begin{cases} t>0\\ t<0\end{cases}, \tag{4.10}$$

where the unitary matrices $U^{\pm}_{\mathcal{C}}(x,t,\epsilon)$ play the roles of the phase factors from Section 3.2. The matrices $U^{\pm}_{\mathcal{C}}(x,t,\epsilon)$ satisfy differential equations that lead to time ordered exponentials instead of simple exponentials, so there is not a simple analog of equation (3.41). However, the analog of Lemma 3.2 is true.

Lemma 4.1 *Let $\eta^{\mathcal{C}}(t)$ be the solution of the classical equations of motion (2.2) and (2.3). There exist eigenvectors $\Phi^{\pm}_{\mathcal{C},j}(x,t,\epsilon)$, $\mathcal{C}=\mathcal{A},\mathcal{B}$, $j=1,2$, such that*

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

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

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

Proof:
We give a proof for $\Phi^+_{\mathcal{A},j}(x,t,\epsilon)$ only. The other cases are similar. In order to simplify the notation, we drop the indices $\mathcal{A}$ and $+$. Thus we need to determine $U(x,t,\epsilon)$ such that

$$\Phi_j(x,t,\epsilon) = U(x,t,\epsilon)\,\Phi_j(x,\epsilon) \tag{4.11}$$

for $j = 1, 2$, where

$$\Phi_1(x,\epsilon) = \cos(\theta(x,\epsilon)/2)\psi_1(x,\epsilon) + \mathrm{e}^{-i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_2(x,\epsilon) \tag{4.12}$$

and

$$\Phi_2(x,\epsilon) = \cos(\theta(x,\epsilon)/2)\psi_3(x,\epsilon) + \mathrm{e}^{-i\varphi(x,\epsilon)}\sin(\theta(x,\epsilon)/2)\psi_4(x,\epsilon) \tag{4.13}$$

Let $a(t) \equiv a^{\mathcal{A}}(t)$, and $\eta(t) \equiv \eta^{\mathcal{A}}(t)$ for $t > 0$, and introduce

$$\omega \equiv x - a(t), \tag{4.14}$$
$$\widetilde{U}(\omega,t,\epsilon) \equiv U(\omega + a(t),t,\epsilon), \qquad \text{and} \tag{4.15}$$
$$\widetilde{\Phi_j}(\omega,t,\epsilon) \equiv \Phi_j(\omega + a(t),\epsilon). \tag{4.16}$$

In terms of these new variables, the equation for the entries of $\widetilde{U}$ has the form

$$i\frac{\partial}{\partial t}\widetilde{U}(\omega,t,\epsilon) = M(\omega,t,\epsilon)\widetilde{U}(\omega,t,\epsilon), \tag{4.17}$$

where the precise form for $M(\omega,t,\epsilon)$ can be obtained from page 36 of [16], with

$$\frac{\partial}{\partial t}\tilde{\Phi}_j(\omega,t,\epsilon) = \eta(t)\nabla\Phi_j(\omega + a(t),\epsilon). \tag{4.18}$$

In analogy with the computations of Section 3.2, we compute

$$\begin{aligned}\nabla\Phi_1 = \quad & \left(-\sin(\theta/2)\psi_1 + \mathrm{e}^{-i\varphi}\cos(\theta/2)\psi_2\right)\nabla\theta/2 \\ & +\cos(\theta/2)\nabla\psi_1 + \mathrm{e}^{-i\varphi}\sin(\theta/2)\nabla\psi_2 \\ & -i\nabla\varphi\mathrm{e}^{-i\varphi}\sin(\theta/2)\psi_2,\end{aligned} \tag{4.19}$$

and

$$\begin{aligned}\nabla\Phi_2 \quad & = \left(-\sin(\theta/2)\psi_3 + \mathrm{e}^{-i\varphi}\cos(\theta/2)\psi_4\right)\nabla\theta/2 \\ & +\cos(\theta/2)\nabla\psi_3 + \mathrm{e}^{-i\varphi}\sin(\theta/2)\nabla\psi_4 \\ & -i\nabla\varphi\mathrm{e}^{-i\varphi}\sin(\theta/2)\psi_4.\end{aligned} \tag{4.20}$$

¿From this we can compute the matrix elements of $M(\omega,t,\epsilon)$, which are the analogs of (3.50). The terms of the form

$$\begin{aligned}\langle\widetilde{\Phi_1}|\frac{\partial}{\partial t}\widetilde{\Phi_1}\rangle = \quad & -i\eta\nabla\varphi\sin^2(\theta/2) + \cos^2(\theta/2)\langle\psi_1|\eta\nabla\psi_1\rangle + \sin^2(\theta/2)\langle\psi_2|\eta\nabla\psi_2\rangle \\ & +\sin(\theta/2)\cos(\theta/2)\left(\mathrm{e}^{-i\varphi}\langle\psi_1|\eta\nabla\psi_2\rangle + \mathrm{e}^{i\varphi}\langle\psi_2|\eta\nabla\psi_1\rangle\right)\end{aligned} \tag{4.21}$$

and

$$\langle\widetilde{\Phi_2}|\frac{\partial}{\partial t}\widetilde{\Phi_2}\rangle = \quad -i\eta\nabla\varphi\sin^2(\theta/2) + \cos^2(\theta/2)\langle\psi_3|\eta\nabla\psi_1\rangle + \sin^2(\theta/2)\langle\psi_4|\eta\nabla\psi_4\rangle$$
$$+\sin(\theta/2)\cos(\theta/2)\left(\mathrm{e}^{-i\varphi}\langle\psi_3|\eta\nabla\psi_4\rangle + \mathrm{e}^{i\varphi}\langle\psi_4|\eta\nabla\psi_3\rangle\right) \tag{4.22}$$

both satisfy the estimates from the proof of Lemma 3.2. Because $\{\,\psi_1,\,\psi_2,\,\psi_3,\,\psi_4\,\}$ are mutually orthogonal, there is considerable simplification of the terms

$$\langle\widetilde{\Phi_1}|\frac{\partial}{\partial t}\widetilde{\Phi_2}\rangle = \langle\cos(\theta/2)\psi_1 + e^{-i\varphi}\sin(\theta/2)\psi_2|\cos(\theta/2)\nabla\psi_3 + e^{-i\varphi}\sin(\theta/2)\nabla\psi_4\rangle \tag{4.23}$$

and

$$\langle\widetilde{\Phi_2}|\frac{\partial}{\partial t}\widetilde{\Phi_1}\rangle = \langle\cos(\theta/2)\psi_3 + e^{-i\varphi}\sin(\theta/2)\psi_4|\cos(\theta/2)\nabla\psi_1 + e^{-i\varphi}\sin(\theta/2)\nabla\psi_2\rangle. \tag{4.24}$$

¿From these formulas, we easily see that these terms have no singular behavior for small t and fixed $\epsilon > 0$. From the convergent Dyson series for $\widetilde{U}(\omega,t,\epsilon)$ from equation (4.17) with initial condition $\widetilde{U}(\omega,0,\epsilon) = I\!I$, we then conclude that

$$\widetilde{U}(\omega,t,\epsilon) = \widetilde{U}(\omega,0,\epsilon) + \mathcal{O}(t/\epsilon^{1-\kappa}). \tag{4.25}$$

This implies the lemma. □

The following analog of Lemma 3.3 is proved by the same techniques we used to prove Lemma 3.3.

Lemma 4.2 *For x in the support of $F(\|x-a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, $\mathcal{C}=\mathcal{A},\mathcal{B}$, we have for $t<0$,*

$$\begin{aligned}
\Phi^-_{\mathcal{A},1}(x,\epsilon) &= \psi_2(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),\\
\Phi^-_{\mathcal{B},1}(x,\epsilon) &= -\psi_1(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),\\
\Phi^-_{\mathcal{A},2}(x,\epsilon) &= \psi_4(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),\\
\Phi^-_{\mathcal{B},2}(x,\epsilon) &= -\psi_3(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),
\end{aligned}$$

and for $t>0$,

$$\begin{aligned}
\Phi^+_{\mathcal{A},1}(x,\epsilon) &= \psi_1(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),\\
\Phi^+_{\mathcal{B},1}(x,\epsilon) &= \psi_2(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),\\
\Phi^+_{\mathcal{A},2}(x,\epsilon) &= \psi_3(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}),\\
\Phi^+_{\mathcal{B},2}(x,\epsilon) &= \psi_4(x,\epsilon) + \mathcal{O}(\epsilon/t^{1/2}).
\end{aligned}$$

Our main result of this section is the following:

Theorem 4.1 *Let $h(x,\epsilon)$ be a hamiltonian such that $h_{\|}(x,\epsilon)$ is characterized by (1.14) and (1.20). Let $\psi(x,t)$ be a solution of the corresponding Schrödinger equation (1.15) such that*

$$\begin{aligned}\psi(x,-T) &= e^{\left(i\frac{S^{\mathcal{B}}(-T)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(-T)(x-a^{\mathcal{B}}(-T))}{\epsilon^2}\right)} \\ &\quad\times\ \varphi_l(A^{\mathcal{B}}(-T),B^{\mathcal{B}}(-T),\epsilon^2,0,a^{\mathcal{B}}(-T),x)\Phi^-_{\mathcal{B},1}(x,-T,\epsilon)+\mathcal{O}(\epsilon^q),\end{aligned}$$

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

$$\begin{aligned}\psi(x,t) &= e^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\ &\quad\times\ \varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\Phi^-_{\mathcal{B},1}(x,t,\epsilon)+\mathcal{O}(\epsilon^p),\end{aligned}$$

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 in (3.92), (3.96) and (3.105) with $y=(x-a(t))/\epsilon$, $s=t/\epsilon$, and finally for $\epsilon^{1-\xi}\le t\le T$:

$$\begin{aligned}\psi(x,t) = &\ -e^{-\pi r/2\eta_1^0}e^{\left(i\frac{S^{\mathcal{A}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{A}}(t)(x-a^{\mathcal{A}}(t))}{\epsilon^2}\right)} \\ &\quad\times\ \varphi_l(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,0,a^{\mathcal{A}}(t),x)\Phi^+_{\mathcal{A},1}(x,t,\epsilon) \\ &+e^{-\pi r/4\eta_1^0}\sqrt{\frac{\pi r}{\eta_1^0}}\frac{e^{i\lambda(\epsilon)}}{\Gamma\left(1+\frac{ir}{2\eta_1^0}\right)} \\ &\quad\times e^{\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}+i\frac{\eta^{\mathcal{B}}(t)(x-a^{\mathcal{B}}(t))}{\epsilon^2}\right)} \\ &\quad\times\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,0,a^{\mathcal{B}}(t),x)\Phi^+_{\mathcal{B},1}(x,t,\epsilon)+\mathcal{O}(\epsilon^p),\end{aligned}$$

where $\lambda(\epsilon)$ is given in (3.129). The corresponding statement with $\Phi^-_{\mathcal{B},2}$ in place of $\Phi^-_{\mathcal{B},1}$ is true with ψ_1 and ψ_2 replaced by ψ_3 and ψ_4, respectively.

The proof of this theorem is essentially the same as that for Theorem 3.1. There is no change in the semiclassical mechanics, and the lemmas of this section handle the adiabatic electronic states for the outer solutions. The inner solutions for the two different values of j do not mix with one another to leading order because of the block diagonal form of (1.14).

One can, of course, take linear combinations of the two solutions described by this theorem. The transition probabilities for Type 2 Avoided Crossings are the same as those presented immediately after the statement of Theorem 3.1 for Type 1 Avoided Crossings.

References

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

[2] Combes, J.-M.: On the Born–Oppenheimer Approximation. In: *International Symposium on Mathematical Problems in Theoretical Physics.* ed. by H. Araki. Berlin, Heidelberg, New York: Springer 1975.

[3] Combes, J.-M.: The Born–Oppenheimer Approximation. In: *The Schrödinger Equation.* ed. by W. Thirring, P. Urban. Wien, New York: Springer 1977.

[4] Combes, J.-M., Duclos P., and Seiler R.: The Born–Oppenheimer Approximation. In *Rigorous Atomic and Molecular Physics.* ed. by G. Velo, A. Wightman. New York: Plenum 1981.

[5] Gradshteyn, I. S. and Ryzhik, I. M.: *Table of Integrals, Series, and Products.* New York: Academic Press 1980.

[6] Hagedorn, G. A.: A Time–Dependent Born–Oppenheimer Approximation. *Commun. Math. Phys.* **77**, 1–19 (1980).

[7] Hagedorn, G. A.: Semiclassical Quantum Mechanics IV: Large Order Asymptotics and More General States in More than One Dimension. *Ann. Inst. H. Poincaré Sect. A* **42**, 363–374 (1985).

[8] Hagedorn, G. A.: High Order Corrections to the Time–Dependent Born–Oppenheimer Approximation I: Smooth Potentials. *Ann. Math.* **124**, 571–590 (1986). Erratum **126**, 219 (1987).

[9] Hagedorn, G. A.: High Order Corrections to the Time–Independent Born–Oppenheimer Approximation I: Smooth Potentials. *Ann. Inst. H. Poincaré Sect. A* **47**, 1–19 (1987).

[10] Hagedorn, G. A.: High Order Corrections to the Time–Independent Born–Oppenheimer Approximation II: Diatomic Coulomb Systems. *Commun. Math. Phys.* **116**, 23–44 (1988).

[11] Hagedorn, G. A.: High Order Corrections to the Time–Dependent Born–Oppenheimer Approximation II: Coulomb Systems. *Commun. Math. Phys.* **117**, 387–403 (1988).

[12] Hagedorn, G. A.: Multiple Scales and the Time–Independent Born–Oppenheimer Approximation. In: *Differential Equations and Applications.* ed. by R. Aftabizadeh. New York: Marcel Dekker 1989.

[13] Hagedorn, G. A.: Electron Energy Level Crossings in the Time–Dependent Born–Oppenheimer Approximation. *Theor. Chimica Acta.* **77**, 163–190 (1990).

[14] Hagedorn, G. A.: Proof of the Landau–Zener Formula in an Adiabatic Limit with Small Eigenvalue Gaps. *Commun. Math. Phys.* **136**, 433–449 (1991).

[15] Hagedorn, G. A.: Time–Reversal Invariance and the Time–Dependent Born–Oppenheimer Approximation. In *Forty More Years of Ramifications: Spectral Asymptotics and Its Applications,* (Discourses in Mathematics and Its Applications, No. 1). ed. by S. A. Fulling and F. J. Narcowich. College Station: Texas A & M University Mathematics Department 1992.

[16] Hagedorn, G. A.: Molecular Propagation Through Electronic Eigenvalue Crossings, *Memoirs Amer. Math. Soc.* **536**, (1994).

[17] Hagedorn, G. A.: Effects of Electron Energy Level Crossings on Molecular Propagation. *Proceedings of the 1994 GIT-UAB International Conference on Differential Equations and Mathematical Physics.* (to appear).

[18] Hagedorn, G. A.: Classification and Normal Forms for Avoided Crossings of Quantum Mechanical Energy Levels. Preprint, Virginia Polytechnic Institute and State University.

[19] Hagedorn, G. A., and Joye, A.: (in preparation).

[20] Herrin, J. S.: The Born–Oppenheimer Approximation: Straight–Up and with a Twist. Ph. D. Dissertation, University of Virginia, 1990.

[21] Joye, A.: Non-trivial Prefactors in Adiabatic Transition Probabilities Induced by High Order Complex Degeneracies. *J. Phys. A* **26**, 6517–6540 (1993).

[22] Joye, A.: Proof of the Landau–Zener Formula. *Asymptotic Analysis* **9**, 209–258 (1994).

[23] Joye, A.: Exponential Asymptotics in a Singular Limit for n-Level Scattering Systems. Preprint CNRS Marseille CPT–95/P.3216.

[24] Joye, A., Kunz, H., and Pfister, C.-E.: Exponential Decay and Geometric Aspect of Transition Probabilities in the Adiabatic Limit. *Ann. Phys.* **208**, 299–332 (1991).

[25] Joye, A., Mileti, G., and Pfister, C.-E.: Interferences in Adiabatic Transition Probabilities Mediated by Stokes Lines. *Phys. Rev. A* **44**, 4280–4295 (1991).

[26] Joye, A. and Pfister, C.-E.: Full Asymptotic Expansion of Transition Probabilities in the Adiabatic Limit. *J. Phys. A.* **24**, 753–766 (1991).

[27] Joye, A. and Pfister, C.-E.: Absence of Geometrical Correction to the Landau-Zener Formula. *Phys. Lett. A* **169**, 62–66 (1992).

[28] Joye, A. and Pfister, C.-E.: Superadiabatic Evolution and Adiabatic Transition Probability between Two Non–Degenerate Levels Isolated in the Spectrum. *J. Math. Phys.* **34**, 454–479 (1993).

[29] Joye, A. and Pfister, C.-E.: Non-abelian Geometric Effect in Quantum Adiabatic Transitions. *Phys. Rev. A* **48**, 2598–2608 (1993).

[30] Joye, A. and Pfister, C.-E.: Quantum Adiabatic Evolution, in *Leuven Conference Proceedings; On the Three Levels Micro- Meso- and Macro-Approaches in Physics*, M. Fannes, C. Meas, A. Verbeure edts., Plenum, New York, 139-148 (1994).

[31] Joye, A., Pfister, C.-E. : Semi-Classical Asymptotics beyond All Orders for Simple Scattering Systems, *SIAM J.Math.Anal.* **26**, 944–977 (1995).

[32] Kargol, A.: The Infinite Time Limit for the Time–Dependent Born–Oppenheimer Approximation. *Commun. Math. Phys.* **166**, 129–148 (1994).

[33] Kato, T.: On the Adiabatic Theorem in Quantum Mechanics. *J. Phys. Soc. Jpn.* **5**, 435–439 (1950).

[34] Klein, M.: On the Mathematical Theory of Predissociation. *Ann. Phys.* **178**, 48–73 (1987).

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

[36] Klein, M., Martinez, A., and Wang, X. P.: On the Born–Oppenheimer Approximation of Wave Operators in Molecular Scattering Theory. Université de Nantes preprint, 1992.

[37] Martin, Ph.A. and Nenciu G.: Semi-Classical Inelastic S-Matrix for One-Dimensional N-States Systems, *Rev.Math.Phys.* **7**, 193–242 (1995).

[38] Martinez, A.: Développements Asymptotiques et Effet Tunnel dans l'Approximation de Born–Oppenheimer. *Ann. Inst. H. Poincaré Sect. A* **50**, 239–257 (1989).

[39] Martinez, A.: Développements Asymptotiques dans l'Approximation de Born–Oppenheimer. *Journées E. D. P. de St. Jean-de-Monts* (1988).

[40] Martinez, A.: Resonances dans l'Approximation de Born–Oppenheimer I. *J. Diff. Eq.* **91**, 204–234 (1991).

[41] Martinez, A.: Resonances dans l'Approximation de Born–Oppenheimer II. Largeur de Résonances. *Commun. Math. Phys.* **135**, 517–530 (1991).