Molecular Propagation through Small Avoided Crossings of Electron Energy Levels

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Abstract

This is the second of two papers on the propagation of molecular wave packets through avoided crossings of electronic energy levels in a limit where the gap between the levels shrinks as the nuclear masses are increased. An earlier paper deals with the simplest two types of generic, minimal multiplicity avoided crossings, in which the levels essentially depend on only one of the nuclear configuration parameters. The present paper deals with propagation through the remaining four types of generic, minimal multiplicity avoided crossings, in which the levels depend on more than one nuclear configuration parameter.

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1 Introduction

This is the second of a pair of papers on the propagation of molecular wave packets through avoided crossings of electronic energy levels in a limit where the gap between the levels shrinks as the nuclear masses are increased. Generic, minimal multiplicity avoided crossings can be classified into six types [19]. Our first paper [20] deals with Types 1 and 2; the present paper deals with Types 3, 4, 5, and 6.

In Type 1 and Type 2 avoided crossings, the electron energy levels essentially depend on only one nuclear configuration parameter. Because of rotational symmetry, this is the case for all diatomic molecules. The results of [20] show that in Type 1 and Type 2 avoided crossings, transitions between the levels are correctly described by the Landau–Zener formula.

In Type 3, 4, 5, and 6 avoided crossings, the electron energy levels essentially depend (respectively) on 2, 2, 3, and 4 nuclear configuration parameters [19]. In practice, these arise in polyatomic molecules, or in diatomic or polyatomic systems in external fields. Molecular propagation through these more complicated avoided crossings is not governed directly by the Landau–Zener formula, and electronic transition probabilites depend on the shape of the nuclear wave packet. Intuitively, this is because different pieces of the wave packet feel different size minimum gaps between the electronic levels. As we explain in more detail below, the correct transition probability can be determined by decomposing the nuclear wave packet into infinitesimal pieces, using a different Landau–Zener formula for each infinitesimal piece, and then doing an integration.

Electron energy levels are functions of the nuclear configuration parameters, determined by discrete quantum mechanical bound state energies of the electrons for each fixed classical nuclear configuration. Their relevance to molecular propagation is tied to the time–dependent Born–Oppenheimer approximation, which exploits 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 quantum state in response to the relatively slow nuclear motion. They 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 intuition is the basis for rigorous asymptotic expansions of solutions to the molecular time–dependent Schrödinger equation [7, 9, 12, 16, 17]. However, the validity of the approximation depends on the assumption that the electron energy level of interest is well isolated from the rest of the spectrum of the electronic Hamiltonian. This assumption is violated near an Avoided Crossing.

Readers interested in the mathematical literature concerning the validity of Born–Oppenheimer approximations should consult [3, 4, 5, 7, 9, 10, 11, 12, 13, 14, 16, 17, 18, 20, 21, 33, 35, 36, 37, 39, 40, 41, 42].

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

$$H(\epsilon) \;=\; \sum_{j=1}^{K} -\frac{\epsilon^4}{2M_j}\,\Delta_{x_j} \;-\; \sum_{j=K+1}^{N} \frac{1}{2m_j}\,\Delta_{x_j} \;+\; \sum_{i<j} V_{ij}(x_i-x_j). \tag{1.1}$$

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

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_x \,+\, h(x). \tag{1.2}$$

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

The time–dependent Schrödinger equation that we study is

$$i\,\epsilon^2\,\frac{\partial\psi}{\partial t} \;=\; H(\epsilon)\,\psi, \tag{1.3}$$

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" [2] 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 (1.1). We only require the Hamiltonian to be of the form (1.2). 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 (1.2) to allow the electron Hamiltonian to depend on ϵ as well as x. We study solutions to equation (1.3) with Hamiltonians of the form

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_x \,+\, h(x,\,\epsilon), \tag{1.4}$$

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 [11, 12, 36].

Precise statements of our results require a considerable amount of notation and are presented in Theorems 3.1, 4.1, 4.2, and 4.3 for Type 3, 4, 5, and 6 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.

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 avoided crossings couple the two levels to leading order in ϵ, and the interesting transitions between the levels occur in the time interval in which the inner solution is valid. To leading order, the Schrödinger equation for the inner solution is hyperbolic. As a result, it makes sense to describe the motion of each infinitesimal piece of the wave function along its characteristic. Along the various characteristics, the wave function feels various different minimum gaps between the eigenvalues. The Landau–Zener formula describes the correct transition probability along each individual characteristic. The transition probability for the entire wave function is correctly obtained by applying the Landau–Zener formula for each infinitesimal piece of the wave function and then integrating over the nuclear configuration space. The transition probability depends on the shape of the wave packet as it encounters the avoided crossing.

To describe the various Types of Avoided Crossings, we recall several results from [19]. For convenience, we use the notation

$$\mathcal{O}(m) = \mathcal{O}\left(\left\{\left(\sum_{j=1}^{n} x_j^2\right) \ + \ \epsilon^2\right\}^{m/2}\right). \tag{1.5}$$

Assume without loss of generality that 0 is a generic point of Γ, and that we are given a classical nuclear momentum vector η^0 that is transversal to Γ. We decompose

$$h(x,\epsilon) = h_{||}(x,\epsilon) + h_{\perp}(x,\epsilon) \tag{1.6}$$

with

$$h_{||}(x,\epsilon) = h(x,\epsilon)P(x,\epsilon) \tag{1.7}$$

and

$$h_{\perp}(x,\epsilon) = h(x,\epsilon)(\mathbb{I} - P(x,\epsilon)) \tag{1.8}$$

where $P(x,\epsilon)$ is a spectral projector for $h(x,\epsilon)$ associated with $E_{\mathcal{A}}(x,\,\epsilon)$ and $E_{\mathcal{B}}(x,\,\epsilon)$.

Type 1 and 2 Avoided Crossings have the codimension of Γ equal to 1. We will not discuss them here since they have already been studied in [20].

Type 3 and 4 Avoided Crossings have the codimension of Γ equal to 2. For these two types of Avoided Crossings, we choose an orthogonal coordinate system for the nuclear configurations in which the x_1 and x_2 coordinate directions are perpendicular to Γ at $x=0$; the x_3, x_4, $\dots x_n$ coordinate directions are parallel to Γ at $x=0$; and so that the vector η^0 has the form

$$\eta^0 = \begin{pmatrix} \eta_1^0 \\ 0 \\ \eta_3^0 \\ \eta_4^0 \\ \vdots \\ \eta_n^0 \end{pmatrix}. \tag{1.9}$$

The eigenvalues involved in a Type 3 Avoided Crossing are non-degenerate. One can choose [19] an orthonormal basis $\{\psi_1(x,\epsilon), \psi_2(x,\epsilon)\}$ of $P(x,\epsilon)\mathcal{H}$, which is regular in (x,ϵ) around $(0,0)$, such that

$$h_{||}(x,\epsilon) = h_1(x,\epsilon) + \widetilde{V}(x,\epsilon), \tag{1.10}$$

where $h_1(x,\epsilon)$ is represented in this basis by the matrix

$$\begin{pmatrix} \beta(x,\epsilon) & \gamma(x,\epsilon)+i\delta(x,\epsilon) \\ \gamma(x,\epsilon)-i\delta(x,\epsilon) & -\beta(x,\epsilon) \end{pmatrix} \tag{1.11}$$

and $\widetilde{V}(x,\epsilon)$ is represented by $\frac{1}{2}\,\mathrm{trace}(h(x,\epsilon)P(x,\epsilon))$ times the 2×2 identity matrix. The function $\widetilde{V}(x,\epsilon)$ is regular in (x,ϵ) near the origin, and

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1 + b_2x_2 + b_3\epsilon + \mathcal{O}(2) \\ \gamma(x,\epsilon) &= c_2x_2 + c_3\epsilon + \mathcal{O}(2) \\ \delta(x,\epsilon) &= d_3\epsilon + \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0) \end{aligned} \tag{1.12}$$

with $b_1>0$, $c_2>0$, $b_2\in I\!R$, $c_3\in I\!R$, and $d_3\in I\!R$. Generically, d_3 is non-zero, which we henceforth assume. The two energy levels involved in the Avoided Crossing are thus

$$\begin{aligned} E_{\substack{A\\B}} &= \widetilde{V}(x,\epsilon) \pm \sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2} \\ &= \widetilde{V}(x,\epsilon) \pm \sqrt{(b_1x_1+b_2x_2+b_3\epsilon)^2+(c_2x_2+c_3\epsilon)^2+(d_3\epsilon)^2 + \mathcal{O}(3)}. \end{aligned} \tag{1.13}$$

Figure 1 shows graphs of two electron energy levels near a typical Type 3 Avoided Crossing.

Our results for molecular propagation through Type 3 Avoided Crossings are stated precisely in theorem 3.1. To illustrate these results, we present a simple example with two nuclear degrees of freedom represented by the coordinates x_1 and x_2. The electrons belong to a two level system with electron Hamiltonian

$$\begin{pmatrix} x_1 & x_2+i\epsilon \\ x_2-i\epsilon & -x_1 \end{pmatrix}.$$

We choose an initial wave packet associated with the lower electronic level. The nuclei approach the origin along the negative x_1-axis in a state that is a Gaussian to leading

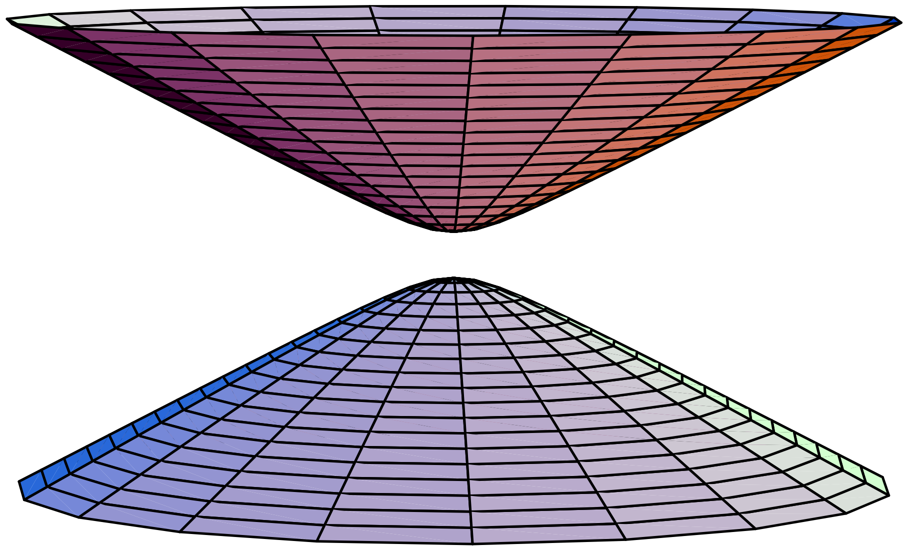

Figure 1: Graphs of electron energy levels with a Type 3 Avoided Crossing.

order in ϵ. The nuclear position and momentum uncertainties are proportional to ϵ, and the center of the Gaussian approximately follows a classical path $a(t)$. Figure 2 gives a graphical representation of this situation immediately before the nuclei encounter the avoided crossing. The left half of the figure corresponds to the lower electronic level, and the right half corresponds to the upper electronic level. For each of the two levels, the figure shows contour plots of the nuclear probability density as functions of the variable $y = (x - a(t))/\epsilon$. This is a natural variable that moves along the classical path with the nuclei.

Immediately after the nuclei have moved through the avoided crossing, the system has non-trivial components in each of the electronic levels, as depicted in figure 3.

To leading order, these final nuclear probability densities on the upper and lower surfaces are the initial nuclear probability density depicted on the left side of figure 2 multiplied by $e^{-f(y_2)}$ and $1 - e^{f(y_2)}$, respectively. Here

$$f(y_2) \;=\; \frac{\pi}{4\eta_1^0}\,(y_2^2 + 1),$$

where the nuclear momentum is concentrated near

$$\eta(0) \;=\; \begin{pmatrix} \eta_1^0 \\ 0 \end{pmatrix}$$

at the time when $a(t) = 0$. The physical intuition associated with this result is the following: The nuclei pass through the avoided crossing during a time interval whose length is on the order of ϵ. During that short time, to leading order, the nuclei simply translate through the avoided crossing. For each fixed value of y, the electron state propagates independently, and at time t, the electron Hamiltonian has an energy gap of size $2\sqrt{(\eta_1^0 t + y_1)^2 + y_2^2 + 1}$. The traditional Landau–Zener formula for a time dependent Hamiltonian with this size

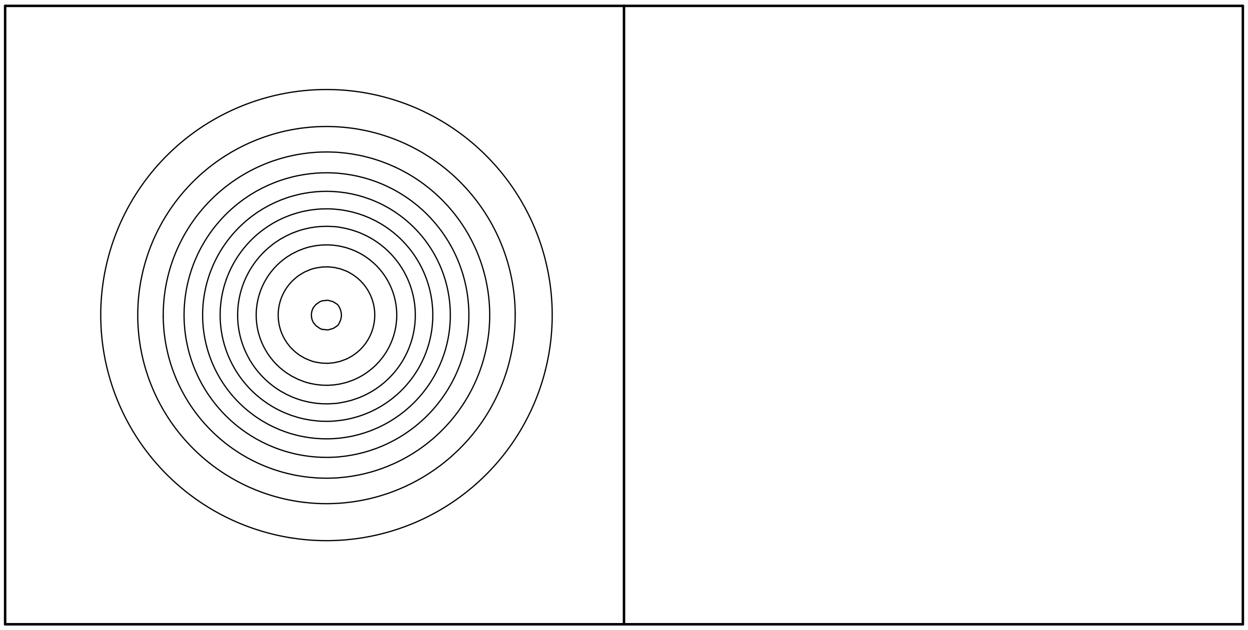

Figure 2: Probability densities before encountering Type 3 Avoided Crossing.

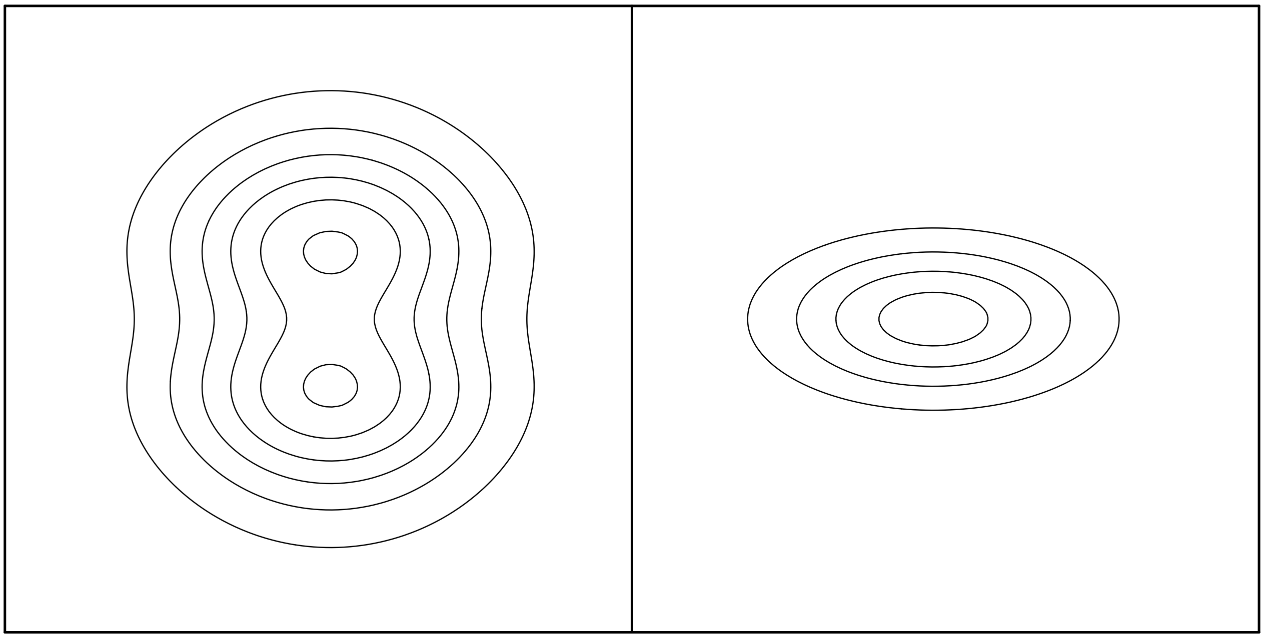

Figure 3: Probability densities after encountering a Type 3 Avoided Crossing.

gap predicts an electronic transition probability of $e^{-f(y_2)}$ as the system moves through the avoided crossing. Theorem 3.1 confirms this intuition.

Type 4 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 $(0,0)$. The operator $h_{||}$ satisfies

$$h_{||}(x,\epsilon) = h_1(x,\epsilon) + \widetilde{V}(x,\epsilon), \tag{1.14}$$

where $h_1(x,\epsilon)$ is represented in this basis by the matrix

$$\begin{pmatrix} \beta(x,\epsilon) & \gamma(x,\epsilon)+i\delta(x,\epsilon) & 0 & 0 \\ \gamma(x,\epsilon)-i\delta(x,\epsilon) & -\beta(x,\epsilon) & 0 & 0 \\ 0 & 0 & \beta(x,\epsilon) & \gamma(x,\epsilon)-i\delta(x,\epsilon) \\ 0 & 0 & \gamma(x,\epsilon)+i\delta(x,\epsilon) & -\beta(x,\epsilon) \end{pmatrix}, \tag{1.15}$$

and $\widetilde{V}(x,\epsilon)$ is represented by $\frac{1}{4}\,\mathrm{trace}(h(x,\epsilon)P(x,\epsilon))$ times the 4×4 identity matrix. The function $\widetilde{V}(x,\epsilon)$ is regular in (x,ϵ) near the origin, and

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1 + b_2x_2 + b_3\epsilon + \mathcal{O}(2) \\ \gamma(x,\epsilon) &= c_2x_2 + c_3\epsilon + \mathcal{O}(2) \\ \delta(x,\epsilon) &= d_3\epsilon + \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0). \end{aligned} \tag{1.16}$$

The two energy levels involved in the Avoided Crossing are thus

$$\begin{aligned} E_{\substack{A\\B}} &= \widetilde{V}(x,\epsilon) \pm \sqrt{\beta(x,\epsilon)^2 + \gamma(x,\epsilon)^2 + \delta(x,\epsilon)^2 + \mathcal{O}(2)} \\ &= \widetilde{V}(x,\epsilon) \pm \sqrt{(b_1x_1+b_2x_2+b_3\epsilon)^2 + (c_2x_2+c_3\epsilon)^2 + (d_3\epsilon)^2 \,+\, \mathcal{O}(3)}. \end{aligned} \tag{1.17}$$

Type 5 Avoided Crossings have the codimension of Γ equal to 3 and the multiplicity of the eigenvalues equal to 2. We choose an orthogonal coordinate system for the nuclear configurations in which the x_1, x_2, and x_3 coordinate directions are perpendicular to Γ at $x=0$; the x_4, x_5, $\dots x_n$ coordinate directions are parallel to Γ at $x=0$; and so that the vector η^0 has the form

$$\eta^0 = \begin{pmatrix} \eta_1^0 \\ 0 \\ 0 \\ \eta_4^0 \\ \eta_5^0 \\ \vdots \\ \eta_n^0 \end{pmatrix}. \tag{1.18}$$

We 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 $(0,0)$. The operator $h_{||}(x,\epsilon)$ satisfies (1.14), where $h_1(x,\epsilon)$ is represented in this basis by the matrix

$$\begin{pmatrix} \beta(x,\epsilon) & 0 & \gamma(x,\epsilon)+i\delta(x,\epsilon) & \zeta(x,\epsilon)+i\xi(x,\epsilon) \\ 0 & \beta(x,\epsilon) & -\zeta(x,\epsilon)+i\xi(x,\epsilon) & \gamma(x,\epsilon)-i\delta(x,\epsilon) \\ \gamma(x,\epsilon)-i\delta(x,\epsilon) & -\zeta(x,\epsilon)-i\xi(x,\epsilon) & -\beta(x,\epsilon) & 0 \\ \zeta(x,\epsilon)-i\xi(x,\epsilon) & \gamma(x,\epsilon)+i\delta(x,\epsilon) & 0 & -\beta(x,\epsilon) \end{pmatrix}, \tag{1.19}$$

and $\widetilde{V}(x,\epsilon)$ is represented by $\frac{1}{4}\,\mathrm{trace}(h(x,\epsilon)P(x,\epsilon))$ times the 4×4 identity matrix. The function $\widetilde{V}(x,\epsilon)$ is regular in (x,ϵ) near the origin, and

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1+b_2x_2+b_3x_3+b_4\epsilon+\mathcal{O}(2) \\ \gamma(x,\epsilon) &= c_2x_2+c_4\epsilon+\mathcal{O}(2) \\ \delta(x,\epsilon) &= d_3x_3+d_4\epsilon+\mathcal{O}(2) \\ \zeta(x,\epsilon) &= e_4\epsilon+\mathcal{O}(2) \\ \xi(x,\epsilon) &= \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0). \end{aligned}$$

We assume the generically satisfied condition $e_4\neq 0$. The two energy levels involved in the Avoided Crossing are thus

$$\begin{aligned} & E_{\substack{A\\B}} \\ &= \widetilde{V}(x,\epsilon)\pm\sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2+\zeta(x,\epsilon)^2+\xi(x,\epsilon)^2} \\ &= \widetilde{V}(x,\epsilon)\pm\sqrt{\left(\sum_{j=1}^{3}b_jx_j\;+b_4\epsilon\right)^2+(c_2x_2+c_4\epsilon)^2+(d_3x_3+d_4\epsilon)^2+(e_4\epsilon)^2\;+\;\mathcal{O}(3)}. \end{aligned} \tag{1.20}$$

Type 6 Avoided Crossings have the codimension of Γ equal to 4 and the multiplicity of the eigenvalues equal to 2. We choose an orthogonal coordinate system for the nuclear configurations in which the x_1, x_2, x_3, and x_4 coordinate directions are perpendicular to Γ at $x=0$; the x_5, x_6, $\ldots x_n$ coordinate directions are parallel to Γ at $x=0$; and so that the vector η^0 has the form

$$\eta^0=\begin{pmatrix}\eta_1^0\\0\\0\\0\\\eta_5^0\\\eta_6^0\\\vdots\\\eta_n^0\end{pmatrix}. \tag{1.21}$$

We 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 $(0,0)$. The operator $h_{||}(x,\epsilon)$ satisfies (1.14), where $h_1(x,\epsilon)$ is represented in this basis by the matrix

$$\begin{pmatrix} \beta(x,\epsilon) & 0 & \gamma(x,\epsilon)+i\delta(x,\epsilon) & \zeta(x,\epsilon)+i\xi(x,\epsilon) \\ 0 & \beta(x,\epsilon) & -\zeta(x,\epsilon)+i\xi(x,\epsilon) & \gamma(x,\epsilon)-i\delta(x,\epsilon) \\ \gamma(x,\epsilon)-i\delta(x,\epsilon) & -\zeta(x,\epsilon)-i\xi(x,\epsilon) & -\beta(x,\epsilon) & 0 \\ \zeta(x,\epsilon)-i\xi(x,\epsilon) & \gamma(x,\epsilon)+i\delta(x,\epsilon) & 0 & -\beta(x,\epsilon) \end{pmatrix}, \tag{1.22}$$

and $\widetilde{V}(x,\epsilon)$ is represented by $\frac{1}{4}\,\mathrm{trace}(h(x,\epsilon)P(x,\epsilon))$ times the 4×4 identity matrix. The function $\widetilde{V}(x,\epsilon)$ is regular in (x,ϵ) near the origin, and

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1+b_2x_2+b_3x_3+b_4x_4+b_5\epsilon+\mathcal{O}(2) \\ \gamma(x,\epsilon) &= c_2x_2+c_5\epsilon+\mathcal{O}(2) \\ \delta(x,\epsilon) &= d_3x_3+d_5\epsilon+\mathcal{O}(2) \\ \zeta(x,\epsilon) &= e_4x_4+e_5\epsilon+\mathcal{O}(2) \\ \xi(x,\epsilon) &= f_5\epsilon+\mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0). \end{aligned}$$

We assume the generically satisfied condition $f_5\neq 0$. The two energy levels involved in the Avoided Crossing are thus

$$\begin{aligned} & E_{\substack{A\\B}} \\ =\ & \widetilde{V}(x,\epsilon)\pm\sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2+\zeta(x,\epsilon)^2+\xi(x,\epsilon)^2} \\ =\ & \widetilde{V}(x,\epsilon) \\ & \pm\sqrt{\left(\sum_{j=1}^4 b_jx_j+b_5\epsilon\right)^2+(c_2x_2+c_5\epsilon)^2+(d_3x_3+d_5\epsilon)^2+(e_4x_4+e_5\epsilon)^2+(f_5\epsilon)^2+\mathcal{O}(3)}. \end{aligned} \tag{1.23}$$

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 state and prove our main result for Type 3 Avoided Crossings, Theorem 3.1. In Section 4 we state our main results, Theorems 4.1, 4.2, and 4.3, for Type 4, 5, and 6 Avoided Crossings, respectively.

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1.1 Convenient Changes of Variables

We begin with Type 3 Avoided Crossings. It is convenient to remove the ϵ-dependence in the leading order of $\beta(x,\epsilon)$ and $\gamma(x,\epsilon)$ in (1.11), so we introduce new variables that are implicitly defined by the relations

$$\begin{aligned} b_1x_1' \,+\, b_2x_2' &= b_1x_1 \,+\, b_2x_2 \,+\, b_3\epsilon \qquad\qquad \text{and} && (1.24)\\ c_2x_2' &= c_2x_2 \,+\, c_3\epsilon. && (1.25)\end{aligned}$$

Explicitly, this change of variables is given by

$$\begin{aligned} x_1' &= x_1 \,+\, \frac{\epsilon}{b_1}\left(b_3 - \frac{b_2c_3}{c_2}\right), && (1.26)\\ x_2' &= x_2 \,+\, \frac{c_3\epsilon}{c_2}, && (1.27)\\ x_j' &= x_j \qquad (j>2). && (1.28)\end{aligned}$$

When we change variables, the Schrödinger equation

$$i\epsilon^2\frac{\partial}{\partial t}\psi(x,t) = -\frac{\epsilon^4}{2}\Delta\psi(x,t) + h(x,\epsilon)\psi(x,t) \tag{1.29}$$

for $\psi(x,t)$ becomes

$$i\epsilon^2\frac{\partial}{\partial t}\phi(x',t) = -\frac{\epsilon^4}{2}\Delta\phi(x',t) + h(x(x',\epsilon),\epsilon)\phi(x',t), \tag{1.30}$$

for

$$\phi(x',t) = \psi(x(x',\epsilon),t), \tag{1.31}$$

with

$$h_{||}(x(x',\epsilon),\epsilon) = \begin{pmatrix} b_1x_1'+b_2x_2' & c_2x_2'+id_3\epsilon \\ c_2x_2'-id_3\epsilon & -b_1x_1'-b_2x_2'\end{pmatrix} \,+\, \widetilde{V}(x(x',\epsilon),\epsilon)I\!I \,+\, \mathcal{O}(2), \tag{1.32}$$

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

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1 + b_2x_2 + \mathcal{O}(2) && (1.33)\\ \gamma(x,\epsilon) &= c_2x_2 + \mathcal{O}(2) \\ \delta(x,\epsilon) &= d_3\epsilon + \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0). \end{aligned}$$

In the new variables, the two relevant energy levels are

$$\begin{aligned} E_{\substack{A\\B}} &= \widetilde{V}(x,\epsilon) \,\pm\, \sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2} \\ &= \widetilde{V}(x,\epsilon) \,\pm\, \sqrt{(b_1x_1+b_2x_2)^2+(c_2x_2)^2+(d_3\epsilon)^2 \,+\, \mathcal{O}(3)}. && (1.34)\end{aligned}$$

For Type 4 Avoided Crossings, we make the same change of variables, which leads to the matrix (1.15) for h_1 with leading behavior for β, γ, δ, and $\widetilde{V}$ given by (1.33). In the new variables, the two relevant energy levels are

$$\begin{aligned} E_{\mathcal{A} \atop \mathcal{B}} &= \widetilde{V}(x,\epsilon) \pm \sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2} \\ &= \widetilde{V}(x,\epsilon) \pm \sqrt{(b_1x_1+b_2x_2)^2+(c_2x_2)^2+(d_3\epsilon)^2 + \mathcal{O}(3)}. \end{aligned} \tag{1.35}$$

For Type 5 Avoided Crossings, we make the change of variables defined implicitly by the following:

$$\begin{aligned} b_1x_1' + b_2x_2' + b_3x_3' &= b_1x_1 + b_2x_2 + b_3x_3 + b_4\epsilon \\ c_2x_2' &= c_2x_2 + c_4\epsilon \\ d_3x_3' &= d_3x_3 + d_4\epsilon. \end{aligned} \tag{1.36}$$

This change of variables leads to the Schrödinger equation (1.30) with h_1 represented by (1.19) with the following local behavior around $x=0$ and $\epsilon=0$:

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1+b_2x_2+b_3x_3+\mathcal{O}(2) \qquad (1.37)\\ \gamma(x,\epsilon) &= c_2x_2+\mathcal{O}(2) \\ \delta(x,\epsilon) &= d_3x_3+\mathcal{O}(2) \\ \zeta(x,\epsilon) &= e_4\epsilon+\mathcal{O}(2) \\ \xi(x,\epsilon) &= \mathcal{O}(2) \\ \widetilde{V}(x,\epsilon) &= \mathcal{O}(0). \end{aligned}$$

In the new variables, the two relevant energy levels are

$$\begin{aligned} & E_{\mathcal{A} \atop \mathcal{B}} \\ &= \widetilde{V}(x,\epsilon) \pm \sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2+\zeta(x,\epsilon)^2+\xi(x,\epsilon)^2} \\ &= \widetilde{V}(x,\epsilon) \pm \sqrt{(b_1x_1+b_2x_2+b_3x_3)^2+(c_2x_2)^2+(d_3x_3)^2+(e_4\epsilon)^2 + \mathcal{O}(3)}. \end{aligned} \tag{1.38}$$

For Type 6 Avoided Crossings, we make the change of variables defined implicitly by the following:

$$\begin{aligned} b_1x_1' + b_2x_2' + b_3x_3' + b_4x_4' &= b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_5\epsilon \\ c_2x_2' &= c_2x_2 + c_5\epsilon \\ d_3x_3' &= d_3x_3 + d_5\epsilon \\ e_4x_4' &= e_4x_4 + e_5\epsilon. \end{aligned} \tag{1.39}$$

This change of variables leads to the Schrödinger equation (1.30) with h_1 represented by (1.22) with the following local behavior around $x=0$ and $\epsilon=0$:

$$\begin{aligned} \beta(x,\epsilon) &= b_1x_1+b_2x_2+b_3x_3+b_4x_4+\mathcal{O}(2) \qquad (1.40)\\ \gamma(x,\epsilon) &= c_2x_2+\mathcal{O}(2) \end{aligned}$$

$$\begin{aligned}
\delta(x,\epsilon) &= d_3 x_3 + \mathcal{O}(2)\\
\zeta(x,\epsilon) &= e_4 x_4 + \mathcal{O}(2)\\
\xi(x,\epsilon) &= f_5 \epsilon + \mathcal{O}(2)\\
\widetilde{V}(x,\epsilon) &= \mathcal{O}(0).
\end{aligned}$$

In the new variables, the two relevant energy levels are

$$\begin{aligned}
&E_{\genfrac{}{}{0pt}{}{\mathcal{A}}{\mathcal{B}}}\\
&= \widetilde{V}(x,\epsilon) \pm \sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2+\zeta(x,\epsilon)^2+\xi(x,\epsilon)^2}\\
&= \widetilde{V}(x,\epsilon) \pm \sqrt{\left(\sum_{j=1}^{4} b_j x_j\right)^2 + (c_2x_2)^2+(d_3x_3)^2+(e_4x_4)^2+(f_5\epsilon)^2 + \mathcal{O}(3)}. \qquad (1.41)
\end{aligned}$$

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 the later sections to prove our main results.

The small $|t|$ and ϵ behavior of these quatities is not simple, due to the presence of two natural time scales. When $|t|$ is smaller than $\epsilon^{2/3}$, an "inner" perturbation expansion is valid, in which the natural time variable is $s=t/\epsilon$. This expansion is matched to "outer" expansions that are valid for t greater than ϵ. The natural time variable for these expansions is t.

We present the detailed analysis for Type 3 Avoided Crossings. At the end of this section we describe what modifications need to be made to handle the other types of avoided crossings.

We define

$$V^{\genfrac{}{}{0pt}{}{\mathcal{A}}{\mathcal{B}}}(x,\epsilon) = \widetilde{V}(x,\epsilon) \pm \sqrt{\beta^2(x,\epsilon)+\gamma^2(x,\epsilon)+\delta^2(x,\epsilon)} \qquad (2.1)$$

where $x \in I\!R^n$, $\epsilon > 0$, and β, γ, and δ satisfy (1.33). Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions of the classical equations of motion

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

with initial conditions

$$\begin{aligned}
a^{\mathcal{C}}(0) &= 0 &(2.3)\\
\eta^{\mathcal{C}}(0) &= \eta^0(\epsilon), &(2.4)
\end{aligned}$$

where $\eta^0(\epsilon) = \eta^0 + \mathcal{O}(\epsilon)$, η^0 has the form described by (1.9), and the $\mathcal{O}(\epsilon)$ term depends on whether $\mathcal{C}$ is $\mathcal{A}$ or $\mathcal{B}$.

It follows from (1.33) that $|\beta(x,\epsilon)|$, $|\gamma(x,\epsilon)|$ and $|\delta(x,\epsilon)|$ are $\mathcal{O}(0)$, so using estimates of the type $\beta/\sqrt{\beta^2+\gamma^2+\delta^2} \leq 1$, we see that

$$\|\nabla V^{\mathcal{C}}(x,\epsilon)\| = \mathcal{O}(0). \tag{2.5}$$

This implies the existence and uniqueness of the solutions to (2.2) for small times.

2.1 Small t Asymptotics

We wish to compute the asymptotics of the solution of (2.2), (2.3) when both t and ϵ tend to zero. We first 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 sufficiently small, 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 use the contraction mapping principle argument used to prove Lemma 2.1 of [20]. The argument goes through without change except that equation (2.15) of [20] must be replaced by

$$\begin{aligned} & \beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)|_{x=\zeta(s,\epsilon)} \\ = \quad & (b_1\zeta_1(s,\epsilon) + b_2\zeta_2(s,\epsilon))^2 + (c_2\zeta_2(s,\epsilon))^2 + (d_3\epsilon)^2 + \mathcal{O}(3). \end{aligned} \tag{2.6}$$

Because η^0 has the form (1.9), $|\zeta_1(s,\epsilon)| > c|s|$, and $\zeta_2(s,\epsilon) = \mathcal{O}(s^2)$. It follows that

$$\beta^2(x,\epsilon) + \gamma^2(x,\epsilon) + \delta^2(x,\epsilon)|_{x=\zeta(s,\epsilon)} \geq cs^2, \tag{2.7}$$

for sufficiently small s. This estimate replaces estimate (2.16) of [20], and the rest of the proof follows exactly as in [20]. □

We also have the following result, which is standard because $\widetilde{V}(x,\epsilon)$ is a regular function:

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 the Inner Solution

We now compute the asymptotics of the classical motion in the inner temporal region, in which t is small compared with $\epsilon^{2/3}$. In this regime we use the rescaled quantities s and $z^{\mathcal{C}}(s)$ that are defined by

$$t = \epsilon s, \tag{2.8}$$

$$a^{\mathcal{C}}(t) = \epsilon z^{\mathcal{C}}(s). \tag{2.9}$$

In order to do the matching to outer solutions, we study the asymptotic behavior of the inner solution in the limits

$$\begin{cases} \epsilon \to 0, \\ \epsilon s^3 \to 0, \\ |s| \to \infty. \end{cases} \tag{2.10}$$

In terms of the new variables, equations (2.2) and (2.3) are

$$\begin{aligned} &\frac{d^2}{ds^2} z^{\mathcal{C}}(s) = -\epsilon \nabla V^{\mathcal{C}}(\epsilon z^{\mathcal{C}}(s), \epsilon), \\ &\frac{d}{ds} z^{\mathcal{C}}(0) = \eta^0(\epsilon), \\ &z^{\mathcal{C}}(0) = 0. \end{aligned} \tag{2.11}$$

To simplify notation, we define

$$b = \begin{pmatrix} b_1 \\ b_2 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \qquad c = \begin{pmatrix} 0 \\ c_2 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \qquad \text{and} \qquad \rho(\epsilon) = \frac{b_1\, \eta_1^0(\epsilon)}{|d_3|} > 0. \tag{2.12}$$

Proposition 2.1 *Let $z^{\mathcal{C}}(s)$ be the solution of (2.11). We have the following asymptotic behaviors as $\epsilon \to 0$, $s \to \pm\infty$ and $\epsilon s^3 \to 0$:*

$$z^{\mathcal{C}}(s) = z_0^{\mathcal{C}}(s) + \epsilon z_1^{\mathcal{C}}(s) + \mathcal{O}(\epsilon^2 s^3), \tag{2.13}$$

$$\frac{d}{ds} z^{\mathcal{C}}(s) = \frac{d}{ds} z_0^{\mathcal{C}}(s) + \epsilon \frac{d}{ds} z_1^{\mathcal{C}}(s) + \mathcal{O}(\epsilon^2 s^2), \tag{2.14}$$

where

$$\begin{aligned} z_0^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = \quad & \eta^0(\epsilon) s, \\ z_1^{\substack{\mathcal{A}\\ \mathcal{B}}}(s) = \quad & -\nabla \widetilde{V}(0,\epsilon) \frac{s^2}{2} \pm \left[\frac{s}{\rho(\epsilon)} - \frac{s}{2\rho(\epsilon)} \sqrt{(\rho(\epsilon)s)^2 + 1} \right. \\ & \left. + \frac{1}{2\rho(\epsilon)^2} \ln\left(\rho(\epsilon)s + \sqrt{(\rho(\epsilon)s)^2 + 1} \right) \right] b. \end{aligned} \tag{2.15}$$

Proof:
We first do formal perturbation calculations and then prove the appropriate estimates. We begin by expanding the potential $V^{\mathcal{C}}(\epsilon z^{\mathcal{C}}(s),\epsilon)$ around the origin in $I\!R^{n+1}$ and inserting an *a priori* expansion of the type

$$z^{\mathcal{C}}(s) = z_0^{\mathcal{C}}(s) + \epsilon z_1^{\mathcal{C}}(s) + \epsilon^2 z_2^{\mathcal{C}}(s) + \cdots \tag{2.16}$$

in (2.11). We formally solve the resulting equation order by order in ϵ. To avoid conflicts in notation, we denote the j^{th} component of $z^{\mathcal{C}}(s)$ by $w_j^{\mathcal{C}}(s)$.

From (1.9), (2.3), and lemma 2.1, we know that

$$z^{\mathcal{C}}(s) = \begin{pmatrix} \eta_1^0(\epsilon) \\ 0 \\ \eta_3^0(\epsilon) \\ \vdots \\ \eta_n^0(\epsilon) \end{pmatrix} s \;+\; \mathcal{O}(\epsilon s^2). \tag{2.17}$$

By explicit calculation, we see that

$$\begin{aligned} -\nabla V^{\mathcal{A}}_{\mathcal{B}}(\epsilon z^{\mathcal{A}}_{\mathcal{B}}(s),\epsilon) = & -\; \nabla\widetilde{V}(0,0) + \mathcal{O}(1) \\ & \mp \left[\begin{pmatrix} b_1^2 \epsilon w_1^{\mathcal{A}}_{\mathcal{B}}(s) \\ b_1 b_2 \epsilon w_1^{\mathcal{A}}_{\mathcal{B}}(s) \\ 0 \\ \vdots \\ 0 \end{pmatrix} + \mathcal{O}(2) \right] \frac{1}{\sqrt{b_1^2(\epsilon w_1^{\mathcal{A}}_{\mathcal{B}}(s))^2 + d_3^2\epsilon^2 + \mathcal{O}(3)}} \\ = & -\; \nabla\widetilde{V}(0,0) + \mathcal{O}(1) \\ & \mp \left[\, b \;+\; \mathcal{O}(1) \,\right] \frac{\eta_1^0(\epsilon) s}{\sqrt{(\eta_1^0(\epsilon)s)^2 + (d_3/b_1)^2 + \mathcal{O}(\epsilon s^3)}}. \end{aligned} \tag{2.18}$$

Here $\mathcal{O}(n)$ is to be understood with ϵz in place of x.

We substitute (2.16) and (2.18) into equation (2.11) and formally equate like orders in ϵ on the two sides of the resulting equation. We learn nothing new at zeroth order. At first order we have

$$\frac{d^2}{ds^2}\, z_1^{\mathcal{C}}(s) \;=\; -\nabla\widetilde{V}(0,0) \;\mp\; \frac{\eta_1^0(\epsilon)\, s}{\sqrt{(\eta_1^0(\epsilon)s)^2 + (d_3/b_1)^2}}\, b. \tag{2.19}$$

Integrating and using $\frac{d}{ds} z_1^{\mathcal{C}}(0) = 0$, we obtain

$$\frac{d}{ds}\, z_1^{\mathcal{C}}(s) \;=\; -\nabla\widetilde{V}(0,0)\, s \;\mp\; \left[\frac{1}{\eta_1^0(\epsilon)} \sqrt{(\eta_1^0(\epsilon)s)^2 + (d_3/b_1)^2} \;-\; \frac{|d_3|}{\eta_1^0(\epsilon) b_1} \right] b. \tag{2.20}$$

We integrate again ([6], p. 82) and use $z_1^{\mathcal{C}} = 0$ to obtain

$$\begin{aligned} z_1^{\mathcal{C}}(s) \;=\; & -\nabla\widetilde{V}(0,0)\,\frac{s^2}{2} \pm \frac{s}{\rho(\epsilon)}\, b \\ & \mp \left[\frac{s}{2\rho(\epsilon)} \sqrt{\rho(\epsilon)^2 s^2 + 1} \;+\; \frac{1}{2\rho(\epsilon)^2} \ln\left(\sqrt{\rho(\epsilon)^2 s^2 + 1} + \rho(\epsilon) s \right) \right] b. \end{aligned} \tag{2.21}$$

Hence, formally,

$$\begin{aligned}
z^{\mathcal{C}}(s) &= \eta_1^0(\epsilon)s \\
&+\epsilon\left(-\nabla\widetilde{V}(0,0)\frac{s^2}{2}\pm b\frac{s}{\rho(\epsilon)}\right) &(2.22)\\
&\mp\epsilon\left(\left[\frac{s}{2\rho(\epsilon)}\sqrt{\rho(\epsilon)^2s^2+1}+\frac{1}{2\rho(\epsilon)^2}\ln\left(\sqrt{\rho(\epsilon)^2s^2+1}+\rho(\epsilon)s\right)\right]b\right)\\
&+\mathcal{O}(\epsilon^2). &(2.23)
\end{aligned}$$

To prove the estimates (2.13) and (2.14), we now simply mimic the end of the proof of Proposition 2.1 of [20]. □

Corollary 2.1 *By further expanding (2.15), we see that in the same time regime, (2.13) implies*

$$\begin{aligned}
z^{\mathcal{A}}_{\mathcal{B}}(s) = \quad & \eta^0(\epsilon)s-\nabla\widetilde{V}(0,\epsilon)\epsilon\frac{s^2}{2}\pm\frac{\epsilon s}{\rho(\epsilon)}b\\
&\mp\mathrm{sign}(s)\left[\frac{\epsilon s^2}{2}+\frac{\epsilon\ln|s|}{2\rho(\epsilon)^2}+\frac{\epsilon}{4\rho(\epsilon)^2}+\frac{\epsilon\ln(2\rho(\epsilon))}{2\rho(\epsilon)^2}\right]b\\
&+\mathcal{O}(\epsilon/s^2)+\mathcal{O}(\epsilon^2s^3). &(2.24)
\end{aligned}$$

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

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

$$s \le \epsilon^{-\xi}, \text{ with } 0<\xi<1/3. \tag{2.25}$$

2.3 Asymptotics for Outer Solution

The outer solutions are valid approximations when $|t|$ is large compared with ϵ. Because we must match the inner solution, we study the asymptotics of these solutions in the limits

$$\begin{cases} \epsilon\to 0,\\ t\to 0,\\ |t|/\epsilon\to\infty. \end{cases} \tag{2.26}$$

To obtain the outer solutions of (2.2) and (2.3), we assume an expansion of the form

$$a^{\mathcal{C}}(t)=a_0^{\mathcal{C}}(t)+g_1(\epsilon)a_1^{\mathcal{C}}(t)+g_2(\epsilon)a_2^{\mathcal{C}}(t)+\cdots \tag{2.27}$$

and substitute it into the equation. For small $|t|$ asymptotics, 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 $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solutions of (2.2) and (2.3), subject to the initial conditions $a^{\mathcal{C}}(0)=0$ and $\eta^{\mathcal{C}}(0)=\eta^0(\epsilon)$. In the regime $\epsilon\to 0$, $t\to 0$, $|t|/\epsilon\to\infty$ and $t^3/\epsilon^2\to 0$ the outer solutions have asymptotics*

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

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

Proof:
This proposition is proved by mimicking the proof of Proposition 2.2 of [20]. □

2.4 Classical Action Integrals

We now determine the asymptotics in the outer regime of classical action integrals which determine phases when we construct quantum mechanical wave functions for the nuclei. Let

$$S^{\mathcal{C}}(t) \;=\; \int_0^t\left(\frac{\eta^{\mathcal{C}}(t')^2}{2}-V^{\mathcal{C}}(a^{\mathcal{C}}(t'),\epsilon)\right)\,dt' \tag{2.28}$$

$$\;=\; {\eta^0}^2(\epsilon)\frac{t}{2}\;-\;V^{\mathcal{C}}(a^{\mathcal{C}}(0),\epsilon)t\;+\;\int_0^t\eta^{\mathcal{C}}(t')^2\,dt', \tag{2.29}$$

and let

$$S(t) \;=\; \int_0^t\left(\frac{\eta(t')^2}{2}-\widetilde{V}(a(t'),\epsilon)\right)\,dt' \tag{2.30}$$

$$\;=\; \int_0^t\eta(t')^2dt'-{\eta^0}^2(\epsilon)\frac{t}{2}-\widetilde{V}(a(0),\epsilon)t, \tag{2.31}$$

From lemma 2.2 we easily deduce

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

$$S(t)={\eta^0}^2(\epsilon)\frac{t}{2}-\widetilde{V}(0,\epsilon)t-\eta^0(\epsilon)\nabla\widetilde{V}(0,\epsilon)t^2+\mathcal{O}(t^3), \tag{2.32}$$

uniformly in ϵ.

From proposition 2.2, and the formula

$$V^{\mathcal{A}}_{\mathcal{B}}(0,\epsilon)=\widetilde{V}(0,\epsilon)\;\pm\;d_3\epsilon\;+\;\mathcal{O}(\epsilon^2), \tag{2.33}$$

we obtain

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*

$$\begin{aligned} S^{\mathcal{A}}_{\mathcal{B}}(t) = \quad & S_0^{\mathcal{A}\atop\mathcal{B}}(\epsilon,\mathrm{sign}(t))-\widetilde{V}(0,\epsilon)t+{\eta^0}^2(\epsilon)\frac{t}{2}-\eta^0(\epsilon)\nabla\widetilde{V}(0,\epsilon)t^2\pm\epsilon|d_3|t \\ & \mp\mathrm{sign}(t)\left(\eta_1^0(\epsilon)b_1t^2+\frac{d_3^2\epsilon^2}{\eta_1^0(\epsilon)b_1}\ln|t|\right)+\mathcal{O}(t^3)+\mathcal{O}(\epsilon^4/t^2)+\mathcal{O}(\epsilon^3\ln|t|). \end{aligned}$$

2.5 Different Initial Momenta

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

$$\begin{aligned} a(0) &= 0 \\ \eta(0) &= \eta^0 \end{aligned} \tag{2.34}$$

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

$$\begin{aligned} a^{\mathcal{C}}(0) &= 0 \\ \eta^{\mathcal{C}}(0) &= \eta^0(\epsilon) = \eta^0 + \mathcal{O}(\epsilon). \end{aligned} \tag{2.35}$$

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*

$$\begin{aligned} & \eta^{\substack{\mathcal{A}\\\mathcal{B}}}(t)(a(t) - a^{\substack{\mathcal{A}\\\mathcal{B}}}(t)) \\ = \; & \mp|d_3|\epsilon t - (\eta^0(\epsilon) - \eta^0)\eta^0(\epsilon)t \\ & \pm\mathrm{sign}(t)\left[\frac{b_1\eta_1^0(\epsilon)}{2}t^2 + \frac{\epsilon^2 d_3^2}{2b_1\eta_1^0(\epsilon)}\left(\ln\left(\frac{2b_1\eta_1^0(\epsilon)|t|}{|d_3|\epsilon}\right) + \frac{1}{2}\right)\right] \\ & +\mathcal{O}(t^3) + \mathcal{O}(\epsilon^4/t^2) + \mathcal{O}(t\epsilon^2\ln\epsilon) \end{aligned}$$

and

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

$$\begin{aligned} S^{\substack{\mathcal{A}\\\mathcal{B}}}(t) &= S_0^{\substack{\mathcal{A}\\\mathcal{B}}}(\epsilon, \mathrm{sign}(t)) + S(t) + ({\eta^0}^2(\epsilon) - {\eta^0}^2)\frac{t}{2} \pm \epsilon|d_3|t \\ & \mp\mathrm{sign}(t)\left(\eta_1^0(\epsilon)b_1t^2 + \frac{d_3^2\epsilon^2}{\eta_1^0(\epsilon)b_1}\ln|t|\right) \\ & +\mathcal{O}(t^3) + \mathcal{O}(\epsilon^4/t^2) + \mathcal{O}(\epsilon^3\ln|t|). \end{aligned}$$

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

The semiclassical wave packets for the nuclei depend on 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

$$\begin{aligned} \frac{d}{dt}A^{\mathcal{C}}(t) &= iB^{\mathcal{C}}(t) \\ \frac{d}{dt}B^{\mathcal{C}}(t) &= iV^{(2)}(a^{\mathcal{C}}(t),\epsilon)A^{\mathcal{C}}(t), \end{aligned} \tag{2.36}$$

with the initial conditions

$$A^{\mathcal{C}}(0) = A_0, \qquad B^{\mathcal{C}}(0) = B_0, \tag{2.37}$$

where $a^{\mathcal{C}}(t)$ is the solution of (2.2) and (2.3). Let us determine the leading order behavior of $V^{(2)}(a^{\mathcal{C}}(t),\epsilon)$. By explicit computation we get, (omitting the arguments (x,ϵ))

$$\begin{aligned} V^{(2)} = \quad & \widetilde{V}^{(2)} \pm \left(|\nabla\beta\rangle\langle\nabla\beta| + |\nabla\gamma\rangle\langle\nabla\gamma| + |\nabla\delta\rangle\langle\nabla\delta|\right)(\beta^2+\gamma^2+\delta^2)^{-1/2} \\ & +(\beta\beta^{(2)}+\gamma\gamma^{(2)}+\delta\delta^{(2)})(\beta^2+\gamma^2+\delta^2)^{-1/2} \\ & -|\beta\nabla\beta+\gamma\nabla\gamma+\delta\nabla\delta\rangle\langle\beta\nabla\beta+\gamma\nabla\gamma+\delta\nabla\delta|(\beta^2+\gamma^2+\delta^2)^{-3/2}. \end{aligned} \tag{2.38}$$

Thus, from (1.33) and some simple estimates, we see that

$$\begin{aligned} V^{(2)} \;=\; & \widetilde{V}^{(2)} \\ \pm\, & \frac{(\gamma^2+\delta^2)|\nabla\beta\rangle\langle\nabla\beta| + (\beta^2+\delta^2)|\nabla\gamma\rangle\langle\nabla\gamma| - \beta\gamma\left(|\nabla\beta\rangle\langle\nabla\gamma| + |\nabla\gamma\rangle\langle\nabla\beta| + \mathcal{O}(3)\right)}{(\beta^2+\gamma^2+\delta^2)^{3/2}}. \end{aligned} \tag{2.39}$$

Explicitly, this has the form

$$\begin{aligned} V^{(2)} &= \widetilde{V}^{(2)} \\ &\pm \frac{1}{(\beta^2+\gamma^2+\delta^2)^{3/2}}\left[\mathcal{O}(3) \;+\; (\gamma^2+\delta^2)\begin{pmatrix} b_1^2 & b_1b_2 & 0 & \dots & 0 \\ b_1b_2 & b_2^2 & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix}\right. \\ &\left. \qquad + (\beta^2+\delta^2)\begin{pmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & c_2^2 & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix} \;-\; \beta\gamma\begin{pmatrix} 0 & b_1c_2 & 0 & \dots & 0 \\ b_1c_2 & 2b_1c_2 & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix}\right]. \end{aligned} \tag{2.40}$$

Using this expression, we obtain the following result for the solutions to (2.36) and (2.37):

Proposition 2.3 *Let $A^{\mathcal{C}}(t)$ and $B^{\mathcal{C}}(t)$ be the solutions of (2.36) and (2.37). In the regime $\epsilon \to 0$, $|t| \to 0$, $\epsilon/|t| \to 0$, and $|t \ln^2 \epsilon| \to 0$, we have the following asymptotics:*

$$A^{\mathcal{A}}_{\mathcal{B}}(t) \;=\; A_0 \;+\; \mathcal{O}\left(|t|\,|\ln\epsilon|\right), \tag{2.41}$$

$$B^{\mathcal{A}}_{\mathcal{B}}(t) \;=\; B_0 \pm \frac{i\,\mathrm{sign}(t)}{\rho(\epsilon)}\left[MA_0 \;+\; \ln\left(\frac{2\rho(\epsilon)|t|}{\epsilon}\right)NA_0\right] \;+\; \mathcal{O}\left(|t|\,\ln^2\epsilon \;+\; \frac{\epsilon^2}{t^2}\right), \tag{2.42}$$

where

$$M \;=\; \frac{1}{|d_3|}|b\rangle\langle b| \;=\; \begin{pmatrix} b_1^2/|d_3| & b_1b_2/|d_3| & 0 & \dots & 0 \\ b_1b_2/|d_3| & b_2^2/|d_3| & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix} \tag{2.43}$$

and

$$N \;=\; \frac{1}{|d_3|}|c\rangle\langle c| \;=\; \begin{pmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & c_2^2/|d_3| & 0 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix}. \tag{2.44}$$

Proof:
To study solutions to (2.36) and (2.37) we first consider various quantities that occur in (2.40) with x replaced by $a^{\mathcal{C}}(t) = \eta^0(\epsilon)t + \mathcal{O}(t^2)$. By tedious, but straightforward calculations, we obtain the following estimates

$$\begin{aligned} \frac{\beta^2+\delta^2}{(\beta^2+\gamma^2+\delta^2)^{3/2}} &= \frac{1}{|d_3|\,\sqrt{\rho(\epsilon)^2t^2+\epsilon^2}} + \mathcal{O}\left((t^2+\epsilon^2)^0\right) \\ \frac{\gamma^2+\delta^2}{(\beta^2+\gamma^2+\delta^2)^{3/2}} &= \frac{\epsilon^2}{|d_3|\,(\rho(\epsilon)^2t^2+\epsilon^2)^{3/2}} + \mathcal{O}\left((t^2+\epsilon^2)^0\right) \\ \frac{\beta\,\gamma}{(\beta^2+\gamma^2+\delta^2)^{3/2}} &= \mathcal{O}\left((t^2+\epsilon^2)^0\right). \end{aligned}$$

From these estimates, it follows that for small t and ϵ,

$$V^{(2)}(a^{\substack{\mathcal{A}\\ \mathcal{B}}}(t),\epsilon) \;=\; \pm\left(\frac{\epsilon^2}{(\rho(\epsilon)^2t^2+\epsilon^2)^{3/2}}\,M \;+\; \frac{1}{(\rho(\epsilon)^2t^2+\epsilon^2)^{1/2}}\,N\right) + \mathcal{O}\left((t^2+\epsilon^2)^0\right). \tag{2.45}$$

We can solve (2.36) and (2.37) if and only if we can solve

$$A^{\mathcal{C}}(t,\epsilon) = A_0 + itB_0 - \int_0^t\int_0^s V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\,A^{\mathcal{C}}(r,\epsilon)\,dr. \tag{2.46}$$

For each fixed positive ϵ, this equation can be solved by iteration for small $|t|$.

For $T>0$, we define a norm on bounded operator valued functions of t and ϵ by

$$|||\,D(\cdot,\cdot)\,||| \;=\; \sup_{\{\epsilon\le T,\,|t\,\ln\,t|\le T,\,|t\,\ln\,\epsilon|\le T\}} \|\,D(t,\epsilon)\,\|.$$

From (2.46), we see that for positive ϵ,

$$\begin{aligned} \|A^{\mathcal{C}}(t,\epsilon)-A_0\| &= \left\| itB_0 - \int_0^t ds\int_0^s V^{(2)}(a^{\mathcal{C}}(r,\epsilon))A^{\mathcal{C}}(r,\epsilon)\,dr\right\| \\ &\le |t|\,\|B_0\| + \left|\int_0^t ds\int_0^s \|V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\|\,|||A^{\mathcal{C}}(\cdot,\cdot)-A_0|||\,dr\right| \\ &\qquad + \left|\int_0^t ds\int_0^s \|V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\|\,\|A_0\|\,dr\right| \\ &\le |t|\,\|B_0\| \\ &\quad + \left|\int_0^t ds\int_0^s \|V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\|\,dr\right|\left(|||A^{\mathcal{C}}(\cdot,\cdot)-A_0|||+\|A_0\|\right). \end{aligned} \tag{2.47}$$

From (2.45) and explicit calculation, we see that for positive ϵ,

$$\begin{aligned}
&\left| \int_0^s \|V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\| \, dr \right| \\
\leq\ & C_1|s| + C_2 \int_0^{|s|} \frac{\epsilon^2\, dr}{(\rho(\epsilon)^2 r^2 + \epsilon^2)^{3/2}} + C_3 \int_0^{|s|} \frac{dr}{\sqrt{\rho(\epsilon)^2 r^2 + \epsilon^2}} \qquad (2.48)\\
=\ & C_1|s| + C_2 \frac{|s|}{\sqrt{\rho(\epsilon)^2 s^2 + \epsilon^2}} + C_3 \frac{1}{\rho(\epsilon)} \ln \left(\frac{\rho(\epsilon)|s|}{\epsilon} + \sqrt{\frac{\rho(\epsilon)^2 s^2}{\epsilon^2} + 1} \right).
\end{aligned}$$

By explicit integration, we see from this estimate that

$$\begin{aligned}
&\left| \int_0^t ds \int_0^s \|V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\| \, dr \right| \\
\leq\ & C_4 t^2 + C_5 \frac{\sqrt{\rho(\epsilon)^2 t^2 + \epsilon^2} - \epsilon}{\rho(\epsilon)^2} \qquad (2.49)\\
& + C_6 \frac{1}{\rho(\epsilon)^2} \left| \epsilon - \sqrt{\rho(\epsilon)^2 t^2 + \epsilon^2} + \rho(\epsilon)|t| \left(\ln \left(\rho(\epsilon)|t| + \sqrt{\rho(\epsilon)^2 t^2 + \epsilon^2} \right) - \ln \epsilon \right) \right|.
\end{aligned}$$

For sufficiently small T, $|\, t \ln t \,| \leq T$, $|\, t \ln \epsilon \,| \leq T$, and $\epsilon \leq T$, this quantity is bounded by

$$\begin{aligned}
&\left| \int_0^t ds \int_0^s \|V^{(2)}(a^{\mathcal{C}}(r,\epsilon))\| \, dr \right| \\
\leq\ & C_7\,|t| + C_8\,|t \ln |t|\,| + C_9\,|t \ln \epsilon\,| \qquad (2.50)\\
\leq\ & \mathcal{O}(\,T\,).
\end{aligned}$$

It now follows from (2.47) that for sufficiently small T, $|||A^{\mathcal{C}}(\cdot,\cdot) - A_0|||$ is bounded. This, (2.47), and (2.50) imply conclusion (2.41) of the proposition.

To prove (2.42), we use

$$\begin{aligned}
B^{\mathcal{C}}(t) &= B_0 + i \int_0^t V^{(2)}(a^{\mathcal{C}}(s,\epsilon))\, A^{\mathcal{C}}(s)\, ds \qquad (2.51)\\
&= B_0 + i \int_0^t V^{(2)}(a^{\mathcal{C}}(s,\epsilon))\, A_0\, ds + i \int_0^t V^{(2)}(a^{\mathcal{C}}(s,\epsilon))\, (A^{\mathcal{C}}(s) - A_0)\, ds
\end{aligned}$$

From (2.45) and explicit integration,

$$\begin{aligned}
&\int_0^t V^{(2)}(a^{\mathcal{C}}(s,\epsilon))\, A_0\, ds \qquad (2.52)\\
=\ & \mathrm{sign}(t) \left(\frac{|t|}{\sqrt{\rho(\epsilon)^2 t^2 + \epsilon^2}} M A_0 + \frac{1}{\rho(\epsilon)} \ln \left(\frac{\rho(\epsilon) t}{\epsilon} + \sqrt{\frac{\rho(\epsilon)^2 t^2}{\epsilon^2} + 1} \right) N A_0 \right) + \mathcal{O}(|t|).
\end{aligned}$$

Furthermore, from (2.47), (2.48), and(2.50),

$$\begin{aligned}
&\left\| \int_0^t V^{(2)}(a^{\mathcal{C}}(s,\epsilon))\, (A^{\mathcal{C}}(s) - A_0)\, ds \right\| \qquad (2.53)\\
\leq\ & \int_0^t \|V^{(2)}(a^{\mathcal{C}}(s,\epsilon))\|\, \|A^{\mathcal{C}}(s) - A_0\|\, ds \qquad (2.54)\\
\leq\ & [\, C_1|t| + C_2 + \mathcal{O}(\ln |t| + \ln \epsilon) \,]\ [\, C_7|t| + \mathcal{O}(|t| \ln |t| + |t| \ln \epsilon) \,]. \qquad (2.55)
\end{aligned}$$

For t and ϵ in the regime covered by the proposition, this last quantity is $\mathcal{O}(\, t \ln^2 \epsilon \,)$.

Conclusion (2.42) is now an easy consequence of (2.51), (2.52), and (2.53). $\square$

2.7 Alterations for Other Types of Avoided Crossings

The analysis presented above is identical for Type 4 Avoided Crossings.

For Type 5 Avoided Crossings, one must make the following substitutions in the above results, but the techniques of proof remain the same.

$$b = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \rho(\epsilon) = \frac{b_1 \eta_1^0(\epsilon)}{|e_4|}, \quad M = \frac{1}{|e_4|}\,|b\rangle\langle b|, \quad \text{and} \quad N = \frac{1}{|e_4|}\,(\,|c\rangle\langle c| \,+\, |d\rangle\langle d|\,)\,.$$

Similarly, for Type 6 Avoided Crossings, one must make the following substitutions, but the techniques of proof remain the same.

$$b = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \ \rho(\epsilon) = \frac{b_1 \eta_1^0(\epsilon)}{|f_5|}, \ M = \frac{1}{|f_5|}\,|b\rangle\langle b|, \text{ and } N = \frac{1}{|f_5|}\,(\,|c\rangle\langle c| \,+\, |d\rangle\langle d| \,+\, |e\rangle\langle e|\,)\,.$$

3 Propagation through Type 3 Avoided Crossings

We now have all the ingredients 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 $\epsilon \to 0$. We first present the building blocks and give their main properties.

3.1 Semiclassical Nuclear Wave Packets

The semiclassical motion of the nuclei is described by wave packets which correspond to the classical phase space trajectory, and of width $\mathcal{O}(\epsilon)$. These are the same wave packets that are used in [8, 17, 20].

Let n denote the dimension of the nuclear configuration space. 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 $\mathbb{R}^n$ as a subset of $\mathbb{C}^n$, and let e_i denote the i^{th} standard basis vector in $\mathbb{R}^n$ or $\mathbb{C}^n$. The inner product on $\mathbb{R}^n$ or $\mathbb{C}^n$ is $\langle\, v,\, w\,\rangle = \sum_{j=1}^n \overline{v_j} w_j$.

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

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

and

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

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 $v_1,\, v_2,\, \dots,\, v_m$ be m arbitrary non–zero vectors in $\mathbb{C}^n$. Then

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

One can prove [8] that these functions do not depend on the ordering of the vectors $v_1,\, v_2,\, \dots,\, v_m$.

Let A be 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

$$\mathcal{H}_l(A;\, x) \;=\; \widetilde{\mathcal{H}}_{|l|}(\underbrace{U_A e_1, \dots, U_A e_1}_{l_1\ entries}, \underbrace{U_A e_2, \dots, U_A e_2}_{l_2\ entries}, \dots, \underbrace{U_A e_n, \dots, U_A e_n}_{l_n\ entries};\, x) \tag{3.4}$$

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:*

$$A \text{ and } B \text{ are invertible;} \tag{3.5}$$

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

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

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

Let $a \in \mathbb{R}^n$, $\eta \in \mathbb{R}^n$, 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.

We encourage the reader to consult Section 3.1 of [20] for several remarks concerning this definition. 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

$$i\hbar\,\frac{\partial\Psi}{\partial t} \;=\; -\,\frac{\hbar^2}{2}\,\Delta\,\Psi \;+\; V(x)\,\Psi \tag{3.9}$$

has an approximate solution of the form

$$e^{iS(t)/\hbar}\,\varphi_l(A(t),B(t),\hbar,a(t),\eta(t),x) \;+\; O(\hbar^{1/2}). \tag{3.10}$$

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

$$\frac{\partial a}{\partial t}(t) \;=\; \eta(t), \tag{3.11}$$

$$\frac{\partial \eta}{\partial t}(t) \;=\; -V^{(1)}(a(t)). \tag{3.12}$$

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

$$S(t) \;=\; \int_{-T}^{t}\left(\frac{(\eta(s))^2}{2}\;-\;V(a(s))\right)\,ds. \tag{3.13}$$

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

$$\frac{\partial A}{\partial t}(t) \;=\; iB(t), \tag{3.14}$$

$$\frac{\partial B}{\partial t}(t) \;=\; iV^{(2)}(a(t))\,A(t). \tag{3.15}$$

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 [8].

In order to control certain errors, we introduce a cutoff function that is supported near the classical path. Let F be a C^∞ cutoff function

$$F : I\!R^+ \mapsto I\!R, \tag{3.16}$$

such that

$$\begin{cases} F(r) = 1 & 0 \le r \le 1 \\ F(r) = 0 & r \ge 2 \end{cases} \tag{3.17}$$

The wave functions we construct below contain the following cutoff function as a factor:

$$F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'}) \tag{3.18}$$

where $0 < \delta'$ is chosen below, and $\mathcal{C} = \mathcal{A},\mathcal{B}$. Multiplication of our semiclassical wave packets by this function leads to exponentially small errors in ϵ.

3.2 Choice of Eigenvectors

In this section we construct the electronic eigenvectors and their phases on the support of the cutoff function $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$. Although the electronic hamiltonian is independent of time, it is convenient to choose specific time dependent electronic eigenvectors. The electrons follow the motion of the nuclei in an adiabatic way, so the suitable instantaneous electronic eigenvectors must satisfy a parallel transport condition to take into account geometric phases that arise. The 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, $|t| > \epsilon^{1-\xi}$ for suitable ξ, with $0 < \delta' < \xi < 1$. We have two sets of dynamic eigenvectors, denoted by $\Phi^{\pm}_{\mathcal{C}}(x, t, \epsilon)$, where the label $\pm$, refers to positive and negative times.

Let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ be the solution of the classical equations of motion (2.2) and (2.3). Our goal is to construct normalized eigenvectors $\Phi^{\pm}_{\mathcal{C}}(x, t, \epsilon)$ that solve

$$\langle \Phi^{\pm}_{\mathcal{C}}(x, t, \epsilon),\, \left(\partial/\partial t + \eta^{\mathcal{C}}(t)\cdot\nabla\right) \Phi^{\pm}_{\mathcal{C}}(x, t, \epsilon)\rangle \equiv 0 \tag{3.19}$$

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 non-zero time t, these vectors exist, are unique up to constant overall phase factors, and are eigenvectors of $h_1(x, \epsilon)$ associated with $E_{\mathcal{C}}(x, \epsilon)$ for any time, see [17].

We need asymptotic information about these eigenvectors, so we construct them explicitly. We define polar coordinates $(r,\, \theta,\, \phi)$ by the relations

$$\begin{aligned} \beta(x, \epsilon) &= r\,\cos\,\theta & (3.20)\\ \gamma(x, \epsilon) &= r \sin\,\theta\,\cos\,\phi & (3.21)\\ \delta(x, \epsilon) &= r\,\sin\,\theta\,\sin\,\phi. & (3.22) \end{aligned}$$

Then, in the basis $\{\,\psi_1(x, \epsilon),\, \psi_2(x, \epsilon)\}$, we construct the following static eigenvectors for $h_1(x,\, \epsilon)$:

$$\begin{aligned} \Phi^{-}_{\mathcal{A}} &= \begin{pmatrix} e^{i\phi}\,\cos\,\theta/2 \\ \sin\,\theta/2 \end{pmatrix} & (3.23)\\ \Phi^{-}_{\mathcal{B}} &= \begin{pmatrix} -\,\sin\,\theta/2 \\ e^{-i\phi}\,\cos\,\theta/2 \end{pmatrix} & (3.24) \end{aligned}$$

for $\pi/2 < \theta \leq \pi$, and

$$\begin{aligned} \Phi^{+}_{\mathcal{A}} &= \begin{pmatrix} \cos\,\theta/2 \\ e^{-i\phi}\,\sin\,\theta/2 \end{pmatrix} & (3.25)\\ \Phi^{+}_{\mathcal{B}} &= \begin{pmatrix} -e^{i\phi}\,\sin\,\theta/2 \\ \cos\,\theta/2 \end{pmatrix} & (3.26) \end{aligned}$$

for $0 \leq \theta \leq \pi/2$.

Lemma 3.1 *Suppose $0 < \delta' < \xi < 1$, and $|t| > \epsilon^{1-\xi}$. Define $\mu(\epsilon, t) = \max\{\,|t|,\, \epsilon^{1-\delta'}/|t|\,\}$, and let $a^{\mathcal{C}}(t)$ and $\eta^{\mathcal{C}}(t)$ solve equations (2.2) and (2.3). For x in the support of $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, $\mathcal{C} = \mathcal{A},\, \mathcal{B}$, we have for $t < 0$,*

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

and for $t > 0$,

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

Proof:
Let x belong to the support of $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$. Then $x = a^{\mathcal{C}}(t) + \omega$, where $\|\omega\| \leq 2\epsilon^{1-\delta'} \ll |t|$, so

$$\begin{aligned}
x_1 &= \eta^0_1 t + \mathcal{O}(t^2) + \mathcal{O}(\epsilon^{1-\delta'}),\\
x_2 &= \mathcal{O}(t^2) + \mathcal{O}(\epsilon^{1-\delta'}),\\
x_j &= \mathcal{O}(|t|) + \mathcal{O}(\epsilon^{1-\delta'}), \qquad \text{for } j \geq 3.
\end{aligned}$$

Thus,

$$\begin{aligned}
x_1 &= \eta^0_1 t + \mathcal{O}(|t|\mu(\epsilon,t)),\\
x_2 &= \mathcal{O}(|t|\mu(\epsilon,t)),\\
x_j &= \mathcal{O}(|t|), \qquad \text{for } j \geq 3.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\beta(x,\epsilon) &= b_1\eta^0_1 t + \mathcal{O}(|t|\mu(\epsilon,t)), && (3.27)\\
\gamma(x,\epsilon) &= \mathcal{O}(|t|\mu(\epsilon,t)), && (3.28)\\
\delta(x,\epsilon) &= d_3\epsilon + \mathcal{O}(|t|\mu(\epsilon,t)) = \mathcal{O}(|t|\mu(\epsilon,t)). && (3.29)
\end{aligned}$$

From these estimates, it follows that

$$\begin{aligned}
\frac{\beta(x,\epsilon)}{r} &= \frac{\text{sign}(t)}{\sqrt{1+\frac{\gamma^2+\delta^2}{\beta^2}}} = \text{sign}(t)\left(1 + \frac{\mathcal{O}\left((|t|\mu(\epsilon,t))^2\right)}{\mathcal{O}(t^2)}\right)^{-1/2} = \text{sign}(t) + \mathcal{O}\left(\mu(\epsilon,t)^2\right),\\
\frac{\gamma(x,\epsilon)}{r} &= \mathcal{O}(\mu(\epsilon,t)),\\
\frac{\delta(x,\epsilon)}{r} &= \mathcal{O}(\mu(\epsilon,t)).
\end{aligned}$$

Since $\sin^2(\theta/2) = \frac{1}{2}(1-\cos(\theta))$, and $\cos^2(\theta/2) = 1 - \sin^2(\theta/2)$, we see that

$$\begin{aligned}
\sin^2(\theta/2) &= \left\{\begin{matrix} 0 & \text{if } t>0 \\ 1 & \text{if } t<0 \end{matrix}\right\} + \mathcal{O}\left(\mu(\epsilon,t)^2\right) \qquad \text{and} && (3.30)\\
\cos^2(\theta/2) &= \left\{\begin{matrix} 1 & \text{if } t>0 \\ 0 & \text{if } t<0 \end{matrix}\right\} + \mathcal{O}\left(\mu(\epsilon,t)^2\right).
\end{aligned}$$

The lemma follows. □

We now construct the dynamic eigenvectors.

Lemma 3.2 *Suppose* $0 < \delta' < \xi < \frac{1}{3}$, $|t| > \epsilon^{1-\xi}$, *and* $|t| < \epsilon^{\kappa}$ *for some* $\kappa > \frac{1}{2}$. *Let* $a^{\mathcal{C}}(t)$ *and* $\eta^{\mathcal{C}}(t)$ *solve the classical equations of motion (2.2) and (2.3). There exist eigenvectors* $\Phi^{\pm}_{\mathcal{C}}(x,t,\epsilon)$, $\mathcal{C} = \mathcal{A}, \mathcal{B}$, *that solve (3.19) and satisfy*

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

for all x *in the support of* $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$.

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 $+$, and let $a(t) \equiv a^{\mathcal{A}}(t)$ and $\eta(t) \equiv \eta^{\mathcal{A}}(t)$ for $t > 0$. We again let $\mu(\epsilon,t) = \max\{\,|t|,\, \epsilon^{1-\delta'}/|t|\,\}$.

Solutions of (3.19) have the form

$$\Phi(x,t,\epsilon) = \Phi(x,\epsilon)\mathrm{e}^{i\lambda(x,t,\epsilon)}, \tag{3.31}$$

where $\lambda(x,t,\epsilon)$ is a real valued function that satisfies the equation

$$i\frac{\partial}{\partial t}\lambda(x,t,\epsilon) + i\eta(t)\cdot\nabla\lambda(x,t,\epsilon) + \langle\Phi(x,\epsilon),\, \eta(t)\cdot\nabla\Phi(x,\epsilon)\rangle = 0. \tag{3.32}$$

We introduce

$$\omega \equiv x - a(t) \tag{3.33}$$

and define

$$\widetilde{\lambda}(\omega,t,\epsilon) \equiv \lambda(\omega + a(t),t,\epsilon), \tag{3.34}$$
$$\widetilde{\Phi}(\omega,t,\epsilon) \equiv \Phi(\omega + a(t),\epsilon). \tag{3.35}$$

In the new variables, equation (3.32) for $\widetilde{\lambda}$ is

$$i\frac{\partial}{\partial t}\widetilde{\lambda}(\omega,t,\epsilon) = -\langle\widetilde{\Phi}(\omega,t,\epsilon),\, \frac{\partial}{\partial t}\widetilde{\Phi}(\omega,t,\epsilon)\rangle \tag{3.36}$$

where

$$\frac{\partial}{\partial t}\widetilde{\Phi}(\omega,t,\epsilon) = \eta(t)\cdot\nabla\Phi(\omega + a(t),\epsilon). \tag{3.37}$$

Dropping the arguments, we have

$$\begin{aligned}\nabla\Phi = \quad & \left(-\sin(\theta/2)\psi_1 + \mathrm{e}^{-i\varphi}\cos(\theta/2)\psi_2\right)\nabla\theta/2 \\ & + \cos(\theta/2)\nabla\psi_1 + \mathrm{e}^{-i\varphi}\sin(\theta/2)\nabla\psi_2 \\ & -i\nabla\varphi\mathrm{e}^{-i\varphi}\sin(\theta/2)\psi_2.\end{aligned} \tag{3.38}$$

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

$$\begin{aligned}\langle\widetilde{\Phi},\, \frac{\partial}{\partial t}\widetilde{\Phi}\rangle = \; & - \; i\eta\nabla\varphi\sin^2(\theta/2) + \cos^2(\theta/2)\langle\psi_1|\eta\nabla\psi_1\rangle + \sin^2(\theta/2)\langle\psi_2|\eta\nabla\psi_2\rangle \\ & + \; \sin(\theta/2)\cos(\theta/2)\left(\mathrm{e}^{-i\varphi}\langle\psi_1|\eta\nabla\psi_2\rangle + \mathrm{e}^{i\varphi}\langle\psi_2|\eta\nabla\psi_1\rangle\right).\end{aligned} \tag{3.39}$$

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

$$\tilde{\lambda}(\omega, t, \epsilon) = \int_0^t \Big(\eta(t')\nabla\varphi \sin^2(\theta(\omega + a(t'), \epsilon)/2) + \mathcal{O}(0)\Big)\, dt', \tag{3.40}$$

where we have now fixed the constant of integration.

We claim that $|\eta \cdot \nabla\varphi \sin^2 \theta/2|$ is bounded on the support of $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$. We note that

$$\varphi(x, \epsilon) = \cot^{-1}(\gamma(x, \epsilon)/\delta(x, \epsilon)), \tag{3.41}$$

provided $\delta(x, \epsilon)$ is different from zero. However, on the support of $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$ with $|t| < \epsilon^{\kappa}$,

$$\begin{aligned} \delta(x, \epsilon) &= d_3\epsilon + \mathcal{O}(x^2 + \epsilon^2) \\ &= d_3\epsilon + \mathcal{O}(t^2 + \epsilon^2) \\ &\geq C\epsilon, \qquad \text{for some positive } C. \end{aligned}$$

By the mean value theorem,

$$\begin{aligned} \sqrt{y^2 + z^2} &= |y| + |z| \frac{\zeta}{\sqrt{y^2 + \zeta^2}} \qquad \text{for some } \zeta \in [\,0,\ |z|\,] \\ &\leq |y| + |z|. \end{aligned}$$

Thus,

$$2 \sin^2 \theta/2 = 1 - \cos\theta = \frac{r - \beta}{r} = \frac{\sqrt{\beta^2 + \gamma^2 + \delta^2} - \beta}{r}$$

satisfies

$$\Big| 2 \sin^2 \theta/2 \Big| \leq \frac{\sqrt{\gamma^2 + \delta^2}}{\sqrt{\beta^2 + \gamma^2 + \delta^2}}.$$

From (3.41) we therefore see that

$$\begin{aligned} \Big| \eta \cdot \nabla\varphi \sin^2 \theta/2 \Big| &\leq \frac{|\,\gamma\,\eta \cdot \nabla\delta\,| + |\,\delta\,\eta \cdot \nabla\gamma\,|}{\sqrt{\gamma^2 + \delta^2}\,\sqrt{\beta^2 + \gamma^2 + \delta^2}} \\ &\leq \frac{|\,\eta \cdot \nabla\gamma\,| + |\,\eta \cdot \nabla\delta\,|}{\sqrt{\beta^2 + \gamma^2 + \delta^2}} \end{aligned}$$

However, on the support of $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$,

$$\begin{aligned} \sqrt{\beta^2 + \gamma^2 + \delta^2} &\geq C|t|, \qquad \text{for some } C, \\ |\,\eta \cdot \nabla\delta\,| &= \mathcal{O}(|t|), \qquad \text{and} \\ |\,\eta \cdot \nabla\gamma\,| &= \eta_0 \cdot c + \mathcal{O}(|t|) \\ &= \mathcal{O}(|t|), \qquad \text{since } \eta_0 \cdot c = 0. \end{aligned} \tag{3.42}$$

Thus, $\eta \cdot \nabla\varphi \sin^2 \theta/2$ is bounded, and by virtue of (3.40),

$$\tilde{\lambda}(\omega, t, \epsilon) = \tilde{\lambda}_0(\omega). + \mathcal{O}(|t|).$$

This implies the lemma since we can arbitrarily take $\tilde{\lambda}_0(\omega) \equiv 0$. $\square$

3.3 The 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 $t = 0$:

$$\begin{aligned}
a^{\mathcal{B}}(0) &= 0, \\
\eta^{\mathcal{B}}(0) &= \eta^0, \\
S^{\mathcal{B}}(0) &= 0, \\
A^{\mathcal{B}}(0) &= A_0, \qquad\qquad \text{and} \\
B^{\mathcal{B}}(t) &\sim B_0 + \frac{i|d_3|}{b_1\eta_1^0}\left[MA_0 + \ln\left(\frac{2b_1\eta_1^0|t|}{|d_3|\epsilon}\right) NA_0\right],
\end{aligned}$$

where A_0 and B_0 satisfy the hypotheses in the definition of the functions φ_l, and the asymptotic condition for $B^{\mathcal{B}}(t)$ is to hold for small values of ϵ, $|t|$, $\epsilon/|t|$, and $|t\,\ln^2\,\epsilon\,|$. 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 3.3 *Suppose $0 < \delta' < \xi < 1$. For any $-T \leq t \leq -\epsilon^{1-\xi}$, there is an approximation $\psi_{OI}(x,t)$ to the exact solution $\psi(x,t)$ to the Schrödinger equation, such that*

$$\psi_{OI}(x,t) = F\left(\frac{\|x-a^{\mathcal{B}}(t)\|}{\epsilon^{1-\delta'}}\right) e^{iS^{\mathcal{B}}(t)/\epsilon^2}\varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x)\ \Phi_{\mathcal{B}}^{-}(x,t,\epsilon) \tag{3.43}$$

and

$$\psi(x,t) = \psi_{OI}(x,t) + \mathcal{O}(\epsilon^{\xi}), \tag{3.44}$$

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 [17]. For $-T \leq t \leq -\epsilon^{1-\xi}$ and x in the support of the cut off function $F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'})$, $\frac{1}{E_A(x)-E_{\mathcal{B}}(x)}$ 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

$$\Psi(x,t) = F(\|x-a^{\mathcal{B}}(t)\|/\epsilon^{1-\delta'})\, e^{iS^{\mathcal{B}}(t)/\epsilon^2}\,\left(\Psi_0(x,t) + \epsilon^2\Psi_2^{\perp}(x,\,t)\right) \tag{3.45}$$

where

$$\Psi_0(x,t) = \varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x)\,\Phi_{\mathcal{B}}^{-}(x,t,\epsilon) \tag{3.46}$$

and

$$\begin{aligned}\Psi_2^{\perp}(x,t) &= i\varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x)\\ &\quad\times \left(\Phi_{\mathcal{A}}^-(x,t,\epsilon)\, \frac{1}{E_{\mathcal{A}}(x)-E_{\mathcal{B}}(x)} \langle\, \Phi_{\mathcal{A}}^-(x,t,\epsilon),\, \left(\frac{\partial}{\partial t} + \eta^{\mathcal{B}}\cdot\nabla_x\right)\, \Phi_{\mathcal{B}}^-(x,t,\epsilon)\,\rangle \right.\\ &\qquad\left. + r_{\mathcal{B}\mathcal{A}}(x,\epsilon) P_{\perp}^{\mathcal{A}\mathcal{B}}(x,\epsilon) \left(\frac{\partial}{\partial t} + \eta^{\mathcal{B}}\cdot\nabla_x\right) \Phi_{\mathcal{B}}^-(x,t,\epsilon)\right),\end{aligned} \tag{3.47}$$

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

The expression (3.45) 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

$$\zeta(x,t,\epsilon) = i\epsilon^2 \frac{\partial \Psi}{\partial t} - H(\epsilon)\Psi. \tag{3.48}$$

For $-T \le t \le -\epsilon^{1-\xi}$, 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 [17], 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 (3.45). Our error term $\zeta(x,t,\epsilon)$ differs formally from that of Section 6 of [17] because our eigenfunctions have time dependence and the ones in Section 6 of [17] 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 [17], 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 [17]. So, it is not surprising that our error term satisfies the same estimate

$$\|\zeta(\cdot,t,\epsilon)\| \le C\,\epsilon^3 |t|^{-2} \tag{3.49}$$

as the corresponding error term in Section 6 of [17].

We obtain the desired estimate by using the estimate (3.49) and lemma 3.3 of [17]. $\square$

Lemma 3.4 *Suppose $0 < \delta' < \xi < \frac{1}{3}$, $t < -\epsilon^{1-\xi}$, and $|t| < \epsilon^{\kappa}$ for some $\kappa > \frac{1}{2}$, and let $y = \frac{x-a(t)}{\epsilon}$. Then the approximate solution of lemma 3.3 has the following asymptotics:*

$$\begin{aligned}\psi_{OI}(x,t) &= -\,F(\epsilon^{\delta'}\|y\|) \exp\left(i\frac{S(t)}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} - i\frac{b_1\eta_1^0 t^2}{2\epsilon^2} + i\frac{d_3^2\left[\frac{1}{2} - \ln\left(\frac{|d_3\epsilon t|}{2b_1\eta_1^0}\right)\right]}{2b_1\eta_1^0}\right)\\ &\quad\times\ \exp\left(-i\frac{|d_3|}{2b_1\eta_1^0}\,\langle\, y,\, \left[M\ +\ \ln\left(\frac{2b_1\eta_1^0|t|}{|d_3|\epsilon}\right)\ N\right]\ y\rangle\right)\\ &\quad\times\ \exp\left(-i\frac{|d_3|b\cdot y}{b_1\eta_1^0} - i\frac{t\,b\cdot y}{\epsilon}\right)\end{aligned}$$

$$
\times \ \exp\left(i\frac{\eta_0\cdot y}{\epsilon}\right)\ \epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\ \psi_1(x,\epsilon)
+\ \mathcal{O}(\epsilon^{\alpha}), \tag{3.50}
$$

for some $\alpha > 0$.

Proof:
We make a sequence of replacements in formula (3.43). With each replacement, we make an error that is acceptably small because of earlier results.

We introduce the notation $y^{\mathcal{C}} = (x - a^{\mathcal{C}}(t))/\epsilon$, and using proposition 2.2, we replace

$$
F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|) \qquad \text{by} \qquad F(\epsilon^{\delta'}\|y\|).
$$

Next we use proposition 2.2 and corollary 2.2 to replace the factor

$$
\exp\left(i\frac{\eta^{\mathcal{B}}(t)\cdot y^{\mathcal{B}}}{\epsilon}\right) \qquad \text{by}
$$

$$
\exp\left(i\frac{\eta_0\cdot y}{\epsilon} - i\frac{|d_3|b\cdot y}{b_1\eta_1^0} - i\frac{t\,b\cdot y}{\epsilon} + i\frac{|d_3|t}{\epsilon} + i\frac{b_1\eta_1^0t^2}{2\epsilon^2} + i\frac{d_3^2}{2b_1\eta_1^0}\left(\ln\,\frac{2b_1\eta_1^0|t|}{|d_3|\epsilon} + \frac{1}{2}\right)\right).
$$

We use lemma 3.1 of [20] and proposition 2.2 to replace

$$
\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),0,x) \qquad \text{by} \qquad \varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a(t),0,x).
$$

We then use lemma 3.1 of [20] and proposition 2.3 to replace

$$
\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a(t),0,x) \qquad \text{by}
$$

$$
\exp\left(-i\frac{|d_3|}{2b_1\eta_1^0}\,\langle y,\,\left[M\,+\,\ln\left(\frac{2b_1\eta_1^0|t|}{|d_3|\epsilon}\right)\,N\right]\,y\rangle\right)\ \epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y).
$$

By corollary 2.3 we can replace

$$
\exp\left(i\frac{S^{\mathcal{B}}(t)}{\epsilon^2}\right) \qquad \text{by} \qquad \exp\left(i\frac{S(t)}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} - i\frac{|d_3|t}{\epsilon} - i\frac{b_1\eta_1^0t^2}{\epsilon^2} - i\frac{d_3^2\ln\,|t|}{\eta_1^0b_1}\right).
$$

Finally, using lemmas 3.1 and 3.2, we replace

$$
\Phi_{\mathcal{B}}^-(x,t,\epsilon) \qquad \text{by} \qquad -\ \psi_1(x,\epsilon)
$$

The lemma follows. □

3.4 The Inner Solution

For small times we use a different approximation that is constructed by means of the classical quantities associated with the potential $\widetilde{V}(x,\epsilon)$. Let $a(t)$, $\eta(t)$, and $S(t)$ be the classical quantities that satisfy the initial conditions

$$
\begin{aligned}
a(0) &= 0\\
\eta(0) &= \eta^0\\
S(0) &= 0.
\end{aligned} \tag{3.51}
$$

In the rescaled variables

$$\begin{cases} y = (x - a(t))/\epsilon, \\ \quad s = t/\epsilon, \end{cases} \tag{3.52}$$

the Schrödinger equation is

$$i\epsilon\frac{\partial}{\partial s}\psi - i\epsilon\eta(\epsilon s)\nabla_y\psi = -\frac{\epsilon^2}{2}\Delta_y\psi + h(a(\epsilon s) + \epsilon y, \epsilon)\psi. \tag{3.53}$$

We look for an approximate solution of the form

$$\psi(y, s, \epsilon) \;=\; F(\|y\|\epsilon^{\delta'})\exp\left(i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{\eta(\epsilon s)y}{\epsilon}\right)\chi(y, s, \epsilon), \tag{3.54}$$

with

$$\begin{aligned} \chi(y, s, \epsilon) = \quad & \{f(y, s, \epsilon)\psi_1(a(\epsilon s) + \epsilon y, \epsilon) + g(y, s, \epsilon)\psi_2(a(\epsilon s) + \epsilon y, \epsilon) \\ & + \psi_\perp(a(\epsilon s) + \epsilon y, \epsilon)\}, \end{aligned} \tag{3.55}$$

where $\psi_\perp(x, \epsilon) \in (I\!I - P(x, \epsilon))\mathcal{H}$ and f, g are scalar functions. Anticipating exponential spatial fall off of the solution, we insert (3.54) in (3.53) and neglect the derivatives of F. Making use of the decomposition (1.10) and eliminating the overall "classical phase" and cut-off F, we have

$$\begin{aligned} & i\epsilon\psi_1\frac{\partial}{\partial s}f + i\epsilon\psi_2\frac{\partial}{\partial s}g + i\epsilon\frac{\partial}{\partial s}\psi_\perp + (\tilde{V}(a) + \epsilon y\nabla_x\tilde{V}(a))(f\psi_1 + g\psi_2 + \psi_\perp) \\ & + i\epsilon^2 f\eta\nabla_x\psi_1 + i\epsilon^2 g\eta\nabla_x\psi_2 + i\epsilon^2\eta\nabla_x\psi_\perp \\ = \quad & -\epsilon^4\Delta_x\psi_\perp/2 - \epsilon^4 f\Delta_x\psi_1/2 - \epsilon^4 g\Delta_x\psi_2/2 - \epsilon^3\nabla_y f\nabla_x\psi_1 \\ & -\epsilon^3\nabla_y g\nabla_x\psi_2 - \epsilon^2\psi_1\Delta_y f - \epsilon^2\psi_2\Delta_y g + h^\perp\psi_\perp + h_1(f\psi_1 + g\psi_2) \\ & +\tilde{V}(a + \epsilon y)(f\psi_1 + g\psi_2 + \psi_\perp). \end{aligned} \tag{3.56}$$

We assume the solutions have expansions of the form

$$\begin{aligned} f(y, s, \epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)f_j(y, s), \\ g(y, s, \epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)g_j(y, s), \\ \psi_\perp(x, t, \epsilon) &= \sum_{j=0}^{\infty}\nu_j(\epsilon)\psi_{\perp j}(x, t), \end{aligned} \tag{3.57}$$

with asymptotic scales $\nu_j(\epsilon)$ to be determined by matching. We insert these expansions in (3.56). Using the behaviors (1.33) and lemma 2.2 we see that the lowest order terms yield

$$\begin{aligned} & i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}f_0(y, s)\psi_1(a(\epsilon s) + \epsilon y, \epsilon) + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s}g_0(y, s)\psi_2(a(\epsilon s) + \epsilon y, \epsilon) \\ = \quad & h_\perp(a(\epsilon s) + \epsilon y, \epsilon)\psi_\perp(a(\epsilon s) + \epsilon y, \epsilon s, \epsilon) \\ & +\epsilon\nu_0(\epsilon)h_{11}(y, s)\left(f_0(y, s)\psi_1(a(\epsilon s) + \epsilon y, \epsilon) + g_0(y, s)\psi_2(a(\epsilon s) + \epsilon y, \epsilon)\right) \end{aligned} \tag{3.58}$$

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

$$\begin{pmatrix} b_1\eta_1^0 s + b_1 y_1 + b_2 y_2 & c_2 y_2 + i d_3 \\ c_2 y_2 - i d_3 & -b_1\eta_1^0 s - b_1 y_1 - b_2 y_2 \end{pmatrix}.$$

By matching the incoming outer solution, we obtain

$$\nu_j(\epsilon) h_\perp(a(\epsilon s)+\epsilon y,\epsilon)\psi_{\perp j}(a(\epsilon s)+\epsilon y,\epsilon s) = 0 \tag{3.59}$$

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

$$\psi_{\perp j}(x,t) = 0, \quad j=0,1,\cdots,m-1. \tag{3.60}$$

By projecting with $P(x,\epsilon)$ and $(\mathit{I\!I} - P(x,\epsilon))$, we split the remaining equation for order $\epsilon\nu_0(\epsilon) = \nu_m(\epsilon)$,

$$\begin{aligned} & i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s} f_0\psi_1 + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s} g_0\psi_2 \\ = \quad & \nu_m(\epsilon) h_\perp\psi_\perp + \epsilon\nu_0(\epsilon) h_{11}(f_0\psi_1 + g_0\psi_2), \end{aligned} \tag{3.61}$$

into

$$\begin{aligned} i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s} f_0\psi_1 + i\epsilon\nu_0(\epsilon)\frac{\partial}{\partial s} g_0\psi_2 &= \epsilon\nu_0(\epsilon) h_{11}(f_0\psi_1 + g_0\psi_2) \qquad \text{and} \\ \nu_m(\epsilon) h_\perp \psi_{\perp m} &= 0. \end{aligned} \tag{3.62}$$

The second equation gives $\psi_{\perp m} = 0$. The first one is equivalent to

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix} = \begin{pmatrix} b_1\eta_1^0 s + b_1 y_1 + b_2 y_2 & c_2 y_2 + i d_3 \\ c_2 y_2 - i d_3 & -b_1\eta_1^0 s - b_1 y_1 - b_2 y_2 \end{pmatrix}\begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix}. \tag{3.63}$$

The general solution of this equation can be found exactly in terms of parabolic cylinder functions [6].

$$\begin{aligned} \begin{pmatrix} f_0(y,s) \\ g_0(y,s) \end{pmatrix} \quad = \quad & C_1(y)\begin{pmatrix} \frac{(1-i)(c_2y_2+id_3)}{2\sqrt{b_1\eta_1^0}} D_{p_u-1}\left(\frac{(-1+i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \\ D_{p_u}\left(\frac{(-1+i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \end{pmatrix} \\ & + C_2(y)\begin{pmatrix} D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \\ \frac{(-1-i)(c_2y_2-id_3)}{2\sqrt{b_1\eta_1^0}} D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \end{pmatrix}, \end{aligned} \tag{3.64}$$

where

$$p_l \;=\; -p_u \;=\; -\,i\,\frac{c_2^2 y_2^2 + d_3^2}{2b_1\eta_1^0}.$$

We define our inner approximation by

$$\begin{aligned} \psi_I(y,s) = \quad & F \quad (\|y\|\epsilon^{\delta'})\ \exp\left(i\frac{S(\epsilon s)}{\epsilon^2} + i\frac{\eta(\epsilon s)y}{\epsilon}\right) \\ & \times\ \left[\,\nu_0(\epsilon) f_0(y,s)\psi_1(a(\epsilon s)+\epsilon y,\epsilon) + \nu_0(\epsilon) g_0(y,s)\psi_2(a(\epsilon s)+\epsilon y,\epsilon)\,\right], \end{aligned} \tag{3.65}$$

with f_0 and g_0 as above. To match (3.50) on the $\mathcal{B}$ level, we need

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

This forces us to take

$$C_1(y) \equiv 0, \tag{3.66}$$

because the second component of the first term on the right hand side of (3.64) does not tend to zero as $s \to -\infty$. We see this by using the asymptotic formula 1 of 9.246 of [6],

$$D_q(z) \;=\; e^{-z^2/4}\, z^q \left(1 - \mathcal{O}\left(\left|\frac{q}{z}\right|^2\right)\right), \qquad \text{for} \qquad \arg\, z < \frac{3\pi}{4}, \tag{3.67}$$

and noting that $\|y\|/s = \mathcal{O}(\epsilon^{\xi-\delta'}) \to 0$ due to the cutoff.

The second component of the second term on the right hand side of (3.64) does tend to zero as $s \to -\infty$. Formula (3.67) and some simple estimates show that on the support of $F(\|y\|\epsilon^{\delta'})$,

$$D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \;=\; \mathcal{O}(|s|^{-1}).$$

Thus, the first component of the second term on the right hand side of (3.64) determines $C_2(y)$ by matching (3.50). As $s \to -\infty$, that component has the following asymptotics by (3.67):

$$\begin{aligned}
&D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right)\\
&= \exp\left(-i\frac{(b_1\eta_1^0 s + b\cdot y)^2}{2b_1\eta_1^0} + \frac{\pi(c_2^2y_2^2 + d_3^2)}{8b_1\eta_1^0}\right)\\
&\quad\times \exp\left(-i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\left[\ln\left(\sqrt{\frac{2}{b_1\eta_1^0}}\right) + \ln\left(b_1\eta_1^0|s| - b\cdot y\right)\right]\right)\\
&\quad\times \left(1 + \mathcal{O}(|s|^{-2})\right).
\end{aligned}$$

In the matching regime, $\|y\|/|s| \to 0$, so by a fairly lengthy calculation, this quantity matches (3.50) if we choose $\nu_0(\epsilon) = 1$ and $C_2(y)$ to be

$$\begin{aligned}
C_2(y) \;=\; & -\epsilon^{-n/2}\,\varphi_l(A_0, B_0, 1, 0, 0, y)\, \exp\left(\frac{-\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right)\\
&\times \exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} - i\frac{d_3^2}{b_1\eta_1^0}\ln\epsilon + i\frac{d_3^2}{4b_1\eta_1^0} - i\frac{d_3^2}{2b_1\eta_1^0}\ln|d_3| + i\frac{3d_3^2}{4b_1\eta_1^0}\ln(2b_1\eta_1^0)\right)\\
&\times \exp\left(-i\frac{c_2^2y_2^2}{4b_1\eta_1^0}\ln(2b_1\eta_1^0) + i\frac{c_2^2y_2^2}{2b_1\eta_1^0}\ln|d_3| - i\frac{|d_3|b\cdot y}{b_1\eta_1^0}\right).
\end{aligned} \tag{3.68}$$

The following result deals with the validity of the inner approximate solution.

Lemma 3.5 *Suppose $0 < \delta' < \xi < 1/3$, $\kappa > \frac{1}{2}$, and $1-\xi > \kappa$. The function $\Psi_I(x,t) = \psi_I((x-a(t))/\epsilon, t/\epsilon)$ is a valid approximation of a solution $\psi(x,t)$ to the Schrödinger equation for $-\epsilon^{1-\xi} \le t \le \epsilon^{1-\xi}$, in the sense that as $\epsilon \to 0$,*

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

Furthermore, in the matching regime, $-\epsilon^{\kappa} < t < -\epsilon^{1-\xi}$, the inner and outer solutions agree in the sense that

$$\| \Psi_{IO}(\cdot,t) - \Psi_I(\cdot,t) \| = \mathcal{O}(\epsilon^{\alpha})$$

for some $\alpha > 0$.

Proof:
The first result is proved by mimicking the proofs of proposition 3.1 of [20] and lemma 3.5 of [20]. The second result is proved by combining lemma 3.4 and simple estimates based on the calculations presented above. □

We need the large positive s asymptotics of the inner solution to match it to an outgoing outer solution. To obtain these asymptotics, we use formula 3 of 9.246 of [6],

$$D_q(z) \;=\; e^{-z^2/4}\, z^q \left(1 - \mathcal{O}\left(\left|\frac{q}{z}\right|^2\right)\right) - \frac{\sqrt{2\pi}}{\Gamma(-q)}\, e^{-q\pi i}\, e^{z^2/4}\, z^{-q-1} \left(1 - \mathcal{O}\left(\left|\frac{q}{z}\right|^2\right)\right),$$

for $\quad -\frac{5\pi}{4} < \arg\, z < \frac{\pi}{4}$.

From this formula, the first component of the second term in (3.64) has large s asymptotics (omitting the factor $C_2(y)$)

$$\begin{aligned}
& D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \\
&= \exp\left(-i\frac{(b_1\eta_1^0 s + b\cdot y)^2}{2b_1\eta_1^0} - \frac{3\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right) \\
&\qquad \times \exp\left(-i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\ \ln\left(\sqrt{\frac{2}{b_1\eta_1^0}}\ (b_1\eta_1^0 s + b\cdot y)\right)\right) \\
&\qquad \times \left(1 + \mathcal{O}(|s|^{-2})\right) \\
&\quad + \mathcal{O}\left(|s|^{-1}\right).
\end{aligned} \tag{3.69}$$

The second component of the second term in (3.64) has large s asymptotics (again omitting the factor $C_2(y)$)

$$\begin{aligned}
& \frac{(-1-i)(c_2y_2 - id_3)}{2\sqrt{b_1\eta_1^0}}\, D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \\
&= \frac{(1+i)(c_2y_2 - id_3)}{2\sqrt{b_1\eta_1^0}} \quad \frac{\sqrt{2\pi}\, e^{i\pi}\, e^{-\frac{\pi(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}}}{\Gamma\left(1 + i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)}
\end{aligned}$$

$$
\begin{aligned}
&\quad\times\ \exp\left(i\frac{(b_1\eta_1^0 s + b\cdot y)^2}{2b_1\eta_1^0} \;+\; \frac{3\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right) \\
&\quad\times\ \exp\left(i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\ \ln\left(\sqrt{\frac{2}{b_1\eta_1^0}}\ (b_1\eta_1^0 s + b\cdot y)\right)\right) \\
&\quad\times\ \left(\,1 \,+\, \mathcal{O}(|s|^{-2})\,\right) \\
&+\mathcal{O}\left(|s|^{-1}\right) \\
=\ & \frac{(-1-i)(c_2y_2-id_3)}{\sqrt{2b_1\eta_1^0}}\quad \frac{\sqrt{\pi}}{\Gamma\left(1+i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)} \\
&\quad\times\ \exp\left(i\frac{(b_1\eta_1^0 s + b\cdot y)^2}{2b_1\eta_1^0} \;-\; \frac{\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right) \\
&\quad\times\ \exp\left(i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\ \ln\left(\sqrt{\frac{2}{b_1\eta_1^0}}\ (b_1\eta_1^0 s + b\cdot y)\right)\right) \\
&\quad\times\ \left(\,1 \,+\, \mathcal{O}(|s|^{-2})\,\right) \\
&+\mathcal{O}\left(|s|^{-1}\right). \qquad (3.70)
\end{aligned}
$$

3.5 Outgoing Outer Solution

To construct the outer solution for positive times, we use the classical quantities associated with the $\mathcal{A}$ and $\mathcal{B}$ levels that satisfy the following initial conditions:

$$
\begin{aligned}
a^{\mathcal{A}}(0) &= 0, \qquad (3.71) \\
\eta^{\mathcal{A}}(0) &= \eta^0 - \frac{2|d_3|\epsilon}{b_1\eta_1^0}\ b, \\
S^{\mathcal{A}}(0) &= 0, \\
A^{\mathcal{A}}(0) &= \left((A_0A_0^*)^{-1} + \frac{\pi}{b_1\eta_1^0}\,|c\rangle\langle c| \right)^{-1/2} \\
B^{\mathcal{A}}(t) &\sim \left(B_0A_0^{-1} + \frac{\pi}{b_1\eta_1^0}\,|c\rangle\langle c| \right)\ A^{\mathcal{A}}(0) + \frac{i|d_3|}{b_1\eta_1^0}\left[MA^{\mathcal{A}}(0) + \ln\left(\frac{2b_1\eta_1^0 t}{|d_3|\epsilon}\right) NA^{\mathcal{A}}(0)\right],
\end{aligned}
$$

$$
\begin{aligned}
a^{\mathcal{B}}(0) &= 0, \qquad (3.72) \\
\eta^{\mathcal{B}}(0) &= \eta^0, \\
S^{\mathcal{B}}(0) &= 0, \\
A^{\mathcal{B}}(0) &= A_0, \\
B^{\mathcal{B}}(t) &\sim B_0 - \frac{i|d_3|}{b_1\eta_1^0}\ \ln\left(\frac{d_3^2}{2b_1\eta_1^0}\right) NA_0 - \frac{i|d_3|}{b_1\eta_1^0}\left[MA_0 + \ln\left(\frac{2b_1\eta_1^0 t}{|d_3|\epsilon}\right) NA_0\right].
\end{aligned}
$$

Here the asymptotic conditions for $B^{\mathcal{C}}(t)$ are to be satisfied in the regime where t, ϵ, ϵ/t, and $t\ln^2(\epsilon)$ are all small. It is convenient to define the quantity

$$B_1^{\mathcal{A}}(t) \;=\; B_0 + \frac{i|d_3|}{b_1\eta_1^0}\left[MA_0 + \ln\left(\frac{2b_1\eta_1^0 t}{|d_3|\epsilon}\right) NA_0\right].$$

One should note the difference in initial momentum with the classical quantities associated with the $\mathcal{B}$ level, (3.43). As explained earlier, the corresponding loss in kinetic energy equals the gain in potential energy, to leading order.

One should also note that the complicated expressions for the $A^{\mathcal{C}}$'s and $B^{\mathcal{C}}$'s are determined in order to satisfy conditions (3.5)–(3.8).

The following lemma describes the outgoing outer solution.

Lemma 3.6 *Suppose $0 < \delta' < \xi < 1/3$, and $1/2 < \kappa < 1-\xi$. For $\epsilon^{1-\xi} \le t \le T$, the outgoing outer solution $\psi_{OO}(x,t)$ agrees with an exact solution of the Schrödinger equation up to $\mathcal{O}(\epsilon^{\xi})$ errors and matches the inner solution for $\epsilon^{\kappa} < t < \epsilon^{1-\xi}$. It has the form*

$$\begin{aligned}&\psi_{OO}(x,t) \qquad\qquad (3.73)\\ =\;& F\left(\frac{\|x-a^{\mathcal{A}}(t)\|}{\epsilon^{1-\delta'}}\right) e^{iS^{\mathcal{A}}(t)/\epsilon^2}\sum_{|m|\le|l|} d_m^{\mathcal{A}}\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\;\Phi_{\mathcal{A}}^{+}(x,t,\epsilon)\\ &+F\left(\frac{\|x-a^{\mathcal{B}}(t)\|}{\epsilon^{1-\delta'}}\right) e^{iS^{\mathcal{B}}(t)/\epsilon^2}\sum_{m} d_m^{\mathcal{B}}\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\;\Phi_{\mathcal{B}}^{+}(x,t,\epsilon),\end{aligned}$$

where the first summation is finite, and the $d_m^{\mathcal{B}}$ in the second summation decrease more rapidly than any inverse power of $|m|$.

Proof:
The validity of the approximation is proved by mimicking the proof of lemma 3.3. However, one must also check that formula (3.73) matches the inner solution.

Checking the matching is straigtforward, but very tedious. We assume $\epsilon^{\kappa} < t < \epsilon^{1-\xi}$ and separately show that the first and second components of (3.65) match the first and second terms on the right hand side of (3.73), respectively. We show these two results by sequences of approximate equalities. At each step we make an error that is $\mathcal{O}(\epsilon^{\alpha})$ for some $\alpha > 0$.

The first component of (3.65) is

$$F(\epsilon^{\delta'}\|y\|)\,\exp\left(i\frac{S}{\epsilon^2}+i\frac{\eta\cdot y}{\epsilon}\right)\,C_2(y)\,D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1y_1 + b_2y_2)\right).$$

By the explicit formula for $C_2(y)$ and formula (3.69), this approximately equals

$$\begin{aligned}&-F(\epsilon^{\delta'}\|y\|)\,\exp\left(i\frac{S}{\epsilon^2}+i\frac{\eta\cdot y}{\epsilon}\right)\,\epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\,\exp\left(-\frac{\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right)\\ &\times\,\exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}-i\frac{d_3^2}{b_1\eta_1^0}\ln\epsilon+i\frac{d_3^2}{4b_1\eta_1^0}-i\frac{d_3^2}{2b_1\eta_1^0}\ln|d_3|+i\frac{3d_3^2}{4b_1\eta_1^0}\ln(2b_1\eta_1^0)\right)\\ &\times\,\exp\left(-i\frac{c_2^2y_2^2}{4b_1\eta_1^0}\ln(2b_1\eta_1^0)+i\frac{c_2^2y_2^2}{2b_1\eta_1^0}\ln|d_3|-i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0}\right)\end{aligned}$$

$$\times\ \exp\left(-i\frac{b_1\eta_1^0 s^2}{2} - is\,b\cdot y - i\frac{(b\cdot y)^2}{2b_1\eta_1^0} - \frac{3\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right)$$
$$\times\ \exp\left(-i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\ \ln\left(\sqrt{\frac{2}{b_1\eta_1^0}}\,(b_1\eta_1^0 s + b\cdot y)\right)\right). \tag{3.74}$$

By making a small error, we can drop the $b\cdot y$ term in the logarithm in the final term in this expression. Also, by proposition 2.2, we make a small error by replacing $F(\epsilon^{-\delta'}\|y\|)$ by $F(\epsilon^{-\delta'}\|y^{\mathcal{A}}\|)$. Thus, simple calculations show that (3.74) approximately equals

$$\begin{aligned}
& -F(\epsilon^{\delta'}\|y^{\mathcal{A}}\|)\ \ \epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\ \exp\left(-\frac{\pi(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)\\
& \times\ \exp\left(-i\frac{|d_3|}{2b_1\eta_1^0}\langle\, y,\ M\,y\,\rangle - i\frac{c_2^2y_2^2}{2b_1\eta_1^0}\ \ln\left(\frac{2b_1\eta_1^0 s}{|d_3|}\right)\right)\\
& \times\ \exp\left(i\frac{\eta\cdot y}{\epsilon} - i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0} - is\,b\cdot y\right)\\
& \times\ \exp\left(i\frac{S}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} - i\frac{b_1\eta_1^0 s^2}{2} + i\frac{d_3^2}{4b_1\eta_1^0} + i\frac{d_3^2}{2b_1\eta_1^0}\ \ln\left(\frac{2b_1\eta_1^0}{|d_3|\epsilon^2 s}\right)\right)\\
= \quad & -F(\epsilon^{\delta'}\|y^{\mathcal{A}}\|)\ \ \epsilon^{-n/2}\,\varphi_l(A_0,B_1^{\mathcal{A}}(t),1,0,0,y)\ \exp\left(-\frac{\pi(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)\\
& \times\ \exp\left(i\frac{\eta\cdot y}{\epsilon} - i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0} - is\,b\cdot y\right)\\
& \times\ \exp\left(i\frac{S}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} - i\frac{b_1\eta_1^0 s^2}{2} + i\frac{d_3^2}{4b_1\eta_1^0} + i\frac{d_3^2}{2b_1\eta_1^0}\ \ln\left(\frac{2b_1\eta_1^0}{|d_3|\epsilon^2 s}\right)\right).
\end{aligned}$$

By lemma 3.1 of [20] and proposition 2.3, this approximately equals

$$\begin{aligned}
& -F(\epsilon^{\delta'}\|y^{\mathcal{A}}\|)\ \ \epsilon^{-n/2}\sum_{|m|\le|l|}\tilde{d}_m^{\mathcal{A}}\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),1,0,0,y)\\
& \times\ \exp\left(i\frac{\eta\cdot y}{\epsilon} - i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0} - is\,b\cdot y\right)\\
& \times\ \exp\left(i\frac{S}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} - i\frac{b_1\eta_1^0 s^2}{2} + i\frac{d_3^2}{4b_1\eta_1^0} + i\frac{d_3^2}{2b_1\eta_1^0}\ \ln\left(\frac{2b_1\eta_1^0}{|d_3|\epsilon^2 s}\right)\right),
\end{aligned} \tag{3.75}$$

where the numbers $\tilde{d}_m^{\mathcal{A}}$ are defined by the relation

$$\exp\left(-\frac{\pi\,d_3^2}{2b_1\eta_1^0}\right)\ \mathcal{H}_l(A_0;\,|A_0|^{-1}y)\ =\ \left[\frac{\det\,A^{\mathcal{A}}(0)}{\det\,A_0}\right]^{1/2}\sum_{|m|\le|l|}\tilde{d}_m^{\mathcal{A}}\,\mathcal{H}_m(A^{\mathcal{A}}(0);\,|A^{\mathcal{A}}(0)|^{-1}y).$$

One may see that the sum is finite and compute the $\tilde{d}_m^{\mathcal{A}}$ by equating coefficients of the monomials involved in this expression.

We now note the following estimates, the last of which follows from proposition 2.2:

$$\left(\eta^{\mathcal{A}}(0) - \eta^0\right) \ =\ -2|d_3|\epsilon + \mathcal{O}(\epsilon^2), \tag{3.76}$$
$$\eta^{\mathcal{A}}(0)^2 - {\eta^0}^2 \ =\ -4|d_3|\epsilon + \mathcal{O}(\epsilon^2), \tag{3.77}$$
$$\eta^{\mathcal{A}}(t) - \eta(t) \ =\ \frac{\epsilon|d_3|}{b_1\eta_1^0}b - t\,b + \mathcal{O}(\epsilon^2/t) + \mathcal{O}(t^2) + \mathcal{O}(\epsilon^4/t^3). \tag{3.78}$$

Using these, lemma 3.1 of [20], and corollary 2.2, we see that (3.75) approximately equals

$$
\begin{aligned}
&-F(\epsilon^{\delta'}\|y^{\mathcal{A}}\|)\ \ \epsilon^{-n/2} \sum_{|m|\le|l|} \tilde{d}_m^{\mathcal{A}}\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),1,0,0,y^{\mathcal{A}})\\
&\times\ \exp\left(i\frac{\eta^{\mathcal{A}}\cdot y^{\mathcal{A}}}{\epsilon}\ -\ i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0}\ -\ is\,b\cdot y\ +\ i\frac{\left(\eta(t)-\eta^{\mathcal{A}}(t)\right)\cdot y}{\epsilon}\right)\\
&\times\ \exp\left(i\frac{S}{\epsilon^2}\ +\ i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}\ -\ i\frac{b_1\eta_1^0 s^2}{2}\ +\ i\frac{d_3^2}{4b_1\eta_1^0}\ +\ i\frac{d_3^2}{2b_1\eta_1^0}\,\ln\left(\frac{2b_1\eta_1^0}{|d_3|\epsilon^2 s}\right)\right)\\
&\times\ \exp\left(i\frac{|d_3|t}{\epsilon}+i\frac{(\eta^{\mathcal{A}}(0)-\eta^0)\cdot\eta^{\mathcal{A}}(0)t}{\epsilon^2}-i\frac{b_1\eta_1^{\mathcal{A}}(0)}{2\epsilon^2}t^2-i\frac{d_3^2}{2b_1\eta_1^{\mathcal{A}}(0)}\left[\frac{1}{2}+\ln\left(\frac{2b_1\eta_1^{\mathcal{A}}(0)t}{|d_3|\epsilon}\right)\right]\right).
\end{aligned}
$$

Using (3.76), (3.78), and the definition of $\eta^{\mathcal{A}}(0)$, we see that this quantity approximately equals

$$
\begin{aligned}
&-F(\epsilon^{\delta'}\|y^{\mathcal{A}}\|) \sum_{|m|\le|l|} \tilde{d}_m^{\mathcal{A}}\ \varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\\
&\times\ \exp\left(i\frac{S}{\epsilon^2}\ +\ i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}\ -\ ib_1\eta_1^0 s^2\ +\ i\frac{|d_3|t}{\epsilon}\ -\ i\frac{d_3^2}{b_1\eta_1^{\mathcal{A}}(0)}\,\ln\,t\right).
\end{aligned}
\tag{3.79}
$$

We define $d_m^{\mathcal{A}}\ =\ -\,e^{i\frac{S_0^{\mathcal{B}}(\epsilon,-)-S_0^{\mathcal{A}}(\epsilon,+)}{\epsilon^2}}\ \tilde{d}_m^{\mathcal{A}}$, apply corollary 2.3, and recall that we are studying the first component of the inner solution. By using lemmas 3.1 and 3.2, we see that (3.79) matches the following approximate solution to the full Schrödinger equation.

$$
F(\epsilon^{\delta'}\|y^{\mathcal{A}}\|)\ e^{iS^{\mathcal{A}}(t)/\epsilon^2} \sum_{|m|\le|l|} d_m^{\mathcal{A}}\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\ \Phi_{\mathcal{A}}^{+}(x,t,\epsilon).
$$

This is the first term of (3.73).

We now concentrate on the second component of (3.65), which equals

$$
\begin{aligned}
&F(\epsilon^{\delta'}\|y\|)\ \exp\left(i\frac{S}{\epsilon^2}+i\frac{\eta\cdot y}{\epsilon}\right)\ C_2(y)\\
&\times\ \frac{(-1-i)(c_2y_2-id_3)}{2\sqrt{b_1\eta_1^0}}\ D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b_1y_1+b_2y_2)\right).
\end{aligned}
$$

By the explicit formula for $C_2(y)$ and formula (3.70), this approximately equals

$$
\begin{aligned}
&-F(\epsilon^{\delta'}\|y\|)\ \exp\left(i\frac{S}{\epsilon^2}+i\frac{\eta\cdot y}{\epsilon}\right)\ \epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\ \exp\left(-\frac{\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right)\\
&\times\ \exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}-i\frac{d_3^2}{b_1\eta_1^0}\,\ln\,\epsilon\,+i\frac{d_3^2}{4b_1\eta_1^0}-i\frac{d_3^2}{2b_1\eta_1^0}\,\ln\,|d_3|\,+i\frac{3d_3^2}{4b_1\eta_1^0}\,\ln\,(2b_1\eta_1^0)\right)\\
&\times\ \exp\left(-i\frac{c_2^2y_2^2}{4b_1\eta_1^0}\,\ln\,(2b_1\eta_1^0)+i\frac{c_2^2y_2^2}{2b_1\eta_1^0}\,\ln\,|d_3|\ -i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0}\right)\\
&\times\ \frac{(-1-i)(c_2y_2-id_3)}{\sqrt{2b_1\eta_1^0}}\quad\frac{\sqrt{\pi}}{\Gamma\left(1+i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)}
\end{aligned}
$$

$$\times\ \exp\left(i\frac{(b_1\eta_1^0 s + b\cdot y)^2}{2b_1\eta_1^0} - \frac{\pi(c_2^2y_2^2+d_3^2)}{8b_1\eta_1^0}\right)$$
$$\times\ \exp\left(i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\ \ln\left(\sqrt{\frac{2}{b_1\eta_1^0}}\ (b_1\eta_1^0 s + b\cdot y)\right)\right). \tag{3.80}$$

As with (3.74), we drop the $b\cdot y$ in the logarithm in the final factor and we replace $F(\epsilon^{-\delta'}\|y\|)$ by $F(\epsilon^{-\delta'}\|y^{\mathcal{B}}\|)$. Thus, simple calculations show that (3.80) approximately equals

$$F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|)\ \ \sqrt{\frac{\pi}{2b_1\eta_1^0}}\ \ \frac{(1+i)(c_2y_2-id_3)}{\Gamma\left(1+i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)}$$
$$\times\ \epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\ \exp\left(-\frac{\pi(c_2^2y_2^2+d_3^2)}{4b_1\eta_1^0}\right)$$
$$\times\ \exp\left(i\frac{|d_3|}{2b_1\eta_1^0}\langle\, y,\ M\,y\,\rangle + i\frac{c_2^2y_2^2}{2b_1\eta_1^0}\ \ln\left(\frac{2b_1\eta_1^0 s}{|d_3|}\right) + i\frac{c_2^2y_2^2}{2b_1\eta_1^0}\ \ln\left(\frac{d_3^2}{2b_1\eta_1^0}\right)\right)$$
$$\times\ \exp\left(i\frac{\eta\cdot y}{\epsilon} - i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0} + is\,b\cdot y\right)$$
$$\times\ \exp\left(i\frac{S}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} + i\frac{b_1\eta_1^0 s^2}{2} + i\frac{d_3^2}{4b_1\eta_1^0} + i\frac{d_3^2}{2b_1\eta_1^0}\ \ln\left(\frac{4b_1^2{\eta_1^0}^2 s}{|d_3|\epsilon^2}\right)\right).$$

By lemma 3.1 of [20] and proposition 2.3, this approximately equals

$$F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|)\ \ \sqrt{\frac{\pi}{2b_1\eta_1^0}}\ \ \frac{(1+i)(c_2y_2-id_3)}{\Gamma\left(1+i\frac{(c_2^2y_2^2+d_3^2)}{2b_1\eta_1^0}\right)}$$
$$\times\ \epsilon^{-n/2}\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y)\ \exp\left(-\frac{\pi(c_2^2y_2^2+d_3^2)}{4b_1\eta_1^0}\right)$$
$$\times\ \exp\left(i\frac{\eta\cdot y}{\epsilon} - i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0} + is\,b\cdot y\right)$$
$$\times\ \exp\left(i\frac{S}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} + i\frac{b_1\eta_1^0 s^2}{2} + i\frac{d_3^2}{4b_1\eta_1^0} + i\frac{d_3^2}{2b_1\eta_1^0}\ \ln\left(\frac{4b_1^2{\eta_1^0}^2 s}{|d_3|\epsilon^2}\right)\right).$$

Using lemma 3.1 of [20], lemmas 2.1 and 2.2, and corollary 2.2, we see that this approximately equals

$$F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|)\ \ \sqrt{\frac{\pi}{2b_1\eta_1^0}}\ \ \frac{(1+i)(c_2y_2^{\mathcal{B}}-id_3)}{\Gamma\left(1+i\frac{(c_2^2(y_2^{\mathcal{B}})^2+d_3^2)}{2b_1\eta_1^0}\right)}$$
$$\times\ \epsilon^{-n/2}\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}})\ \exp\left(-\frac{\pi(c_2^2(y_2^{\mathcal{B}})^2+d_3^2)}{4b_1\eta_1^0}\right)$$
$$\times\ \exp\left(i\frac{\eta^{\mathcal{B}}\cdot y^{\mathcal{B}}}{\epsilon} - i\frac{|d_3|\,b\cdot y}{b_1\eta_1^0} + is\,b\cdot y + i\frac{\left(\eta(t)-\eta^{\mathcal{B}}(t)\right)\cdot y}{\epsilon}\right)$$
$$\times\ \exp\left(i\frac{S}{\epsilon^2} + i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2} + i\frac{b_1\eta_1^0 s^2}{2} + i\frac{d_3^2}{4b_1\eta_1^0} + i\frac{d_3^2}{2b_1\eta_1^0}\ \ln\left(\frac{4b_1^2{\eta_1^0}^2 s}{|d_3|\epsilon^2}\right)\right)$$

$$
\begin{aligned}
&\times\ \exp\left(-i\frac{|d_3|t}{\epsilon}\ +\ i\frac{b_1\eta_1^0}{\epsilon^2}t^2\ +\ i\frac{d_3^2}{2b_1\eta_1^0}\left[\frac{1}{2}\ +\ \ln\left(\frac{2b_1\eta_1^0 t}{|d_3|\epsilon}\right)\right]\right)\\
=\ & F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|)\ \sqrt{\frac{\pi}{2b_1\eta_1^0}}\ \ \frac{(1+i)(c_2y_2^{\mathcal{B}}-id_3)}{\Gamma\left(1+i\frac{(c_2^2(y_2^{\mathcal{B}})^2+d_3^2)}{2b_1\eta_1^0}\right)}\\
&\times\ \varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\ \exp\left(-\ \frac{\pi(c_2^2(y_2^{\mathcal{B}})^2+d_3^2)}{4b_1\eta_1^0}\right)\\
&\times\ \exp\left(i\frac{S}{\epsilon^2}\ +\ i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}\ +\ ib_1\eta_1^0 s^2\ -\ i\frac{|d_3|t}{\epsilon}\ +\ i\frac{d_3^2}{b_1\eta_1^0}\ln\,t\right)\\
&\times\ \exp\left(i\frac{d_3^2}{2b_1\eta_1^0}\ +\ i\frac{d_3^2}{2b_1\eta_1^0}\ln\left(\frac{8b_1^3{\eta_1^0}^3}{d_3^2}\right)\right)
\end{aligned}
$$

From corollary 2.3 we see that this approximately equals

$$
\begin{aligned}
&\exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}\ -\ i\frac{S_0^{\mathcal{B}}(\epsilon,+)}{\epsilon^2}\ +\ i\frac{d_3^2}{2b_1\eta_1^0}\ +\ i\frac{d_3^2}{2b_1\eta_1^0}\ln\left(\frac{8b_1^3{\eta_1^0}^3}{d_3^2}\right)\right)\\
&\times\ \sqrt{\frac{\pi}{2b_1\eta_1^0}}\ \ \frac{(1+i)(c_2y_2^{\mathcal{B}}-id_3)}{\Gamma\left(1+i\frac{(c_2^2(y_2^{\mathcal{B}})^2+d_3^2)}{2b_1\eta_1^0}\right)}\ \exp\left(-\ \frac{\pi(c_2^2(y_2^{\mathcal{B}})^2+d_3^2)}{4b_1\eta_1^0}\right)\\
&\times\ F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|)\ e^{iS^{\mathcal{B}}(t)/\epsilon^2}\ \varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x).
\end{aligned}
\tag{3.81}
$$

Here, the first line is simply a constant phase, and the product of the first two lines, which we call $G(y_2^{\mathcal{B}})$, is an entire function of $y_2^{\mathcal{B}}$. From the asymptotics of the Gamma and Polygamma functions [1], G and all its derivatives grow at worst polynomially for real $y_2^{\mathcal{B}}$. From this it follows that

$$
G(y_2^{\mathcal{B}})\ \varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)
$$

is a Schwartz function. It consequently [43] has a convergent series expansion of the form

$$
\begin{aligned}
&G(y_2^{\mathcal{B}})\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\\
=\ &\sum_m k_m^{\mathcal{B}}(t)\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x),
\end{aligned}
\tag{3.82}
$$

where the coefficients

$$
k_m^{\mathcal{B}}(t)\ =\ \langle\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}}),\ G(y_2^{\mathcal{B}})\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}})\rangle
$$

decay faster than any negative power of $|m|$ for each fixed t. The semiclassical wave packets $\varphi_j(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}})$ satisfy $i\frac{\partial\psi}{\partial t}\ =\ K(t)\,\psi$, where $K(t)$ is the operator $-\frac{1}{2}\,\Delta_{y^{\mathcal{B}}}\ +\ \frac{1}{2}\langle y^{\mathcal{B}},\ E_{\mathcal{B}}^{(2)}(a^{\mathcal{B}}(t))\,y^{\mathcal{B}}\rangle$. Using this, we compute the derivative of $k_m^{\mathcal{B}}(t)$,

$$
\begin{aligned}
&\frac{\partial k_m^{\mathcal{B}}}{\partial t}(t)\\
=\ & i\,\langle\,K(t)\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}}),\ G(y_2^{\mathcal{B}})\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}})\rangle\\
&-i\langle\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}}),\ G(y_2^{\mathcal{B}})\,K(t)\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),1,0,0,y^{\mathcal{B}})\rangle
\end{aligned}
$$

$$
\begin{aligned}
= \quad & -\langle\, \varphi_m(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), 1, 0, 0, y^{\mathcal{B}}),\ \frac{i}{2}\ \left(\Delta_{y^{\mathcal{B}}}\, G(y_2^{\mathcal{B}})\right)\ \varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), 1, 0, 0, y^{\mathcal{B}})\rangle \\
& -\langle\, \varphi_m(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), 1, 0, 0, y^{\mathcal{B}}),\ i\ \left(\nabla_{y^{\mathcal{B}}}\, G(y_2^{\mathcal{B}})\right) \cdot \nabla_{y^{\mathcal{B}}}\, \varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), 1, 0, 0, y^{\mathcal{B}})\rangle.
\end{aligned} \tag{3.83}
$$

The first inner product on the right hand side of (3.83) is bounded by $C_N(1+|m|)^{-N}$, where N is arbitrary and C_N can be chosen independent of t. The second inner product on the right hand side of (3.83) is bounded by $C_N\,|\ln(t/\epsilon)|(1+|m|)^{-N}$ where N is arbitrary and C_N can be chosen independent of t.

By integrating these estimates with respect to t, we see that $d_m^{\mathcal{B}} = \lim_{t\to 0} k_m^{\mathcal{B}}(t)$ exists and that the right hand side of (3.82) approximately equals

$$
\sum_m d_m^{\mathcal{B}}\, \varphi_m(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x).
$$

Since we are studying the second component of the inner solution, lemmas 3.1 and 3.2 now show that (3.81) matches the following approximate solution to the full Schrödinger equation.

$$
F(\epsilon^{\delta'}\|y^{\mathcal{B}}\|)\ e^{iS^{\mathcal{B}}(t)/\epsilon^2}\ \sum_m d_m^{\mathcal{B}}\, \varphi_m(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x)\ \Phi_{\mathcal{B}}^{+}(x, t, \epsilon).
$$

This is the second term of (3.73). □

Remarks.

1. Suppose one chooses $l=0$ so that the incoming outer nuclear wave packet is a Gaussian. Then the part of the outgoing outer solution that is associated with the $\mathcal{A}$ surface also has a Gaussian nuclear wave packet. The absolute square of the nuclear wave packet for the part associated with the $\mathcal{B}$ surface is the difference between two Gaussians. The infinite series expansion is required because the $G(y_2)$ factor gives rise to complicated phases.

2. Our calculations show that to leading order, the probability of an electronic transition from the $\mathcal{B}$ surface to the $\mathcal{A}$ surface is

$$
\begin{aligned}
P_{\mathcal{B}\to\mathcal{A}} \quad &\approx \quad \sum_{|m|\le|l|} \left|\tilde{d}_m^{\mathcal{A}}\right|^2 \ = \ \sum_{|m|\le|l|} \left|d_m^{\mathcal{A}}\right|^2 \\
&= \quad \int_{I\!R^n} |\varphi_l(A_0, B_0, 1, 0, 0, y)|^2\ e^{-\frac{\pi(c_2^2 y_2^2 + d_3^2)}{b_1 \eta_1^0}}\ dy.
\end{aligned}
$$

For the case $l=0$, we have the simple expression

$$
\tilde{d}_0^{\mathcal{A}} \quad = \quad \left[\frac{\det\ A_0}{\det\ A^{\mathcal{A}}(0)}\right]^{1/2}\ \exp\left(-\frac{\pi d_3^2}{2 b_1 \eta_1^0}\right).
$$

So, to leading order the transition probability is

$$
P_{\mathcal{B}\to\mathcal{A}} \quad \approx \quad \left[\frac{\det\ A_0}{\det\ A^{\mathcal{A}}(0)}\right]\ \exp\left(-\frac{\pi d_3^2}{b_1 \eta_1^0}\right).
$$

For codimension 2 crossings we obtain the same formula [17], except that d_3 is zero for codimension 2 crossings. Thus, the leading order transition probability depends algebraically on η_1^0 in the crossing case, but exponentially in the avoided crossing case. Although our error estimates are not uniform in η_1^0 as $\eta_1^0 \to 0$, this might provide a way to distinguish true crossings from avoided crossings.

We now summarize the main results of this section.

Theorem 3.1 *Let $h(x,\epsilon)$ be a hamiltonian such that $h_{||}(x,\epsilon)$ is characterized by (1.10), (1.11), and (1.33). Let $\psi(x,t)$ be a solution of the corresponding Schrödinger equation (1.29) such that*

$$\begin{aligned}\psi(x,-T) &= e^{iS^{\mathcal{B}}(-T)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(-T),B^{\mathcal{B}}(-T),\epsilon^2,a^{\mathcal{B}}(-T),\eta^{\mathcal{B}}(-T),x)\ \Phi^-_{\mathcal{B}}(x,-T,\epsilon)\\ &\quad +\ \mathcal{O}(\epsilon^q)\end{aligned}$$

for some positive q. Then, for any $0<\xi<1/3$, there exists a positive p such that in the limit $\epsilon\to 0$, we have

$$\psi(x,t) \;=\; e^{iS^{\mathcal{B}}(t)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\ \Phi^-_{\mathcal{B}}(x,t,\epsilon)\ +\ \mathcal{O}(\epsilon^p),$$

for $-T\le t\le -\epsilon^{1-\xi}$. For $-\epsilon^{1-\xi}\le t\le \epsilon^{1-\xi}$, we have

$$\psi(x,t) \;=\; e^{iS(t)/\epsilon^2+i\eta(t)(x-a(t))/\epsilon^2}\,\left(\,f_0(y,s)\,\psi_1(x,\epsilon)\ +\ g_0(y,s)\,\psi_2(x,\epsilon)\,\right)\ +\ \mathcal{O}(\epsilon^p),$$

where f_0 and g_0 are defined by (3.64), (3.66), and (3.68) with $y=(x-a(t))/\epsilon$ and $s=t/\epsilon$. Finally, for $\epsilon^{1-\xi}\le t\le T$,

$$\begin{aligned}\psi(x,t) &= e^{iS^{\mathcal{A}}(t)/\epsilon^2}\sum_{|m|\le|l|} d^{\mathcal{A}}_m\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\,\Phi^+_{\mathcal{A}}(x,t,\epsilon)\\ &\quad+\ e^{iS^{\mathcal{B}}(t)/\epsilon^2}\sum_{m} d^{\mathcal{B}}_m\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\,\Phi^+_{\mathcal{B}}(x,t,\epsilon)\\ &\quad+\ \mathcal{O}(\epsilon^p),\end{aligned}$$

where the $d^{\mathcal{A}}_m$ and $d^{\mathcal{B}}_m$ are specified in the proof of lemma 3.6.

4 Type 4, 5, and 6 Avoided Crossings

In this section we make precise statements of our results for Type 4, 5, and 6 Avoided Crossings. The proofs of these results are obtained by simply mimicking arguments from Section 3, so we do not present the details.

4.1 Type 4 Avoided Crossings

Since the matrix (1.15) is the direct sum of (1.11) and its conjugate, the only substantial difference between Type 3 Avoided Crossings and Type 4 Avoided Crossings is the degeneracy of the electronic states. For Type 4 Avoided Crossings, the following lemma plays the role of lemmas 3.1 and 3.2. The proof of this lemma is an extension of the proofs of lemmas 3.1 and 3.2. Similar arguments may also be found in Section 4.2 of [20].

Lemma 4.1 *Consider a system with a Type 4 Avoided Crossing. Suppose* $0 < \delta' < \xi < \frac{1}{3}$, $|t| > \epsilon^{1-\xi}$. *Define* $\mu(\epsilon, t) = \max\{\,|t|,\ \epsilon^{1-\delta'}/|t|\,\}$, *and let* $a^{\mathcal{C}}(t)$ *and* $\eta^{\mathcal{C}}(t)$ *solve equations (2.2) and (2.3). For* x *in the support of* $F(\|x - a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, *there exist orthonormal eigenvectors* $\Phi^{\pm}_{\mathcal{C},j}(x, t, \epsilon)$ *for* $\mathcal{C} = \mathcal{A},\ \mathcal{B},\ t \gtrless 0$, *and* $j = 1,\ 2$, *that correspond to* $E_{\mathcal{C}}(x,\ \epsilon)$ *and solve*

$$\langle \Phi^{\pm}_{\mathcal{C},j}(x, t, \epsilon),\ \left(\partial/\partial t + \eta^{\mathcal{C}}(t)\cdot\nabla\right)\Phi^{\pm}_{\mathcal{C},k}(x, t, \epsilon)\rangle \equiv 0 \qquad (j,\ k\ =\ 1,\ 2). \tag{4.1}$$

If in addition, $|t| < \epsilon^{\kappa}$ *for some* $\kappa > \frac{1}{2}$, *then for* $t < 0$,

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

and for $t > 0$,

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

Our main result for Type 4 Avoided Crossings is the following:

Theorem 4.1 *Let* $h(x, \epsilon)$ *be a hamiltonian such that* $h_{\|}(x, \epsilon)$ *is characterized by (1.14), (1.15), and (1.33). Let* $a^{\mathcal{C}}(t)$, $\eta^{\mathcal{C}}$, $A^{\mathcal{C}}$, $B^{\mathcal{C}}$, *and* $S^{\mathcal{C}}$ *be defined as in Section 2. For* $j = 1,\ 2$, *let* $\psi_j(x, t)$ *be a solution of the Schrödinger equation (1.29) such that*

$$\begin{aligned}
\psi_j(x, -T) \;=\;& e^{iS^{\mathcal{B}}(-T)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(-T), B^{\mathcal{B}}(-T), \epsilon^2, a^{\mathcal{B}}(-T), \eta^{\mathcal{B}}(-T), x)\ \Phi^{-}_{\mathcal{B},j}(x, -T, \epsilon)\\
&+\ \mathcal{O}(\epsilon^q)
\end{aligned}$$

for some positive q. *Then, for any* $0 < \xi < 1/3$, *there exists a positive* p *such that in the limit* $\epsilon \to 0$, *we have*

$$\psi_j(x, t) \;=\; e^{iS^{\mathcal{B}}(t)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x)\ \Phi^{-}_{\mathcal{B},j}(x, t, \epsilon)\ +\ \mathcal{O}(\epsilon^p),$$

for $-T \le t \le -\epsilon^{1-\xi}$. *For* $-\epsilon^{1-\xi} \le t \le \epsilon^{1-\xi}$, *in the basis* $\{\,\psi_1(x, \epsilon),\ \cdots,\ \psi_4(x, \epsilon)\,\}$, *we have*

$$\begin{aligned}
\psi_1(x, t) \;=\;& e^{iS(t)/\epsilon^2 + i\eta(t)(x-a(t))/\epsilon^2}\ C_2(y)\\
&\times \begin{pmatrix} D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right)\\[1ex] \frac{(-1-i)(c_2 y_2 - i d_3)}{2\sqrt{b_1\eta_1^0}}\, D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right)\\[1ex] 0\\ 0 \end{pmatrix}\\
&+\ \mathcal{O}(\epsilon^p)\,,
\end{aligned}$$

and

$$
\begin{aligned}
\psi_2(x,t) &= e^{iS(t)/\epsilon^2 + i\eta(t)(x-a(t))/\epsilon^2}\, C_2(y) \\
&\quad \times \begin{pmatrix} 0 \\ 0 \\ D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \\ \frac{(-1-i)(c_2 y_2 + i d_3)}{2\sqrt{b_1\eta_1^0}} D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1 y_1 + b_2 y_2)\right) \end{pmatrix} \\
&\quad + \mathcal{O}(\epsilon^p)\,,
\end{aligned}
$$

where C_2 is defined by (3.68), $p_l = -i\frac{c_2^2 y_2^2 + d_3^2}{2b_1\eta_1^0}$, $y = (x-a(t))/\epsilon$, and $s = t/\epsilon$. Finally, for $\epsilon^{1-\xi} \le t \le T$,

$$
\begin{aligned}
\psi_j(x,t) &= e^{iS^{\mathcal{A}}(t)/\epsilon^2} \sum_{|m|\le|l|} d^{\mathcal{A}}_{m,j}\, \varphi_m(A^{\mathcal{A}}(t), B^{\mathcal{A}}(t), \epsilon^2, a^{\mathcal{A}}(t), \eta^{\mathcal{A}}(t), x)\, \Phi^+_{\mathcal{A},j}(x,t,\epsilon) \\
&\quad + e^{iS^{\mathcal{B}}(t)/\epsilon^2} \sum_{m} d^{\mathcal{B}}_{m,j}\, \varphi_m(A^{\mathcal{B}}(t), B^{\mathcal{B}}(t), \epsilon^2, a^{\mathcal{B}}(t), \eta^{\mathcal{B}}(t), x)\, \Phi^+_{\mathcal{B},j}(x,t,\epsilon) \\
&\quad + \mathcal{O}(\epsilon^p),
\end{aligned}
$$

where the $d^{\mathcal{A}}_{m,j}$ and $d^{\mathcal{B}}_{m,j}$ are computed by the process used in the proof of lemma 3.6.

4.2 Type 5 Avoided Crossings

Type 5 Avoided Crossings have more complicated electronic structure, so we present a few more of the details. To specify the static eigenvectors analogous to those in lemma 3.1, we define a coordinate system by the following relations, with $0 \le r$, $0 \le \theta < \pi$, $0 \le \phi < \frac{\pi}{2}$, and $0 \le \mu < 2\pi$:

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

where $\beta(x,\epsilon)$, $\gamma(x,\epsilon)$, $\delta(x,\epsilon)$, and $\zeta(x,\epsilon)$ are given by (1.37). The static eigenvectors are then given by

$$
\begin{aligned}
\Phi^-_{\mathcal{A},1}(x,\epsilon) &= \begin{pmatrix} \cos\,\frac{\theta}{2}\,\cos\,\phi \\ e^{-i\mu}\,\cos\,\frac{\theta}{2}\,\sin\,\phi \\ 0 \\ \sin\,\frac{\theta}{2} \end{pmatrix}, \\
\Phi^-_{\mathcal{A},2}(x,\epsilon) &= \begin{pmatrix} -e^{i\mu}\,\cos\,\frac{\theta}{2}\,\sin\,\phi \\ \cos\,\frac{\theta}{2}\,\cos\,\phi \\ -\sin\,\frac{\theta}{2} \\ 0 \end{pmatrix},
\end{aligned}
$$

$$\Phi^-_{\mathcal{B},1}(x,\epsilon) \;=\; \begin{pmatrix} -\sin\frac{\theta}{2} \\ 0 \\ e^{-i\mu}\cos\frac{\theta}{2}\sin\phi \\ \cos\frac{\theta}{2}\cos\phi \end{pmatrix},$$

$$\Phi^-_{\mathcal{B},2}(x,\epsilon) \;=\; \begin{pmatrix} 0 \\ -\sin\frac{\theta}{2} \\ -\cos\frac{\theta}{2}\cos\phi \\ e^{i\mu}\cos\frac{\theta}{2}\sin\phi \end{pmatrix},$$

for $\pi/2 < \theta \leq \pi$, and

$$\Phi^+_{\mathcal{A},1}(x,\epsilon) \;=\; \begin{pmatrix} \cos\frac{\theta}{2} \\ 0 \\ e^{-i\mu}\sin\frac{\theta}{2}\sin\phi \\ \sin\frac{\theta}{2}\cos\phi \end{pmatrix},$$

$$\Phi^+_{\mathcal{A},2}(x,\epsilon) \;=\; \begin{pmatrix} 0 \\ \cos\frac{\theta}{2} \\ -\sin\frac{\theta}{2}\cos\phi \\ e^{i\mu}\sin\frac{\theta}{2}\sin\phi \end{pmatrix},$$

$$\Phi^+_{\mathcal{B},1}(x,\epsilon) \;=\; \begin{pmatrix} -e^{i\mu}\sin\frac{\theta}{2}\sin\phi \\ \sin\frac{\theta}{2}\cos\phi \\ \cos\frac{\theta}{2} \\ 0 \end{pmatrix},$$

$$\Phi^+_{\mathcal{B},2}(x,\epsilon) \;=\; \begin{pmatrix} -\sin\frac{\theta}{2}\cos\phi \\ -e^{-i\mu}\sin\frac{\theta}{2}\sin\phi \\ 0 \\ \cos\frac{\theta}{2} \end{pmatrix},$$

for $0 \leq \theta < \pi/2$.
Using these definitions and mimicking the proofs of lemmas 3.1 and 3.2, we have the following analog of lemma 4.1:

Lemma 4.2 *Consider a system with a Type 5 Avoided Crossing. Suppose* $0 < \delta' < \xi < \frac{1}{3}$, $|t| > \epsilon^{1-\xi}$. *Define* $\mu(\epsilon,t) = \max\{\,|t|,\ \epsilon^{1-\delta'}/|t|\,\}$, *and let* $a^{\mathcal{C}}(t)$ *and* $\eta^{\mathcal{C}}(t)$ *solve equations (2.2) and (2.3). For* x *in the support of* $F(\|x-a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, *there exist orthonormal eigenvectors* $\Phi^{\pm}_{\mathcal{C},j}(x,t,\epsilon)$ *for* $\mathcal{C} = \mathcal{A},\ \mathcal{B}$, $t \gtrless 0$, *and* $j = 1,\ 2$, *that correspond to* $E_{\mathcal{C}}(x,\ \epsilon)$ *and solve (4.1). If in addition,* $|t| < \epsilon^{\kappa}$ *for some* $\kappa > \frac{1}{2}$, *then for* $t < 0$,

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

and for $t > 0$,

$$\Phi^+_{\mathcal{A},1}(x,t,\epsilon) = \psi_1(x,\epsilon) + \mathcal{O}(\mu(\epsilon,t)),$$

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

Our main result for Type 5 Avoided Crossings is the following:

Theorem 4.2 *Let $h(x,\epsilon)$ be a hamiltonian such that $h_{||}(x,\epsilon)$ is characterized by (1.14), (1.19), and (1.37). Let $a^{\mathcal{C}}(t)$, $\eta^{\mathcal{C}}$, $A^{\mathcal{C}}$, $B^{\mathcal{C}}$, and $S^{\mathcal{C}}$ be the quantities from Section 2.7 appropriate for Type 5 Avoided Crossings. For $j=1,\,2$, let $\psi_j(x,t)$ be a solution of the Schrödinger equation (1.29) such that*

$$
\begin{aligned}
\psi_j(x,-T) &= e^{iS^{\mathcal{B}}(-T)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(-T),B^{\mathcal{B}}(-T),\epsilon^2,a^{\mathcal{B}}(-T),\eta^{\mathcal{B}}(-T),x)\ \Phi^-_{\mathcal{B},j}(x,-T,\epsilon)\\
&\quad +\ \mathcal{O}(\epsilon^q)
\end{aligned}
$$

for some positive q. Then, for any $0<\xi<1/3$, there exists a positive p such that in the limit $\epsilon\to 0$, we have

$$
\psi_j(x,t) = e^{iS^{\mathcal{B}}(t)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\ \Phi^-_{\mathcal{B},j}(x,t,\epsilon)\ +\ \mathcal{O}(\epsilon^p),
$$

for $-T\le t\le -\epsilon^{1-\xi}$. For $-\epsilon^{1-\xi}\le t\le \epsilon^{1-\xi}$, in the basis $\{\,\psi_1(x,\epsilon),\,\cdots,\,\psi_4(x,\epsilon)\,\}$, we have

$$
\begin{aligned}
\psi_1(x,t) &= e^{iS(t)/\epsilon^2+i\eta(t)(x-a(t))/\epsilon^2}\ C_2(y)\\
&\quad\times\begin{pmatrix}
D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b\cdot y)\right)\\
0\\
\frac{(-1-i)(c_2y_2-id_3y_3)}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b\cdot y)\right)\\
\frac{(-1-i)e_4}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b\cdot y)\right)
\end{pmatrix}\\
&\quad+\ \mathcal{O}(\epsilon^p)\,,
\end{aligned}
$$

and

$$
\begin{aligned}
\psi_2(x,t) &= e^{iS(t)/\epsilon^2+i\eta(t)(x-a(t))/\epsilon^2}\ C_2(y)\\
&\quad\times\begin{pmatrix}
0\\
D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b\cdot y)\right)\\
\frac{(1+i)e_4}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b\cdot y)\right)\\
\frac{(-1-i)(c_2y_2+id_3y_3)}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s+b_1y_1+b_2y_2)\right)
\end{pmatrix}\\
&\quad+\ \mathcal{O}(\epsilon^p)\,,
\end{aligned}
$$

where $C_2(y)$ is defined by

$$\begin{aligned}
C_2(y) &= -\,\epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\,\exp\left(\frac{-\pi(c_2^2y_2^2+d_3^2y_3^2+e_4^2)}{8b_1\eta_1^0}\right)\\
&\times\ \exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}-i\frac{e_4^2}{b_1\eta_1^0}\ \ln\,\epsilon\,+i\frac{e_4^2}{4b_1\eta_1^0}-i\frac{e_4^2}{2b_1\eta_1^0}\ \ln\,|e_4|\,+i\frac{3e_4^2}{4b_1\eta_1^0}\ \ln\,(2b_1\eta_1^0)\right)\\
&\times\ \exp\left(-i\frac{c_2^2y_2^2+d_3^2y_3^2}{4b_1\eta_1^0}\ \ln\,(2b_1\eta_1^0)+i\frac{c_2^2y_2^2+d_3^2y_3^2}{2b_1\eta_1^0}\ \ln\,|e_4|\,-i\frac{|e_4|b\cdot y}{b_1\eta_1^0}\right),
\end{aligned}$$

$p_l\ =\ -\,i\frac{c_2^2y_2^2+d_3^2y_3^2+e_4^2}{2b_1\eta_1^0}$, *$y=(x-a(t))/\epsilon$, and $s=t/\epsilon$. Finally, for $\epsilon^{1-\xi}\le t\le T$,*

$$\begin{aligned}
\psi_j(x,t) &= e^{iS^{\mathcal{A}}(t)/\epsilon^2}\sum_{|m|\le|l|} d_{m,j}^{\mathcal{A}}\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\,\Phi_{\mathcal{A},j}^{+}(x,t,\epsilon)\\
&+\ e^{iS^{\mathcal{B}}(t)/\epsilon^2}\sum_{m} d_{m,j}^{\mathcal{B},1}\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\,\Phi_{\mathcal{B},1}^{+}(x,t,\epsilon)\\
&+\ e^{iS^{\mathcal{B}}(t)/\epsilon^2}\sum_{m} d_{m,j}^{\mathcal{B},2}\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\,\Phi_{\mathcal{B},2}^{+}(x,t,\epsilon)\\
&+\ \mathcal{O}(\epsilon^p),
\end{aligned}$$

where the $d_{m,j}^{\mathcal{A}}$ and $d_{m,j}^{\mathcal{B},k}$ are computed by the process used in the proof of lemma 3.6. The initial conditions for the semiclassical quantities in the expression for $\psi_j(x,t)$ for $t\ge\epsilon^{1-\xi}$ are the analogs of formulas (3.71) and (3.72) after one has taken into account the appropriate alterations from section 2.7.

4.3 Type 6 Avoided Crossings

Type 6 Avoided Crossings have even more complicated electronic structure. To specify the static eigenvectors analogous to those in lemma 3.1, we define a coordinate system by the following relations, with $0\le r$, $0\le\theta<\pi$, $0\le\phi<\frac{\pi}{2}$, $0\le\mu<2\pi$, and $0\le\omega<2\pi$:

$$\begin{aligned}
r &= \sqrt{\beta(x,\epsilon)^2+\gamma(x,\epsilon)^2+\delta(x,\epsilon)^2+\zeta(x,\epsilon)^2+\xi(x,\epsilon)^2},\\
\beta(x,\epsilon) &= r\,\cos\,\theta,\\
\gamma(x,\epsilon) &= r\,\sin\,\theta\,\sin\,\phi\,\cos\,\mu,\\
\delta(x,\epsilon) &= r\,\sin\,\theta\,\sin\,\phi\,\sin\,\mu,\\
\zeta(x,\epsilon) &= r\,\sin\,\theta\,\cos\,\phi\,\cos\,\omega,\\
\xi(x,\epsilon) &= r\,\sin\,\theta\,\cos\,\phi\,\sin\,\omega,
\end{aligned}$$

where $\beta(x,\epsilon)$, $\gamma(x,\epsilon)$, $\delta(x,\epsilon)$, $\zeta(x,\epsilon)$, and $\xi(x,\epsilon)$ are given by (1.40). The static eigenvectors are then given by

$$\Phi_{\mathcal{A},1}^{-}(x,\epsilon)\ =\ \begin{pmatrix} e^{i\omega}\,\cos\,\frac{\theta}{2}\,\cos\,\phi\\ e^{-i\mu}\,\cos\,\frac{\theta}{2}\,\sin\,\phi\\ 0\\ \sin\,\frac{\theta}{2}\end{pmatrix},$$

$$\Phi^-_{\mathcal{A},2}(x,\epsilon) \;=\; \begin{pmatrix} -e^{i\mu}\cos\frac{\theta}{2}\sin\phi \\ e^{-i\omega}\cos\frac{\theta}{2}\cos\phi \\ -\sin\frac{\theta}{2} \\ 0 \end{pmatrix},$$

$$\Phi^-_{\mathcal{B},1}(x,\epsilon) \;=\; \begin{pmatrix} -\sin\frac{\theta}{2} \\ 0 \\ e^{-i\mu}\cos\frac{\theta}{2}\sin\phi \\ e^{-i\omega}\cos\frac{\theta}{2}\cos\phi \end{pmatrix},$$

$$\Phi^-_{\mathcal{B},2}(x,\epsilon) \;=\; \begin{pmatrix} 0 \\ -\sin\frac{\theta}{2} \\ -e^{i\omega}\cos\frac{\theta}{2}\cos\phi \\ e^{i\mu}\cos\frac{\theta}{2}\sin\phi \end{pmatrix},$$

for $\pi/2 < \theta \leq \pi$, and

$$\Phi^+_{\mathcal{A},1}(x,\epsilon) \;=\; \begin{pmatrix} \cos\frac{\theta}{2} \\ 0 \\ e^{-i\mu}\sin\frac{\theta}{2}\sin\phi \\ e^{-i\omega}\sin\frac{\theta}{2}\cos\phi \end{pmatrix},$$

$$\Phi^+_{\mathcal{A},2}(x,\epsilon) \;=\; \begin{pmatrix} 0 \\ \cos\frac{\theta}{2} \\ -e^{i\omega}\sin\frac{\theta}{2}\cos\phi \\ e^{i\mu}\sin\frac{\theta}{2}\sin\phi \end{pmatrix},$$

$$\Phi^+_{\mathcal{B},1}(x,\epsilon) \;=\; \begin{pmatrix} -e^{i\mu}\sin\frac{\theta}{2}\sin\phi \\ e^{-i\omega}\sin\frac{\theta}{2}\cos\phi \\ \cos\frac{\theta}{2} \\ 0 \end{pmatrix},$$

$$\Phi^+_{\mathcal{B},2}(x,\epsilon) \;=\; \begin{pmatrix} -e^{i\omega}\sin\frac{\theta}{2}\cos\phi \\ -e^{-i\mu}\sin\frac{\theta}{2}\sin\phi \\ 0 \\ \cos\frac{\theta}{2} \end{pmatrix},$$

for $0 \leq \theta < \pi/2$.

Using these definitions and mimicking the proofs of lemmas 3.1 and 3.2, we have the following analog of lemma 4.1:

Lemma 4.3 *Consider a system with a Type 6 Avoided Crossing. Suppose* $0 < \delta' < \xi < \frac{1}{3}$, $|t| > \epsilon^{1-\xi}$. *Define* $\mu(\epsilon,t) = \max\{\,|t|,\ \epsilon^{1-\delta'}/|t|\,\}$, *and let* $a^{\mathcal{C}}(t)$ *and* $\eta^{\mathcal{C}}(t)$ *solve equations (2.2) and (2.3). For* x *in the support of* $F(\|x-a^{\mathcal{C}}(t)\|/\epsilon^{1-\delta'})$, *there exist orthonormal eigenvectors* $\Phi^{\pm}_{\mathcal{C},j}(x,t,\epsilon)$ *for* $\mathcal{C} = \mathcal{A},\ \mathcal{B}$, $t \gtrless 0$, *and* $j = 1,\ 2$, *that correspond to* $E_{\mathcal{C}}(x,\ \epsilon)$ *and solve (4.1). If in addition,* $|t| < \epsilon^{\kappa}$ *for some* $\kappa > \frac{1}{2}$, *then for* $t < 0$,

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

and for $t > 0$,

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

Our main result for Type 6 Avoided Crossings is the following:

Theorem 4.3 *Let* $h(x,\epsilon)$ *be a hamiltonian such that* $h_{||}(x,\epsilon)$ *is characterized by (1.14), (1.22), and (1.40). Let* $a^{\mathcal{C}}(t)$, $\eta^{\mathcal{C}}$, $A^{\mathcal{C}}$, $B^{\mathcal{C}}$, *and* $S^{\mathcal{C}}$ *be the quantities from Section 2.7 appropriate for Type 6 Avoided Crossings. For* $j = 1,\ 2$, *let* $\psi_j(x,t)$ *be a solution of the Schrödinger equation (1.29) such that*

$$\begin{aligned}
\psi_j(x,-T) &= e^{iS^{\mathcal{B}}(-T)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(-T),B^{\mathcal{B}}(-T),\epsilon^2,a^{\mathcal{B}}(-T),\eta^{\mathcal{B}}(-T),x)\ \Phi^-_{\mathcal{B},j}(x,-T,\epsilon)\\
&\quad +\ \mathcal{O}(\epsilon^q)
\end{aligned}$$

for some positive q. *Then, for any* $0 < \xi < 1/3$, *there exists a positive* p *such that in the limit* $\epsilon \to 0$, *we have*

$$\psi_j(x,t) = e^{iS^{\mathcal{B}}(t)/\epsilon^2}\,\varphi_l(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\ \Phi^-_{\mathcal{B},j}(x,t,\epsilon)\ +\ \mathcal{O}(\epsilon^p),$$

for $-T \le t \le -\epsilon^{1-\xi}$. *For* $-\epsilon^{1-\xi} \le t \le \epsilon^{1-\xi}$, *in the basis* $\{\,\psi_1(x,\epsilon),\ \cdots,\ \psi_4(x,\epsilon)\,\}$, *we have*

$$\begin{aligned}
\psi_1(x,t) &= e^{iS(t)/\epsilon^2+i\eta(t)(x-a(t))/\epsilon^2}\ C_2(y)\\
&\quad\times\begin{pmatrix}
D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b\cdot y)\right)\\
0\\
\frac{(-1-i)(c_2y_2-id_3y_3)}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b\cdot y)\right)\\
\frac{(-1-i)(e_4y_4-if_5)}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b\cdot y)\right)
\end{pmatrix}\\
&\quad+\ \mathcal{O}(\epsilon^p)\,,
\end{aligned}$$

and

$$\begin{aligned}
\psi_2(x,t) &= e^{iS(t)/\epsilon^2+i\eta(t)(x-a(t))/\epsilon^2}\ C_2(y)\\
&\quad\times\begin{pmatrix}
0\\
D_{p_l}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b\cdot y)\right)\\
\frac{(1+i)(e_4y_4+if_5)}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b\cdot y)\right)\\
\frac{(-1-i)(c_2y_2+id_3y_3)}{2\sqrt{b_1\eta_1^0}}D_{p_l-1}\left(\frac{(-1-i)}{\sqrt{b_1\eta_1^0}}(b_1\eta_1^0 s + b_1y_1+b_2y_2)\right)
\end{pmatrix}\\
&\quad+\ \mathcal{O}(\epsilon^p)\,,
\end{aligned}$$

where C_2 *is defined by*

$$
\begin{aligned}
&C_2(y)\\
=\;& -\,\epsilon^{-n/2}\,\varphi_l(A_0,B_0,1,0,0,y)\,\exp\left(\frac{-\pi(c_2^2y_2^2+d_3^2y_3^2+e_4^2y_4^2+f_5^2)}{8b_1\eta_1^0}\right)\\
&\times\;\exp\left(i\frac{S_0^{\mathcal{B}}(\epsilon,-)}{\epsilon^2}-i\frac{f_5^2}{b_1\eta_1^0}\ \ln\,\epsilon\,+i\frac{f_5^2}{4b_1\eta_1^0}-i\frac{f_5^2}{2b_1\eta_1^0}\ \ln\,|f_5|\,+i\frac{3f_5^2}{4b_1\eta_1^0}\ \ln\,(2b_1\eta_1^0)\right)\\
&\times\;\exp\left(-i\frac{c_2^2y_2^2+d_3^2y_3^2+e_4^2y_4^2}{4b_1\eta_1^0}\ \ln\,(2b_1\eta_1^0)+i\frac{c_2^2y_2^2+d_3^2y_3^2+e_4^2y_4^2}{2b_1\eta_1^0}\ \ln\,|f_5|\,-i\frac{|f_5|b\cdot y}{b_1\eta_1^0}\right),
\end{aligned}
$$

$p_l\;=\;-\,i\frac{c_2^2y_2^2+d_3^2y_3^2+e_4^2y_4^2+f_5^2}{2b_1\eta_1^0}$, $y=(x-a(t))/\epsilon$, *and* $s=t/\epsilon$. *Finally, for* $\epsilon^{1-\xi}\le t\le T$,

$$
\begin{aligned}
\psi_j(x,t)\;=\;& e^{iS^{\mathcal{A}}(t)/\epsilon^2}\sum_{|m|\le|l|}d_{m,j}^{\mathcal{A}}\,\varphi_m(A^{\mathcal{A}}(t),B^{\mathcal{A}}(t),\epsilon^2,a^{\mathcal{A}}(t),\eta^{\mathcal{A}}(t),x)\,\Phi_{\mathcal{A},j}^{+}(x,t,\epsilon)\\
&+\;e^{iS^{\mathcal{B}}(t)/\epsilon^2}\sum_{m}d_{m,j}^{\mathcal{B},1}\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\,\Phi_{\mathcal{B},1}^{+}(x,t,\epsilon)\\
&+\;e^{iS^{\mathcal{B}}(t)/\epsilon^2}\sum_{m}d_{m,j}^{\mathcal{B},2}\,\varphi_m(A^{\mathcal{B}}(t),B^{\mathcal{B}}(t),\epsilon^2,a^{\mathcal{B}}(t),\eta^{\mathcal{B}}(t),x)\,\Phi_{\mathcal{B},2}^{+}(x,t,\epsilon)\\
&+\;\mathcal{O}(\epsilon^p),
\end{aligned}
$$

where the $d_{m,j}^{\mathcal{A}}$ *and* $d_{m,j}^{\mathcal{B},k}$ *are computed by the process used in the proof of lemma 3.6. The initial conditions for the semiclassical quantities in the expression for* $\psi_j(x,t)$ *for* $t\ge\epsilon^{1-\xi}$ *are the analogs of formulas (3.71) and (3.72) after one has taken into account the appropriate alterations from section 2.7.*

References

[1] Abromowitz, M. and Stegun, I. A.: *Handbook of Mathematical Functions.* New York: Dover 1968.

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

[3] 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.

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

[5] 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.

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

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

[8] 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).

[9] 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).

[10] 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).

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

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

[13] 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.

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

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

[16] 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.

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

[18] Hagedorn, G. A.: Effects of Electron Energy Level Crossings on Molecular Propagation. *Differential Equations and Mathematical Physics. Proceedings of the International Conference. University of Alabama at Birmingham March 13–17, 1994.* ed. by I. Knowles, 85–95, 1995.

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

[20] Hagedorn, G. A., and Joye, A.: Landau–Zener Transitions through Small Electronic Gaps in the Born–Oppenheimer Approximation. Preprint, Virginia Polytechnic Institute and State University.

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

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

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

[24] Joye, A.: Exponential Asymptotics in a Singular Limit for n-Level Scattering Systems. Preprint CNRS Marseille CPT–95/P.3216, *SIAM J. Math. Anal.* (to appear).

[25] 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).

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

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

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

[29] 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).

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

[31] 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).

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

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

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

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

[36] 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).

[37] 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.

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

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

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

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

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

[43] Reed, M. and Simon, B.: *Methods of Modern Mathematical Physics I: Functional Analysis.* New York, London: Academic Press 1972.