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Electron energy level crossings in the time-dependent Born-Oppenheimer approximation

George A. Hagedorn*
Department of Mathematics and Center for Transport Theory and Mathematical Physics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0123, USA

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Summary. We summarize the results of a mathematical study of the time-dependent Born-Oppenheimer approximation near crossings of two non-degenerate electron energy surfaces. We illustrate our techniques by relatively simple examples that contain the essential ingredients of the general cases. We discuss all generic types of crossings of two non-degenerate electron energy surfaces.

Key words: Born-Oppenheimer approximation – Level crossings – Adiabatic approximation – Semiclassical approximation

1. Introduction

The familiar time-dependent Born-Oppenheimer approximation provides a useful description of molecular dynamics. One chooses a simple isolated electron energy surface and propagates the nuclei semiclassically in the effective potential generated by this surface. The electronic wave function propagates with an adiabatic dependence on the nuclear configurations.

This approximation breaks down as the nuclei approach a configuration at which the chosen electron energy surface fails to remain isolated from the rest of the electronic energy spectrum. The simplest way this can happen is if two such electron energy surfaces cross one another. In this paper we discuss how the approximation can be adapted to accommodate such crossings.

We have mathematical proofs that in the large nuclear mass limit, our approximations are asymptotic to solutions to the full Schrödinger equation in very general situations. These proofs are technically very complicated, and the

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technicalities obscure the basic ideas that are involved. We plan to publish them in the mathematical physics literature.

The goal of the present paper is to present the basic ideas with as little technical complication as possible. For this reason, we analyze specific simple examples, rather than study the general cases. These examples have been chosen to illustrate all the principal ideas without burdening the reader with lengthy calculations.

In all of our examples, the electronic Hilbert space is two dimensional, and the electronic Hamiltonians are 2×2 matrices. To the order of approximation that we calculate, the behavior produced in these examples is the same as that produced in the infinite dimensional case with Hamiltonians that are differential operators. In the general case, there are adiabatic corrections that involve states other than the two whose energies cross. As in general adiabatic situations [1, 2], these corrections give rise to terms that are of second order in the expansion parameter we use. The terms we present in this paper are of at most first order. Thus, the relevance of our results to interesting systems is not affected by the non-existence of general diabatic bases [3–6].

In the general case of the crossing of two non-degenerate electronic states $\Phi_{\mathscr{A}}(x)$ and $\Phi_{\mathscr{B}}(x)$, the eigenvectors may be discontinuous near the crossing. However, one can always choose two orthonormal vectors $\Phi_1(x)$ and $\Phi_2(x)$ that depend smoothly on the nuclear configuration x, and that span the same subspace as the pair $\Phi_{\mathscr{A}}(x)$ and $\Phi_{\mathscr{B}}(x)$. As a consequence of the adiabatic aspects of the problem indicated in the previous paragraph, the first order Born-Oppenheimer approximation depends only on the following four matrix elements of the electron Hamiltonian:

$$\begin{array}{ll} \langle \Phi_1(x), h(x)\Phi_1(x)\rangle & \langle \Phi_1(x), h(x)\Phi_2(x)\rangle \\ \langle \Phi_2(x), h(x)\Phi_1(x)\rangle & \langle \Phi_2(x), h(x)\Phi_2(x)\rangle. \end{array}$$

The other matrix elements are only relevant in the higher orders of approximation.

The wave functions we study are all highly localized in the nuclear configuration space near some classical path $a(t)$. As a result of this localization, the standard time-dependent Born-Oppenheimer approximation is valid unless $a(t)$ is very close to the crossing configuration (the larger the nuclear masses, the closer $a(t)$ can get before the standard approximation breaks down). For our low order Born-Oppenheimer results, when $a(t)$ is near a general crossing, one may approximate the four matrix elements by their first order Taylor series approximations. The higher order Taylor series terms for the matrix elements do not affect the low order Born-Oppenheimer propagation. Thus, for a low order Born-Oppenheimer approximation, the critical aspects of a level crossing (even in the realistic infinite dimensional case) are determined by the first order Taylor series approximations to the four relevant electron Hamiltonian matrix elements.

The examples presented in this paper give rise to the same crossing phenomena as the general cases, because their first order Taylor series coefficients at the crossing are representative of the generic cases. What happens at a crossing depends on the local behavior of the four electron Hamiltonian matrix elements, and our examples contain generic local behavior.

The initial states we have chosen in this paper all are standard time-dependent Born-Oppenheimer states that are associated with one arbitrary non-degenerate electron energy surface. They have Gaussian dependence on the nuclear configurations. Our techniques apply if the Gaussian $\phi_0(A, B, \epsilon^2, a, \eta, x)$ is replaced by any of the functions $\phi_k(A, B, \epsilon^2, a, \eta, x)$ of Sect. 2. Since the Schrödinger equation is linear, the superposition principle holds and one may take finite linear combinations of the resulting approximate solutions. However, the error estimates are not uniform in the multi-index k, and we have proved our results only for initial conditions that are finite linear combinations of the ϕ_k. One should be warned that the different initial conditions give rise to different probabilities for the final state to end up on one or the other electron energy surfaces. The probabilities reported in Sects. 4 and 5 are valid only for the specific initial states we have chosen. To compute what happens for the other initial states, one must go through the procedure that we outline in Sects. 3–5 for the specific state of interest. The calculations are straightforward, but messy and lengthy.

For electron Hamiltonians with analytic dependence on the nuclear configurations, there are four generic types of electronic energy level crossings. The various types arise from different symmetry situations [7, 8]. In this paper, we discuss three of these situations. The case we omit concerns Hamiltonians that commute with an anti-unitary operator whose square is -1. In systems with non-trivial spin effects, but no external magnetic fields, the time reversal operator is such an anti-unitary operator if the number of electrons is odd. In such systems all states are degenerate, and one expects non-trivial dynamical considerations to play a role, even away from a crossing [9]. Molecules with an odd number of electrons exhibit this Kramer's degeneracy [7].

The three types we study give rise to dramatically different phenomena as the nuclear configurations go through the crossing. It is convenient to label the three types of crossings by the codimensions of the submanifolds on which the two electron energy surfaces are in contact with one another. The codimension reflects the number of nuclear coordinates that typically must be adjusted in order to reach the crossing. The cases we study have codimensions 1, 2, and 3. In the Kramer's doublet situation that we do not study, generic crossings have codimension five [7–9].

Codimension 1 crossings are the most elementary. They generically do not occur unless the electron Hamiltonian has a symmetry and the two surfaces involved in the crossing are associated with different symmetry classes. In this case, the electron energies and electron wave functions can be chosen to be analytic functions of the nuclear configurations. Except in degenerate situations, the separation between the two electron energy surfaces vanishes linearly as nuclear configurations approach the crossing.

To illustrate our techniques for a codimension 1 crossing, we have chosen the following example: The electron Hilbert space is the two dimensional complex space $\mathbb{C}^2$, and the nuclear configurations are described by a single real parameter, $x \in \mathbb{R}$. The electron Hamiltonian is

$$h_1(x) = \begin{bmatrix} -x \sin^2(x) & x \sin(x) \cos(x) \\ x \sin(x) \cos(x) & -x \cos^2(x) \end{bmatrix}. \tag{1.1}$$

The electron energy levels are $E_{\mathscr{A}}(x) = 0$ and $E_{\mathscr{B}}(x) = -x$. The corresponding eigenvectors are

$$\Phi_{\mathscr{A}}(x) = \begin{pmatrix} \cos(x) \\ \sin(x) \end{pmatrix}, \quad \text{and} \quad \Phi_{\mathscr{B}}(x) = \begin{pmatrix} -\sin(x) \\ \cos(x) \end{pmatrix}.$$

If the nuclear mass is ϵ^{-4}, then the relevant Schrödinger equation is

$$i\epsilon^2 \frac{\partial \psi}{\partial t} = -\frac{\epsilon^4}{2} \frac{\partial^2 \psi}{\partial x^2} + h_1(x)\psi, \tag{1.2}$$

where $\psi(x, t)$ has two components. One should note that the time scale has been chosen as in the usual time-dependent Born-Oppenheimer approximation [10], so that the nuclear motion has a semiclassical limit that is non-trivial as ϵ tends to 0.

In Sect. 3 we choose a specific traditional Born-Oppenheimer state associated with the $E_{\mathscr{A}}$ surface that is localized in x near a negative value a, and has momentum localized near a positive value η. We propagate this state through the crossing. After passing through the crossing, the wave function is a superposition of two traditional Born-Oppenheimer states: one for the $E_{\mathscr{A}}$ surface, and one for the $E_{\mathscr{B}}$ surface. For small ϵ, the amplitude of the $E_{\mathscr{A}}$ component is $1 + o(\epsilon)$, and the amplitude of the $E_{\mathscr{B}}$ component is $(2\pi\eta)^{1/2}\epsilon + o(\epsilon)$.

The zeroth order Born-Oppenheimer term is not significantly affected by a codimension 1 crossing. In a temporal boundary layer of duration $O(\epsilon)$ when the zeroth order term is passing through the crossing, the $E_{\mathscr{B}}$ component is generated as a first order correction. We have not calculated higher order corrections, but we would expect them to be very complicated and have orders $\epsilon^{n(k)} \log^{m(k)}(\epsilon)$.

Codimension 2 crossings are generic if the electron Hamiltonian commutes with a conjugation (i.e., an anti-unitary operator whose square is the identity) and either no symmetries are involved or the relevant electronic wave functions belong to the same symmetry class. (For finite dimensional Hamiltonians, this means that in addition to being self-adjoint, the Hamiltonian is unitarily equivalent to a real symmetric matrix.) This situation is probably the one of greatest interest in quantum chemistry. For example, if there is no external magnetic field and either spin effects are ignored or there are an even number of electrons, then the Hamiltonian commutes with the time reversal. In this situation time reversal is a conjugation [7].

In generic codimension 2 crossings, the electron energy levels depend continuously on the nuclear configurations, but are not differentiable. In addition, the associated electron eigenfunctions are not continuous functions of the nuclear configurations near the crossing. Interesting phenomena, such as Berry phases result from the structure of these discontinuities [11–13].

The canonical example of a codimension 2 crossing is the following: The electron Hilbert space is the two dimensional complex space $\mathbb{C}^2$, and the nuclear configurations are described by a two real parameters, $(x_1, x_2) \in \mathbb{R}^2$. The electron Hamiltonian is

$$h_2(x_1, x_2) = \begin{bmatrix} x_1 & x_2 \\ x_2 & -x_1 \end{bmatrix}. \tag{1.3}$$

The electron energy levels are $E_{\mathscr{A}}(x) = (x_1^2 + x_2^2)^{1/2}$ and $E_{\mathscr{B}}(x) = -(x_1^2 + x_2^2)^{1/2}$. We choose the corresponding eigenvectors to be

$$\Phi_{\mathscr{A}}(x) = \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{pmatrix}, \quad \text{and} \quad \Phi_{\mathscr{B}}(x) = \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix},$$

where $\theta = \tan^{-1}(x_2/x_1)$ is the usual polar coordinate. We choose the branch of the inverse tangent so that $-x/2 \leqslant \theta < 3\pi/2$. One can multiply our choice of eigenvectors by odd powers of the phase factor $e^{i\theta/2}$ to avoid having a cut. We have not done so, because we want to work with real eigenvectors whenever possible. The advantage of real eigenvectors is that if $\Phi(x)$ is real and normalized, then $\langle \Phi(x), \eta \cdot \nabla \Phi(x) \rangle = 0$ for any vector η. If $\Phi(x)$ were not real, then this equation could fail for almost all choices of η. Although one could use complex eigenvectors, one would not be able to use formulas from Section 3 of [10] without making appropriate alterations.

One might expect the presence of a cut would cause difficulties, but it does not. The nuclear wave functions we use are localized near a point $a(t)$, and we only use the eigenfunctions when $a(t)$ is sufficiently far from the crossing. Whenever we use $\Phi_{\mathscr{A}}(x)$ or $\Phi_{\mathscr{B}}(x)$ in our analysis, they always appear multiplied by a function that is zero in a neighborhood of the cut. Of course, the exact solution to the Schrödinger equation is not zero in the neighborhood of the cut, even though the approximate one is. The exact solution is, however, sufficiently small in the neighborhood so that the error estimates still hold. When $a(t)$ is near the crossing, the wave function is not small near the cut. In that situation we use different techniques that make no reference whatsoever to the electron eigenfunctions. Since the eigenfunctions are not used, the cut is irrelevant. The technique of asymptotic matching is used to connect the various solutions to one another to obtain results for the whole time interval of interest. The matching uniquely determines a single valued wave function, and there is no ambiguity concerning the sign or phase of the wave function at any stage.

The matching process is the same one used in standard WKB theory near a turning point. In the interior of the classically forbidden region and in the interior of the classically allowed region, outer solutions are valid. They involve exponentials times factors that blow up near the turning point. Near the turning point, one rescales the problem and finds inner solutions that are valid approximations. They involve Airy functions. Asymptotic matching connects these solutions to one another. Our analysis is completely analogous.

The Schrödinger equation we study in the codimension 2 case is

$$i\epsilon^2 \frac{\partial \psi}{\partial t} = -\frac{\epsilon^4}{2}\left(\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_2^2}\right) + h_2(x_1, x_2)\psi, \tag{1.4}$$

where $\psi(x_1, x_2, t)$ has two components.

In Section 4 we choose an initial Born-Oppenheimer state associated with the $E_{\mathscr{A}}$ energy level that is localized near the point $(a, 0)$ and localized in momentum near $(\eta, 0)$, where $a < 0$ and $\eta > 0$. After we have propagated the state through the crossing, then to leading order, the wave function is a superposition of two Born-Oppenheimer components: one for the $E_{\mathscr{A}}$ surface, and one for the $E_{\mathscr{B}}$

surface. The $E_{\mathscr{B}}$ component is a traditional Born-Oppenheimer state. The $E_{\mathscr{A}}$ component has a slightly greater position uncertainty than the traditional Born-Oppenheimer states.

In contrast to the codimension 1 case, both components have amplitudes that are $O(1)$ as ϵ tends to 0. For the specific state we study, the probability of finding the system in the $E_{\mathscr{B}}$ state after the crossing is $(1+\pi/\eta_0)^{-1/2}+o(1)$, where η_0 is the speed at which the nuclei move through the crossing. The probability of finding the system in the $E_{\mathscr{A}}$ state is $1-(1+\pi/\eta_0)^{-1/2}+o(1)$. Thus, the probabilities depend critically on the rate at which the system passes through the crossing.

Codimension 3 crossings are generic for general self-adjoint electron Hamiltonians if there are no symmetries or if the relevant electron wave functions belong to the same symmetry class. Such systems are not time reversal invariant, but occur, for example, when there are external magnetic fields. The analysis of a non-degenerate codimension 3 crossing is similar to the codimension 2 case, but is complicated by the involvement of another degree of freedom for the nuclei and some nontrivial topology involving the choice of electronic eigenfunctions.

We illustrate the techniques for a codimension 3 crossing by the following example: The electron Hilbert space is the two dimensional complex space $\mathbb{C}^2$, and the nuclear configurations are described by a three real parameters, $(x_1, x_2, x_3) \in \mathbb{R}^3$. The electron Hamiltonian is

$$h_3(x_1, x_2, x_3) = \begin{bmatrix} x_3 & x_1+ix_2 \\ x_1-ix_2 & -x_3 \end{bmatrix}. \tag{1.5}$$

The electron energy levels are $E_{\mathscr{A}}(x) = (x_1^2+x_2^2+x_3^2)^{1/2}$ and $E_{\mathscr{B}}(x) = -(x_1^2+x_2^2+x_3^2)^{1/2}$. To avoid singularities caused by the topology of the situation, we make different choices of the eigenvectors, depending on the sign of x_3. We let θ and φ be the usual spherical coordinates with $0 \leqslant \theta \leqslant \pi$ and $0 \leqslant \varphi < 2\pi$. If $0 \leqslant \theta \leqslant \pi/2$, we choose the eigenvectors to be

$$\Phi_{\mathscr{A}}^{+}(x) = \begin{pmatrix} \cos(\theta/2) \\ e^{-i\varphi}\sin(\theta/2) \end{pmatrix}, \quad \text{and} \quad \Phi_{\mathscr{B}}^{+}(x) = \begin{pmatrix} -e^{i\varphi}\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix}.$$

If $\pi/2 < \theta \leqslant \pi$, we choose the eigenvectors to be

$$\Phi_{\mathscr{A}}^{-}(x) = \begin{pmatrix} e^{i\varphi}\cos(\theta/2) \\ \sin(\theta/2) \end{pmatrix}, \quad \text{and} \quad \Phi_{\mathscr{B}}^{-}(x) = \begin{pmatrix} -\sin(\theta/2) \\ e^{-i\varphi}\cos(\theta/2) \end{pmatrix}.$$

We will not make use of these eigenvectors near the $x_3 = 0$ plane, so the discontinuity will not cause difficulties. Although these eigenvectors are not real, they satisfy $\langle \Phi_{\cdot}(x), \eta \cdot \nabla \Phi_{\cdot}(x) \rangle = 0$ as long as η points along the third coordinate axis and $x_3 \neq 0$. This allows us to use formulas from [10] verbatim, since we have chosen initial conditions that have $\eta(t)$ pointing along the x_3 axis. As in the codimension 2 case, we will never make use of the eigenfunctions near the cut on the $x_3 = 0$ plane. The asymptotic matching procedure uniquely determines single valued inner and outgoing outer solutions. There is no phase ambiguity.

The Schrödinger equation we study in the codimension 3 case is:

$$i\epsilon^2 \frac{\partial \psi}{\partial t} = -\frac{\epsilon^4}{2}\left(\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_2^2} + \frac{\partial^2 \psi}{\partial x_3^2}\right) + h_3(x_1, x_2, x_3)\psi, \tag{1.6}$$

where $\psi(x_1, x_2, x_3, t)$ has two components.

In Sect. 5 we choose an initial Born-Oppenheimer state associated with the $E_{\mathscr{A}}$ energy level that is localized near the point $(0, 0, a)$ and localized in momentum near $(0, 0, \eta)$, where $a < 0$ and $\eta > 0$. After passing through the crossing, the wave function is again a superposition of two Born-Oppenheimer states associated with the $E_{\mathscr{A}}$ and $E_{\mathscr{B}}$ surfaces. As in the codimension 2 case, both components have amplitudes that are $O(1)$ as ϵ tends to 0, and the $E_{\mathscr{A}}$ component has a somewhat larger spatial uncertainty than traditional Born-Oppenheimer states. For the specific state we study, the probability of finding the system in the $E_{\mathscr{B}}$ state after the crossing is $(1 + \pi/\eta_0)^{-1} + o(1)$, where η_0 is the speed at which the nuclei move through the crossing. The probability of finding the system in the $E_{\mathscr{A}}$ state is $1 - (1 + \pi/\eta_0)^{-1} + o(1)$.

We employ the same basic strategy to approximately solve the Schrödinger equations for the three cases. Before the nuclei encounter the crossing, we use previously developed techniques [10] to construct the solutions. These "outer" solutions become singular and fail to be accurate as the nuclei get close to the crossing. We use the method of matched asymptotic expansions with general order functions [14] to match these outer solutions to "inner" solutions that are valid while the nuclei are actually going through the crossing. After the nuclei are away from the crossing, we match the inner solutions to appropriate outer solutions. The outer solutions are standard time-dependent Born-Oppenheimer solutions. The inner solutions are obtained by rescaling the time variable to conform to the physical situation. The crossing of energy surfaces gives rise to a new time scale when the nuclei are near the crossing. The inner solutions are constructed as functions of the rescaled time $s = t/\epsilon$. The most difficult aspect of the rigorous proof involves demonstrating that there are appropriate time intervals during which both the outer and inner expansions are valid.

By examining the inner solutions we observe a Franck–Condon principle. In the temporal boundary layer when the inner solutions are valid, the nuclei essentially move with constant speed. Their large masses prevent them from accelerating significantly during this brief time interval. The electrons, however, exhibit complicated dynamics in the temporal boundary layer.

Born-Oppenheimer approximations have received very little attention from mathematicians [10, 15–23], and there are only three mathematical papers [10, 18, 21] that consider the time-dependent approximation. Eigenvalue crossings in the adiabatic approximation have also received very little attention [2, 24–30] and only one paper [2] considers adiabatic crossings for systems with infinite dimensional Hilbert spaces. As far as the author is aware, the results described in the present paper represent the only attempt to construct a rigorous general theory for level crossings in the Born-Oppenheimer limit for molecular systems.

In Sects. 3–5 we precisely describe the results for our examples without

proofs. The proofs are outlined in the Appendix. The full proofs that handle general situations with infinite dimensional electron Hamiltonians will be published in the mathematics literature.

Remark 1. Although our techniques apply in generic situations, specific details depend on the particular situation. Different initial conditions may produce different probabilities for transition from one surface to another at a crossing.

Remark 2. In Sects. 4 and 5, we arbitrarily took initial conditions associated with the upper surface. If one were to start with the analogous Gaussian nuclear wave functions on the lower surface, the transition probabilities and the qualitative structure of the solutions would be the same, except for the interchange of the $\mathscr{A}$'s and $\mathscr{B}$'s. The classical action integrals, positions, momenta, and uncertainty matrices would be different, because the roles of the two electron energy surfaces before and after the crossings would be reversed.

Remark 3. The codimension 2 and 3 cases are fundamentally different from the codimension 1 case because of the singular structure of the electronic eigenfunctions associated with the geometric phase. This singular behavior enhances the coupling between the two surfaces. As a consequence, both surfaces are involved to leading order in the codimension 2 and 3 cases, while only one is involved to leading order in the codimension 1 case.

Remark 4. The temporal and spatial scaling properties of the differential equations and initial conditions for molecular systems are much more subtle than one might naively expect. The Born-Oppenheimer limit discussed in this paper is the distinguished limiting process in which all the various terms of the differential equations play significant roles. Other choices of the temporal scaling or spatial scaling as ϵ tends to zero may produce different phenomena. However, they tend to have less interesting structure because some terms in the equations dominate while others become unimportant.

2. Notation for wave packets

In Sects. 3–5, we will use special n-dimensional semiclassical wave packets [31, 32]. In general cases, much more complicated wave functions are required. However, the examples we present have been chosen so that the matrices, A and B are always diagonal. This drastically simplifies the formulas.

We first establish our notation for Gaussian wave functions.

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

A and B are invertible;

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

and $(\operatorname{Re} BA^{-1})^{-1} = AA^*$.

Let $a \in \mathbb{R}^n$, $\eta \in \mathbb{R}^n$, and $\epsilon > 0$. We define

$$\phi_0(A, B, \epsilon^2, a, \eta, x) = \pi^{-n/4}\epsilon^{-n/2}[\det A]^{-1/2} \times \exp\{-(x-a)\cdot BA^{-1}(x-a)/2\epsilon^2 + i\eta\cdot(x-a)/\epsilon^2\}.$$

Intuitively, this is a semiclassical wave packet in which ϵ^2 plays the role of h. The wave packet is concentrated near position a and has momentum concentrated near η. The position and momentum uncertainties in the j^{th} coordinate direction are proportional to $\epsilon|A_{jj}|$ and $\epsilon|B_{jj}|$, respectively [31, 32].

In the codimension 2 and 3 cases, Gaussian wave packets are not sufficient for the analysis. We also need the following Hermite polynomials times Gaussians:

Definition. Choose A, B, a, and η as in the above definition. For each multi-index $k = (k_1, k_2, \ldots, k_n)$ of non-negative integers, we define

$$\phi_k(A, B, \epsilon^2, a, \eta, x) = \phi_0(A, B, \epsilon^2, a, \eta, x) \times \prod_{j=1}^{n} 2^{-k_j/2}(k_j!)^{-1/2}\left(\frac{\overline{A_{jj}}}{A_{jj}}\right)^{k_j/2} H_{k_j}(\epsilon^{-1}|A_{jj}|^{-1}(x-a))$$

For each fixed choice of A, B, a, and η, the functions $\phi_k(A, B, \epsilon^2, a, \eta, x)$ form an orthonormal basis of wave packets. These wave packets propagate in a simple way [31, 32] in the semiclassical limit. All out nuclear wave functions will be constructed from superpositions of these functions.

Warning! If A and B are not diagonal, then the definition above is not the proper definition. The natural basis in the general case involves polynomials that are much more complicated than products of Hermite polynomials [10, 32]. For generic electron energy level surfaces, non-diagonal A's and B's cannot be avoided, even if no crossings are present. The evolution equations [10] for these uncertainty matrices produce off-diagonal terms in generic situations. The electron Hamiltonians for our examples have been chosen to illustrate the principal ideas in as simple a context as possible.

3. Codimension 1 crossings

In this section, we study particular crossing solutions to Eq. (1.2) modulo errors that are $o(\epsilon^\alpha)$ for some $\alpha > 1$. A simple connection formula that connects the solution before the crossing to the solution after the crossing is obtained (see Eq. (3.4)). The techniques involved in obtaining these solutions are adaptations of the techniques [2] used to handle adiabatic crossings.

When the nuclear wave function is localized away from the crossing, Eq. (1.2) can be solved to arbitrarily high order by traditional Born-Oppenheimer solutions [10]. We have chosen one such solution associated with the $E_{\mathscr{A}}$ electron energy level, that is moving toward the crossing for $-1 \leqslant t \leqslant -c < 0$. Up to errors that are $O(\epsilon^2)$, this solution is

$$e^{iS^{\mathscr{A}}(t)/\epsilon^2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{A}}(x). \tag{3.1}$$

Here

$$a^{\mathscr{A}}(t) = \eta_0 t,$$
$$\eta^{\mathscr{A}}(t) = \eta_0,$$
$$S^{\mathscr{A}}(t) = \eta_0^2 t/2,$$
$$A^{\mathscr{A}}(t) = 1 + it,$$

and

$$B^{\mathscr{A}}(t) = 1$$

are the classical position, classical momentum, classical action, and semiclassical uncertainty matrices for the nuclei.

By carefully estimating the errors, one can prove that (3.1) is a solution to equation (1.2) modulo errors that are $O(\epsilon^{2-\gamma})$, on the extended time interval $-1 \leqslant t \leqslant -C\epsilon^{\gamma}$, provided $0 \leqslant \gamma < 1$. These extended interval error estimates are non-trivial and tedious in general cases. One must insert spatial cut-offs, include parts of the second and third order corrections to the wave function, estimate a large number of error terms, and then remove the cut-offs.

Next, we define the inner solution that matches this outer solution. Since the inner solution involves the $E_{\mathscr{B}}$ electron energy surface, we need the appropriate classical position, momentum, action, and semiclassical uncertainty matrices for that surface. They are

$$a^{\mathscr{B}}(t) = \eta_0 t + t^2/2,$$
$$\eta^{\mathscr{B}}(t) = \eta_0 + t,$$
$$S^{\mathscr{B}}(t) = \eta_0^2 t/2 + \eta_0 t^2 + t^3/3,$$
$$A^{\mathscr{B}}(t) = 1 + (i + 1/\eta_0)t,$$

and

$$B^{\mathscr{B}}(t) = 1 - i/\eta_0.$$

The derivation of the inner solution also involves rescalings of the independent variables. We define a rescaled time variable $s(t) = t/\epsilon$ and two rescaled position variables $y_{\mathscr{A}}(x, t) = (x - a_{\mathscr{A}})/\epsilon$ and $y_{\mathscr{B}}(x, t) = (x - a_{\mathscr{B}})/\epsilon$. Since we want only one position variable instead of two, we arbitrarily choose $y_{\mathscr{A}}$ as an independent variable, and use $y_{\mathscr{B}} = y_{\mathscr{A}} + (a^{\mathscr{A}} - a^{\mathscr{B}})/\epsilon = y_{\mathscr{A}} - \epsilon s^2/2$ only as a convenient shorthand notation.

In the rescaled variables s and $y_{\mathscr{A}}$, the Schrödinger equation (1.2) has the form

$$i\epsilon \frac{\partial \psi}{\partial s} - i\epsilon \eta^{\mathscr{A}} \frac{\partial \psi}{\partial y_{\mathscr{A}}} = -\frac{\epsilon^2}{2} \frac{\partial^2 \psi}{\partial y_{\mathscr{A}}^2} + h_1(a^{\mathscr{A}} + \epsilon y_{\mathscr{A}})\psi. \tag{3.2}$$

We make the ansatz that the inner solution has the form

$$\psi(y_{\mathscr{A}}, s) = e^{iS^{\mathscr{A}}/\epsilon^2} e^{i\eta^{\mathscr{A}} y_{\mathscr{A}}/\epsilon} f(\epsilon, s, y_{\mathscr{A}}) \Phi_{\mathscr{A}}(a^{\mathscr{A}} + \epsilon y_{\mathscr{A}}) + e^{iS^{\mathscr{B}}/\epsilon^2} e^{i\eta^{\mathscr{B}} y_{\mathscr{B}}/\epsilon} g(\epsilon, s, y_{\mathscr{B}}) \Phi_{\mathscr{B}}(a^{\mathscr{A}} + \epsilon y_{\mathscr{A}}). \tag{3.3}$$

We assume the functions f and g have asymptotic expansions

$$f(\epsilon, s, y_{\mathscr{A}}) = \sum_{n=0}^{\infty} v_n(\epsilon) f_n(s, y_{\mathscr{A}})$$

and

$$g(\epsilon, s, y_{\mathscr{B}}) = \sum_{n=0}^{\infty} v_n(\epsilon) g_n(s, y_{\mathscr{B}}),$$

where the order functions $v_j(\epsilon)$ are the arbitrary functions that will be determined by matching the outer solutions.

We substitute the expression (3.3) into Eq. (3.2). In the resulting expression we expand all analytic dependence on ϵ in its power series in powers of ϵ. We then equate like powers of ϵ on the two sides of the resulting equation, order by order. By matching the incoming outer solution, we learn that $v_0(\epsilon) = 1$, and $v_1(\epsilon) = \epsilon$. Furthermore, we find

$$f_0 = \epsilon^{-1/2} \phi_0(A^{\mathscr{A}}(0), B^{\mathscr{A}}(0), 1, 0, 0, y_{\mathscr{A}}),$$

$$g_0 = 0,$$

$$f_1 = \frac{is}{2} \frac{\partial^2}{\partial y_{\mathscr{A}}^2} \epsilon^{-1/2} \phi_0(A^{\mathscr{A}}(0), B^{\mathscr{A}}(0), 1, 0, 0, y_{\mathscr{A}}),$$

and

$$g_1 = -\eta_0 \epsilon^{-1/2} \phi_0(A^{\mathscr{B}}(0), B^{\mathscr{B}}(0), 1, 0, 0, y_{\mathscr{B}}) \int_{-\infty}^{s + y_{\mathscr{B}}/\eta_0} e^{-i\eta_0 r^2/2}\, dr.$$

By another wearisome error analysis, this approximate inner solution agrees with an exact solution up to $O(\epsilon^{4\gamma' - 2})$ errors for $|t| < \epsilon^{\gamma'}$. If we choose $3/4 < \gamma' < 1$, this time interval intersects the interval of validity for the outer solution. In their respective intervals of validity, the two solutions agree with exact solutions up to $o(\epsilon)$ errors, and in the overlap region, the two solutions agree with one another to first order. So, the matching is justified. By similar rigorous analysis, we can explicitly write down the positive time first order outer solution that matches the inner solution. It is valid for $\epsilon^{\gamma} < t$ and is given by the formula

$$e^{iS^{\mathscr{A}}(t)/\epsilon^2} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x) \Phi_{\mathscr{A}}(x)$$
$$+ \epsilon(-1 + i)\pi^{1/2} \eta_0^{1/2}\, e^{iS^{\mathscr{B}}(t)/\epsilon^2} \phi_0(A^{\mathscr{B}}(t), B^{\mathscr{B}}(t), \epsilon^2, a^{\mathscr{B}}(t), \eta^{\mathscr{B}}(t), x) \Phi_{\mathscr{B}}(x). \quad (3.4)$$

Remark 1. Note that in our example,

$$\left\langle \Phi_{\mathscr{B}}(x), \frac{d\Phi_{\mathscr{A}}}{dx}(x) \right\rangle = 1$$

for all x. In more general situations, the order ϵ connection coefficient contains the additional factor

$$\left\langle \Phi_{\mathscr{B}}(0), \frac{d\Phi_{\mathscr{A}}}{dx}(0) \right\rangle$$

if the crossing occurs at $x = 0$.

Remark 2. The inner solution involves two time scales, s and t. By doing a multiple scales expansion that involves both time scales, one obtains a more aesthetic form for the approximate inner solution:

$$f_0 = \epsilon^{-1/2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, y_{\mathscr{A}}),$$

$$g_0 = 0,$$

$$f_1 = 0,$$

and

$$g_1 = -\eta_0\epsilon^{-1/2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, y_{\mathscr{A}}) \int_{-\infty}^{s + y_{\mathscr{A}}/\eta_0} e^{-i\eta_0 r^2/2}\, dr.$$

Of course, for times when the inner solution is a valid approximation, this approximate solution is first order equivalent to the one presented above.

4. Codimension 2 crossings

In this section, we study particular crossing solutions to Eq. (1.4) modulo errors that are $o(1)$. In contrast to the codimension 1 case, codimension 2 crossings drastically alter the zeroth order wave functions. Although the connection formulas are much more complicated, the probabilities for ending up on one surface or the other remain relatively simple in the leading order approximation.

When the nuclear wave function is localized away from the crossing, Eq. (1.4) can be solved to arbitrarily high order by traditional Born-Oppenheimer solutions [10]. We have chosen one such solution associated with the $E_{\mathscr{A}}$ electron energy level, that is moving toward the crossing for $-\eta_0 \leqslant t \leqslant -c < 0$. Up to errors that are $O(\epsilon^1)$, this solution is

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{A}}(x) \quad (4.1)$$

where F is a smooth cut off function that takes the value 1 when its argument is less than one and takes the value 0 when its argument is greater than 2. The number $\delta > 0$ will be chosen later to be very small. In addition,

$$a^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 t + t^2/2 \\ 0 \end{pmatrix},$$

$$\eta^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 + t \\ 0 \end{pmatrix},$$

$$S^{\mathscr{A}}(t) = \eta_0^2 t/2 + \eta_0 t^2 + t^3/3,$$

$$A_{11}^{\mathscr{A}}(t) = 1 + it,$$

$$B_{11}^{\mathscr{A}}(t) = 1,$$

$$A_{12}^{\mathscr{A}}(t) = A_{21}^{\mathscr{A}}(t) = B_{12}^{\mathscr{A}}(t) = B_{21}^{\mathscr{A}}(t) = 0,$$

$$A_{22}^{\mathscr{A}}(t) = 1 + \frac{t\log|t|}{\eta_0} + \left(i - \frac{1}{\eta_0}\right)t + \frac{t^2\log|t|}{2\eta_0^2} + \left(\frac{i}{2\eta_0} - \frac{3}{2\eta_0^2}\right)t^2 + O(t^3)$$

and

$$B_{22}^{\mathscr{A}}(t) = -\frac{i\log|t|}{\eta_0} + 1 - \frac{it\log|t|}{\eta_0^2} + \left(\frac{1}{\eta_0} + \frac{5i}{2\eta_0^2}\right)t + O(t^2)$$

are the classical position, classical momentum, classical action, and semiclassical uncertainty matrices for the nuclei. The functions A_{22} and B_{22} are obtained by solving a system of ordinary differential equations by the classical power series method of Frobenius. The logarithms arise from a regular singular point at $t = 0$ in the equations. We have exhibited all logarithms that occur in the formulas. The $O(t^3)$ and $O(t^2)$ terms in the formulas represent errors that are analytic functions of t.

By carefully estimating the errors, one can prove that (4.1) is a solution to Eq. (1.4) modulo errors that are $O(\epsilon^{1-\gamma})$, on the extended time interval $-1 \leqslant t \leqslant -C\epsilon^{\gamma}$, provided $0 \leqslant \gamma < 1 - \delta$. These extended interval error estimates are tedious as in the codimension 1 case. One must include part of the second order correction to the wave function and estimate a large number of error terms. One should note that the presence of the cut off function F in (4.1) causes the wave function to be zero on the x_2 axis for $t < -C\epsilon^{\gamma}$ for small ϵ. Thus, the expression (4.1) is continuous and single valued.

Next, we obtain the inner solution that matches the outer solution. We let $y_1 = (x_1 - \eta_0 t)/\epsilon$ and $y_2 = x_2/\epsilon$, and we define the rescaled time variable $s = t/\epsilon$. We then seek a solution of the form

$$\psi = e^{i\eta_0 y_1/\epsilon}\, e^{i\eta_0^2 s/2\epsilon} \begin{pmatrix} f_\epsilon(s, y_1, y_2) \\ g_\epsilon(s, y_1, y_2) \end{pmatrix}$$

that matches the outer solution (4.1). To leading order in the small ϵ limit, one finds that the solution has the form

$$\psi = e^{i\eta_0 y_1/\epsilon}\, e^{i\eta_0^2 s/2\epsilon} K_\epsilon(y_1, y_2) \begin{pmatrix} \dfrac{(1-i)y_2}{2\eta_0^{1/2}}\, D_{p-1}((-1+i)\eta_0^{-1/2}(\eta_0 s + y_1)) \\ D_p((-1+i)\eta_0^{-1/2}(\eta_0 s + y_1)) \end{pmatrix}, \quad (4.2)$$

where D_q is the parabolic cylinder function [33] of order q, $p = iy_2^2/2\eta_0$, and

$$K_\epsilon(y_1, y_2) = \pi^{-1/2}\epsilon^{-1}\, e^{-iy_1^2/2\eta_0}\, e^{-iy_2^2\log(2\eta_0)/4\eta_0}\, e^{i(\log\epsilon)y_2^2/2\eta_0}\, e^{-\pi y_2^2/8\eta_0}\, e^{-(y_1^2+y_2^2)/2}.$$

The approximate inner solution (4.2) agrees with an exact solution up to $o(1)$ errors for times t that satisfy $|t| < \epsilon^{\gamma'}$ for $\gamma' > 2/3$. If we choose δ sufficiently small, this interval overlaps the interval of validity for the outer solution for negative times. The matching is consequently justified.

We next match the inner solution (4.2) to positive time outer solutions. The piece of the wave function that ends up on the $E_{\mathscr{A}}$ surface is the simpler of the

two, because it is a Gaussian to leading order. If we set $d = (1 + \pi/\eta_0)^{1/2}$, then to leading order, this component is

$$d^{-1/2} F\left(\frac{|x - a^{\mathscr{B}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{B}}(t)/\epsilon^2} \phi_0(A^{\mathscr{B}}(t), B^{\mathscr{B}}(t), \epsilon^2, a^{\mathscr{B}}(t), \eta^{\mathscr{B}}(t), x) \Phi_{\mathscr{B}}(x), \quad (4.3)$$

where

$$a^{\mathscr{B}}(t) = \begin{pmatrix} \eta_0 t + t^2/2 \\ 0 \end{pmatrix},$$

$$\eta^{\mathscr{B}}(t) = \begin{pmatrix} \eta_0 t + t \\ 0 \end{pmatrix},$$

$$S^{\mathscr{B}}(t) = \eta_0^2 t/2 + \eta_0 t^2 + t^3/3,$$

$$A_{11}^{\mathscr{B}}(t) = 1 + it,$$

$$B_{11}^{\mathscr{B}}(t) = 1,$$

$$A_{12}^{\mathscr{B}}(t) = A_{21}^{\mathscr{B}}(t) = B_{12}^{\mathscr{B}}(t) = B_{21}^{\mathscr{B}}(t) = 0,$$

$$A_{22}^{\mathscr{B}}(t) = d^{-1} + \frac{t \log|t|}{\eta_0 d} + \left(id - \frac{1}{\eta_0 d}\right) t + \frac{t^2 \log|t|}{2\eta_0^2 d} + \left(\frac{id}{2\eta_0} - \frac{3}{2\eta_0^2 d}\right) t^2 + O(t^3)$$

and

$$B_{22}^{\mathscr{B}}(t) = -\frac{i \log|t|}{\eta_0 d} + d - \frac{it \log|t|}{\eta_0^2 d} + \left(\frac{d}{\eta_0} + \frac{5i}{2\eta_0^2 d}\right) t + O(t^2).$$

The probability of finding the system propagating on the $E_{\mathscr{B}}$ surface is thus

$$d^{-1} = \left(1 + \frac{\pi}{\eta_0}\right)^{-1/2}.$$

The $E_{\mathscr{A}}$ component is more complicated. The asymptotics of the parabolic cylinder functions [33] contain terms that involve the following function:

$$G(y_2) = \frac{(1-i)y_2}{2\eta_0^{1/2}} \frac{(2\pi)^{1/2}}{\Gamma\left(1 - \frac{iy_2^2}{2\eta_0}\right)} e^{-\pi y_2^2/4\eta_0}.$$

By using the asymptotics of the gamma, digamma, and polygamma functions [34], one can prove that the odd function $G(y_2)\, e^{-y_2^2/2}$ belongs to the class of Schwartz functions. From this it follows [31, 35] that G has a convergent expansion in odd order Hermite polynomials

$$G(y_2) = \sum_{j=1}^{\infty} c_j 2^{-j/2} (j!)^{-1/2} H_j(y_2),$$

with coefficients c_j that decay faster than any inverse power of j.

We let k_j denote the multi-index $k_j = (0, j)$. Then the $E_{\mathscr{A}}$ component of the outer solution for positive times is, to leading order,

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2} \sum_{j=1}^{\infty} c_j \phi_{k_j}(A^{\mathscr{A}}(\epsilon, t), B^{\mathscr{A}}(\epsilon, t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x) \Phi_{\mathscr{A}}(x), \tag{4.4}$$

where

$$a^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 t - t^2/2 \\ 0 \end{pmatrix},$$

$$\eta^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 t - t \\ 0 \end{pmatrix},$$

$$S^{\mathscr{A}}(t) = \eta_0^2 t/2 - \eta_0 t^2 + t^3/3,$$

$$A_{11}^{\mathscr{A}}(t) = 1 + it\left(1 + \frac{2i}{\eta_0}\right),$$

$$B_{11}^{\mathscr{A}}(t) = 1 + \frac{2i}{\eta_0},$$

$$A_{12}^{\mathscr{A}}(t) = A_{21}^{\mathscr{A}}(t) = B_{12}^{\mathscr{A}}(t) = B_{21}^{\mathscr{A}}(t) = 0,$$

$$A_{22}^{\mathscr{A}}(\epsilon, t) = 1 + \frac{t \log t}{\eta_0} + \left(i - \frac{1}{\eta_0} - \frac{\log(2\eta_0)}{\eta_0} + \frac{2 \log \epsilon}{\eta_0}\right) t + \frac{t^2 \log t}{2\eta_0^2}$$
$$- \left(\frac{i}{2\eta_0} + \frac{3}{2\eta_0^2} - \frac{\log(2\eta_0)}{2\eta_0^2} + \frac{2 \log \epsilon}{2\eta_0^2}\right) t^2 + O(t^3)$$

and

$$B_{22}^{\mathscr{A}}(\epsilon, t) = \frac{i \log t}{\eta_0} + 1 + \frac{i \log(2\eta_0)}{\eta_0} - \frac{2i \log \epsilon}{\eta_0} - \frac{it \log|t|}{\eta_0^2}$$
$$+ \left(-\frac{1}{\eta_0} + \frac{5i}{2\eta_0^2} - \frac{i \log(2\eta_0)}{\eta_0^2} + \frac{2i \log \epsilon}{\eta_0^2}\right) t + O(t^2).$$

Remark 1. The ϵ-dependence of $A_{22}^{\mathscr{A}}(\epsilon, t)$ and $B_{22}^{\mathscr{A}}(\epsilon, t)$ makes (4.4) different from the usual Born-Oppenheimer states. For positive t, the position and momentum uncertainties in (4.4) are proportional to $\epsilon \log \epsilon$ rather than ϵ.

Remark 2. It is not much more difficult to propagate an initial state of ϕ_k rather than ϕ_0. The analysis is essentially the same, although the probabilities of ending up on the two surfaces are very different. By superposition of these states, one can send in a fairly general nuclear wave function.

Remark 3. Because of the presence of the cut off function F, none of the functions (4.1), (4.3), and (4.4) that involve the discontinuous electronic eigenfunctions is non-zero near the cut on the x_2 axis. Thus our approximate solutions are all single valued and continuous.

5. Codimension 3 crossings

The analysis of solutions to Eq. (1.6) is very similar to that for Eq. (1.4). We will consequently only present the results of the calculations in this section.

For $-\eta_0 \leqslant t \leqslant -c < 0$ we choose the initial approximate solution to be

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x) \Phi_{\mathscr{A}}^{-}(x), \quad (5.1)$$

where F is cut off as in Sect. 4, and

$$a^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 t + t^2/2 \\ 0 \\ 0 \end{pmatrix},$$

$$\eta^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 + t \\ 0 \\ 0 \end{pmatrix},$$

$$S^{\mathscr{A}}(t) = \eta_0^2 t/2 + \eta_0 t^2 + t^3/3,$$

$$A_{11}^{\mathscr{A}}(t) = 1 + it,$$

$$B_{11}^{\mathscr{A}}(t) = 1,$$

$$A_{22}^{\mathscr{A}}(t) = A_{33}^{\mathscr{A}}(t) = 1 + \frac{t \log|t|}{\eta_0} + \left(i - \frac{1}{\eta_0}\right) t + \frac{t^2 \log|t|}{2\eta_0^2} + \left(\frac{i}{2\eta_0} - \frac{3}{2\eta_0^2}\right) t^2 + O(t^3),$$

$$B_{22}^{\mathscr{A}}(t) = B_{33}^{\mathscr{A}}(t) = -\frac{i \log|t|}{\eta_0} + 1 - \frac{it \log|t|}{\eta_0^2} + \left(\frac{1}{\eta_0} + \frac{5i}{2\eta_0^2}\right) t + O(t^2),$$

and the off-diagonal entries of $A^{\mathscr{A}}$ and $B^{\mathscr{A}}$ are all 0.

The approximate inner solution that matches (5.1) is

$$\psi = e^{i\eta_0 y_3/\epsilon} e^{i\eta_0^2 s/2\epsilon} K_\epsilon(y_1, y_2, y_3) \times \begin{pmatrix} \dfrac{(1-i)(y_1 + iy_2)}{2\eta_0^{1/2}} D_{p-1}((-1+i)\eta_0^{-1/2}(\eta_0 s + y_3)) \\ D_p((-1+i)\eta_0^{-1/2}(\eta_0 s + y_3)) \end{pmatrix}, \quad (5.2)$$

where $s = t/\epsilon$, $y_1 = x_1/\epsilon$, $y_2 = x_2/\epsilon$, $y_3 = (x_3 - \eta_0 t)/\epsilon$, $p = i(y_1^2 + y_2^2)/2\eta_0$, and

$$K_\epsilon(y_1, y_2, y_3) = \pi^{-3/4} \epsilon^{-3/2} e^{-iy_3^2/2\eta_0} e^{-i(y_1^2 + y_2^2)\log(2\eta_0)/4\eta_0} \times e^{i(\log \epsilon)(y_1^2 + y_2^2)/2\eta_0} e^{-\pi(y_1^2 + y_2^2)/8\eta_0} e^{-(y_1^2 + y_2^2 + y_3^2)/2}.$$

The inner solution (5.2) matches an outer solution for positive times that is a sum of two components. If we set $d = (1 + \pi/\eta_0)^{1/2}$ as in Sect. 4, then to leading order, the $E_{\mathscr{B}}$ component is

$$d^{-1} F\left(\frac{|x - a^{\mathscr{B}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{B}}(t)/\epsilon^2} \phi_0(A^{\mathscr{B}}(t), B^{\mathscr{B}}(t), \epsilon^2, a^{\mathscr{B}}(t), \eta^{\mathscr{B}}(t), x) \Phi_{\mathscr{B}}^{+}(x), \quad (5.3)$$

where

$$a^{\mathscr{B}}(t) = \begin{pmatrix} \eta_0 t + t^2/2 \\ 0 \\ 0 \end{pmatrix},$$

$$\eta^{\mathscr{B}}(t) = \begin{pmatrix} \eta_0 t + t \\ 0 \\ 0 \end{pmatrix},$$

$$S^{\mathscr{B}}(t) = \eta_0^2 t/2 + \eta_0 t^2 + t^3/3,$$

$$A_{11}^{\mathscr{B}}(t) = 1 + it,$$

$$B_{11}^{\mathscr{B}}(t) = 1,$$

$$A_{22}^{\mathscr{B}}(t) = A_{33}^{\mathscr{B}}(t) = d^{-1} + \frac{t \log|t|}{\eta_0 d} + \left(id - \frac{1}{\eta_0 d}\right) t + \frac{t^2 \log|t|}{2\eta_0^2 d} + \left(\frac{id}{2\eta_0} - \frac{3}{2\eta_0^2 d}\right) t^2 + O(t^3),$$

$$B_{22}^{\mathscr{B}}(t) = B_{33}^{\mathscr{B}}(t) = -\frac{i \log|t|}{\eta_0 d} + d - \frac{it \log|t|}{\eta_0^2 d} + \left(\frac{d}{\eta_0} + \frac{5i}{2\eta_0^2 d}\right) t + O(t^2),$$

and the off-diagonal entries of $A^{\mathscr{B}}$ and $B^{\mathscr{B}}$ are all 0. The probability of finding the system propagating on the $E_{\mathscr{B}}$ surface is thus

$$d^{-2} = \left(1 + \frac{\pi}{\eta_0}\right)^{-1}.$$

The $E_{\mathscr{A}}$ component is more complicated. We set

$$G(y_1, y_2) = \frac{(1-i)(y_1 + iy_2)}{2\eta_0^{1/2}} \frac{(2\pi)^{1/2}}{\Gamma\left(1 - \dfrac{i(y_1^2 + y_2^2)}{2\eta_0}\right)} e^{-\pi(y_1^2 + y_2^2)/4\eta_0}.$$

The function G has a convergent Hermite polynomial expansion

$$G(y_1, y_2) = \sum_{j,l=1}^{\infty} c_{j,l} 2^{-(j+l)/2} (j!)^{-1/2} (l!)^{-1/2} H_j(y_1) H_l(y_2),$$

with coefficients $c_{j,l}$ that decay faster than any inverse power of $j + l$.

We let $k_{j,l}$ denote the multi-index $k_{j,l} = (j, l, 0)$. Then the $E_{\mathscr{A}}$ component of the outer solution for positive times is, to leading order,

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2} \Phi_{\mathscr{A}}^{+}(x) \times \sum_{j,l=1}^{\infty} c_{j,l} \phi_{k_{j,l}}(A^{\mathscr{A}}(\epsilon, t), B^{\mathscr{A}}(\epsilon, t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x) e^{i\varphi(x)}, \quad (5.4)$$

where $\varphi(x)$ is the azimuthal spherical coordinate for x,

$$a^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 t - t^2/2 \\ 0 \\ 0 \end{pmatrix},$$

$$\eta^{\mathscr{A}}(t) = \begin{pmatrix} \eta_0 - t \\ 0 \\ 0 \end{pmatrix},$$

$$S^{\mathscr{A}}(t) = \eta_0^2 t/2 - \eta_0 t^2 + t^3/3,$$

$$A_{11}^{\mathscr{A}}(t) = 1 + it\left(1 + \frac{2i}{\eta_0}\right),$$

$$B_{11}^{\mathscr{A}}(t) = 1 + \frac{2i}{\eta_0},$$

$$A_{22}^{\mathscr{A}}(\epsilon, t) = A_{33}^{\mathscr{A}}(\epsilon, t) = 1 + \frac{t \log t}{\eta_0} + \left(i - \frac{1}{\eta_0} - \frac{\log(2\eta_0)}{\eta_0} + \frac{2 \log \epsilon}{\eta_0}\right) t + \frac{t^2 \log t}{2\eta_0^2}$$
$$- \left(\frac{i}{2\eta_0} + \frac{3}{2\eta_0^2} - \frac{\log(2\eta_0)}{2\eta_0^2} + \frac{2 \log \epsilon}{2\eta_0^2}\right) t^2 + O(t^3),$$

$$B_{22}^{\mathscr{A}}(\epsilon, t) = B_{33}^{\mathscr{A}}(\epsilon, t) = \frac{i \log t}{\eta_0} + 1 + \frac{i \log(2\eta_0)}{\eta_0} - \frac{2i \log \epsilon}{\eta_0} - \frac{it \log|t|}{\eta_0^2}$$
$$+ \left(-\frac{1}{\eta_0} + \frac{5i}{2\eta_0^2} - \frac{i \log(2\eta_0)}{\eta_0^2} + \frac{2i \log \epsilon}{\eta_0^2}\right) t + O(t^2),$$

and the off-diagonal entries of $A^{\mathscr{A}}$ and $B^{\mathscr{A}}$ are all 0.

Appendix

In this appendix we provide some further details for the codimension 1 and 2 examples. Rigorous mathematical proofs follow the outlines we present, but require numerous estimates of norms of error terms. The codimension 3 case is very similar to the codimension 2 case, so we will not discuss it here.

All our results rely on the following lemma that is a simple variant of Lemma 2.1 of [2]. In our applications, the variable r of the lemma is a rescaled time $r = \epsilon^{-b} t$ for some $b \geqslant 0$, and typically $a = 2 - b$.

Lemma A1. *Suppose $H(\epsilon)$ is a family of self-adjoint operators for $\epsilon > 0$. Suppose $\psi(r, \epsilon)$ belongs to the domain of $H(\epsilon)$, is continuously differentiable in r, and approximately solves the Schrödinger equation in the sense that*

$$i\epsilon^a \frac{\partial \psi}{\partial r}(r, \epsilon) = H(\epsilon)\psi(r, \epsilon) + \zeta(r, \epsilon), \tag{A.1}$$

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

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

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

$$i\epsilon^a \frac{\partial \Psi}{\partial r}(r, \epsilon) = H(\epsilon)\Psi(r, \epsilon) \tag{A.2}$$

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

$$\|\Psi(r, \epsilon) - \psi(r, \epsilon)\| \leqslant \epsilon^{-a} \int_{T_1(\epsilon)}^{T_2(\epsilon)} \mu(r, \epsilon)\, dr. \tag{A.3}$$

Proof. By the unitarity of the propagator $e^{-irH(\epsilon)/\epsilon^a}$ for Eq. (A.2) and the fundamental theorem of calculus, the quantity on the left-hand side of (A.3) can be estimated as follows:

$$\begin{aligned}
&\|e^{-i(r-r_0)H(\epsilon)/\epsilon^a}\psi(r_0, \epsilon) - \psi(r, \epsilon)\| \\
&\quad = \|\psi(r_0, \epsilon) - e^{i(r-r_0)H(\epsilon)/\epsilon^a}\psi(r, \epsilon)\| \\
&\quad = \left\| \int_{r_0}^{r} \frac{\partial}{\partial s}\left(\psi(r_0, \epsilon) - e^{i(s-r_0)H(\epsilon)/\epsilon^a}\psi(s, \epsilon)\right) ds \right\| \\
&\quad = \left\| \int_{r_0}^{r} \left(-i\epsilon^{-a}\, e^{i(s-r_0)H(\epsilon)/\epsilon^a} H(s, \epsilon)\psi(s, \epsilon) - e^{i(s-r_0)H(\epsilon)/\epsilon^a} \frac{\partial \psi}{\partial s}(s, \epsilon) \right) ds \right\| \\
&\quad = \left\| \int_{r_0}^{r} i\epsilon^{-a}\, e^{i(s-r_0)H(\epsilon)/\epsilon^a} \zeta(s, \epsilon)\, ds \right\| \\
&\quad \leqslant \epsilon^{-a} \int_{T_1(\epsilon)}^{T_2(\epsilon)} \mu(r, \epsilon)\, dr.
\end{aligned}$$

This proves the lemma. □

A1. Sketch of the proof for the codimension 1 case

To justify the claims in Sect. 3, we begin by proving that expression (3.1) agrees with an exact solution to Eq. (1.2) up to an error that is $O(\epsilon^{2-\gamma})$ for $-1 \leqslant t \leqslant -C\epsilon^{\gamma}$, for appropriate choices of γ. To do this, we first note that modulo $O(\epsilon^n)$ errors for any n, expression (3.1) is equal to

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}, \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{A}}(x), \tag{A.4}$$

where $0 < \delta < 1 - \gamma$, and F is a smooth cut-off function that takes the value 1 when its argument is less than 1 and takes the value 0 when its argument is greater than 2. The error here is of infinite order because of the rapid fall off of ϕ_0.

Next, we add parts of the second and third order correction terms to (A.4). These additions are required for the proof because we are analyzing a singular

perturbation problem. If one tries to work with (A.4) without the additions, the analysis breaks down. Intuitively, this break down is due to small amplitude, high frequency oscillations in the solution if one uses (A.4) at some given time as the initial condition. Because the frequency is high, the time derivative is large, even though the amplitude of the oscillations is small. The addition of the correction terms to the initial conditions yields a solution that does not have the high frequency oscillations. We can obtain a good enough estimate on its time derivative to use Lemma A.1 to prove that our approximate solution stays near an exact solution.

These correction terms are given by Eqs. (3.6) and (3.11) of [10] (for our special example, $\psi_1 = 0$, so the formulas are not so complicated). On the time interval $-1 \leqslant t \leqslant -C\epsilon^{\gamma}$, we make an $O(\epsilon^{2-\gamma})$ error by replacing (A.4) by

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2}$$

$$\times \Big[\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{A}}(x)$$

$$- \epsilon^2 \frac{i\eta^{\mathscr{A}}(t)}{x} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{B}}(x)$$

$$+ \epsilon^3 \frac{1}{x} \frac{B^{\mathscr{A}}(t)}{A^{\mathscr{A}}(t)} \frac{x - a^{\mathscr{A}}(t)}{\epsilon} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{B}}(x) \Big]. \tag{A.5}$$

To facilitate the calculations with this expression, we use the multiple scales notation of [10] to rewrite it as

$$F(\epsilon^{\delta}|y|)\, e^{iS^{\mathscr{A}}(t)/\epsilon^2}\, e^{i\eta^{\mathscr{A}}(t)y/\epsilon}[\psi_0(x, y, t) + \epsilon^2\psi_2^{\perp}(x, y, t) + \epsilon^3\psi_3^{\perp}(x, y, t)],$$

where $y = (x - a^{\mathscr{A}}(t))/\epsilon$,

$$\psi_0(x, y, t) = \epsilon^{-1/2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, y)\Phi_{\mathscr{A}}(x).$$

$$\psi_2^{\perp}(x, y, t) = \frac{-i\eta^{\mathscr{A}}(t)}{x} \epsilon^{-1/2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, y)\Phi_{\mathscr{B}}(x),$$

and

$$\psi_3^{\perp}(x, y, t) = \frac{1}{x} \frac{B^{\mathscr{A}}(t)}{A^{\mathscr{A}}(t)} y\epsilon^{-1/2}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, y)\Phi_{\mathscr{B}}(x).$$

By explicit calculation, expression (A.5) approximately solves Eq. (1.2) in the sense of Lemma A1 with $a = 2$ and remainder $\zeta(\epsilon, x, y, t)$. Some of the terms in this remainder contain derivatives of F. Their norms are smaller than any power of ϵ because $\delta > 0$ and ϕ_0 falls off exponentially in y. The other terms in the remainder have finite order norms. They are

$$F(\epsilon^{\delta}|y|)\, e^{iS^{\mathscr{A}}(t)/\epsilon^2}\, e^{i\eta^{\mathscr{A}}(t)y/\epsilon}$$

$$\times\Bigg[-i\epsilon^4\eta^{\mathscr{A}}\frac{\partial}{\partial x}\psi_{\frac{1}{2}}^{\perp}(x,y,t)-\epsilon^5\eta^{\mathscr{A}}\frac{\partial}{\partial x}\psi_{\frac{1}{3}}^{\perp}(x,y,t)$$

$$-\epsilon^5\frac{\partial^2}{\partial x\,\partial y}\psi_{\frac{1}{2}}^{\perp}(x,y,t)-\epsilon^6\frac{\partial^2}{\partial x\,\partial y}\psi_{\frac{1}{3}}^{\perp}(x,y,t)$$

$$-\frac{\epsilon^4}{2}\frac{\partial^2}{\partial x^2}\psi_0(x,y,t)-\frac{\epsilon^6}{2}\frac{\partial^2}{\partial x^2}\psi_{\frac{1}{2}}^{\perp}(x,y,t)-\frac{\epsilon^7}{2}\frac{\partial^2}{\partial x^2}\psi_{\frac{1}{3}}^{\perp}(x,y,t)\Bigg].$$

We estimate the norms of each of these seven terms, making use of the relationship $0<\delta<1-\gamma$. The norms of the seven terms (in the order presented above) are $O(\epsilon^4|t|^{-2})$, $O(\epsilon^5|t|^{-2})$, $O(\epsilon^5|t|^{-2})$, $O(\epsilon^6|t|^{-2})$, $O(\epsilon^4)$, $O(\epsilon^6|t|^{-3})$, and $O(\epsilon^7|t|^{-3})$. We integrate these estimates up to time $t=-C\epsilon^{\gamma}$. For γ close to 1, the integral that has lowest order is the first one. It is of order $\epsilon^{4-\gamma}$. Thus, by the lemma, expression (A.5) agrees with an exact solution of Eq. (1.2) up to an $O(\epsilon^{2-\gamma})$ error for $-1\leqslant t\leqslant -C\epsilon^{\gamma}$. Since (A.4) agrees with (A.5) to the same order, (A.4) also agrees with an exact solution of Eq. (1.2) up to an $O(\epsilon^{2-\gamma})$ error for $-1\leqslant t\leqslant -C\epsilon^{\gamma}$. This establishes all the claims of Sect. 3 for the outer solution for negative times.

For the inner solution, we defined the rescaled variables $s=t/\epsilon$, and $y_{\mathscr{A}}=(x-a^{\mathscr{A}})/\epsilon$. For convenience, we also set $y_{\mathscr{B}}=(x-a^{\mathscr{B}})/\epsilon=y_{\mathscr{A}}-\epsilon s^2/2$. We make the ansatz that the inner solution has the form (3.3), and substitute expression (3.3) into Eq. (3.2). In the resulting equation, we expand all dependence on ϵ that is analytic in ϵ in its Taylor series. After some cancellations, the lowest order terms that occur in the resulting equation are of order $\epsilon v_0(\epsilon)$. These lowest order terms require

$$i\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon}\frac{\partial f_0}{\partial s}\Phi_{\mathscr{A}}(a^{\mathscr{A}}(0))$$

$$+\, i\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 s^2}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon}\, e^{isy_{\mathscr{A}}}\, e^{-i\eta_0 s^2/2}\frac{\partial g_0}{\partial s}\Phi_{\mathscr{B}}(a^{\mathscr{A}}(0))$$

$$=0.$$

Because of the orthogonality of the wave functions $\Phi_{\mathscr{A}}(a^{\mathscr{A}}(0))$ and $\Phi_{\mathscr{B}}(a^{\mathscr{A}}(0))$, the two terms on the left hand side of this equation must each vanish. This can only happen if

$$\frac{\partial f_0}{\partial s}=0$$

and

$$\frac{\partial g_0}{\partial s}=0.$$

Thus, f_0 and g_0 have trivial s dependence, but may have non-trivial spatial dependence. The spatial dependence is determined by formally matching the

inner solution to the incoming outer solution to lowest order. This forces $v_0(\epsilon) = 1$,

$$f_0 = \epsilon^{-1/2}\phi_0(A^{\mathscr{A}}(0), B^{\mathscr{A}}(0), 1, 0, 0, y_{\mathscr{A}})$$

and

$$g_0 = 0.$$

We now consider the next higher order terms. If $\lim_{\epsilon \to 0} v_1(\epsilon)/\epsilon = \infty$, then by an analysis similar to that for the leading order terms, we find that

$$\frac{\partial f_1}{\partial s} = 0 \quad \text{and} \quad \frac{\partial g_1}{\partial s} = 0.$$

Matching to the outer solution forces f_1 and g_1 to be identically 0. If $\lim_{\epsilon \to 0} v_1(\epsilon)/\epsilon = 0$, then we obtain equations that cannot be solved. So, we conclude that we should choose $v_1(\epsilon) = \epsilon$. With this choice, the next order terms in the perturbation expansion require

$$\begin{aligned}
& i\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon} \frac{\partial f_1}{\partial s} \Phi_{\mathscr{A}}(a^{\mathscr{A}}(0)) \\
& \quad + i\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 s^2}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon}\, e^{isy_{\mathscr{A}}/\epsilon}\, e^{-i\eta_0 s^2/2} \frac{\partial g_1}{\partial s} \Phi_{\mathscr{B}}(a^{\mathscr{A}}(0)) \\
& = -i\eta_0\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon} f_0 \frac{\partial \Phi_{\mathscr{A}}}{\partial x}(a^{\mathscr{A}}(0)) \\
& \quad - i\eta_0\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 s^2}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon}\, e^{isy_{\mathscr{A}}}\, e^{-i\eta_0 s^2/2} g_0 \frac{\partial \Phi_{\mathscr{B}}}{\partial x}(a^{\mathscr{A}}(0)) \\
& \quad - \tfrac{1}{2}\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon} \frac{\partial^2 f_0}{\partial y_{\mathscr{A}}^2} \Phi_{\mathscr{A}}(a^{\mathscr{A}}(0)) \\
& \quad - \tfrac{1}{2}\, e^{i\eta_0^2 s/2\epsilon}\, e^{i\eta_0 s^2}\, e^{i\eta_0 y_{\mathscr{A}}/\epsilon}\, e^{isy_{\mathscr{A}}}\, e^{-i\eta_0 s^2/2} \frac{\partial^2 g_0}{\partial y_{\mathscr{B}}^2} \Phi_{\mathscr{B}}(a^{\mathscr{A}}(0)).
\end{aligned}$$

We split this into two equations by separately studying the components that are multiples of the two orthogonal electronic states $\Phi_{\mathscr{A}}(a^{\mathscr{A}}(0))$ and $\Phi_{\mathscr{B}}(a^{\mathscr{A}}(0))$. After a little algebra, the multiples of $\Phi_{\mathscr{A}}(a^{\mathscr{A}}(0))$ require

$$\frac{\partial f_1}{\partial s} = \frac{i}{2} \frac{\partial^2 f_0}{\partial y_{\mathscr{A}}^2}.$$

The multiples of $\Phi_{\mathscr{B}}(a^{\mathscr{A}}(0))$ require

$$\frac{\partial g_1}{\partial s} = -\eta_0\, e^{-i\eta_0 s^2/2}\, e^{-isy_{\mathscr{A}}} f_0(s, y_{\mathscr{A}}).$$

These two equations are easy to solve explicitly for the solutions that match the outer solution. The results are

$$f_1 = \frac{is}{2} \frac{\partial^2 f_0}{\partial y_{\mathscr{A}}^2}$$

and

$$g_1 = -\eta_0 f_0(s, y_{\mathscr{A}}) \int_{-\infty}^{s} e^{-i\eta_0 s'^2/2} e^{-is' y_{\mathscr{A}}} ds'$$

$$= -\eta_0 f_0(s, y_{\mathscr{A}}) \int_{-\infty}^{s + y_{\mathscr{A}}/\eta_0} e^{-i\eta_0 r^2/2} dr. \tag{A.6}$$

To prove the accuracy of the approximate inner solution, we simply apply Lemma A1 with $a = 1$. When we substitute our approximate solution into Eq. (3.2), the largest term in the remainder term $\zeta(s, \epsilon)$ is due to the Taylor series errors. It's norm is bounded by $\mu(s, \epsilon) = \epsilon^3 s^3$. So, from the conclusion to Lemma A1, our approximate inner solution agrees with an exact solution to (3.2) up to an error that is bounded by a constant times $\epsilon^2 s^4$. If we keep $|t| < \epsilon^{\gamma'}$, then $|s| < \epsilon^{\gamma' - 1}$, so the error is $O(\epsilon^{4\gamma' - 2})$. Since we are only doing a first order calculation, this is acceptable as long as we take $\gamma' > 3/4$.

When $-\epsilon^{\gamma'} < t < -\epsilon^{\gamma}$ with $3/4 < \gamma' < \gamma < 1$, the inner and outer approximate solutions agree with one another up to $o(\epsilon)$ errors. This is proved by subtracting one wave function from the other, and estimating the norm of the resulting expression by standard integration and Taylor series estimates.

The positive time outer approximate solution is generated in the same way as the negative time outer approximate solution. However, the particular solution must be chosen to match the inner solution. To do this matching, we must study the large s asymptotics of the inner solution. This is trivial, except for the integral term in (A.6). By integrating by parts,

$$\int_{-\infty}^{s + y_{\mathscr{A}}/\eta_0} e^{-i\eta_0 r^2/2} dr \sim (1 - i)\pi^{1/2} \eta^{-1/2} - \frac{i}{y_{\mathscr{A}} + \eta_0 s} e^{-i(y_{\mathscr{A}} + \eta_0 s)^2/2\eta_0}.$$

With this asymptotic information, we obtain the positive time analog to (A.5). The first order outer solution with parts of the second and third order terms included is

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2}$$

$$\times \Bigg[\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{A}}(x)$$

$$- \epsilon^2 \frac{i\eta^{\mathscr{A}}(t)}{x} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{B}}(x)$$

$$+ \epsilon^3 \frac{1}{x} \frac{B^{\mathscr{A}}(t)}{A^{\mathscr{A}}(t)} \frac{x - a^{\mathscr{A}}(t)}{\epsilon} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{B}}(x) \Bigg]$$

$$+ \epsilon(-1 + i)\pi^{1/2} \eta_0^{1/2} F\left(\frac{|x - a^{\mathscr{B}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{B}}(t)/\epsilon^2}$$

$$\times \Bigg[\phi_0(A^{\mathscr{B}}(t), B^{\mathscr{B}}(t), \epsilon^2, a^{\mathscr{B}}(t), \eta^{\mathscr{B}}(t), x)\Phi_{\mathscr{B}}(x)$$

$$- \epsilon^2 \frac{i\eta^{\mathscr{B}}(t)}{x} \phi_0(A^{\mathscr{B}}(t), B^{\mathscr{B}}(t), \epsilon^2, a^{\mathscr{B}}(t), \eta^{\mathscr{B}}(t), x)\Phi_{\mathscr{A}}(x) \Bigg]. \tag{A.7}$$

This expression agrees with the inner solution up to $o(\epsilon)$ errors in the positive time matching region $\epsilon^\gamma < t < \epsilon^\gamma$. Also, by another application of Lemma A1 with $a = 2$, (A.7) agrees with an exact solution to equation (1.2) up to an $O(\epsilon^{2-\gamma})$ error for $t > \epsilon^\gamma$. Finally, (A.7) is equal to (3.4) up to an $O(\epsilon^{2-\gamma})$ error for $t > \epsilon^\gamma$.

This completes the outline of the proof of our results for the codimension 1 example of Sect. 3.

A2. Sketch of the proof for the codimension 2 case

The basic ideas for proving our codimension 2 results are the same as those for the proof of the codimension 1 results. However, the codimension 2 case is more difficult because the electronic eigenvalues are not differentiable at the crossing, and the electronic eigenvectors are not even continuous near the crossing.

We begin by proving that the negative time outer solution (4.1) agrees with an exact solution to (1.4) up to an error that is $O(\epsilon^{1-\gamma})$ for $-1 \leqslant t \leqslant -C\epsilon^\gamma$ for appropriate choices of γ. To do this, we first add part of the second order correction term to (4.1). This term is given by Eq. (3.6) of [10]. For $-1 \leqslant t \leqslant -C\epsilon^\gamma$, we make an $O(\epsilon^{2-2\gamma})$ error by replacing (4.1) by

$$F\left(\frac{|x - a^{\mathscr{A}}(t)|}{\epsilon^{1-\delta}}\right) e^{iS^{\mathscr{A}}(t)/\epsilon^2}$$

$$\times \Bigg[\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{A}}(x)$$

$$+ \epsilon^2 \frac{i|\eta^{\mathscr{A}}(t)|x_2}{2|x|^3} \phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), \epsilon^2, a^{\mathscr{A}}(t), \eta^{\mathscr{A}}(t), x)\Phi_{\mathscr{B}}(x) \Bigg]. \quad \text{(A.8)}$$

As in the codimension 1 case, calculations with this expression are facilitated by using the notation of [10]. In this notation, (A.8) is expressed as

$$F(\epsilon^\delta|z|)\, e^{iS^{\mathscr{A}}(t)/\epsilon^2}\, e^{i\eta^{\mathscr{A}}(t)\cdot z/\epsilon}[\psi_0(x, z, t) + \epsilon^2\psi_2^\perp(x, z, t)],$$

where $z = (x - a^{\mathscr{A}}(t))/\epsilon$,

$$\psi_0(x, z, t) = \epsilon^{-1}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\Phi_{\mathscr{A}}(x),$$

and

$$\psi_2^\perp(x, z, t) = \frac{i}{2|x|}\epsilon^{-1}\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\eta^{\mathscr{A}} \cdot \nabla_x \Phi_{\mathscr{A}}(x).$$

By explicit calculation, (A.8) approximately solves (1.4) in the sense of Lemma A1, with $a = 2$ and remainder $\zeta(\epsilon, x, z, t)$. As in the codimension 1 case, the terms in the remainder that contain derivatives of F are of infinite order. Twelve terms of finite order contribute to $\zeta(\epsilon, x, z, t)$. They are

$$
\begin{aligned}
&\epsilon^{-1}F(\epsilon^{\delta}|z|)\, e^{iS^{\mathscr{A}}(t)/\epsilon^2}\, e^{i\eta^{\mathscr{A}}(t)\cdot z/\epsilon} \\
&\quad\times\Bigg\{-\epsilon^4\frac{1}{2|x|}\,\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\frac{\partial\eta^{\mathscr{A}}}{\partial t}\cdot\nabla_x\Phi_{\mathscr{A}}(x) \\
&\quad-\epsilon^4\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\left(\eta^{\mathscr{A}}\cdot\nabla_x\frac{1}{2|x|}\right)(\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x)) \\
&\quad-\epsilon^4\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\frac{1}{2|x|}\,\eta^{\mathscr{A}}\cdot\nabla_x(\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x)) \\
&\quad+[E_{\mathscr{A}}(a^{\mathscr{A}}+\epsilon z)-\tilde{E}_{\mathscr{A}}(a^{\mathscr{A}},\epsilon z)]\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\Phi_{\mathscr{A}}(x) \\
&\quad-i\epsilon^2[E_{\mathscr{A}}(a^{\mathscr{A}}+\epsilon z)-\tilde{E}_{\mathscr{A}}(a^{\mathscr{A}},\epsilon z)]\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\frac{1}{2|x|}\,\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x) \\
&\quad-\epsilon^3\nabla_z\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\cdot\nabla_x\Phi_{\mathscr{A}}(x) \\
&\quad+i\epsilon^5\left(\nabla_z\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\cdot\nabla_x\frac{1}{2|x|}\right)\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x) \\
&\quad+i\epsilon^5\frac{1}{2|x|}\,\nabla_z\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\cdot\nabla_x(\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x)) \\
&\quad-\frac{\epsilon^4}{2}\,\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\Delta_x\Phi_{\mathscr{A}}(x) \\
&\quad+i\frac{\epsilon^6}{2}\,\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\left(\Delta_x\frac{1}{2|x|}\right)\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x) \\
&\quad+i\epsilon^6\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\left(\nabla_x\frac{1}{2|x|}\right)\cdot\nabla_x(\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x)) \\
&\quad+i\frac{\epsilon^6}{2}\,\phi_0(A^{\mathscr{A}}(t), B^{\mathscr{A}}(t), 1, 0, 0, z)\frac{1}{2|x|}\,\Delta_x(\eta^{\mathscr{A}}\cdot\nabla_x\Phi_{\mathscr{A}}(x))\Bigg\},
\end{aligned}
$$

where $\tilde{E}_{\mathscr{A}}(a^{\mathscr{A}}, \epsilon z)$ is the second order Taylor series approximation to $E_{\mathscr{A}}(a^{\mathscr{A}}+\epsilon z)$ in the variable ϵz.

We estimate the norms of each of these terms, making use of the relationship $0<\delta<1-\gamma$. They are (in the order presented above) $O(\epsilon^4|t|^{-3})$, $O(\epsilon^5|t|^{-4})$, $O(\epsilon^6|t|^{-5}+\epsilon^5|t|^{-4})$, $O(\epsilon^3|t|^{-2})$, $O(\epsilon^6|t|^{-5})$, $O(\epsilon^3|t|^{-1}\log|t|)$, $O(\epsilon^5|t|^{-3}\log|t|)$, $O(\epsilon^5|t|^{-3}\log|t|)$, $O(\epsilon^4|t|^{-2})$, $O(\epsilon^7|t|^{-5})$, $O(\epsilon^7|t|^{-5})$, and $O(\epsilon^6|t|^{-4})$. We integrate these estimates up to time $t=-C\epsilon^{\gamma}$. For γ close to 1, the integral that has smallest order is fourth one. It is of order $\epsilon^{3-\gamma}$. Thus, by Lemma A1, expression (A.8) agrees with an exact solution (1.4) up to an $O(\epsilon^{1-\gamma})$ error for $-1\leqslant t\leqslant -C\epsilon^{\gamma}$. Since (4.1) agrees with (A.8) to order $\epsilon^{2-2\gamma}$, (4.1) also agrees with an exact solution to (1.4) up to an $O(\epsilon^{1-\gamma})$ error for $-1\leqslant t\leqslant -C\epsilon^{\gamma}$. This proves the claims of Sect. 4 for the negative time outer solution.

For the inner solution we define rescaled variables $s=t/\epsilon$, $y_1=(x_1-\eta_0 t)/\epsilon$, and $y_2=x_2/\epsilon$, and make the ansatz that the inner solution has the form

$$
\psi = e^{i\eta_0 y_1/\epsilon}\, e^{i\eta_0^2 s/2\epsilon}\begin{pmatrix} f_\epsilon(s, y_1, y_2) \\ g_\epsilon(s, y_1, y_2)\end{pmatrix}. \tag{A.9}
$$

When we substitute this into (1.4), we find that f and g must satisfy

$$i\frac{\partial}{\partial s}\begin{pmatrix} f \\ g \end{pmatrix} = -\frac{\epsilon}{2}\Delta_y \begin{pmatrix} f \\ g \end{pmatrix} + \begin{pmatrix} \eta_0 s + y_1 & y_2 \\ y_2 & -\eta_0 s - y_1 \end{pmatrix}\begin{pmatrix} f \\ g \end{pmatrix}. \tag{A.10}$$

If f and g have asymptotic expansions for small ϵ, then the leading terms must satisfy

$$i\frac{\partial}{\partial s}\begin{pmatrix} f_0 \\ g_0 \end{pmatrix} = \begin{pmatrix} \eta_0 s + y_1 & y_2 \\ y_2 & -\eta_0 s - y_1 \end{pmatrix}\begin{pmatrix} f_0 \\ g_0 \end{pmatrix}.$$

The solutions to this equations can be written explicitly in terms of parabolic cylinder functions. They are

$$\begin{pmatrix} f_0(s, y_1, y_2) \\ g_0(s, y_1, y_2) \end{pmatrix} = K_\epsilon(y_1, y_2)\begin{pmatrix} \dfrac{(1-i)y_2}{2\eta_0^{1/2}} D_{p-1}((-1+i)\eta_0^{-1/2}(\eta_0 s + y_1)) \\ D_p((-1+i)\eta_0^{-1/2}(\eta_0 s + y_1)), \end{pmatrix}$$

where $K_\epsilon(y_1, y_2)$ is arbitrary and $p = iy_2^2/2\eta_0$. To determine $K_\epsilon(y_1, y_2)$ we formally match the inner solution to the negative time outer solution for small t but large s. By using the asymptotics of the parabolic cylinder functions [33], we find that

$$K_\epsilon(y_1, y_2) = \pi^{-1/2}\epsilon^{-1}\, e^{-iy_1^2/2\eta_0}\, e^{-iy_2^2 \log(2\eta_0)/4\eta_0}\, e^{i(\log \epsilon)y_2^2/2\eta_0}\, e^{-\pi y_2^2/8\eta_0}\, e^{-(y_1^2+y_2^2)/2}.$$

With this choice of $K_\epsilon(y_1, y_2)$, we must prove that the inner solution (A.9) agrees with an exact solution to (A.10) up to a tolerable error on a time interval that intersects the interval of validity of the outer solution. We do this by applying Lemma A1 with $a = 0$. When we substitute (A.9) into (A.10), the two sides of the equation agree up to a remainder

$$\zeta(\epsilon, s, y_1, y_2) = -\frac{\epsilon}{2}\Delta_y \begin{pmatrix} f_0(s, y_1, y_2) \\ g_0(s, y_1, y_2) \end{pmatrix}.$$

We calculate this Laplacian explicitly, and find that its norm (integrated with respect to dx) is bounded by a constant times ϵs^2. The most rapid growth in s comes from the second derivatives of the parabolic cylinder functions; the growth in y does not cause trouble because of the exponential decay in the function $K_\epsilon(y_1, y_2)$. If $|t| < \epsilon^{\gamma'}$, then $|s| < \epsilon^{\gamma'-1}$, and for s in this interval, Lemma A1 shows that the approximate inner solution agrees with an exact solution up to an error of order

$$\epsilon \int_{-\epsilon^{\gamma'-1}}^{\epsilon^{\gamma'-1}} s^2\, ds = O(\epsilon^{3\gamma'-2}).$$

This error is tolerable as long as $\gamma' > 2/3$.

If we choose $2/3 < \gamma' < \gamma < 1$, then the negative time outer solution and the inner solution are both valid for $-C\epsilon^{\gamma'} < t < -C\epsilon^{\gamma}$. Furthermore, the two solutions agree with one another in this interval up to $o(1)$ errors, and the matching is justified.

For the positive time outer solution, we mimic the analysis of the negative time outer solution. The positive time outer solution is given by expressions (4.3)

and (4.4). The particular form of these expressions is chosen to match the asymptotics [33] of the parabolic cylinder functions when s is large, but t is small. Because of the rapid fall off of the c_j in (4.4), we can estimate the errors for each terms of (4.4) individually, with estimates that grow polynomially in j. The process of estimation of the errors is essentially identical to that used for the negative time outer solution, wo we do not describe the details here.

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