

Mathematical Analysis of Born–Oppenheimer Approximations

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Dedicated to Barry Simon in celebration of his 60th birthday.

ABSTRACT. We review mathematical results concerning Born–Oppenheimer approximations in molecular quantum mechanics.

Introduction

The goal of this paper is to review rigorous mathematical results concerning Born–Oppenheimer approximations. We make no attempt to cover the enormous physics and chemistry literature on the subject.

We begin with a description of the development of the subject in Section 1 without any precise mathematical statements. We present more precise results concerning the standard time–dependent Born–Oppenheimer approximation in Section 2. We describe the time–independent approximation in Section 3. In Section 4, we discuss extensions of the time–dependent approximation to accommodate electron energy level crossings. Finally, in Section 5, we discuss the analogous extensions to accommodate avoided crossings with small gaps.

1. A Historical Introduction

In 1927, just one year after the publication of the Schrödinger equation, Max Born and J. Robert Oppenheimer published a truly remarkable paper [5] on molecular quantum mechanics. A year later, Fritz London published a little–known paper [69] that contained the idea that a related approximation should apply to the dynamics of molecules involved in a chemical reaction.

The paper [5] is famous, and essentially everything that is known about the structure of molecular bound states relies on the approximation developed in it. By contrast, paper [69] is almost unknown and hardly ever cited, but its ideas are the basis for almost everything that is known about molecular dynamics.

Both of these papers exploit the disparity between the masses of nuclei and the masses of electrons. The protons and neutrons that make up nuclei have masses that

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are 1836 times the mass of an electron. Using this large mass ratio, the two papers develop the following physical intuition: Because of their much smaller masses, electrons typically move very rapidly compared to the nuclei. So, the electrons can quickly adjust their state in response to the slow nuclear motion. If they start in their n^{th} bound state, they stay in their n^{th} bound state, determined as though the nuclei were not moving. These electronic bound states and electronic energies depend on the nuclear positions, and the electronic energy levels play the roles of effective potentials for the nuclear motion. Furthermore, because of their large masses, the nuclei obey a semiclassical approximation.

From this intuition, Born and Oppenheimer developed a quantitative model for molecular bound states (in which the nuclei could vibrate and the whole molecule could rotate), and London presented a qualitative model for understanding chemical reactions.

These approximations agreed well with experimental results, but rigorous verification of their validity was not established for half a century. Mathematicians had missed an enormous opportunity to make a contribution to chemical physics much earlier.

Born and Oppenheimer recognized the role of the expansion parameter ϵ , where ϵ^4 was the electron mass divided by the mean nuclear mass. They expanded the energy of a molecule formally through fourth order in ϵ and found a zeroth order approximation for the full molecular wave function. Their expansion for the energy was particularly beautiful. The zeroth order term was the electronic energy with the nuclei at an optimal configuration. The first order term was zero. The second order term was the energy of the harmonic approximation to the vibrational motion of the nuclei. The third order term was zero. The fourth order term contained the energies of the rotational motion, anharmonic corrections to the nuclear vibrations, and non-adiabatic corrections to the electron energy.

The spectra of small molecules reflect this structure. Electronic transitions are typically in the ultraviolet or visible ranges. The much lower energy vibrational transitions are in the infrared. Even lower still are the rotational transitions that are in the microwave range.

Without going into technicalities, we can describe the zeroth and second order terms more precisely. We let the vector X denote the positions of the nuclei in the center of mass frame of reference. The electron Hamiltonian $h(X)$ is then defined as the sum of the quantum mechanical kinetic energy operator for the electrons plus the total potential energy of the electrons and the nuclei. It is a self-adjoint operator on the Hilbert space for the electrons that depends parametrically on X . Discrete eigenvalues of $h(X)$ (that are chosen to depend continuously on X) are called electron energy levels.

Born and Oppenheimer assumed that some electronic level $E(X)$ had a local minimum at some point X_0 . The zeroth order term in their expansion was $E(X_0)$. They then approximated $E(X)$ by its second order Taylor series near X_0 . This led to an exactly solvable Harmonic oscillator problem that gave the vibrational levels at second order in ϵ .

The first rigorous paper in this subject was published in 1973 by Seiler [88]. He verified the formal results of Born and Oppenheimer for an exactly solvable, but unphysical, harmonic oscillator model. A rigorous proof of the validity of the conclusions of Born and Oppenheimer for a physically realistic model was announced

[10] in 1975, and the proof was published by Combes, Duclos, and Seiler [11, 12] in 1980.

The ideas of London’s work were made precise to leading order in ϵ and proved in 1980, under the assumption that the potentials between the particles were smooth [26].

The next developments came roughly five years later. In both the time-independent [28] and time-dependent [27] situations, rigorous expansions were developed to arbitrarily high order in ϵ under the assumption of smooth potentials. These papers relied on the powerful bookkeeping tool called the “Method of Multiple Scales” from the applied mathematics literature. The technique gave a systematic way of separating adiabatic correction terms from semiclassical correction terms. In retrospect, Born and Oppenheimer had used their brilliant physical intuition to do exactly this separation of terms, one by one, through the fourth order calculation.

The high order results led to the question of whether or not one could do the expansions to arbitrary order in ϵ for Coulomb potentials. This was a delicate technical problem because the singularities of the Coulomb interactions between the electrons and the nuclei gave rise to cusps in the electronic wave functions. As a result, many expressions from the smooth potential case did not make sense in the Coulomb case because of a lack of differentiability.

In 1986, Hunziker [48] proved that electron energy levels were analytic as functions of the nuclear positions, even in the Coulomb case. By exploiting his techniques, Born–Oppenheimer expansions to all orders in ϵ were developed for the time-dependent case in [30]. The time-independent expansion was developed to arbitrary order for diatomic molecules in [29], and for general molecules in [66]. These papers were technically very complicated, but the underlying idea was quite simple: Hunziker’s results showed that the electron wave function had directional derivatives of all orders in certain directions in the nuclear configuration space. By setting up the expansion in just the right way, one needed only those directional derivatives.

Similar questions have arisen in scattering theory. For situations with smooth potentials, see [62, 83, 64, 84]. For Coulomb potentials, see [65, 54].

Fairly recently, Nenciu, Martinez, Sordani, Panati, Spohn, and Teufel [75, 81, 82, 91, 92, 94] have developed new approaches to the subject of the time-dependent approximation. These papers consider isolated subsets of the spectrum of $h(X)$ that may be more general than a simple isolated eigenvalue. They do a more general adiabatic approximation for the electrons, and take the semiclassical limit for the nuclei as an independent step, only when necessary or desired. When the chosen subset of the spectrum of $h(X)$ contains many states, the associated nuclear evolution can be complicated.

The underlying innovation of these papers is related to what is done in some practical computations in chemical physics. The semiclassical approximation for the nuclei can lead to larger errors than the adiabatic approximation for the electrons in real systems. Thus, even when considering only one electronic level $E(X)$, some chemical computations handle the nuclei quantum mechanically using the effective potential $E(X)$. Since there are fewer approximations, this should be expected to yield better results. From a technical point of view, pseudodifferential methods

tend to be the most effective tools regarding these issues for providing mathematical justification of these approximations.

The next development in this subject was the study of the effects of electron energy level crossings for the time-dependent approximation. A basic assumption of the standard theory was that if the electrons were in their n^{th} energy level, then this level was isolated from all other electronic levels.

The first step in addressing what would happen when this assumption was not satisfied was to classify level crossings. Since the early days of quantum mechanics [95], it has been known that crossings generically occur on submanifolds of various codimensions, depending on symmetry considerations. Generic crossings of electronic levels with the minimal multiplicity allowed by the symmetry group were classified in [32] and [33]. As expected, the most striking distinction between these crossings was the codimension of the set of nuclear positions where the levels crossed. These were codimensions 1, 2, 3, and 5.

The second step was to propagate molecular wave packets through each of these crossings. This was first done in [33]. For codimension 1 crossings, the leading order result is that the system simply follows the smooth energy level as though no crossing had occurred. However, a new component of order ϵ can be created that propagates according to the dynamics of the other smooth electronic level as the wave packet moves through the crossing. In the higher codimension cases, the leading order wave packet splits into two components as the system moves through the crossing. One piece follows one electronic level and the other piece follows the other level. In contrast to the codimension 1 cases, the final probabilities for ending up on one surface or the other depend strongly on the detailed structure of the nuclear wave packet just before it hits the crossing.

Propagation through crossings can play a significant role in chemical reactions because it provides a mechanism for the electrons to move efficiently from one level to another. For example, a key reaction in human eyesight relies on propagation through a codimension 2 level crossing in the chromophore retinal in the protein rhodopsin. See, *e.g.*, [46] and the references cited there.

In the last several years, other approaches to the study of level crossings have been developed. Fermanian–Kammerer and Gérard [16, 17, 18, 19, 20, 21] introduced objects called two-scale measures that resolve the coupling of levels in an ϵ -dependent neighborhood of the crossing submanifold. In subsequent works, Lasser and Teufel [67, 68] lifted these results to Wigner functions. These approaches provide a very nice phase space description of propagation through level crossings. In particular, they can accommodate quite general initial conditions at the price of losing information on the phases of the wave function. For example, Fermanian–Kammerer and Lasser [22] describe the time behavior of the wave function’s Wigner measure for codimension 2 crossings, and Lasser and Teufel [68] have developed an elegant branching process that describes the splitting of the wave function in the codimension 2, 3, and 5 cases. For an application to the specific molecule Pyrazine, see [23].

Colin de Verdière [7, 8] has developed another approach that can handle phase space level crossings that are more general than those that occur in the Born–Oppenheimer context. This approach is based on the construction of microlocal normal forms for matrix valued symbols in a neighborhood of phase space level

crossings. It provides a description of the propagation of WKB–type states as well as semiclassical wave packets through the crossings.

A related subject is the motion through “avoided crossings.” These are nuclear configurations where two electronic levels approach very close to one another, but do not actually cross. A classification of generic avoided crossings is given in [34]. The authors have studied propagation through avoided crossings with small gaps between levels in [36, 37]. In these papers, two electronic levels are assumed to have an avoided crossing in which the gap between the two levels is $O(\epsilon)$. Under these circumstances, the leading order wave function splits into two pieces, one that propagates on the upper level and one that propagates on the lower level. In case the levels involved in an avoided crossing are known only approximately through perturbation theory in ϵ , Exner and Joye [14] show that the same conclusions hold as well.

Rousse [85, 86] has generalized these results to study the case where the gaps are $O(\epsilon^p)$ for p in an interval around 1. For $p < 1$ the leading order term ignores the avoided crossing. For $p > 1$, the system behaves as though there were an actual crossing. The critical case $p = 1$ is that studied in [36, 37].

There are recent results about pushing the standard time–dependent approximation even further when the electronic Hamiltonian is analytic in the nuclear configuration variable. In the absence of crossings, the authors proved [40] that by optimal truncation of the time–dependent expansion, one obtains approximations in which the errors behave like $C_1 \exp\{-C_2/\epsilon^2\}$, where $C_2 > 0$. The optimal truncation involves the following: When expanding to order ϵ^N , the error terms have norms $C_N \epsilon^N$. By very careful estimation of these errors, one can prove that $C_N \leq AB^N \sqrt{N!}$. The exponential estimates are obtained when N is chosen to behave like $N \sim g/\epsilon^2$ for an appropriate choice of g . Descriptions of exponentially accurate results that use pseudodifferential operator techniques can be found in [75, 76, 81, 91].

Under appropriate hypotheses, results with exponentially accurate error bounds have been proved in the context of stationary scattering theory. See, *e.g.*, [70, 60, 58, 2].

For some very special systems, the large time asymptotics of the leading order exponentially small non–adiabatic correction terms for solutions to the time–dependent Schrödinger equation have been determined in [42]. These transitions are associated with avoided crossings with a fixed gap as $\epsilon \rightarrow 0$. The transition amplitudes and the momenta of the nuclei after the transitions are larger than what one might naïvely guess. Also the form for the nuclear wave function is not what one might naïvely guess in some cases.

In [42], the time development is hidden. A very nice open problem is to understand how these non–adiabatic terms arise as a function of time. Although this has not been solved, preliminary steps towards the solution can be found in [41, 3, 4].

In the last decade, there have been more results concerning the time–independent approximation. Sordani [89] has examined highly excited rotational states of diatomic molecules. Rousse [86, 87] has studied highly excited vibrational states when the nuclei have one degree of freedom. In this case, a Bohr–Sommerfeld

condition determines the correct vibrational levels for the nuclei. Rouse holds the energy fixed as $\epsilon \rightarrow 0$, so the nuclei are in vibrational state n , where $n = O(\epsilon^{-2})$.

Very recently, Hagedorn and Toloza have applied optimal truncation techniques to the time-independent Born–Oppenheimer approximation. They did this first [44] for a toy model with just two electronic levels and the nuclei with one degree of freedom. They generalized this to fairly realistic electron Hamiltonians [45], but with the nuclei restricted to one degree of freedom.

In the last 25 years, many other interesting developments have occurred in closely related areas.

Resonances. In traditional two-body scattering, tunnelling effects often give rise to resonances. In molecular systems there are more such mechanisms. For example, non-adiabatic transitions by the electrons can allow a system to escape from a well. This leads to the theory of predissociation. Klein [63] studied predissociation in 1987. Martinez studied resonances and proved that in many instances, they had exponentially long lifetimes [71, 72, 73, 74]. Resonances associated with codimension 2 level crossings have also been studied by Nédélec [77, 78, 79, 80] and Fujiié, Lasser and Nédélec [24].

Resolvent Estimates. Many detailed results on scattering matrices and cross sections depend on (weighted) estimates for the resolvent of the Hamiltonian near its spectrum. For molecular systems, Jecko [49, 50, 51, 52] has studied these estimates in a variety of circumstances, including situations related to level crossings. These papers construct conjugate operators in the sense of Mourre for the Hamiltonian, which is a challenge when the levels may cross.

Molecules Interacting with Laser Pulses. With the development of ultra-short laser pulses, enormous amounts of information about molecular dynamics can be obtained experimentally. Much of the theory related to these experiments relies on the idea that electrons absorb photons on such a short time scale that the nuclei do not have time to move. Jilcott [55, 56] has made this idea precise and has proven its validity. Hagedorn, Rouse, and Jilcott [43] have corrected a calculational error in [55, 56] and have examined transition amplitudes to different vibrational levels for the nuclei when a laser pulse causes an electronic transition. Electronic transitions typically excite $O(\epsilon^{-1})$ different vibrational states. The paper [43] rigorously calculates the Franck–Condon factors that govern the strengths of the associated spectral lines.

Results related to Berry Phases. Many papers on Born–Oppenheimer approximations assume the chosen electronic level $E(X)$ has multiplicity 1, and that the phases of the electronic eigenstates can be chosen in accordance with the “adiabatic connection” on the bundle of eigenstates over the nuclear configuration manifold. When this cannot be done, the system displays Berry phases. Herrin and Howland [47] examine a diatomic model that has a Berry phase associated with rotations of the whole molecule. They observe that the rotational energy levels are altered in this case. In related work, Faure and Zhilinskii [15] demonstrate a precise link between geometrical properties of electronic eigenspaces and the structure of the spectrum of the full molecular Hamiltonian.

Time–Independent Information about Crossings and Avoided Crossings.

Time–Independent techniques can yield information about transitions between levels associated with avoided crossings. For example, in models where the nuclei have only one degree of freedom and the electronic Hilbert space is finite dimensional, the time–independent Schrödinger equation is equivalent to a system of ODE’s. In this representation, the $\epsilon \rightarrow 0$ limit looks formally like an adiabatic problem where X has become the time variable. The situation is more complicated than the standard adiabatic problem because the resulting Hamiltonian is not self–adjoint. However, in some situations, exponentially small scattering amplitudes associated with avoided crossings can be calculated quite explicitly. See, *e.g.*, [70, 60, 57, 58, 9, 61].

Also, solutions to the time–independent Schrödinger equation near codimension 2 crossings have been found in [25].

Chemistry without the Born–Oppenheimer Approximation? One can ask whether or not certain fundamental concepts used in chemistry can be formulated without the Born–Oppenheimer approximation. For example, when there are isomers and/or identical nuclei in the system, do chemical structure diagrams make sense if the nuclei and electrons are simply treated as quantum particles? For a recent discussion of this topic, see the review article [93].

2. The Standard Time–Dependent Approximation

In this section we describe the coherent state approach to the time–dependent Born–Oppenheimer approximation in some detail. This approach yields a rather simple, complete description of the molecular wave function, although it requires special initial conditions and the semiclassical approximation for the nuclei. The more sophisticated approaches described in Section 1 can allow more general initial nuclear states and/or avoid the semiclassical treatment of the nuclei. However, many of them study Wigner distributions on phase space rather than wave functions for the nuclei.

To make precise statements, we need some preliminary notation and results concerning semiclassical wave packets for the nuclei. We have tried to minimize the technicalities, but some are unavoidable.

2.1. Semiclassical Wave Packets. The “coherent state” approach to semiclassical quantum mechanics makes use of generalizations of the usual harmonic oscillator eigenfunctions. These wave packets are described in detail in [35]. Although the notation is different, they coincide with “generalized squeezed states” [13].

In d dimensions, these states are $\varphi_j(A, B, \hbar, a, \eta, x)$, where j is an d –dimensional multi-index, A and B are complex $d \times d$ matrices, a and η are d –dimensional vectors, and x is the d –dimensional variable. We always assume A and B satisfy

$$B^t A - A^t B = 0, \quad \text{and}$$

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

where the superscript t denotes the transpose. The first of these conditions is equivalent to BA^{-1} being symmetric, *i.e.*, (real symmetric) + i (real symmetric). The second condition is equivalent to $(\text{Re } BA^{-1})^{-1} = AA^*$. We let $|A|$ denote the positive square root of AA^* .

When the multi-index j equals zero, these states are the complex Gaussians

$$\varphi_0(A, B, \hbar, a, \eta, x) = \pi^{-d/4} \hbar^{d/4} [\det A]^{-1/2}$$

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

Physically, a represents a classical position, and η represents a classical momentum. The position uncertainty is given by the covariance matrix $\hbar^{1/2}|A|$ and the momentum uncertainty is given by $\hbar^{1/2}|B|$. The choice of square root for $[\det A]^{-1/2}$ is arbitrary, but is chosen to depend continuously on time when A depends on time.

For non-zero values of j , the easiest way to define the semiclassical wave packets is to introduce raising operators [35]. These act on Schwartz functions ψ by

$$\begin{aligned} & (\mathcal{A}_m(A, B, \hbar, a, \eta)^* \psi)(x) \\ &= \frac{1}{\sqrt{2\hbar}} \left(\left[\sum_{n=1}^d \bar{B}_{nm}(x_n - a_n) - i \sum_{n=1}^d \bar{A}_{nm} \left(-i\hbar \frac{\partial}{\partial x_n} - \eta_n \right) \right] \psi \right)(x). \end{aligned}$$

For any non-zero multi-index j , we define

$$\begin{aligned} \varphi_j(A, B, \hbar, a, \eta, \cdot) &= \frac{1}{\sqrt{j!}} (\mathcal{A}_1(A, B, \hbar, a, \eta)^*)^{j_1} (\mathcal{A}_2(A, B, \hbar, a, \eta)^*)^{j_2} \\ &\quad \times \cdots (\mathcal{A}_d(A, B, \hbar, a, \eta)^*)^{j_d} \varphi_0(A, B, \hbar, a, \eta, \cdot). \end{aligned}$$

For fixed a, η, A , and B , these functions form an orthonormal basis of $L^2(\mathbb{R}^d)$, indexed by j . Numerous properties of these functions are discussed in [35]. The main property that we need is that modulo an $O(\hbar^{1/2})$ error, $e^{iS(t)/\hbar} \varphi_j(A(t), B(t), \hbar, a(t), \eta(t), x)$ satisfies the time-dependent Schrödinger equation

$$(2.1) \quad i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2} \Delta \psi + V(x) \psi$$

if $V \in C^3(\mathbb{R}^d)$ is bounded below, $V(x) \leq C e^{Mx^2}$, and

$$(2.2) \quad \dot{a}(t) = \eta(t)$$

$$(2.3) \quad \dot{\eta}(t) = -(\nabla V)(a(t))$$

$$(2.4) \quad \dot{S}(t) = \frac{\eta(t)^2}{2} - V(a(t))$$

$$(2.5) \quad \dot{A}(t) = iB(t)$$

$$(2.6) \quad \dot{B}(t) = iV^{(2)}(a(t))A(t).$$

Here $V^{(2)}$ denotes the Hessian matrix $\frac{\partial^2 V}{\partial X_i \partial X_k}$. The solution to (2.2)–(2.6) is completely determined by the classical phase space flow generated by the potential V .

By taking time-dependent superpositions of the $e^{iS(t)/\hbar} \varphi_j(A(t), B(t), \hbar, a(t), \eta(t), x)$ (with finitely many different j) this result can be improved to give $O(\hbar^{m/2})$ accurate approximations for any m if $V \in C^{m+3}(\mathbb{R}^d)$.

When V is analytic, these results can be improved by using optimal truncation techniques to produce approximations with $O(e^{-\Gamma/\hbar})$ errors [38, 39]. Similar results on the propagation of observables can also be found [6].

2.2. Electron Energy Levels and Phases of Eigenstates. A basic assumption of the standard Born–Oppenheimer approximation is that the electron Hamiltonian $h(X)$, acting as a self-adjoint operator on the electronic Hilbert space \mathcal{H}_{el} , depends smoothly (in the strong resolvent sense) on X for all X in some connected open set $\mathcal{X} \subset \mathbb{R}^d$. We further assume that $h(X)$ has an isolated non-degenerate eigenvalue $E(X)$ that depends smoothly on $X \in \mathcal{X}$. The function $E(X)$ is called an electron energy level.

For simplicity in this discussion, we assume that the eigenvector $\Phi(X)$ corresponding to $E(X)$ can be chosen so that

$$(2.7) \quad \langle \Phi(X), v \cdot \nabla_X \Phi(X) \rangle = 0$$

for any vector v . This condition is satisfied if \mathcal{X} has trivial homology groups and $h(X)$ commutes with a conjugation for all $X \in \mathcal{X}$. In this case (2.7) is satisfied if $\Phi(X)$ is chosen to equal its conjugate. In more complicated situations with Longuet–Higgins phases or Berry phases, we can use a time-dependent choice of phase of $\Phi(X)$ to satisfy the appropriate analog of (2.7).

2.3. The Multiple Scales Technique for the Time-Dependent Approximation. One way or another, all the mathematical results on the time-dependent Born–Oppenheimer approximation make use of two length scales in the nuclear variables. The authors’ favorite way of doing this is to use the method of multiple scales.

The choice of time variable for the time-dependent Schrödinger equation can be made so that the nuclear motion has a non-trivial limit. After this and some trivial rescaling of the nuclear variables, the equation we wish to solve can be written as

$$(2.8) \quad i \epsilon^2 \frac{\partial \Psi}{\partial t} = - \frac{\epsilon^4}{2} \Delta_X \Psi + h(X) \Psi,$$

where $\Psi \in L^2(\mathbb{R}^d, \mathcal{H}_{el})$.

Since ϵ^2 appears in (2.8) precisely where \hbar appears in (2.1), we make use of the semiclassical wave packets. The chosen electron energy level $E(X)$ plays the role of the potential in the equations (2.2)–(2.6) in the Born–Oppenheimer situation.

The method of multiple scales replaces the nuclear configuration variable X by two variables

$$x = X \quad \text{and} \quad y = (X - a(t))/\epsilon,$$

where $a(t)$ describes the classical configuration for the nuclei. Rather than attempting to solve (2.8) directly, we first study solutions $\tilde{\Psi}(x, y, t)$ to

$$(2.9) \quad i \epsilon^2 \frac{\partial \tilde{\Psi}}{\partial t} = - \frac{\epsilon^4}{2} \Delta_x \tilde{\Psi} - \epsilon^3 \nabla_x \cdot \nabla_y \tilde{\Psi} - \frac{\epsilon^2}{2} \Delta_y \tilde{\Psi} \\ + [h(x) - E(x)] \tilde{\Psi} + E(a(t) + \epsilon y) \tilde{\Psi}.$$

Then we obtain a solution $\Psi(X, t)$ to (2.8) as $\Psi(X, t) = \tilde{\Psi}\left(X, \frac{X-a(t)}{\epsilon}, t\right)$.

Anticipating the same dynamical phases as in the semiclassical wave packets, we look for solutions to (2.9), of the form

$$\tilde{\Psi}(x, y, t) = e^{iS(t)/\epsilon^2} e^{i\eta(t)\cdot y/\epsilon} \chi(x, y, t).$$

Then $\chi(x, y, t)$ must satisfy

$$\begin{aligned} i\epsilon^2 \frac{\partial \chi}{\partial t} = & \left[-\frac{\epsilon^4}{2} \Delta_x - \epsilon^3 \nabla_x \cdot \nabla_y - \frac{\epsilon^2}{2} \Delta_y - i\epsilon^2 \eta(t) \cdot \nabla_x \right. \\ & + [E(a(t) + \epsilon y) - E(a(t)) - \epsilon (\nabla E)(a(t)) \cdot y] \\ & \left. + [h(x) - E(x)] \right] \chi \end{aligned}$$

We substitute a formal expansion

$$\chi(x, y, t) = \psi_0(x, y, t) + \epsilon \psi_1(x, y, t) + \epsilon^2 \psi_2(x, y, t) + \dots$$

into this equation, expand $E(a(t) + \epsilon y)$ in its Taylor series in powers of ϵ , and equate terms of equal powers of ϵ on the two sides of the resulting expression.

Order 0. The $O(\epsilon^0)$ terms require

$$[h(x) - E(x)] \psi_0(x, y, t) = 0.$$

Thus,

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

where g_0 is, as of yet, not determined.

Order 1. The $O(\epsilon^1)$ terms require

$$[h(x) - E(x)] \psi_1(x, y, t) = 0.$$

Thus,

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

where g_1 is, as of yet, not determined.

Order 2. The $O(\epsilon^2)$ terms are much more complicated. They require

$$i\dot{\psi}_0 = -\frac{1}{2} \Delta_y \psi_0 + E^{(2)}(a(t)) \frac{y^2}{2} \psi_0 - i\eta(t) \cdot \nabla_x \psi_0 + [h(x) - E(x)] \psi_2,$$

where the dot $\dot{}$ denotes the time derivative, and $E^{(2)}(a) \frac{y^2}{2}$ denotes $\frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial x_i \partial x_j}(a) y_i y_j$. The utility of the multiple scales technique now becomes evident because we can separate this equation into parts. The first part consists of all components that are in the $\Phi(x)$ direction in the electronic Hilbert space. The second part consists of all components that are orthogonal to $\Phi(x)$ in the electronic Hilbert space. Equality must be satisfied for both of these components.

The two equations we obtain are

$$(2.10) \quad i\dot{g}_0 + i\eta(t) \cdot \nabla_x g_0 = -\frac{1}{2} \Delta_y g_0 + E^{(2)}(a(t)) \frac{y^2}{2} g_0,$$

and

$$(2.11) \quad [h(x) - E(x)] \psi_2(x, y, t) = i g_0(x, y, t) \eta(t) \cdot (\nabla_x \Phi)(x).$$

For any j , equation (2.10) is solved by

$$g_0(x, y, t) = \epsilon^{-d/2} e^{iS(t)/\epsilon^2} \phi_j(A(t), B(t), 1, a(t), \eta(t), y),$$

where $E(X)$ plays the role of the potential in determining the solution to (2.2)–(2.6). Note that these solutions have no x dependence, and if we substitute $(X - a(t))/\epsilon$ for y , they are normalized in $L^2(\mathbb{R}^d)$. We henceforth assume that each such function g_n is independent of x . This removes some of the ambiguity of expressing functions of X in terms of either x or y .

To solve (2.11), we note that $[h(x) - E(x)]$ is invertible as an operator on the orthogonal complement of the span of $\Phi(x)$. We denote this inverse by $r(x)$, and then,

$$\psi_2(x, y, t) = \psi_2^\perp + \psi_2^\parallel,$$

where

$$\psi_2^\perp = i g_0(y, t) r(x) \eta(t) \cdot (\nabla_x \Phi)(x)$$

and

$$\psi_2^\parallel = g_2(x, y, t) \Phi(x),$$

with $g_2(x, y, t)$ not yet determined.

Order $n \geq 3$. The higher order terms are dealt with in the same way, although the technical details are more complicated. We project the $O(\epsilon^n)$ equation into the $\Phi(x)$ direction and into the direction perpendicular to $\Phi(x)$ in the electronic Hilbert space. In the $\Phi(x)$ direction, we determine g_{n-2} and hence ψ_{n-2}^\parallel by using techniques associated with the semiclassical wave packets. In the orthogonal direction we employ the reduced resolvent operator $r(x)$ to determine ψ_n^\perp . Thus, the multiple scales bookkeeping allows us to separate terms that we treat by semiclassical techniques from those that we handle by adiabatic techniques. For the details, see [27, 31, 33].

After doing these formal calculations, a rigorous proof of the validity of the time-dependent approximation is a consequence of the following lemma. We apply this lemma to the function

$$\begin{aligned} \Psi_\epsilon(X, t) &= \sum_{n=0}^N \epsilon^n \psi_n \left(X, \frac{X - a(t)}{\epsilon}, t \right) \\ &+ \epsilon^{N+1} \psi_{N+1}^\perp \left(X, \frac{X - a(t)}{\epsilon}, t \right) + \epsilon^{N+2} \psi_{N+2}^\perp \left(X, \frac{X - a(t)}{\epsilon}, t \right) \end{aligned}$$

to obtain the result with an $O(\epsilon^{N+1})$ error.

LEMMA 2.1. *Given a molecular wave function $\Psi_\epsilon(X, t)$, define*

$$\zeta_\epsilon(x, t) = i \epsilon^2 \frac{\partial \Psi_\epsilon}{\partial t}(X, t) + \frac{\epsilon^4}{2} (\Delta_X \Psi_\epsilon)(X, t) - h(X) \Psi_\epsilon(X, t).$$

If $\|\zeta(\cdot, t)\| \leq \mu(\epsilon, t)$, then $\Psi_\epsilon(X, t)$ differs in norm from the exact solution to (2.8) with initial condition $\Psi_\epsilon(X, 0)$ by at most $\int_0^t \mu(\epsilon, s) ds / \epsilon^2$.

When $h(\cdot)$ satisfies an analyticity condition we can improve these results further by employing an optimal truncation technique. We obtain a time-dependent approximation with an error bound of the form $O(\exp(-\Gamma/\epsilon^2))$ by using the above construction and choosing $N \sim g/\epsilon^2$ for an appropriate choice of g . The technical details can be found in [40].

3. The Time-Independent Approximation

We can use the Method of Multiple Scales to construct quasimodes and quasi-energies for the time-independent Born-Oppenheimer approximation also. The results of [11] show that under appropriate hypotheses, these quasienergies correspond exactly to the low-lying eigenvalues of the full Hamiltonian. For simplicity, we present the formal calculations near an isolated minimum of an electron energy level. In most cases of interest, after the removal of the center of mass motion of the molecule, there is still a two or three dimensional rotational symmetry that causes the minimum to be attained on a non-trivial manifold (isomorphic to the two-sphere S^2 or the full rotation group $SO(3)$). This physical situation is technically more complicated because degenerate perturbation theory is required.

In our example, we assume that an electron energy level $E(X)$ has a local minimum at some point $X = a$ with the second derivative matrix $E^{(2)}(a)$ strictly positive. Again, to avoid degenerate perturbation theory, we assume the square roots ω_k of the eigenvalues of this matrix are not rational multiples of one another. We then introduce the two variables

$$x = X \quad \text{and} \quad y = \frac{X - a}{\epsilon}.$$

We then look for approximate solutions to the equation

$$(3.1) \quad -\frac{\epsilon^4}{2} \Delta_x \tilde{\Psi} - \epsilon^3 \nabla_x \cdot \nabla_y \tilde{\Psi} - \frac{\epsilon^2}{2} \Delta_y \tilde{\Psi} + [h(x) - E(x)] \tilde{\Psi} \\ + E(a + \epsilon y) \tilde{\Psi} + \sum_{n=4}^{\infty} \epsilon^n (T_n(x) - T_n(a + \epsilon y)) \tilde{\Psi} = \mathcal{E}(\epsilon) \tilde{\Psi}.$$

The operators $T_n(\cdot)$ will be chosen during the perturbation calculations so that certain functions will be independent of x .

We now substitute formal series expansions

$$\mathcal{E}(\epsilon) = \mathcal{E}_0 + \epsilon \mathcal{E}_1 + \epsilon^2 \mathcal{E}_2 + \dots \\ \tilde{\Psi} = \psi_0 + \epsilon \psi_1 + \epsilon^2 \psi_2 + \dots$$

into (3.1). We then expand $E(a + \epsilon y)$ and $T_n(a + \epsilon y)$ in their Taylor series in powers of ϵ and equate terms of the same orders on the two sides of the resulting equation.

Order 0. The order ϵ^0 terms require

$$[h(x) - E(x)] \psi_0(x, y) + E(a) \psi_0(x, y) = \mathcal{E}_0 \psi_0(x, y).$$

This equation has solutions

$$\mathcal{E}_0 = E(a),$$

and

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

where g_0 is not yet determined. We later choose $T_4(x)$ so that g_0 has no x dependence.

Order 1. After some cancellations, the order ϵ^1 terms require

$$[h(x) - E(x)] \psi_1(x, y) + (\nabla E)(a) \cdot y \psi_0(x, y) = \mathcal{E}_1 \psi_0(x, y).$$

Since $E(x)$ has a local minimum at a , $(\nabla E)(a) = 0$. Thus, we learn that

$$\mathcal{E}_1 = 0,$$

and

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

where g_1 is not yet determined. We later choose $T_5(x)$ so that g_1 has no x dependence.

Order 2. After some simplification, the order ϵ^2 terms require

$$[h(x) - E(x)] \psi_2(x, y) - \frac{1}{2} (\Delta_y \psi_0)(x, y) + E^{(2)}(a) \frac{y^2}{2} \psi_0(x, y) = \mathcal{E}_2 \psi_0(x, y).$$

We project this equation into the span of $\Phi(x)$ and into the direction orthogonal to $\Phi(x)$ in the electronic Hilbert space to obtain two conditions:

$$-\frac{1}{2} (\Delta_y g_0)(y) + E^{(2)}(a) \frac{y^2}{2} g_0(y) = \mathcal{E}_2 g_0$$

and

$$[h(x) - E(x)] \psi_2(x, y) = 0.$$

The first of these equations is a harmonic oscillator problem. We obtain $g_0(y)$ as a product of Hermite polynomials times a Gaussian, and

$$\mathcal{E}_2 = \sum_{k=1}^d \left(n_k + \frac{1}{2} \right) \omega_k,$$

where each vibrational quantum number n_k is a non-negative integer. The second equation simply tells us that

$$\psi_2(x, y) = g_2(x, y) \Phi(x).$$

We will choose $T_6(x)$ so that g_2 has no x dependence.

Order 3. The order ϵ^3 terms require

$$[h(x) - E(x)] \psi_3 + \left(-\frac{1}{2} \Delta_y + E^{(2)}(a) \frac{y^2}{2} - \mathcal{E}_2 \right) \psi_1$$

$$- (\nabla_y g_0) \cdot (\nabla_x \Phi)(x) + E^{(3)}(a) \frac{y^3}{3!} \psi_0 = \mathcal{E}_3 \psi_0.$$

We again project into the $\Phi(x)$ direction and the perpendicular direction in the electron Hilbert space. For the terms in the $\Phi(x)$ direction, we also project into the $g_0(y)$ direction and the perpendicular direction in $L^2(\mathbb{R}^d, dy)$.

Thus, we get three conditions. From the terms orthogonal to $\Phi(x)$, we have

$$[h(x) - E(x)] \psi_3 = (\nabla_y g_0) \cdot (\nabla_x \Phi)(x).$$

By applying the reduced resolvent operator $r(x)$ for $[h(x) - E(x)]$, we obtain

$$\psi_3(x, y) = g_3(x, y) \Phi(x) + r(x) (\nabla_y g_0) \cdot (\nabla_x \Phi)(x).$$

We will choose $T_7(x)$ so that g_3 has no x dependence. Since any homogeneous cubic polynomial in y times $g_0(y)$ is orthogonal to $g_0(y)$, the terms in the direction of $g_0(y) \Phi(x)$, require

$$\mathcal{E}_3 = 0.$$

The terms that are multiples of $\Phi(x)$ but orthogonal to $g_0(y)$ require

$$\left(-\frac{1}{2}\Delta_y + E^{(2)}(a)\frac{y^2}{2} - \mathcal{E}_2\right) g_1 = -E^{(3)}(a)\frac{y^3}{3!} g_0.$$

We do not precisely normalize our quasimodes, so we can take g_1 orthogonal to g_0 . We then solve the equation for g_1 by applying the reduced resolvent operator for $\left(-\frac{1}{2}\Delta_y + E^{(2)}(a)\frac{y^2}{2} - \mathcal{E}_2\right)$.

Order 4. The order ϵ^4 terms require

$$\begin{aligned} [h(x) - E(x)] \psi_4 + \left(-\frac{1}{2}\Delta_y + E^{(2)}(a)\frac{y^2}{2} - \mathcal{E}_2\right) \psi_2 \\ - (\nabla_y g_1) \cdot (\nabla_x \Phi)(x) - \frac{1}{2} g_0(y) (\Delta_x \Phi)(x) + E^{(3)}(a)\frac{y^3}{3!} \psi_1 \\ + E^{(4)}(a)\frac{y^4}{4!} \psi_0 + T_4(x) \psi_0 - T_4(a) \psi_0 = \mathcal{E}_4 \psi_0. \end{aligned}$$

We break this into three equations by taking the same projections as for the order ϵ^3 terms. The multiples of $g_0(y) \Phi(x)$ yield

$$\begin{aligned} -\frac{1}{2} \langle \Phi(x), \Delta_x \Phi(x) \rangle_{\mathcal{H}_{el}} + \langle g_0(y), E^{(3)}(a)\frac{y^3}{3!} g_1(y) \rangle_y \\ + \langle g_0(y), E^{(4)}(a)\frac{y^4}{4!} g_0(y) \rangle_y + T_4(x) - T_4(a) = \mathcal{E}_4. \end{aligned}$$

We can solve this equation by taking

$$T_4(x) = \frac{1}{2} \langle \Phi(x), \Delta_x \Phi(x) \rangle_{\mathcal{H}_{el}}$$

and

$$\mathcal{E}_4 = -T_4(a) + \langle g_0(y), E^{(3)}(a)\frac{y^3}{3!} g_1(y) \rangle_y + \langle g_0(y), E^{(4)}(a)\frac{y^4}{4!} g_0(y) \rangle_y.$$

We solve the other two equations by applying the reduced resolvents of $[h(x) - E(x)]$ and $\left(-\frac{1}{2}\Delta_y + E^{(2)}(a)\frac{y^2}{2} - \mathcal{E}_2\right)$ as we did for the order ϵ^3 terms.

Order $n \geq 5$. At higher orders, we simply mimic what we did for the order ϵ^4 . The order ϵ^n terms determine $T_n(x)$, \mathcal{E}_n , the component of ψ_n orthogonal to $\Phi(x)$, and $g_{n-2}(y)$.

We do these formal calculations to any order $n \geq 2$. We then drop the terms in the wave functions and energy that have not yet been determined. Next, we replace x by X and y by $(X - a)/\epsilon$ in $\tilde{\Psi}$ to obtain the quasimode Ψ_ϵ . We easily check that

$$\|H(\epsilon) \Psi_\epsilon - \mathcal{E}(\epsilon) \Psi_\epsilon\| = O(\epsilon^{n+1}),$$

where $H(\epsilon)$ is the full Hamiltonian. The spacing between levels is $O(\epsilon^2)$ for our simple model, so this yields non-trivial spectral information.

Hagedorn and Toloza attempted to apply optimal truncation techniques to this expansion, but could not get the required estimates because of difficulties with the

$T_n(x)$. By abandoning the multiple scales technique and working just in the y variable, they succeeded in applying optimal truncation techniques to a different expansion. By doing so, they obtained quasimodes with errors of order $\exp(-\Gamma/\epsilon^2)$ for some models [44, 45].

4. Propagation through Level Crossings

We present fewer details in this section because the subject is more technical. Again, we present a summary of the authors’ work on the subject. The other approaches deal with Wigner distributions on phase space instead of the wave functions and rely heavily on pseudodifferential operator techniques and two-scale measures.

Before studying propagation through level crossings it is necessary to study the structure of different kinds of level crossings. This subject is studied in [32] and Chapter 2 of [33], which we now briefly summarize without any proofs.

Symmetry considerations are central to the classification of different types of crossings. In quantum mechanics, symmetry operations may or may not involve time reversing operators, which are anti-unitary (*i.e.*, they have all the properties of unitary operators, except that they have $U(\lambda\psi) = \bar{\lambda}U(\psi)$ instead of $U(\lambda\psi) = \lambda U(\psi)$). Thus, standard group representation theory is not sufficient, and one must allow “corepresentations” which involve linear and anti-linear operators.

The relevant symmetry group G is the set of all X -independent unitary and anti-unitary operators on the electron Hilbert space that commute with the electron Hamiltonian $h(X)$ for all X . Each electron energy level is associated with an irreducible representation (or corepresentation) of G . Minimal multiplicity irreducible representations are one dimensional, and minimal multiplicity irreducible corepresentations are either one or two dimensional. In standard situations, the two dimensional irreducible corepresentations occur when electron spin is taken into account and the molecule has an odd number of electrons. We henceforth consider only electronic levels of the minimal multiplicity allowed by the representations or corepresentations.

Generic crossings of levels associated with inequivalent irreducible (co)representations are the simplest. The two eigenvalues are simply two different functions of X , and they generically take equal values on a codimension 1 submanifold. Near the crossing, the electronic eigenfunctions associated with the two levels can be chosen to depend smoothly on X . So, in a basis that depends smoothly on X , the two levels are described by a diagonal matrix. In [32, 33], these are crossings of types A, C, D, E, F, G, and H. Crossings of type A involve eigenvalues corresponding to inequivalent representations. The others come from eigenvalues that correspond to inequivalent corepresentations, and irreducible corepresentations, themselves come in three different types.

The situation is much more interesting when two levels associated with equivalent (co)representations cross. In [32, 33], these are crossings of types B, I, J, and K, and the manifolds where the levels are equal generically have codimensions 3, 2, 3, and 5, respectively.

The type B situation occurs when there are no time-reversing operators in the symmetry group. Near the crossing, the behavior of the two levels is similar to that

of the general traceless Hermitian matrix

$$\begin{pmatrix} X_1 & X_2 + iX_3 \\ X_2 - iX_3 & -X_1 \end{pmatrix},$$

whose eigenvalues are $\pm\sqrt{X_1^2 + X_2^2 + X_3^2}$. The eigenvectors cannot be chosen to depend smoothly on X and have non-trivial Berry phases.

The type I situation comes from a one dimensional corepresentation. The behavior of the levels near the crossing is similar to that of the general traceless real symmetric matrix

$$\begin{pmatrix} X_1 & X_2 \\ X_2 & -X_1 \end{pmatrix},$$

whose eigenvalues are $\pm\sqrt{X_1^2 + X_2^2}$. The eigenvectors cannot be chosen to depend smoothly on X , and they exhibit a degenerate Berry phase that is frequently called a Longuet-Higgins phase. If the eigenvectors are locally chosen to be real, then they pick up a minus sign as the parameter X is moved around the crossing manifold. The chemists use the term ‘‘conical intersection’’ for these crossings. For our specific example, the plot of the eigenvalues with (X_1, X_2) horizontally and energy vertically yields the cone $E^2 = X_1^2 + X_2^2$ with the crossing at the vertex.

The type K crossings come from a two dimensional irreducible corepresentation. Their local behavior is like the direct sum of a type B matrix and its conjugate. The canonical example is

$$\begin{pmatrix} X_1 & X_2 + iX_3 & 0 & 0 \\ X_2 - iX_3 & -X_1 & 0 & 0 \\ 0 & 0 & X_1 & X_2 - iX_3 \\ 0 & 0 & X_2 + iX_3 & -X_1 \end{pmatrix},$$

whose eigenvalues are $\pm\sqrt{X_1^2 + X_2^2 + X_3^2}$ and are doubly degenerate.

Type J crossings occur on codimension 5 submanifolds. The canonical example is the matrix

$$\begin{pmatrix} X_1 & 0 & X_2 + iX_3 & X_4 + iX_5 \\ 0 & X_1 & -X_4 + iX_5 & X_2 - iX_3 \\ X_2 - iX_3 & -X_4 - iX_5 & -X_1 & 0 \\ X_4 - iX_5 & X_2 + iX_3 & 0 & -X_1 \end{pmatrix},$$

whose eigenvalues are $\pm\sqrt{X_1^2 + X_2^2 + X_3^2 + X_4^2 + X_5^2}$ and are doubly degenerate. The bundles of eigenvectors have a ‘‘non-Abelian Berry phase’’ that is given by a 2×2 unitary matrix instead of a complex number. The complicated geometrical structure of these bundles is described in [1].

The main results of [33] describe what happens when a standard time-dependent Born-Oppenheimer wave packet encounters any of the types of generic, minimal multiplicity crossings. At codimension 1 crossings, nothing interesting happens to leading order in ϵ . The zeroth order wave packet follows the smooth electron energy level as though the second level were not there. Depending on the behavior of the derivatives of the electron states with respect to the nuclear coordinates, a term of order ϵ associated with the second level can be created as the zeroth order term passes through the crossing. All other levels of $h(X)$ are involved only at second order in ϵ , so they are irrelevant through first order.

The higher codimension crossings cause much more significant effects because the electronic states are singular near the crossings. In [33], propagation through these crossings is studied by using matched asymptotic expansions. The analysis is very technical, but the underlying idea is quite simple. One proves that there exist two numbers ξ and ξ' that satisfy $\frac{2}{3} < \xi' < \xi < 1$, such that all of the following results can be proven.

An incoming standard Born–Oppenheimer state away from the crossing is chosen so that its associated classical position $a(t)$ hits the crossing submanifold at some time that we take to be $t = 0$. The leading order standard approximation agrees with an exact solution up to errors of order ϵ^{p_1} for some $p_1 > 0$ for all $t \in [-T, -\epsilon^\kappa)$, for all $\kappa < \xi$.

Next, an “inner expansion” is derived that agrees with an exact solution up to errors of order ϵ^{p_2} for some $p_2 > 0$ when $|t| < \epsilon^{\xi'}$. This wave packet is arranged so that it agrees with the incoming wave packet up to errors of order ϵ^{p_3} with $p_3 > 0$ for times $t = -\epsilon^\kappa$ with $\xi' < \kappa < \xi$ where both expansions are valid.

For small positive times ϵ^κ with $\xi' < \kappa < \xi$, a similar matching is done to outgoing standard time–dependent Born–Oppenheimer states that have errors of order ϵ^{p_1} for $t \in (\epsilon^\kappa, T]$, when $\kappa < \xi$. So, for any time $t \in [-T, T]$, at least one of the three expansions is valid to leading order in ϵ .

The inner expansion is obtained by replacing the original time variable t by a rescaled time $s = t/\epsilon$ and replacing the original variable X by $y = (X - a(t))/\epsilon$. In the new variables, a formal asymptotic expansion is substituted into the Schrödinger equation. The leading order terms satisfy a hyperbolic PDE that has very simple characteristics. Along each characteristic, it can be solved explicitly in terms of parabolic cylinder functions of complex order and complex argument. The behavior of these special functions is known well enough to yield a proof that the matching can be done rigorously.

When a wave packet propagates through these crossings, it splits at leading order, ϵ^0 , into two separate wave packets. One piece propagates according to the dynamics of one electronic level involved in the crossing. The other piece has dynamics governed by the second level. These separate wave packets have complicated phases, but their absolute values can be found in a relatively simple way because the leading order equation for the inner solution is hyperbolic. Along each characteristic one finds that a Landau–Zener formula dictates the probability to end up on the upper or lower of the two levels. However, there is a different minimal gap between the electronic levels felt along different characteristics. The parts of the wave function that go right through the crossing manifold feel no gap, and they follow the smooth electronic level. If they start on the lower level, they go to the upper level, and *vice versa*. The pieces of the wave function that stay far from the crossing (on a distance scale of order ϵ) obey the adiabatic theorem and stay on the same level because they feel a relatively large gap. The Landau–Zener formula gives the precise result for intermediate gaps.

The techniques underlying the crossing results of Fermanian–Kammerer, Gérard, Teufel, and Lasser [16, 17, 18, 19, 20, 21, 22, 23, 67, 68] rely on two–scale measures to resolve the behavior of solutions when they are a distance of order ϵ from the crossing submanifold. By concentrating on Wigner functions instead of wave functions, these techniques yield somewhat cleaner results because they

do not yield phase information that is contained in the wave packets. Lasser and Teufel have developed a very nice algorithm for the propagation of Wigner functions through crossings.

5. Propagation through Avoided Crossings with Small Gaps

The authors have also studied what happens when wave packets go through avoided crossings with small gaps. An avoided crossing is a situation where two levels get close to one another, but do not actually cross. The expression “small gaps” refers to levels that come an $O(\epsilon)$ distance from one another.

For this small gap situation, the electron Hamiltonian must depend on ϵ . That may appear to be unphysical, but for real molecules, there is a fixed value of ϵ , and levels can have avoided crossings that have gaps that are roughly equal to ϵ . Gaps on the order of ϵ are the most interesting. As commented in Section 1, Rousse [85, 86] has shown that avoided crossings with gaps of order ϵ^p with $p < 1$ yield give rise to trivial phenomena to leading order. When $p > 1$, they behave like actual crossings.

As in the case of crossings, there are several different types of generic, minimal multiplicity avoided crossings. They are classified, and normal forms are found for each type in [34]. In that paper, avoided crossings are defined as crossings that have been perturbed in a generic way to produce avoided crossings. Canonical examples of electron Hamiltonians of each type with gaps of size 2δ are given by the following matrices:

Type 1 $E(X_1) = \pm\sqrt{X_1^2 + \delta^2}$ (multiplicity 1).

$$\begin{pmatrix} X_1 & \delta \\ \delta & -X_1 \end{pmatrix}$$

Type 2 $E(X_1) = \pm\sqrt{X_1^2 + \delta^2}$ (multiplicity 2).

$$\begin{pmatrix} X_1 & \delta & 0 & 0 \\ \delta & -X_1 & 0 & 0 \\ 0 & 0 & X_1 & \delta \\ 0 & 0 & \delta & -X_1 \end{pmatrix}$$

Type 3 $E(X_1, X_2) = \pm\sqrt{X_1^2 + X_2^2 + \delta^2}$ (multiplicity 1).

$$\begin{pmatrix} X_1 & X_2 + i\delta \\ X_2 - i\delta & -X_1 \end{pmatrix}$$

Type 4 $E(X_1, X_2) = \pm\sqrt{X_1^2 + X_2^2 + \delta^2}$ (multiplicity 2).

$$\begin{pmatrix} X_1 & X_2 + i\delta & 0 & 0 \\ X_2 - i\delta & -X_1 & 0 & 0 \\ 0 & 0 & X_1 & X_2 - i\delta \\ 0 & 0 & X_2 + i\delta & -X_1 \end{pmatrix}$$

Type 5 $E(X_1, X_2, X_3) = \pm\sqrt{X_1^2 + X_2^2 + X_3^2 + \delta^2}$ (multiplicity 2).

$$\begin{pmatrix} X_1 & 0 & X_2 + iX_3 & \delta \\ 0 & X_1 & -\delta & X_2 - iX_3 \\ X_2 - iX_3 & -\delta & -X_1 & 0 \\ \delta & X_2 + iX_3 & 0 & -X_1 \end{pmatrix}$$

Type 6 $E(X_1, X_2, X_3, X_4) = \pm\sqrt{X_1^2 + X_2^2 + X_3^2 + X_4^2 + \delta^2}$ (multiplicity 2).

$$\begin{pmatrix} X_1 & 0 & X_2 + iX_3 & X_4 + i\delta \\ 0 & X_1 & -X_4 + i\delta & X_2 - iX_3 \\ X_2 - iX_3 & -X_4 - i\delta & -X_1 & 0 \\ X_4 - i\delta & X_2 + iX_3 & 0 & -X_1 \end{pmatrix}$$

Papers [36, 37] study the propagation of wave packets through each type of avoided crossings when δ is taken to be $O(\epsilon)$. The underlying basic idea is again to use matched asymptotic expansions as in the case of actual crossings. Although the analysis is quite similar, there is the additional technical complication that the classical mechanics for the nuclei now depends on ϵ in a complicated way as $\epsilon \rightarrow 0$.

The results for each type of avoided crossing are somewhat similar to those for codimension 2, 3, and 5 crossings. As the wave packet propagates through the avoided crossing, it splits at leading order into two pieces. One piece propagates according to the dynamics of the upper level and the other piece propagates according to the dynamics of the lower level. The leading order inner solutions again involve hyperbolic PDE's whose solutions can be written in terms of parabolic cylinder functions. A Landau–Zener formula describes the transition probability along each characteristic.

Similar difficulties occur when the molecular Hamiltonian of [36] is known only by means of perturbation series. However, the perturbation theory of Born–Oppenheimer wave packets in presence of avoided crossings can still be performed. See [14].

Although no one seems to have used them to do so, the techniques of Colin de Verdière, Fermanian–Kammerer, Gérard, Lasser, and Teufel can almost certainly produce analogous results.

If the gap is small and fixed, instead of being $O(\epsilon)$, then transitions associated with avoided crossings are $O(\exp(-\Gamma/\epsilon^2))$. Under rather restrictive hypotheses, the large time behavior of the leading order non-adiabatic component is found in [42]. The nuclear variable X is restricted to one dimension and the electron Hamiltonian is an $n \times n$ matrix that depends analytically on X , with appropriate limiting behavior as $X \rightarrow \pm\infty$. In the remote past, the allowed incoming states include the product of a semiclassical wave packet ϕ_j in X times an electronic eigenfunction.

If the initial electronic level and a second level have a single avoided crossing with a sufficiently small gap, then the leading order transition wave function on the second level is Gaussian, with norm of order $\epsilon^{-j} \exp(-\alpha/\epsilon^2)$ for a precise $\alpha > 0$. Both its amplitude and its average momentum are larger than what one would obtain by treating the nuclei as classical point particles and applying the Landau–Zener formula for the electrons.

The proof in [42] uses generalized eigenfunction expansions associated with the full Hamiltonian and a WKB technique [57, 58] that is valid for complex X .

Results of a similar nature, but for more general systems of PDE's are obtained in [59]. Further time-independent generalized eigenfunction results are obtained in [60, 70, 58].

The results of [42] describe only the large time behavior. It is a beautiful open problem to analyze the dynamics up to this exponential accuracy when the gap is fixed and small.

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