Non–Adiabatic Transitions in a Simple Born–Oppenheimer Scattering System

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We study non–adiabatic scattering transitions in the Born–Oppenheimer limit for a molecular Schrödinger operator in which the nuclei have one degree of freedom and the electron Hamiltonian is a 2×2 matrix.

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1. Introduction

We describe non–adiabatic transitions in a simple Born–Oppenheimer scattering system. The detailed proofs are long and technical. They can be found in Ref. 4. These transitions are difficult to study because they are exponentially small and cannot be determined by perturbation theory.

We study scattering theory for the equation

$$i\,\epsilon^2\,\frac{\partial \psi}{\partial t} \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2 \psi}{\partial x^2} \;+\; h(x)\,\psi \tag{1}$$

in the Born–Oppenheimer limit $\epsilon \to 0$. Here we assume $h(x)$ is a 2×2 matrix that depends parametrically on x and has an analytic continuation to a sufficiently wide strip about the real axis. We also assume $h(x)$ approaches limits $h(\pm\infty)$ sufficiently rapidly, as $\operatorname{Re} x \to \pm\infty$, uniformly in the strip. We further assume that the

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eigenvalues of $h(x)$ are never equal for real x. A typical example is

$$h(x) \;=\; \begin{pmatrix} \tanh(x) & 1 \\ 1 & -\tanh(x) \end{pmatrix}.$$

To describe solutions to equation (1), we introduce 1–dimensional semiclassical wave packets for the nuclei

$$\varphi_k(A,\, B,\, \epsilon^2,\, a,\, \eta,\, x) = \pi^{-1/4}\, \epsilon^{-1/2}\, 2^{-k/2}\, (k!)^{-1/2}\, \overline{A}^{k/2}/A^{(k+1)/2}\, H_k((x-a)/(|A|\,\epsilon)) \times \exp\left(-\frac{B\,(x-a)^2}{2\,A\,\epsilon^2} \;+\; i\,\eta\,(x-a)/\epsilon^2 \right).$$

We always impose the condition that $\mathrm{Re}\,\overline{A}\,B \;=\; 1$. Under this condition, $\{\, \varphi_k(A,\, B,\, \epsilon^2,\, a,\, \eta,\, \cdot)\,\}$ is an orthonormal basis of $L^2(\mathbb{R})$ for fixed A, B, ϵ, a, and η when $k = 0,\, 1,\, 2,\, \cdots$. A detailed discussion of these wave packets may be found in Ref. 2.

For each k, there is a solution to equation (1) of the form

$$\psi(x,\, t) \;=\; e^{iS(t)/\epsilon^2}\, \varphi_k(A(t),\, B(t),\, \epsilon^2,\, a(t),\, \eta(t),\, x)\; \Phi_1(x) \;+\; O(\epsilon),$$

where $\Phi_1(x)$ is an eigenvector of $h(x)$ that depends smoothly on x and has phase chosen to obey the adiabatic connection. (If $h(x)$ is real symmetric for real x then $\Phi_1(x)$ can be chosen real for all real x.) The quantities $A(t)$, $B(t)$, $a(t)$, $\eta(t)$, and $S(t)$ are determined by the classical phase space flow with the eigenvalue $E_1(x)$ corresponding to $\Phi_1(x)$ being used as an effective potential.[1] This result can be improved by optimally truncating the associated perturbation expansion.[3] We obtain

$$\psi(x,\, t) \;=\; e^{iS(t)/\epsilon^2} \sum_{n=0}^{N(\epsilon)} \epsilon^n\; \psi_n(x,\, t,\, \epsilon) \;+\; O\left(\exp\left(-\Gamma/\epsilon^2\right)\right). \tag{2}$$

Here $\Gamma > 0$, and the $\psi_n(x,\, t,\, \epsilon)$ have the form

$$\psi_n(x,\, t,\, \epsilon) = \sum_{j=0}^{3n+3+k} c_{j,k}(t,\, \epsilon)\, \varphi_j(A(t),\, B(t),\, \epsilon^2,\, a(t),\, \eta(t),\, x)\; \Phi_1(x) + \sum_{j=0}^{3n+3+k} d_{j,k}(t,\, \epsilon)\, \varphi_j(A(t),\, B(t),\, \epsilon^2,\, a(t),\, \eta(t),\, x)\; \Phi_2(x),$$

where $\{\Phi_1(x),\, \Phi_2(x)\}$ is the basis of eigenvectors for $h(x)$.

2. Non–Adiabatic Transitions

The approximate solution (2) is concentrated near a single classical orbit with position $a(t)$ determined by classical mechanics with the effective potential $E_1(x)$. Our main goal is to compute the leading order correction to this solution that obeys the classical mechanics governed by the second electronic potential energy surface $E_2(x)$.

We further assume that the two levels $E_1(x)$ and $E_2(x)$ have a single avoided crossing with a sufficiently small, but positive minimum gap between them. We assume that this avoided crossing is associated with a crossing for some complex value of x inside the strip of analyticity of $h(x)$.

By inserting energy cut offs, we assume that we are studying states whose energy lies strictly above the maxima of both electronic levels $E_1(\cdot)$ and $E_2(\cdot)$. Of course we also assume that the classical energy

$$\frac{\eta(t)^2}{2} \;+\; E_1(a(t))$$

satisfies this condition. Then one can find the leading order non-adiabatic contribution that is in the error term in formula (2).[4]

There are several surprises. First, the leading order transition probability is strictly greater than what one would obtain by naïvely applying the Landau–Zener formula to the Schrödinger equation

$$i\,\epsilon^2\,\frac{\partial \phi}{\partial t} \;=\; h(a(t))\,\phi. \tag{3}$$

Since the nuclei are localized near $a(t)$, and the Landau–Zener formula correctly describes the non–adiabatic transtions for solutions to (3), one might expect this to yield the correct leading order result for (1), but it is wrong. Second, one might expect classical energy conservation to predict the momentum of the nuclei after a non–adiabatic transtion has occurred. This, too, is simply the wrong leading order result. The true average nuclear momentum after the transition is strictly greater than this prediction. Third, for a fixed value of k, when the incoming state is asymptotic in the remote past to

$$e^{iS(t)/\epsilon^2}\,\varphi_k(A(t),\,B(t),\,\epsilon^2,\,a(t),\,\eta(t),\,x)\;\Phi_1(x),$$

then for sufficiently small ϵ, the leading order non–adiabatic contribution in the remote future is asymptotic to

$$C_1\;\exp(-\,C_2/\epsilon^2)\;\epsilon^{-k}\;e^{i\widetilde{S}(t)/\epsilon^2}\,\varphi_0(\widetilde{A}(t),\,\widetilde{B}(t),\,\epsilon^2,\,\widetilde{a}(t),\,\widetilde{\eta}(t),\,x)\;\Phi_2(x),$$

with $C_1 \neq 0$ and $C_2 > 0$. Here, $\widetilde{A}(t)$, $\widetilde{B}(t)$, $\widetilde{a}(t)$, $\widetilde{\eta}(t)$, and $\widetilde{S}(t)$ are determined by the classical phase space flow for the potential energy $E_2(x)$. We should comment that under our hypotheses on the energy, $\eta(t)$ never changes sign. The particular $\widetilde{\eta}(t)$ that arises also must have constant sign, and the sign is the same as that of $\eta(t)$. Any transitions that change direction are exponentially smaller in $1/\epsilon^2$ because of our assumption that the minimum gap between E_1 and E_2 is sufficiently small.

So, for a wide variety of incoming states, the leading order outgoing non–adiabatic term is always a complex Gaussian.

3. Comments about the Proof

We prove our main result by first studying the generalized eigenfunctions of the full Hamiltonian. These are solutions to the equation

$$-\frac{\epsilon^4}{2}\frac{\partial^2\psi}{\partial x^2} \;+\; h(x)\,\psi \;=\; \mathcal{E}\;\psi.$$

For each $\mathcal{E}$ above the maxima of $E_j(\cdot)$, there are four independent solutions to this equation. One is incoming from the left and associated with E_1; one is incoming from the right and associated with E_1. The other two are similarly incoming from the left and right and associated with E_2. For small ϵ we perform a WKB analysis of these solutions, and since we are interested in the transitions, we extend this analysis to complex values of x so that we can integrate the full Schrödinger equation around the crossing point of E_1 and E_2 in the complex plane.

We decompose our wave packets as superpositions of these generalized eigenfunctions. From the complex WKB analysis, we can compute the leading order non–adiabatic scattering component of each generalized eigenfunction. Computing the non–adiabatic transition wave packet then becomes an exercise in finding the asymptotics of an integral that arises from the superposition. This is quite tedious, but can be done quite explicitly.[4]

One thus gets the correct leading order transition component of the wave function. One also can understand why the naïve approach is wrong.

In the naïve approach, one computes the average momentum of the nuclei as they go through the transition. One then uses this in the Landau–Zener calculation. However, the higher momentum components of the wave function are much more likely to make a transition than the slower components. To get the correct results, one must compute the transition probability for each component and then average over the components. This yields a higher total transition probability than what one gets by averaging first. It also explains why the simple energy conservation calculation yields the wrong momentum prediction. The faster parts of the wave function are more likely to make a transition.

Finally, when using a φ_k as the incoming wave packet with $k > 0$, one can see why the non–adiabatic transition component is a Gaussian if ϵ is sufficiently small. The extra shift in momentum associated with the faster parts of the wave function being more likely to make a transition just affects the Gaussian factor in the formula for the φ_k in momentum space. (When one Fourier transforms from position space to momentum space, $\varphi_k(A,\, B,\, \epsilon^2,\, a,\, \eta,\, x)$ becomes $(-i)^k\, e^{-i\eta a/\epsilon^2}\, \varphi_k(B,\, A,\, \epsilon^2,\, \eta,\, -a,\, p)$.) The Hermite polynomial factor $H_k((p-\eta)/(|B|\,\epsilon))$ does not get shifted. The momentum space wave packet is largest near the point where the Gaussian is centered, and near this shifted point, the Hermite polynomial is approximately equal to its highest order term, which is a constant times $\left((p-\eta)/(|B|\,\epsilon)\right)^k$. This times the shifted Gaussian is approximately another constant times ϵ^{-k} times another Gaussian.

Thus, all of the results that are surprising arise from the rapid increase of the

transition probability as a function of the momentum when one examines the generalized wave functions.

4. Generalizations

Similar results hold for $m \times m$ matrices $h(x)$ whose spectra display suitable avoided crossings. Incoming states, given as superpositions of generalized eigenvectors, can also be accommodated, provided the corresponding energy density is sharply peaked around some value above that of the relevant electronic energy levels.[4]

These ideas have been further generalized in Ref. 5 to tackle the semiclassical study of waves driven by systems of autonomous PDEs in $1+1$ space-time dimensions in a scattering regime. Consider operators of the form

$$\mathcal{R}(x,\, i\epsilon\partial/\partial t,\, i\epsilon\partial/\partial x) \;=\; \sum_{\substack{0\le l\le m\\ 0\le n\le r}} A_{ln}(x)\,(i\epsilon\partial/\partial x)^l\,(i\epsilon\partial/\partial t)^n$$

where $A_{ln}(x)$ are $d \times d$ matrices, analytic in x in some strip, which tend rapidly enough to limits as $\mathrm{Re}\, x \to \pm\infty$, uniformly in the strip.

The main assumptions are made on the modes on the system, which are the roots $\{k_j(x,\, E)\}_{j=1,\cdots,md}$ of the dispertion relation $\det \mathcal{R}(x,\, E,\, k) = 0$. We assume they are real valued in some energy window, do not to cross as x varies in $\mathbb{R}$, and display some avoided crossing. Under these assumptions, the generalized eigenvectors, $\psi_\epsilon(x,\, E) \in \mathbb{C}^d$, solutions to $\mathcal{R}(x,\, E,\, i\epsilon\partial/\partial x)\,\psi_\epsilon(x,\, E) = 0$, can be expanded in a basis of polarization vectors associated with the different modes. Superpositions of generalized eigenvectors yield exact solutions to the evolution equation in $L^2(\mathbb{R})$

$$\mathcal{R}(x,\, i\epsilon\partial/\partial t,\, i\epsilon\partial/\partial x)\,\Psi_\epsilon(x,\, t) \;=\; 0.$$

By selecting solutions which live on a specific mode in the remote past with a group velocity that makes them go through an avoided crossing, it is possible to compute the asymptotics as $\epsilon \to 0$ of the exponentially small part of the solution which makes a transition to the closest mode, for large but finite values of x and t.

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