Non–Adiabatic Transitions caused by Avoided Crossings of Electron Energy Levels

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Outline of the talk

1. Various Types of Generic Avoided Crossings

2. Semiclassical Wave Packets and the Time–Dependent Born–Oppenheimer Approximation

3. Born–Oppenheimer Propagation through Avoided Crossings with Small Gaps

4. Born–Oppenheimer Propagation through the Simplest Avoided Crossings with Fixed Gaps

Various Types of Avoided Crossings

We define avoided crossings with small gaps as generically perturbed crossings.

Let the electron Hamiltonian $h(X, \delta)$ have two discrete eigenvalues $E_{\mathcal{A}}(X, \delta)$ and $E_{\mathcal{B}}(X, \delta)$ that are isolated from the rest of the spectrum.

Assume $E_{\mathcal{A}}(0, 0) = E_{\mathcal{B}}(0, 0)$, but that there are no other crossings.

Assume minimal multiplicity allowed by the symmetry group.

Study generic situations in which the degeneracy splits for all $\delta > 0$.

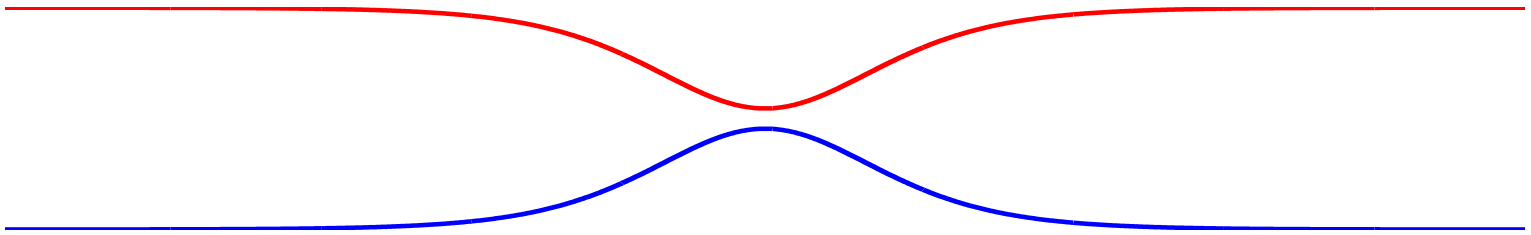
Choose coordinates for the joint spectral subspace for $E_{\mathcal{A}}$ and $E_{\mathcal{B}}$.
In those coordinates, $h(X, \delta)$ is represented by a $2n \times 2n$ matrix.

Subtract $\dfrac{1}{2n}\left(E_{\mathcal{A}}(X, \delta) + E_{\mathcal{B}}(X, \delta)\right)$ times the $2n \times 2n$ identity matrix.

Type 1 X is one–dimensional and the eigenvalues are simple.

The first order Taylor series is $\begin{pmatrix} b_1 X + b_2 \delta & c_2 \delta \\ c_2 \delta & -b_1 X - b_2 \delta \end{pmatrix}$.

The Canonical Example $\begin{pmatrix} X & \delta \\ \delta & -X \end{pmatrix}$; eigenvalues $\pm\sqrt{X^2 + \delta^2}$.



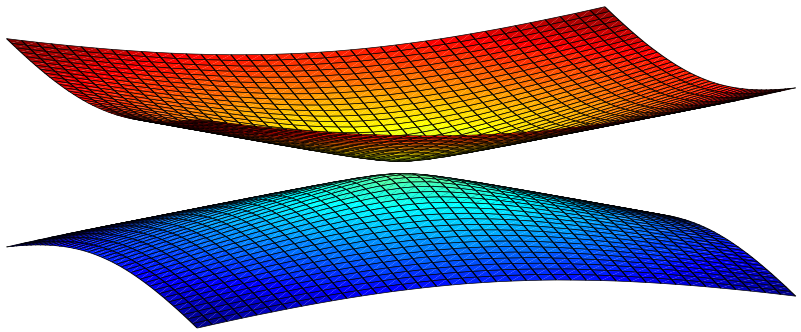
Canonical Examples of the other Five Types' Taylor Expansions

Type 2. X one–dimensional and $n = 2$.

$$\begin{pmatrix} X & \delta & 0 & 0 \\ \delta & -X & 0 & 0 \\ 0 & 0 & X & \delta \\ 0 & 0 & \delta & -X \end{pmatrix}; \qquad \text{eigenvalues } \pm\sqrt{X^2+\delta^2}.$$

Type 3. X two–dimensional and $n = 1$.

$$\begin{pmatrix} X_1 & X_2 + i\,\delta \\ X_2 - i\,\delta & -X_1 \end{pmatrix}; \qquad \text{eigenvalues } \pm\sqrt{X_1^2+X_2^2+\delta^2}.$$



Type 4. X is two dimensional and $n = 2$.

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

Eigenvalues $\pm\sqrt{X_1^2 + X_2^2 + \delta^2}$.

Type 5. X is three–dimensional and $n = 2$.

$$\begin{pmatrix} X_1 & 0 & X_2 + i\,X_3 & \delta \\ 0 & X_1 & -\delta & X_2 - i\,X_3 \\ X_2 - i\,X_3 & -\delta & -X_1 & 0 \\ \delta & X_2 + i\,X_3 & 0 & -X_1 \end{pmatrix}$$

Eigenvalues $\pm\sqrt{X_1^2 + X_2^2 + X_3^2 + \delta^2}$.

Type 6. X is four–dimensional and $n = 2$.

$$\begin{pmatrix} X_1 & 0 & X_2 + i\,X_3 & X_4 + i\,\delta \\ 0 & X_1 & -X_4 + i\,\delta & X_2 - i\,X_3 \\ X_2 - i\,X_3 & -X_4 - i\,\delta & -X_1 & 0 \\ X_4 - i\,\delta & X_2 + i\,X_3 & 0 & -X_1 \end{pmatrix}$$

Eigenvalues $\pm\sqrt{X_1^2 + X_2^2 + X_3^2 + X_4^2 + \delta^2}$.

Semiclassical Wave Packets

To state time–dependent results in their most explicit form,
we need to discuss semiclassical wave packets $\phi_k(A, B, \hbar, a, \eta, x)$.

- These are generalizations of Harmonic oscillator states.
- They coincide with generalized squeezed states.
- In the molecular context, $\hbar$ will be ϵ^2.

$\{\, \phi_k(A, B, \hbar, a, \eta, x) \,\}$ is an orthonormal basis of $L^2(\mathbb{R}^d)$
as k ranges over d–dimensional multi–indices.

- $a \in \mathbb{R}^d$ represents a classical position.
- $\eta \in \mathbb{R}^d$ represents a classical momentum.
- A and B are complex invertible $d \times d$ matrices that satisfy
  $A^t B - B^t A = 0$ and $A^* B + B^* A = 2\, I$.
  The position uncertainty is determined by $\epsilon\, |A|$, and
  the momentum uncertainty is determined by $\epsilon\, |B|$.

$$\phi_0(A, B, \hbar, a, \eta, x) \;=\; \pi^{-d/4}\ \hbar^{-d/4}\ (\det(A))^{-1/2}$$

$$\times\ \exp\Big\{ -(x-a)\cdot BA^{-1}(x-a)/(2\hbar) \;+\; i\eta\cdot(x-a)/\hbar \Big\}.$$

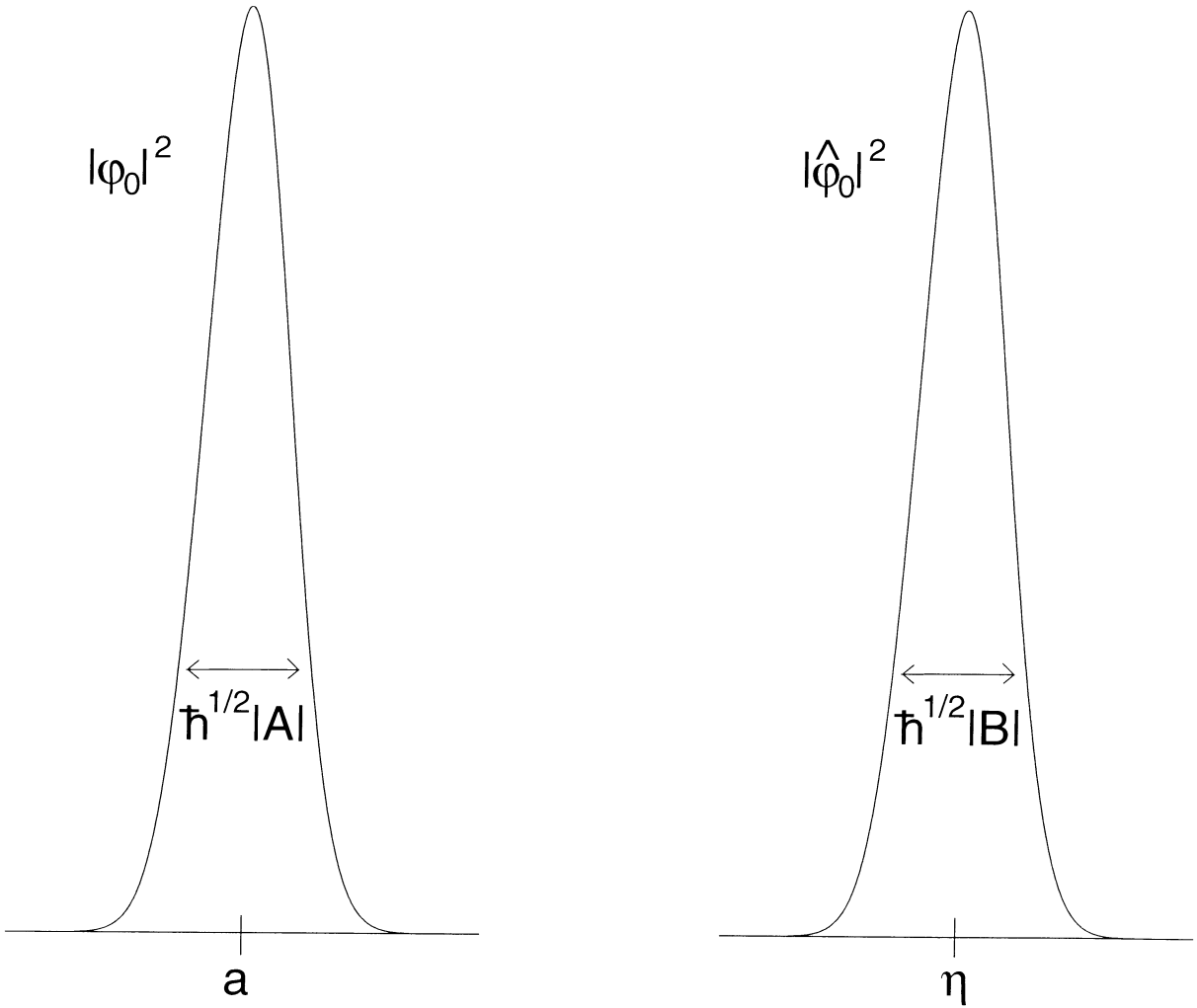
There are raising and lowering operators with the same algebraic properties as with the Harmonic oscillator.

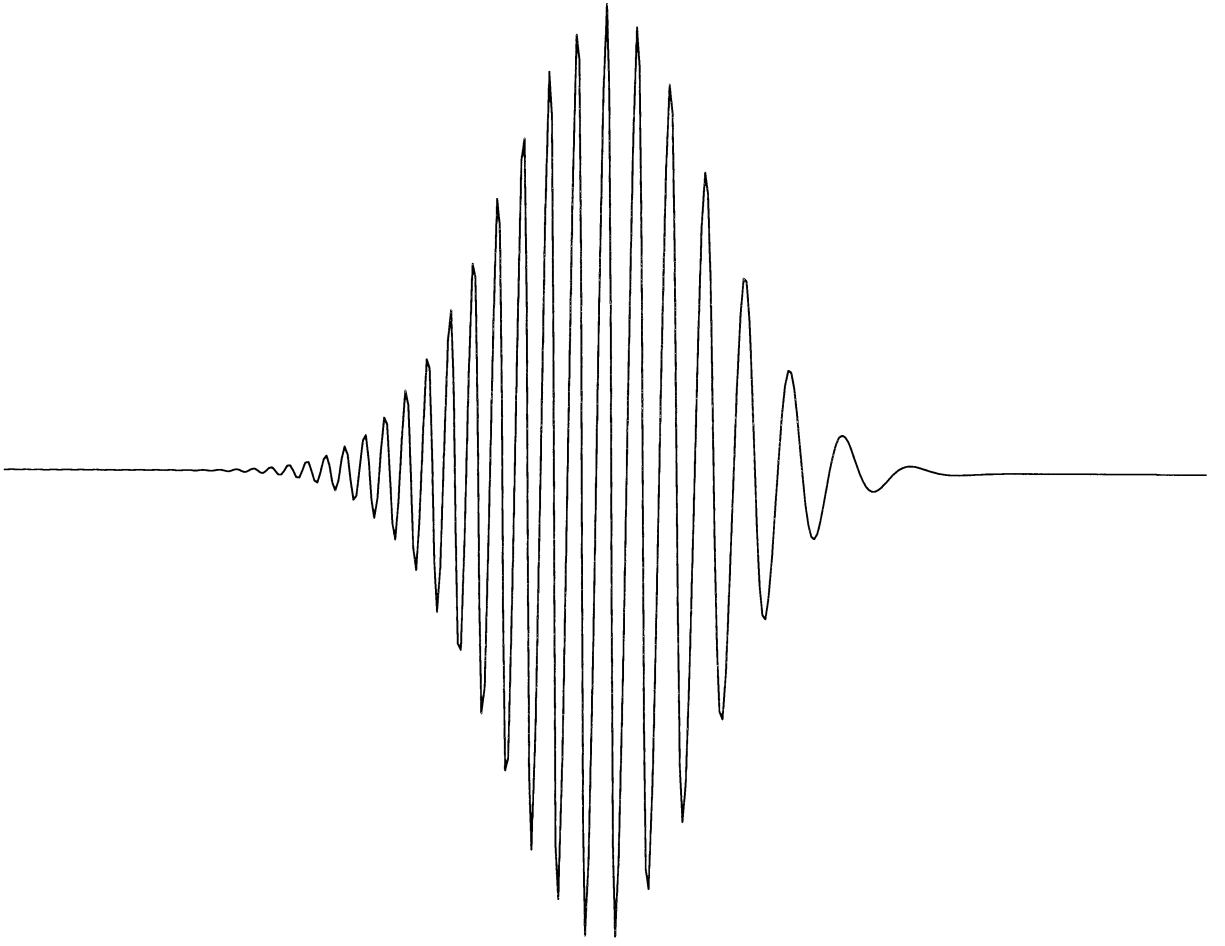
Define the Fourier Transform

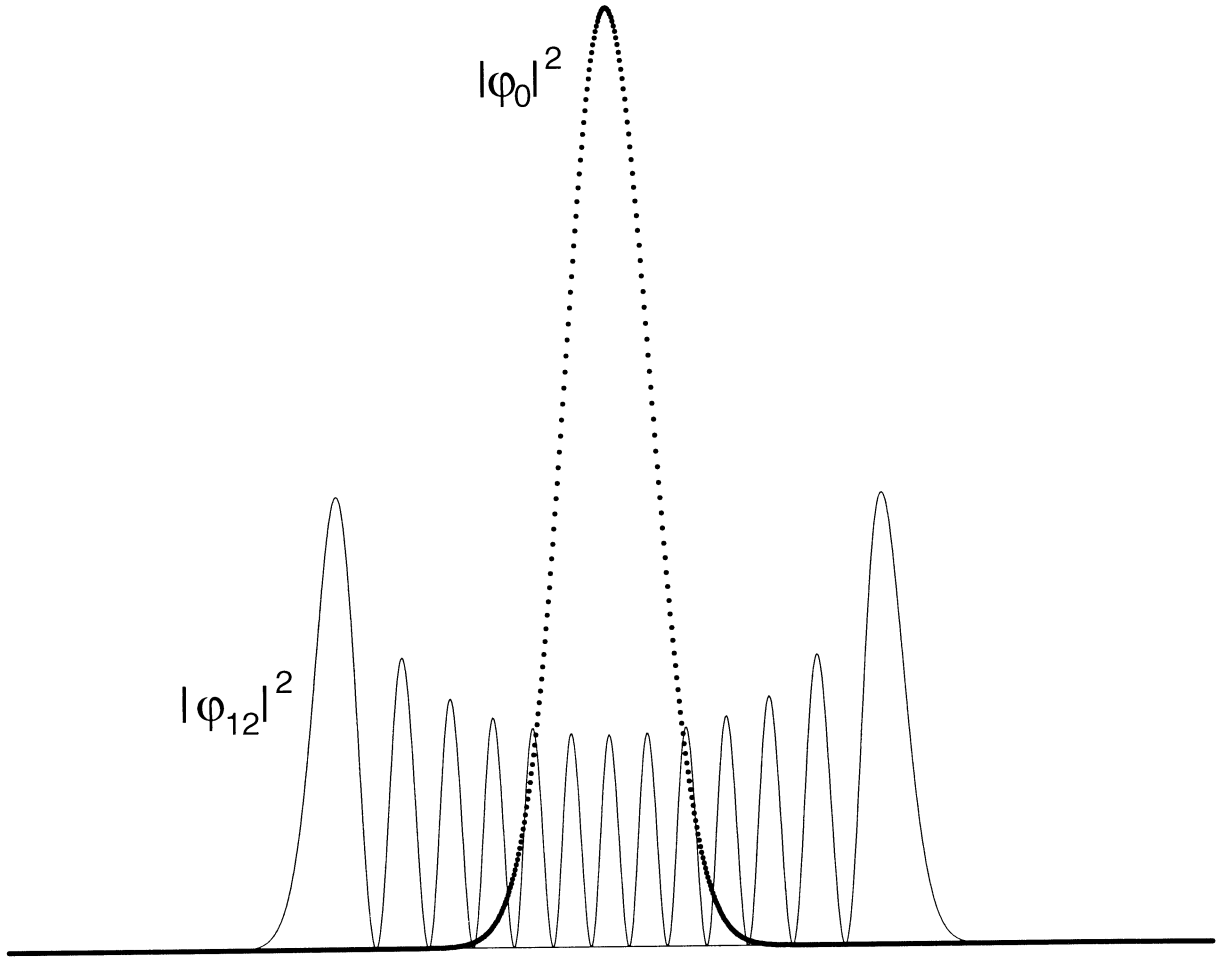
$$(\mathcal{F}_\hbar\, f)(\xi) \;=\; (2\pi\hbar)^{-d/2} \int_{\mathbb{R}^d} f(x)\ e^{-i\xi\cdot x/\hbar}\ dx.$$

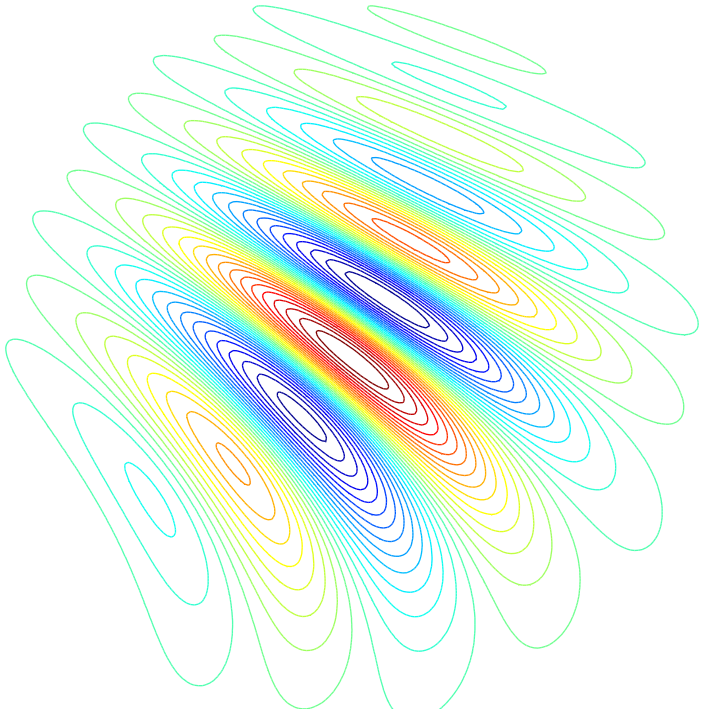
Then

$$(\mathcal{F}_\hbar\, \phi_k(A, B, \hbar, a, \eta, \cdot))(\xi) \;=\; e^{-ia\cdot\eta/\hbar}\ \phi_k(B, A, \hbar, \eta, -a, \xi).$$


$|\varphi_0|^2$
$\hbar^{1/2}|A|$
a
$|\hat{\varphi}_0|^2$
$\hbar^{1/2}|B|$
η




$|\varphi_0|^2$
$|\varphi_{12}|^2$



The Time–Dependent Born–Oppenheimer Approximation

Suppose $h(X)$ has a simple isolated eigenvalue $E(X)$ with eigenfunction $\Phi(X)$.

$i\,\epsilon^2\,\dfrac{\partial\psi}{\partial t} \;=\; -\,\dfrac{\epsilon^4}{2}\,\Delta_X\,\psi \;+\; h(X)\,\psi$ has a solution of the form

$$e^{i\,S(t)/\epsilon^2}\;\phi_k(A,\,B,\,\hbar,\,a,\,\eta,\,X)\;\Phi(X) \quad + \quad O(\epsilon), \qquad \text{where}$$

$$\begin{aligned}
\dot{a}(t) &= \eta(t), \\
\dot{\eta}(t) &= -\,E^{(1)}(a(t)), \\
\dot{A}(t) &= i\,B(t), \\
\dot{B}(t) &= i\,E^{(2)}(a(t))\;A(t), \\
\dot{S}(t) &= \frac{\eta(t)^2}{2} \;-\; E(a(t)).
\end{aligned}$$

Propagation through Avoided Crossings with Small Gaps

We consider an electron Hamiltonian $h(X, \delta)$
with an avoided crossing, and choose δ proportional to ϵ.

We thus study solutions to the Schrödinger equation

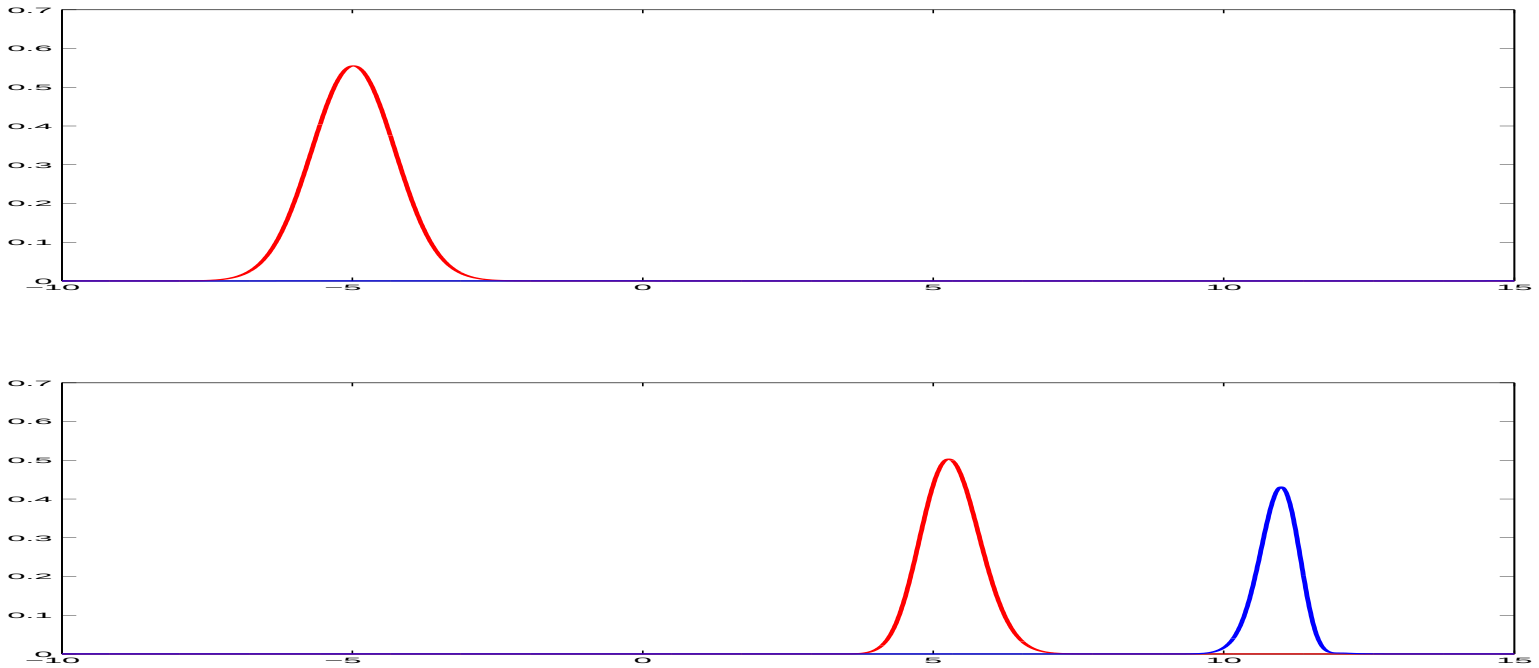
$$i\,\epsilon^2\,\frac{\partial\psi}{\partial t} \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_X\,\psi \;+\; h(X,\,c\,\epsilon)\,\psi.$$

We choose incoming Born–Oppenheimer initial conditions
associated with $E_{\mathcal{A}}$ that would go through the middle of the
avoided crossing.

To leading order, two non–trivial Born–Oppenheimer wavepackets
associated with $E_{\mathcal{A}}$ and $E_{\mathcal{B}}$ emerge from the avoided crossing.

Type 1 and Type 2 The Landau–Zener Formula gives the correct leading order transition amplitude. For the canonical examples, the transition probability is $\exp\left(-\frac{\pi\ \mathrm{gap}^2}{4\,\eta_0\,\epsilon^2}\right)$.

Numerical Simulation $\epsilon = 0.2$, $\mathrm{gap} = 1.5\,\epsilon$, $\eta_0 = 1.625$,
Transition Probability L–Z formula $= 0.34$ numerics $= 0.36$.
Classical energy conservation gives the momentum of the component of the wave function on the new level.



- If the incoming nuclear packet is

$$e^{i\,S(t)/\epsilon^2}\,\phi_k(A_{\mathcal{A}}(t),\,B_{\mathcal{A}}(t),\,\epsilon^2,\,a_{\mathcal{A}}(t),\,\eta_{\mathcal{A}}(t),\,X),$$

  then both leading order outgoing packets are also ϕ_k's.

- The proof uses matched asymptotic expansions.

- We match the incoming Born–Oppenheimer state to an "inner expansion" at small negative times.
  We then match the inner expansion to two outgoing Born–Oppenheimer states for small positive times.

- The explicit inner expansion involves parabolic cylinder functions of complex order and complex argument.

Types 3–6 Again, two leading order wave packets emerge on the two electonic levels.

In the temporal boundary layer for the transition, the Schrödinger equation is asymptotically hyperbolic.

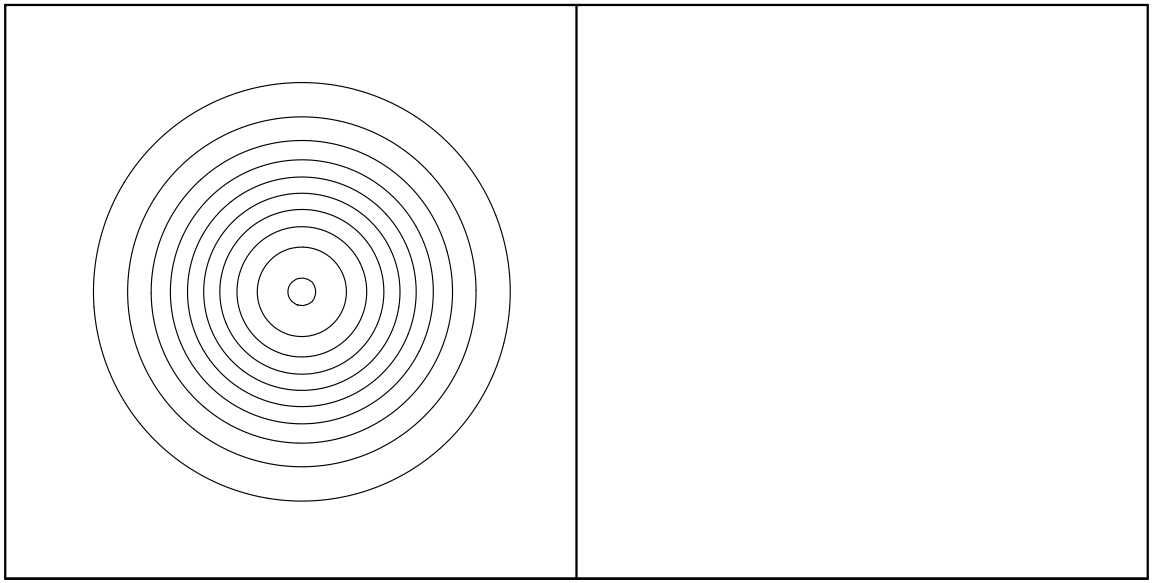
Each piece of the wave function feels its own size gap.

Apply a Landau–Zener formula for each piece's transition probability.

Classical energy conservation gives the momentum of the component of the wave function on the new level.

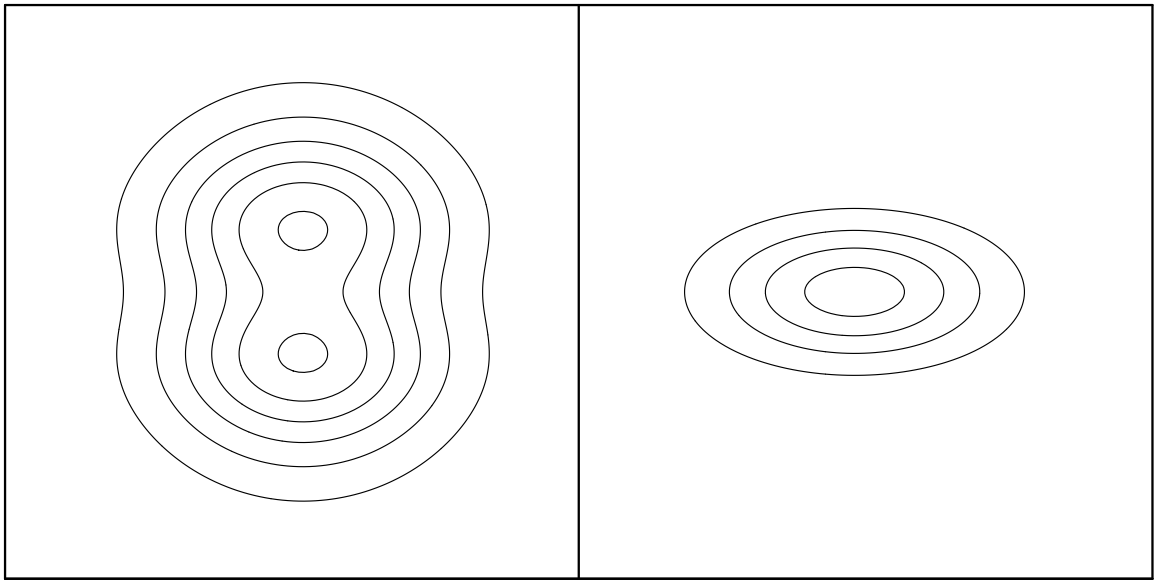
Contour plots for Types 3 and 4:

Incoming



Upper Level Lower Level

Outgoing



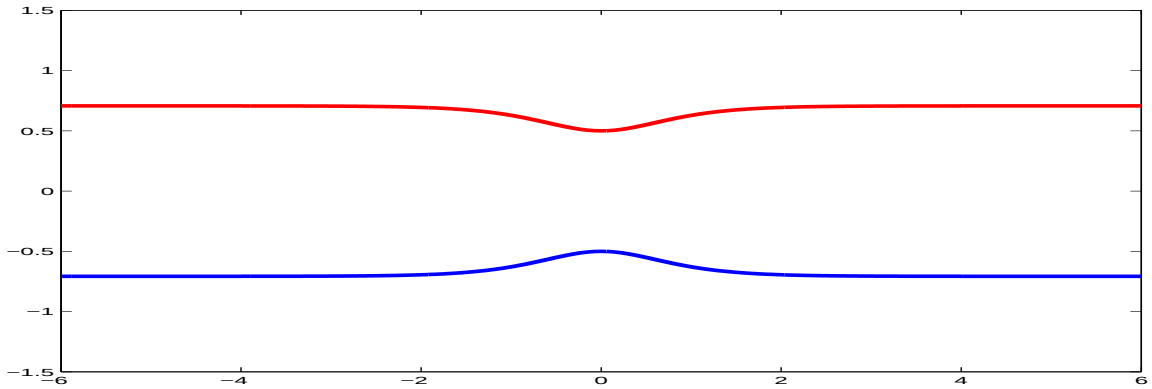
Upper Level Lower Level

Non–Adiabatic Transitions for Fixed Gaps

We only have leading order results for small ϵ
when nuclei have 1 degree of freedom
and the electron Hamiltonian is an analytic $n \times n$ matrix.

Example that illustrates rigorous results

$$h(x) = \frac{1}{2} \begin{pmatrix} 1 & \tanh(x) \\ \tanh(x) & -1 \end{pmatrix}$$



Scattering with large negative t asymptotics

$$e^{iS(t)/\epsilon^2} \phi_k(A(t), B, \epsilon^2, a(t), \eta, x) \ \Phi_{\text{up}}(x).$$

What should we expect?

- The nuclei behave like classical particles (at least for small k).
- The electrons should feel a time–dependent Hamiltonian

$$\widetilde{h}(t) \;=\; \frac{1}{2}\begin{pmatrix} 1 & \tanh(a(t)) \\ \tanh(a(t)) & -1 \end{pmatrix},$$

  and we should simply use the Landau–Zener formula to get the exponentially small transition probability.
- For $\eta = 1$, energy conservation predicts the momentum after the transition to be 1.9566.

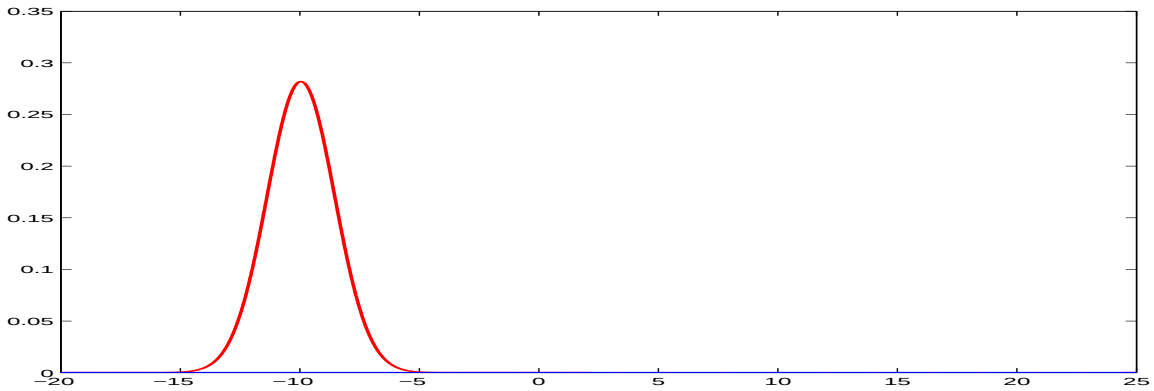
These Predictions Are Wrong!

- The transition amplitude is larger than predicted.
- The momentum after the transition is larger than predicted.

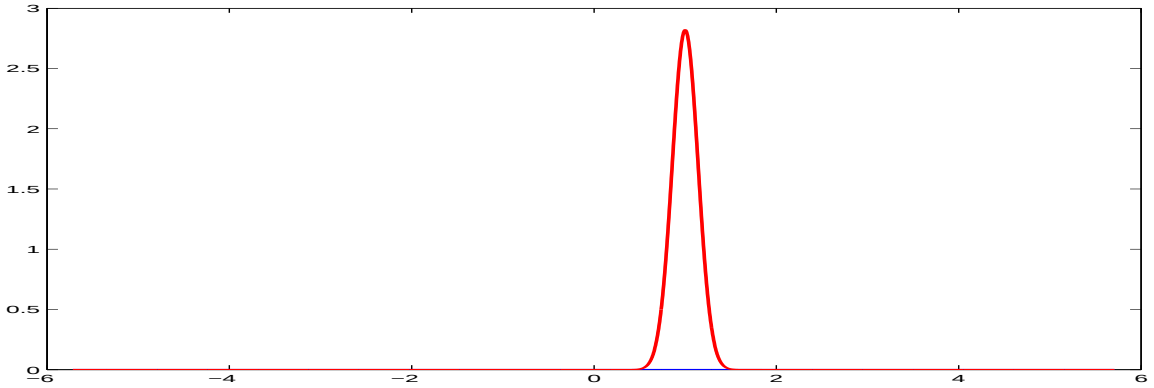
Additional Surprises

- For incoming state ϕ_k, the nuclear wave function after the transition is not what one might naïvely expect.
  - The nuclear wavepacket after transition is a ϕ_0.
  - The transition amplitude is asymptotically of order

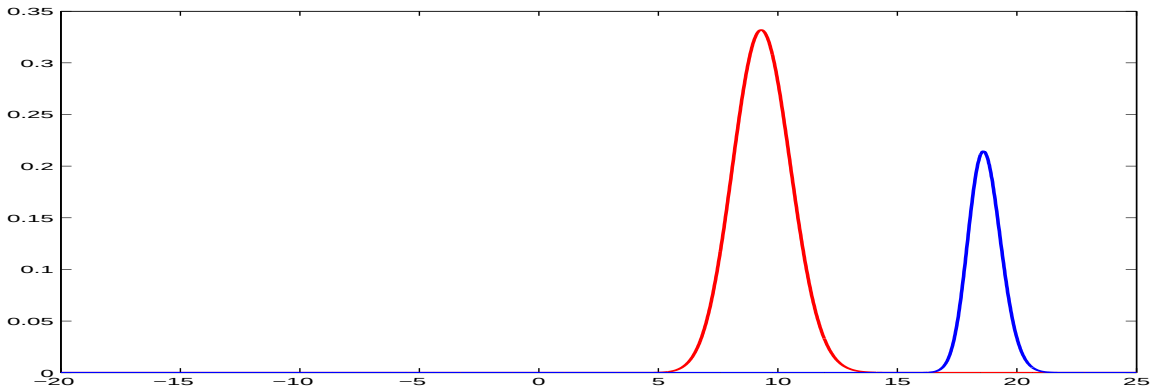
$$\epsilon^{-k} \exp\left(-\alpha/\epsilon^2\right).$$



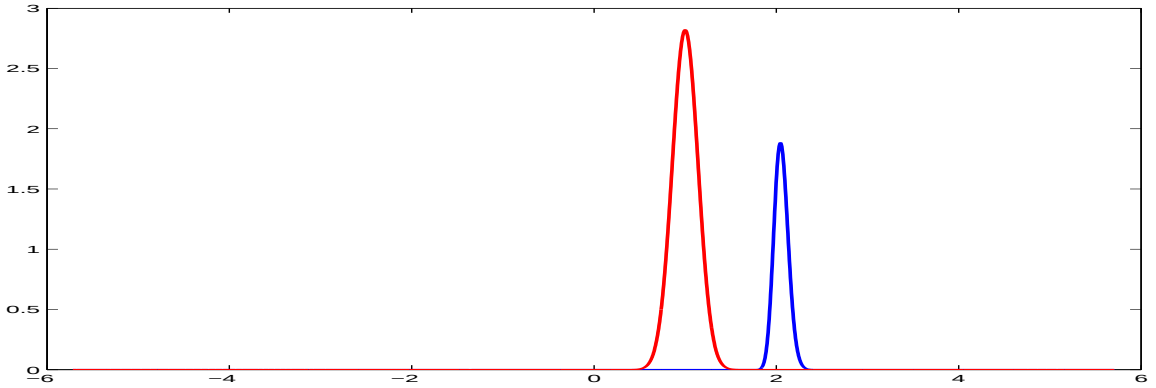
Position space plot at time $t = -10$ of the probability density for being on the upper energy level.



Momentum space plot at time $t = -10$ of the probability density for being on the upper energy level.



Position space probability density at time $t = 9$.
Lower level plot is multiplied by 3×10^8.



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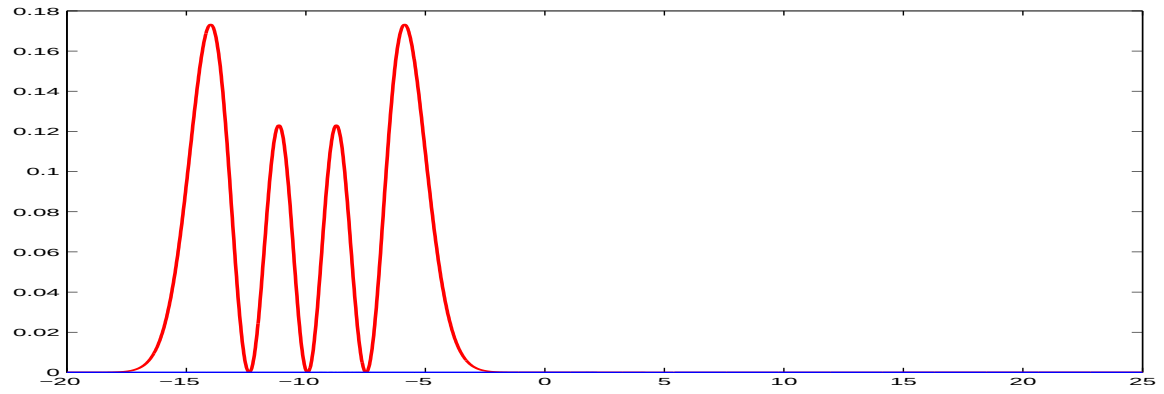

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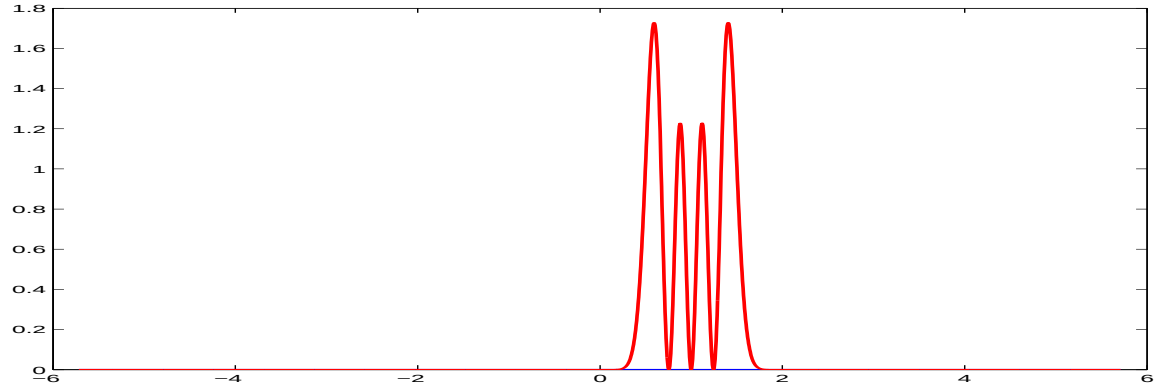
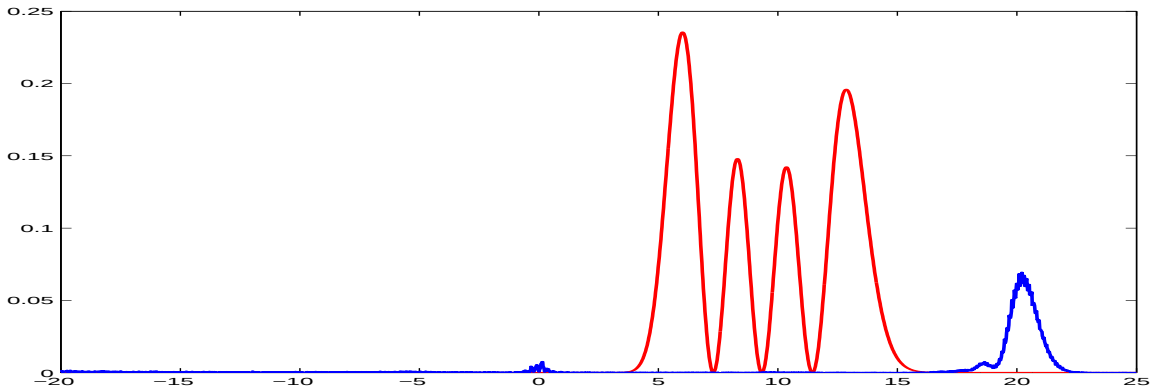
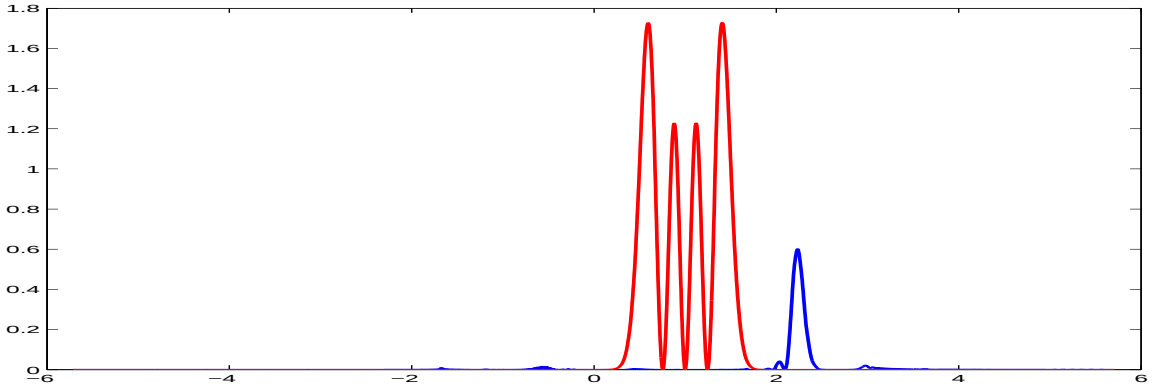


Momentum space probability density at time $t = -10$.



Position space probability density at time $t = 9$.
Plot for the lower level has been multiplied by 10^7.



Momentum space probability density at time $t = 9$.
Plot for the lower level has been multiplied by 10^7.

What's going on, and how do we analyze it?

- We expand $\Psi(x, t)$ in generalized eigenfunctions of $H(\epsilon)$.
- We then do a WKB approximation of the generalized eigenfunctions that is valid for complex x.
- We find that the Landau–Zener formula gives the correct transition amplitude for each generalized eigenfunction.
  This amplitude behaves roughly like $\exp\left(-\dfrac{C}{|p|\,\epsilon^2}\right)$,
  where p is the incoming momentum.
- So, higher momentum components of the wave function are drastically more likely to experience a transition.
  We get the correct result by using Landau–Zener for each p and then averaging.

Why do we always get a Gaussian?

- In the formulas, the extra shift in momentum occurs in the exponent.
- In momentum space ϕ_k all have the same exponential factor. The extra shift does not appear in the polynomial that multiplies the exponential.
- For small ϵ, to leading order, the polynomial factor looks like its largest order term near where the Gaussian is concentrated in momentum.
- $\left(\frac{p}{\epsilon}\right)^k \exp\left(-\frac{(p-\eta)^2}{\epsilon^2}\right)$ is approximately ϵ^{-k} times a Gaussian for $\eta \neq 0$.

Thank you!

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