The Time–Dependent Born–Oppenheimer Approximation and Non–Adiabatic Transitions

George A. Hagedorn
Department of Mathematics, and
Center for Statistical Mechanics, Mathematical Physics,
and Theoretical Chemistry
Virginia Tech
Blacksburg, Virginia 24061–0123

hagedorn@math.vt.edu

University of Illinois at Chicago. 26 March 2014.

Outline

1. Semiclassical Wave Packets.

2. Multiple Scales and the Time–Dependent Born–Oppenheimer Approximation.

3. Non–Adiabatic Transitions associated with Avoided Crossings with Shrinking Gaps.

4. Non–Adiabatic Transitions associated with Avoided Crossings with Fixed Gaps.

One Dimensional Gaussian Semiclassical Wave Packets

The notation may initially seem strange, but it is crucial.

Suppose $a \in \mathbb{R}$, $\eta \in \mathbb{R}$, and $\hbar > 0$.

Suppose A and B are complex numbers that satisfy

$$\mathrm{Re}\left\{\overline{A}\,B\right\} \;=\; 1.$$

We define

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

$$\times \quad \exp\left\{-\,B\,(x-a)^2/(2\,A\,\hbar) \;+\; i\,\eta\,(x-a)/\hbar\right\}.$$

Remarks

- Any complex Gaussian with $\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$ can be written this way.

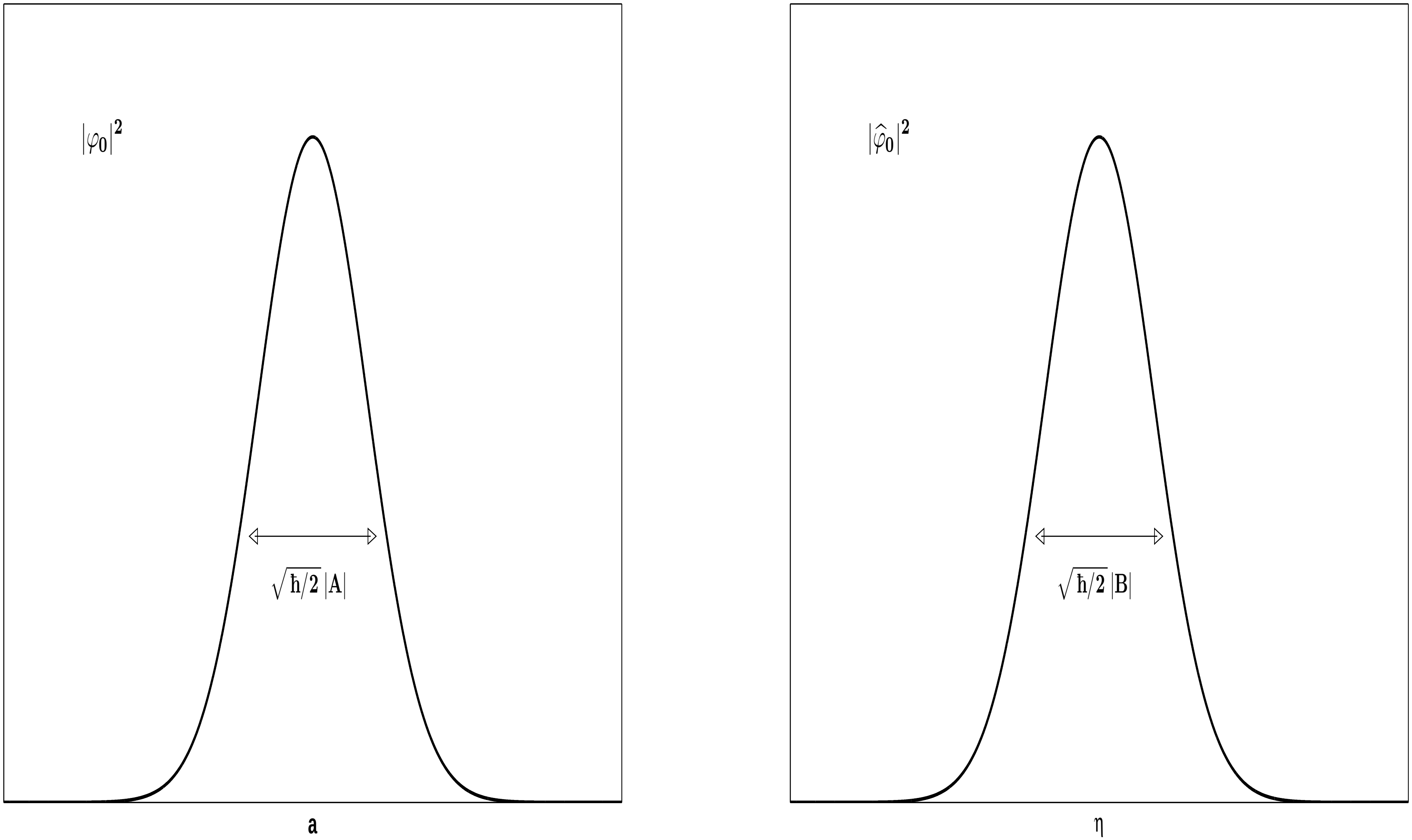
- Define the scaled Fourier transform by

$$(\,\mathcal{F}_\hbar \, f\,)\,(\xi) \;=\; (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} f(x)\, e^{-i\,\xi\,x/\hbar}\, dx.$$

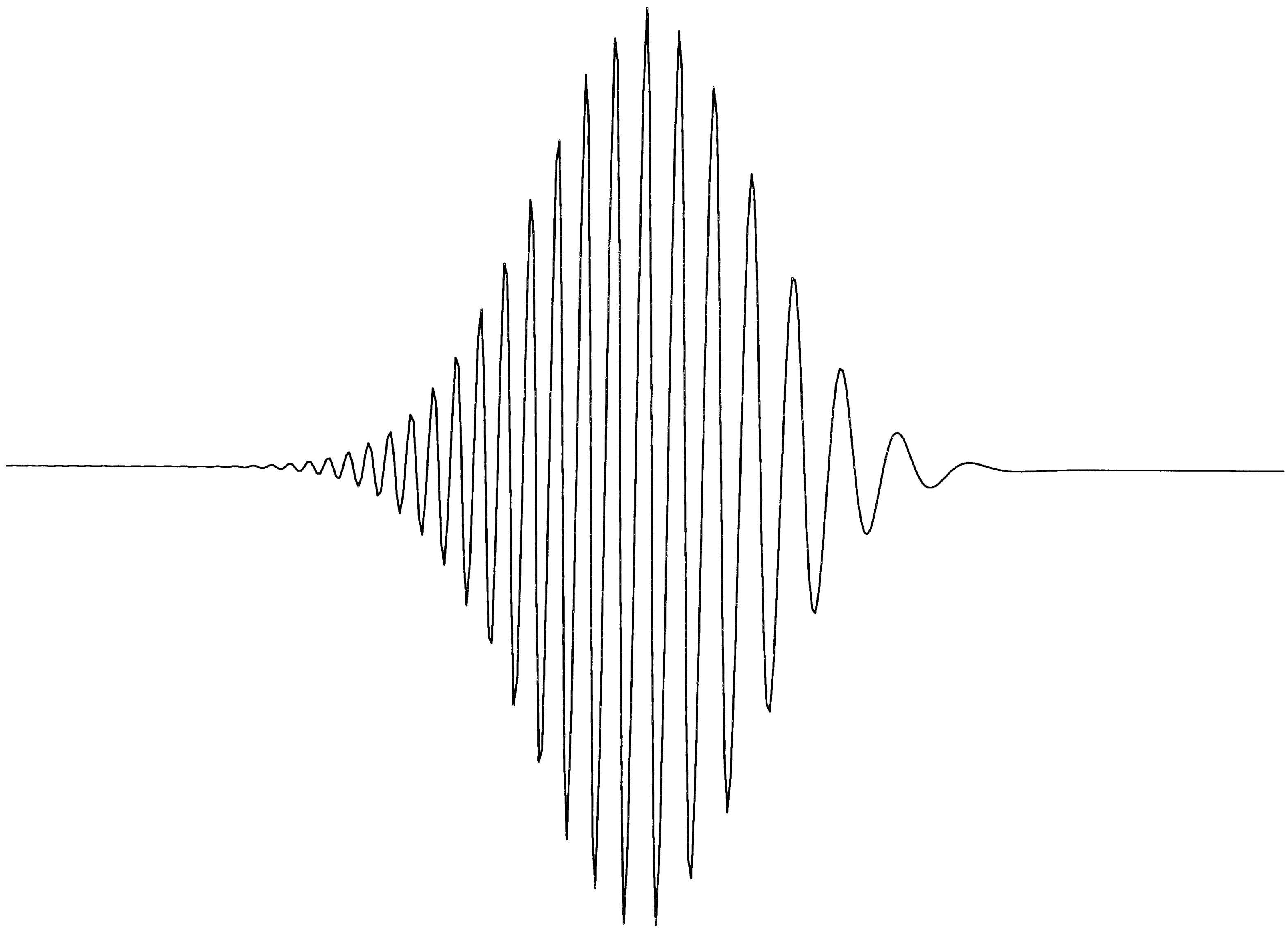
This allows us to go from the position representation to the momentum representation.
(The variable ξ is the momentum variable here.)

Then, by explicit computation,

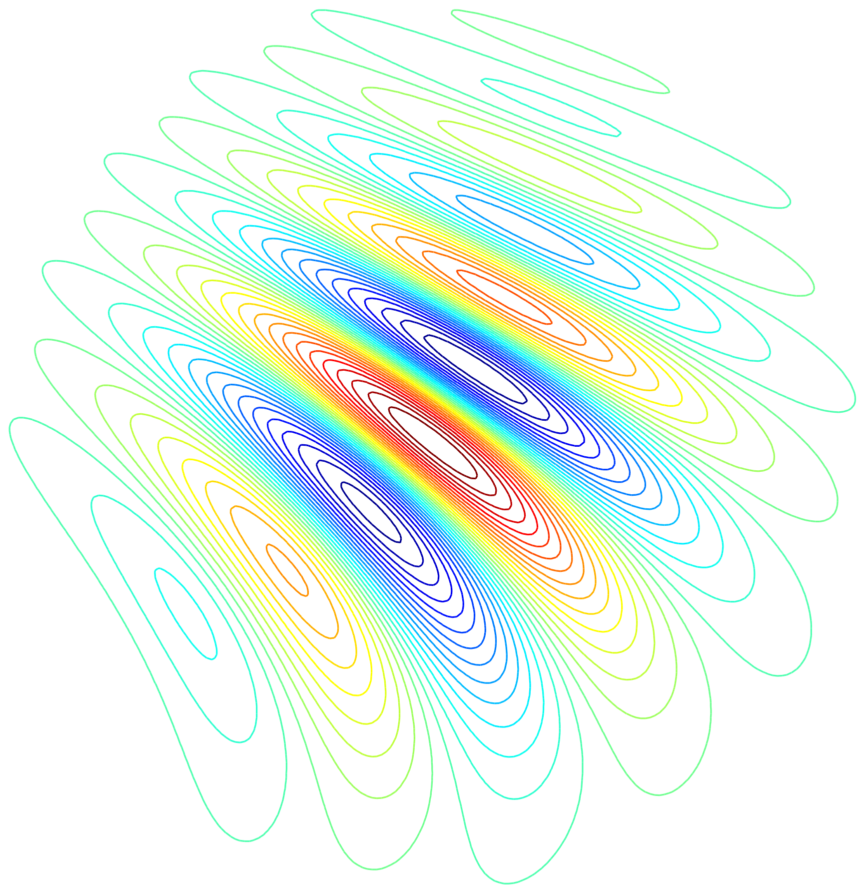
$$(\,\mathcal{F}_\hbar\, \varphi_0(A,\, B,\, \hbar,\, a,\, \eta,\, \cdot\,)\,)\,(\xi) \;=\; e^{-i\,a\,\eta/\hbar}\, \varphi_0(B,\, A,\, \hbar,\, \eta,\, -a,\, \xi).$$



The position density $|\varphi_0(x)|^2$, and momentum density $|\widehat{\varphi}_0(\xi)|^2$.



The real part of a typical $\varphi_0(x)$.



Contour Plot of the real part of a two-dimensional $\varphi_0(x, y)$.

Theorem 1 Suppose $V \in C^3(\mathbb{R})$ satisfies $-M_1 \leq V(x) \leq M_2\, e^{M_3\,|x|^2}$. Suppose $a(t)$, $\eta(t)$, $S(t)$, $A(t)$, and $B(t)$ satisfy

$$\begin{aligned}
\dot{a}(t) &= \eta(t), \\
\dot{\eta}(t) &= -V'(a(t)), \\
\dot{S}(t) &= \eta(t)^2/2 \;-\; V(a(t)), \\
\dot{A}(t) &= i\,B(t), \\
\dot{B}(t) &= i\,V''(a(t))\,A(t).
\end{aligned}$$

Let $\Psi(x,t,\hbar)$ solve $i\,\hbar\,\dfrac{\partial\Psi}{\partial t} \;=\; -\dfrac{\hbar^2}{2}\,\Delta\,\Psi + V\,\Psi$

with $\Psi(x,\,0,\,\hbar) \;=\; e^{iS(0)/\hbar}\,\varphi_0(A(0),\,B(0),\,\hbar,\,a(0),\,\eta(0),\,x)$.

Then for $t \in [0,\,T]$, the approximate solution

$$\psi(x,\,t,\,\hbar) \;=\; e^{iS(t)/\hbar}\,\varphi_0(A(t),\,B(t),\,\hbar,\,a(t),\,\eta(t),\,x)$$

satisfies

$$\|\,\psi(x,\,t,\,\hbar) \;-\; \Psi(x,\,t,\,\hbar)\,\|_{L^2(\mathbb{R})} \;\leq\; C\;\hbar^{1/2}.$$

More General One Dimensional Semiclassical Wave Packets

In analogy with the Harmonic Oscillator, we define raising and lowering operators:

$$(\,\mathcal{A}(A,B,\hbar,a,\eta)^*\,\psi\,)\,(x) \;=\; \frac{1}{\sqrt{2\hbar}}\left(\left[\,\overline{B}\,(x-a)\;-\;i\,\overline{A}\,(-i\hbar\frac{\partial}{\partial x}-\eta)\right]\psi\right)(x)$$

and

$$(\,\mathcal{A}(A,B,\hbar,a,\eta)\,\psi\,)\,(x) \;=\; \frac{1}{\sqrt{2\hbar}}\left(\left[\,B\,(x-a)\,+\,i\,A\,(-i\hbar\frac{\partial}{\partial x}-\eta)\right]\psi\right)(x).$$

Then,

$$\mathcal{A}(A,B,\hbar,a,\eta)\,\mathcal{A}(A,B,\hbar,a,\eta)^*\;-\;\mathcal{A}(A,B,\hbar,a,\eta)^*\,\mathcal{A}(A,B,\hbar,a,\eta)\;=\;1.$$

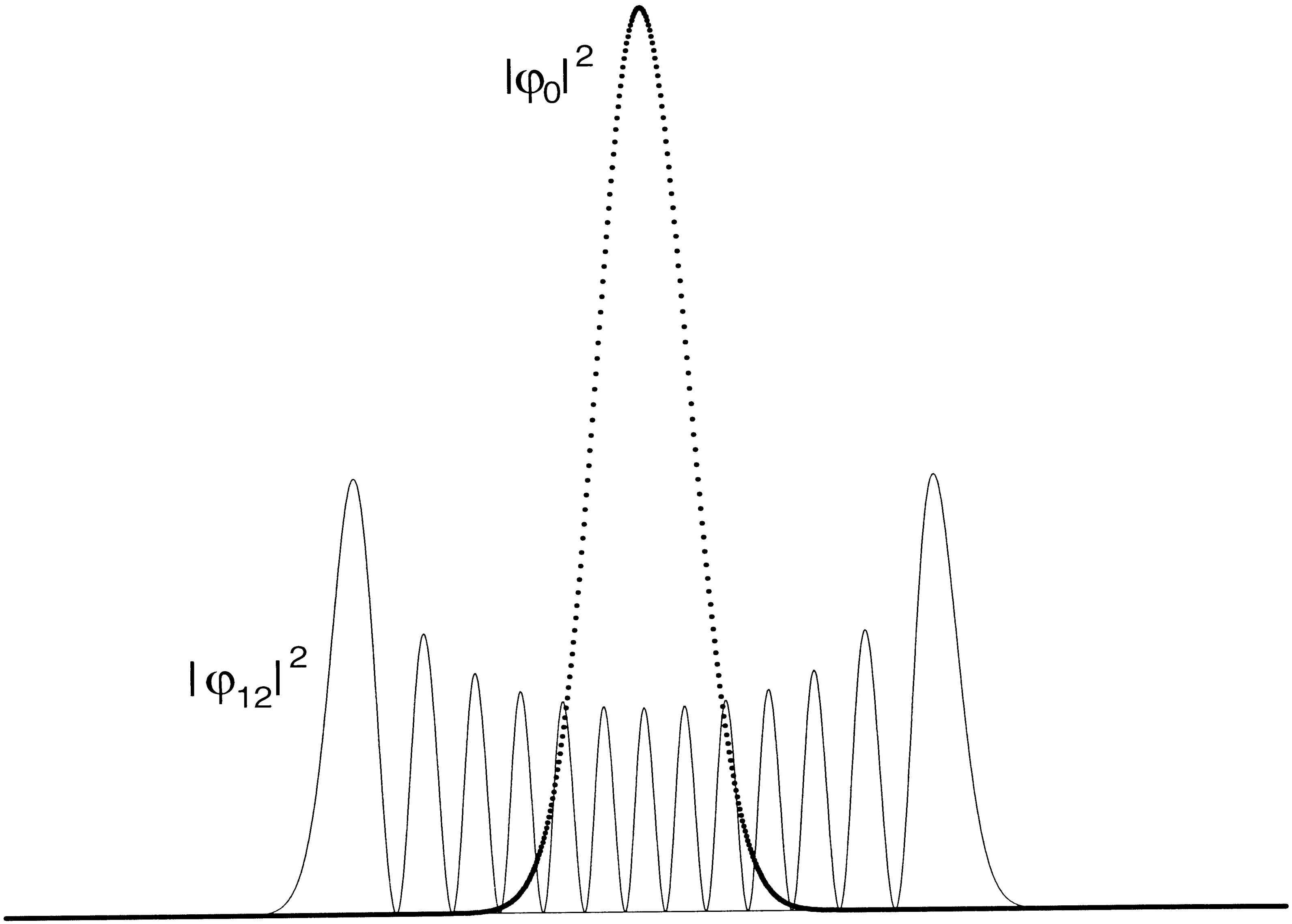
For any non-negative integer j, we define

$$\varphi_j(A,\, B,\, \hbar,\, a,\, \eta,\, x) \;=\; \frac{1}{\sqrt{j!}}\; \big(\mathcal{A}(A,\, B,\, \hbar,\, a,\, \eta)^*\big)^j \;\; \varphi_0(A,\, B,\, \hbar,\, a,\, \eta,\, x).$$

For fixed A, B, $\hbar$, a, and η,

$\Big\{\, \varphi_j(A,\, B,\, \hbar,\, a,\, \eta,\, \cdot\,)\, \Big\}$ is an orthonormal basis of $L^2(\mathbb{R},\, dx)$.

$$\Big(\, \mathcal{F}_\hbar\, \varphi_j(A,\, B,\, \hbar,\, a,\, \eta,\, \cdot\,)\, \Big)\, (\xi) \;=\; (-i)^{|j|}\; e^{-i\, a\, \eta/\hbar}\; \varphi_j(B,\, A,\, \hbar,\, \eta,\, -a,\, \xi).$$



The position probability densities $|\varphi_0(x)|^2$ and $|\varphi_{12}(x)|^2$.

Theorem 1′ Suppose $V \in C^3(\mathbb{R})$ satisfies $-M_1 \le V(x) \le M_2\, e^{M_3\,|x|^2}$. Suppose $a(t)$, $\eta(t)$, $S(t)$, $A(t)$, and $B(t)$ satisfy

$$\begin{aligned}
\dot{a}(t) &= \eta(t), \\
\dot{\eta}(t) &= -V'(a(t)), \\
\dot{S}(t) &= \eta(t)^2/2 \;-\; V(a(t)), \\
\dot{A}(t) &= i\,B(t), \\
\dot{B}(t) &= i\,V''(a(t))\,A(t).
\end{aligned}$$

Let $\Psi(x,t,\hbar)$ solve $i\,\hbar\,\dfrac{\partial \Psi}{\partial t} \;=\; -\,\dfrac{\hbar^2}{2}\,\Delta\,\Psi + V\,\Psi$

with $\Psi(x,\,0,\,\hbar) \;=\; e^{iS(0)/\hbar}\;\varphi_j(A(0),\,B(0),\,\hbar,\,a(0),\,\eta(0),\,x)$.

Then for $t \in [0,\,T]$, the approximate solution

$$\psi(x,\,t,\,\hbar) \;=\; e^{iS(t)/\hbar}\;\varphi_j(A(t),\,B(t),\,\hbar,\,a(t),\,\eta(t),\,x)$$

satisfies

$$\|\,\psi(x,\,t,\,\hbar) \;-\; \Psi(x,\,t,\,\hbar)\,\|_{L^2(\mathbb{R})} \;\le\; C_j\;\hbar^{1/2}.$$

The Time–Dependent Born–Oppenheimer Approximation

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

where the electron Hamiltonian $h(X)$ depends parametrically
on the nuclear configuration X,
but is an operator on the electron Hilbert space $\mathcal{H}_{el}$.

We cannot solve this exactly, so we search for approximate
solutions for small ϵ.

The physical value of ϵ is typically on the order of $\dfrac{1}{10}$.

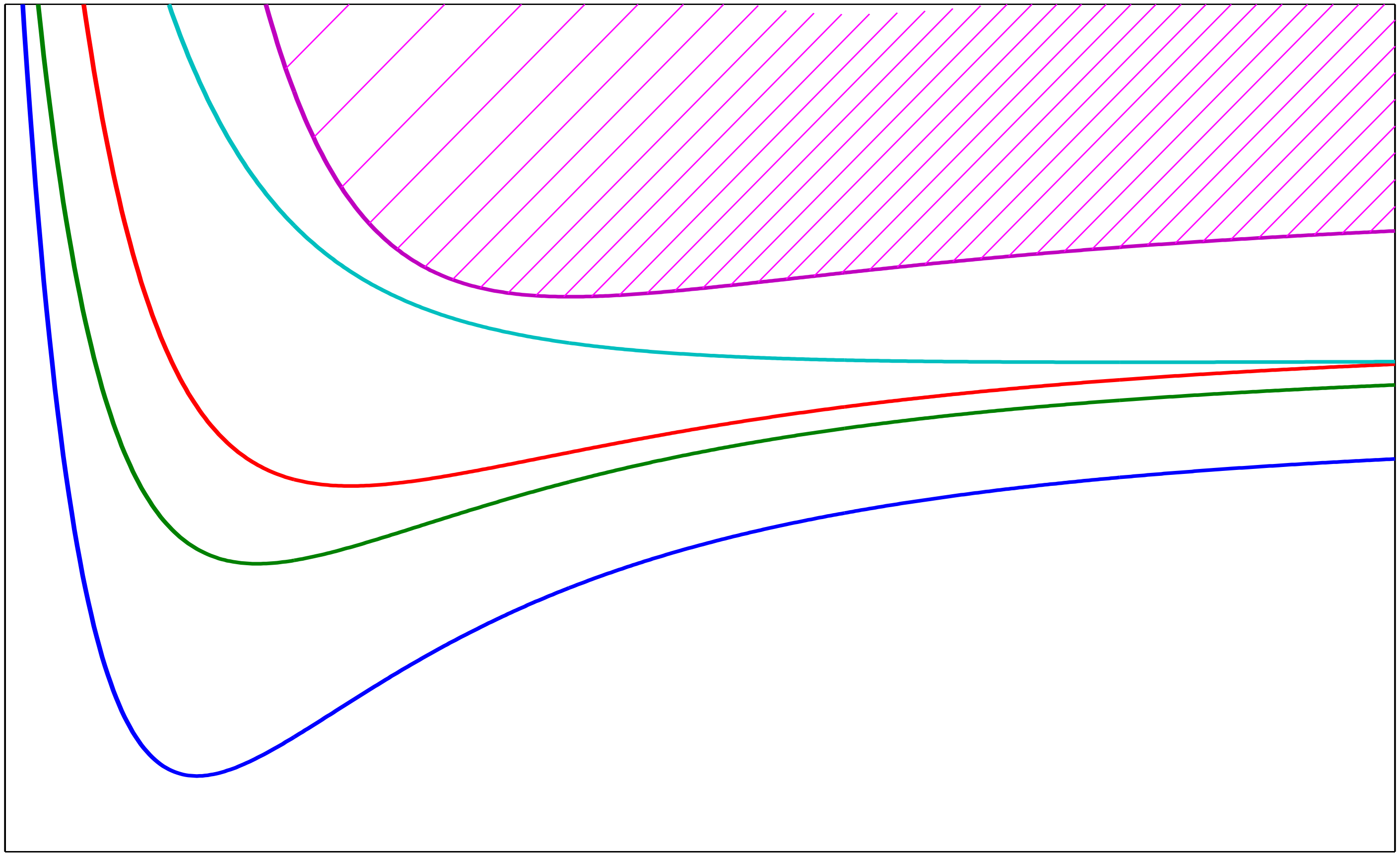
We assume $h(X)$ has an isolated non-degenerate eigenvalue $E(X)$ that depends smoothly on X.

$E(\cdot)$ determines a “Potential Energy Surface.”

We take $\Phi(X)$ to be the corresponding normalized eigenvector.

We choose the phase of $\Phi(X)$ according to the adiabatic connection.

For real operators $h(X)$, we can choose $\Phi(X)$ to be real,
but there are situations where we can only do this locally.



The spectrum of $h(X)$.

The Multiple Scales Technique

The electronic eigenvector dependends on $x = X$.

Nuclear quantum fluctuations occur on a length scale of order ϵ in X.

For small ϵ, $x = X$ and $y = \frac{X - a(t)}{\epsilon}$ behave as independent variables.

To find approximate solutions $\Psi(X)$ to the Schrödinger equation, we search for approximate solutions $\psi(x, y)$, where

$$i\,\epsilon^2\,\frac{\partial \psi}{\partial t} \;=\; -\,\frac{\epsilon^2}{2}\,\Delta_y\,\psi \;-\; \epsilon^3\,\nabla_x\cdot\nabla_y\,\psi \;-\; \frac{\epsilon^4}{2}\,\Delta_x\,\psi$$

$$+\quad [h(x) - E(x)]\,\psi \;+\; E(a(t) + \epsilon y)\,\psi$$

We ultimately take $\Psi(X, t) = \psi\left(X, \frac{X - a(t)}{\epsilon}, t\right)$.

We anticipate the semiclassical motion of the nuclei will play a role, so we make the Ansatz that $\psi(x,\,y,\,t)$ equals

$$e^{i\,S(t)/\epsilon^2}\,e^{i\eta(t)\cdot y/\epsilon}\,\Big(\psi_0(x,\,y,\,t)\;+\;\epsilon\,\psi_1(x,\,y,\,t)\;+\;\epsilon^2\,\psi_2(x,\,y,\,t)\;+\;\cdots\Big).$$

We substitute this into the multiple scales equation.
We also expand $E(a(t)+\epsilon y)$ in its power series in ϵ in the equation.

We then equate terms of the same orders on the two sides of the resulting equation.

Order ϵ^0 $\qquad [h(x)-E(x)]\,\psi_0\;=\;0.$

Thus,

$$\psi_0(x,\,y,\,t)\;=\;g_0(x,\,y,\,t)\;\Phi_0(x).$$

At this point we have no information about g_0.

Order ϵ^1 $\qquad [h(x) - E(x)]\,\psi_1 \;=\; 0.$

Thus,

$$\psi_1(x,\,y,\,t) \;=\; g_1(x,\,y,\,t)\;\Phi_0(x).$$

At this point we have no information about g_1.

Order ϵ^2

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

We separately examine the components of this equation that are in the direction of $\Phi(x)$ and those that are perpendicular to $\Phi(x)$ in $\mathcal{H}_{el}$. This yields two equations that must be solved.

In the $\Phi(x)$ direction we require

$$i\,\frac{\partial g_0}{\partial t} \;=\; -\,\frac{1}{2}\,\Delta_y\, g_0 \,+\, \frac{y\cdot E^{(2)}(a(t))\,y}{2}\,g_0.$$

This is solved exactly by the semiclassical wave packets.

$$g_0(x,\,y,\,t) \;=\; \epsilon^{-n/2}\;\varphi_j(A(t),\,B(t),\,1,\,0,\,0,\,y).$$

The perpendicular components require

$$[h(x)-E(x)]\,\phi_2(x,\,y,\,t) \;=\; i\,g_0(x,\,y,\,t)\;\eta(t)\cdot(\nabla_x\Phi)(x).$$

Thus,

$$\psi_2(x,\,y,\,t) \;=\; i\,g_0(x,\,y,\,t)\,[h(x)-E(x)]_r^{-1}\,\eta(t)\cdot(\nabla_x\Phi)(x)+g_2(x,\,y,\,t)\Phi(x).$$

At order ϵ^k, we simply mimic this process.

The equation that arises from multiples of $\Phi(x)$ is solved by using wavepackets techniques.

The equation for the perpendicular components is solved by applying the reduced resolvent of $h(x)$.

This way we obtain a formal approximate solution.
We then prove rigorous error estimates by using the "magic lemma."

Theorem 2 There exists an exact solution $\chi_\epsilon(X,\,t)$ to the Schrödinger equation that satisfies

$$\left\|\chi_\epsilon(X,\,t)\;-\;\left\{\sum_{k=0}^{K}\epsilon^k\,\psi_k\left(X,\,\frac{X-a(t)}{\epsilon},\,t\right)+\epsilon^{K+1}\psi_{K+1}^{\perp}\left(X,\,\frac{X-a(t)}{\epsilon},\,t\right)\right.\right.$$

$$\left.\left.+\;\epsilon^{K+2}\psi_{K+2}^{\perp}\left(X,\,\frac{X-a(t)}{\epsilon},\,t\right)\right\}\right\|\;\le\;C_K\,\epsilon^{K+1}.$$

Theorem 3 By optimal truncation of the asymptotic series, one can construct an approximate solution

$$\widetilde{\psi}_\epsilon(X,\,t)\;=\;\sum_{k=0}^{K(\epsilon)}\epsilon^k\,\psi_k\left(X,\,\frac{X-a(t)}{\epsilon},\,t\right).$$

There exists an exact solution $\chi_\epsilon(X,\,t)$ to the Schrödinger equation that satisfies

$$\left\|\,\chi_\epsilon(X,\,t)\;-\;\widetilde{\psi}_\epsilon(X,\,t)\,\right\|\;\le\;C\,\exp\left(-\,\frac{\Gamma}{\epsilon^2}\right).$$

Non–Adiabatic Transitions from Avoided Crossings

In the mid–1990's, Alain Joye and I studied propagation through generic avoided crossings with gaps proportional to ϵ.

There are numerous types of avoided crossings. Some examples have

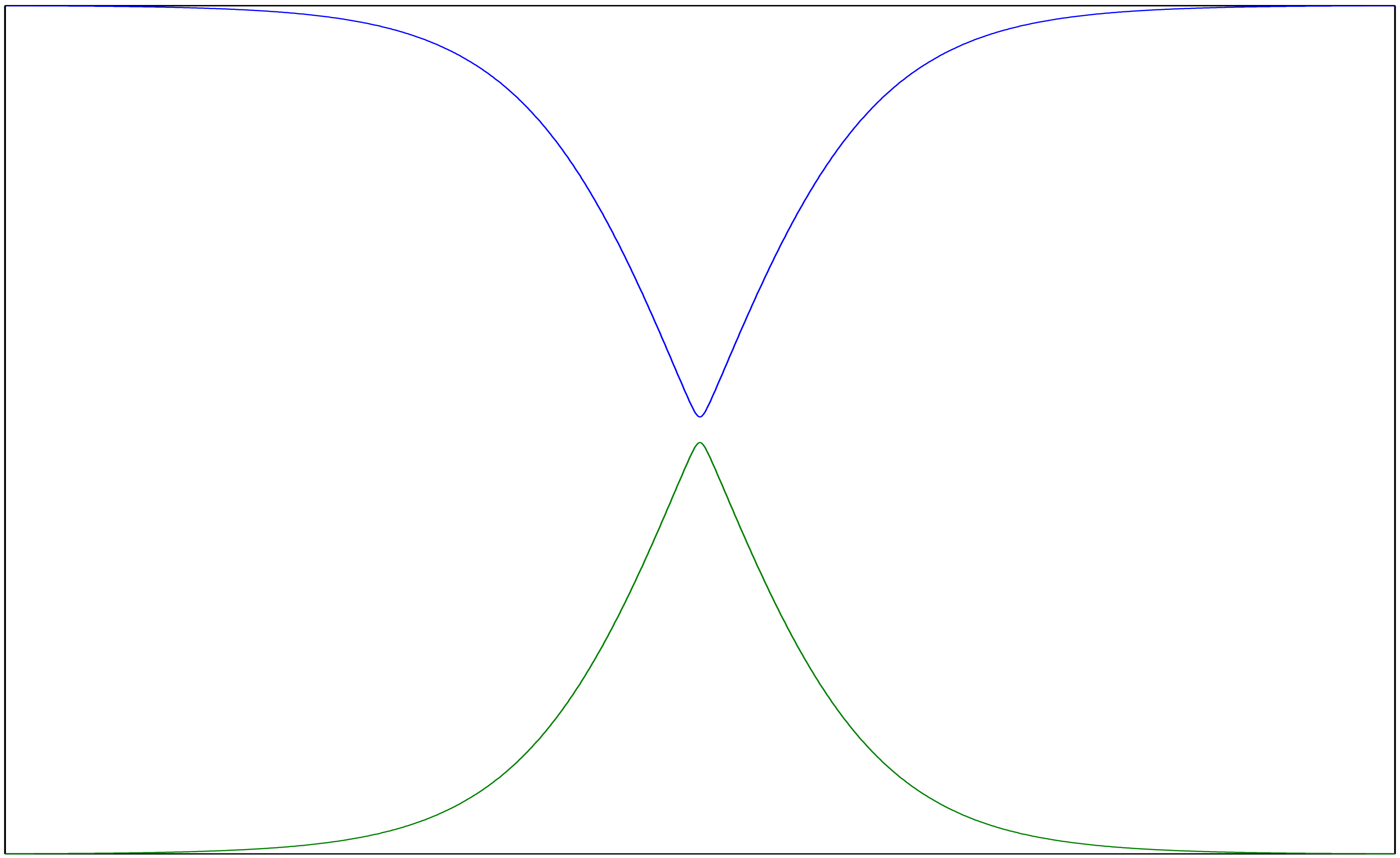
$$h(X) \;=\; \begin{pmatrix} \tanh(X) & c\,\epsilon \\ c\,\epsilon & -\tanh(X) \end{pmatrix} \qquad \text{with } X \in \mathbb{R},$$

$$E(X) \;=\; \pm\,\sqrt{\tanh(X)^2 \,+\, c^2\,\epsilon^2}\;.$$

or

$$h(X_1,\,X_2) \;=\; \begin{pmatrix} \tanh(X_1) & \tanh(X_2) + i\,c\,\epsilon \\ \tanh(X_2) - i\,c\,\epsilon & -\tanh(X_1) \end{pmatrix} \quad \text{with } X_j \in \mathbb{R}.$$

$$E(X_1,\,X_2) \;=\; \pm\,\sqrt{\tanh(X_1)^2 \,+\, \tanh(X_2)^2 \,+\, c^2\,\epsilon^2}\;.$$



An Avoided Crossing with a Small Gap.

In this situation we proved the following:

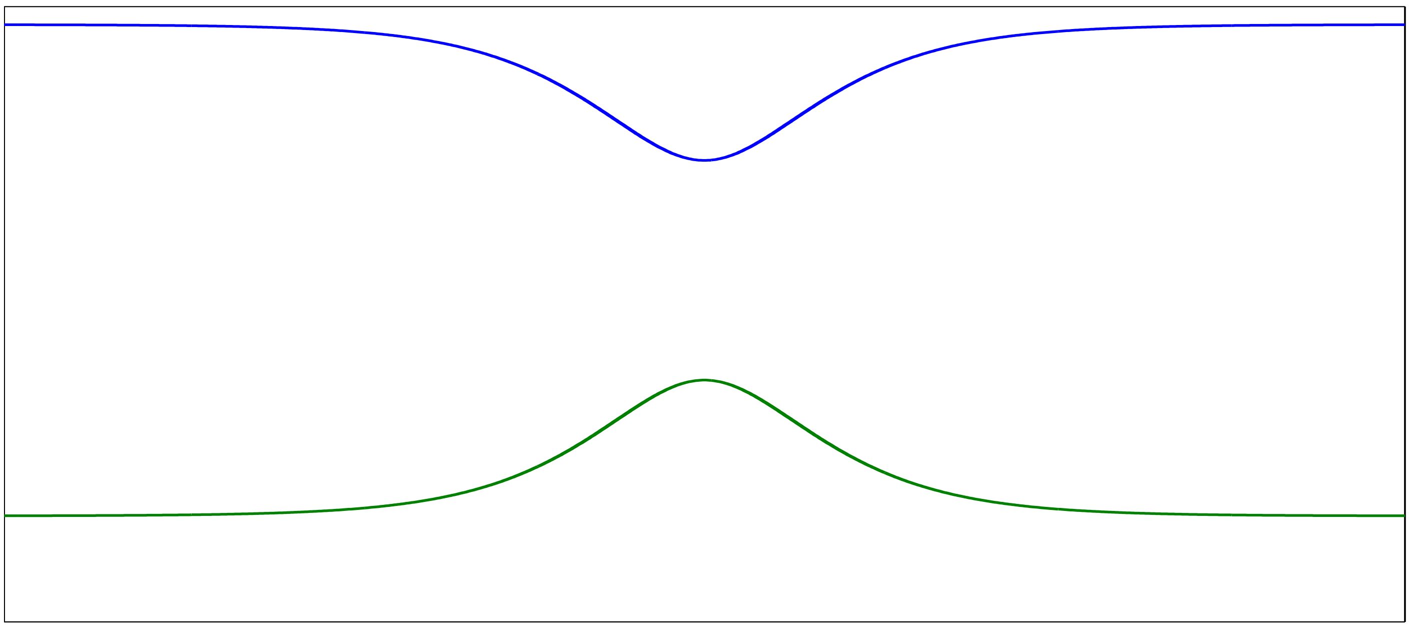
1. For all of the various types of generic avoided crossings, a correctly interpreted Landau–Zener formula gives the correct transition amplitudes.

2. Classical energy conservation gives the momentum after the wave function has gone through the avoided crossings.

3. If one sends in a $\varphi_k(A_{\mathcal{A}}(t),\, B_{\mathcal{A}}(t),\, \epsilon^2,\, a_{\mathcal{A}}(t),\, \eta_{\mathcal{A}}(t),\, X)\,\Phi_{\mathcal{A}}(X)$, then the part of the wave function that makes a non–adiabatic transition is $\varphi_k(A_{\mathcal{B}}(t),\, B_{\mathcal{B}}(t),\, \epsilon^2,\, a_{\mathcal{B}}(t),\, \eta_{\mathcal{B}}(t),\, X)\,\Phi_{\mathcal{B}}(X)$, to leading order after the transition has occurred.

4. Because the gaps are so small, the transition probability is $O(\epsilon^0)$.

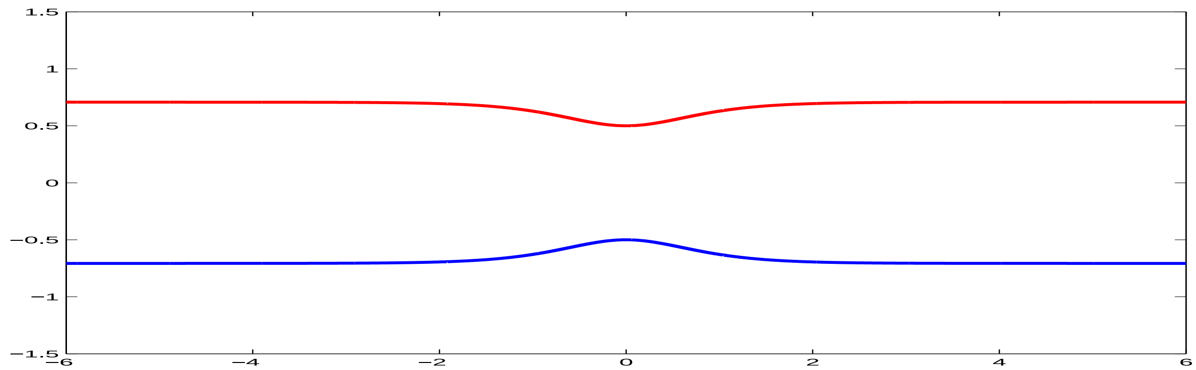
The only known rigorous results for fixed gaps have just one degree of freedom for the nuclei.



An Avoided Crossing with a Fixed Gap.

I shall present these results (obtained with Alain Joye) for the following specific example

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



Scattering with large negative t asymptotics

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

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.

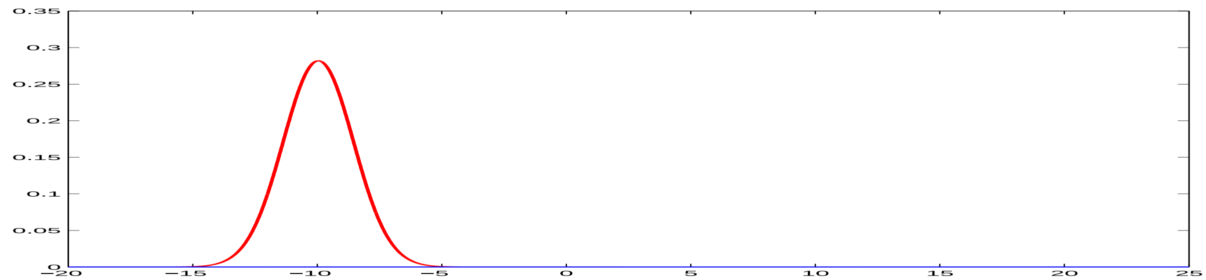
These predictions are wrong!

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

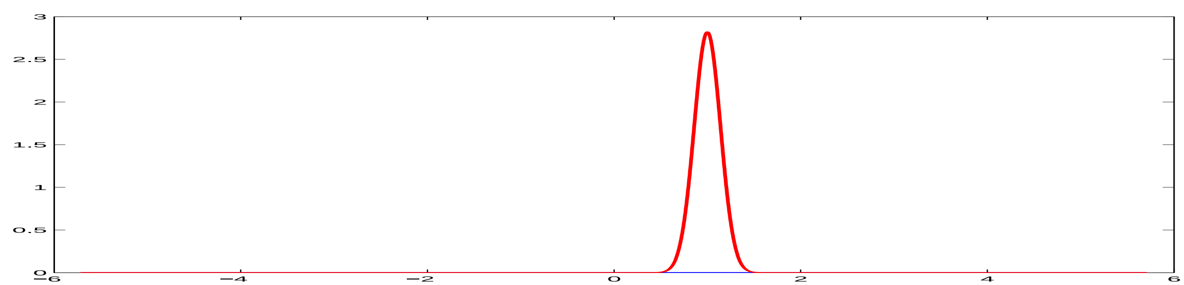
Additional Surprises

- 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

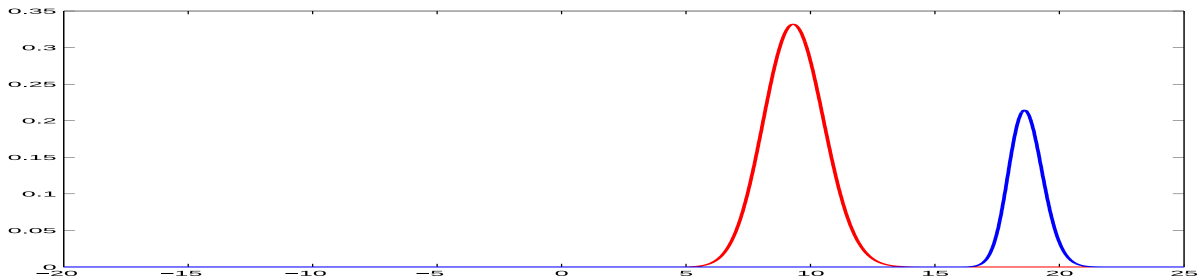
$$\epsilon^{-k} \exp\left(-\alpha/\epsilon^2\right).$$



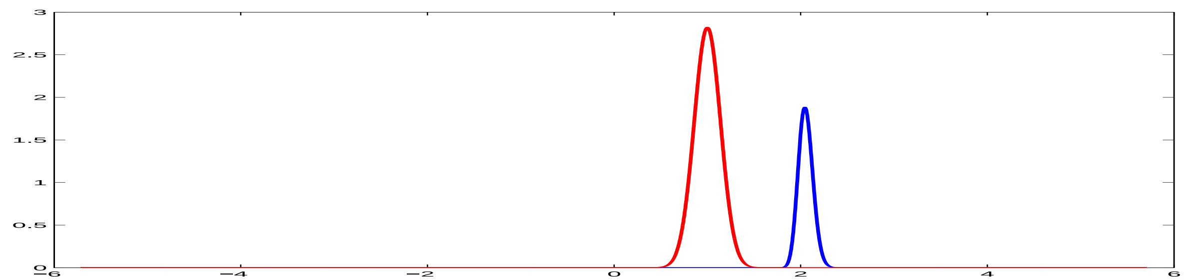
Position space plot at time $t = -10$ of the probability density for being on the upper energy level.



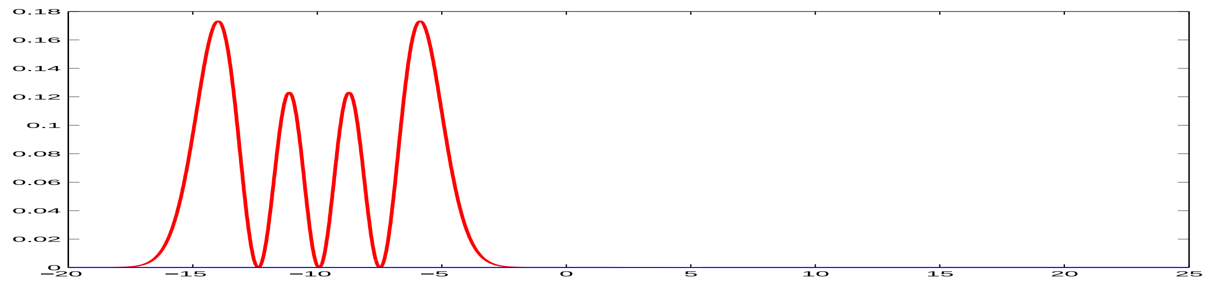
Momentum space plot at time $t = -10$ of the probability density for being on the upper energy level.



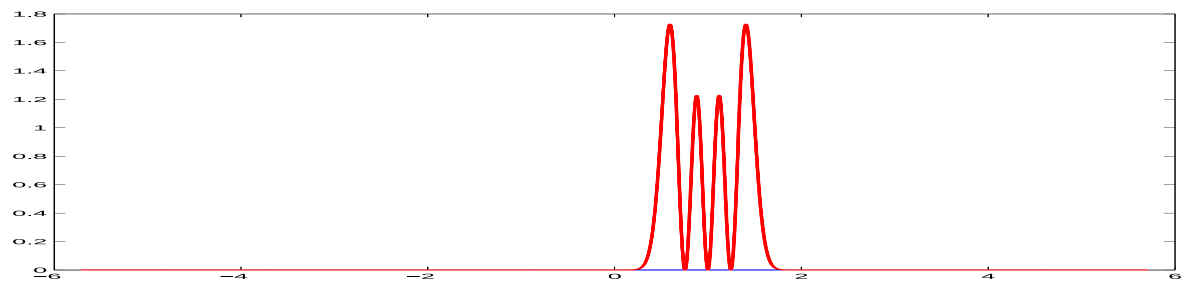
Position space probability density at time $t = 9$.
Lower level plot is multiplied by 3×10^8.



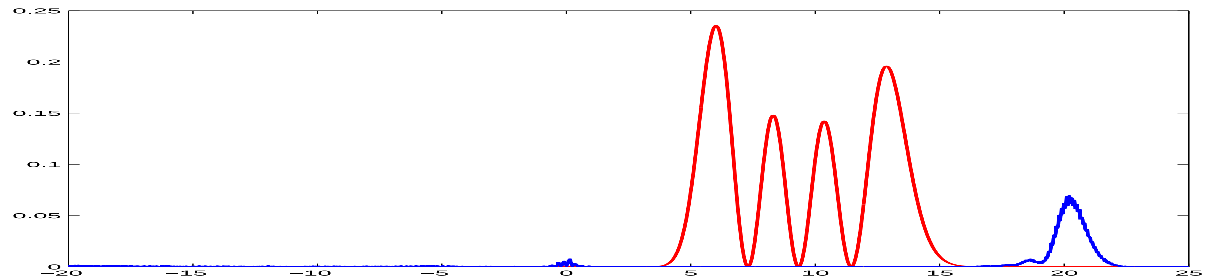
Momentum space probability density at time $t = 9$.
Lower level plot is multiplied by 3×10^8.



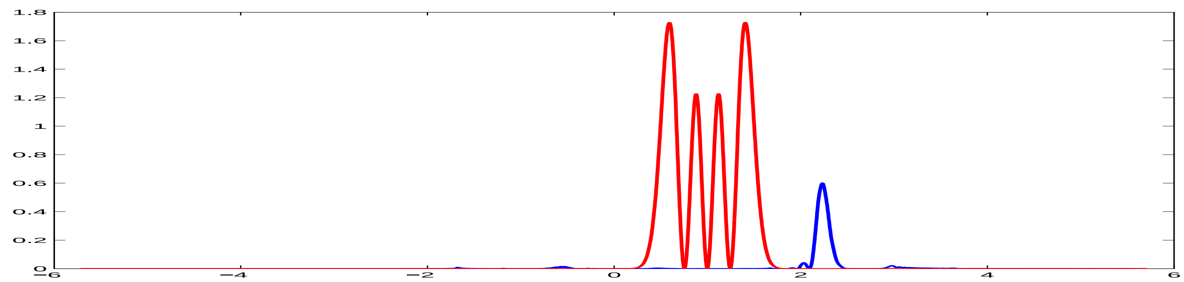
Position space probability density at time $t = -10$.



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 very much!