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

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

hagedorn@math.vt.edu

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Outline

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2. The Time–Dependent Born–Oppenheimer Approximation

3. Exponentially Small Non–Adiabatic Scattering Transitions

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 $\epsilon\, |B|$.

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

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

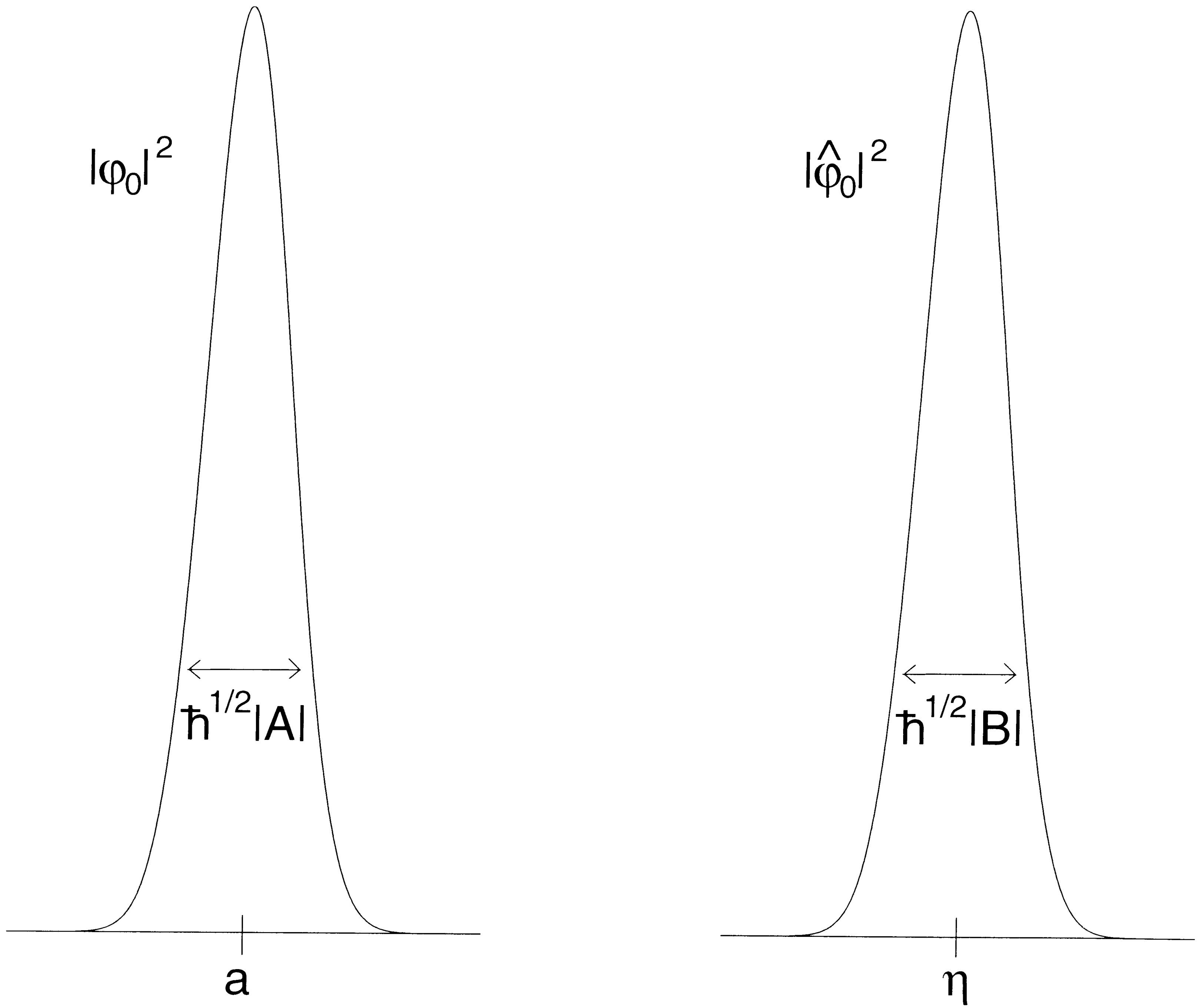
There are raising and lowering operators with the same algebraic properties as with the Harmonic oscillator.

Define the Fourier Transform

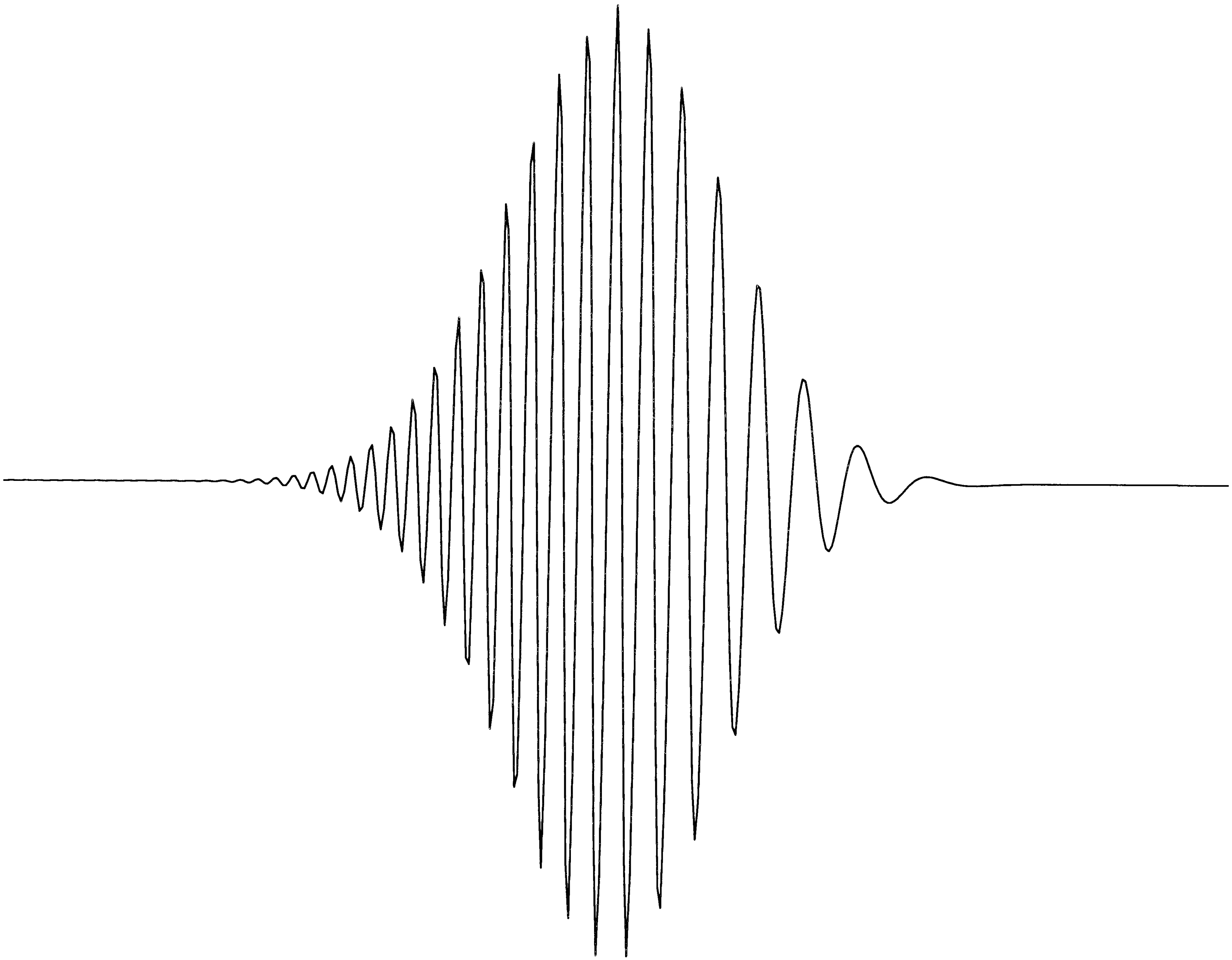
$$(\mathcal{F}_\hbar f)(\xi) \;=\; (2\pi\hbar)^{-d/2}\int_{\mathbb{R}^d} f(x)\;e^{-i\xi\cdot x/\hbar}\;dx.$$

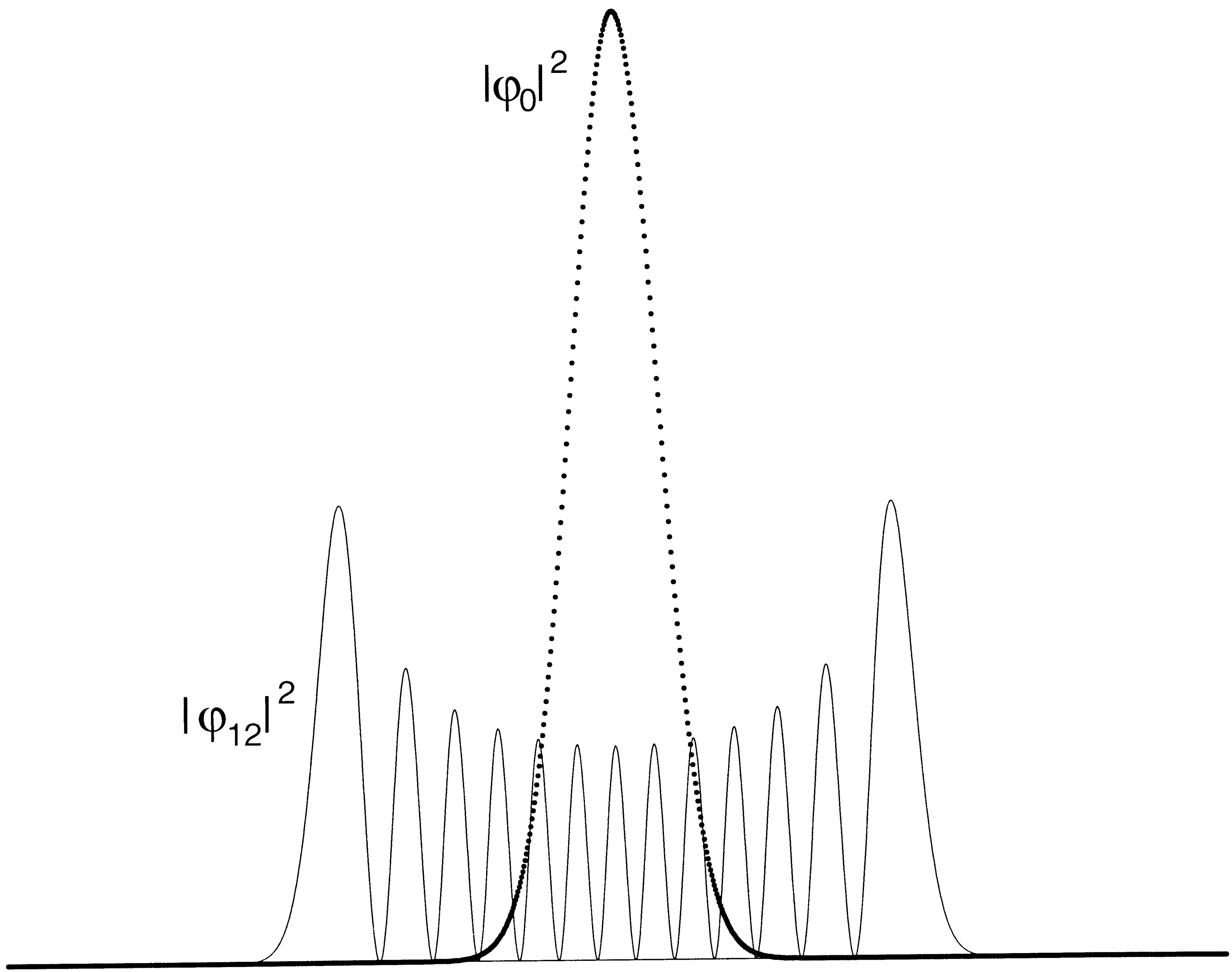
Then

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

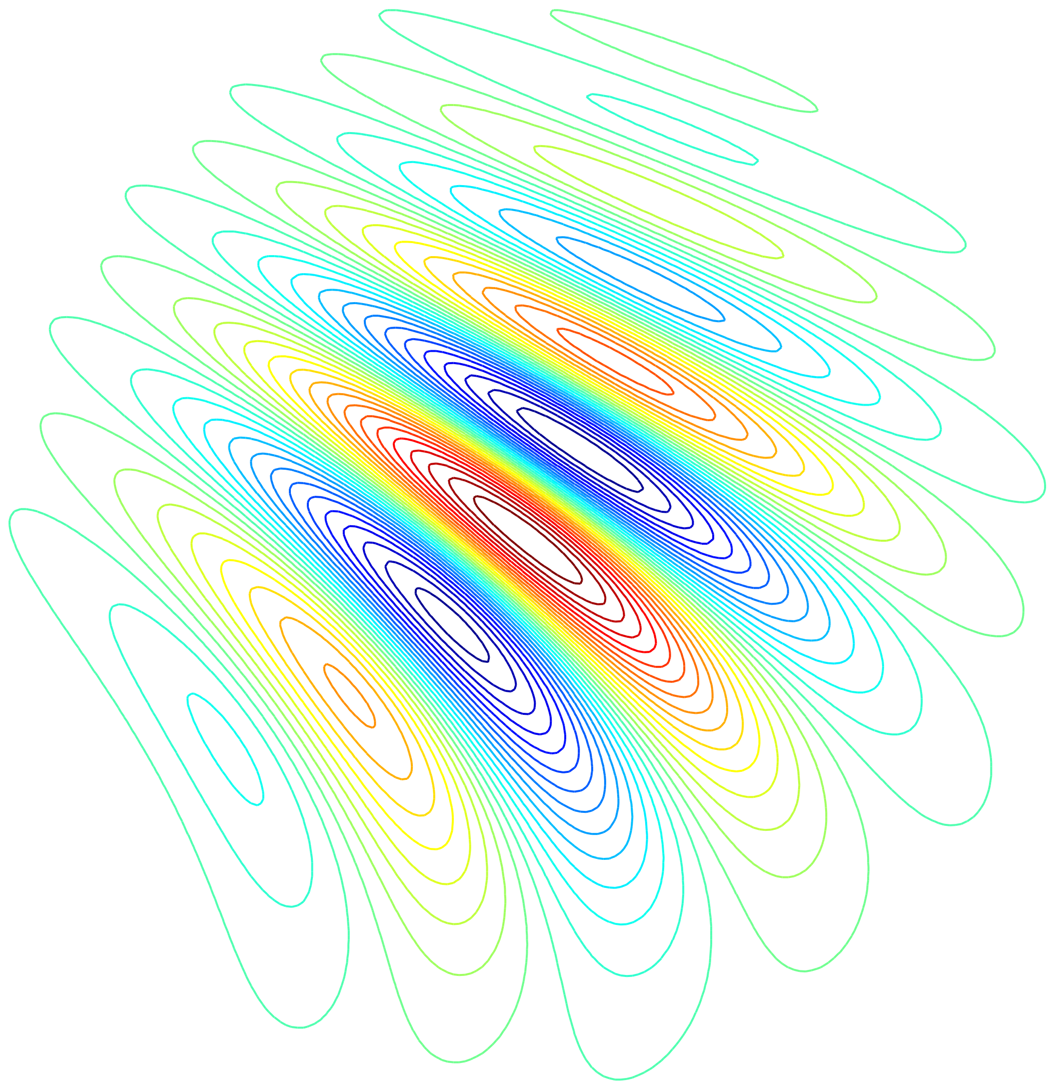


$|\varphi_0|^2$
$\hbar^{1/2}|A|$
a
$|\hat{\varphi}_0|^2$
$\hbar^{1/2}|B|$
η





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



If $V(X)$ is smooth and bounded below, then

$$e^{iS(t)/\hbar} \sum_{|k| \leq K} c_k \; \phi_k(A(t), B(t), \hbar, a(t), \eta(t), X)$$

solves the time–dependent Schrödinger equation

$$i \; \hbar \; \frac{\partial \psi}{\partial t} \; = \; - \; \frac{\hbar^2}{2} \; \Delta_X \; \psi \; + \; V(X) \; \psi,$$

up to an $O(\hbar^{1/2})$ error.

Here

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

If $V(X)$ is quadratic, there is no error.

There are many generalizations of this result.
(Time dependent V's. Higher order in $\hbar^{1/2}$. Approximations with $\exp(-C/\hbar)$ errors from optimal truncation.)

Faou, Gradinaru, and Lubich recently developed a numerical algorithm for solving semiclassical time–dependent Schrödinger equations that is based on these wave packets.

It scales very well as the space dimension and/or the approximation order are increased.

The Time–Dependent Born–Oppenheimer Approximation

Molecular Hamiltonians can be written as

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_X \;+\; h(X),$$

where the electron Hamiltonian $h(X)$ depends parametrically on the nuclear configuration X.

We wish to find approximate solutions to

$$i\;\epsilon^2\,\frac{\partial\Psi}{\partial t} \;=\; H(\epsilon)\;\Psi.$$

Born–Oppenheimer Approximations treat the electrons and nuclei separately, while respecting the coupling between them.

STEP 1. For each configuration X of the nuclei, solve the electronic eigenvalue problem.

$$h(X)\ \Phi(X,x) \ = \ E(X)\ \Phi(X,x).$$

- The various different discrete eigenvalues $E(X)$ that depend continuously on X are called electron energy levels.

STEP 2. Use the semiclassical wave packets for the nuclei with an electron energy level $E(X)$ playing the role of the potential.

Hypotheses

- Assume the resolvent of $h(X)$ is smooth in X.
- Assume $E(X)$ is a non–degenerate level for all X, and let $\Phi(X)$ be an associated normalized eigenvector with phase chosen so $\langle\, \Phi(X,\cdot),\, \nabla_X \Phi(X,\cdot)\,\rangle_{\mathcal{H}_{\mathrm{el}}} = 0$.
- Solve the semiclassical equations of motion

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

Theorem 1 The time–dependent Schrödinger equation has a solution of the form $\Psi_{N,\epsilon}(X,\,x,\,t) \;+\; error_{N,\epsilon}$,

where $$\Psi_{N,\epsilon}(X,\,x,\,t) \quad = \quad \sum_{n=0}^{N} \psi_{n,\epsilon}(X,\,x,\,t)\;\epsilon^n$$

and $\|\,error_{N,\epsilon}\,\| \quad \leq \quad C_N\,\epsilon^{N+1}$, for $t \;\in\; [0,\,T]$.

The zeroth order term in the expansion is

$$\psi_{0,\epsilon}(X,\,x,\,t)$$

$$= \quad e^{iS(t)/\epsilon^2} \quad \Phi(X,x) \sum_{|k|\leq K} c_k\;\phi_k(A(t),B(t),\epsilon^2,a(t),\eta(t),X),$$

where the c_k and K are arbitrary.

Theorem 2 Under analyticity assumptions on $h(X)$, we can choose $N(\epsilon) = O(\epsilon^{-2})$, such that the Schrödinger equation has a solution of the form $\quad \Psi_{N(\epsilon),\epsilon} \quad + \quad error_\epsilon,$

where $\quad \| \, error_\epsilon \, \| \quad \leq \quad C \ \exp\left(-\frac{\Gamma}{\epsilon^2}\right), \qquad$ for $t \ \in \ [0, T]$.

Furthermore, given any $b > 0$, this $N(\epsilon)$ can be chosen so that there exist D and $\gamma > 0$, such that

$$\int_{|X-a(t)|>b} \left\| \, \Psi_{N(\epsilon),\epsilon}(X, x, t) \, \right\|^2_{\mathcal{H}_{\text{el}}} \ dX \quad \leq \quad D \ \exp\left(-\frac{\gamma}{\epsilon^2}\right).$$

Remarks

- Semiclassical wave packet techniques handle the nuclear motion.
- An adiabatic expansion handles the electronic states.
- We use the Method of Multiple Scales to separate semiclassical terms from adiabatic terms in the perturbation calculations.
- The analog of Theorem 1 is proven for Coulomb potentials.
- Theorem 2 follows from Theorem 1 and the estimate

  $\| error_{N-1,\epsilon} \| \leq \alpha \, \beta^N \, N^{N/2} \, \epsilon^N$ by a simple calculation.
- The form of the error estimate in Theorem 2 is optimal. Our approximation ignores tunnelling by the nuclei and non–adiabatic transitions by the electrons.

Remarks (continued)

- There are several other approaches. See, for example,
  - C. Fermanian–Kammerer, P. Gérard.
  - G. Panati, H. Spohn, S. Teufel.
  - C. Lasser, C. Fermanian–Kammerer.
  - A. Martinez, V. Sordoni.

Exponentially Small Non–Adiabatic Transitions

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.

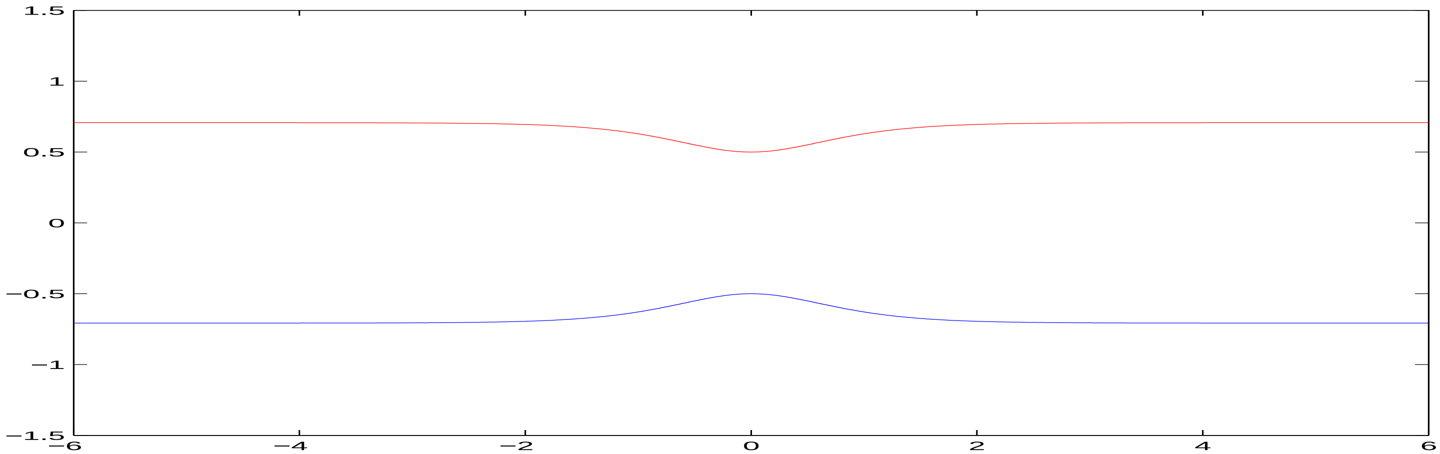
For further simplicity, let $n = 2$.

Assume $h(X)$ approaches limits as $X \to \pm\infty$ sufficiently rapidly,
and that there is one avoided crossing of the eigenvalues.

We can find the leading order exponentially small
non–adiabatic correction for the scattering theory when
the total energy is strictly above all the eigenvalues of $h(\cdot)$.

Example that illustrates the rigorous results

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



Scattering with large negative t asymptotics

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

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.

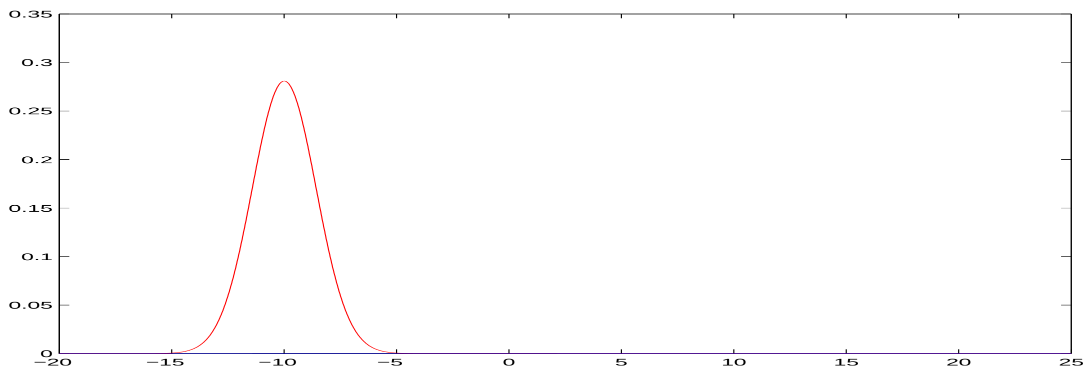
This intuitive picture is wrong!

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

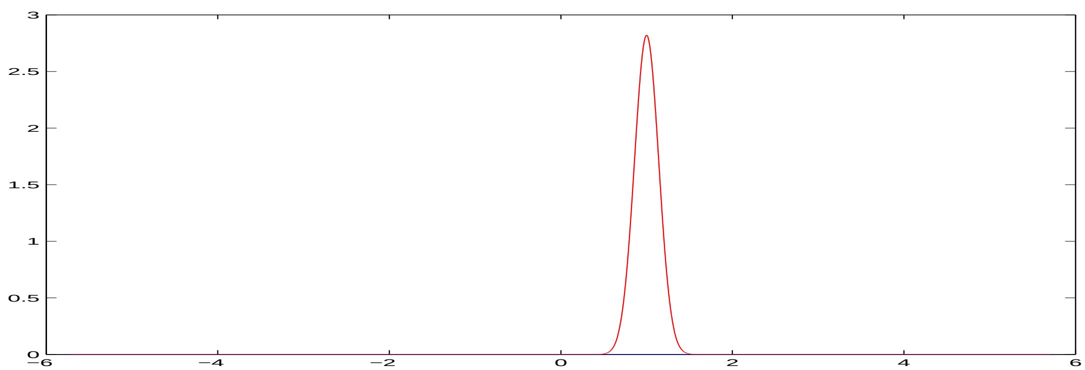
Additional Surprises

- 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

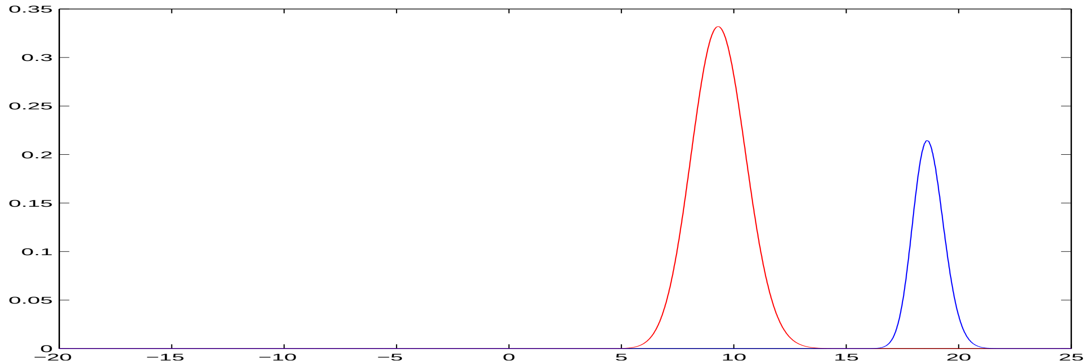
$$\epsilon^{-k} \exp\left(-\alpha/\epsilon^2\right).$$



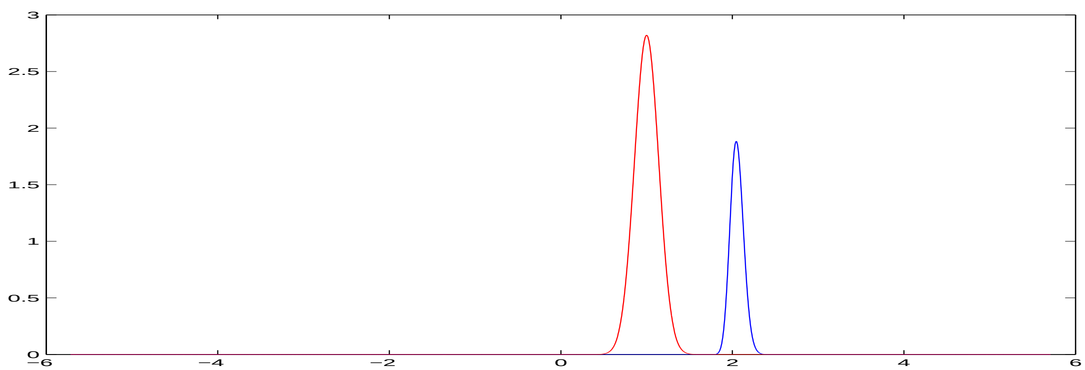
Position space plot at time $t = -10$ of the probability density for being on the upper energy level.



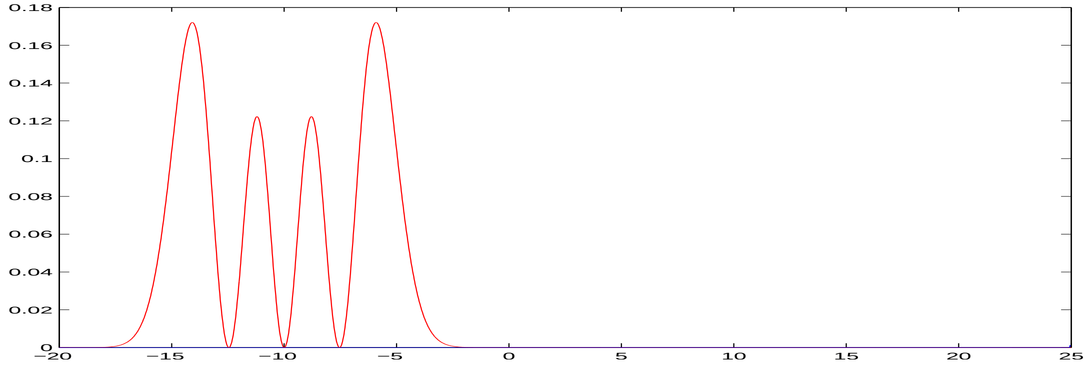
Momentum space plot at time $t = -10$ of the probability density for being on the upper energy level.



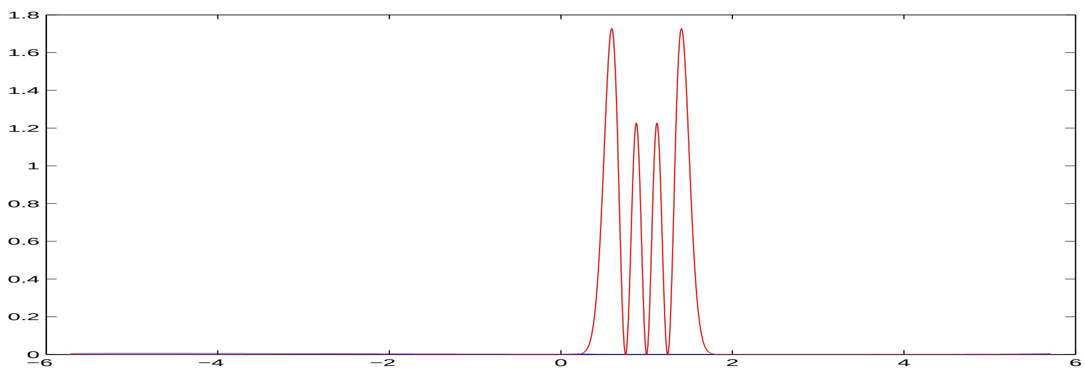
Position space probability density at time $t = 9$.
Lower level plot is multiplied by 3×10^8.



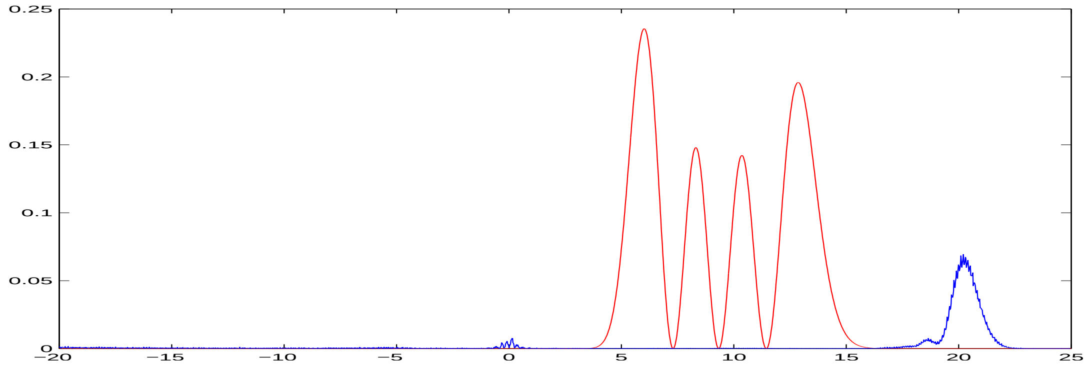
Momentum space probability density at time $t = 9$.
Lower level plot is multiplied by 3×10^8.



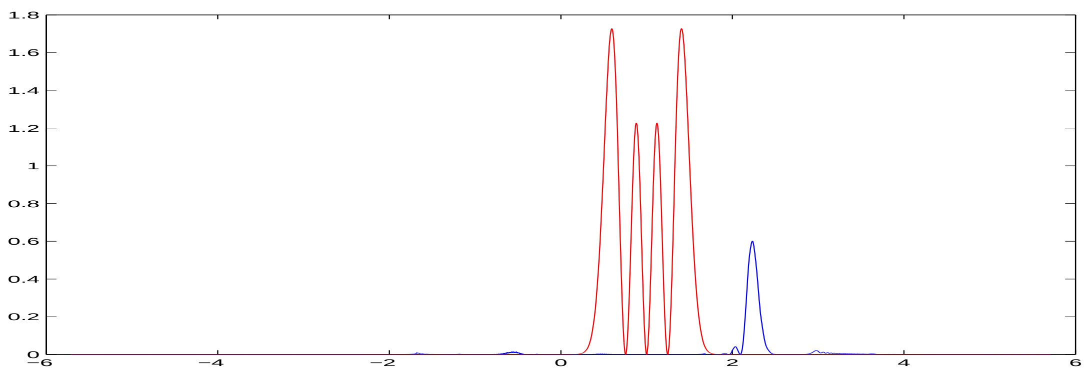
Position space probability density at time $t = -10$.



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 $\exp\left(-\frac{C}{|p|\,\epsilon^2}\right)$, 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 $\eta \neq 0$.