

Photo-dissociation of molecules: mathematics meets quantum chemistry

Ben Goddard

School of Mathematics, University of Edinburgh
and The Maxwell Institute for Mathematical Sciences

ScotCHEM 2017

Joint work with Volker Betz (TU Darmstadt),
Tim Hurst (Edinburgh), Uwe Manthe (Bielefeld)
and Stefan Teufel (Tübingen)

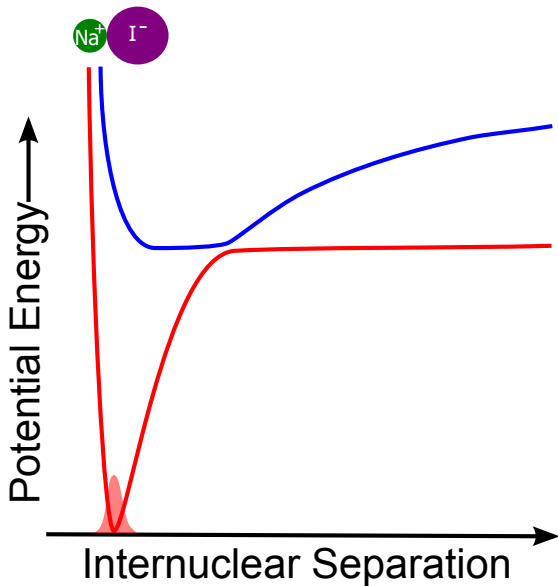


MAXWELL INSTITUTE FOR
MATHEMATICAL SCIENCES

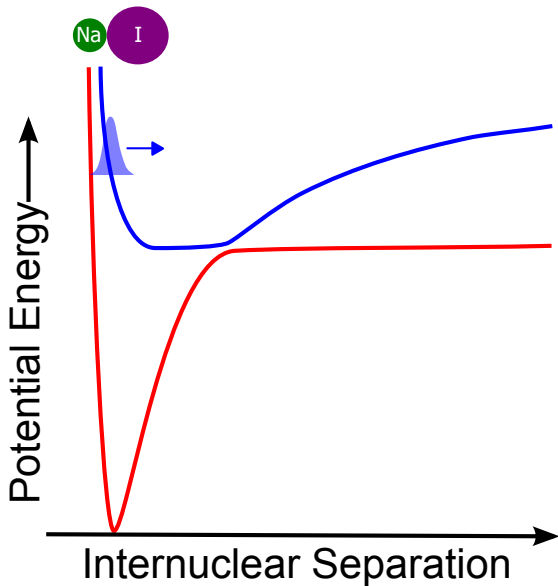
EPSRC

Engineering and Physical Sciences
Research Council

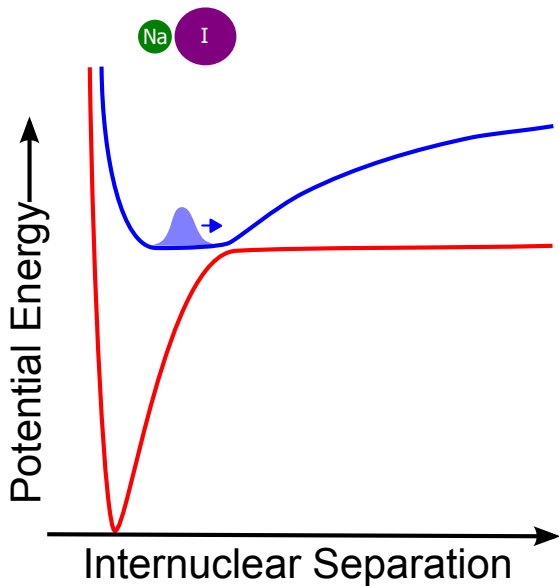
Example: Photo-Dissociation of NaI



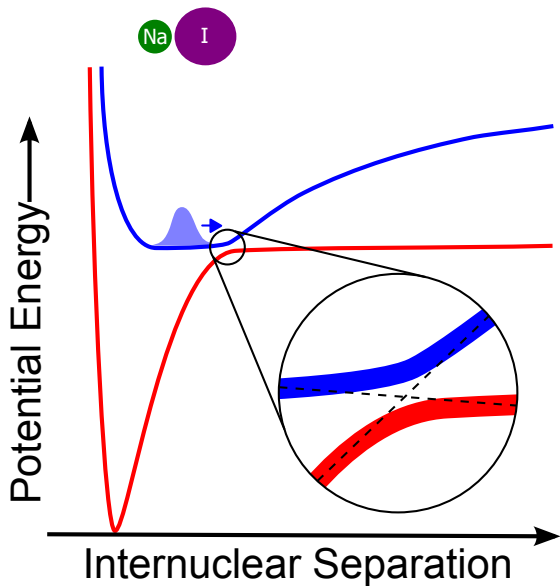
Example: Photo-Dissociation of NaI



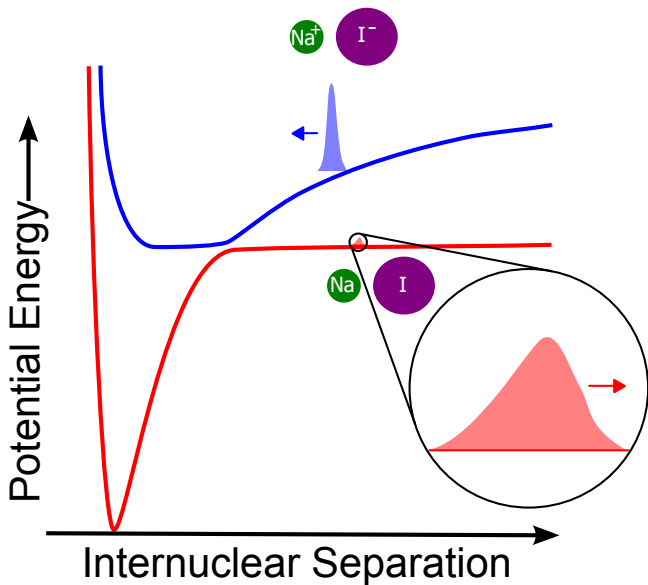
Example: Photo-Dissociation of NaI



Example: Photo-Dissociation of NaI



Example: Photo-Dissociation of NaI



Questions

Assume initial wavefunction lies on the upper level:

- ① How large is the transition probability onto the lower?
- ② What is the precise form of the transmitted wavefunction?
- ③ What happens to the transmitted wavepacket?

Questions

Assume initial wavefunction lies on the upper level:

- 1 How large is the transition probability onto the lower?
- 2 What is the precise form of the transmitted wavefunction?
- 3 What happens to the transmitted wavepacket?

Challenges

Due to the presence of a small parameter $\epsilon = \sqrt{m_e/m_n}$:

- Wavefunctions are rapidly oscillating (typical frequency $1/\epsilon$);
- Transmitted wavepacket is exponentially small (in $1/\epsilon$ and the gap);
- Requires very high accuracy numerics.

Questions

Assume initial wavefunction lies on the upper level:

- 1 How large is the transition probability onto the lower?
- 2 What is the precise form of the transmitted wavefunction?
- 3 What happens to the transmitted wavepacket?

Challenges

Due to the presence of a small parameter $\epsilon = \sqrt{m_e/m_n}$:

- Wavefunctions are rapidly oscillating (typical frequency $1/\epsilon$);
- Transmitted wavepacket is exponentially small (in $1/\epsilon$ and the gap);
- Requires very high accuracy numerics.

Aim

Compute the transmitted wavepacket using only single-level (Born-Oppenheimer) dynamics.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\hbar\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\hbar^2}{2m_n}\Delta_{\mathbf{x}_n} - \frac{\hbar^2}{2m_e}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

V_n = Coulomb repulsion between nuclei.

V_e = Coulomb repulsion between electrons.

$V_{n,e}$ = Coulomb attraction between nuclei and electrons.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\hbar\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\hbar^2}{2m_n}\Delta_{\mathbf{x}_n} - \frac{\hbar^2}{2m_e}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- Atomic units: $\hbar = m_e = 1$.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{1}{2m_n}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- Atomic units: $\hbar = m_e = 1$.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{1}{2m_n}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- **Atomic units:** $\hbar = m_e = 1$.
- $m_n \gg m_e$, for simplicity $m_{n,i} = \varepsilon^{-2}$ for all i .

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- **Atomic units:** $\hbar = m_e = 1$.
- $m_n \gg m_e$, for simplicity $m_{n,i} = \varepsilon^{-2}$ for all i .

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- **Atomic units:** $\hbar = m_e = 1$.
- $m_n \gg m_e$, for simplicity $m_{n,i} = \varepsilon^{-2}$ for all i .
- **Motion of nuclei very slow:** $t \mapsto t/\varepsilon$.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\varepsilon\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- **Atomic units:** $\hbar = m_e = 1$.
- $m_n \gg m_e$, for simplicity $m_{n,i} = \varepsilon^{-2}$ for all i .
- **Motion of nuclei very slow:** $t \mapsto t/\varepsilon$.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\varepsilon\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = H\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- **Atomic units:** $\hbar = m_e = 1$.
- $m_n \gg m_e$, for simplicity $m_{n,i} = \varepsilon^{-2}$ for all i .
- **Motion of nuclei very slow:** $t \mapsto t/\varepsilon$.
- Define **electronic Hamiltonian** $H_e(\mathbf{x}_n)$.

The role of ε (Chemistry/Maths scalings)

For N_n nuclei with positions \mathbf{x}_n and N_e electrons with positions \mathbf{x}_e ,

$$i\varepsilon\partial_t\psi(\mathbf{x}_n, \mathbf{x}_e, t) = \left(-\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}_n} + H_e(\mathbf{x}_n) \right)\psi(\mathbf{x}_n, \mathbf{x}_e, t),$$

with

$$H = -\frac{\varepsilon^2}{2}\Delta_{\mathbf{x}_n} - \frac{1}{2}\Delta_{\mathbf{x}_e} + V_n(\mathbf{x}_n) + V_e(\mathbf{x}_e) + V_{n,e}(\mathbf{x}_n, \mathbf{x}_e).$$

- Atomic units: $\hbar = m_e = 1$.
- $m_n \gg m_e$, for simplicity $m_{n,i} = \varepsilon^{-2}$ for all i .
- Motion of nuclei very slow: $t \mapsto t/\varepsilon$.
- Define electronic Hamiltonian $H_e(\mathbf{x}_n)$.

The two-band Schrödinger equation

Two-level system with one degree of freedom:

$$i\varepsilon\partial_t \begin{pmatrix} \psi_1(x, t) \\ \psi_2(x, t) \end{pmatrix} = \left(-\frac{\varepsilon^2}{2}\partial_x^2\mathbf{I} + V(x) + d(x)\mathbf{I} \right) \begin{pmatrix} \psi_1(x, t) \\ \psi_2(x, t) \end{pmatrix}, \text{ with}$$

$$V(x) = \rho(x) \begin{pmatrix} \cos(\theta(x)) & \sin(\theta(x)) \\ \sin(\theta(x)) & -\cos(\theta(x)) \end{pmatrix}.$$

\mathbf{I} is the 2×2 unit matrix, x the nuclear separation.

Assume $\rho \geq \delta > 0$; an avoided crossing with gap at least 2δ .

δ should be small and independent of ε .

Nuclei move a distance of order one in a time of order one.

Adiabatic representation

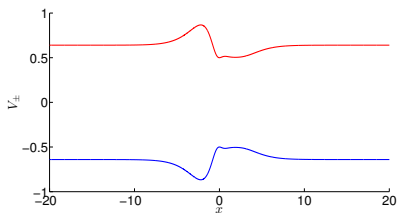
For

$$U_0(x) = \begin{pmatrix} \cos(\theta(x)/2) & \sin(\theta(x)/2) \\ \sin(\theta(x)/2) & -\cos(\theta(x)/2) \end{pmatrix}, \quad \psi_a(x, t) = U_0(x)\psi(x, t),$$

we obtain

$$i\varepsilon\partial_t\psi_a(x, t) = H_0\psi_a(x, t), \quad \text{with}$$

$$H_0 = U_0 H U_0^* = -\frac{\varepsilon^2}{2}\partial_x^2 \mathbf{I} + \begin{pmatrix} \rho(x) + d(x) + \varepsilon^2 \frac{\theta'(x)^2}{8} & -\varepsilon \frac{\theta'(x)}{2} \cdot (\varepsilon\partial_x) - \varepsilon^2 \frac{\theta''(x)}{4} \\ \varepsilon \frac{\theta'(x)}{2} \cdot (\varepsilon\partial_x) + \varepsilon^2 \frac{\theta''(x)}{4} & -\rho(x) + d(x) + \varepsilon^2 \frac{\theta'(x)^2}{8} \end{pmatrix}.$$



Adiabatic representation

For

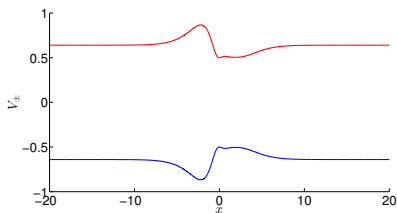
$$U_0(x) = \begin{pmatrix} \cos(\theta(x)/2) & \sin(\theta(x)/2) \\ \sin(\theta(x)/2) & -\cos(\theta(x)/2) \end{pmatrix}, \quad \psi_a(x, t) = U_0(x)\psi(x, t),$$

we obtain

$$i\varepsilon\partial_t\psi_a(x, t) = H_0\psi_a(x, t), \quad \text{with}$$

$$H_0 = U_0 H U_0^* = -\frac{\varepsilon^2}{2}\partial_x^2 \mathbf{I} + \begin{pmatrix} \rho(x) + d(x) + \varepsilon^2 \frac{\theta'(x)^2}{8} & -\varepsilon \frac{\theta'(x)}{2} \cdot (\varepsilon\partial_x) - \varepsilon^2 \frac{\theta''(x)}{4} \\ \varepsilon \frac{\theta'(x)}{2} \cdot (\varepsilon\partial_x) + \varepsilon^2 \frac{\theta''(x)}{4} & -\rho(x) + d(x) + \varepsilon^2 \frac{\theta'(x)^2}{8} \end{pmatrix}.$$

To leading order, the dynamics decouple: Born-Oppenheimer approximation.



Adiabatic representation

For

$$U_0(x) = \begin{pmatrix} \cos(\theta(x)/2) & \sin(\theta(x)/2) \\ \sin(\theta(x)/2) & -\cos(\theta(x)/2) \end{pmatrix}, \quad \psi_a(x, t) = U_0(x)\psi(x, t),$$

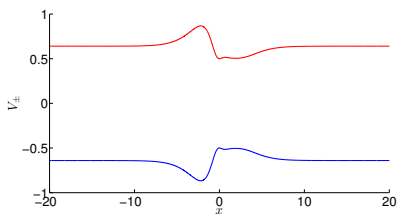
we obtain

$$i\varepsilon\partial_t\psi_a(x, t) = H_0\psi_a(x, t), \quad \text{with}$$

$$H_0 = U_0 H U_0^* = -\frac{\varepsilon^2}{2}\partial_x^2 \mathbf{I} + \begin{pmatrix} \rho(x) + d(x) + \varepsilon^2 \frac{\theta'(x)^2}{8} & -\varepsilon \frac{\theta'(x)}{2} \cdot (\varepsilon\partial_x) - \varepsilon^2 \frac{\theta''(x)}{4} \\ \varepsilon \frac{\theta'(x)}{2} \cdot (\varepsilon\partial_x) + \varepsilon^2 \frac{\theta''(x)}{4} & -\rho(x) + d(x) + \varepsilon^2 \frac{\theta'(x)^2}{8} \end{pmatrix}.$$

To leading order, the dynamics decouple: Born-Oppenheimer approximation.

Couplings given to first order by the first off-diagonal terms; semiclassical wavefunctions oscillate with frequency $1/\varepsilon$.



What do typical dynamics look like?

Superadiabatic representations

We need a better representation than the adiabatic one.

Superadiabatic representations

We need a better representation than the adiabatic one.

Idea: Find a unitary transformation U_n such that $\psi_n = U_n \psi$ solves (to leading order in ε)

$$i\varepsilon \partial_t \psi_n = \begin{pmatrix} -\frac{\varepsilon^2}{2} \partial_x^2 + \rho(x) + d(x) & \varepsilon^{n+1} K_{n+1}^+ \\ \varepsilon^{n+1} K_{n+1}^- & -\frac{\varepsilon^2}{2} \partial_x^2 - \rho(x) + d(x) \end{pmatrix} \psi_n.$$

Superadiabatic representations

We need a better representation than the adiabatic one.

Idea: Find a unitary transformation U_n such that $\psi_n = U_n \psi$ solves (to leading order in ε)

$$i\varepsilon \partial_t \psi_n = \begin{pmatrix} -\frac{\varepsilon^2}{2} \partial_x^2 + \rho(x) + d(x) & \varepsilon^{n+1} K_{n+1}^+ \\ \varepsilon^{n+1} K_{n+1}^- & -\frac{\varepsilon^2}{2} \partial_x^2 - \rho(x) + d(x) \end{pmatrix} \psi_n.$$

U_n is known to exist, but is basically impossible to apply numerically.

Superadiabatic representations

We need a better representation than the adiabatic one.

Idea: Find a unitary transformation U_n such that $\psi_n = U_n \psi$ solves (to leading order in ε)

$$i\varepsilon \partial_t \psi_n = \begin{pmatrix} -\frac{\varepsilon^2}{2} \partial_x^2 + \rho(x) + d(x) & \varepsilon^{n+1} K_{n+1}^+ \\ \varepsilon^{n+1} K_{n+1}^- & -\frac{\varepsilon^2}{2} \partial_x^2 - \rho(x) + d(x) \end{pmatrix} \psi_n.$$

U_n is known to exist, but is basically impossible to apply numerically.

However, we can find the coupling elements K_n (which are differential operators) via a (complicated) recursion.

Superadiabatic representations

We need a better representation than the adiabatic one.

Idea: Find a unitary transformation U_n such that $\psi_n = U_n \psi$ solves (to leading order in ε)

$$i\varepsilon \partial_t \psi_n = \begin{pmatrix} -\frac{\varepsilon^2}{2} \partial_x^2 + \rho(x) + d(x) & \varepsilon^{n+1} K_{n+1}^+ \\ \varepsilon^{n+1} K_{n+1}^- & -\frac{\varepsilon^2}{2} \partial_x^2 - \rho(x) + d(x) \end{pmatrix} \psi_n.$$

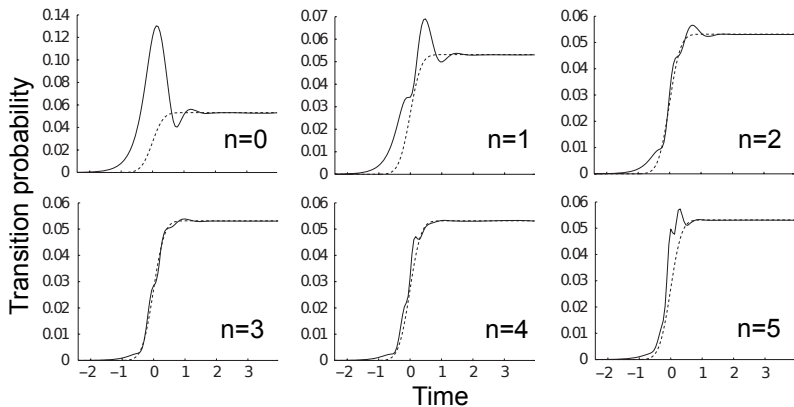
U_n is known to exist, but is basically impossible to apply numerically.

However, we can find the coupling elements K_n (which are differential operators) via a (complicated) recursion.

Approximation: Keep only the leading term corresponding to the highest derivative in K_n .

Justified rigorously for high momentum. How well does this work in general?

What does a typical transition look like?



Explicit formula

For **any** semiclassical ϕ

$$\widehat{\psi}_n^{\varepsilon}(k, t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}} \frac{\eta^* + k}{2|\eta^*|} e^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta^*|} e^{-i\frac{\tau_r}{2\delta\varepsilon}(k-\eta^*)} \widehat{\phi}^{\varepsilon}(\eta^*) \chi_{k^2 > 4\delta}$$

- Independent of n , uses only local information.
- Nonadiabatic transitions decouple in momentum space.

Explicit formula

For **any** semiclassical ϕ

$$\widehat{\psi}_n^{\varepsilon}(k, t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}^-} \frac{\eta^* + k}{2|\eta^*|} e^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta^*|} e^{-i\frac{\tau_r}{2\delta\varepsilon}(k-\eta^*)} \widehat{\phi}^{\varepsilon}(\eta^*) \chi_{k^2 > 4\delta}$$

- Independent of n , uses only local information.
- Nonadiabatic transitions decouple in momentum space.
- $\eta^* = \text{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum k due to energy conservation.

Explicit formula

For **any** semiclassical ϕ

$$\widehat{\psi}_n^{\varepsilon}(k, t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}^-} \frac{\eta^* + k}{2|\eta^*|} e^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta^*|} e^{-i\frac{\tau_r}{2\delta\varepsilon}(k-\eta^*)} \widehat{\phi}^{\varepsilon}(\eta^*) \chi_{k^2 > 4\delta}$$

- Independent of n , uses only local information.
- Nonadiabatic transitions decouple in momentum space.
- $\eta^* = \text{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum k due to energy conservation.
- $\chi_{k^2 > 4\delta}$ is also from energy conservation.

Explicit formula

For **any** semiclassical ϕ

$$\widehat{\psi}_n^{\varepsilon}(k, t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}} \frac{\eta^* + k}{2|\eta^*|} e^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta^*|} e^{-i\frac{\tau_r}{2\delta\varepsilon}(k-\eta^*)} \widehat{\phi}^{\varepsilon}(\eta^*) \chi_{k^2 > 4\delta}$$

- Independent of n , uses only local information.
- Nonadiabatic transitions decouple in momentum space.
- $\eta^* = \text{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum k due to energy conservation.
- $\chi_{k^2 > 4\delta}$ is also from energy conservation.
- $\tau = \tau_r + i\tau_c = 2 \int_0^{q_c} \rho(z) dz$ with q_c the complex zero of ρ closest of the real line. Contributes a Landau-Zener factor, causing the exponential smallness in ε .

Explicit formula

For **any** semiclassical ϕ

$$\widehat{\psi}_n^- \varepsilon(k, t) \approx e^{-\frac{i}{\varepsilon} t \hat{H}^-} \frac{\eta^* + k}{2|\eta^*|} e^{-\frac{\tau_c}{2\delta\varepsilon} |k - \eta^*|} e^{-i\frac{\tau_r}{2\delta\varepsilon} (k - \eta^*)} \widehat{\phi}^\varepsilon(\eta^*) \chi_{k^2 > 4\delta}$$

- Independent of n , uses only local information.
- Nonadiabatic transitions decouple in momentum space.
- $\eta^* = \text{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum k due to energy conservation.
- $\chi_{k^2 > 4\delta}$ is also from energy conservation.
- $\tau = \tau_r + i\tau_c = 2 \int_0^{q_c} \rho(z) dz$ with q_c the complex zero of ρ closest of the real line. Contributes a Landau-Zener factor, causing the exponential smallness in ε .
- $k - \sqrt{k^2 - 4\delta} \approx 2\delta/k$, so larger momentum wavepackets are more likely to make the transition.

Explicit formula

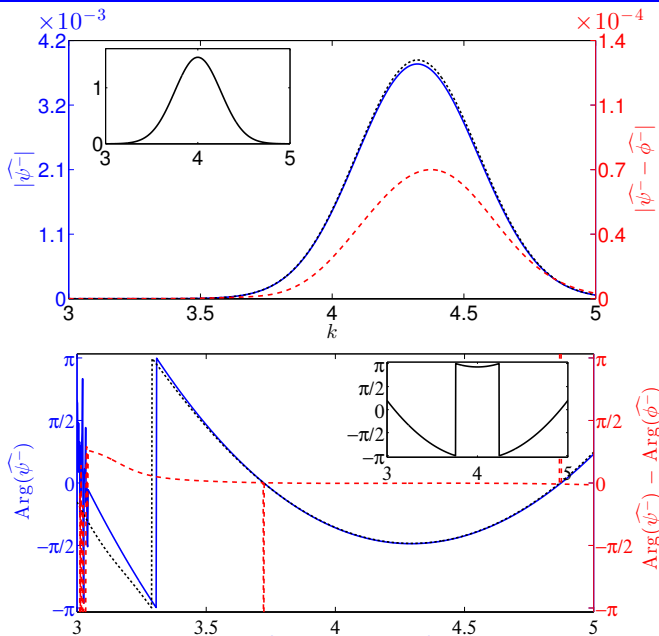
For **any** semiclassical ϕ

$$\widehat{\psi}_n^-{}^\varepsilon(k, t) \approx e^{-\frac{i}{\varepsilon}t\hat{H}^-} \frac{\eta^* + k}{2|\eta^*|} e^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta^*|} e^{-i\frac{\tau_r}{2\delta\varepsilon}(k-\eta^*)} \widehat{\phi}^\varepsilon(\eta^*) \chi_{k^2 > 4\delta}$$

- Independent of n , uses only local information.
- Nonadiabatic transitions decouple in momentum space.
- $\eta^* = \text{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum k due to energy conservation.
- $\chi_{k^2 > 4\delta}$ is also from energy conservation.
- $\tau = \tau_r + i\tau_c = 2 \int_0^{q_c} \rho(z) dz$ with q_c the complex zero of ρ closest of the real line. Contributes a Landau-Zener factor, causing the exponential smallness in ε .
- $k - \sqrt{k^2 - 4\delta} \approx 2\delta/k$, so larger momentum wavepackets are more likely to make the transition.
- For large momentum, small momentum uncertainty, gives Landau-Zener transition probability.

- ① Evolve initial wave packet on upper level using B-O dynamics until centre of mass reaches the transition point.
- ② Apply formula to the wave packet.
- ③ Evolve resulting transmitted wave packet using B-O dynamics on lower level, until the centre of mass reaches the scattering region.

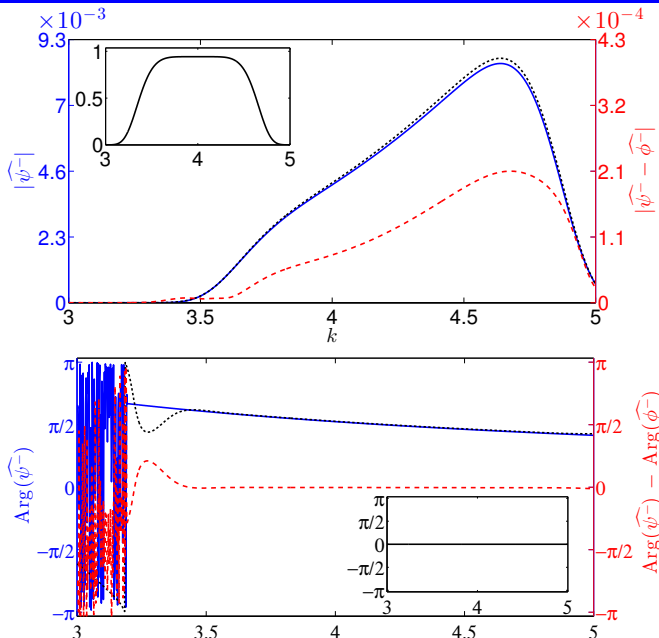
Numerics 1: Gaussian Wavepacket, $\varepsilon = 1/40$



$$P(\text{Transition}) = 5.8 \times 10^{-6}$$

$$L^2 \text{ Relative Error} = 0.019$$

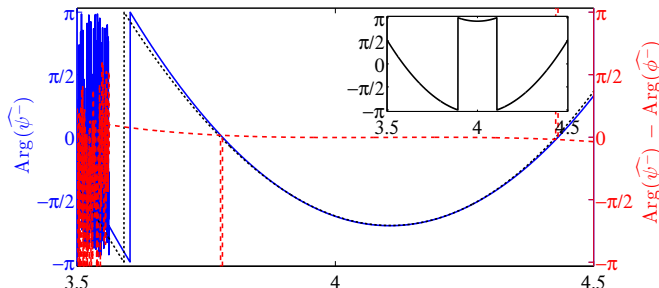
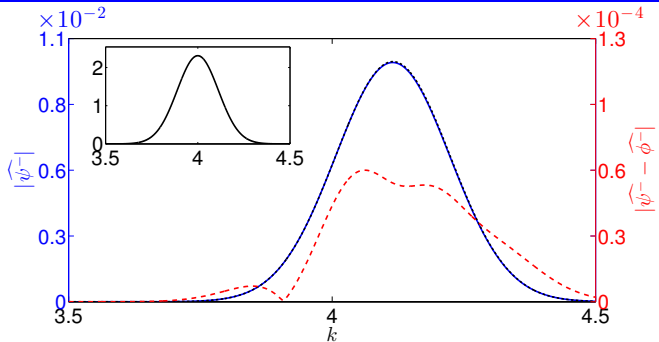
Numerics 2: Non-Gaussian Wavepacket, $\varepsilon = 1/40$



$$P(\text{Transition}) = 4.5 \times 10^{-5}$$

$$L^2 \text{ Relative Error} = 0.024$$

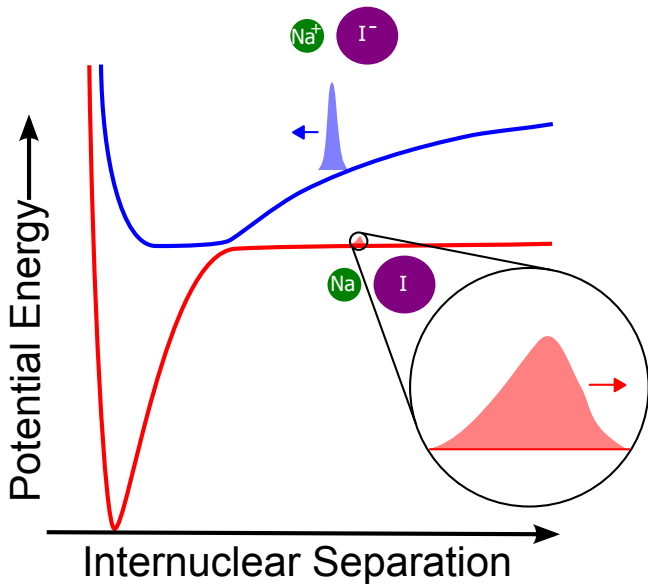
Numerics 3: Gaussian Wavepacket, $\varepsilon = 1/200$



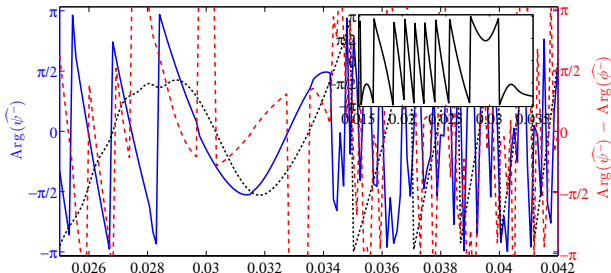
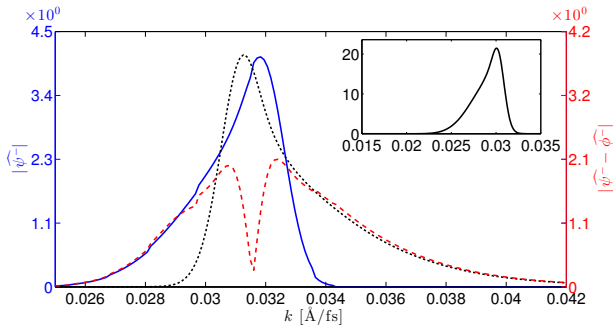
$$P(\text{Transition}) = 1.8 \times 10^{-5}$$

$$L^2 \text{ Relative Error} = 0.007$$

Back to NaI



Numerics 4: NaI, $\varepsilon = 0.00531$



$$P(\text{Transition}) = 3.4 \times 10^{-2} \quad L^2 \text{ Relative Error} = 0.706$$

What went wrong?

We have three main assumptions:

- The slope of the potential is small;
- The wavepacket is semiclassical [width order $\epsilon^{1/2}$];
- The potential is locally flat.

These are all related.

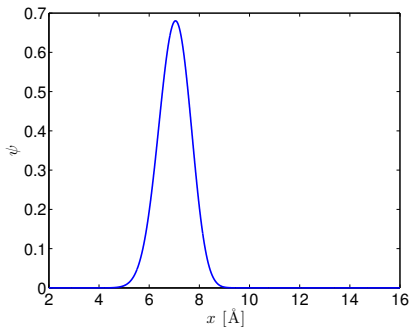
What went wrong?

We have three main assumptions:

- The slope of the potential is small;
- The wavepacket is semiclassical [width order $\epsilon^{1/2}$];
- The potential is locally flat.

These are all related.

Main issue: The wavepacket is actually quite broad.



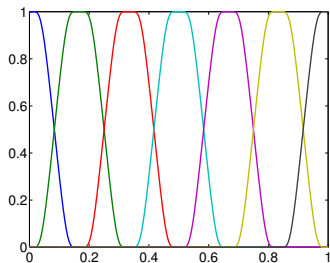
Linearity to the rescue!

We're solving

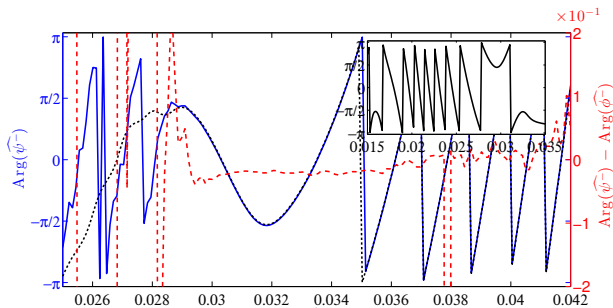
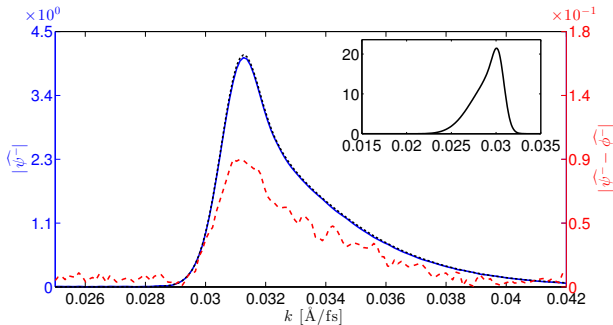
$$i\varepsilon\partial_t\psi = H\psi.$$

Since it's linear, we can:

- 'Slice' the incoming wavepacket in space (partition of unity);
- Evolve each slice to the crossing point;
- Apply our formula;
- Recombine slices by evolving away from crossing point.



Numerics 5: NaI, $\varepsilon = 0.00531$, 30 slices



$P(\text{Transition}) = 3.4 \times 10^{-2}$
 L^2 Relative Error = 0.024
 18 / 19

Summary and open problems

We have:

- A vastly simplified model for transitions.
- Applicable to real-life systems.
- Extended this to cases where the slope at the crossing is not small.

To do:

- Extend to higher dimensions.
- Understand the asymptotics of the coupling elements.
- Prove rigorous error estimates.

V. Betz, BDG, S. Teufel, *Proc. R. Soc. A* **465** 3553–3580 (2009)

V. Betz, BDG, *Phys. Rev. Lett.* **103** 213001 (2009)

V. Betz, BDG, *SIAM J. Sci. Comput.* **33**(5) 2247–2276 (2011)

V. Betz, BDG, U. Manthe, *J. Chem. Phys.* **144** 224109 (2016)