Photo-dissociation of molecules: mathematics meets quantum chemistry

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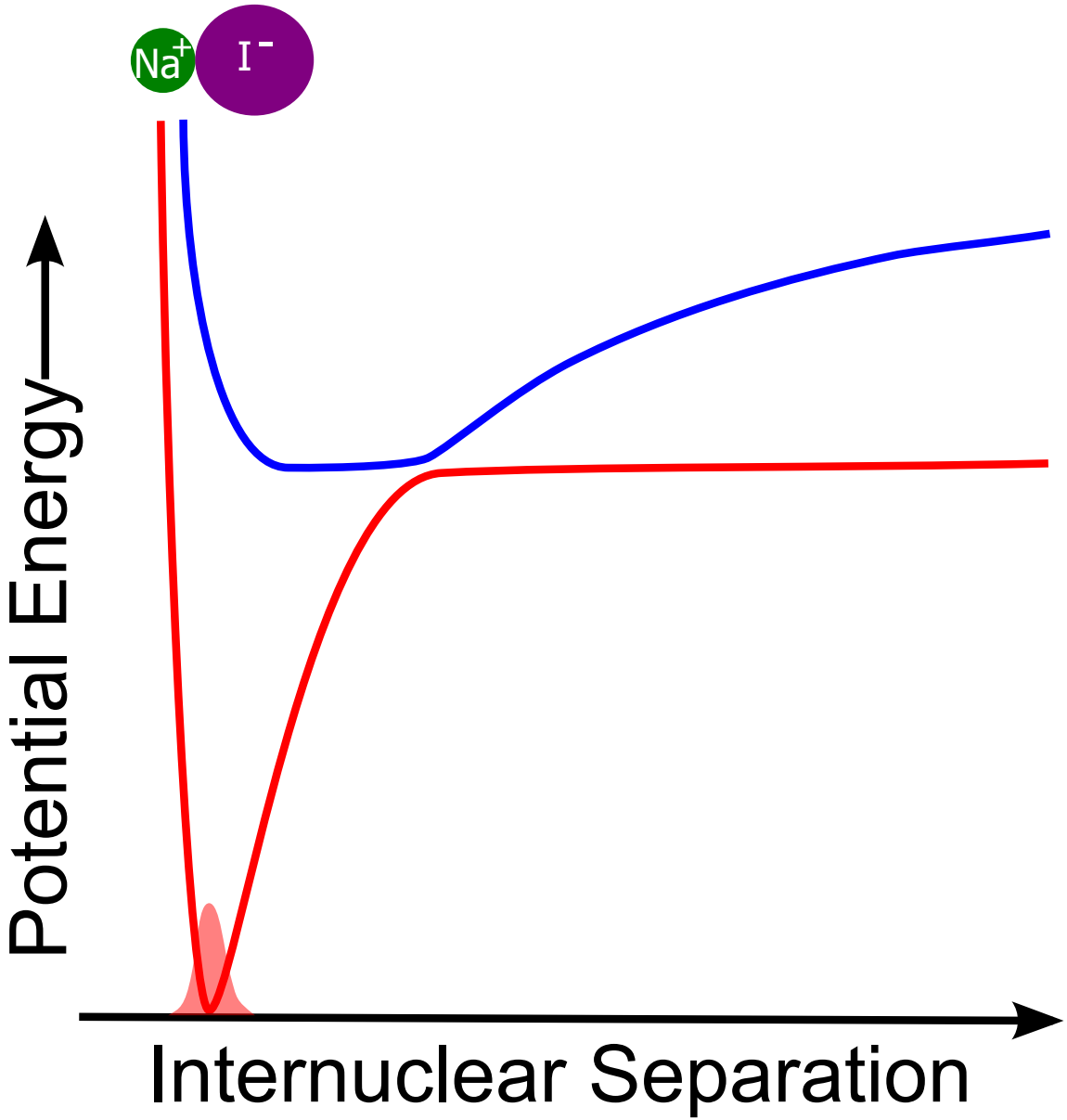
MAXWELL INSTITUTE FOR MATHEMATICAL SCIENCES

EPSRC
Engineering and Physical Sciences Research Council

Example: Photo-Dissociation of NaI



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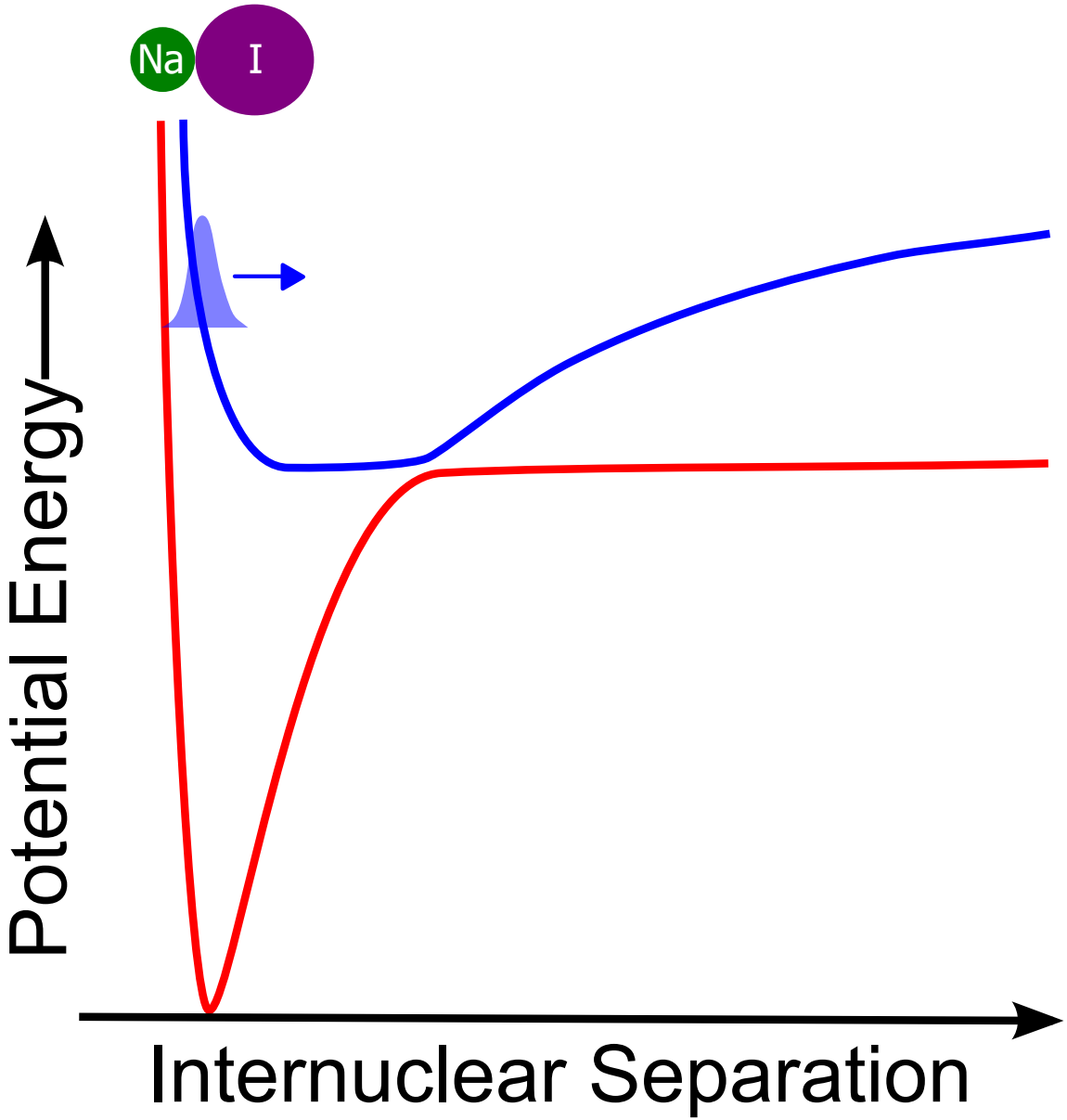

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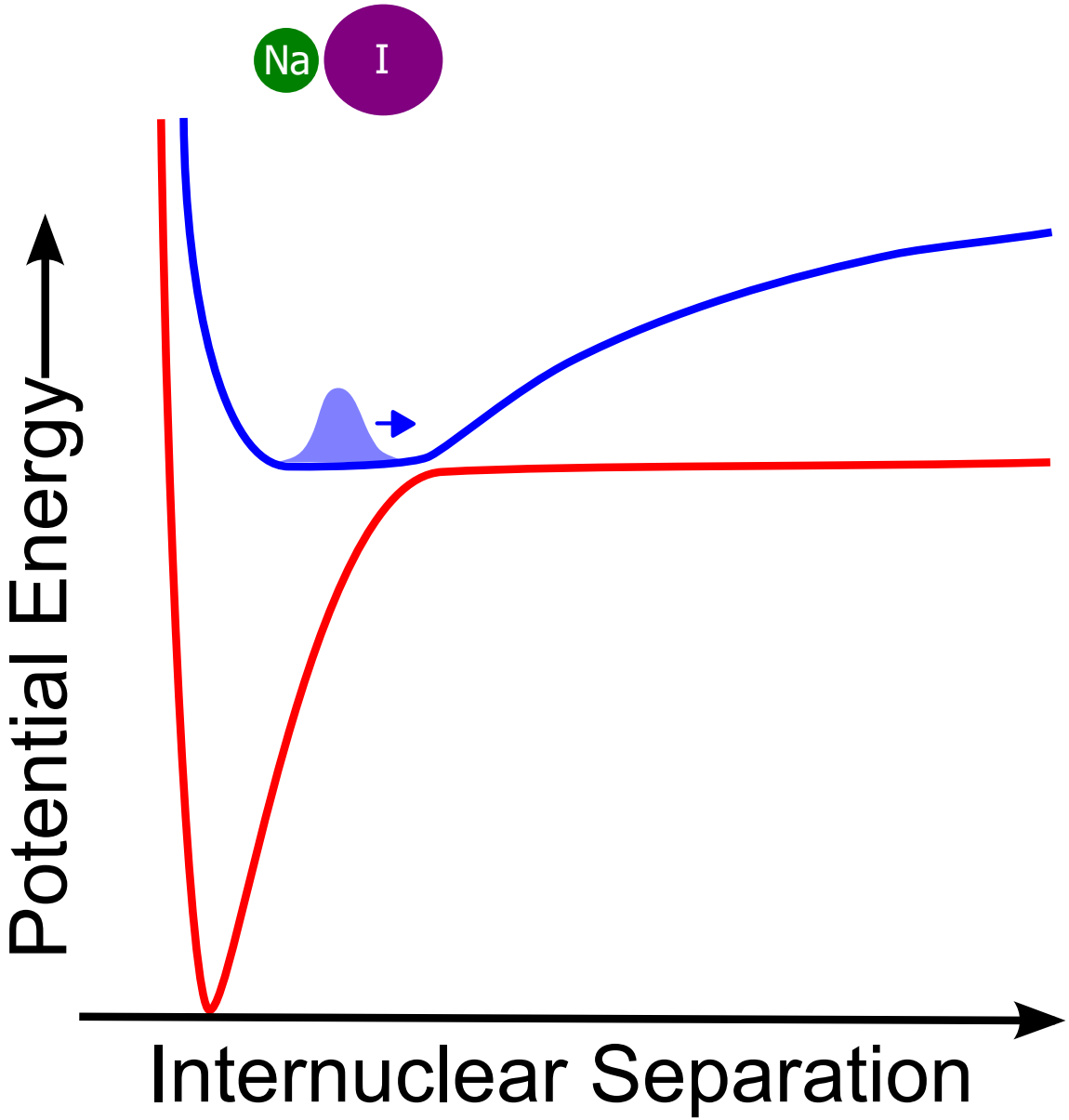

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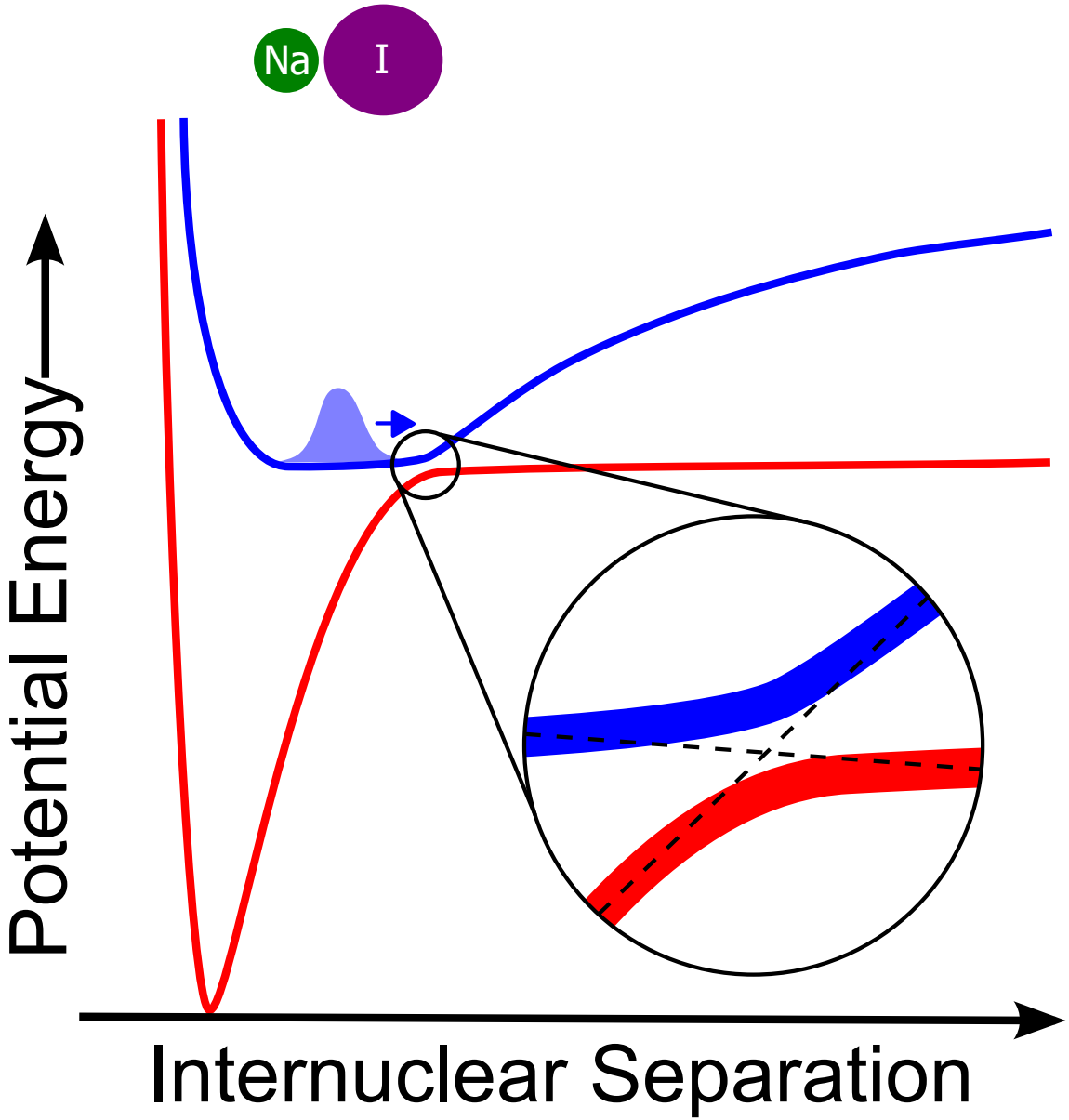

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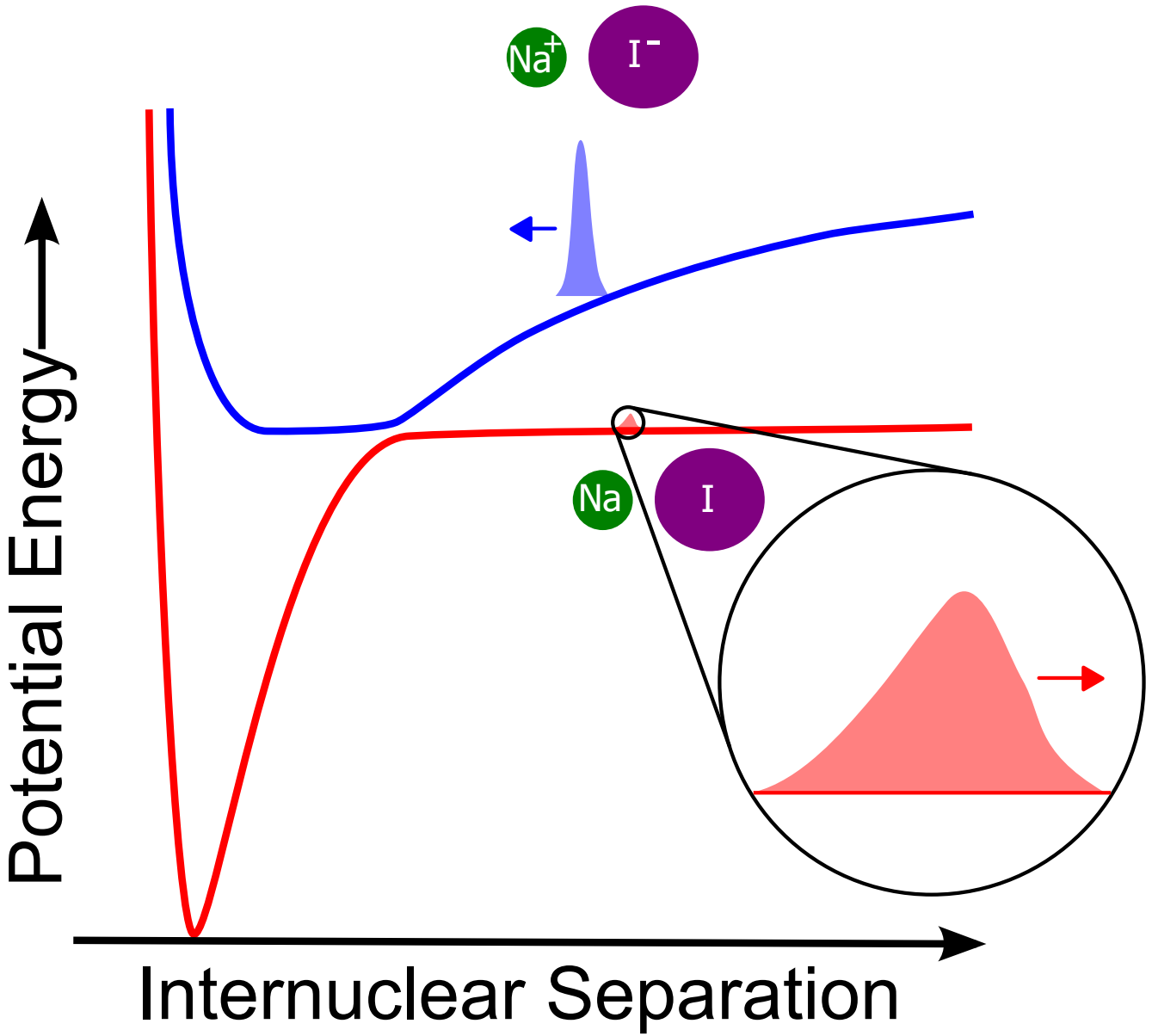

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Due to the presence of a small parameter $\epsilon = \sqrt{m_e/m_n}$:

- Wavefunctions are rapidly oscillating (typical frequency $1/\epsilon$);
- Transmitted wavepacket is exponentially small (in $1/\epsilon$ and the gap);
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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 $\mathbf{x}_{\mathrm{n}}$ and N_{e} electrons with positions $\mathbf{x}_{\mathrm{e}}$,

$$\mathrm{i}\hbar\partial_t\psi(\mathbf{x}_{\mathrm{n}},\mathbf{x}_{\mathrm{e}},t) = H\psi(\mathbf{x}_{\mathrm{n}},\mathbf{x}_{\mathrm{e}},t),$$

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$$H = -\frac{\hbar^2}{2m_{\mathrm{n}}}\Delta_{\mathbf{x}_{\mathrm{n}}} - \frac{\hbar^2}{2m_{\mathrm{e}}}\Delta_{\mathbf{x}_{\mathrm{e}}} + V_{\mathrm{n}}(\mathbf{x}_{\mathrm{n}}) + V_{\mathrm{e}}(\mathbf{x}_{\mathrm{e}}) + V_{\mathrm{n,e}}(\mathbf{x}_{\mathrm{n}},\mathbf{x}_{\mathrm{e}}).$$

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

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The two-band Schrödinger equation

Two-level system with one degree of freedom:

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

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

$\mathbf{I}$ 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

$$U_0(x) = \begin{pmatrix} \cos\left(\theta(x)/2\right) & \sin\left(\theta(x)/2\right) \\ \sin\left(\theta(x)/2\right) & -\cos\left(\theta(x)/2\right) \end{pmatrix}, \ \psi_{\mathrm{a}}(x,t) = U_0(x)\psi(x,t),$$

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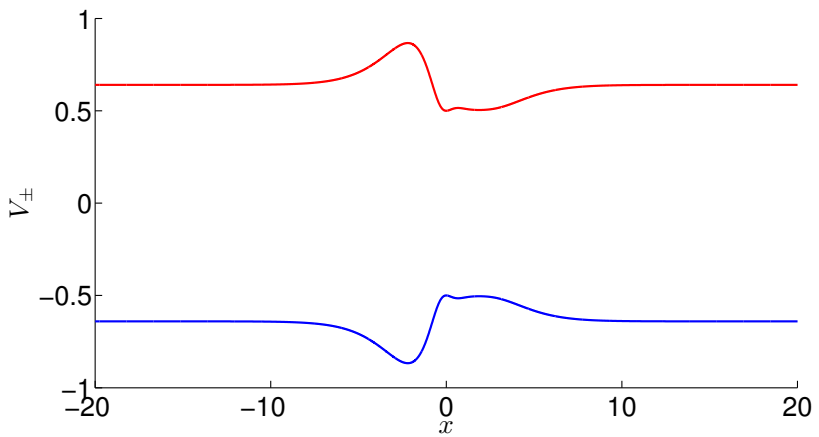

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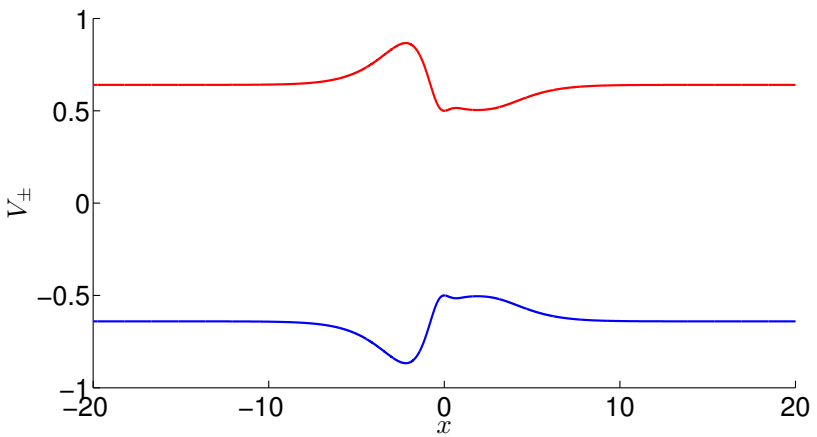
To leading order, the dynamics decouple: Born-Oppenheimer approximation.



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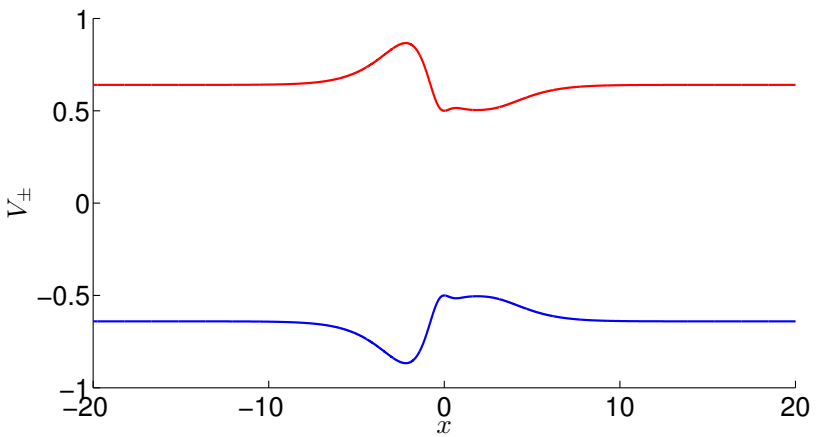
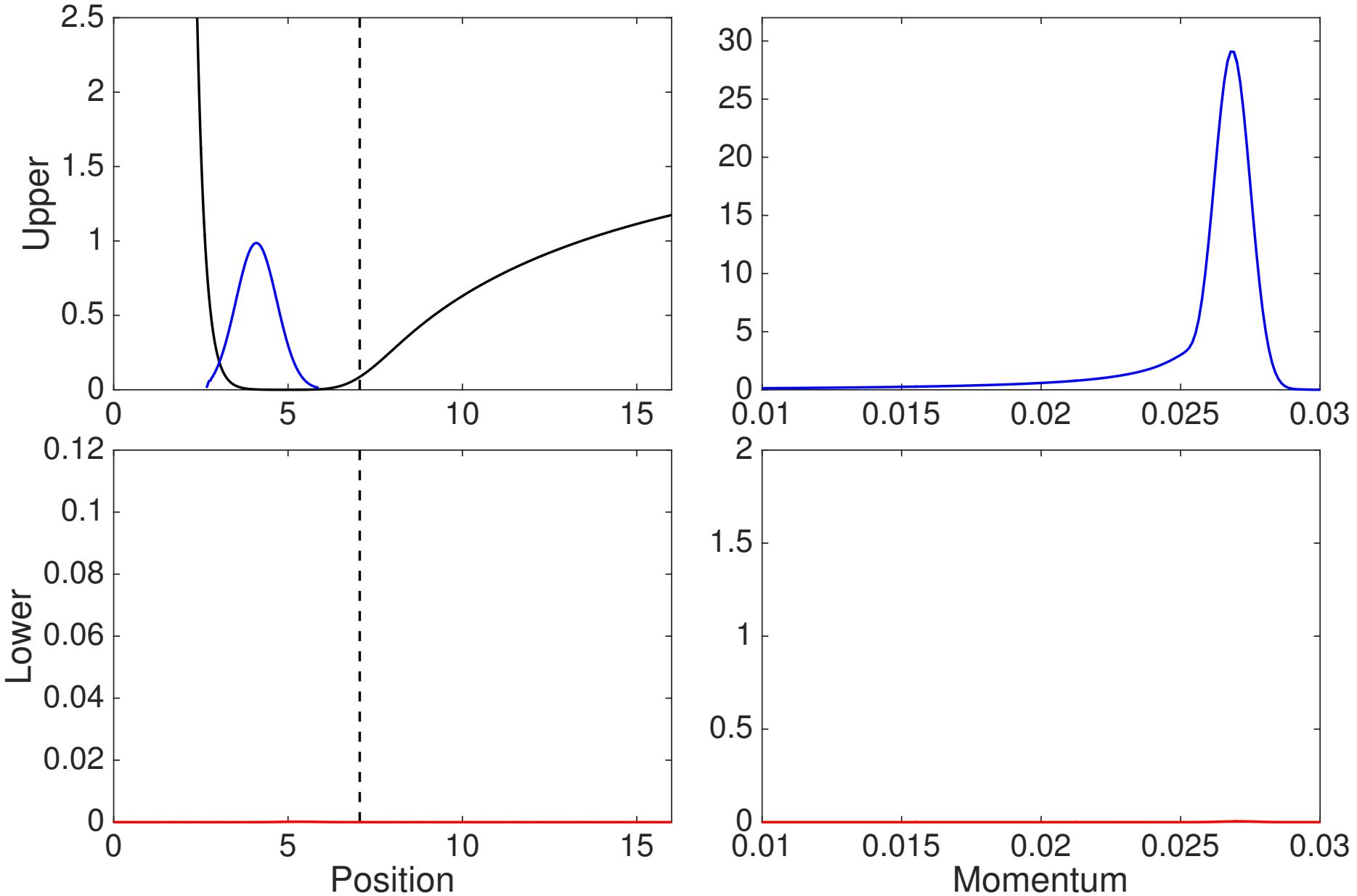


Couplings given to first order by the first off-diagonal terms; semiclassical wavefunctions oscillate with frequency $1/\varepsilon$.

What do typical dynamics look like?



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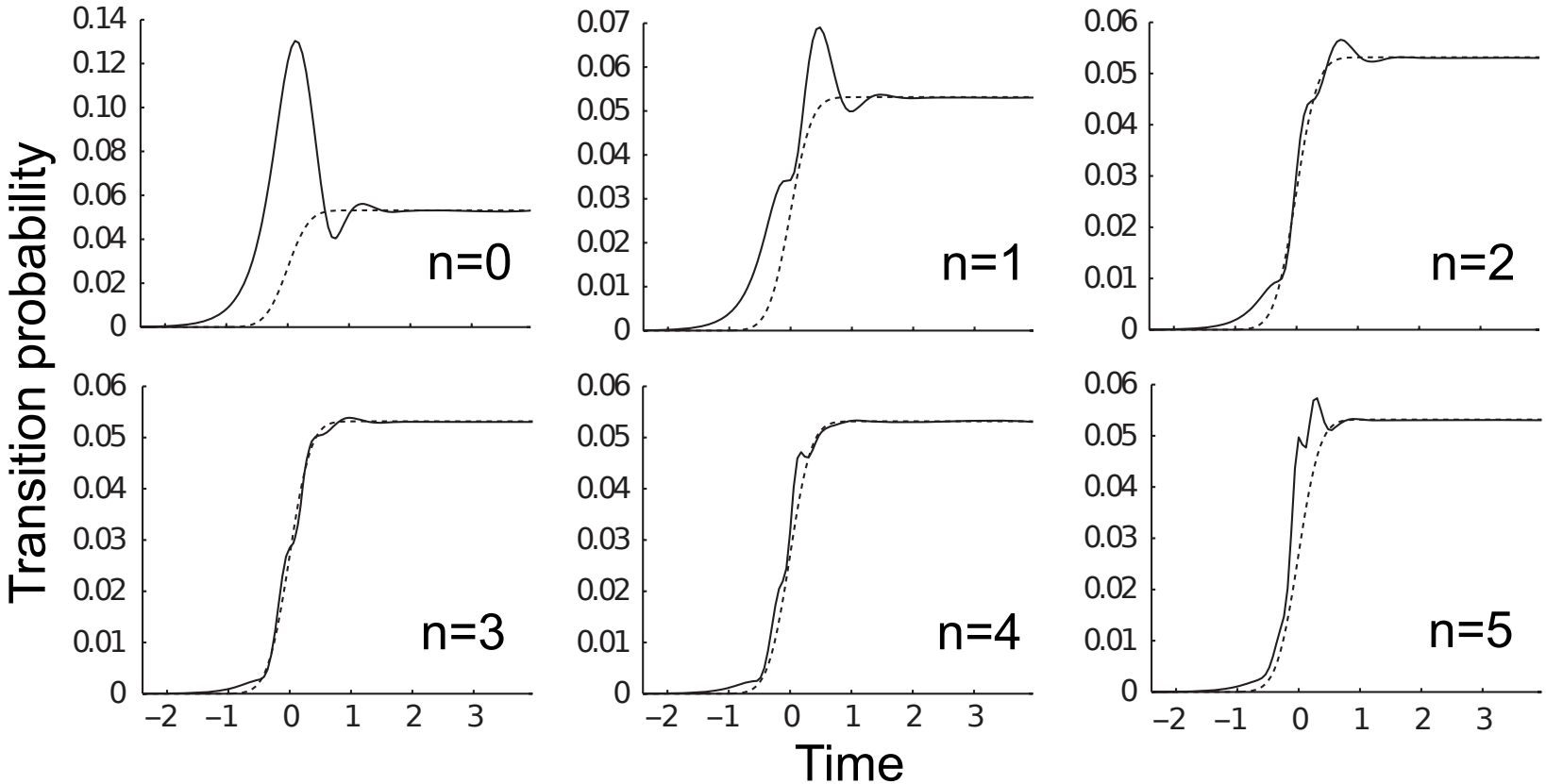
Approximation: Keep only the leading term corresponding to the highest derivative in K_n.

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

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

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- For large momentum, small momentum uncertainty, gives Landau-Zener transition probability.

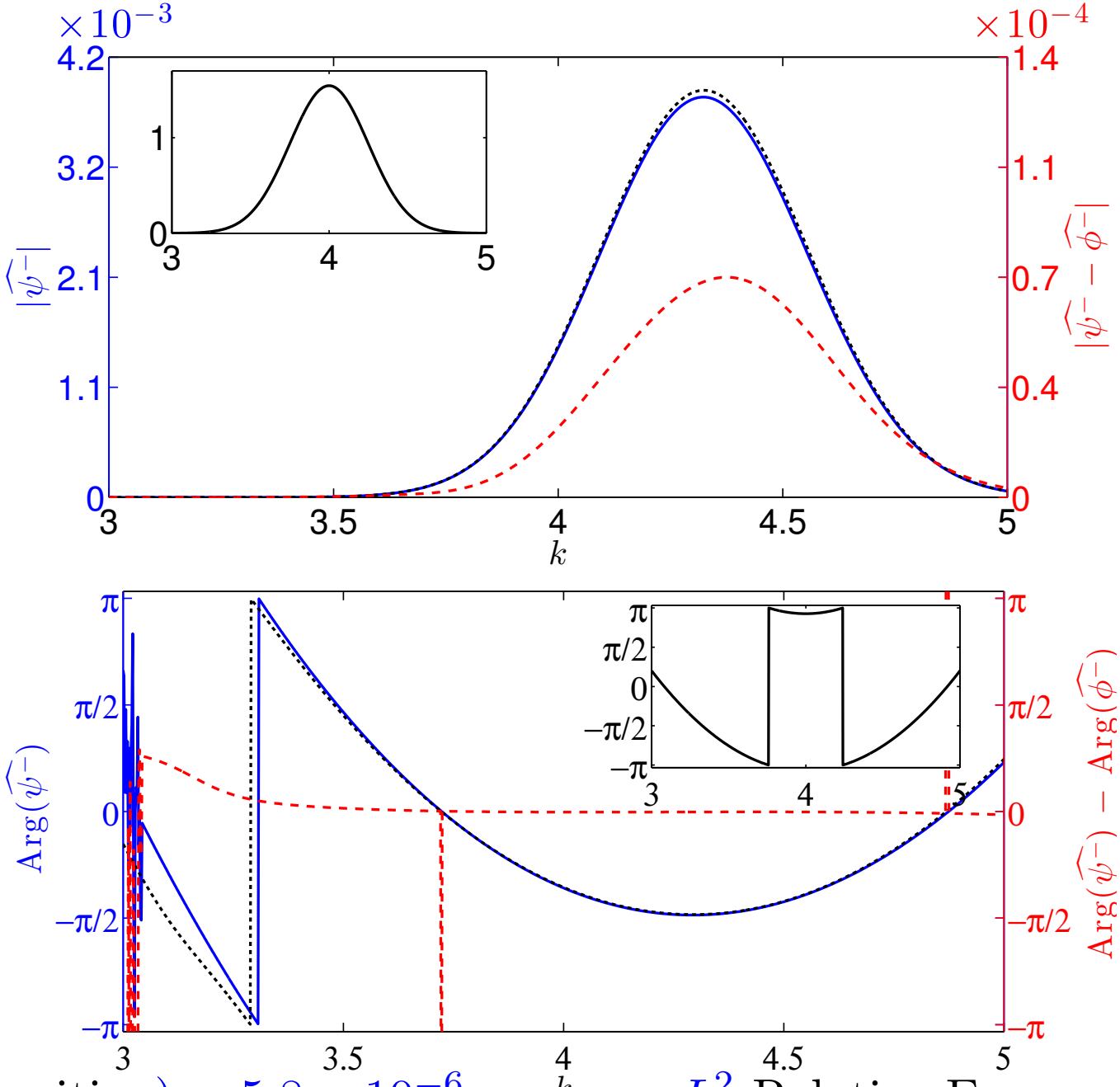
Algorithm

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.

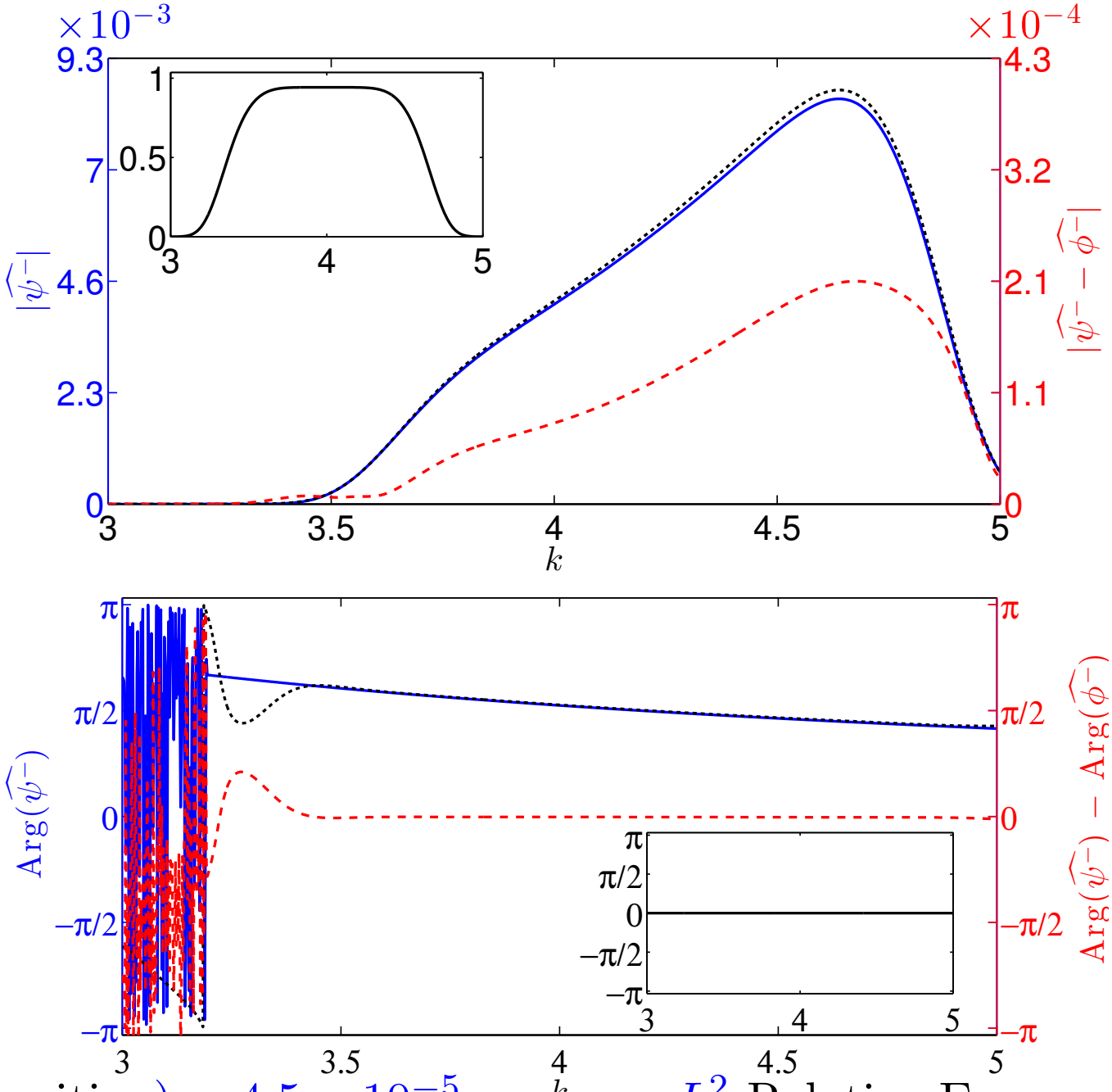
3. Evolve resulting transmitted wave packet using B-O dynamics on lower level, until the centre of mass reaches the scattering region.

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



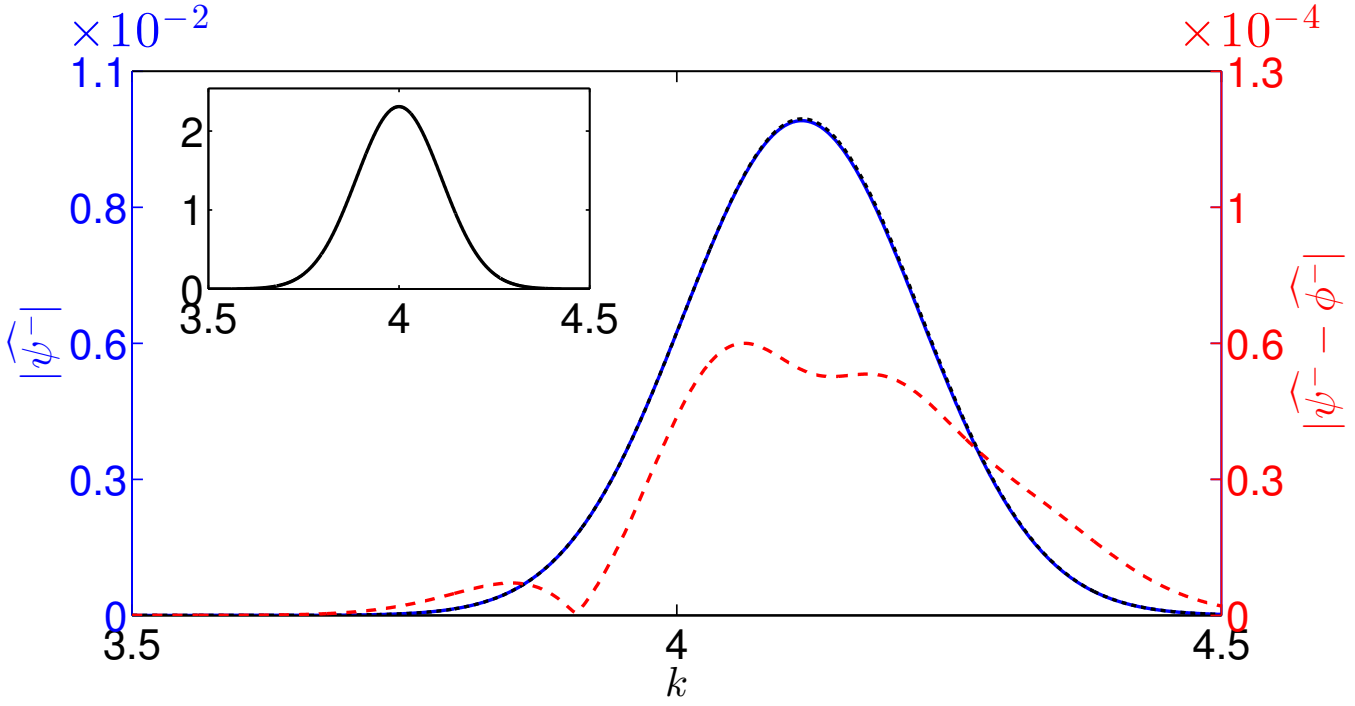
$P(\text{Transition}) = 5.8 \times 10^{-6}$ L^2 Relative Error $= 0.019$

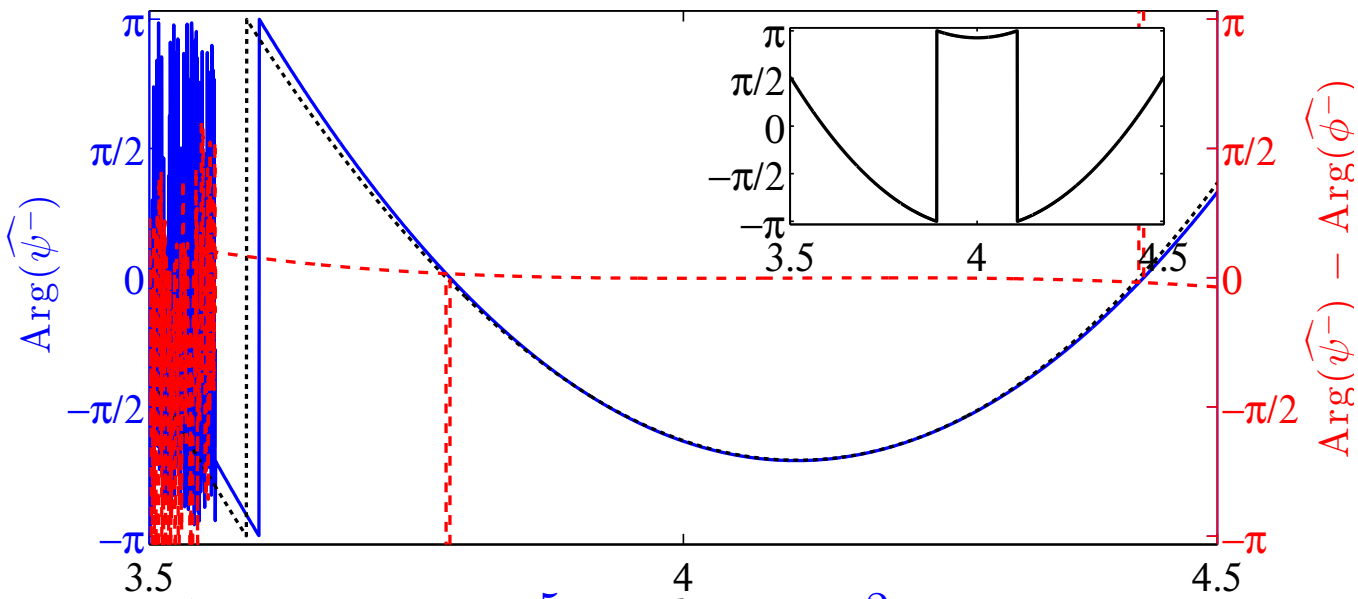
Numerics 2: Non-Gaussian Wavepacket, $\varepsilon = 1/40$



$P(\text{Transition}) = 4.5 \times 10^{-5}$ L^2 Relative Error $= 0.024$

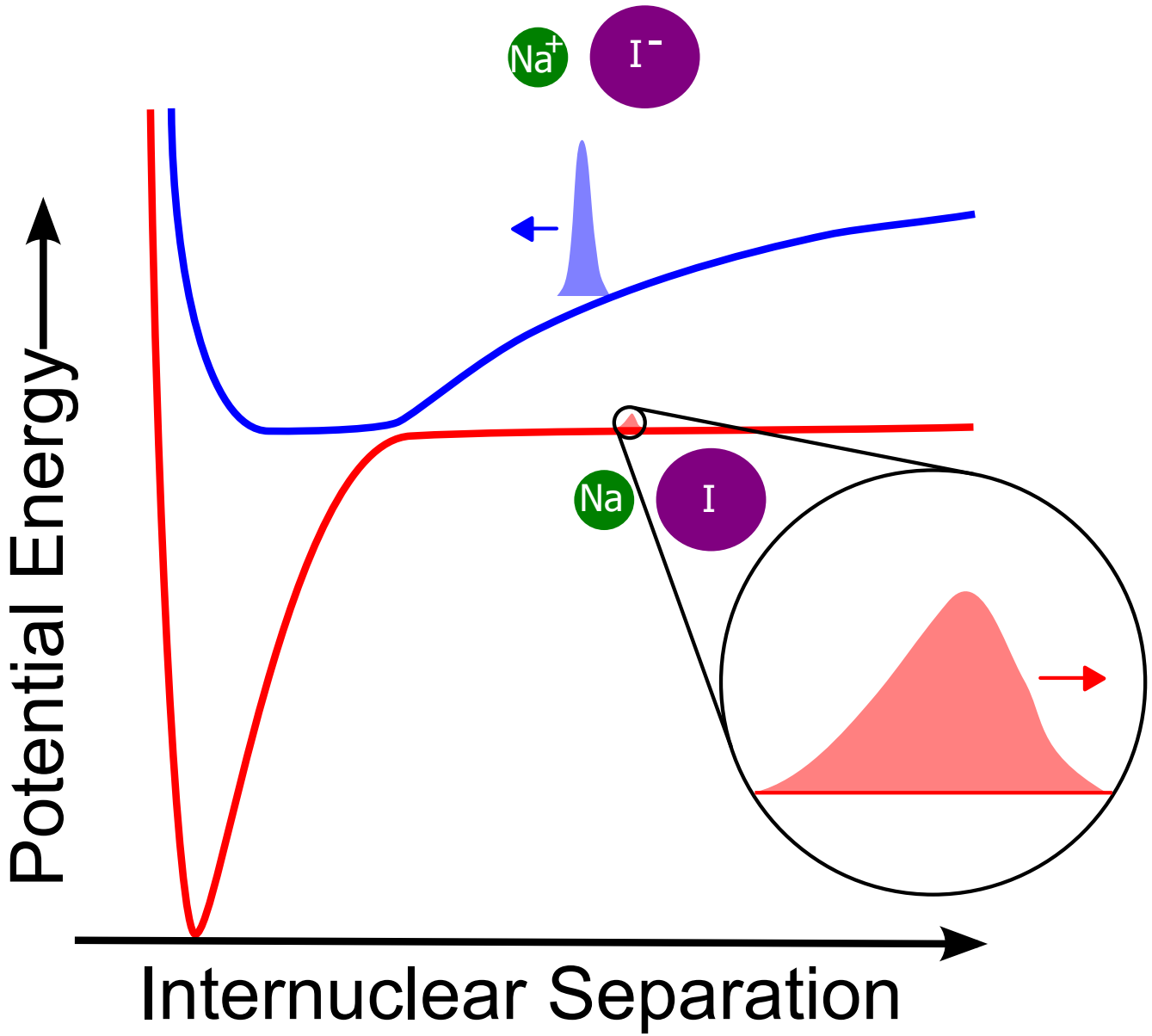
Numerics 3: Gaussian Wavepacket, $\varepsilon = 1/200$



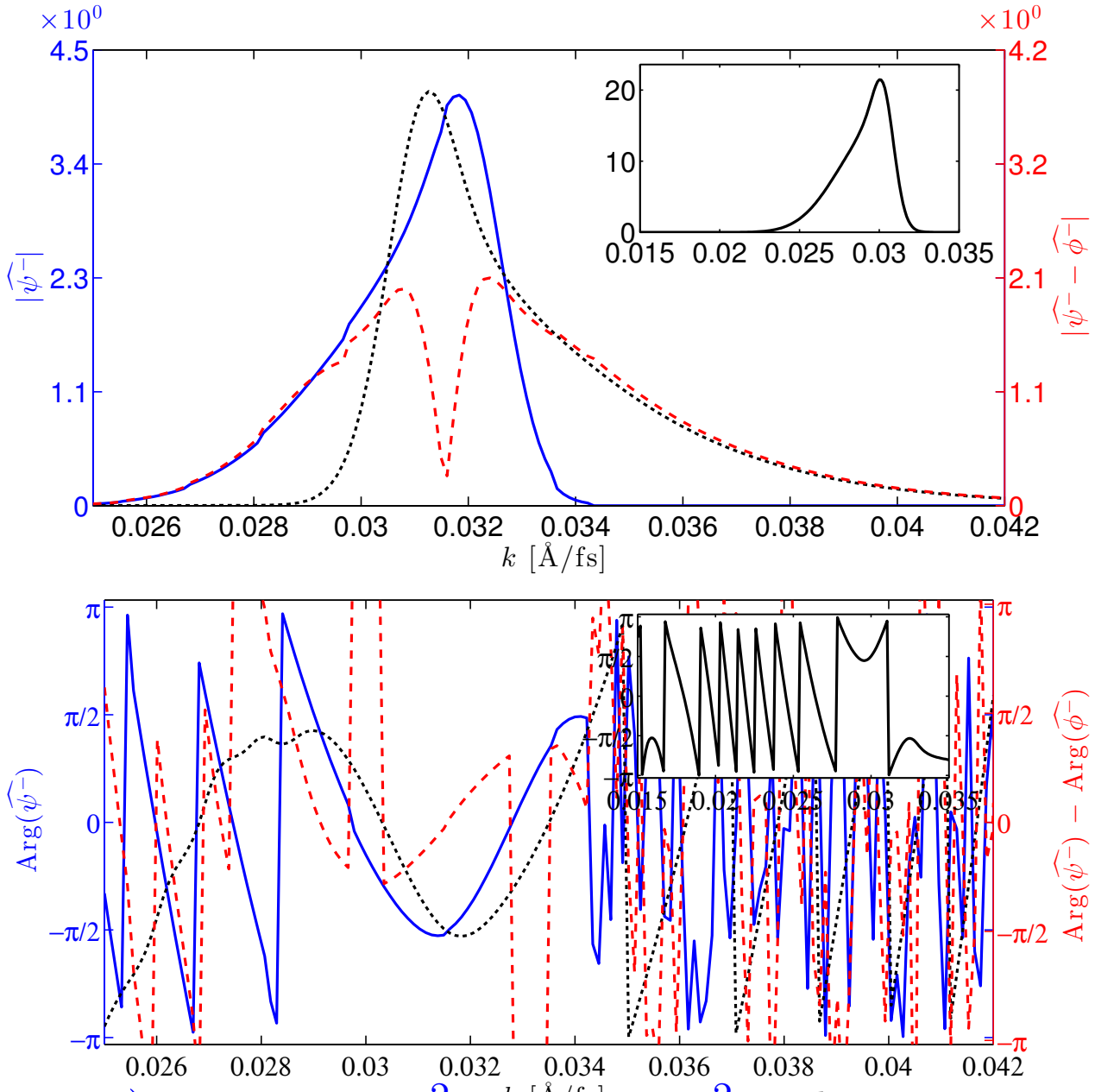


$P(\text{Transition}) = 1.8 \times 10^{-5}$ L^2 Relative Error $= 0.007$

Back to NaI



Numerics 4: NaI, $\varepsilon = 0.00531$



$P(\text{Transition}) = 3.4 \times 10^{-2}$ L^2 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:

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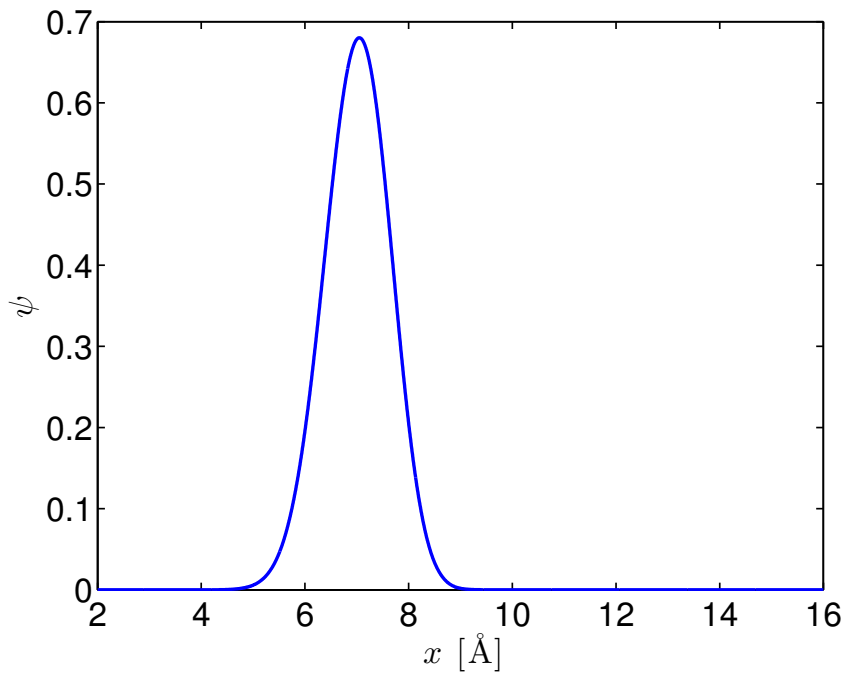
These are all related.

Main issue: The wavepacket is actually quite broad.



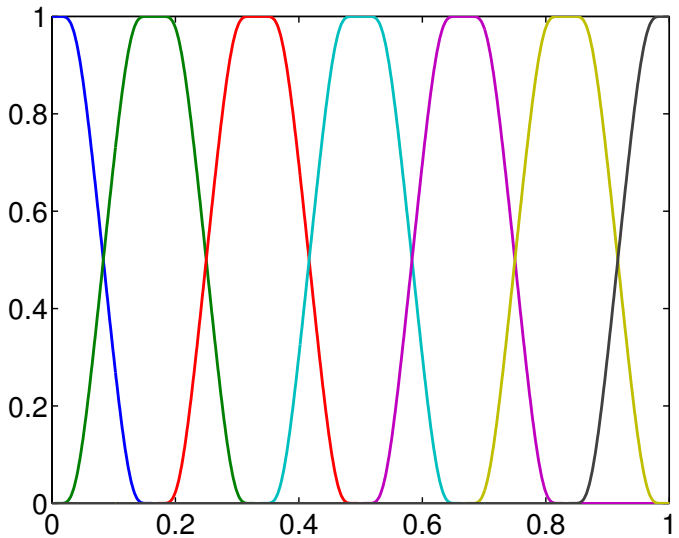
Linearity to the rescue!

We're solving

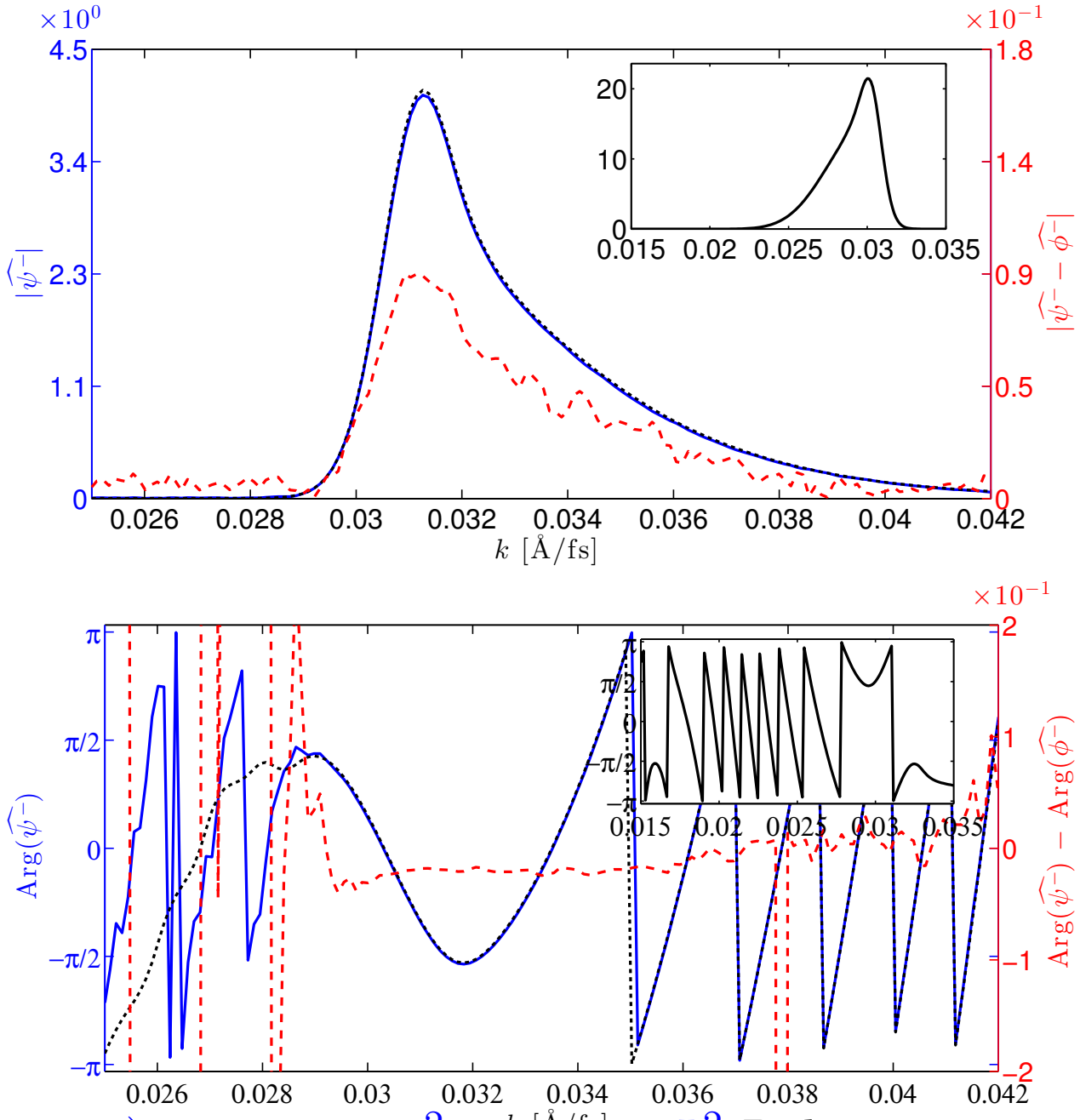
$$\mathrm{i}\varepsilon\partial_t\psi = H\psi.$$

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 $= 0.024$

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.

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