Transitions through avoided crossings in diatomic molecules

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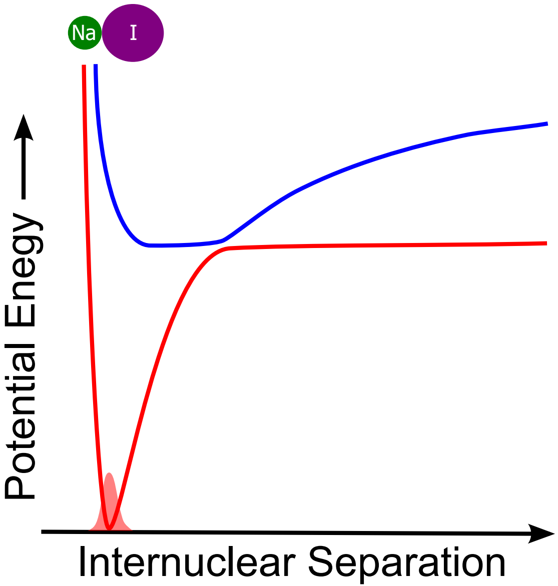
Example: Photo-Dissociation of NaI



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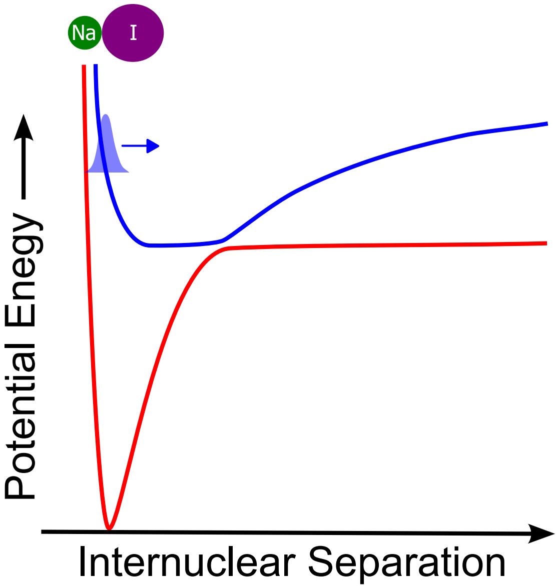

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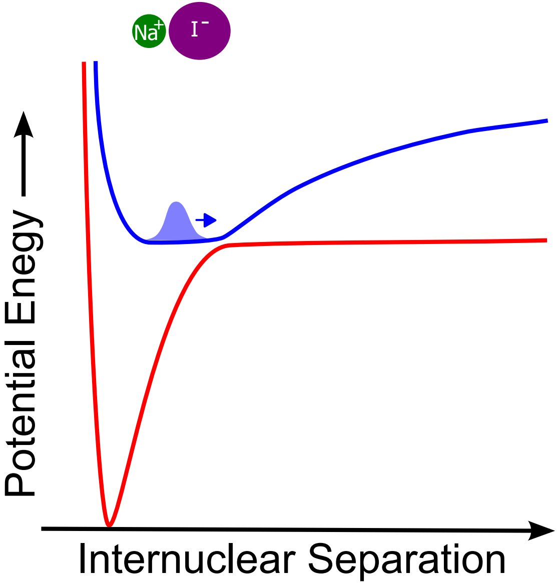

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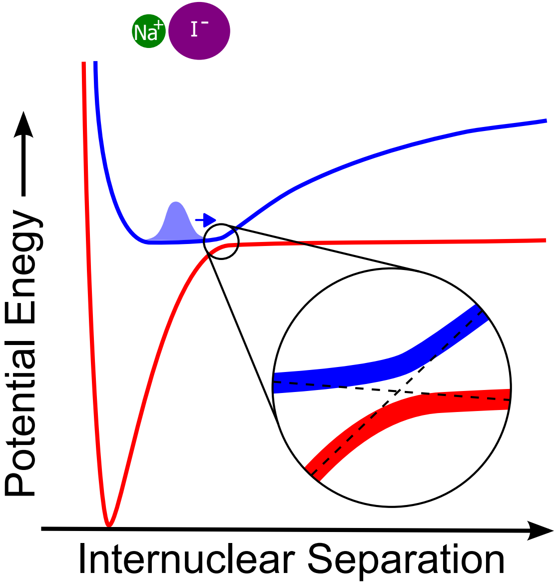

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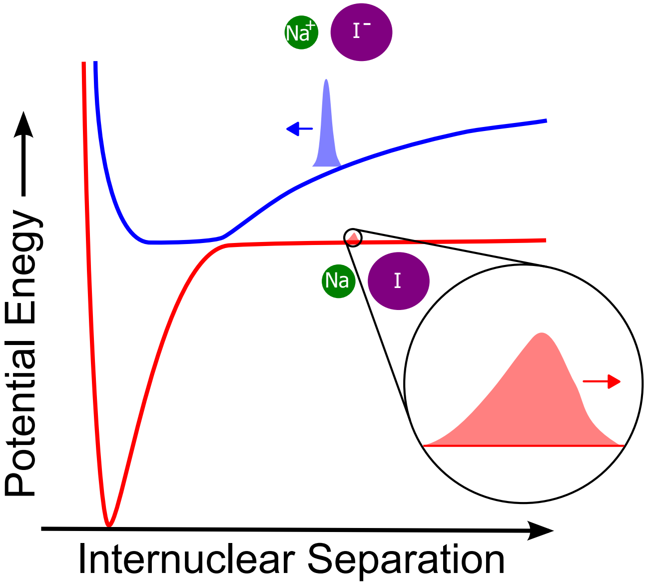

Questions and some answers

Assume initial wavefunction lies in upper adiabatic subspace.

1. How large is the transition probability into the lower adiabatic subspace?
2. What is the precise form of the transmitted wavefunction?

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1. How large is the transition probability into the lower adiabatic subspace?
2. What is the precise form of the transmitted wavefunction?

- Transitions between components of ψ_{a} are order ε globally.
- Usually exponentially small in the scattering regime.
- Under suitable assumptions, there exist unitaries U_n such that the components of the corresponding ψ_n decouple up to errors of $\mathcal{O}(\varepsilon^{n+1})$.
  This is the n-th superadiabatic representation.
- Optimizing over n allows decoupling up to exponentially small (in ε) errors.
- If V becomes constant sufficiently quickly for $|x| \to \infty$, U_n agrees with U_0 up to errors involving the derivative of V.

The two-band Schrödinger equation

Two-level system with one degree of freedom:

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

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

$\mathbf{I}$ is the 2×2 unit matrix, x is the nuclear position, $\varepsilon > 0$ is the square root of the mass ratio, and $\psi \in L^2(\mathrm{d}x, \mathbb{C}^2)$.

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Corresponds to an avoided crossing with gap at least 2δ.

The time scale ensures that the nuclei move a distance of order one in a time of order one.

Adiabatic representation

For

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

we obtain

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

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

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

$$\theta'(x) = \frac{\mathrm{i}\gamma}{x - \mathrm{i}q_c} - \frac{\mathrm{i}\gamma}{x + \mathrm{i}q_c} + \theta_r(x), \qquad \tau_\delta = 2\int_0^{q_c}\rho(z)\mathrm{d}z.$$

Superadiabatic representations

To leading order in ε,

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

Coupling elements K_n given by a complicated recursion.
Hence

$$\psi_{-,n}(x,t) = -\mathrm{i}\varepsilon^n \int_{-\infty}^{t} \left(\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}(t-s)H^-}\, K_{n+1}^{-}\, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}sH^+}\, \psi_{+,0} \right)(x)\, \mathrm{d}s$$

or in Fourier space

$$\widehat{\psi_{-,n}}^{\varepsilon}(k,t) = -\varepsilon^n \frac{\mathrm{i}}{\sqrt{2\pi\varepsilon}} \int_{-\infty}^{t} \left(\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}(t-s)\hat{H}^-}\, J_{n+1}^{-}\, \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}s\hat{H}^+}\, \widehat{\psi_{+,0}}^{\varepsilon} \right)(k)\, \mathrm{d}s.$$

Notation: $\widehat{f}^{\varepsilon}(k) = \frac{1}{\sqrt{2\mathrm{i}\varepsilon}} \int_{\mathbb{R}} \mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}kq}\, f(q)\mathrm{d}q = \frac{1}{\sqrt{\varepsilon}}\hat{f}\left(\frac{k}{\varepsilon}\right)$.

Integral Formulation

For ϕ on upper level, well away from the crossing, the transmitted wave packet in the n-th superadiabatic basis ψ_n^- satisfies

$$\widehat{\psi_n^-}^{\varepsilon}(k,t) \approx -\frac{1}{4\pi\varepsilon}\,\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}t\hat{H}^-(k)}\int_{-\infty}^{t}\mathrm{d}s\int_{\mathbb{R}}\mathrm{d}\eta\,(k+\eta)(1-\tfrac{2\lambda s}{k+\eta})^{n+1}\big(\tfrac{k^2-\eta^2}{4\delta}\big)^{n}$$
$$\times\ \mathrm{e}^{-\frac{\tau_c}{2\delta\varepsilon}|k-\eta|}\,\mathrm{e}^{-\frac{\mathrm{i}\tau_r}{2\delta\varepsilon}(k-\eta)}\,\mathrm{e}^{\frac{\mathrm{i}}{2\varepsilon}\big((k^2-\eta^2-4\delta)s-(k-\eta)\lambda s^2\big)}\,\widehat{\phi}^{\varepsilon}(\eta),$$

where $\hat{H}^-(k)$ is the B-O propagator in the lower level, $\tau_\delta =: \tau_r + \mathrm{i}\tau_c$ and $d(x) = d_0 + \lambda x + \mathcal{O}(x^2)$.

Idea: The integrand is quickly oscillating so we use a stationary phase argument around $s = 0$, $\eta = \eta^* = \sqrt{k^2 - 4\delta}$.

Plausible assumptions on the width of the wavepacket ($\mathcal{O}(\varepsilon^{1/2})$) lead to explicit Gaussian integrals.

Main Result for Gaussian wave packets

For $\widehat{\phi}^{\varepsilon}(\eta) = \exp\big(-c(\eta-p_0)^2/\varepsilon + \mathrm{i}x_0\eta/\varepsilon\big)$,

$$\widehat{\psi_n^-}^{\varepsilon}(k,t) \approx \frac{\mathrm{e}^{-\frac{\mathrm{i}}{\varepsilon}t\hat{H}^-}}{2\sqrt{4\alpha_{2,0}\alpha_{0,2}-\alpha_{1,1}^2}} \exp\Big[\frac{\alpha_{2,0}\alpha_{0,1}^2+\alpha_{0,2}\alpha_{1,0}^2-\alpha_{1,0}\alpha_{0,1}\alpha_{1,1}}{\alpha_{1,1}^2-4\alpha_{2,0}\alpha_{0,2}}\Big]$$

$$\times\,(\eta^*+k)\,\mathrm{e}^{-\frac{\tau_c}{2\delta\epsilon}|k-\eta^*|}\;\mathrm{e}^{-\mathrm{i}\frac{\tau_r}{2\delta\epsilon}(k-\eta^*)}\;\mathrm{e}^{-\mathrm{i}\varphi(p_0)}\,\widehat{\phi}^{\varepsilon}(\eta^*)\chi_{k^2>4\delta},$$

with

$$\alpha_{2,0} = -\tfrac{n_0\varepsilon}{4\delta} - \tfrac{n_0\eta^{*2}\varepsilon}{8\delta^2} - c$$

$$\alpha_{1,0} = -\tfrac{n_0\eta^*\varepsilon^{1/2}}{2\delta} - \tfrac{2c(\eta^*-p_0)}{\varepsilon^{1/2}} + \tfrac{\mathrm{sgn}(k)\tau_c}{2\delta\varepsilon^{1/2}} + \mathrm{i}\tfrac{\tau_r}{2\delta\varepsilon^{1/2}} + \mathrm{i}\tfrac{x_0}{\varepsilon^{1/2}}$$

$$\alpha_{1,1} = -\mathrm{i}\eta^* + \tfrac{2(n_0+1)\lambda\varepsilon}{(k+\eta^*)^2}$$

$$\alpha_{0,1} = -\tfrac{2(n_0+1)\varepsilon^{1/2}\lambda}{k+\eta^*}$$

$$\alpha_{0,2} = -\mathrm{i}\tfrac{2\delta\lambda}{(k+\eta^*)} - \tfrac{2(n_0+1)\lambda^2\varepsilon}{(k+\eta^*)^2}$$

$$\varphi(p_0) = -\tfrac{(n_0+1)^2\varepsilon\lambda a_0\delta}{2(n_0+1)^2\lambda^2\varepsilon^2+2\delta^2a_0^2} - \tfrac{1}{2}\arctan\big(\tfrac{a_0\delta}{(n_0+1)\varepsilon\lambda}\big) + \mathrm{sgn}(\lambda p_0)\tfrac{\pi}{4}$$

with n_0 given by the solution of three quadratic equations.

Simplification for small λ

For any semiclassical ϕ

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

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

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- The complex part of τ contributes a Landau-Zener factor, causing the exponential smallness in ε.

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- The complex part of τ contributes a Landau-Zener factor, causing the exponential smallness in ε.
- $k - \sqrt{k^2 - 4\delta} \approx 2\delta/k^2$, so larger momentum wavepackets are more likely to make the transition.
- 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. [E.g. Strang splitting or Hagedorn wavepackets.]

2. Transform resulting wave packet into momentum space and decompose into a linear combination of complex Gaussians. [For initial Gaussian, is Gaussian with error order $\epsilon^{1/2}$. Not required if λ small.]

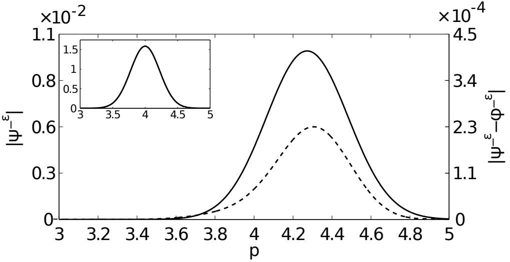
3. Apply formula to each complex Gaussian and take the corresponding linear combination.

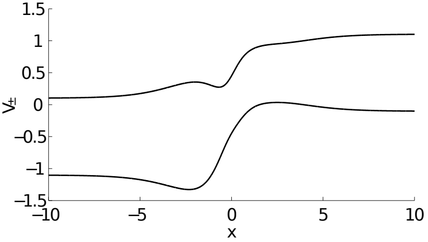
4. Evolve resulting transmitted wave packet using B-O dynamics on lower level, until the centre of mass reaches the scattering region. [As in (1)].

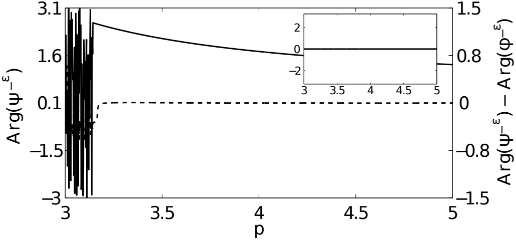
Numerics 1: Gaussian Wavepacket

$$\widehat{\phi}^{\varepsilon}(\eta) = \exp\big(-c(\eta - p_0)^2/\varepsilon + \mathrm{i}x_0\eta/\varepsilon\big)$$

$$\varepsilon = 1/40;\ p_0 = 4;\ c = 1/2;\ x_0 = 0;\ \tau = -0.15992 + 0.52951\mathrm{i}$$







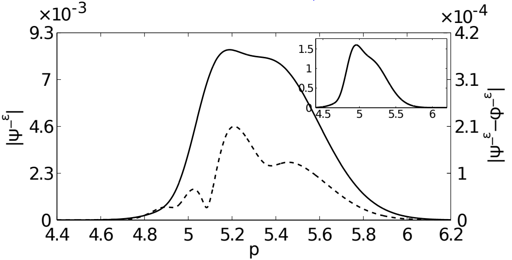
$P(\text{Transition}) = 3.9 \times 10^{-5}$

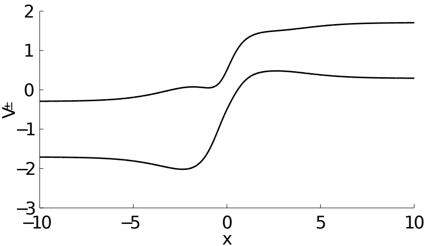
L^2 Relative Error $= 0.021$

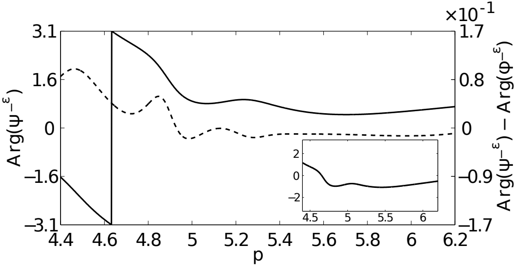
Numerics 2: Non-Gaussian Wavepacket

$$\widehat{\phi}^{\varepsilon}(\eta) = \sum_{j=1}^{3} (-1)^{j+1} \widehat{\phi}_j^{\varepsilon}(\eta), \quad \widehat{\phi}_j^{\varepsilon}(\eta) = \exp\left(-c_j(\eta - p_{0,j})^2/\varepsilon + \mathrm{i} x_{0,j}\eta/\varepsilon\right)$$

$$\varepsilon = 1/50;\ \tau = -0.16611 + 0.537721\mathrm{i}$$







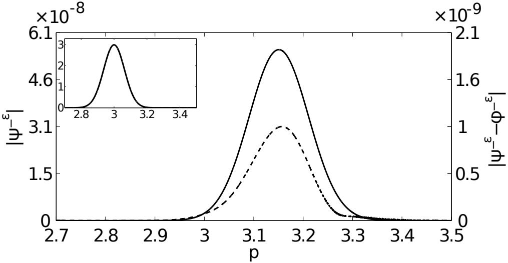
$P(\text{Transition}) = 3.5 \times 10^{-5}$

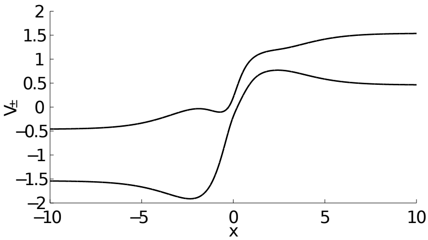
L^2 Relative Error $= 0.018$

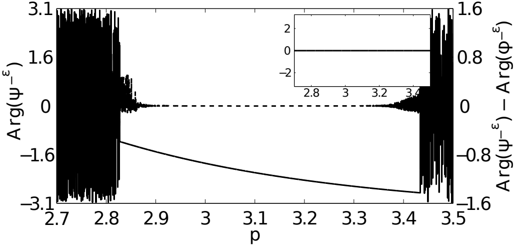
Numerics 3: Gaussian Wavepacket, small ε

$$\widehat{\phi}^{\varepsilon}(\eta) = \exp\big(-c(\eta - p_0)^2/\varepsilon + \mathrm{i}x_0\eta/\varepsilon\big)$$

$$\varepsilon = 1/500;\ p_0 = 3;\ c = 1/2;\ x_0 = 0;\ \tau = -0.02331 + 0.11040\mathrm{i}$$



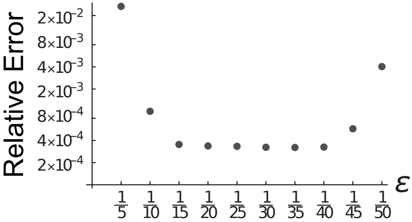




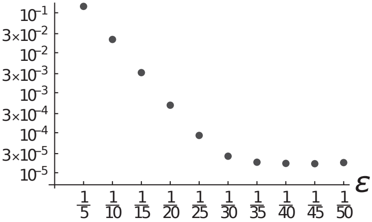
$P(\text{Transition}) = 3.4 \times 10^{-16}$

L^2 Relative Error $= 0.018$

Asymptotics for fixed p



$p_0 = 2$



$p_0 = 5$

- Excellent agreement for wide range of ε.
- Not asymptotically correct for fixed p.
- However, small ε and fixed p gives very small transition probability (e.g. $p_0 = 2$, $\varepsilon = 1/50$ gives $\|\psi_-\|_2^2 \approx 6 \times 10^{-10}$).
- Actual error much better than we can prove with *a priori* estimates.

Conclusions and outlook

We have derived a closed-form approximation to the transmitted wavefunction, which is accurate for a large range of potentials and values of ε.

- Understand the heuristic phase correction and physical interpretation of the results.
- Apply the method to real-life systems.
- Extend the result to higher dimensions (work in progress).
- (Related) Understand the asymptotics of K_n^-.
- Prove rigorous error estimates.