Spawning of wavepackets in 1D non-adiabatic transitions

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Outline

Time-dependent Schrödinger equation

$$i\varepsilon^2 \frac{\partial}{\partial t} |\psi\rangle = \underbrace{(T + V)}_{H} |\psi\rangle$$

where

$$T := -\frac{1}{2}\varepsilon^4 \frac{\partial^2}{\partial x^2} \qquad V := V(x)$$

- Time evolution for a state $|\psi\rangle$
- Kinetic operator T and potential $V(x)$
- Semi-classical scaling $\varepsilon^2 \approx 10^{-2}, 10^{-3}, \ldots$
- Recover classical mechanics for $\varepsilon \to 0$

Wavefunction

Representation of the wavefunction

- Separation of variables
- Basis set expansion
  - very successful idea → Roothaan equations in Hartree-Fock

$$\begin{aligned}\psi(x,t) &= \sum_k c_k(t)\,\phi_k(x) \\ &= \sum_k c_k(t)\,\phi_k[\Pi(t)](x)\end{aligned}$$

Parameters:

$$\Pi(t) := \{P(t), Q(t), p(t), q(t)\}$$

Expansion coefficients:

$$c(t) := (c_0(t), \ldots, c_K(t))$$

Semiclassical wavepackets

Definition of the basis functions

- Basis functions: product of a Gaussian times a polynomial

$$\phi_0(x) := \left(\pi\varepsilon^2\right)^{-\frac{1}{4}} Q^{-\frac{1}{2}} \exp\left(\frac{i}{2\varepsilon^2} P Q^{-1} (x-q)^2 + \frac{i}{\varepsilon^2} p (x-q)\right)$$

- Parameters $P \in \mathbb{C}$, $Q \in \mathbb{C}$
- Position $q \in \mathbb{R}$ and momentum $p \in \mathbb{R}$
- Construct ϕ_k by applying the *raising operator* $\mathcal{R}$

$$\phi_k := \frac{1}{\sqrt{k!}} \mathcal{R}^k \phi_0$$

- $\{\phi_i\}_i$ complete basis of L^2 for fixed P, Q, p, q

Semiclassical wavepackets

Definition of a wavepacket

- General wavepacket as linear combination

$$\Phi\left(x\right) := e^{\frac{iS}{\varepsilon^2}} \sum_{k=0}^{K} c_k \phi_k\left(x\right)$$

- In theory $K = \infty$, practically $K \leq 512$
- Time propagation of wavepackets:
  - propagate parameters P, Q, p, q
  - propagate coefficients $\{c_i\}_i$
- *Wavepackets stay in this mathematical form*
- Explicit algorithm $\rightarrow$ my Bachelor Thesis

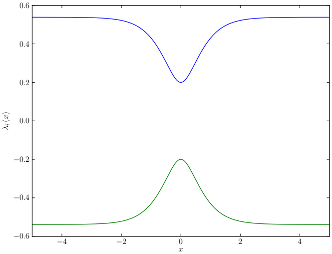
Non-adiabatic potentials

- Potential $V(x)$ with *multiple* energy levels $\lambda_i(x)$
- Wavepackets can *jump* to other levels
- and *split up* over different levels
- Energy levels do never cross

Very simple example

$$V(x) = \begin{bmatrix} \frac{1}{2}\tanh(x) & \delta \\ \delta & -\frac{1}{2}\tanh(x) \end{bmatrix}$$

- $0 < \delta \in \mathbb{R}$



Non-adiabatic potentials

Technical details

- Potential $V(x)$ is a matrix
  - Matrix valued TDSE
  - Vector valued wavefunction
- Wavepackets of the form:

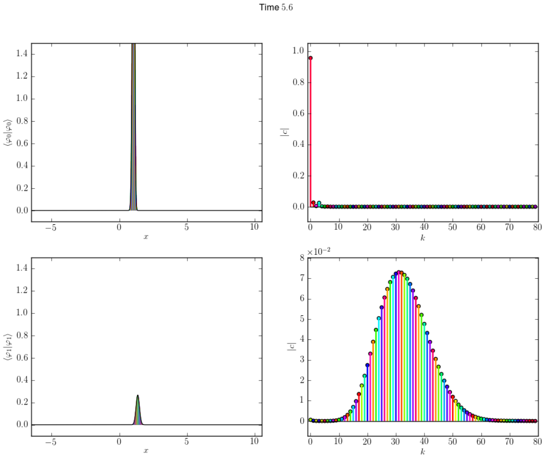
$$|\Psi\rangle = \begin{pmatrix} \Phi_0 \\ \vdots \\ \Phi_{N-1} \end{pmatrix}$$

- Usually homogeneous: same Π for all Φ_i
  - *really* a good idea?
  - no, not always $\rightarrow$ *spawning*

Video of the time evolution without spawning

Spawning

Motivating example



Spawning

In the non-adiabatic setting

- Goal: reduce basis size K
  - transformation to *better* basis
- Split up wavepackets: $|\Psi\rangle = |\Psi_0\rangle + |\Psi_1\rangle$
- Each $|\Psi_i\rangle$ has own set Π_i
  - Important if Π_0 and Π_1 differ too much
  - Allows smaller basis size for Ψ_0, Ψ_1
- Important:
  - Spawning may solve problems arising in *long-time* simulations
  - It does *not* help with difficulties at the avoided crossing

Spawning

In the non-adiabatic setting

- Split up wavepackets: $|\Psi\rangle \approx |\Psi_0\rangle + |\Psi_1\rangle = |\Psi'\rangle$
- Reason: part Φ_1 on lower level λ_1 travels faster
- Before split up by spawning:
  - $$|\Psi\rangle = \begin{pmatrix} \Phi_0 \\ \Phi_1 \end{pmatrix}$$
  - Single set Π for both Φ_i
  - Probably big basis necessary: K is large
- After split up by spawning:
  - $$|\Psi'\rangle = \begin{pmatrix} \Phi'_0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \Phi'_1 \end{pmatrix}$$
  - Each Φ'_i has own parameter set Π_i
  - Hopefully each Ψ'_i needs only much smaller basis

Spawning

Mathematical problem description

Given a linear combination $\sum_{k=\alpha}^{\beta} c_k \phi_k \left[\Pi\right](x)$ *with* $\alpha \geq 0$ *and* $\beta \leq K$ *find a new, optimal basis of* L^2*. More precisely, find a new set* $\tilde{\Pi}$ *of parameters. Then do a basis expansion in the new basis* $\sum_{k=\alpha}^{\beta} \tilde{c}_k \phi_k [\tilde{\Pi}]$ *resulting in new coefficients* $\tilde{c}$*.*

Spawning

Parameter estimation in detail

- A fragment: $w := \sum_{k=\alpha}^{\beta} c_k \phi_k$
- Estimate optimal $\tilde{\Pi}$ for w via expectation values

$$\tilde{q} := \frac{\langle w \,|\, x \,|\, w \rangle}{\langle w \,|\, w \rangle} = \frac{\sqrt{2\varepsilon^2}}{\sum_{k=\alpha}^{\beta} \overline{c_k} c_k} \Re \left(Q \sum_{k=\alpha+1}^{\beta} \overline{c_k} c_{k-1} \sqrt{k} \right) + q$$

$$\tilde{p} := \frac{\left\langle w \,\middle|\, -i\varepsilon^2 \frac{\partial}{\partial x} \,\middle|\, w \right\rangle}{\langle w \,|\, w \rangle} = \frac{\sqrt{2\varepsilon^2}}{\sum_{k=\alpha}^{\beta} \overline{c_k} c_k} \Re \left(P \sum_{k=\alpha+1}^{\beta} \overline{c_k} c_{k-1} \sqrt{k} \right) + p$$

- Similar procedure for $\tilde{Q}$ and $\tilde{P}$
- Non-adiabatic setting: $\Phi_1 \equiv w$ and $\alpha = 0$, $\beta = K$

Spawning

Change of basis

- Find the expansion coefficients $\tilde{c}_k$
- Different strategies possible
  - *Lumping*
  - *Basis projection*
  - ...
- Both have advantages and drawbacks
  - *Basis projection* is the cleaner solution

Spawning

Basis projection

- Project w to first μ new basis functions $\tilde{\phi}_k := \phi_k[\tilde{\Pi}]$

$$\tilde{c}_i := \frac{\left\langle w \,\middle|\, \tilde{\phi}_i \right\rangle}{\langle w \,|\, w \rangle}$$

- Do these integrals with highly accurate quadrature

$$\tilde{c}_i = \varepsilon \cdot Q_0 \sum_{r=0}^{R-1} \overline{\sum_{k=\alpha}^{\beta} c_k \phi_k\left(\gamma_r\right)} \cdot \tilde{\phi}_i\left(\gamma_r\right) \cdot \omega_r \,.$$

- Finally assign the coefficients

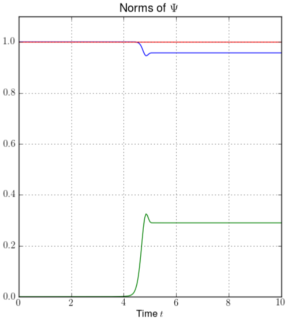
$$\tilde{c} := \begin{pmatrix} \tilde{c}_0 & \cdots & \tilde{c}_\mu & \tilde{c}_{\mu+1} = 0 & \cdots & \tilde{c}_{\eta-1} = 0 \end{pmatrix}$$

$$\begin{pmatrix} c_\alpha & \cdots & c_\beta \end{pmatrix} := 0 \,.$$

Spawning

Spawning criteria

- An oracle telling us if and when to spawn
  - Spawn to early is *very bad*
  - Spawn to late is of little risk



- Simple threshold based criterion
  - $\langle w, w \rangle \geq \tau$
  - asymptotic value $\approx \tau$
  - but a priori unknown!
- More advanced criteria possible

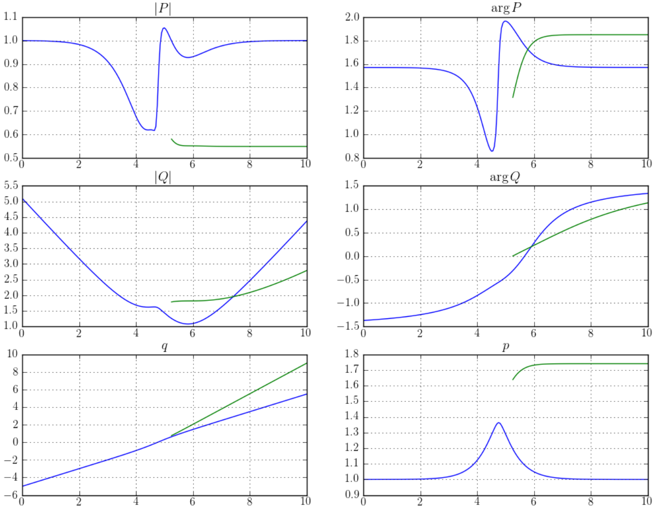
Implementation

- Implementation on top of `WaveBlocks`
  - My code framework from the Bachelor Thesis
  - Currently about 8k lines of python code (core only)
  - Highly modular and easily extendable
  - Object oriented python code using `numpy` for numerics
- Adding spawning algorithms was really easy
  - Only 4 new classes
    - Parameter estimation routines
    - Change of basis routines
    - Code that checks for spawning during time propagation
  - About 500 lines of new code (w/o data analysis and plotting)

python powered

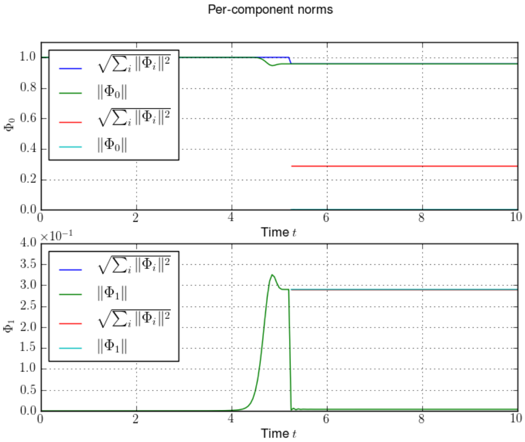
An example

Estimated parameters



An example

Norms



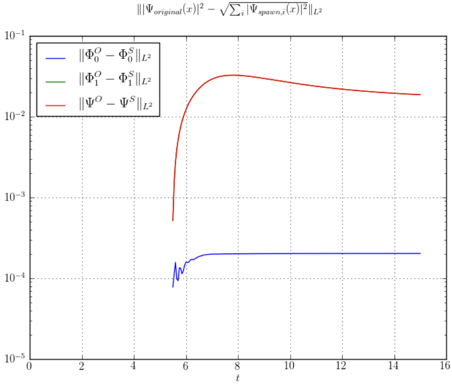
An example

Video

Video of the time evolution with spawning

An example

Spawning error



- *Systematic* ways to reduce the spawning error

Current research

Refine spawning in the *non-adiabatic* case

- Open issues with parameter estimation
- Can we improve the change of basis?
- Compare spawn criteria and find best one
- Propagation algorithm in case the interaction of the spawned packets can not be neglected (hard!)
- Adaptive basis size (almost done)

Thanks for your attention

Questions?

More information on the topic

- The full thesis:
  `http://n.ethz.ch/~raoulb/research/term_thesis/main.pdf`
- The `WaveBlocks` source code:
  `http://waveblocks.origo.ethz.ch/`
  svn `http://svn.origo.ethz.ch/waveblocks/`