Algorithms for non-adiabatic transitions with one-dimensional wavepackets

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Outline

Time-dependent Schrödinger equation

Semi-classical scaling

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

where

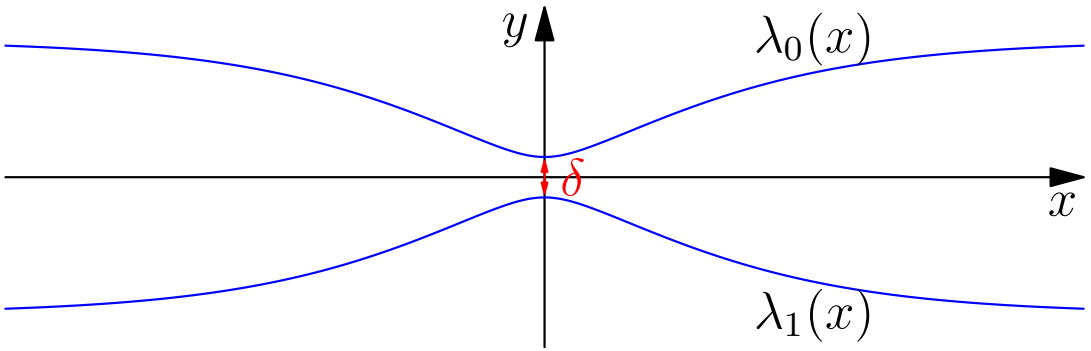
$$T := -\frac{1}{2}\varepsilon^4 \frac{\partial^2}{\partial x^2} \qquad V := V(x)$$

- 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 $\varepsilon \to 0$

Time-dependent Schrödinger equation

The non-adiabatic potential

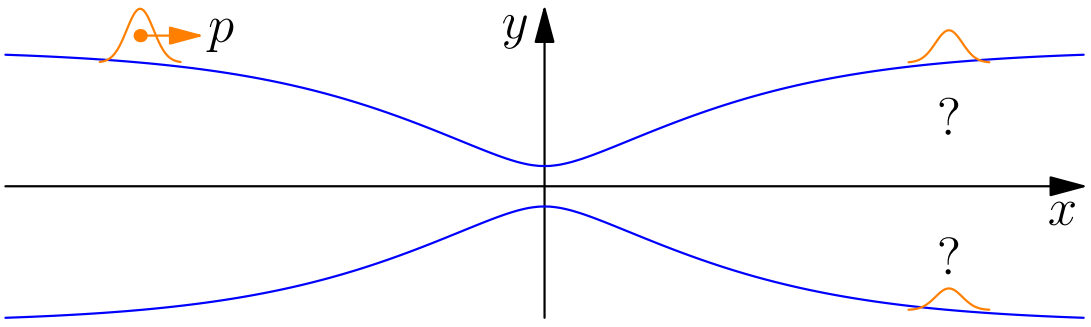
- Non-adiabatic potential V with an *avoided crossing*
- $V(x)$ is a matrix dependent on x
- *Energy levels* given by the eigenvalues $\lambda_i(x)$
- There is an *energy gap* δ



- $|\Psi\rangle$ is a vector

Time-dependent Schrödinger equation

Initial values



- Put a wavepacket $|\Psi\rangle$ somewhere
- Add an initial impulse
- See what happens at (and after) the avoided crossing

Analytical solution and operator splitting method

- Analytical solution available but useless

$$|\psi(t)\rangle = e^{-\frac{i}{\varepsilon^2}Ht}|\psi(0)\rangle = \exp\left(\frac{-i}{\varepsilon^2}Tt + \frac{-i}{\varepsilon^2}Vt\right)|\psi(0)\rangle$$

- Solution:
  - Time evolution by a symmetric Lie-Trotter splitting of H
  - Unitary propagator
  - State-of-the-art method, is called the *exact solution*

Operator splitting method

Time stepping and numerical issues

A single time step τ:

$$|\psi(t+\tau)\rangle = e^{-\frac{i}{2\varepsilon^2}\tau V(x)}\mathcal{F}^{-1}\left(e^{-\frac{i}{\varepsilon^2}\tau T(\omega)}\mathcal{F}\left(e^{-\frac{i}{2\varepsilon^2}\tau V(x)}|\psi(x,t)\rangle\right)\right)$$

- Compute matrix exponential
  - of V in position space
  - of T in momentum space
- Solution can be highly oscillatory!
- Need a very fine $\mathcal{O}\left(\varepsilon^2\right)$ grid on the whole domain
- Boundary effects due to Fourier Transformation

Semiclassical wavepackets

Definition of the basis functions

- Basis functions: product of a Gaussian times a polynomial

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

- Construct ϕ_k by applying the *raising operator* $\mathcal{R}$

$$\mathcal{R} = \frac{i}{\sqrt{2\varepsilon^2}}\left(\overline{P}(x-q) + i\varepsilon^2 \overline{Q}\left(\frac{\partial}{\partial x} - p\right)\right)$$

- We get then

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

Semiclassical wavepackets

Definition of a wavepacket

- General state on one energy level as linear combination

$$\Phi(x) := e^{\frac{iS}{\varepsilon^2}} \sum_{k=0}^{K-1} c_k \phi_k(x)$$

- We need a vector of multiple Φ
- Global parameter set $\Pi := \{P, Q, S, p, q\}$
- Individual coefficients $c := (c_0, \ldots, c_{K-1})^T$

$$|\Psi\rangle := \left| \begin{pmatrix} \Phi_0(x) \\ \vdots \\ \Phi_{N-1}(x) \end{pmatrix} \right\rangle$$

Theorems about exact propagation

Plug $|\Psi\rangle$ into the TDSE and propagate

- Exact propagation only changes the values of Π
- We have exact propagation iff
  - $H = T$
  - $H = U$ where U is quadratic
- Otherwise: propagation changes the values of c
  - $H = W$ where $W = V - U$ is the non-quadratic remainder
- Split the Schrödinger equation and propagate by T, U and W separately

The algorithm

Require: A semiclassical wavepacket $|\Psi(t)\rangle$
Require: The set Π of Hagedorn parameters of Ψ

// Propagate with the kinetic operator

$$q^{(j+\frac{1}{2})} := q^{(j)} + \frac{\tau}{2} p^{(j)}$$

$$Q^{(j+\frac{1}{2})} := Q^{(j)} + \frac{\tau}{2} P^{(j)}$$

$$S^{(j+\frac{1}{2},-)} := S^{(j)} + \frac{\tau}{4} p^{(j)\mathsf{T}} p^{(j)}$$

// Propagate with the local quadratic potential

$$p^{(j+1)} := p^{(j)} - \tau \nabla \lambda_\chi \left(q^{(j+1/2)}\right)$$

$$P^{(j+1)} := P^{(j)} - \tau \nabla^2 \lambda_\chi \left(q^{(j+1/2)}\right) Q^{(j+1/2)}$$

$$S^{(j+1/2,+)} := S^{(j+1/2,-)} - \tau \lambda_\chi \left(q^{(j+1/2)}\right)$$

// Propagate with the non-quadratic remainder

The algorithm, continued

// Stack the coefficient vectors c^n of all components
$C^{(j)} := \left(c^0, \ldots, c^{N-1}\right)^{\mathsf{T}}$
// Assemble the block matrix $\mathbf{F}$
$\mathbf{F}^{(j+1/2)} := \left(F_{r,c}\right)_{r,c} \quad \forall r, c \in 0, \ldots, N-1$
// Propagate the coefficients
$C^{(j+1)} := \exp\left(-\tau \frac{i}{\varepsilon^2} \mathbf{F}^{(j+1/2)}\right) C^{(j)}$
// Split the coefficients
$\left(c^0, \ldots, c^{N-1}\right) := C^{(j+1)}$
// Propagate with the kinetic operator again
$q^{(j+1)} := q^{(j+1/2)} + \frac{\tau}{2} p^{(j+1)}$
$Q^{(j+1)} := Q^{(j+1/2)} + \frac{\tau}{2} P^{(j+1)}$
$S^{(j+1)} := S^{(j+1/2,+)} + \frac{\tau}{4} p^{(j+1)\mathsf{T}} p^{(j+1)}$
return $\left|\Psi\left(t+\tau\right)\right\rangle$

Some final remarks

- Wavepackts work very well for simple potentials
- Some open issues for more complex potentials
  - Several parameters to choose, for example the basis size
- Gridless method
  - but we need very high order quadrature
  - and the matrix exponential of a full matrix
- Unbounded domains possible

Two energy levels with a single avoided crossing

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

$$\varepsilon = 0.2$$

$$\delta = 0.5 \cdot \varepsilon$$

$$|\Psi\rangle = \left|\begin{pmatrix} \phi_2(x) \\ 0 \end{pmatrix}\right\rangle$$

$$\Pi = \{P, Q, S, p, q\} = \{1.0i, 1.0 - 6.0i, 0.0, 1.0, -6.0\}$$

Two avoided crossings in series

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

where

$$\Theta := \tanh(x-\rho)\tanh(x+\rho)$$

and $\rho = 3.0$

Three energy levels with multiple avoided crossings

$$V(x) = \begin{pmatrix} \Theta + \Xi & \delta_1 & \delta_2 \\ \delta_1 & -\Theta & 0 \\ \delta_2 & 0 & 1 - \Xi \end{pmatrix}$$

where

$$\Theta := \tanh(x + \rho) \quad \text{and} \quad \Xi := \tanh(x - \rho)$$

and $\rho = 3.0$

Current and future work

An active topic of research

- Improve for more complicated potentials, more energy levels
  - Spawning of new packets during simulation
  - Multiple parameter sets Π
- Find evidence (or proof) for conjectures about convergence
- Go to higher dimensional space
  - Sparse packets for reducing the number of coefficients c
- ...
- Much more interesting work!

Thanks for your attention

More information on the topic

- The full thesis:

  `http://www.sam.math.ethz.ch/~raoulb/research/bachelor_thesis/tex/main.pdf`

- More simulation results:

  `http://www.sam.math.ethz.ch/~raoulb/research/bachelor_thesis`

- The python source code (outdated):

  `https://github.com/raoulbq/WaveBlocks`