Wavepacket propagation in D-dimensional non-adiabatic crossings

Raoul Bourquin

Dr. Vasile Grădinaru
Prof. Dr. Ralf Hiptmair

Seminar for Applied Mathematics, ETH Zurich
Spring semester 2012

Outline

Time-dependent Schrödinger equation

Semi-classical scaling

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

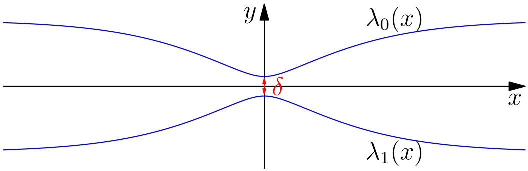
where

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

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

The non-adiabatic potential

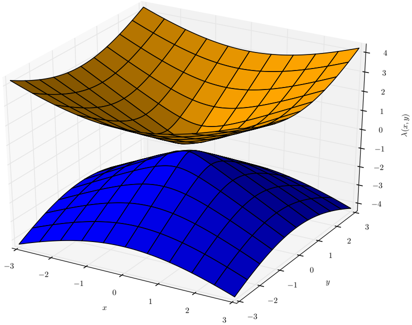
- Non-adiabatic potential $\mathbf{V}$ with N energy levels
- $\mathbf{V}(\underline{x})$ is a matrix dependent on $\underline{x} \in \mathbb{R}^D$
- *Energy levels* given by the eigenvalues $\lambda_i(\underline{x})$
- Levels can cross or show *avoided crossings*
  - There is an *energy gap* δ



The non-adiabatic potential

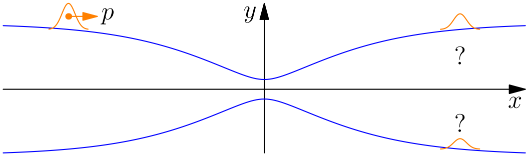
A two-dimensional example

$$\mathbf{V}(x,y) := \begin{pmatrix} x & \sqrt{y^2+\delta^2} \\ \sqrt{y^2+\delta^2} & -x \end{pmatrix}$$



Time-dependent Schrödinger equation

Initial values



- Put a wavepacket $|\Psi\rangle$ somewhere
- Add an initial momentum (optional)
- See what happens at (and after) the avoided crossing
- Expect some *transitions*, magnitude of amplitudes?

Wavefunction

Representation of the wavefunction

- Separation of variables
- Basis set expansion
  - very successful idea ($\rightarrow$ Roothaan equations in Hartree-Fock)
- Parametrised basis functions

$$\begin{aligned}\psi\left(\underline{x}, t\right) &= \sum_{\underline{k}\in\mathfrak{K}} c_{\underline{k}}\left(t\right)\phi_{\underline{k}}\left(\underline{x}\right)\\ &= \sum_{\underline{k}\in\mathfrak{K}} c_{\underline{k}}\left(t\right)\phi_{\underline{k}}\left[\Pi\left(t\right)\right]\left(\underline{x}\right)\end{aligned}$$

Parameters:

$$\Pi\left(t\right) := \left\{\underline{q}\left(t\right), \underline{p}\left(t\right), \mathbf{Q}\left(t\right), \mathbf{P}\left(t\right)\right\}$$

Expansion coefficients:

$$\underline{c}\left(t\right) := \left\{c_{\underline{k}}\left(t\right)\right\}_{\underline{k}\in\mathfrak{K}}$$

Semi-classical wavepackets

Definition of the basis functions

- Basis functions: product of a Gaussian times a polynomial
- Ground state

$$\phi_{\underline{0}}[\Pi]\left(\underline{x}\right) := (\pi\varepsilon^2)^{-\frac{D}{4}} (\det \mathbf{Q})^{-\frac{1}{2}} \cdot \exp\left(\frac{i}{2\varepsilon^2} \left\langle (\underline{x}-\underline{q}), \mathbf{P}\mathbf{Q}^{-1}(\underline{x}-\underline{q}) \right\rangle + \frac{i}{\varepsilon^2} \left\langle \underline{p}, (\underline{x}-\underline{q}) \right\rangle \right)$$

- Parameters $\mathbf{Q} \in \mathbb{C}^{D\times D}$, $\mathbf{P} \in \mathbb{C}^{D\times D}$
- Position $\underline{q} \in \mathbb{R}^D$ and momentum $\underline{p} \in \mathbb{R}^D$
- Construct $\phi_{\underline{k}}$ by applying the *raising operator* $\mathcal{R}$
- $\left\{\phi_{\underline{k}}\right\}_{\underline{k}}$ complete basis of L^2 for fixed Π

Semi-classical wavepackets

Raising operators

- Define the *raising operator* [1]

$$\mathcal{R} := \begin{pmatrix} \mathcal{R}_0 \\ \vdots \\ \mathcal{R}_{D-1} \end{pmatrix} = \frac{i}{\sqrt{2\varepsilon^2}} \left(\mathbf{P}^{\mathrm{H}} \left(\underline{x} - \underline{q} \right) - \mathbf{Q}^{\mathrm{H}} \left(\left(-i\varepsilon^2 \nabla_x \right) - \underline{p} \right) \right)$$

- Apply to the ground state

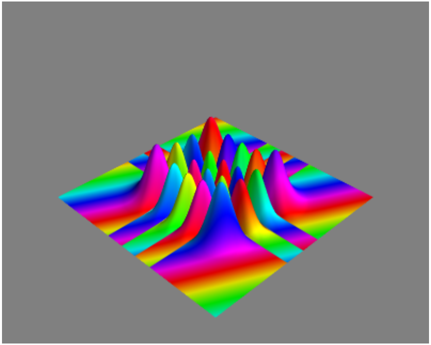
$$\phi_{\underline{k}} := \frac{1}{\sqrt{\underline{k}!}} \mathcal{R}_0^{k_0} \mathcal{R}_1^{k_1} \cdots \mathcal{R}_{D-1}^{k_{D-1}} \phi_{\underline{0}}$$

- Higher order functions $\phi_{\underline{k}}$

[1] for details, see [2]

Semi-classical wavepackets

Basis function example



- Example of $\phi_{4,3}(x, y)$

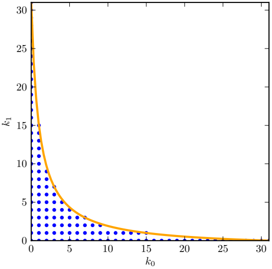
Semi-classical wavepackets

Basis shapes

- *Basis shapes* specify the set $\mathfrak{K}$
- Finite subset of $\mathbb{N}_0^D$

Hyperbolic cut basis shape

$$\mathfrak{K}(K) := \left\{ \underline{k} \in \mathbb{N}_0^D : \prod_{d=0}^{D-1} (1 + k_d) \leq K \right\}$$



- Full hypercubic set grows $\mathcal{O}\left(K^D\right)$
- This one grows $\mathcal{O}\left(K \log(K)^{D-1}\right)$

Semi-classical wavepackets

Definition of a wavepacket

- General wavepacket as linear combination

$$\Phi\left(\underline{x}\right) := e^{\frac{iS}{\varepsilon^2}} \sum_{\underline{k} \in \mathfrak{K}} c_{\underline{k}} \phi_{\underline{k}}\left(\underline{x}\right)$$

- In theory $\mathfrak{K} = \mathbb{N}_0^D$, practically $|\mathfrak{K}| < 200$
- We need a vector of multiple Φ
  - Global parameter set $\Pi := \{\underline{q}, \underline{p}, \mathbf{Q}, \mathbf{P}, S\}$
  - Individual coefficients $\left\{c_{\underline{k}}^{j}\right\}_{\underline{k}}$ per component Φ_j

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

Propagation of semi-classical wavepackets

- Time propagation of wavepackets [2]
  - propagate parameters $\mathbf{Q}$, $\mathbf{P}$, $\underline{q}$, $\underline{p}$ and S
  - propagate all coefficients $\left\{c_{\underline{k}}\right\}_{\underline{k}}$
- *Wavepackets stay in the same mathematical form*

[2] generalised algorithm of [1]

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 $\underline{c}$
  - $H = W$ where $W = V - U$ is the non-quadratic remainder
- Split the Schrödinger equation and propagate by T, U and W separately

Propagation of semi-classical wavepackets

Update rules

- Kinetic operator T part

$$\underline{q}(t) = \underline{q}(0) + t\,\underline{p}(0)$$
$$\mathbf{Q}(t) = \mathbf{Q}(0) + t\,\mathbf{P}(0)$$
$$S(t) = S(0) + \frac{1}{2} t\,\underline{p}(0)^{\mathsf{T}}\underline{p}(0)$$

- Potential part, quadratic approximation $U(\underline{x})$

$$\underline{p}(t) = \underline{p}(0) - t\,\nabla U(\underline{q}(0))$$
$$\mathbf{P}(t) = \mathbf{P}(0) - t\,\nabla^2 U(\underline{q}(0))\mathbf{Q}(0)$$
$$S(t) = S(0) - t\,U(\underline{q}(0))$$

Propagation of semi-classical wavepackets

Galerkin approximation

- Galerkin approximation

$$\forall \underline{k} \in \mathfrak{K} \quad \langle \phi_{\underline{k}}, (i\varepsilon^2 \partial_t - W)u \rangle = 0$$

- Non-quadratic remainder $W(\underline{x})$ part

$$\underline{c}(t) = \exp\left(-\frac{i}{\varepsilon^2} t \mathbf{F}\right) \underline{c}(0)$$

- with

$$\mathbf{F} = \begin{pmatrix} & \vdots & \\ \cdots & \langle \phi_{\underline{k}}, W \phi_{\underline{l}} \rangle & \cdots \\ & \vdots & \end{pmatrix}$$

Some final remarks

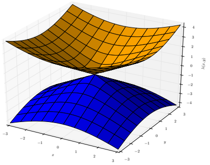
- Wavepackts work very well for simpler potentials
- Some open issues for more complex potentials
  - Several parameters to choose, for example the basis size
- Gridless method
  - but we need very high order quadrature
  - and the matrix exponential of a full matrix
    - Iterative methods like Arnoldi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

A simulation example

Missed conic crossing

- Take the potential

$$\mathbf{V}(x,y) := \begin{pmatrix} x & \sqrt{y^2+\delta^2} \\ \sqrt{y^2+\delta^2} & -x \end{pmatrix}$$



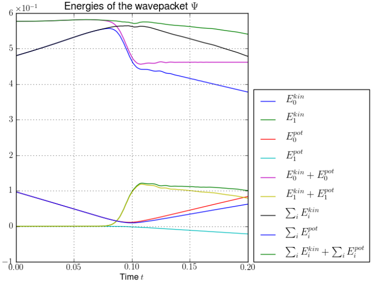
- Set $\delta = 0$ and $\varepsilon = 0.01$
- Initial parameters Π

$$\underline{q} = \begin{pmatrix} -0.1 \\ \alpha\varepsilon \end{pmatrix} \quad \underline{p} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \mathbf{Q} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \mathbf{P} = \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} \quad S = 0$$

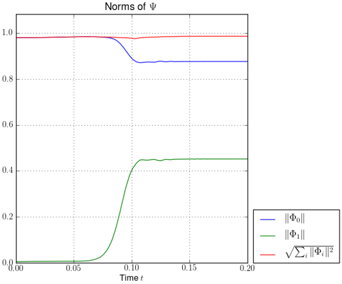
- Timestep $\tau = 0.001$
- Start with a Gaussian $\phi_{\underline{0}}$
- Vary α

A simulation example

Missed conic crossing, $\alpha = 1.0$



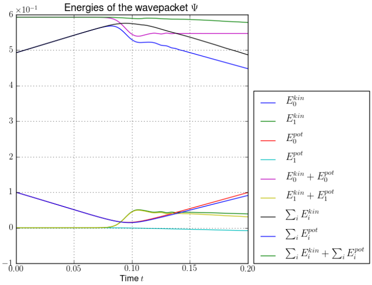
(a)



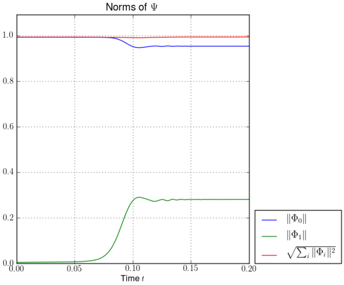
(b)

A simulation example

Missed conic crossing, $\alpha = 1.5$



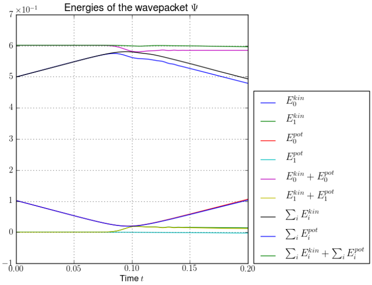
(c)



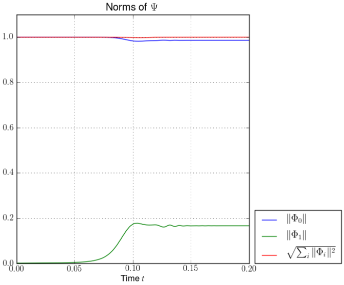
(d)

A simulation example

Missed conic crossing, $\alpha = 2.0$



(e)



(f)

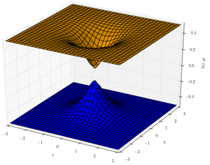
Another simulation example

An avoided crossing

- Take the potential

$$\mathbf{V}(x,y) := \begin{pmatrix} \frac{1}{2}\xi & \delta \\ \delta & -\frac{1}{2}\xi \end{pmatrix}$$

where $\xi := \tanh\left(\sqrt{x^2+y^2}\right)$



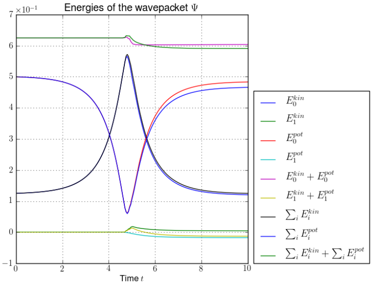
- Initial parameters Π

$$\underline{q} = \begin{pmatrix} -3 \\ 0 \end{pmatrix} \quad \underline{p} = \begin{pmatrix} 0.5 \\ 0 \end{pmatrix} \quad \mathbf{Q} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \mathbf{P} = \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} \quad S = 0$$

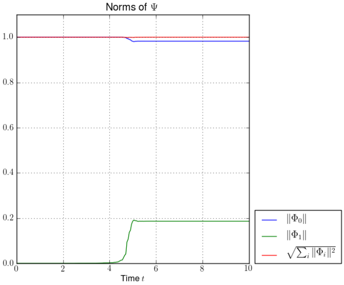
- Timestep $\tau = 0.01$
- Start with a Gaussian $\phi_{\underline{0}}$
- Vary ε and δ

Another simulation example

An avoided crossing with $\varepsilon = 0.01$ and $\delta = 0.05$



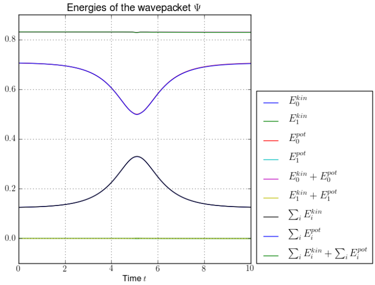
(g)



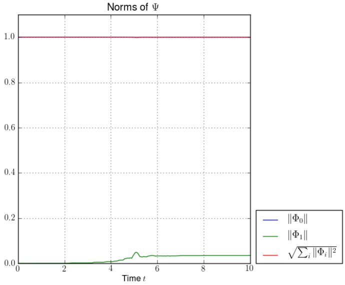
(h)

Another simulation example

An avoided crossing with $\varepsilon = 0.01$ and $\delta = 0.5$



(i)



(j)

Current and future work

Some ideas

- Apply the algorithms to real chemical problems
  - For example Pyrazine ($C_4H_4N_2$), see [3]
  - or Methyl iodide (ICH_3), see [4]
- Use code to simulate
  - In even higher dimensions $D > 3$
  - More than 2 energy levels
- Improve propagation for very small ε

Thanks for your attention

More information on the topic

- The full thesis:

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

E. Faou, V. Gradinaru, and C. Lubich.
Computing semiclassical quantum dynamics with Hagedorn wavepackets.
SIAM Journal on Scientific Computing, 31(4):3027–3041, 2009.

G. A. Hagedorn.
Raising and lowering operators for semiclassical wave packets.
Annals of Physics, 269(1):77–104, 1998.

C. Lasser and T. Swart.
Single switch surface hopping for a model of pyrazine.
The Journal of Chemical Physics, 129(3):034302, 2008.

S.-Y. Lee and E. J. Heller.
Exact time-dependent wave packet propagation: Application to the photodissociation of methyl iodide.
The Journal of Chemical Physics, 76(6):3035–3044, 1982.