Propagation of Wave Packets and Herman-Kluk Propagators

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Introduction

Schedule of the talk.

1. Quantum Dynamics. Systems of Schrödinger time-evolution equations.
2. Scalar case. How to trade solving high dimensional oscillating equations into solving ODEs ? Egorov theorem, thawed or frozen gaussians approximation, “non-hopping algorithm”.
3. Systems. Zoology of systems, revisiting the scalar methods, the need of “hopping” algorithms.

Quantum Dynamics

Schrödinger equations

- Born-Oppenheimer Approximation

$$i\varepsilon\partial_t\psi^\varepsilon = \widehat{H}\psi^\varepsilon, \;\; \psi^\varepsilon(0,x) = \psi_0^\varepsilon(x),$$

$$H = -\frac{\varepsilon^2}{2}|\xi|^2 + V(x),$$

V matrix-valued, self-adjoint, with subquadratic growth,

$$z = (x,\xi) \in \mathbb{R}^{2d}, \;\; (t,x) \in \mathbb{R}\times\mathbb{R}^d, \;\; \psi^\varepsilon \in L^2(\mathbb{R}^d, \mathbb{C}^N).$$

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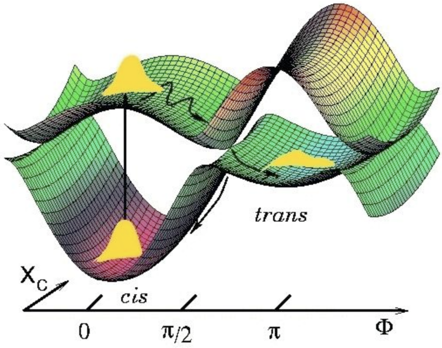
$\Longrightarrow$ The aim: Describe

1. $\psi^\varepsilon(t) = \mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{H}}\psi_0^\varepsilon$
2. $(\widehat{a}\,\psi^\varepsilon(t),\psi^\varepsilon(t))_{L^2(\mathbb{R}^d,\mathbb{C}^N)}$, $a \in \mathcal{C}_0^\infty(\mathbb{R}^{2d},\mathbb{C}^{N,N})$.

What is known about H ? and ε

- Energy surfaces - Pyrazine



cf. Köppel and Yarkony

- Who is ε ?

For molecular dynamics, $\varepsilon = \sqrt{\frac{m_e}{m_N}}$.

Algorithms from the 70s

Underlying ideas:

- Key point: solving ODEs instead of PDEs by developing ansatz based on classical quantities.
- Key tools: Propagation of wave packets + Gaussian frame.

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- Key tools: Propagation of wave packets + Gaussian frame.

A large range of methods:

- Frozen gaussians & Thawed gaussians approximations,
  from chemistry Heller 1981, Herman-Kluk 1984, Kay 1994, Domcke & all 2019
  to mathematics Rousse-Swart 2009, Robert 2010, Lasser-Sattleger 2017.
- Surface hopping semi-groups,
  Tully Preston 1971, FK Lasser 2012, Kube Lasser Weber 2009, Lu 2018.
- Variational methods, MCTDH and G-MCTDH,
  Worth, Lasorne, Burghardt & Römer 2013, Lubich 2015.

Scalar equations

$H = h\,\mathrm{Id}$ for h real-valued.

Egorov theorem

- Egorov Theorem: for any observable a

$$\left(\widehat{a}\,\psi^\varepsilon(t),\psi^\varepsilon(t)\right)_{L^2(\mathbb{R}^d,\mathbb{C})}=\left(\widehat{a\circ\Phi^t_h}\,\psi^\varepsilon(t),\psi^\varepsilon(t)\right)_{L^2(\mathbb{R}^d,\mathbb{C})}+O(\varepsilon^2)$$

where $t\mapsto\Phi^t_h(z_0)$ is the classical trajectory

$$\dot\Phi^t_h(z_0)=Jdh(\Phi^t_h(z_0)),\;\;\Phi^0_h(z_0)=z_0.$$

$$h(x,\xi)=\frac{|\xi|^2}{2}+V(x),\;\;J=\begin{pmatrix}0 & \mathrm{Id}\\ -\mathrm{Id} & 0\end{pmatrix}.$$

- Numerical realization

1. Sample the initial Wigner transform $\Longrightarrow$ $(z_j,w_j)_{1\leq j\leq N}$
2. Propagate the weighted points:

$$(\Phi^t_h(z_j),w_j),\;\;1\leq j\leq N.$$

3. Sum-up at finite time:

$$\left(\widehat{a}\,\psi^\varepsilon(t),\psi^\varepsilon(t)\right)_{L^2(\mathbb{R}^d,\mathbb{C})}\sim\sum_{j=1}^N a\left(\Phi^t_h(z_j)\right)w_j.$$

Bargmann formula

- Gaussian: Let Γ in the positive half Siegel space,

$$g_0^\Gamma(x) = c_\Gamma \, \mathrm{e}^{i\Gamma x\cdot x}, \quad \|g_0^\Gamma\|_{L^2(\mathbb{R}^d)} = 1, \quad {}^t\Gamma = \Gamma, \quad \mathrm{Im}\,\Gamma > 0.$$

- Gaussian wave packets: Let $z = (q,p) \in \mathbb{R}^{2d}$,

$$g_z^{\Gamma,\varepsilon}(x) = \varepsilon^{-\frac{d}{4}} g_0^\Gamma\left(\frac{x-q}{\sqrt{\varepsilon}}\right) \mathrm{e}^{\frac{i}{\varepsilon}p\cdot(x-q)}$$

- Bargmann transform: Decomposition of $\psi \in L^2(\mathbb{R}^d)$ on Gaussians

$$\psi(x) = (2\pi\varepsilon)^{-d} \int_{z\in\mathbb{R}^{2d}} \langle g_z^\varepsilon, \psi\rangle g_z^\varepsilon(x) dz, \quad \psi \in L^2(\mathbb{R}^d)$$

where $g_z^{i\mathrm{Id},\varepsilon} = g_z^\varepsilon$.

Bargmann formula

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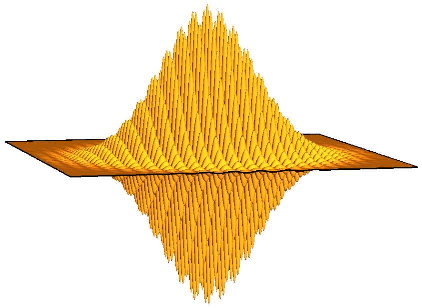
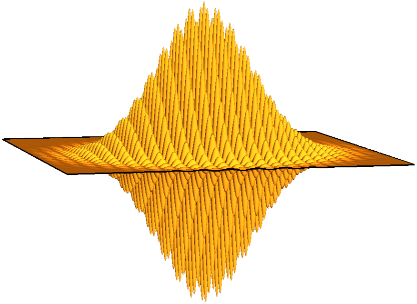


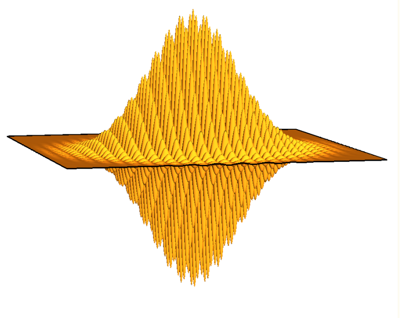
Bargmann formula

$$\psi_0^\varepsilon(x) = (2\pi\varepsilon)^{-d} \int_{z\in\mathbb{R}^{2d}} \langle g_z^\varepsilon, \psi_0^\varepsilon \rangle g_z^\varepsilon(x) dz, \quad \psi \in L^2(\mathbb{R}^d)$$



Bargmann formula

$$\mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{H}^{\varepsilon}}\psi_0^{\varepsilon}(x) = (2\pi\varepsilon)^{-d}\int_{z\in\mathbb{R}^{2d}}\langle g_z^{\varepsilon},\psi_0^{\varepsilon}\rangle \mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{H}^{\varepsilon}} g_z^{\varepsilon}(x)dz.$$



Wave packet propagation:

$$\mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{H}^{\varepsilon}} g_z^{\varepsilon}(x) = \mathrm{e}^{\frac{i}{\varepsilon}S(t,z)}\, g_{\Phi_H^t(z)}^{\Gamma(t,z),\varepsilon}(x) + O(\sqrt{\varepsilon})$$

Thawed Gaussian propagator for scalar equations

Theorem (Kay 2006, Rousse & Swart 2009, Robert 2010)

$$\mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{H}}\psi_0^\varepsilon = (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}} \langle g_z^\varepsilon, \psi_0^\varepsilon\rangle \mathrm{e}^{\frac{i}{\varepsilon}S(t,z)} g_{\Phi_h^t(z)}^{\Gamma(t,z),\varepsilon} dz + O(\varepsilon) \ \ in \ \ L^2(\mathbb{R}^d),$$

Classical quantities

- $\Phi_h^t(z) = (q(t), p(t))$ is the classical trajectory arising from z.
- $S(t,z)$ is the classical action, $\dot{S} = p\cdot\dot{q} - h(q,p)$, $S(0)=0$.
- $\Gamma(t,z) = (C(t,z)+iD(t,z))(A(t,z)+iB(t,z))^{-1}$

  where $F(t,z) = \begin{pmatrix} A(t,z) & B(t,z) \\ C(t,z) & D(t,z)\end{pmatrix}$ satisfies

$$\partial_t F = J\,\mathrm{Hess}_z h(t,\Phi_h^t(z))F(t), \ \ F(0) = \mathrm{Id}_{\mathbb{R}^{2d}}.$$

Frozen Gaussian propagator for scalar equations

Theorem (Kay 2006, Rousse & Swart 2009, Robert 2010)

$$e^{-\frac{i}{\varepsilon}t\widehat{H}}\psi_0^\varepsilon = (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}}\langle g_z^\varepsilon, \psi_0^\varepsilon\rangle u(t,z) e^{\frac{i}{\varepsilon}S(t,z)} g^\varepsilon_{\Phi_h^t(z)} dz + O(\varepsilon) \ \ in \ \ L^2(\mathbb{R}^d),$$

$$with \ \ u(t,z) = 2^{-d/2}\det{}^{1/2}\left(A(t,z)+D(t,z)+i(C(t,z)-B(t,z))\right).$$

Key points of the proof [Robert 2010]:

1. Wave packet propagation

$$e^{-\frac{i}{\varepsilon}t\widehat{H}^\varepsilon} g_z^\varepsilon(x) = e^{\frac{i}{\varepsilon}S(t,z)}\, g^{\Gamma(t,z),\varepsilon}_{\Phi_H^t(z)}(x) + O(\sqrt{\varepsilon})$$

2. Treat the remainder in $O(\sqrt{\varepsilon})$ in order to obtain $O(\varepsilon)$ (integration by parts).
3. Turn the width $\Gamma(t,z)$ of the Gaussian into the prefactor $u(t,z)$ by an evolution argument drawing a path form $\Gamma_0 = i\mathrm{Id}$ to $\Gamma_1 = \Gamma(t,0,z)$.

Frozen Gaussian propagator for scalar equations

Algorithmic realization [Lasser & Sattleger 2017]

1. Initial Sampling of the data by a Monte Carlo procedure

$$\psi_0^\varepsilon(x) \sim (2\pi\varepsilon)^{-d} \sum_{1\leq j\leq N} r_0^\varepsilon(z_j) g_{z_j}^\varepsilon$$

with $z_1, \cdots, z_N$ i.i.d. according to the probability measure

$$\mu_0^\varepsilon(dz) = \left(\int |\langle g_z, \psi_0^\varepsilon \rangle| dz \right)^{-1} |\langle g_z, \psi_0^\varepsilon \rangle| dz.$$

2. Transport of the sample points + classical quantities

$$z_j(t) = \Phi_h^t(z_j), \;\; S(t, z_j), \;\; u(t, z_j), \;\; 1 \leq j \leq N.$$

3. Quadrature formula

$$\psi^\varepsilon(t,x) \sim (2\pi\varepsilon)^{-d} \sum_{1\leq j\leq N} r_0^\varepsilon(z_j) \mathrm{e}^{\frac{i}{\varepsilon} S(t,z_j)} u(t,z_j) g^\varepsilon_{\Phi^t_{z_j}}.$$

What about systems ?

Which systems ? which data ?

- The data is chosen on an energy surface:

$$\psi_0^\varepsilon = \widehat{\vec{V}_0}\phi_0^\varepsilon$$

with $\phi_0^\varepsilon \in L^2(\mathbb{R}^d, \mathbb{C})$ and $H(z)\vec{V}_0(z) = h(z)\vec{V}_0(z)$.

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- How is h ?

1. Gapped eigenvalue: there exists $\delta_0 > 0$ such that

$$d\left(h(z), \sigma(H(z)) \setminus \{h(z)\}\right) > \delta_0.$$

2. Crossings: let $h =: h_1$ and h_2, eigenvalues of H,

$$\Upsilon := \{z \in \mathbb{R}^{2d},\ \ h_1(z) = h_2(z)\} \neq \emptyset.$$

Classification according to the dimension of Υ (Hagedorn 1994), its geometric properties (Colin de Verdière 2003, FK & Gérard 2002) $\Longrightarrow$ normal forms and transition formulas.

Time-dependent eigenvectors

Adiabatic decoupling: If $\psi_0^\varepsilon = \widehat{\vec{V}_0}\phi_0^\varepsilon + O(\varepsilon)$ with $H\vec{V}_0 = h\vec{V}_0$, then

$$\psi^\varepsilon(t) = \widehat{\vec{V}(t)}\mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{h}}\phi_0^\varepsilon + O(\varepsilon)$$

where $H\vec{V} = h\vec{V}$ is given by parallel transport:

$$\partial_t\vec{V} + \xi\cdot\nabla_x\vec{V} - \nabla h\cdot\vec{V} = \Omega\vec{V}, \quad \vec{V}(0) = \vec{V}_0.$$

$$\Omega(x,\xi) = (\mathrm{Id} - \Pi(x))\xi\cdot\nabla\Pi(x).$$

$\Longrightarrow$

- Egorov theorem for matrix-valued symbols.
- Thawed/Frozen Gaussian aproximation of the propagator.

Gapped systems - Thawed Gaussian propagator

- Propagation of the Gaussian WP:

$$\mathrm{e}^{-i\frac{t}{\varepsilon}\widehat{H}}(\vec{V}_0 g_z^\varepsilon) = \mathrm{e}^{\frac{i}{\varepsilon}S(t,z)} g^{\varepsilon,\Gamma(t)}_{\Phi_h^t(z)} \vec{V}(t) + O(\sqrt{\varepsilon})..$$

Proposition (FLR 2019)

$$\mathrm{e}^{-i\frac{t}{\varepsilon}\widehat{H}}\psi_0^\varepsilon = (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{2d}} \langle g_z^\varepsilon, v_0^\varepsilon\rangle \; u(t,z)\vec{V}(t,\Phi_h^t(z)) \; \mathrm{e}^{\frac{i}{\varepsilon}S(t,z)} \; g^\varepsilon_{\Phi_h^t(z)} \, dz + O(\varepsilon).$$

- A vector-valued prefactor:

$$\vec{U}(t,z) = u(t,z)\vec{V}(t,\Phi_h^t(z)).$$

What about systems with crossings ?

Systems with crossings - surface hoppings

Key ideas:

- Far from the crossing set: adiabatic regime.
- Close to the crossing set: generate new trajectories when the trajectories reach a hopping hypersurface

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- Far from the crossing set: adiabatic regime.
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Good news:

- For "generic" conical crossings, the time-dependent eigenvector exists up to the crossing.

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Two questions:

- Which hopping hypersurface ?
  $\Longrightarrow$ minimal gap condition (FK Lasser 2012 - expectation values).
- Which weight on the new trajectories ?
  $\Longrightarrow$ Transition coefficients arising from the analysis of the normal forms model problems (starting from Landau and Zener 1930's).

Systems with codimension 1 crossings

- $N \geq 2$, $H = h_1\Pi_1 + h_2\Pi_2$.
- The functions h_1, h_2, Π_1 and Π_2 are smooth

$$h_1 = v + f, \;\; h_2 = v - f, \;\; v = \frac{1}{2}\mathrm{Tr}\, H, \;\; f \;\; \text{gap}.$$

- Classical quantities associated with h_j, $j \in \{1, 2\}$

$$\Phi_j^{t,t_0}(z), \; S_j(t, t_0, z), \; F_j(t, t_0, z), \; \Gamma_j(t, t_0, z), \; u_j(t, t_0, z), \; \vec{U}_j(t, t_0, z), \ldots$$

Systems with codimension 1 crossings

- Generic codimension 1 crossing:

$$\mu(z) := \frac{1}{2}(\partial_t f + \{v, f\}(z)) \neq 0, \ \ \forall z \in \Upsilon.$$

$\Longrightarrow$ The trajectories are transverse to the crossing hypersurface

$$\Upsilon = \{f(q) = 0\}.$$

- If $z \in \mathbb{R}^d$, $t^\flat(z)$ is the crossing time

$$\Phi_1^{t^\flat(z),0}(z) = z^\flat(z) \in \Upsilon.$$

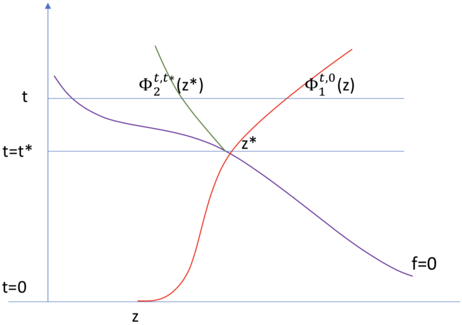
- With $\vec{V}_1 = \Pi_1 \vec{V}_1$, we associate $\vec{V}_1(t, 0, z)$ and $\vec{V}_2(t, t^\flat, z)$ with

$$\vec{V}_2(t^\flat, t^\flat, z) = \vec{V}_1(t^\flat, 0, z)^\perp.$$

- We associate with $z \in \mathbb{R}^{2d}$

$$S^\flat(z) = S_1(t^\flat, 0, z), \ \ \alpha^\flat(z) = \|(\partial_t \Pi_1 + \{v, \Pi_1\})\vec{V}_1(t^\flat, z^\flat)\|_{\mathbb{C}^N}.$$

Systems with codimension 1 crossings



Propagation of a Wave Packet

Propagation of Gaussian wave packets

Theorem (Hagedorn 94, Watson & Weinstein 18 , CFK Lasser Robert 19)

Assume $\psi_0^\varepsilon = \widehat{\vec{V}_1} g^\varepsilon_{z_0}$, *then in* $L^2(\mathbb{R}^d)$

$$\mathrm{e}^{-\frac{i}{\varepsilon}t\widehat{H}}\psi_0^\varepsilon = \widehat{\vec{V}}_1(t)v_1^\varepsilon(t) + \sqrt{\varepsilon}\,\mathbf{1}_{t>t^\flat}\,\widehat{\vec{V}}_2(t)v_2^\varepsilon(t) + O(\varepsilon^{2/3})$$

- $v_1^\varepsilon(t)$ *solves* $i\varepsilon\partial_t v_1^\varepsilon = \widehat{h}_1 v_1^\varepsilon,\;\; v_1^\varepsilon(0) = g^\varepsilon_{z_0}$.
- $v_2^\varepsilon(t)$ *solves* $i\varepsilon\partial_t v_2^\varepsilon = \widehat{h}_2 v_2^\varepsilon,\;\; v_2^\varepsilon(t^\flat) = \alpha^\flat\,\mathrm{e}^{iS^\flat/\varepsilon} g^{\Gamma^\flat,\varepsilon}_{z^\flat}$,

where $\alpha^\flat$, $S^\flat$, $\Gamma^\flat$ *are classical quantities associated with the crossing point* $z^\flat$.

The result extends to non gaussian wave packets data:

$$\varepsilon^{-\frac{d}{4}} a\left(\frac{x-q}{\sqrt{\varepsilon}}\right)\mathrm{e}^{\frac{i}{\varepsilon}p\cdot(x-q)},\;\; a\in\mathcal{S}(\mathbb{R}^d).$$

Frozen Gaussian app. for codim 1 crossings

Theorem (CFK. Lasser Robert, *still writing...*)

Assume $\psi_0^\varepsilon = \widehat{\vec{V}}_1 v_0^\varepsilon$. *then*

$$\psi^\varepsilon(t,x) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \mathrm{e}^{\frac{i}{\varepsilon} S_1(t,0,z)} \vec{U}_1^\varepsilon(t,0,z) \langle g_z^\varepsilon, v_0^\varepsilon \rangle g^\varepsilon_{\Phi_1^{t,0}(z)}(x) dz$$

$$+\sqrt{\varepsilon}\,(2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \mathbf{1}_{t^\flat(z)<t} \alpha^\flat(z) \mathrm{e}^{\frac{i}{\varepsilon} S^\flat(z)} \mathrm{e}^{\frac{i}{\varepsilon} S_2(t,t^\flat,z^\flat)} \vec{U}_2^\varepsilon(t,t^\flat,z^\flat)$$

$$\times \langle g_z^\varepsilon, v_0^\varepsilon \rangle g^\varepsilon_{\Phi_2^{t,t^\flat}(z^\flat)}(x) dz + o(\sqrt{\varepsilon})$$

with vector-valued Herman-Kluk prefactors

$$\vec{U}_1^\varepsilon(t,0,z) = \vec{V}_1\left(t,0,\Phi_1^{t,0}(z)\right) u_1(t,0,z),$$

$$\vec{U}_2^\varepsilon(t,t^\flat,z^\flat) = \vec{V}_2\left(t,t^\flat,\Phi_2^{t,t^\flat(z)}(z^\flat)\right) u_2(t,t^\flat,z^\flat).$$

Frozen Gaussian solver for codimension 1 crossings

Assume $\psi_0^\varepsilon = \widehat{\vec{V}}_1 v_0^\varepsilon$.

1. Initial sampling of v_0^ε: $\Longrightarrow$ N weighted sample points
$$(z_1, r_1), \dots, (z_N, r_N).$$
2. Transport along Φ_1^t: $\Longrightarrow z_1^{(1)}(t), \quad \dots \quad, z_N^{(1)}(t)$, the actions $S_1(t,0,z_j)$ and prefactors $\vec{U}_1(t,0,z_j)$.
3. Branching process: If $f(z_j(t))$ changes of sign at time $t_j^\flat$. Generate $z_j^{(2)}(t)$ on the mode h_2 with starting point $z_j^\flat := z_j^{(1)}(t_j^\flat)$. Set $r_j^\flat := \alpha(z_j^\flat)\mathrm{e}^{\frac{i}{\varepsilon}S_1(t_j^\flat,0,z_j)} r_j$.
4. Conclusion:
$$\psi^\varepsilon(t,x) \sim (2\pi\varepsilon)^{-d} \sum_{1\leq j\leq N} r_j \mathrm{e}^{\frac{i}{\varepsilon}S_1(t,0,z_j)} \vec{U}_1(t,0,z_j) g^\varepsilon_{z_j^{(1)}(t)}$$
$$+\sqrt{\varepsilon} \sum_{t_j^\flat < t} r_j^\flat \mathrm{e}^{\frac{i}{\varepsilon}S_2(t,t_j^\flat,z_j^\flat)} \vec{U}_2(t,t_j^\flat,z_j^{(2)}(t)) g^\varepsilon_{z_j^{(2)}(t)}$$

Conclusion

- Better estimates for expectation value than for wave function .
- For systems, parallel transport + hopping trajectories with deterministic branching process.
- Codimension 2 and 3 crossing (including Dirac points):
  1. single switch surface hopping for observables (transitions at leading order)
  2. thawed & frozen gaussian approximations (work in progress with Lysianne Hari and Stephanie Gamble).