Towards a mathematical understanding of surface hopping methods

Zhennan Zhou

Duke University
zhennan@math.duke.edu

November 2016, Duke University
KI-Net: Young Researchers Workshop 2016

Joint with

Jianfeng Lu (Duke University)

Outline

Introduction and previous work

The path integral formulation

Numerical tests and discussions

Future directions and final comments

The fundamental equation

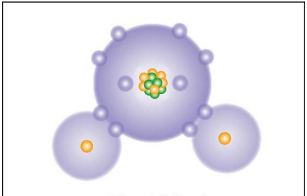
The Schrödinger equation for nuclei and electrons (in atomic unit)

$$i\partial_t u = -\frac{1}{2M}\Delta_x u - \frac{1}{2}\Delta_r u + V(x,r)u,$$

where $x \in \mathbb{R}^m$ the position of nuclei and $r \in \mathbb{R}^n$ the position of electrons. After rescaling

$$i\varepsilon\partial_t u = -\frac{\varepsilon^2}{2}\Delta_x u - \frac{1}{2}\Delta_r u + V(x,r)u,$$

where $\varepsilon = \sqrt{1/M} \ll 1$ (about $1/100$ for hydrogen nucleus).

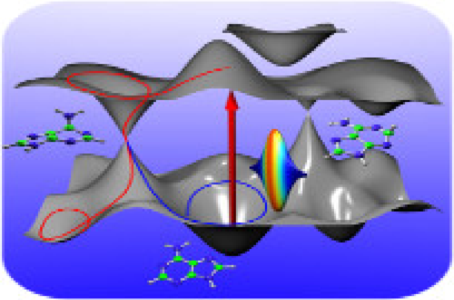


Water Molecule

The famous quote

P.A.M. Dirac, 1929

The fundamental laws necessary to the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known,



The famous quote

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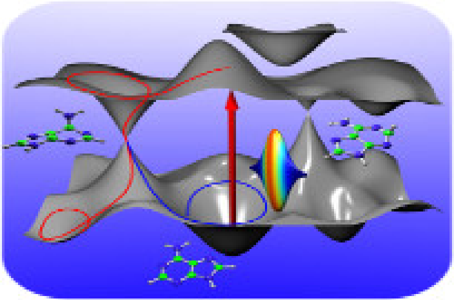
The fundamental laws necessary to the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficult lies only in the fact that application of these laws leads to equations that are too complex to be solved.



The solution to the curse of dimensionality

The dimension is too high! Let us try to separate the nucleus and electron degrees of freedom

$$i\varepsilon\partial_t u = -\frac{\varepsilon^2}{2}\Delta_x u - \frac{1}{2}\Delta_r u + V(x,r)u =: -\frac{\varepsilon^2}{2}\Delta_x u + H_e(x)u.$$

Denote $\Psi_k(r;x)$ as the eigenstates of $H_e(x)$

$$H_e(x)\Psi_k(r;x) = E_k(x)\Psi_k(r;x),$$

where x enters as a parameter. These are called adiabatic states.

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It is a whole different story how to approximate the above eigenvalue problem, *aka* the electronic structure theory, which we will not go into today ...

The adiabatic approximation

Recall that

$$i\varepsilon\partial_t u = -\frac{\varepsilon^2}{2}\Delta_x u - \frac{1}{2}\Delta_r u + V(x,r)u =: -\frac{\varepsilon^2}{2}\Delta_x u + H_e(x)u,$$

and $\Psi_k(r;x)$ (adiabatic states) are the eigenstates of $H_e(x)$

$$H_e(x)\Psi_k(r;x) = E_k(x)\Psi_k(r;x).$$

(Time-dependent) Born-Oppenheimer approximation:

$$u(t,x,r) \approx u_0(t,x)\Psi_0(r;x),$$

with u_0 solving the nuclei Schrödinger equation

$$i\varepsilon\partial_t u_0(t,x) = -\frac{\varepsilon^2}{2}\Delta_x u_0 + E_0(x)u_0.$$

The semi-classical approximation

Nuclei Schrödinger equation on the energy surface $E_0(x)$:

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It is still impractical to solve, as this is a PDE on $\mathbb{R}^m$.

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To make it practical, recall that $\varepsilon \ll 1$. The semiclassical limit $\varepsilon \to 0$ gives the Hamilton dynamics for the nuclei with Hamiltonian $\frac{1}{2}|p|^2 + E_0(q)$.

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}t} &= -\nabla_q E_0(q);\\ \frac{\mathrm{d}q}{\mathrm{d}t} &= p.\end{aligned}$$

This is known as the ab initio molecular dynamics, since the interaction potential E_0 is given by a first principle calculations.

Thus, from Schrödinger equations to molecular dynamics, we have made two approximations:

(a) Adiabatic approximation: $u(t, x, r) = u_0(t, x)\Psi_0(r; x)$;

(b) Semiclassical approximation.

(a) is justified if $E_0(x)$ (ground state) as an energy surface is well separated from $E_1(x)$ (excited state).

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This is however often not the case, for applications like photoexcited dynamics, electron transfer and surface chemistry, where the Born-Oppenheimer approximation falls apart.

Instead, we would need to consider components of excited states:

$$u(t, x, r) = \sum_i u_i(t, x)\Psi_i(r; x),$$

and to make the notation simple, we will just consider two states (generalization is straightforward):

$$u(t, x, r) = u_0(t, x)\Psi_0(r; x) + u_1(t, x)\Psi_1(r; x).$$

Two state wave function:

$$u(t,x,r) = u_0(t,x)\Psi_0(r;x) + u_1(t,x)\Psi_1(r;x).$$

Substitute into the Schrödinger equation, we get

$$i\varepsilon\partial_t \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} = -\frac{\varepsilon^2}{2}\Delta_x \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} + \begin{pmatrix} E_0 & \\ & E_1 \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix}$$
$$-\varepsilon^2 \sum_{j=1}^{m} \begin{pmatrix} d_{00} & d_{01} \\ d_{10} & d_{11} \end{pmatrix}_j \partial_{x_j} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} - \frac{\varepsilon^2}{2} \begin{pmatrix} D_{00} & D_{01} \\ D_{10} & D_{11} \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix},$$

where for $k, l = 0, 1$

$$D_{kl}(x) = \langle \Psi_l(r;x), \Delta_x \Psi_k(r;x) \rangle_r,$$
$$\big(d_{kl}(x)\big)_j = \langle \Psi_l(r;x), \partial_{x_j} \Psi_k(r;x) \rangle_r.$$

As before, it is almost hopeless trying to directly simulate the matrix Schrödinger equation, and thus we still need to consider the semiclassical approximation.

Tully's fewest switch surface hopping [JChP 1990]

Semiclassical approximation to the matrix Schrödinger equation

$$i\varepsilon\partial_t \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} = -\frac{\varepsilon^2}{2}\Delta_x \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} + \begin{pmatrix} E_0 & \\ & E_1 \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} - \varepsilon^2 \sum_{j=1}^{m} \begin{pmatrix} d_{00} & d_{01} \\ d_{10} & d_{11} \end{pmatrix}_j \partial_{x_j} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix}$$

Intuition: Without the coupling d term, it is really just propagation on one of the energy surfaces, and hence very similar to the ab initio molecular dynamics, however, we need to "modify" the dynamics so to account the coupling terms.

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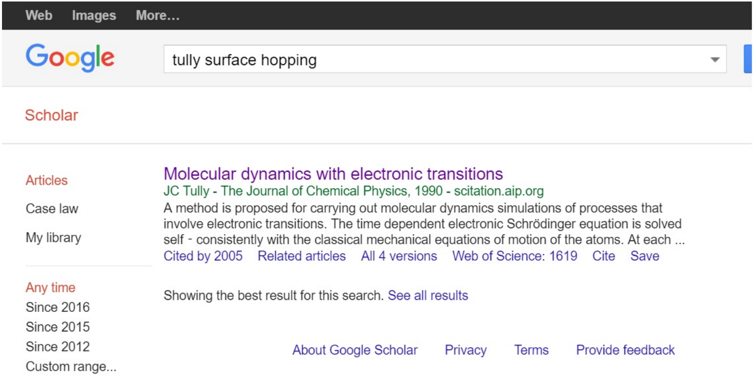
Denote a trajectory as $(q(t), p(t))$, the FSSH algorithm proposes to solve along the trajectory a "fictitious" ODE system of ($k = 1, 2$)

$$i\varepsilon\dot{c}_k(t) = E_k(q(t))c_k(t) - i\varepsilon \sum_j c_j(t)p(t) \cdot d_{kj}(q(t)),$$

and $(|c_0(t)|^2, |c_1(t)|^2)$ is understood as "population" on each energy surface along the trajectory. Q: Where this equation comes from???

Why studying surface hopping (FSSH) ?

Widely used in chemistry with many applications and increasing popularity



tully surface hopping

Molecular dynamics with electronic transitions

JC Tully - The Journal of Chemical Physics, 1990 - scitation.aip.org

A method is proposed for carrying out molecular dynamics simulations of processes that involve electronic transitions. The time dependent electronic Schrödinger equation is solved self - consistently with the classical mechanical equations of motion of the atoms. At each ...

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“empirically guessed / designed” attempts try to “correct” it

Previous works

- "Surface hopping" is also sometimes used for a very different "older" algorithm, which relies on Landau-Zener asymptotics. This asymptotics has been rigorously justified by the work of G. Hagedorn, C. Lasser, S. Teufel and others, also numerical work by C. Lasser, S. Jin and others.

  The FSSH type algorithms are for more general situations, and is quite different in many ways.

- In the chemistry / physics literature, often the starting point to "understand" the FSSH algorithm is the Kapral-Ciccotti equation, which is an extension of the usual Moyal's evolution equation for Wigner distribution to the matrix Schrödinger equations. So far,

  we don't see how to justify the "derivation" of FSSH from Wigner distribution, and it seems highly skeptical, at best.

Why studying surface hopping?

Even theoretical chemists find the algorithm mysterious, and are still wondering about whether the algorithm is correct (and in which sense) and can be derived ...

This is an area full of opportunities for applied mathematicians and rich of mathematical ideas:

- semiclassical analysis
- stochastic simulation
- multiscale modeling
- high dimensional PDEs
- applied harmonic analysis ...

Surface hopping as a path integral

The surface hopping is an asymptotically convergent path integral representation for the matrix Schrödinger equation! Similar to using Feynman-Kac formula to stochastically solve reaction-diffusion equations.

$$i\varepsilon\partial_t \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} = -\frac{\varepsilon^2}{2}\Delta_x \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} + \begin{pmatrix} E_0 & \\ & E_1 \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix} - \varepsilon^2 \sum_{j=1}^{m} \begin{pmatrix} d_{00} & d_{01} \\ d_{10} & d_{11} \end{pmatrix}_j \partial_{x_j} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix}$$

We have

$$u(t,x) = \mathcal{Z}_0 \mathbb{E}\, F(x; \{\widetilde{z}(s)\}_{0\le s\le t}) + \mathcal{O}(\varepsilon),$$

where

- $\mathbb{E}$ stands for expectation over the path space of $\widetilde{z}(s) = \big(z(s), l(s)\big) = \big(q(s), p(s), l(s)\big)$,
- $\mathcal{Z}_0$ is a normalization factor, and
- F is a functional depends on the trajectory $\widetilde{z}$

  (exact expression, unfortunately quite long and requires more notations, will be given later).

Surface hopping trajectory ensemble

Trajectory (path space) average

$$u(t,x) = \mathcal{Z}_0 \mathbb{E}\, F(x; \{\widetilde{z}(s)\}_{0\le s\le t}) + \mathcal{O}(\varepsilon),$$

The trajectory follows a Markov switching process

$$\mathrm{d}z(t) = \mathrm{d}(q(t), p(t)) = \Big(p(t), -\nabla_q E_{l(t)}\big(q(t)\big)\Big)\, \mathrm{d}t,$$

$$\mathbb{P}\big(l(t+\delta t) = l \mid l(t) = k,\ z(t) = z\big) = \delta_{kl} + \lambda_{kl}(z)\delta t + o(\delta t)$$

with rate matrix

$$\lambda(z) = \begin{pmatrix} \lambda_{00}(z) & \lambda_{01}(z) \\ \lambda_{10}(z) & \lambda_{11}(z) \end{pmatrix} = \begin{pmatrix} -|p\cdot d_{01}(q)| & |p\cdot d_{01}(q)| \\ |p\cdot d_{10}(q)| & -|p\cdot d_{10}(q)| \end{pmatrix}.$$

- $l(t)$ follows a (nonhomogeneous) Poisson process with state dependent jumping intensity $\lambda(z)$; it contains a.s. finite number of jumps.
- $z(t)$ follows the Hamiltonian flow on energy surface $l(t)$;

A rigorous surface hopping algorithm

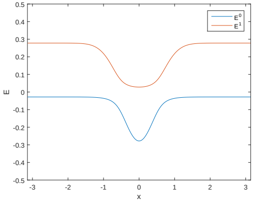
The path integral representation readily suggests an algorithm for approximating u:

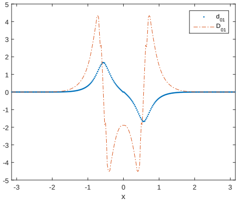
$$
\begin{aligned}
u(t,x,r) &= \mathcal{Z}_0 \, \mathbb{E} \, F(x; \{\widetilde{z}(s)\}_{0\le s\le t}) + \mathcal{O}(\varepsilon) \\
&= \frac{\mathcal{Z}_0}{M} \sum_{i=1}^{M} F(x; \{\widetilde{z}^i(s)\}_{0\le s\le t}) + \mathcal{O}\Big(\frac{1}{\sqrt{M}}\Big) + \mathcal{O}(\varepsilon),
\end{aligned}
$$

where $\widetilde{z}^i$ is i.i.d. realization of the trajectory.

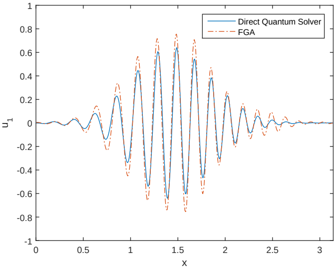
- With our mathematical understanding of the surface hopping algorithm (in particular, what it really tries to compute), it is natural to design more efficient algorithms.
- We remark that our algorithm actually offers an approximation to the wave function (and hence physical observables, transition rate, etc.)

Example (0) Sampling error with direct Monte Carlo





Solution and surface hopping approximation, $\varepsilon = 1/32$



(N_0 trajs)

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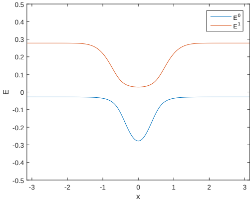

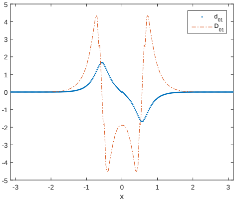

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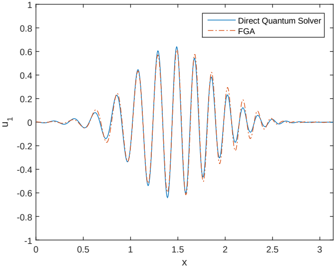

($3N_0$ trajs)

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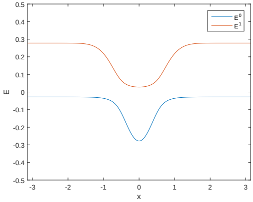

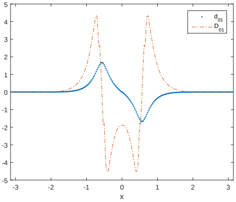

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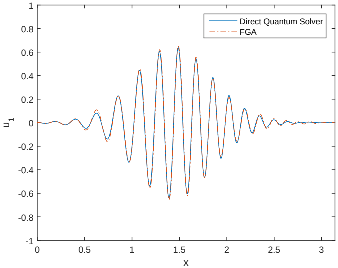


($5N_0$ trajs)

The Frozen Gaussian approximation and other semiclassical approaches

Before giving the detailed expression of F, let us go back to

$$i\varepsilon\partial_t u = -\frac{\varepsilon^2}{2}\Delta_x u + E(x)u.$$

The frozen Gaussian approximation (aka Herman-Kluk propagator) [Herman-Kluk 1984; Kay 1994; Swart-Rousse 2009; Lu-Yang 2011]

$$u_{\mathsf{FGA}}(t,x) = \frac{1}{(2\pi\varepsilon)^{3m/2}} \int_{\mathbb{R}^{2m}} A(t,q,p) e^{\frac{i}{\varepsilon}\Theta(t,x,q,p)} \,\mathrm{d}q\,\mathrm{d}p.$$

Somewhat unexpectedly (not at all clear from first sight), the surface hopping algorithm is actually a natural generalization of the frozen Gaussian approximation to the matrix Schrödinger equation!

Recall that most chemical derivations are trying to start from the Moyal's equation for Wigner function (*i.e.*, Kapral-Ciccotti equation) ...

Note: the various ways towards semiclassical approximation: WKB (geometric optics), Gaussian packets, Wigner distribution ...

The surface hopping ansatz

We assume the following **deterministic** ansatz, referred as surface hopping ansatz, for the solution to the matrix Schrödinger equation

$$u_{\text{FGASH}}(T,x) = |0\rangle \Big(u^{(0)}(T,x) + u^{(2)}(T,x) + \cdots \Big) + |1\rangle \Big(u^{(1)}(T,x) + u^{(3)}(T,x) + \cdots \Big), \quad (1)$$

where $|0\rangle = \binom{1}{0}$ and $|1\rangle = \binom{0}{1}$ denotes the quantum state associated with each surface.

The wave function $u^{(n)}$ stands for the contribution with n surface hops before time t, starting from surface E_0. In particular, for trajectories with even number of hops, the electronic state ends at $|0\rangle$, and trajectories with odd number of hops contribute to $|1\rangle$. This explains the above linear combination.

We denote a sequence $\{t_k\}_{k=1}^n$ for the hopping times satisfying

$$0 \leq t_1 \leq t_2 \leq \cdots \leq t_n \leq T,$$

at which time the trajectory switches from one energy surface to the other. The ansatz for $u^{(n)}$ is given by

$$u^{(n)}(T,x) = \frac{1}{(2\pi\varepsilon)^{3m/2}} \int \mathrm{d}q \, \mathrm{d}p \int_{0 \leq t_1 \leq \cdots \leq t_n \leq T} \mathrm{d}T_{n:1} \\ \tau^{(1)} \cdots \tau^{(n)} \, A^{(n)} \, \exp\left(\frac{i}{\varepsilon}\Theta^{(n)}\right), \tag{2}$$

where the hopping coefficient $\tau^{(k)}$ is defined as

$$\tau^{(k)} = -p(t_k) \cdot d_{l(t_k^+)l(t_k^-)}(q(t_k)), \tag{3}$$

and $\mathrm{d}T_{n:1} = \mathrm{d}t_1 \cdots \mathrm{d}t_n$. Note that in the above ansatz, we integrate over all possible hopping times for n hops in the time interval $[0,T]$. Given $\{t_k\}_{k=1}^n$ and z_0, the trajectory $\widetilde{z}(t)$ for $0 \leq t \leq T$ is specified.

The choice of the hopping coefficient $\tau^{(k)}$ is essential for the term by term matching in the surface hopping ansatz.

The term

$$A(t)\exp\left(\frac{i}{\varepsilon}\Theta(t,x)\right)$$

resembles the familiar amplitude $A(t)$ and phase $\Theta(t,x)$ expression from the Herman-Kluk propagator.

In particular, the phase term Θ takes the following form

$$\Theta(t,x) = S(t) + \frac{i}{2}|x - q(t)|^2 + p(t)\cdot(x - q(t)), \tag{4}$$

where $S(t)$ is the classical action associated with the trajectory and recall that $z(t) = (p(t), q(t))$ is the momentum and position of the trajectory.

Recall that, the position and momentum $z(t) = (p(t), q(t))$ evolves by a Hamiltonian flow on the energy surface $l(t)$:

$$\begin{cases} \dot{q}(t) = p(t); \\ \dot{p}(t) = -\nabla_q E_{l(t)}(q(t)). \end{cases} \tag{5}$$

Substitute the ansatz into the matrix Schrödinger equations and carry out asymptotic calculations, we obtain the amplitude A and action S solve the ODEs

$$\dot{S}(t) = \frac{1}{2} p(t)^2 - E_{l(t)}(q(t)), \tag{6}$$

$$\begin{aligned} \dot{A}(t) = {} & \frac{1}{2} A \operatorname{tr}\Big(Z(t)^{-1} \big(\partial_z p(t) - i \partial_z q(t) \nabla_q^2 E_{l(t)}(q(t)) \big) \Big) \\ & - A \, d_{l(t)l(t)}(q(t)) \cdot p(t), \end{aligned} \tag{7}$$

which are also continuous through jumps.

Theorem (Lu-Z., arXiv:1602.06459)

With some assumptions on E, d and D,
(a) the surface hopping ansatz $u_{\textit{FGASH}}$ converges absolutely,
and (b) we have

$$\|u - u_{\textit{FGASH}}\|_{L^2} = \mathcal{O}(\varepsilon).$$

The FGA-SH method can be interpreted as a path integral formulation of the matrix Schrödinger equation in the spirit of surface hopping. It approximates the solution $u = \binom{u_0}{u_1}$ as

$$\begin{aligned} u(T, x) &= u_{\text{FGASH}}(T, x) + \mathcal{O}(\varepsilon) \\ &= \mathbb{E}_{\widetilde{z}} \mathcal{F}\bigl(x; \{\widetilde{z}(s)\}_{0 \le s \le T}\bigr) + \mathcal{O}(\varepsilon), \end{aligned} \tag{8}$$

where the average is taken over an ensemble of trajectories we describe before.

The functional $\mathcal{F}$ is then given by

$$\mathcal{F}\big(x;\{\widetilde{z}(t)\}_{0\le t\le T}\big) = |l(T)\rangle \, \frac{\mathcal{Z}_0}{|A_0(\widetilde{z}(0))|} \times \\ \times A(T)\exp\Big(\frac{i}{\varepsilon}\Theta(T,x)\Big)\exp\Big(w(T)\Big)\prod_{k=1}^{n}\frac{\tau^{(k)}}{|\tau^{(k)}|}\,, \qquad (9)$$

which depends on the trajectory $\widetilde{z}$ up to time T.

The weighting factor w in (9) solves the ODE

$$\dot{w}(t) = \lambda_{1-l(t),l(t)}, \qquad (10)$$

with initial condition $w(0) = 0$. Thus, it is the accumulated jumping intensity of the trajectory.

The weight of a trajectory

For the algorithmic purpose, we remark that we can combine A with the weighting factor w as

$$\Gamma(t) = \frac{A(t)}{|A(0)|} \exp\bigl(w(t)\bigr), \tag{11}$$

which solves the ODE

$$\begin{aligned} \dot{\Gamma}(t) = \frac{1}{2}\Gamma \operatorname{tr}\Bigl(Z(t)^{-1}\bigl(\partial_z p(t) - i\partial_z q(t)\nabla_q^2 E_{l(t)}(q(t))\bigr)\Bigr) \\ + \Gamma\Bigl(\bigl|p(t)\cdot d_{(1-l(t))l(t)}(q(t))\bigr| - p(t)\cdot d_{l(t)l(t)}(q(t))\Bigr) \end{aligned} \tag{12}$$

with initial condition $\Gamma(0;\widetilde{z}(0)) = A_0(\widetilde{z}(0))/|A_0(\widetilde{z}(0))|$.

The quantity $|\Gamma(t)|$ will be treated as the weight of the trajectory in our algorithm. Thus we will prune trajectories with small weight, and branch trajectories with larger weights to reduce the variance of the stochastic sampling algorithm.

Modified path integral (with birth/death branching)

After propagating the trajectories till $t = T$, due to the birth/death branching process, the path integral is approximated by

$$u_{\text{FGA-SH}}(T, x) \approx \frac{\mathcal{Z}_0}{M(0)} \sum_{\alpha=1}^{M(T)} |l_\alpha(T)\rangle \, \gamma_\alpha(T) \times \\ \times \exp\Big(\frac{i}{\varepsilon} \Theta_\alpha(T, x)\Big) \prod_{k=1}^{n_\alpha} \frac{\tau_\alpha^{(k)}}{\left|\tau_\alpha^{(k)}\right|}, \quad (13)$$

where $M(T)$ denotes the number of trajectory at time T and we use subscript α explicitly to emphasize the dependence of these quantities on the right hand side on each trajectory.

We also remark that $|\gamma_\alpha| \approx 1$ due to the branching process, so it mainly contributes to a phase factor in the summation.

Propagation of trajectories

The algorithm starts by sampling a collection of initial points for the trajectories and estimate $\mathscr{Z}_0$.

The propagation of the trajectories are carried out as follows: For each time step of size Δt, the following steps are performed in order:

1. Evolve the position and momentum $p(t), q(t)$ by the Hamiltonian dynamics on the current surface $l(t)$.
2. Evolve the other (q, p) dependent quantities (phase, amplitude, weighting...) according to the current surface of the trajectory $l(t)$.
3. Hopping attempts. The probability that a surface hop occurs within the time interval $(t, t + \Delta t)$ is given by $\Delta t \lambda_{(1-l(t))l(t)}$. When hopping, $l(t)$ is changed, and the phase change is recorded.
4. (optional) Birth/death branching.

Example (1) Convergence test with various ε

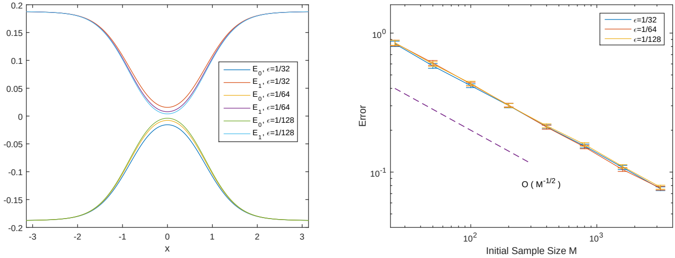


Figure: Left: Eigenvalues of H_e for $\varepsilon = \frac{1}{32}$, $\frac{1}{64}$ and $\frac{1}{128}$. Right: Empirical average of the error in the wave functions with confidence intervals.

Example (2) Effect of weighting factor w

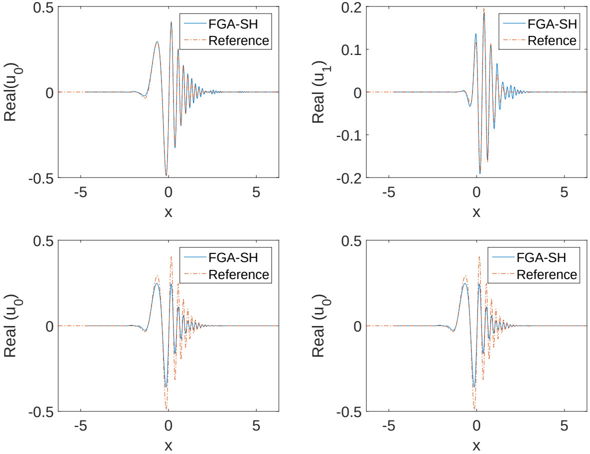


Figure: Top: FGA-SH solutions with the weighting factor. Bottom: FGA-SH solutions without the weighting factor.

Example (2) Effect of weighting factor w

	avg. error	Variance	TR mean	Variance
w/o w.f.	0.2695	9.5780e-03	0.1772	1.0339e-02
with w.f.	0.0678	7.5759e-03	0.2386	1.2106e-02

Table: Numerical error in the wave functions, and average transition rates with and without the weighting factor. The reference transition rate is given by 0.2443; the inclusion of the weighting factor reduces the relative error from 27.5% to 2.33%.

The non-homogeneous and state dependent Poisson process (which is involved in all version of surface hopping algorithms) requires the crucial correction terms in averaging,

while as far as we have seen, the chemistry literature seems to have missed such correction terms ...

Example (3) Initial condition with different momentum

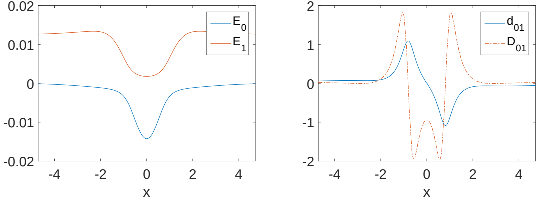
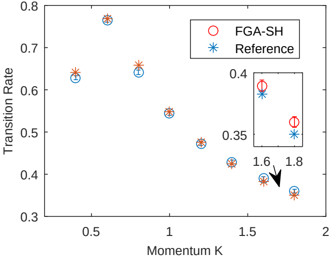


Figure: Left: Eigenvalues of H_e. Right: the coupling vectors of H_e.



Example (3) Initial condition with different momentum

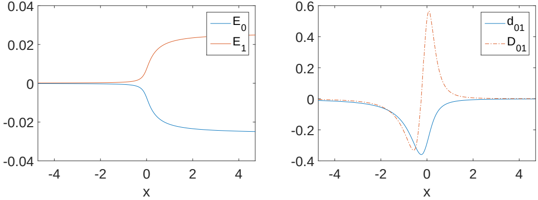
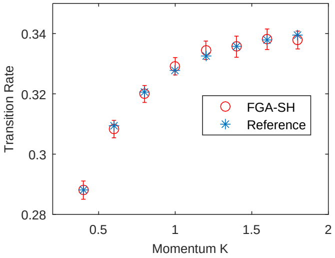


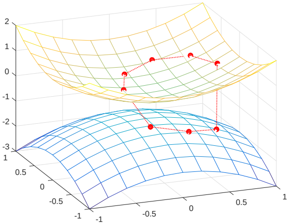
Figure: Left: Eigenvalues of H_e. Right: the coupling vectors of H_e.



Future directions

Well, this is not, however, the end of the story, but rather...

- It provides a framework to approximate a wide of class of matrix form differential equations.
- By the similar spirit, many nonadiabatic phenomenon can be studied, like thermal equilibrium sampling of nonadiabatic systems. (work in preparation)
- and many fresh ideas....



Thank you for your attention!

Email: `zhennan@math.duke.edu`

URL: `http://www.math.duke.edu/~zhennan/`

- Jianfeng Lu and Zhennan Zhou, Frozen Gaussian approximation with surface hopping for mixed quantum-classical dynamics: A mathematical justification of surface hopping algorithms, arXiv:1602.06459
- Jianfeng Lu and Zhennan Zhou, Improved sampling and validation of frozen Gaussian approximation with surface hopping algorithm for nonadiabatic dynamics, Journal of Chemical Physics, 145, 124109 (2016).