Metal Surfaces: Nonadiabatic Dynamics and Surface Hopping

A mathematically exact approach

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Overview

1. Backgrounds

2. Our algorithm and results

3. Discussions

Born-Oppenheimer approximation

The following setup, known as Born-Oppenheimer approximation, is often used by people as the default setting in most quantum chemistry related calculations without even realizing it:

- The nuclei are much heavier than the electrons and therefore move much slower. One regards the nuclei as classical particles.
- Adiabatic[1] assumption: ignore the couplings between different electronic states. (for example, in many MD calculations, only consider the ground state potential energy surface).

However, the B-O approximation and adiabatic assumption breaks down in many chemistry systems, such as surface chemistry, graphene, vibration-rotation systems, ...
We need to go beyond the B-O approximation.

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[1]The word *adiabatic* has very different meanings in different settings.

Beyond the B-O approximation

Scientifically, there could be many reasons why B-O approximation breaks down. For example,

- If the nuclei is too light, a classical treatment will be too wrong, it has to be treated as a quantum particle. A typical example is the Hydrogen bond.

However, even if the nuclei is heavy enough, if there are band crossings or small band gaps, the adiabatic assumption will break down. In such cases, if molecular dynamics is carried out using only the ground state energy, the result will make no sense.

Beyond the B-O approximation: surface hopping

- Physical intuition: the electron does not maintain on the ground state potential energy surface, it hops between different energy surfaces.
- Historically: first proposed by Tully [3], works in simple scenarios. Over the past 30 years, hundreds of versions of surface hopping.

Molecular dynamics with electronic transitions
JC **Tully** - The Journal of Chemical Physics, 1990 - aip.scitation.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…
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Problem: no gurantee to be *correct*, each version only works in the specific scenario.

Metal surfaces

- Molecule-metal interfaces are related to many different phenomenon in experimental chemistry, such as chemisorption, electrochemistry, heterogeneous catalysis and molecular junctions.
- The breakdown of BO approximations at metal surfaces leads to many interesting physical phenomenon: such as electronic friction, electron transfer, and energy transfer.

Metal surfaces
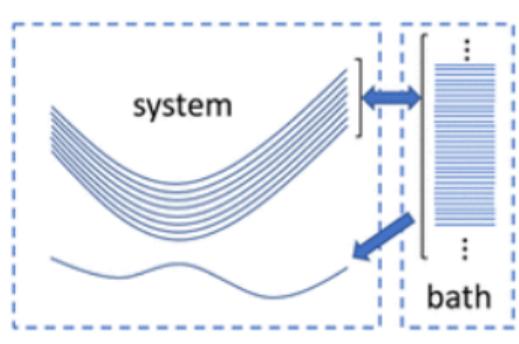
- Difficulty (other than the breakdown of BO approximation): continuous spectrum.
- For a continous spectrum $[\mathcal{E}_a, \mathcal{E}_b]$, if discretized into N orbitals, computational cost all existing methods will scale at least $O(N)$ while $N \to \infty$.
- But some physics in condensed matter system can only be recovered when N is really large. Therefore $O(N)$ is still not practical.

Metal surfaces

The quantum dynamics of nuclei at metal surfaces are described by the Newns-Anderson model, also known as the Anderson-Holstein model

$$
\begin{aligned}
\hat{H} = {} & \frac{\hat{p}^2}{2m_{\mathrm{n}}} + U_1(\hat{x}) + h(\hat{x})\hat{d}^\dagger\hat{d} \\
& + \int_{\mathcal{E}_a}^{\mathcal{E}_b} (\mathcal{E} - \mu)\hat{c}_{\mathcal{E}}^\dagger\hat{c}_{\mathcal{E}}\mathrm{d}\mathcal{E} + \int_{\mathcal{E}_a}^{\mathcal{E}_b} \left(V(\mathcal{E}, \hat{x})\hat{c}_{\mathcal{E}}^\dagger\hat{d} + \bar{V}(\mathcal{E}, \hat{x})\hat{d}^\dagger\hat{c}_{\mathcal{E}} \right) \mathrm{d}\mathcal{E}.
\end{aligned}
\tag{1}
$$

- $\hat{p}$ is the momentum operator, $\hat{x}$ is the position operator, m_{n} is the mass of the nuclei.
- $U_1(\hat{x})$ is the nuclear potential for the neutral molecule, $U_1(\hat{x}) + h(\hat{x})$ is the nuclear potential for the charged molecule.
- $\hat{d}$ and $\hat{d}^\dagger$ are the annihilation and creation operators for the electronic ground state of the molecule, $\hat{c}_{\mathcal{E}}$ and $\hat{c}_{\mathcal{E}}^\dagger$ are the annihilation and creation operators for metal electronic orbitals with energy level $\mathcal{E} \in [\mathcal{E}_a, \mathcal{E}_b]$. μ is the chemical potential.
- $V(\mathcal{E}, x)$ describes the coupling between the molecule and metal orbitals, and $\bar{V}(\mathcal{E}, x)$ means the complex conjugate of $V(\mathcal{E}, x)$.

Nondimensionalization

After nondimensionalization, the above model becomes

$$\begin{aligned}
\hat{H}_{\text{non}} &= -\frac{\varepsilon^2}{2}\nabla_{\tilde{x}}^2 + \tilde{U}_1(\tilde{x}) + \tilde{h}(\tilde{x})\hat{d}^\dagger\hat{d} \\
&\quad + \int_{\tilde{\mathcal{E}}_a}^{\tilde{\mathcal{E}}_b}(\tilde{\mathcal{E}} - \tilde{\mu})\hat{c}_{\tilde{\mathcal{E}}}^\dagger\hat{c}_{\tilde{\mathcal{E}}}\mathrm{d}\mathcal{E} + \varepsilon\int_{\tilde{\mathcal{E}}_a}^{\tilde{\mathcal{E}}_b}\left(\tilde{V}(\tilde{\mathcal{E}},\tilde{x})\hat{c}_{\mathcal{E}}^\dagger\hat{d} + \bar{V}(\mathcal{E},\hat{x})\hat{d}^\dagger\hat{c}_{\mathcal{E}}\right)\mathrm{d}\mathcal{E}
\end{aligned} \quad (2)$$

where we call ε the semiclassical parameter. In first quantization, this is

$$\begin{cases}
\mathrm{i}\varepsilon\partial_t\psi_0(t,x) = -\dfrac{\varepsilon^2}{2}\Delta\psi_0(t,x) + U_0(x)\psi_0(t,x) + \varepsilon\displaystyle\int_{\mathcal{E}_a}^{\mathcal{E}_b}\mathrm{d}\tilde{\mathcal{E}}\,V(\tilde{\mathcal{E}},x)\psi_1(t,\tilde{\mathcal{E}},x) \\
\mathrm{i}\varepsilon\partial_t\psi_1(t,\mathcal{E},x) = -\dfrac{\varepsilon^2}{2}\Delta\psi_1(t,\mathcal{E},x) + \left(U_1(x) + \mathcal{E}\right)\psi_1(t,\mathcal{E},x) + \varepsilon\bar{V}(\mathcal{E},x)\psi_0(t,x)
\end{cases} \quad (3)$$

The numerical challenges are

- Small ε leads to very oscillatory wavefunction.
- Discretization number N of continuous spectrum $[\mathcal{E}_a, \mathcal{E}_b]$ might be large.
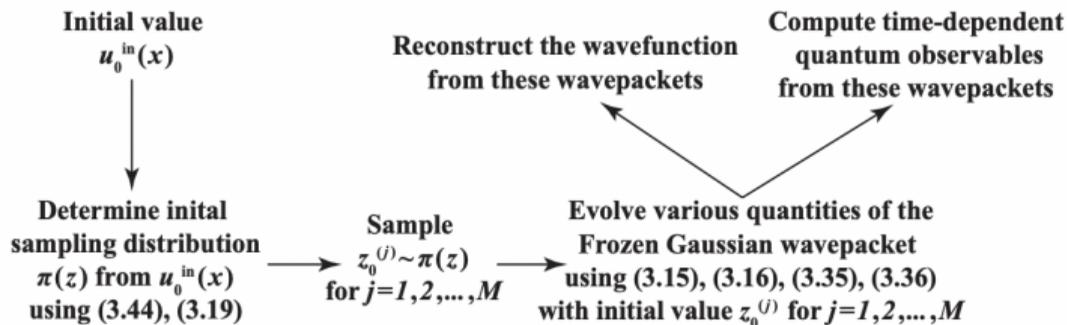
Our goal

$$
\begin{cases}
\mathrm{i}\varepsilon\partial_t\psi_0(t,x) = -\dfrac{\varepsilon^2}{2}\Delta\psi_0(t,x) + U_0(x)\psi_0(t,x) + \varepsilon\displaystyle\int_{\mathcal{E}_a}^{\mathcal{E}_b} \mathrm{d}\tilde{\mathcal{E}}\, V(\tilde{\mathcal{E}},x)\psi_1(t,\tilde{\mathcal{E}},x) \\[4mm]
\mathrm{i}\varepsilon\partial_t\psi_1(t,\mathcal{E},x) = -\dfrac{\varepsilon^2}{2}\Delta\psi_1(t,\mathcal{E},x) + \left(U_1(x)+\mathcal{E}\right)\psi_1(t,\mathcal{E},x) + \varepsilon\bar{V}(\mathcal{E},x)\psi_0(t,x)
\end{cases}
\tag{4}
$$

Design an algorithm for this system, whose computational cost does not (essentially) depend on both the semiclassical parameter ε and the number of metal orbitals N.

Mathematical details

Check all the details (very lengthy) in our article [2] [1].

- We represent the wavefunction using frozen Gaussians. This is how we deal with oscillatory wavefunctions.
- We derive the hopping probabilities using time dependent perturbation theory, whose error can be controlled by semiclassical analysis.


```
Initial value                                    Reconstruct the wavefunction         Compute time-dependent
  u_0^in(x)                                      from these wavepackets               quantum observables
                                                                                      from these wavepackets

     │
     ▼
Determine inital              Sample            Evolve various quantities of the
sampling distribution         z_0^(j)~π(z)      Frozen Gaussian wavepacket
π(z) from u_0^in(x)           for j=1,2,...,M    using (3.15), (3.16), (3.35), (3.36)
using (3.44), (3.19)                            with initial value z_0^(j) for j=1,2,...,M
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[2] Zhen Huang, Limin Xu, and Zhennan Zhou. Efficient frozen gaussian sampling algorithms for nonadiabatic quantum dynamics at metal surfaces. arXiv preprint arXiv:2206.02173, 2022
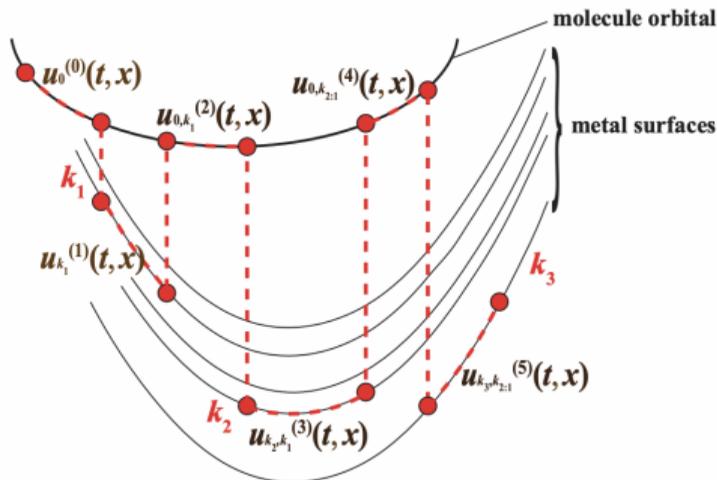
Surface Hopping

Figure 1: Illustration of the surface hopping ansatz: $k_1, k_2, k_3 \in \{1, 2, \cdots, N\}$ represents the indices of the metal orbitals that the wave packet has hopped onto. $u_0^{(0)}$ represents the wave packet that hasn't ever hopped; $u_{k_1}^{(1)}$ represents the wave packet that has hopped once and is on the k_1-th metal surface; $u_{0,k_1}^{(2)}$ represents the wave packet that has hopped twice and was on the k_1-th metal surface before the second jump; $u_{k_2,k_1}^{(3)}$ represents the wave packet that has hopped three times, is currently on the k_2-th metal surface and was on the k_1-th metal surfaces in history. The meaning of $u_{0,k_{2:1}}^{(4)}$ and $u_{k_3,k_{2:1}}^{(5)}$ could be determined similarly.

Why our surface hopping methods?

- The hopping probability is **correct**. (With both mathematical proof [2] and extensive experiments).

- For metal surface, our method's computational cost is independent of both ε and N (With both mathematical proof and extensive experiments [1]).

Theorem 4.1. *For system* (1.1) *with initial value* (3.44), *let M be the sample size. With assumption 1, the sampling error* $\mathrm{Err}_M(t, N)$ *of the FGS algorithm (Algorithm 1) satisfies the following inequality:*

$$\mathrm{Err}_M(t, N) \leq \frac{1}{\sqrt{M}} K(t) \prod_{j=1}^{m} \left(\frac{1+a_j}{\sqrt{a_j}} \right)^{\frac{1}{2}}, \qquad (4.6)$$

where $K(t)$ is independent of both the semiclassical parameter ε and the number of metal orbitals N .

Computational cost

The sample size required to reach a certain threshold is independent of N and ε:
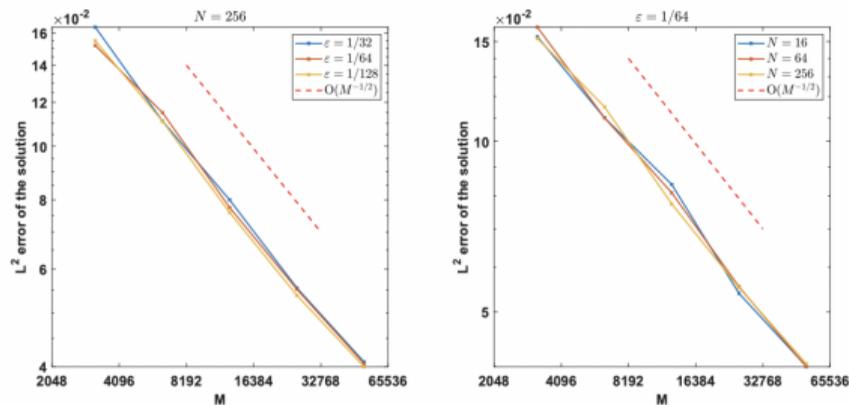

Figure 5: (**Example 1**) The L^2 error versus the sample size M, for fixed $N = 256$ with various $\epsilon = \frac{1}{32}, \frac{1}{64}, \frac{1}{128}$ (left) and for fixed $\varepsilon = \frac{1}{64}$ with various $N = 16, 64, 256$ (right).

Accuracy

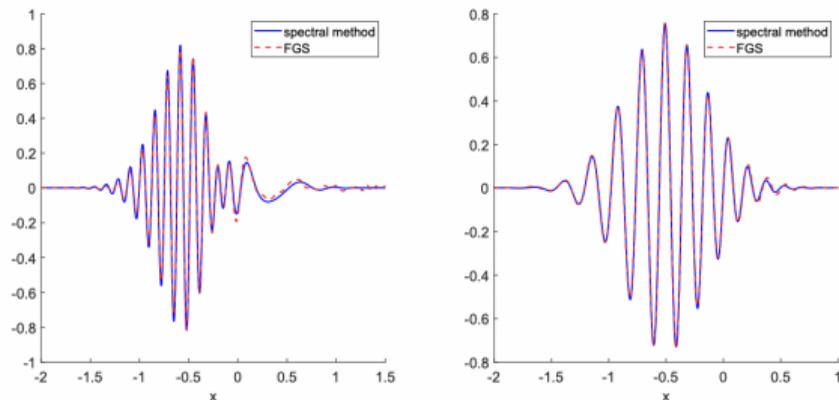Accuracy, verified by a toy case:

Figure 6: Left (Example 2): The real part of $u_0(t,x)$ at $t = 1.4$ with $\varepsilon = 0.04, N = 5, M = 16000$. Right (Example 3): The real part of $u_0(t,x)$ at $t = 1$ with $\varepsilon = 1/16, N = 5, M = 10000$.

Application of our methods

Our method could be used to explore many physics of the metal surface system, for example the finite temperature effect:
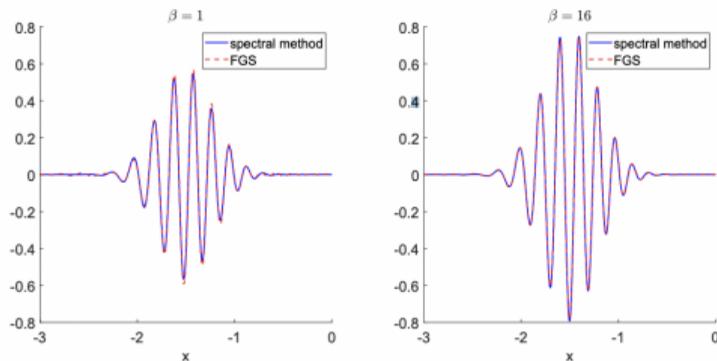

Figure: Wave function of metal orbitals.

From a physical point of view, a higher temperature (i.e. a smaller β) induces more electron transfer (bigger amplitude for wave functions of metal orbitals).
This is a very toy example, more scientific stories are under way... (ongoing work).

Discussions

Future directions of our work:

- Strong interaction limit
- Open quantum system setup
- Mathematical analysis of electronic friction

Surface hopping is a specific kind of molecular dynamics with hopping. Could we use neural networks to help do surface hopping? (Since neural networks have already been used to do molecular dynamics).

- Surface hopping + deep learning potentials?

📄 Zhen Huang, Limin Xu, and Zhennan Zhou.
Efficient frozen gaussian sampling algorithms for nonadiabatic quantum dynamics at metal surfaces.
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📄 Jianfeng Lu and Zhennan Zhou.
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Mathematics of Computation, 87(313):2189–2232, 2018.

📄 John C Tully.
Molecular dynamics with electronic transitions.
The Journal of Chemical Physics, 93(2):1061–1071, 1990.