Nonadiabatic Dynamics for Nanoscale Materials

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Ehrenfest Dynamics

Total energy of electrons and nuclei

\[ E_{\text{tot}} = \frac{M \ddot{R}}{2} + V(R(t)) + \text{Tr}_x \rho(x) H(x; R(t)) \]

is conserved

\[ \frac{dE_{\text{tot}}}{dt} = 0 \]

time-dependent Hellmann-Feynman theorem gives Newton equation

\[ M \dddot{R} = -\vec{\nabla}_R V - \text{Tr}_x \rho(x) \vec{\nabla}_R H(x; R(t)) \]

quantum force

(time-dependent Hellmann-Feynman theorem)
Why Surface Hopping Needed?

Average surface is not physical
Fewest Switches Surface Hopping


Based on probability $|c_i|^2$

(becomes effectively Ehrenfest)

Fewest Switches

based on flux, $d|c_i|^2/dt$
Fewest Switches Surface Hopping

Tully, *JCP* 93, 1061 (1990)

a.k.a., quantum-master equation with time-dependent transition rates:
- non-perturbative
- correct short time dynamics

Trajectory branching: Tully, *JCP* 93, 1061 (1990)

Within TDDFT:
Craig, Duncan, Prezhdo *PRL* 95, 163001 (2005)

Detailed balance, due to hop rejection, needed for thermodynamic equilibrium:
Parahdekar, Tully *JCP* 122, 094102 (2005)
Electron density derives from Kohn-Sham orbitals

\[ \rho(x) = \sum_p \left| \phi_p(x) \right|^2 \]

\[ |\Psi\rangle = |\phi_{1}(x_1,t)\phi_{2}(x_2,t)\ldots\phi_{N}(x_N,t)\rangle_{SD} \]

DFT functional \( H \) depends on nuclear evolution \( R(t) \)

Variational principle gives

\[ i\hbar \frac{\partial \phi_p(x,t)}{\partial t} = H\phi_p(x,t) \quad p = 1, 2, \ldots \]

Orbitals are expanded in adiabatic KS basis

\[ \phi_p(x,t) = \sum c_p^\alpha(t) \chi^\alpha(x) \]

\[ H(x;R(t))\chi^\alpha(x;R(t)) = \varepsilon^\alpha(R(t))\chi^\alpha(x;R(t)) \]

\[ i\hbar \frac{\dot{c}^\alpha}{\dot{c}^\beta} = \sum_\beta c_\beta \left( \varepsilon_\beta \delta_{\alpha\beta} - i\hbar \langle \chi^\alpha | \nabla_R | \chi^\beta \rangle \cdot \dot{R} \right) \]
Time-Domain Kohn-Sham Equations: Ehrenfest vs. Surface Hopping

- **Ehrenfest**: adiabatic KS basis can be viewed as *numerical representation*
  

  main challenge – evaluation of NA coupling

- **Surface Hopping**: requires definition of “states” for hopping;
  KS basis gives *0th order adiabatic states*

Craig, Duncan, Prezhdo *PRL* **95**, 163001 (2005)
Surface Hopping in Many-Body Kohn-Sham Basis
Craig, Duncan, Prezhdo Phys. Rev. Lett. 95, 163001 (2005)

\[ | \varphi_a \varphi_b \cdots \varphi_p \rangle = \sum_{j \neq k \neq \cdots \neq l}^{N_e} C_{j \cdots l}(t) | \tilde{\varphi}_j \tilde{\varphi}_k \cdots \tilde{\varphi}_l \rangle \]

\[ i\hbar \frac{\partial}{\partial t} C_{q \cdots v}(t) = \sum_{a \cdots p}^{N_e} C_{a \cdots p}(t) \left[ E_{q \cdots v} \delta_{aq} \cdots \delta_{pv} + D_{a \cdots p; q \cdots r} \cdot \dot{\mathbf{R}} \right]. \]

\[ D_{a \cdots p; q \cdots r} \cdot \dot{\mathbf{R}} = -i\hbar \langle \tilde{\varphi}_a \tilde{\varphi}_b \cdots \tilde{\varphi}_p | \frac{\partial}{\partial t} | \tilde{\varphi}_q \tilde{\varphi}_r \cdots \tilde{\varphi}_v \rangle \]

\( D \) is non-zero only if different in one orbital, very sparse

Multiple excitons in \( \text{Si}_{29}\text{H}_{24} \): 25 VB and 24 CB orbitals

\( 98,101 \text{ states} = \text{ground}+600\text{SE}+97,500\text{DE} \)

Hyeon-Deuk, Prezhdo Nano Lett. 11, 1845 (2011); ACS Nano 6, 1239 (2012)
Why Surface Hopping in Kohn-Sham Representation Works


- KS close to LR/TDDFT (in contrast to HF and CIS)
- No bond-breaking, conformational changes.
- Many-electrons, single excitation small perturbation
- Averaging over many initial conditions and pathways
Classical Path Approximation
Useful for Nanoscale Systems

1. DFT functional (Hamiltonian) depends on ground state density, even though the true density does evolve
2. Ground and excited state nuclear trajectories are similar

Justification:
1. Excitation of 1 or 2 electrons out of hundreds does not change density and forces much
2. Thermal fluctuations are larger than differences in equilibrium geometries of ground and excited electronic states

Key Advantages – allows use of ground state trajectory, while still performing TDKS & SH for electronic state populations – electronic and nuclear timestep separation (1as & 1fs)
Theoretical Questions

Perspective: *JPC Lett.* 7 2100 (2016)

- How to couple quantum and classical dynamics? quantum back-reaction on classical variables
- Can one do better than classical mechanics for nuclear motion? zero-point motion, tunneling, branching, loss of coherence

Decoherence induced surface hopping (DISH) *JCP* 137, 22A545 (2012)
Coherence penalty functional (CPF) *JCP* 140, 194107 (2014)
Global flux surface hopping (GFSH) *JCTC* 10, 3598 (2014)
Second quantized surface hopping (SQUASH) *PRL* 113, 153003 (2014)
FSSH in Liouville space *JPCL* 6, 3827 (2015)
GFSH in Liouville space, *JCP-Rapid* 143, 191102 (2015)
FSSH probability depends on NA coupling, which diverges

\[ d_{ij}^k = \frac{\alpha p_{ki} p_{kj}}{E_j - E_i} \]

Linjun Wang pointed out that in FSSH sum of all hoping probabilities is

\[ \sum_{i}^N g_i = dt \cdot \frac{-d(c_a^* c_a) / dt}{c_a^* c_a} \]

Obtains problematic probability

\[ g_j = \sum_{i}^N g_i - \sum_{i\neq j}^N g_i \]

One tests if this is true (self-consistency).
Self-Consistent FSSH


FSSH: $dt=0.1\text{fs}$; SC-FSSH: $dt=1\text{fs}$

Population of right-most site

$$H = H_e + H_n$$

$$H_n = \frac{1}{2} \sum_i \left( K \xi_i^2 + m v_i^2 \right)$$

$$H_e = \sum_{i}^{N-1} J |i\rangle\langle i+1| + |i+1\rangle\langle i| + \sum_{i}^{N} \alpha |i\rangle\langle i| $$
Self-Consistent FSSH


FSSH: $dt=0.0001\text{fs}$; SC-FSSH: $dt=1\text{fs}$

Population of right-most site

\[ H = H_e + H_n \]

\[ H_n = \frac{1}{2} \sum_i \left( Kx_i^2 + mv_i^2 \right) \]

\[ H_e = \sum_{i}^{N-1} J|i\rangle\langle i+1| + |i+1\rangle\langle i| + \sum_{i}^{N} \alpha x_i |i\rangle \langle i| \]
Auger Processes in Nanomaterials

Electron-hole energy exchange is a 2-particle process, has super-exchange channel

Also:
- Multiple-exciton generation and recombination
- Singlet fission (via intermediate charge transfer states)
- Auger-assisted electron transfer

Top channel is allowed by Schrodinger equation level, but forbidden in FSSH due to hop rejection
Global Flux Surface Hopping


Re-sum all fluxes
Then $1 \rightarrow 2$ and $2 \rightarrow 3$ cancel and $1 \rightarrow 3$ appears

$V_{11}(x) = 0$, $V_{22}(x) = 0.01$, $V_{33}(x) = 0.005$

$V_{12}(x) = V_{21}(x) = 0.001e^{-x^2/2}$

$V_{23}(x) = V_{32}(x) = 0.01e^{-x^2/2}$

$V_{13}(x) = V_{31}(x) = 0$

$k = 4-7$ super-exchange regime
Auger Electron-Hole Relaxation and Hole Trapping in CdSe QD


HDT ligated Cd$_{33}$Se$_{33}$

- Hole is localized on surface, ligand tail not important
- Bottleneck not achieved: hole trapping is too slow, not because hole still couples to electron

FSSH underestimates rate by a factor of 4 in this case
FSSH in Liouville Space


\[ \frac{d|\psi(t)\rangle}{dt} = \frac{1}{i\hbar} \hat{H}|\psi(t)\rangle, \quad \hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)| \]

\[ \frac{d\hat{\rho}(t)}{dt} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}] \]

\[ \frac{d|\rho\rangle}{dt} = \frac{1}{i\hbar} \hat{L}|\rho\rangle \]

One trajectory at a time
Normal FSSH

Questions for coherence states, \( i \neq j \)

- Energy: \( E_{ij} = (E_{ii} + E_{jj})/2 \), similar to quantum-classical Liouville
- Interpretation of trajectories on \( ij \): assign half to \( ii \), half to \( jj \)
- Direction of velocity rescaling for transition \( ij \rightarrow kl \):
  add NA coupling vectors \( NA_{ik} + NA_{jl} \)
• FSSH in diabatic representation is better than adiabatic
• Big improvement in adiabatic using Liouville (better treatment of coherence)
Super-exchange is obtained
Decoherence & Quantum Zeno Effect


With decoherence: \[ P_{12} = |T_{12}|^2 + |T_{12}|^2 + \ldots \]
Without decoherence \[ P_{12} = |T_{12} + T_{12} + \ldots|^2 \]

Decoherence makes transitions less likely
\[ 0.1^2 + 0.1^2 < (0.1 + 0.1)^2 \]

atom

alive
cat
dead
Stochastic Mean-Field
(decoherence gives branching)


No ad hoc expressions for hopping probability

Cat Density

quantum Brownian motion

\[ d\Psi = -iH\Psi dt - \frac{\gamma}{2} L^+ L\Psi dt + \sqrt{\gamma} L\Psi dW \]

friction noise
Decoherence Induced Surface Hopping (DISH)


Evolve in an adiabatic state.
Hop when a decoherence event occurs.
Use normal quantum probabilities.
Rescale velocity as before in SH.

Advantages
1. Includes decoherence
2. Gives branching
3. Nuclear evolution in pure states

Corresponds to a piece-wise continuous stochastic Schrödinger equation
Coherence Penalty Functional


- Retain computational efficiency of Ehrenfest – no stochastic sampling: 1 trajectory, ordinary differential equations
- Penalize development of coherence

\[
\frac{i\hbar}{\partial t} \frac{\partial c_i(t)}{\partial t} = \sum_j \left[ E_i(R(t)) \delta_{i,j} - i\hbar P M d_{ij} \right] c_j(t)
\]

\[
H = \sum_i \frac{E_i}{2\hbar} (q_i^2 + p_i^2) - \frac{P}{M} \sum_{i,j} d_{ij} p_i q_j
\]

\[
q_i = \text{Re}(c_i), \quad p_i = \text{Im}(c_i)
\]

\[
\dot{q}_i = -\frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}
\]
Coherence Penalty Functional


- Retain computational efficiency of Ehrenfest – no stochastic sampling: 1 trajectory, ordinary differential equations
- Penalize development of coherence

\[
\begin{align*}
\frac{i\hbar}{\partial t} & \frac{\partial c_i(t)}{\partial t} = \sum \left[ E_i (R(t)) \delta_{i,j} - i\hbar \frac{P}{M} d_{ij} \right] c_j(t) \\
H & = \sum_i \frac{E_i}{2\hbar} (q_i^2 + p_i^2) - \frac{P}{M} \sum_{i,j} d_{ij} p_i q_j \\
\tilde{H} & = H + \sum_{i \neq j} \lambda_{ij} (q_i^2 + p_i^2) (q_j^2 + p_j^2) \\
(q_i^2 + p_i^2)(q_j^2 + p_j^2) & = |c_i^* c_j|^2
\end{align*}
\]

\[q_i = \text{Re}(c_i) \quad p_i = \text{Im}(c_i)\]

\[
\begin{align*}
\dot{q}_i & = -\frac{\partial H}{\partial p_i} \\
\dot{p}_i & = -\frac{\partial H}{\partial q_i}
\end{align*}
\]

states with large coherence are energy maxima

coherence measure \(\lambda_{ij}\) - decoherence rate
Phonon Bottleneck in CdSe QD


**Cd<sub>33</sub>Se<sub>33</sub>**

**Cd<sub>33</sub>Se<sub>33</sub>/Zn<sub>78</sub>S<sub>78</sub>**

d~2.0 nm

Experiment: 1 ns


Calculation: 0.7 ns  
without decoherence: 0.003 ns
PYXAID: PYthon eXtension of Ab Initio Dynamics


*ibid.* **10**, 789 (2014)

Python interfaced with Quantum Espresso, VASP

In DFTB+: Pal, Trivedi, Akimov, Aradi, Frauenheim, Prezhdo

*JCTC* **12** 1436 (2016)

Fragment approach in Gamess: Negben, Prezhdo

*JPC A* **120** 7205 (2016)

Overview of new methods
Perspective Article in
*JPC Lett.* **7** 2100 (2016)
Why is there no Marcus inverted region?

\[ k(r) \propto e^{-\frac{[\Delta G(r)+\lambda]^2}{4\lambda RT}} \]
Auger-assisted ET


- Normally, excess energy goes to phonons
- In QDs, hole excitation accompanies ET
- Then, hole transfers energy to phonons
Plasmon-driven ET


– traditional view

– our calculation
Experimental Evidence


Quantum yield is independent of excitation energy, in contrast to traditional model.

$$QY(\omega) = \frac{(h\omega - E_B)^2}{4E_F h\omega}$$
Gold Rods on MoS$_2$

Long, Fang, Prezhdo & co-workers *Chem*, accepted

Traditional mechanism holds

Coupling is weak:
- Plasmon-like excitations have no density on MoS$_2$
- MoS$_2$ is fully chemically saturated

Au pyramid on TiO$_2$  
Au pyramid on MoS$_2$  
Au rod on MoS$_2$
Hot Luminescence in FAPbBr$_3$


- Organic-inorganic perovskite luminesces at both low (>1ns) and high (200ps) energies
- Purely inorganic perovskite emits only at low energy
- Origin of high energy luminescence?
High energy: delocalized (free) carriers, larger coupling, faster decay
Low energy: localized (polaron) carriers, smaller coupling, slower decay

Different “chromophores” can also arise from ion rich phases, electrically ordered phases, grain boundaries, defects, etc.
In Lieu of Conclusions

- **Nonadiabatic MD with TDDFT**
  - Classical path approximation for SH
  - Self-consistent FSSH (trivial crossings)
  - Global flux surface hopping
  - Surface hopping in Liouville space
  - Decoherence induced surface hopping
  - Coherence penalty functional

- **Applications**
  - Phonon-bottleneck in QDs
  - Auger assisted ET
  - Plasmon-driven ET
  - Hot luminescence in perovskites