Nonadiabatic Molecular Dynamics with Kohn-Sham DFT: Modeling Nanoscale Materials

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Outline

- Nonadiabatic MD with Kohn-Sham DFT
  - Advantages & Validity
  - Quantum Backreaction & Branching (Nuclear Dynamics)
  - Decoherence & Zero-Point Energy

- Carbon Nanotubes & Nanoribbons
  - Luminescence Quenching
  - Singlet-Triplet Transitions
  - Structural Defects
Adiabatic vs. Nonadiabatic MD

Nonadiabatic MD: Coupling between potential surfaces opens channels for system to change electronic states.

transition allowed

weak coupling

strong coupling

electrons treated quantum-mechanically

nuclei treated classically
Time-Domain DFT for Nonadiabatic Molecular Dynamics

Electron density derives from Kohn-Sham orbitals

\[ \rho(x) = \sum_p |\varphi_p(x)|^2 \]

\[ |\Psi\rangle = |\varphi_p(x_1,t)\varphi_q(x_2,t)\cdots\varphi_v(x_N,t)\rangle_{SD} \]

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

Variational principle gives

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

Orbitals are expanded in adiabatic KS basis

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

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

\[ i\hbar \dot{c}_\alpha = \sum_\beta c_\beta \left( \varepsilon^\beta \delta_{\alpha\beta} - i\hbar \langle \chi^\alpha | \nabla_R | \chi^\beta \rangle \cdot \dot{R} \right) \]
\[
|\varphi_a \varphi_b \cdots \varphi_p\rangle = \sum_{j \neq k \neq \cdots \neq l}^{N_e} C_{j \cdots l}(t) |\tilde{\varphi}_j \tilde{\varphi}_k \cdots \tilde{\varphi}_l\rangle
\]

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

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

non-zero only if different in one orbital
Open Theoretical Questions

✓ How to couple quantum and classical dynamics?
  quantum influence on classical trajectory

✓ Can one do better than classical mechanics for nuclear motion?
  zero-point motion, tunneling, branching, loss of coherence
Nuclear Evolution: Ehrenfest


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

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

quantum force
Nuclear Evolution: Surface Hopping

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)
1. KS excitations close to LR/TDDFT (in contrast to HF and CIS)
2. No bond-breaking, conformational changes, etc.
3. Many-electron systems, single excitation is a small perturbation
4. Averaging over many initial conditions and pathways

Electron Transfer Example:
KS and LR agree better for PW91 (pure DFT) than B3LYP (hybrid).
Small Molecule With Isomerization

Tapavicza, Tavernelli, Rothlisberger

KS/TDDFT works well even in this case?!
Schroedinger Cat and Decoherence

System - radioactive atom; Bath - cat

In Nanomaterials
System - electrons, spins; Bath - phonons
Franck-Condon Factor and Decoherence

\[ \sum_{\{B_2\}} \left| \langle B_1 | B_2 \rangle \right|^2 \delta(E_1 - E_2) \]

\[ = \int e^{i(E_1 - E_2)t/\hbar} \langle B_1(t) | B_2(t) \rangle \, dt \]

Bath (vibrational) wave functions diverge

This affects evolution of (electronic) system
Decoherence and Surface Hopping

Reduced density matrix:

\[
\begin{pmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{pmatrix} \rightarrow
\begin{pmatrix}
\rho_{11} & \rho_{12}\langle B_2 | B_1 \rangle \\
\rho_{21}\langle B_1 | B_2 \rangle & \rho_{22}
\end{pmatrix}
\]

\[\rho = \langle B | \rho^{S-B} | B \rangle\] on decoherence time scale

\[\rho_{12} \rightarrow 0\]

hopping probability \[P_{12} \sim \rho_{12}\]
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 \[ |0.1|^2 + |0.1|^2 < |0.1 + 0.1|^2 \]
Stochastic Mean-Field (SMF)


Stochastic Schrodinger equation in place of regular SE in Ehrenfest

\[ \langle d\Psi \rangle = -iH\Psi dt - \gamma \frac{1}{2} \left( L^*L\Psi \right) dt + \sqrt{\gamma} L\Psi dW \]

\( L \) – system-bath interaction
\( \gamma \) – decoherence rate

**Advantages**

1. Includes decoherence
2. Gives branching
3. Infinitesimal velocity rescalings
Decoherence Induced Surface Hopping (DISH)

- Evolve in an adiabatic state.
- Hop when a decoherence event occurs.
- Rescale velocity as before in SH.

Advantages

1. Includes decoherence
2. Gives branching
3. Nuclear evolution in pure states
Quantized Hamilton Dynamics


\[
\frac{d \langle q \rangle}{dt} = \langle p \rangle; \quad \frac{d \langle p \rangle}{dt} = -\langle q \rangle - \langle q^2 \rangle
\]

but \[\langle q^2 \rangle \neq \langle q \rangle \langle q \rangle\] and

\[
\frac{d \langle q^2 \rangle}{dt} = \langle pq + qp \rangle \equiv 2 \langle pq \rangle_s
\]

\[
\frac{d \langle pq \rangle_s}{dt} = \langle p^2 \rangle - \langle q^2 \rangle - \langle q^3 \rangle
\]

the infinite hierarchy is terminated by a closure

\[\langle q^3 \rangle \approx 3 \langle q^2 \rangle \langle q \rangle - 2 \langle q \rangle^3\]
Harmonic Oscillator in Mapped QHD-2

\[ \hbar' \rightarrow \hbar' \]

\[ \text{mass} \rightarrow \text{mass} \]

QHD-2 takes care of zero-point-energy
Metastable Cubic Potential in Mapped QHD-2

\( h\hbar \) mass

QHD-2 gives tunneling

\( \hbar mass \)
Quantum-Classical Lie Bracket


\[
[A,B]_{qc} = -\frac{i}{\hbar}[A,B] + \frac{1}{2}(\{A,B\} - \{B,A\})
\]

quantum commutator + classical Poisson bracket

starting point for many methods:
Ehrenfest, multiconfiguration quantum-classical

problems with Jacobi identity:

\[
[[A,B]_{qc},C]_{qc} + [[B,C]_{qc},A]_{qc} + [[C,A]_{qc},B]_{qc} = 0
\]

Alternative definition:

\[
[A,B]_{qc} = -\frac{i}{\hbar}[A,B] - i \left. \frac{\partial[A,B]}{\partial \hbar} \right|_{\hbar=0}
\]
Bohmian Quantum-Classical Mechanics


\( \psi(r,t) = \sqrt{\rho(r,t)} e^{iS(r,t)/\hbar} \) gives Newton eq. \( m\ddot{r} = -\nabla_r \left[ V(r) + Q(r) \right] \)

with non-local quantum potential \( Q(r) = -\frac{\hbar^2}{2m} \frac{\nabla^2_r \sqrt{\rho(r)}}{\sqrt{\rho(r)}} \)

Quantum (r) – Classical (R)

\( M\ddot{R} = -\nabla_R \left[ V_R(R) + V_{rR}(r,R) \right] \) drop \( Q(R), Q(r,R) \)

\( m\ddot{r} = -\nabla_r \left[ V_r(r) + V_{rR}(r,R) + Q(r) \right] \)

Advantage

Branching
Highly simplified representation of O$_2$ interacting with Pt


\[
H(q,Q) = T_q + T_Q + V_q(q) + V_q(Q) + V_{qQ}(q,Q)
\]

\[
V_q(Q) = \frac{M\Omega^2 Q^2}{2}
\]

\[
V_q(q) = a(e^{-2b(q-c)} - 2e^{-b(q-c)})
\]

\[
V_{qQ}(q,Q) = Ae^{-B(q-Q)}
\]

1. Bohmian approach fixes asymptotic behavior
2. Bohmian and MF err at short times due to ZPE
KS-SH works well with nanoscale materials, even small molecules
- KS excitations are close to LR/TDDFT (in contrast to HF and CIS)
- Usually no bond-breaking, conformational changes, etc.
- Many-electron systems, single excitation is a small perturbation
- Averaging over many initial conditions and pathways

FSSH gives (approx.) detailed balance, essential in applications

Decoherence effects are essential in many-atom systems

Stochastic Mean-Field (SMF) and Decoherence Induced SH (DISH) “derive” a SH algorithm from decoherence

Zero-point-energy, tunneling and decoherence are included in Quantized Hamilton Dynamics (QHD)

Bohmian quantum-classical formulation naturally gives branching
"The beauty of this is that it is only of theoretical importance, and there is no way it can be of any practical use whatsoever."
"The beauty of this is that it is only of theoretical importance, and there is no way it can be of any practical use whatsoever."
\[ \overrightarrow{C_h} = n\overrightarrow{a_1} + m\overrightarrow{a_2} \]

Metallic (red dots) if \( n-m = 0 \) (mod 3)

Zigzag
\( \theta = 0 \)

Chiral
\( \theta = 30 \)

Armchair
Electron-Phonon Relaxation and Phonon Modes

Ma, Valkunas, Dexheimer, Bachilo, Fleming

*PRL* 94, 157402 (2005)

High frequency optical G-modes

Low frequency acoustic radial breathing modes (RBM)

* – graphite background
Luminescence Quenching and Ground State Recovery


Multiple luminescence quenching timescales in literature:

\sim 20\text{ps}, 200\text{ps} and 10\text{ns}

Luminescence yields are generally low \textless 1\%, i.e. quenching is efficient
Defects

Stone-Wales defect
bond rotation

7557 defect
C$_2$ inserts across hexagon

transition
density
Defects and Density of States

Ideal (6,4) tube

bond rotation
(Stone-Wales defect)

$C_2$ inserts across hexagon
(7557 defect)

Defect states both in the gap and inside bands

$C_2$ addition creates a distinct state
Decoherence Times & Fluorescence Linewidth

<table>
<thead>
<tr>
<th>Tube</th>
<th>$\tau$ (fs)</th>
<th>$A$</th>
<th>$\omega$ (fs$^{-1}$)</th>
<th>Linewidth (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,4)</td>
<td>59.6</td>
<td>0.086</td>
<td>0.32</td>
<td>11.0</td>
</tr>
<tr>
<td>(8,4)</td>
<td>51.2</td>
<td>0.061</td>
<td>0.30</td>
<td>12.8</td>
</tr>
<tr>
<td>(7,0)</td>
<td>24.5</td>
<td>-</td>
<td>0</td>
<td>26.9</td>
</tr>
<tr>
<td>7557</td>
<td>18.4</td>
<td>0.88</td>
<td>0.12</td>
<td>35.8</td>
</tr>
<tr>
<td>SW</td>
<td>48.0</td>
<td>0.062</td>
<td>0.25</td>
<td>13.7</td>
</tr>
<tr>
<td>50K</td>
<td>955</td>
<td>0.0056</td>
<td>0.30</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Experiment

10 meV (suspended)
25 meV (surfactant)

Defects create stronger electron-phonon coupling and can be detected by broader lines

$$f(t) = \exp\left(\frac{-t}{\tau}\right) \frac{1 + A \cos(\omega t)}{1 + A}$$
Active Phonon Modes

(8,4)  
n-m=1 mod 3

(6,4)  
n-m=2 mod 3

(7,0)  
n-m=1 mod 3

SW  7557
Fluorescence Decay (FSSH)

Defects notably decrease lifetime, explain multiple decay components.

No T-dependence: cancellation of changes in NA coupling and decoherence.
Comparison of FSSH with DISH

FSSH and DISH give similar results
DISH uses decoh. as SH algorithm
Poisson and fixed coh. times similar
Triplets & Phosphorescence Decay

Jablonsky diagram

- **S_0**
- **S_1**
- **T_1**
- **NA**
- **NA + SO**

**Triplets provide new decay pathway**

Spin-Orbit (SO) coupling is on the same order as NA coupling, but SO coupling fluctuates less.
Triplets & Phosphorescence Decay

Triplets decay ~5 times more slowly than singlets

Decay rate is proportional to square of SO coupling and inverse energy gap

Larger tubes – weaker coupling (due to smaller curvature), but also smaller energy gaps

<table>
<thead>
<tr>
<th>Transition</th>
<th>Gap (eV)</th>
<th>Coupling (meV)</th>
<th>ISC Time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1-T_1$</td>
<td>0.35</td>
<td>1.0</td>
<td>362</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>62.2</td>
</tr>
<tr>
<td>$T_1-S_0$</td>
<td>1.05</td>
<td>1.0</td>
<td>1,082</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>1.0</td>
<td>1,392</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>548</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>238</td>
</tr>
</tbody>
</table>
Transition Densities

Stone-Wales defect
bond rotation

7557 defect
$C_2$ inserts across hexagon

Ideal (16,16)

7557

SW
Phonon Modes

Opposite to tubes: weaker electron-phonon coupling in defects compared to ideal ribbon
Decoherence Time & Fluorescence Linewidth

<table>
<thead>
<tr>
<th>Ribbon</th>
<th>$\tau$ (fs)</th>
<th>$\omega$ (fs(^{-1}))</th>
<th>$A$</th>
<th>$\Gamma$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(16,16)</td>
<td>23.5/25.8</td>
<td>0.259/0.257</td>
<td>0.024/0.069</td>
<td>28.0/25.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\tau_e$ (fs)</th>
<th>$\tau_g$ (fs)</th>
<th>$B$</th>
<th>$\Gamma$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7557</td>
<td>41.8/48.9</td>
<td>39.9/35.7</td>
<td>0.38/0.30</td>
<td>16.1/16.5</td>
</tr>
<tr>
<td>SW</td>
<td>69.8/57.3</td>
<td>42.3/46.0</td>
<td>0.54/0.44</td>
<td>11.5/12.9</td>
</tr>
</tbody>
</table>

Opposite to tubes: wider lines in ideal ribbon than in defects
Fluorescence Decay (FSSH)

- Defects speed up relaxation, same as in tubes.
- Ribbons decay more slowly than tubes due to smaller electronic overlaps.
Comparison of FSSH with DISH

FSSH and DISH give similar results
DISH uses decoh. as SH algorithm
Poisson and fixed coh. times similar
Apparent Paradoxes

Tubes vs. Ribbons
Ideal ribbons show wider lines, i.e. faster dephasing, but slower relaxation than ideal tubes. ??

Ideal vs. Defects
Defects accelerate relaxation in both tubes and ribbons; however, defects make lines broader in tubes and narrower in ribbons. ??

\[
k_{1 \rightarrow 2}^{qm} = \frac{2\pi}{\hbar} \left| \sum_n \frac{i\hbar}{M_n} \langle 1 | \nabla_n | 2 \rangle \langle \hat{p}_n \rangle \right|^2 
\times \prod_m |\langle i_m | f_m \rangle|^2 \delta(E_{1i} - E_{2f}) \left( \frac{1}{T} \right)
\]
Summary for Carbon Tubes/Ribbons

- Luminescence quenching – 3 timescales, as in experiment
  Tubes: 150ps ideal, 50ps defects, 700ps triplet channel
  Ribbons: 300ps ideal, 100ps defects

- Phonons: C-C stretch in ideal systems
  low frequency modes with defects

- No T-dependence by decoherence correction

- DISH and FSSH results are similar, DISH is “more justified”

*Phys. Rev. Lett.* 96 187401 (2006); *Phys. Rev. Lett.* 98 189901 (2007);
*Nano Lett.* 7 3260 (2007); *Phys. Rev. Lett.*, 100 197402 (2008);
*Nature Nanotech.* 4 190 (2008); *Pure & Appl. Chem.* 80 1433 (2008);
*Nano Lett.* 8 2126 (2008); *Nano Lett.* 8 2510 (2008);