Molecular Dynamics with Electronic Transitions

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Breakdown Of Quantum Adiabatic Theorem

The probability of changing an instantaneous energy eigenstate is significant:

1. when approached near the region of strong coupling i.e., the energy difference between two instantaneous eigenstates is small.

2. The approach velocity near the region of strong coupling is large.

What does this imply for us?

We cannot restrict ourselves with dynamics on just **a single potential energy surface(PES)** to describe host of dynamical processes!

A tough nut to crack

This leads us to the following problem:

To model non-adiabatic dynamics in various physical and chemical systems

There are multiple approaches to conquer our problem:

- Full quantum-mechanical treatment of nuclei and electrons.
- Semi-classical approaches which treats nuclei as classical particles and electrons from a quantum mechanical perspective.

However, we must consider variety of **factors** before proceeding with any of the above approach. We will adopt the second route!

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Aim & Motivation

Objective

To model non-adiabatic effects in **molecular dynamic technique** and incorporate **electronic transitions**

What is molecular dynamics?

Key Idea

The atomic motions are governed by the laws of classical mechanics subject to some multi-dimensional force field

Why molecular dynamics for atomic motions?

Potential Advantage

Molecular dynamics approach can treat atomic motions in full dimensionality

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A Primer

Two things to reconcile: **Molecular dynamics** and **electronic transitions**. What sort of a method are we aiming?

- A method which self-consistently treats classical and quantum degrees of freedom. Why?

- A method which only incorporates one kind of quantum effect(electronic transitions) while ignoring others(tunneling, zero point motion, etc). Does it even make physical sense?

Key Argument

The prominence of the two kinds of quantum effects are controlled by independent parameters!

- Practical regime: **Short wavelength limit**

Desired attributes of the method

Let us look at some properties that are desirable in any extension of MD to incorporate electronic transitions:

1. The method must be practical.
2. Trajectories must split into branches.
3. Energy conservation, momentum conservation and unitarity.
4. The method should be applicable to any number of coupled states and any number of entries into and exits from regions of strong electronic coupling.
5. The method should be applicable to any kind of electronic coupling, not just localized avoided crossings.
6. Any electronic representation should be acceptable.
7. Electronic coherence should be described correctly.
8. Limiting case: The method should be a molecular dynamics approach.
9. The method must be accurate.

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Math begins!

Let us start by considering the total Hamiltonian describing electronic and nuclear motion,

$$\mathcal{H} = T_{\mathbf{R}} + \mathcal{H}_0(\mathbf{r}, \mathbf{R}) \tag{1}$$

where $\mathcal{H}_0(\mathbf{r}, \mathbf{R})$ is the electronic Hamiltonian for a fixed nuclear coordinate $\mathbf{R}$ and $T_{\mathbf{R}}$ is the nuclear kinetic energy operator. Let us now select any **orthonormal** and **real** set of electronic basis functions $\varphi_j(\mathbf{r}; \mathbf{R})$ that depend parametrically on nuclear positions.

Time for some definitions:

$$V_{ij}(\mathbf{R}) = \langle \varphi_i(\mathbf{r}; \mathbf{R}) | \mathcal{H}_0(\mathbf{r}, \mathbf{R}) | \varphi_j(\mathbf{r}; \mathbf{R}) \rangle \tag{2}$$

non-adiabatic coupling vector

$$\mathbf{d}_{ij}(\mathbf{R}) = \langle \varphi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} \varphi_j(\mathbf{r}; \mathbf{R}) \rangle \tag{3}$$

We also assume that atomic motions can be described by some trajectory which is a continuous functions of time,

$$\mathbf{R} = \mathbf{R}(t)$$

Math continues!

Let $\psi(\mathbf{r}, \mathbf{R}, t)$ describe the electronic state at time t. We expand it in terms of basis functions,

$$\psi(\mathbf{r}, \mathbf{R}, t) = \sum_j c_j(t) \phi_j(\mathbf{r}; \mathbf{R}) \qquad (4)$$

Substituting (4) into time-dependent Schrodinger equation and taking an inner product with respect to $\phi_k(\mathbf{r}, \mathbf{R})$,

$$i\hbar \sum_j \dot{c}_j \phi_j + i\hbar \sum_j c_j \dot{\phi}_j = \sum_j c_j \mathcal{H}_0 \phi_j \qquad (5)$$

$$i\hbar \dot{c}_k + i\hbar \sum_j c_j \left\langle \phi_k \middle| \dot{\phi}_j \right\rangle = \sum_j c_j V_{kj} \qquad (6)$$

$$i\hbar \dot{c}_k = \sum_j c_j \left(V_{kj} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kj} \right) \qquad (7)$$

Math continues!

We will shift to density matrix representation $\left(a_{kj} = c_k c_j^*\right)$. (7) becomes

$$i\hbar \dot{a}_{kj} = \sum_l \left\{ a_{lj} \left[V_{kl} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kl} \right] - a_{kl} \left[V_{lj} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{lj} \right] \right\} \qquad (8)$$

The populations satisfy

The populations satisfy

$$\dot{a}_{kk} = \sum_{l \neq k} b_{kl} \qquad (9)$$

where,

$$b_{kl} = \frac{2}{\hbar} Im(a_{kl}^* V_{kl}) - 2Re(a_{kl}^* \dot{\mathbf{R}} \cdot \mathbf{d}_{kl}) \qquad (10)$$

Brainstorming - Algorithm

- Develop a procedure for self-consistent selection of the trajectory $\mathbf{R}(t)$ that best satisfies the attributes.
- A trajectory must move on a single PES, not some weighted average.
- The simplest way to achieve this is to require that the each trajectory always moves on a single PES, interrupted only by the possibility of sudden switches from one state to another that occur in infinitesimal time.

Fewest Switches

The algorithm for switching the states in an infinitesimal time minimizes the number of state switches.

Let us try to derive the stochastic algorithm for the two level(PES) case.

Switching algorithm for the two level case

Consider two levels $|1\rangle$ and $|2\rangle$ and N number of trajectories. Let a'_{11} and a'_{22} be the populations of state 1 and 2 respectively at time $t_1 = t$.

Respective trajectories at $t_1 = t$

$$N'_1 = a'_{11}N \qquad N'_2 = a'_{22}N \qquad (11)$$

After an infinitesimal time Δt, the populations change $a'_{11} \to a_{11}$ and $a'_{22} \to a_{22}$.(Assume $a_{11} < a'_{11}$)

Respective trajectories at $t_2 = t + \Delta t$

$$N_1 = a_{11}N \qquad N_2 = a_{22}N \qquad (12)$$

There are multiple ways that trajectories can switch between these two states.

Two level case(continued)

The fewest switches criterion in this case gives:

> **Probability that one of the initial N_1 trajectories would switch**
>
> $$P_{\text{switch}}(1 \to 2) = \frac{(a_{11}' - a_{11})N}{a_{11}'N} \approx \frac{\dot{a}_{22}\Delta t}{a_{11}} \qquad (13)$$

Therefore, the algorithm for switching is as follows:

- A trajectory is in state 1 at integration step i.
- The trajectory is integrated one time interval Δt, on state 1, to step i+1.
- (7) or (8) is also integrated to obtain state probabilities at step i+1, a_{11} and a_{22}.
- A uniform random number ζ between 0 and 1 is generated.
- A state will switch from 1 to 2 if

$$\frac{\Delta t b_{21}}{a_{11}} > \zeta \qquad (14)$$

Extension to multi-state case

The algorithm can be generalised to many electronic states as follows:

- **Initial conditions** to be specified for all the classical trajectories according to some classical ensemble distribution and initial electronic density matrix elements a_{kj}. Typically, only a single electronic state k will be populated.

- The classical mechanical equations are integrated by the force provided by the gradient of the current PES(V_{kk}). (7) or (8) are also integrated along this trajectory.

- The switching probability g_{kj} from the current state to all other states j are computed from density matrix elements and

$$g_{kj} = \frac{\Delta b_{jk}}{a_{kk}} \tag{15}$$

A switch from state j to k occurs if

$$\sum_{l \leq k-1} g_{jl} < \zeta < \sum_{l \leq k} g_{jl} \tag{16}$$

Algorithm(continue)

- If no switch occurs, return to step 2. If switch occurs, re-scale the velocities in the direction of non-adiabatic coupling vector(if switch between $k \to k'$, then rescaling in the direction of $\mathbf{d}_{kk'}$) to conserve the total energy.

- Return to step 2, after the re-adjustment of velocities.

1. J.Tully, J. Chem. Phys.93, 1061 (1990);

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