

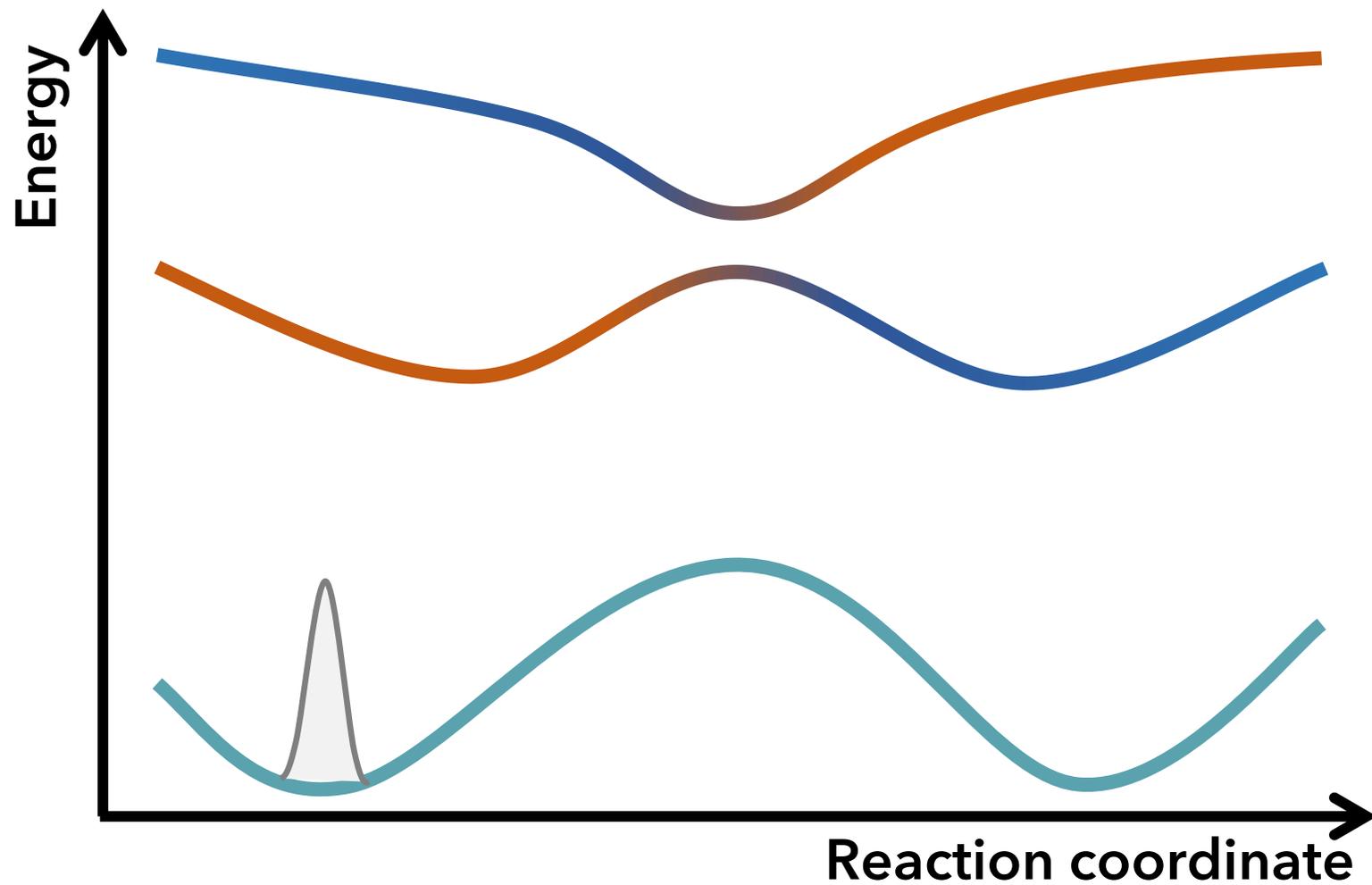


# L8 – Classical Mechanics 4

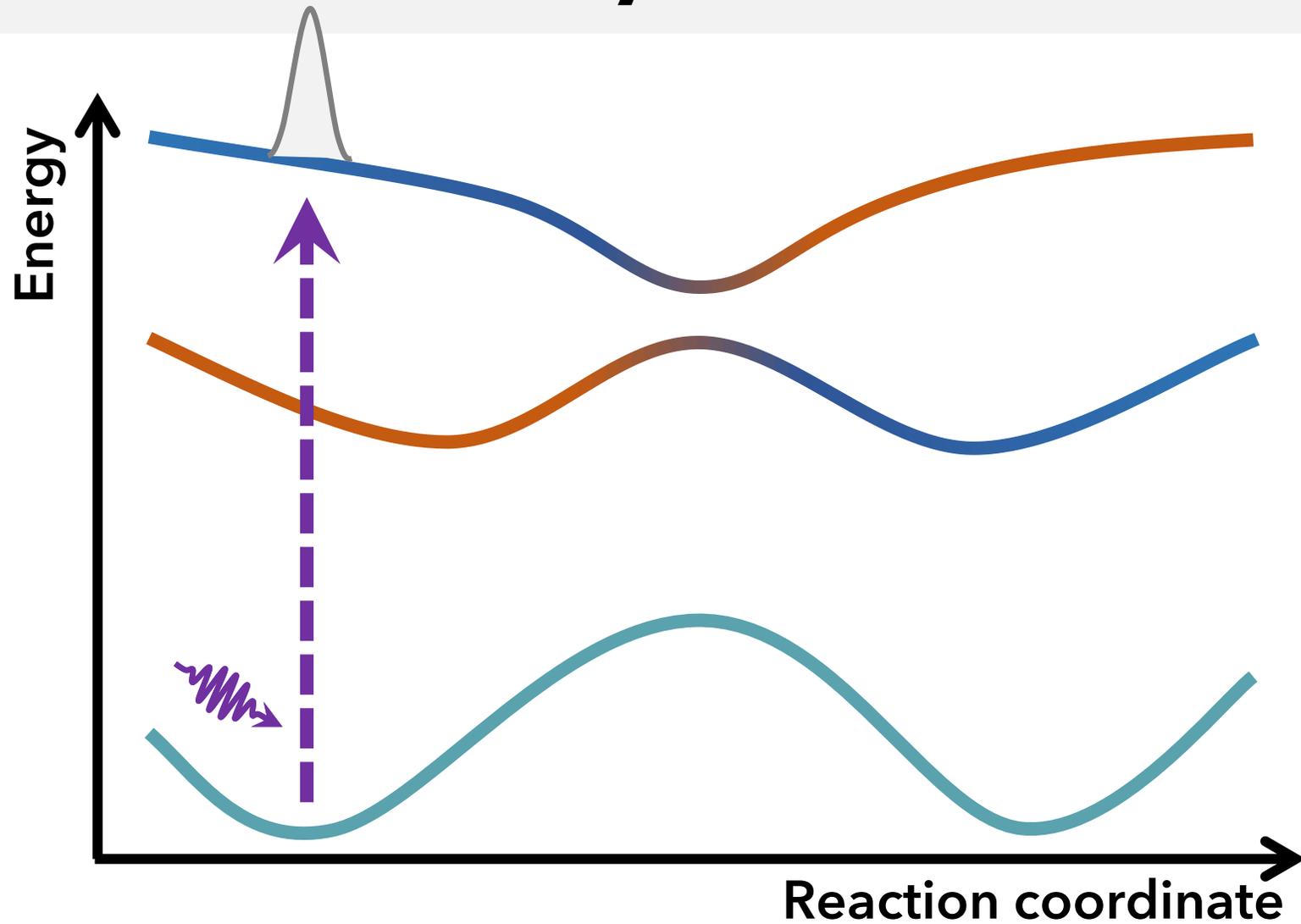
Mixed quantum classical dynamics  
Hamilton and Lagrange formulations

# Mixed Quantum-Classical Dynamics

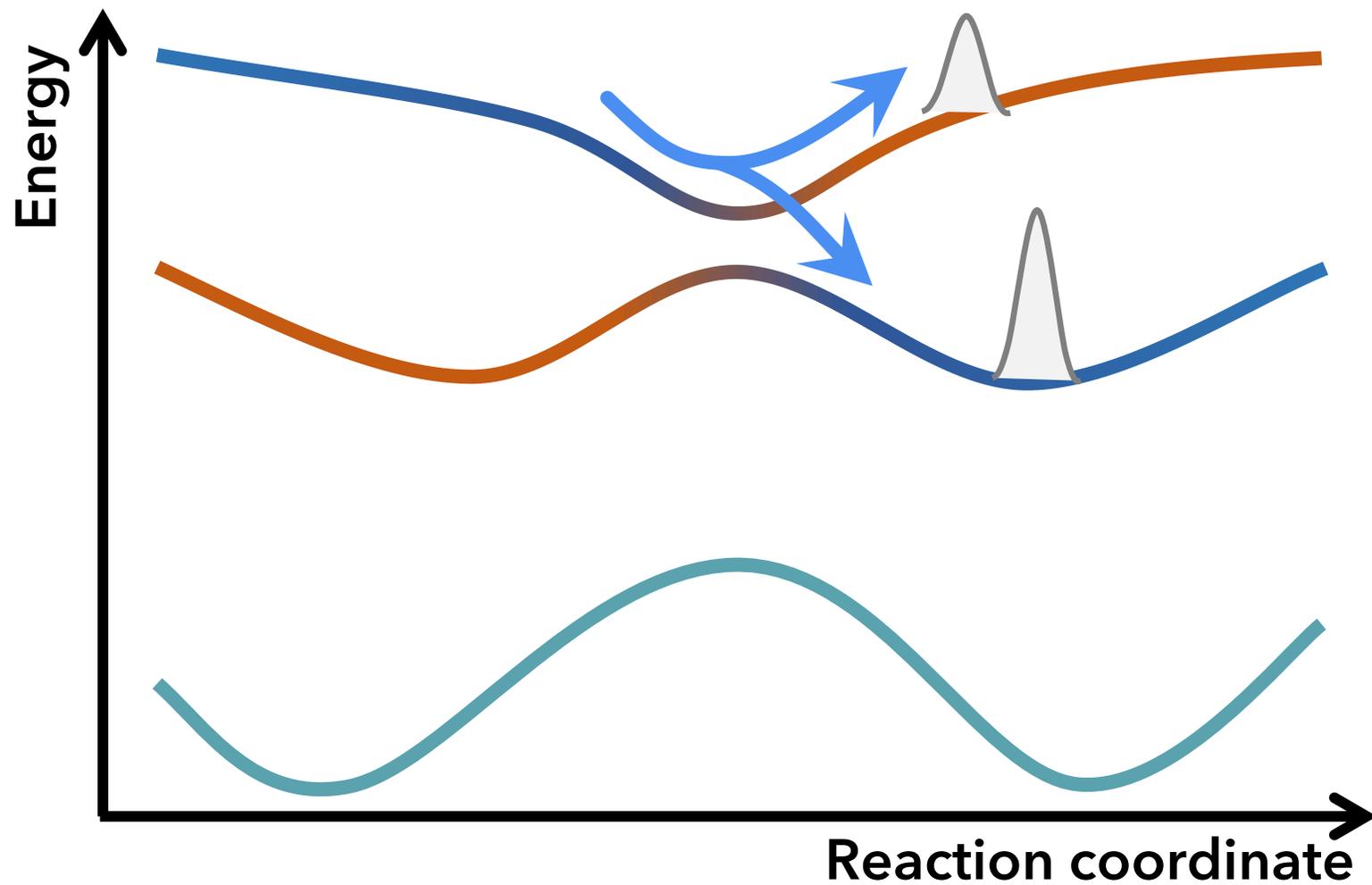
# Nonadiabatic dynamics



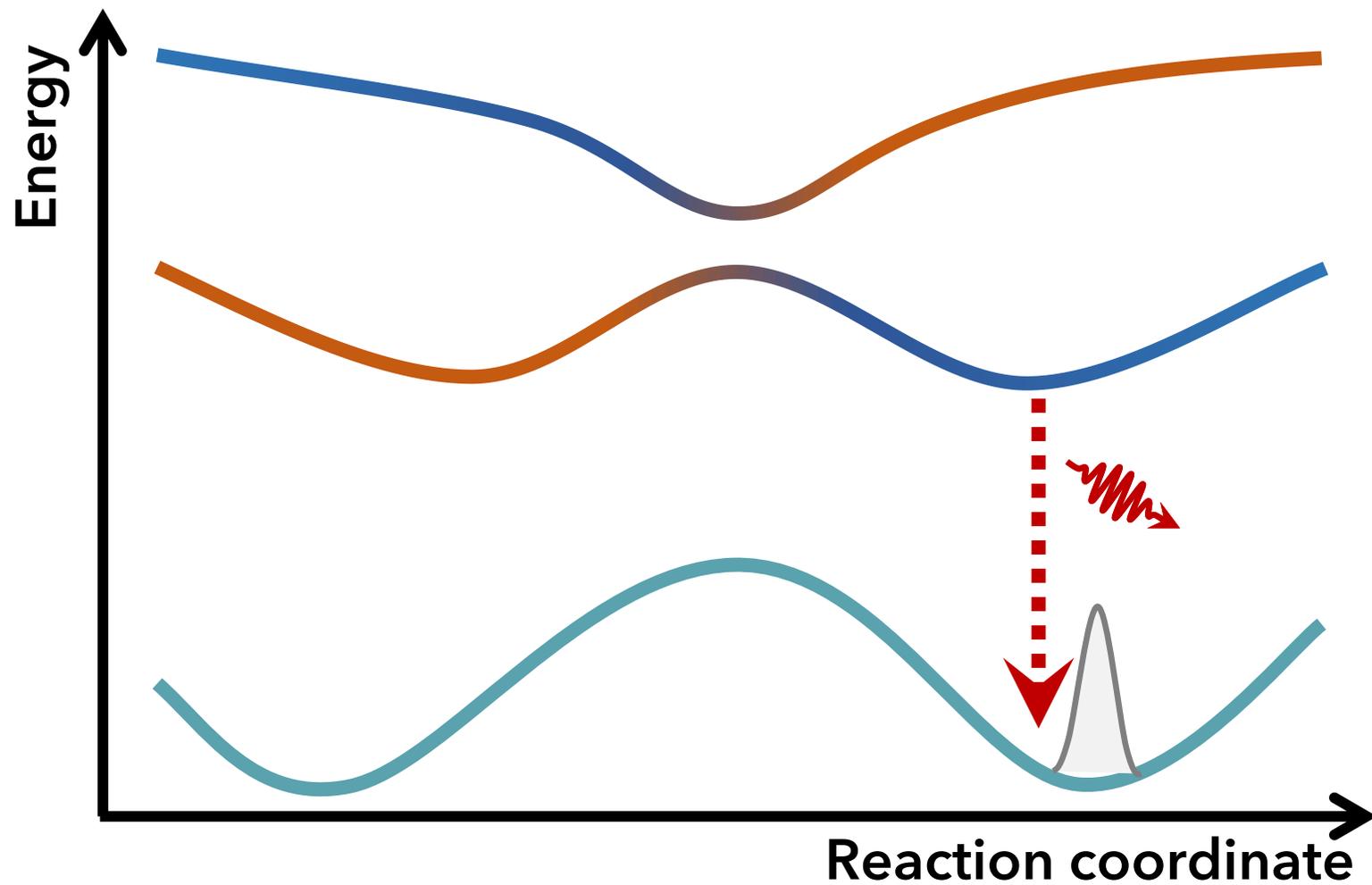
# Nonadiabatic dynamics



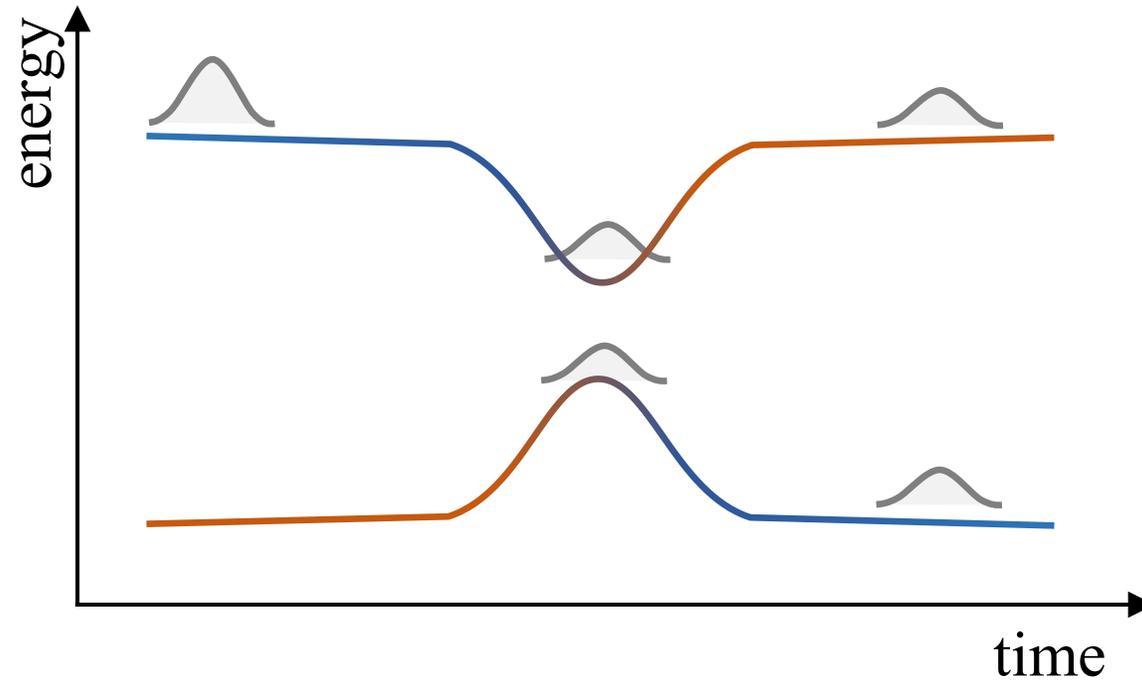
# Nonadiabatic dynamics



# Nonadiabatic dynamics



Photoinduced phenomena in molecules involve the **time evolution of the nuclear wavepacket** through a manifold of electronic states



Modeling these processes requires considering the **coupling between the nuclear and electronic motions** (**nonadiabatic** regime)

# Mixed quantum-classical (MQC) dynamics

1. Nuclei are treated via *classical trajectories*
2. Electrons are treated *quantum mechanically*
3. A nonadiabatic algorithm introduces *post Born-Oppenheimer effects*

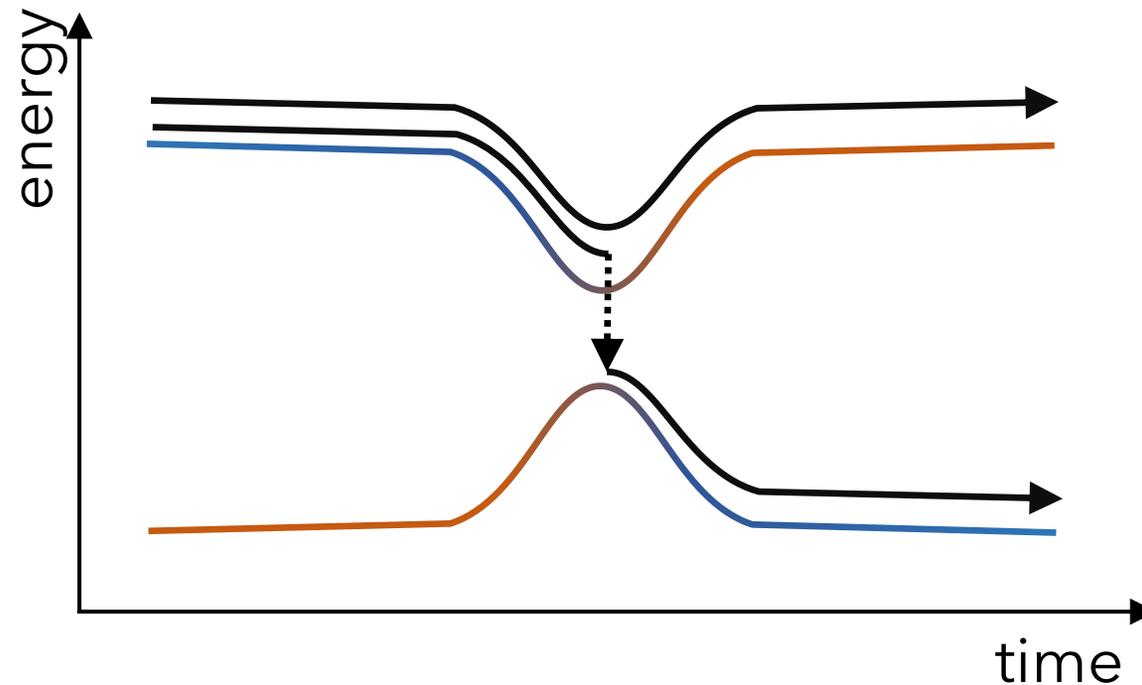
Crespo-Otero; Barbatti. *Chem Rev* **2018**, 118, 7026

Tully. *Faraday Discuss.* **1998**, 110, 407

# **Standard Methods for NA-MQC: Trajectory surface hopping**

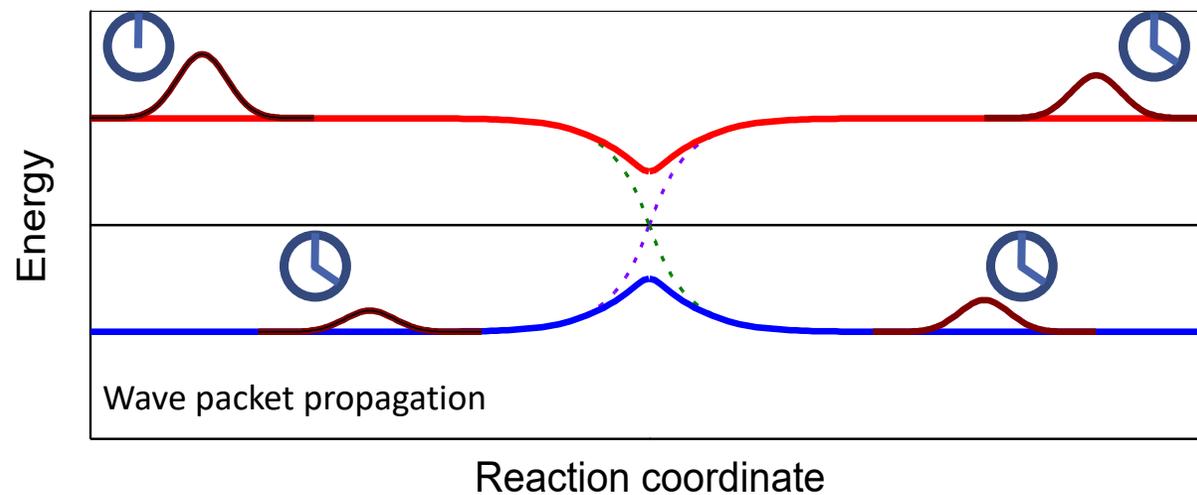
# Surface Hopping Dynamics

- Propagate nuclei via classical trajectories on a single PES
- Allow trajectory to change PES via a stochastic algorithm
- Compute hop probabilities by solving electrons quantum mechanically



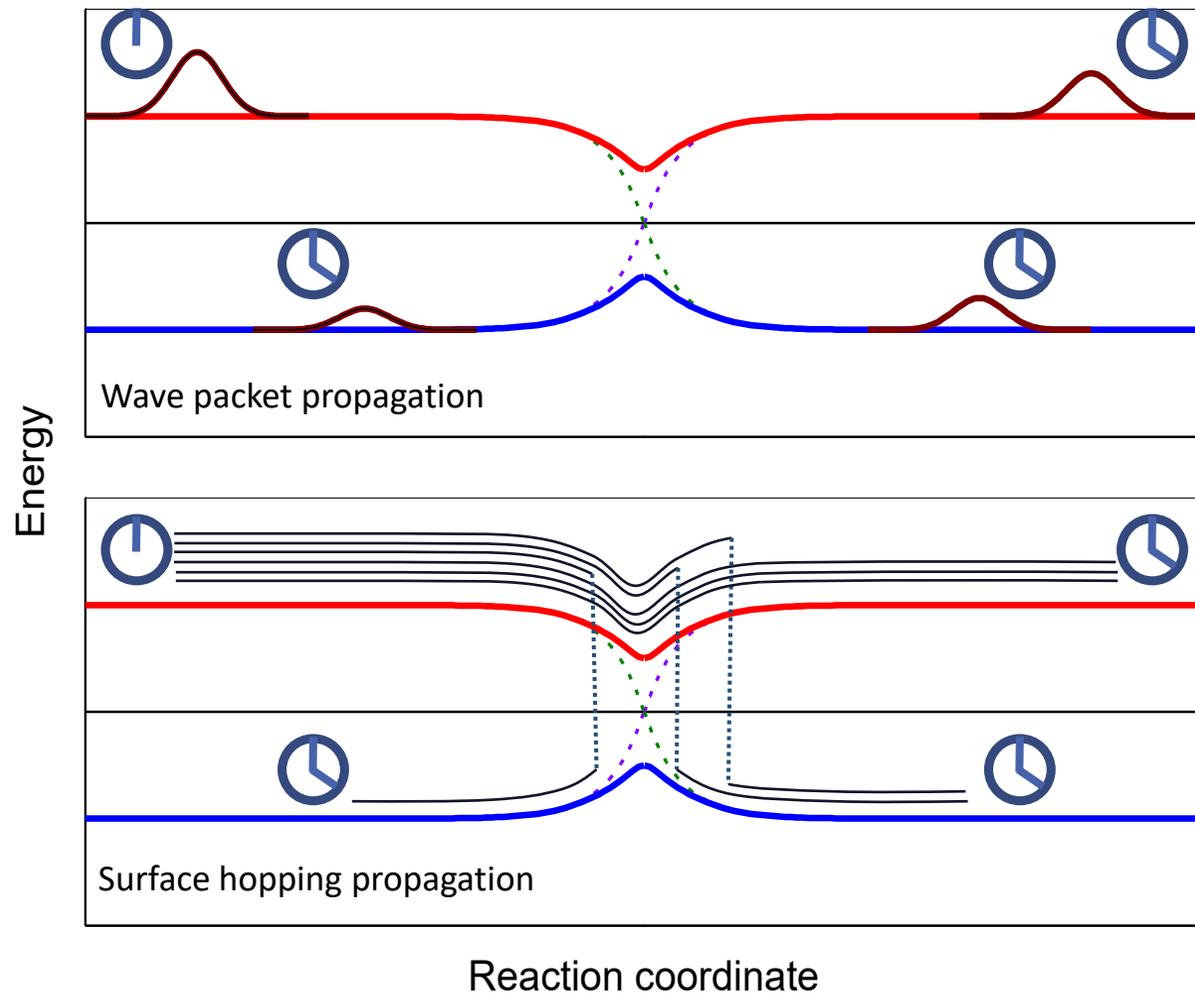
Fundamental paper:

Tully. *J Chem Phys* **1990**, 93, 1061



## MCTDH

$$\left( \hat{T}_{nuc} + E_K(\mathbf{R}) - \sum_L N_{KL}(\mathbf{R}) \right) \chi_K(\mathbf{R}) = i\hbar \frac{\partial \chi_K(\mathbf{R})}{\partial t}$$



## MCTDH

$$\left( \hat{T}_{nuc} + E_K(\mathbf{R}) - \sum_L N_{KL}(\mathbf{R}) \right) \chi_K(\mathbf{R}) = i\hbar \frac{\partial \chi_K(\mathbf{R})}{\partial t}$$

## Surface Hopping

$$\frac{d^2 \mathbf{R}_\alpha}{dt^2} = \frac{-\nabla_\alpha E_K(\mathbf{R})}{M_\alpha}$$

$$r_t \begin{cases} < P_{1 \rightarrow 0}(N_{01}) & \rightarrow K = 0 \\ \geq P_{1 \rightarrow 0}(N_{01}) & \rightarrow K = 1 \end{cases}$$

EOM: *Fewest-Switches Surface Hopping (FSSH)* (adiabatic representation):

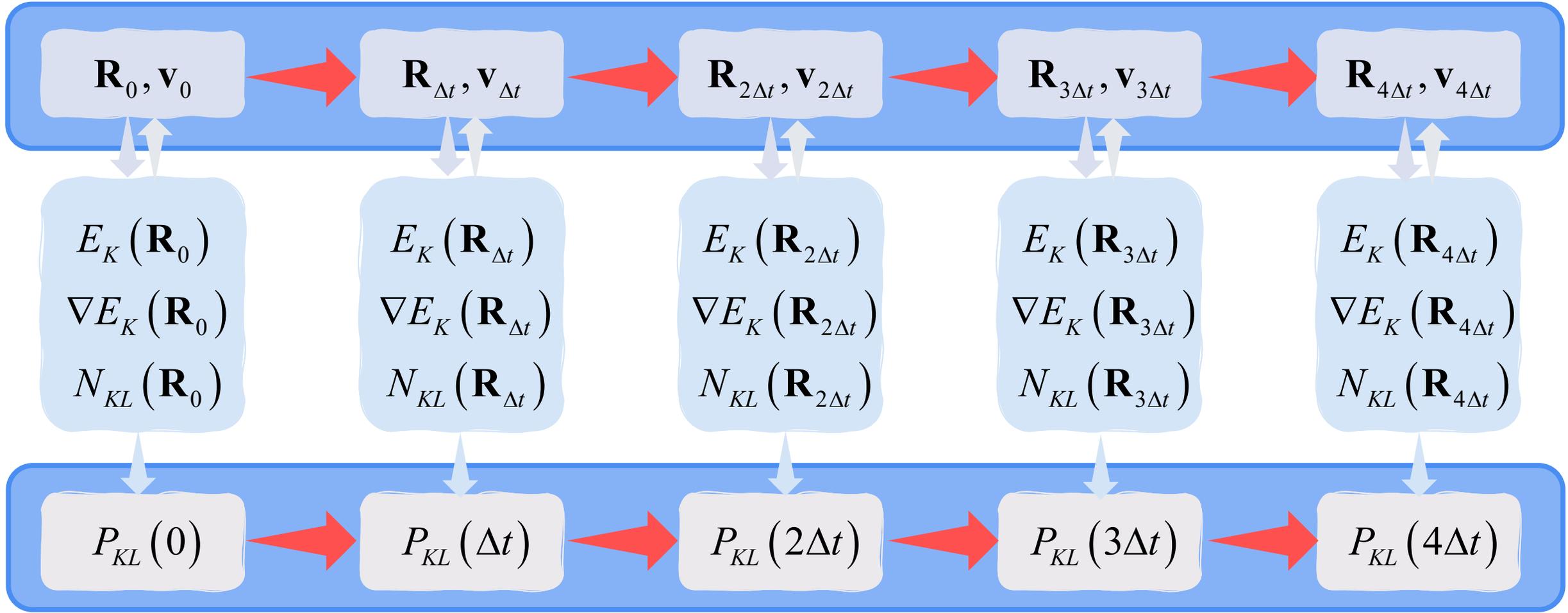
$$\frac{d^2 \mathbf{R}_\alpha}{dt^2} = \frac{1}{M_\alpha} \mathbf{F}(\mathbf{R}) \quad \mathbf{F}(\bar{\mathbf{R}}) = -\nabla_\alpha E_L$$

$$\frac{dc_J}{dt} = \sum_K -c_K \left( \frac{i}{\hbar} E_K + \sigma_{JK} \right) \quad \sigma_{JK}(\mathbf{R}) \equiv \left\langle \psi_J \left| \frac{\partial \psi_K}{\partial t} \right. \right\rangle$$

$$P_{L \rightarrow J}^{FSSH} = \max \left[ 0, \frac{-2\Delta t}{|c_L|^2} \text{Re}(\sigma_{LJ} c_J c_L^*) \right]$$

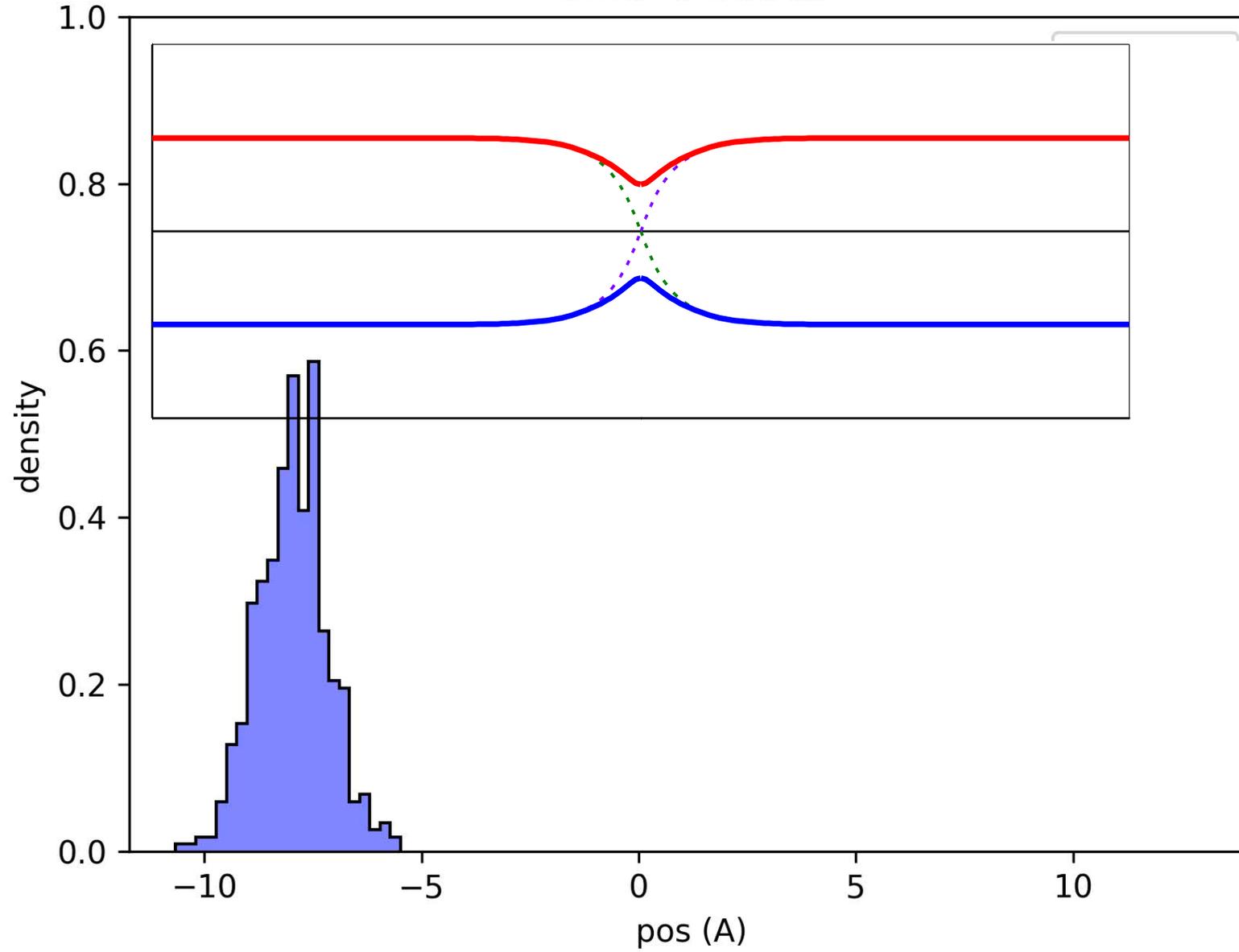
$$\sum_{K=1}^{J-1} P_{L \rightarrow K}^{FSSH} < r_t \leq \sum_{K=1}^J P_{L \rightarrow J}^{FSSH}$$

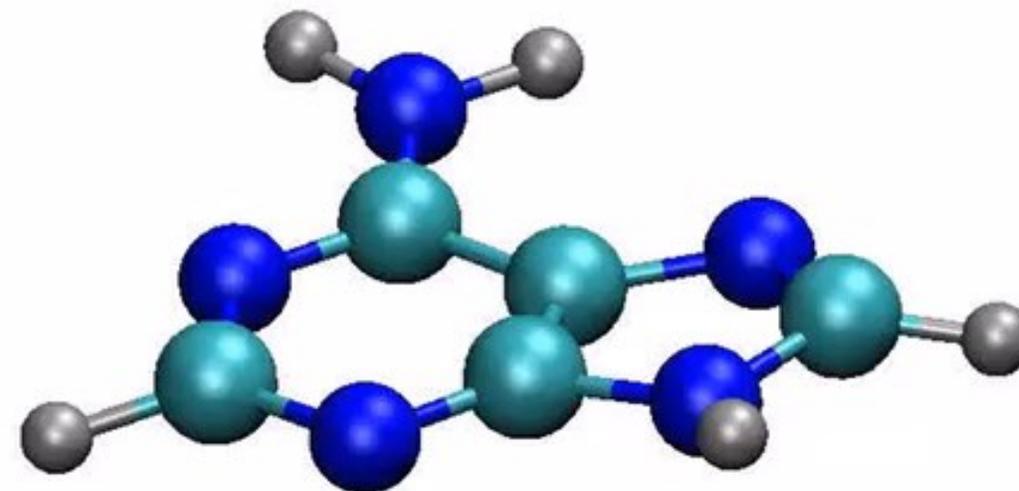
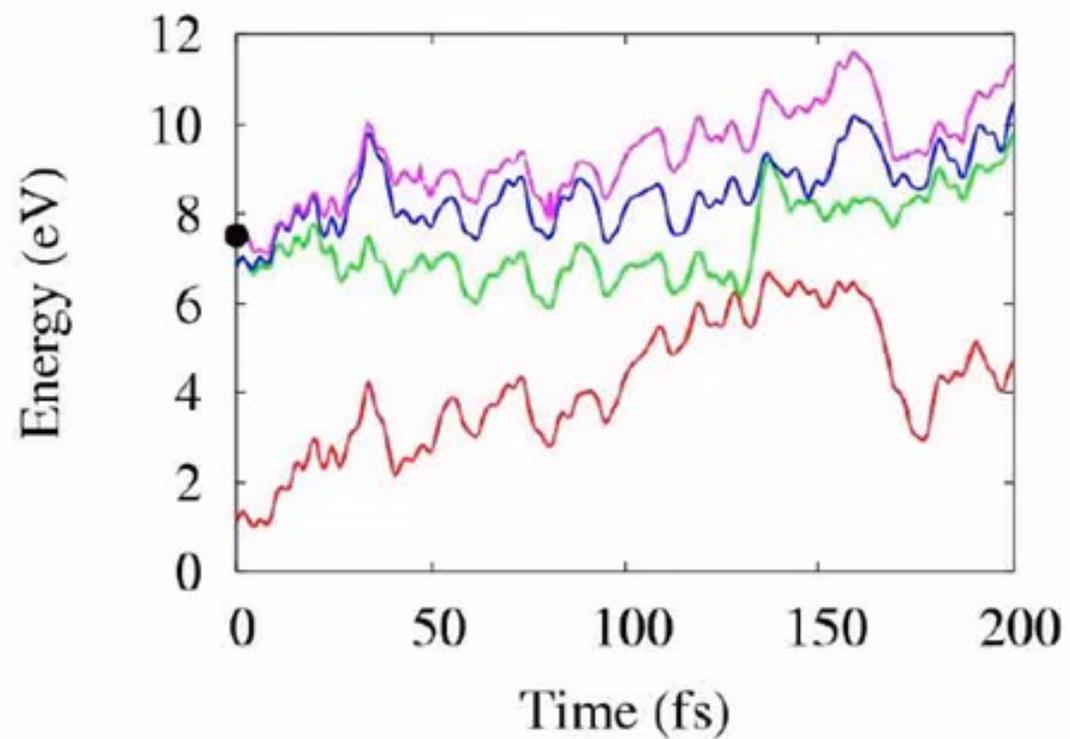
# EOM propagation





time 0.000 fs





## **Pros:**

- Clear and intuitive background
- Easy to implement

## **Cons:**

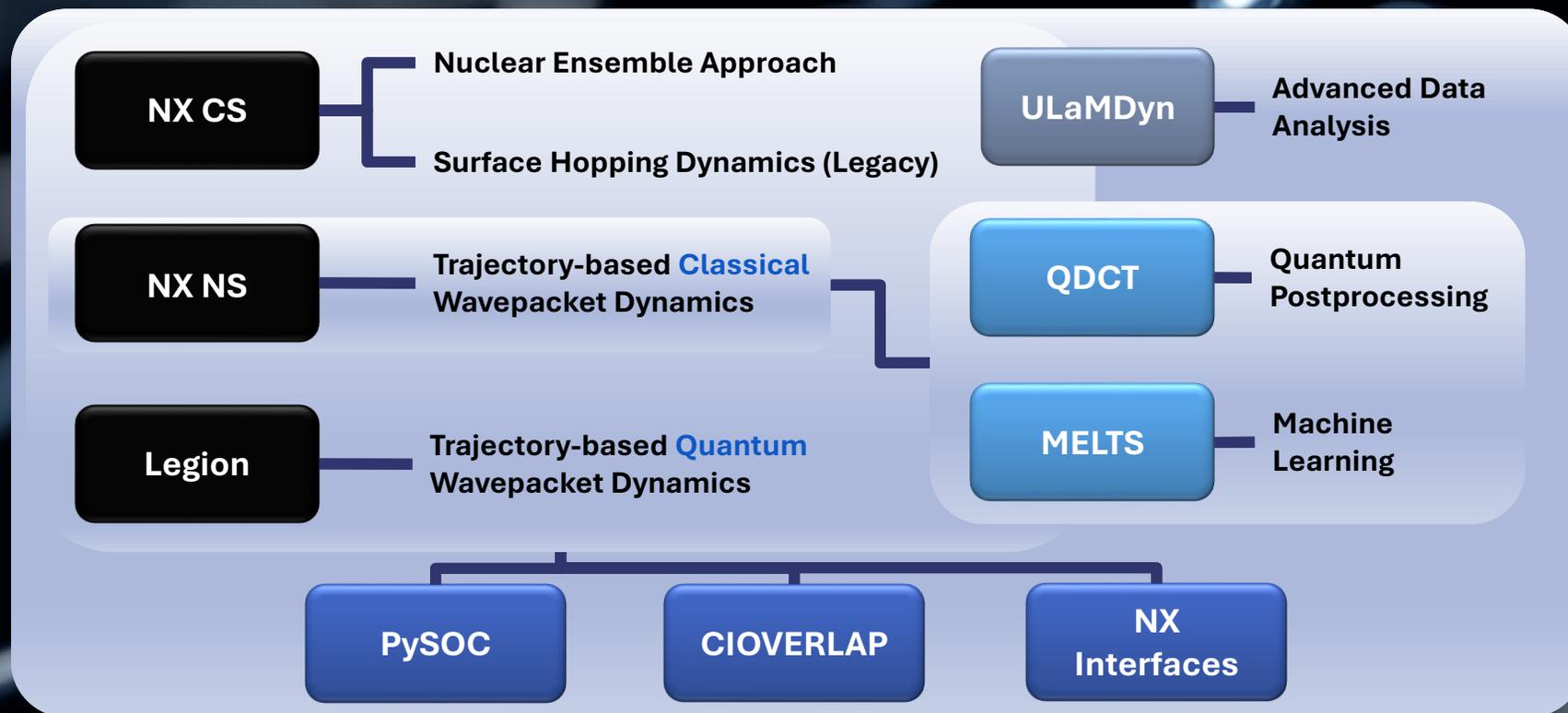
- Inconsistent coherence treatment
- Lack of global info (tunneling, quantum interference, etc.)

To know more:

Tully. *Faraday Discuss* **1998**, 110, 407

Barbatti. *WIREs: Comp Mol Sci* **2011**, 1, 620

# The Newton-X Platform



newtonx.org

# Costs of dynamics

# Dynamics may be expensive

$$T_{total} \approx N_{\text{Trajectories}} \times N_{\text{Single Points}} \times T_{\text{Single Point}}$$

How much does dynamics cost? [tinyurl.com/dyncost](https://tinyurl.com/dyncost)  
How many trajectories should we run? [tinyurl.com/trajs](https://tinyurl.com/trajs)

# Dynamics may be expensive

$$T_{total} \approx N_{\text{Trajectories}} \times \left( \frac{\tau_{\text{chem process}}}{\Delta \tau} \right) \times T_{\text{Single Point}}$$

|                              |                       |
|------------------------------|-----------------------|
| $N_{\text{Trajectories}}$    | = 100 trajectories    |
| $T_{\text{Single Point}}$    | = 6 min = 0.1 CPUh    |
| $\tau_{\text{chem process}}$ | = 500,000 fs = 0.5 ns |
| $\Delta \tau$                | = 0.5 fs              |

$$T_{total} \approx 10 \text{ MCPUh}$$

|              |                   |
|--------------|-------------------|
| Price 1 CPUh | = 0.02 € (France) |
|--------------|-------------------|

|                |          |
|----------------|----------|
| Price 10 MCPUh | = 200 k€ |
|----------------|----------|

How much does dynamics cost? [tinyurl.com/dyncost](https://tinyurl.com/dyncost)

How many trajectories should we run? [tinyurl.com/trajs](https://tinyurl.com/trajs)

# Dynamics leaves a huge carbon footprint

1 CPUh @ 32 GB = 1.3 g CO<sub>2</sub>e 

10 MCPUh = 13 tCO<sub>2</sub>e



11.5 tCO<sub>2</sub>e/year

|   |        |
|---|--------|
|    | → × 2  |
|    | → × 7  |
|   | → × 10 |
|  | → × 12 |
|  | → × 14 |

# The Lagrange equation

Second Newton's law:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$$

Left: 
$$m_i \frac{d}{dt} \frac{d\mathbf{r}_i}{dt} = \frac{d}{dt} \left( m_i \frac{d\mathbf{r}_i}{dt} \right) = \frac{d}{dt} (m_i \mathbf{v}_i) = \frac{d\mathbf{p}_i}{dt}$$

Right: 
$$\mathbf{F}_i = -\nabla_i V = -\frac{\partial V}{\partial \mathbf{r}_i} \quad (\text{conservative})$$

Second Newton's law for a conservative system:

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial V}{\partial \mathbf{r}_i}$$

Second Newton's law:

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial V}{\partial \mathbf{r}_i}$$

We want to write it in terms of the kinetic energy:

$$T = \frac{1}{2} \sum_k m_k \mathbf{v}_k^2 = \frac{1}{2} \sum_k m_k \dot{\mathbf{r}}_k^2$$

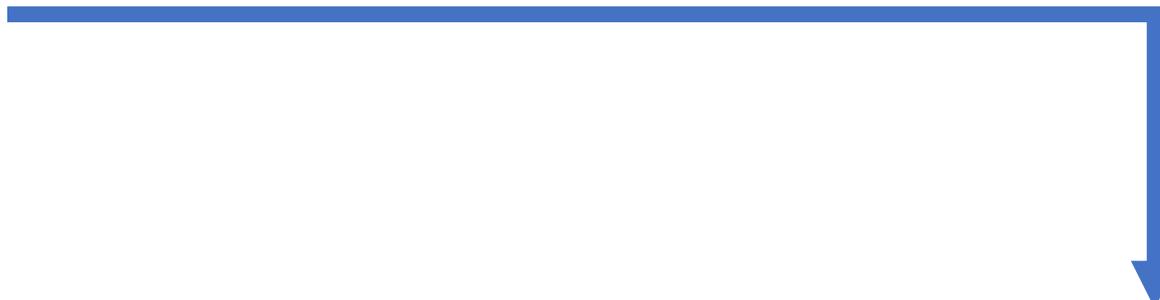
Take the partial derivative

$$\frac{\partial T}{\partial \dot{\mathbf{r}}_i} = \frac{\partial}{\partial \dot{\mathbf{r}}_i} \left( \frac{1}{2} \sum_k m_k \dot{\mathbf{r}}_k^2 \right) = m_i \dot{\mathbf{r}}_i = \mathbf{p}_i$$

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{\mathbf{r}}_i} = \frac{d\mathbf{p}_i}{dt}$$

Replacing

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{\mathbf{r}}_i} = \frac{d\mathbf{p}_i}{dt} \text{ into } \frac{d\mathbf{p}_i}{dt} = -\frac{\partial V}{\partial \mathbf{r}_i} \text{ gives}$$

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{\mathbf{r}}_i} = -\frac{\partial V}{\partial \mathbf{r}_i}$$


Note that

$$\frac{\partial (T(\dot{\mathbf{r}}_i) - V(\mathbf{r}_i))}{\partial \dot{\mathbf{r}}_i} = \frac{\partial T(\dot{\mathbf{r}}_i)}{\partial \dot{\mathbf{r}}_i}$$

$$\frac{\partial (T(\dot{\mathbf{r}}_i) - V(\mathbf{r}_i))}{\partial \mathbf{r}_i} = -\frac{\partial V(\mathbf{r}_i)}{\partial \mathbf{r}_i}$$

$$\frac{d}{dt} \left( \frac{\partial (T - V)}{\partial \dot{\mathbf{r}}_i} \right) = \frac{\partial (T - V)}{\partial \mathbf{r}_i}$$

or

$$\frac{d}{dt} \left( \frac{\partial (T - V)}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial (T - V)}{\partial \mathbf{r}_i} = 0$$

$$\frac{d}{dt} \left( \frac{\partial(T-V)}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial(T-V)}{\partial \mathbf{r}_i} = 0$$

Define **Lagrangian** function

$$L \equiv T - V$$

We obtain the **Lagrange's equations**

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial L}{\partial \mathbf{r}_i} = 0$$

The Lagrange's equations can be written in terms of **generalized coordinates**  $\mathbf{q}_i$

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\mathbf{q}}_i} \right) - \frac{\partial L}{\partial \mathbf{q}_i} = 0 \quad L = T - V$$

Where  $\mathbf{q}_i$  are functions of  $\mathbf{r}_i$

$$\mathbf{q}_i = \mathbf{q}_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$$

$$\mathbf{r}_i = \mathbf{r}_i(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N, t)$$

Generalized coordinates allow including constraints  
(solid bodies, motion on surfaces, walls, etc.)

Generalized coordinates do not need to have length dimensions  
(angles, Fourier expansion amplitudes, etc.)

The Lagrange's equations are still valid for forces obtained from velocity-dependent potentials

$$V = V(\mathbf{q}, \dot{\mathbf{q}})$$

For example, an electric charge  $e$  with mass  $m$  moving with velocity  $\mathbf{v}$  in a region with electric field  $\mathbf{E}$  and magnetic field  $\mathbf{B}$ :

$$\mathbf{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

The Lagrangian  $L = T - V$  is

$$L = \frac{1}{2}mv^2 - e(\phi - \mathbf{A} \cdot \mathbf{v})$$

Inserting it into Lagrange's equation yields

$$m \frac{d^2\mathbf{r}}{dt^2} = e[\mathbf{E} + (\mathbf{v} \times \mathbf{B})]$$

# Car-Parrinello molecular dynamics (CPMD)

# Car-Parrinello Lagrangian

$$L = \underbrace{\frac{1}{2} \left( \sum_{\alpha}^{nuclei} M_{\alpha} \dot{\mathbf{R}}_{\alpha}^2 + \mu \sum_i^{orbitals} \langle \dot{\psi}_i | \dot{\psi}_i \rangle \right)}_{\text{Generalized T}} - \underbrace{E[\mathbf{R}, \{\psi\}] + \sum_{ij} \Lambda_{ij} \left( \langle \psi_i | \psi_j \rangle - \delta_{ij} \right)}_{\text{Generalized V}}$$

Orthogonality constraint

$\mu$  - fictitious electron mass

$\psi_i$  - Kohn-Sham orbitals

## Car-Parrinello EOM

$$M_{\alpha} \ddot{\mathbf{R}}_{\alpha} = -\nabla_{\alpha} E[\mathbf{R}, \{\psi\}] + \sum_{ij} \Lambda_{ij} \nabla_{\alpha} \langle \psi_i | \psi_j \rangle$$

$$\mu \ddot{\psi}_i = -h(\mathbf{R}, \{\psi\}) \psi_i + \sum_j \Lambda_{ij} \psi_j$$

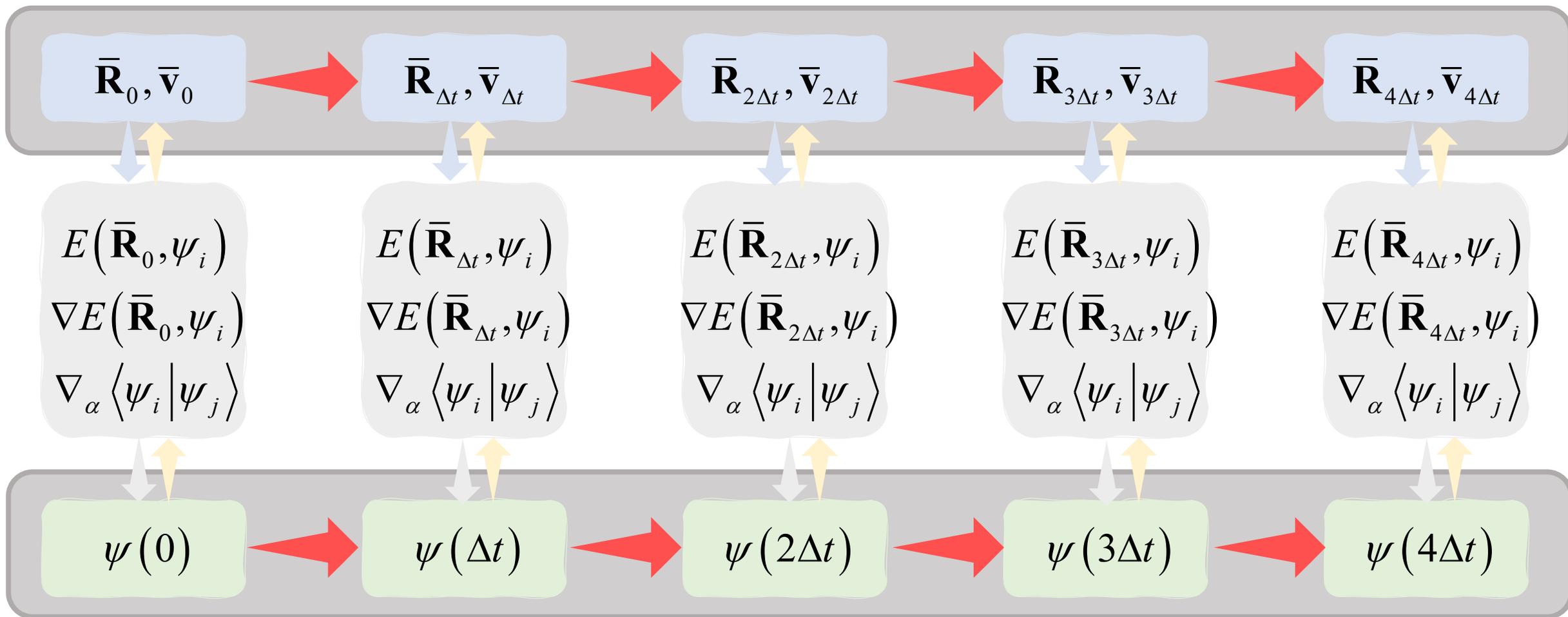
$\mu$  - fictitious electron mass

$\psi_i$  - Kohn-Sham orbitals

$h$  - One particle Hamiltonian

# CPMD

## Classical EOM



## Quantum EOM

QM treatment of electrons allows CPMD to capture electronic effects, such as charge transfer, bond breaking, and formation.

CPMD depends on the parameter  $\mu$ .

CPMD is more expensive than BOMD.

Costs are alleviated with plane wave basis sets.

BOMD is more advantageous for non-reactive dynamics.

CPMD can be run with CPMD and CP2K programs.

# Hamilton's equations

For regular coordinates

$$\frac{\partial L}{\partial \dot{\mathbf{r}}} = \frac{\partial (T(\dot{\mathbf{r}}) - V(\mathbf{r}))}{\partial \dot{\mathbf{r}}} = \frac{\partial}{\partial \dot{\mathbf{r}}} \left( \frac{1}{2} m \dot{\mathbf{r}}^2 \right) = m \dot{\mathbf{r}} = \mathbf{p}$$

It motivated defining the generalized (canonical) momentum

$$\mathbf{p} \equiv \frac{\partial L}{\partial \dot{\mathbf{q}}}$$

It is possible to reformulate the equations of motion from

$$(\mathbf{q}, \dot{\mathbf{q}}, t)$$

to

$$(\mathbf{q}, \mathbf{p}, t)$$

To do that, we define the **Hamiltonian** function as

$$H(\mathbf{q}, \mathbf{p}, t) \equiv \dot{\mathbf{q}}\mathbf{p} - L(\mathbf{q}, \dot{\mathbf{q}}, t)$$

$$H(\mathbf{q}, \mathbf{p}, t) \equiv \dot{\mathbf{q}}\mathbf{p} - L(\mathbf{q}, \dot{\mathbf{q}}, t)$$

Now, we take the derivatives

$$\text{In } \mathbf{p}: \quad \frac{\partial H(\mathbf{q}, \mathbf{p}, t)}{\partial \mathbf{p}} = \frac{\partial(\dot{\mathbf{q}}\mathbf{p})}{\partial \mathbf{p}} - \frac{\partial L(\mathbf{q}, \dot{\mathbf{q}}, t)}{\partial \mathbf{p}} = \dot{\mathbf{q}} = \frac{d\mathbf{q}}{dt}$$

$$\text{In } \mathbf{q}: \quad \frac{\partial H(\mathbf{q}, \mathbf{p}, t)}{\partial \mathbf{q}} = \frac{\partial(\dot{\mathbf{q}}\mathbf{p})}{\partial \mathbf{q}} - \frac{\partial L(\mathbf{q}, \dot{\mathbf{q}}, t)}{\partial \mathbf{q}} = -\frac{\partial L(\mathbf{q}, \dot{\mathbf{q}}, t)}{\partial \mathbf{q}}$$

$$\underbrace{\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\mathbf{q}}} \right)}_{\mathbf{p} \equiv \frac{\partial L}{\partial \dot{\mathbf{q}}}} - \frac{\partial L}{\partial \mathbf{q}} = 0 \quad \longrightarrow \quad \frac{d}{dt}(\mathbf{p}) - \left( -\frac{\partial H}{\partial \mathbf{q}} \right) = 0 \quad \longrightarrow \quad \frac{\partial H}{\partial \mathbf{q}} = -\frac{d\mathbf{p}}{dt}$$

The Lagrange's equations

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\mathbf{q}}} \right) - \frac{\partial L}{\partial \mathbf{q}} = 0$$

become the Hamilton's equations

$$\begin{aligned} \frac{d\mathbf{q}}{dt} &= \frac{\partial H}{\partial \mathbf{p}} \\ \frac{d\mathbf{p}}{dt} &= -\frac{\partial H}{\partial \mathbf{q}} \end{aligned}$$

with the Hamiltonian defined as

$$H(\mathbf{q}, \mathbf{p}, t) \equiv \dot{\mathbf{q}}\mathbf{p} - L(\mathbf{q}, \dot{\mathbf{q}}, t)$$

If:

1. The equations defining the generalized coordinates  $\mathbf{q}$  do not depend explicitly on time.
2. The forces are derivable from a conservative potential.

then, the Hamiltonian is the total energy

$$H = T + V = E$$

**Taking a step back**

## Classical Mechanics

The state of a classical system is determined by solving

$$\begin{aligned}\frac{d\mathbf{q}}{dt} &= \frac{\partial H}{\partial \mathbf{p}} \\ \frac{d\mathbf{p}}{dt} &= -\frac{\partial H}{\partial \mathbf{q}}\end{aligned}$$

for both  $\mathbf{q}$  and  $\mathbf{p}$ .

For a conservative system, the Hamiltonian **function** is

$$H = T + V$$

## Quantum Mechanics

The state of a quantum system is determined by solving

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle$$

either for

$$\psi(\mathbf{q}) = \langle \mathbf{q} | \psi \rangle$$

or

$$\psi(\mathbf{p}) = \langle \mathbf{p} | \psi \rangle$$

For a conservative system, the Hamiltonian **operator** is

$$\hat{H} = \hat{T} + \hat{V}$$

**many**

Quantum Statistical  
Mechanics

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}]$$

Classical Statistical  
Mechanics

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}$$

**few**

Quantum  
Mechanics

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle$$

Classical  
Mechanics

$$\frac{dq}{dt} = \frac{\partial H}{\partial p} \quad \frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

**small**

**large**

To know more:

Lagrange's equations, Hamilton's equations

- Goldstein, Classical mechanics. **1980**. Ch 1, 2, 8

Mixed quantum-classical methods

- Crespo-Otero; Barbatti. *Chem Rev* **2018**, 118, 7026

Cost of dynamics

- How much does dynamics cost? [tinyurl.com/dyncost](https://tinyurl.com/dyncost)
- How many trajectories should we run? [tinyurl.com/trajs](https://tinyurl.com/trajs)