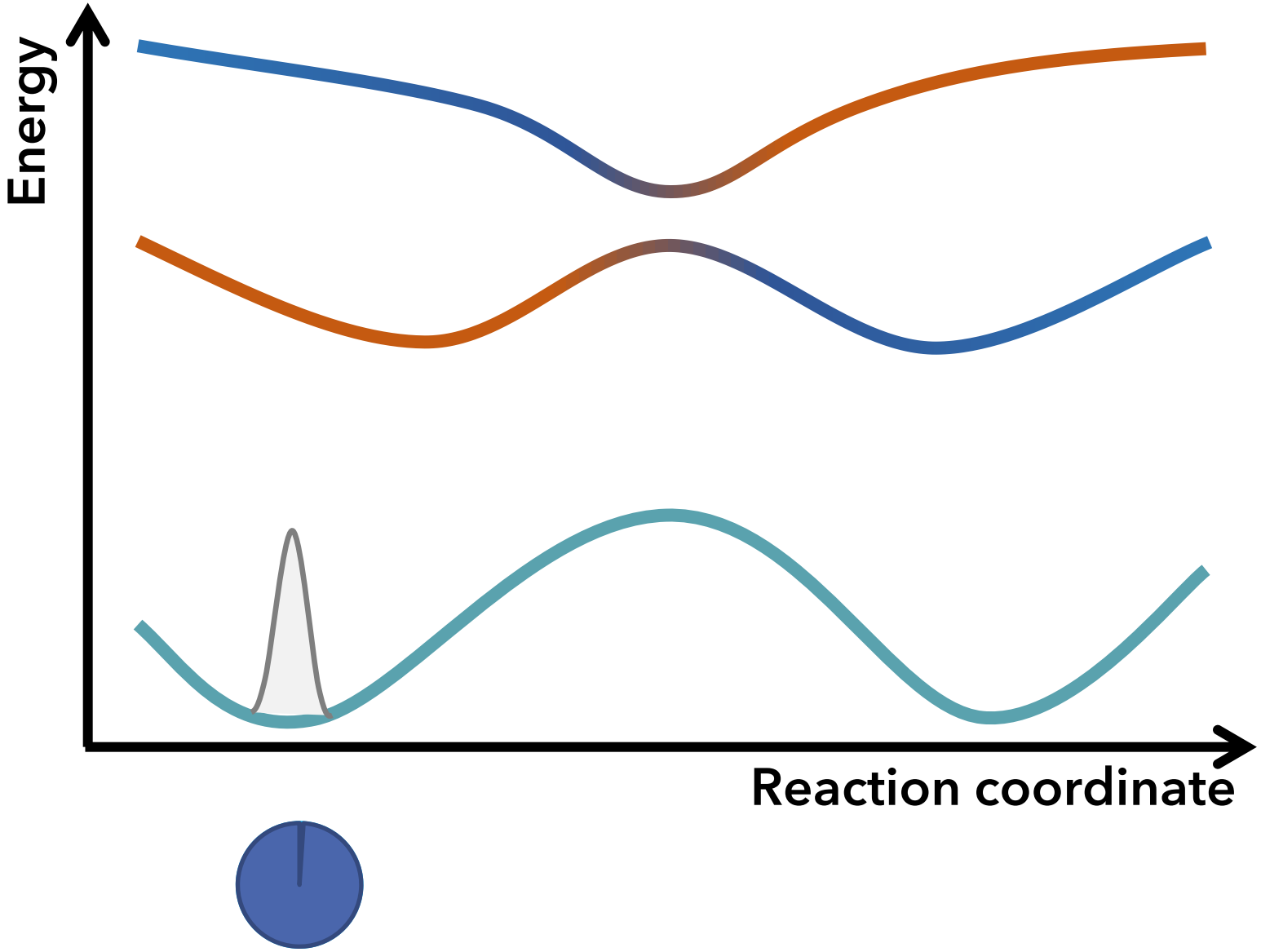
L8 – Classical Mechanics 4

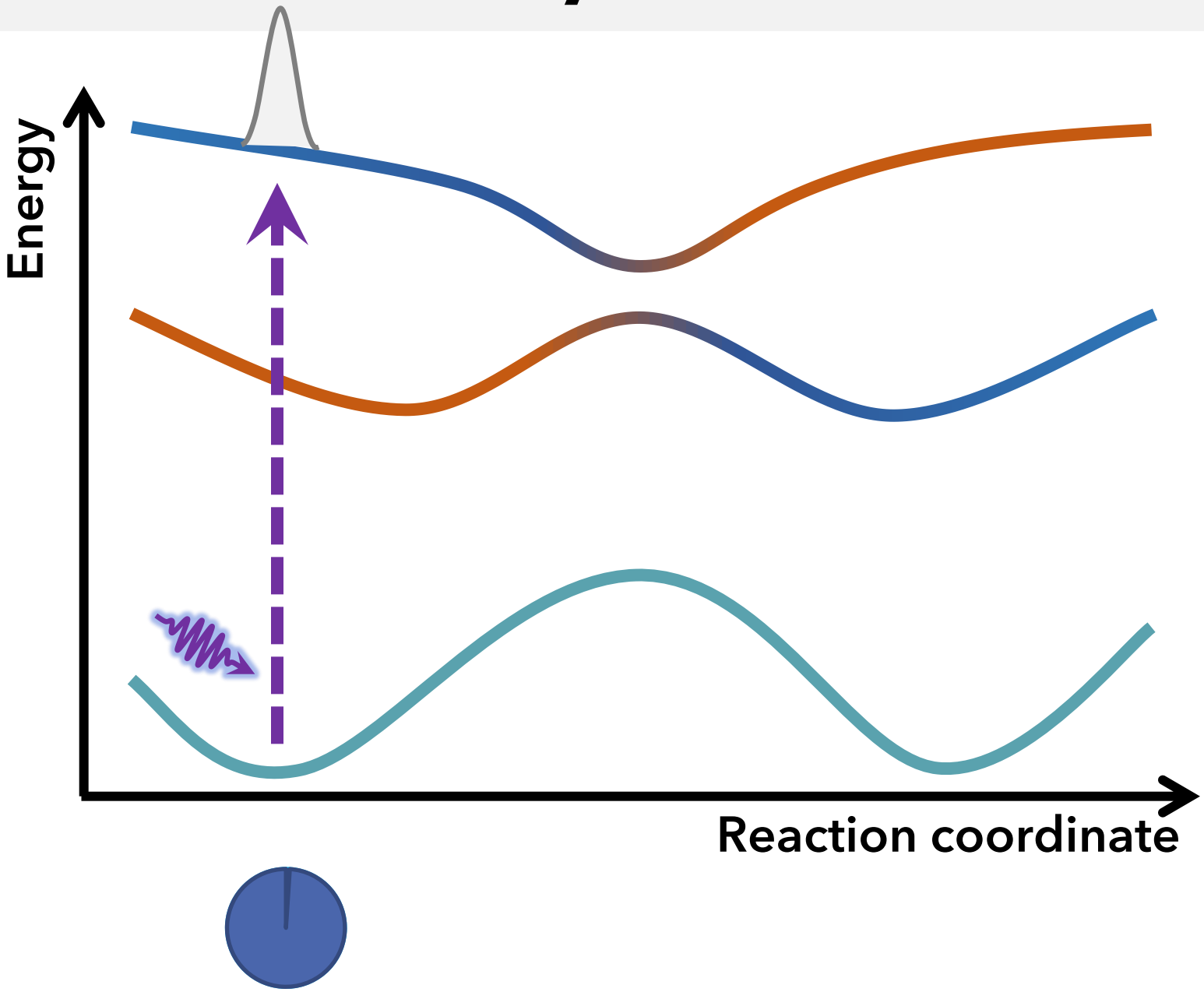
Mixed quantum classical dynamics
Hamilton and Lagrange formulations

Mixed Quantum-Classical Dynamics

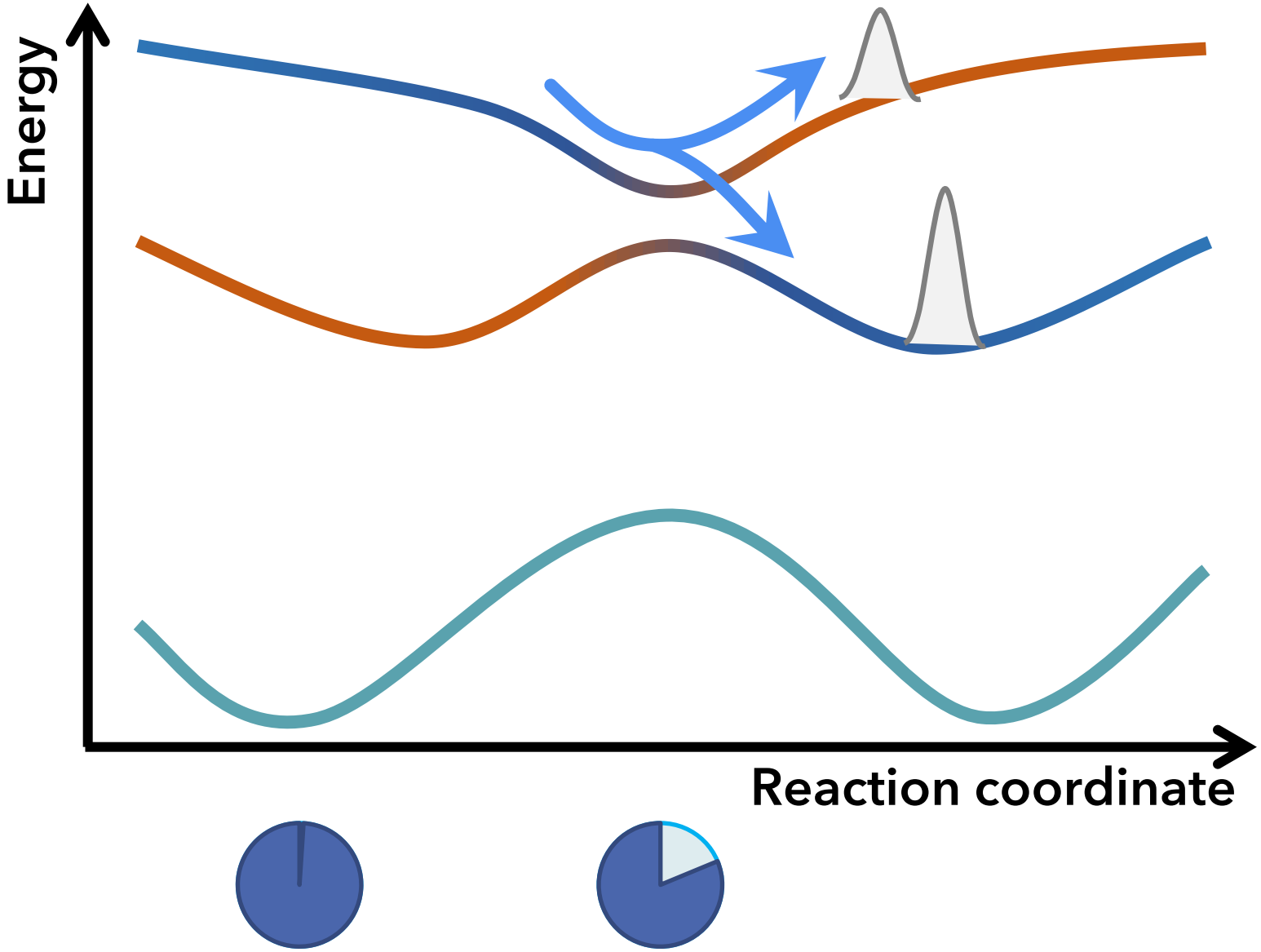
Nonadiabatic dynamics



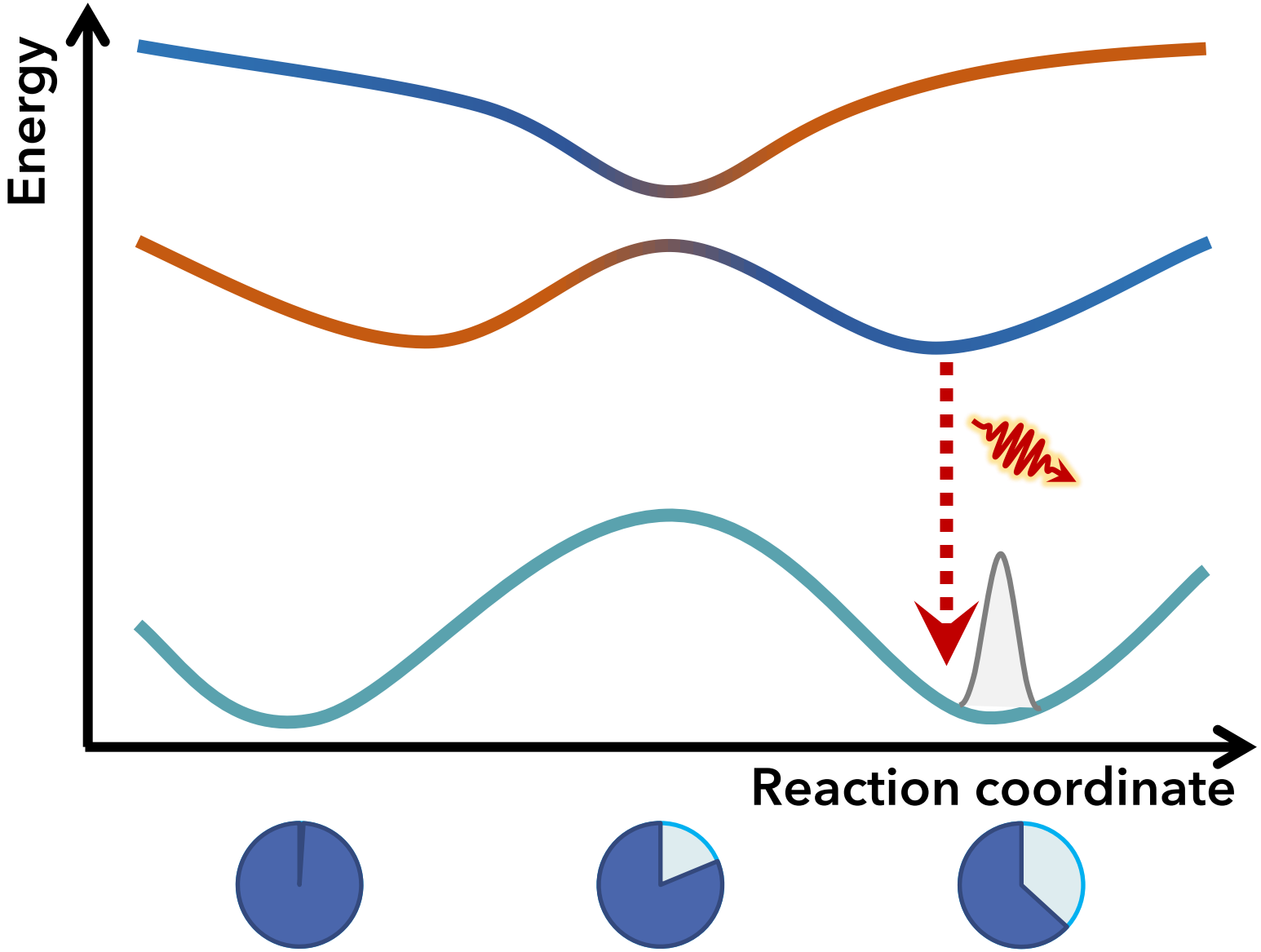
Nonadiabatic dynamics



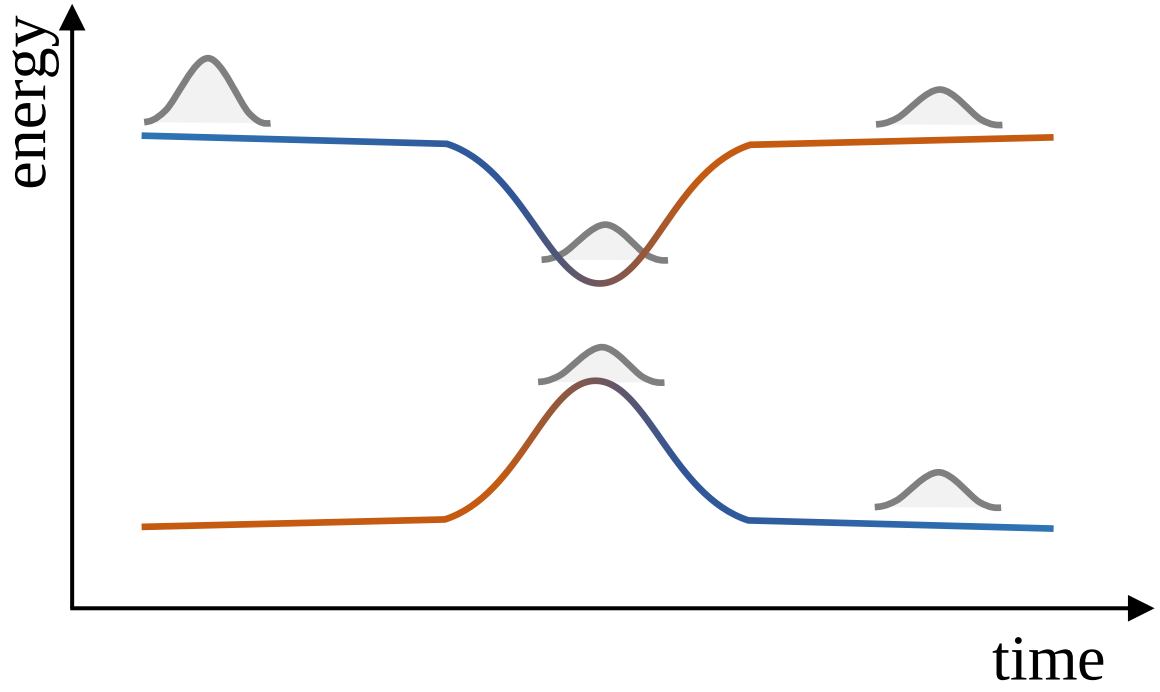
Nonadiabatic dynamics



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

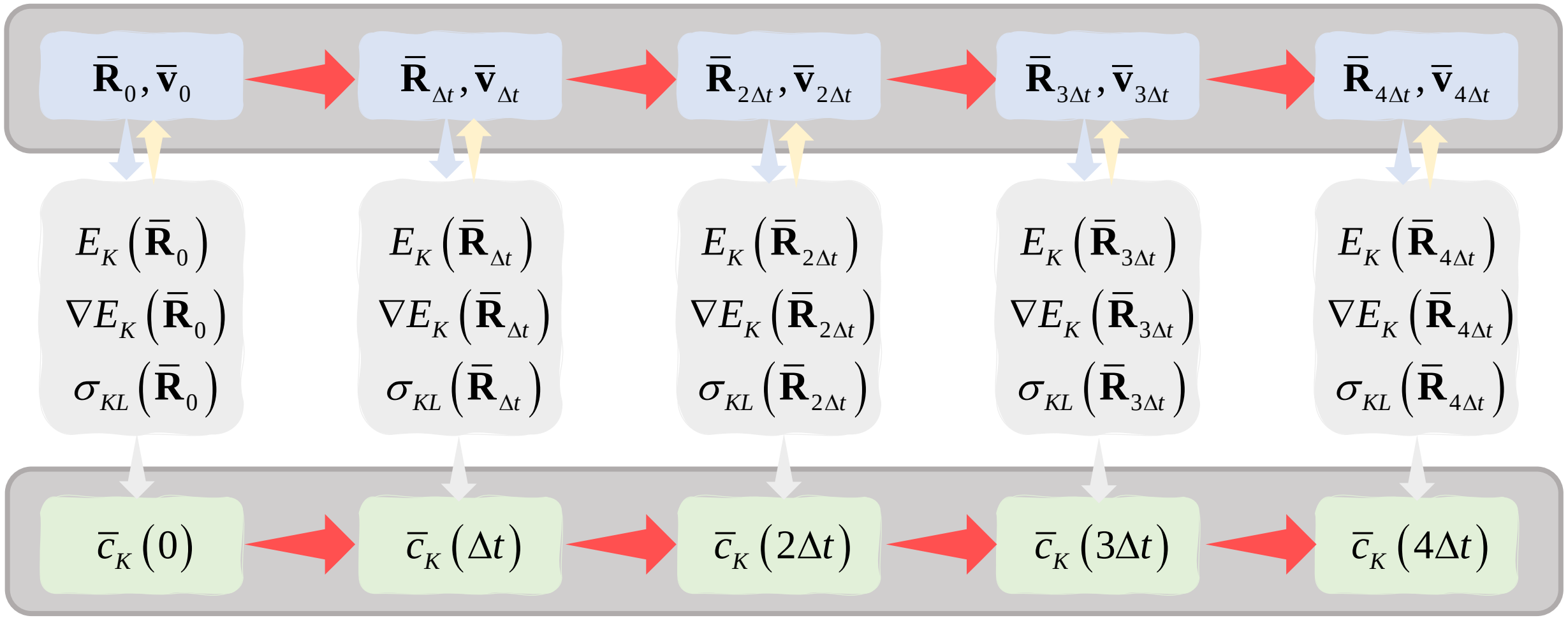
1. Nuclei are treated via *classical trajectories*

2. Electrons are treated *quantum mechanically*

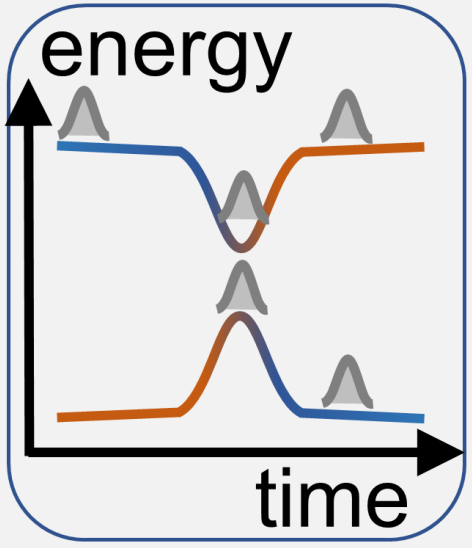
3. A nonadiabatic algorithm introduces *post Born-Oppenheimer effects*

Crespo-Otero; Barbatti. *Chem Rev* **2018**, *118*, 7026
Tully. *Faraday Discuss.* **1998,** *110*, 407

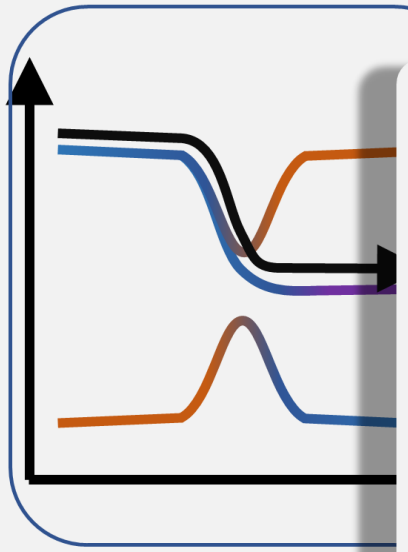
MQC Dynamics



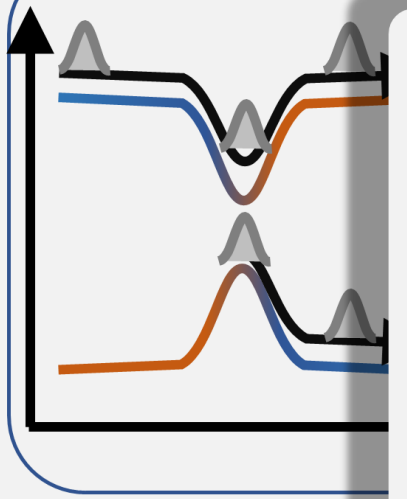
Exact



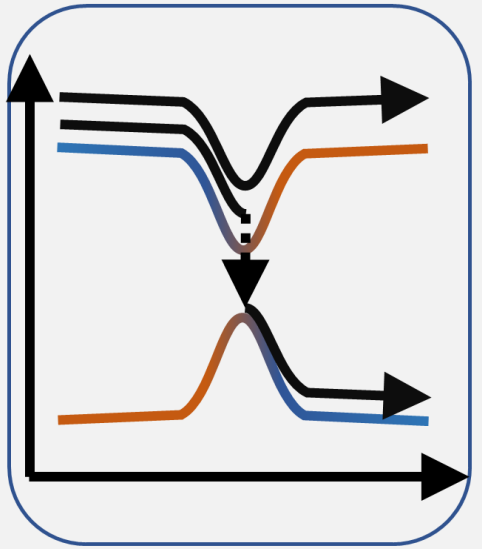
Averaging



Spawning



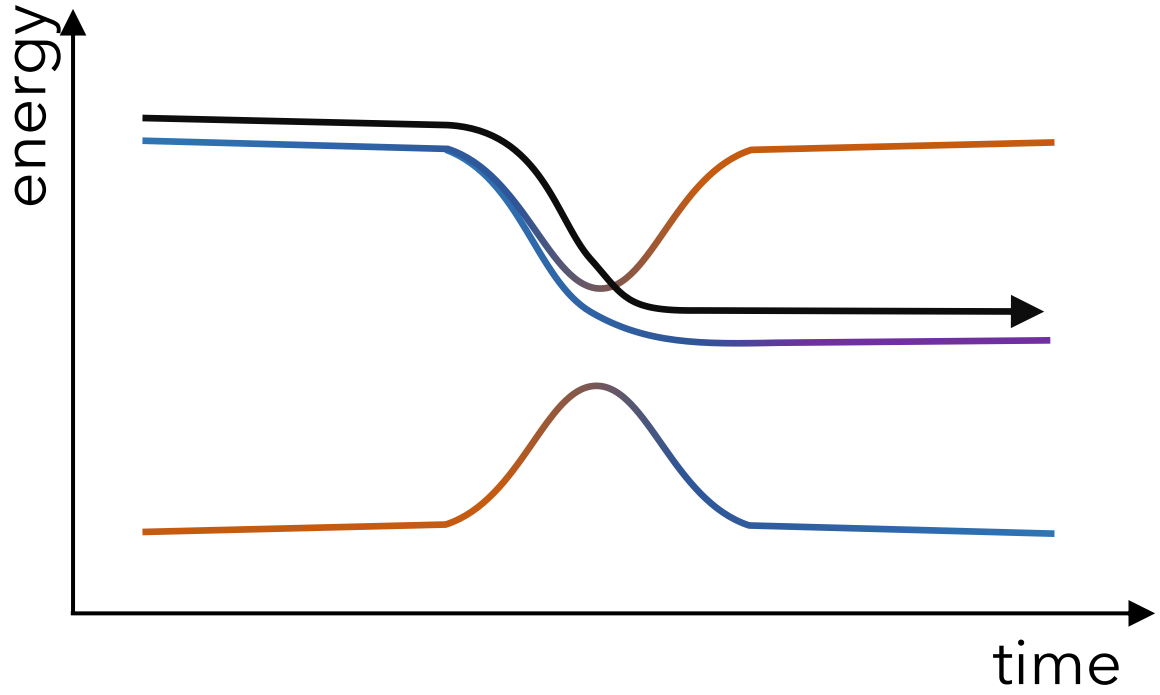
Hopping



Standard Methods for MQCD
Mean field Ehrenfest

Mean-Field Ehrenfest Dynamics

- Propagate nuclei via classical trajectories on an averaged PES
- Compute the weights for the average solving electronic problem quantum mechanically



Derivation of EOM:
de Carvalho; Bouduban; Curchod; Tavernelli. *Entropy* **2014,** *16*, 62

The Equations-of-Motion (EOM) are

$$\frac{d^2\mathbf{R}_\alpha}{dt^2} = \frac{1}{M_\alpha}\mathbf{F}(\mathbf{R}) \qquad \mathbf{F}(\mathbf{R}) = -\sum_{IJ} c_I^* c_J \langle \psi_I | \nabla \hat{H}_e | \psi_J \rangle$$

$$\frac{dc_J}{dt} = \sum_K -c_K \left(\frac{i}{\hbar} H_{JK} + \sigma_{JK} \right)$$

$$H_{JK}(\bar{\mathbf{R}}) \equiv \left\langle \psi_J \middle| \hat{H}_e \middle| \psi_K \right\rangle$$

$$\sigma_{JK}(\bar{\mathbf{R}}) \equiv \left\langle \psi_J \middle| \frac{\partial \psi_K}{\partial t} \right\rangle$$

Pros:

- Clear and intuitive background
- Easy to implement
- It is the basis for electronic structure methods like TDHF and TDKS

Cons:

- Overcoherence
- Wrong asymptotic limits
- Lack of global info (tunneling, quantum interference, etc.)

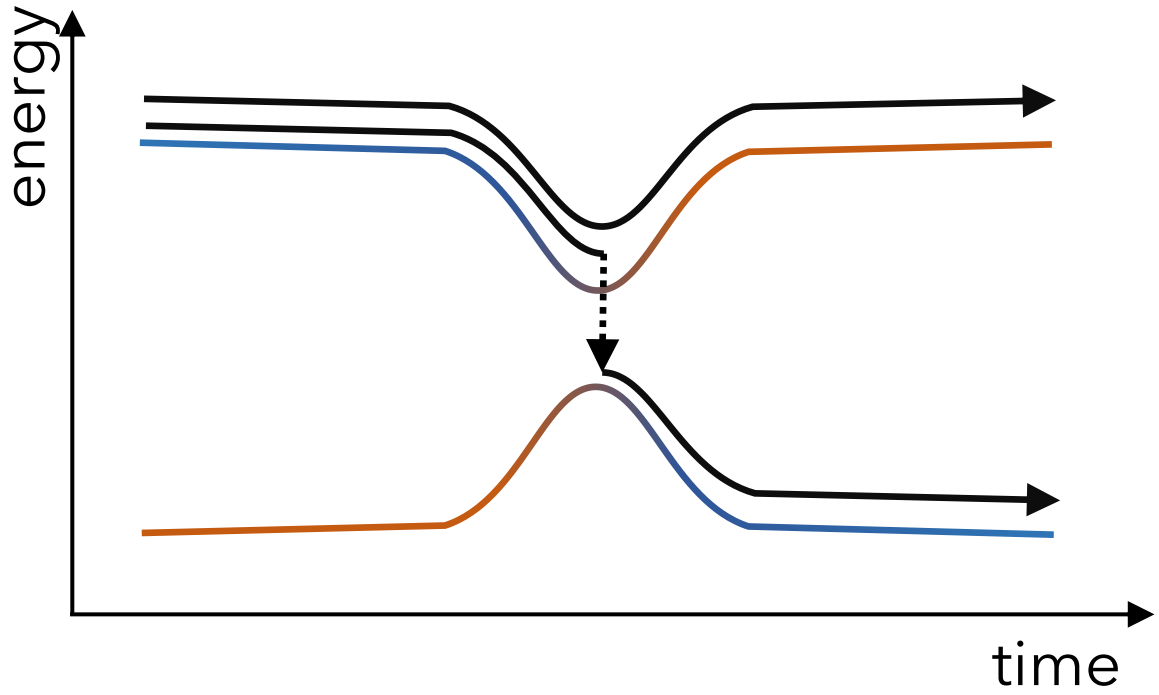
To know more:

- Tully. *Faraday Discuss* **1998,** *110*, 407
- Zhu *et al. J Chem Phys* **2004**, *120*, 5543
- de Carvalho; Bouduban; Curchod; Tavernelli. *Entropy* **2014,** *16*, 62

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

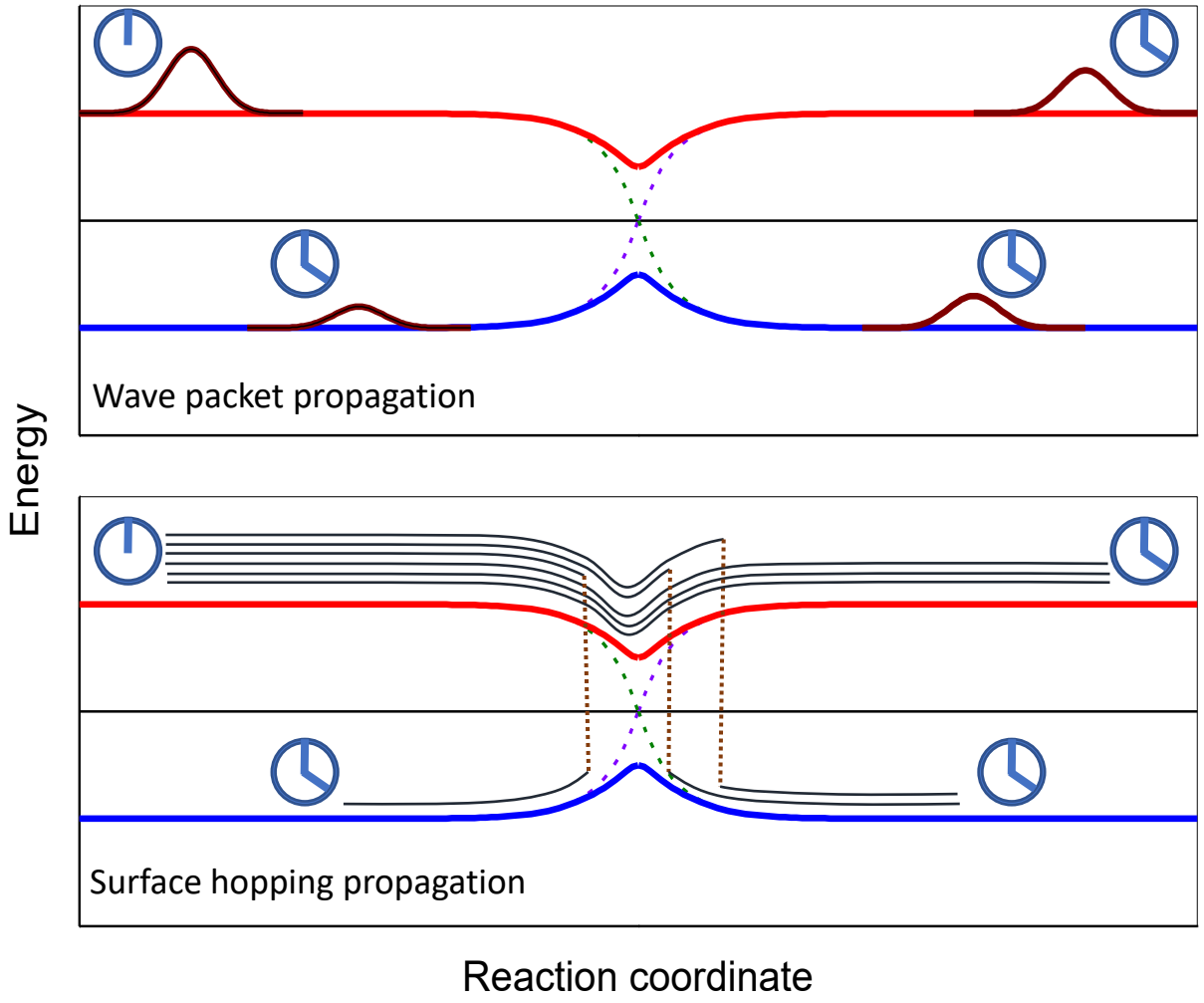
EOM: *Fewest-Switches Surface Hopping* (FSSH) (adiabatic representation):

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

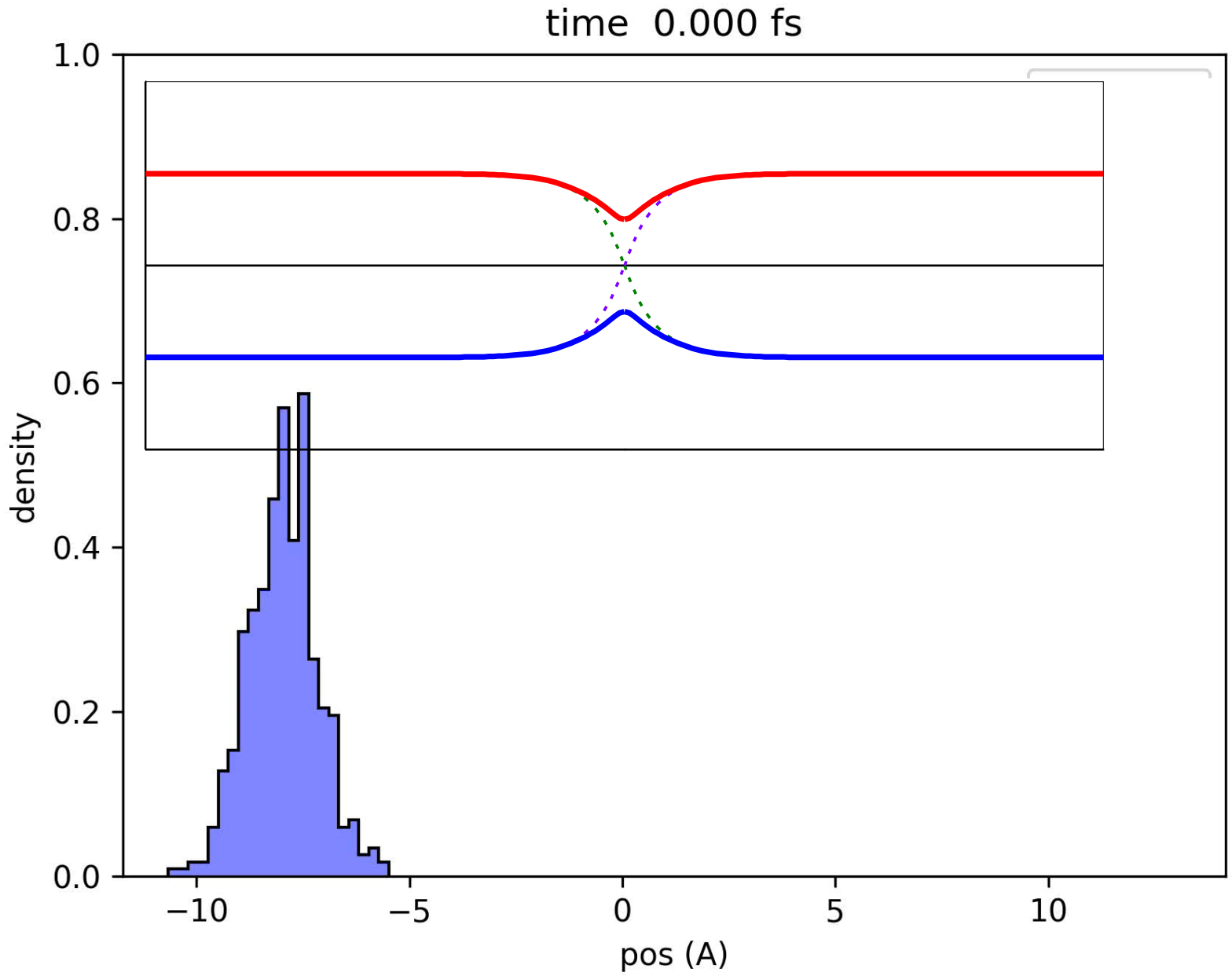
$$\frac{dc_J}{dt} = \sum_K -c_K\left(\frac{i}{\hbar}E_K + \sigma_{JK}\right) \qquad \sigma_{JK}(\mathbf{R}) \equiv \left\langle \psi_J \middle| \frac{\partial \psi_K}{\partial t} \right\rangle$$

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

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



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


time 0.000 fs
1.0
0.8
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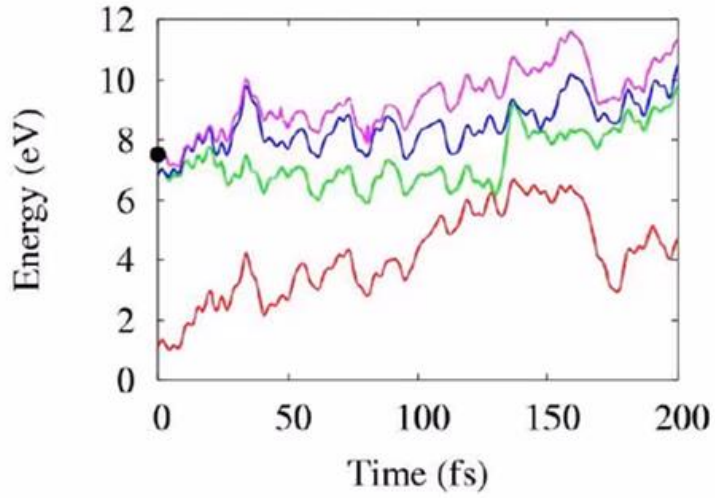
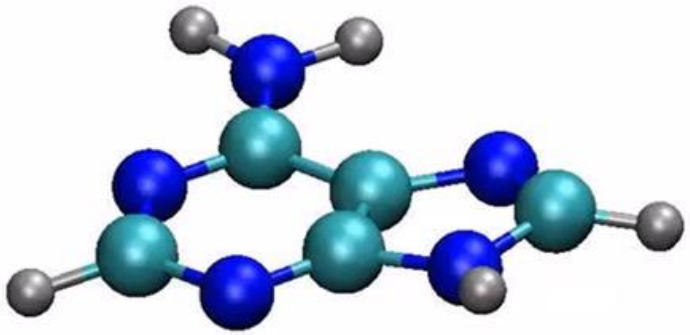
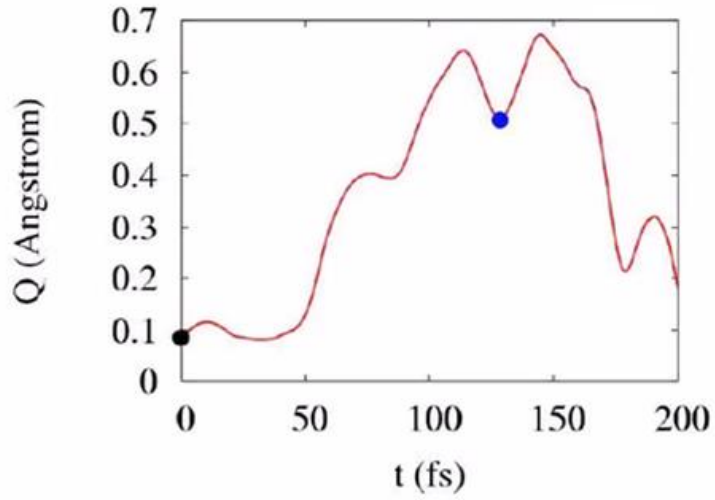
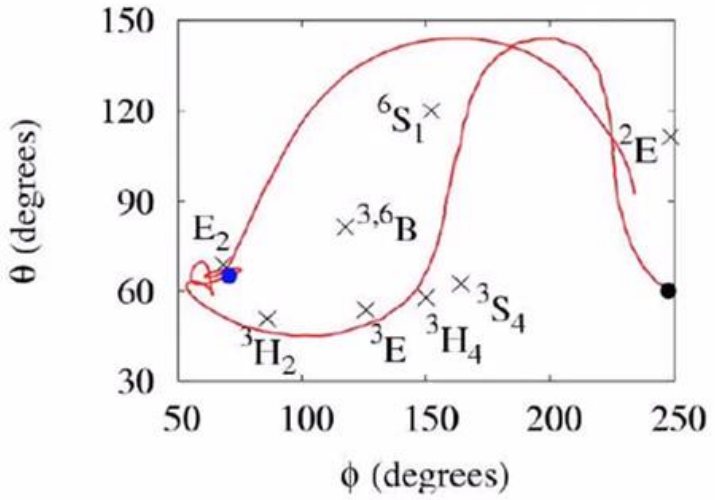
pos (A)

youtube.com/user/mbarbatti









Barbatti; Lischka. *JACS* **2008,** *130*, 6831

Pros:

- Clear and intuitive background
- Easy to implement
- Decoherence problems not as severe as in MFE

Cons:

- Still overcoherence
- Lack of global info (tunneling, quantum interference, etc.)

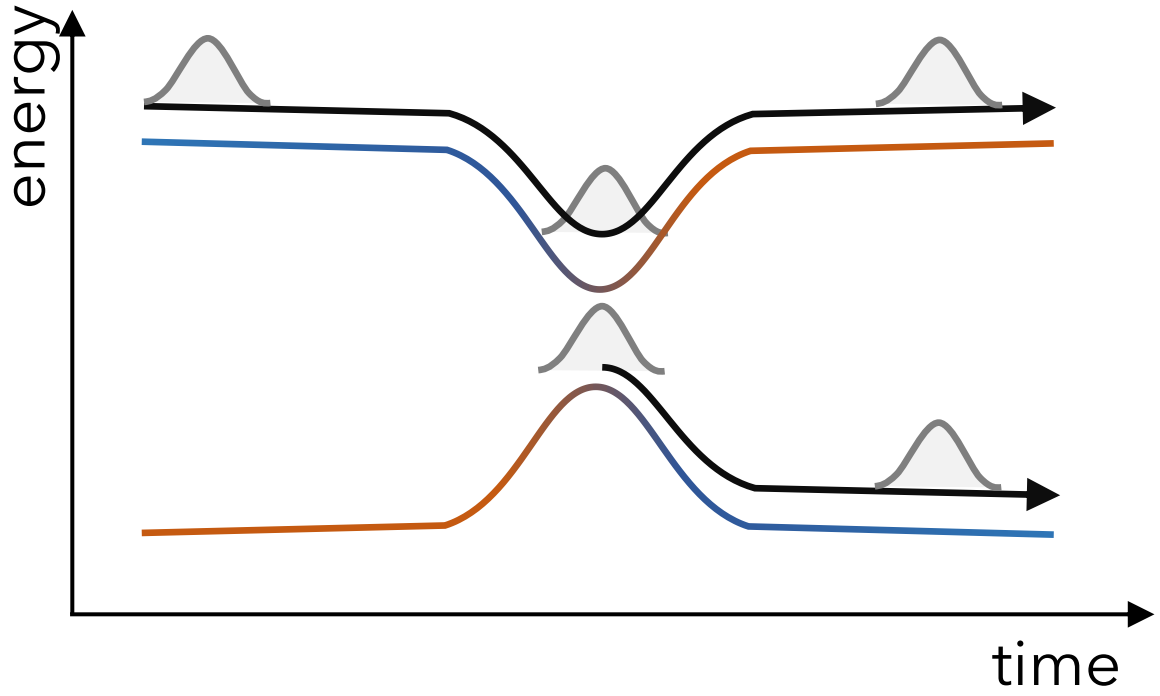
To know more:

Tully. *Faraday Discuss* **1998,** *110*, 407
Barbatti. *WIREs: Comp Mol Sci* **2011,** *1*, 620

Standard Methods for NA-MQC: Multiple spawning

Multiple Spawning Dynamics

- Nuclear wave function is expanded in frozen Gaussians
- Gaussians centers are propagated classically
- Number of Gaussian changes with time (spawning events)



Good starting point:
Curchod; Martínez. *Chem Rev* ***2018***, *118*, 3305

MS Dynamics

Pros:

- In the limit, MS gives the exact solution

Cons:

- Expensive
- Difficult to implement

To know more:

Curchod; Martínez. *Chem Rev* ***20*18**, *118*, 3305
Worth; Robb; Lasorne. *Mol Phys* **2008,** *106*, 2077
Makhov; Glover; Martinez; Shalashilin. *J Chem Phys* **2014,** *141*, 054110

Newton-X

Newtonian Dynamics Close to the X-Seam

- Surface hopping & Nuclear ensemble simulations
- Freeware
- Open source

Barbatti *et al*. *JCTC* **2022,** *18*, 6851
Barbatti *et al*. *WIREs: Comp Mol Sci* **2014**, *4*, 26
Barbatti *et al*. *J Photochem Photobiol, A* **2007**, *190*, 228

Newtonian Dynamics Close to the X-Seam

- Simulations with MRCI, MCSCF, CASPT2, ADC(2), TDDFT, TD-DFTB, FOMO-CI, OM2/CI, Analytical models, ML potentials

- Interfaces to Columbus, Turbomole, Gaussian, Bagel, Gamess, CP2K, DFTB+, ORCA, Mopac (Pisa), MNDO, ORCA, Molcas, MLatom

Barbatti *et al. JCTC* **2022,** *18*, 6851

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
How many trajectories should we run? 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

$T_{total} \approx 10$ MCPUh

Price 1 CPUh = 0.02 € (France)

Price 10 MCPUh = 200 k€

How much does dynamics cost? tinyurl.com/dyncost
How many trajectories should we run? tinyurl.com/trajs

Dynamics leaves a huge carbon footprint

1 CPUh @ 32 GB = 1.3 g CO_2e

10 MCPUh = 13 tCO_2e

11.5 tCO_2e/year

→ × 2

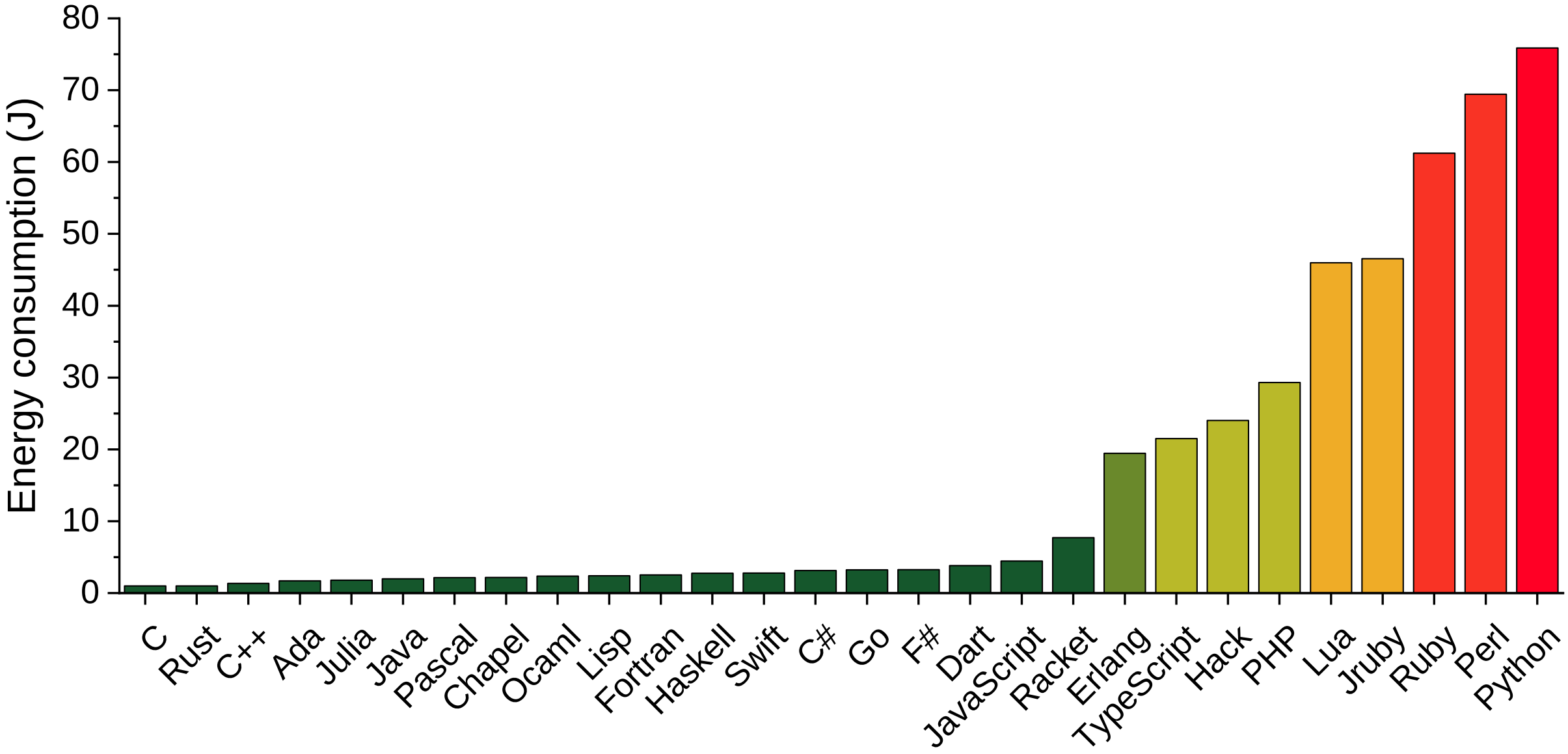
→ × 7

→ × 10

→ × 12

→ × 14

www.green-algorithms.org



Pereira *et al*. *Sci Comput Program* 2021, *205*, 102609
sites.google.com/view/energy-efficiency-languages

The Lagrange equation

Second Newton's law:

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

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

Right: $\mathbf{F}_i = -\nabla_i V = -\dfrac{\partial V}{\partial \mathbf{r}_i}$ (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

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

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

Note that

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

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

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

or

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

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

Define **Lagrangian** function

$$L \equiv T - V$$

We obtain the **Lagrange's equations**

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

Goldstein, Classical mechanics. **1980**

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

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

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

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

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

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

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

For example, an electric charge *e* with mass *m* moving with velocity **v** in a region with electric field **E** and magnetic field **B**:

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

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

The Lagrangian $L = T - V$ is

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

Inserting it into Lagrange's equation yields

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

Car-Parrinello molecular dynamics (CPMD)

Car-Parrinello Lagrangian

Orthogonality constraint

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

Generalized T

Generalized V

μ - fictitious electron mass

ψ_i – Kohn-Sham orbitals

Hutter. *WIREs* **2012**, *2*, 604

Car-Parrinello EOM

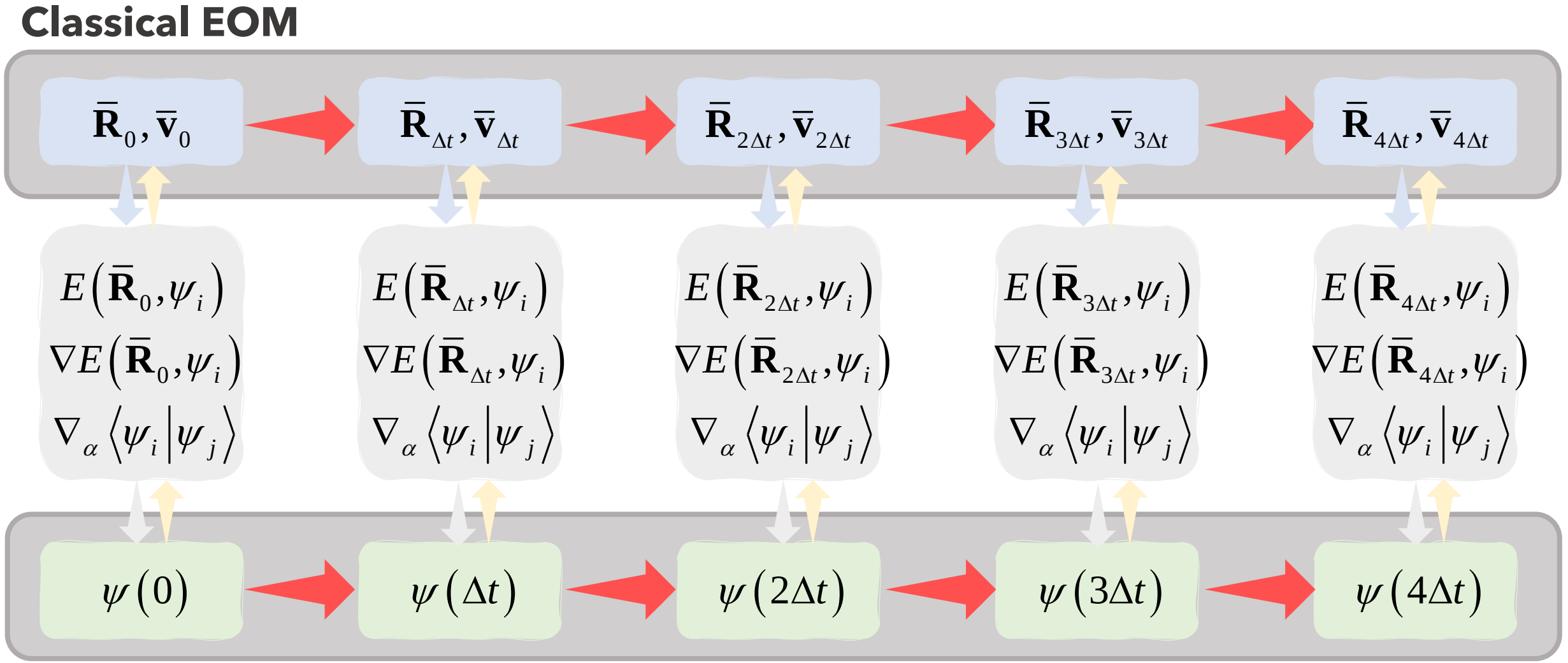
$$M_\alpha \ddot{\mathbf{R}}_\alpha = -\nabla_\alpha E\left[\mathbf{R},\{\psi\}\right] + \sum_{ij} \Lambda_{ij} \nabla_\alpha \left\langle \psi_i \middle| \psi_j \right\rangle$$

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

μ - fictitious electron mass
ψ_i – Kohn-Sham orbitals
h – One particle Hamiltonian

Hutter. *WIREs* **2012**, *2*, 604

CPMD


Classical EOM
$\bar{\mathbf{R}}_0, \bar{\mathbf{v}}_0$
$\bar{\mathbf{R}}_{\Delta t}, \bar{\mathbf{v}}_{\Delta t}$
$\bar{\mathbf{R}}_{2\Delta t}, \bar{\mathbf{v}}_{2\Delta t}$
$\bar{\mathbf{R}}_{3\Delta t}, \bar{\mathbf{v}}_{3\Delta t}$
$\bar{\mathbf{R}}_{4\Delta t}, \bar{\mathbf{v}}_{4\Delta t}$
$E(\bar{\mathbf{R}}_0, \psi_i)$
$\nabla E(\bar{\mathbf{R}}_0, \psi_i)$
$\nabla_\alpha \langle \psi_i | \psi_j \rangle$
$E(\bar{\mathbf{R}}_{\Delta t}, \psi_i)$
$\nabla E(\bar{\mathbf{R}}_{\Delta t}, \psi_i)$
$\nabla_\alpha \langle \psi_i | \psi_j \rangle$
$E(\bar{\mathbf{R}}_{2\Delta t}, \psi_i)$
$\nabla E(\bar{\mathbf{R}}_{2\Delta t}, \psi_i)$
$\nabla_\alpha \langle \psi_i | \psi_j \rangle$
$E(\bar{\mathbf{R}}_{3\Delta t}, \psi_i)$
$\nabla E(\bar{\mathbf{R}}_{3\Delta t}, \psi_i)$
$\nabla_\alpha \langle \psi_i | \psi_j \rangle$
$E(\bar{\mathbf{R}}_{4\Delta t}, \psi_i)$
$\nabla E(\bar{\mathbf{R}}_{4\Delta t}, \psi_i)$
$\nabla_\alpha \langle \psi_i | \psi_j \rangle$
$\psi(0)$
$\psi(\Delta t)$
$\psi(2\Delta t)$
$\psi(3\Delta t)$
$\psi(4\Delta t)$
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 μ.

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

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

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

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

to

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

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

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

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

Now, we take the derivatives

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

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

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

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

$$\frac{d\mathbf{q}}{dt}=\frac{\partial H}{\partial \mathbf{p}}$$

$$\frac{d\mathbf{p}}{dt}=-\frac{\partial H}{\partial \mathbf{q}}$$

with the Hamiltonian defined as

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

If:

1. The equations defining the generalized coordinates **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

$$\frac{d\mathbf{q}}{dt} = \frac{\partial H}{\partial \mathbf{p}}$$

$$\frac{d\mathbf{p}}{dt} = -\frac{\partial H}{\partial \mathbf{q}}$$

for both **q** and **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

few

small

large

Quantum Statistical Mechanics

$$i\hbar\frac{\mathrm{d}\rho}{\mathrm{d}t}=\left[\hat{H},\rho\right]$$

Classical Statistical Mechanics

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

Quantum Mechanics

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

Classical Mechanics

$$\frac{d\mathbf{q}}{dt}=\frac{\partial H}{\partial\mathbf{p}}\quad\frac{d\mathbf{p}}{dt}=-\frac{\partial H}{\partial\mathbf{q}}$$

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
- How many trajectories should we run? tinyurl.com/trajs

Papers available for download at:
amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX (Ask me for the password)