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Nonadiabatic Molecular Dynamics: Concepts, Methods, and Emerging Tools

II– Dynamics

Molecular problem

$$\hat{H}(\mathbf{R},\mathbf{r})\Psi(\mathbf{R},\mathbf{r}) = \varepsilon\Psi(\mathbf{R},\mathbf{r})$$

with

$$\hat{H}(\mathbf{R},\mathbf{r}) = \hat{T}_{nuc}(\mathbf{R}) + \hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})$$

✚

Born-Huang wave function

$$\Psi(\mathbf{R},\mathbf{r}) = \sum_n \varphi_n(\mathbf{r};\mathbf{R})\chi_n(\mathbf{R})$$

✚

Adiabatic approximation

$$\left\langle \varphi_{n'} \middle| \nabla^2_{\mathbf{R}} \varphi_n \right\rangle = \left\langle \varphi_{n'} \middle| \nabla_{\mathbf{R}} \varphi_n \right\rangle = 0$$

〓

Time-independent adiabatic formulation

Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc}(\mathbf{R}) + E(\mathbf{R})\right)\chi(\mathbf{R}) = \varepsilon\chi(\mathbf{R})$$

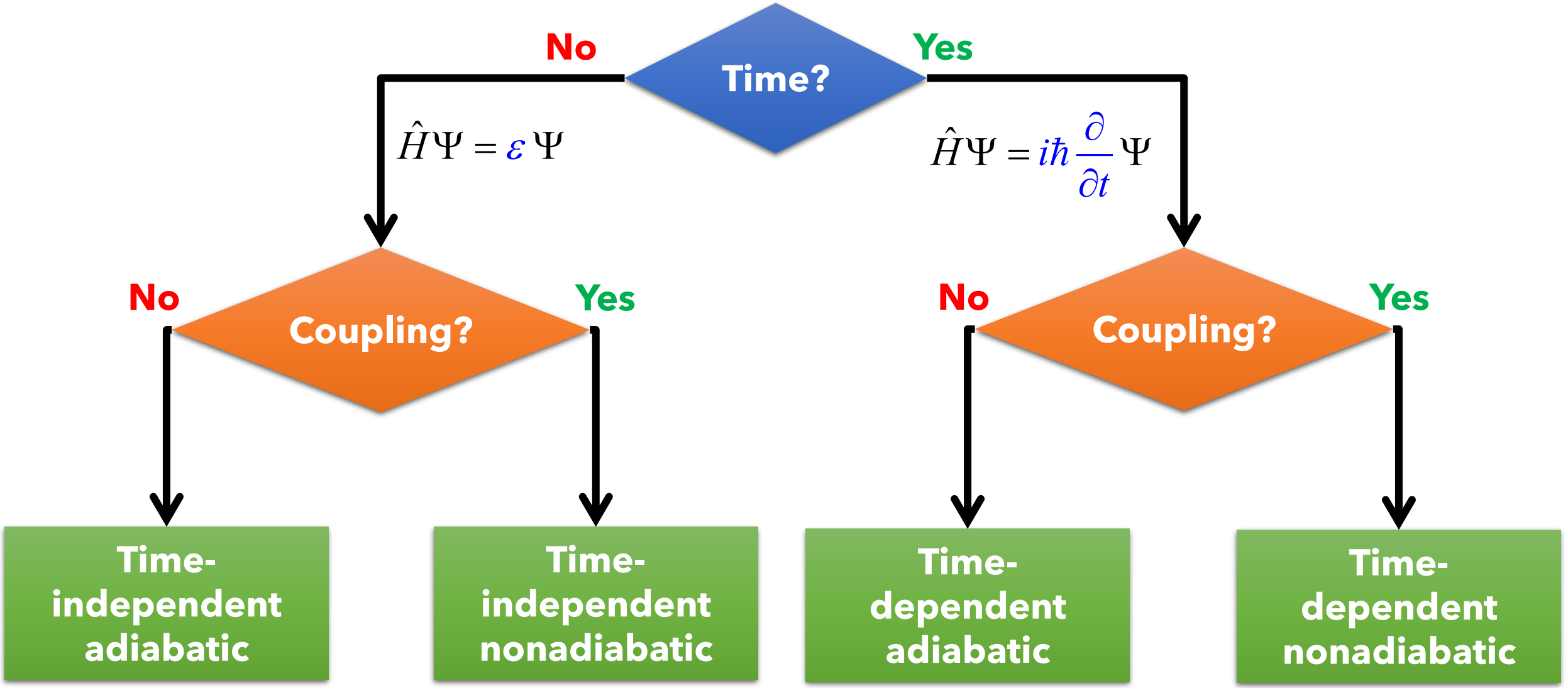
Electronic Schrödinger equation

$$\left(\hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})\right)\varphi(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r};\mathbf{R})$$

BO molecular wave function

$$\Psi^{BO}(\mathbf{R},\mathbf{r}) = \varphi(\mathbf{r};\mathbf{R})\chi(\mathbf{R})$$

Born-Oppenheimer-Huang formulation



Born-Oppenheimer-Huang formulation

Electronic Schrödinger equation

$$\left(\hat{T}_{elec} + V\right)\varphi_n = E_n\varphi_n$$

Nuclear Schrödinger equation

Adiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n = 0$$

Nonadiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Molecular wave function

$$\Psi = \varphi_n\chi_n$$

$$\Psi = \sum_m \varphi_n\chi_n$$

Adiabatic approximation

Born-Oppenheimer-Huang formulation

Electronic Schrödinger equation

$$\left(\hat{T}_{elec} + V\right)\varphi_n = E_n\varphi_n$$

Coupling terms

$$\hat{N}_{nm}\chi_n = \left[2\mathbf{F}_{mn}\cdot\nabla + G_{mn}\right]\chi_n$$

Nuclear Schrödinger equation

Adiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n = 0$$

Nonadiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Molecular wave function

$$\Psi = \varphi_n\chi_n$$

$$\Psi = \sum_m \varphi_n\chi_n$$

First-order nonadiabatic coupling vector

$$\mathbf{F}_{nm} = \begin{bmatrix} F_{nm,1,X} & F_{nm,1,Y} & F_{nm,1,Z} \\ F_{nm,2,X} & F_{nm,2,Y} & F_{nm,2,Z} \\ \vdots & \vdots & \vdots \\ F_{nm,N_{at},X} & F_{nm,N_{at},Y} & F_{nm,N_{at},Z} \end{bmatrix}$$

$$F_{nm,\alpha,X} = \left\langle \varphi_n \left| \frac{\partial \varphi_m}{\partial X_\alpha} \right\rangle \right.$$

$$= \int d\mathbf{r} \varphi_n^* \left(\mathbf{r}; \mathbf{R}_\alpha \right) \frac{\partial \varphi_m \left(\mathbf{r}; \mathbf{R}_\alpha \right)}{\partial X_\alpha}$$

$$\mathbf{F}_{mn}\left(\mathbf{R}\right) = \left\langle \varphi_m \left(\mathbf{r}; \mathbf{R} \right) \middle| \nabla_{\mathbf{R}} \varphi_n \left(\mathbf{r}; \mathbf{R} \right) \right\rangle_{\mathbf{r}}$$

For the more info, see the appendix to this presentation.

Second-order scalar coupling

$$G_{mn} = \begin{bmatrix} G_{mn,1} \\ G_{mn,2} \\ \vdots \\ G_{mn,N_{at}} \end{bmatrix} \qquad G_{mn,\alpha} = \left\langle \varphi_m \left| \frac{\partial^2 \varphi_n}{\partial X_\alpha^2} \right\rangle + \left\langle \varphi_m \left| \frac{\partial^2 \varphi_n}{\partial Y_\alpha^2} \right\rangle + \left\langle \varphi_m \left| \frac{\partial^2 \varphi_n}{\partial Z_\alpha^2} \right\rangle \right. \right. \right.$$

$$\begin{aligned} G_{mn}(\mathbf{R}) &= \left\langle \varphi_m(\mathbf{r};\mathbf{R}) \middle| \nabla_{\mathbf{R}}^2 \varphi_n(\mathbf{r};\mathbf{R}) \right\rangle_{\mathbf{r}} \\ &= \nabla \cdot \mathbf{F}_{mn}(\mathbf{R}) + \mathbf{F}_{mn}(\mathbf{R}) \cdot \mathbf{F}_{mn}(\mathbf{R}) \end{aligned}$$

Usually, G = 0 is assumed in trajectory-based nonadiabatic dynamics.

Adiabatic approximation

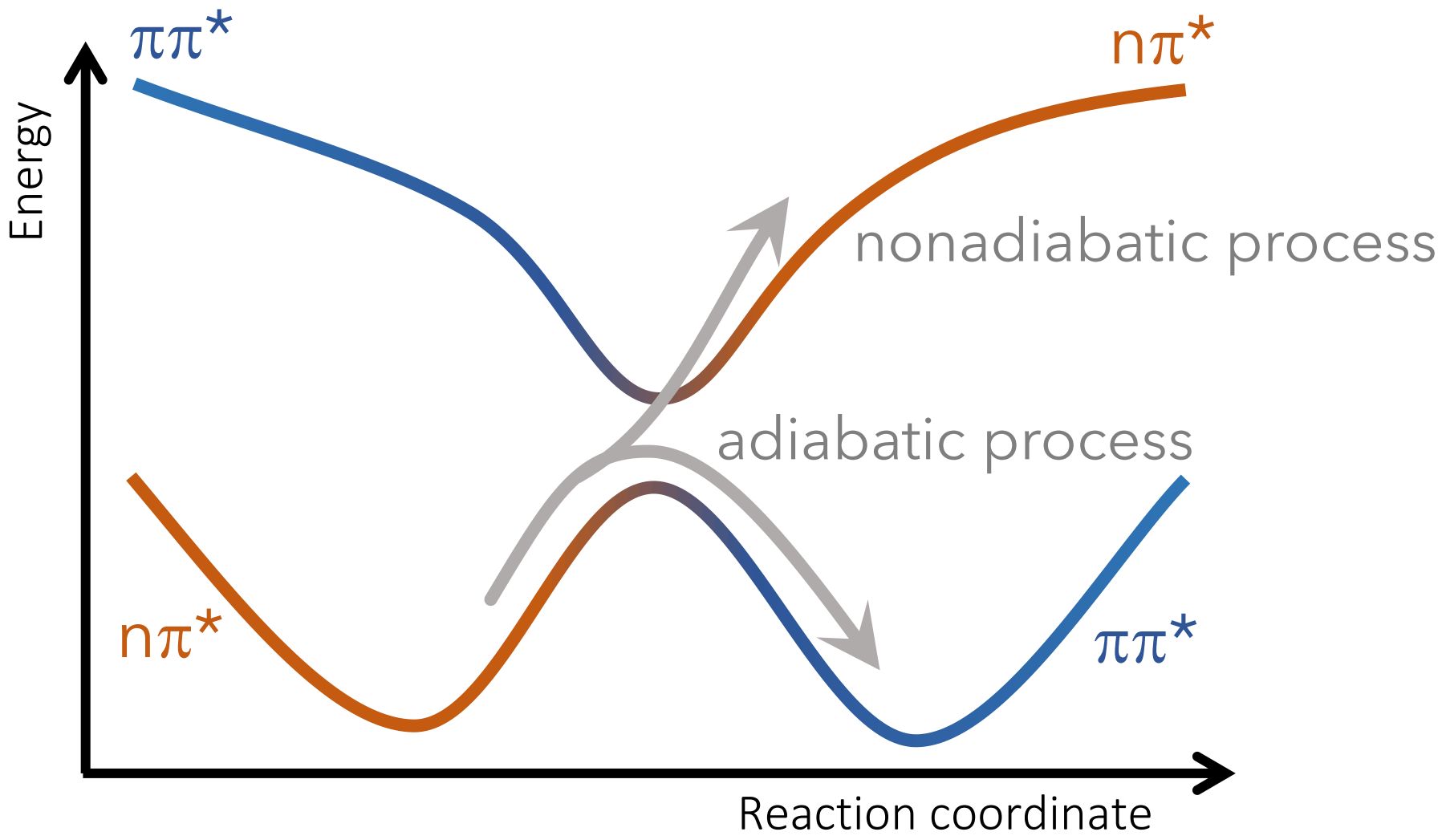
All coupling terms between electronic states are null.

$$\hat{N}_{nm}(\mathbf{R})\,\chi_n(\mathbf{R}) = 0$$

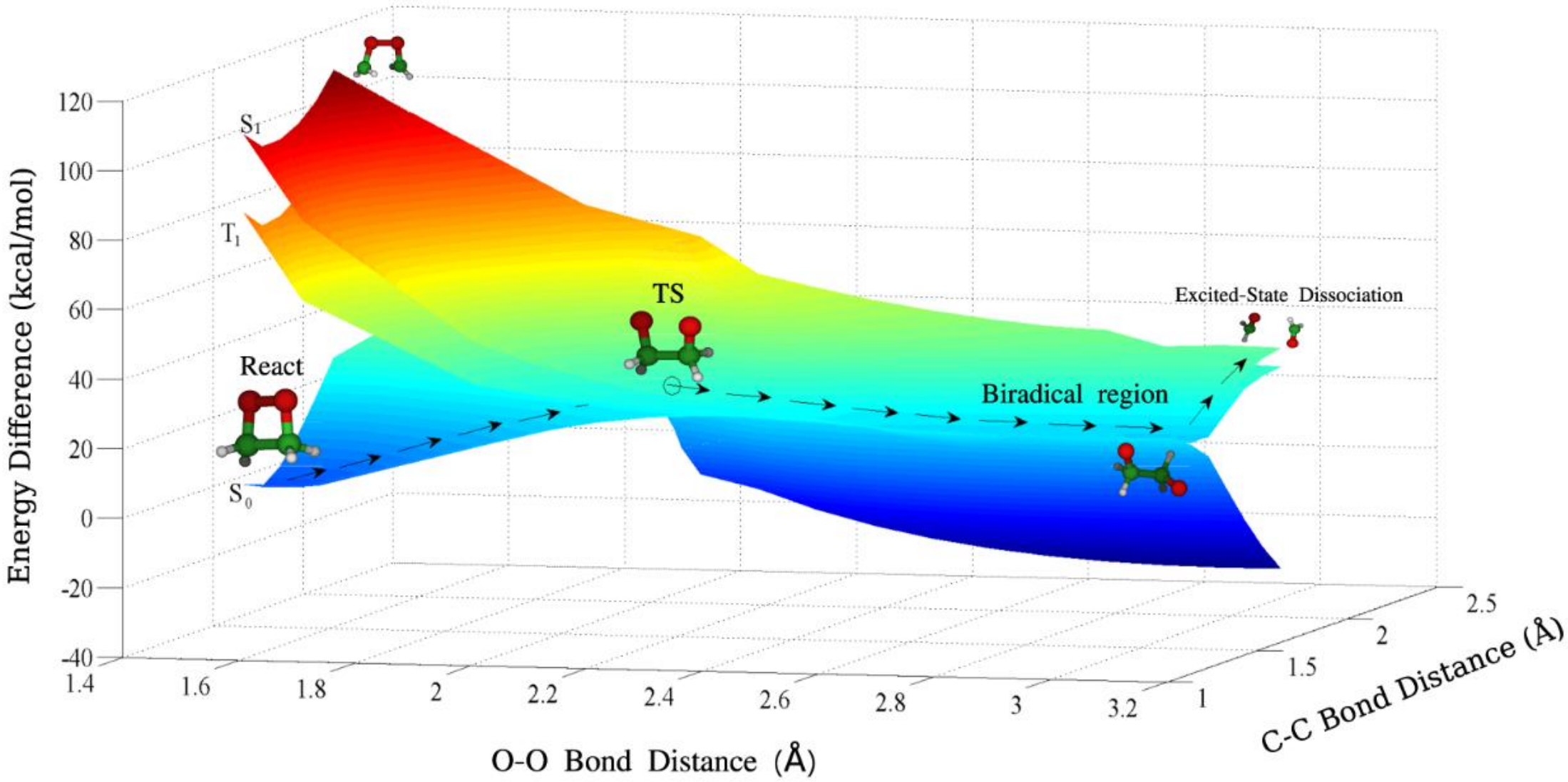
In practical terms, it means:

$$\left\langle \varphi_m \middle| \nabla^2_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} = 0$$

$$\left\langle \varphi_m \middle| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} = 0$$


ππ*
nπ*
Energy
nonadiabatic process
adiabatic process
nπ*
ππ*
Reaction coordinate

1,2-Dioxetane decomposition (bioluminescence)



Farahani *et al*. *JCTC* **2013**, *9*, 5404

Electronic structure

Born-Oppenheimer-Huang formulation

Electronic Schrödinger equation

$$\left(\hat{T}_{elec} + V\right)\varphi_n = E_n\varphi_n$$

Nuclear Schrödinger equation

Adiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n = 0$$

Nonadiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Molecular wave function

$$\Psi_n = \varphi_n\chi_n$$

$$\Psi = \sum_m \varphi_n\chi_n$$

Quantum chemistry's primary goal

Given a nuclear geometry **R**, solve the electronic Schrödinger equation in the adiabatic approximation

$$\left(\hat{T}_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)=E_n\left(\mathbf{R}\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)$$

to get electronic energies E_n and electronic wave function φ_n for state n.

Electronic structure methods

Wave-function based

$$\varphi_n(\mathbf{r};\mathbf{R})$$

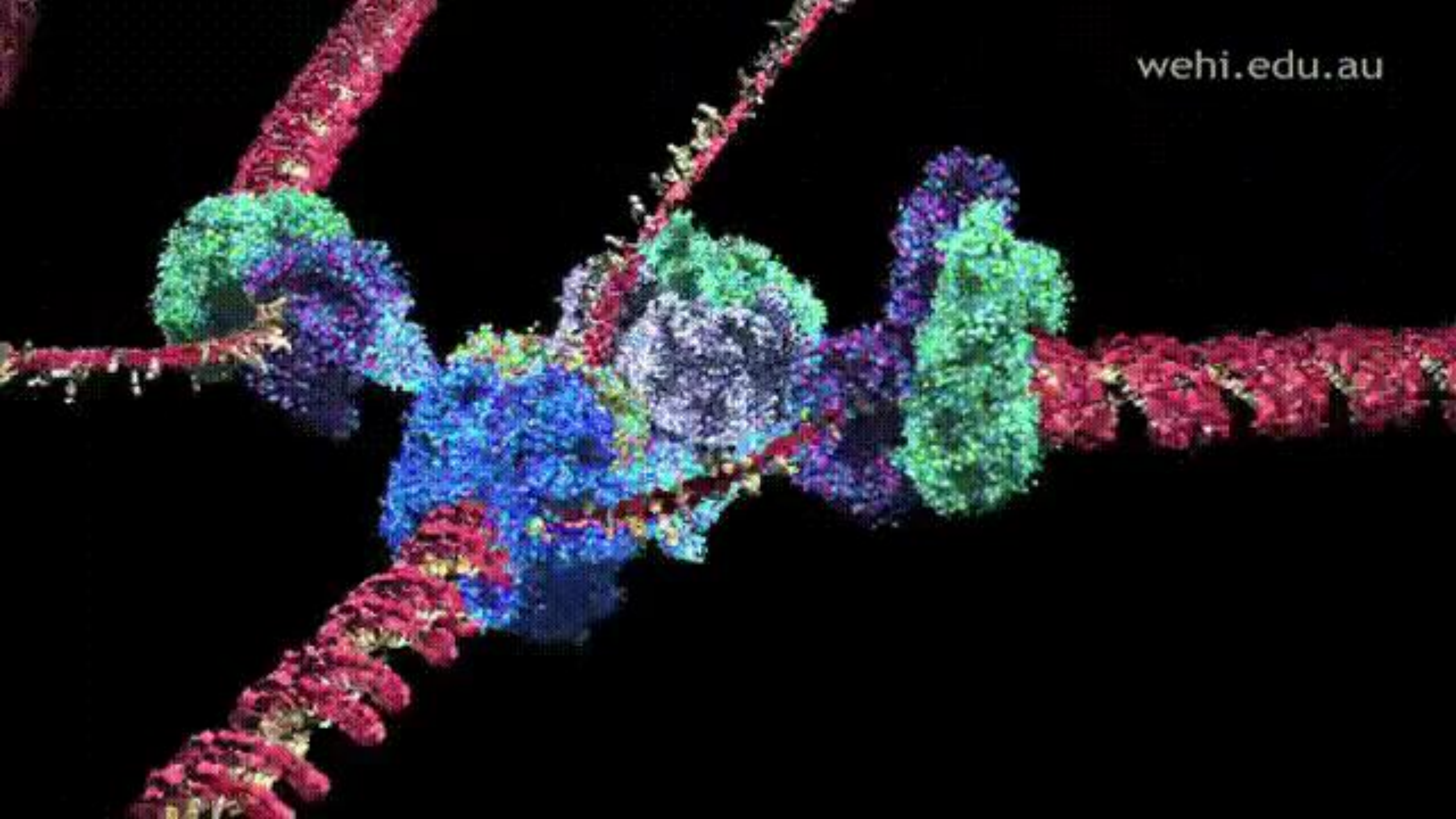
- Hartree-Fock
- MP
- CC
- CASSCF
- CASPT2
- CI
- ADC
- ...

Density based

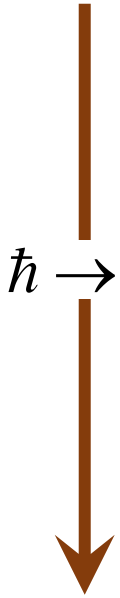
$$\rho_n(\mathbf{r};\mathbf{R})$$

- DFT
- DFTB
- TDDFT
- TDA
- DFT-CI
- REKS
- BSE
- ...

The classical nuclear motion


wehi.edu.au

Quantum nuclear motion



$\hbar \to 0$

Classical nuclear motion

Time-dependent adiabatic nuclear equation

$$\left(\hat{T}_{nuc} + E(\mathbf{R}) - i\hbar\frac{\partial}{\partial t}\right)\chi(\mathbf{R},t) = 0$$

Newton's nuclear equation

$$M_\alpha \frac{d^2\mathbf{R}_\alpha}{dt^2} = \mathbf{F}_\alpha$$

Hamilton-Jacobi formulation of classical mechanics

$$M_\alpha \frac{d^2\mathbf{R}_\alpha}{dt^2} = \mathbf{F}_\alpha$$

$$\frac{\partial S}{\partial t} + H\left(\mathbf{R}, \nabla S, t\right) = 0$$

$$S\left(\mathbf{R}, t\right) = \int_{t_0}^{t} L d\tau$$

$$\mathbf{p} = \nabla S$$

S: Action
L = *T* – *V:* Lagrangian
H = *T* + *V:* Hamiltonian

Classical limit of the Schrödinger equation $\left(\hbar \to 0\right)$

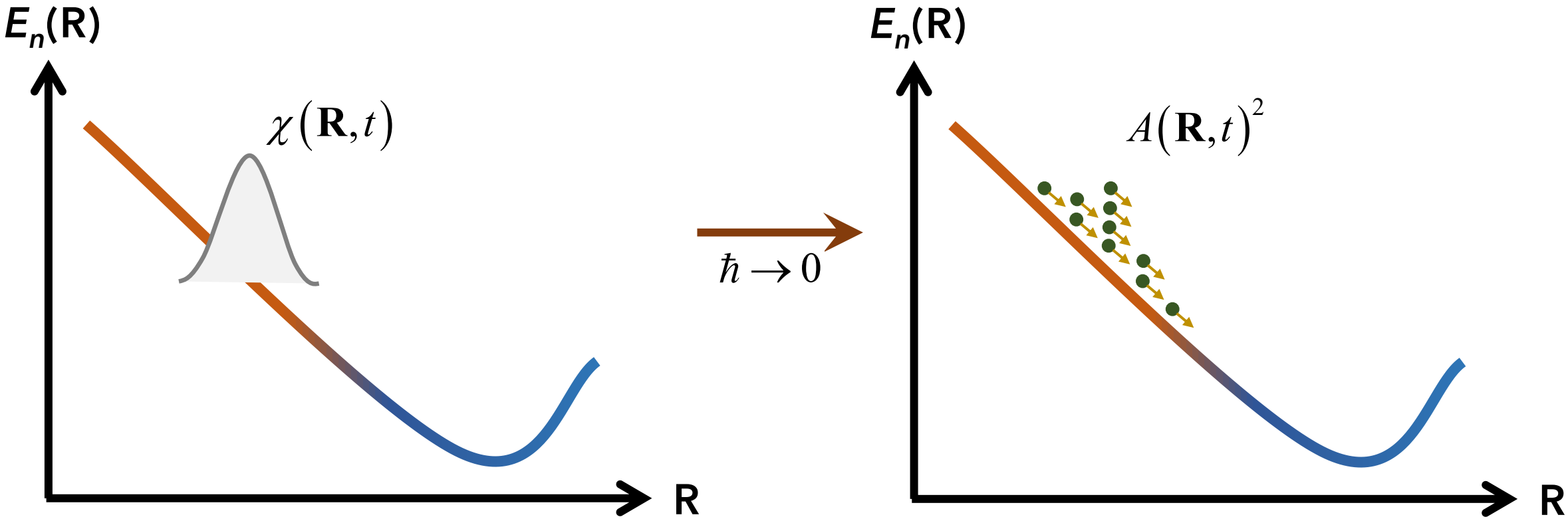
$$\frac{\partial S\left(\mathbf{R},t\right)}{\partial t} + H\left(\mathbf{R},\nabla S,t\right) = 0$$

$$\frac{\partial A\left(\mathbf{R},t\right)^2}{\partial t} + \frac{1}{\mathbf{M}}\nabla \cdot \left(A^2\left(\mathbf{R},t\right)\nabla S\left(\mathbf{R},t\right)\right) = 0$$

See demonstration in the appendix

"In the classical approximation, $\chi(\mathbf{R},t)$ describes **a fluid of non-interacting classical particles** of mass **M** (statistical mixture) and subject to the potential $E_n(\mathbf{R})$. The density and current density at each point of space are at all times respectively equal to the probability density A^2 and the probability current density $A^2\nabla S/\mathbf{M}$ of the quantum particles at that point."

- Messiah, *Quantum Mechanics*, p. 223



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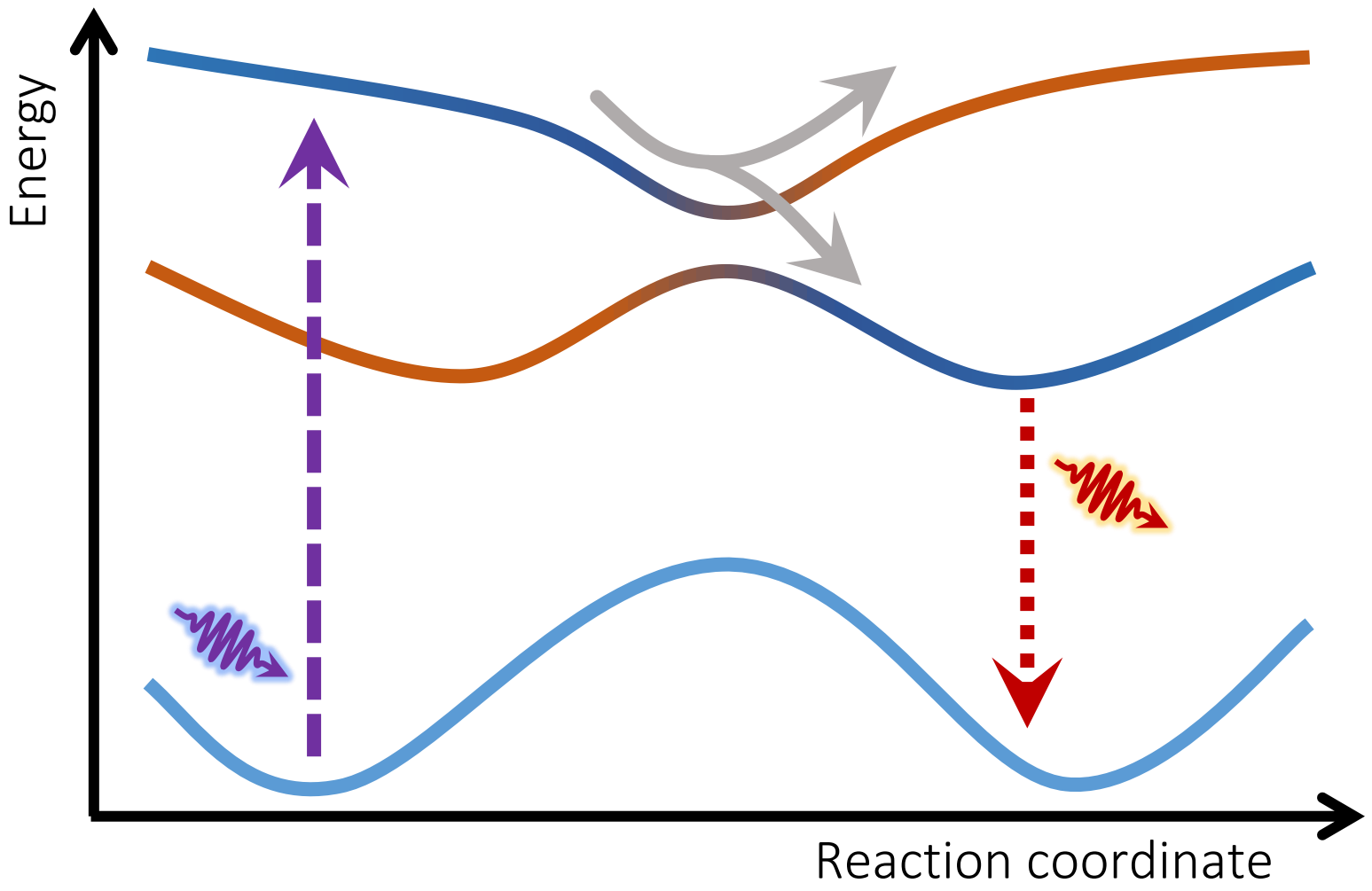
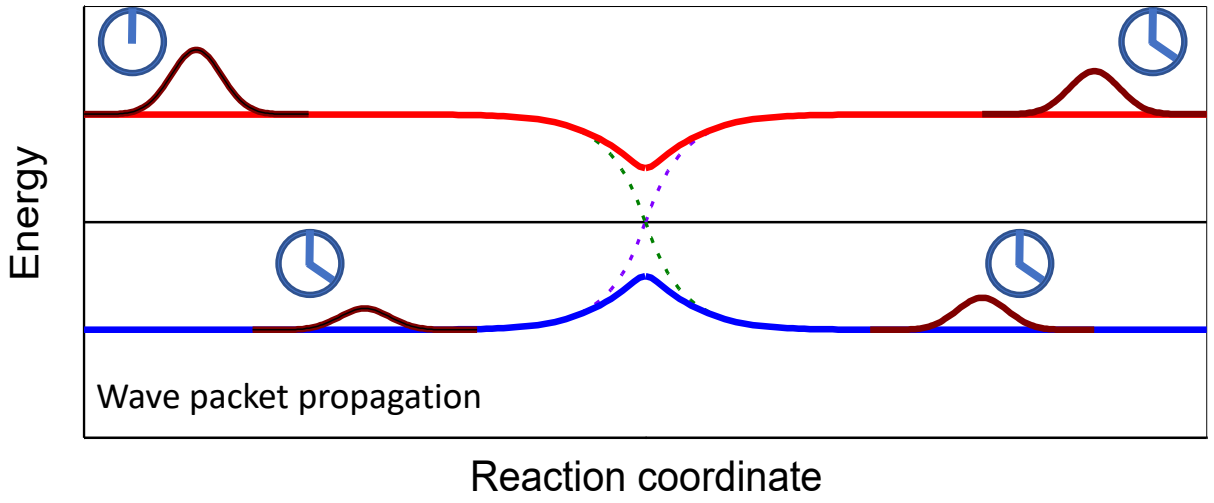
- Messiah, *Quantum Mechanics*, p. 223

This classical limit of the nuclear Schrödinger equation is the formal reason we can do molecular dynamics of molecules.

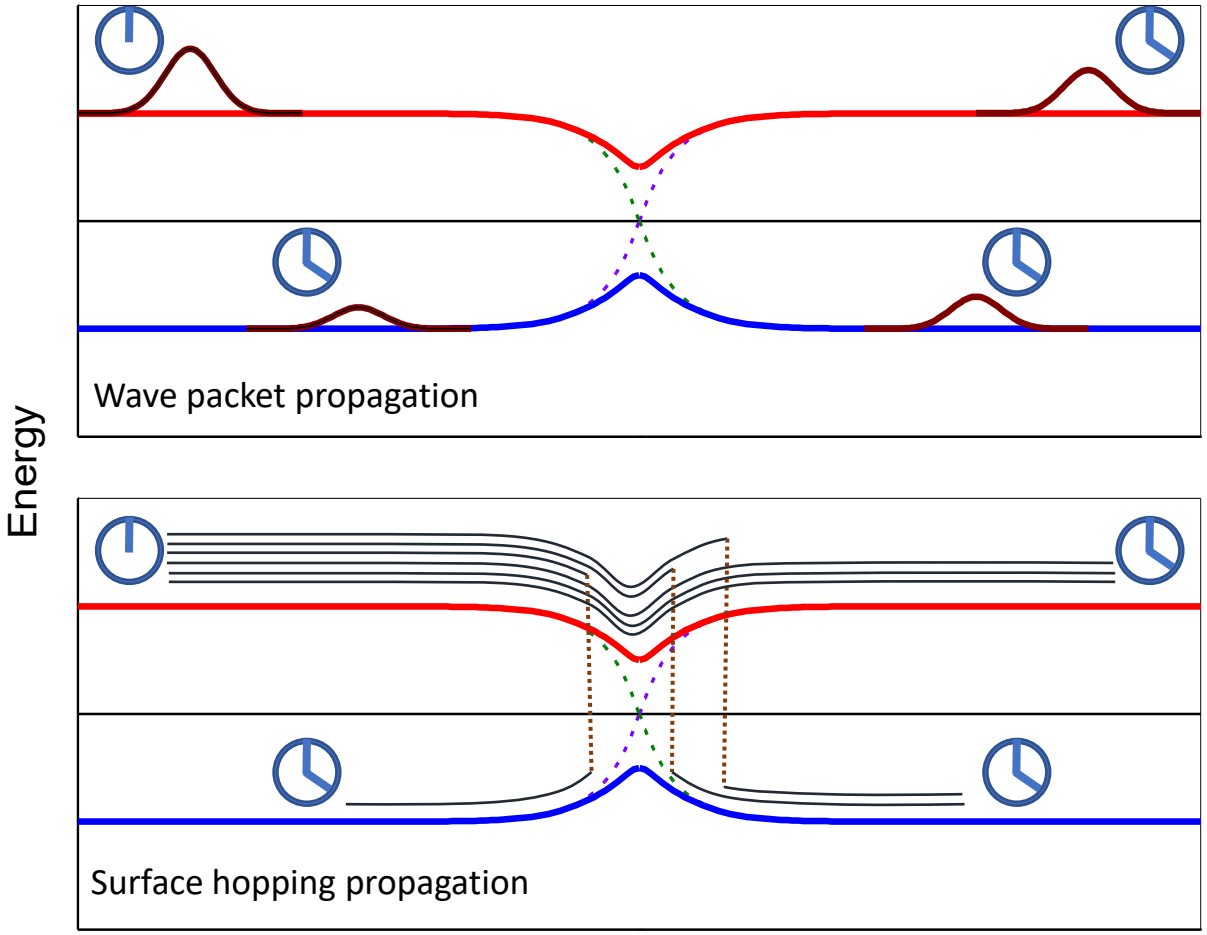
Nonadiabatic dynamics



- EM fields (photoabsorption, stimulated emission)
- Diabatic mixing (internal conversion, intersystem crossing)
- Vacuum fluctuations (fluorescence, phosphorescence)



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



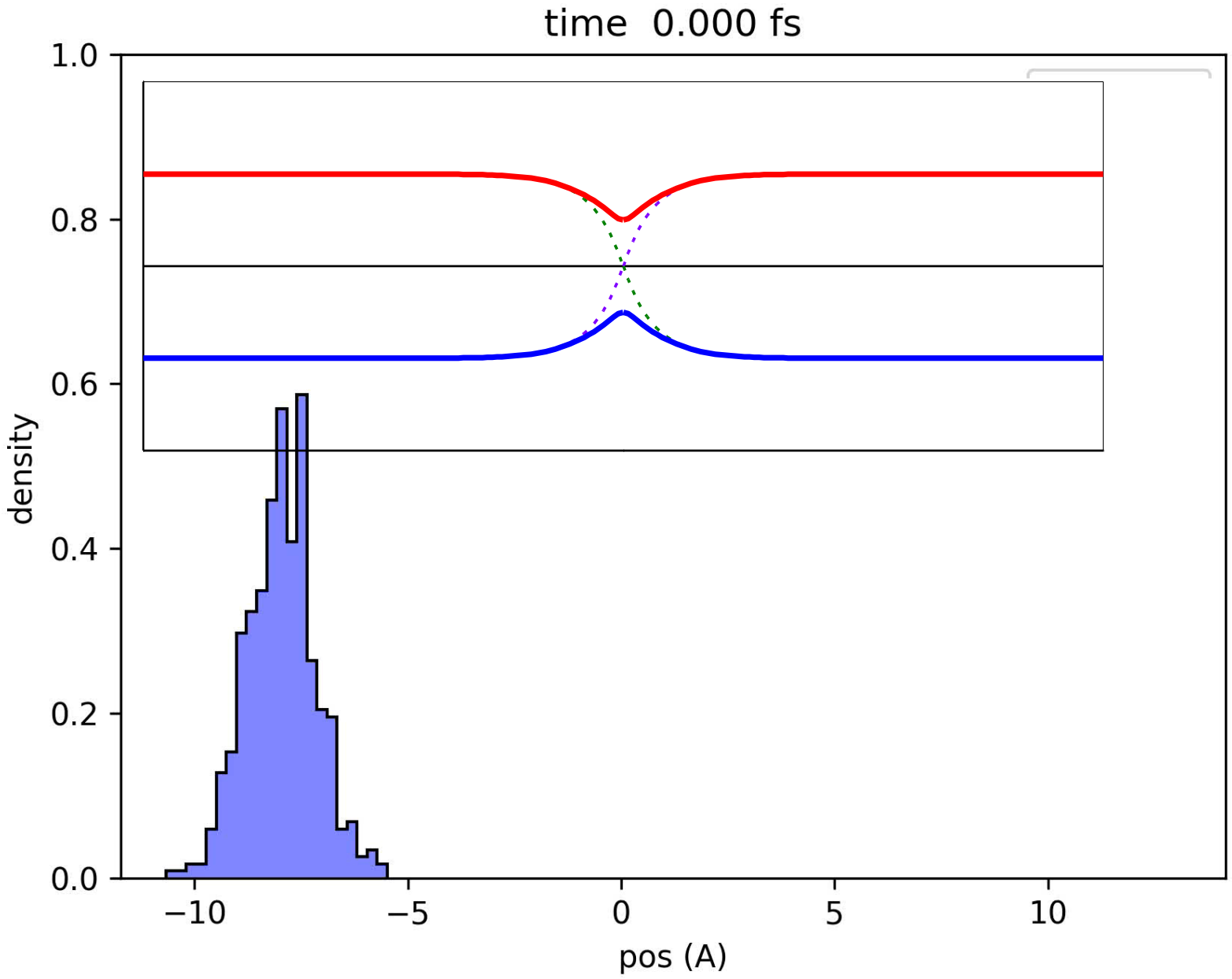
$$\left(\hat{T}_{nuc} + E_K(\mathbf{R}) - \sum_L N_{KL}(\mathbf{R})\right)\chi_K(\mathbf{R}) = i\hbar\frac{\partial\chi_K(\mathbf{R})}{\partial t}$$

Surface Hopping

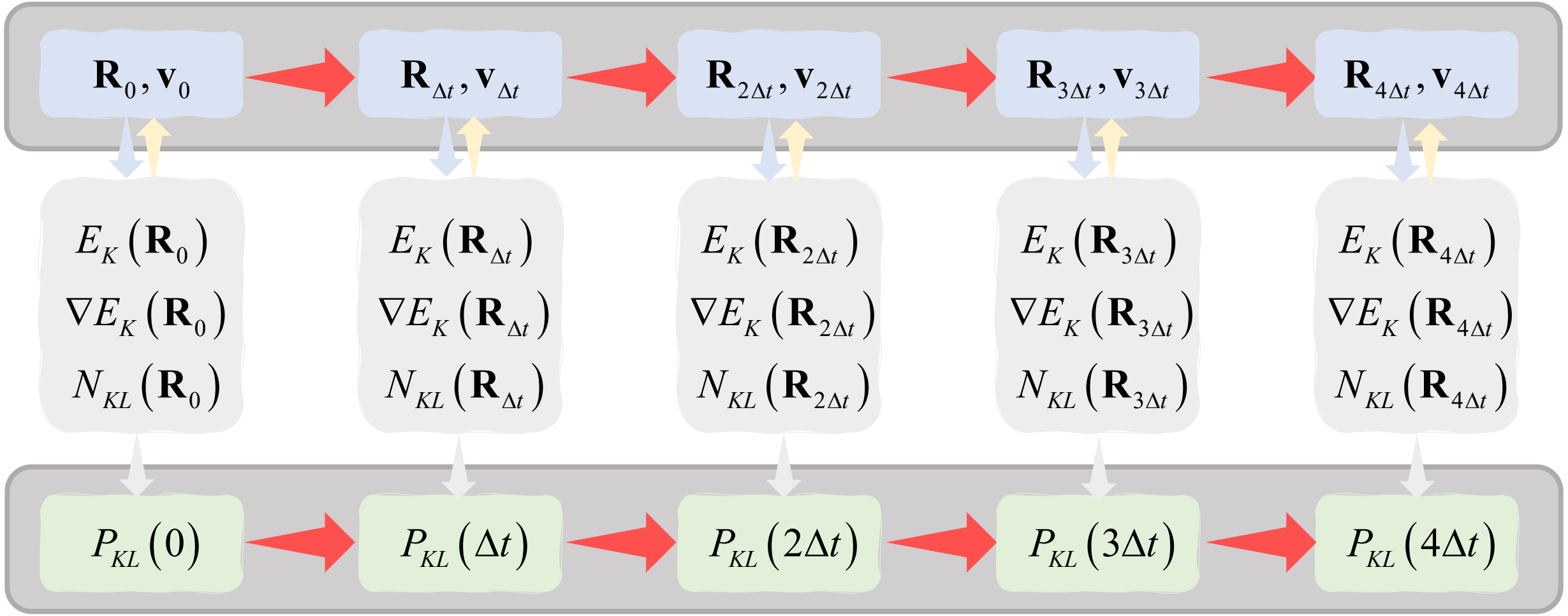
$$\frac{d^2\mathbf{R}_\alpha}{dt^2} = \frac{-\nabla_\alpha E_K(\mathbf{R})}{M_\alpha}$$

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

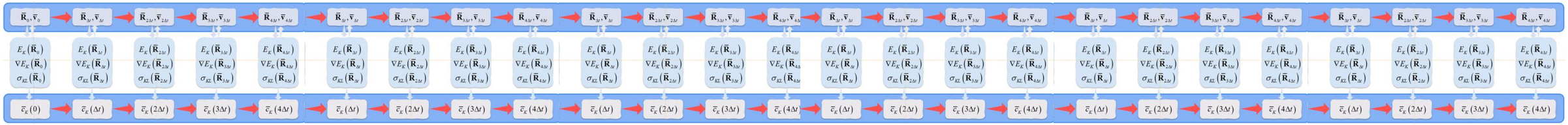
Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026


time 0.000 fs
1.0
0.8
0.6
0.4
0.2
0.0
density
−10
−5
0
5
10
pos (A)

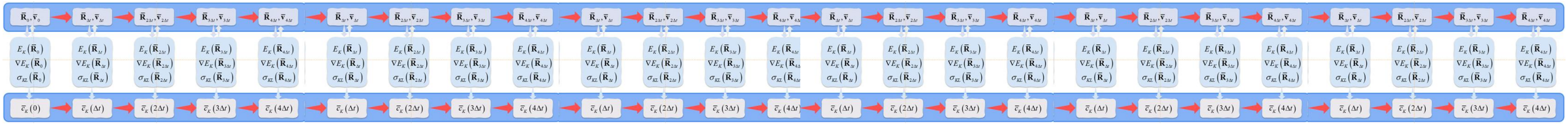
Equations of motion propagation



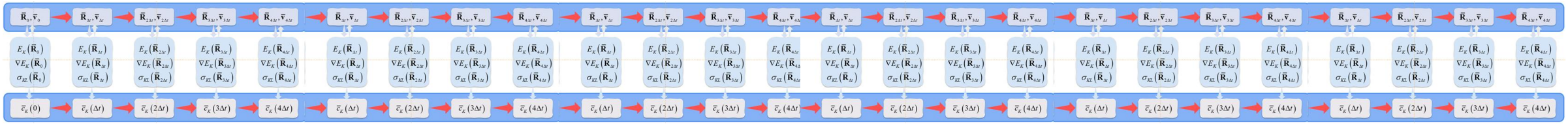
TRAJ 1



TRAJ 2



TRAJ 3



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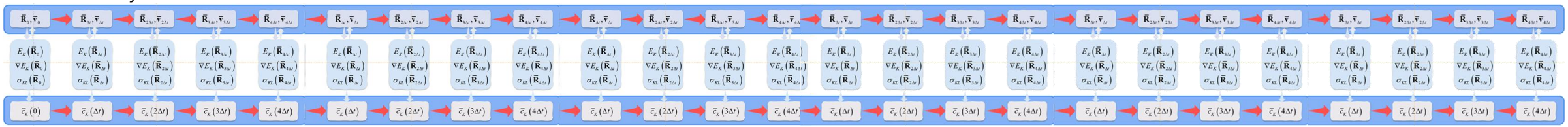
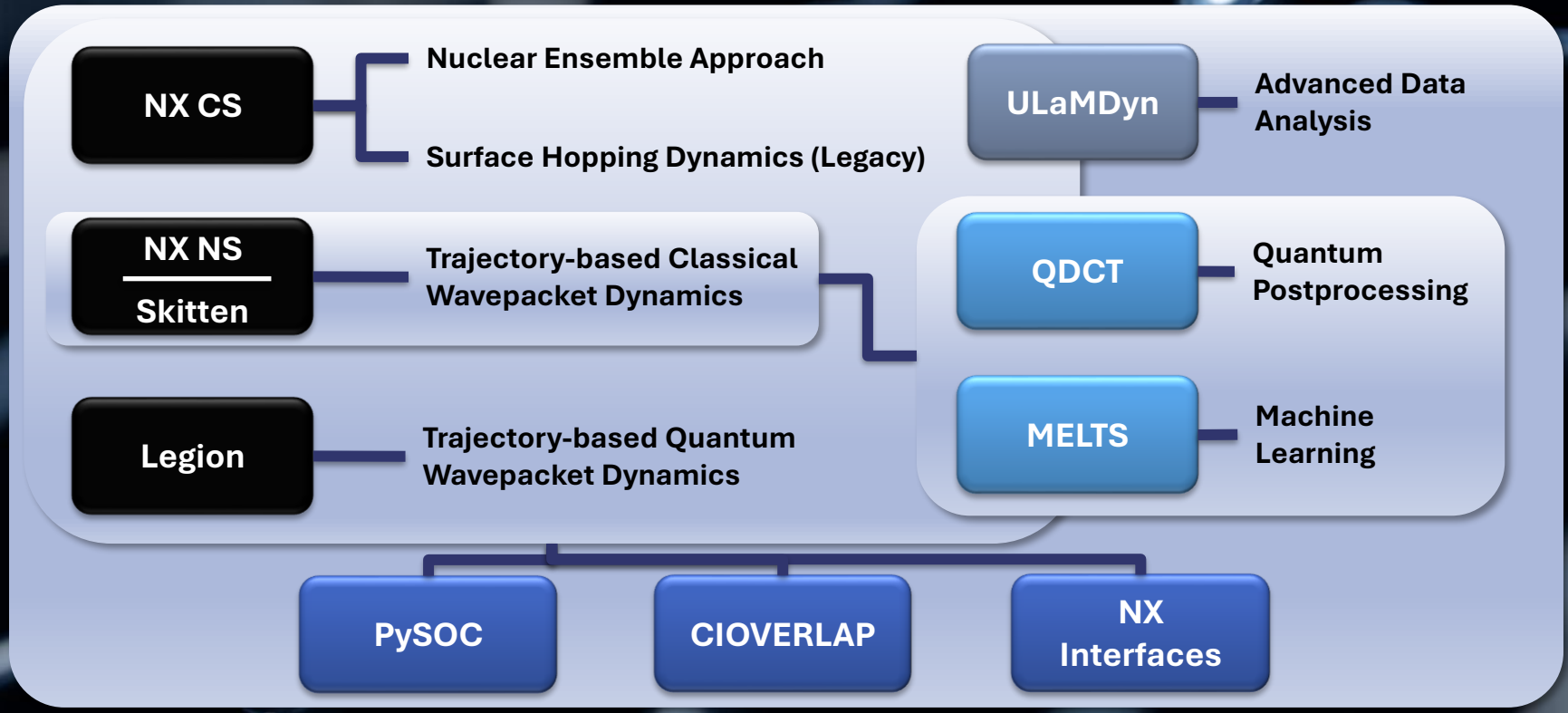
TRAJ N_{traj}



The Newton-X Platform



newtonx.org

amU Aix Marseille Université
Institut de Chimie Radicalaire
Theoretical Chemistry Team

Newtonian Dynamics Close to the X-Seam

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

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

Newtonian Dynamics Close to the X-Seam

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

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

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

To know more:

Quantum chemistry:

- **DFT:** Sherril, tinyurl.com/dftsherril
- **Insights on quantum chemistry:** Barbatti. *Pure Appl Chem* **2025**

Nonadiabatic couplings and conical intersections

- Sicilia *et al*. *J Phys Chem A* **2007,** *111*, 2182

Mixed quantum-classical nonadiabatic dynamics

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

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Appendix: Nonadiabatic coupling vector properties

Nonadiabatic coupling vector

$$\mathbf{F}_{nm}\left(\mathbf{R}\right) \equiv \left\langle \varphi_n\left(\mathbf{r};\mathbf{R}\right) \middle| \nabla_{\mathbf{R}} \varphi_m\left(\mathbf{r};\mathbf{R}\right) \right\rangle_{\mathbf{r}}$$

$$\mathbf{F}_{mn} = -\mathbf{F}_{nm}$$

$$\mathbf{F}_{nm} = \frac{\left\langle \varphi_n \middle| \nabla_{\mathbf{R}} H_{elec} \middle| \varphi_m \right\rangle_{\mathbf{r}}}{\left(E_m - E_n\right)}$$

The nonadiabatic coupling vector is antisymmetric

$$\nabla_{\mathbf{R}} \langle \varphi_n | \varphi_m \rangle = \langle \nabla_{\mathbf{R}} \varphi_n | \varphi_m \rangle + \langle \varphi_n | \nabla_{\mathbf{R}} \varphi_m \rangle = 0$$

$$\mathbf{F}_{mn} = \langle \nabla_{\mathbf{R}} \varphi_n | \varphi_m \rangle = -\langle \varphi_n | \nabla_{\mathbf{R}} \varphi_m \rangle = -\mathbf{F}_{nm}$$

$$\mathbf{F}_{mn} = -\mathbf{F}_{nm}$$

The nonadiabatic coupling vector transports the wave function

$$\left|\varphi_n\left(\mathbf{R}_0+\delta\mathbf{R}\right)\right\rangle=\left|\varphi_n\left(\mathbf{R}_0\right)\right\rangle+\nabla\left|\varphi_n\left(\mathbf{R}_0\right)\right\rangle\cdot\delta\mathbf{R}$$

$$\nabla\left|\varphi_n\right\rangle=\sum_m\mathbf{c}_{nm}\left|\varphi_m\right\rangle$$

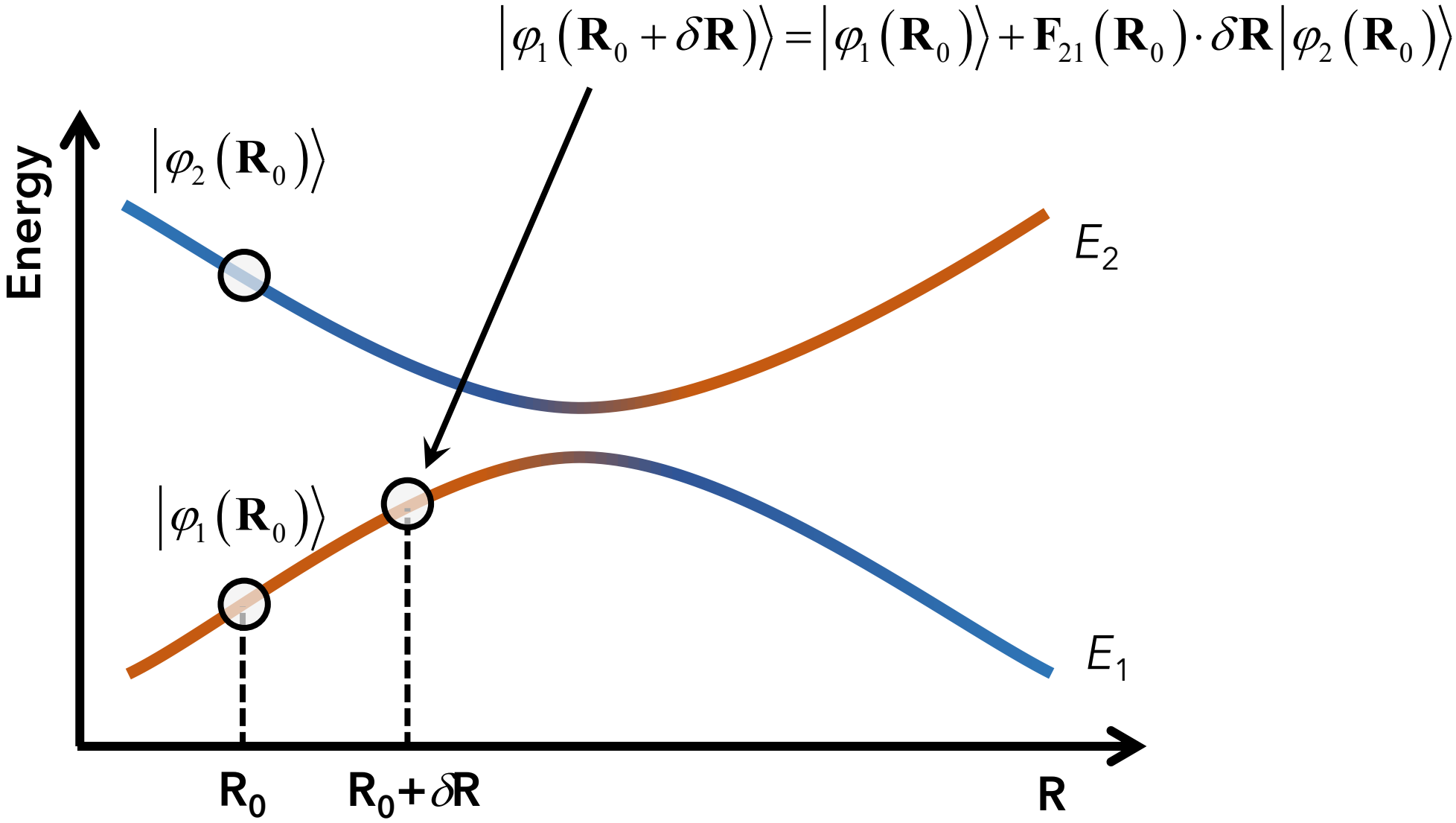
$$\left\langle\varphi_k\left|\nabla\varphi_n\right\rangle=\sum_m\mathbf{c}_{nm}\left\langle\varphi_k\left|\varphi_m\right\rangle\right.\right.$$

$$=\sum_m\mathbf{c}_{nm}\delta_{km}=\mathbf{c}_{nk}$$

$$\mathbf{c}_{nk}=\mathbf{F}_{kn}=-\mathbf{F}_{nk}\rightarrow\nabla\left|\varphi_n\right\rangle=\sum_m\mathbf{F}_{mn}\left|\varphi_m\right\rangle$$

$$\left|\varphi_n\left(\mathbf{R}_0+\delta\mathbf{R}\right)\right\rangle=\left|\varphi_n\left(\mathbf{R}_0\right)\right\rangle+\sum_m\mathbf{F}_{mn}\left(\mathbf{R}_0\right)\left|\varphi_m\left(\mathbf{R}_0\right)\right\rangle\cdot\delta\mathbf{R}$$

Baer, *Beyond Born-Oppenheimer*. **2006**


$\left|\varphi_1\left(\mathbf{R}_0+\delta\mathbf{R}\right)\right\rangle=\left|\varphi_1\left(\mathbf{R}_0\right)\right\rangle+\mathbf{F}_{21}\left(\mathbf{R}_0\right)\cdot\delta\mathbf{R}\left|\varphi_2\left(\mathbf{R}_0\right)\right\rangle$
Energy
$\left|\varphi_2\left(\mathbf{R}_0\right)\right\rangle$
E_2
$\left|\varphi_1\left(\mathbf{R}_0\right)\right\rangle$
E_1
$\mathbf{R}_0$
$\mathbf{R}_0+\delta\mathbf{R}$
R

The nonadiabatic coupling vector diverges at degeneracies

$$\left\langle \varphi_n \left| H_{elec} \right| \varphi_m \right\rangle = 0$$

$$\nabla_{\mathbf{R}} \left\langle \varphi_n \left| H_{elec} \right| \varphi_m \right\rangle = \left\langle \nabla_{\mathbf{R}} \varphi_n \left| H_{elec} \right| \varphi_m \right\rangle + \left\langle \varphi_n \left| \nabla_{\mathbf{R}} H_{elec} \right| \varphi_m \right\rangle + \left\langle \varphi_n \left| H_{elec} \right| \nabla_{\mathbf{R}} \varphi_m \right\rangle$$

$$= E_m \left\langle \nabla_{\mathbf{R}} \varphi_n \left| \varphi_m \right\rangle + \left\langle \varphi_n \left| \nabla_{\mathbf{R}} H_{elec} \right| \varphi_m \right\rangle + E_n \left\langle \varphi_n \left| \nabla_{\mathbf{R}} \varphi_m \right\rangle \right.$$

$$E_m \mathbf{F}_{mn} + \left\langle \varphi_n \left| \nabla_{\mathbf{R}} H_{elec} \right| \varphi_m \right\rangle + E_n \mathbf{F}_{nm} = 0$$

$$\left\langle \varphi_n \left| \nabla_{\mathbf{R}} H_{elec} \right| \varphi_m \right\rangle = \left(E_m - E_n \right) \mathbf{F}_{nm}$$

$$\mathbf{F}_{nm} = \frac{\left\langle \varphi_n \left| \nabla_{\mathbf{R}} H_{elec} \right| \varphi_m \right\rangle}{\left(E_m - E_n \right)}$$

At the state crossing:

$$\lim_{E_m = E_n} \left(\left| \mathbf{F}_{nm} \right| \right) \to \infty$$

Appendix: Demonstration of the classical limit of the Nuclear Schrödinger Equation

Messiah. Quantum Mechanics, 1961 (vol 1, p. 222)

1. Start with the Nuclear Schrödinger equation in TD-BOA:

$$T_{nuc}\left(\mathbf{R}\right)h_n\left(\mathbf{R},t\right)+E_n\left(\mathbf{R}\right)h_n\left(\mathbf{R},t\right)-i\hbar\frac{\partial h_n\left(\mathbf{R},t\right)}{\partial t}=0$$

2. Assume the nuclear wave function in polar form

$$h_n\left(\mathbf{R},t\right)=A\left(\mathbf{R},t\right)\exp\left(\frac{i}{\hbar}S\left(\mathbf{R},t\right)\right)$$

3. Use the nuclear kinetic energy operator

$$T_{nuc}=-\frac{\hbar^2}{2\mathbf{M}}\nabla^2$$

4. After a lot of algebra, we get ....

Messiah. Quantum Mechanics, 1961 (vol 1, p. 222)

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]+E_n(\mathbf{R})\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$-i\hbar\partial_t\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]=0$$

Now, we make a lot of algebraic manipulation

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]+E_n(\mathbf{R})\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$-i\hbar\partial_t\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]=0$$

$$\nabla^2\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]=\nabla\cdot\nabla\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$=\nabla\cdot\left[\nabla A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+A(\mathbf{R},t)\nabla\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$=\nabla\cdot\left[\nabla A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+\frac{i}{\hbar}A(\mathbf{R},t)\nabla S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$\nabla^2\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]=\nabla\cdot\left[\nabla A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]+\nabla\cdot\left[\frac{i}{\hbar}A(\mathbf{R},t)\nabla S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$=\left[\nabla^2 A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+\nabla A(\mathbf{R},t)\cdot\nabla\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$+\left[\frac{i}{\hbar}\nabla A(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+\frac{i}{\hbar}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+\frac{i}{\hbar}A(\mathbf{R},t)\nabla S(\mathbf{R},t)\cdot\nabla\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$=\nabla^2 A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+\frac{2i}{\hbar}\nabla A(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)$$

$$+\frac{i}{\hbar}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)-\frac{1}{\hbar^2}A(\mathbf{R},t)\left(\nabla S(\mathbf{R},t)\right)^2\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]+E_n(\mathbf{R})\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]$$

$$-i\hbar\partial_t\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]=0$$

$$\partial_t\left[A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)\right]=\partial_t A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+A(\mathbf{R},t)\partial_t\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)$$

$$=\partial_t A(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)+\frac{i}{\hbar}A(\mathbf{R},t)\partial_t S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)$$

$$-\frac{\hbar^2}{2\mathbf{M}}\left[\nabla^2 A(\mathbf{R},t)+\frac{2i}{\hbar}\nabla A(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)+\frac{i}{\hbar}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)-\frac{1}{\hbar^2}A(\mathbf{R},t)\left(\nabla S(\mathbf{R},t)\right)^2\right]$$
$$+E_n(\mathbf{R})A(\mathbf{R},t)-i\hbar\partial_t A(\mathbf{R},t)+A(\mathbf{R},t)\partial_t S(\mathbf{R},t)=0$$

Separate real and imaginary terms

$$-\frac{\hbar^2}{2\mathbf{M}}\left[\nabla^2 A(\mathbf{R},t)+\frac{2i}{\hbar}\nabla A(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)+\frac{i}{\hbar}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)-\frac{1}{\hbar^2}A(\mathbf{R},t)\left(\nabla S(\mathbf{R},t)\right)^2\right]$$

$$+E_n(\mathbf{R})A(\mathbf{R},t)-i\hbar\partial_t A(\mathbf{R},t)+A(\mathbf{R},t)\partial_t S(\mathbf{R},t)=0$$

$$\partial_t S(\mathbf{R},t)+\frac{1}{2\mathbf{M}}\left(\nabla S(\mathbf{R},t)\right)^2+E_n(\mathbf{R})-\frac{\hbar^2}{2\mathbf{M}}\frac{\nabla^2 A(\mathbf{R},t)}{A(\mathbf{R},t)}=0$$

$$\partial_t A(\mathbf{R},t)+\frac{1}{\mathbf{M}}\left[\nabla A(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)+\frac{1}{2}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)\right]=0$$

Multiply the second equation by 2*A*

$$2A(\mathbf{R},t)\partial_t A(\mathbf{R},t)+\frac{2A(\mathbf{R},t)}{\mathbf{M}}\left[\nabla A(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)+\frac{1}{2}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)\right]=0$$

$$\partial_t A(\mathbf{R},t)^2+\frac{1}{\mathbf{M}}\left[\nabla A^2(\mathbf{R},t)\cdot\nabla S(\mathbf{R},t)+A(\mathbf{R},t)^2\nabla^2 S(\mathbf{R},t)\right]=0$$

$$\partial_t A(\mathbf{R},t)^2+\frac{1}{\mathbf{M}}\nabla\cdot\left[A^2(\mathbf{R},t)\nabla S(\mathbf{R},t)\right]=0$$

Classical limit

$$\partial_t S(\mathbf{R},t)+\frac{1}{2\mathbf{M}}\left(\nabla S(\mathbf{R},t)\right)^2+E_n(\mathbf{R})-\frac{\hbar^2}{2\mathbf{M}}\frac{\nabla^2 A(\mathbf{R},t)}{A(\mathbf{R},t)}=0$$

$$\lim \hbar \to 0$$

$$\partial_t S(\mathbf{R},t)+\frac{1}{2\mathbf{M}}\left(\nabla S(\mathbf{R},t)\right)^2+E_n(\mathbf{R})=0$$

$$T_{nuc}=\frac{1}{2\mathbf{M}}\left(\nabla S(\mathbf{R},t)\right)^2$$

$$H=T_{nuc}+E_n(\mathbf{R})$$

$$\partial_t S+H(\mathbf{R},\nabla S,t)=0$$

That's the Hamilton-Jacobi equation!