



# L3 – Quantum Mechanics 3

Beyond Born-Oppenheimer

Previously on...

# **Computational simulations of nanosystems**

Field-free non-relativistic molecular problem

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

with

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

Born-Huang wave function

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

Adiabatic approximation

$$\langle \varphi_{n'} | \nabla_{\mathbf{R}}^2 \varphi_n \rangle_{\mathbf{r}} \chi_n + 2 \langle \varphi_{n'} | \nabla_{\mathbf{R}} \varphi_n \rangle_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} \chi_n = 0$$

Time-independent Born-Oppenheimer adiabatic formulation

BO molecular wave function

$$\Psi_n^{BO}(\mathbf{R}, \mathbf{r}) = \varphi_n(\mathbf{r}; \mathbf{R}) \chi_n(\mathbf{R})$$

Nuclear Schrödinger equation

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

Electronic Schrödinger equation

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

1. For fixed  $\mathbf{R}$ , Solve the *electronic* Schrödinger equation to get  $E_n(\mathbf{R})$  and  $\varphi(\mathbf{r};\mathbf{R})$

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

2. Solve *nuclear* Schrödinger equation on the electronic potential  $E_n(\mathbf{R})$  to get  $\chi_n(\mathbf{R})$  and  $\varepsilon$

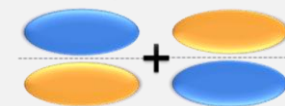
$$\left(\hat{T}_{nuc}(\mathbf{R}) + E_n(\mathbf{R})\right) \chi_n(\mathbf{R}) = \varepsilon \chi_n(\mathbf{R})$$

# To solve the electronic equation:

4. Use WF to get the final electronic WF or density



3. Use MOs to build electronic wave function (WF) guess



2. Use AOs to build molecular orbitals (MO)



1. Define atomic orbital (AO) basis



With this procedure, the electronic equation becomes

$$\mathbf{H}(E, \mathbf{C})\mathbf{C} = E\mathbf{C}$$

↑            ↑            ↑  
everything is unknown!

Such a problem is solved with a self-consistent approach (SFC):

1. Guess an approximated  $E^{(0)}$  and  $\mathbf{C}^{(0)}$  and solve

$$\mathbf{H}(E^{(0)}, \mathbf{C}^{(0)})\mathbf{C}^{(1)} = E^{(1)}\mathbf{C}^{(1)}$$

2. Use  $E^{(1)}$  and  $\mathbf{C}^{(1)}$  to solve

$$\mathbf{H}(E^{(1)}, \mathbf{C}^{(1)})\mathbf{C}^{(2)} = E^{(2)}\mathbf{C}^{(2)}$$

3. Continue the iterations until

$$E^{(N)} = E^{(N-1)}$$

**A bit of history**



**Max Born**  
**(1882 - 1970)**





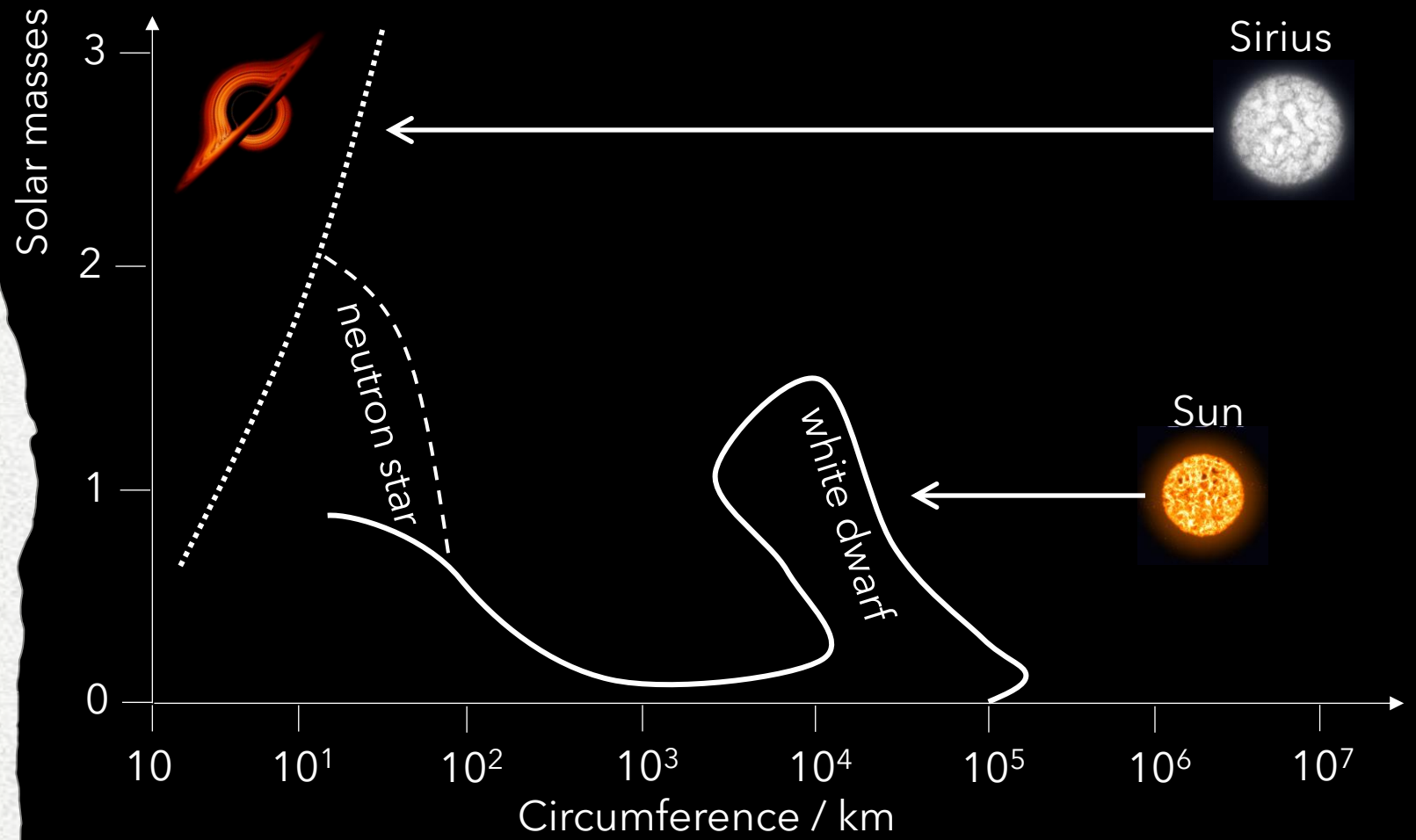
Born rule

$$P(\alpha) = |\langle \alpha | \Psi \rangle|^2$$



# J. Robert Oppenheimer (1904 - 1967)





# ANNALEN DER PHYSIK

## VIERTE FOLGE. BAND 84

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### 1. *Zur Quantentheorie der Molekeln;* *von M. Born und R. Oppenheimer*

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Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel, die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von Kramers und Pauli (Kreisel mit eingebautem Schwungrad) darstellt. Ferner ergibt sich eine Rechtfertigung der von Franck und Condon angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Molekeln erläutert.

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$$(15) \quad \left\{ H_0 \left( x, \frac{\partial}{\partial x}; \xi, \mathcal{V} \right) - V_n(\xi) \right\} \varphi_n(x; \xi, \mathcal{V}) = 0$$

$$\left[ H_{elec} - E_n(\mathbf{R}) \right] \varphi_n(\mathbf{r}; \mathbf{R}) = 0$$

"The most important goal of our investigation is to prove that the function  $V_n(\xi)$  plays the role of a potential for nuclear motion."

B&O, 1927

$$\kappa = \left( \frac{m}{M} \right)^{1/4}$$

Develop Hamiltonian, wave function, and energies in a perturbative series in  $\kappa$ .

$$f(\mathbf{R} + \kappa\boldsymbol{\rho}) = f^{(0)} + \kappa f^{(1)} + \kappa^2 f^{(2)} + \dots$$

Solve the equation for each order

$$(35) \left\{ \begin{array}{l} \text{a) } (H_0^0 - W^0) \psi^0 = 0, \\ \text{b) } (H_0^0 - W^0) \psi^{(1)} = (W^{(1)} - H_0^{(1)}) \psi^0, \\ \text{c) } (H_0^0 - W^0) \psi^{(2)} = (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0) \psi^0 \\ \quad + (W^{(1)} - H_0^{(1)}) \psi^{(1)}, \\ \text{d) } (H_0^0 - W^0) \psi^{(3)} = (W^{(3)} - H_0^{(3)} - H_{\zeta\vartheta}^0 - H_{\zeta\zeta}^{(1)}) \psi^0 \\ \quad + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0) \psi^{(1)} + (W^{(1)} - H_0^{(1)}) \psi^{(2)}, \\ \text{e) } (H_0^0 - W^0) \psi^{(4)} = (W^{(4)} - H_0^{(4)} - H_{\vartheta\vartheta}^0 - H_{\zeta\vartheta}^{(1)} - H_{\zeta\zeta}^{(2)}) \psi^0 \\ \quad + (W^{(3)} - H_0^{(3)} - H_{\zeta\vartheta}^0 - H_{\zeta\zeta}^{(1)}) \psi^{(1)} \\ \quad + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^0) \psi^{(2)} + (W^{(1)} - H_0^{(1)}) \psi^{(3)}, \\ \dots \end{array} \right.$$

[the second order] represents the equation for harmonic nuclear vibration

$$(46) \quad \left\{ H_{\zeta\zeta}^0 \left( \boldsymbol{\xi}, \frac{\delta^2}{\partial \zeta_i \partial \zeta_j} \right) + \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \xi_i \partial \xi_j} - W_n^{(2)} \right\} \chi_n = 0.$$

$$\left( T_{nuc}(\mathbf{R}) + \frac{1}{2} \sum_{ij} \frac{\partial^2 E_n(\mathbf{R}_0)}{\partial R_i \partial R_j} R_i R_j - \varepsilon_n \right) \chi_n(\mathbf{R}) = 0$$



"The nuclear vibrations correspond to terms of second order and the rotations to fourth order in the energy, while the first and third order terms vanish. The absence of the first order terms is related to the existence of an equilibrium position of the nuclei, in which the electronic energy for stationary nuclei is at a minimum."

B&O 1927

**It has, however, been found, in particular by studying molecular vibrations, that the adiabatic model has a wider application than predicted by this theory. There exists in fact another method which contains this practical result, with the only modification that the potential energy of the nuclei is not the energy eigenvalue of the electronic state considered, but a slightly different quantity. This method has the further advantage that it leads to a system of simultaneous equations for all electronic states which represent the coupling of electronic and nuclear motion in a rigorous way.**

## Born-Huang wave function

$$(H - E)\Psi(x, X) = 0; \quad (\text{VIII.4})$$

we try to solve it by an expansion

$$\Psi(x, X) = \sum_n \psi_n(X) \phi_n(x, X). \quad (\text{VIII.5})$$

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

# Adiabatic approximation

# Adiabatic approximation

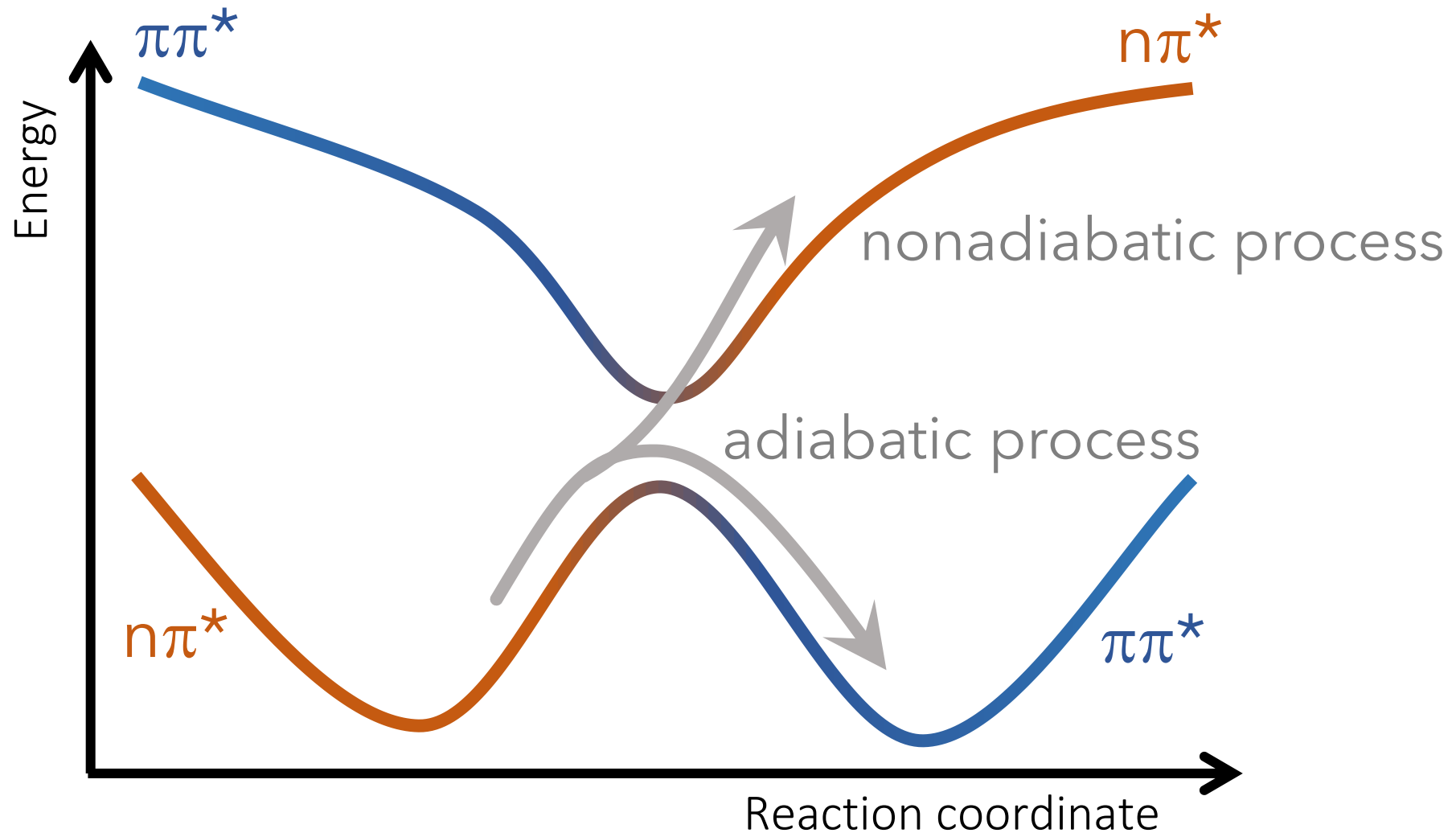
$$\hat{N}_{n'n}(\mathbf{R})\chi_n(\mathbf{R}) = -\sum_{\rho=1}^{3N_{at}} \frac{\hbar^2}{2M_\rho} \left[ \left\langle \varphi_{n'} \left| \frac{\partial^2 \varphi_n}{\partial \mathbf{R}_\rho^2} \right\rangle_{\mathbf{r}} \chi_n + 2 \left\langle \varphi_{n'} \left| \frac{\partial \varphi_n}{\partial \mathbf{R}_\rho} \right\rangle_{\mathbf{r}} \frac{\partial \chi_n}{\partial \mathbf{R}_\rho} \right] = 0$$

or to simplify the notation:

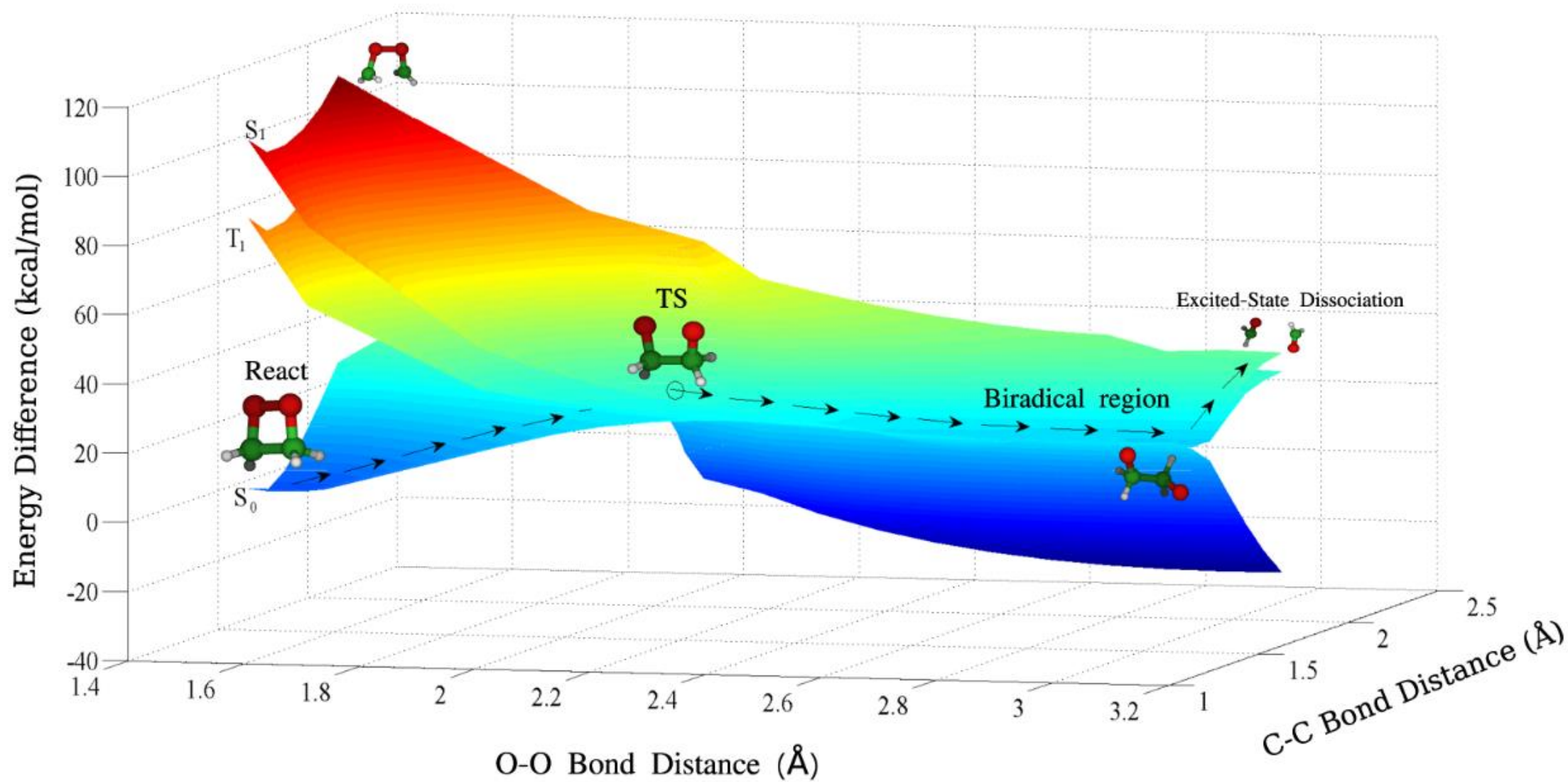
$$\hat{N}_{n'n}(\mathbf{R})\chi_n(\mathbf{R}) = -\frac{\hbar^2}{2\mathbf{M}} \left[ \left\langle \varphi_{n'} \left| \nabla_{\mathbf{R}}^2 \varphi_n \right\rangle_{\mathbf{r}} \chi_n + 2 \left\langle \varphi_{n'} \left| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} \chi_n \right] = 0$$

$$\left\langle \varphi_{n'} \left| \nabla_{\mathbf{R}}^2 \varphi_n \right\rangle_{\mathbf{r}} = 0$$

$$\left\langle \varphi_{n'} \left| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} = 0$$



# 1,2-Dioxetane decomposition (bioluminescence)





A frog resting comfortably in tepid water does not notice the water slowly brought to a boil.

The unfortunate animal is cooked to death in an *adiabatic* process.

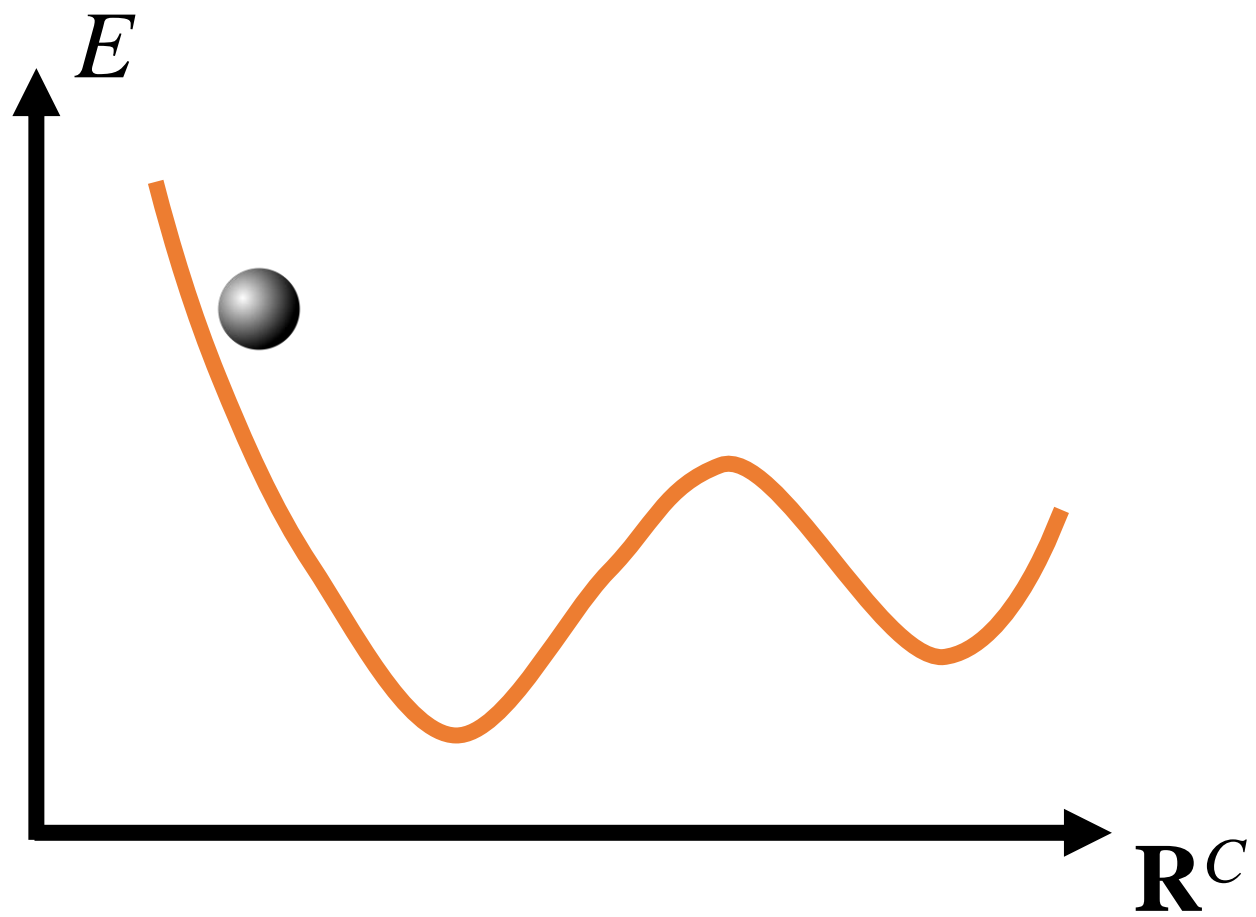


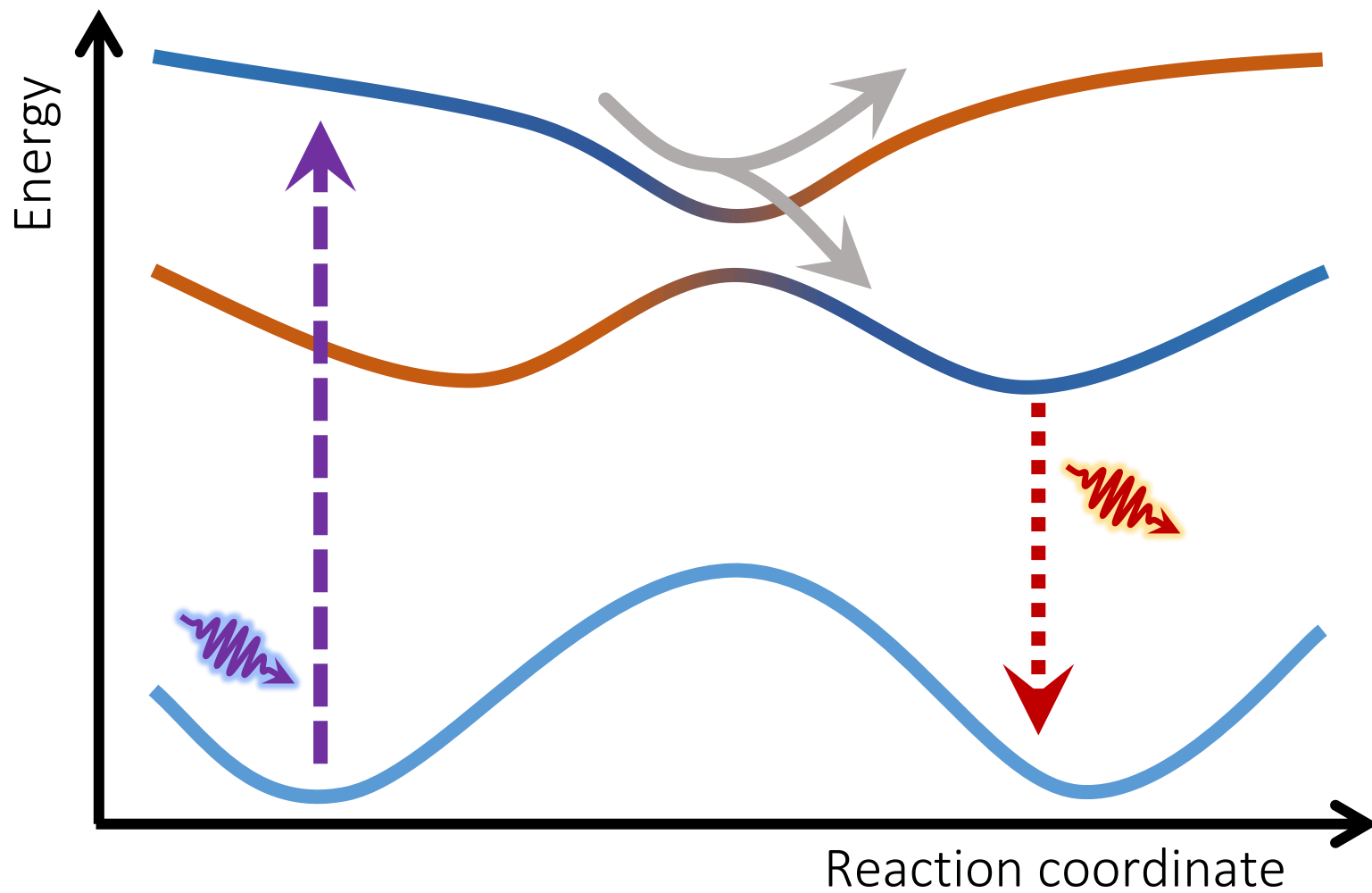
Another frog dropped into boiling water will immediately jump out of the pan.

The poor animal is hurt, but a *nonadiabatic* process saves it.



# Beyond the adiabatic approximation





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

# Nonadiabatic expansion

$$\hat{H}_{n'}(\mathbf{R})\chi_{n'}(\mathbf{R}) - \varepsilon \chi_{n'}(\mathbf{R}) + \sum_n \hat{N}_{nn'}(\mathbf{R})\chi_n(\mathbf{R}) = 0$$

where  $\hat{H}_{n'}(\mathbf{R}) = \hat{T}_{nuc} + E_{n'}(\mathbf{R})$

$$\hat{N}_{n'n}(\mathbf{R}) = -\frac{\hbar^2}{2\mathbf{M}} \left[ 2\mathbf{F}_{n'n}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} + G_{n'n}(\mathbf{R}) \right]$$

$$\mathbf{F}_{n'n}(\mathbf{R}) \equiv \left\langle \varphi_{n'}(\mathbf{r}; \mathbf{R}) \left| \nabla_{\mathbf{R}} \varphi_n(\mathbf{r}; \mathbf{R}) \right. \right\rangle_{\mathbf{r}}$$

$$G_{n'n}(\mathbf{R}) \equiv \left\langle \varphi_{n'}(\mathbf{r}; \mathbf{R}) \left| \nabla_{\mathbf{R}}^2 \varphi_n(\mathbf{r}; \mathbf{R}) \right. \right\rangle_{\mathbf{r}}$$

## Time-independent Born-Huang nonadiabatic formulation

Electronic Schrödinger equation

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

Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc} + E_{n'} - \varepsilon\right)\chi_{n'} - \frac{\hbar^2}{2\mathbf{M}} \sum_n [2\mathbf{F}_{n'n} \cdot \nabla + G_{n'n}] \chi_n = 0$$

Born-Huang molecular wave function

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

## Second-order scalar coupling

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

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

# First-order nonadiabatic coupling vector

$$\mathbf{F}_{nm} = \begin{bmatrix} F_{nm,1,X} & F_{nm,1,Y} & F_{nm,1,Z} \\ F_{nm,2,X} & F_{nm,2,Y} & F_{nm,2,Z} \\ \vdots & \vdots & \vdots \\ F_{nm,N_{at},X} & F_{nm,N_{at},Y} & F_{nm,N_{at},Z} \end{bmatrix} \quad F_{nm,\alpha,X} = \left\langle \varphi_n \left| \frac{\partial \varphi_m}{\partial X_\alpha} \right. \right\rangle$$



# Nonadiabatic coupling vector

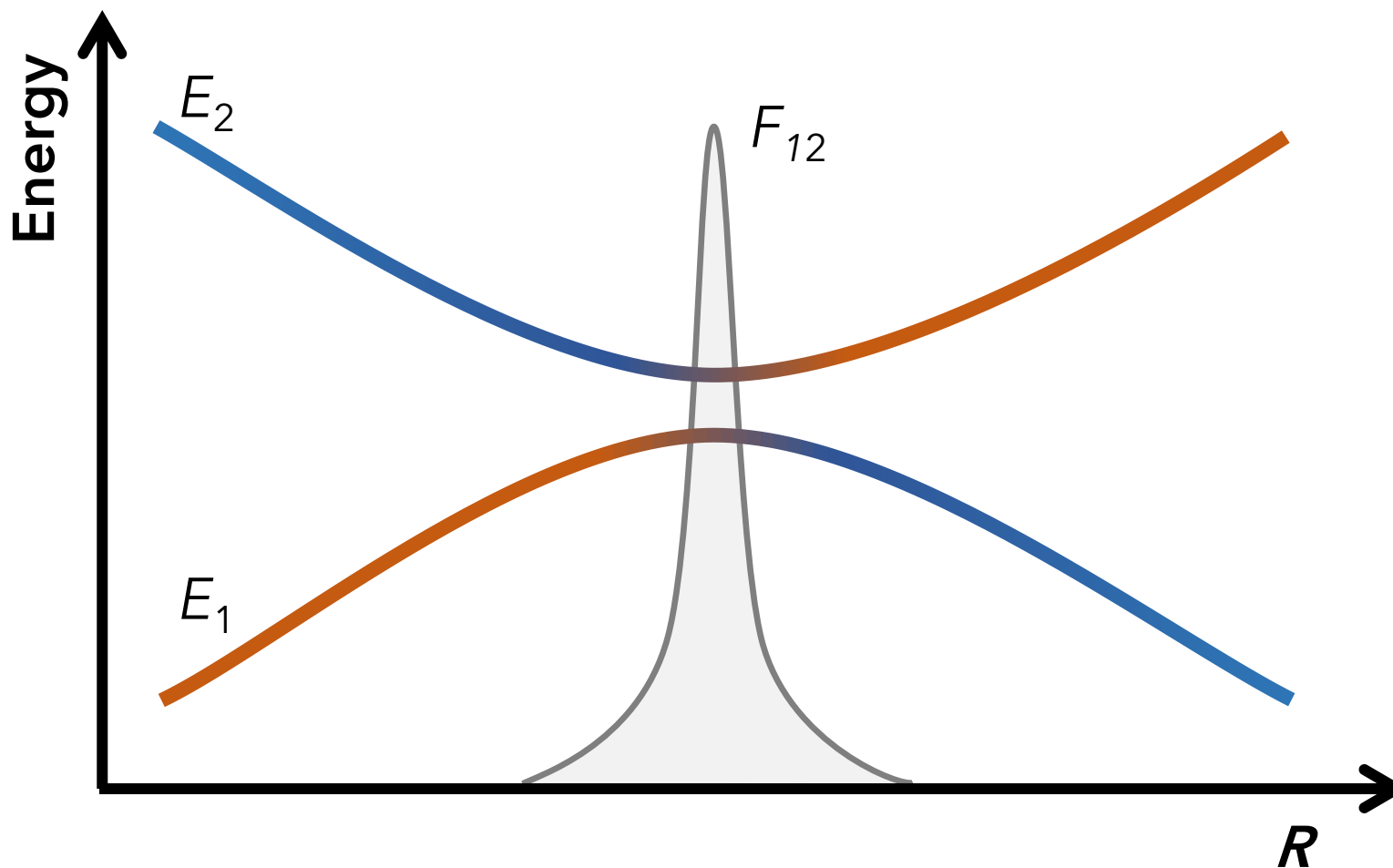
$$\mathbf{F}_{nm}(\mathbf{R}) \equiv \left\langle \varphi_n(\mathbf{r}; \mathbf{R}) \left| \nabla_{\mathbf{R}} \varphi_m(\mathbf{r}; \mathbf{R}) \right. \right\rangle_{\mathbf{r}}$$

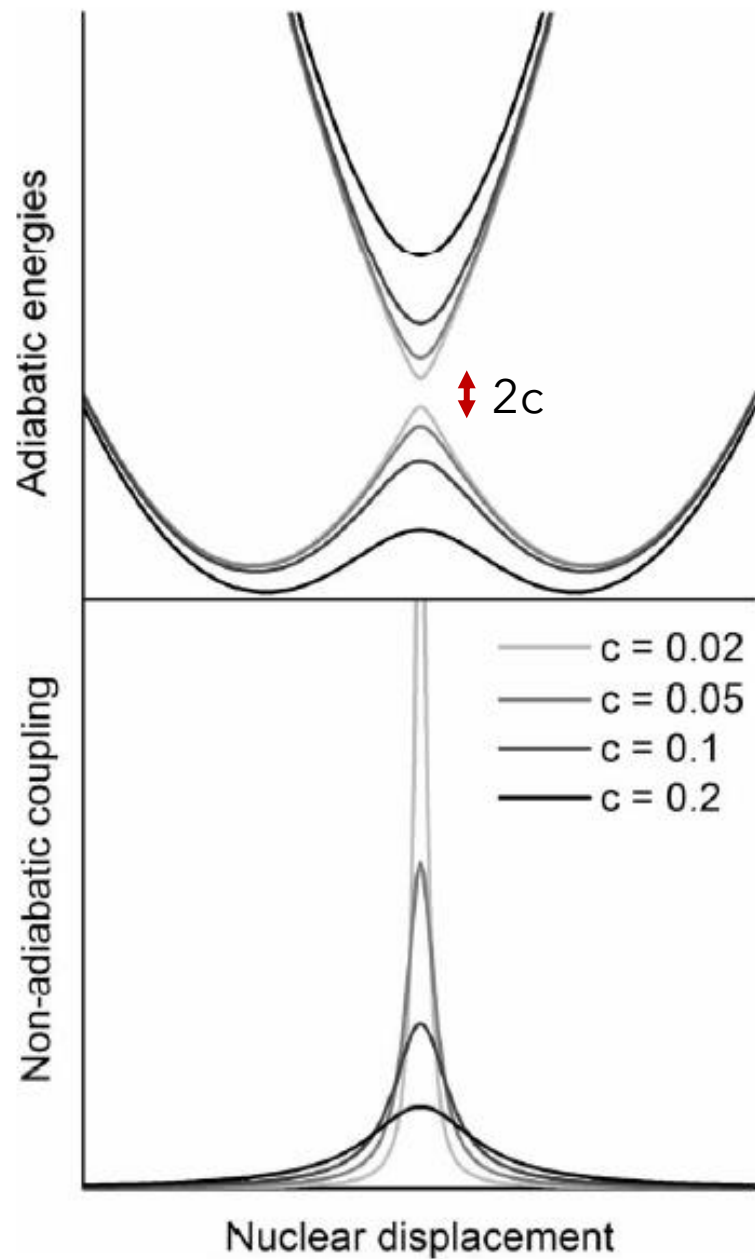
$$\mathbf{F}_{mn} = -\mathbf{F}_{nm}$$

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

For the demonstration, see the appendix to this presentation.

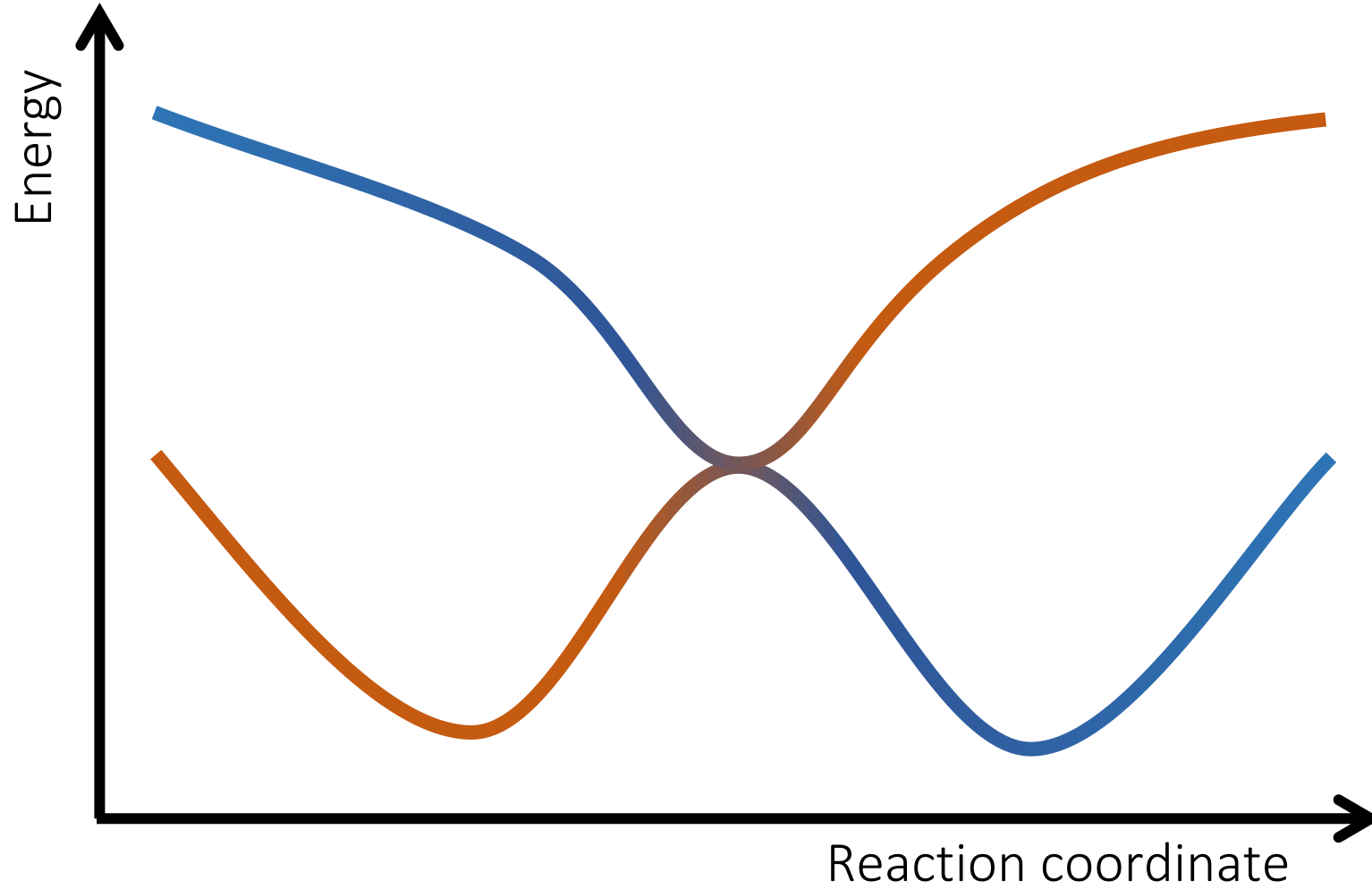
$$F_{12}(R) \approx \frac{1}{2} \sqrt{\frac{1}{\Delta E_{21}} \frac{\partial^2 \Delta E_{21}}{\partial R^2}} \quad \left( \text{for } \frac{1}{\Delta E_{21}} \frac{\partial^2 \Delta E_{21}}{\partial R^2} \geq 0 \right)$$





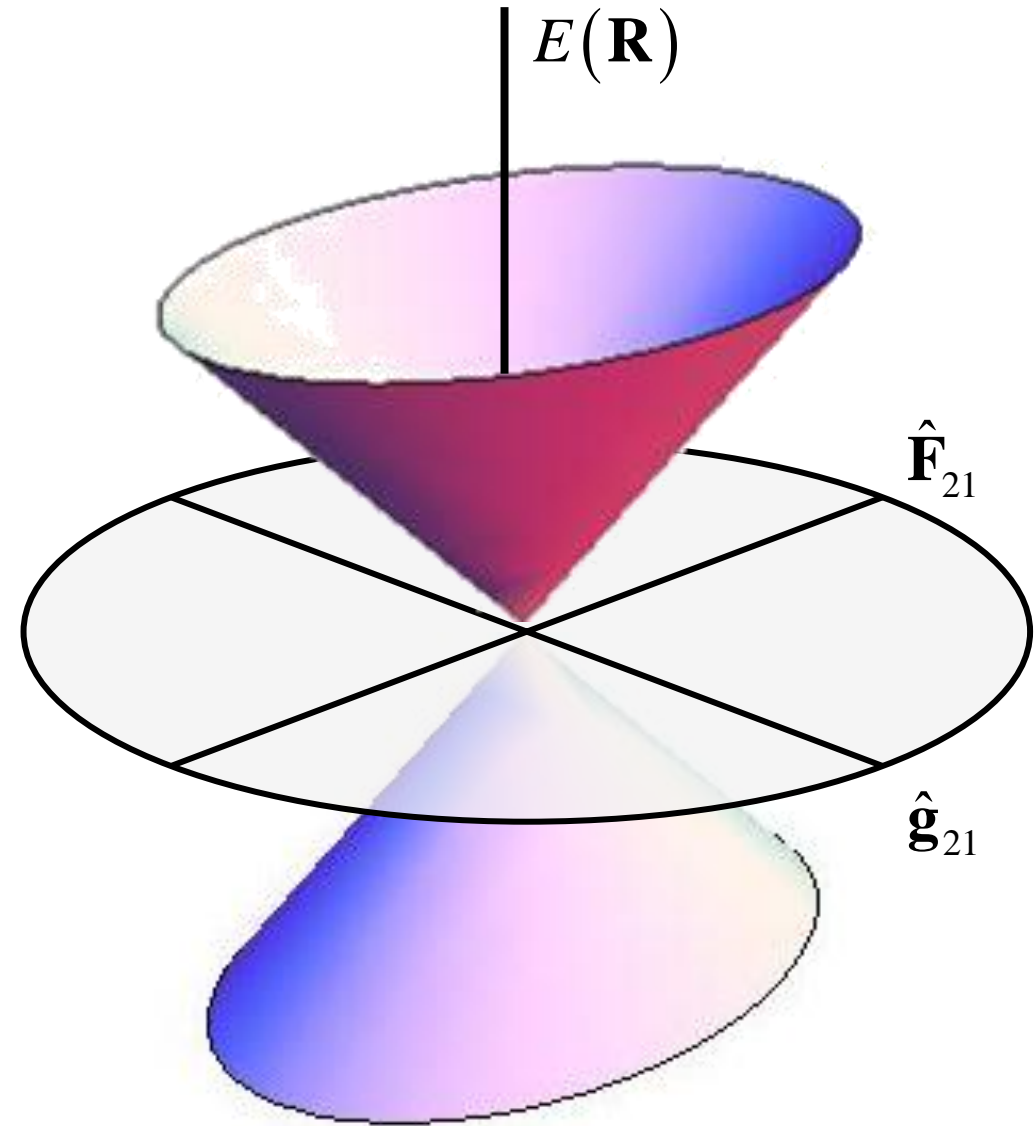
Can two potential energy surface touch?

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0)$$



# Conical intersection

$$E_{1,2}(\mathbf{R}_0 + \Delta\mathbf{R}) = \frac{(E_1(\mathbf{R}_0) + E_2(\mathbf{R}_0))}{2} \pm \sqrt{\left(\frac{1}{2}\mathbf{g}_{21}(\mathbf{R}_0) \cdot \Delta\mathbf{R}\right)^2 + (\Delta E_{12}(\mathbf{R}_0)\mathbf{F}_{21}(\mathbf{R}_0) \cdot \Delta\mathbf{R})^2}$$



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

For the demonstration, see the appendix to this presentation.

# Nonadiabatic dynamics

# Time-dependent nonadiabatic expansion

$$\hat{H}_{n'}(\mathbf{R})\chi_{n'}(\mathbf{R},t) - i\hbar \frac{\partial \chi_{n'}(\mathbf{R},t)}{\partial t} + \sum_n \hat{N}_{n'n}\chi_{n'}(\mathbf{R},t) = 0$$

where

$$\hat{H}_{n'}(\mathbf{R}) = \hat{T}_{nuc} + E_{n'}(\mathbf{R})$$

$$\hat{N}_{n'n}(\mathbf{R}) = -\frac{\hbar^2}{2\mathbf{M}} \left[ G_{n'n}(\mathbf{R}) + 2\mathbf{F}_{n'n}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} \right]$$

## Time-dependent Born-Huang nonadiabatic formulation

Electronic Schrödinger equation

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

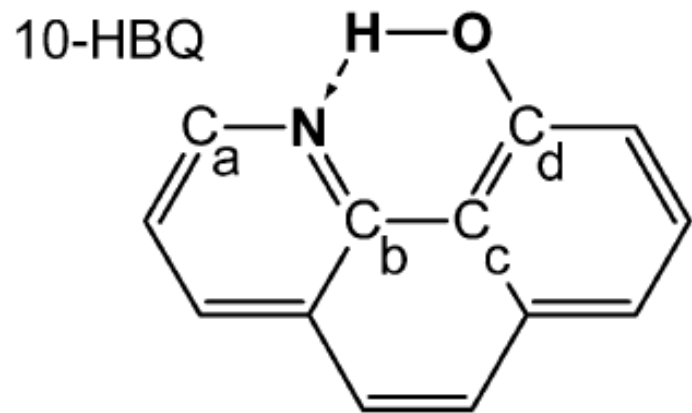
Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc} + E_{n'} - i\hbar\partial_t\right)\chi_{n'} - \frac{\hbar^2}{2\mathbf{M}} \sum_n \left[2\mathbf{F}_{n'n} \cdot \nabla + G_{n'n}\right]\chi_n = 0$$

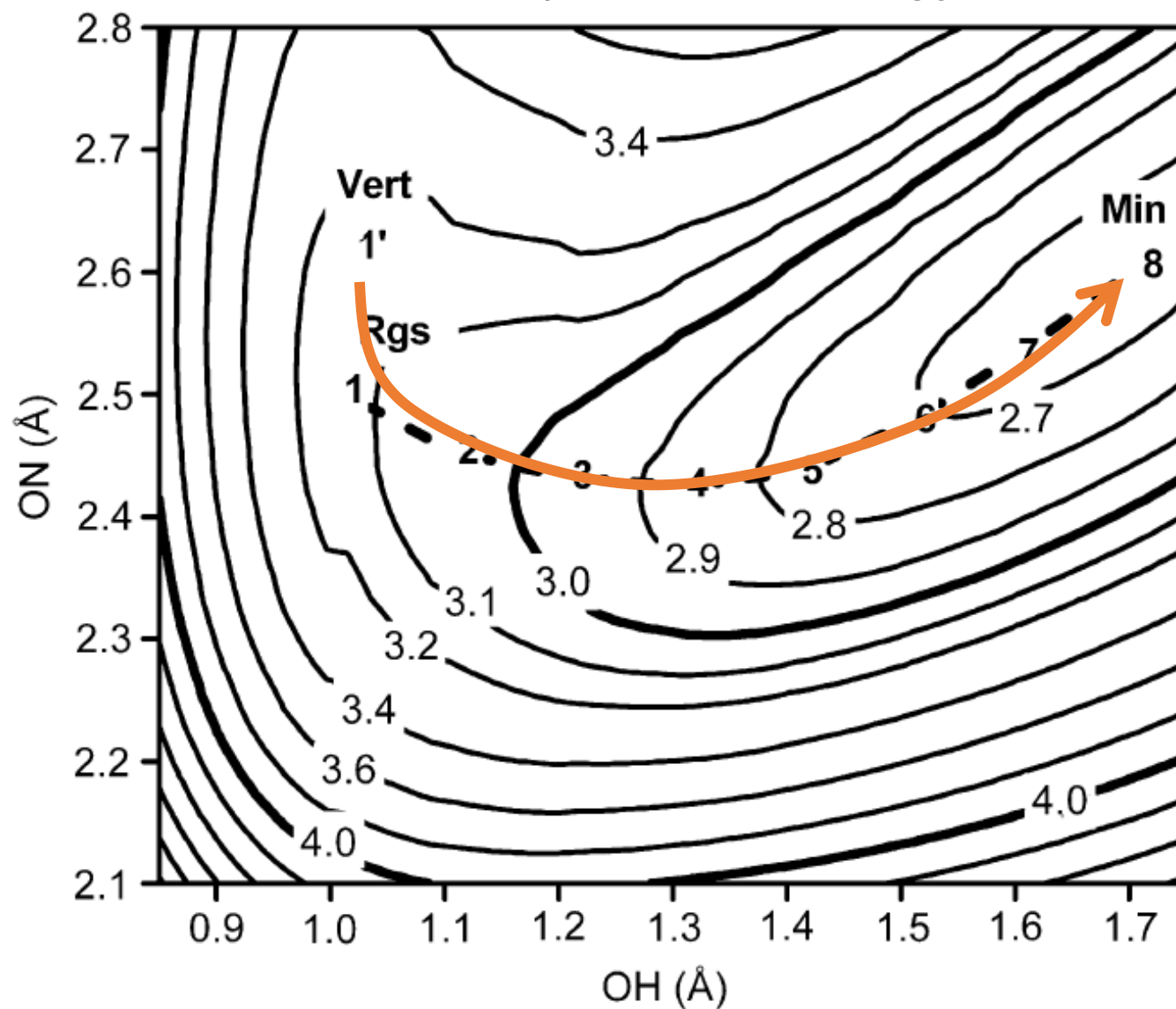
Born-Huang molecular wave function

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

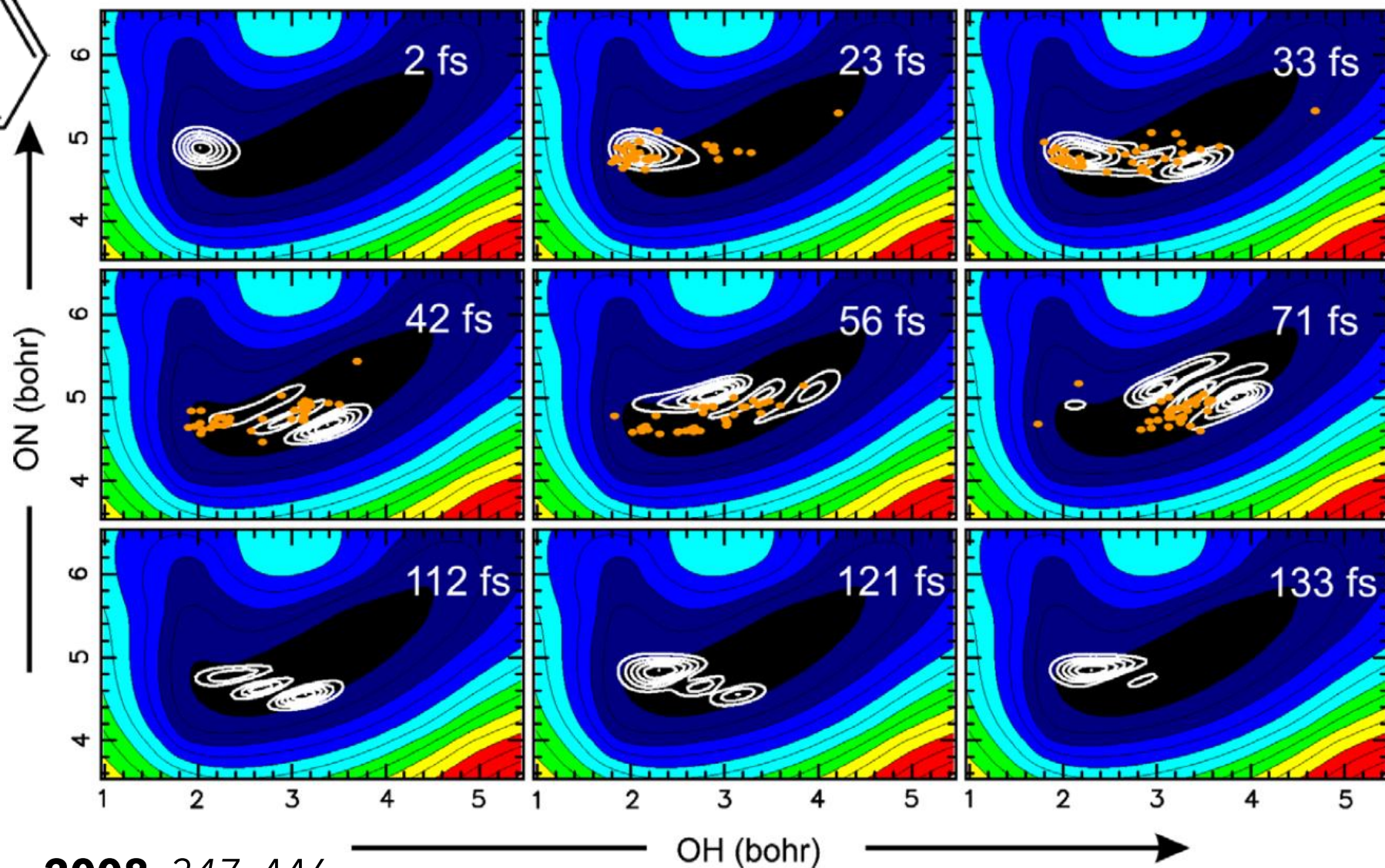
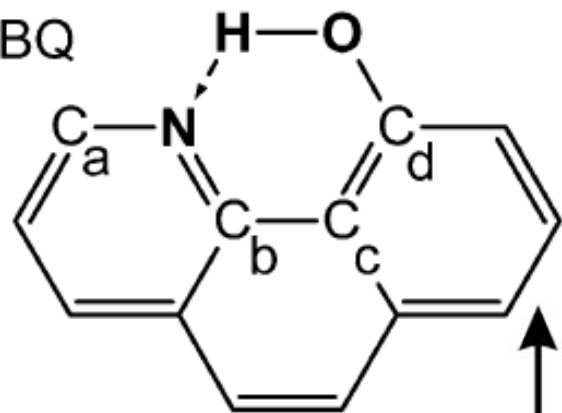


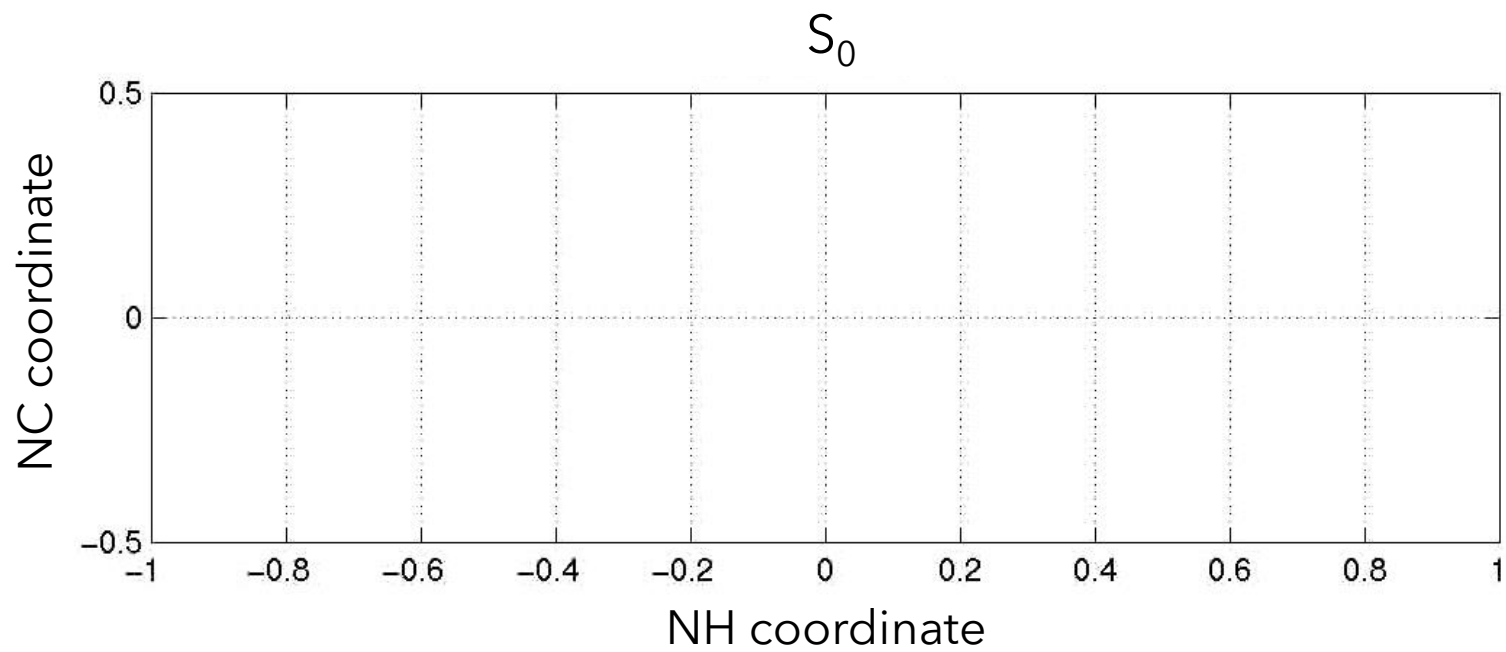
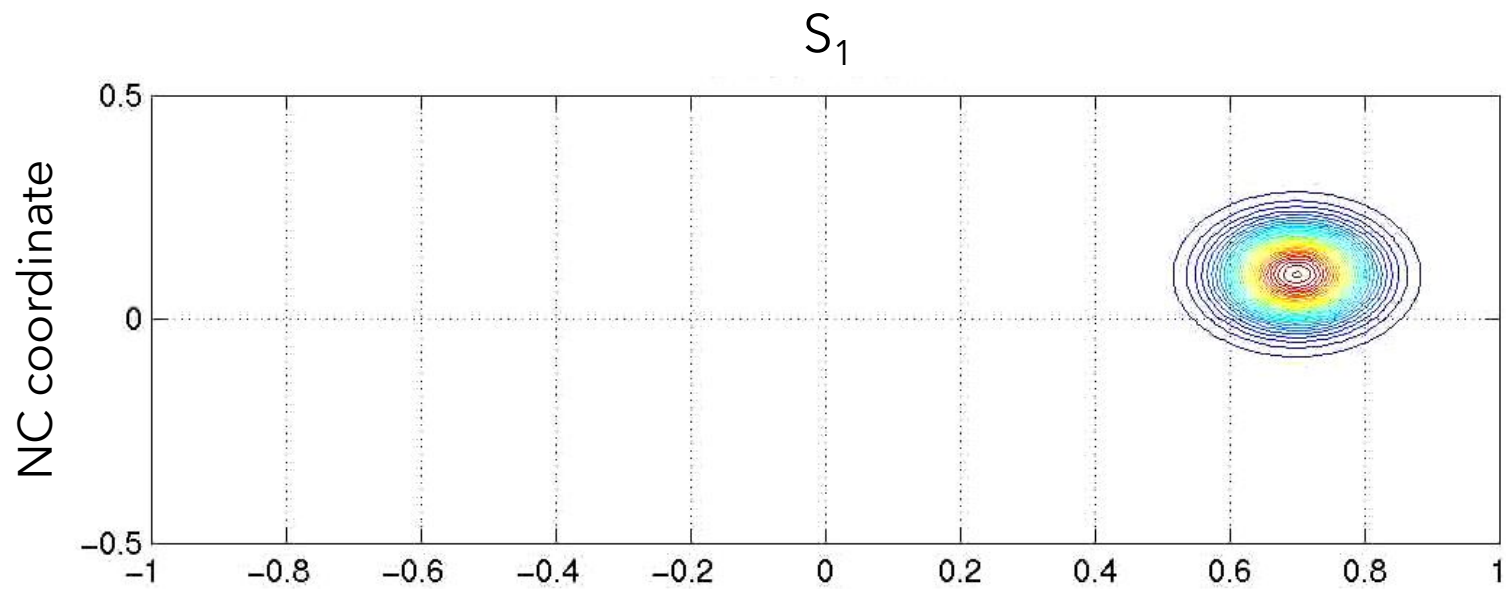
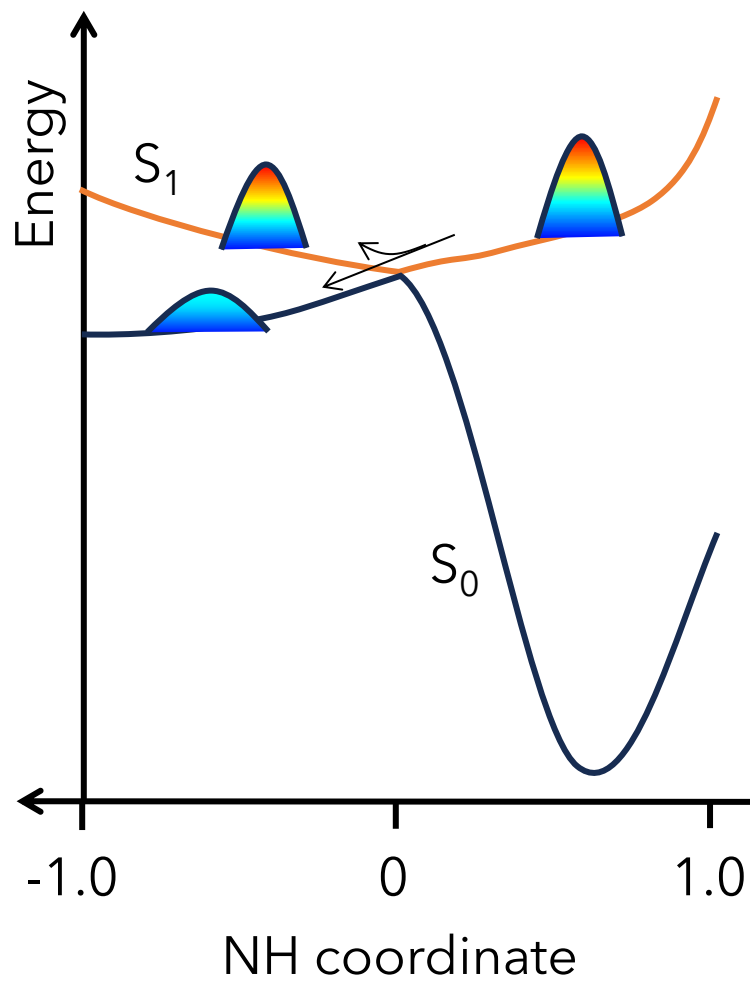
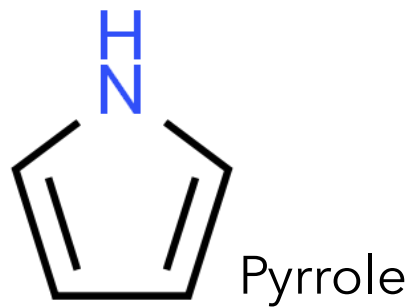


First excited potential energy surface



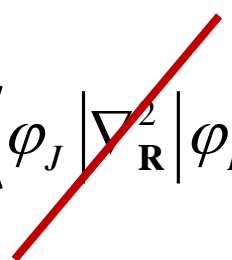
10-HBQ



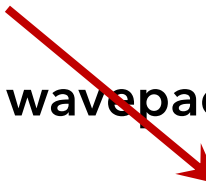


# Terms mediating nonadiabatic transitions

## Quantum wavepacket (e.g. MCTDH)


$$\langle N_{JI}^{ki} \rangle = \frac{\hbar^2}{\mathbf{M}} \left\langle \chi_k^{(J)} \left| \left\langle \varphi_J \left| \nabla_{\mathbf{R}} \left| \varphi_I \right\rangle_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} + \frac{\hbar^2}{2\mathbf{M}} \left\langle \chi_k^{(J)} \left| \left\langle \varphi_J \left| \nabla_{\mathbf{R}}^2 \left| \varphi_I \right\rangle_{\mathbf{r}} \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \right.$$


## Trajectory-guided quantum wavepacket (e.g. Multiple spawning)

$$\langle N_{JI}^{ki} \rangle \approx \frac{\hbar^2}{\mathbf{M}} \left\langle \chi_k^{(J)} \left| \nabla_{\mathbf{R}} \right| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \cdot \left\langle \varphi_J \left| \nabla_{\mathbf{R}} \left| \varphi_I \right\rangle_{\mathbf{r}} \right|_{\mathbf{R}^C}$$


$\mathbf{R}^C$  is the classical nuclear position

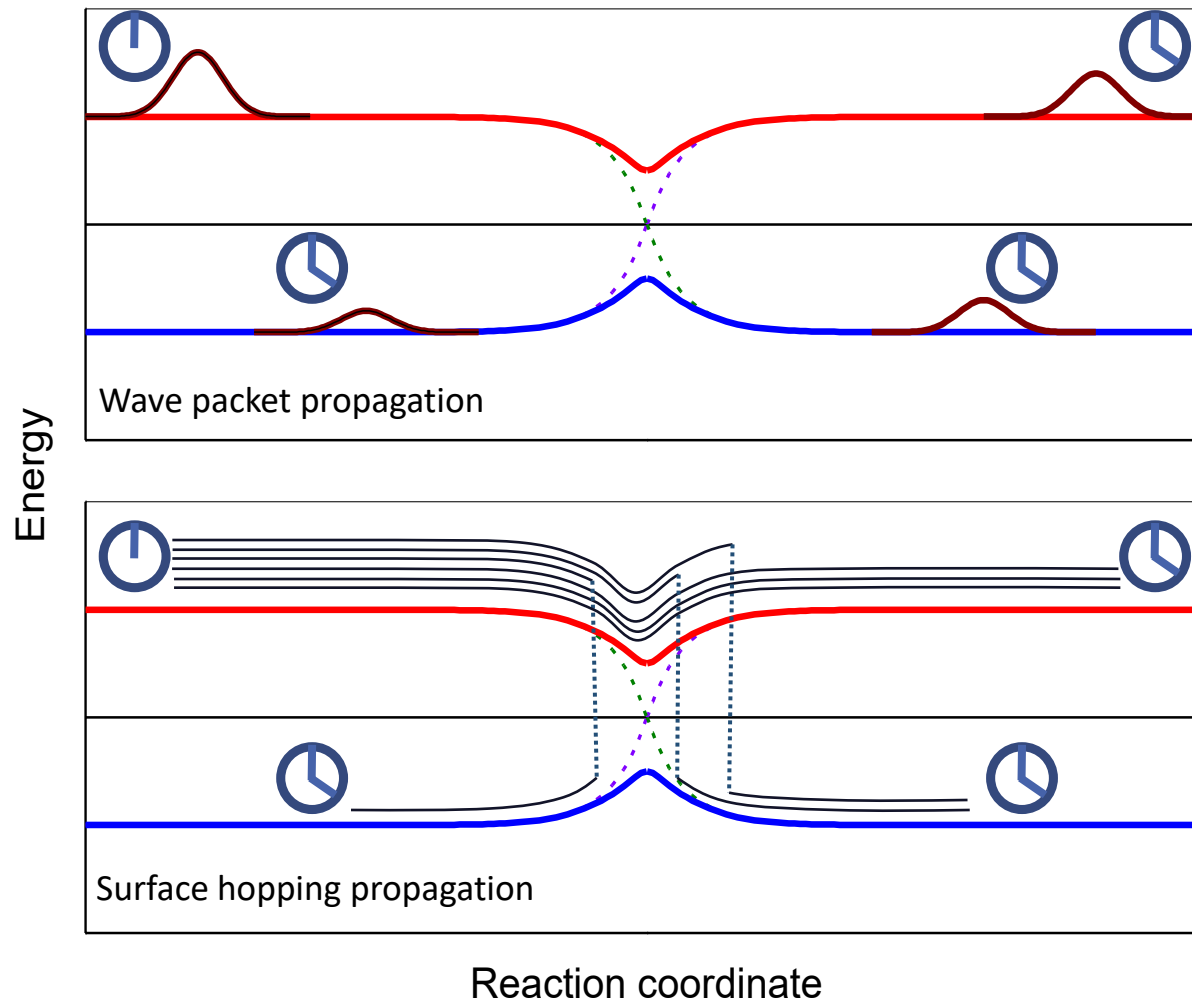
## Classical wavepacket (e.g. Surface hopping)

$$\langle N_{JI} \rangle \approx \frac{i\hbar}{\mathbf{M}} \mathbf{p}^C \cdot \left\langle \varphi_J \left| \nabla_{\mathbf{R}} \left| \varphi_I \right\rangle_{\mathbf{r}} \right|_{\mathbf{R}^C}$$


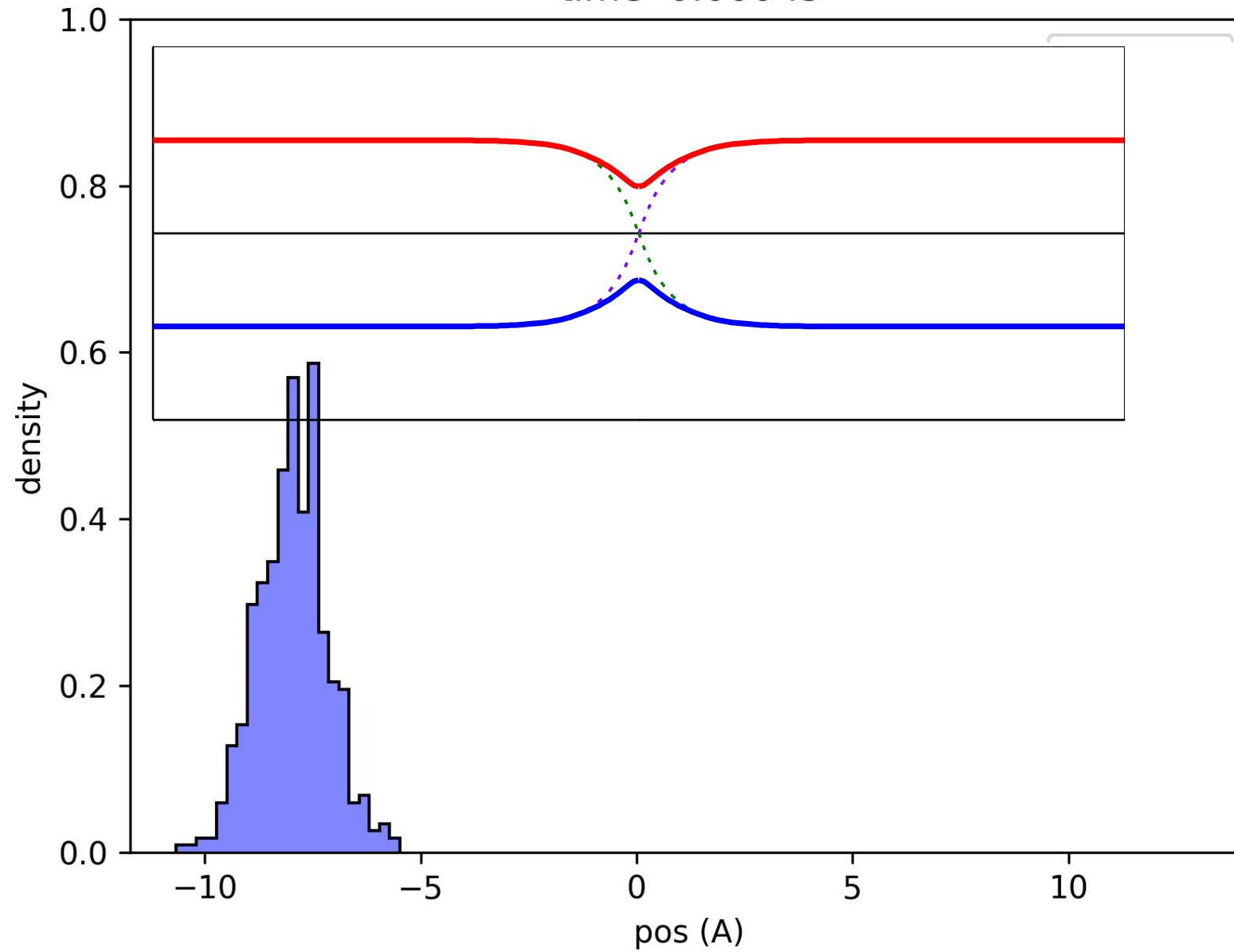
$\mathbf{p}^C$  is the classical nuclear momentum

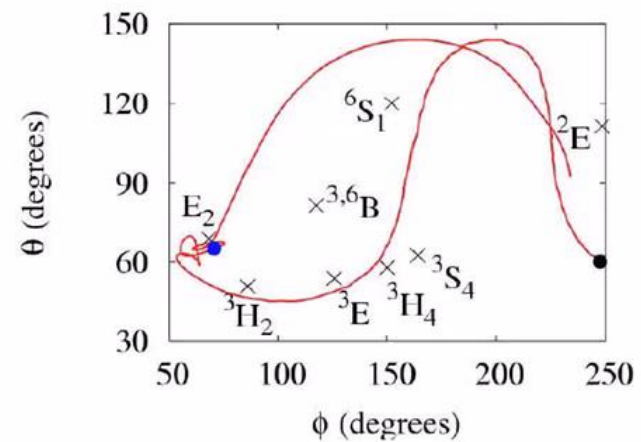
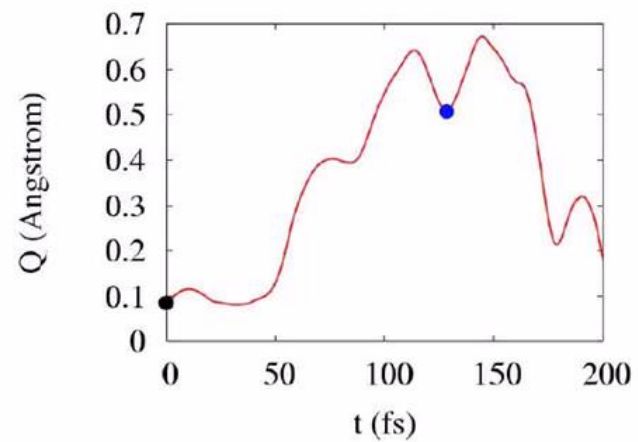
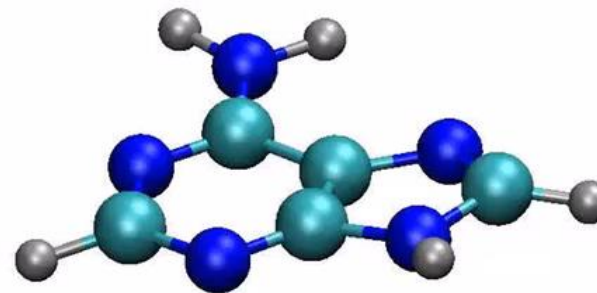
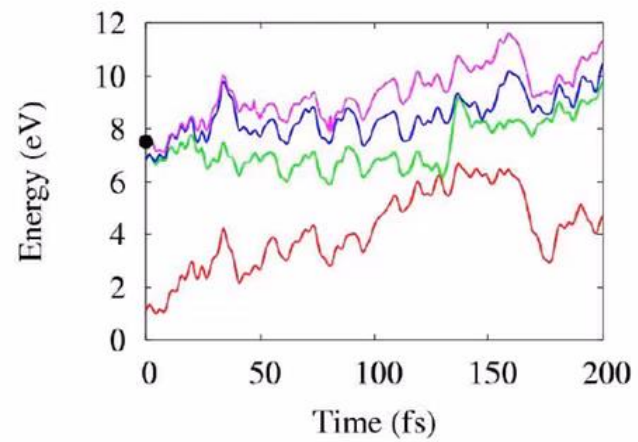
# Mixed quantum-classical (MQC) dynamics

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



time 0.000 fs







## **Software for full quantum dynamics**

Quantics

[www2.chem.ucl.ac.uk/worthgrp/quantics/](http://www2.chem.ucl.ac.uk/worthgrp/quantics/)

## **Software for multiple spawning**

PySpawn

[github.com/blevine37/pySpawn17](https://github.com/blevine37/pySpawn17)

## **Software for surface hopping (developed by my group)**

Newton-X

[www.newtonx.org](http://www.newtonx.org)

# Born-Oppenheimer-Huang formulation

## Electronic Schrödinger equation

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

## Nuclear Schrödinger equation

Adiabatic

Nonadiabatic

Time-independent

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

Time-independent

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

Time-dependent

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

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

$$\Psi_n = \varphi_n\chi_n$$

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

To know more:

Nonadiabatic couplings and conical intersections

- Sicilia *et al.* *J Phys Chem A* **2007**, 111, 2182
- Worth; Cederbaum. *Annu Rev Phys Chem* **2004**, 55, 127

Nonadiabatic dynamics

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

Available for download at:

[amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX](https://amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX)

Ask me for the password.

# Demonstration of a conical intersection

Diabatic basis  $\{|\nu_i\rangle\}$

$$H_D = \begin{bmatrix} \langle \nu_1 | H_{elec} | \nu_1 \rangle & \langle \nu_1 | H_{elec} | \nu_2 \rangle \\ \langle \nu_2 | H_{elec} | \nu_1 \rangle & \langle \nu_2 | H_{elec} | \nu_2 \rangle \end{bmatrix} \equiv \begin{bmatrix} V_a & c \\ c & V_b \end{bmatrix} \quad \langle \nu_1 | \nabla \nu_2 \rangle = 0$$

$$V_n(\mathbf{R}_0) = E_n(\mathbf{R}_0)$$

$$|\nu_n(\mathbf{R}_0)\rangle = |\varphi_n(\mathbf{R}_0)\rangle$$

$$|\nu_n(\mathbf{R})\rangle = \mathbf{U}(\theta) |\varphi_n(\mathbf{R})\rangle$$

Adiabatic energies

$$\begin{bmatrix} V_a - E & c \\ c & V_b - E \end{bmatrix} = 0$$

$$(V_a - E)(V_b - E) - c^2 = 0$$

$$E_{1,2} = \frac{(V_a + V_b)}{2} \pm \sqrt{\left(\frac{V_a - V_b}{2}\right)^2 + c^2}$$

Crossing condition

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) \text{ if } (V_a(\mathbf{R}_0) = V_b(\mathbf{R}_0)) \\ \text{and } (c(\mathbf{R}_0) = 0)$$

$$E_{1,2} = \frac{(V_a + V_b)}{2} \pm \sqrt{\left(\frac{V_a - V_b}{2}\right)^2 + c^2}$$

$$\begin{aligned} V_a(\mathbf{R}) &= V_a(\mathbf{R}_0) + \nabla_{\mathbf{R}} V_a(\mathbf{R}_0) \cdot \Delta\mathbf{R} \\ &= E_1(\mathbf{R}_0) + \nabla_{\mathbf{R}} E_1(\mathbf{R}_0) \cdot \Delta\mathbf{R} \\ &= E_1(\mathbf{R}_0) + \mathbf{g}_1(\mathbf{R}_0) \cdot \Delta\mathbf{R} \end{aligned}$$

$$V_b(\mathbf{R}) = E_2(\mathbf{R}_0) + \mathbf{g}_2(\mathbf{R}_0) \cdot \Delta\mathbf{R}$$

Near the crossing point

$$\frac{V_b - V_a}{2} = \frac{1}{2} \mathbf{g}_{12}(\mathbf{R}_0) \cdot \Delta\mathbf{R}$$

$$E_{1,2} = \frac{(V_a + V_b)}{2} \pm \sqrt{\left(\frac{V_a - V_b}{2}\right)^2 + c^2}$$

$$c(\mathbf{R}) = c(\mathbf{R}_0) + \nabla_{\mathbf{R}} c(\mathbf{R}_0) \cdot \Delta \mathbf{R}$$

$$\begin{aligned} \nabla_{\mathbf{R}} c(\mathbf{R}_0) &= \nabla_{\mathbf{R}} \langle \nu_b(\mathbf{R}_0) | H_{elec}(\mathbf{R}_0) | \nu_a(\mathbf{R}_0) \rangle \\ &= \langle \nabla_{\mathbf{R}} \nu_b(\mathbf{R}_0) | H_{elec}(\mathbf{R}_0) | \nu_a(\mathbf{R}_0) \rangle \\ &\quad + \langle \nu_b(\mathbf{R}_0) | \nabla_{\mathbf{R}} H_{elec}(\mathbf{R}_0) | \nu_a(\mathbf{R}_0) \rangle \\ &\quad + \langle \nu_b(\mathbf{R}_0) | H_{elec}(\mathbf{R}_0) | \nabla_{\mathbf{R}} \nu_a(\mathbf{R}_0) \rangle \end{aligned}$$



$$\begin{aligned}\nabla_{\mathbf{R}}c(\mathbf{R}_0) &= V_a \left\langle \nabla_{\mathbf{R}}\psi_b(\mathbf{R}_0) \left| \psi_a(\mathbf{R}_0) \right. \right\rangle^{=0} \\ &\quad + \left\langle \psi_b(\mathbf{R}_0) \left| \nabla_{\mathbf{R}}H_{elec}(\mathbf{R}_0) \right| \psi_a(\mathbf{R}_0) \right\rangle \\ &\quad + V_b \left\langle \psi_b(\mathbf{R}_0) \left| \nabla_{\mathbf{R}}\psi_a(\mathbf{R}_0) \right. \right\rangle^{=0}\end{aligned}$$

$$\begin{aligned}\nabla_{\mathbf{R}}c(\mathbf{R}_0) &= \left\langle \varphi_2(\mathbf{R}_0) \left| \nabla_{\mathbf{R}}H_{elec}(\mathbf{R}_0) \right| \varphi_1(\mathbf{R}_0) \right\rangle \\ &= (E_1 - E_2)\mathbf{F}_{21}\end{aligned}$$

$$c(\mathbf{R}) = c(\mathbf{R}_0) + \Delta E_{12}(\mathbf{R}_0)\mathbf{F}_{21}(\mathbf{R}_0) \cdot \Delta\mathbf{R}$$

Near the crossing point

$$c = \Delta E_{12}(\mathbf{R}_0)\mathbf{F}_{21}(\mathbf{R}_0) \cdot \Delta\mathbf{R}$$

# Nonadiabatic coupling vector properties

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

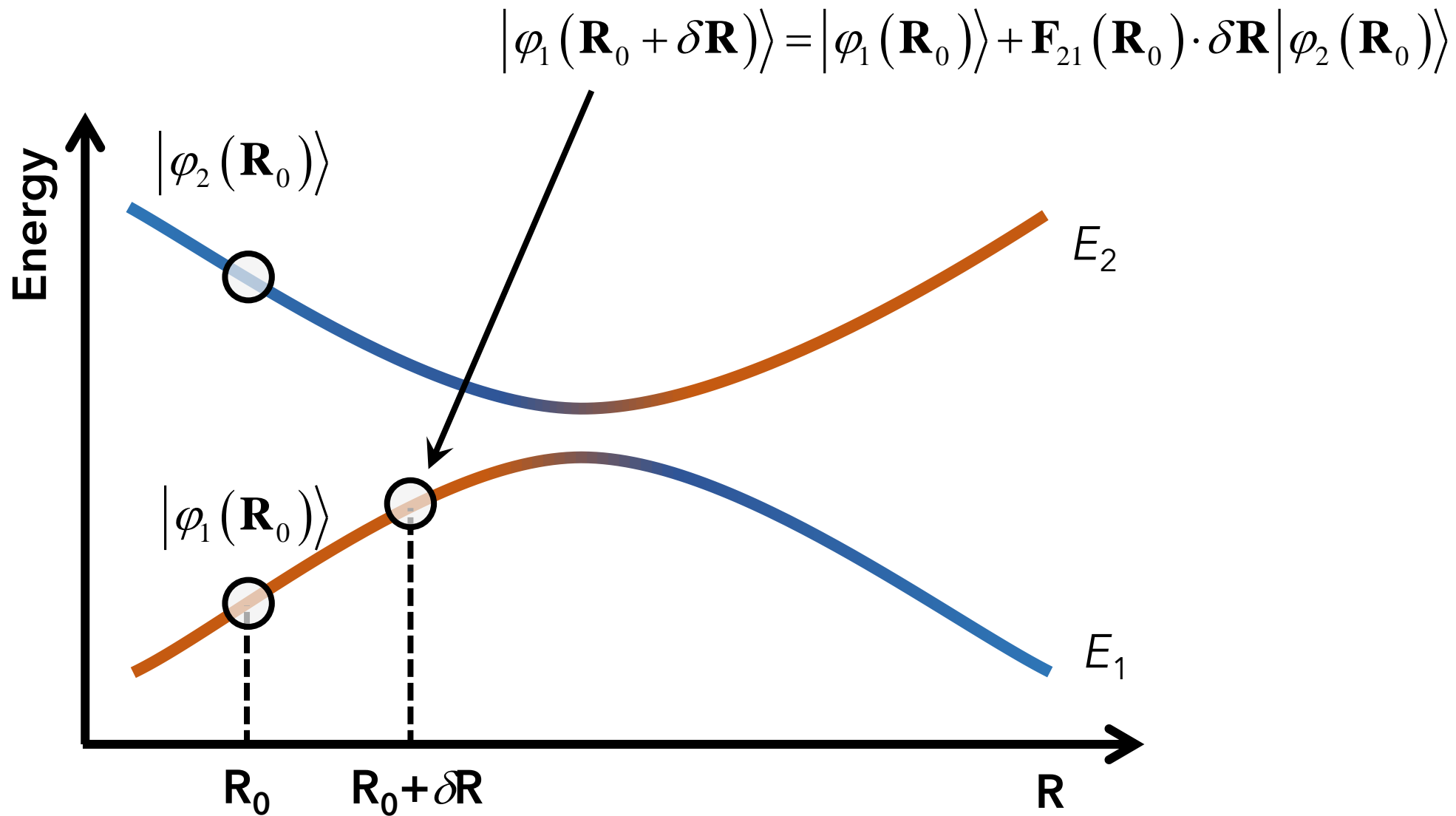
$$|\varphi_n(\mathbf{R}_0 + \delta\mathbf{R})\rangle = |\varphi_n(\mathbf{R}_0)\rangle + \nabla|\varphi_n(\mathbf{R}_0)\rangle \cdot \delta\mathbf{R}$$

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

$$\begin{aligned} \langle\varphi_k|\nabla\varphi_n\rangle &= \sum_m \mathbf{c}_{nm} \langle\varphi_k|\varphi_m\rangle \\ &= \sum_m \mathbf{c}_{nm} \delta_{km} = \mathbf{c}_{nk} \end{aligned}$$

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

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



The nonadiabatic coupling vector diverges at degeneracies

$$\langle \varphi_n | \mathbf{H}_{elec} | \varphi_m \rangle = 0$$

$$\begin{aligned} \nabla_{\mathbf{R}} \langle \varphi_n | \mathbf{H}_{elec} | \varphi_m \rangle &= \langle \nabla_{\mathbf{R}} \varphi_n | \mathbf{H}_{elec} | \varphi_m \rangle + \langle \varphi_n | \nabla_{\mathbf{R}} \mathbf{H}_{elec} | \varphi_m \rangle + \langle \varphi_n | \mathbf{H}_{elec} | \nabla_{\mathbf{R}} \varphi_m \rangle \\ &= E_m \langle \nabla_{\mathbf{R}} \varphi_n | \varphi_m \rangle + \langle \varphi_n | \nabla_{\mathbf{R}} \mathbf{H}_{elec} | \varphi_m \rangle + E_n \langle \varphi_n | \nabla_{\mathbf{R}} \varphi_m \rangle \end{aligned}$$

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

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

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

At the state crossing:

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