# L3 - Quantum Mechanics 3

## Beyond Born-Oppenheimer

Previously on...

# Computational simulations of nanosystems

Field-free non-relativistic molecular problem

$$H\left(\mathbf{R},\mathbf{r}\right)\Psi^{k}\left(\mathbf{R},\mathbf{r}\right)=\varepsilon_{k}\Psi^{k}\left(\mathbf{R},\mathbf{r}\right)$$

with

$$H\left(\mathbf{R},\mathbf{r}\right)=T_{nuc}\left(\mathbf{R}\right)+T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)$$

Born-Huang wave function

$$\Psi_{k}\left(\mathbf{R},\mathbf{r}\right)=\sum_{nj}c_{nj}^{k}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{nj}\left(\mathbf{R}\right)$$

Adiabatic approximation

$$\left\langle \varphi_{n'}\left|\nabla_{\mathbf{R}}^{2}\varphi_{n}\right.\right\rangle_{\mathbf{r}}\chi_{nj}+2\left\langle \varphi_{n'}\left|\nabla_{\mathbf{R}}\varphi_{n}\right.\right\rangle_{\mathbf{r}}\cdot\nabla_{\mathbf{R}}\chi_{nj}=0$$

## Time-independent BO adiabatic formulation

BO molecular wave function

$$\Psi_{nj}^{BO}\left(\mathbf{R},\mathbf{r}\right)=\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{nj}\left(\mathbf{R}\right)$$

Nuclear Schrödinger equation

$$\left(T_{nuc}\left(\mathbf{R}\right)+E_{n}\left(\mathbf{R}\right)\right)\chi_{nj}\left(\mathbf{R}\right)=\varepsilon_{nj}\chi_{nj}\left(\mathbf{R}\right)$$

Electronic Schrödinger equation

$$\left(T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)=E_{n}\left(\mathbf{R}\right)\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)$$

1. Solve electronic Schrödinger equation to get $E_n(\mathbf{R})$ and φ

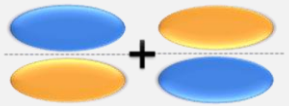
$$\left(T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)=E_n\left(\mathbf{R}\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)$$

2. Solve nuclear Schrödinger equation on the electronic potential $E_n(\mathbf{R})$

$$\left(T_{nuc}\left(\mathbf{R}\right)+E_n\left(\mathbf{R}\right)\right)\chi_{nj}\left(\mathbf{R}\right)=\varepsilon_{nj}\chi_{nj}\left(\mathbf{R}\right)$$

# 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

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

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

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

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

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

3. Continue the iterations until

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

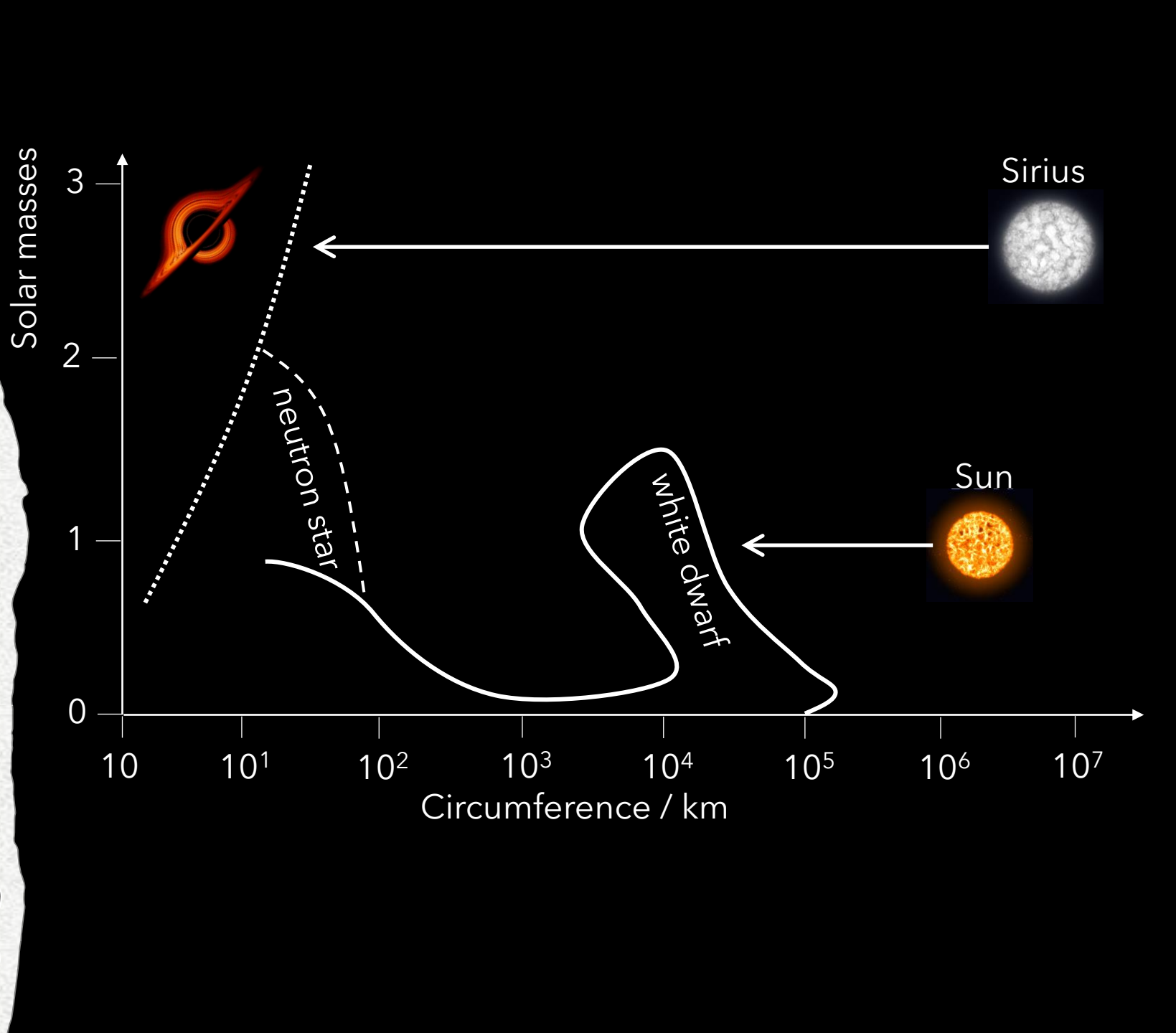
# A bit of history

# Max Born
# (1882 - 1970)

Born rule

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

# J. Robert Oppenheimer (1904 - 1967)


Solar masses
3
2
1
0
Sirius
Sun
neutron star
white dwarf
10
10¹
10²
10³
10⁴
10⁵
10⁶
10⁷
Circumference / km

1927 № 20

ANNALEN DER PHYSIK

VIERTE FOLGE. BAND 84

# 1. *Zur Quantentheorie der Molekeln;*

*von M. Born und R. Oppenheimer*

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.

Born; Oppenheimer. *Annalen der Physik* **1927,** *389*, 457

Born; Oppenheimer, In *Quantum chemistry*, World Scientific, 2000; pp 1

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

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

"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 κ.

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

Solve the equation for each order

$$
(35)\quad \begin{cases}
\text{a)}\ (H_0^0 - W^0)\,\psi^0 = 0\,, \\
\text{b)}\ (H_0^0 - W^0)\,\psi^{(1)} = (W^{(1)} - H_0^{(1)})\,\psi^0\,, \\
\text{c)}\ (H_0^0 - W^0)\,\psi^{(2)} = (W^{(2)} - H_0^{(2)} - H^0_{\zeta\zeta})\,\psi^0 \\
\qquad\qquad + (W^{(1)} - H_0^{(1)})\,\psi^{(1)}\,, \\
\text{d)}\ (H_0^0 - W^0)\,\psi^{(3)} = (W^{(3)} - H_0^{(3)} - H^0_{\zeta\vartheta} - H^{(1)}_{\zeta\zeta})\,\psi^0 \\
\qquad\qquad + (W^{(2)} - H_0^{(2)} - H^0_{\zeta\zeta})\,\psi^{(1)} + (W^{(1)} - H_0^{(1)})\,\psi^{(2)}\,, \\
\text{e)}\ (H_0^0 - W^0)\,\psi^{(4)} = (W^{(4)} - H_0^{(4)} - H^0_{\vartheta\vartheta} - H^{(1)}_{\zeta\vartheta} - H^{(2)}_{\zeta\zeta})\,\psi^0 \\
\qquad\qquad + (W^{(3)} - H_0^{(3)} - H^0_{\zeta\vartheta} - H^{(1)}_{\zeta\zeta})\,\psi^{(1)} \\
\qquad\qquad + (W^{(2)} - H_0^{(2)} - H^0_{\zeta\zeta})\,\psi^{(2)} + (W^{(1)} - H_0^{(1)})\,\psi^{(3)}\,, \\
\quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{cases}
$$

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

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

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

“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. Dynamical Theory of Crystal Lattices, 1954, p. 406

# Born-Huang wave function

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

we try to solve it by an expansion

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

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

Born; Huang. Dynamical Theory of Crystal Lattices, 1954, p. 406

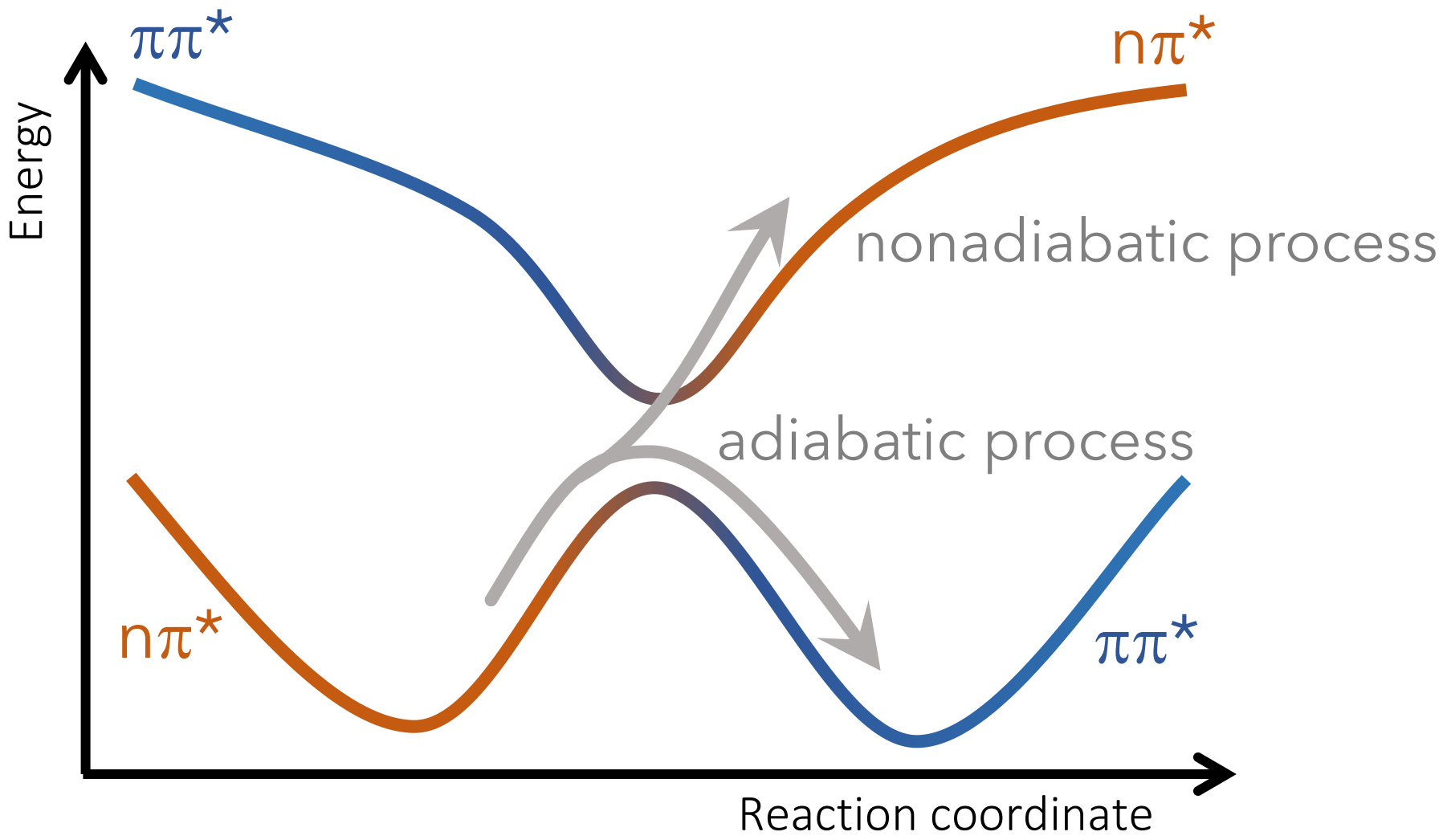
# Adiabatic approximation

# Adiabatic approximation

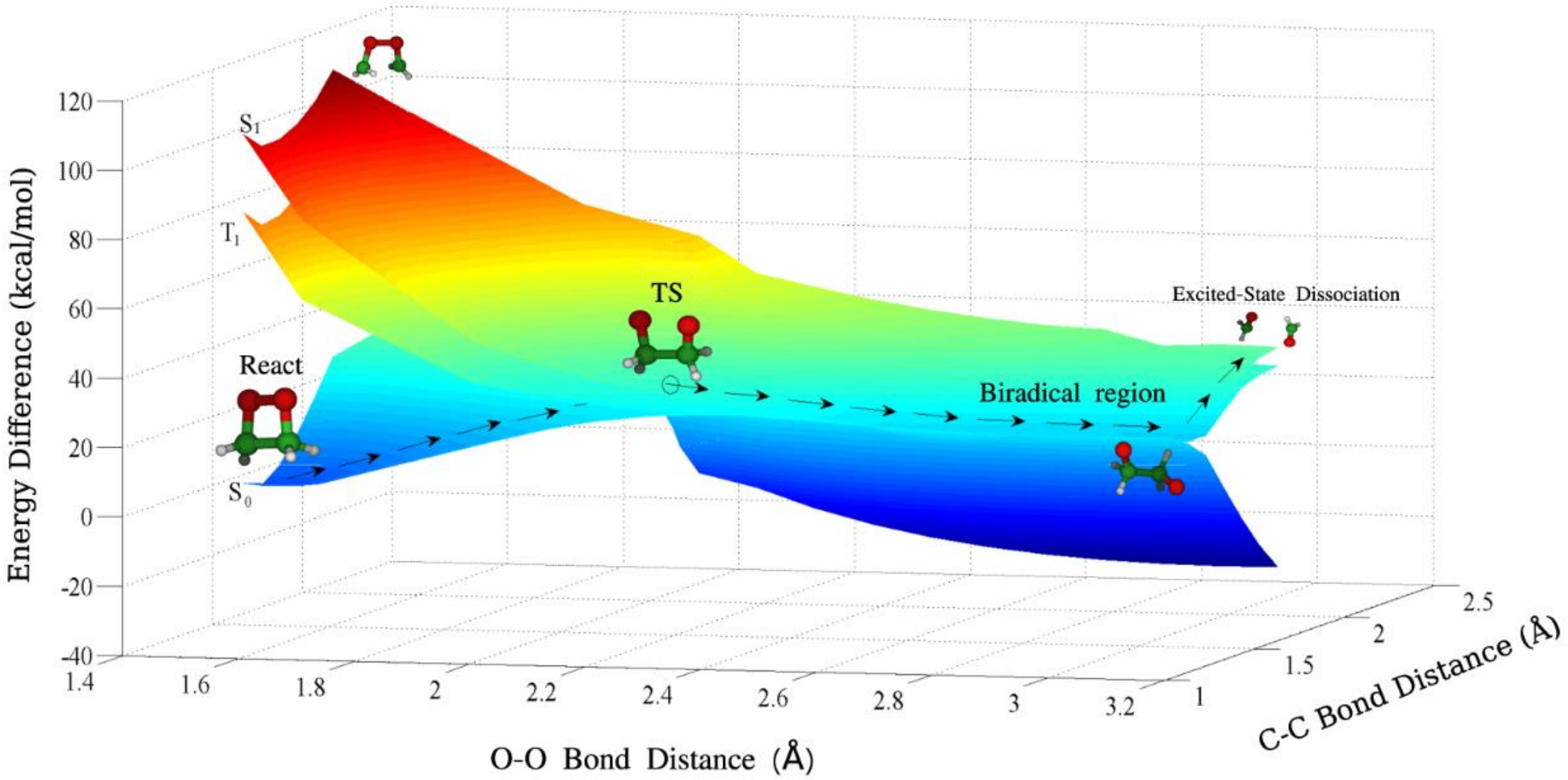
$$N_{n'n}(\mathbf{R}) = -\frac{\hbar^2}{2\mathbf{M}}\left[\left\langle \varphi_{n'} \middle| \nabla^2_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} h_n^k + 2\left\langle \varphi_{n'} \middle| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} h_n^k \right] = 0$$

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

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


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

# 1,2-Dioxetane decomposition (bioluminescence)




Farahani *et al. J Chem Theory Comput* **2013**, *9*, 5404

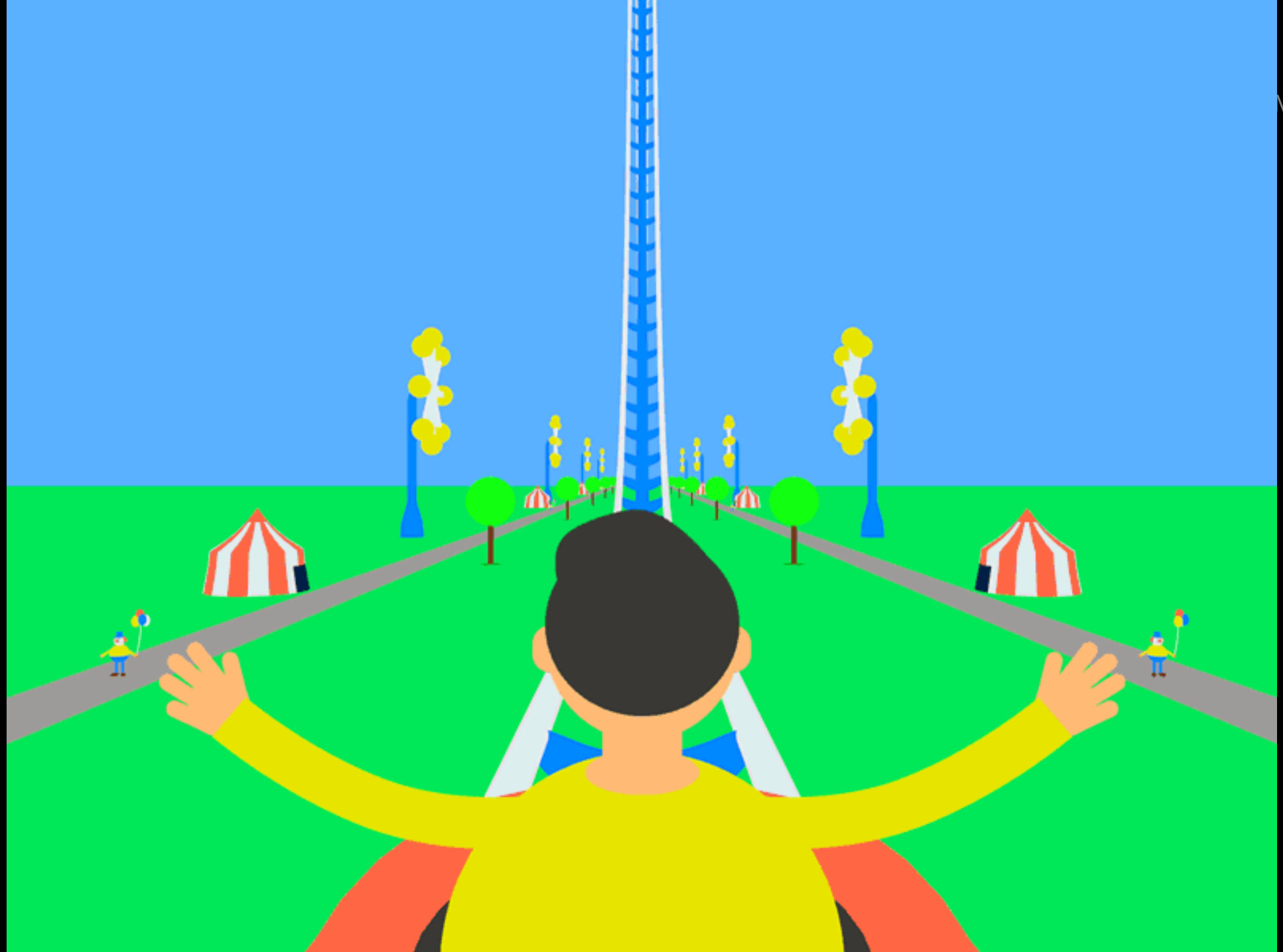
A frog resting comfortably in tepid water does not notice the water slowing brought to a boil.

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

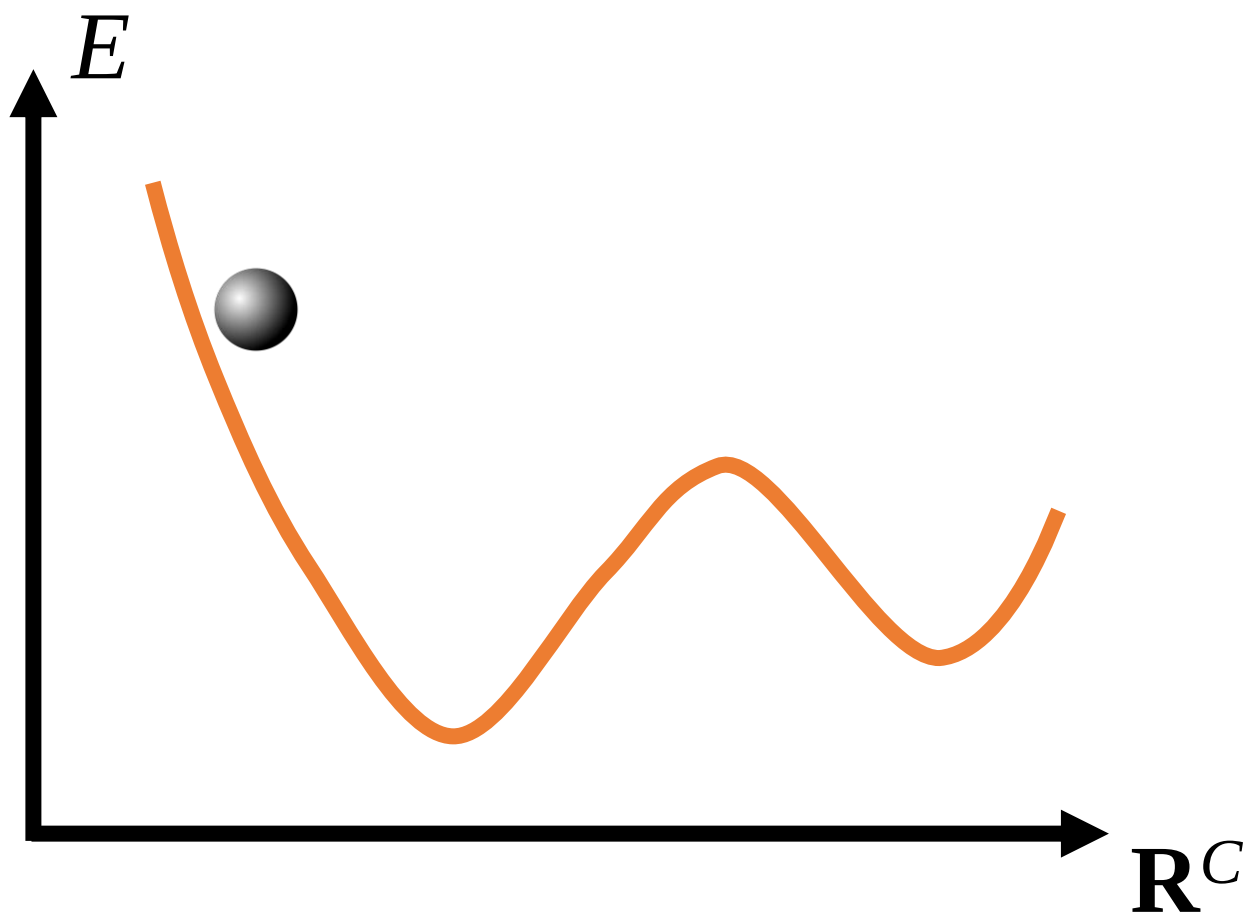
Another frog dropped into boiling water will immediately jump out of the pan.

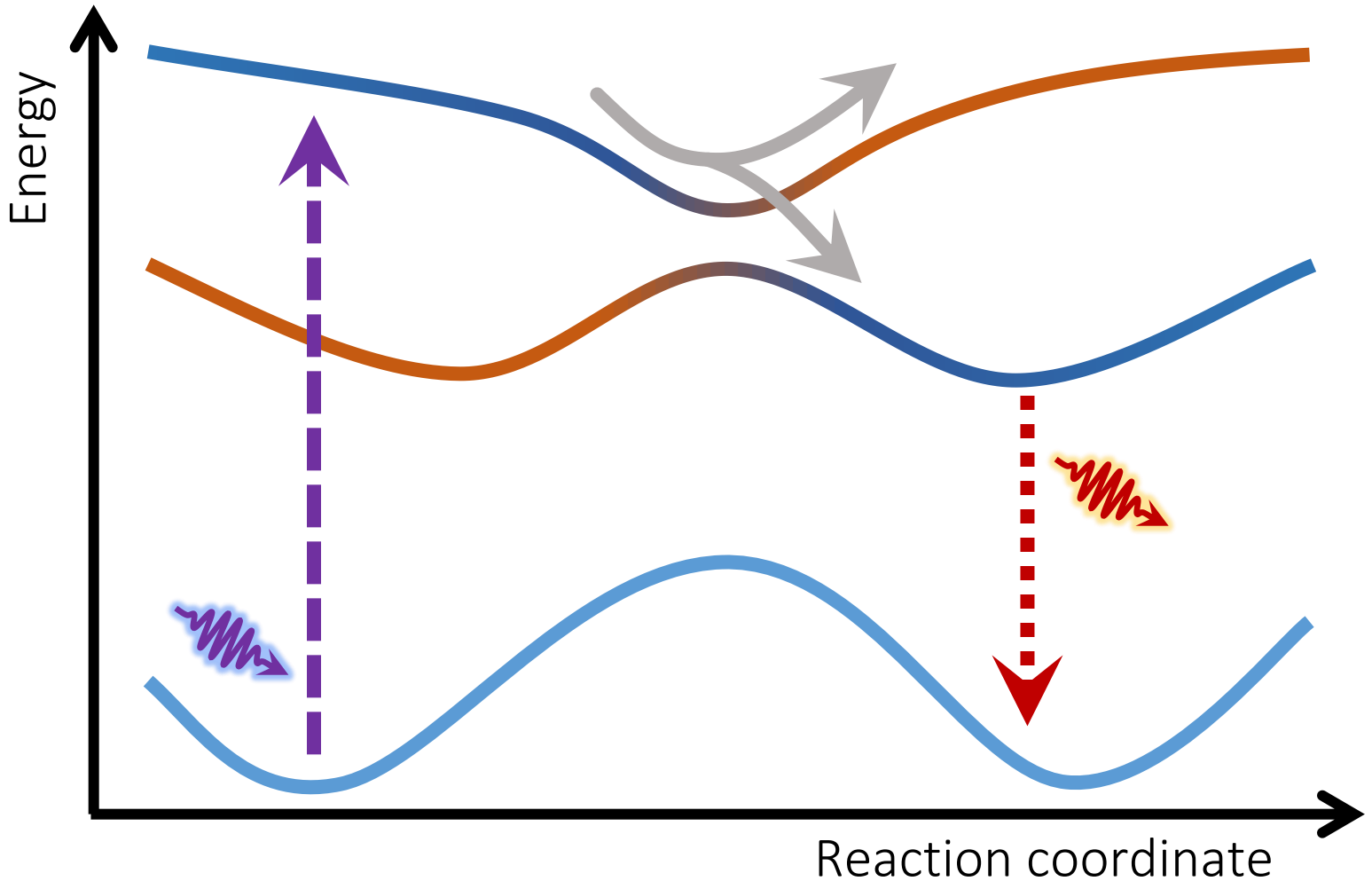
The poor animal is hurt, but a *nonadiabatic* process saves it.

# Beyond the adiabatic approximation



LIGHT AND
MOLECULES


E
$\mathbf{R}^C$




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

# Nonadiabatic expansion

$$H_{n'}(\mathbf{R})h_{n'}^{k}(\mathbf{R})-\varepsilon_k h_{n'}^{k}(\mathbf{R})+\sum_{n} N_{nn'}(\mathbf{R})=0$$

$$\text{where } H_{n'}(\mathbf{R})=T_{nuc}+E_{n'}(\mathbf{R})$$

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

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

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

# Time-independent Born-Huang nonadiabatic formulation

Nuclear Schrödinger equation

$$\left(T_{nuc} + E_{n'} - \varepsilon\right) h_{n'} - \frac{\hbar^2}{2\mathbf{M}} \sum_n \left[2\mathbf{F}_{n'n} \cdot \nabla + G_{n'n}\right] h_n = 0$$

Electronic Schrödinger equation

$$\left(T_{elec} + V\right) \varphi_n = E_n \varphi_n$$

Born-Huang molecular wave function

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

# Second-order scalar coupling

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

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

# First-order nonadiabatic coupling vector

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

# Nonadiabatic coupling vector

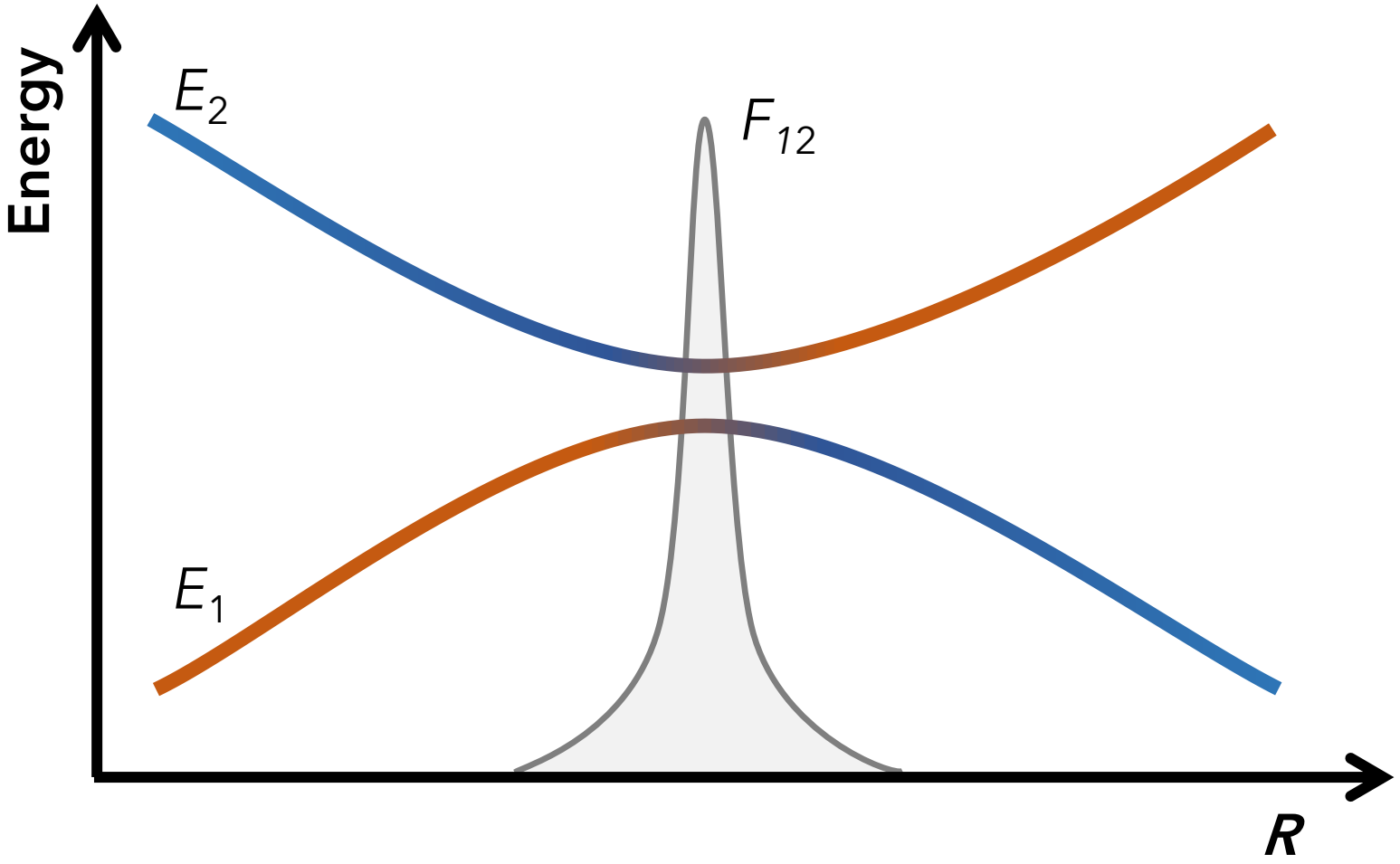
$$\mathbf{F}_{nm}\left(\mathbf{R}\right) \equiv \left\langle \varphi_n\left(\mathbf{r};\mathbf{R}\right) \middle| \nabla_{\mathbf{R}} \varphi_m\left(\mathbf{r};\mathbf{R}\right) \right\rangle_{\mathbf{r}}$$

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

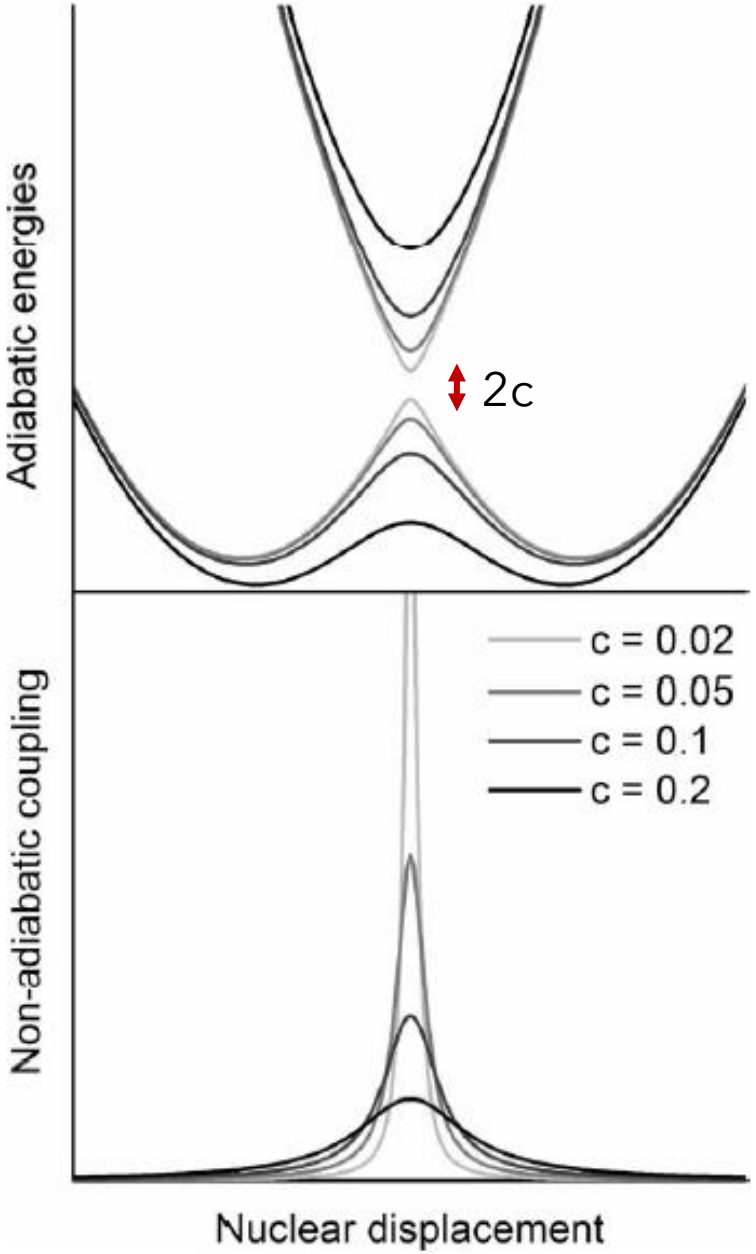
$$\mathbf{F}_{nm} = \frac{\left\langle \varphi_n \middle| \nabla_{\mathbf{R}} H_{elec} \middle| \varphi_m \right\rangle_{\mathbf{r}}}{\left(E_m - E_n\right)}$$

For the demonstration, see the appendix to this presentation.

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



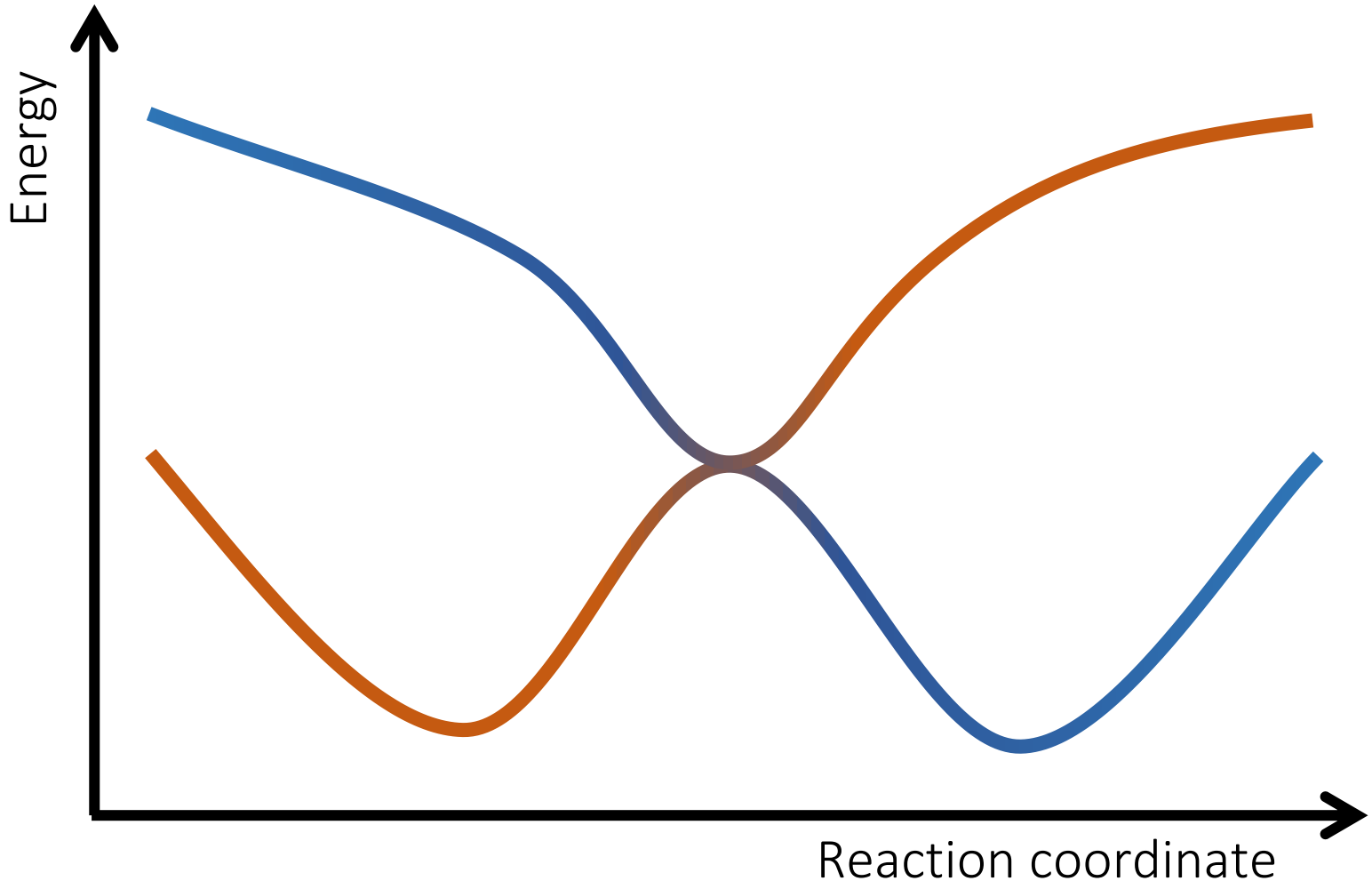

Baeck; An. *J Chem Phys* **2017,** *146*, 064107




Plasser *et al. J Chem Phys* **2012,** *137*, 22A514

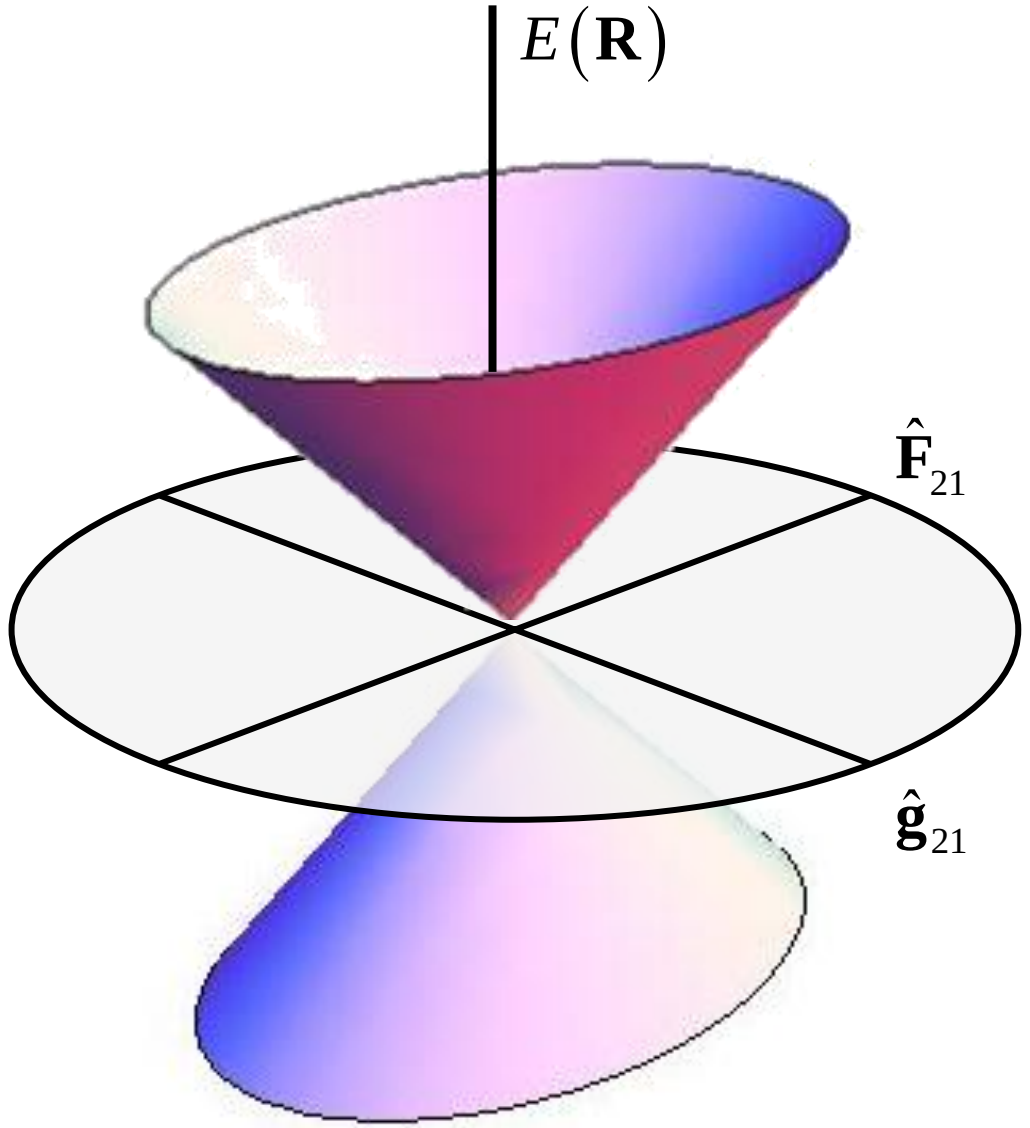
Can two potential energy surface touch?

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



# Conical intersection

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




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

# Nonadiabatic dynamics

# Time-dependent nonadiabatic expansion

$$H_{n'}\left(\mathbf{R}\right)h_{n'}^{k}\left(\mathbf{R},t\right)-i\hbar\partial_{t}h_{n'}^{k}\left(\mathbf{R},t\right)+\sum_{n}N_{n'n}\left(\mathbf{R},t\right)=0$$

*where*

$$H_{n'}\left(\mathbf{R}\right)=T_{nuc}+E_{n'}\left(\mathbf{R}\right)$$

$$N_{n'n}\left(\mathbf{R},t\right)=-\frac{\hbar^{2}}{2\mathbf{M}}\left[G_{n'n}\left(\mathbf{R}\right)h_{n}^{k}\left(\mathbf{R},t\right)+2\mathbf{F}_{n'n}\left(\mathbf{R}\right)\cdot\nabla_{\mathbf{R}}h_{n}^{k}\left(\mathbf{R},t\right)\right]$$

# Time-dependent Born-Huang nonadiabatic formulation

Nuclear Schrödinger equation

$$\left(T_{nuc} + E_{n'} - i\hbar\partial_t\right)h_{n'} - \frac{\hbar^2}{2\mathbf{M}}\sum_n \left[2\mathbf{F}_{n'n}\cdot\nabla + G_{n'n}\right]h_n = 0$$

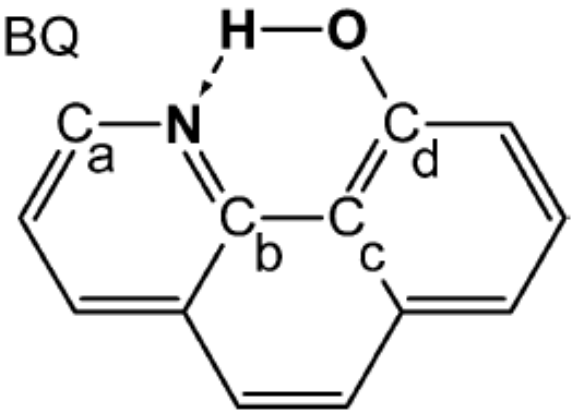
Electronic Schrödinger equation

$$\left(T_{elec} + V\right)\varphi_n = E_n\varphi_n$$

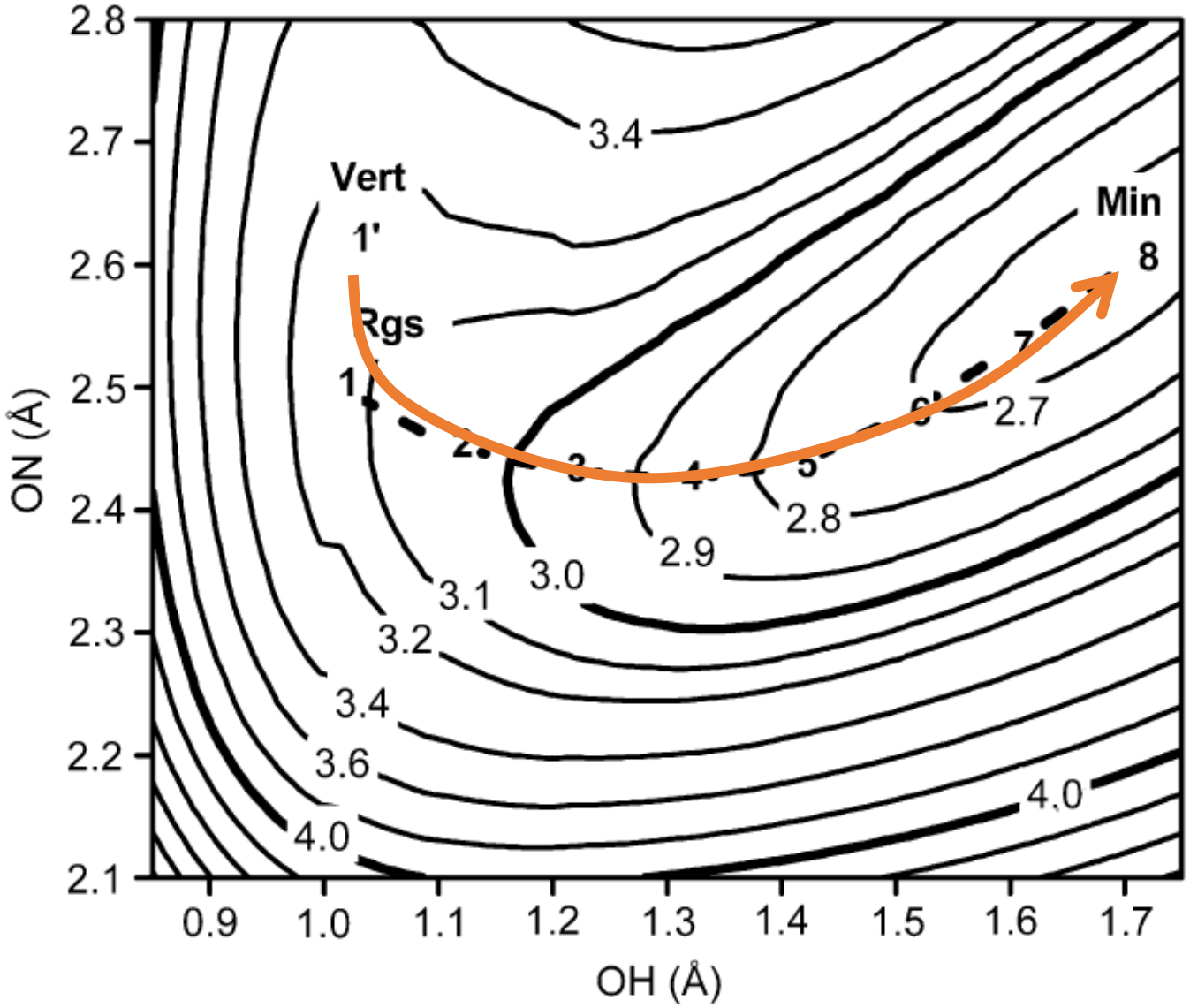
Born-Huang molecular wave function

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

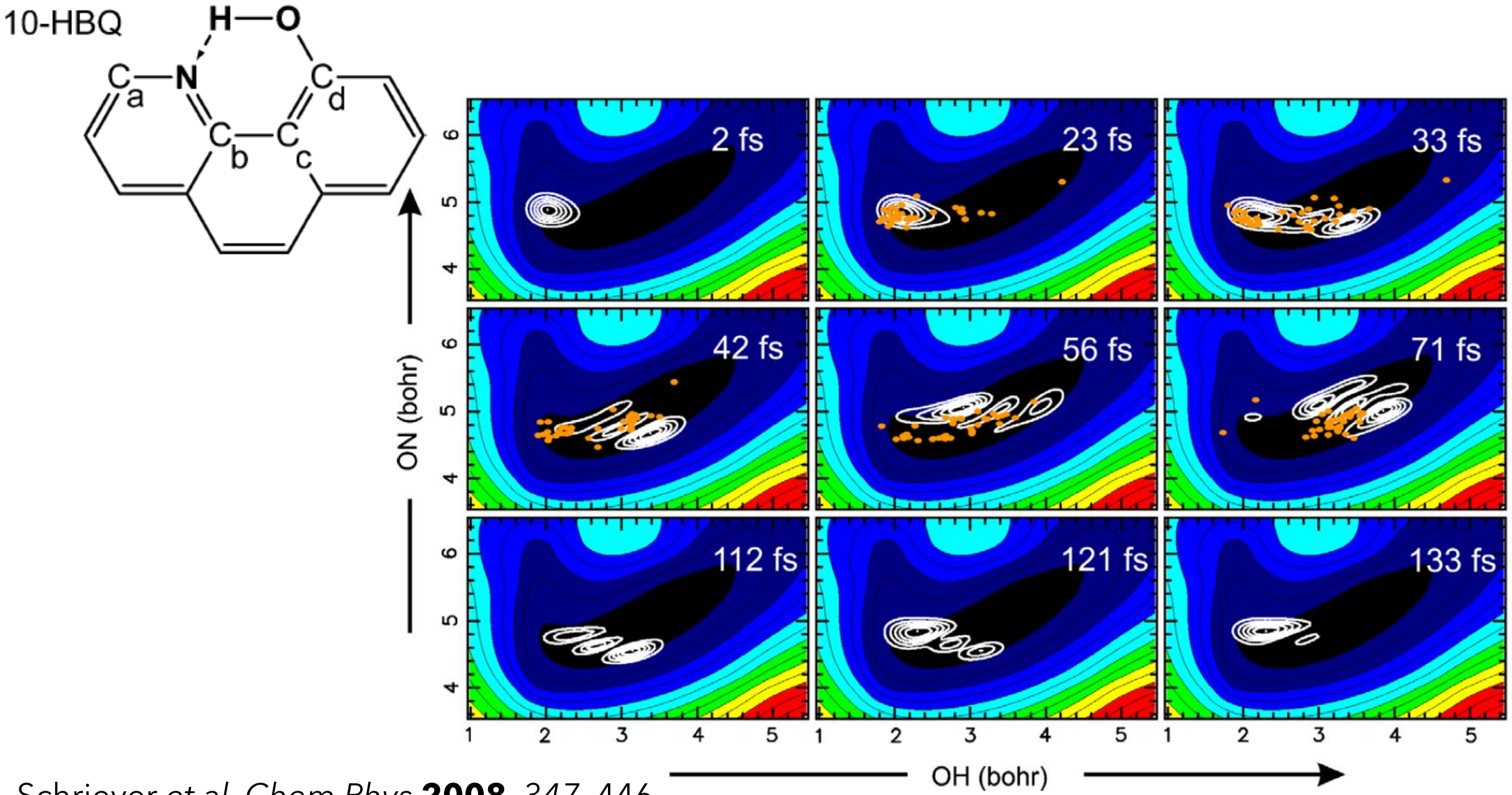
10-HBQ



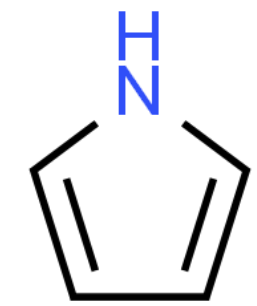

First excited potential energy surface



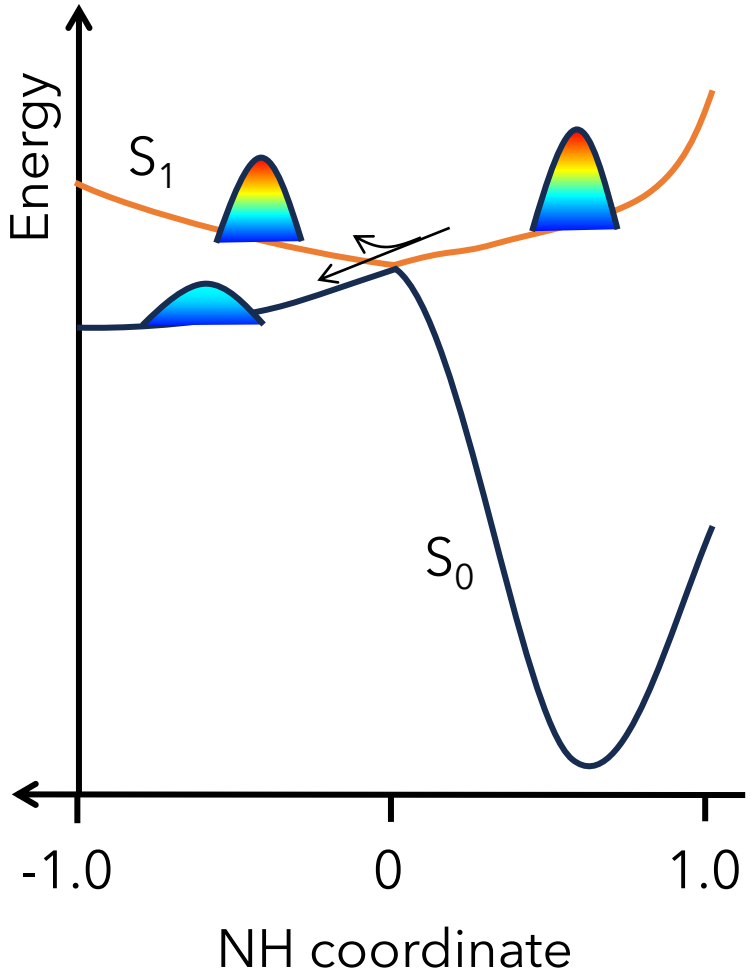

Schriever *et al. Chem Phys* **2008**, *347*, 446

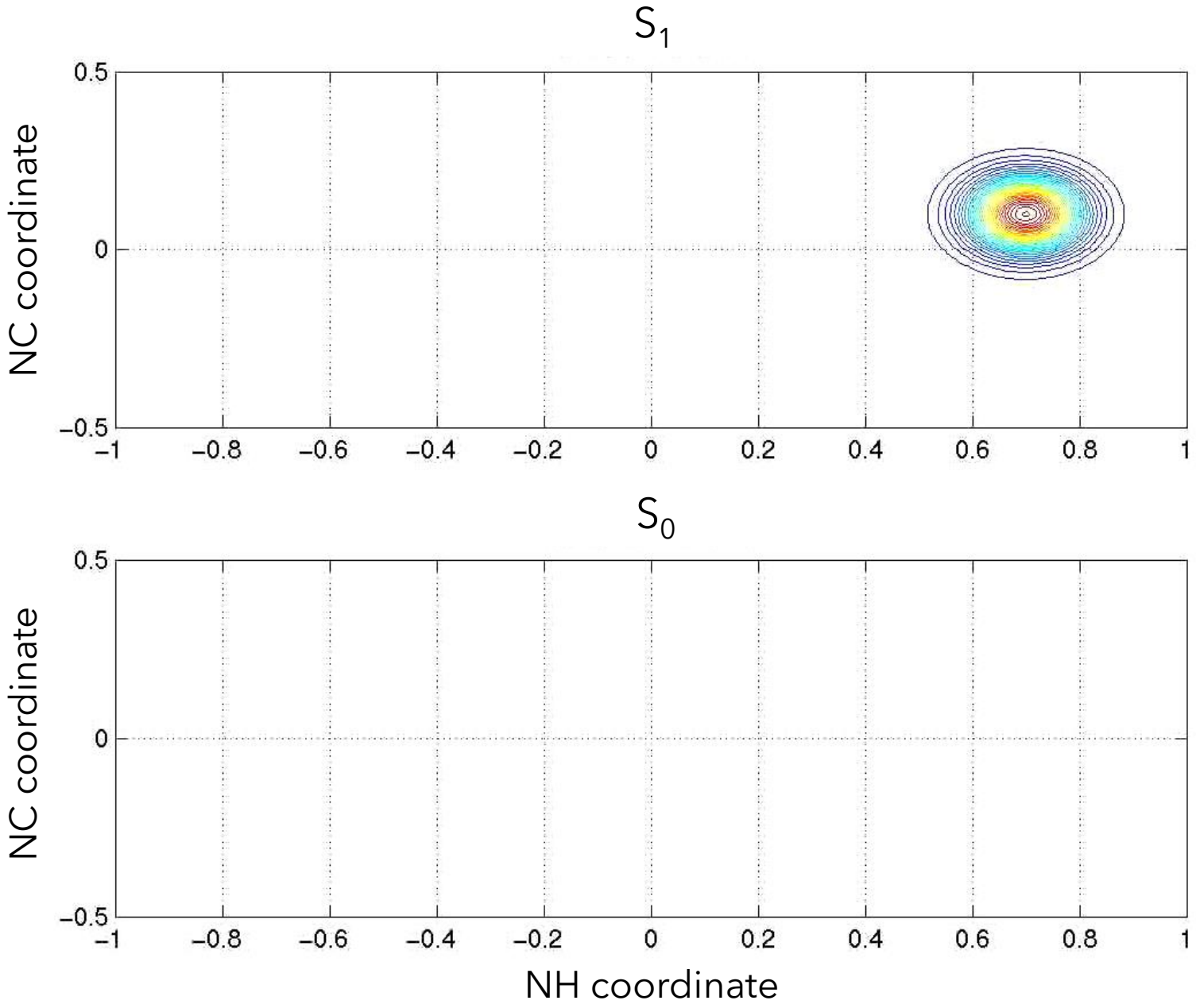



Schriever *et al. Chem Phys* **2008**, *347*, 446


H
N

Pyrrole


Energy
S1
S0
-1.0
0
1.0
NH coordinate


S1
S0
NC coordinate
NC coordinate
0.5
0
−0.5
−1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
0.6
0.8
1
NH coordinate

# Terms mediating nonadiabatic transitions

**Full time-dependent Schrödinger equation**

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

**Multiple spawing**

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

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

**Surface hopping**

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

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

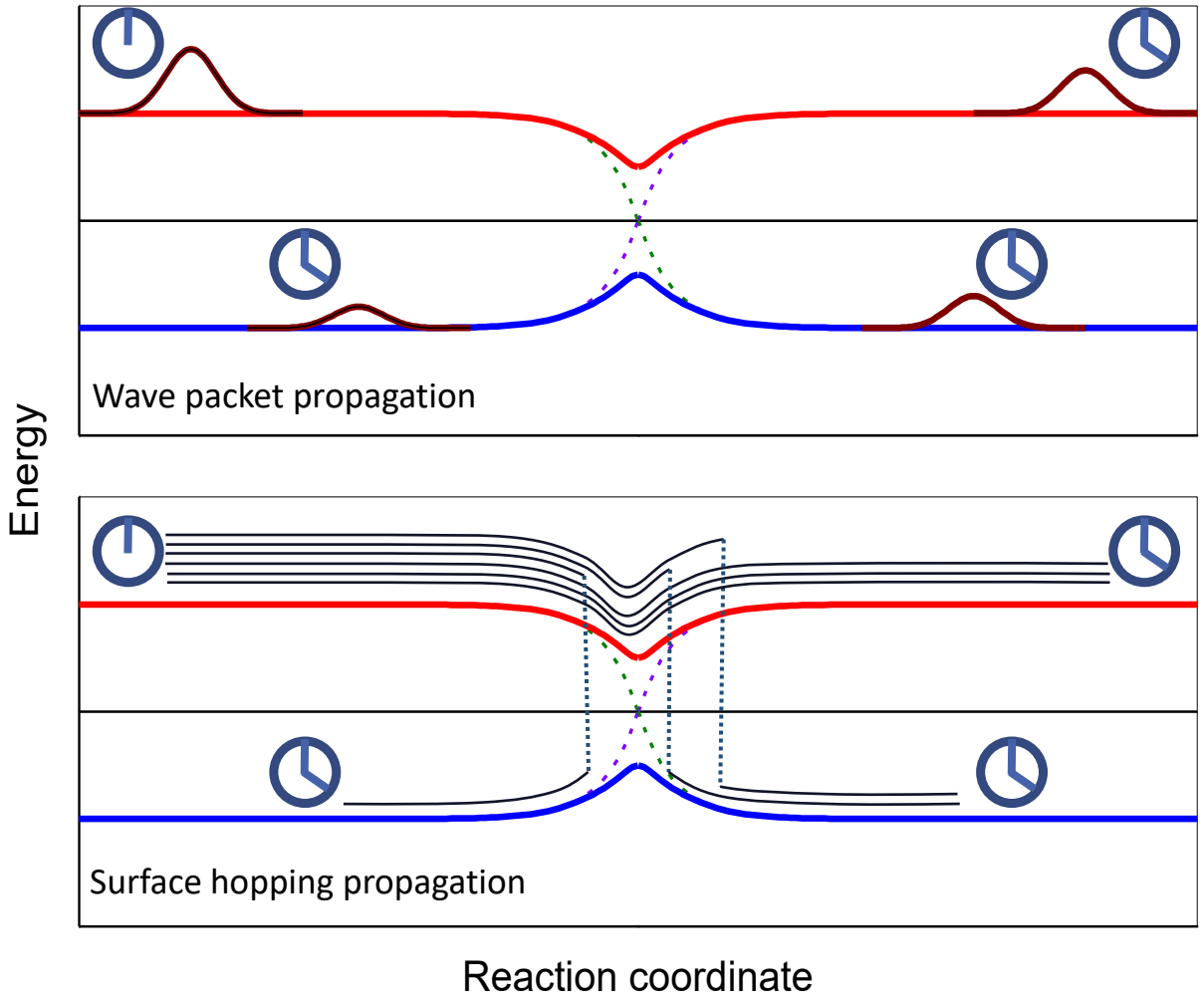
# Mixed quantum-classical (MQC) dynamics

1. Nuclei are treated via *classical trajectories*

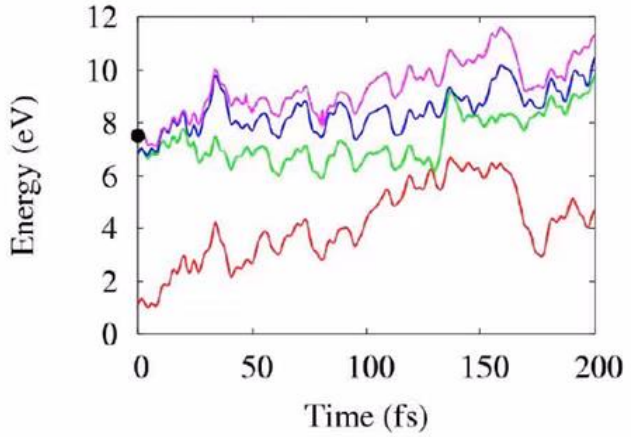
2. Electrons are treated *quantum mechanically*

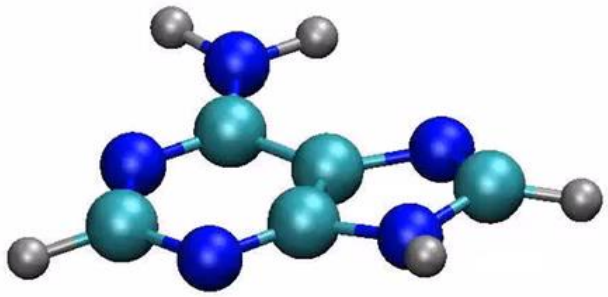
3. A nonadiabatic algorithm introduces *post Born-Oppenheimer effects*

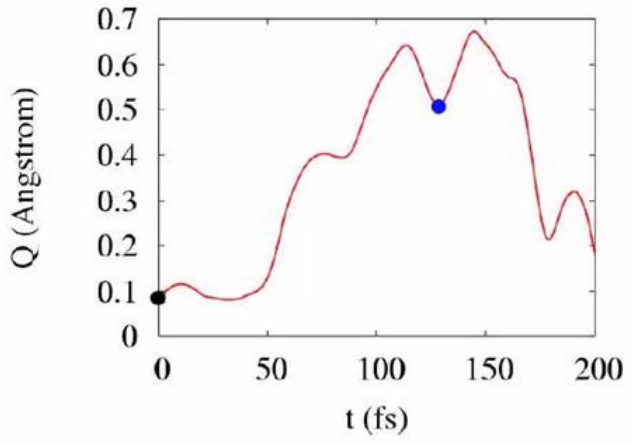
Tully. *Faraday Discuss.* **1998,** *110*, 407

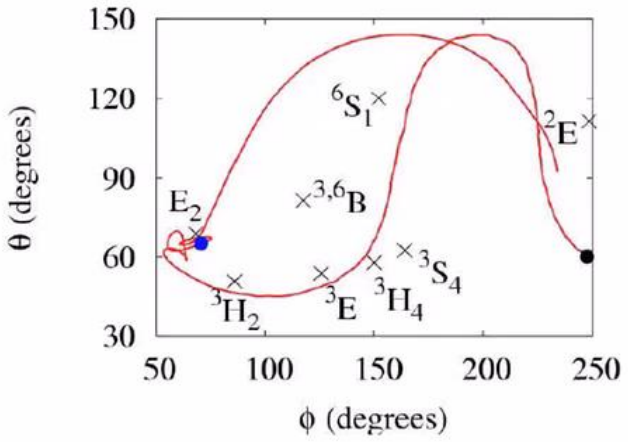



Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026






youtube.com/user/mbarbatti

## Quasi-classical independent-trajectories formulation

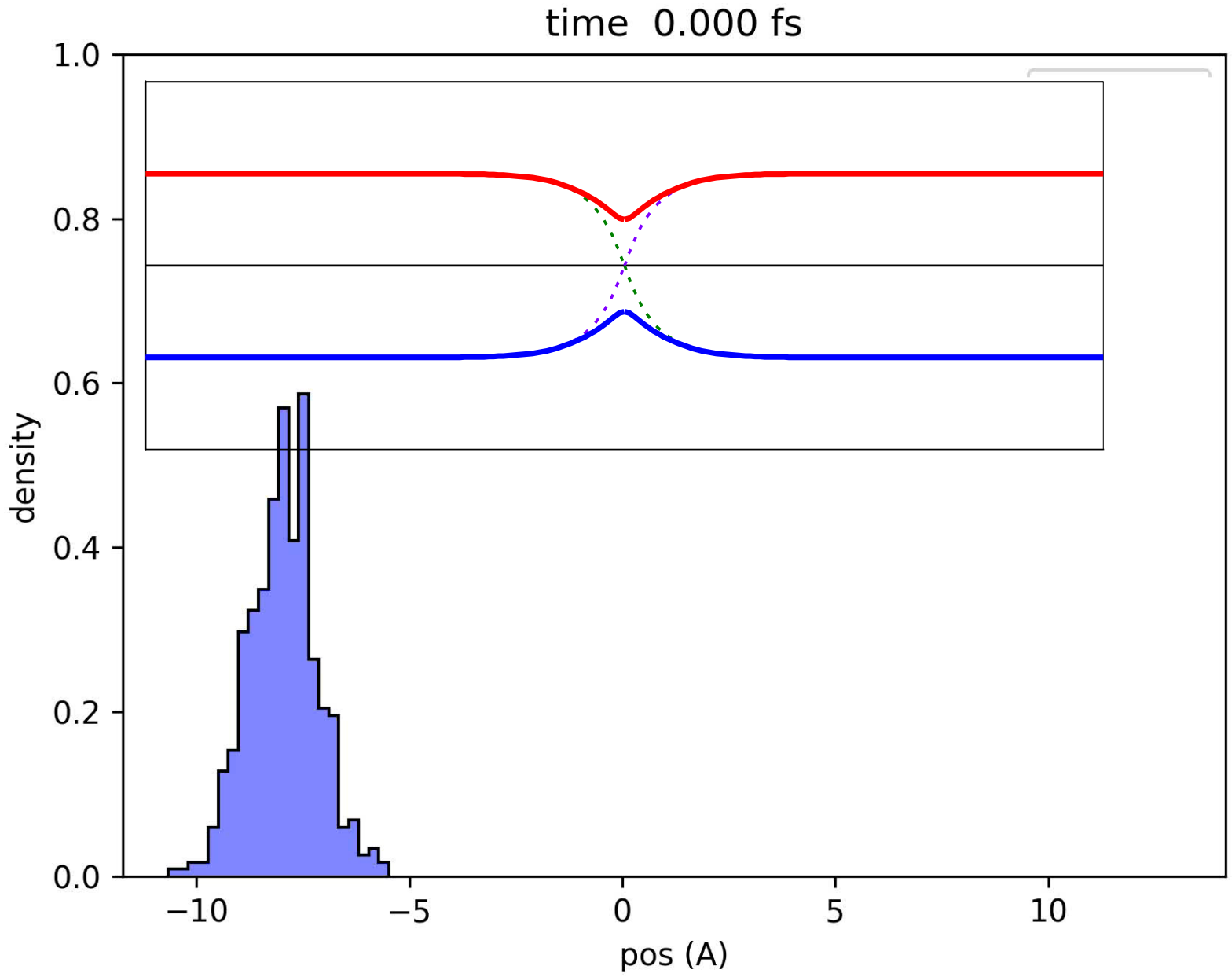
$$\phi^{(i)}\left(\mathbf{r},t\right)=\sum_{n}c_{n}^{(i)}\left(t\right)\varphi\left(\mathbf{r};\mathbf{R}_{i}^{C}\left(t\right)\right)$$

$$\left|h_{n}\left(\mathbf{R},t\right)\right|^{2}=\frac{1}{N_{traj}}\sum_{n,i}\delta_{\mathbf{R}}\left(\mathbf{R}_{i}^{C}\left(t\right)\right)$$

$$\int d\mathbf{R}\left|h_{n}\left(\mathbf{R},t\right)\right|^{2}=\frac{1}{N_{traj}}\sum_{i}\left|c_{n}^{(i)}\left(t\right)\right|^{2}=\left\langle\left|c_{n}\left(t\right)\right|^{2}\right\rangle$$

*i* counts trajectories
*n* counts states

Dirac measure $\delta_{x}\left(A\right)=\begin{cases}1 & x=A\\ 0 & x\neq A\end{cases}$


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

**Software for full quantum dynamics**
Quantics
www2.chem.ucl.ac.uk/worthgrp/quantics/

**Software for multiple spawning**
PySpawn
github.com/blevine37/pySpawn17

**Software for surface hopping (developed by my group)**
Newton-X
www.newtonx.org

# Born-Oppenheimer-Huang formulation

**Electronic Schrödinger equation**

$$\left(T_{elec} + V\right)\varphi_n = E_n \varphi_n$$

**Nuclear Schrödinger equation**

Adiabatic

Time-independent

$$\left(T_{nuc} + E_n - \varepsilon\right)h_n = 0$$

Time-dependent

$$\left(T_{nuc} + E_n - i\hbar\partial_t\right)h_n = 0$$

Nonadiabatic

Time-independent

$$\left(T_{nuc} + E_n - \varepsilon\right)h_n + \sum_m N_{nm}h_m = 0$$

Time-dependent

$$\left(T_{nuc} + E_n - i\hbar\partial_t\right)h_n + \sum_m N_{nm}h_m = 0$$

**Molecular wave function**

$$\Psi_n = \varphi_n h_n$$

$$\Psi = \sum_m \varphi_n h_n$$

# 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
Ask me for the password.

# Demonstration of a conical intersection

Diabatic basis $\left\{\left|\upsilon_i\right\rangle\right\}$

$$H_D = \begin{bmatrix} \left\langle \upsilon_1 \left| H_{elec} \right| \upsilon_1 \right\rangle & \left\langle \upsilon_1 \left| H_{elec} \right| \upsilon_2 \right\rangle \\ \left\langle \upsilon_2 \left| H_{elec} \right| \upsilon_1 \right\rangle & \left\langle \upsilon_2 \left| H_{elec} \right| \upsilon_2 \right\rangle \end{bmatrix} \equiv \begin{bmatrix} V_a & c \\ c & V_b \end{bmatrix}$$

$$\left\langle \upsilon_1 \left| \nabla \upsilon_2 \right\rangle = 0 \right.$$

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

$$\left|\upsilon_n\left(\mathbf{R}_0\right)\right\rangle = \left|\varphi_n\left(\mathbf{R}_0\right)\right\rangle$$

$$\left|\upsilon_n\left(\mathbf{R}\right)\right\rangle = \mathbf{U}\left(\theta\right)\left|\varphi_n\left(\mathbf{R}\right)\right\rangle$$

## Adiabatic energies

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

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

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

## Crossing condition

$$E_1\left(\mathbf{R}_0\right) = E_2\left(\mathbf{R}_0\right) \text{ if } \quad \left(V_a\left(\mathbf{R}_0\right) = V_b\left(\mathbf{R}_0\right)\right)$$

$$\text{and } \left(c\left(\mathbf{R}_0\right) = 0\right)$$

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

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

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

Near the crossing point

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

Worth; Cederbaum. *Annu Rev Phys Chem* **2004,** *55*, 127

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

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

$$\begin{aligned}
\nabla_{\mathbf{R}} c\left(\mathbf{R}_0\right) &= \nabla_{\mathbf{R}} \left\langle \upsilon_b\left(\mathbf{R}_0\right) \middle| H_{elec}\left(\mathbf{R}_0\right) \middle| \upsilon_a\left(\mathbf{R}_0\right) \right\rangle \\
&= \left\langle \nabla_{\mathbf{R}} \upsilon_b\left(\mathbf{R}_0\right) \middle| H_{elec}\left(\mathbf{R}_0\right) \middle| \upsilon_a\left(\mathbf{R}_0\right) \right\rangle \\
&+ \left\langle \upsilon_b\left(\mathbf{R}_0\right) \middle| \nabla_{\mathbf{R}} H_{elec}\left(\mathbf{R}_0\right) \middle| \upsilon_a\left(\mathbf{R}_0\right) \right\rangle \\
&+ \left\langle \upsilon_b\left(\mathbf{R}_0\right) \middle| H_{elec}\left(\mathbf{R}_0\right) \middle| \nabla_{\mathbf{R}} \upsilon_a\left(\mathbf{R}_0\right) \right\rangle
\end{aligned}$$

$$\nabla_{\mathbf{R}} c(\mathbf{R}_0) = V_a \left\langle \nabla_{\mathbf{R}} \upsilon_b(\mathbf{R}_0) \middle| \upsilon_a(\mathbf{R}_0) \right\rangle^{=0}$$
$$+ \left\langle \upsilon_b(\mathbf{R}_0) \middle| \nabla_{\mathbf{R}} H_{elec}(\mathbf{R}_0) \middle| \upsilon_a(\mathbf{R}_0) \right\rangle$$
$$+ V_b \left\langle \upsilon_b(\mathbf{R}_0) \middle| \nabla_{\mathbf{R}} \upsilon_a(\mathbf{R}_0) \right\rangle^{=0}$$

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

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

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

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

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

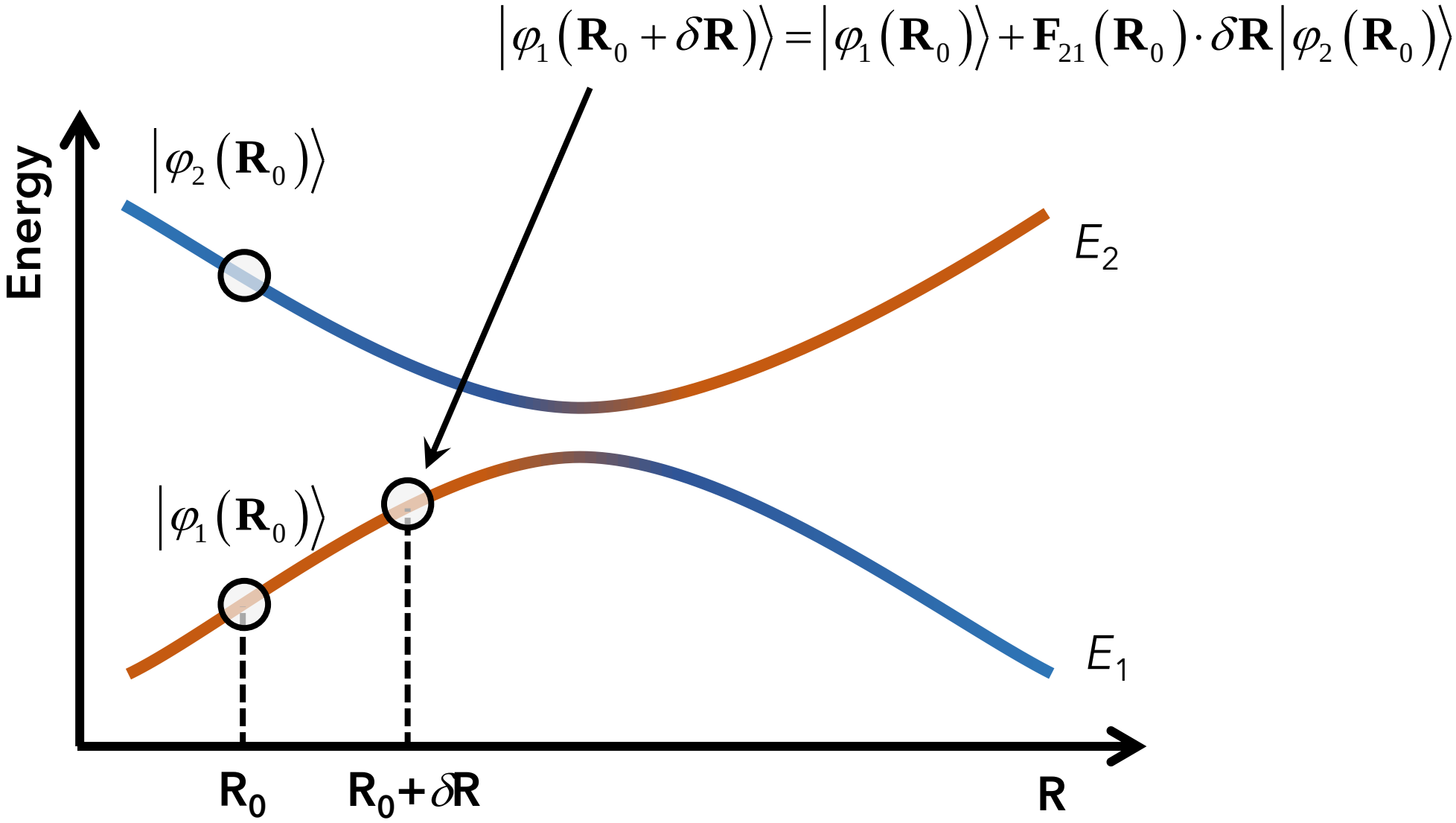
$$\left\langle\varphi_k\left|\nabla\varphi_n\right\rangle=\sum_m\mathbf{c}_{nm}\left\langle\varphi_k\left|\varphi_m\right\rangle\right.\right.$$

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

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

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

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:

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