L3 - Quantum Mechanics 3

Beyond Born-Oppenheimer

Previously on...

Computational simulations of nanosystems

Field-free non-relativistic molecular problem

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

with

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

Born-Huang wave function

$$\Psi\left(\mathbf{R},\mathbf{r}\right)=\sum_{n}c_{n}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{n}\left(\mathbf{R}\right)$$

Adiabatic approximation

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

Time-independent Born-Oppenheimer adiabatic formulation

BO molecular wave function

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

Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc}\left(\mathbf{R}\right)+E_{n}\left(\mathbf{R}\right)\right)\chi_{n}\left(\mathbf{R}\right)=\varepsilon\,\chi_{n}\left(\mathbf{R}\right)$$

Electronic Schrödinger equation

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

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

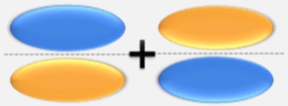
$$\left(\hat{T}_{elec}(\mathbf{r}) + \hat{V}(\mathbf{r},\mathbf{R})\right)\varphi_n(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\varphi_n(\mathbf{r};\mathbf{R})$$

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

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

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

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

everything is unknown!

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

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

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

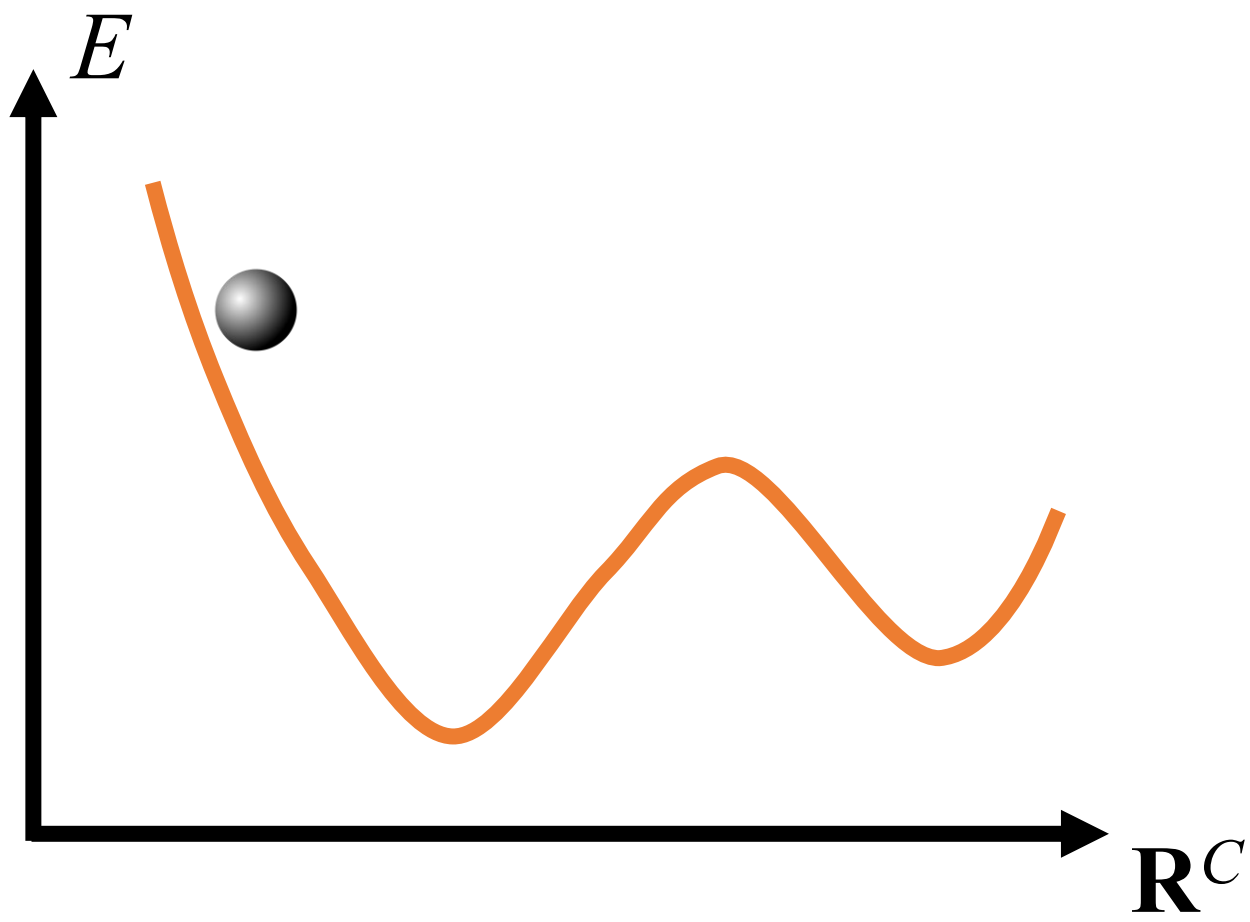
2. Use $E^{(1)}$ and $\mathbf{C}^{(1)}$ to solve

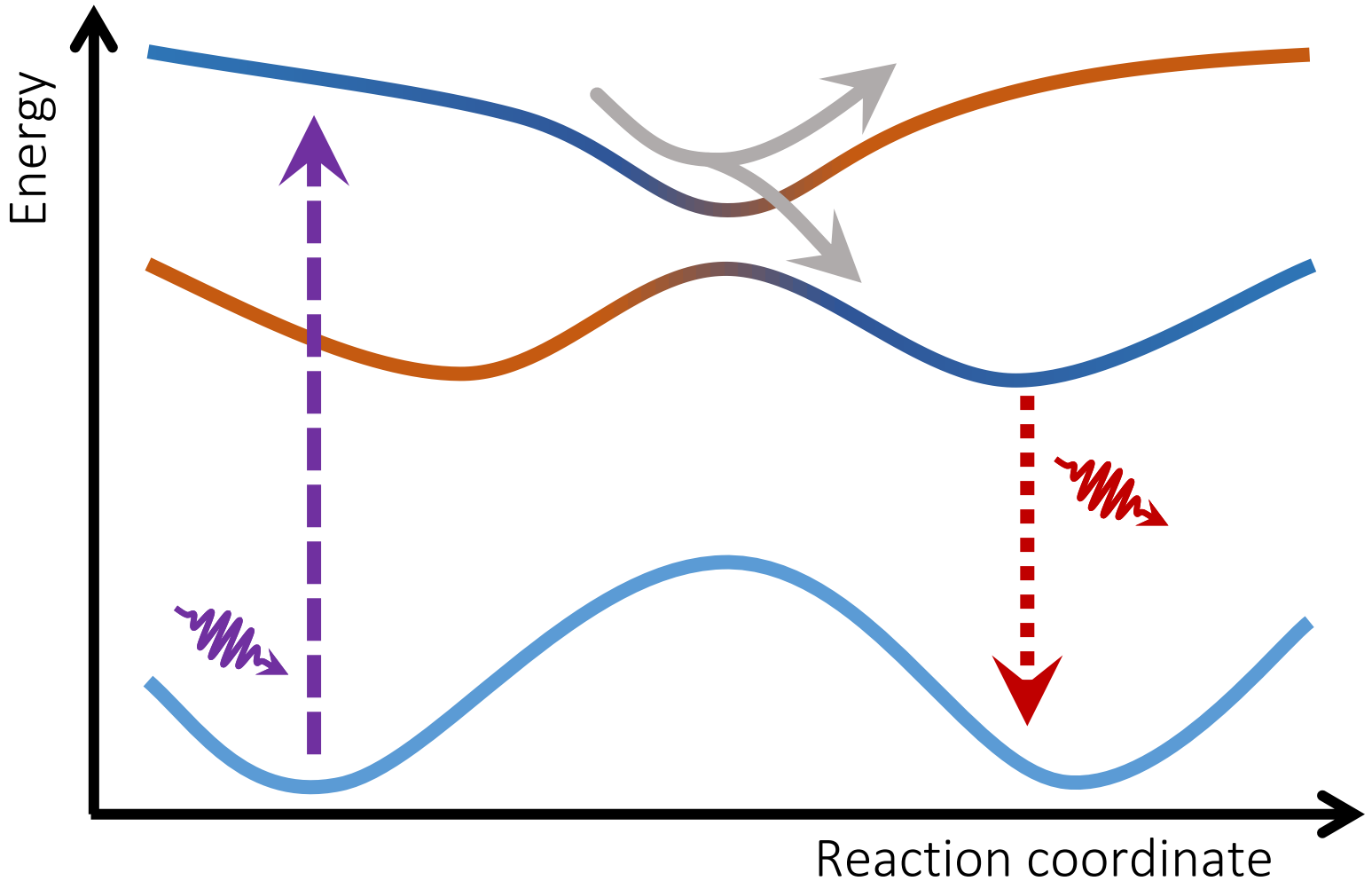
$$\mathbf{H}\left(E^{(1)},\mathbf{C}^{(1)}\right)\mathbf{C}^{(2)} = E^{(2)}\mathbf{C}^{(2)}$$

3. Continue the iterations until

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

Beyond the adiabatic approximation


E
$\mathbf{R}^C$



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

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

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

Born-Huang molecular wave function

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

Nonadiabatic coupling vector

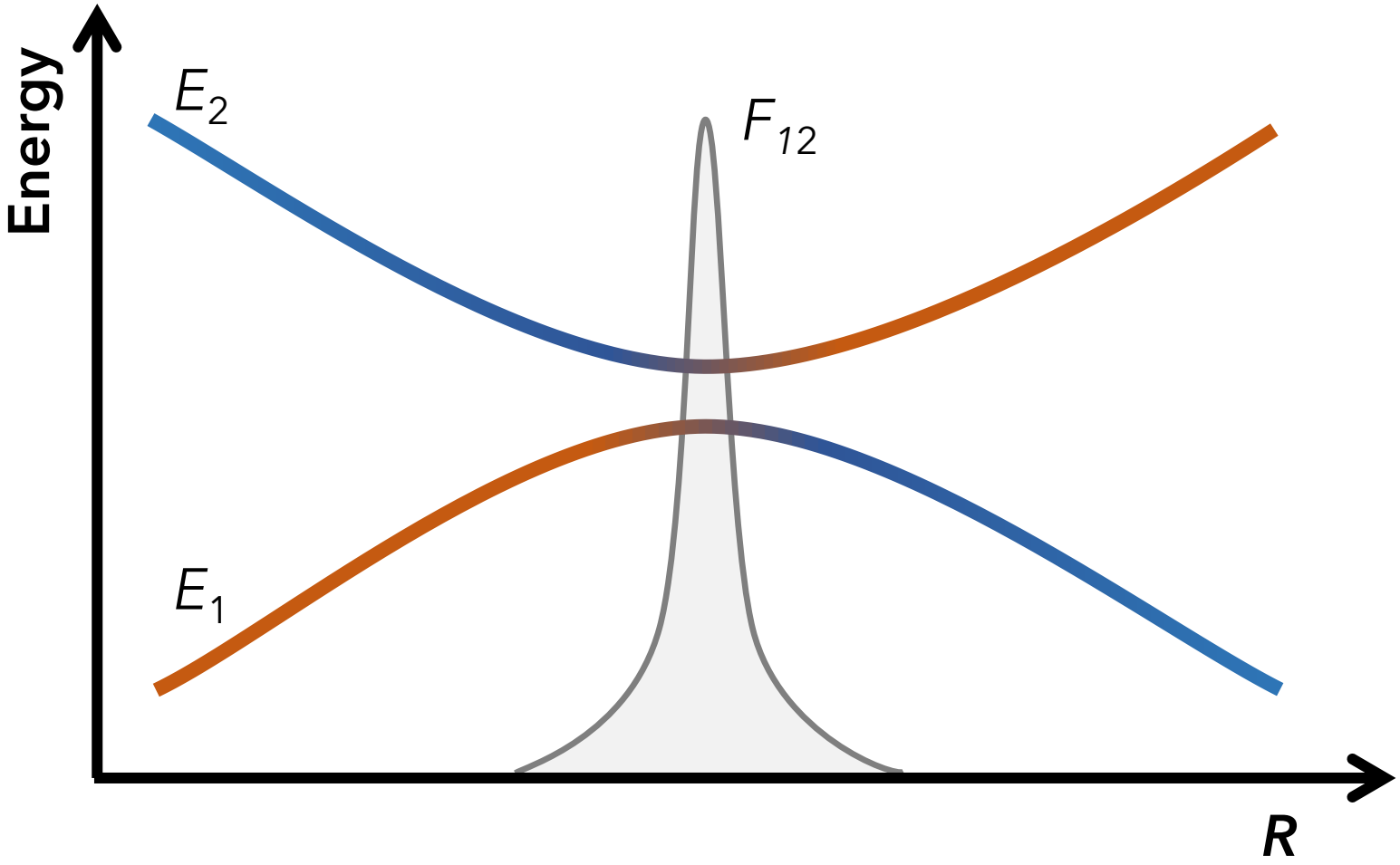
$$\mathbf{F}_{nm}\left(\mathbf{R}\right) \equiv \left\langle \varphi_n\left(\mathbf{r};\mathbf{R}\right) \middle| \nabla_{\mathbf{R}} \varphi_m\left(\mathbf{r};\mathbf{R}\right) \right\rangle_{\mathbf{r}}$$

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

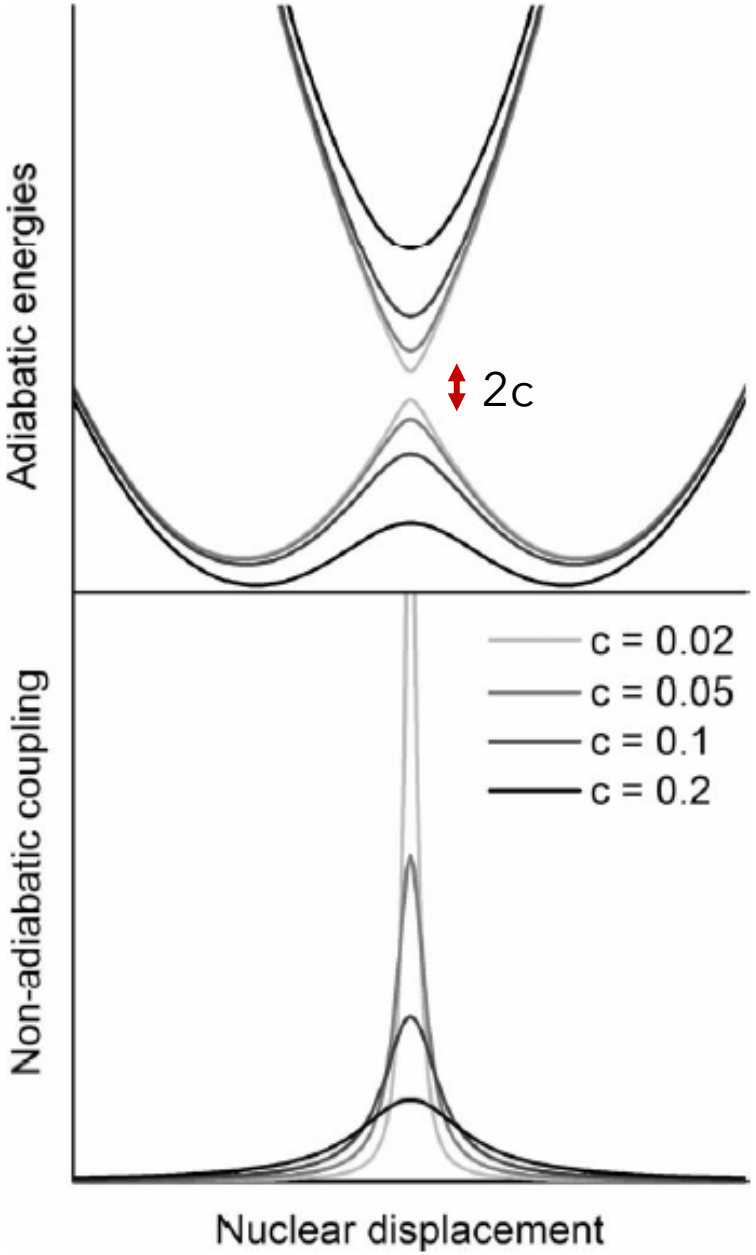
$$\mathbf{F}_{nm} = \frac{\left\langle \varphi_n \middle| \nabla_{\mathbf{R}} H_{elec} \middle| \varphi_m \right\rangle_{\mathbf{r}}}{\left(E_m - E_n\right)}$$

For the demonstration, see the appendix to this presentation.

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



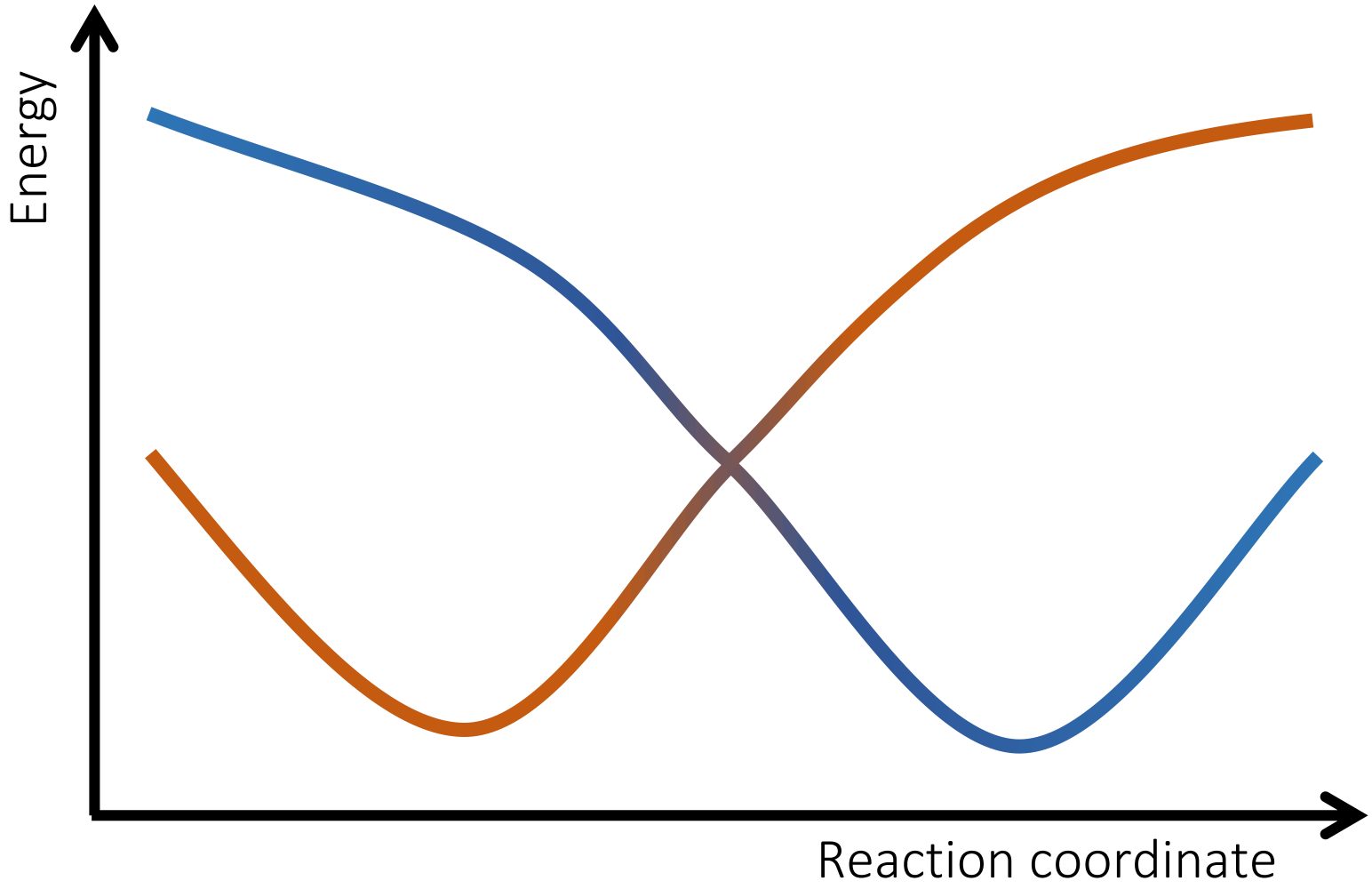
Baeck; An. *J Chem Phys* **2017,** *146*, 064107



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

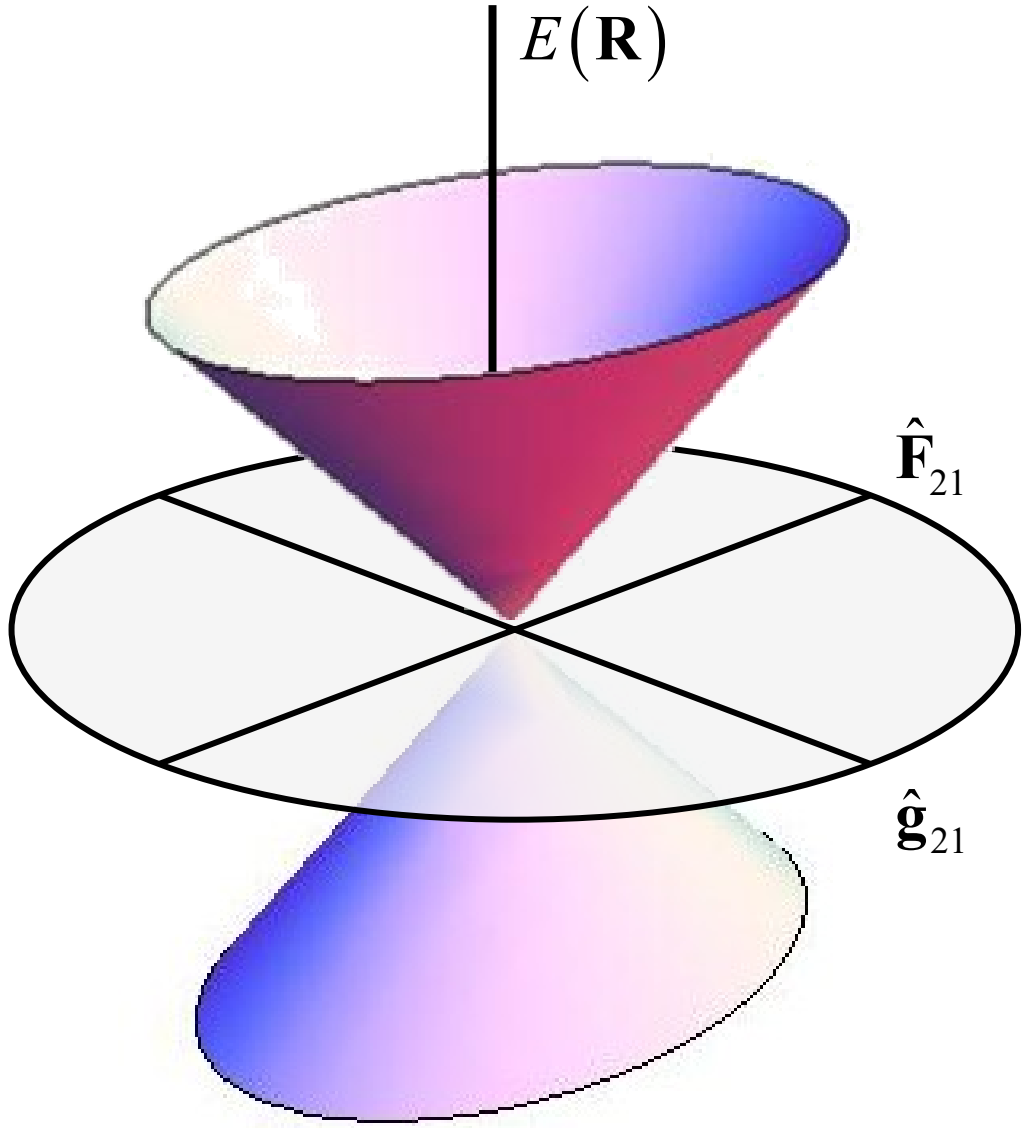
Can two potential energy surface touch?

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



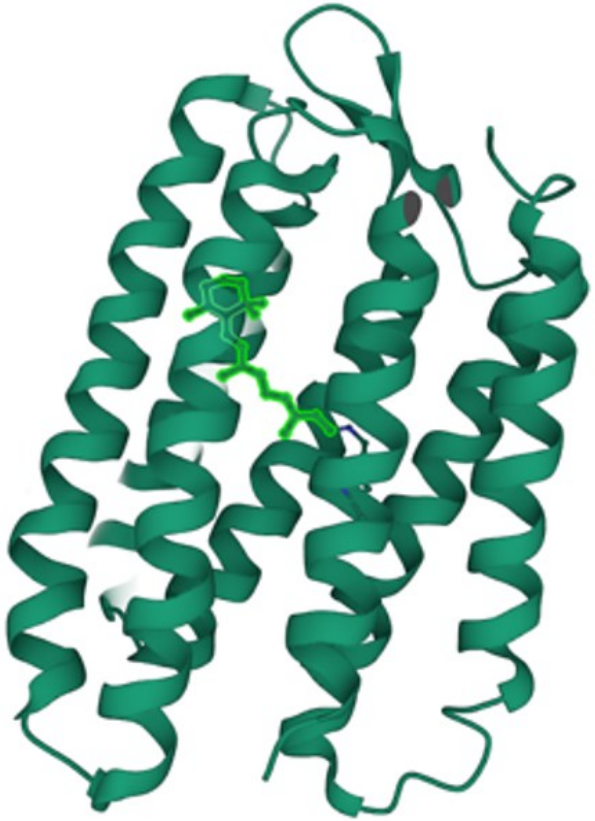
Conical intersection

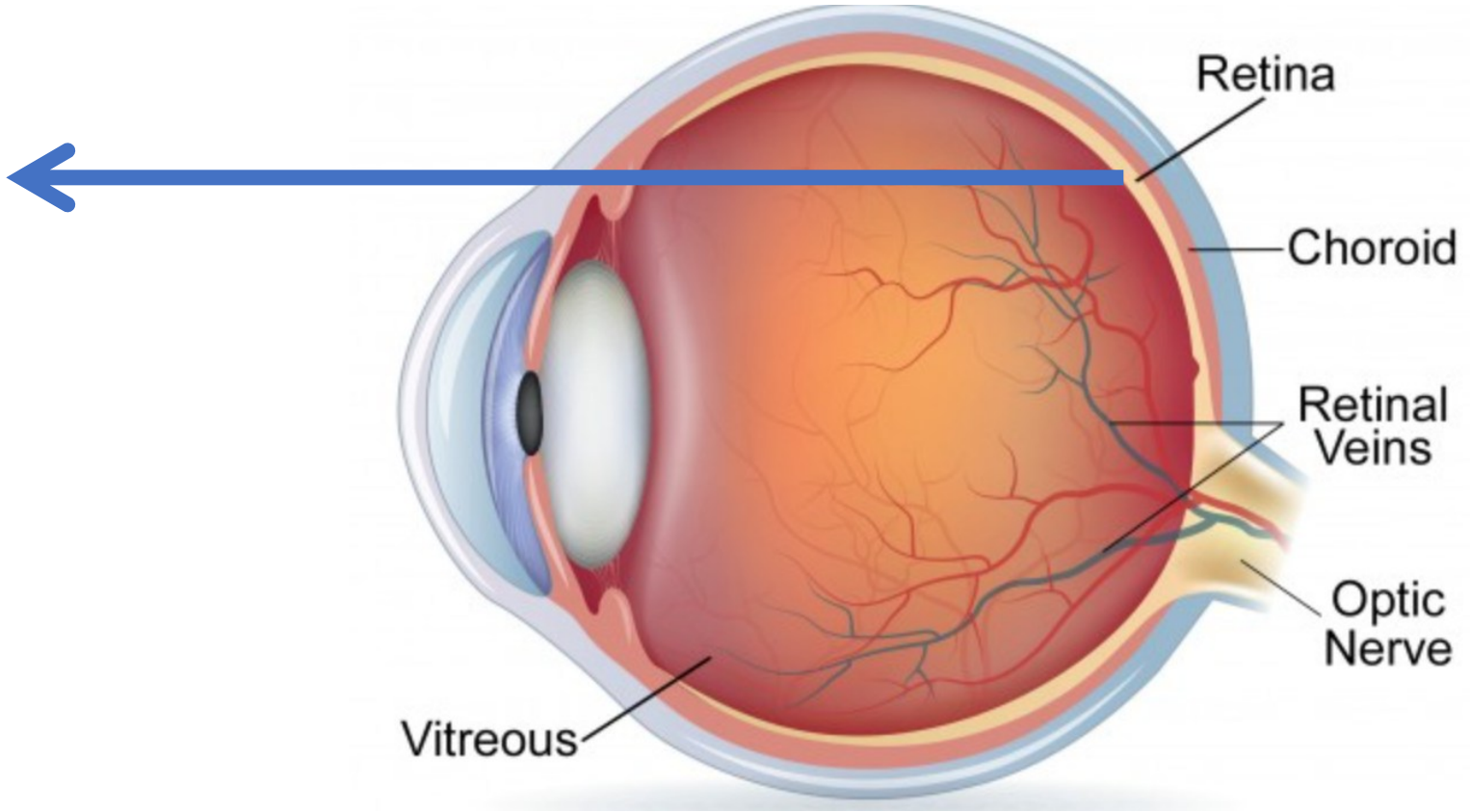
$$E_{1,2}\left(\mathbf{R}_0+\Delta\mathbf{R}\right)=\frac{\left(E_1\left(\mathbf{R}_0\right)+E_2\left(\mathbf{R}_0\right)\right)}{2}\pm\sqrt{\left(\frac{1}{2}\mathbf{g}_{21}\left(\mathbf{R}_0\right)\cdot\Delta\mathbf{R}\right)^2+\left(\Delta E_{12}\left(\mathbf{R}_0\right)\mathbf{F}_{21}\left(\mathbf{R}_0\right)\cdot\Delta\mathbf{R}\right)^2}$$



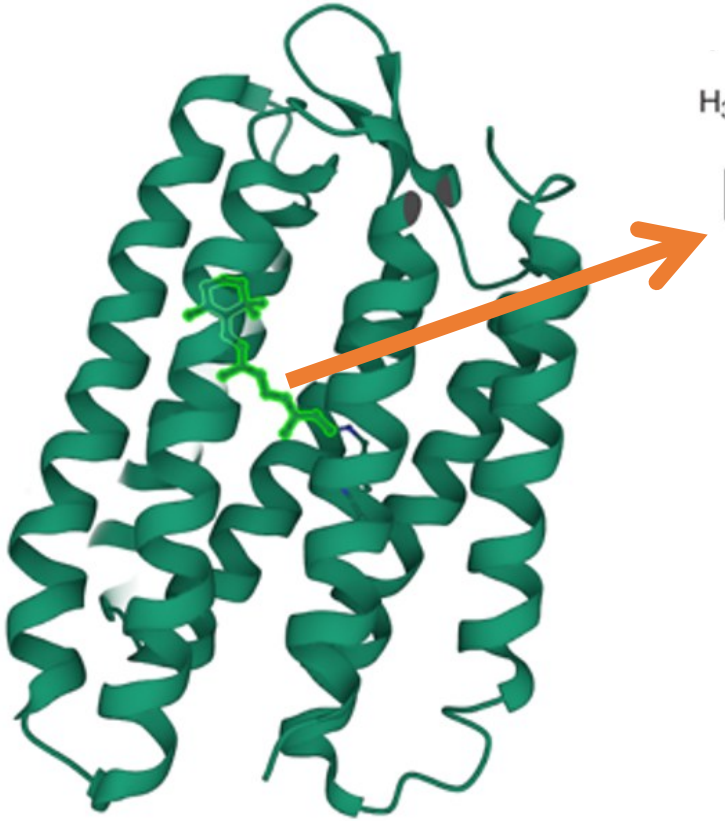
Sicilia *et al. J Phys Chem A* **2007,** *111*, 2182
For the demonstration, see the appendix to this presentation.

bacteriorhodopsin

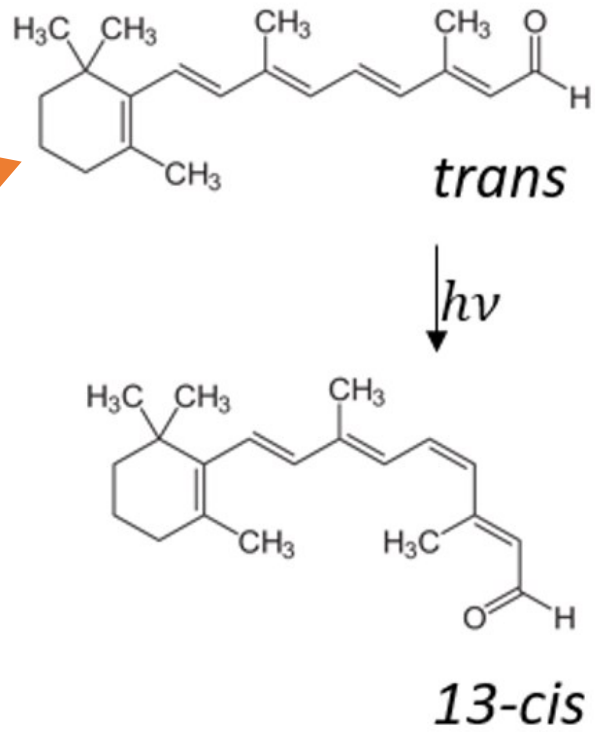


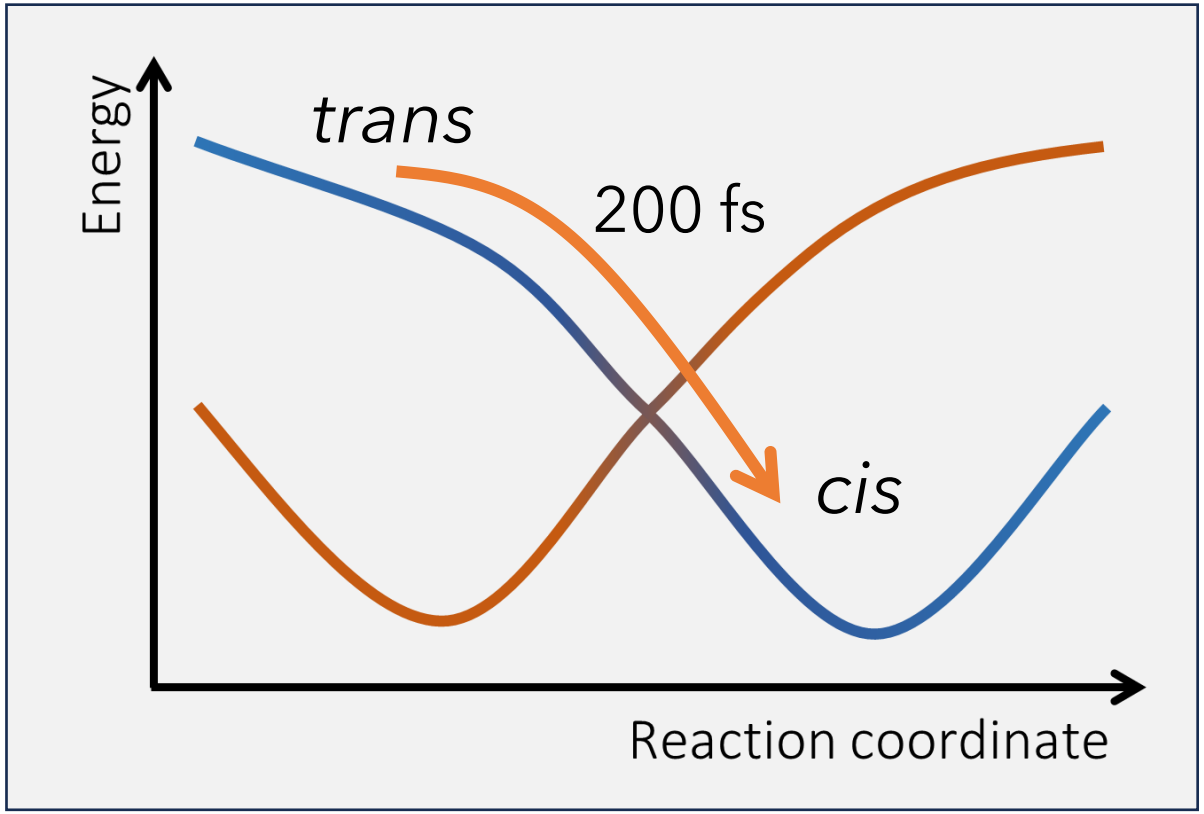


bacteriorhodopsin

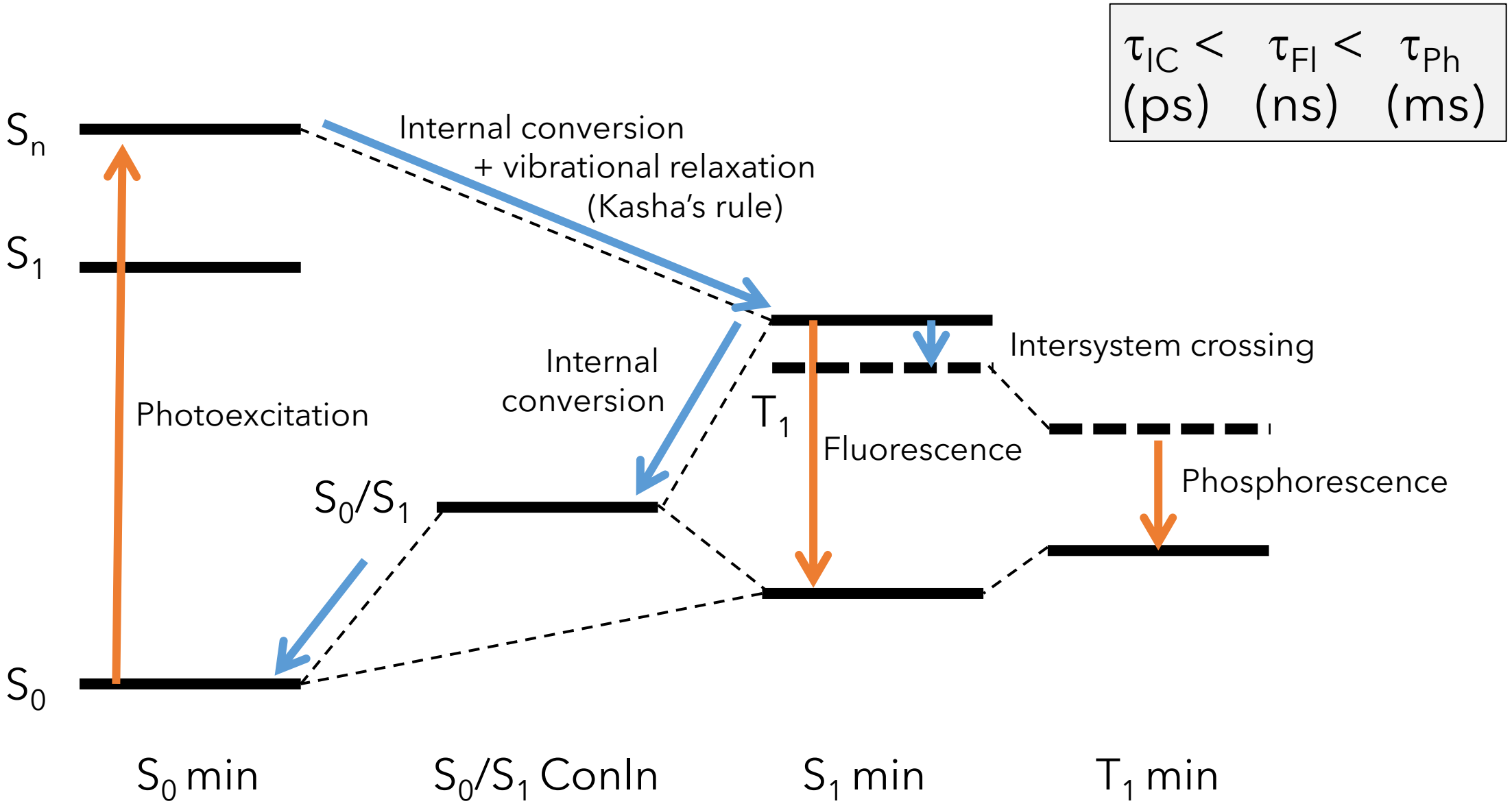


retinal





Gozem *et al. Chem Rev* **2017**, *117*, 13502


τ_{IC} < τ_{FI} < τ_{Ph}
(ps) (ns) (ms)
S_n
S_1
S_0
Internal conversion
+ vibrational relaxation
(Kasha's rule)
Photoexcitation
Internal
conversion
S_0/S_1
T_1
Intersystem crossing
Fluorescence
Phosphorescence
S_0 min
S_0/S_1 ConIn
S_1 min
T_1 min

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

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

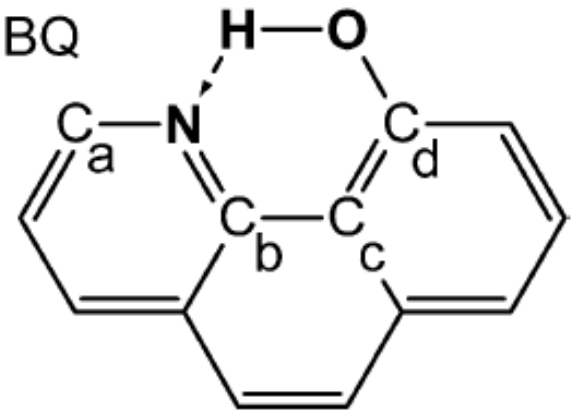
Nuclear Schrödinger equation

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

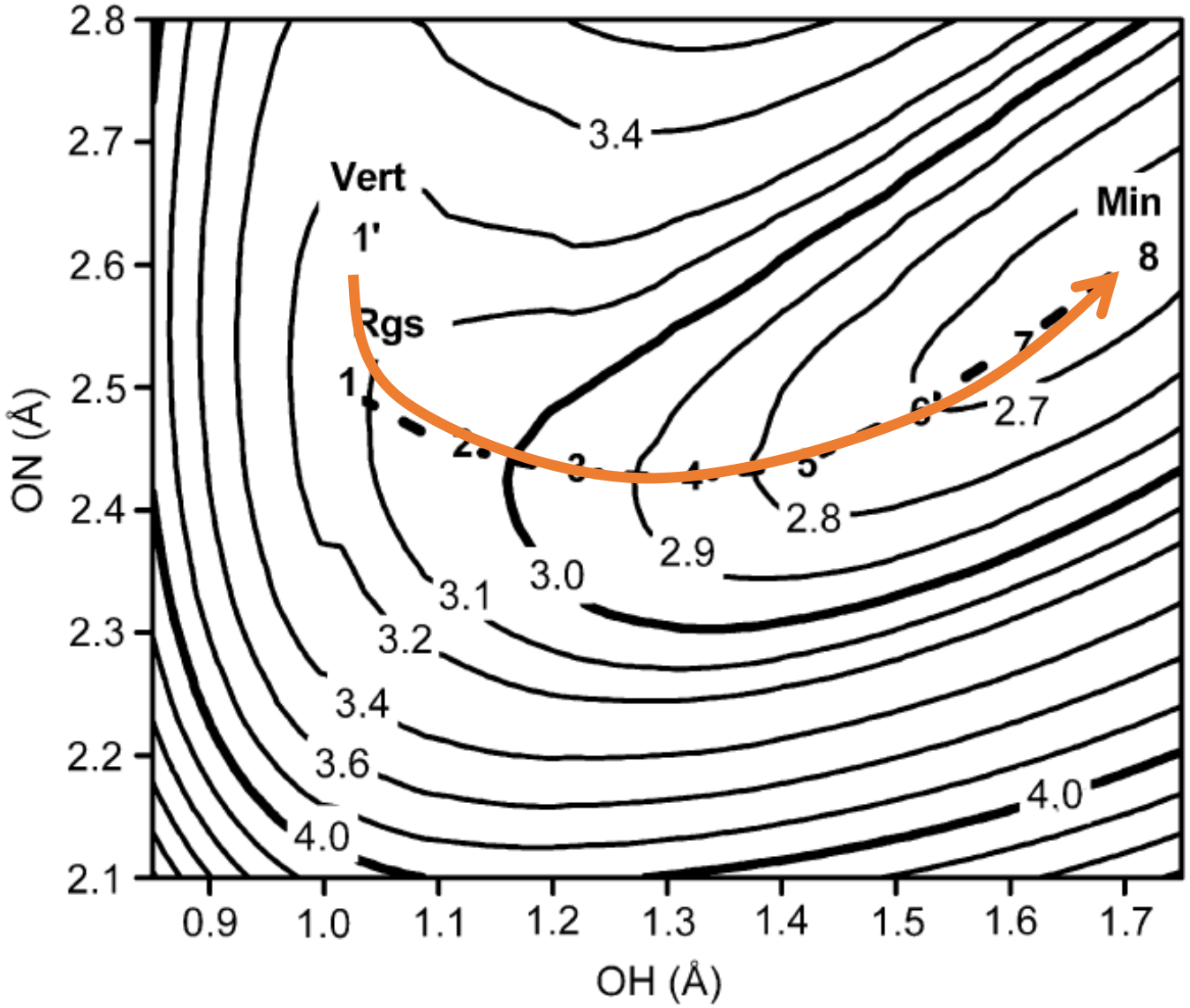
Born-Huang molecular wave function

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

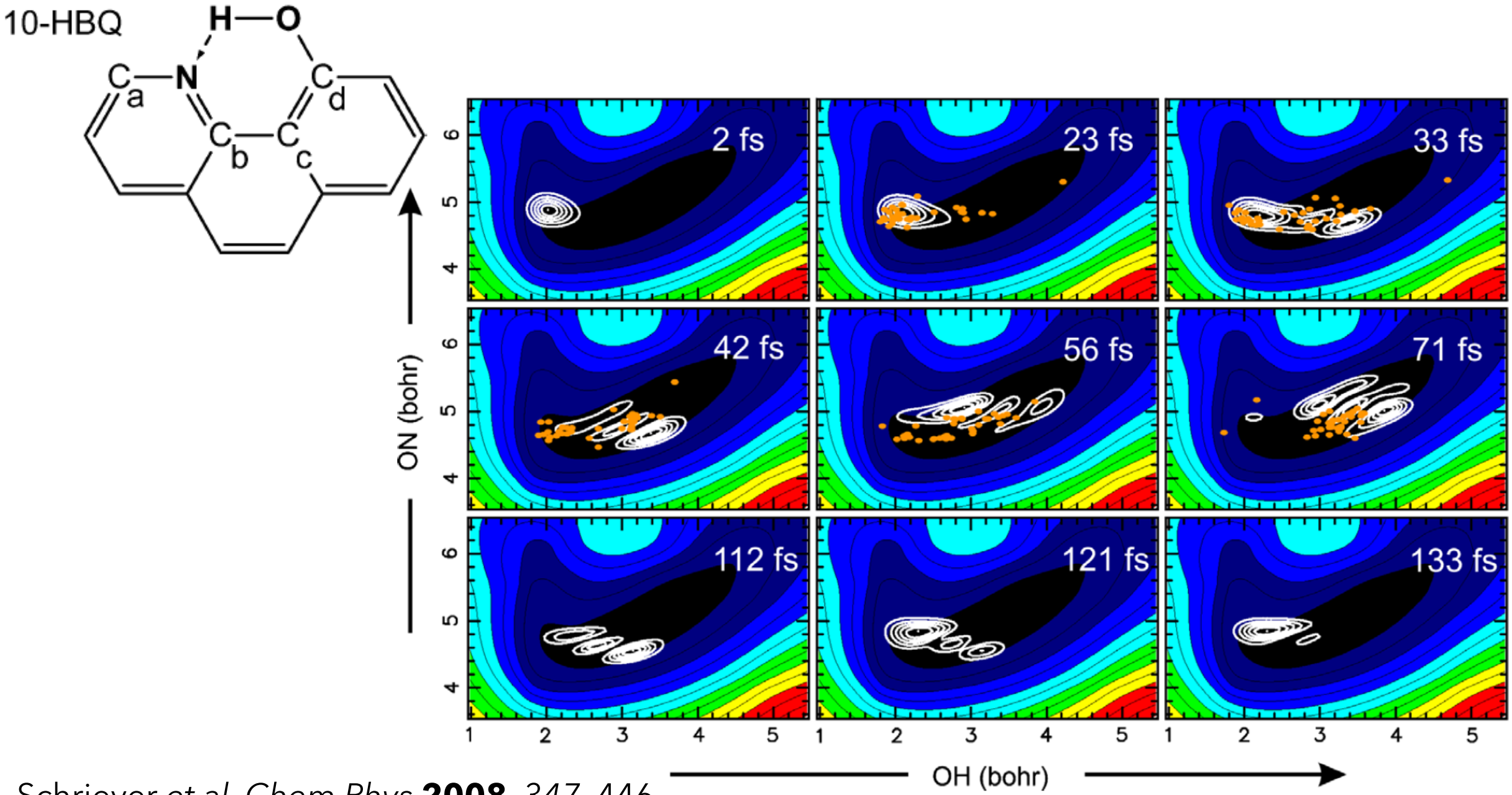
10-HBQ



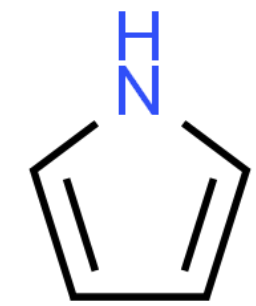
First excited potential energy surface



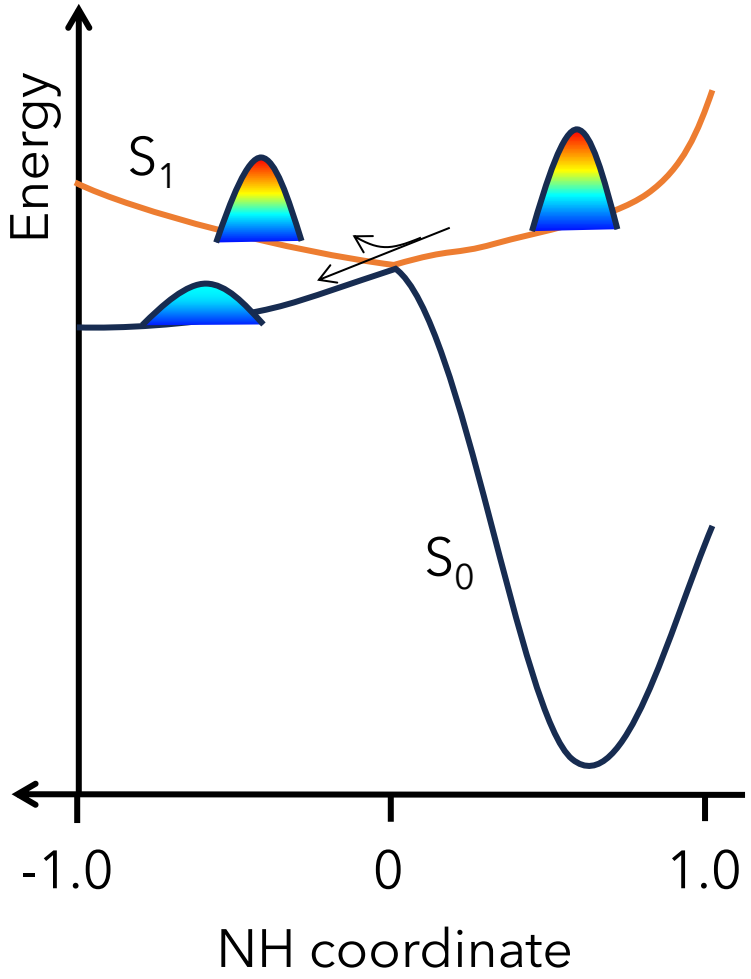
Schriever *et al. Chem Phys* **2008**, *347*, 446

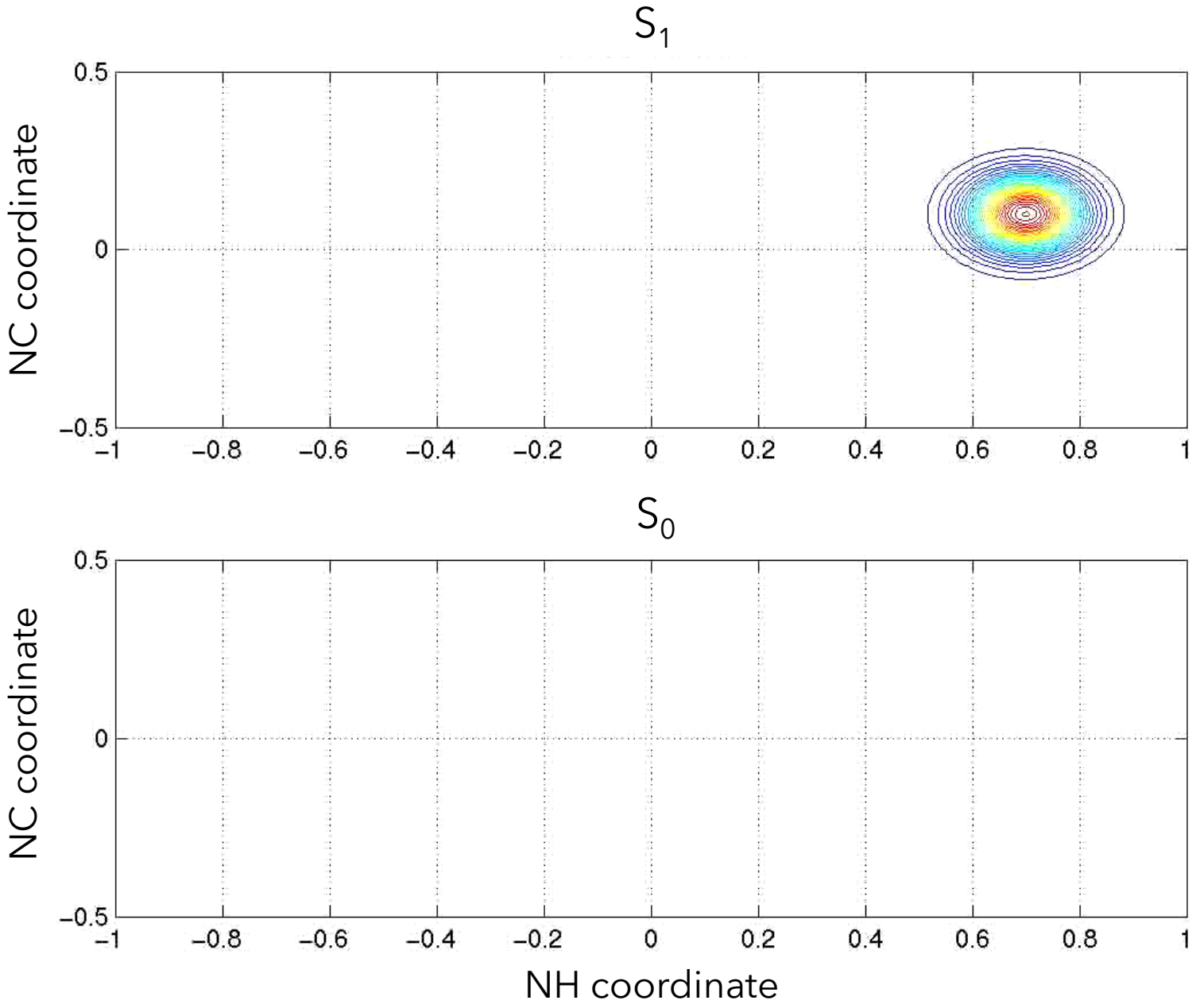


Schriever *et al. Chem Phys* **2008**, *347*, 446


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

Quantum wavepacket (e.g. MCTDH)

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

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

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

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

Classical wavepacket (e.g. 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

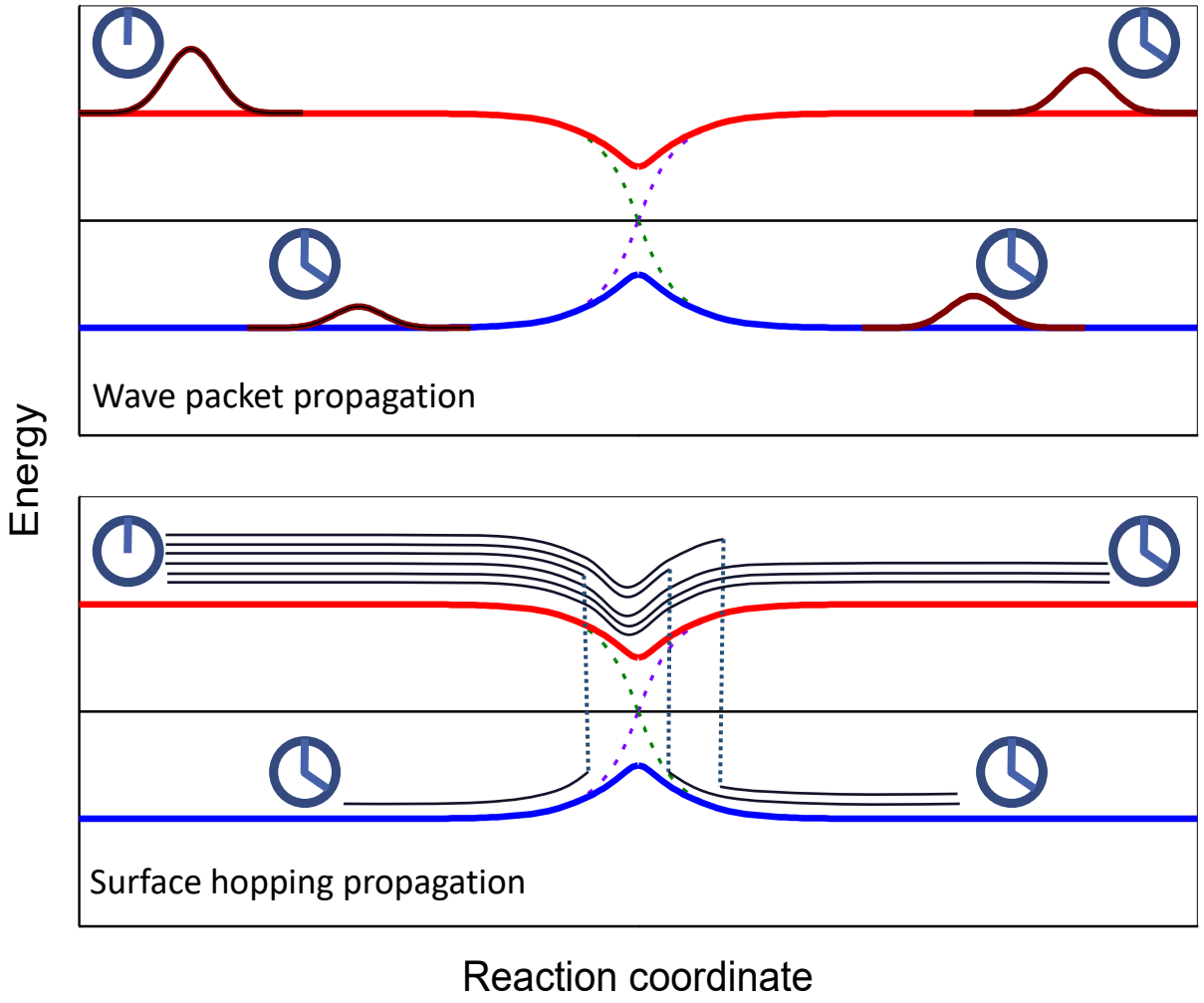
Mixed quantum-classical (MQC) dynamics

1. Nuclei are treated via *classical trajectories*

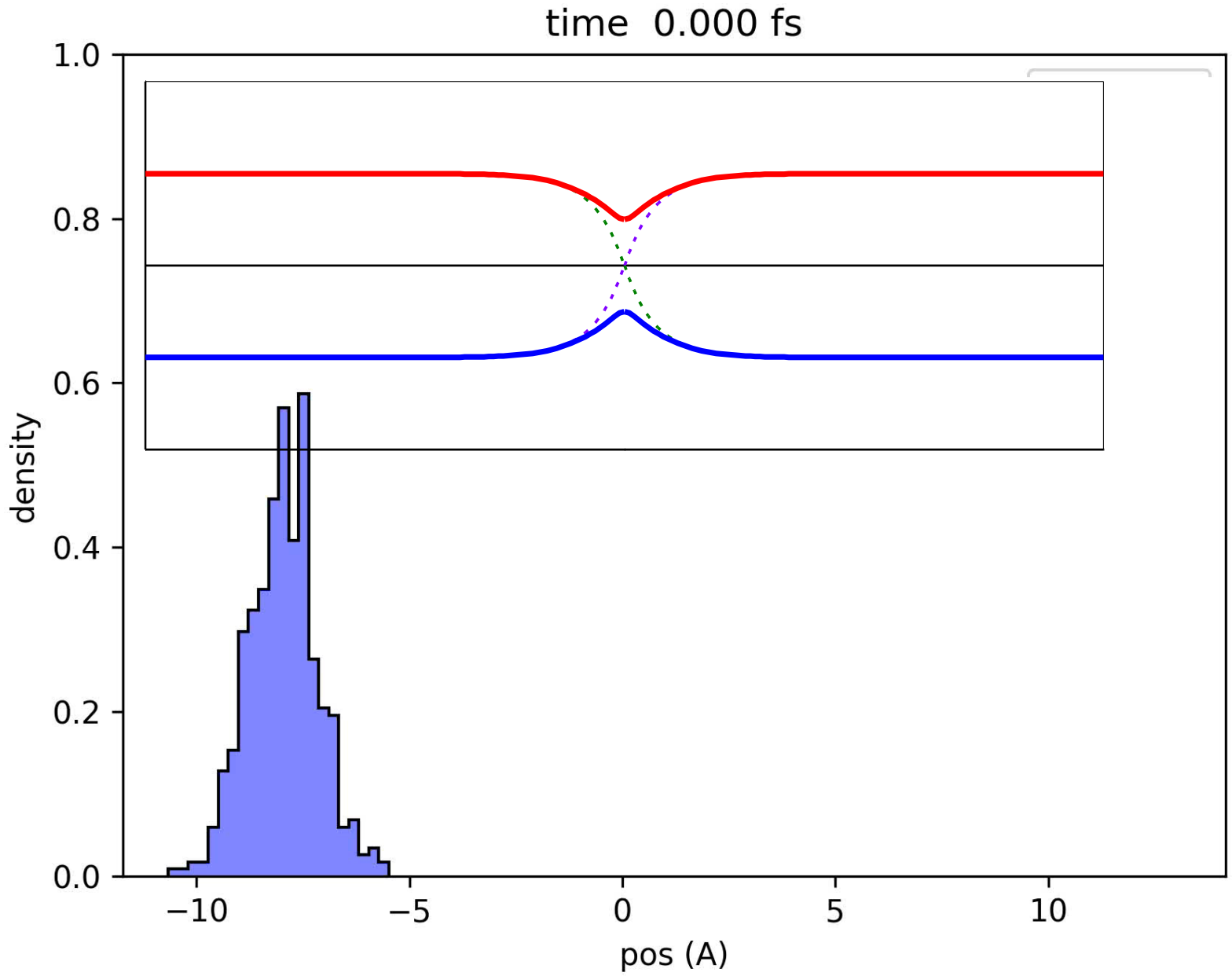
2. Electrons are treated *quantum mechanically*

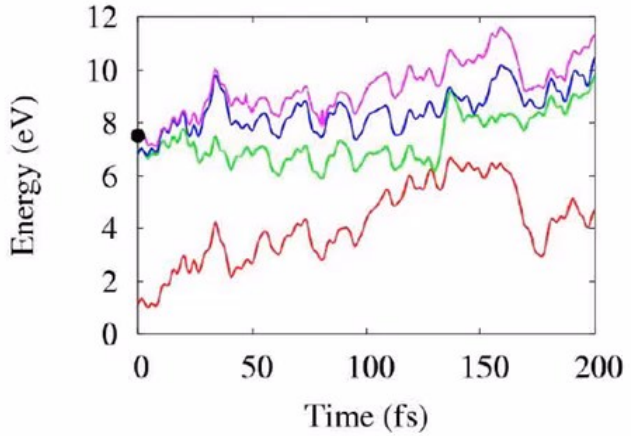
3. A nonadiabatic algorithm introduces *post Born-Oppenheimer effects*

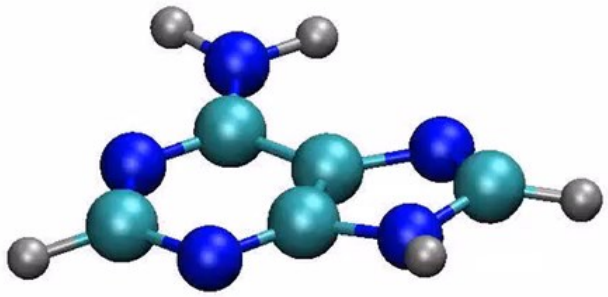
Tully. *Faraday Discuss.* **1998,** *110*, 407

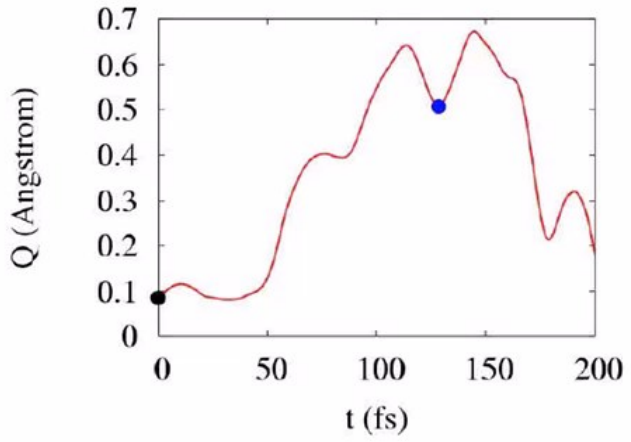


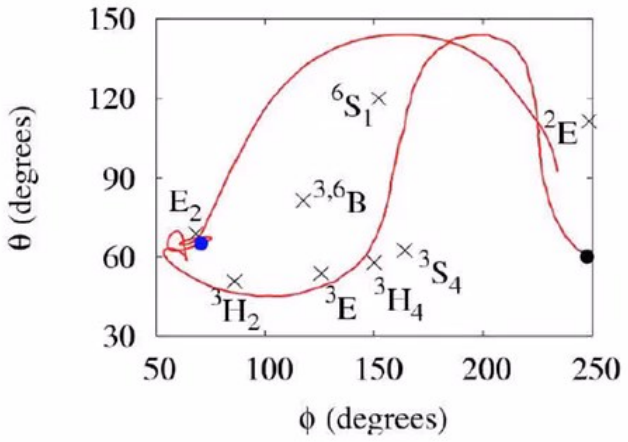
Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026


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









youtube.com/user/mbarbatti

Software for full quantum dynamics

Quantics

www2.chem.ucl.ac.uk/worthgrp/quantics/

Software for surface hopping & multiple spawning (developed by my group)

Newton-X

www.newtonx.org

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

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

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

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

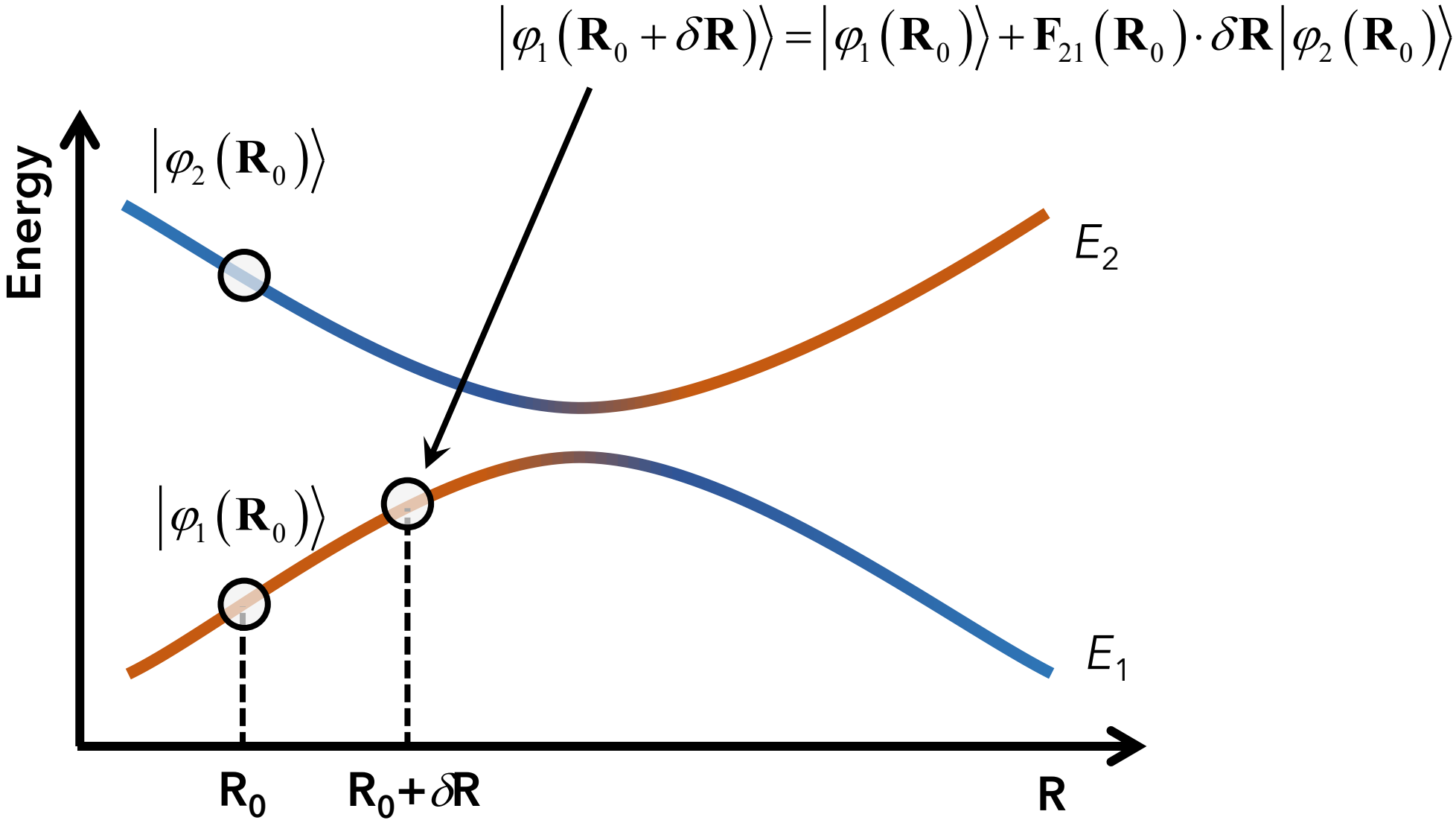
$$\left\langle\varphi_k\left|\nabla\varphi_n\right\rangle=\sum_m\mathbf{c}_{nm}\left\langle\varphi_k\left|\varphi_m\right\rangle\right.\right.$$

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

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

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

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:

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