Nonadiabatic Dynamics
current methods and challenges

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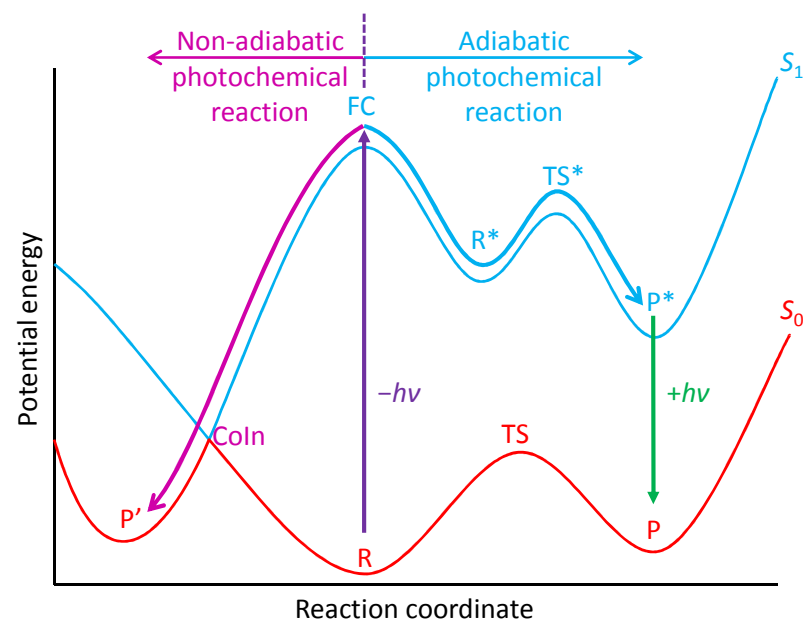*CNRS – Université de Montpellier*

Summer School EMIE-UP
Multiscale Dynamics in Molecular Systems
August 2019

1. Introduction

2. Beyond the Born-Oppenheimer Approximation

3. Non-Adiabatic Processes

4. Methods

5. Examples of Application

6. Conclusions and Outlooks

1. Introduction

"Nonadiabatic dynamics": a tentative definition

Field

Computational and theoretical description of molecular processes induced upon UV-visible light absorption and starting in electronic excited states

Methods

Quantum/semiclassical molecular dynamics (time evolution of the molecular geometry governed by potential energy surfaces and non-adiabatic couplings) and electronic structure (set of coupled excited states)
→ both challenging compared to ground-state simulations

Objective

Simulation of time/energy-resolved processes at the molecular level from the promotion to the excited electronic state, if possible to the formation of products or regeneration of reactants back in the electronic ground state

Applications

Electronic spectroscopy (photoabsorption, photoionisation)
Photochemistry, photophysics, chemiluminescence [atto/femto]
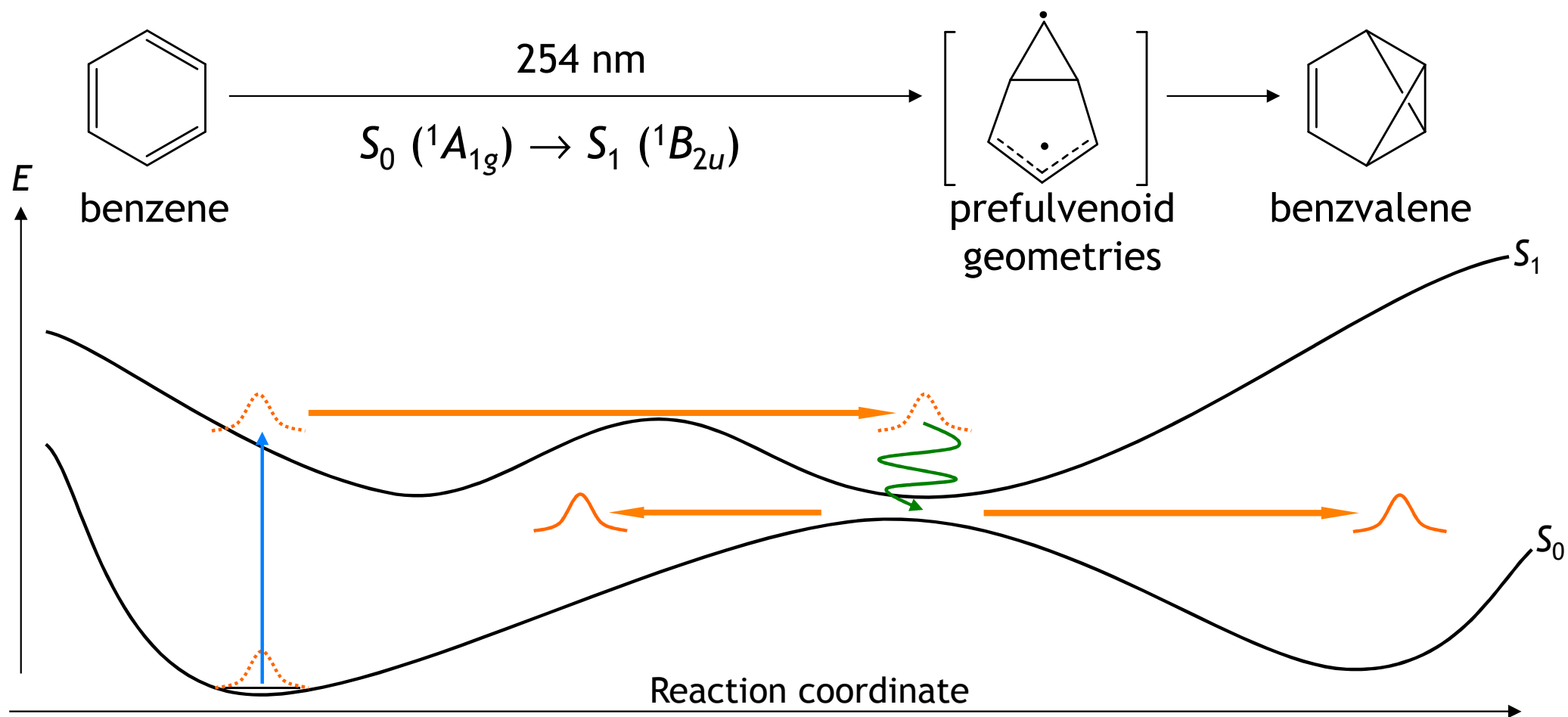
Electronic spectroscopy

- Franck-Condon approximation
- Electric dipole approximation
- Wavepacket evolution (time)
- Absorption spectrum (energy)

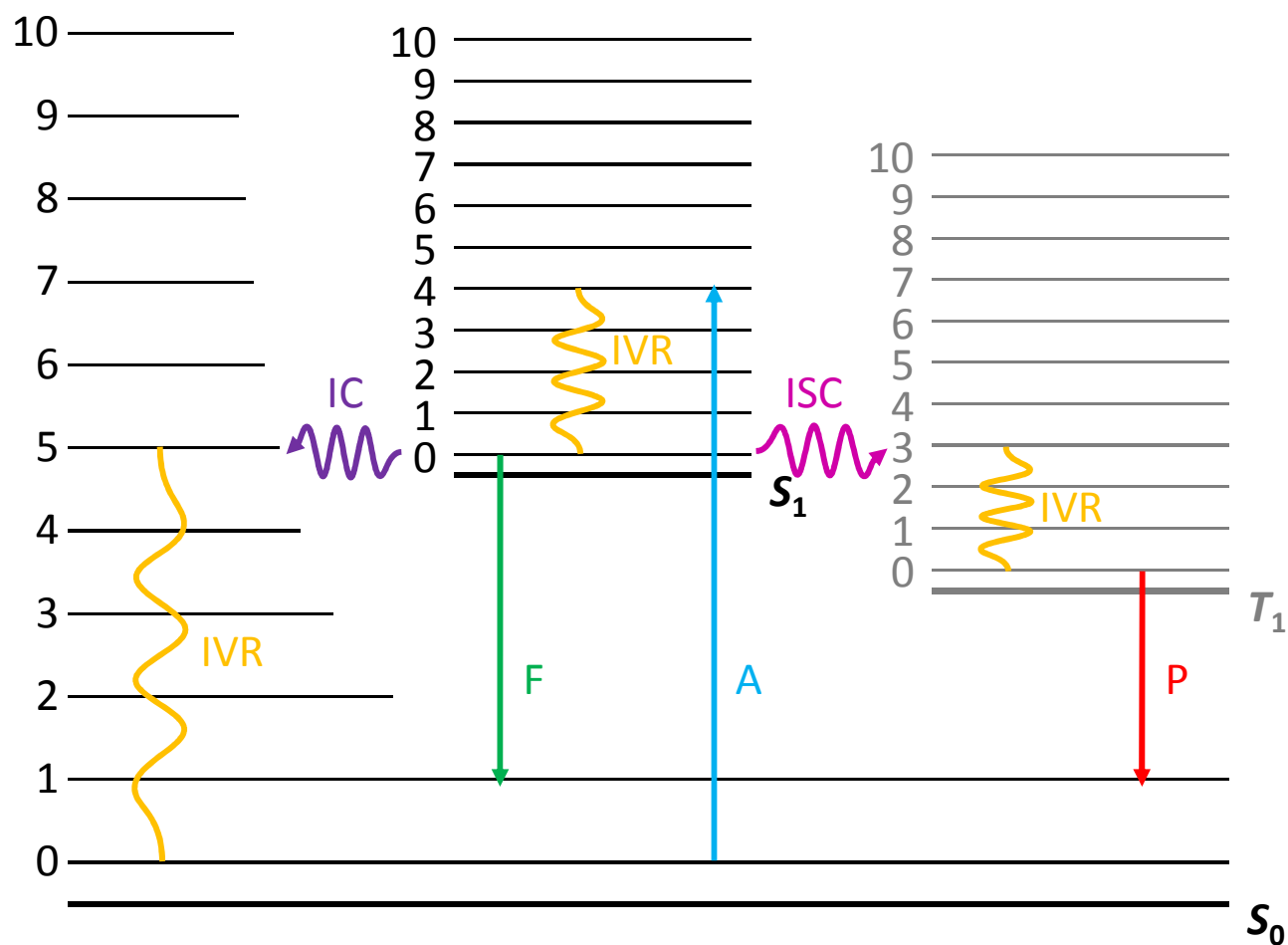*Example: ππ* benzene (vibrational progression in mode 1: totally symmetric breathing)*
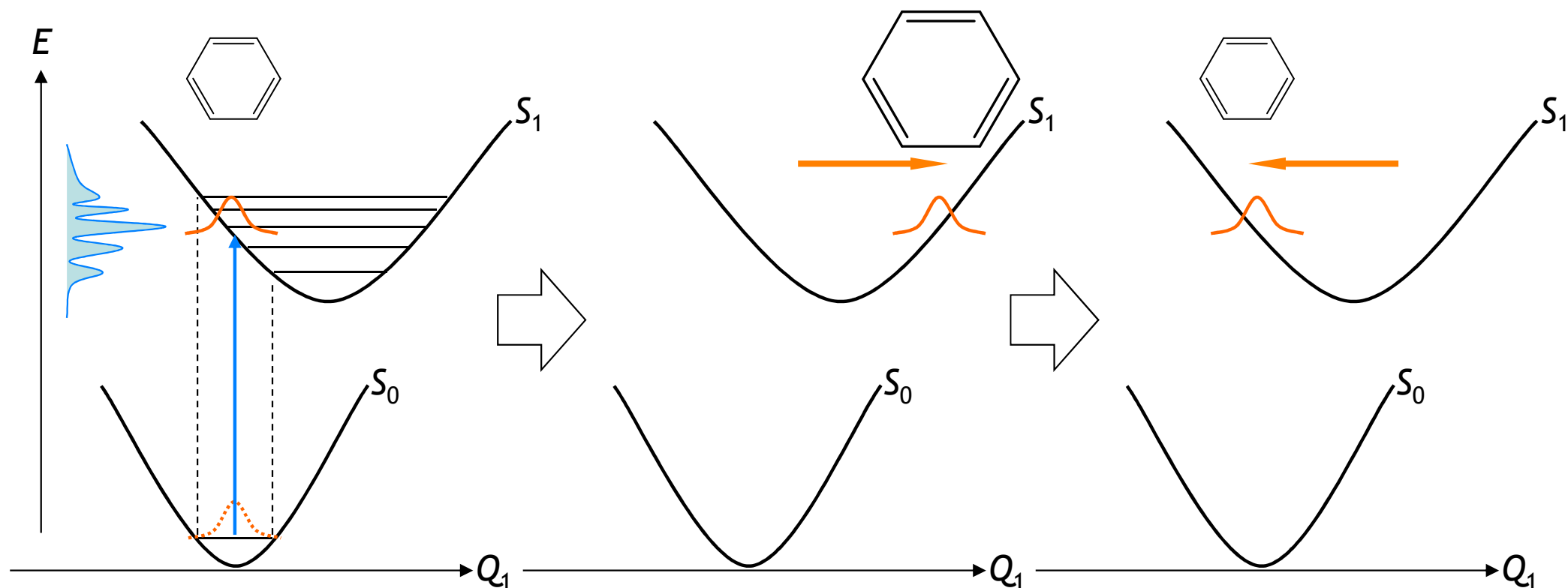
Photochemistry

- Intramolecular vibrational redistribution
- Internal conversion
- Photostability *vs.* photoreactivity

254 nm

$S_0 \ (^1A_{1g}) \rightarrow S_1 \ (^1B_{2u})$

benzene

$\left[\text{prefulvenoid} \right]$
prefulvenoid
geometries

benzvalene

E

S_1

S_0

Reaction coordinate

Spectroscopic picture (photophysics): Jablonski diagram

Radiative: **A**bsorption, **F**luorescence, **P**hosphorescence

Radiationless: **I**ntramolecular **V**ibrational **R**edistribution, **I**nternal **C**onversion, **I**nter**S**ystem **C**rossing

Molecular theoretical chemistry: role of the geometry

Structure (thermodynamics, spectroscopy) and reactivity (mechanism, kinetics)

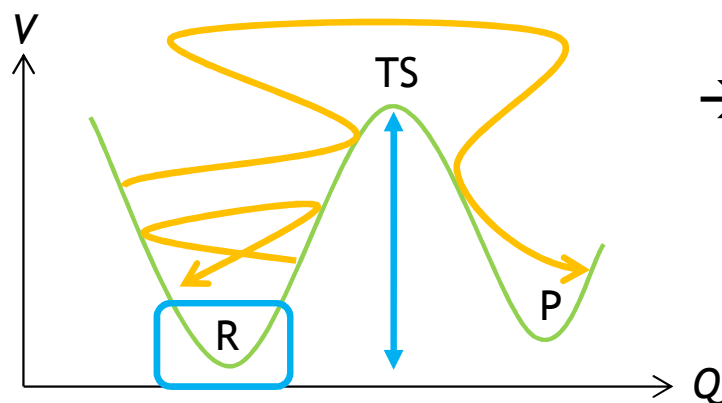**Quantum chemistry** ⟷ Potential energy surface ⟷ **Molecular dynamics**
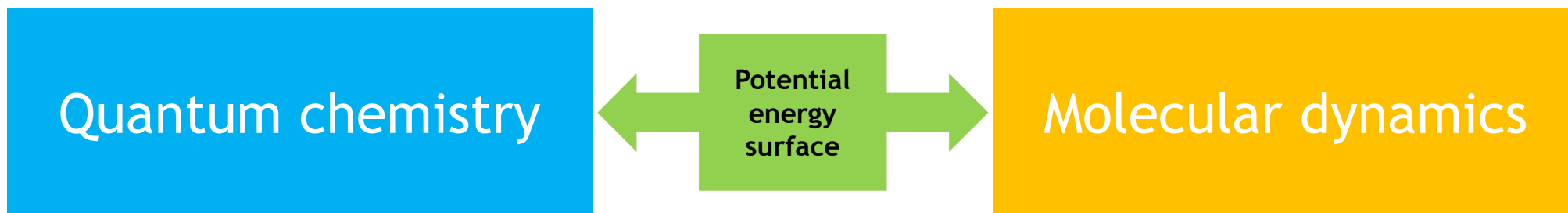
Electronic energy
(at various positions of the nuclei)

→ Static approach
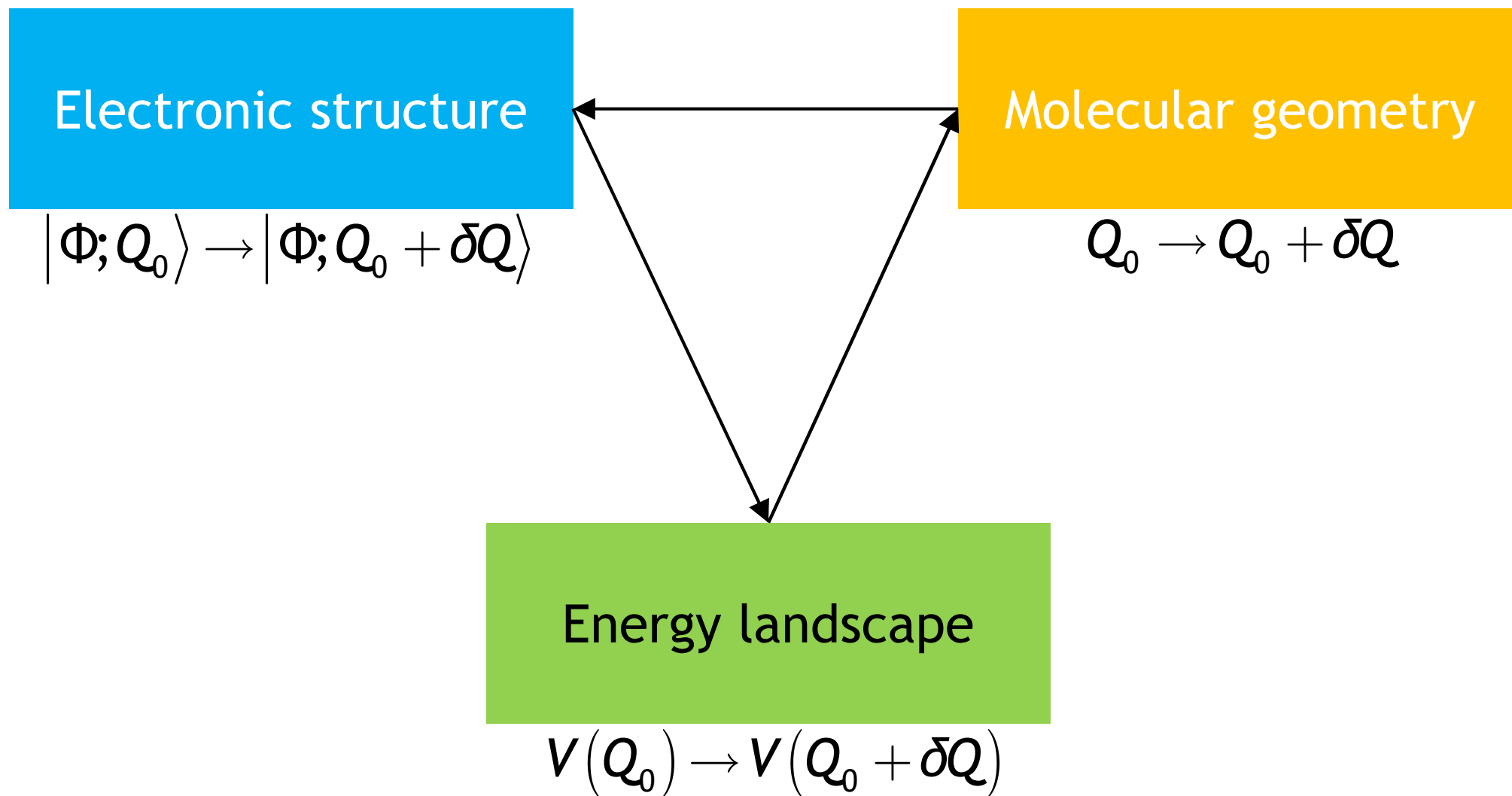
Nuclear motion
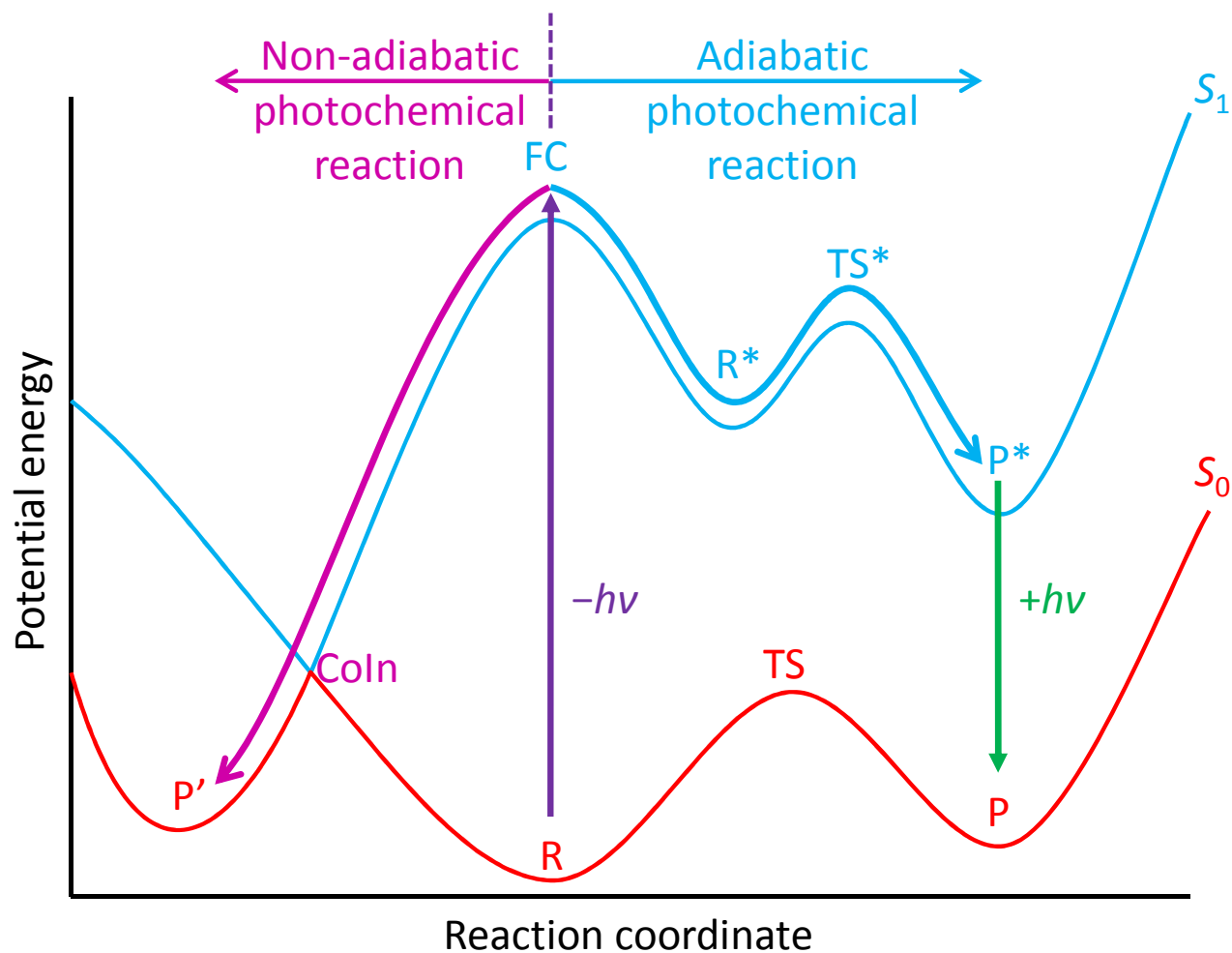(in the mean field of the electrons)

→ Dynamical approach

Reciprocal influence between
the electronic structure and the molecular geometry

Interplay between topography and motion

Electronic structure

$$\left|\Phi;Q_0\right\rangle \rightarrow \left|\Phi;Q_0+\delta Q\right\rangle$$

Molecular geometry

$$Q_0 \rightarrow Q_0 + \delta Q$$

Energy landscape

$$V(Q_0) \rightarrow V(Q_0 + \delta Q)$$

# Mechanistic picture (photochemistry): reaction path

Adiabatic reaction: radiative deactivation after excited-state product is formed

Non-adiabatic reaction: radiationless decay to ground-state product through conical intersection (CoIn)

Photochemistry *vs.* thermal chemistry

- The system does not start from around an equilibrium geometry
- The slope on S_1 creates an initial driving force (skiing rather than hiking)
- The system will develop momentum as it escapes the Franck-Condon region
- The trajectory can easily deviate from the minimum energy path (bottom of the valley connecting R to P through TS)

   → molecular dynamics simulations
- State crossings are likely to happen

   → non-adiabatic (vibronic) effects

   → quantum dynamics
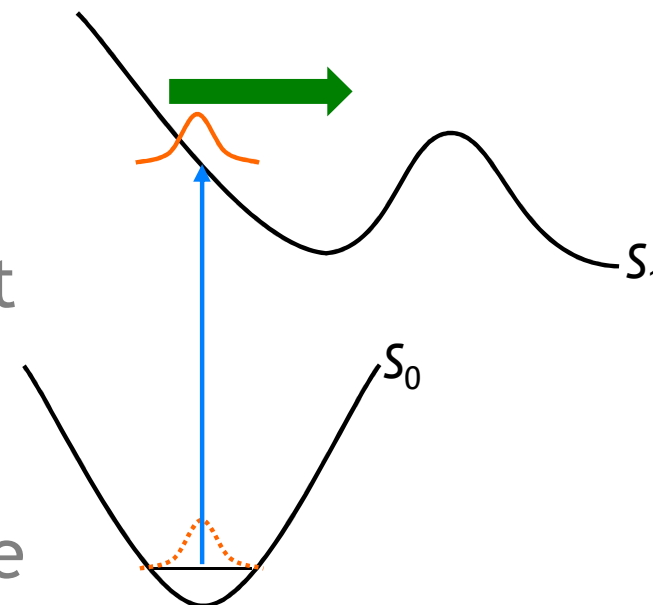
2. Beyond the Born-Oppenheimer Approximation

Reactant

Product
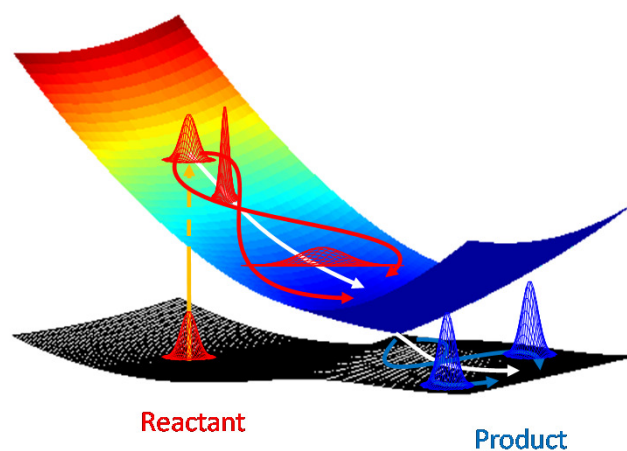
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a. Adiabatic Electronic States

b. Adiabatic Partition of the Molecular Schrödinger Equation

c. Non-Adiabatic Couplings

d. Conical Intersections

e. Diabatic Electronic States

Formalism: prerequisites

$$\left(uv\right)'' = u\left(v\right)'' + 2\left(u\right)'\left(v\right)' + \left(u\right)'' v$$

$$\begin{bmatrix} a & c \\ c & b \end{bmatrix} \xrightarrow{\text{eigenvalues}} e_{\pm} = \frac{a+b}{2} \pm \sqrt{\left(\frac{a-b}{2}\right)^2 + c^2}$$

$$e_+ - e_- = 0 \Leftrightarrow \sqrt{\left(\frac{a-b}{2}\right)^2 + c^2} = 0 \Leftrightarrow \begin{cases} a-b = 0 \\ c = 0 \end{cases}$$

Common ground: the molecular Hamiltonian

- Non-relativistic
- Electrostatic
- Electronic (r) and nuclear (R) coordinates

→ Direct solution extremely expensive and rarely useful

$$\hat{H}_{\text{mol}} = -\sum_{J=1}^{N} \frac{\hbar^2}{2M_J} \Delta_{\vec{R}_J}$$

$$-\sum_{j=1}^{n} \frac{\hbar^2}{2m_e} \Delta_{\vec{r}_j}$$

$$+\sum_{J=1}^{N-1} \sum_{K>J}^{N} \frac{Z_J Z_K e^2}{4\pi\varepsilon_0} \frac{1}{\left\| \vec{R}_J - \vec{R}_K \right\|}$$

$$+\sum_{j=1}^{n-1} \sum_{k>j}^{n} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\left\| \vec{r}_j - \vec{r}_k \right\|}$$

$$-\sum_{J=1}^{N} \sum_{j=1}^{n} \frac{Z_J e^2}{4\pi\varepsilon_0} \frac{1}{\left\| \vec{R}_J - \vec{r}_j \right\|}$$

The adiabatic partition: electronic/nuclear separation

- Nuclei at least 1800 heavier than electrons
- Time scale separation

  Electronic ~ 0.1 fs

  Vibrational ~ 10 fs

- Energy scale separation

  Electronic ~ 50 000 cm^{-1}

  Vibrational ~ 500 cm^{-1}

→ Problem solved in two sequential steps

1) Electronic, relaxed at each geometry (quantum chemistry)

2) Nuclear, in the electronic mean field (molecular dynamics)

Starting point: Born-Oppenheimer (BO) approximation

$$\hat{H}_{\mathrm{mol}}\left(\partial_q, q, \partial_Q, Q\right) = \hat{T}_{\mathrm{nuc}}\left(\partial_Q\right) + \hat{H}_{\mathrm{el}}\left(\partial_q, q; Q\right)$$

$$\forall Q, \quad \hat{H}_{\mathrm{el}}\left(\partial_q, q; Q\right)\Phi(q; Q) = E_{\mathrm{el}}(Q)\Phi(q; Q)$$

Starting point: Born-Oppenheimer (BO) approximation

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$$\boxed{\forall Q, \ E_{\text{el}}(Q) \equiv V(Q)}$$

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$$\boxed{\forall Q, \quad E_{\text{el}}(Q) \equiv V(Q)}$$

$$\left[-\frac{\hbar^2}{2m}\partial_Q^2 + V(Q)\right]\varphi_v(Q) = E_{\text{mol},v}\,\varphi_v(Q)$$

$$\underbrace{\phantom{-\frac{\hbar^2}{2m}\partial_Q^2 + V(Q)}}_{\text{BO}}$$
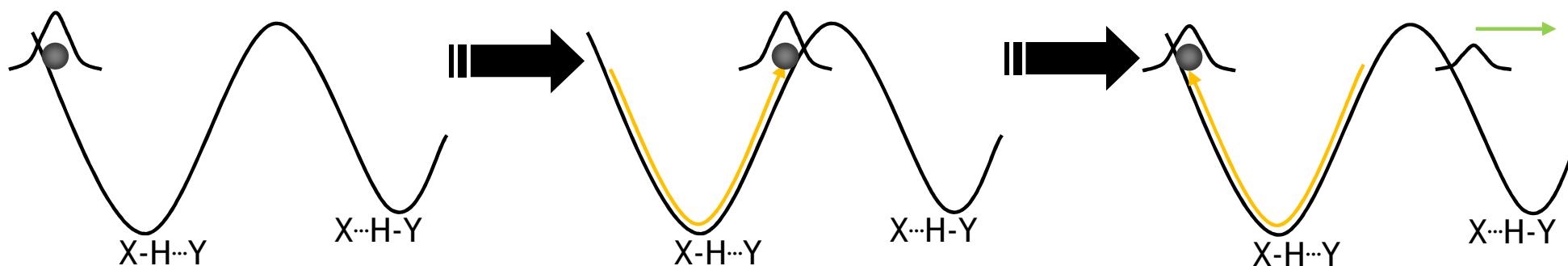
Quantum or classical dynamics: equations of motion

nuclear wavepacket

$$\left[-\frac{\hbar^2}{2m}\partial_Q^2 + \underbrace{V(Q)}_{\text{potential energy surface}} \right]\psi(Q,t) = i\hbar\partial_t\psi(Q,t)$$
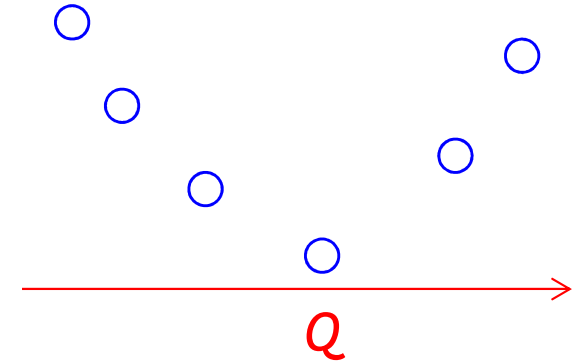
nuclear trajectory

$$m\partial_t^2 Q(t) = -\underbrace{\left[\partial_Q V(Q)\right]_{Q(t)}}_{\text{local force}}$$
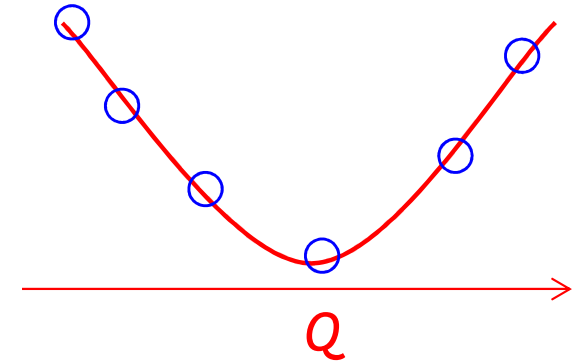
H transfer with tunnelling: non-classical behaviour

Potential energy surface: explicit function of Q

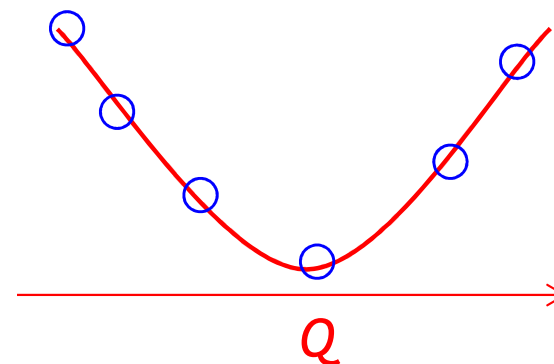$$\boxed{\forall Q,\ E_{el}(Q)} \rightarrow \text{sampling}$$

Potential energy surface: explicit function of Q

$$\boxed{\forall Q,\ E_{el}(Q) \equiv V(Q)} \longrightarrow \text{sampling and fitting}$$

Potential energy surface: explicit function of Q

$$\boxed{\forall Q,\ E_{el}(Q) \equiv V(Q)} \rightarrow \text{sampling and fitting}$$
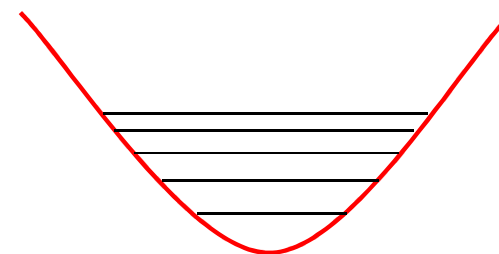

Example: linear harmonic oscillator

$$V(Q) = V_0 + \frac{1}{2}k_0(Q - Q_0)^2$$

Parameters: $Q_0,\ V_0 = V(Q_0),\ k_0 = \left[\partial_Q^2 V(Q)\right]_{Q_0}$

$$\boxed{\underbrace{\left[-\frac{\hbar^2}{2m}\partial_Q^2 + V(Q)\right]}_{\text{BO}}\varphi_v(Q) = E_{\text{mol},v}\varphi_v(Q)}$$

Potential energy surface: many-(many!)-body expansion

$$V\left(Q_1, \cdots, Q_{3N-6}\right) = V_0^{(0)}$$

$$+ \sum_{j=1}^{3N-6} V_j^{(0)} \left(Q_j - Q_j^{(0)}\right)$$

$$+ \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} V_{jk}^{(0)} \left(Q_j - Q_j^{(0)}\right)\left(Q_k - Q_k^{(0)}\right) +$$

$$+ \frac{1}{6} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} \sum_{l=1}^{3N-6} V_{jkl}^{(0)} \left(Q_j - Q_j^{(0)}\right)\left(Q_k - Q_k^{(0)}\right)\left(Q_l - Q_l^{(0)}\right) + \cdots$$

- Unknown form (not $1/r_{12}$) → sampling and fitting
- More than two-body terms: multidimensional integrals $<\phi|V|\phi>$, not limited to $(\mu\nu||\lambda\eta)$
- The very bottleneck in quantum dynamics!

Photochemistry often involves radiationless decay

- Example: first step of the vision process:

  retinal photoisomerisation → no fluorescence!
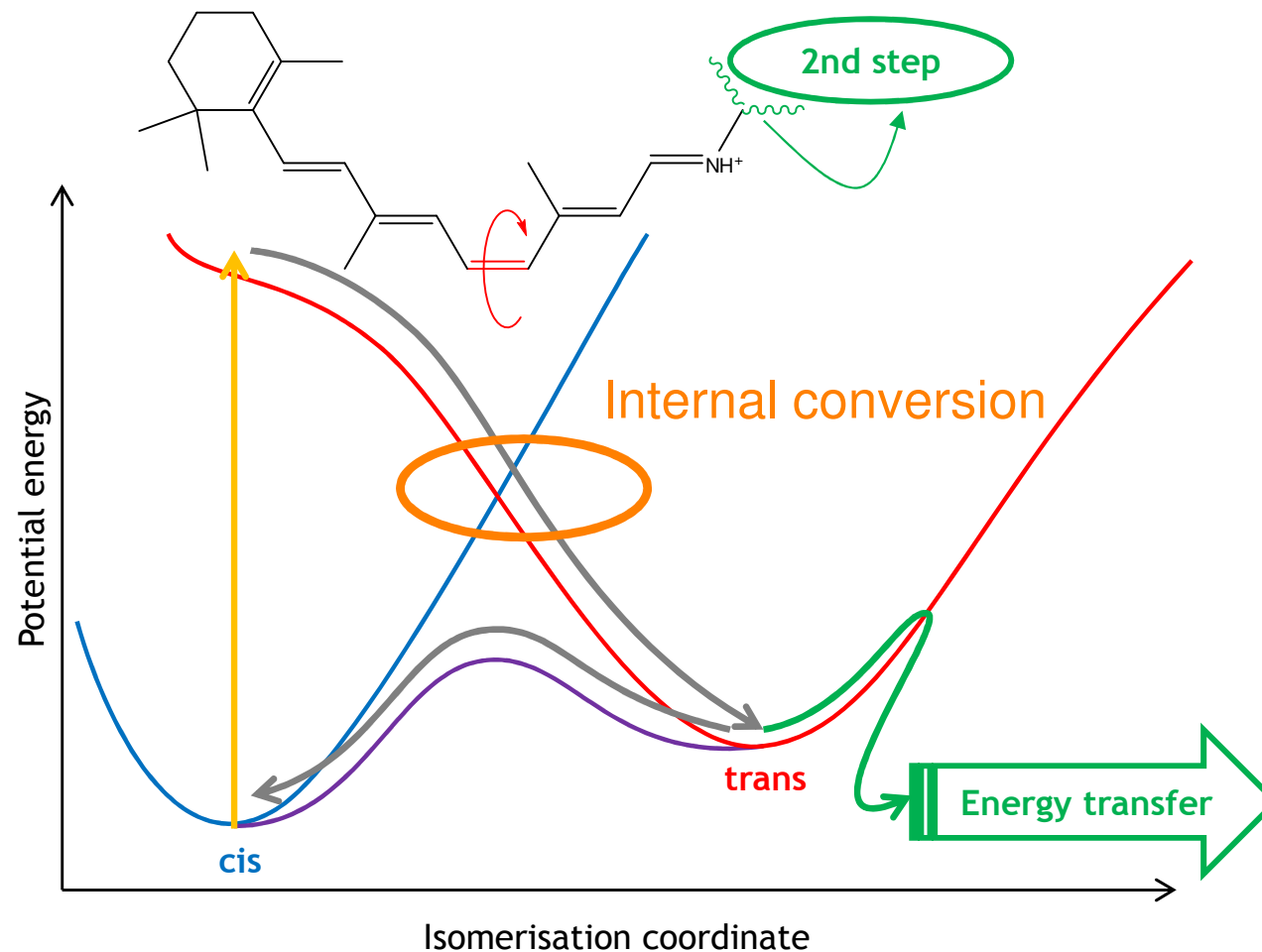
Why and where does it happen?

- When the Born-Oppenheimer approximation is no longer valid

- Vibronic coupling between the electronic states and the nuclear motion: non-adiabatic coupling

- Strong effect when the electronic energy separation is small (~ vibrational, so similar time scales)

- Explanation of internal conversion (if same spin)

- *NB*: intersystem crossing (if different spins) due to spin-orbit coupling (relativistic origin)

Beyond Born-Oppenheimer

$$\Psi_{mol}(q,Q,t) = \underbrace{\psi_s(Q,t)}_{nuc}\underbrace{\Phi_s(q;Q)}_{el} \Rightarrow \text{BO approximation}$$

$$\text{Beyond BO} \Rightarrow \Psi_{mol}(q,Q,t) = \sum_s \underbrace{\psi_s(Q,t)}_{nuc}\underbrace{\Phi_s(q;Q)}_{el}$$

$$\left(\text{or } \Psi_{mol}\left(q,Q,\boxed{t}\right) = \underbrace{\tilde{\psi}\left(Q,\boxed{t}\right)}_{nuc}\underbrace{\tilde{\Phi}\left(q;Q,\boxed{t}\right)}_{el} \quad \text{``Exact factorisation''} \right)$$

$\hat{H}_{el}(\partial_q, q; Q)$: no longer replaced by a single of its eigenvalues, $V_s(Q)$

$\rightarrow$ matrix (ss' indices) of "potential energies" wrt. Q

$\hat{T}_{nuc}(Q,\partial_Q) \sim -\dfrac{\hbar^2}{2m}\partial_Q^2$: acts on both $\psi_s(Q,t)$ and $\Phi_s(q;Q)$

$\rightarrow$ non-adiabatic-coupling matrix (ss' indices) wrt. Q

Refresher: Riemannian vector derivative

$\{\vec{u}_s(x)\}$ parametric orthonormal basis set (~rotating frame):

$$\vec{v}(x) = \sum_s v_s(x)\vec{u}_s(x), \quad v_s(x) = \vec{u}_s(x) \cdot \vec{v}(x)$$

$$(uv)' = (u)'v + u(v)'$$

$$(uv)'' = (u)''v + 2(u)'(v)' + u(v)''$$

$$\vec{v}''(x) = \sum_s \left(v_s''(x)\vec{u}_s(x) + \boxed{2v_s'(x)\vec{u}_s'(x) + v_s(x)\vec{u}_s''(x)}\right),$$

$$\vec{u}_s(x) \cdot \vec{v}''(x) = v_s''(x) + \boxed{2\sum_p v_p'(x)\left(\vec{u}_s(x) \cdot \vec{u}_p'(x)\right) + \sum_p v_p(x)\left(\vec{u}_s(x) \cdot \vec{u}_p''(x)\right)}$$

Non-adiabatic coupling (general principle)

$\left\{ \left| \Phi_s ; x \right\rangle \right\}$ parametric orthonormal basis set (~rotating frame):

$$\left| \Psi ; x \right\rangle = \sum_s \psi_s(x) \left| \Phi_s ; x \right\rangle, \quad \psi_s(x) = \left\langle \Phi_s ; x \middle| \Psi ; x \right\rangle$$

$$\left| \Psi'' ; x \right\rangle = \sum_s \left(\psi_s''(x) \left| \Phi_s ; x \right\rangle + \boxed{2\psi_s'(x) \left| \Phi_s' ; x \right\rangle + \psi_s(x) \left| \Phi_s'' ; x \right\rangle} \right),$$

$$\left\langle \Phi_s ; x \middle| \Psi'' ; x \right\rangle = \psi_s''(x) + \boxed{2\sum_p \psi_s'(x) \left\langle \Phi_s ; x \middle| \Phi_p' ; x \right\rangle + \sum_p \psi_s(x) \left\langle \Phi_s ; x \middle| \Phi_p'' ; x \right\rangle}$$

Representation of the wavefunctions

$$\Psi_{\text{mol}}(q,Q,t) = \sum_s \underbrace{\psi_s(Q,t)}_{\text{nuc}} \underbrace{\Phi_s(q;Q)}_{\text{el}}$$

$$\forall Q, \ \hat{H}_{\text{el}}(q;Q)\Phi_s(q;Q) = V_s(Q)\Phi_s(q;Q)$$

$$\hat{T}_{\text{nuc}}(\partial_Q) = -\frac{\hbar^2}{2m}\partial_Q^2$$

Representation explicit with respect to Q

but implicit with respect to q (could be $p = \hbar k$)

$$\Phi_s(q;Q) \rightarrow |\Phi_s;Q\rangle$$

$$\hat{H}_{\text{el}}(\partial_q, q; Q) \rightarrow \hat{H}_{\text{el}}(Q)$$

$$\left|\Psi_{\text{mol}}(Q,t)\right\rangle = \sum_s \underbrace{\psi_s(Q,t)}_{\text{nuc}} \underbrace{|\Phi_s;Q\rangle}_{\text{el}}$$

Vibronic non-adiabatic couplings

$$\hat{H}_{\text{mol}}\left(Q\right) = -\frac{\hbar^2}{2m}\boxed{\partial_Q^2} + \hat{H}_{\text{el}}\left(Q\right)$$

$$\hat{H}_{\text{mol}}\left(Q\right)\left|\Psi_{\text{mol}}\left(Q,t\right)\right\rangle = i\hbar\partial_t\left|\Psi_{\text{mol}}\left(Q,t\right)\right\rangle$$

$$\left|\Psi_{\text{mol}}\left(Q,t\right)\right\rangle = \sum_s \psi_s\left(Q,t\right)\left|\Phi_s;Q\right\rangle$$

$$\left\langle\Phi_s;Q\right|\cdots\right\rangle = \int_{\{q\}}\Phi_s^*\left(q;Q\right)\cdots dq$$

$$\underbrace{\left[-\frac{\hbar^2}{2m}\boxed{\partial_Q^2} + V_s\left(Q\right)\right]}_{\hat{\mathcal{H}}_s^{\text{BO}}(Q)}\psi_s\left(Q,t\right) + \sum_p \hat{\Lambda}_{sp}\left(Q\right)\psi_p\left(Q,t\right) = i\hbar\partial_t\psi_s\left(Q,t\right)$$

$$\hat{\Lambda}_{sp}\left(Q\right) = -\frac{\hbar^2}{m}\left\langle\Phi_s;Q\left|\boxed{\partial_Q}\Phi_p;Q\right\rangle\boxed{\partial_Q} - \frac{\hbar^2}{2m}\left\langle\Phi_s;Q\left|\boxed{\partial_Q^2}\Phi_p;Q\right\rangle\right.$$

Non-adiabatic photochemistry: a non-classical field

Radiationless decay mechanisms → the nuclei behave as quantum-mechanically as the electrons (~ΔE, ~Δt)

$$i\hbar\partial_t \begin{bmatrix} \psi_0(Q,t) \\ \psi_1(Q,t) \end{bmatrix} = \begin{bmatrix} \hat{\mathcal{H}}_0^{BO} & 0 \\ 0 & \hat{\mathcal{H}}_1^{BO} \end{bmatrix} \begin{bmatrix} \psi_0(Q,t) \\ \psi_1(Q,t) \end{bmatrix} + \begin{bmatrix} \hat{\Lambda}_{00} & \hat{\Lambda}_{01} \\ \hat{\Lambda}_{10} & \hat{\Lambda}_{11} \end{bmatrix} \begin{bmatrix} \psi_0(Q,t) \\ \psi_1(Q,t) \end{bmatrix}$$

- Nuclear wavepacket (Q,t) with two (or more) components
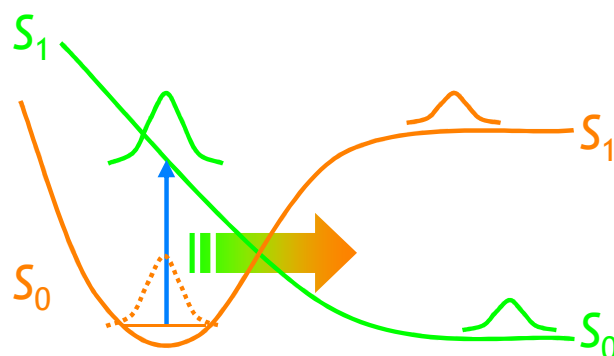
$$P^{(s)}(t) = \int\limits_{\{Q\}} \left| \psi_s(Q,t) \right|^2 dQ$$

- Vibronic non-adiabatic coupling (non-Born-Oppenheimer) → electronic population transfer

Matrix Hellmann-Feynman theorem (general principle)

$$\hat{H}\left|\Phi_b\right\rangle = E_b\left|\Phi_b\right\rangle$$

$$\hat{H} = \hat{H}^\dagger$$

$$\left\langle\Phi_a\right|\hat{H} = E_a\left\langle\Phi_a\right|$$

$$\left\langle\Phi_a\middle|\Phi_b\right\rangle = \delta_{ab}$$

derivative with respect to an **external parameter**:

$$\left\langle\Phi_a\middle|\Phi_b\right\rangle' = \left\langle\Phi_a'\middle|\Phi_b\right\rangle + \left\langle\Phi_a\middle|\Phi_b'\right\rangle = 0$$

Matrix Hellmann-Feynman theorem (general principle)

$$\left\langle \Phi_a \left| \hat{H} \right| \Phi_b \right\rangle = \delta_{ab} E_a$$

$$\left\langle \Phi_a \left| \hat{H} \right| \Phi_b \right\rangle' =$$

$$\left\langle \Phi_a' \left| \hat{H} \right| \Phi_b \right\rangle + \left\langle \Phi_a \left| \hat{H} \right| \Phi_b' \right\rangle + \left\langle \Phi_a \left| \hat{H}' \right| \Phi_b \right\rangle =$$

$$E_b \left\langle \Phi_a' \middle| \Phi_b \right\rangle + E_a \left\langle \Phi_a \middle| \Phi_b' \right\rangle + \left\langle \Phi_a \left| \hat{H}' \right| \Phi_b \right\rangle =$$

$$\left(E_a - E_b \right) \left\langle \Phi_a \middle| \Phi_b' \right\rangle + \left\langle \Phi_a \left| \hat{H}' \right| \Phi_b \right\rangle = \delta_{ab} E_a'$$

Matrix Hellmann-Feynman theorem (general principle)

$$a = b : \quad E'_a = \left\langle \Phi_a \left| \hat{H}' \right| \Phi_a \right\rangle$$

$$a \neq b : \quad \left\langle \Phi_a \middle| \Phi'_b \right\rangle = \frac{\left\langle \Phi_a \left| \hat{H}' \right| \Phi_b \right\rangle}{E_b - E_a}$$

Link with 1ˢᵗ-order perturbation and response theories

$$\hat{H} = \hat{H}^0 + \hat{H}' \textcolor{red}{\delta x}$$

$$\hat{H}^0 \left| \Phi_s^0 \right\rangle = V_s^0 \left| \Phi_s^0 \right\rangle$$

$$\hat{H} \left| \Phi_s \right\rangle = V_s \left| \Phi_s \right\rangle$$

$$V_s = V_s^0 + \underbrace{V_s' \textcolor{red}{\delta x}}_{\textcolor{red}{\text{energy correction}}} + \dots$$

$$\left| \Phi_s \right\rangle = \left| \Phi_s^0 \right\rangle + \underbrace{\sum_p \left| \Phi_p^0 \right\rangle \left\langle \Phi_p^0 \middle| \Phi_s' \right\rangle \textcolor{red}{\delta x}}_{\textcolor{red}{\text{wavefunction response}}} + \dots$$

$$V_s' = \left\langle \Phi_s^0 \middle| \hat{H}' \middle| \Phi_s^0 \right\rangle$$

$$\left\langle \Phi_p^0 \middle| \Phi_s' \right\rangle = \frac{\left\langle \Phi_p^0 \middle| \hat{H}' \middle| \Phi_s^0 \right\rangle}{V_s^0 - V_p^0}$$

Matrix Hellmann-Feynman theorem here

$$\left(V_s\left(Q\right)-V_p\left(Q\right)\right)\left\langle\Phi_s;Q\left|\partial_Q\Phi_p;Q\right\rangle\right. + \left\langle\Phi_s;Q\left|\partial_Q\hat{H}_{el}\left(Q\right)\right|\Phi_p;Q\right\rangle = \delta_{sp}\partial_Q V_s\left(Q\right)$$

$$s=p: \quad \underbrace{\partial_Q V_s\left(Q\right)}_{\text{adiabatic gradient}} = \left\langle\Phi_s;Q\left|\partial_Q\hat{H}_{el}\left(Q\right)\right|\Phi_s;Q\right\rangle$$

$$s\neq p: \quad \underbrace{\left\langle\Phi_s;Q\left|\partial_Q\Phi_p;Q\right\rangle\right.}_{\text{1st-order non-adiabatic coupling}} = \frac{\left\langle\Phi_s;Q\left|\partial_Q\hat{H}_{el}\left(Q\right)\right|\Phi_p;Q\right\rangle}{V_p\left(Q\right)-V_s\left(Q\right)}$$

Analytic derivatives

$$\left\langle \Phi_s ; Q \middle| \partial_Q \hat{H}_{\text{el}}(Q) \middle| \Phi_p ; Q \right\rangle = \int_{\{q\}} \underbrace{\Phi_s^*(q;Q) \Phi_p(q;Q)}_{\rightarrow \text{transition density}} \partial_Q \underbrace{V_{\text{el-nuc}}(q;Q)}_{\rightarrow v_{\text{ext}}(q;Q)} dq$$

$$+ \delta_{sp} \partial_Q V_{\text{nuc-nuc}}(Q)$$

Two-state model

$$\begin{bmatrix} H_{00} & H_{01} \\ H_{01} & H_{11} \end{bmatrix} = \frac{H_{00} + H_{11}}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} -\dfrac{H_{11} - H_{00}}{2} & H_{01} \\ H_{01} & \dfrac{H_{11} - H_{00}}{2} \end{bmatrix}$$

$\downarrow$ eigenvalues

$$V_{0,1} = \frac{H_{00} + H_{11}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{00}}{2}\right)^2 + \left(H_{01}\right)^2}$$

Conical intersection

$$\frac{V_1 - V_0}{2} = \sqrt{\left(\frac{H_{11} - H_{00}}{2}\right)^2 + \left(H_{01}\right)^2}$$

$$\frac{V_1 - V_0}{2} = 0 \Leftrightarrow \begin{cases} H_{11} - H_{00} = 0 \\ H_{01} = 0 \end{cases}$$

Adiabatic surfaces
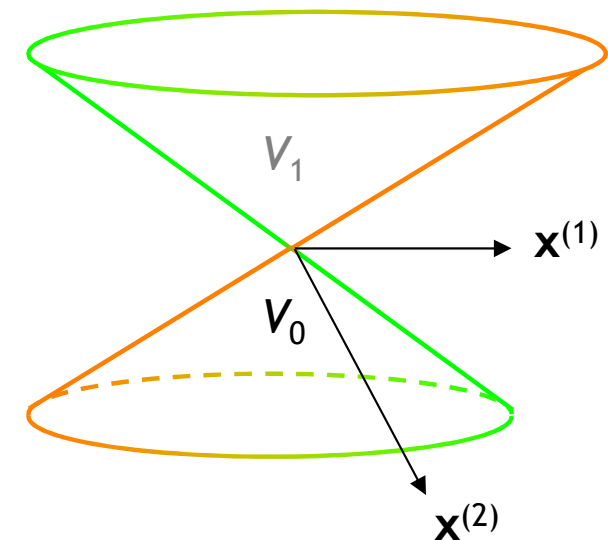
Degeneracy lifted at first order along 2D branching space

- $\mathbf{x}^{(1)}$ || gradient of $(H_{11} - H_{00})/2$
- $\mathbf{x}^{(2)}$ || gradient of H_{01}

Conical intersections: divergence and cusp

$$\left\langle \Phi_0; \mathbf{Q} \middle| \nabla_{\mathbf{Q}} \Phi_1; \mathbf{Q} \right\rangle = \frac{\left\langle \Phi_0; \mathbf{Q} \middle| \nabla_{\mathbf{Q}} \hat{H}_{\text{el}}(\mathbf{Q}) \middle| \Phi_1; \mathbf{Q} \right\rangle}{V_1(\mathbf{Q}) - V_0(\mathbf{Q})} \to \infty$$
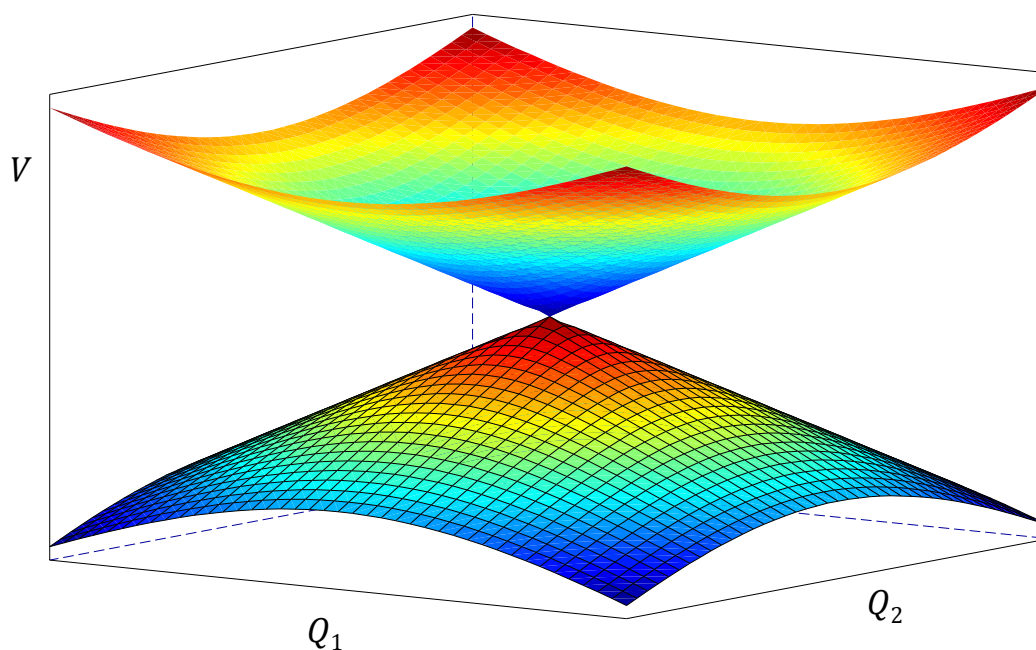
$$\frac{V_1(\mathbf{Q}_0 + \delta\mathbf{Q}) - V_0(\mathbf{Q}_0 + \delta\mathbf{Q})}{2} = 0 + \underbrace{\sqrt{\left(\mathbf{x}^{(1)} \cdot \delta\mathbf{Q}\right)^2 + \left(\mathbf{x}^{(2)} \cdot \delta\mathbf{Q}\right)^2}}_{\text{gradient: ill-defined (cusp)}} + \cdots$$

Non-adiabatic photochemistry around conical intersections

Reactant

Product
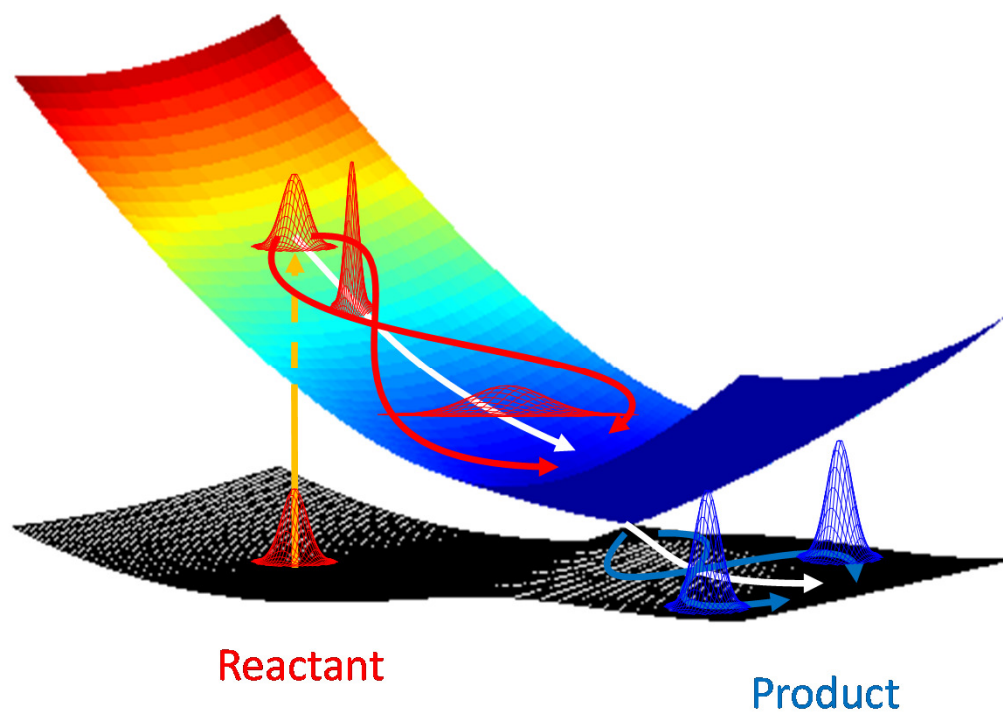
- Adiabatic representation (BO states)

- **Divergent** non-adiabatic coupling and **cusp** of the potential energy surfaces at the conical intersection

- **Problem for QD: integrals require regular functions of Q**

Molecular symmetry

- Diatom (one coordinate): crossing only if different symmetry (Wigner non-crossing rule)
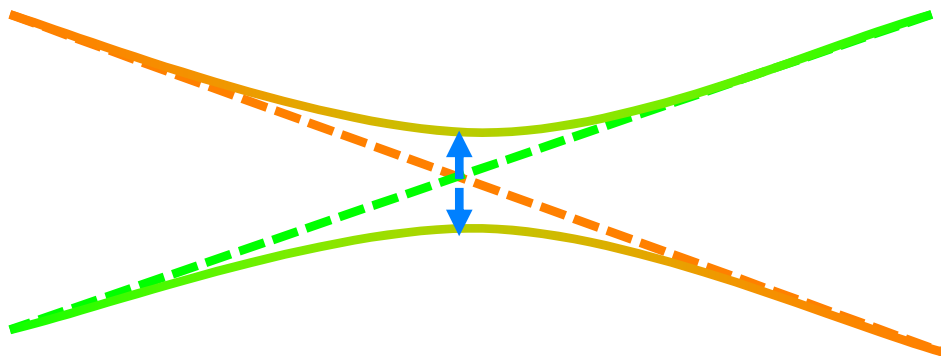
- Jahn-Teller:

two degenerate electronic states (E)

→ two equivalent vibrations (E)
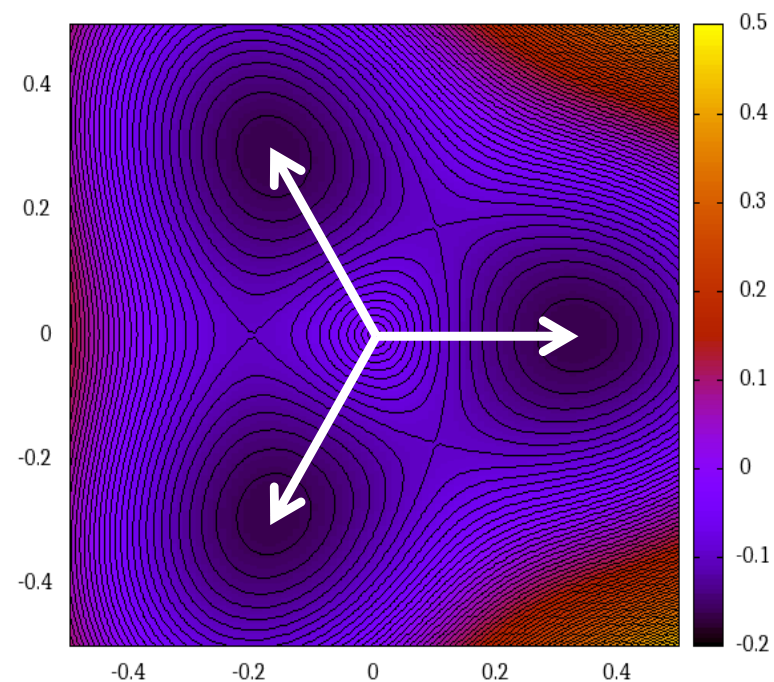
Molecular symmetry

- Symmetry-induced conical intersection: allowed crossing between states of different symmetries (Γ_A and Γ_B), coupling of $\Gamma_A \otimes \Gamma_B$ symmetry → non-zero when symmetry gets broken (states mix)

$$\begin{bmatrix} \langle A|\hat{H}_{el}|A\rangle & \langle A|\hat{H}_{el}|B\rangle \\ \langle B|\hat{H}_{el}|A\rangle & \langle B|\hat{H}_{el}|B\rangle \end{bmatrix}$$

- Accidental conical intersection: probable because large number of degrees of freedom (often related to high-symmetry Jahn-Teller prototype)

Getting rid of singularities: diabatisation

- Unitary transformation minimising the non-adiabatic coupling

$$\mathbf{U} = \begin{bmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{bmatrix}$$

$$\langle \Phi_0; Q | \partial_Q \Phi_1; Q \rangle \to \infty \xrightarrow{\hspace{4cm}} \langle \Phi_0'; Q | \partial_Q \Phi_1'; Q \rangle \approx 0$$

$$\mathbf{H} = \mathbf{U}\mathbf{V}\mathbf{U}^\dagger$$

- Electronic Hamiltonian matrix no longer diagonal

$$\begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix} = \frac{V_0 + V_1}{2}\mathbf{1} + \frac{V_1 - V_0}{2}\begin{bmatrix} -\cos 2\varphi & -\sin 2\varphi \\ -\sin 2\varphi & \cos 2\varphi \end{bmatrix}$$

Two states: explicit relationships

- Rotation angle

$$\tan 2\varphi(Q) = -\frac{2H_{01}(Q)}{H_{11}(Q) - H_{00}(Q)}$$

- Condition to make the diabatic derivative coupling zero

$$\langle \Phi_0; Q | \partial_Q \Phi_1; Q \rangle = \underbrace{\langle \Phi_0'; Q | \partial_Q \Phi_1'; Q \rangle}_{\approx 0} - \partial_Q \varphi(Q)$$

$$\Rightarrow \partial_Q \varphi(Q) \approx -\langle \Phi_0; Q | \partial_Q \Phi_1; Q \rangle$$

- Never fully achieved in practice: various types of quasi-diabatic states, all based on a smoothness condition of the wavefunction or the energy, the dipole moment, etc.

Why quasi-diabatic states?

- Infinite basis set required

  (unless isolated Hilbert subspace)

$$\partial_Q \left\langle \Phi_0; Q \middle| \partial_Q \Phi_1; Q \right\rangle$$

$$= \left\langle \Phi_0; Q \middle| \partial_Q^2 \Phi_1; Q \right\rangle + \left\langle \partial_Q \Phi_0; Q \middle| \partial_Q \Phi_1; Q \right\rangle$$

$$= \left\langle \Phi_0; Q \middle| \partial_Q^2 \Phi_1; Q \right\rangle + \sum_{s=0}^{\infty} \left\langle \partial_Q \Phi_0; Q \middle| \Phi_s; Q \right\rangle \left\langle \Phi_s; Q \middle| \partial_Q \Phi_1; Q \right\rangle$$

$$= \left\langle \Phi_0; Q \middle| \partial_Q^2 \Phi_1; Q \right\rangle - \sum_{s=0}^{\infty} \left\langle \Phi_0; Q \middle| \partial_Q \Phi_s; Q \right\rangle \left\langle \Phi_s; Q \middle| \partial_Q \Phi_1; Q \right\rangle$$

Diabatisation *a priori* or *a posteriori*

diab

Working space
(*N* configurations)

Target subspace
(*n* adiabatic states)

Model subspace
(*n* diabatic states)
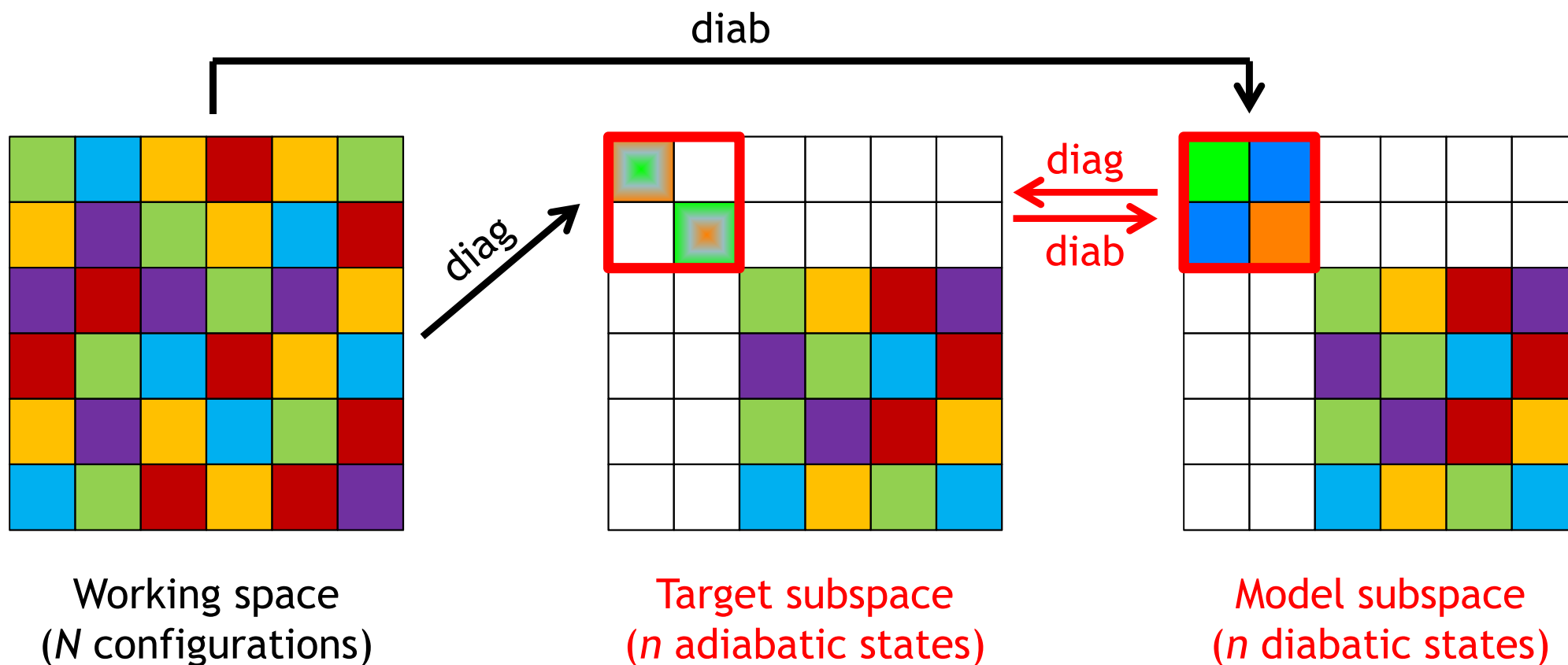
- Configuration contraction wrt. static correlation yielding well-behaved model states equivalent to the target states (*n* out of *N*)

→ effective Hamiltonian

Diabatisation by ansatz: smooth Hamiltonian matrix
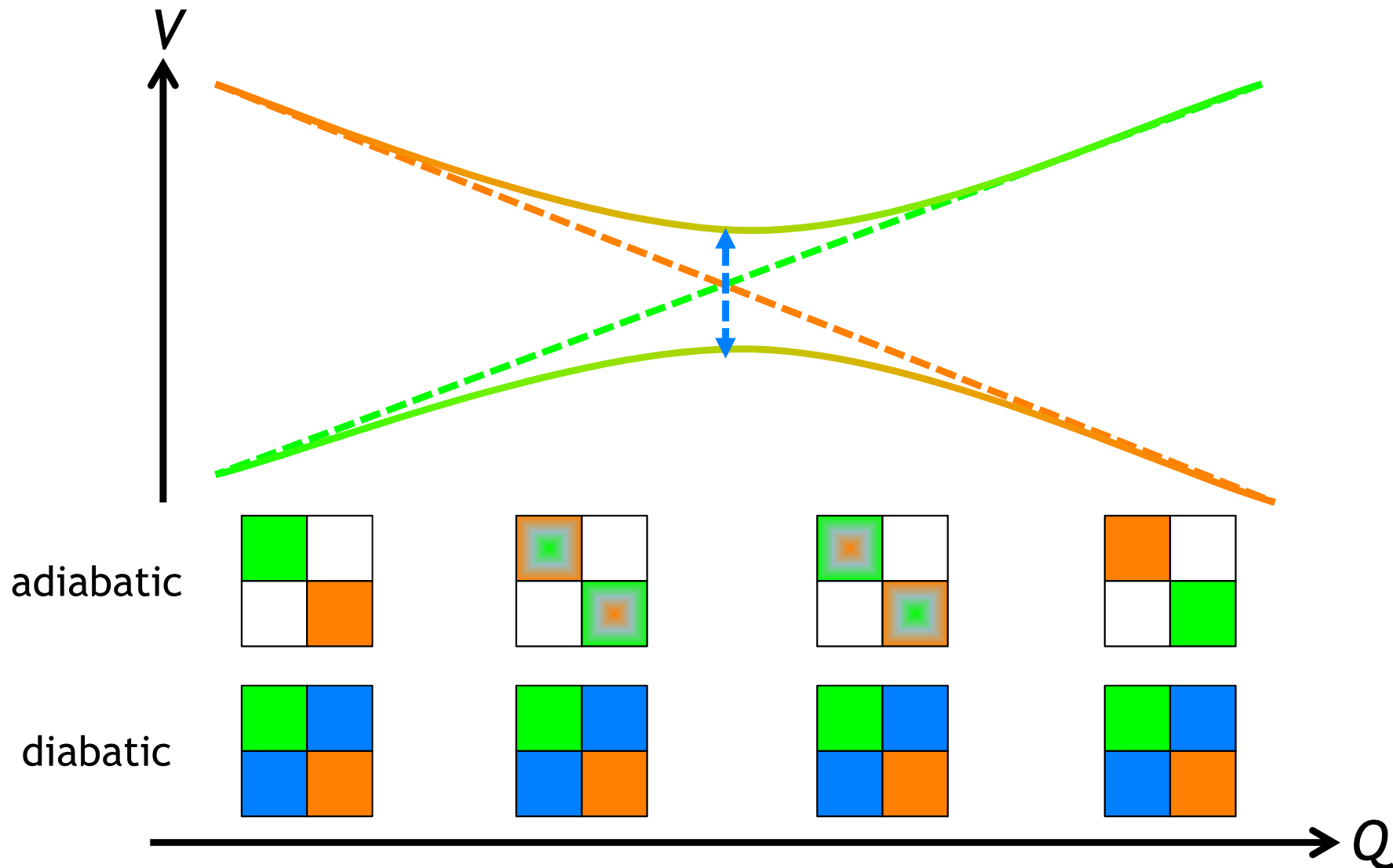
- Electronic structure preserved wrt. geometry variation

Consequence: smoother PES with no cusp

Diabatic
surfaces

Diabatic
potential coupling $\longleftrightarrow$

Adiabatic
surfaces
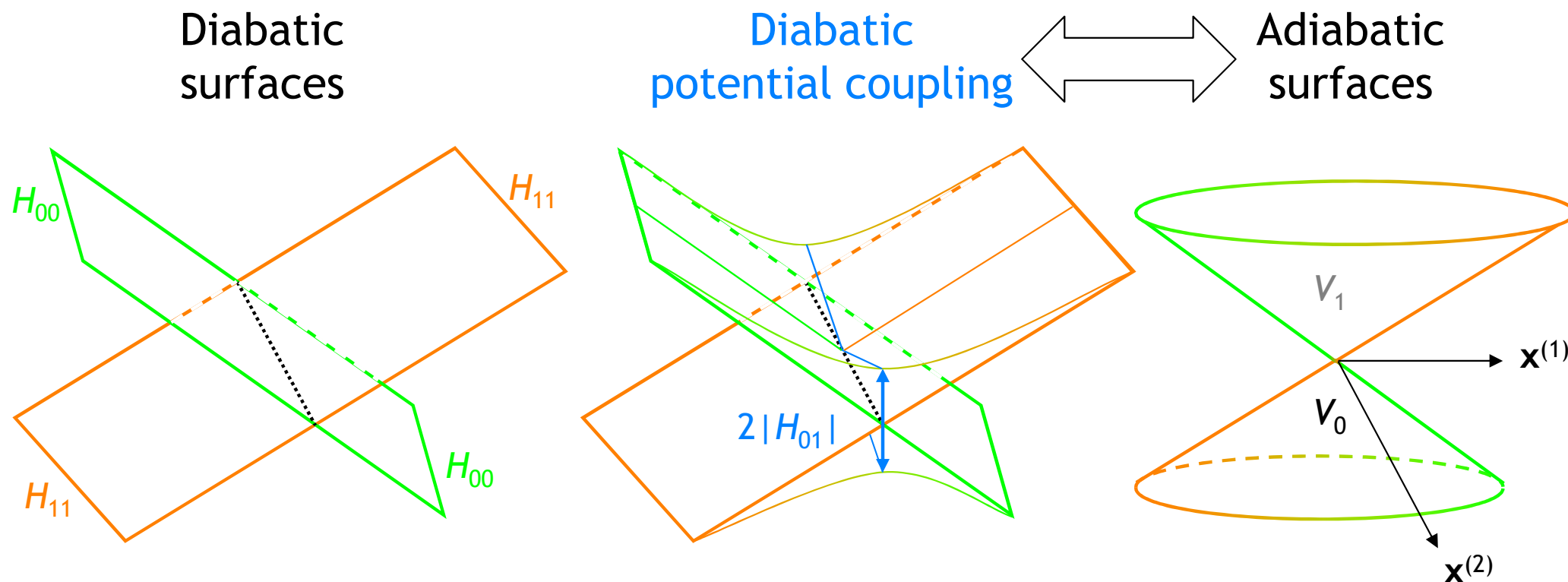
$$\frac{V_1 - V_0}{2} = \sqrt{\left(\frac{H_{11} - H_{00}}{2}\right)^2 + \left(H_{01}\right)^2}$$

Degeneracy lifted at first order
along 2D branching space

- $\mathbf{x}^{(1)}$ || gradient of $H_{11} - H_{00}$
- $\mathbf{x}^{(2)}$ || gradient of H_{01}

Intuitive chemical interpretation

- Walsh correlation diagrams
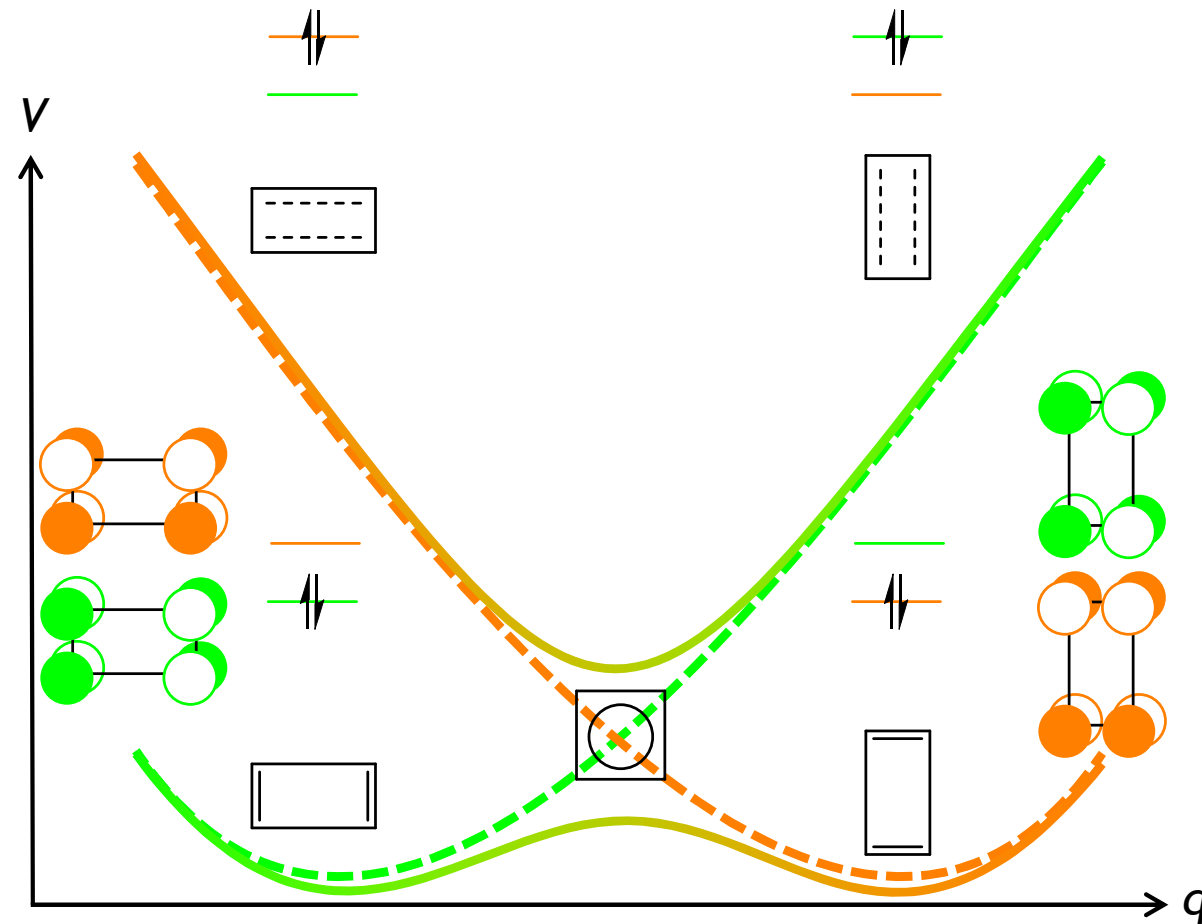
Photochemistry: ES and GS multiple wells and crossings

$(\pi\pi^*)$

$(\pi\sigma^*)$

$(n\pi^*)$

$(ref)_{mr}$

$(ref)_{bp}$
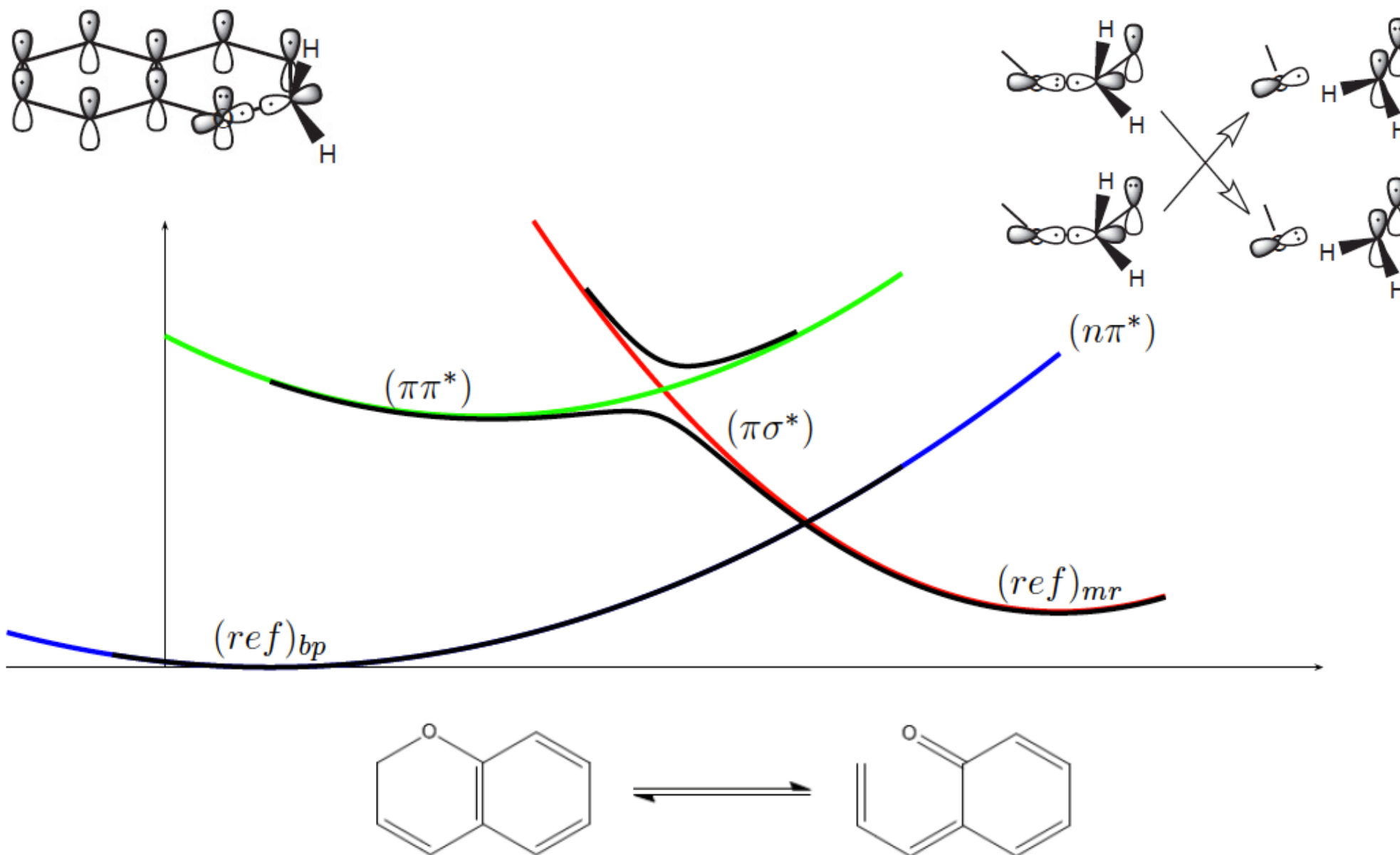
Thermal chemistry: GS local coupled states

- Marcus theory of electron transfer reactions
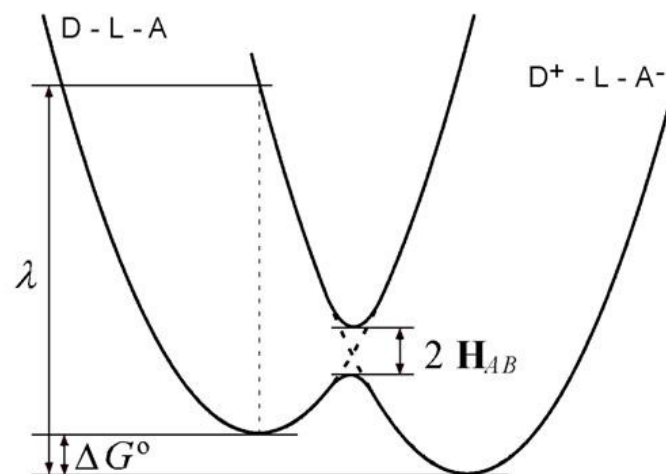
- Valence bond: transition barriers as avoided crossings
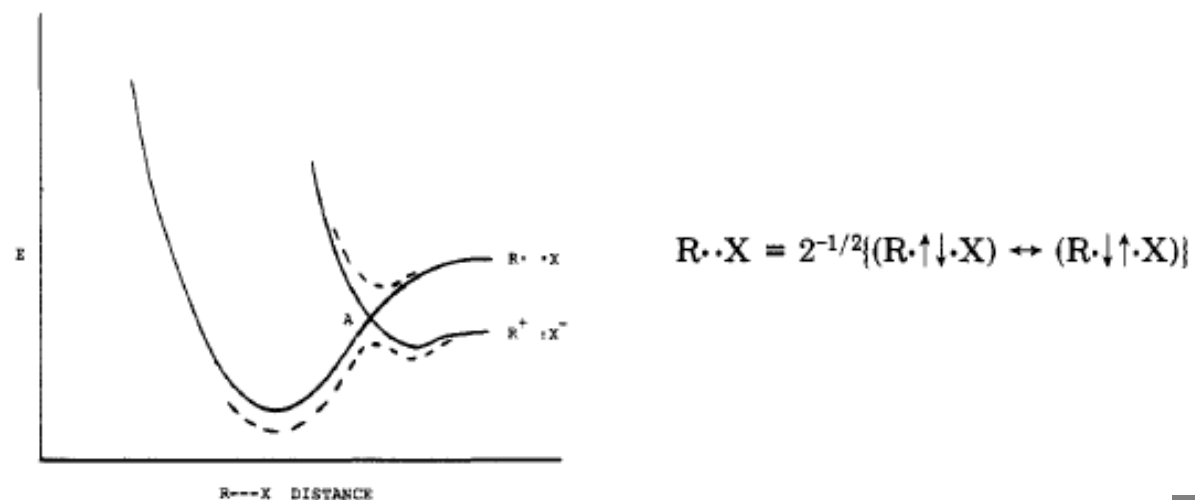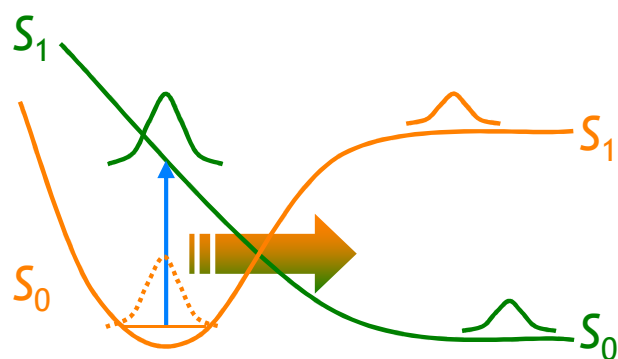
$$R \cdot \cdot X = 2^{-1/2}\{(R \cdot \uparrow \downarrow \cdot X) \leftrightarrow (R \cdot \downarrow \uparrow \cdot X)\}$$

3. Non-adiabatic Processes

a. Non-Adiabatic Quantum Dynamics

b. Radiationless Decay

c. Electronic State Crossings

Born-Oppenheimer quantum dynamics

- **Time-dependent** molecular Schrödinger equation within the Born-Oppenheimer approximation

$$i\hbar \frac{\partial}{\partial t} \psi\left(\vec{R},t\right) = \hat{H}_{\vec{R}}^{BO(s)} \psi\left(\vec{R},t\right)$$

$$\hat{H}_{\vec{R}}^{BO(s)} = \hat{T}_{\vec{R}} + V_s^{adia}\left(\vec{R}\right)$$

- Nuclear kinetic energy operator

  and potential energy surface

- Wavepacket for the nuclear motion (R,t)

  $\rightarrow$ amplitude of probability to be at geometry R at time t

Example: H transfer with tunnelling

X-H⋯Y   X⋯H-Y   X-H⋯Y   X⋯H-Y   X-H⋯Y   X⋯H-Y
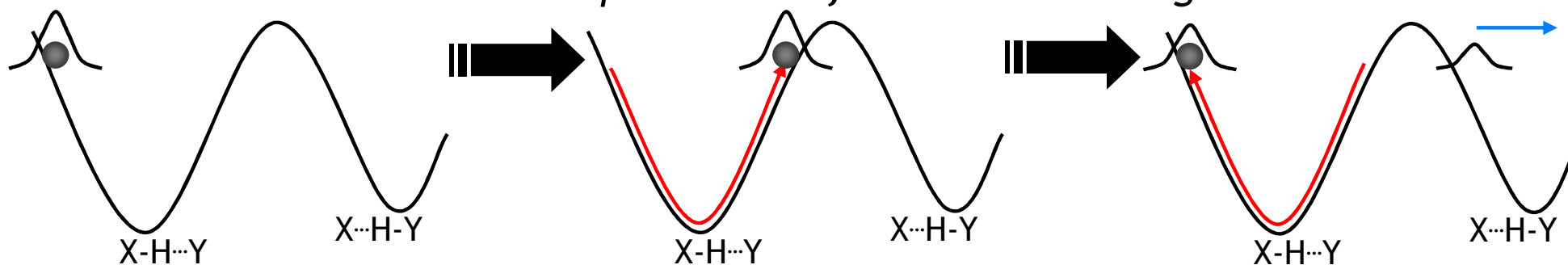
Non-adiabatic quantum dynamics

- **Time-dependent** molecular Schrödinger equation for two vibronically coupled singlet electronic states, S_0 and S_1,

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi^{(0)}(\vec{R},t) \\ \psi^{(1)}(\vec{R},t) \end{bmatrix} = \begin{bmatrix} \hat{\mathcal{H}}_{\vec{R}}^{(00)} & \hat{\mathcal{H}}_{\vec{R}}^{(01)} \\ \hat{\mathcal{H}}_{\vec{R}}^{(10)} & \hat{\mathcal{H}}_{\vec{R}}^{(11)} \end{bmatrix} \begin{bmatrix} \psi^{(0)}(\vec{R},t) \\ \psi^{(1)}(\vec{R},t) \end{bmatrix}$$

- Two-component wavepacket for the nuclear motion (R,t)

- Non-adiabatic coupling terms (non-Born-Oppenheimer)
  $\rightarrow$ transfer of electronic population

Example: photodissociation with internal conversion
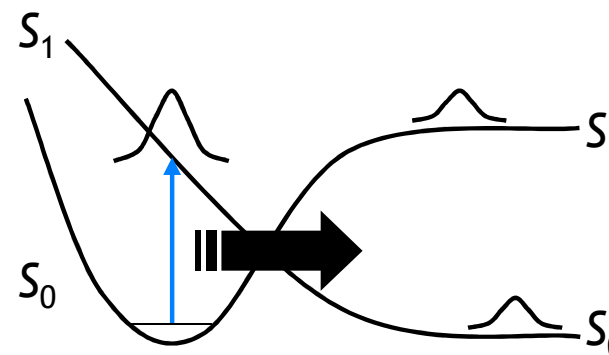
Representations of the molecular Hamiltonian

$$\hat{\mathcal{H}}_{\vec{R}}^{(ss')} = \left\langle s; \vec{R} \left| \hat{H}_{\text{mol}} \right| s'; \vec{R} \right\rangle = \hat{T}_{\vec{R}} \delta_{ss'} + \hat{\Lambda}_{\vec{R}}^{(ss')} + \left\langle s; \vec{R} \left| \hat{H}_{\text{el}}(\vec{R}) \right| s'; \vec{R} \right\rangle$$

General form

$$\begin{bmatrix} \hat{\mathcal{H}}^{(00)} & \hat{\mathcal{H}}^{(01)} \\ \hat{\mathcal{H}}^{(10)} & \hat{\mathcal{H}}^{(11)} \end{bmatrix} = \begin{bmatrix} \hat{T} & 0 \\ 0 & \hat{T} \end{bmatrix} + \begin{bmatrix} \hat{\Lambda}^{(00)} & \hat{\Lambda}^{(01)} \\ \hat{\Lambda}^{(10)} & \hat{\Lambda}^{(11)} \end{bmatrix} + \begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix}$$

Adiabatic electronic states

$$\begin{bmatrix} \hat{\mathcal{H}}^{(00)} & \hat{\mathcal{H}}^{(01)} \\ \hat{\mathcal{H}}^{(10)} & \hat{\mathcal{H}}^{(11)} \end{bmatrix} = \begin{bmatrix} \hat{T} & 0 \\ 0 & \hat{T} \end{bmatrix} + \begin{bmatrix} \hat{\Lambda}^{(00)} & \hat{\Lambda}^{(01)} \\ \hat{\Lambda}^{(10)} & \hat{\Lambda}^{(11)} \end{bmatrix} + \begin{bmatrix} V_0 & 0 \\ 0 & V_1 \end{bmatrix}$$

Zero potential coupling (H_{01})
→ Output of quantum chemistry

NB: diagonal scalar corrections $\Lambda^{(00)}$, $\Lambda^{(11)}$ (Born-Huang approximation)

Diabatic electronic states

$$\begin{bmatrix} \hat{\mathcal{H}}^{(00)} & \hat{\mathcal{H}}^{(01)} \\ \hat{\mathcal{H}}^{(10)} & \hat{\mathcal{H}}^{(11)} \end{bmatrix} = \begin{bmatrix} \hat{T} & 0 \\ 0 & \hat{T} \end{bmatrix} + \begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix}$$

Zero kinetic coupling ($\Lambda^{(01)}$)
→ Easier for quantum dynamics (no singularity at conical intersection)

Electronic population

- Time-resolved population of each electronic state = integral of the density within the electronic state

$$P^{(s)}(t) = \int\limits_{\{\vec{R}\}} \left| \psi^{(s)}\left(\vec{R}, t\right) \right|^2 d\tau$$
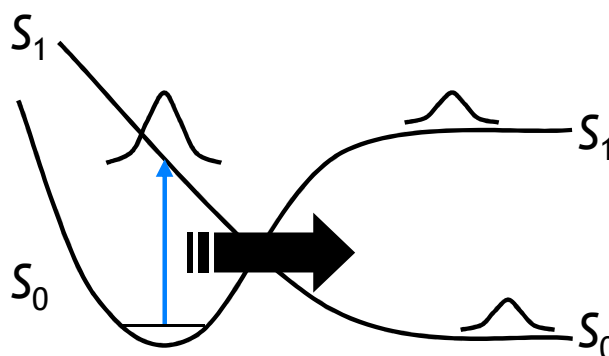
- Normalisation condition

$$\sum_{s} P^{(s)}(t) = 1$$

- Transfer of population due to non-adiabatic coupling

$$i\hbar \frac{\partial}{\partial t} \psi^{(s)}\left(\vec{R}, t\right) = \underbrace{\hat{\mathcal{H}}_{\vec{R}}^{(ss)} \psi^{(s)}\left(\vec{R}, t\right)}_{\substack{\text{conservation term} \\ \text{(Born-Oppenheimer)}}} + \underbrace{\sum_{s' \neq s} \hat{\mathcal{H}}_{\vec{R}}^{(ss')} \psi^{(s')}\left(\vec{R}, t\right)}_{\substack{\text{creation/dissipation terms} \\ \text{(non-adiabatic coupling)}}}$$

Radiationless decay

- Internal conversion = population transfer between singlet states

- No light emission: vibronic (non-adiabatic) coupling

- Very efficient at or near conical intersections

$$\left\langle 0^{\text{adia}}; \vec{R} \,\middle|\, \vec{\nabla}_{\vec{R}} \,\middle|\, 1^{\text{adia}}; \vec{R} \right\rangle = \frac{\left\langle 0^{\text{adia}}; \vec{R} \,\middle|\, \vec{\nabla}_{\vec{R}} \hat{H}_{\text{el}}\left(\vec{R}\right) \,\middle|\, 1^{\text{adia}}; \vec{R} \right\rangle}{V_1^{\text{adia}}\left(\vec{R}\right) - V_0^{\text{adia}}\left(\vec{R}\right)}$$

Photostability *vs.* photoreactivity

- Internal conversion can regenerate the electronic ground state in the reactant or product regions
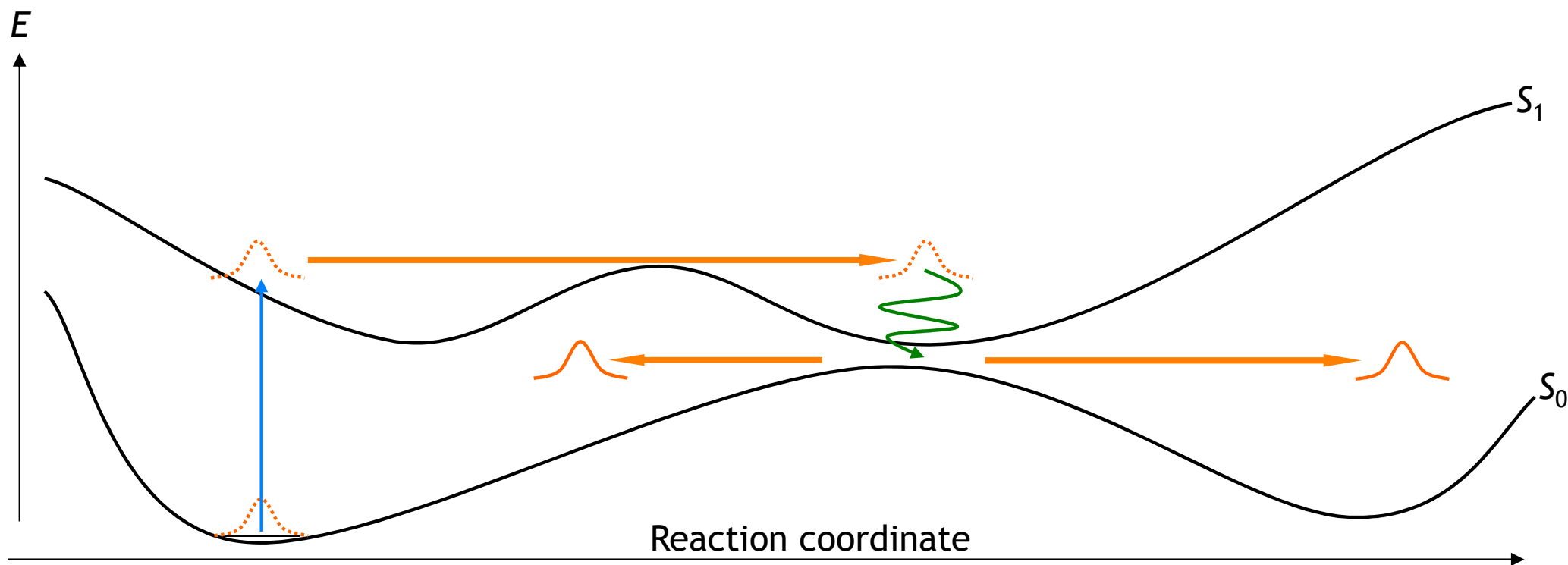
Role of the crossing topography

Sloped conical intersection
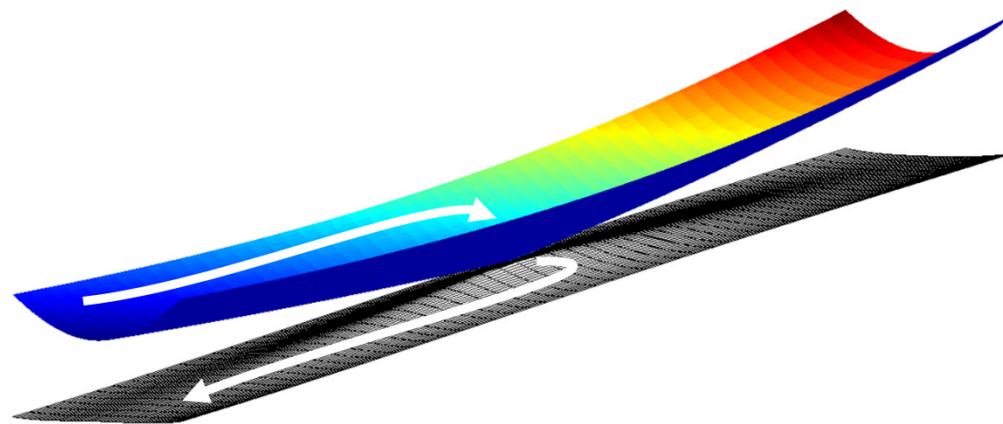
Peaked conical intersection
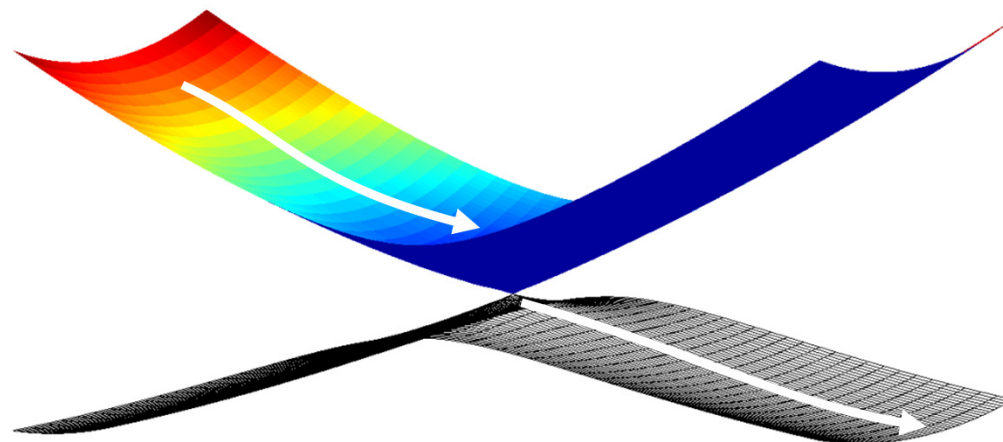
Retinal photoreactivity
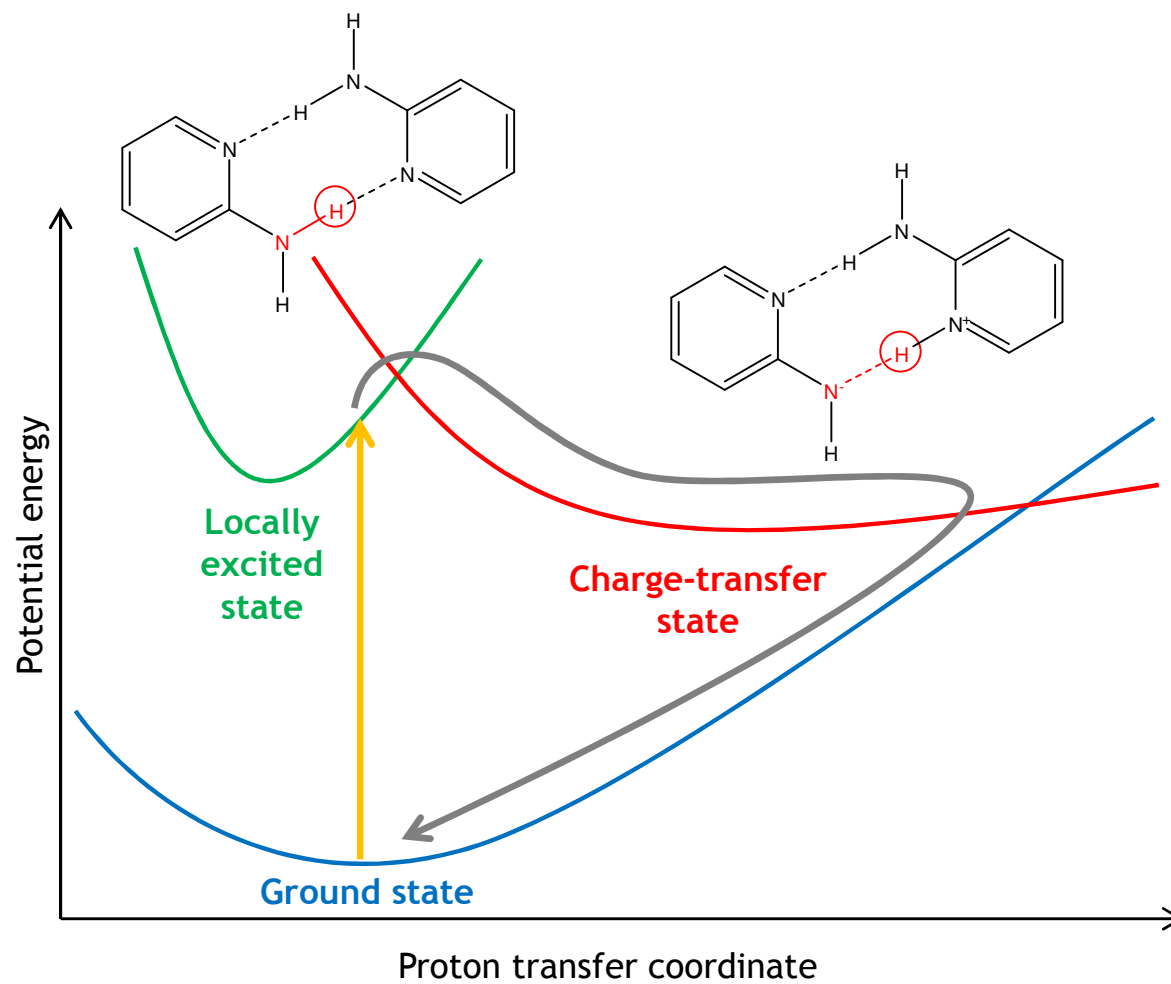
2nd step

Energy transfer

Potential energy

cis

trans

Isomerisation coordinate

DNA photostability

4. Methods
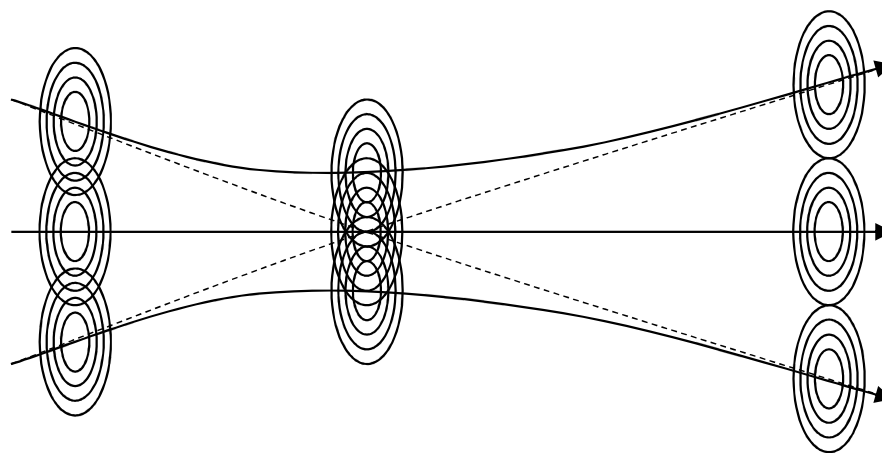
a. Grid-Based Methods

    "Exact" methods

    MCTDH

b. Direct (on-the-Fly) Methods

    Gaussian-Based Quantum Dynamics

    Trajectory-Based Dynamics → cf. F. Agostini's talk

State of the art

Grid-based quantum dynamics → electronic spectroscopy

Vibronic coupling Hamiltonian model (local expansion of the diabatic potential surfaces and couplings)

- Benchmark: pyrazine: 10 atoms (24D) / 3 coupled electronic states
- Valid only for small amplitude motions
- Global potential energy surfaces on a large grid: difficult and expensive

Trajectory-based mixed dynamics → photochemistry

Swarm of classical trajectories + probability of electronic transfer

- Most applications up to date (not accurate but useful for mechanistic purposes)
- Approximate treatment of non-adiabatic events
- 'On-the-fly' calculation of the potential energy or force field

+ A more quantum strategy: direct quantum dynamics

- Moving Gaussian functions (centre follows a 'quantum trajectory')
- Approximate quantum dynamics with 'on-the-fly' potential energy surfaces

Hierarchy of methods
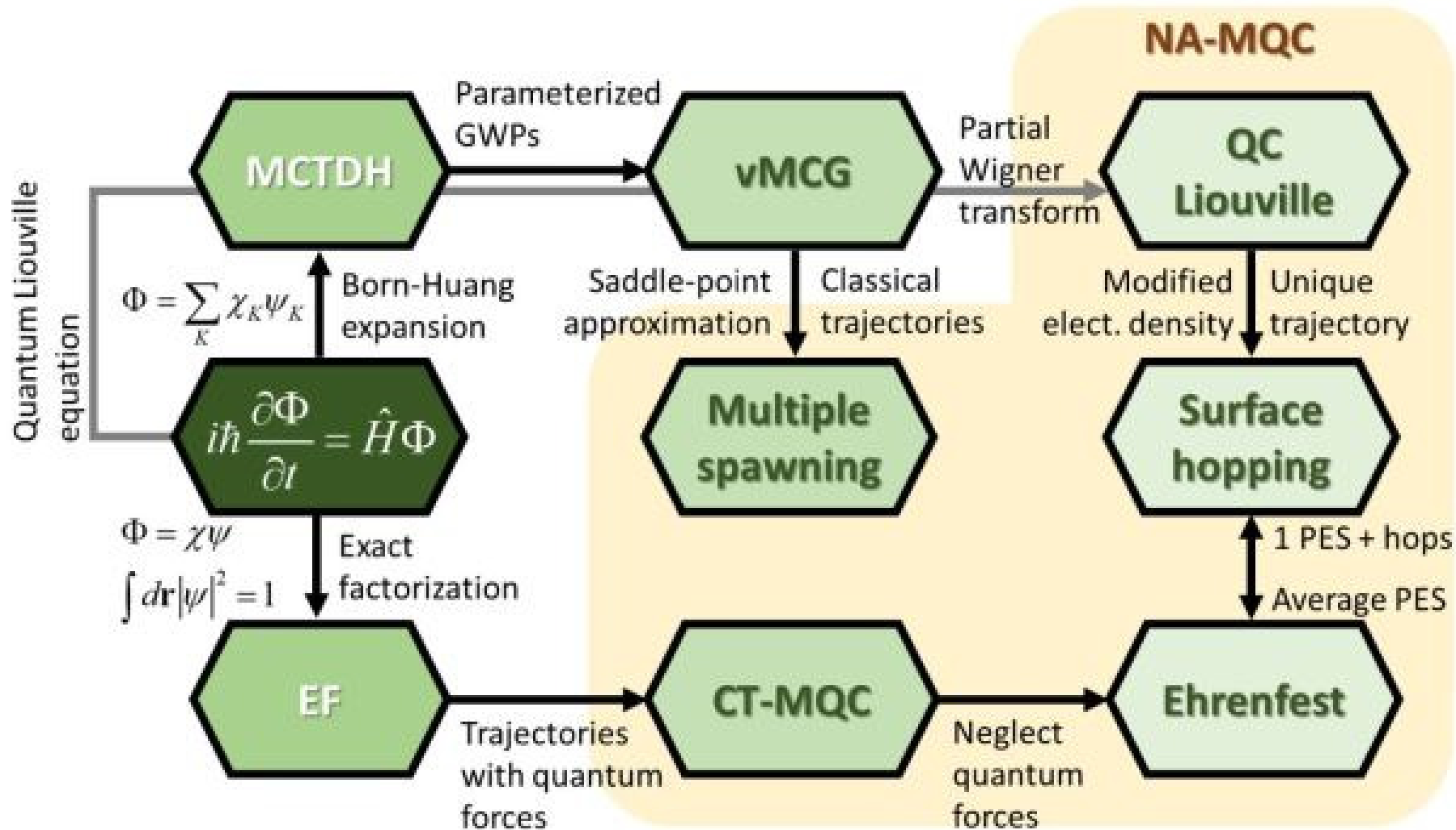
NA-MQC : nonadiabatic mixed quantum-classical
approximations → trajectory-based methods
(courtesy: Mario Barbatti)

First step: initial condition

- Initial condition = initial wavepacket
- Electric dipole + Franck-Condon approximation
  → Heller picture: sudden projection on S_1 of the vibrational ground state in S_0

$$\left|\psi\left(\vec{R}, t=0\right)\right\rangle = \sum_s \psi^{(s)}\left(\vec{R}, t=0\right)\left|s; \vec{R}\right\rangle$$

$$\psi^{(1)}\left(\vec{R}, t=0\right) = \varphi_0^{(0)}\left(\vec{R}\right)$$

$$\psi^{(0)}\left(\vec{R}, t=0\right) = 0$$
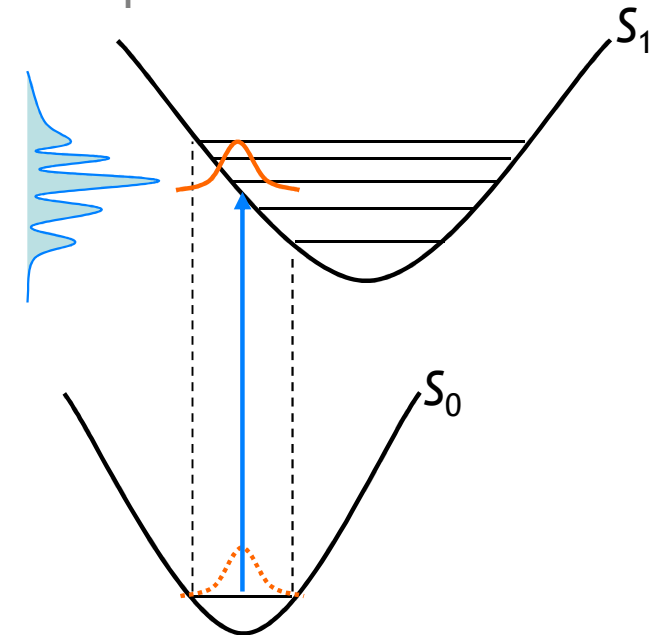
- Possible to include t-dependent laser pulse and R-dependent electric dipole

S_1

S_0

Second step: propagation

- Solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\left|\psi\left(\vec{R},t\right)\right\rangle = \hat{\mathcal{H}}_{\vec{R}}\left|\psi\left(\vec{R},t\right)\right\rangle$$

- The wavepacket evolves in time driven by the molecular Hamiltonian (often in a diabatic representation)

$$\hat{\mathcal{H}}_{\vec{R}} = \sum_{s,s'}\left|s;\vec{R}\right\rangle \hat{\mathcal{H}}_{\vec{R}}^{(ss')}\left\langle s';\vec{R}\right|$$

- "Exact" propagator (numerical integration)

$$\left|\psi\left(\vec{R},t+\Delta t\right)\right\rangle = e^{-\frac{i}{\hbar}\hat{\mathcal{H}}_{\vec{R}}\Delta t}\left|\psi\left(\vec{R},t\right)\right\rangle$$

- MCTDH (variational convergence)

$$\left\langle \delta\psi\left(\vec{R},t\right)\right|\hat{\mathcal{H}}_{\vec{R}} - i\hbar\frac{\partial}{\partial t}\left|\psi\left(\vec{R},t\right)\right\rangle$$

Approximate propagator

- Example: split-operator (Fourier transform R-space/K-space)

$$\begin{bmatrix} \psi^{\text{adia}(0)}\left(\vec{R}, t+\Delta t\right) \\ \psi^{\text{adia}(1)}\left(\vec{R}, t+\Delta t\right) \end{bmatrix} \approx \begin{bmatrix} e^{-\frac{1}{2}\frac{i}{\hbar}V_0^{\text{adia}}\left(\vec{R}\right)\Delta t} & 0 \\ 0 & e^{-\frac{1}{2}\frac{i}{\hbar}V_1^{\text{adia}}\left(\vec{R}\right)\Delta t} \end{bmatrix}$$

$$T\left(\vec{K}\right) = \sum_J \frac{\hbar^2}{2M_J}\vec{K}_J \cdot \vec{K}_J$$

$$\mathbf{U}^{\dagger}_{\text{adia}\leftarrow\text{dia}} \begin{bmatrix} \mathcal{F}^{-1}_{\vec{R}\leftarrow\vec{K}} e^{-\frac{i}{\hbar}T\left(\vec{K}\right)\Delta t} \mathcal{F}_{\vec{K}\leftarrow\vec{R}} & 0 \\ 0 & \mathcal{F}^{-1}_{\vec{R}\leftarrow\vec{K}} e^{-\frac{i}{\hbar}T\left(\vec{K}\right)\Delta t} \mathcal{F}_{\vec{K}\leftarrow\vec{R}} \end{bmatrix} \mathbf{U}_{\text{dia}\leftarrow\text{adia}}$$

$$\begin{bmatrix} e^{-\frac{1}{2}\frac{i}{\hbar}V_0^{\text{adia}}\left(\vec{R}\right)\Delta t} & 0 \\ 0 & e^{-\frac{1}{2}\frac{i}{\hbar}V_1^{\text{adia}}\left(\vec{R}\right)\Delta t} \end{bmatrix} \begin{bmatrix} \psi^{\text{adia}(0)}\left(\vec{R}, t\right) \\ \psi^{\text{adia}(1)}\left(\vec{R}, t\right) \end{bmatrix}$$

- Other typical propagator: Chebyshev polynomial expansion

MultiConfiguration Time-Dependent Hartree (MCTDH)

- Nuclear coordinates → f internal degrees of freedom

$$\vec{R} \to \mathbf{Q} = \left\{ Q_1, \ldots, Q_f \right\}$$

- Similar to one-state case

  Hartree product of SPF ~ configuration

  SPF ~ molecular orbital

  expansion of the SPF in a primitive basis set ~ LCAO

$$\left| \psi(\mathbf{Q}, t) \right\rangle = \sum_{s} \psi^{(s)}(\mathbf{Q}, t) \left| s; \mathbf{Q} \right\rangle$$

$$\psi^{(s)}(\mathbf{Q}, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} \underbrace{A_{j_1,\ldots,j_f}^{(s)}(t)}_{\text{coefficient}} \underbrace{\prod_{\kappa=1}^{f} \underbrace{\varphi_{j_\kappa}^{(\kappa, s)}(Q_\kappa, t)}_{\text{SPF}}}_{\text{Hartree product}}$$

- Extra electronic degree of freedom (s) in the equations of motion

Comparison: 3D example

- Standard methods (equivalent to full CI expansion)

primitive basis set (mathematical functions, equivalent to AOs):

$$\left\{f_{j_1}^{(1)}(Q_1)\right\}_{j_1=1}^{N_1} \otimes \left\{f_{j_2}^{(2)}(Q_2)\right\}_{j_2=1}^{N_2} \otimes \left\{f_{j_3}^{(3)}(Q_3)\right\}_{j_3=1}^{N_3}$$

$$\psi(Q_1,Q_2,Q_3,t) = \sum_{j_1=1}^{N_1}\sum_{j_2=1}^{N_2}\sum_{j_3=1}^{N_3} \underbrace{A_{j_1j_2j_3}(t)}_{\text{coefficient}} \underbrace{f_{j_1}^{(1)}(Q_1)f_{j_2}^{(2)}(Q_2)f_{j_3}^{(3)}(Q_3)}_{\text{configuration}}$$

- Large basis set → $N_1N_2N_3$ configurations (3D functions) and expansion coefficients

Comparison: 3D example

- MCTDH method (equivalent to MCSCF)

  single-particle functions (variational, equivalent to MOs):

$$\left\{\varphi_{k_1}^{(1)}(Q_1,t)\right\}_{k_1=1}^{n_1} \otimes \left\{\varphi_{k_2}^{(2)}(Q_2,t)\right\}_{k_2=1}^{n_2} \otimes \left\{\varphi_{k_3}^{(3)}(Q_3,t)\right\}_{k_3=1}^{n_3}$$

$$\psi(Q_1,Q_2,Q_3,t) = \sum_{k_1=1}^{n_1}\sum_{k_2=1}^{n_2}\sum_{k_3=1}^{n_3}\underbrace{A_{k_1k_2k_3}(t)}_{\text{coefficient}}\underbrace{\varphi_{k_1}^{(1)}(Q_1,t)\varphi_{k_2}^{(2)}(Q_2,t)\varphi_{k_3}^{(3)}(Q_3,t)}_{\text{configuration}}$$

$$\varphi_{k_\kappa}^{(\kappa)}(Q_\kappa,t) = \sum_{j_\kappa=1}^{N_\kappa}C_{j_\kappa}^{(\kappa,k_\kappa)}(t)f_{j_\kappa}^{(\kappa)}(Q_\kappa) \quad ; \kappa = 1,2,3$$

- Contraction scheme $\rightarrow$ $n_1n_2n_3 << N_1N_2N_3$ configurations (3D functions) and expansion A-coefficients, but extra "LCAO" C-coefficients

Comparison: 3D example

- ML(multilayer)-MCTDH method (hierarchical contraction)

intermediate correlated functions (groups of coordinates):

$$\left\{\varphi_{k_{12}}^{(12)}\left(Q_1,Q_2,t\right)\right\}_{k_{12}=1}^{n_{12}} \otimes \left\{\varphi_{k_3}^{(3)}\left(Q_3,t\right)\right\}_{k_3=1}^{n_3}$$

$$\psi\left(Q_1,Q_2,Q_3,t\right) = \sum_{k_{12}=1}^{n_{12}}\sum_{k_3=1}^{n_3} \underbrace{A_{k_{12}k_3}\left(t\right)}_{\text{coefficient}} \underbrace{\varphi_{k_{12}}^{(12)}\left(Q_1,Q_2,t\right)\varphi_{k_3}^{(3)}\left(Q_3,t\right)}_{\text{first layer }\{1,2\}\{3\}}$$

$$\varphi_{k_{12}}^{(12)}\left(Q_1,Q_2,t\right) = \sum_{l_1=1}^{m_1}\sum_{l_2=1}^{m_2} \underbrace{B_{l_1l_2}^{(12,k_{12})}\left(t\right)}_{\text{coefficient}} \underbrace{\xi_{l_1}^{(1)}\left(Q_1,t\right)\xi_{l_2}^{(2)}\left(Q_2,t\right)}_{\text{second layer }\{1\}\{2\}}$$

- Smaller vectors but more complicated equations of motion

Quantum dynamics: the curse of dimensionality

QD: rigorous and accurate but...

PES required as an analytical expression fitted to a grid of data points

→ grid-based methods

Representing a multiD function is expensive

- Exponential scaling

Fitting procedures are complicated and system-dependent

- Constrained optimisation techniques

Much grid space is wasted

- High or far regions: seldom explored

→ trajectory-based methods

PES calculated on-the-fly as in classical MD

Gaussian-based quantum dynamics

- The variational multiconfiguration Gaussian (vMCG) method
- Time-dependent Gaussian basis set (local around centres)

$$\psi(Q,t) = \sum_j A_j(t) g_j(Q,t)$$
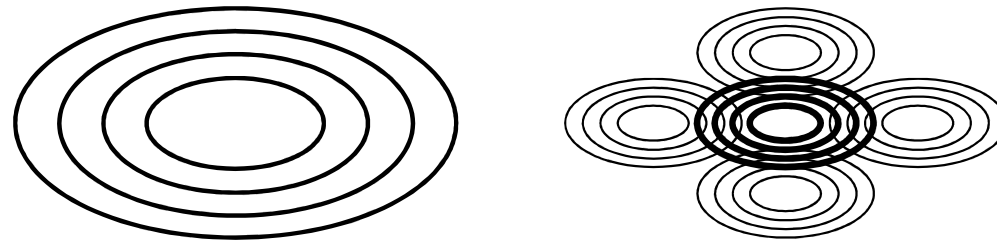
- Coupled 'quantum trajectories': position, momentum, and phase at centre of Gaussian functions

Equations of motion implemented in a development version (QUANTICS, London) of the Heidelberg MCTDH package
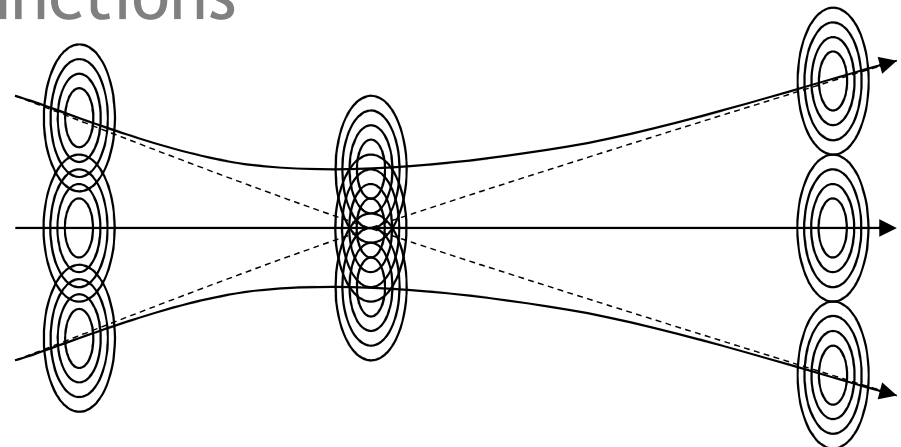
Direct dynamics implementation (DD-vMCG)

- **Diabatic** picture for dynamics
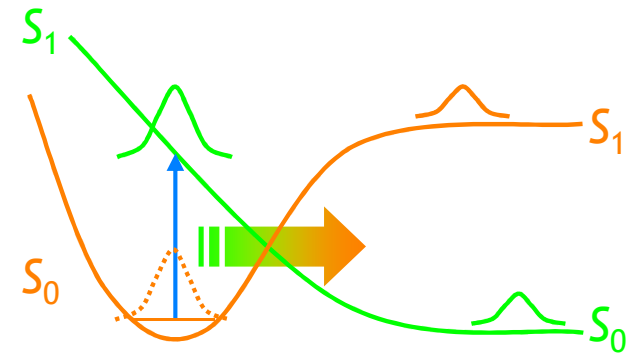
- **Adiabatic** picture for on-the-fly quantum chemistry

$$
\begin{bmatrix} \hat{\mathcal{H}}^{(00)} & \hat{\mathcal{H}}^{(01)} \\ \hat{\mathcal{H}}^{(10)} & \hat{\mathcal{H}}^{(11)} \end{bmatrix} = \begin{bmatrix} \hat{T} & 0 \\ 0 & \hat{T} \end{bmatrix} + \underbrace{\mathbf{U}_{\text{dia}\leftarrow\text{adia}} \begin{bmatrix} V_0 & 0 \\ 0 & V_1 \end{bmatrix} \mathbf{U}^{\dagger}_{\text{adia}\leftarrow\text{dia}}}_{\begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix}}
$$

- Diabatic transformation (**U**):
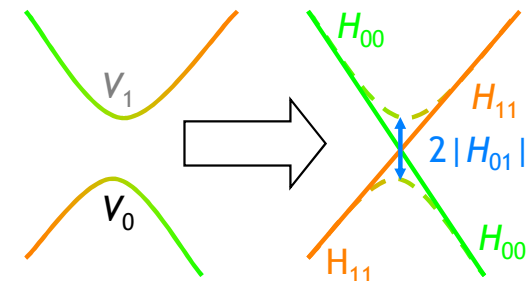
Diabatisation: start with linear vibronic-coupling model

- $\mathbf{x}^{(1)}$ and $\mathbf{x}^{(2)}$ (branching space): lift degeneracy at a selected conical intersection ($\mathbf{Q}^{\text{ref}}$)

$$kQ_1 = \mathbf{x}^{(1)} \cdot \left(\mathbf{Q} - \mathbf{Q}^{\text{ref}}\right)$$

$$\lambda Q_2 = \mathbf{x}^{(2)} \cdot \left(\mathbf{Q} - \mathbf{Q}^{\text{ref}}\right)$$

$$\mathbf{x}^{(1)} = \frac{1}{2} \nabla_{\mathbf{Q}} \left(H_{11} - H_{00}\right)$$

$$\mathbf{x}^{(2)} = \nabla_{\mathbf{Q}} H_{01}$$
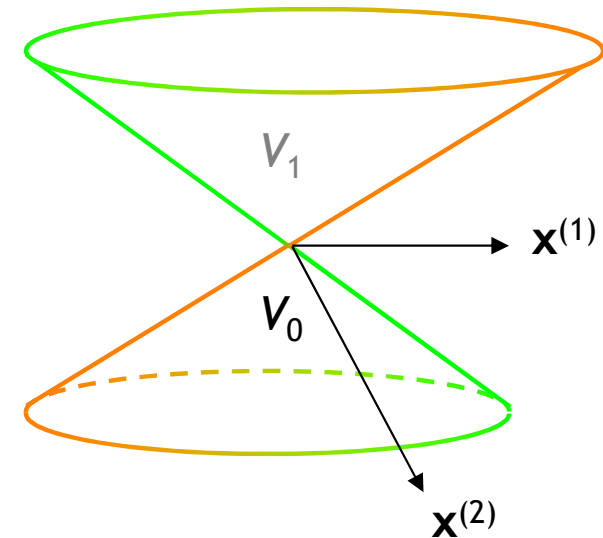
- Simplest diabatic Hamiltonian

$$\mathbf{W}(\mathbf{Q}) = \begin{bmatrix} -kQ_1 & \lambda Q_2 \\ \lambda Q_2 & kQ_1 \end{bmatrix}$$

And generate regularised Hamiltonian

$$\begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix} = \mathbf{U}_{\text{dia}\leftarrow\text{adia}} \begin{bmatrix} V_0 & 0 \\ 0 & V_1 \end{bmatrix} \mathbf{U}^{\dagger}_{\text{adia}\leftarrow\text{dia}}$$
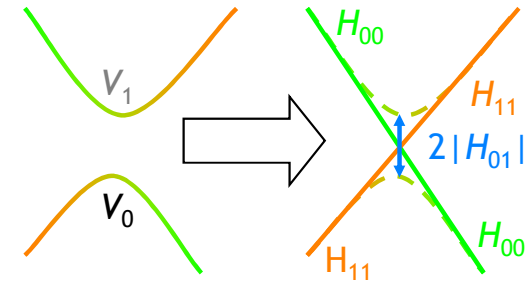
- First-order expansion of the adiabatic energy difference and rescaling

$$\hat{\mathcal{H}}_{\mathbf{Q}} = \hat{T}_{\mathbf{Q}}\mathbf{1} + \Sigma(\mathbf{Q})\mathbf{1} + \frac{\Delta(\mathbf{Q})}{\Delta^{(1)}(\mathbf{Q})}\mathbf{W}^{(1)}(\mathbf{Q})$$

$$\Sigma(\mathbf{Q}) = \frac{V_0(\mathbf{Q}) + V_1(\mathbf{Q})}{2}, \quad \Delta(\mathbf{Q}) = \frac{V_1(\mathbf{Q}) - V_0(\mathbf{Q})}{2}$$

$$\mathbf{W}^{(1)}(\mathbf{Q}) = \begin{bmatrix} -\mathbf{x}^{(1)}\cdot\delta\mathbf{Q} & \mathbf{x}^{(2)}\cdot\delta\mathbf{Q} \\ \mathbf{x}^{(2)}\cdot\delta\mathbf{Q} & \mathbf{x}^{(1)}\cdot\delta\mathbf{Q} \end{bmatrix}, \quad \Delta^{(1)}(\mathbf{Q}) = \sqrt{\left[\mathbf{x}^{(1)}\cdot\delta\mathbf{Q}\right]^2 + \left[\mathbf{x}^{(2)}\cdot\delta\mathbf{Q}\right]^2}$$

Advantage: effective Hamiltonian

- Exact eigenvalues (adiabatic data) at any point

$$\begin{bmatrix} V_0(\mathbf{Q}) & 0 \\ 0 & V_1(\mathbf{Q}) \end{bmatrix} = \Sigma(\mathbf{Q})\mathbf{1} + \frac{\Delta(\mathbf{Q})}{\Delta^{(1)}(\mathbf{Q})} \underbrace{\mathbf{U}^{(1)\dagger}_{\text{adia}\leftarrow\text{dia}}(\mathbf{Q})\mathbf{W}^{(1)}(\mathbf{Q})\mathbf{U}^{(1)}_{\text{dia}\leftarrow\text{adia}}(\mathbf{Q})}_{\begin{bmatrix} -\Delta^{(1)}(\mathbf{Q}) & 0 \\ 0 & \Delta^{(1)}(\mathbf{Q}) \end{bmatrix}}$$

- Approximate rotation angle $\varphi^{(1)}$ and non-adiabatic coupling (first-order contribution inducing the singularity around $\mathbf{Q}^{\text{ref}}$)

$$\nabla_{\mathbf{Q}}\varphi^{(1)}(\mathbf{Q}) \approx -\left\langle \Phi_0;\mathbf{Q} \,\middle|\, \nabla_{\mathbf{Q}}\Phi_1;\mathbf{Q} \right\rangle$$

Interface quantum chemistry – quantum dynamics

Local Harmonic Approximation

R_2

R_1

$$\left[R_{1j}(t), R_{2j}(t) \right]$$

Database

Quantum Chemistry

Potential energy and derivatives

$$\left\{ g_j\!\left(\vec{R}, t\right) \right\}$$

$$\left\{ A_j(t) \right\}$$

Quantum Dynamics

$$\left\{ g_j\!\left(\vec{R}, t + \Delta t\right) \right\}$$

$$\left\{ A_j(t + \Delta t) \right\}$$
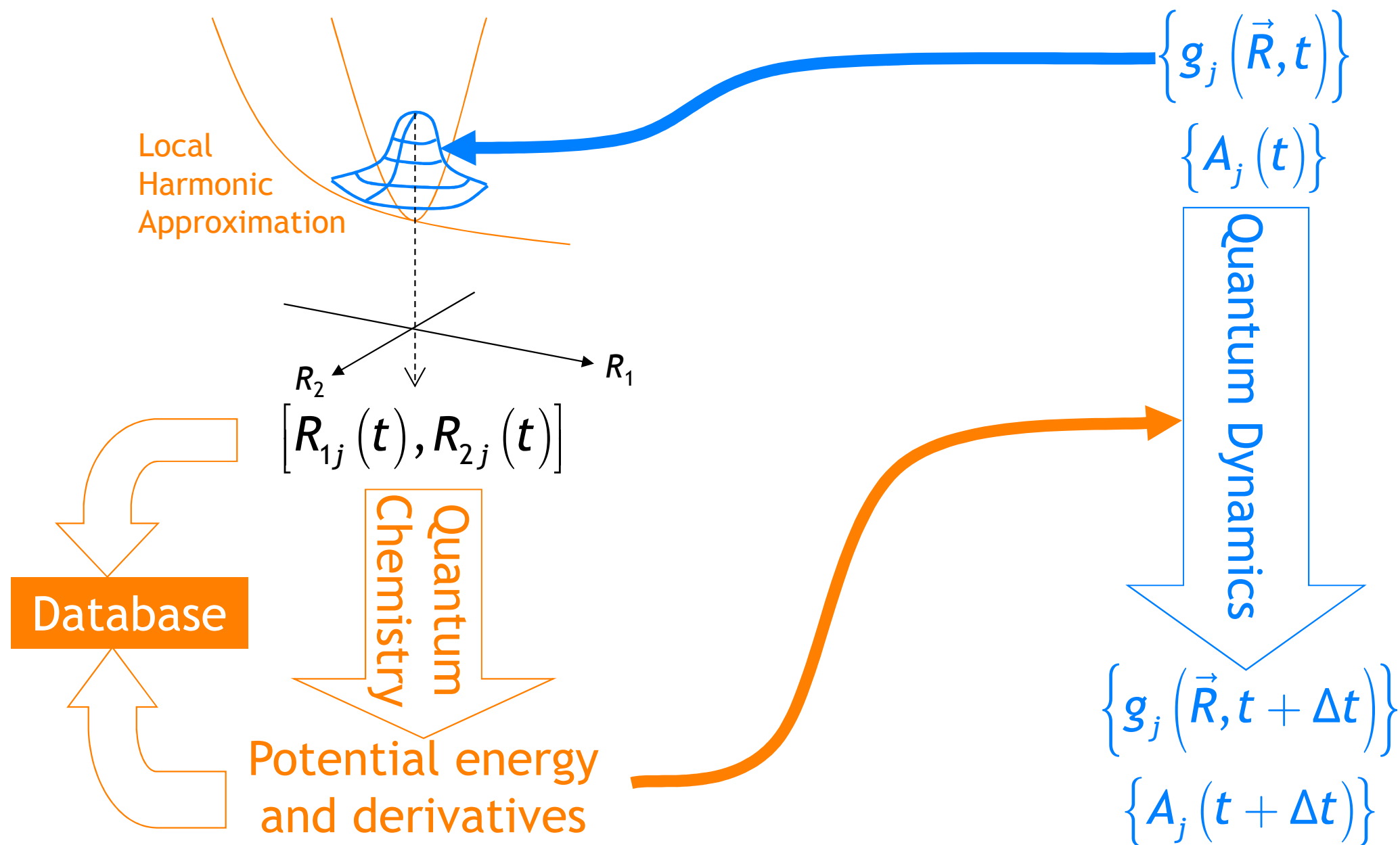
Gross Gaussian populations

- Non-orthogonal basis set: ambiguous attribution of how much of the density is given by each Gaussian function
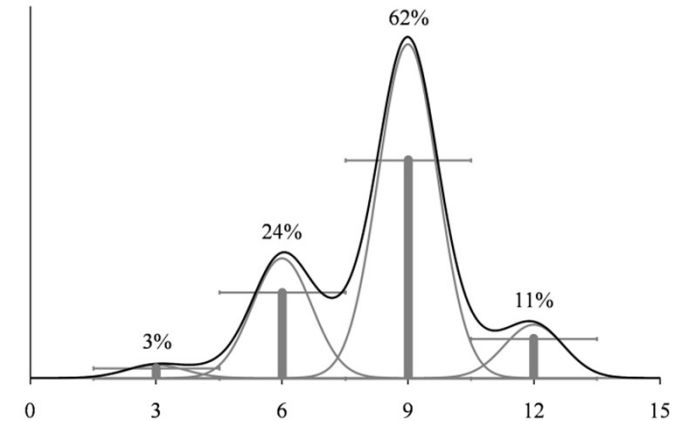
$$\left|\psi^{(s)}\left(\vec{R},t\right)\right|^2 = \sum_{k,j} A_k^{(s)*}(t)\, A_j^{(s)}(t)\, g_k^{(s)*}\left(\vec{R},t\right) g_j^{(s)}\left(\vec{R},t\right)$$

- Solution: Mulliken-like population (*Cf.* atomic orbitals, not orthogonal)

$$S_{kj}(t) = \int_{\{\vec{R}\}} g_k^{(s)*}\left(\vec{R},t\right) g_j^{(s)}\left(\vec{R},t\right) d\tau$$

$$GGP_j^{(s)}(t) = \Re \sum_k A_k^{(s)*}(t)\, A_j^{(s)}(t)\, S_{kj}(t)$$

$$P^{(s)}(t) = \sum_j GGP_j^{(s)}(t)$$

$$\sum_s \sum_j GGP_j^{(s)}(t) = 1$$

Ab initio Multiple Spawning (AIMS)

- Similar expansion as vMCG

$$\left|\psi\left(\vec{R},t\right)\right\rangle = \sum_s \sum_j A_j^{(s)}\left(t\right) g_j^{(s)}\left(\vec{R},t\right)\left|s;\vec{R}\right\rangle$$
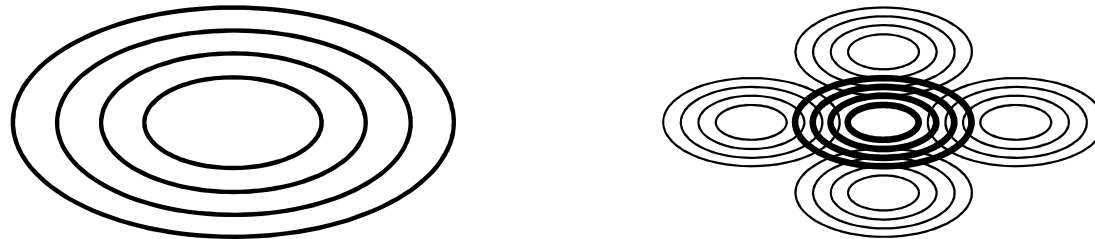
- Difference: quantum evolution for the coefficients but classical equations of motion for the centres of the Gaussian functions
- Drawback: convergence is slower (classical motion)
- Advantage: the basis set can increase (spawning) when necessary → when the wavepacket reaches a conical intersection

Mixed quantum-classical (semiclassical) trajectories

- Statistical sampling (positions and velocities) of the initial wavepacket

$$\left| \psi\left(\vec{R}, t\right) \right\rangle \rightarrow \left\{ \vec{R}^{(k)}(t), \vec{V}^{(k)}(t) \right\}_k$$
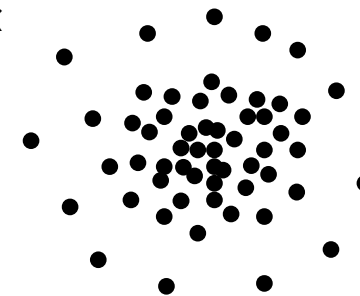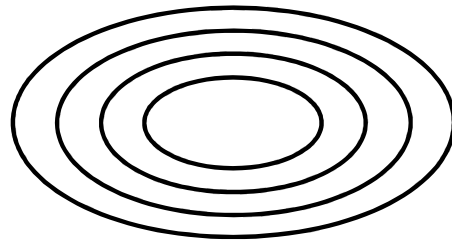
- Swarm of trajectories driven by Newton's classical equations of motion far from conical intersection

- Diabatic state-transfer probability when the energy gap becomes small (surface hopping) calculated from approximate quantum equations (*e.g.*, Landau-Zener formula)

$$P_{1 \to 0}^{(k)}(t) = \exp\left[-\frac{2\pi}{\hbar} \frac{\left(H_{01}^2\right)_{\vec{R}^{(k)}(t)}}{\left| \vec{V}^{(k)}(t) \cdot \vec{\nabla}_{\vec{R}}\left(H_{11} - H_{00}\right)_{\vec{R}^{(k)}(t)} \right|} \right]$$

5. Examples of Application
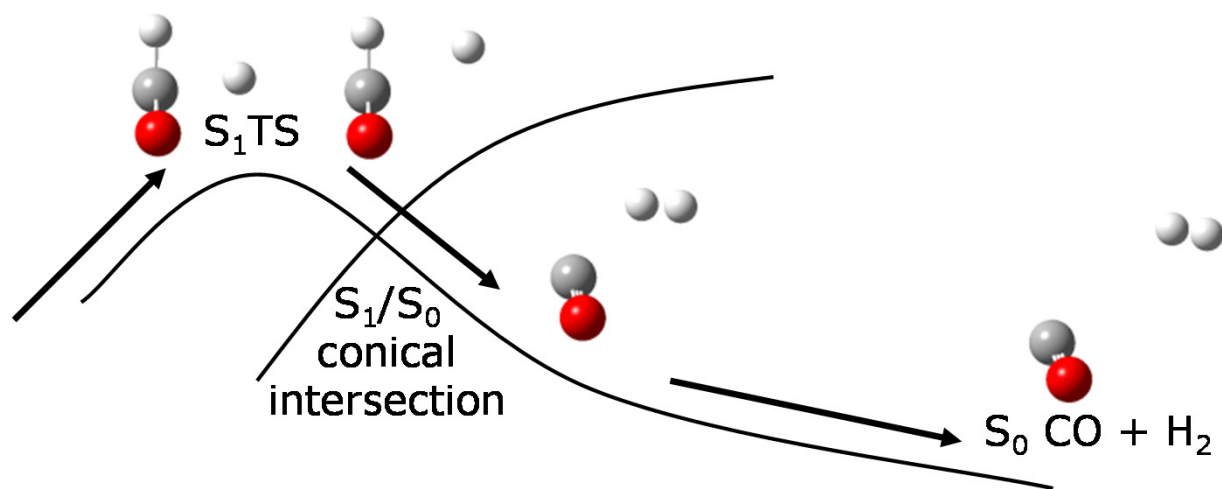
S$_1$TS

S$_1$/S$_0$ conical intersection

S$_0$ CO + H$_2$

Electronic spectroscopy: absorption spectrum

- Franck-Condon approximation
- Electric dipole approximation
- Wavepacket evolution
- Absorption spectrum: Fourier transform of the autocorrelation function

$$\sigma(\omega) \propto \omega \int_{-\infty}^{+\infty} e^{i\left(\frac{E_0}{\hbar}+\omega\right)t} C(t)\, dt, \text{ where } C(t) = \langle \Psi(t=0) | \Psi(t) \rangle$$
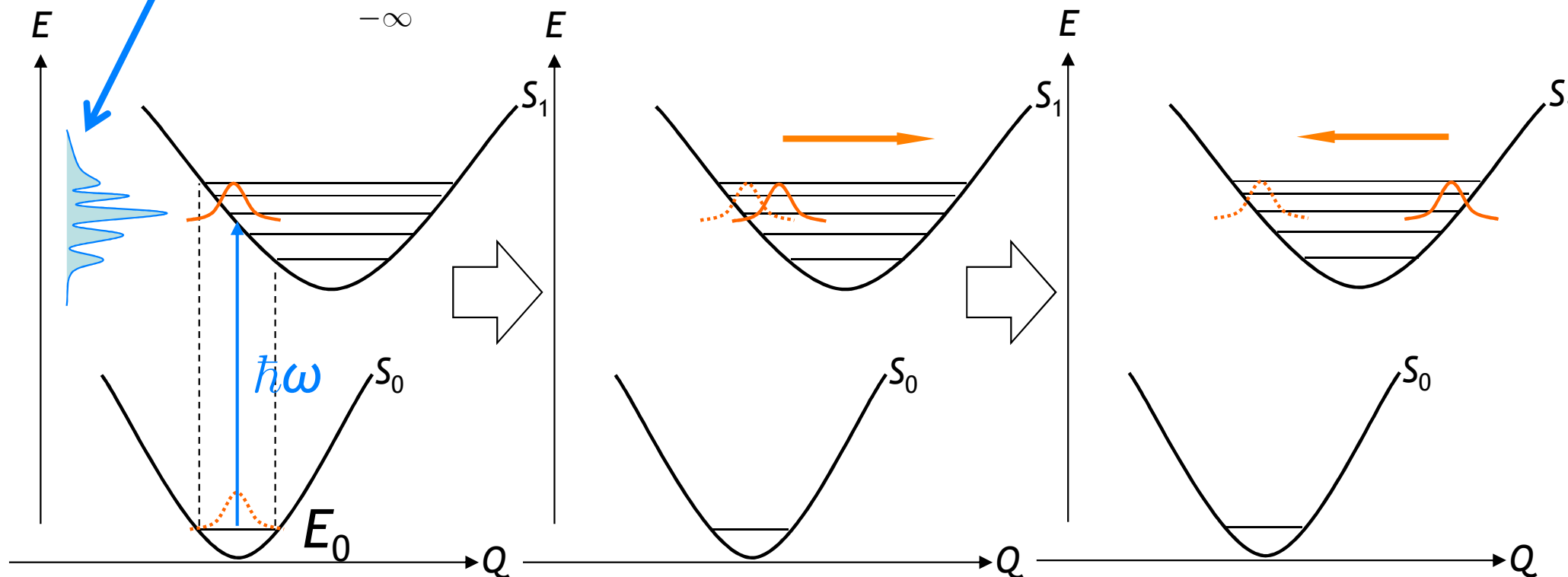
$S_2 \leftarrow S_0$ pyrazine absorption spectrum (MCTDH)

- Vibronic (non-adiabatic) coupling between S_2 and S_1
- Intensity borrowed by dark state from bright state
- Benchmark for MCTDH with vibronic coupling Hamiltonian model
  10 atoms (24D) / 3 electronic states
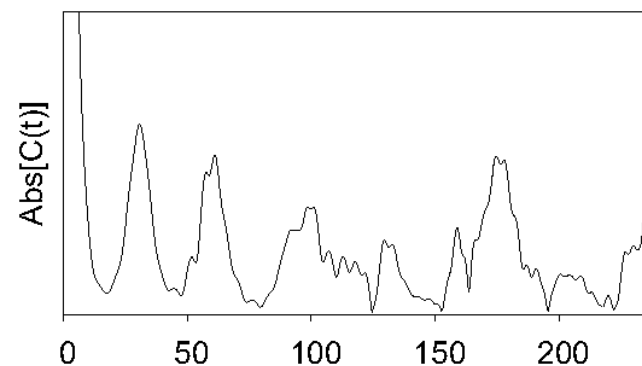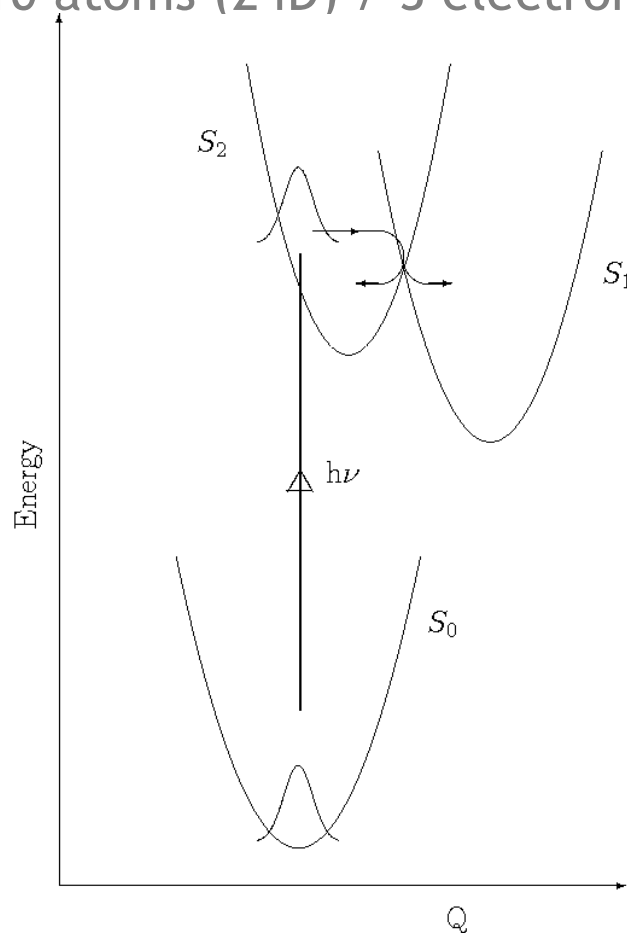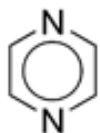
$$I(\omega) = I_0 e^{-\sigma(\omega)c\ell}$$
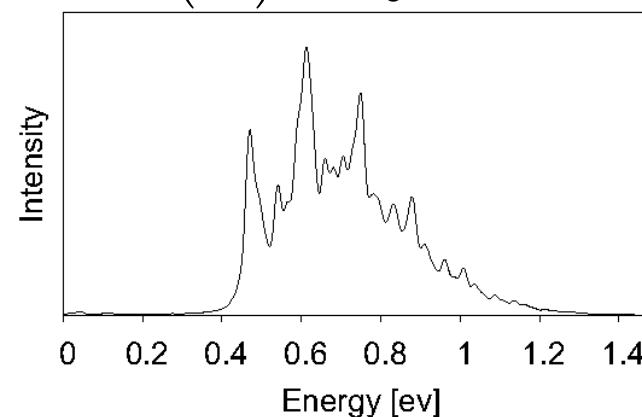
$S_2 \leftarrow S_0$ pyrazine absorption spectrum (MCTDH)

- Quadratic vibronic coupling Hamiltonian model

$$\hat{\mathcal{H}}_Q^{\text{dia}} = \sum_i \frac{\hbar\omega_i}{2}\left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right)\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} -\Delta & 0 \\ 0 & \Delta \end{bmatrix}$$

$$+ \sum_{i \in G_1}\begin{bmatrix} a_i & 0 \\ 0 & b_i \end{bmatrix}Q_i + \sum_{i,j \in G_2}\begin{bmatrix} a_{ij} & 0 \\ 0 & b_{ij} \end{bmatrix}Q_i Q_j$$

$$+ \sum_{i \in G_3}\begin{bmatrix} 0 & c_i \\ c_i & 0 \end{bmatrix}Q_i + \sum_{i,j \in G_4}\begin{bmatrix} 0 & c_{ij} \\ c_{ij} & 0 \end{bmatrix}Q_i Q_j$$

- Parameters fitted to *ab initio* calculations after diagonalisation
- Four groups of coordinates (G_1 to G_4) depending on irreducible representations in D_{2h}

$S_2 \leftarrow S_0$ pyrazine absorption spectrum (MCTDH)

Using all 24 degrees of freedom
→ spectrum converged *vs.* experiment
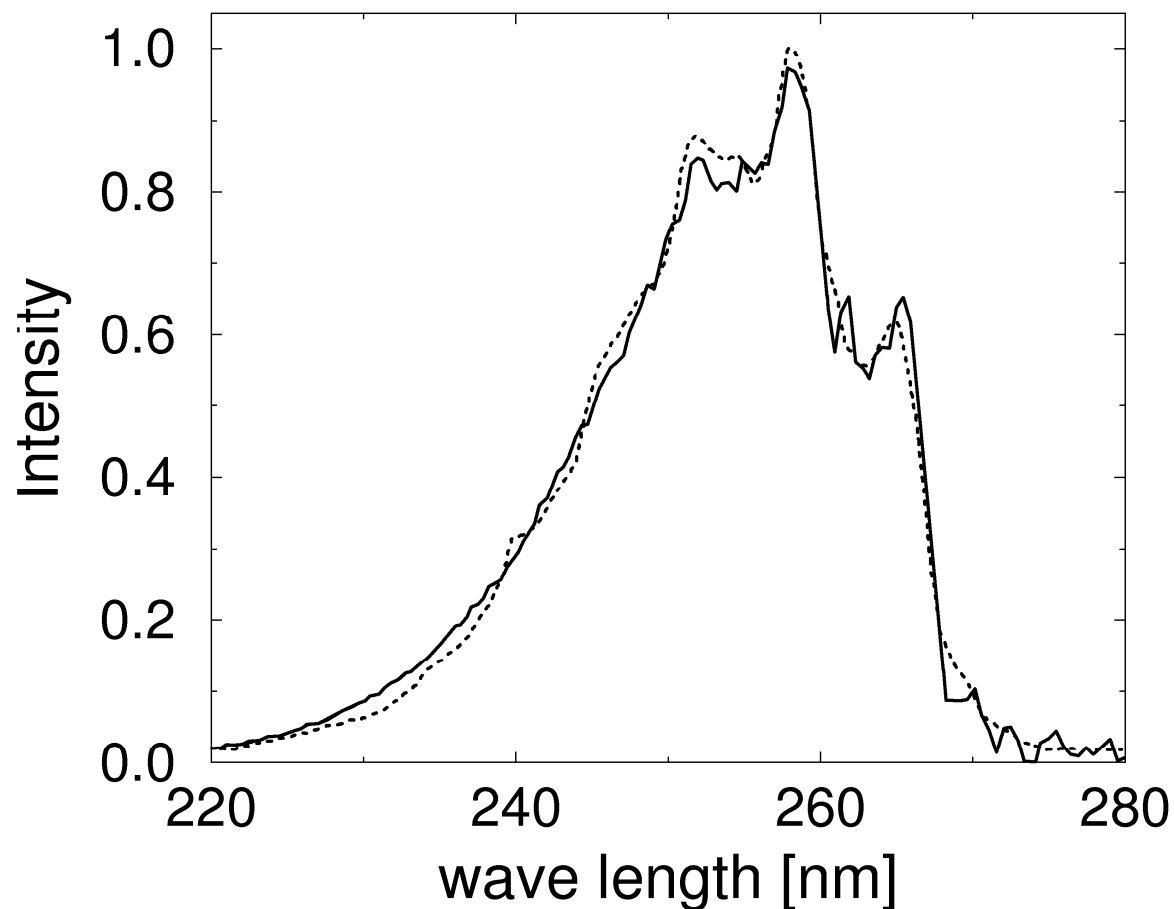
Heme photodissociation with SO coupling (ML-MCTDH)
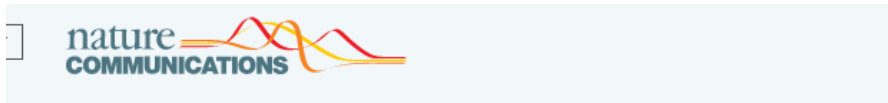

179 el. states (S/T/Q), 15 vib. modes, 1 ps simulations
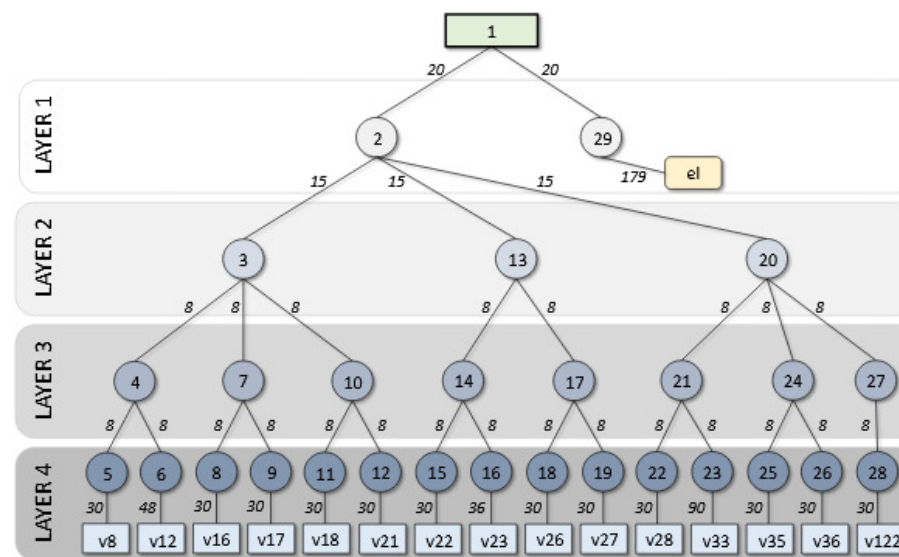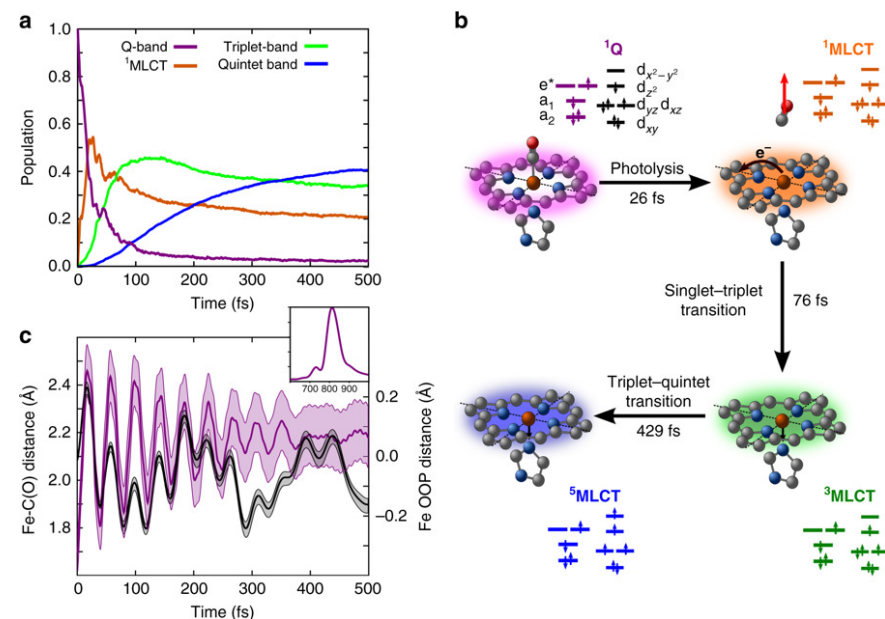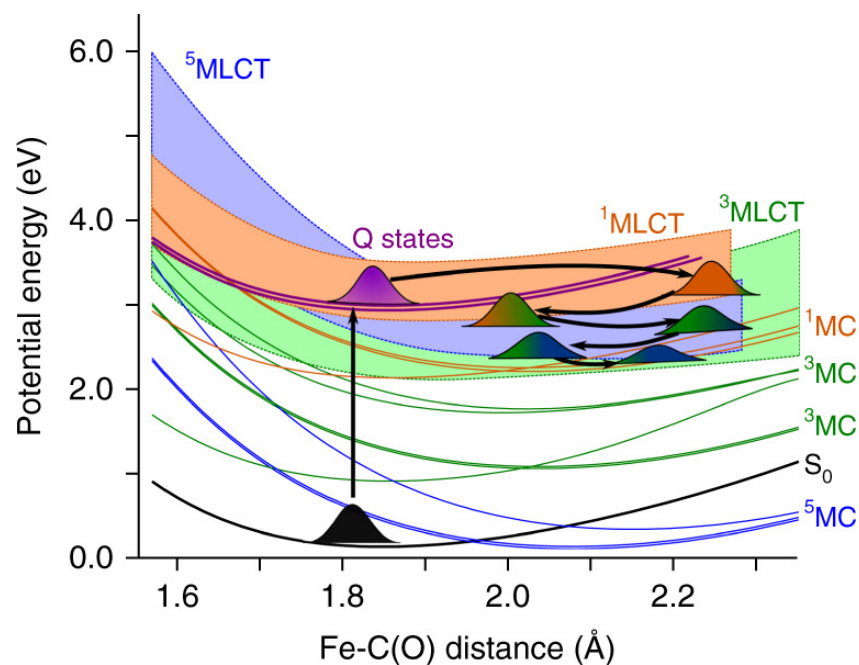
S_1/S_0 formaldehyde photodissociation (DD-vMCG)

- After S_1 photoexcitation (n_O, π^*_{CO}), formaldehyde dissociates to H + HCO or H_2 + CO
- At low energy, Fermi-Golden-Rule decay to S_0 (slow decay at large energy gap) followed by ground-state reactivity
- At medium energy, involvement of the triplet T_1
- At higher energy, possible to overcome the S_1 TS followed by direct decay to S_0 products through conical intersection
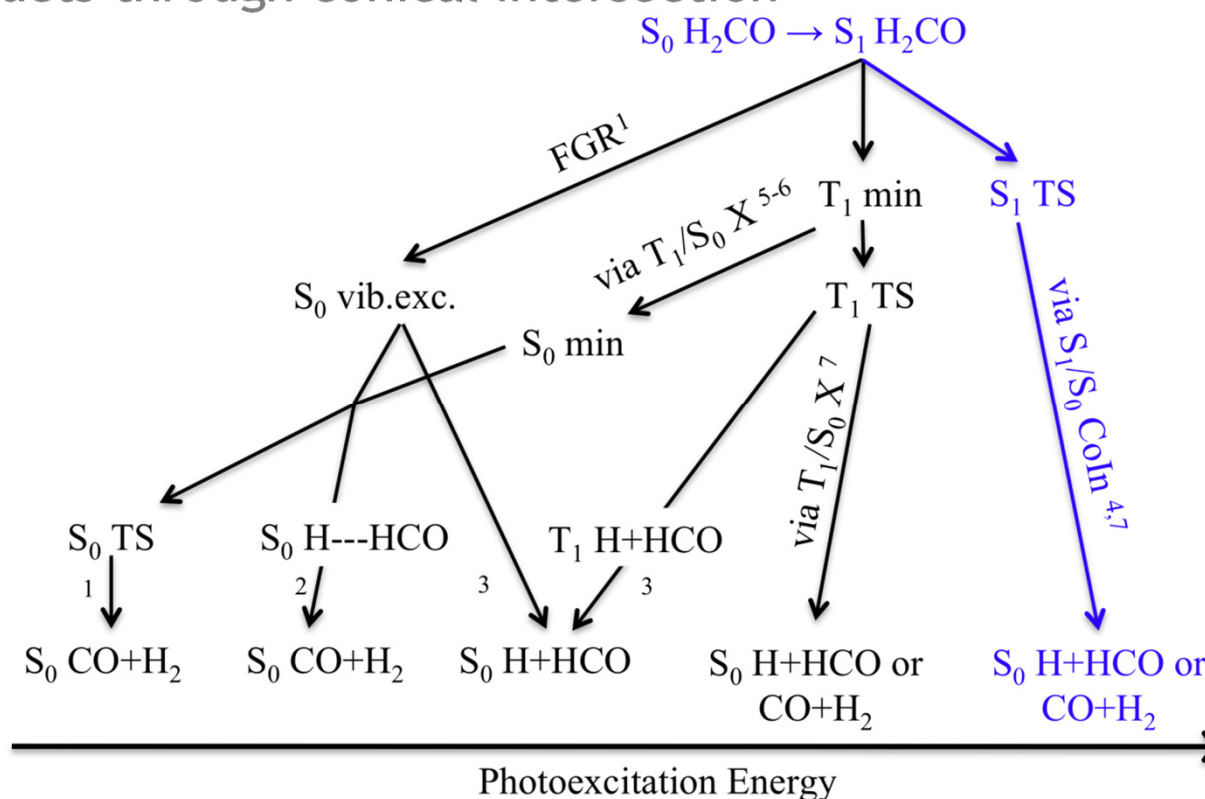
S_1/S_0 formaldehyde photodissociation (DD-vMCG)

The S_1 TS is directly connected to the S_1/S_0 conical intersection

S$_1$TS

S_1/S_0
conical
intersection

S_0 CO + H$_2$
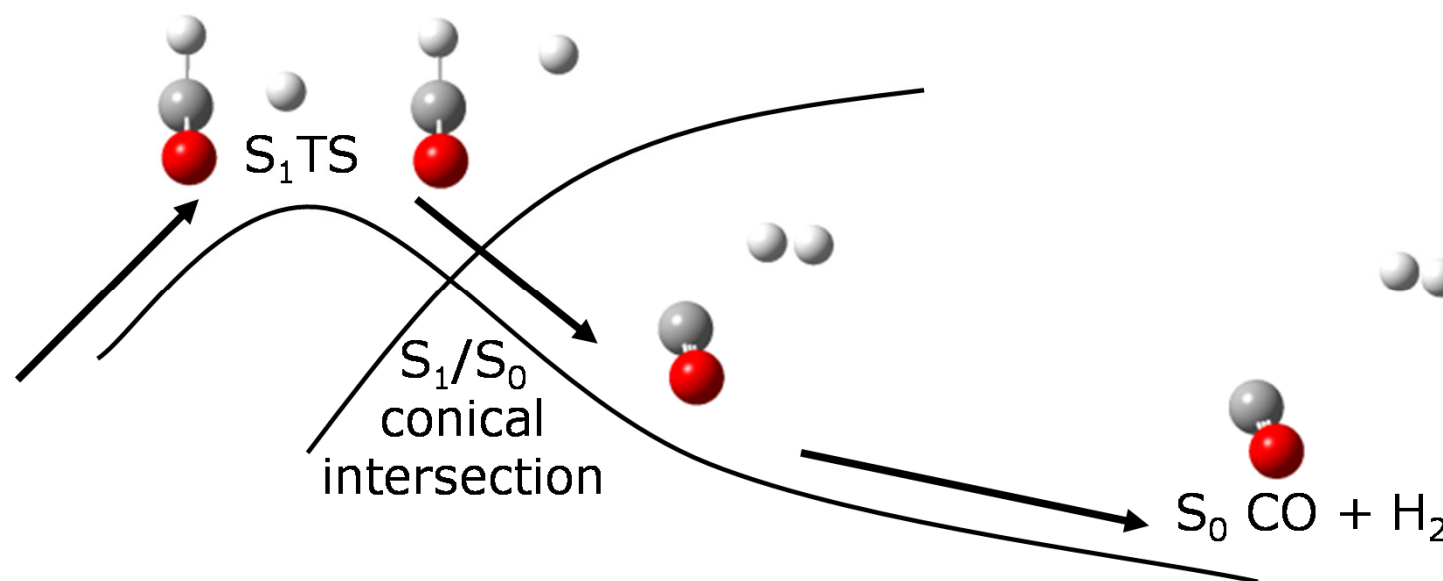
S_1/S_0 formaldehyde photodissociation (DD-vMCG)

## Influence of initial conditions

Initial geometry and momentum:
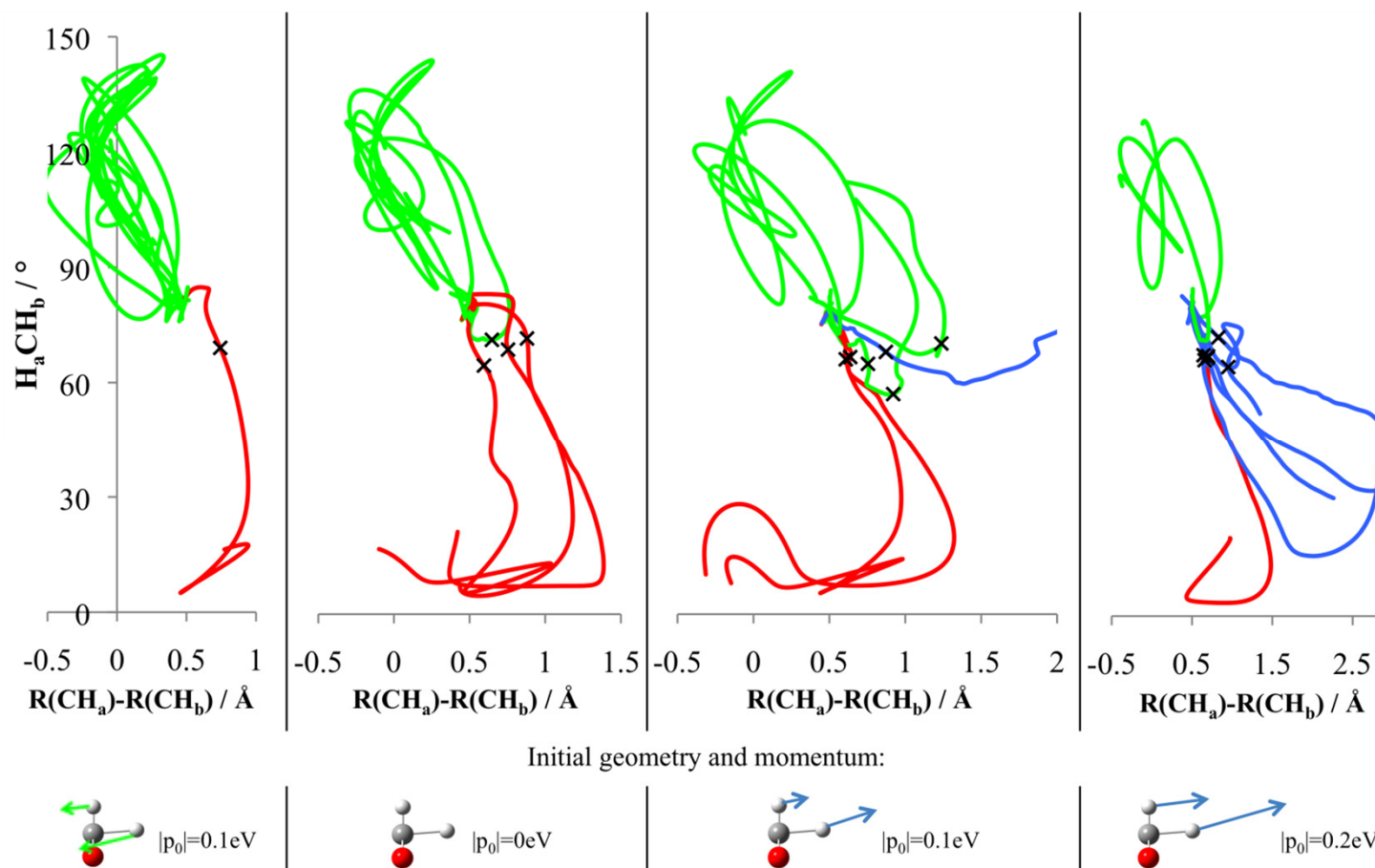
S_1/S_0 formaldehyde photodissociation (DD-vMCG)

Distribution of products (final geometry and electronic state)
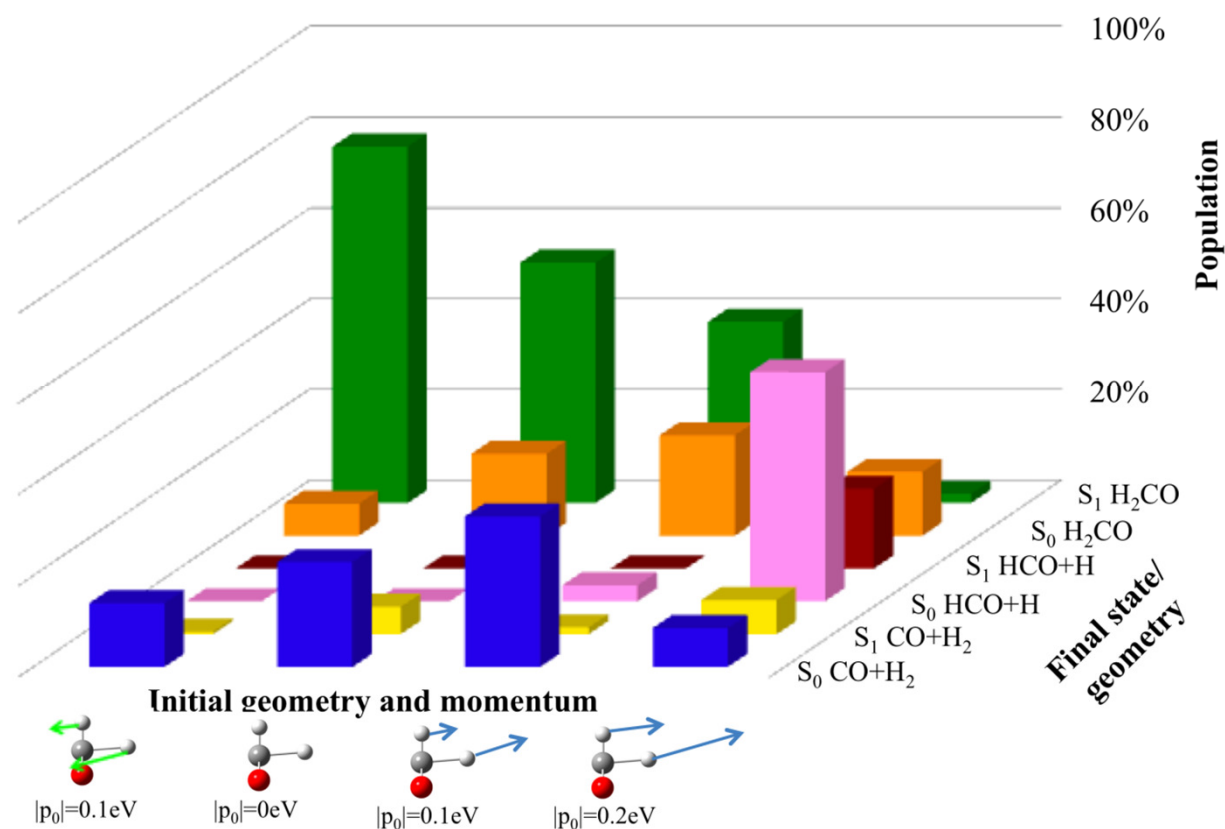
Some recent test cases with new diabatisation (DD-vMCG)

- Butatriene cation

     2/3/4-state 2-dimensional diabatic matrix (global): smooth
     → surfaces and populations depend on number of states

- Formamidic acid

     6-state 12-dimensional diabatic matrix (global): smooth
     → 24 Gaussian functions: 80% dissociation (various fragments)
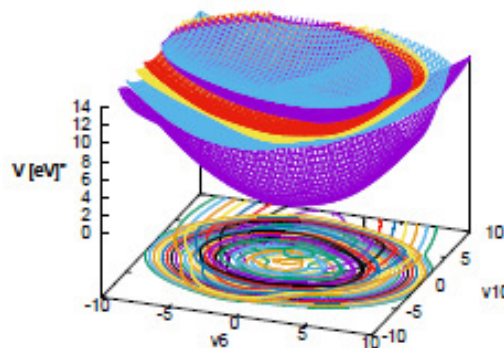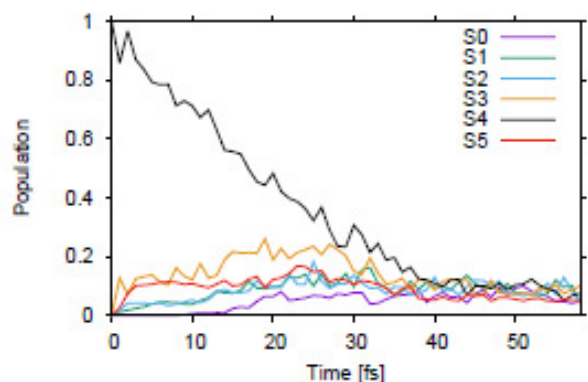
Trajectory Analysis	
Product	No.
O-H break	14
HN-CO	6
N-CH-O	2
NH + CO	1
HNC-H-O	1

- Ozone

     8 Gaussian functions with CASPT2: spectrum in correct place
     → took a student only one week compared to one year for the original work with grid-based quantum dynamics!

6. Conclusions and Outlooks

Excited-state dynamics is still a growing field of theoretical and physical chemistry (applications to laser-driven control, influence of the environment in large systems or condensed matter...)

Developments are still required to treat photochemical reactivity with as much accuracy as electronic spectroscopy (cheaper quantum chemistry methods for excited states, general procedures to produce accurate potential energy surfaces and couplings for large-amplitude deformations of the geometry...)

Summer School EMIE-UP
Multiscale Dynamics in Molecular Systems
August 2019

Outlooks: attophysics and attochemistry

é'

State 2

Cation

State 1

Attosecond pulse

Neutral

Hole

0.000 fs

1.306 fs
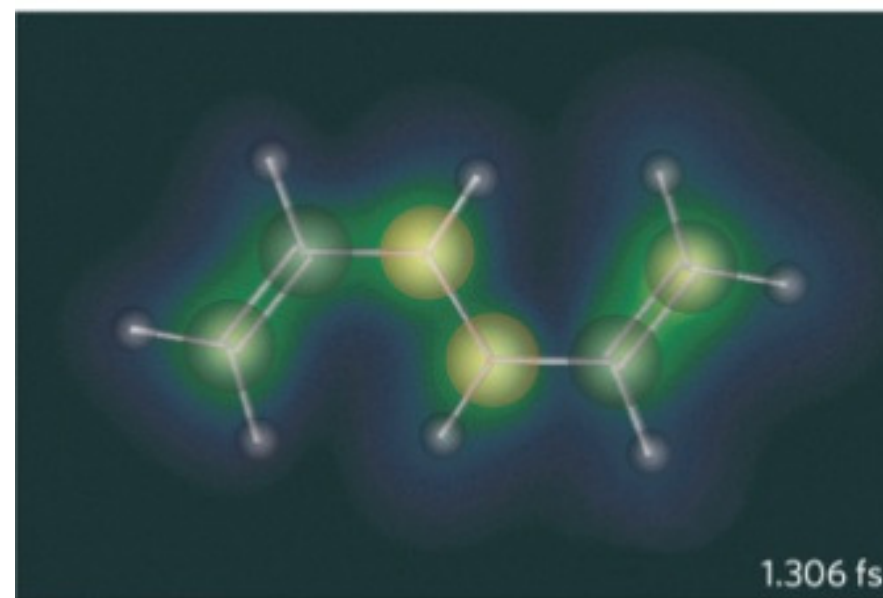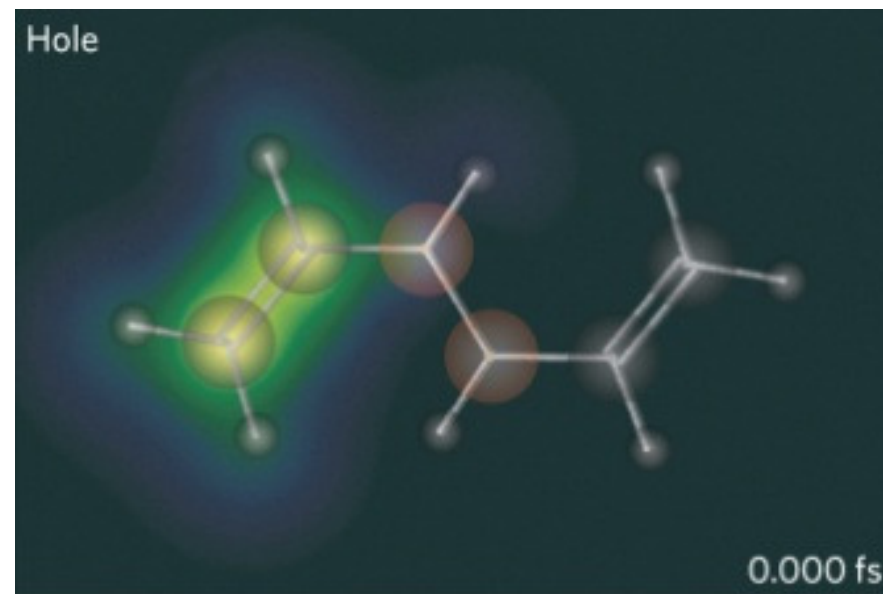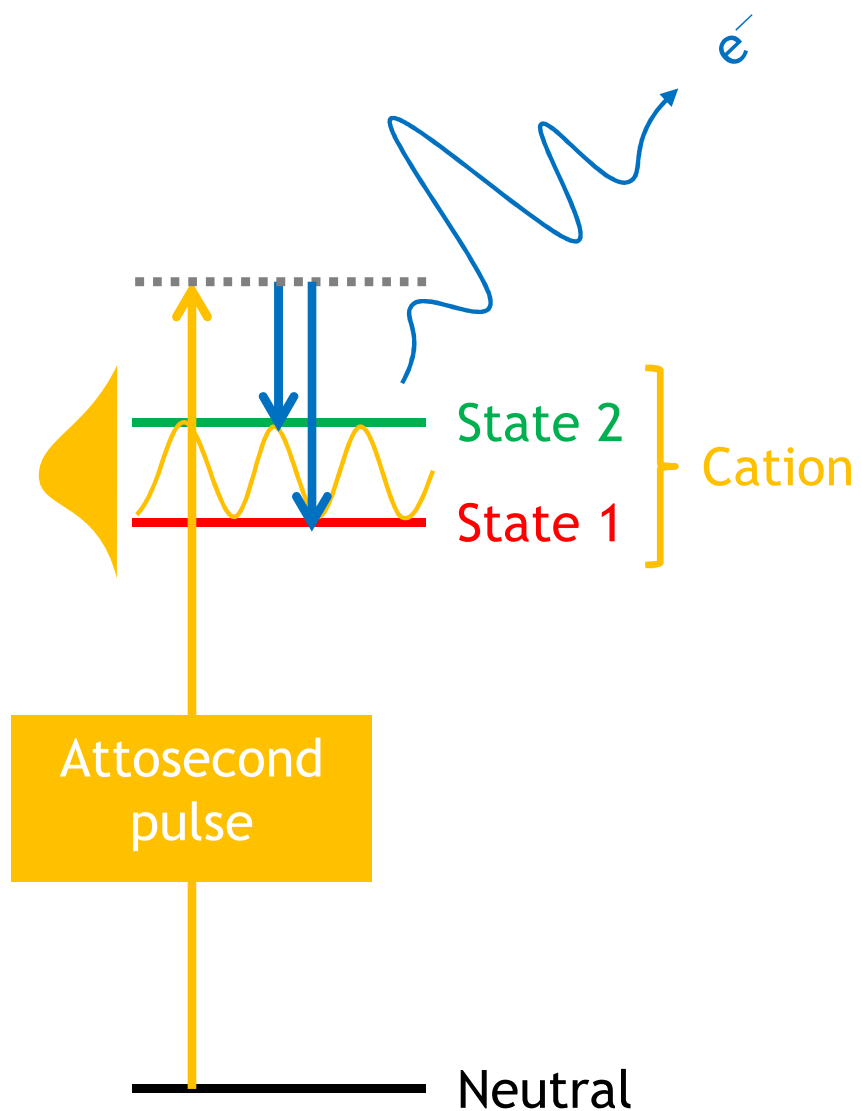
# Beyond WPs: dissipative quantum dynamics (system-bath)

THE JOURNAL OF PHYSICAL CHEMISTRY B
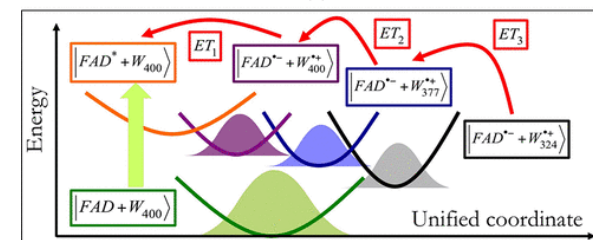
Article

Cite This: J. Phys. Chem. B 2018, 122, 126−136

pubs.acs.org/JPCB

Multidimensional Quantum Mechanical Modeling of Electron Transfer and Electronic Coherence in Plant Cryptochromes: The Role of Initial Bath Conditions

David Mendive-Tapia,[*,†,‡] Etienne Mangaud,[§] Thiago Firmino,[⊥] Aurélien de la Lande,[⊥] Michèle Desouter-Lecomte,[⊥] Hans-Dieter Meyer,[‡] and Fabien Gatti[*,‖]
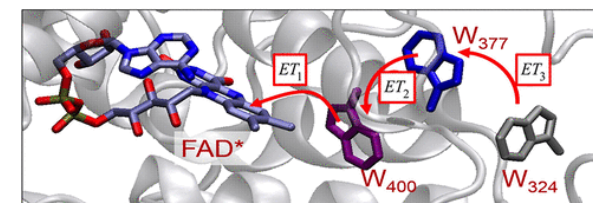
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PAPER • OPEN ACCESS

Non-Markovianity in the optimal control of an open quantum system described by hierarchical equations of motion

E Mangaud[1], R Puthumpally-Joseph[2,3], D Sugny[2,4,8], C Meier[1], O Atabek[5] and M Desouter-Lecomte[6,7,8]

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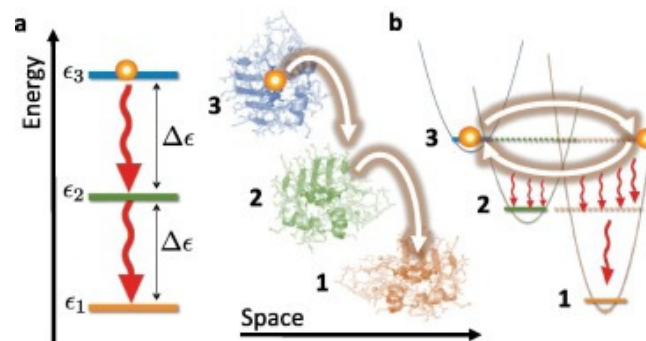
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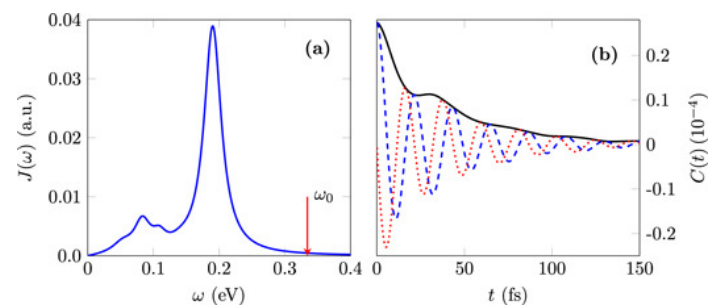
Chemical Physics
Available online 1 June 2019, 110392
In Press, Accepted Manuscript ⓘ

Visualising the role of non-perturbative environment dynamics in the dissipative generation of coherent electronic motion

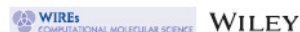A.W. Chin [a, b], E. Mangaud [b, c], V. Chevet [d], O. Atabek [d], M. Desouter-Lecomte [a, e]

Some recent reviews...

OVERVIEW

WIREs COMPUTATIONAL MOLECULAR SCIENCE — WILEY

Different flavors of nonadiabatic molecular dynamics

Federica Agostini[1] | Basile F. E. Curchod[2]

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Email: federica.agostini@u-psud.fr

Funding information
Durham University

The Born-Oppenheimer approximation constitutes a cornerstone of our understanding of molecules and their reactivity, partly because it introduces a somewhat simplified representation of the *molecular wavefunction*. However, when a molecule absorbs light containing enough energy to trigger an electronic transition, the simplistic nature of the molecular wavefunction offered by the Born-Oppenheimer approximation breaks down as a result of the now non-negligible coupling between nuclear and electronic motion, often coined *nonadiabatic couplings*. Hence, the description of nonadiabatic processes implies a change in our representation of the molecular wavefunction, leading eventually to the design of new theoretical tools to describe the fate of an electronically-excited molecule. This Overview focuses on this quantity—the total molecular wavefunction—and the different approaches proposed to describe theoretically this complicated object in non-Born-Oppenheimer conditions, namely the Born-Huang and Exact-Factorization representations. The way each representation depicts the appearance of nonadiabatic effects is then revealed by using a model of a coupled proton–electron transfer reaction. Applying approximations to the formally exact equations of motion obtained within each representation leads to the derivation, or proposition, of different strategies to simulate the nonadiabatic dynamics of molecules. Approaches like quantum dynamics with fixed and time-dependent grids, traveling basis functions, or mixed quantum/classical like surface hopping, Ehrenfest dynamics, or coupled-trajectory schemes are described in this Overview.

This article is categorized under:
  Theoretical and Physical Chemistry > Reaction Dynamics and Kinetics
  Software > Simulation Methods
  Theoretical and Physical Chemistry > Spectroscopy

KEYWORDS
Born-Oppenheimer approximation, excited-state dynamics, nonadiabatic dynamics, photochemistry

1 | INTRODUCTION—NONADIABATIC DYNAMICS

A set of moving nuclei, held together by electrons—this can summarize a common and simple depiction of a molecule. This vision, however, indirectly implies that nuclear motion can be somehow separated from the electronic one, and that electrons quantum-mechanically glue the nuclei in a specific way. Both are direct consequences of invoking the so-called

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CHEMICAL REVIEWS

Review — Cite This: Chem. Rev. 2018, 118, 7026–7068 — pubs.acs.org/CR

Recent Advances and Perspectives on Nonadiabatic Mixed Quantum–Classical Dynamics

Rachel Crespo-Otero[*,†] and Mario Barbatti[*,‡]

[†] School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom
[‡] Aix Marseille Univ, CNRS, ICR, Marseille, France

ABSTRACT: Nonadiabatic mixed quantum–classical (NA-MQC) dynamics methods form a class of computational theoretical approaches in quantum chemistry tailored to investigate the time evolution of nonadiabatic phenomena in molecules and supermolecular assemblies. NA-MQC is characterized by a partition of the molecular system into two subsystems: one to be treated quantum mechanically (usually but not restricted to electrons) and another to be dealt with classically (nuclei). The two subsystems are connected through nonadiabatic couplings terms to enforce self-consistency. A local approximation underlies the classical subsystem, implying that direct dynamics can be simulated, without needing precomputed potential energy surfaces. The NA-MQC split allows reducing computational costs, enabling the treatment of realistic molecular systems in diverse fields. Starting from the three most well-established methods—mean-field Ehrenfest, trajectory surface hopping, and multiple spawning—this review focuses on the NA-MQC dynamics methods and programs developed in the last 10 years. It stresses the relations between approaches and their domains of application. The electronic structure methods most commonly used together with NA-MQC dynamics are reviewed as well. The accuracy and precision of NA-MQC simulations are critically discussed, and general guidelines to choose an adequate method for each application are delivered.

CONTENTS

ACS Publications — 7026 — © 2018 American Chemical Society — DOI: 10.1021/acs.chemrev.8b00177 — Chem. Rev. 2018, 118, 7026–7068

… and books

Multidimensional Quantum Dynamics
Edited by Hans-Dieter Meyer, Fabien Gatti and Graham A. Worth
WILEY-VCH
MCTDH Theory and Applications

Applications of Quantum Dynamics in Chemistry
Lecture Notes in Chemistry 98
Fabien Gatti
Benjamin Lasorne
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André Nauts
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Molecular Quantum Dynamics
Physical Chemistry in Action
Fabien Gatti *Editor*
From Theory to Applications
Springer

Quantum Chemistry and Dynamics of Excited States: Methods and Applications

Edited by Leticia González and Roland Lindh

(to be released, 2019)

WILEY

Further reading

- Michl, J. and Bonačić-Koutecký, V., *Electronic Aspects of Organic Photochemistry*, New York, Wiley, 1990.
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