Born-Oppenheimer Approximation

central to chemistry

separation slow (nuclear) and fast (electronic) motion

light electrons: QM (HF, DFT, ...), classical (MM)

heavy nuclei: QM (wavepacket/grid), classical (MD)

crux: nuclei move on single electronic PES

large energy gap between electronic states

derivation of Born-Oppenheimer

terms couple nuclear motion on different electronic PES

break down of Born-Oppenheimer approximation

small energy gap between electronic states

near surface crossings (degeneracies)

radiationless transition

adiabatic and diabatic electronic states

Born-Oppenheimer Approximation

molecular Schrödinger equation

$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi \qquad H\Psi = E\Psi$$

molecular Hamilton operator

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R})$$

with

$$T_N = -\frac{1}{2}\sum_i^{N_N}\frac{\hbar^2}{M_i}\nabla^2_{\mathbf{R}}$$

$$T_e = -\frac{\hbar^2}{2m_e}\sum_i^{n_e}\nabla^2_{\mathbf{r}}$$

$$U(\mathbf{r}, \mathbf{R}) = \frac{e^2}{4\pi\epsilon_0}\left(\sum_I^{N_N}\sum_{J>I}^{N_N}\frac{Z_I Z_J}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_I^{N_N}\sum_k^{n_e}\frac{Z_I}{|\mathbf{r}_k - \mathbf{R}_B|} + \sum_j^{n_e}\sum_{k>j}^{n_e}\frac{1}{|\mathbf{r}_k - \mathbf{r}_j|}\right)$$

Born-Oppenheimer Approximation

molecular Hamilton operator

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R})$$

step 1: clamped nuclei

separation of fast and slow degrees of freedom

$$T_N = 0$$

always possible, not an approximation!

sometimes wrong choice: coupling between ‘fast’ and ‘slow’ motions

consider only electronic degrees of freedom

$$H^e = T_e + U(\mathbf{r}, \mathbf{R})$$

electronic Schrödinger equation in field of fixed nuclei

$$H^e \psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R})$$

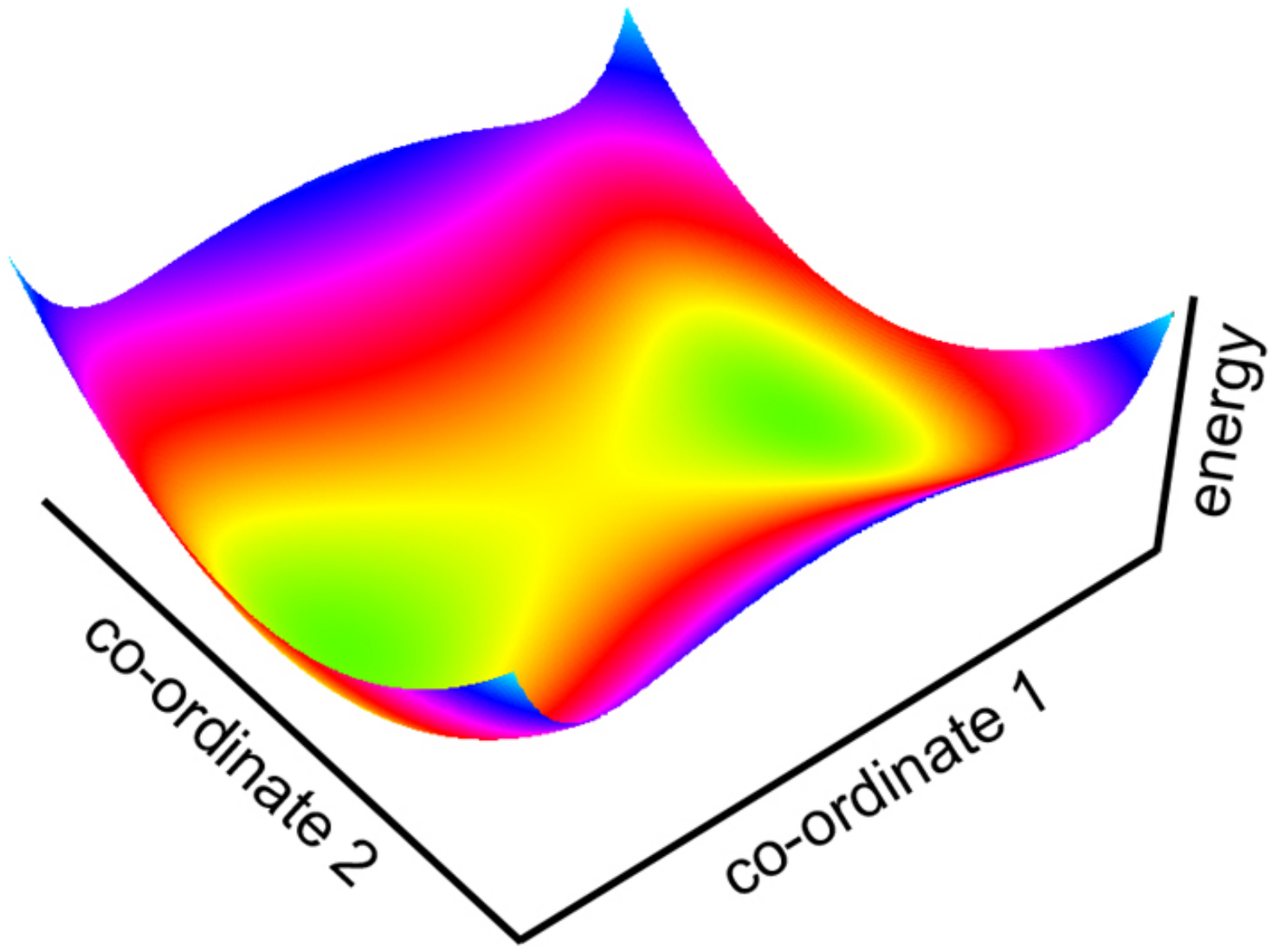
$i \geq 1$: CI, SA-CASSCF, MRCI

Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

electronic potential energy surface (PES)



Born-Oppenheimer Approximation

electronic Schrödinger equation in field of fixed nuclei

diagonalize electronic Hamiltonian

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

solution form orthogonal basis

adiabatic electronic states

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i(\mathbf{r};\mathbf{R})^* \psi_j(\mathbf{r};\mathbf{R}) d\mathbf{r} = \delta_{ij}$$

Born representation: expansion in electronic basis

expansion coefficients are nuclear wave functions

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_j \chi_j(\mathbf{R})\psi_j(\mathbf{r};\mathbf{R}),$$

no approximations so far!

Born-Oppenheimer Approximation

molecular wave function in Born representation

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_j \chi_j(\mathbf{R})\psi_j(\mathbf{r};\mathbf{R}),$$

$$H^e\psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

molecular Hamiltonian

$$H = T_N + T_e + U(\mathbf{r},\mathbf{R}) = T_N + H^e(\mathbf{R})$$

substitute and multiply from left by $\langle\psi_i|$ and integrate

$$\sum_j \langle\psi_i|H|\psi_j\rangle\chi_j(\mathbf{R}) = E\sum_j \langle\psi_i|\psi_j\rangle\chi_j(\mathbf{R})$$

Born-Oppenheimer Approximation

substitute and multiply from left by $\langle\psi_i|$ and integrate

$$\sum_j \langle\psi_i|H|\psi_j\rangle\chi_j(\mathbf{R}) = E\sum_j \langle\psi_i|\psi_j\rangle\chi_j(\mathbf{R})$$

using short-hand notation

$$\begin{aligned} H_{ij}(\mathbf{R}) &= \langle\psi_i(\mathbf{r};\mathbf{R})|H|\psi_j(\mathbf{r};\mathbf{R})\rangle \\ &= \langle\psi_i(\mathbf{r};\mathbf{R})|T_N|\psi_j(\mathbf{r};\mathbf{R})\rangle + V_i(\mathbf{R})\delta_{ij} \end{aligned}$$

coupled differential equations

$$\sum_j H_{ij}(\mathbf{R})\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R})$$

Born-Oppenheimer Approximation

elements of nuclear kinetic energy matrix

$$
\begin{aligned}
\langle\psi_i|T_N|\psi_j\rangle|\chi_j\rangle &= \frac{-\hbar^2}{2M_k}\langle\psi_i|\nabla^2_{\mathbf{R}}|\psi_j\rangle|\chi_j\rangle \\
&= \frac{-\hbar^2}{2M_k}\left(\langle\psi_i|\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{R}}|\psi_j\rangle\right)|\chi_j\rangle \\
&= \frac{-\hbar^2}{2M_k}\left(\langle\psi_i|\nabla_{\mathbf{R}}|\left[\nabla_{\mathbf{R}}\psi_j\right]\rangle + \langle\psi_i|\nabla_{\mathbf{R}}|\psi_j\rangle\nabla_{\mathbf{R}}\right)|\chi_j\rangle \\
&= \frac{-\hbar^2}{2M_k}(\langle\psi_i|\left[\nabla^2_{\mathbf{R}}\psi_j\right]\rangle + \langle\psi_i|\left[\nabla_{\mathbf{R}}\psi_j\right]\rangle\nabla_{\mathbf{R}} + \\
&\quad \langle\psi_i|\left[\nabla_{\mathbf{R}}\psi_j\right]\rangle\nabla_{\mathbf{R}} + \langle\psi_i|\psi_j\rangle\nabla^2_{\mathbf{R}})|\chi_j\rangle \\
&= \frac{-\hbar^2}{2M_k}(\langle\psi_i|\left[\nabla^2_{\mathbf{R}}\psi_j\right]\rangle + 2\langle\psi_i|\left[\nabla_{\mathbf{R}}\psi_j\right]\rangle\nabla_{\mathbf{R}} + \langle\psi_i|\psi_j\rangle\nabla^2_{\mathbf{R}})|\chi_j\rangle \\
&= \frac{-\hbar^2}{2M_k}(G_{ij} + 2\mathbf{F}_{ij}\nabla_{\mathbf{R}})|\chi_j\rangle + T_N\delta_{ij}|\chi_j\rangle \\
&= \left(T_N\delta_{ij} - \Lambda_{ij}\right)|\chi_j\rangle
\end{aligned}
$$

Born-Oppenheimer Approximation

substitute and multiply from left by $\langle\psi_i|$ and integrate

$$\sum_j H_{ij}(\mathbf{R})\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R})$$

collect all couplings in special operator

$$H_{ij}(\mathbf{R}) = \left[T_N + V_i(\mathbf{R})\right]\delta_{ij} - \Lambda_{ij}$$

coupled equations

coupling between nuclear wave packets on different electronic PES

coupling due to nuclear kinetic energy operator operating on electrons

kind of resonance with energy exchange

$$\left[T_N + V_i(\mathbf{R})\right]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R})$$

Born-Oppenheimer Approximation

coupled equations

$$\left[T_N + V_i(\mathbf{R})\right]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R})$$

non-adiabatic coupling operator matrix elements

$$\Lambda_{ij}(\mathbf{R}) = \sum_k \frac{\hbar^2}{2M_k}\left[2\mathbf{F}^k_{ij}(\mathbf{R})\nabla_{\mathbf{R}_k} + G^k_{ij}(\mathbf{R})\right]$$

with elements

$$\mathbf{F}^k_{ij}(\mathbf{R}) = \langle\psi_i(\mathbf{r};\mathbf{R})|\nabla_{\mathbf{R}_k}\psi_j(\mathbf{r};\mathbf{R})\rangle$$ non-adiabatic coupling vector

$$G^k_{ij}(\mathbf{R}) = \langle\psi_i(\mathbf{r};\mathbf{R})|\nabla^2_{\mathbf{R}_k}\psi_j(\mathbf{r};\mathbf{R})\rangle$$ scalar coupling

inversely proportional to nuclear mass!

small terms due to mass difference, but...

Born-Oppenheimer Approximation

non-adiabatic coupling vector

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} \psi_j(\mathbf{r};\mathbf{R}) \rangle$$

using the following relation

$$\nabla_{\mathbf{R}} H^e(\mathbf{r};\mathbf{R}) \psi_j(\mathbf{r};\mathbf{R}) = \nabla_{\mathbf{R}} V_j(\mathbf{R}) \psi_j(\mathbf{r};\mathbf{R})$$

and some lines of algebra to show that

Hellman-Feynmann term

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r};\mathbf{R}) \rangle}{V_j - V_i}$$

... coupling inversely proportional to energy gap!

Born-Oppenheimer Approximation

non-adiabatic coupling matrix element

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} \psi_j(\mathbf{r};\mathbf{R}) \rangle$$

no diagonal elements

$$\mathbf{F}_{ii}^{k}(\mathbf{R}) = 0$$

because

$$\begin{aligned}
\nabla_{\mathbf{R}} \langle \psi_i | \psi_i \rangle &= 0 \\
\langle \nabla_{\mathbf{R}} \psi_i | \psi \rangle + \langle \psi_i | \nabla_{\mathbf{R}} \psi_i \rangle &= 0 \\
\langle \psi_i | \nabla_{\mathbf{R}} \psi \rangle + \mathrm{c.c} &= 0
\end{aligned}$$

Born-Oppenheimer Approximation

nuclear Schrödinger in Born representation

$$\left[T_N + V_i(\mathbf{R})\right]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R})$$

coupling between nuclear wavepackets on different PES

Born-Oppenheimer approximation: $\Lambda = \Lambda_{ii}$

$$\left[T_N + V_i(\mathbf{R}) - \Lambda_{ii}\right]\chi_i(\mathbf{R}) = E\chi_i(\mathbf{R})$$

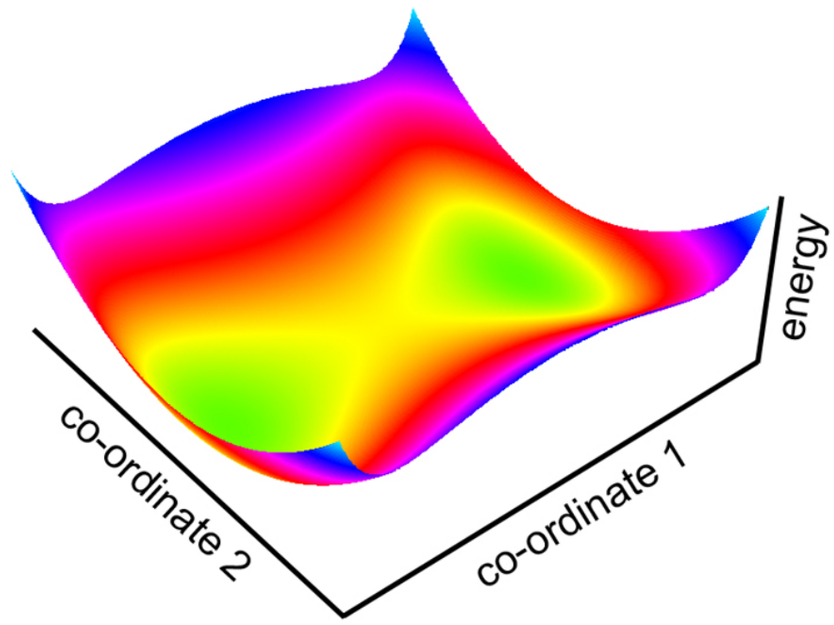
nuclear wavepackets restricted to single electronic PES

$$\Psi_i^{\mathrm{tot}}(\mathbf{R},\mathbf{r}) = \chi_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

adiabatic approximation: $\Lambda = 0$

$$\left[T_N + V_i(\mathbf{R})\right]\chi_i(\mathbf{R}) = E\chi_i(\mathbf{R})$$

mostly used in quantum chemistry



Born-Oppenheimer Approximation

nuclear Schrödinger in Born representation

$$\left[T_N + V_i(\mathbf{R})\right]\chi_i(\mathbf{R}) - \sum_j \Lambda_{ij}\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R})$$

using atomic units and *scaled* coordinates

$$T_N = -\frac{1}{2M}\nabla^2_{\mathbf{R}}$$

$$\Lambda_{ij} = \frac{1}{2M}\left(2\mathbf{F}_{ij}\cdot\nabla_{\mathbf{R}} + G_{ij}\right))$$

$$\mathbf{F}_{ij} = \langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \qquad G_{ij} = \langle\psi_i|\nabla^2_{\mathbf{R}}\psi_j\rangle$$

Born-Oppenheimer Approximation

using atomic units and scaled coordinates

$$T_N = -\frac{1}{2M}\nabla^2_{\mathbf{R}}$$

$$\Lambda_{ij} = \frac{1}{2M}\left(2\mathbf{F}_{ij}\cdot\nabla_{\mathbf{R}} + G_{ij}\right)$$

$$\mathbf{F}_{ij} = \langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle \qquad G_{ij} = \langle\psi_i|\nabla^2_{\mathbf{R}}\psi_j\rangle$$

using the relation

$$\mathbf{G} = \nabla_{\mathbf{R}}\cdot\mathbf{F} + \mathbf{F}\cdot\mathbf{F}$$

one arrives at

$$\left[-\frac{1}{2M}\left(\nabla_{\mathbf{R}} + \mathbf{F}\right)^2 + \mathbf{V}\right]\boldsymbol{\chi} = E\boldsymbol{\chi}$$

Born-Oppenheimer Approximation

nuclear Schrödinger in vector notation

$$\left[-\frac{1}{2M}\left(\nabla_{\mathbf{R}}+\mathbf{F}\right)^2+\mathbf{V}\right]\boldsymbol{\chi}=E\boldsymbol{\chi}$$

<u>dressed</u> kinetic energy operator

$$\tilde{T}_N=-\frac{1}{2M}\left(\nabla_{\mathbf{R}}+\mathbf{F}\right)^2 \qquad \mathbf{F}_{ij}=\langle\psi_i|\nabla_{\mathbf{R}}\psi_j\rangle$$

non local & non diagonal

couples nuclear dynamics on multiple electronic PES

induces radiationless transitions!

potential energy operator

local & diagonal

no coupling

Born-Oppenheimer Approximation

non-adiabatic coupling vector

$$\mathbf{F}_{ij}^{k}(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r};\mathbf{R}) \rangle}{V_j - V_i}$$

inversely proportional with gap!

break down of adiabatic approximation!

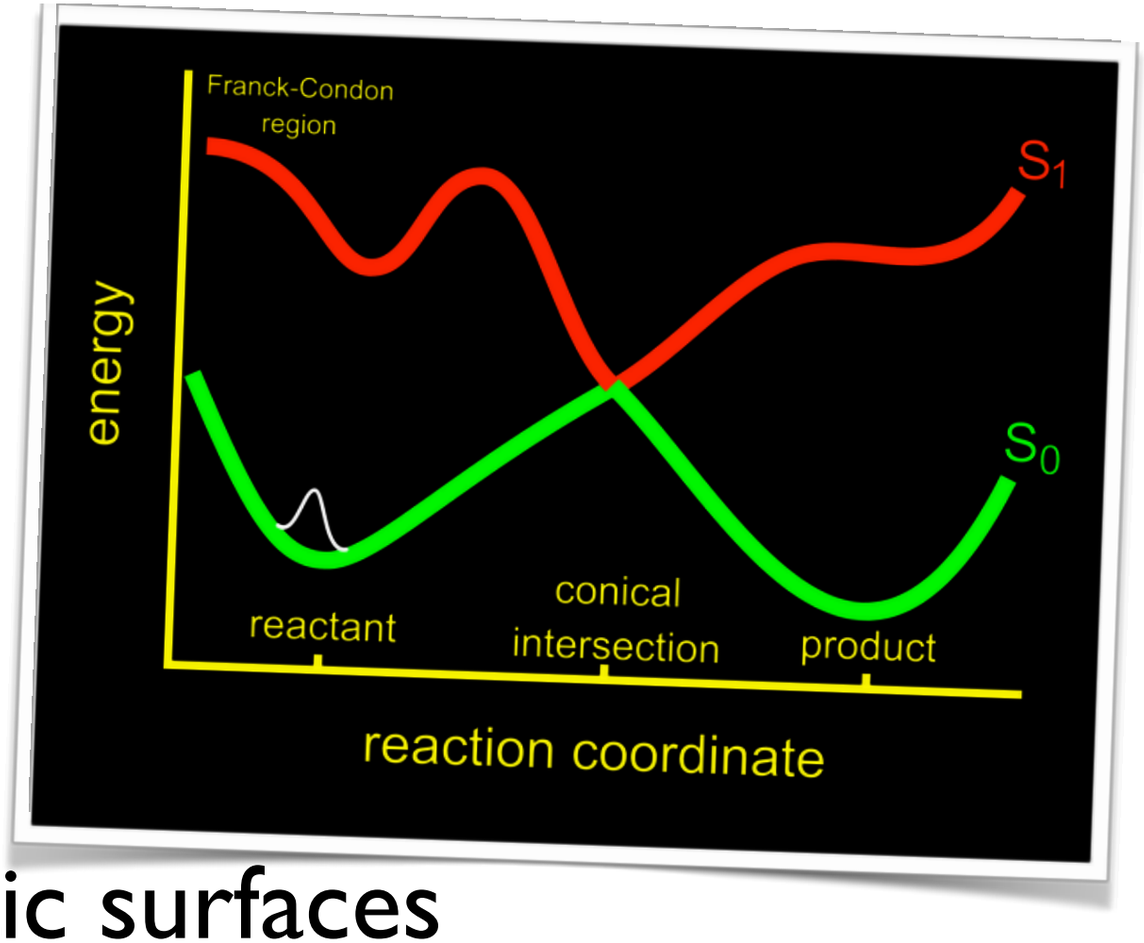
non-adiabatic dynamics

multiple surfaces

branching

interference/coherence

photochemistry



intersection between adiabatic surfaces

Born-Oppenheimer Approximation

adiabatic electronic basis

diagonal & local potential matrix

$$\langle \psi_i | H^e | \psi_j \rangle = \delta_{ij} V_j$$

non-diagonal & non-local nuclear kinetic energy matrix

$$\langle \psi_i | T_N | \psi_j \rangle = -\frac{1}{2M} \left(\nabla_{\mathbf{R}} + \langle \psi_i | \nabla_{\mathbf{R}} | \psi_j \rangle \right)^2$$

coupling in $\mathbf{F}$

diabatic representation

non-diagonal & local potential matrix

$$\langle \varphi_i | H^e | \varphi_j \rangle = W_{ij}$$

coupling in $\mathbf{W}$

diagonal nuclear kinetic energy matrix

$$\langle \varphi_i | T_N | \varphi_j \rangle = -\frac{\delta_{ij}}{2M} \nabla^2_{\mathbf{R}}$$

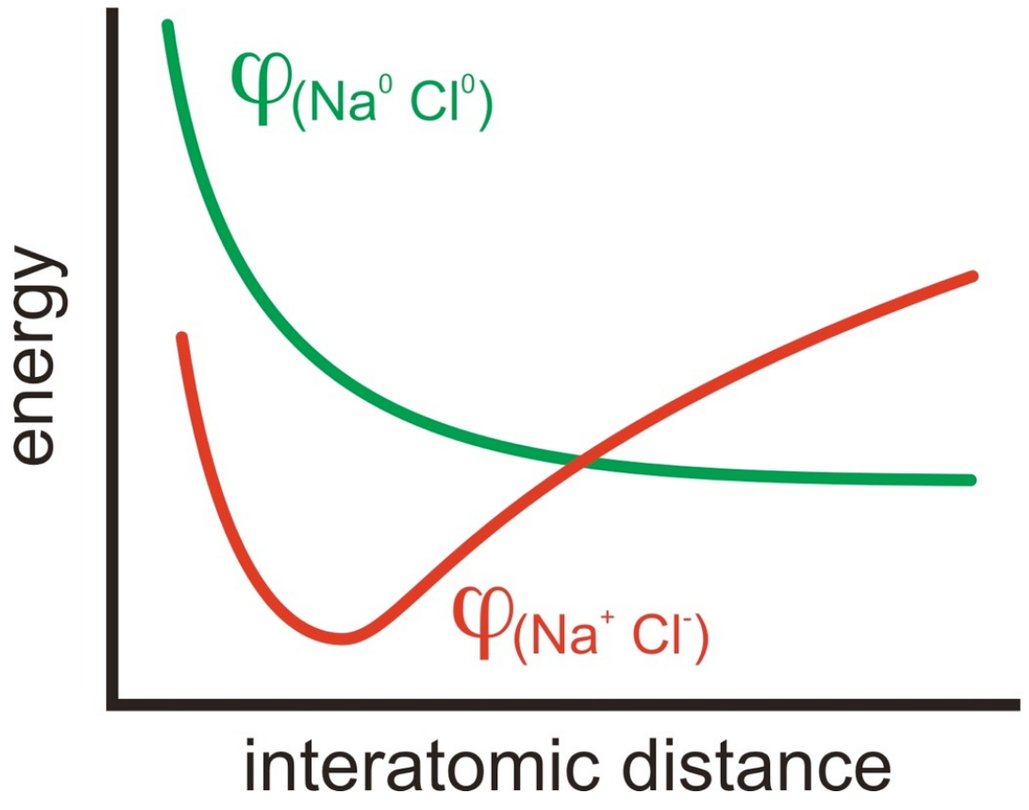
Born-Oppenheimer Approximation

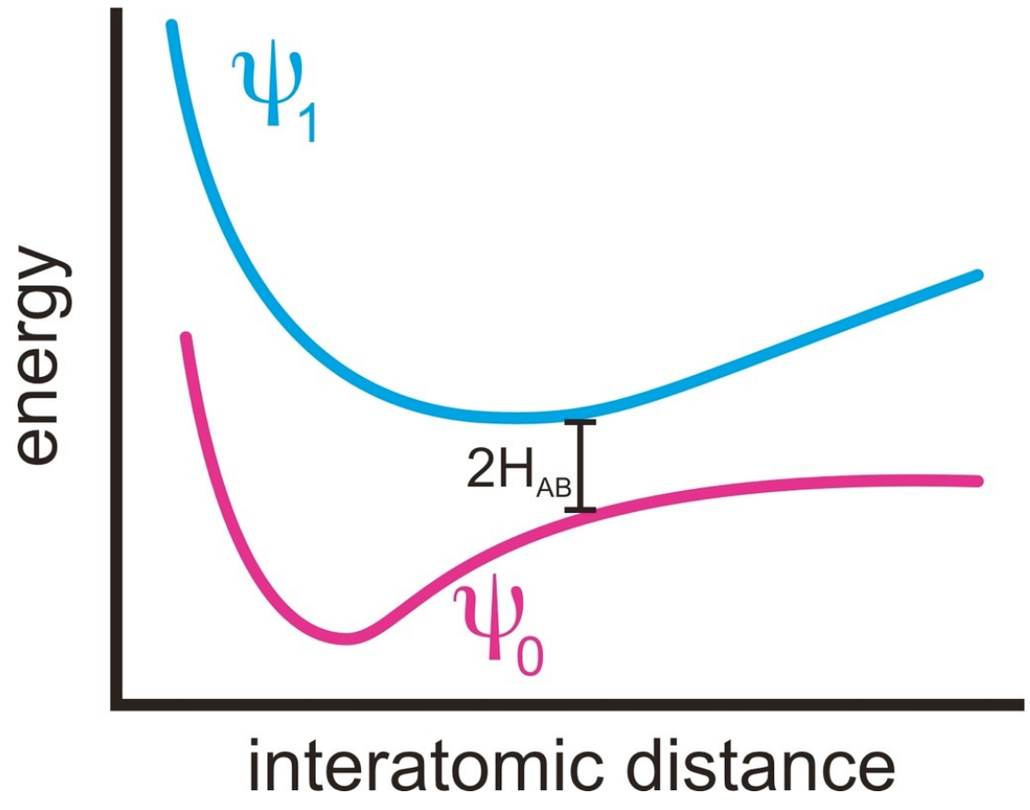
diabatic electronic basis

electronic character preserved

adiabatic electronic basis

electronic character mixed





Born-Oppenheimer Approximation

diabatic representation

non-diagonal & local potential matrix

$$\langle \varphi_i | H^e | \varphi_j \rangle = W_{ij}$$

diagonal nuclear kinetic energy matrix

$$\langle \varphi_i | T_N | \varphi_j \rangle = -\frac{\delta_{ij}}{2M} \nabla^2_{\mathbf{R}}$$

molecular Hamiltonian

$$H_{ij} = T_N \delta ij + W_{ij}$$

molecular Schrödinger equation

$$\sum_j H_{ij}\chi_j = T_N \chi_i + \sum_j W_{ij}\chi_j = E\chi_i$$

$$\mathbf{H}\boldsymbol{\chi} = \left[T_N \mathbf{1} + \mathbf{W}(\mathbf{R})\right]\boldsymbol{\chi} = E\boldsymbol{\chi}$$

Born-Oppenheimer Approximation

construction of diabatic basis

unitary transformation for each nuclear configuration

$$\varphi_i(\mathbf{r};\mathbf{R}) = \sum_j \psi_j(\mathbf{r};\mathbf{R}) U_{ji}(\mathbf{R})$$

construction of diabatic Hamiltonian

kinetic energy (diagonal)

$$T_N^d \mathbf{1} = \mathbf{U}^\dagger \tilde{\mathbf{T}}_N \mathbf{U}$$

dressed kinetic energy operator

$$\tilde{\mathbf{T}}_N = -\frac{1}{2M}\left(\nabla_{\mathbf{R}} + \mathbf{F}\right)^2 \qquad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

transformation should nullify non-adiabatic coupling

Born-Oppenheimer Approximation

construction of diabatic Hamiltonian

dressed kinetic energy operator

$$\tilde{\mathbf{T}}_N = -\frac{1}{2M}\left(\nabla_{\mathbf{R}} + \mathbf{F}\right)^2 \qquad \mathbf{F}_{ij} = \langle \psi_i | \nabla_{\mathbf{R}} \psi_j \rangle$$

transformation should nullify non-adiabatic coupling

$$\begin{aligned}
\langle \varphi_i | \nabla_{\mathbf{R}} \varphi_j \rangle &= \sum_k \sum_l U^*_{ki}(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} U_{lj}(\mathbf{R}) \psi_l \rangle \\
&= \sum_k \sum_l \left[U^*_{ki}(\mathbf{R} \langle \psi_k | \psi_l \rangle \nabla_{\mathbf{R}} U_{lj}(\mathbf{R}) + U^*_{ki}(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} | \psi_l \rangle U_{lj}(\mathbf{R}) \right] \\
&= \underline{\sum_k U^*_{ki} \nabla_{\mathbf{R}} U_{kj}} + \underline{\sum_k \sum_l U^*_{ki}(\mathbf{R}) \langle \psi_k | \nabla_{\mathbf{R}} | \psi_l \rangle U_{lj}(\mathbf{R})}
\end{aligned}$$

find $\mathbf{U}$ such that

$$\underline{\mathbf{U^T F U}} + \underline{\mathbf{U^T} \nabla_{\mathbf{R}} \mathbf{U}} = \mathbf{0}$$

Born-Oppenheimer Approximation

derivation

separation between fast and slow degrees of freedom

nuclei move on single adiabatic PES

ignore non-adiabatic coupling

breakdown

small energy gap between electronic PES

at intersections infinite non-adiabatic coupling

nuclear displacement couple different adiabatic states

highly complicated nuclear wave function

switch to diabatic basis

only electronic coupling

unitary transformation

Conical Intersection

surface crossings

funnels for photochemical reactions

conditions for crossing between two electronic states

adiabatic representation

two coordinates needed to locate intersection

two coordinates needed to lift degeneracy

topology of intersection

double cone

$2N$-8 dimensional hyperline

properties of intersection

Berry phase

singularity due to separation between electronic and nuclear motion

compensated by nuclear wavefunction (complicated!)

Conical Intersection

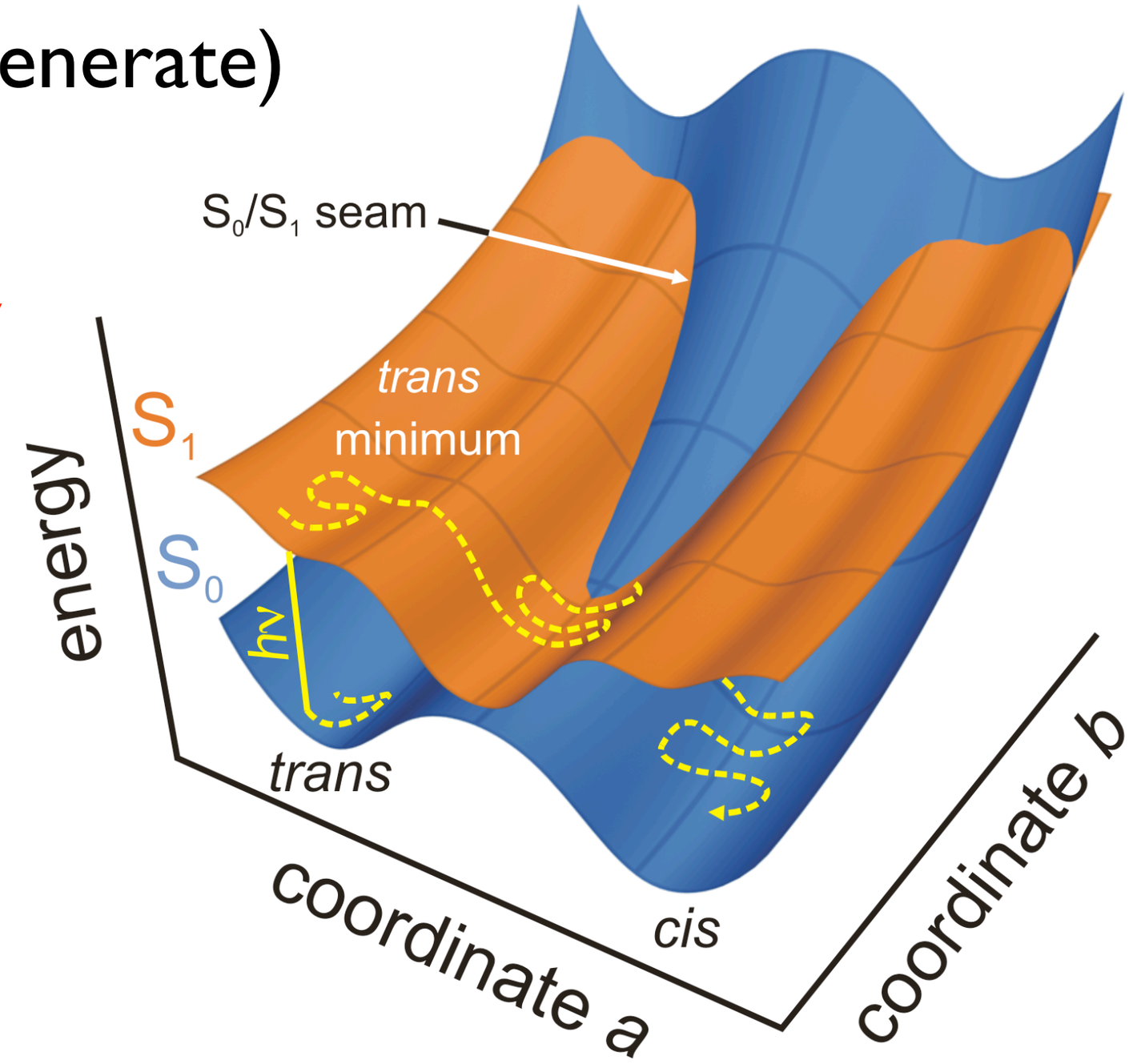
adiabatic surfaces

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

can cross (are degenerate)

$$V_i(\mathbf{R}) = V_j(\mathbf{R})$$

radiationless decay



Conical Intersection

adiabatic surfaces

$$H^e \psi_i(\mathbf{r};\mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r};\mathbf{R})$$

can cross (are degenerate)

$$V_i(\mathbf{R}) = V_j(\mathbf{R})$$

break-down of Born-Oppenheimer

non-adiabatic coupling becomes infinite!

$$\mathbf{F}_{ij}^k(\mathbf{R}) = \frac{\langle \psi_i(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r};\mathbf{R}) \rangle}{V_j - V_i}$$

switch to diabatic basis

no non-adiabatic coupling

back to adiabatic basis by diagonalizing $\mathbf{W}$

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

$$V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

construct mixed diabatic/adiabatic basis at $\mathbf{R}_0$

via unitary transformation

$$\{\varphi_2, \varphi_1, \psi_3, ..., \psi_n\}$$

orthonormal

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} \quad \langle\varphi_I|\varphi_J\rangle = \delta_{IJ} \quad \langle\varphi_I|\psi_j\rangle = 0$$

diabatic and adiabatic energies for two lowest states

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_1(\mathbf{R}_0)$$

adiabatic wave functions

$$\psi_1 = c_{11}\varphi_1 + c_{12}\varphi_2 \qquad \psi_2 = c_{21}\varphi_1 + c_{22}\varphi_2$$

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

$$V_1(\mathbf{R}_0) = V_2(\mathbf{R}_0)$$

transformation to mixed diabatic/adiabatic basis at $\mathbf{R}_0$

diabatic electronic energies

$$E_1(\mathbf{R}_0) = E_2(\mathbf{R}_0) = V_1(\mathbf{R}_0) = V_1(\mathbf{R}_0)$$

$$\mathbf{W}(\mathbf{R}_0) = \mathbf{V}(\mathbf{R_0})$$

$$W_{ij} = H_{ij} = \langle \varphi_i | H^e | \varphi_j \rangle$$

$$\mathbf{W}(\mathbf{R_0}) = \begin{pmatrix} H_{11}(\mathbf{R_0}) & H_{12}(\mathbf{R_0}) \\ H_{12}(\mathbf{R_0}) & H_{22}(\mathbf{R_0}) \end{pmatrix}$$

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

diabatic electronic energies

$$\mathbf{W}(\mathbf{R_0}) = \begin{pmatrix} H_{11}(\mathbf{R_0}) & H_{12}(\mathbf{R_0}) \\ H_{12}(\mathbf{R_0}) & H_{22}(\mathbf{R_0}) \end{pmatrix}$$

adiabatic electronic energies

diagonalize $\mathbf{W}$

$$V_1(\mathbf{R_0}) = \left(\frac{H_{11}+H_{22}}{2}\right) - \sqrt{\left(\frac{H_{11}-H_{22}}{2}\right)^2 + H_{12}^2}$$

$$V_2(\mathbf{R_0}) = \left(\frac{H_{11}+H_{22}}{2}\right) + \sqrt{\left(\frac{H_{11}-H_{22}}{2}\right)^2 + H_{12}^2}$$

degeneracy (crossing) if

$$H_{11} = H_{22} \wedge H_{12} = 0$$

independent: 2 coordinates required to locate degeneracy

degeneracy preserved in N-8 remaining internal coordinates

Conical Intersection

degeneracy between two electronic states at $\mathbf{R}_0$

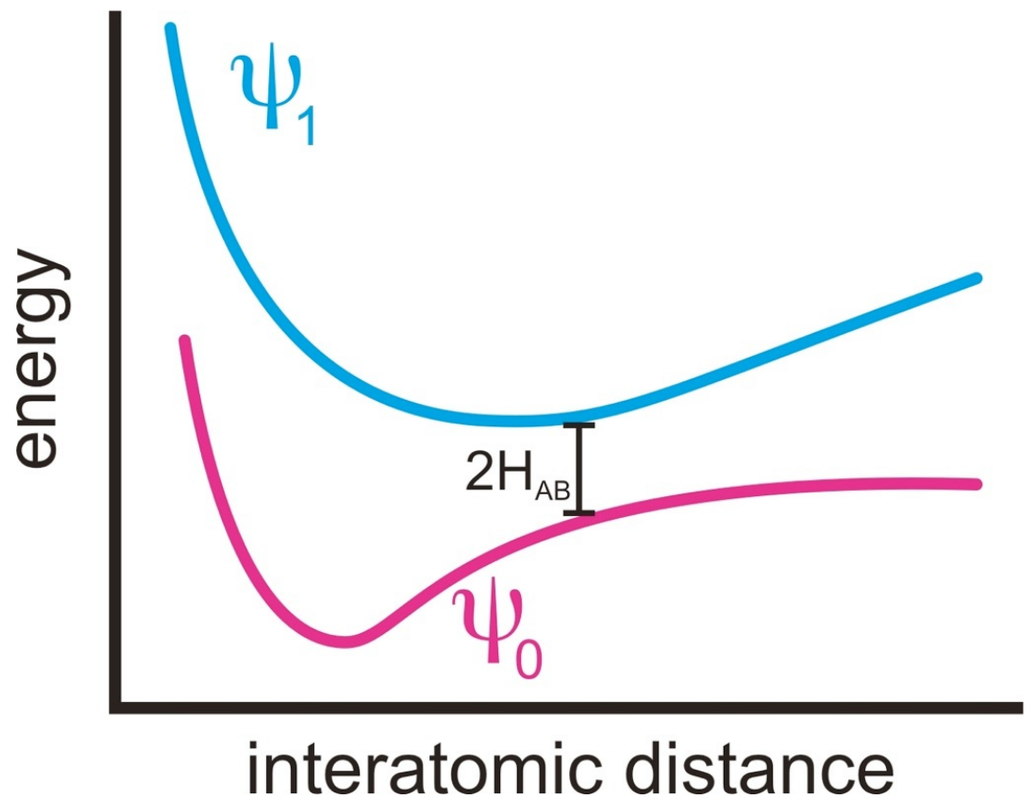
two coordinates required to locate degeneracy

degeneracy (crossing) if

$$H_{11} = H_{22} \wedge H_{12} = 0$$

non-crossing rule

diatomics



Conical Intersection

topology of intersection

expand $\mathbf{W}$ around $\mathbf{R}_0$

$$\mathbf{W}(\mathbf{R}-\mathbf{R}_0) = \mathbf{W}^{(0)} + \mathbf{W}^{(1)} + \mathbf{W}^{(2)} + \ldots$$

zeroth order term

$$\mathbf{W}^{(0)} = \frac{E_A+E_B}{2}\mathbf{1} + \begin{pmatrix} -\frac{E_B-E_A}{2} & 0 \\ 0 & \frac{E_B-E_A}{2} \end{pmatrix}$$

offset, set to zero for convenience

$$\mathbf{W}^{(0)} = \mathbf{0}$$

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}}\left(\frac{H_{11}+H_{22}}{2}\right)\cdot\Delta\mathbf{R} + \nabla_{\mathbf{R}}\left(\frac{H_{11}-H_{22}}{2}\right)\Delta\mathbf{R} & \nabla_{\mathbf{R}}H_{12}\cdot\Delta\mathbf{R} \\ \nabla_{\mathbf{R}}H_{12}\cdot\Delta\mathbf{R} & \nabla_{\mathbf{R}}\left(\frac{H_{11}+H_{22}}{2}\right)\cdot\Delta\mathbf{R} - \nabla_{\mathbf{R}}\left(\frac{H_{11}-H_{22}}{2}\right)\Delta\mathbf{R} \end{pmatrix}$$

$$\Delta\mathbf{R} = \mathbf{R}_0 - \mathbf{R}$$

Conical Intersection

topology of intersection

first order term

$$\mathbf{W}^{(1)} = \begin{pmatrix} \nabla_{\mathbf{R}} \left(\frac{H_{11}+H_{22}}{2}\right) \cdot \Delta\mathbf{R} + \nabla_{\mathbf{R}} \left(\frac{H_{11}-H_{22}}{2}\right) \Delta\mathbf{R} & \nabla_{\mathbf{R}} H_{12} \cdot \Delta\mathbf{R} \\ \nabla_{\mathbf{R}} H_{12} \cdot \Delta\mathbf{R} & \nabla_{\mathbf{R}} \left(\frac{H_{11}+H_{22}}{2}\right) \cdot \Delta\mathbf{R} - \nabla_{\mathbf{R}} \left(\frac{H_{11}-H_{22}}{2}\right) \Delta\mathbf{R} \end{pmatrix}$$

$$\mathbf{W}^{(1)} = \begin{pmatrix} \mathbf{s} \cdot \Delta\mathbf{R} + \mathbf{g} \cdot \Delta\mathbf{R} & \mathbf{h} \cdot \Delta\mathbf{R} \\ \mathbf{h} \cdot \Delta\mathbf{R} & \mathbf{s} \cdot \boldsymbol{\Delta}\mathbf{R} - \mathbf{g} \cdot \boldsymbol{\Delta}\mathbf{R} \end{pmatrix}$$

average gradient vector

$$\mathbf{s} = \nabla_{\mathbf{R}} \frac{H_{11} + H_{22}}{2} | \mathbf{R}_0$$

gradient difference vector

$$\mathbf{g} = \nabla_{\mathbf{R}} \frac{H_{11} - H_{22}}{2} | \mathbf{R}_0$$

derivative coupling vector

$$\mathbf{h} = \nabla_{\mathbf{R}} H_{12} | \mathbf{R}_0$$

Conical Intersection

topology of intersection

keeping only terms to first order

$$\mathbf{W}(\Delta\mathbf{R}) \approx \mathbf{W}^{(0)} + \mathbf{W}^{(1)}$$

set zeroth order term to zero (just an offset)

$$\mathbf{W}(\Delta\mathbf{R}) \approx \begin{pmatrix} \mathbf{s}\cdot\Delta\mathbf{R} + \mathbf{g}\cdot\Delta\mathbf{R} & \mathbf{h}\cdot\Delta\mathbf{R} \\ \mathbf{h}\cdot\Delta\mathbf{R} & \mathbf{s}\cdot\boldsymbol{\Delta}\mathbf{R} - \mathbf{g}\cdot\boldsymbol{\Delta}\mathbf{R} \end{pmatrix}$$

diagonalize to get adiabatic PES

$$V_1(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} - \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

$$V_2(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} + \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

Conical Intersection

topology of intersection

eigenvalues of **W**

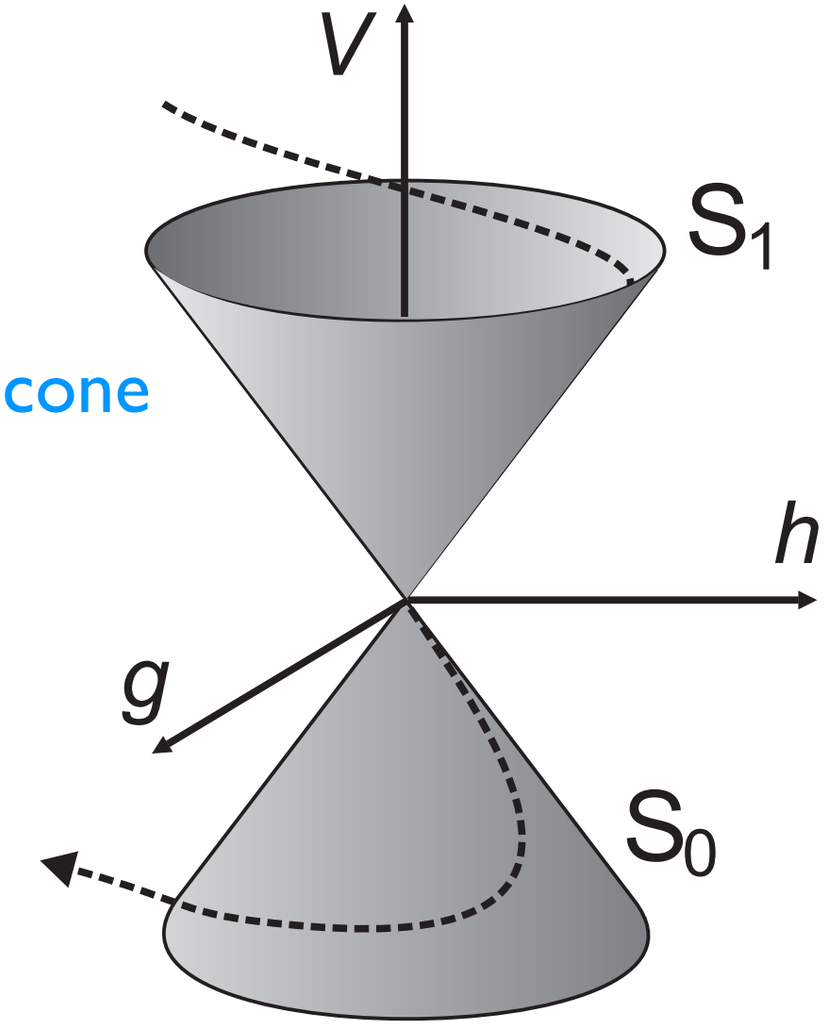
$$V_1(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} - \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

$$V_2(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} + \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

double cone in branching space (g-h space)

adiabatic surfaces touch at tip

average gradient projected on g-h gives tilt of cone



Conical Intersection

topology of intersection

eigenvalues of $\mathbf{W}$

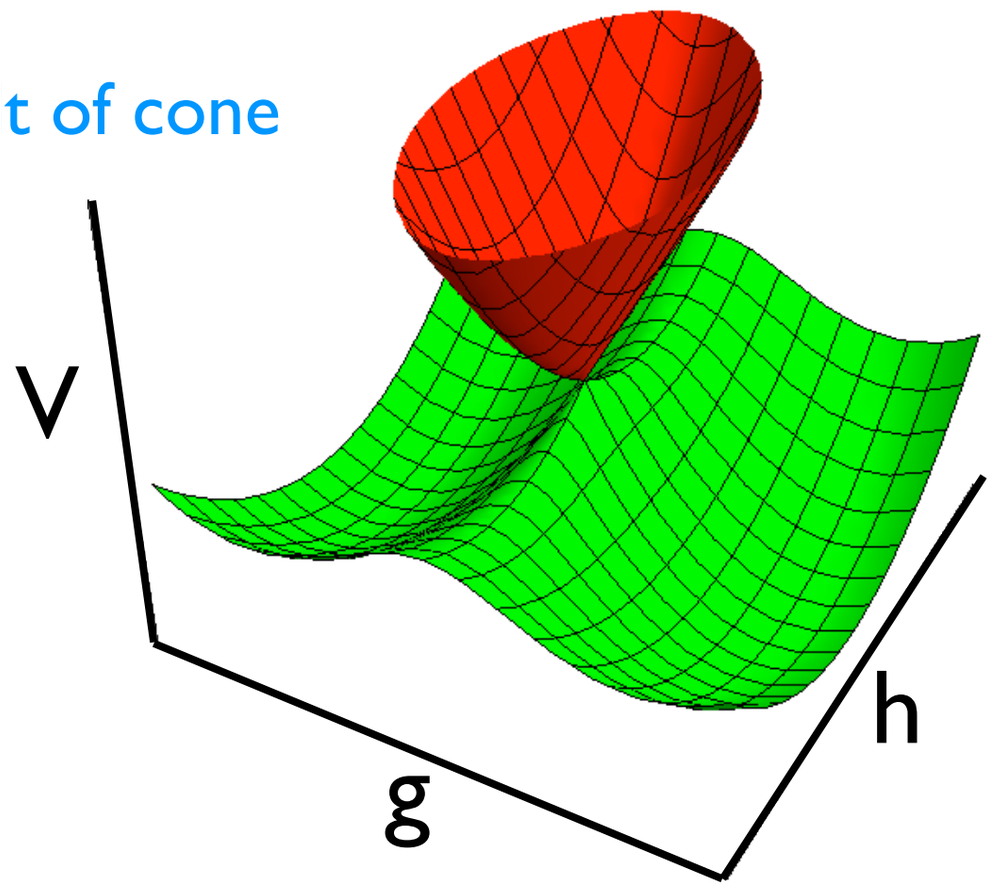
$$V_1(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} - \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

$$V_2(\Delta\mathbf{R}) = \mathbf{s}\cdot\Delta\mathbf{R} + \sqrt{(\mathbf{g}\cdot\Delta\mathbf{R})^2 + (\mathbf{h}\cdot\Delta\mathbf{R})^2}$$

double cone in branching space (g-h space) to first order!

adiabatic surfaces touch at tip

average gradient projected on g-h gives tilt of cone



Conical Intersection

back to adiabatic basis

degeneracy requires (to first order) that

$$\mathbf{g} \cdot \Delta\mathbf{R} = 0 \wedge \mathbf{h} \cdot \Delta\mathbf{R}$$

independent: accidental same-symmetry intersection

two coordinate need to change to locate intersection

single degree of freedom: non-crossing rule in diatomics

degeneracy lifted in branching space

degeneracy maintained in $3N$-8 remaining degree of freedom

Conical Intersection

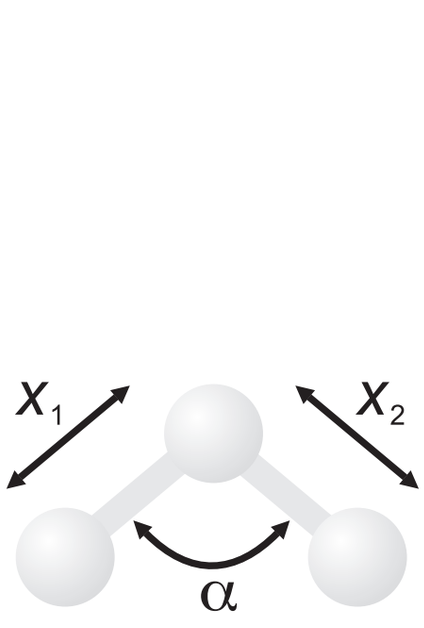
back to adiabatic basis

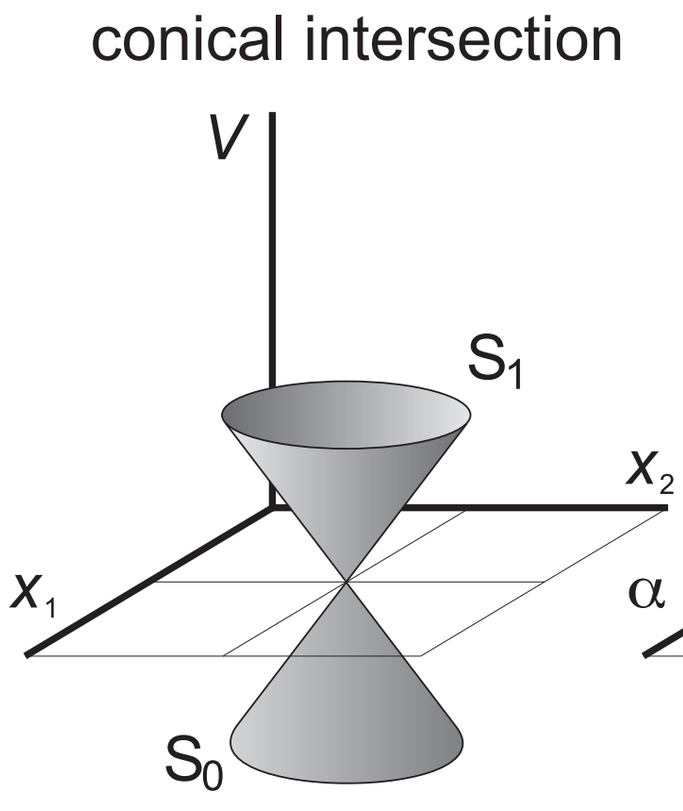
degeneracy lifted in branching space

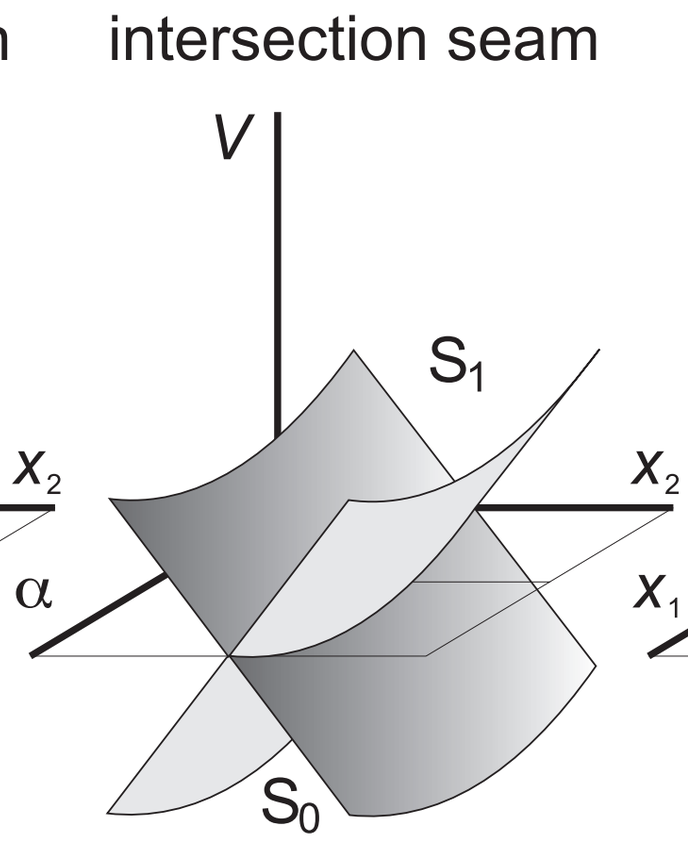
$$\mathbf{x}_1 = \|\mathbf{g}\| \qquad \mathbf{x}_2 = \|\mathbf{h}\|$$

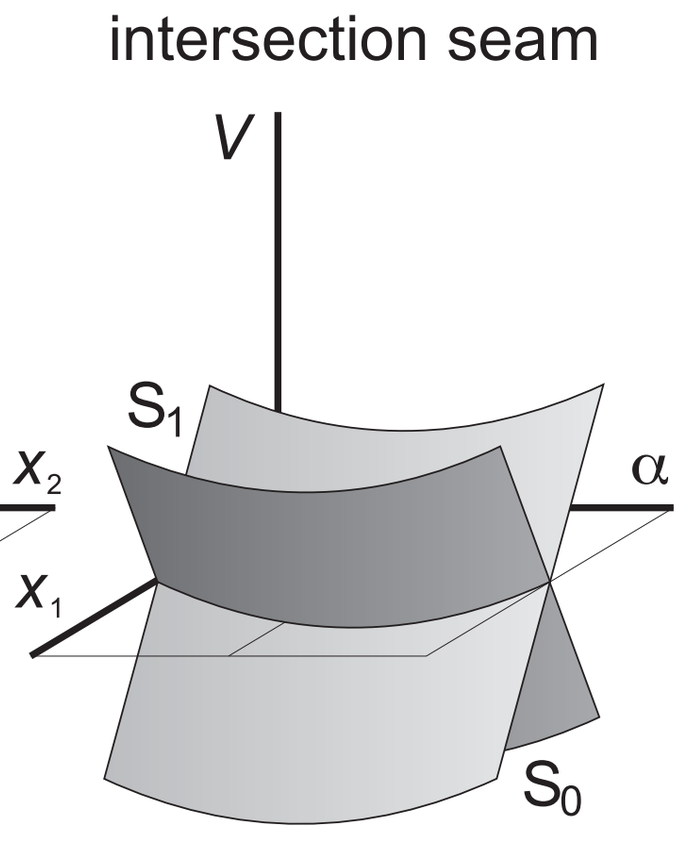
degeneracy maintained in $3N$-8 remaining degree of freedom

tri-atomics: hypothetical example









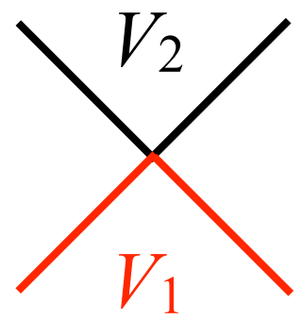
Conical Intersection

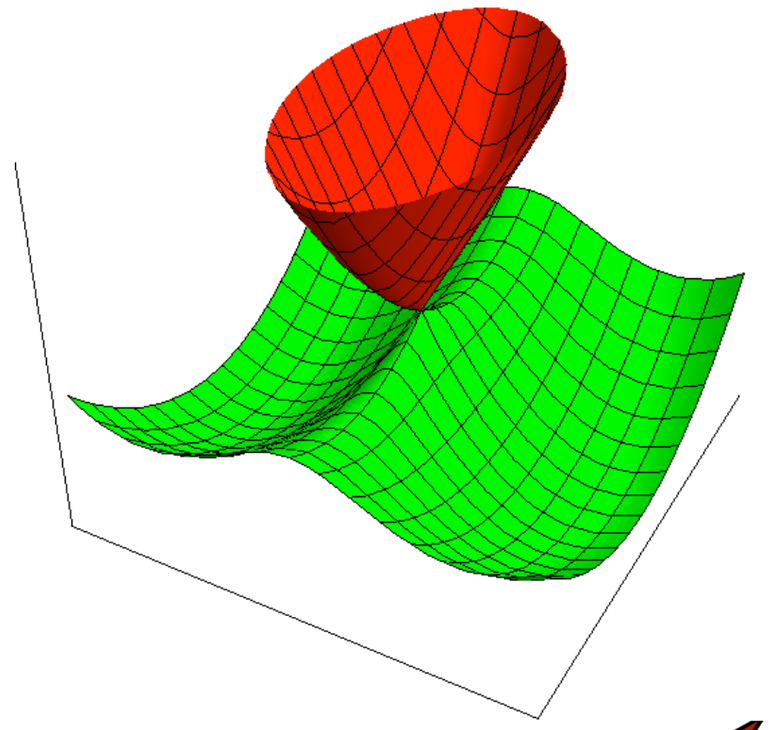
average gradient (**s**)determines tilt of double cone

peaked

photoreactivity

$$\mathbf{s}\cdot\mathbf{g}\approx\mathbf{0}\quad\mathbf{s}\cdot\mathbf{h}\approx\mathbf{0}$$

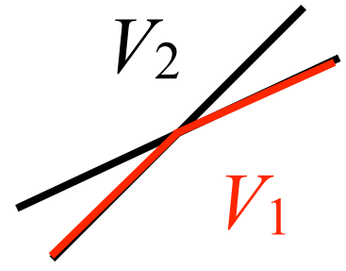


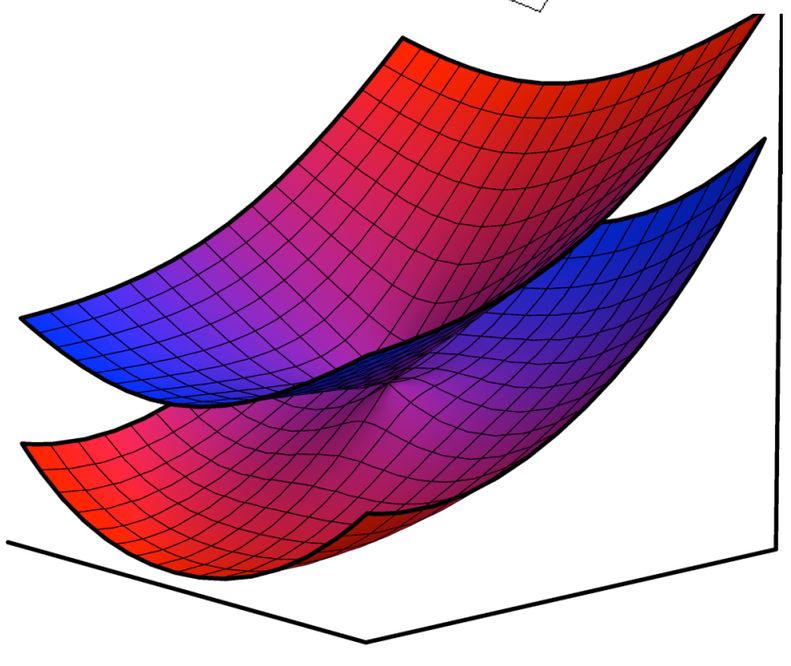


sloped

photostability

$$\mathbf{s}\cdot\mathbf{g}>\mathbf{0}$$





all are $3N$-8 dimensional hyperlines

impossible to hit

compare point in plane

possible to get near

coupling strong enough for transition

Conical Intersection

they are everywhere!

Conical Intersection

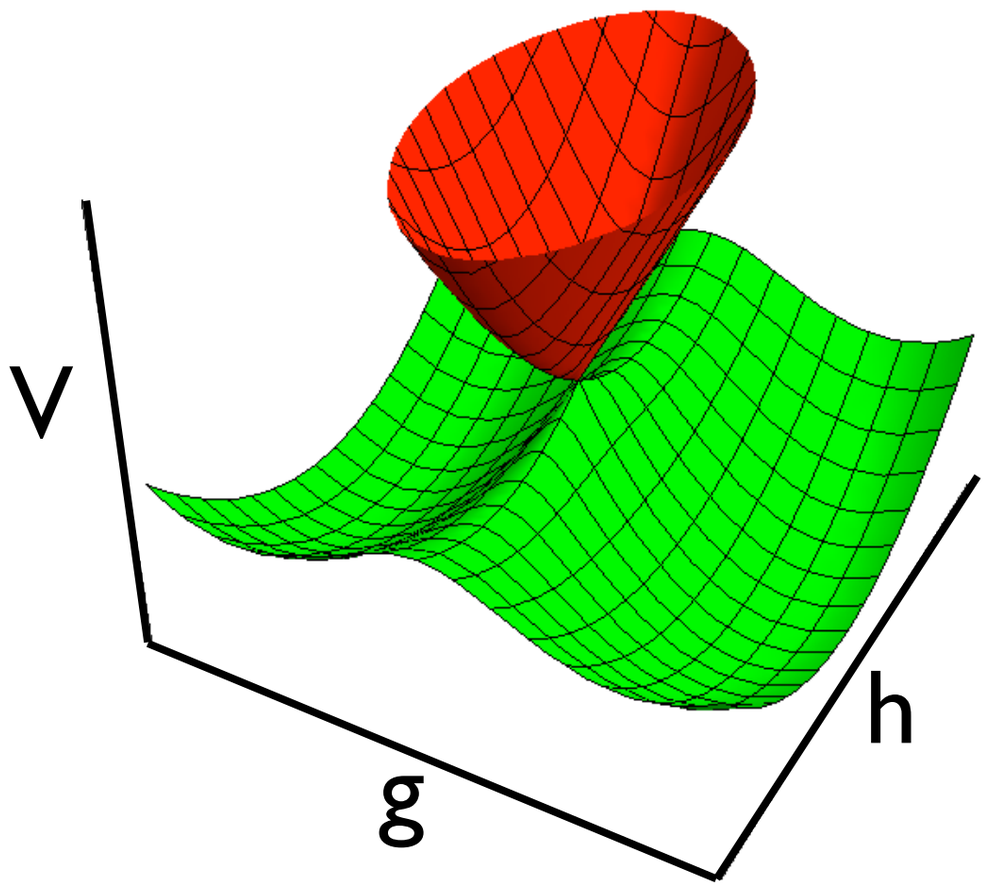
finding them

electronic structure of excited & ground state: SA-CASSCF

optimization on S_1 in N-2 internal degrees of freedom

minimize gap in g-h plane

example for practical



Conical Intersection

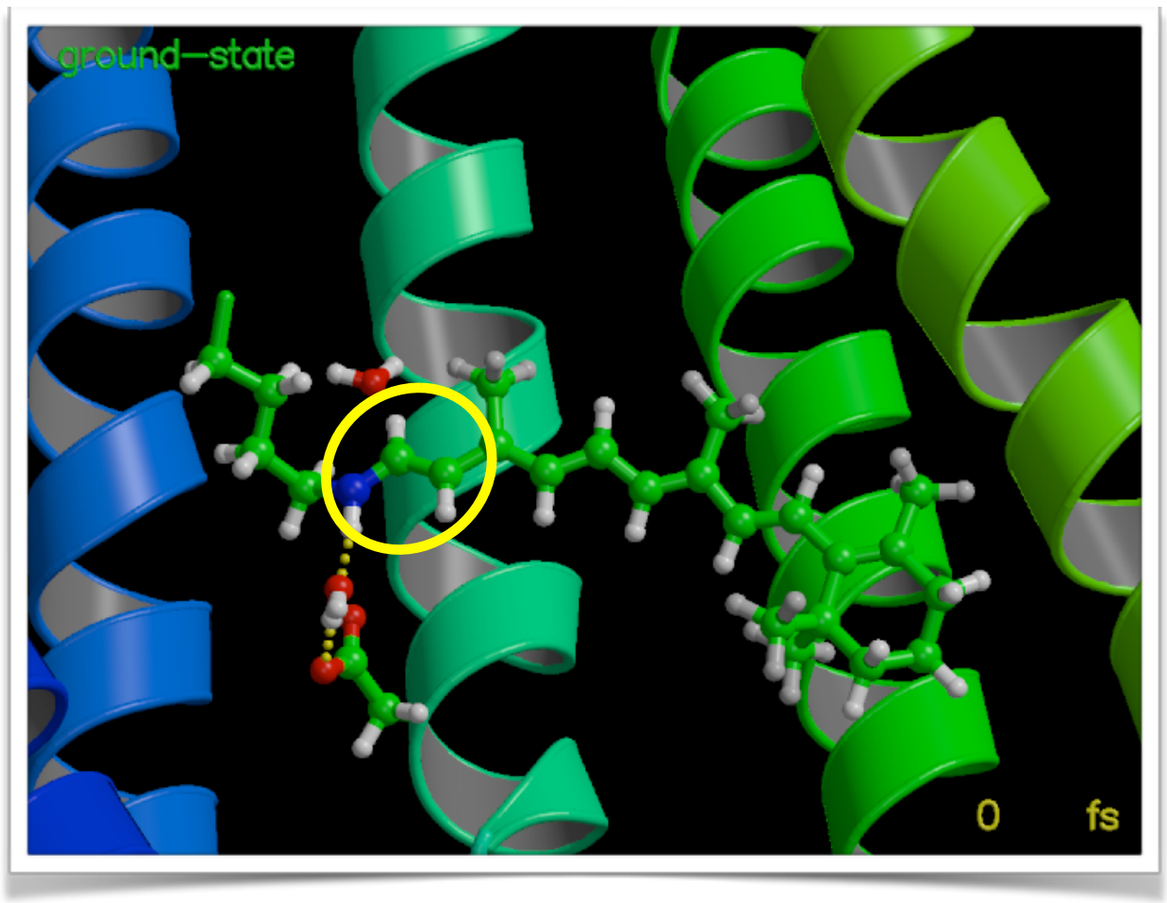
finding them

electronic structure of excited & ground state: SA-CASSCF

optimization on S_1 in N-2 internal degrees of freedom

minimize gap in g-h plane

example for practical: photoisomerization



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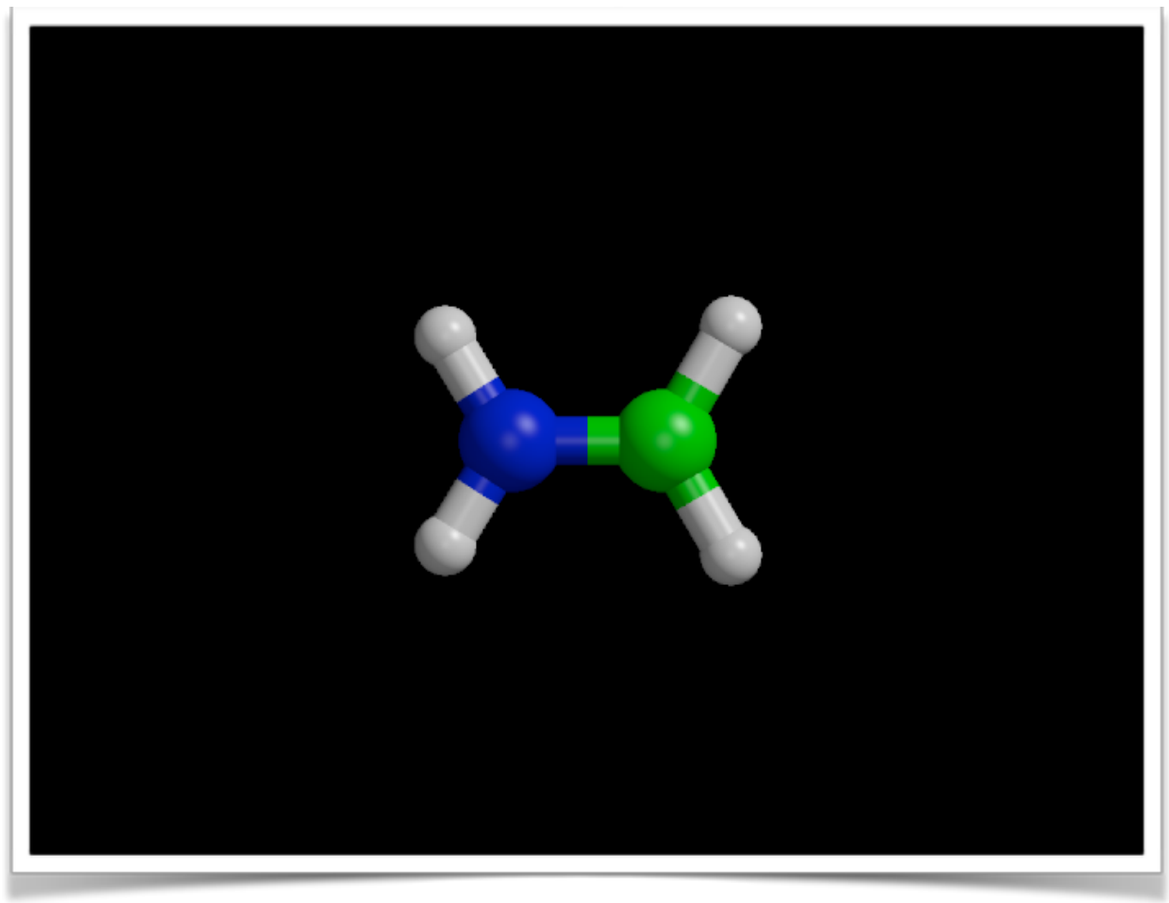

Conical Intersection

example for practical: photoisomerization

optimizing conical intersection in protonated formaldimine