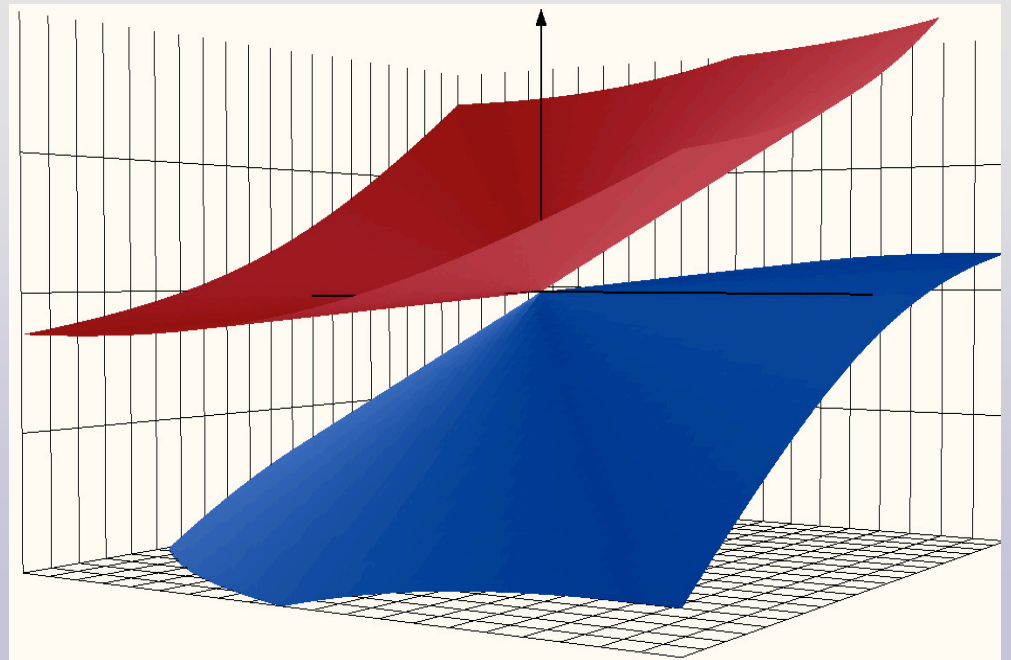
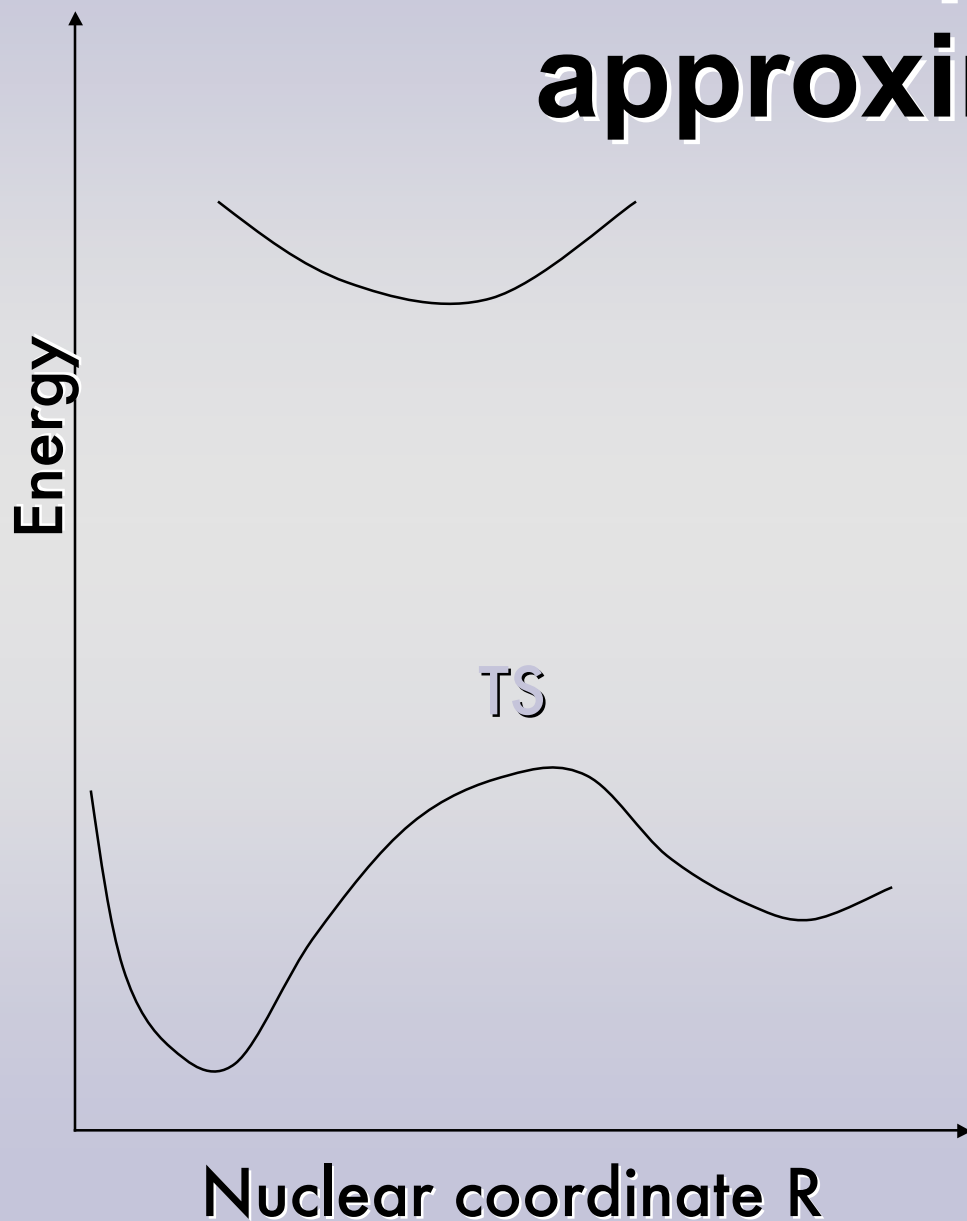


Conical Intersections

Spiridoula Matsika



The Born-Oppenheimer approximation



- The study of chemical systems is based on the separation of nuclear and electronic motion
- The potential energy surfaces (PES) are generated by the solution of the electronic part of the Schrodinger equation. This solution gives an energy for every fixed position of the nuclei. When the energy is plotted as a function of geometries it generates the PES as a $(3N-6)$ dimensional surface.
- Every electronic state has its own PES.
- ▼ On this potential energy surface, we can treat the motion of the nuclei classically or quantum mechanically

Hamiltonian for molecules

The total Hamiltonian operator for a molecular system is the sum of the kinetic energy operators (T) and potential energy operators (V) of all particles (nuclei and electrons). In atomic units the Hamiltonian is:

$$H = T + V$$

$$\begin{aligned}
 H^{tot}(\mathbf{r}, \mathbf{R}) &= \overset{\text{Nuc kinetic En}}{T^N} + \overset{\text{Electr. kinetic En}}{T^e} + \overset{\text{el-el repulsion}}{V^{ee}} + \overset{\text{el-nuc attraction}}{V^{eN}} + \overset{\text{Nuc-nuc repulsion}}{V^{NN}} \\
 &= \sum_{\alpha} \frac{-1}{2M_{\alpha}} \nabla_{\alpha}^2 + \sum_i \frac{-1}{2m_e} \nabla_i^2 + \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha}}{r_{\alpha i}} + \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}} \\
 &= T^N + H^e(\mathbf{r}; \mathbf{R})
 \end{aligned}$$

$$H^T = T^N + H^e = \sum_{\alpha} \frac{-1}{2M_{\alpha}} \nabla_{\alpha}^2 + H^e(\mathbf{r}; \mathbf{R})$$

Assuming that the motion of electrons and nuclei is separable, the Schrodinger equation is separated into an electronic and nuclear part. \mathbf{R} and \mathbf{r} are nuclear and electronic coordinates respectively. The total wavefunction Ψ^T is a product of electronic Ψ_I^e and nuclear χ_I wavefunctions for an I state.

$$\Psi^T(\mathbf{r}, \mathbf{R}) = \chi_I(\mathbf{R}) \Psi_I^e(\mathbf{r}; \mathbf{R})$$

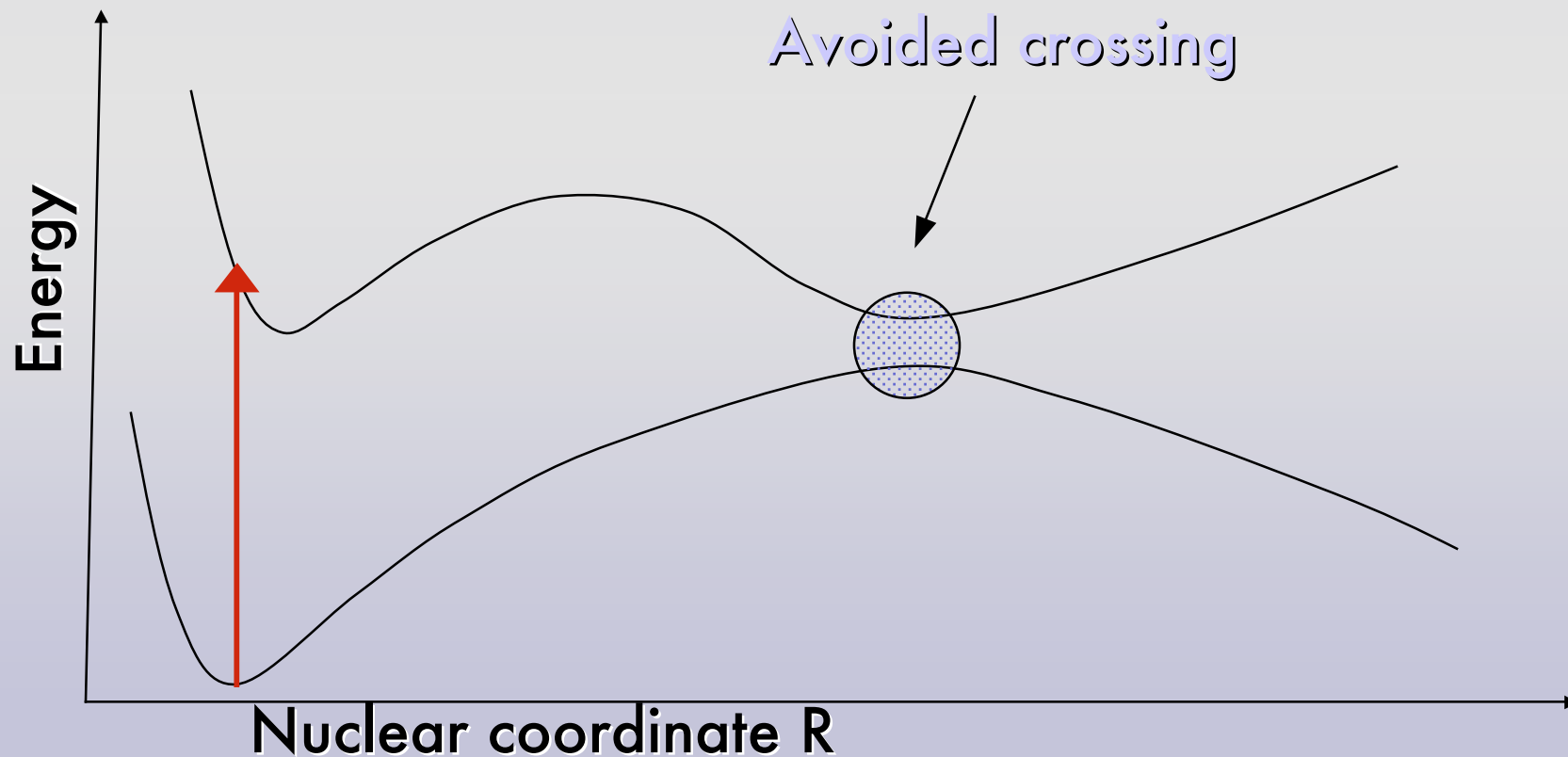
$$H^T \Psi^T = E^T \Psi^T$$

$$H^e \Psi_I^e = E_I^e \Psi_I^e \longrightarrow (T^N + E_I^e) \chi_I = E^T \chi_I$$

Electronic eq.

Nuclear eq.

Nonadiabatic processes are facilitated by the close proximity of potential energy surfaces. When the potential energy surfaces approach each other the BO approximation breaks down. The rate for nonadiabatic transitions depends on the energy gap.



When electronic states approach each other, more than one of them should be included in the expansion

$$\Psi^T(\mathbf{r}, \mathbf{R}) = \sum_{I=1}^{N^a} \chi_I(\mathbf{R}) \Psi_I^e(\mathbf{r}; \mathbf{R}) \quad \text{Born-Huang expansion}$$

If the expansion is not truncated the wavefunction is exact since the set Ψ_I^e is complete. The total Schrodinger equation using the Born-Huang expansion becomes

$$\begin{aligned} & (T^N + \frac{1}{\mu} K^{II} + E_I^e) \chi_I + \\ & + \sum_{J \neq I}^N \frac{1}{2\mu} (-2\mathbf{f}^{IJ} \cdot \nabla \chi_J + K^{IJ} \chi_J) = E^T \chi_I \end{aligned}$$

$$f_{\alpha}^{IJ}(\mathbf{R}) = \left\langle \Psi_I^e \left| \nabla_{\alpha} \Psi_J^e \right. \right\rangle_{\mathbf{r}}$$

$$k^{IJ}(\mathbf{R}) = \left\langle \Psi_I^e \left| \nabla^2 \Psi_J^e \right. \right\rangle_{\mathbf{r}}$$

Derivative coupling: couples the different electronic states

Derivative coupling

$$\mathbf{f}_{IJ} = \langle \Psi_I | \nabla | \Psi_J \rangle = \frac{\langle \Psi_I | \nabla H | \Psi_J \rangle}{E_J - E_I}$$

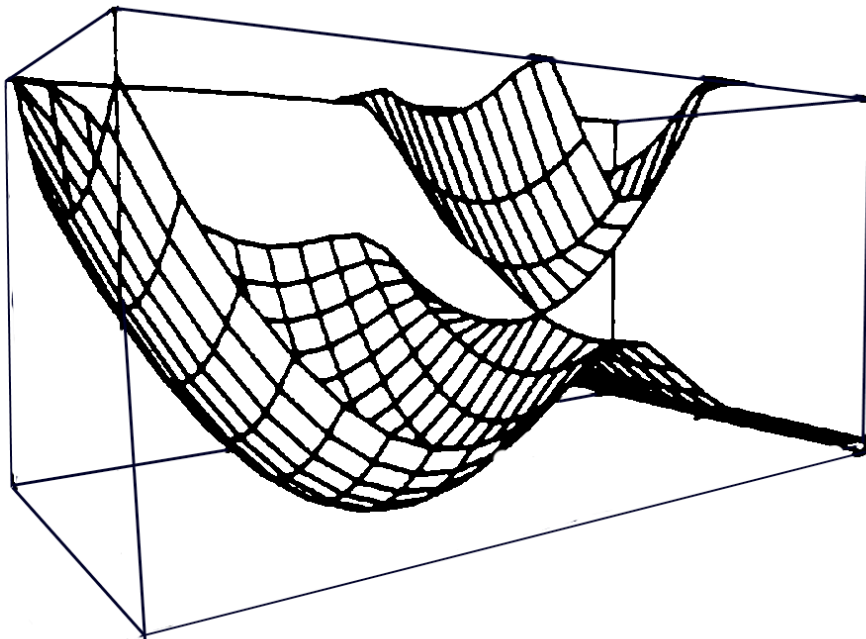
$$\mathbf{f}_{IJ} = -\mathbf{f}_{JI}$$

$$\mathbf{f}_{II} = 0 \quad \longleftarrow \quad \text{For real wavefunctions}$$

$$\langle \Psi_I | \nabla^2 | \Psi_J \rangle = \nabla \cdot \mathbf{f}_{IJ} + \mathbf{f}_{IJ} \cdot \mathbf{f}_{IJ}$$

The derivative coupling is inversely proportional to the energy difference of the two electronic states. Thus the smaller the difference, the larger the coupling. If $\Delta E=0$ f is infinity.

What is a conical intersection



Two adiabatic potential energy surfaces cross. The interstate coupling is large facilitating fast radiationless transitions between the surfaces

The Noncrossing Rule

The adiabatic eigenfunctions are expanded in terms of φ_i

$$\psi_1 = c_{11}\varphi_1 + c_{21}\varphi_2$$

$$\psi_2 = c_{12}\varphi_1 + c_{22}\varphi_2$$

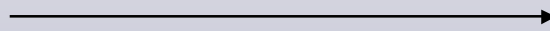
The electronic Hamiltonian is built and diagonalized

$$\mathbf{H}^e = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

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

$$\Delta H = H_{11} - H_{22}$$

The eigenvalues
and eigenfunctions
are:



$$E_{1,2} = \frac{H_{11} + H_{22} \pm \sqrt{\Delta H^2 + H_{12}^2}}{2}$$

$$\psi_1 = \cos \frac{\alpha}{2} \varphi_1 + \sin \frac{\alpha}{2} \varphi_2$$

$$\psi_2 = -\sin \frac{\alpha}{2} \varphi_1 + \cos \frac{\alpha}{2} \varphi_2$$

$$\sin \frac{\alpha}{2} = \frac{H_{12}}{\sqrt{\Delta H^2 + H_{12}^2}}$$

$$\cos \frac{\alpha}{2} = \frac{H_{11} - H_{22}}{\sqrt{\Delta H^2 + H_{12}^2}}$$

In order for the eigenvalues to become degenerate:

$$H_{11}(R) = H_{22}(R)$$

$$H_{12}(R) = 0$$

Since two conditions are needed for the existence of a conical intersection the dimensionality is $N^{\text{int}} - 2$, where N^{int} is the number of internal coordinates

For diatomic molecules there is only one internal coordinate and so states of the same symmetry cannot cross (noncrossing rule). But polyatomic molecules have more internal coordinates and states of the same symmetry can cross.

Conical intersections and symmetry

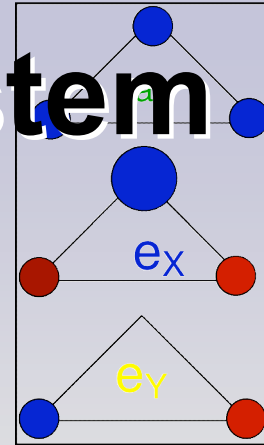
$$\mathbf{H}^e = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

- Symmetry required conical intersections, [Jahn-Teller effect](#)
 - $H_{12}=0$, $H_{11}=H_{22}$ by symmetry
 - seam has dimension N of high symmetry
 - Example: E state in H_3 in D_{3h} symmetry
- Symmetry allowed conical intersections (between states of different symmetry)
 - $H_{12}=0$ by symmetry
 - Seam has dimension N-1
 - Example: A_1 - B_2 degeneracy in C_{2v} symmetry in H_2+OH
- Accidental same-symmetry conical intersections
 - Seam has dimension N-2

$$V = \frac{1}{2} \rho^2 \pm k\rho \quad (4)$$

$$\rho^2 = \rho_0^2 \pm k\rho_0 \quad (7)$$

Example: X3 system



These rotationally symmetric surfaces are depicted schematically in Fig. 1 and characterized there by the JT stabilization energy

$$E_{JT} = \frac{k^2}{2\omega}, \quad (6)$$

occurring at the optimum distortion

$$\rho_0 = k/\omega. \quad (7)$$

The so-called pseudorotational angle ϕ is defined as

$$\phi = \arctan(Q_y/Q_x). \quad (8)$$

The corresponding eigenvector matrix reads

$$S = \begin{pmatrix} \cos(\phi/2) & -\sin(\phi/2) \\ \sin(\phi/2) & \cos(\phi/2) \end{pmatrix}, \quad (9)$$

where the two columns represent the expansion coefficients of the adiabatic wave functions in the diabatic electronic basis. Transforming the complete

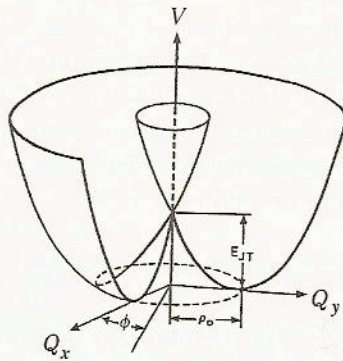
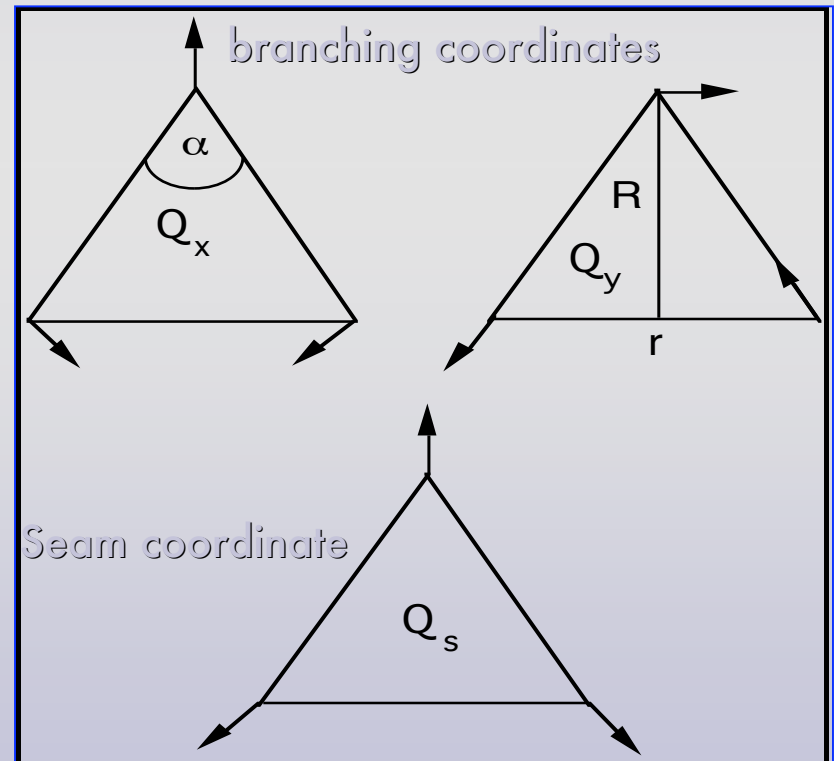
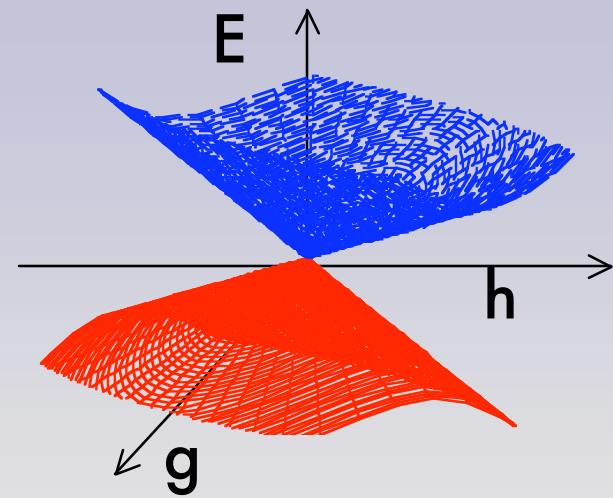


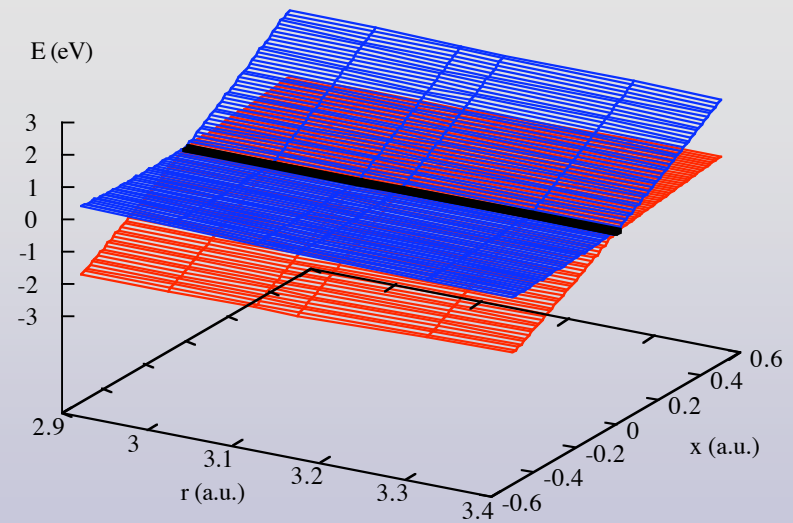
Fig. 1. Perspective drawing of the $E \otimes e$ JT intersection arising for linear coupling (Mexican hat). The rotationally symmetric double cone is located in the figure centre. Also indicated in the figure are the Cartesian displacement coordinates Q_x and Q_y of the JT active mode, the pseudorotational angle ϕ and the energy gain E_{JT} occurring for the optimum distortion ρ_0 .



Two internal coordinates lift the degeneracy linearly: **g-h** or branching plane



$N^{\text{int}}-2$ coordinates form the **seam**: points of conical intersections are connected continuously



The Branching Plane

The Hamiltonian matrix elements are expanded in a Taylor series expansion around the conical intersection

$$\bar{H}(\mathbf{R}) = \bar{H}(\mathbf{R}_0) + \nabla \bar{H}(\mathbf{R}_0) \cdot \delta \mathbf{R}$$

$$\Delta H(\mathbf{R}) = 0 + \nabla \Delta H(\mathbf{R}_0) \cdot \delta \mathbf{R}$$

$$H_{12}(\mathbf{R}) = 0 + \nabla H_{12}(\mathbf{R}_0) \cdot \delta \mathbf{R}$$

Then the conditions for degeneracy are

$$\nabla \Delta H(\mathbf{R}_0) \cdot \delta \mathbf{R} = 0$$

$$\nabla H_{12}(\mathbf{R}_0) \cdot \delta \mathbf{R} = 0$$

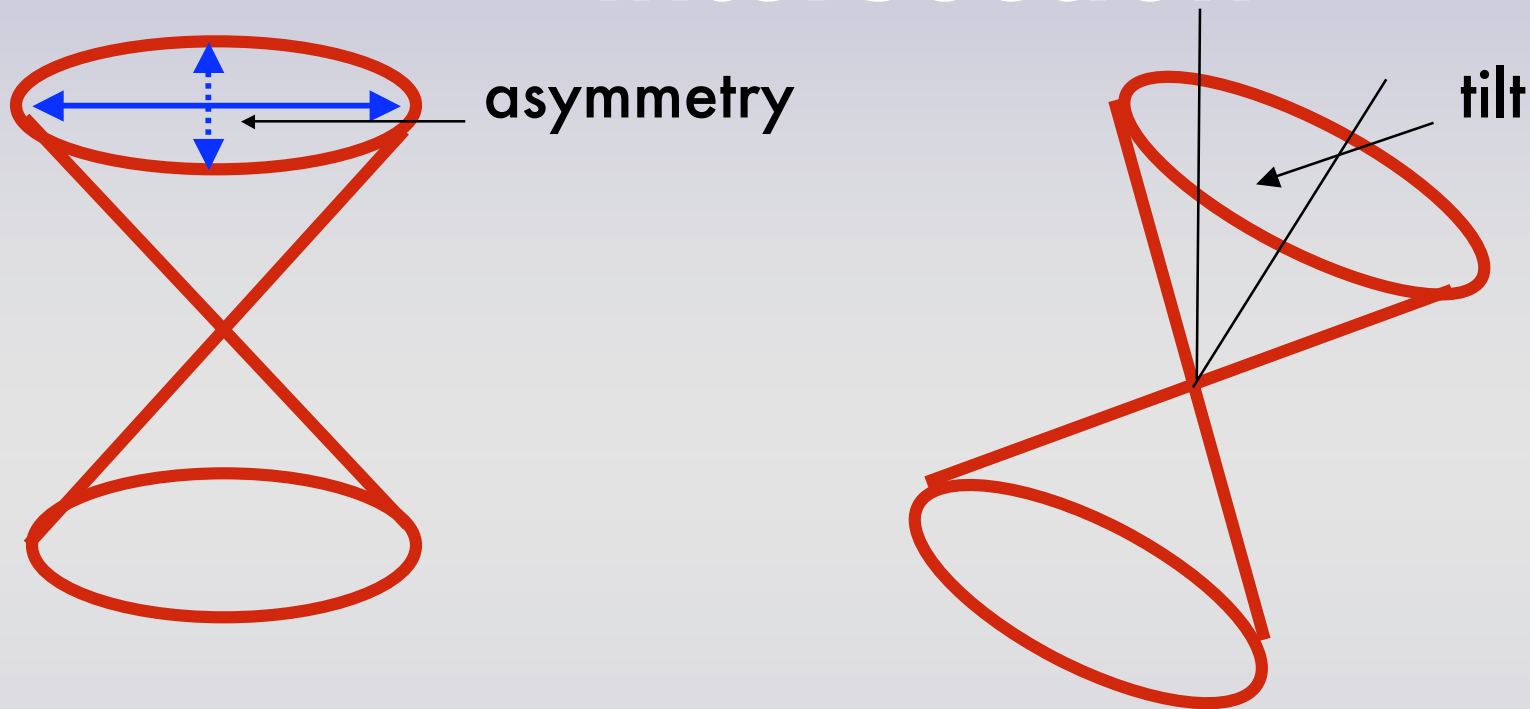
$$\mathbf{g} = \nabla \Delta H$$

$$\mathbf{h} = \nabla H_{12}$$

$$\mathbf{H}^e = (s_x x + s_y y) \mathbf{I} + \begin{pmatrix} gx & hy \\ hy & -gx \end{pmatrix}$$

$$E_{1,2} = s_x x + s_y y \pm \sqrt{(gx)^2 + (hy)^2}$$

Topography of a conical intersection



$$E_{\pm} = E_0 + s_x X + s_y y \pm \sqrt{g^2 X^2 + h^2 y^2}$$

Conical intersections are described in terms of the characteristic parameters g, h, s

Geometric phase effect (Berry phase)

If the angle α changes from α to $\alpha + 2\pi$:

$$\psi_1 = \left(\cos\frac{\alpha}{2}\right)\varphi_1 + \left(\sin\frac{\alpha}{2}\right)\varphi_2$$

$$\psi_2 = -\left(\sin\frac{\alpha}{2}\right)\varphi_1 + \left(\cos\frac{\alpha}{2}\right)\varphi_2$$

$$\psi_1(\alpha + 2\pi) = -\psi_1(\alpha)$$

$$\psi_2(\alpha + 2\pi) = -\psi_2(\alpha)$$

The electronic wavefunction is doubled valued, so a phase has to be added so that the total wavefunction is single valued

$$\Psi^T = e^{iA(R)}\psi(R;r)\chi(R)$$

The geometric phase effect can be used for the identification of conical intersections. If the line integral of the derivative coupling around a loop is equal to π

Adiabatic and Diabatic representation

- Adiabatic representation uses the eigenfunctions of the electronic hamiltonian. The derivative coupling then is present in the total Schrodinger equation
- Diabatic representation is a transformation from the adiabatic which makes the derivative coupling vanish. Off diagonal matrix elements appear. Better for dynamics since matrix elements are scalar but the derivative coupling is a vector.
- Strickly diabatic bases don't exist. Only quasidiabatic where f is very small.

Practically g and h are taken from *ab initio* wavefunctions expanded in a CSF basis

$$\Psi_I^e = \sum_{m=1}^{N^{CSF}} c_m^I \psi_m$$
$$[\mathbf{H}^e(\mathbf{R}) - \mathbf{E}_I(\mathbf{R})] \mathbf{c}^I(\mathbf{R}) = 0$$

Tuning, coupling vectors

$$h_{\alpha}^{IJ}(\mathbf{R}) = \mathbf{c}^I(\mathbf{R}_x)^{\dagger} \frac{\partial \mathbf{H}(\mathbf{R})}{\partial R_{\alpha}} \mathbf{c}^J(\mathbf{R}_x)$$

$$g_{\alpha}^I(\mathbf{R}) = \mathbf{c}^I(\mathbf{R}_x)^{\dagger} \frac{\partial \mathbf{H}(\mathbf{R})}{\partial R_{\alpha}} \mathbf{c}^I(\mathbf{R}_x)$$

$$\mathbf{g}^{IJ}(\mathbf{R}) = \mathbf{g}^I(\mathbf{R}) - \mathbf{g}^J(\mathbf{R})$$

Locating the minimum energy point on the seam of conical intersections

- Projected gradient technique:
 - M. J. Baerpack, M. Robe and H.B. Schlegel
Chem. Phys. Lett. **223**, 269, (1994)
- Lagrange multiplier technique:
 - M. R. Manaa and D. R. Yarkony, *J. Chem. Phys.*, **99**, 5251, (1993)

Locate conical intersections using lagrange multipliers:

$$\Delta E_{ij} + \mathbf{g}^{ji} \cdot \delta \mathbf{R} = 0$$

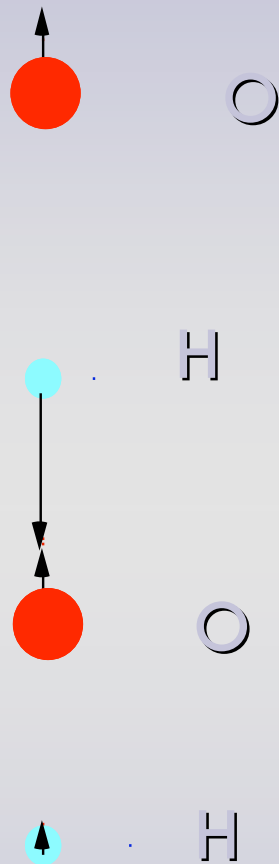
$$\mathbf{h}^{ji} \cdot \delta \mathbf{R} = 0$$

Additional geometrical constrains, K^i , can be imposed. These conditions can be imposed by finding an extremum of the Lagrangian.

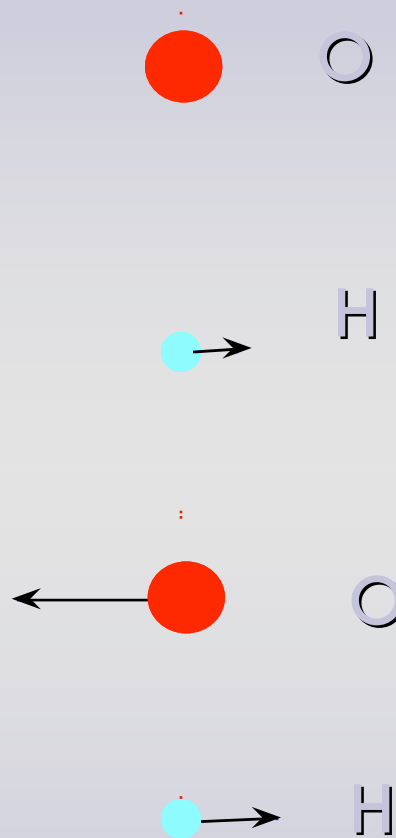
$$L(\mathbf{R}, \xi, \lambda) = E_k + \xi_1 \Delta E_{ij} + \xi_2 H_{ij} + \sum \lambda_i K^i$$

Branching vectors for OH+OH

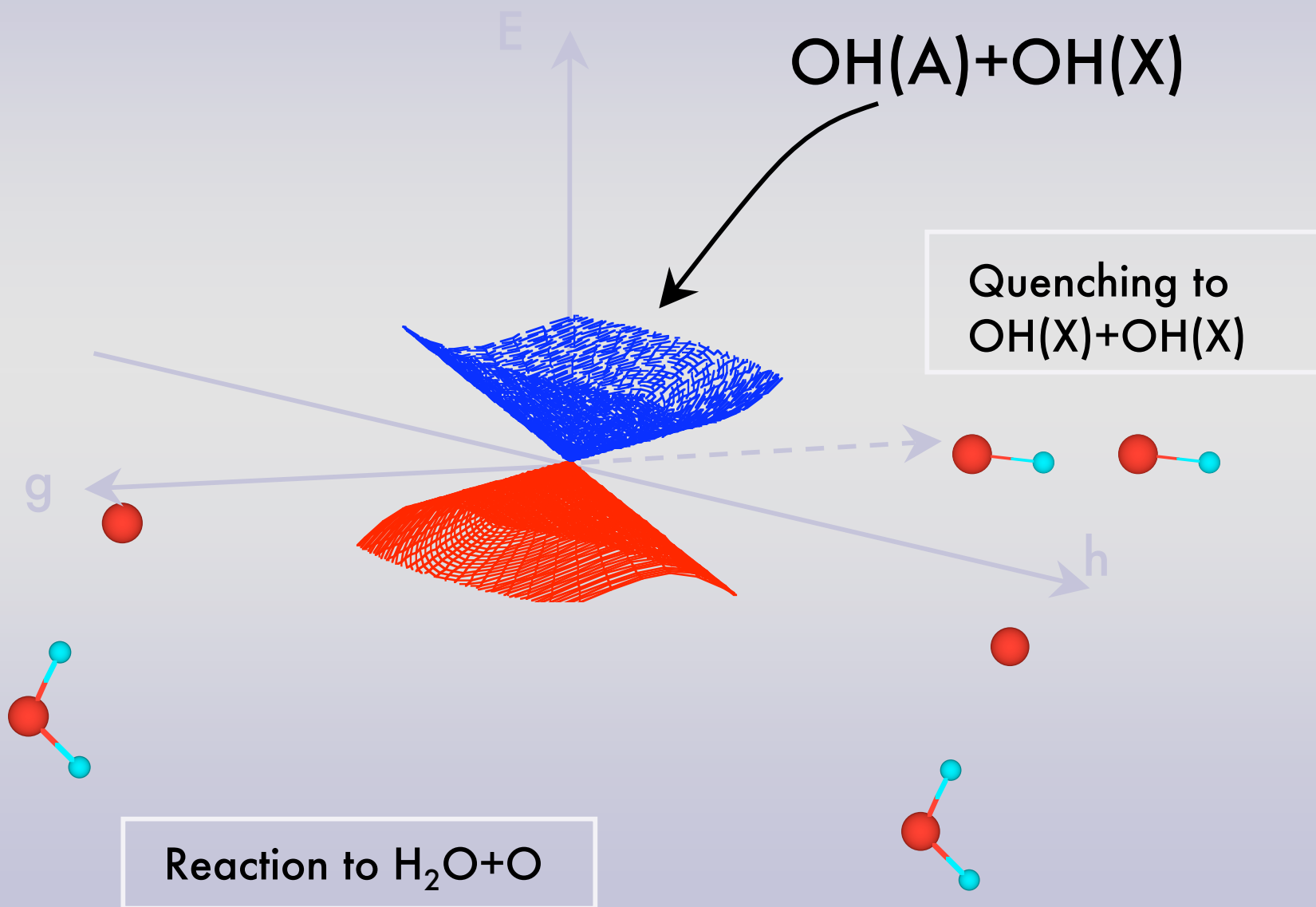
g



h



Routing effect:



Three-state conical intersections

Three state conical intersections can exist between three states of the same symmetry in a system with N^{int} degrees of freedom in a subspace of dimension $N^{\text{int}}-5$

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{12} & H_{22} & H_{23} \\ H_{13} & H_{23} & H_{33} \end{pmatrix}$$

$$H_{11}(\mathbf{R}) = H_{22}(\mathbf{R}) = H_{33}(\mathbf{R}) \\ H_{12}(\mathbf{R}) = H_{13}(\mathbf{R}) = H_{23}(\mathbf{R}) = 0$$

Dimensionality: $N^{\text{int}}-5$, where N^{int} is the number of internal coordinates

J. von Neumann and E. Wigner, *Phys.Z* 30,467 (1929)

Conditions for a conical intersection including the spin-orbit interaction

$$\begin{pmatrix} \Psi_1 & \Psi_2 & \tau\Psi_1 & \tau\Psi_2 \\ \hline H_{11} & H_{12} & 0 & H_{1\tau 2} \\ H_{12}^* & H_{22} & -H_{1\tau 2} & 0 \\ \hline H_{11} & H_{12}^* \\ H_{12} & H_{22} \end{pmatrix}$$

- In general 5 conditions need to be satisfied.
 - $H_{11}=H_{22}$
 - $\text{Re}(H_{12})=0$
 - $\text{Im}(H_{12})=0$
 - $\text{Re}(H_{1\tau 2})=0$, satisfied in C_s symmetry
 - $\text{Im}(H_{1\tau 2})=0$, satisfied in C_s symmetry
- The dimension of the seam is $N^{\text{int}}-5$ or $N^{\text{int}}-3$