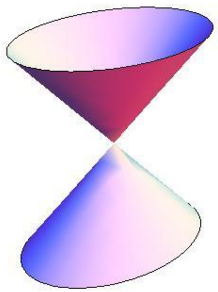
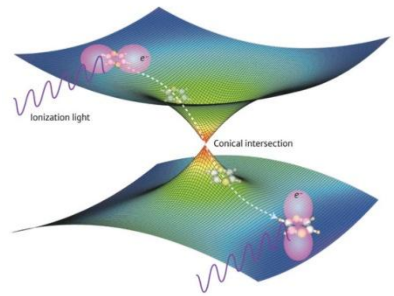
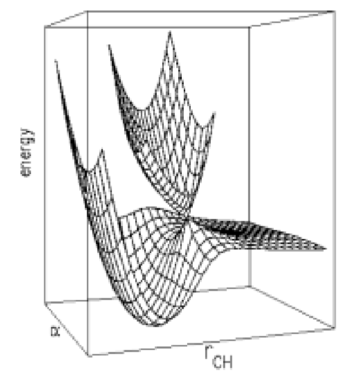
Conical intersections of potential energy surfaces

Ample numerical experience shows that degeneracies are usually of conical shape (degeneracy is lifted in 1st order of the nuclear displacements)





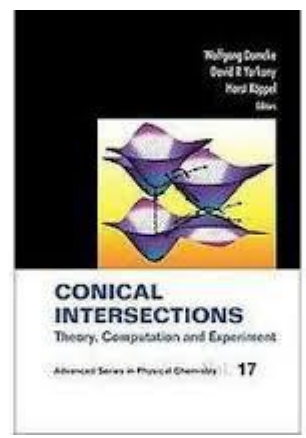


See also: D. Truhlar and A. Mead, Phys. Rev. A 68 (2003) 032501

W. Domcke, D. R. Yarkony and H. Köppel (Eds.)

- *Conical Intersections: Electronic structure, dynamics and spectroscopy*
- *Conical Intersections: Theory, computation and experiment*

(World Scientific, Singapore, 2004 & 2011)



The noncrossing rule and its generalization

J.v. Neumann & E. Wigner, Physik. Zeitschrift, **30** (1929) 467; E. Teller, J. Phys. Chem. **41** (1937) 109

Consider a quasi-degeneracy of potential energy surfaces; at a neighboring geometry the electronic wavefunctions are written as

$$\phi_\pm = c_1\phi_1^{\,0} + c_2\,\phi_2^{\,0}$$

(with the functions $\phi_1^{\,0}$ and $\phi_2^{\,0}$ from the reference geometry). The potential energies $V_\pm$ result from solving

$$\begin{pmatrix} H_{11}\text{-}V_\pm & H_{12} \\ H_{12} & H_{22}\text{-}V_\pm \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad \text{with} \quad H_{ij} = \langle \phi_i^0 \,|\, \hat{H}_{el} \,|\, \phi_j^0 \rangle$$

One has:

$$V_\pm = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2}$$

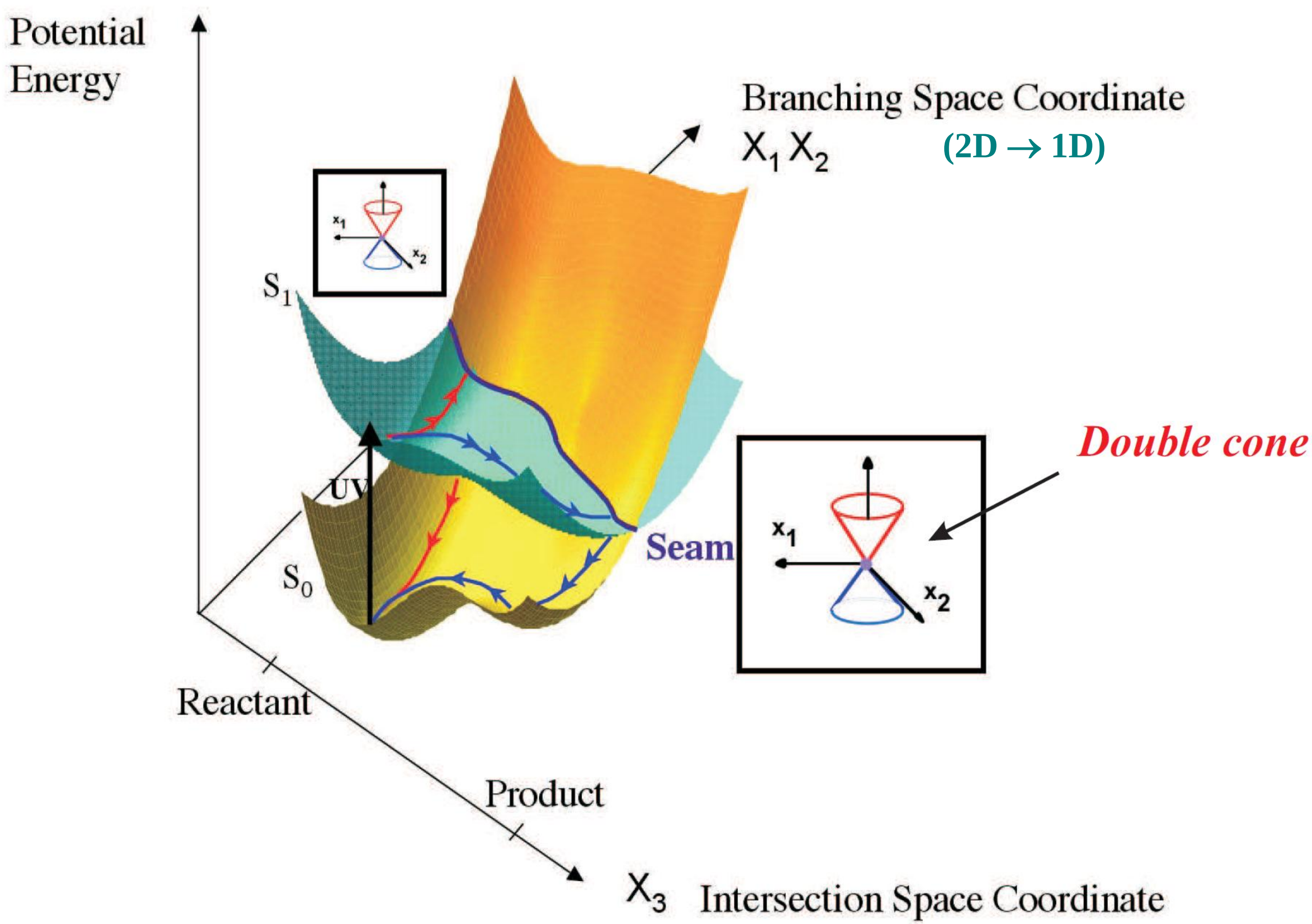
Degeneracy requires: $\mathbf{H_{11} = H_{22}}$ and $\mathbf{H_{12} = 0}$ **,**

i.e., in general the variation of <u>**two**</u> parameters.

==> In diatomic molecules no curve crossing of states with the same symmetry.

<u>For *n* nuclear coordinates:</u>

Dimension of subspace of degeneracy = *n-2* .



The conical intersection hyperline traced out by a co-ordinate X_3 plotted in a space containing the co-ordinate X_3 and one co-ordinate from the degeneracy-lifting space $X_1\ X_2$