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
The noncrossing rule and its generalization


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

$$\begin{pmatrix} H_{11} - V_\pm & H_{12} \\ H_{12} & H_{22} - V_\pm \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad \text{with} \quad H_{ij} = <\phi_i^0 | H_{el} | \phi_j^0>$$

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: $H_{11} = H_{22}$ and $H_{12} = 0$,

i.e., in general the variation of two parameters.

$$\Rightarrow$$ In diatomic molecules no curve crossing of states with the same symmetry.

For $n$ nuclear coordinates:

Dimension of subspace of degeneracy $= n-2$. 
The conical intersection hyperline traced out by a coordinate $X_3$ plotted in a space containing the coordinate $X_3$ and one coordinate from the degeneracy-lifting space $X_1 X_2$. 