B.2) A simple model of vibronic coupling

Use a diabatic electronic basis and expand coupling terms:

$$\mathcal{H} = T_K \mathbf{1} + \mathbf{W}$$

$$\boxed{\begin{aligned} W_{nn}(Q) &= V_0(Q) + E_n + \textstyle\sum_i k_i^{(n)} Q_i + \sum_{i,j} \gamma_{ij}^{(n)} Q_i Q_j + \cdots \\ W_{nn'}(Q) &= \textstyle\sum_i \lambda_i^{(nn')} Q_i + \cdots \qquad (n \neq n') \end{aligned}}$$

with Q_i: normal coordinates of $V_0(Q)$,
and, for instance, $k_i^{(n)} = (\partial V_n / \partial Q_i)_{Q=0}$.

$k_i^{(n)}$ is the gradient of the excited potential energy surface at the Franck-Condon zone centre.

Analogously for the other coupling constants.

The coupling constants can therefore be determined from *ab initio* calculations (few points are needed).

Selection rule for $\lambda_i^{(nn')}$

$$\boxed{\Gamma_n \times \Gamma_Q \times \Gamma_{n'} \supset \Gamma_A}$$

a) *Hamiltonian for a two-state case:*

$$\mathcal{H} = \left(-\frac{1}{2}\sum\omega_i\frac{\partial^2}{\partial Q_i^2}+\frac{1}{2}\sum\omega_i Q_i^2\right)\mathbf{1}+ \left(\begin{array}{cc} E_g+\sum k_j^{(g)}Q_j & \sum\lambda_l Q_l \\ \sum\lambda_l Q_l & E_u+\sum k_j^{(u)}Q_j \end{array}\right)$$

Electronic states with different symmetries → Modes l and j are different.

For a first insight into the phenomena, the g mode will be dropped and only one term will be considered in the off-diagonal element:

$$\mathcal{H} = (-\frac{\omega_u}{2}\frac{\partial^2}{\partial Q_u^2}+\frac{\omega_u}{2}Q_u^2)\mathbf{1}+\left(\begin{array}{cc} E_g & \lambda Q_u \\ \lambda Q_u & E_u \end{array}\right)$$

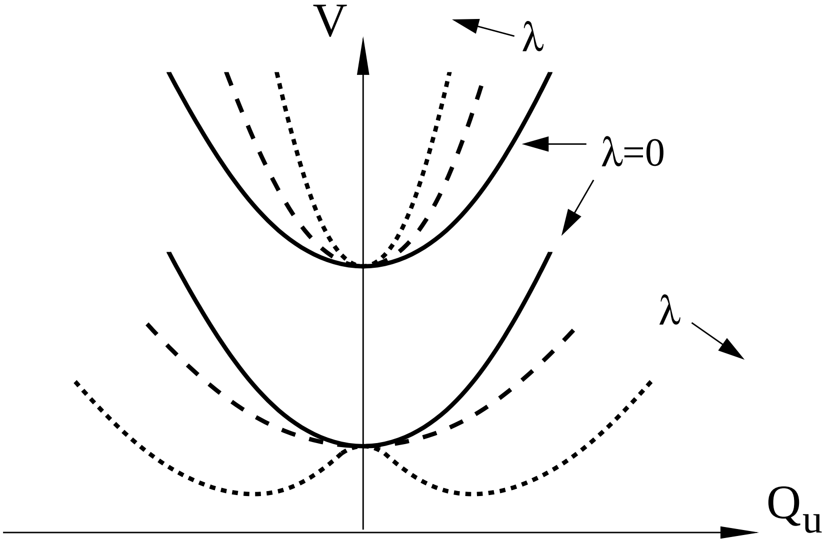
This is almost the simplest case that one can think of, but it still shows many of the representative effects of vibronic interactions.
In the diabatic representation $\mathcal{H}$ is not too descriptive. Let us have a look then at the adiabatic potential energy curves:

$$E = \frac{E_g+E_u}{2} \quad ; \quad \Delta E = \frac{E_g-E_u}{2}$$

$$\Longrightarrow V_\pm = \frac{\omega_u}{2}Q_u^2 + E \pm \sqrt{\Delta E^2+\lambda^2 Q_u^2}$$

$$\text{If } Q_u = 0 \quad \text{then} \quad V_\pm = E \pm \Delta E = \begin{cases} E_g \\ E_u \end{cases},$$

i.e., the diabatic and the adiabatic potential energy curves are identical (how it should be). $Q_u \neq 0$ yields repulsion between the potential energy curves. A qualitative picture is displayed next,



The upper potential energy curves, V_+, are always steeper due to the interaction.

For V_- a double minimun can be obtained for strong couplings: Symmetry breaking.

Repulsion of potential energy curves and symmetry lowering (linear → non-linear; planar → non-planar) are important signs of vibronic interaction with other electronic states.

Calculation of the curvature using Taylor expansion:

$$\begin{aligned} V_{\pm} &= E + \frac{\omega_u}{2} Q_u^2 \pm \Delta E \left(1 + \frac{1}{2} \frac{\lambda^2 Q_u^2}{\triangle E^2} + ... \right) \\ &= E + \frac{\omega_u}{2} Q_u^2 \pm \Delta E \pm \frac{\lambda^2 Q_u^2}{2 \Delta E^2} \\ &= E \pm \Delta E + \frac{1}{2} \left(\omega_u \pm \frac{\lambda^2}{\Delta E} \right) Q_u^2 \end{aligned}$$

$$\boxed{\Longrightarrow \omega_u^{\pm} = \omega_u \pm \tfrac{\lambda^2}{\Delta E}}$$

The change in the curvature is symmetric, as the repulsion of the potential energy curves. The expression for ω_u^- holds only for positive frequences. This yields a critical coupling strength, λ_c, for obtaining a double minimum:

$$\boxed{\lambda_c^2 = \Delta E \cdot \omega_u}$$

If $\lambda > \lambda_c$, $Q_u = 0$ represents a local maximum. The minima are the non-trivial solutions of the equation:

$$0 = \frac{\partial V_-}{\partial Q_u} = \omega_u \; Q_u - \frac{\lambda^2 Q_u}{\sqrt{\Delta E^2 + \lambda^2 Q_u^2}}$$

$$\Longrightarrow Q_u^o = \pm \sqrt{\frac{\lambda^2}{\omega_u^2} - \frac{\Delta E^2}{\lambda^2}}$$

The solutions are real and $\neq 0$ if $\lambda > \lambda_c$. The stabilization energy, E_s, represents the lowering of the minimum of the lower potential energy curve relative to the minimum in the absence of vibronic coupling ($\lambda = 0$) due to an asymmetric distortion:

$$E_s = V_-(0) - V_-(Q_u^o) = \frac{\omega_u}{2}\left(\frac{\lambda}{\omega_u} - \frac{\Delta E}{\lambda}\right)^2$$

This expression is formally always defined, but holds only for $\lambda > \lambda_c$.

Beside the potential energy curves, we are interested also in the non-adiabatic couplings, given by the derivative of the rotation angle, α':

$$\alpha(Q_u) = \frac{1}{2}\arctan\frac{2\,W_{12}}{W_{11} - W_{22}}$$

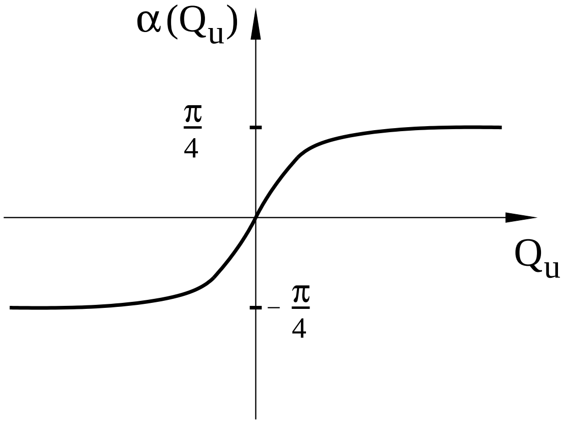
Substituting and differentiating:

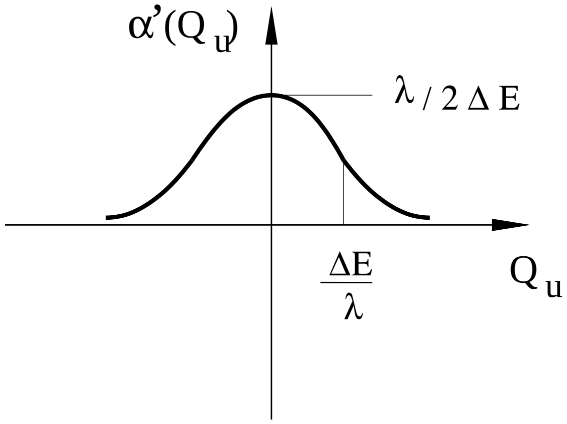
$$\alpha(Q_u) = \frac{1}{2}\arctan\frac{\lambda Q_u}{\Delta E}$$

$$\Longrightarrow \alpha' = \frac{1}{2}\cdot\frac{1}{1 + \frac{\lambda^2 Q_u^2}{\Delta E^2}}\cdot\frac{\lambda}{\Delta E} = \frac{\lambda \Delta E/2}{\Delta E^2 + \lambda^2 Q_u^2}$$

One obtains a Lorentzian curve with a width and a height given by $hwhm = \frac{\Delta E}{\lambda}$ and $\alpha'(0) = \frac{\lambda}{2\Delta E}$, respectively.

The area under the $\alpha'(Q_u)$ curve has to be $\frac{\pi}{2}$ and, therefore, the limits for $\alpha(\pm\infty)$ are $\pm\frac{\pi}{4}$.





One can see from this expression that for fixed values of λ and ω_u, the non-adiabatic effects increase with decreasing ΔE.

Comparison of criteria:

Double minimum: $\lambda^2 > \omega_u \cdot \Delta E$

Non-adiabatic effects: $\lambda > \Delta E,\ \omega_u \geq \Delta E$

For $\omega_u < \Delta E$, the criterium for the double minimum is easier to fulfill than for non-adiabatic effects.

⟶ different validity of the diagonal approximation in the adiabatic and the diabatic basis!

$$\omega_u\, \Delta E < \lambda^2 < \Delta E^2$$

Double minimum / adiabatic app. valid

b) Das vibronische g-u Problem : 2 Moden

Betrachte 2 nichtentartete Zustände verschiedener Symmetrie (‘g’ bzw. ‘u’), eine totalsymmetrische, modulierende Mode Q_g sowie eine nichttotalsymmetrische, koppelnde Mode Q_u :

$$\boxed{\mathbf{H} = \left[T_N + \frac{\omega_g}{2} Q_g^2 + \frac{\omega_u}{2} Q_u^2 \right] \mathbf{1} + \begin{pmatrix} E_1 + k_1 Q_g & \lambda Q_u \\ \lambda Q_u & E_2 + k_2 Q_g \end{pmatrix}}$$

Eigenwerte von $\mathbf{H} - T_N \mathbf{1}$:

$$V_\pm = \frac{\omega_g}{2} Q_g^2 + \frac{\omega_u}{2} Q_u^2 + \frac{E_1 + E_2}{2} + \frac{k_1 + k_2}{2} Q_g \pm \frac{w}{2};$$

$$w = \left\{ \left[E_1 - E_2 + (k_1 - k_2) Q_g \right]^2 + 4 \lambda^2 Q_u^2 \right\}^{1/2}$$

$$\frac{w}{2} = \left[(\Delta + \delta k \cdot Q_g)^2 + \lambda^2 Q_u^2 \right]$$

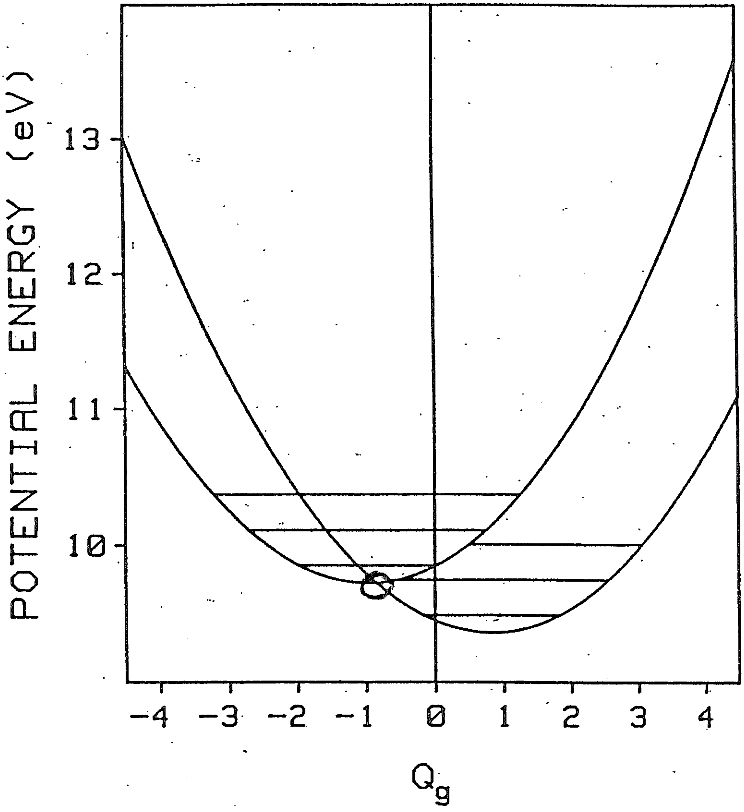
Konische Durchschneidung im Punkt:

$$\boxed{Q_u = 0 \quad ; \qquad Q_g = -\frac{E_1 - E_2}{k_1 - k_2}}$$

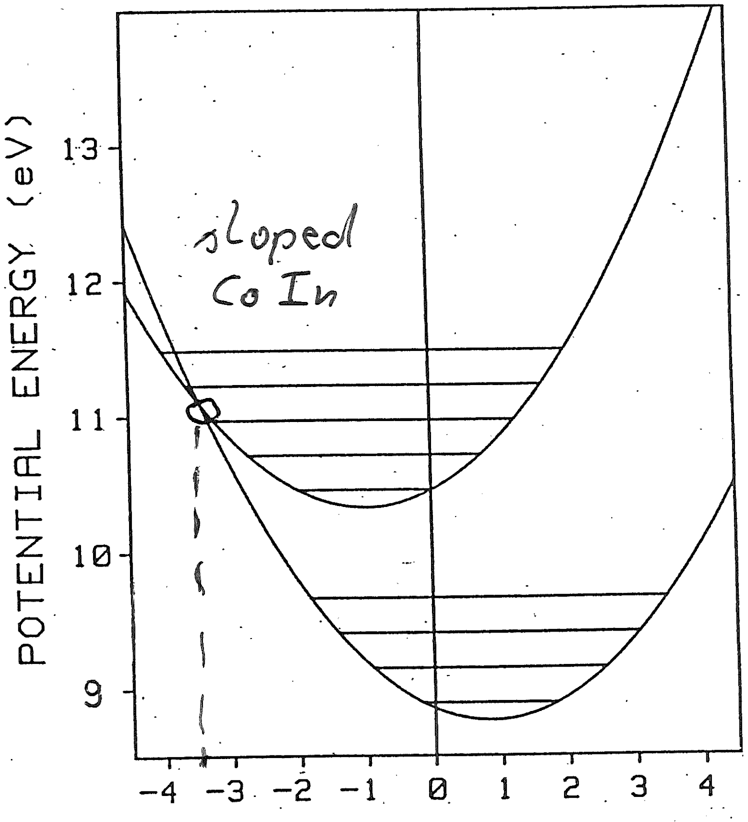
Elektronische Nichtdiagonalterme induzieren Nichtseparabilität der beiden Schwingungsmoden

Darstellung der Q_g-Potentialkurven für zwei verschiedene Werte der Energielücke ΔE (Q_u=0)

$C_4H_4^+$ ΔE=0.4 eV (Prototyp)



ΔE=1.6 eV (Studie)



$$-Q_g = \frac{E_1 - E_2}{k_1 - k_2}$$

Schematische Darstellung der Q_u-Potentialkurven für verschiedene Werte von Q_g