Derivative couplings in LVC approach

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

Substituting and differentiating:

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

$$\Longrightarrow \alpha' = \frac{1}{2} \cdot \frac{1}{1 + \frac{\lambda^2 Q_u^2}{\Delta E^2}} \cdot \frac{\lambda}{\Delta E} = \frac{\lambda \Delta E/2}{\Delta E^2 + \lambda^2 Q_u^2} \equiv \frac{\partial \alpha (Q_g, Q_u)}{\partial Q_u}$$

$$\frac{\partial \alpha (Q_g, Q_u)}{\partial Q_g} = \frac{\lambda Q_u \cdot \Delta k/2}{\Delta E^2 + \lambda^2 Q_u^2}$$

and $\Delta E = E_1 - E_2 + \underbrace{(k_1 - k_2)}_{\Delta k} Q_g$

$$\Longrightarrow \boxed{\begin{aligned} \frac{\partial \alpha}{\partial Q_u} &= \frac{\pi}{2} L_{\frac{\Delta E}{\lambda}} (Q_u) \\ \frac{\partial \alpha}{\partial Q_g} &= \frac{\pi}{2} L_{\frac{\lambda Q_u}{\Delta k}} (Q_g + \delta) \end{aligned}} \qquad \delta = \frac{E_1 - E_2}{k_1 - k_2}$$

Trafo diabat. → adiabat. Basis

Damit wird $\mathcal{H}_{ad} = \mathbf{S}^\dagger \mathcal{H} \mathbf{S} = \mathbf{S}^\dagger T_k \mathbf{S} + \begin{pmatrix} V_1 & 0 \\ 0 & V_2 \end{pmatrix}$

Mit

$$\mathbf{S}^\dagger T_k \mathbf{S} + \mathbf{S}^\dagger \mathbf{S} T_k - \mathbf{S}^\dagger \mathbf{S} T_k$$
$$= T_k - \mathbf{S}^\dagger [\mathbf{S}, T_k] \qquad \text{folgt}$$

$$\mathcal{H}_{ad} = T_k \, \mathbf{1} + \begin{pmatrix} V_1(Q) & 0 \\ 0 & V_2(Q) \end{pmatrix} + \underbrace{\mathbf{S}^\dagger [T_k, \mathbf{S}]}_{-\Lambda}$$

Explizit:

$$S(Q) = \begin{pmatrix} \cos\alpha(Q) & \sin\alpha(Q) \\ -\sin\alpha(Q) & \cos\alpha(Q) \end{pmatrix}$$

$$\boxed{\Rightarrow \Lambda = \begin{pmatrix} -\frac{\omega}{2}\alpha'^2 & \frac{\omega}{2}\alpha'' + \omega\alpha' \frac{\partial}{\partial Q} \\ -\frac{\omega}{2}\alpha'' - \omega\alpha' \frac{\partial}{\partial Q} & -\frac{\omega}{2}\alpha'^2 \end{pmatrix}}$$

for $T_k = -\frac{\omega}{2} \frac{\partial^2}{\partial Q^2}$