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1. Consider the case of conical intersection. The Hamiltonian expressed in the representation of a set of diabatic basis reads

$$\hat{H}_{\mathrm{mol}} = \hat{T}\mathbf{I} + \begin{bmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{bmatrix} \tag{1}$$

with $\hat{T} = -\frac{1}{2}(\partial_x^2 + \partial_y^2)$ and

$$V_{11} = \frac{\omega^2}{2}\left[(x + x_0)^2 + y^2\right], \tag{2}$$

$$V_{22} = \frac{\omega^2}{2}\left[(x - x_0)^2 + y^2\right], \tag{3}$$

$$V_{12} = cy. \tag{4}$$

(a) Prove that the adiabatic potential energy surfaces are

$$W_{1,2} = \frac{1}{2}(V_{11} + V_{22}) \pm \frac{1}{2}\sqrt{(V_{11} - V_{22})^2 + 4V_{12}^2} \tag{5}$$

with the transformation matrix being

$$U(\theta) = \begin{bmatrix} \cos\frac{\theta}{2} & -\sin\frac{\theta}{2} \\ \sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{bmatrix} \tag{6}$$

and

$$\theta = \arctan\frac{cy}{\omega^2 x_0 x} \equiv \arctan\frac{\gamma y}{x}. \tag{7}$$

(b) Plot $W_{1,2}$ and find out where the Born–Oppenheimer approximation breaks down. Set $\omega = x_0 = 1$ and $\gamma = 0.3$.

(c) Further plot θ as a function of $\phi \in [0, 2\pi]$ in two cases: (i) $x^2 + y^2 = 1$, $\phi = \arctan\frac{y}{x}$; (ii) $(x-1)^2 + (y-1)^2 = 1$, $\phi = \arctan\frac{y-1}{x-1}$. Find out the abnormal behavior of θ in the first case and explain it. (Ref: I. G. Ryabinkin, et al. *Acc. Chem. Res.* 2017, **50**, 1785–1793.)