Section 2.5:Quadratic Effects in the $E \times e$-Problem*

We conclude our outline of the $E \times e$ - problem by pointing out that it contains far more points of degeneracy than just the origin, $\rho = 0$, and is thus of considerably higher complexity than suggested by the foregoing discussion. Expanding the potential up to quadratic order, we extend Eq.(2.72) to arrive at

$$\begin{aligned} \mathbf{V} = \ & \tfrac{1}{2}\hbar\omega(Q_\theta^2 + Q_\varepsilon^2)\boldsymbol{\sigma_0} + V_E \begin{pmatrix} -Q_\theta & Q_\varepsilon \\ Q_\varepsilon & Q_\theta \end{pmatrix} \\ & + \tfrac{1}{2}W_E \begin{pmatrix} Q_\varepsilon^2 - Q_\theta^2 & -2Q_\varepsilon Q_\theta \\ -2Q_\varepsilon Q_\theta & Q_\theta^2 - Q_\varepsilon^2 \end{pmatrix}, \end{aligned} \tag{1}$$

where the coupling constant W_E has been introduced as reduced matrix element of second order. Going from the real-valued to the complex-valued diabatic electronic basis, as in the transition from Eq.(2.72) to Eq.(2.73), we find after some algebraic manipulation

$$\mathbf{V} = \frac{1}{2}\hbar\omega\rho^2\boldsymbol{\sigma_0} + V_E\rho\left[1 + \frac{W_E}{V_E}\rho\cos 3\alpha + (\frac{W_E}{2V_E}\rho)^2\right]^{\frac{1}{2}} \begin{pmatrix} 0 & \exp(-i\beta) \\ \exp(i\beta) & 0 \end{pmatrix}. \tag{2}$$

The angle β is defined by [31]

$$\tan\beta = \frac{V_E\sin\alpha - \frac{1}{2}W_E\rho\sin 2\alpha}{V_E\cos\alpha + \frac{1}{2}W_E\rho\cos 2\alpha}. \tag{3}$$

The reader verifies immediately that in the absence of the quadratic effect ($W_E = 0$), the angle β reduces to α, and the first-order formalism described by Eqns.(2.73 - 2.75) is recovered. Since the diabatic coupling matrix in Eq.(2) is analogous to the matrix Eq.(2.75), introducing eigenfunctions analogous to those given by (2.76) leads to the two adiabatic potential energy surfaces:

$$V_\pm^{APES} = \frac{1}{2}\hbar\omega\rho^2 \pm \rho[V_E^2 + V_E W_E\rho\cos 3\alpha + (\frac{1}{2}W_E)^2\rho^2]^{\frac{1}{2}} \tag{4}$$

Inspecting Eq.(4), we find that the quadratic order adds periodic warping to the rim of the Mexican hat profile as shown in Figure 2.2, turning the cylindrical symmetry of the linear problem into threefold symmetry. Further, three more points of degeneracy, i.e. zeros of the square root term in Eq.(4) are added to that at the origin. Their coordinates are $\rho = 2V_E/W_E$ and $\varphi = \pi/3, \pi$, and $5\pi/3$.

Employing, as in Eqns.(2.87,2.88), the single valued representation of the wave functions, and repeating the calculation done for the linear approximation in Eq.(2.89), one arrives at the vector potential for the quadratic model. We stipulate

$$\psi'_+ = \frac{1}{\sqrt{2}}(|E_1\rangle + \exp(i\theta)|E_2\rangle) \tag{5}$$

$$\psi'_- = \frac{1}{\sqrt{2}}(|E_1\rangle - \exp(i\theta)|E_2\rangle) \tag{6}$$

The angle θ is determined as a function of α and ρ from the condition that the pair $\{\psi'_+, \psi'_-\}$ diagonalizes the right hand side of Eq.(2). The most elementary choice that satisfies this condition is $\theta = \beta$. Using this assignment, we compute in analogy to Eq.(2.91) the geometric phase accumulated as the ground state wave function is transported along the loop C_0 that encircles the origin, as shown in Figure 1. This problem is by far less elementary than that posed by the linear case, but is still analytically solvable. The result is [32]

$$\begin{aligned}
\varphi(C_0) &= i \oint_{C_0} \langle \psi_- | \nabla_{\boldsymbol{Q}} \, \psi_- \rangle d\mathbf{Q} = i \oint_{C_0} \frac{i}{2} \nabla_{\boldsymbol{Q}} \, \theta \; d\mathbf{Q} \\
&= -\frac{1}{2} \int_0^{2\pi} \frac{\partial \theta}{\partial \alpha} \, d\alpha \\
&= -\frac{1}{2} \int_0^{2\pi} \frac{V_E^2 - \frac{1}{2} W_E^2 \rho^2 - \frac{1}{2} V_E W_E \rho \cos 3\alpha}{V_E^2 + \frac{1}{4} W_E^2 \rho^2 + \frac{1}{2} V_E W_E \rho \cos 3\alpha} \, d\alpha = -\pi
\end{aligned} \tag{7}$$

Exercise 2.8 : Verify Eq.(7)

Integrating along the curve C_1 in the same, i.e. the counterclockwise sense, we obtain the previous result with inverted sign:

$$\varphi(C_1) = \pi. \tag{8}$$

Further, if we extend the line integral to include both the central and a peripheral intersection, employing for instance the loop C_2 in Figure 2.6 as boundary, the effects of the two enclosed vector potential singularities add up to yield a vanishing geometric phase: $\varphi(C_2) = 0$.

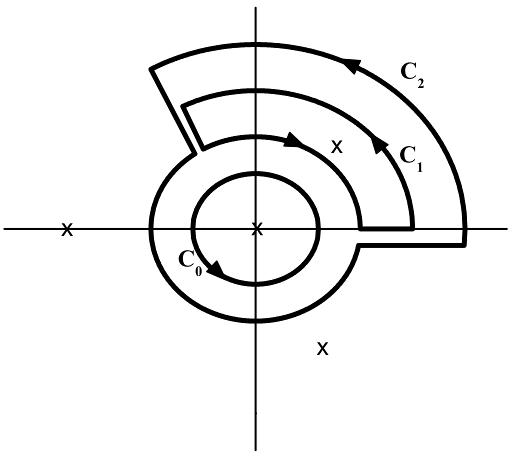

Figure 1: The central and the three peripheral conical intersections of the $E \times e$ Jahn-Teller problem extended to quadratic order. The geometric phases accumulated along the three closed loops C_0, C_1, and C_2 depend on the type and the number of the enclosed conical intersections.

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