On The Theoretical Treatment of Multi – State Born – Oppenheimer System with Dynamical Calculation

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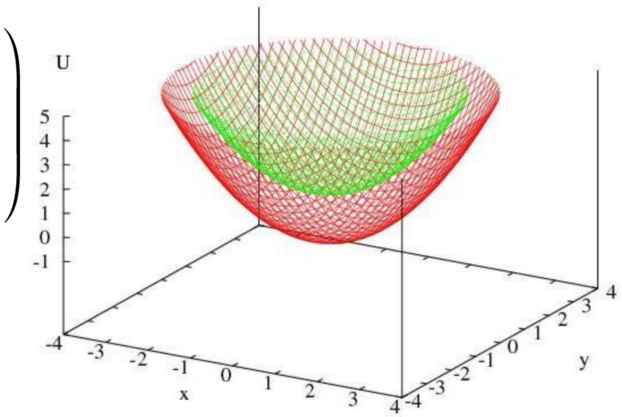
⇨Herzberg and Longuet - Higgins (HLH) studied the Jahn - Teller conical intersection (CI) model.

The Jahn-Teller Model and Longuet-Higgins Phase

The Jahn-Teller model is a “Toy” potential define degeneracy between two electronic states:

$$\hat{H} = \hat{H}_0 + \hat{W}$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\widehat{\nabla}^2 .\mathbf{1} + \frac{\omega}{2}\begin{pmatrix} x^2 + y^2 + \varepsilon & 0 \\ 0 & x^2 + y^2 - \varepsilon \end{pmatrix}$$



$$\hat{W} = k\begin{bmatrix} y & x \\ x & -y \end{bmatrix}$$

$$x = q\cos\theta$$

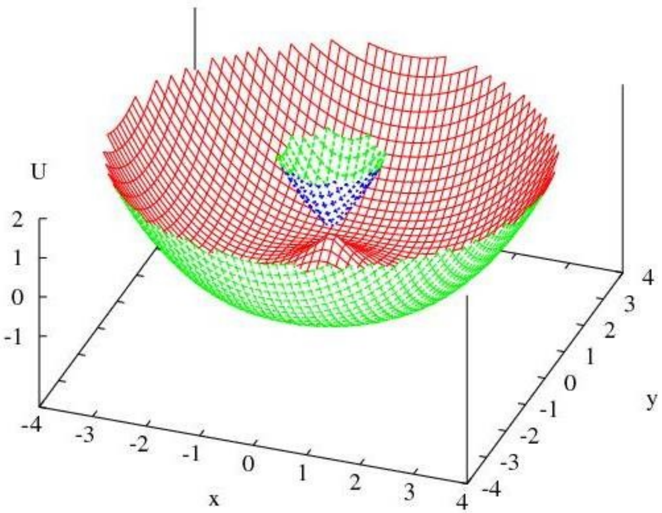
$$y = q\sin\theta$$

The eigenvalues and eigenfunctions are

$$\lambda = \pm kq$$

$$\xi_1 = \left(\frac{1}{\sqrt{\pi}} \cos\frac{\theta}{2}, \frac{1}{\sqrt{\pi}} \sin\frac{\theta}{2} \right)$$

$$\xi_2 = \left(\frac{1}{\sqrt{\pi}} \sin\frac{\theta}{2}, - \frac{1}{\sqrt{\pi}} \cos\frac{\theta}{2} \right)$$



When $\theta \rightarrow \theta + 2\pi$, ξ_1 and ξ_2 change sign

⇨HLH found the existence of multi - valued electronic wavefunction and corrected in ad hoc manner.

$$\xi_1 = \left(\frac{1}{\sqrt{\pi}} \cos\frac{\theta}{2}, \frac{1}{\sqrt{\pi}} \sin\frac{\theta}{2} \right) e^{\frac{i\theta}{2}}$$

$$\xi_2 = \left(\frac{1}{\sqrt{\pi}} \sin\frac{\theta}{2}, - \frac{1}{\sqrt{\pi}} \cos\frac{\theta}{2} \right) e^{\frac{i\theta}{2}}$$

⇨HLH observation pointed out that electron - nuclear separation (BO treatment and approximation) needs care.

The Born - Oppenheimer treatment for three electronic state (N =3)

The Born - Oppenheimer expansion of the wavefunction for the subspace of the Hilbert space along with the total electron-nuclei Hamiltonian in adiabatic representation:

$$\begin{aligned}\Psi(\mathbf{n},\mathbf{e}) &= \sum_{i=1}^{3}\psi_i(\mathbf{n})\xi_i(\mathbf{e},\mathbf{n}),\\ \hat{H} &= \hat{T}_n + \hat{H}_e(\mathbf{e},\mathbf{n}),\end{aligned} \qquad (1)$$

$$\hat{T}_n = -\frac{\hbar^2}{2m}\sum_n \nabla_n^2, \qquad \hat{H}_e(\mathbf{e},\mathbf{n})\xi_i(\mathbf{e},\mathbf{n}) = u_i(\mathbf{n})\xi_i(\mathbf{e},\mathbf{n}),$$

The matrix representation of adiabatic nuclear SE

$$-\frac{\hbar^2}{2m}\nabla^2\psi_j(\mathrm{n}) + \left(u_j(\mathrm{n}) - E\right)\psi_j(\mathrm{n}) - \frac{\hbar^2}{2m}\sum_{i=1}^{N}\left\{2\vec{\tau}_{ji}^{(1)}\vec{\nabla}\psi_i(\mathrm{n}) + \tau_{ji}^{(2)}\psi_i(\mathrm{n})\right\} = 0$$

$$\vec{\tau}_{ij}^{(1)} = \langle\xi_i(\mathbf{e},\mathbf{n})|\vec{\nabla}|\xi_j(\mathbf{e},\mathbf{n})\rangle, \qquad \tau_{ij}^{(2)} = \langle\xi_i(\mathbf{e},\mathbf{n})|\nabla^2|\xi_j(\mathbf{e},\mathbf{n})\rangle, \qquad (2)$$

$$\tau^{(2)} = \vec{\tau}^{(1)}\cdot\vec{\tau}^{(1)} + \vec{\nabla}\vec{\tau}^{(1)}$$

The compact form of kinetically coupled nuclear SE

$$-\frac{\hbar^2}{2m}\begin{pmatrix} \vec{\nabla} & \vec{\tau}_{12} & \vec{\tau}_{13} \\ -\vec{\tau}_{12} & \vec{\nabla} & \vec{\tau}_{23} \\ -\vec{\tau}_{13} & -\vec{\tau}_{23} & \vec{\nabla} \end{pmatrix}^2 \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} + \begin{pmatrix} u_1 - E & 0 & 0 \\ 0 & u_2 - E & 0 \\ 0 & 0 & u_3 - E \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = 0, \qquad (3)$$

where the NAC matrix is defined as:

$$\vec{\boldsymbol{\tau}} = \begin{pmatrix} 0 & \vec{\tau}_{12} & \vec{\tau}_{13} \\ -\vec{\tau}_{12} & 0 & \vec{\tau}_{23} \\ -\vec{\tau}_{13} & -\vec{\tau}_{23} & 0 \end{pmatrix} \qquad (4)$$

Since the three states constitute the sub-Hilbert space, it is possible to transform (**Ψ=AΨ^d**) the adiabatic nuclear SE to the diabatic one as below,

$$\begin{pmatrix} -\frac{\hbar^2}{2m}\nabla^2 - E & 0 & 0 \\ 0 & -\frac{\hbar^2}{2m}\nabla^2 - E & 0 \\ 0 & 0 & -\frac{\hbar^2}{2m}\nabla^2 - E \end{pmatrix} \begin{pmatrix} \psi_1^d \\ \psi_2^d \\ \psi_3^d \end{pmatrix} + \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \begin{pmatrix} \psi_1^d \\ \psi_2^d \\ \psi_3^d \end{pmatrix} = 0, \qquad (5)$$

$$\mathbf{W} = \mathbf{A}^\dagger \mathbf{U} \mathbf{A} \qquad U_{ij} = u_i \delta_{ij}$$

under the condition:

$$\vec{\nabla}\mathbf{A} + \vec{\boldsymbol{\tau}}\mathbf{A} = 0. \qquad (6)$$

Let us define these three rotation matrices [$\mathbf{A}_{12}(\theta_{12})$, $\mathbf{A}_{23}(\theta_{23})$, $\mathbf{A}_{13}(\theta_{13})$] and one of the ways of their product ($\mathbf{A}$) as:

$$\mathbf{A}(\theta_{12},\theta_{23},\theta_{13}) = \mathbf{A}_{12}(\theta_{12})\cdot\mathbf{A}_{23}(\theta_{23})\cdot\mathbf{A}_{13}(\theta_{13})$$

$$= \begin{pmatrix} \cos\theta_{12} & \sin\theta_{12} & 0 \\ -\sin\theta_{12} & \cos\theta_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_{23} & \sin\theta_{23} \\ 0 & -\sin\theta_{23} & \cos\theta_{23} \end{pmatrix} \begin{pmatrix} \cos\theta_{13} & 0 & \sin\theta_{13} \\ 0 & 1 & 0 \\ -\sin\theta_{13} & 0 & \cos\theta_{13} \end{pmatrix}$$

$$= \begin{pmatrix} \begin{matrix}\cos\theta_{12}\cos\theta_{13} \\ -\sin\theta_{12}\sin\theta_{13}\sin\theta_{23}\end{matrix} & \sin\theta_{12}\cos\theta_{23} & \begin{matrix}\cos\theta_{12}\sin\theta_{13} \\ +\sin\theta_{12}\cos\theta_{13}\sin\theta_{23}\end{matrix} \\ \\ \begin{matrix}-\sin\theta_{12}\cos\theta_{13} \\ -\cos\theta_{12}\sin\theta_{13}\sin\theta_{23}\end{matrix} & \cos\theta_{12}\cos\theta_{23} & \begin{matrix}-\sin\theta_{12}\sin\theta_{13} \\ +\cos\theta_{12}\cos\theta_{13}\sin\theta_{23}\end{matrix} \\ \\ -\sin\theta_{13}\cos\theta_{23} & -\sin\theta_{23} & \cos\theta_{13}\cos\theta_{23} \end{pmatrix} \qquad (7)$$

Substituting the above model form of **A** matrix and the anti-symmetric form of $\boldsymbol{\tau}$-matrix in Eq. (6), leads to the following equations[1] for ADT angles:

$$\begin{aligned}
\vec{\nabla}\theta_{12} &= -\vec{\tau}_{12} + \tan\theta_{23}(\vec{\tau}_{13}\cos\theta_{12} - \vec{\tau}_{23}\sin\theta_{12}), && \text{(8a)}\\
\vec{\nabla}\theta_{23} &= -(\vec{\tau}_{13}\sin\theta_{12} + \vec{\tau}_{23}\cos\theta_{12}), && \text{(8b)}\\
\vec{\nabla}\theta_{13} &= -\frac{1}{\cos\theta_{23}}(\vec{\tau}_{13}\cos\theta_{12} - \vec{\tau}_{23}\sin\theta_{12}), && \text{(8c)}
\end{aligned}$$

which in turn brings the explicit form of $\boldsymbol{\tau}$ matrix elements[2] in terms of ADT angles:

$$\begin{aligned}
\vec{\tau}_{12} &= -\vec{\nabla}\theta_{12} - \sin\theta_{23}\vec{\nabla}\theta_{13}, && \text{(9a)}\\
\vec{\tau}_{23} &= \sin\theta_{12}\cos\theta_{23}\vec{\nabla}\theta_{13} - \cos\theta_{12}\vec{\nabla}\theta_{23}, && \text{(9b)}\\
\vec{\tau}_{13} &= -\cos\theta_{12}\cos\theta_{23}\vec{\nabla}\theta_{13} - \sin\theta_{12}\vec{\nabla}\theta_{23}, && \text{(9c)}
\end{aligned}$$

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[1] Z. H. Top and M. Baer, J. Chem. Phys. **66**, 1363 (1977).
[2] Biplab Sarkar and Satrajit Adhikari, J. Chem. Phys. **124**, 074101 (2006);
Biplab Sarkar and Satrajit Adhikari, J. Phys. Chem. A **112**, 9868 (2008).

The analyticity of the Transformation Matrix 'A' for any two nuclear coordinates (*p* and *q*):

$$\frac{\partial}{\partial p}\tau^q_{ij} - \frac{\partial}{\partial q}\tau^p_{ij} = (\boldsymbol{\tau}^q\boldsymbol{\tau}^p)_{ij} - (\boldsymbol{\tau}^p\boldsymbol{\tau}^q)_{ij}, \tag{10}$$

$$\tau^p_{ij} = \langle\xi_i|\nabla_p|\xi_j\rangle, \qquad \tau^q_{ij} = \langle\xi_i|\nabla_q|\xi_j\rangle.$$

The Curl condition in terms of ADT angles:

$$\text{Curl } \tau^{pq}_{12} = [\boldsymbol{\tau}\times\boldsymbol{\tau}]^{pq}_{12} = -\cos\theta_{23}(\nabla_q\theta_{23}\nabla_p\theta_{13} - \nabla_p\theta_{23}\nabla_q\theta_{13}) \tag{11a}$$

$$\begin{aligned}\text{Curl } \tau^{pq}_{23} = [\boldsymbol{\tau}\times\boldsymbol{\tau}]^{pq}_{23} &= \cos\theta_{12}\cos\theta_{23}(\nabla_q\theta_{12}\nabla_p\theta_{13} - \nabla_p\theta_{12}\nabla_q\theta_{13})\\ &- \sin\theta_{12}\sin\theta_{23}(\nabla_q\theta_{23}\nabla_p\theta_{13} - \nabla_p\theta_{23}\nabla_q\theta_{13})\\ &+ \sin\theta_{12}(\nabla_q\theta_{12}\nabla_p\theta_{23} - \nabla_p\theta_{12}\nabla_q\theta_{23})\end{aligned} \tag{11b}$$

$$\begin{aligned}\text{Curl } \tau^{pq}_{13} = [\boldsymbol{\tau}\times\boldsymbol{\tau}]^{pq}_{13} &= \sin\theta_{12}\cos\theta_{23}(\nabla_q\theta_{12}\nabla_p\theta_{13} - \nabla_p\theta_{12}\nabla_q\theta_{13})\\ &+ \cos\theta_{12}\sin\theta_{23}(\nabla_q\theta_{23}\nabla_p\theta_{13} - \nabla_p\theta_{23}\nabla_q\theta_{13})\\ &- \cos\theta_{12}(\nabla_q\theta_{12}\nabla_p\theta_{23} - \nabla_p\theta_{12}\nabla_q\theta_{23})\end{aligned} \tag{11c}$$

The explicit forms of *div* τ_{ij}s are:

$$\begin{aligned}
\text{div } \vec{\tau}_{12} &= 2\sin\theta_{12}\cos\theta_{12}\cos^2\theta_{23}(\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{13}) \\
&- 2\sin\theta_{12}\cos\theta_{12}(\vec{\nabla}\theta_{23}\cdot\vec{\nabla}\theta_{23}) - 3\cos^2\theta_{12}\cos\theta_{23}(\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{23}) \\
&+ \sin^2\theta_{12}\cos\theta_{23}(\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{23}) - \sin\theta_{23}\nabla^2\theta_{13} - \nabla^2\theta_{12} \qquad (12a) \\
\text{div } \vec{\tau}_{23} &= 2\sin\theta_{12}\sin\theta_{23}\cos\theta_{23}(\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{13}) \\
&+ 3\cos\theta_{12}\cos\theta_{23}(\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{23}) + 3\sin\theta_{12}(\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{23}) \\
&+ \sin\theta_{12}\sin\theta_{23}(\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{23}) + \sin\theta_{12}\cos\theta_{23}\nabla^2\theta_{12} - \cos\theta_{12}\nabla^2\theta_{23} \qquad (12b) \\
\text{div } \vec{\tau}_{13} &= 2\sin\theta_{12}\sin\theta_{23}\cos\theta_{23}(\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{12}) \\
&+ 3\sin\theta_{12}\cos\theta_{23}(\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{13}) - 3\cos\theta_{12}(\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{23}) \\
&- \cos\theta_{12}\sin\theta_{23}(\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{23}) - \cos\theta_{12}\cos\theta_{23}\nabla^2\theta_{13} - \sin\theta_{12}\nabla^2\theta_{23} \qquad (12c)
\end{aligned}$$

Moreover, it is possible to show that there are altogether six (6) different ways to take the product of the three rotation matrices [$\mathbf{A}_{12}(\theta_{12})$, $\mathbf{A}_{23}(\theta_{23})$, $\mathbf{A}_{13}(\theta_{13})$], to obtain the ADT matrix (**A**):

$$\mathbf{A} = P_n\{\mathbf{A}_{12}(\theta_{12})\cdot\mathbf{A}_{23}(\theta_{23})\cdot\mathbf{A}_{13}(\theta_{13})\}, \qquad n = 1, \cdot\cdot N!, \qquad (13)$$

Jahn – Teller distortions in the presence of accidental degeneracy: The excited states of Na_3 system

The general form of the diabatic Hamiltonian matrix (3x3) for the electron – nuclear BO system[3]:

$$\hat{\mathrm{H}}(\rho,\phi) = \hat{\mathrm{T}}_{\mathrm{N}}\cdot\mathbf{1} + \hat{\mathrm{H}}_{\mathrm{e}}(\rho,\phi), \qquad \hat{\mathrm{T}}_{\mathrm{N}} = -\frac{\hbar^2}{2\mu}\Big(\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\Big),$$

$$\hat{\mathrm{H}}_{\mathrm{e}}(\rho,\phi) = \begin{pmatrix} \frac{\rho^2}{2} & K\rho e^{i\phi}+\frac{1}{2}g\rho^2e^{-2i\phi} & P\rho e^{-i\phi}+\frac{1}{2}f\rho^2e^{2i\phi} \\ K\rho e^{-i\phi}+\frac{1}{2}g\rho^2e^{2i\phi} & \frac{\rho^2}{2} & P\rho e^{i\phi}+\frac{1}{2}f\rho^2e^{-2i\phi} \\ P\rho e^{i\phi}+\frac{1}{2}f\rho^2e^{-2i\phi} & P\rho e^{-i\phi}+\frac{1}{2}f\rho^2e^{2i\phi} & \epsilon_0+\frac{d\rho^2}{2} \end{pmatrix} \qquad (14)$$

which under the unitary transformation matrix,

$$\hat{\mathrm{U}}_{\mathrm{e}} = \frac{1}{\sqrt{2}}\begin{pmatrix} i & 1 & 0 \\ 1 & i & 0 \\ 0 & 0 & 1+i \end{pmatrix}$$

takes the following form:

$$\hat{\mathrm{H}}_{\mathrm{e}}(\rho,\phi) = \begin{pmatrix} \frac{\rho^2}{2}+U_2 & U_1 & W_1-W_2 \\ U_1 & \frac{\rho^2}{2}-U_2 & W_1+W_2 \\ W_1-W_2 & W_1+W_2 & \epsilon_0+\frac{d\rho^2}{2} \end{pmatrix} \qquad (15)$$

with $U_1 = K\rho\cos\phi + \frac{1}{2}g\rho^2\cos(2\phi)$, and $U_2 = K\rho\sin\phi - \frac{1}{2}g\rho^2\sin(2\phi)$,

where $\rho^2/2$ and $\varepsilon_0 + d\rho^2/2$ are the energies for the E- and A- type states. The potentials W_i's are of the same forms as U_i's but defined in terms of different set of coupling parameters *P* and *f* which replace *K* and *g*, respectively.

[3]F. Cocchini, T. H. Upton and W. Andreoni, J. Chem. Phys. 88, 6068 (1988).

If P and f are zero, the model represents the Jahn – Teller interaction and the eigenvalues of the matrix takes the following form:

$$\begin{aligned} u_1(\rho,\phi) &= \frac{\rho^2}{2} - \sqrt{K^2\rho^2 + \frac{g^2\rho^4}{4} + Kg\rho^3\cos(3\phi)}, \\ u_2(\rho,\phi) &= \frac{\rho^2}{2} + \sqrt{K^2\rho^2 + \frac{g^2\rho^4}{4} + Kg\rho^3\cos(3\phi)}, \end{aligned}$$

where the corresponding eigenvectors are given by:

$$\mathbf{A} = \begin{pmatrix} \sqrt{\frac{v+U_2}{2v}} & -\sqrt{\frac{v-U_2}{2v}} \\ \\ \sqrt{\frac{v-U_2}{2v}} & \sqrt{\frac{v+U_2}{2v}} \end{pmatrix}, \qquad (16)$$

with $\quad v = \left(K^2\rho^2 + \frac{1}{4}g^2\rho^4 + Kg\rho^3\cos 3\phi\right)^{1/2}.$

If K and g are zero, the Hamiltonian becomes pseudo – Jahn – Teller model. In this situation the eigenvalues of the matrix takes the following form:

$$u_1(\rho,\phi) = \frac{1}{2}\left(\epsilon_0 + \frac{d\rho^2}{2} + \frac{\rho^2}{2}\right) - \sqrt{\Delta^2 + 2w}, \qquad (17a)$$

$$u_2(\rho,\phi) = \frac{\rho^2}{2}, \qquad (17b)$$

$$u_3(\rho,\phi) = \frac{1}{2}\left(\epsilon_0 + \frac{d\rho^2}{2} + \frac{\rho^2}{2}\right) + \sqrt{\Delta^2 + 2w}, \qquad (17c)$$

with $\quad \Delta = \frac{1}{2}\left(\epsilon_0 + \frac{d\rho^2}{2} - \frac{\rho^2}{2}\right) \quad$ and $\quad w = W_1^2 + W_2^2 = P^2\rho^2 + \frac{1}{4}f^2\rho^4 + Pf\rho^3\cos(3\phi)$.

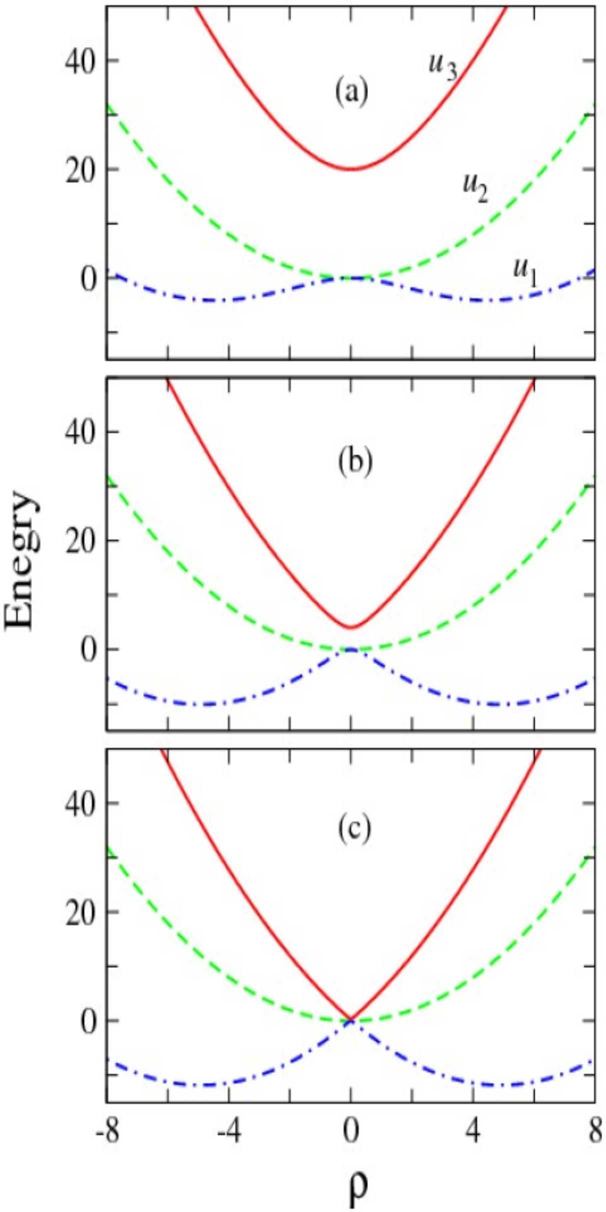


Fig. 1: The three adiabatic potential energy curves [u_1, u_2 and u_3] as functions of ρ with $\varphi = \pi/2$, where (a), (b), (c) are for Δ values 10, 2, and 0.2, respectively.

The columns of the following matrix are the three electronic basis functions:

$$\mathbf{A} = \begin{pmatrix} -\frac{(W_1+W_2)}{\sqrt{2w}} & \frac{(W_1-W_2)}{\sqrt{2w+\{\Delta-\sqrt{\Delta^2+2w}\}^2}} & \frac{(W_1-W_2)}{\sqrt{2w+\{\Delta+\sqrt{\Delta^2+2w}\}^2}} \\ \frac{(W_1-W_2)}{\sqrt{2w}} & \frac{(W_1+W_2)}{\sqrt{2w+\{\Delta-\sqrt{\Delta^2+2w}\}^2}} & \frac{(W_1+W_2)}{\sqrt{2w+\{\Delta+\sqrt{\Delta^2+2w}\}^2}} \\ 0 & \frac{\Delta-\sqrt{\Delta^2+2w}}{\sqrt{2w+\{\Delta-\sqrt{\Delta^2+2w}\}^2}} & \frac{\Delta+\sqrt{\Delta^2+2w}}{\sqrt{2w+\{\Delta+\sqrt{\Delta^2+2w}\}^2}} \end{pmatrix}. \quad (18)$$

Non – adiabatic coupling terms: $\nabla A + \tau A = 0$

Considering two state ADT matrix (Eq. 16), the ρ and φ component of the NAC matrix are analytically calculated as:

$$\boldsymbol{\tau}^{\rho} = \begin{pmatrix} 0 & -\frac{Kg\rho^2}{4v^2}\sin(3\phi) \\ \frac{Kg\rho^2}{4v^2}\sin(3\phi) & 0 \end{pmatrix},$$

and

$$\boldsymbol{\tau}^{\phi} = \begin{pmatrix} 0 & -\frac{-2K^2\rho^2+g^2\rho^4+Kg\rho^3\cos(3\phi)}{4v^2} \\ \frac{-2K^2\rho^2+g^2\rho^4+Kg\rho^3\cos(3\phi)}{4v^2} & 0 \end{pmatrix}$$

On the other hand, we use three state ADT matrix (Eq. 18) and evaluate the analytical forms of ρ and φ component of the NAC matrix elements:

$$\tau_{12}^{\rho} = -\frac{Pf\rho^2\sin(3\phi)}{[2w(2w+\{\Delta-\sqrt{\Delta^2+2w}\}^2)]^{1/2}}, \quad (19a)$$

$$\tau_{13}^{\rho} = -\frac{Pf\rho^2\sin(3\phi)}{[2w(2w+\{\Delta+\sqrt{\Delta^2+2w}\}^2)]^{1/2}}, \quad (19b)$$

$$\tau_{23}^{\rho} = \frac{\Delta\cdot(2P^2\rho+f^2\rho^3+3Pf\rho^2\cos(3\phi))}{2\sqrt{2w}(\Delta^2+2w)}, \quad (19c)$$

and

$$\tau_{12}^{\phi} = \frac{[2P^2\rho^2-f^2\rho^4-Pf\rho^3\cos(3\phi)]}{[2w(2w+\{\Delta-\sqrt{\Delta^2+2w}\}^2)]^{1/2}}, \quad (20a)$$

$$\tau_{13}^{\phi} = \frac{[2P^2\rho^2-f^2\rho^4-Pf\rho^3\cos(3\phi)]}{[2w(2w+\{\Delta+\sqrt{\Delta^2+2w}\}^2)]^{1/2}}, \quad (20b)$$

$$\tau_{23}^{\phi} = -\frac{\Delta\cdot 3Pf\rho^3\sin(3\phi)}{2\sqrt{2w}(\Delta^2+2w)}, \quad (20c)$$

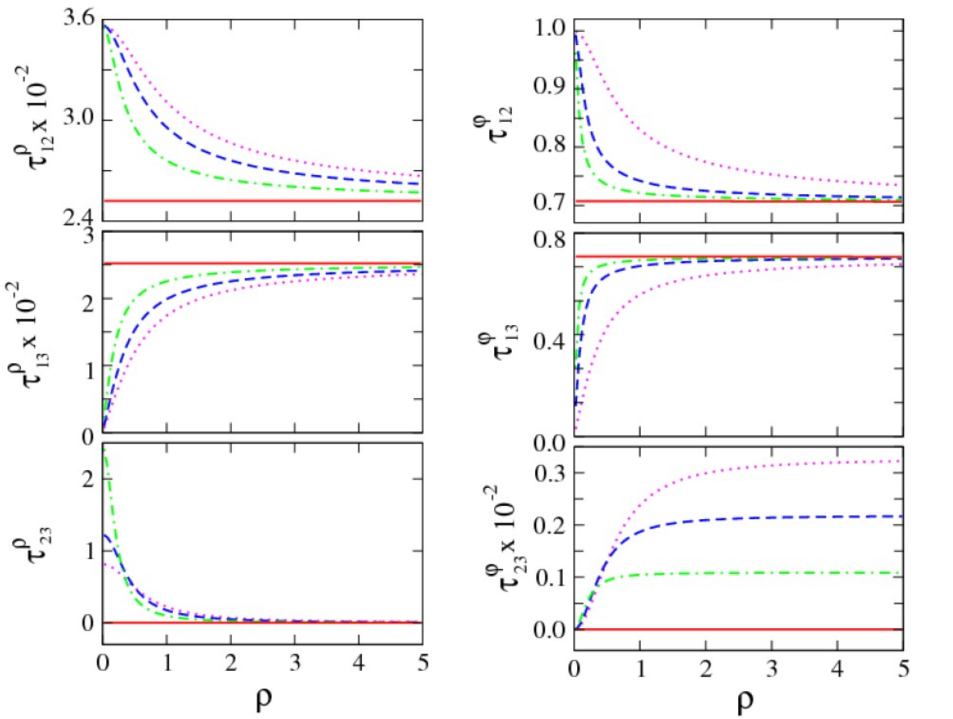


Fig.2. The ρ and φ components of the non-adiabatic coupling elements as functions of ρ at a fixed φ =π /2 with Δ values 3 (···), 2 (−−−), 1 (·-·-·) and 0 (—), respectively.

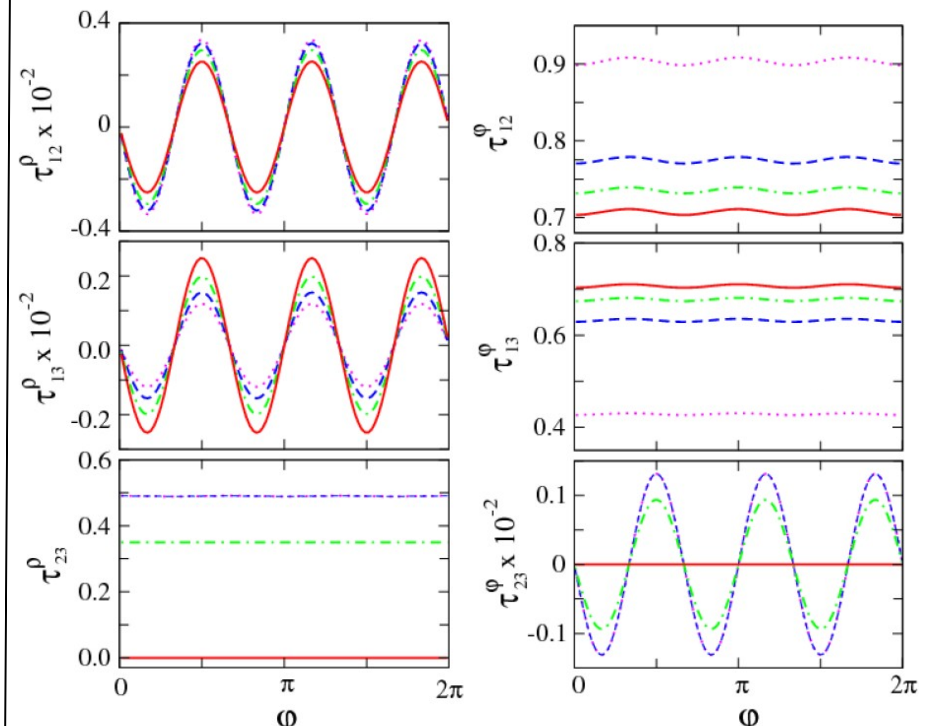


Fig.3. The ρ and φ components of the non-adiabatic coupling elements as functions of φ at a fixed ρ=0.5 with Δ values 3 (···), 2 (−−−), 1 (·-·-·) and 0 (—), respectively.

Curls:

With the analytical form of the NAC matrix for the two - state (JT) case, the Curl appears identically zero:

$$\mathbf{Curl}\boldsymbol{\tau} = \mathbf{0},$$

but for the three – state (*PJT*) case the same appear as the following:

$$\begin{aligned}
\text{Curl } \tau_{12}^{\rho\phi} &= \frac{\Delta}{4w(\Delta^2+2w)[2w+\{\Delta+\sqrt{\Delta^2+2w}\}^2]^{1/2}} \times \Big[-3P^2 f^2 \rho^5 \sin^2(3\phi) \\
&+ \{2P^2\rho^2 - f^2\rho^4 - Pf\rho^3\cos(3\phi)\}\{2P^2\rho + f^2\rho^3 + 3Pf\rho^2\cos(3\phi)\}\Big], \qquad (21a)\\
\text{Curl } \tau_{13}^{\rho\phi} &= \frac{\Delta}{4w(\Delta^2+2w)[2w+\{\Delta-\sqrt{\Delta^2+2w}\}^2]^{1/2}} \times \Big[3P^2 f^2 \rho^5 \sin^2(3\phi) \\
&- \{2P^2\rho^2 - f^2\rho^4 - Pf\rho^3\cos(3\phi)\}\{2P^2\rho + f^2\rho^3 + 3Pf\rho^2\cos(3\phi)\}\Big], \qquad (21b)\\
\text{Curl } \tau_{23}^{\rho\phi} &= 0. \qquad (21c)
\end{aligned}$$

It is important to note that in case of pseudo - JT model situation for each and every ρ and φ points in the configuration space: (a) at $\Delta=0$, *all the Curl elements become identically zero (**Curl $\boldsymbol{\tau}$ = 0**) even with non -zero τ- components*; (b) at $\Delta\neq 0$, *even with diabatic Hamiltonian, at least two Curl elements show up theoretically non - zero contribution*.

On the other hand, if we substitute the components of the τ matrix elements for the three - state in the following first order differential equations:

$$\vec{\nabla}\theta_{12} = -\vec{\tau}_{12} + \tan\theta_{23}(\vec{\tau}_{13}\cos\theta_{12} - \vec{\tau}_{23}\sin\theta_{12}), \tag{22a}$$

$$\vec{\nabla}\theta_{23} = -(\vec{\tau}_{13}\sin\theta_{12} + \vec{\tau}_{23}\cos\theta_{12}), \tag{22b}$$

$$\vec{\nabla}\theta_{13} = -\frac{1}{\cos\theta_{23}}(\vec{\tau}_{13}\cos\theta_{12} - \vec{\tau}_{23}\sin\theta_{12}), \tag{22c}$$

and solve them numerically by using predictor - corrector method to obtain ADT angle (Eq. 22) for various Δ values:

Δ=0 **Δ=2**

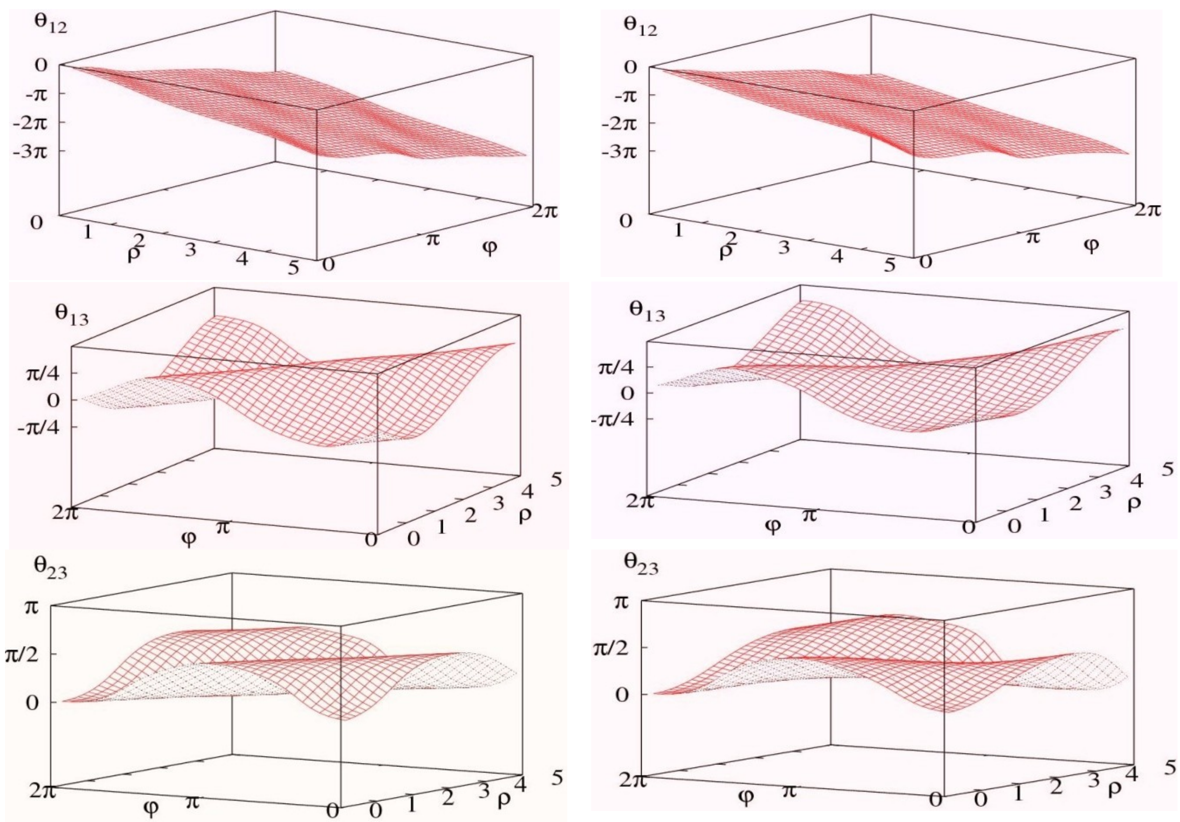


Fig. 4. The ADT angles θ_{12}, θ_{13} and θ_{23} as functions of ρ and φ for Δ = 0 and Δ = 2.

The general analytic form of the curls in terms of those ADT angles are obtained as:

$$\text{Curl } \tau_{12}^{pq} = -\cos\theta_{23}(\nabla_q\theta_{23}\nabla_p\theta_{13} - \nabla_p\theta_{23}\nabla_q\theta_{13}), \tag{23a}$$

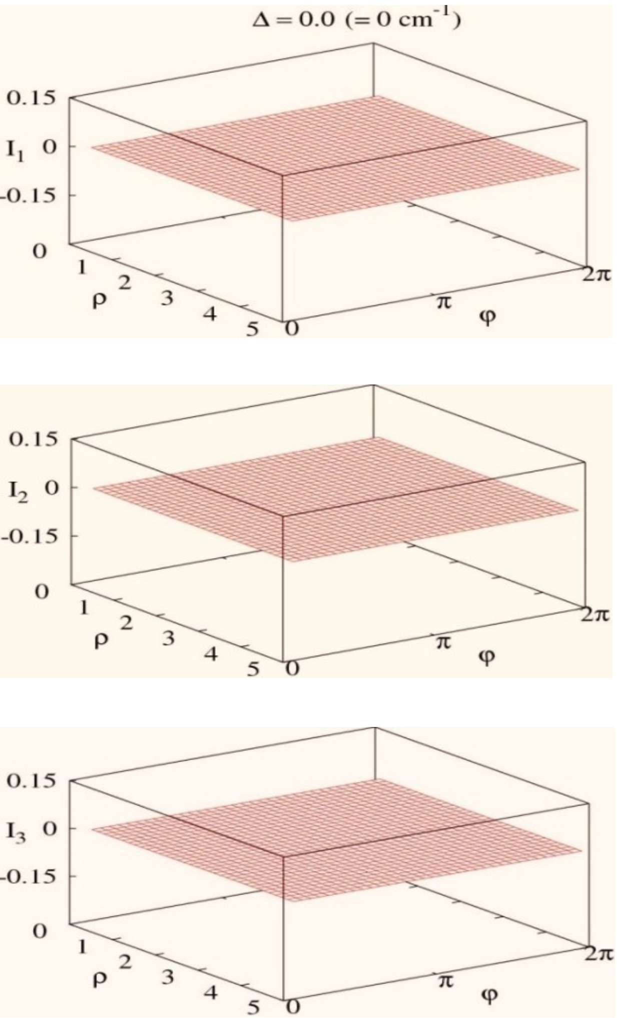
$$\begin{aligned}\text{Curl } \tau_{23}^{pq} &= \cos\theta_{12}\cos\theta_{23}(\nabla_q\theta_{12}\nabla_p\theta_{13} - \nabla_p\theta_{12}\nabla_q\theta_{13}) \\ &- \sin\theta_{12}\sin\theta_{23}(\nabla_q\theta_{23}\nabla_p\theta_{13} - \nabla_p\theta_{23}\nabla_q\theta_{13}) \\ &+ \sin\theta_{12}(\nabla_q\theta_{12}\nabla_p\theta_{23} - \nabla_p\theta_{12}\nabla_q\theta_{23}),\end{aligned} \tag{23b}$$

$$\begin{aligned}\text{Curl } \tau_{13}^{pq} &= \sin\theta_{12}\cos\theta_{23}(\nabla_q\theta_{12}\nabla_p\theta_{13} - \nabla_p\theta_{12}\nabla_q\theta_{13}) \\ &+ \cos\theta_{12}\sin\theta_{23}(\nabla_q\theta_{23}\nabla_p\theta_{13} - \nabla_p\theta_{23}\nabla_q\theta_{13}) \\ &- \cos\theta_{12}(\nabla_q\theta_{12}\nabla_p\theta_{23} - \nabla_p\theta_{12}\nabla_q\theta_{23}),\end{aligned} \tag{23c}$$

where the difference of the cross derivatives, namely, the Identities:

$$I_1 = (\nabla_\rho\theta_{12}\nabla_\phi\theta_{13} - \nabla_\phi\theta_{12}\nabla_\rho\theta_{13}), \qquad I_2 = (\nabla_\rho\theta_{12}\nabla_\phi\theta_{23} - \nabla_\phi\theta_{12}\nabla_\rho\theta_{23}),$$

and $$I_3 = (\nabla_\rho\theta_{13}\nabla_\phi\theta_{23} - \nabla_\phi\theta_{13}\nabla_\rho\theta_{23}) \tag{24a - c}$$



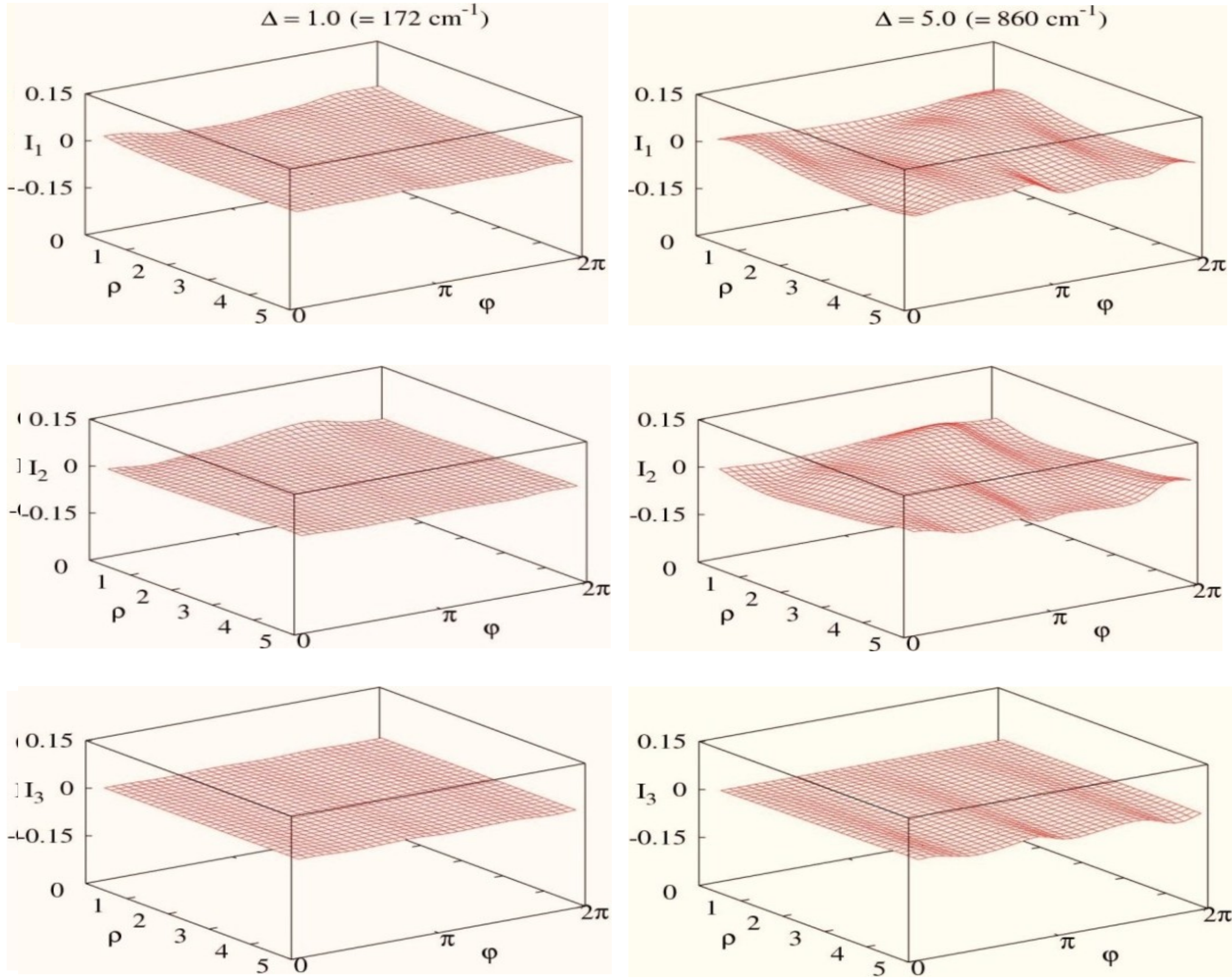


Fig. 5. The difference between the cross deri[...] element with respect to a pair of nuclear coord[...] functions of ρ and φ for Δ = 0 and Δ = 0.5.

Fig. 6. The same as in Fig. (5) but for Δ = 1 and Δ = 5.

Divergences:

$$\text{Div } \vec{\tau}_{12} = \frac{Kg\rho^4 \sin(3\phi)}{4v^4}\left[\frac{1}{2}g^2\rho + Kg\cos(3\phi) + 9(K^2\rho - \frac{1}{4}g^2\rho^3)\right] \quad \text{(for two state (JT))} \tag{25}$$

whereas for three – state:

$$\text{Div } \vec{\tau}_{12} = \text{Div } \vec{\tau}_{13} = \frac{Pf\rho^4 \sin(3\phi)}{2\sqrt{2}w^2}\left[\frac{1}{2}f^2\rho + Pf\cos(3\phi) + 9(P^2\rho - \frac{1}{4}f^2\rho^3)\right], \tag{26a}$$

$$\text{Div } \vec{\tau}_{23} = 0. \tag{26b}$$

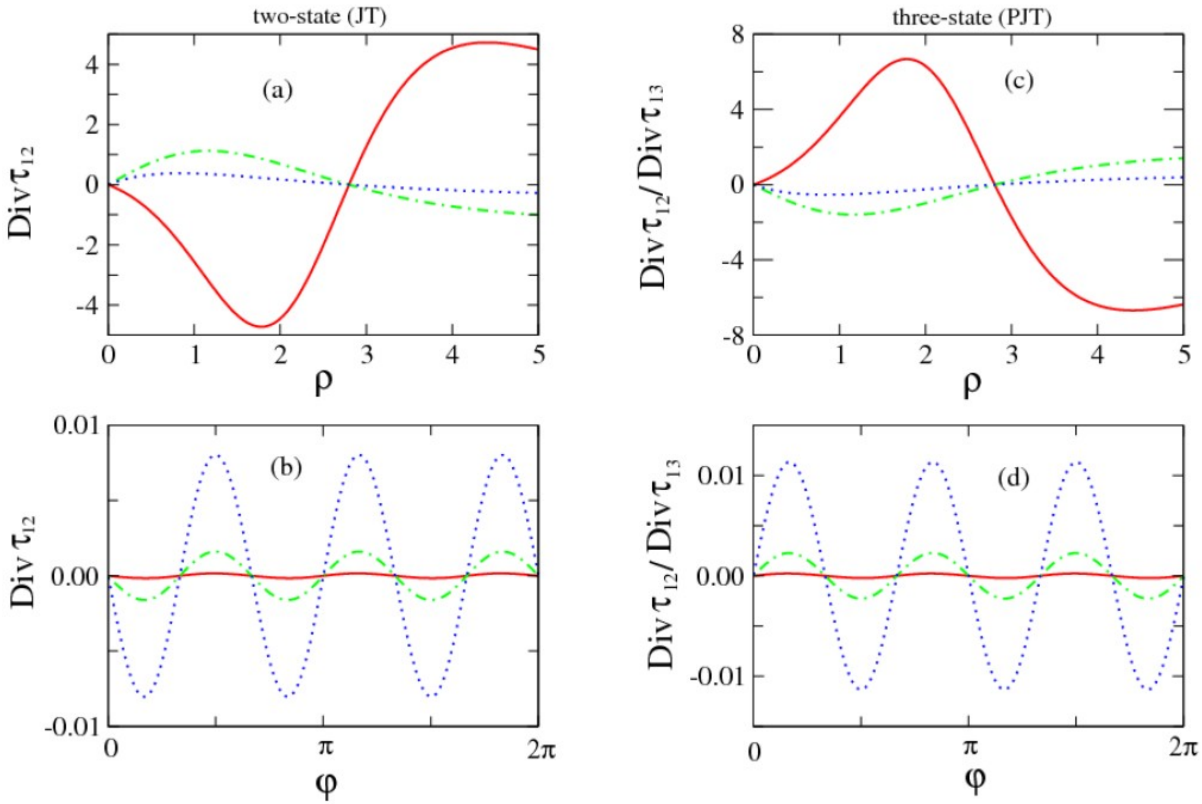


Fig. 7. The Divergence of the non-adiabatic coupling elements for two state (JT) [(a) and (b)] as well as three state (PJT) [(c) and (d)] system. In figure (a) and (c) the divergence is plotted as functions of ρ with φ = π/4(—); π/2(-·-·-); and 7π/12(···), and in (b) and (d) the same is presented as functions of φ with ρ = 0.5 (···); 0.1 (-·-·-); 0.01 (—), respectively.

The transformation matrix, *G* and the Topological matrix, *D*:

For two - state: The transformation matrix, G which diagonalizes the ρ and φ components of the NAC matrix, is given by:

$$\mathbf{G} = \begin{pmatrix} \frac{i}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix},$$

with eigenvalues $\pm i\omega_\rho$ and $i\omega_{\varphi}$, respectively, where

$$\omega_\rho = \frac{Kg\rho^2 \sin 3\phi}{4v^2}, \quad \text{and} \quad \omega_\phi = \frac{-2K^2\rho^2 + g^2\rho^4 + Kg\rho^3 \cos 3\phi}{4v^2}.$$

It has been found that the calculated eigenvalue of the φ component of the NAC matrix (ω_φ) is gauge invariant, i.e., for any fixed ρ value, the following integral appear as:

$$\int_0^{2\pi} \omega_\phi d\phi = \pi, \tag{27}$$

where the topological matrix, $\mathbf{D} = \exp(\int_0^{2\pi} \tau_\phi d\phi) = \mathbf{G} \ \exp(\int_0^{2\pi} \pm i\omega_\phi d\phi) \ \mathbf{G}^\dagger$, derived from ADT condition, ensures uniquely defined diabatic PESs as given by:

$$\mathbf{D} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{28}$$

For three - state: The transformation matrix $\mathbf{G}_\rho$ and $\mathbf{G}_\varphi$, which diagonalizes the ρ and φ component of the NAC matrix, have the following form:

$$\mathbf{G}_x = \begin{pmatrix} \frac{g_3^x}{\omega_x} & \frac{-g_1^x g_3^x - i g_2^x \omega_x}{\sqrt{2}\omega_x \eta_x} & \frac{-g_1^x g_3^x + i g_2^x \omega_x}{\sqrt{2}\omega_x \eta_x} \\ -\frac{g_2^x}{\omega_x} & \frac{g_1^x g_2^x - i g_3^x \omega_x}{\sqrt{2}\omega_x \eta_x} & \frac{g_1^x g_2^x + i g_3^x \omega_x}{\sqrt{2}\omega_x \eta_x} \\ \frac{g_1^x}{\omega_x} & \frac{\eta_x}{\sqrt{2}\omega_x} & \frac{\eta_x}{\sqrt{2}\omega_x} \end{pmatrix}, \quad x \equiv \{\rho, \phi\} \tag{29}$$

where

$g_1^x = \tau_{12}^x$; $g_2^x = \tau_{13}^x$; $g_3^x = \tau_{23}^x$

$$\eta_\rho = \sqrt{(g_2^\rho)^2 + (g_3^\rho)^2} = \left[\left\{ \frac{[Pf\rho^2 \sin(3\phi)]}{[2w(2w + \{\Delta + \sqrt{\Delta^2 + 2w}\}^2)]^{1/2}} \right\}^2 + \left\{ \frac{\Delta \cdot (2P^2\rho + f^2\rho^3 + 3Pf\rho^2 \cos(3\phi))}{2\sqrt{2w}(\Delta^2 + 2w)} \right\}^2 \right]^{\frac{1}{2}}, \tag{30}$$

$$\eta_\phi = \sqrt{(g_2^\phi)^2 + (g_3^\phi)^2} = \left[\left\{ \frac{[2P^2\rho^2 - f^2\rho^4 - Pf\rho^3 \cos(3\phi)]}{[2w(2w + \{\Delta + \sqrt{\Delta^2 + 2w}\}^2)]^{1/2}} \right\}^2 + \left\{ \frac{\Delta \cdot 3Pf\rho^3 \sin(3\phi)}{2\sqrt{2w}(\Delta^2 + 2w)} \right\}^2 \right]^{\frac{1}{2}}, \tag{31}$$

with eigenvalues 0, $\pm i\omega_{\rho/\varphi}$, where

$$\omega_\rho = \sqrt{(g_1^\rho)^2 + (g_2^\rho)^2 + (g_3^\rho)^2}$$

$$= \left[\left\{ \frac{Pf\rho^2 \sin(3\phi}{2w} \right\}^2 + \left\{ \frac{\Delta \cdot (2P^2\rho + f^2\rho^3 + 3Pf\rho^2\cos(3\phi))}{2\sqrt{2w}(\Delta^2 + 2w)} \right\}^2 \right]^{\frac{1}{2}}, \qquad \text{(32a)}$$

and

$$\omega_\phi = \sqrt{(g_1^\phi)^2 + (g_2^\phi)^2 + (g_3^\phi)^2}$$

$$= \left[\left\{ \frac{2P^2\rho^2 - f^2\rho^4 - Pf\rho^3\cos(3\phi)}{2w} \right\}^2 + \left\{ \frac{\Delta \cdot 3Pf\rho^3 \sin(3\phi)}{2\sqrt{2w}(\Delta^2 + 2w)} \right\}^2 \right]^{\frac{1}{2}}. \qquad \text{(32b)}$$

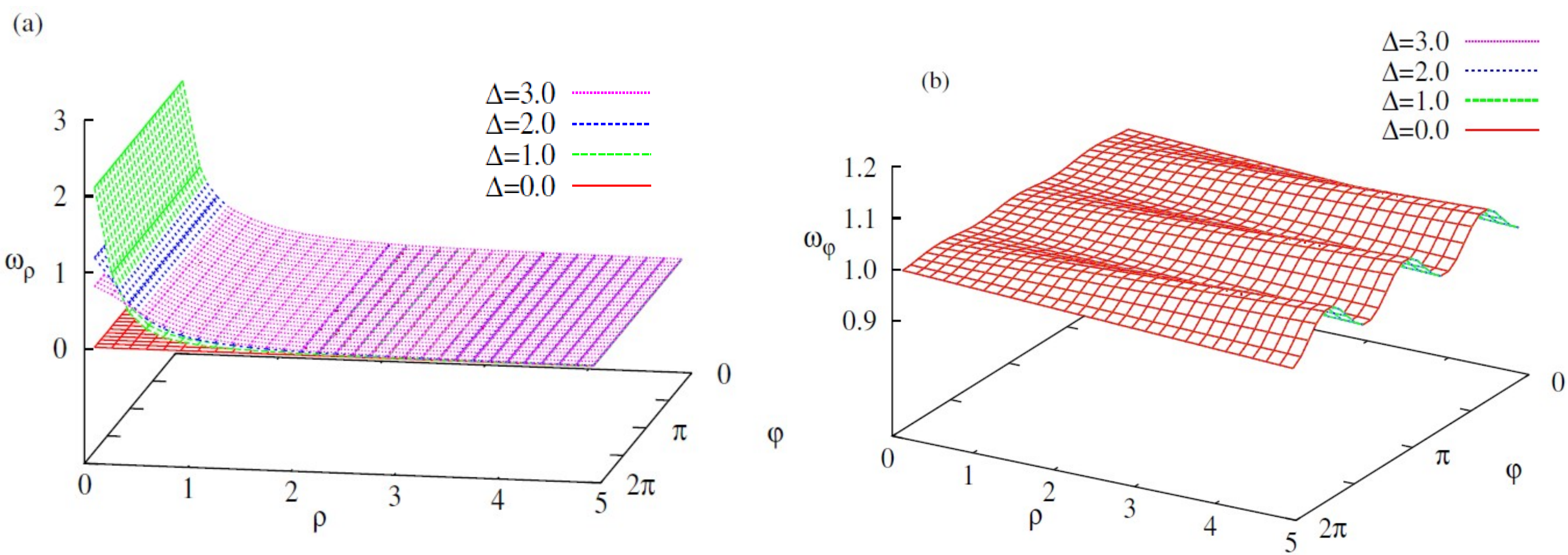


Fig. 8. Eigenvalues (a) ω_ρ and (b) ω_φ of ρ and φ component non-adiabatic coupling matrix, respectively, as functions of ρ and φ for various Δ values.

If we assume the gap between E- and A- type states is zero ($\Delta = 0$), the NAC elements (Eq. 19 and 20) appear as:

$$\tau_{12}^{\rho} = \tau_{13}^{\rho} = -\frac{Pf\rho^2\sin(3\phi)}{2\sqrt{2}w}, \tag{33a}$$

$$\tau_{12}^{\phi} = \tau_{13}^{\phi} = \frac{[2P^2\rho^2 - f^2\rho^4 - Pf\rho^3\cos(3\phi)]}{2\sqrt{2}w}, \tag{33b}$$

$$\tau_{23}^{\rho} = \tau_{23}^{\phi} = 0, \tag{33c}$$

with $\mathbf{Curl\tau = 0}$ and ***G*** matrices for the ρ and φ components (Eq. 29) turns into a constant matrix as given below:

$$\mathbf{G} = \begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & \frac{1}{2} & \frac{1}{2} \end{pmatrix}, \tag{34}$$

where the eigenvalues (Eq. 32) are:

$$\omega_\rho = \frac{Pf\rho^2\sin(3\phi)}{2w}, \quad \text{and} \quad \omega_\phi = \frac{2P^2\rho^2 - f^2\rho^4 - Pf\rho^3\cos(3\phi)}{2w}. \tag{35a - b}$$

Again with the φ component of the NAC matrix the following integral appear as:

$$\int_0^{2\pi} \omega_\phi d\phi = 2\pi, \tag{36}$$

and the topological matrix D is given by

$$\mathbf{D} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{37}$$

Formulation of the EBO equation:

$$-\frac{\hbar^2}{2m}\begin{pmatrix}\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) & 0 & 0\\ 0 & \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) & 0\\ 0 & 0 & \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right)\end{pmatrix}\begin{pmatrix}\chi_1\\ \chi_2\\ \chi_3\end{pmatrix} - \frac{\hbar^2}{2m}\frac{1}{\rho^2}\begin{pmatrix}\frac{\partial}{\partial\phi} & 0 & 0\\ 0 & \frac{\partial}{\partial\phi} & 0\\ 0 & 0 & \frac{\partial}{\partial\phi}\end{pmatrix}^2\begin{pmatrix}\chi_1\\ \chi_2\\ \chi_3\end{pmatrix}$$

$$+\begin{pmatrix}\frac{\rho^2}{2}-E & 0 & W_1-W_2\\ 0 & \frac{\rho^2}{2}-E & W_1+W_2\\ W_1-W_2 & W_1+W_2 & \epsilon_0+\frac{d\rho^2}{2}-E\end{pmatrix}\begin{pmatrix}\chi_1\\ \chi_2\\ \chi_3\end{pmatrix}=0, \quad (38)$$

where it can be transformed, $\boldsymbol{\chi} = \mathbf{A}\,\boldsymbol{\psi}$, to the following form of adiabatic representation:

$$-\frac{\hbar^2}{2m}\begin{pmatrix}\frac{\partial}{\partial\rho} & \tau_{12}^{\rho} & \tau_{13}^{\rho}\\ \tau_{21}^{\rho} & \frac{\partial}{\partial\rho} & \tau_{23}^{\rho}\\ \tau_{31}^{\rho} & \tau_{32}^{\rho} & \frac{\partial}{\partial\rho}\end{pmatrix}^2\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix} - \frac{\hbar^2}{2m}\frac{1}{\rho}\begin{pmatrix}\frac{\partial}{\partial\rho} & \tau_{12}^{\rho} & \tau_{13}^{\rho}\\ \tau_{21}^{\rho} & \frac{\partial}{\partial\rho} & \tau_{23}^{\rho}\\ \tau_{31}^{\rho} & \tau_{32}^{\rho} & \frac{\partial}{\partial\rho}\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix}$$

$$-\frac{\hbar^2}{2m}\frac{1}{\rho^2}\begin{pmatrix}\frac{\partial}{\partial\phi} & \tau_{12}^{\phi} & \tau_{13}^{\phi}\\ \tau_{21}^{\phi} & \frac{\partial}{\partial\phi} & \tau_{23}^{\phi}\\ \tau_{31}^{\phi} & \tau_{32}^{\phi} & \frac{\partial}{\partial\phi}\end{pmatrix}^2\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix} + \begin{pmatrix}u_1(\rho,\phi)-E & 0 & 0\\ 0 & u_2(\rho,\phi)-E & 0\\ 0 & 0 & u_3(\rho,\phi)-E\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\\ \psi_3\end{pmatrix}=0, \quad (39)$$

and thereby, the above equation under the transformation matrix G, ($\psi = G\phi$) leads to:

$$-\frac{\hbar^2}{2m}\begin{pmatrix}\left(\frac{\partial}{\partial\rho}+i\omega_\rho\right)^2 & 0 & 0\\ 0 & \frac{\partial^2}{\partial\rho^2} & 0\\ 0 & 0 & \left(\frac{\partial}{\partial\rho}-i\omega_\rho\right)^2\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\end{pmatrix}-\frac{\hbar^2}{2m}\frac{1}{\rho}\begin{pmatrix}\frac{\partial}{\partial\rho}+i\omega_\rho & 0 & 0\\ 0 & \frac{\partial}{\partial\rho} & 0\\ 0 & 0 & \frac{\partial}{\partial\rho}-i\omega_\rho\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\end{pmatrix}$$

$$-\frac{\hbar^2}{2m}\frac{1}{\rho^2}\begin{pmatrix}\left(\frac{\partial}{\partial\phi}+i\omega_\phi\right)^2 & 0 & 0\\ 0 & \frac{\partial^2}{\partial\phi^2} & 0\\ 0 & 0 & \left(\frac{\partial}{\partial\phi}+i\omega_\phi\right)^2\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\end{pmatrix}$$

$$+\begin{pmatrix}\frac{1}{2}(u_2+u_3)-E & \frac{1}{2\sqrt{2}}(-u_2+u_3) & \frac{1}{2\sqrt{2}}(-u_2+u_3)\\ \frac{1}{2\sqrt{2}}(-u_2+u_3) & \frac{1}{4}(2u_1+u_2+u_3)-E & \frac{1}{4}(-2u_1+u_2+u_3)\\ \frac{1}{2\sqrt{2}}(-u_2+u_3) & \frac{1}{4}(-2u_1+u_2+u_3) & \frac{1}{4}(2u_1+u_2+u_3)-E\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\\ \phi_3\end{pmatrix}=0, \tag{40}$$

i.e.,

$$\mathbf{V}=\mathbf{G}^\dagger\mathbf{U}\mathbf{G}=\begin{pmatrix}\frac{1}{2}(u_2+u_3) & \frac{1}{2\sqrt{2}}(-u_2+u_3) & \frac{1}{2\sqrt{2}}(-u_2+u_3)\\ \frac{1}{2\sqrt{2}}(-u_2+u_3) & \frac{1}{4}(2u_1+u_2+u_3) & \frac{1}{4}(-2u_1+u_2+u_3)\\ \frac{1}{2\sqrt{2}}(-u_2+u_3) & \frac{1}{4}(-2u_1+u_2+u_3) & \frac{1}{4}(2u_1+u_2+u_3)\end{pmatrix}.$$

If the so called BO approximation is imposed considering the dynamics only at enough low energies on the ground state, the upper electronic states become classically closed ($|\psi_1| >> |\psi_i|$, i=2,3) and such approximation on the above equation brings the approximate EBO equation Eq. (41) for the ground state.

On the other hand, since the conical intersection predominantly affects the nuclear wavefunction only at and around its' origin, the approximate EBOs equation can be obtained by incorporating the degeneracy of the adiabatic PESs, namely, $u_1 \cong u_2 \cong u_3$ at and around the same region (CI),

$$-\frac{\hbar^2}{2m}\left\{\left(\frac{\partial}{\partial\rho}+i\omega_\rho\right)^2+\frac{1}{\rho}\left(\frac{\partial}{\partial\rho}+i\omega_\rho\right)+\frac{1}{\rho^2}\left(\frac{\partial}{\partial\phi}+i\omega_\phi\right)^2\right\}\phi_1+(u_1-E)\phi_1=0, \quad \text{(41a)}$$

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\right\}\phi_2+(u_2-E)\phi_2=0, \quad \text{(41b)}$$

$$-\frac{\hbar^2}{2m}\left\{\left(\frac{\partial}{\partial\rho}-i\omega_\rho\right)^2+\frac{1}{\rho}\left(\frac{\partial}{\partial\rho}-i\omega_\rho\right)+\frac{1}{\rho^2}\left(\frac{\partial}{\partial\phi}-i\omega_\phi\right)^2\right\}\phi_3+(u_3-E)\phi_3=0. \quad \text{(41c)}$$

As we wish to perform the dynamics in Cartesian co - ordinates system, the NAC elements and their eigenvalues at $\Delta = 0$ appear as:

$$\tau_{12}^{x} = \tau_{13}^{x} = \frac{f^2 y(x^2+y^2) - 2Pfxy - 2P^2 y}{2\sqrt{2}w}, \quad (42a)$$

$$\tau_{12}^{y} = \tau_{13}^{y} = \frac{2P^2 x - Pf(x^2-y^2) - f^2 x(x^2-y^2) - 2f^2 xy^2}{2\sqrt{2}w}, \quad (42b)$$

$$\tau_{23}^{x} = \tau_{23}^{y} = 0, \quad (42c)$$

and

$$\omega_x = \frac{f^2 y(x^2+y^2) - 2Pfxy - 2P^2 y}{2w}, \quad (43a)$$

$$\omega_y = \frac{2P^2 x - Pf(x^2-y^2) - f^2 x(x^2-y^2) - 2f^2 xy^2}{2w}, \quad (43b)$$

where the corresponding EBO equation for the ground surface at $\Delta = 0$ is given below:

$$-\frac{\hbar^2}{2m}(\nabla_x + i\omega_x)^2\phi_1 - \frac{\hbar^2}{2m}(\nabla_y + i\omega_y)^2\phi_1 + (u_1(x,y) - E)\phi_1 = 0 \quad (44)$$

and the ordinary BO equation is obtained as

$$-\frac{\hbar^2}{2m}\nabla_x^2\phi_1 - \frac{\hbar^2}{2m}\nabla_y^2\phi_1 + (u_1(x,y) - E)\phi_1 = 0. \quad (45)$$

On the contrary, if we include the geometric phase (GP) considering three state BO system through the vector potential derived by Mead and Truhlar approach, the extended single surface equation (S. Adhikari and G. D. Billing, J. Chem. Phys. **111**, 40 (1999)) takes the following forms in polar and Cartesian coordinates:

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\left(\frac{\partial}{\partial\phi}+i\right)^2\right\}\phi_1+(u_1-E)\phi_1=0, \tag{46a}$$

$$-\frac{\hbar^2}{2m}(\nabla_x-i\frac{y}{x^2+y^2})^2\phi_1-\frac{\hbar^2}{2m}(\nabla_y+i\frac{x}{x^2+y^2})^2\phi_1+(u_1(x,y)-E)\phi_1=0. \tag{46b}$$

In case of $\Delta \neq 0$, if we assume that the operators, ∇_x and ∇_y, approximately commute with G_x and G_y, respectively and the NAC matrices, τ^x and τ^y also approximately commutes with each other, the EBO equation may be valid with the following form of ω_x and ω_y:

$$\omega_x = \frac{1}{w(\Delta^2+2w)}\sqrt{\left(W_1\frac{\partial W_2}{\partial x}-W_2\frac{\partial W_1}{\partial x}\right)^2(\Delta^2+2w)^2+\Delta^2 w\frac{1}{8}\left(\frac{\partial w}{\partial x}\right)^2}, \tag{47a}$$

and

$$\omega_y = \frac{1}{w(\Delta^2+2w)}\sqrt{\left(W_1\frac{\partial W_2}{\partial y}-W_2\frac{\partial W_1}{\partial y}\right)^2(\Delta^2+2w)^2+\Delta^2 w\frac{1}{8}\left(\frac{\partial w}{\partial y}\right)^2}, \tag{47b}$$

where

$$W_1\frac{\partial W_2}{\partial x} - W_2\frac{\partial W_1}{\partial x} = \frac{f^2}{2}y(x^2+y^2)-Pfxy-P^2y,$$

$$W_1\frac{\partial W_2}{\partial y} - W_2\frac{\partial W_1}{\partial y} = P^2x-\frac{1}{2}Pf(x^2-y^2)-\frac{1}{2}f^2x(x^2+y^2), \quad \frac{\partial w}{\partial y} = 2P^2y+f^2y(x^2+y^2)-6Pfxy,$$

$$w = P^2(x^2+y^2)+\frac{1}{4}f^2(x^2+y^2)^2+Pfx[4x^2-3(x^2+y^2)].$$

Numerical Calculation Using EBO equation:

1. Photoabsorption Spectrum:

The diabatic wavefunction starting with the initial wavepacket located on the ground state is given by: $\psi^{dia} = A\ \psi^{adia}$ with $\psi^{adia} = (GWP, 0, 0)$. In case of adiabatic calculations, namely, BO and EBO, the corresponding propagations are performed from ground state with the same GWP.

The nuclear wavefunction obtained by FFT - Lancozs method is used to calculate the autocorrelation function (C(t)) and the Fourier transform of C(t) gives photoabsorption spectra,

$$I(\omega) \propto \omega \int_{-\infty}^{\infty} C(t) \exp(i\omega t) dt,$$

where

$$\begin{aligned} C(t) &= \langle \Psi(t) | \Psi(0) \rangle, \\ &= \langle \Psi^{\star}(\frac{t}{2}) | \Psi(\frac{t}{2}) \rangle. \end{aligned}$$

All the numerical calculations has been carried out for the pseudo - Jahn - Teller model situation with the parameter[3] $P = 3.4648$ and $f = 0.0247$ for System **C**

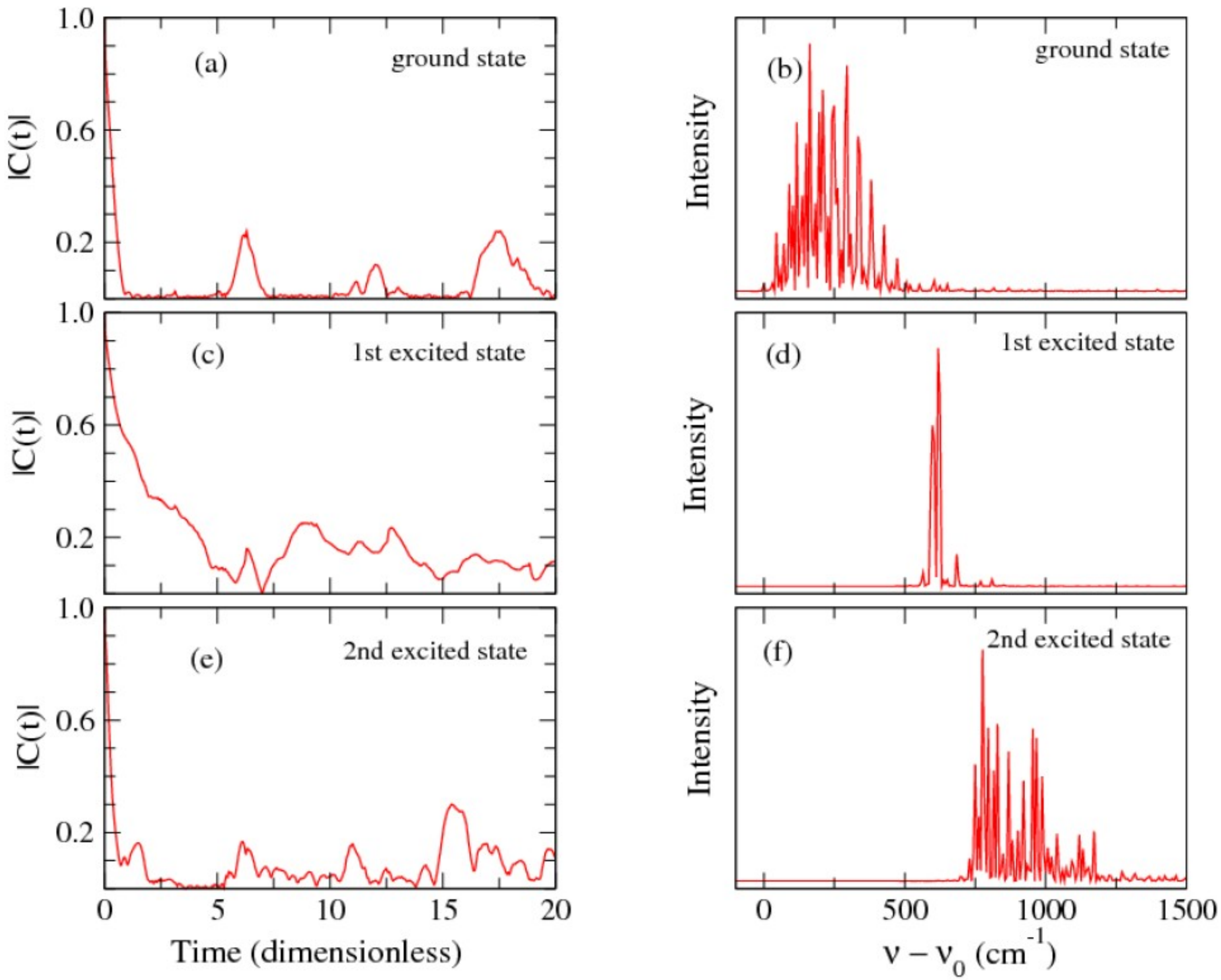


Fig. 9. displays the autocorrelation functions as functions of time (dimensionless) starting with the initial wavefunction placed at (a) ground, (c) first excited and (e) second excited state, whereas figures (b), (d), (f) present the corresponding photoabsorption spectra of those respective states. Calculations are performed by using the three state diabatic Hamiltonian.

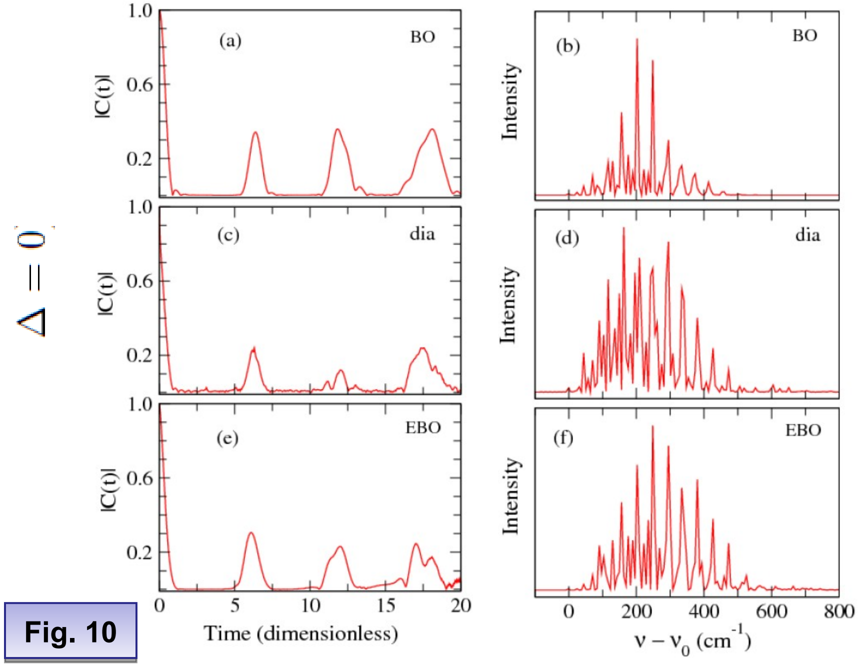


Fig. 10

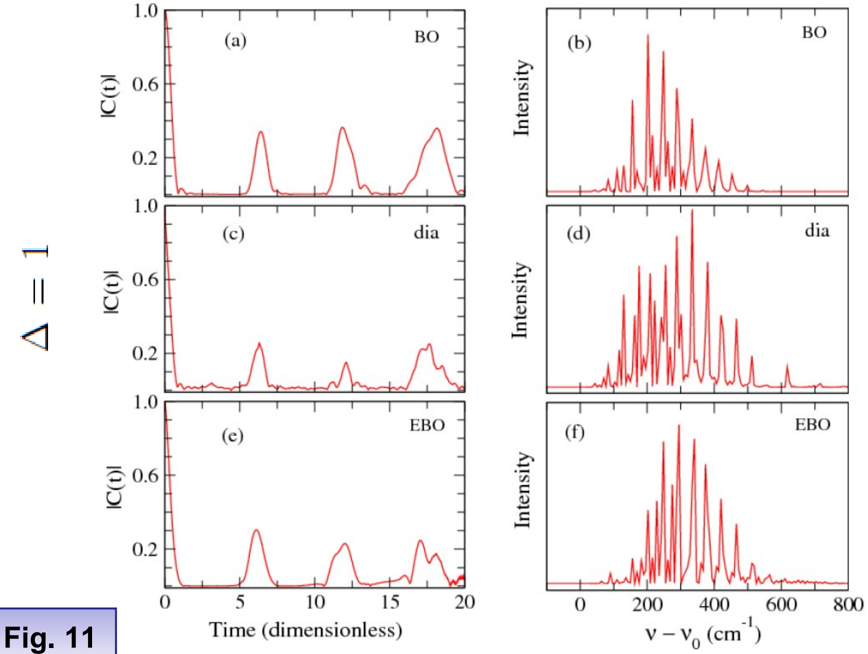


Fig. 11

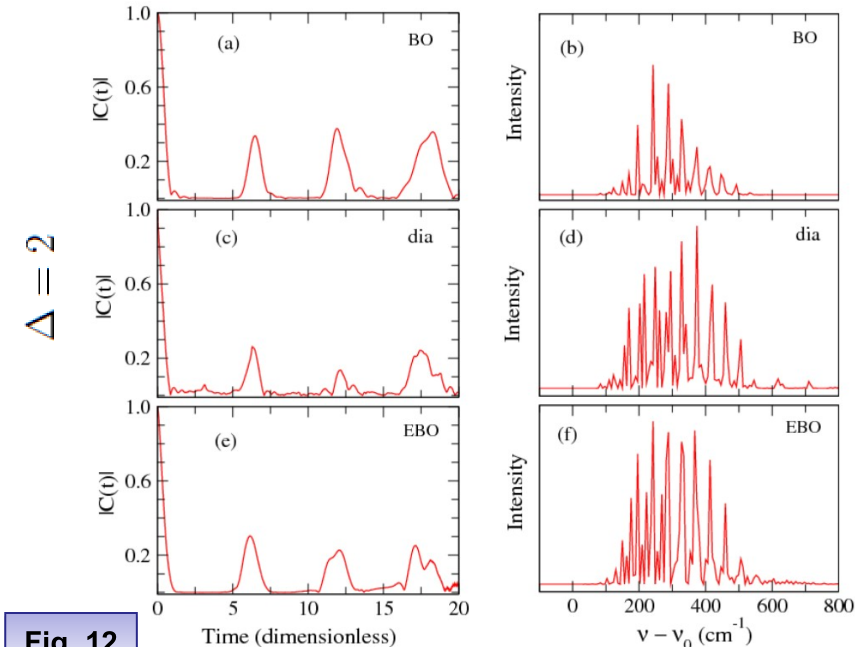


Fig. 12

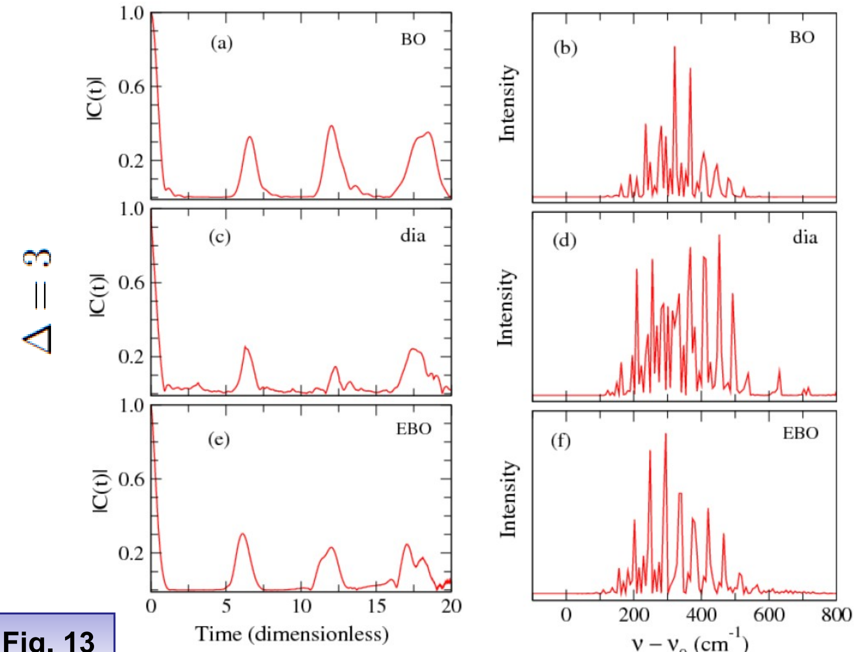


Fig. 13

2. The experimentally measured and theoretically calculated Vibrational Spectrum:

Table I: Experimentally observed absorption lines of Na_3 cluster by resonant two - photon ionization process (TPI)[4] and theoretically (BO, GP and EBO (Δ = 0 and 0.75)) calculated frequencies with parameter[5] P = 3.07 and f =-0.0045.

					$\Delta = 0$		$\Delta = 0.75$	
$\nu_i^{expt} - \nu_0^b$	$\nu_i^{BO} - \nu_0$	δ_{BO}	$\nu_i^{GP} - \nu_0$	δ_{GP}	$\nu_i^{EBO} - \nu_0$	δ_{EBO}	$\nu_i^{EBO} - \nu_0$	δ_{EBO}
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	3.0	0.5	3.2	0.7	3.0	0.5	3.0	0.5
14.5	21.5	7.0	16.7	2.2	16.5	2.0	16.5	2.0
32.5	33.3	0.8	33.9	1.4	32.8	0.3	32.9	0.4
55.0	36.7	−18.3	49.5	−5.5	56.8	1.8	56.9	1.9
82.5	56.8	−25.7	80.5	−1.9	86.0	3.5	86.0	3.5
116.5	108.3	−8.2	111.7	−4.8	120.0	3.5	119.9	3.4
128.0	130.7	2.7	128.5	0.5	127.0	−1.0	126.9	−1.1
133.0	138.3	5.3	137.0	4.0	130.8	−2.2	130.9	−2.1
146.5	156.5	10.0	139.0	−7.5	146.1	−0.4	146.1	−0.4
166.5	165.7	−0.8	175.3	8.8	166.2	−0.3	166.1	−0.4
192.5	192.6	0.1	193.6	1.1	192.6	0.1	192.6	0.1
222.5	192.6	−29.9	208.1	−14.4	225.2	2.7	225.3	2.8
...	234.2	...	247.5	...	246.2	...	246.5	...
254.0	253.7	−0.3	262.6	8.6	254.1	0.1	253.9	−0.1
258.5	258.6	0.1	272.0	13.5	258.6	0.1	258.4	−0.1
280.5	276.4	−4.1	290.8	10.3	277.0	3.5	276.8	−3.7
301.0	285.9	−15.1	306.5	5.5	300.3	−0.7	300.2	−0.8
332.0	330.3	−1.7	331.4	−0.6	330.7	−1.3	330.7	−1.3
369.0	366.8	−2.2	376.4	7.4	366.7	−2.3	366.8	−2.2
376.5	380.5	4.0	388.2	11.7	374.4	−2.1	375.5	−1.0
386.5	397.6	11.1	391.9	5.4	386.7	0.2	386.3	−0.2

$\nu_0 = 15996\ cm^{-1}$

where

$$\delta_x = \nu_i^x - \nu_i^{expt},$$

and

$$\chi^x = \frac{1}{N}\sqrt{\sum_i (\nu_i^x - \nu_i^{expt})^2},$$

$$x \equiv \{\mathrm{BO,GP,EBO}\}.$$

$\chi^{BO} = 2.39$

$\chi^{GP} = 1.53$

$\chi^{EBO}\ (\Delta = 0) = 0.397$

$\chi^{EBO}\ (\Delta = 0.75) = 0.391$

[4]G. Delacrétaz and L. Wöste, Surf. Sci. **156**, 770 (1985).

[5]R. Meiswinkel and H. Köppel, Chem. Phys. **144**, 117 (1990).

Table II(a): Experimentally observed absorption lines (all in cm^{-1}) of Na_3 cluster by resonant two - photon ionization process (TPI) and theoretically (BO, GP and EBO (Δ = 0)) calculated frequencies with[3] P=3.4648 and f = 0.0247.

$\nu_i^{expt} - \nu_0$	$\nu_i^{BO} - \nu_0$	δ_{BO}	$\nu_i^{GP} - \nu_0$	δ_{GP}	$\nu_i^{EBO^0} - \nu_0$	δ_{EBO^0}
00.0	00.0	0.0	0.0	0.0	0.0	0.0
31.0	29.2	−1.8	29.8	−1.2	30.9	−0.1
49.5	40.4	−9.5	43.8	−5.7	49.9	0.4
58.5	54.7	−3.8	49.5	−9.0	55.1	3.4
68.0	62.0	−6.0	54.5	−13.5	69.5	1.5
84.5	86.9	−2.4	85.2	0.7	84.7	0.2
91.0	86.9	−4.1	96.6	5.6	89.4	−1.6
111.0	127.7	16.7	107.0	−4.0	112.6	1.6
130.0	130.8	0.8	125.5	−4.5	130.5	0.4
150.0	150.5	0.5	153.5	3.5	150.3	0.3
157.5	158.2	0.7	160.1	2.6	158.1	0.6
176.0	178.0	2.0	177.8	1.8	177.5	1.5
221.5	223.6	2.1	227.1	5.6	220.9	−0.6
251.5	249.4	−2.1	250.0	−1.5	249.0	−2.5
273.0	269.2	−3.8	271.0	−2.0	273.5	0.5
282.0	280.2	−1.6	292.8	10.8	282.9	0.9
299.5	289.8	−9.7	298.3	−1.2	300.0	0.5
312.5	305.3	−7.2	306.7	−5.8	312.6	0.1
335.0	308.8	−26.2	318.1	−16.9	334.6	−0.4
366.5	364.6	−2.1	364.9	−1.6	365.7	−0.8
391.0	390.5	−0.5	392.4	1.4	391.3	0.3
404.5	391.3	−13.2	417.9	13.4	403.7	−0.8
425.0	433.4	−8.4	433.7	8.7	424.5	−0.5
453.5	482.0	−28.5	454.9	1.4	455.0	1.5
483.0	484.2	1.2	485.1	2.1	483.7	0.7
512.5	492.0	20.5	497.7	−14.8	512.2	−0.3

$\nu_0 = 17307\ cm^{-1}$

$\chi^{BO} = 2.03$

$\chi^{GP} = 1.412$

$\chi^{EBO}\ (\Delta = 0) = 0.226$

[3] F. Cocchini, T. H. Upton and W. Andreoni, J. Chem. Phys. 88, 6068 (1988).

Table II(b): Experimentally observed absorption lines (all in cm^{-1}) of Na_3 cluster by resonant two - photon ionization process (TPI) and theoretically calculated frequencies using present EBO equation for various $\Delta(\neq 0)$ with[3] P = 3.4648 and f = 0.0247.

	$\Delta = 1$		$\Delta = 2$		$\Delta = 3$	
$\nu_i^{expt} - \nu_0$	$\nu_i^{EBO} - \nu_0$	δ_{EBO}	$\nu_i^{EBO} - \nu_0$	δ_{EBO}	$\nu_i^{EBO} - \nu_0$	δ_{EBO}
0.0	0.0	0.0	0.0	0.0	0.0	0.0
31.0	30.9	−0.1	30.9	−0.1	30.8	−0.2
49.5	49.8	0.3	49.6	0.1	49.1	−0.4
58.5	55.0	−3.5	54.9	−3.6	54.7	−3.8
68.0	69.5	1.5	69.3	1.3	69.1	1.1
84.5	84.6	0.1	84.5	0.0	84.3	−0.2
91.0	89.4	−1.6	89.3	−1.7	89.1	−1.9
111.0	112.6	1.6	112.5	1.5	112.3	1.3
130.0	130.5	0.6	130.6	0.6	130.9	0.9
150.0	150.3	0.3	150.3	0.3	150.2	0.2
157.5	158.0	0.5	158.0	0.5	158.0	0.5
176.0	177.4	1.4	177.2	1.2	176.8	0.8
221.5	220.7	−1.8	220.2	−0.7	220.1	−1.4
251.5	249.1	−2.4	249.3	−1.8	249.7	−1.8
273.0	273.5	0.5	273.6	0.6	273.9	0.9
282.0	282.9	0.9	282.9	0.9	283.0	1.0
299.5	299.9	0.4	299.9	0.4	300.1	0.6
312.5	312.6	0.1	312.6	0.1	311.7	−0.8
335.0	334.6	−0.4	334.7	−0.3	335.0	0.0
366.5	365.9	−0.6	366.2	−0.3	366.8	0.3
391.0	391.2	0.2	391.0	0.0	390.5	−0.5
404.5	403.6	−0.9	403.2	−1.3	403.0	−1.5
425.0	424.5	−0.5	424.6	−0.4	426.5	−0.5
453.5	454.9	1.4	454.5	1.0	454.0	0.5
483.0	483.8	0.8	483.3	0.3	482.0	−1.0
512.5	512.3	−0.2	512.3	−0.2	512.4	−0.1

$\chi^{EBO}\,(\Delta = 1) = 0.225$

$\chi^{EBO}\,(\Delta = 2) = 0.211$

$\chi^{EBO}\,(\Delta = 3) = 0.227$

[3] F. Cocchini, T. H. Upton and W. Andreoni, J. Chem. Phys. 88, 6068 (1988).

Finally, it is quite clear from the following figures that the BO vibrational spectrum at high energy region is strongly affected by non - adiabatic coupling terms. Even some cases, eigenspectrum due to non - adiabatic effect changes their position with respect to the unperturbed ones.

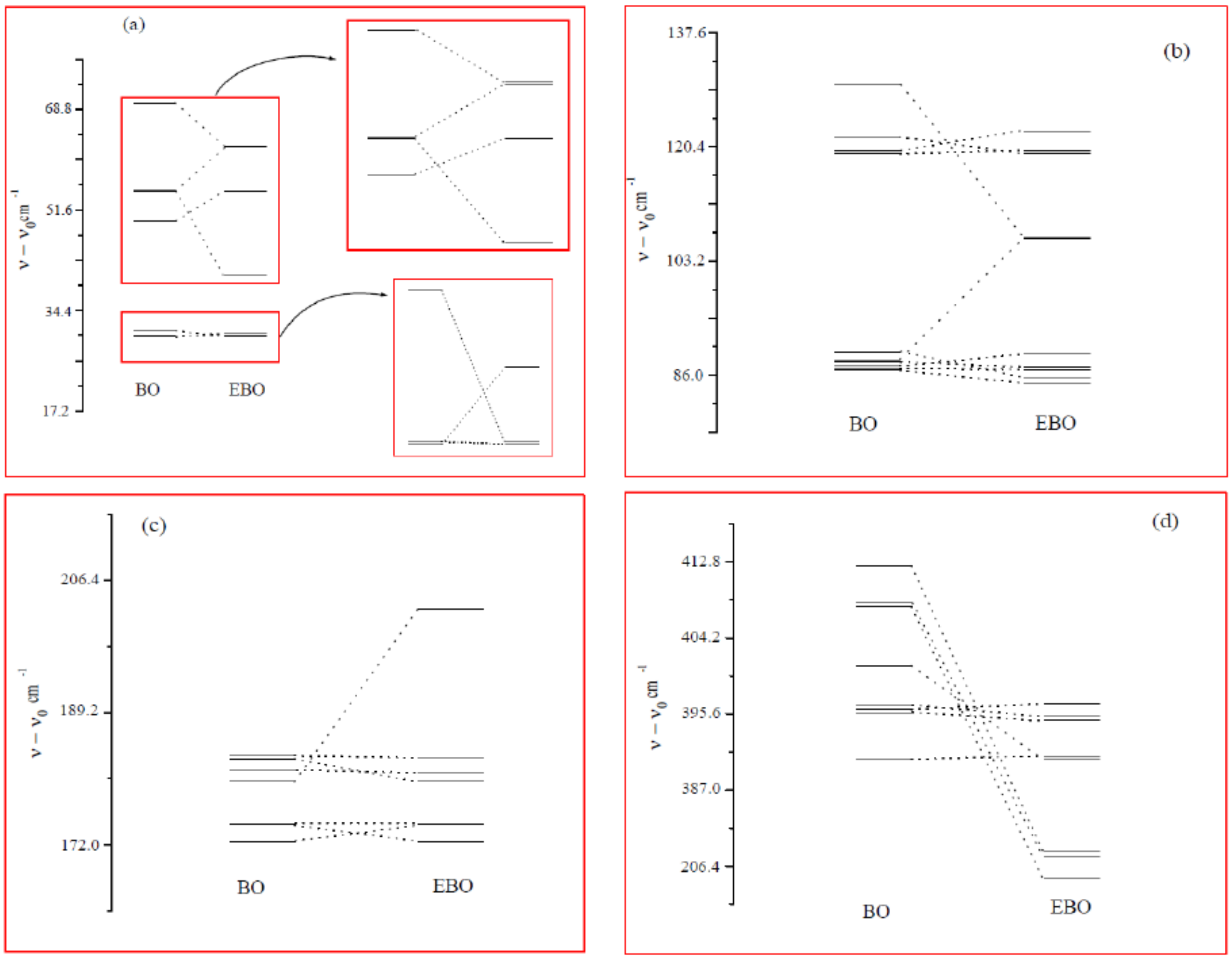


Fig. 14. (a - d) display the vibrational eigenspectrum of the ground adiabatic state under BO and EBO approximation for various frequency ($\nu - \nu_0$; ν_0 = 17307cm^{-1}) range.

Summary:

- The origin of Mead and Truhlar vector potential is the geometry of a molecule, whereas the form of our formulated vector potential depends on the electronic eigenfunctions of a molecule at each nuclear configuration.

- **In case of MT approach:**

  (a) The momentum operator for the angular coordinate only (let say, φ with domain {0, 2π}) undergoes a change from $\nabla_\varphi \rightarrow \nabla_\varphi \pm i\nabla_\varphi A(\varphi)$, where the scalar function A(φ) is the HLH phase argument, an angular function of φ and depends on the geometry of a molecule.

  (b) Such vector potentials $(\nabla_\varphi A(\varphi))$ are usually constant over the entire φ space (with domain 0 to 2π), appear as either half integer or integer and become π or 2π under integration from 0 to 2π.

  (c) There is no scope to introduce any functional form of the MT vector potential arising due the change of electronic eigenfunction with the change of nuclear coordinates.

- **In our approach:**

  (a) The vector potential appears not only for the angular coordinate (φ with domain 0 to 2π) but also for all other nuclear coordinates and show complicated functional form over the nuclear configuration space.

  (b) The formulated vector potential is theoretically valid for a two electronic state system, whether these two states have degeneracy at some point(s)/along a seam or not because the components of the non - adiabatic coupling matrices always commute with each other by construction (**Curl = 0**).

(c) For a three electronic state system the component NAC matrices also commute identically with each other (Curl = 0) if there is three state degeneracy at a point(s) or along a seam. We explore the numerical validity of EBO equation if curl of the non - adiabatic coupling matrix is: (1) Theoretically (identically) zero; (2) Not theoretically zero but virtually numerically zero.

- If we look into this model Hamiltonian for Na_3, the form of the MT vector potential $(\nabla_\varphi A(\varphi))$ will be just n/2 or n, n = 1, 2, 3, ... (see Eq. 46) depending upon two or three state system, which on integration over 0 to 2π will become either π or 2π.

- The form of the vector potentials for the φ component in our approach are such that the same integration for the two state system will provide π (see Eq. 27) and 2π (see Eq. 36) for the three state system.

- As a matter of fact, the requirement of single surface beyond Born - Oppenheimer equation is the following: Whatever be the form of the vector potential, the corresponding differential equation can provide meaningful solution only if the angular component of the vector potential show gauge invariance.

- We have incorporated new results in **Table I** and **Table II** by introducing three state geometric phase through MT vector potential approach. Those results clearly show that the frequencies are far away from experimental ones but reasonably better than BO calculated results.

- Even if we consider non zero Δ, it appears that the curls are not identically zero but the numerical magnitudes of curls are virtually zero upto certain non - zero Δ values. The identities (I_1, I_2 and I_3) clearly show negligibly small values for the entire nuclear configuration space upto Δ = 1.0 (ε_0 ≈172 cm^{-1}) for system **C**.

- We have also calculated the vibrational frequencies for the ground electronic state for system **C** and system **B** as functions of Δ to explore how our EBO equation follow the experimental vibrational spectra, where BO and GP results differ substantially.

Reference:
A. K. Paul, S. Sardar, B. Sarkar and S. Adhikari, **J. Chem. Phys.** (In Press, 2009)

Work in progress

- Our ongoing *ab initio* calculations for non-adiabatic coupling terms of the Na_3 system is to investigate the nature of Curl of the NAC terms to diabatize the adiabatic Schroedinger equation and to explore the numerical justification of the formulated EBO equation.

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thank you

Appendix 1

The Cartesian components of $\nabla\times\tau_{12}$ along the unit vectors, i, j, and k are given by:

$$
\begin{aligned}
\mathrm{Curl}\ \tau_{12}^{yz} &= -\cos\theta_{23}\left[\frac{\partial\theta_{23}}{\partial y}\frac{\partial\theta_{13}}{\partial z}-\frac{\partial\theta_{23}}{\partial z}\frac{\partial\theta_{13}}{\partial y}\right],\\
\mathrm{Curl}\ \tau_{12}^{zx} &= -\cos\theta_{23}\left[\frac{\partial\theta_{23}}{\partial x}\frac{\partial\theta_{13}}{\partial z}-\frac{\partial\theta_{23}}{\partial z}\frac{\partial\theta_{13}}{\partial x}\right],\\
\mathrm{Curl}\ \tau_{12}^{xy} &= -\cos\theta_{23}\left[\frac{\partial\theta_{23}}{\partial x}\frac{\partial\theta_{13}}{\partial y}-\frac{\partial\theta_{23}}{\partial y}\frac{\partial\theta_{13}}{\partial x}\right],
\end{aligned}
$$

whereas it's spherical polar components along the unit vectors, r, θ and φ are:

$$
\begin{aligned}
\mathrm{Curl}\ \tau_{12}^{\theta\phi} &= -\frac{\cos\theta_{23}}{r^2\sin\theta}\left[\frac{\partial\theta_{23}}{\partial\theta}\frac{\partial\theta_{13}}{\partial\phi}-\frac{\partial\theta_{23}}{\partial\phi}\frac{\partial\theta_{13}}{\partial\theta}\right],\\
\mathrm{Curl}\ \tau_{12}^{r\phi} &= -\frac{\cos\theta_{23}}{r\sin\theta}\left[\frac{\partial\theta_{23}}{\partial r}\frac{\partial\theta_{13}}{\partial\phi}-\frac{\partial\theta_{23}}{\partial\phi}\frac{\partial\theta_{13}}{\partial r}\right],\\
\mathrm{Curl}\ \tau_{12}^{r\theta} &= -\frac{\cos\theta_{23}}{r}\left[\frac{\partial\theta_{23}}{\partial r}\frac{\partial\theta_{13}}{\partial\theta}-\frac{\partial\theta_{23}}{\partial\theta}\frac{\partial\theta_{13}}{\partial r}\right].
\end{aligned}
$$

Let us consider the ratios, $A1 = \frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial\theta}} \cdot \frac{\frac{\partial\theta_{13}}{\partial r}}{\frac{\partial\theta_{23}}{\partial r}}$ and $A2 = \frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial\phi}} \cdot \frac{\frac{\partial\theta_{13}}{\partial r}}{\frac{\partial\theta_{23}}{\partial r}}$

and rewrite these quantities by using the chain rule of differentiation,

$$A1 = \frac{\frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial\theta}}}{\frac{\frac{\partial\theta_{23}}{\partial r}}{\frac{\partial\theta_{13}}{\partial r}}} = \frac{\left(1 + \frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial\theta}}{\frac{\partial x}{\partial\theta}} + \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial\theta}}{\frac{\partial x}{\partial\theta}}\right)\left(1 + \frac{\frac{\partial\theta_{13}}{\partial y}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}} + \frac{\frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}}\right)}{\left(1 + \frac{\frac{\partial\theta_{13}}{\partial y}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial\theta}}{\frac{\partial x}{\partial\theta}} + \frac{\frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial\theta}}{\frac{\partial x}{\partial\theta}}\right)\left(1 + \frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}} + \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}}\right)}$$

$$A2 = \frac{\frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial\phi}}}{\frac{\frac{\partial\theta_{23}}{\partial r}}{\frac{\partial\theta_{13}}{\partial r}}} = \frac{\left(1 + \frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial\phi}}{\frac{\partial x}{\partial\phi}} + \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial\phi}}{\frac{\partial x}{\partial\phi}}\right)\left(1 + \frac{\frac{\partial\theta_{13}}{\partial y}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}} + \frac{\frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}}\right)}{\left(1 + \frac{\frac{\partial\theta_{13}}{\partial y}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial\phi}}{\frac{\partial x}{\partial\phi}} + \frac{\frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{13}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial\phi}}{\frac{\partial x}{\partial\phi}}\right)\left(1 + \frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}} + \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x}} \cdot \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}}\right)}$$

The Jacobian determinant for the transformation from Cartesian to polar is given by:

$$J(r,\theta,\phi) = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial y}{\partial \theta} & \frac{\partial z}{\partial \theta} \\ \frac{\partial x}{\partial \phi} & \frac{\partial y}{\partial \phi} & \frac{\partial z}{\partial \phi} \end{vmatrix} = \begin{vmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\phi \\ r\cos\theta\cos\phi & r\cos\theta\sin\phi & -r\sin\theta \\ -r\sin\theta\sin\phi & r\sin\theta\cos\phi & 0 \end{vmatrix}.$$

When the origin of the coordinate system [r=0 (x=0, y=0, z=0)] coincides with the point of conical intersection or even if the point of conical intersection(s) is away from the origin of the coordinate system, parametric representation for the vector equation of the conical surface predicts that various components of Jacobian determinant vanishes at that point (CI).

It is important to note that this transformation remain valid with zero content at r=0, i. e.,

$$\frac{\partial(x,y)}{\partial(r,\theta)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial y}{\partial \theta} \end{vmatrix} = 0 \qquad \Rightarrow \frac{\frac{\partial y}{\partial \theta}}{\frac{\partial x}{\partial \theta}} = \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}},$$

$$\frac{\partial(x,z)}{\partial(r,\theta)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial z}{\partial \theta} \end{vmatrix} = -r\cos\theta = 0 \qquad \Rightarrow \frac{\frac{\partial z}{\partial \theta}}{\frac{\partial x}{\partial \theta}} = \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}},$$

$$\frac{\partial(x,y)}{\partial(r,\phi)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} \\ \frac{\partial x}{\partial \phi} & \frac{\partial y}{\partial \phi} \end{vmatrix} = r\sin^2\theta = 0 \qquad \Rightarrow \frac{\frac{\partial y}{\partial \phi}}{\frac{\partial x}{\partial \phi}} = \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}},$$

$$\frac{\partial(x,z)}{\partial(r,\phi)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \phi} & \frac{\partial z}{\partial \phi} \end{vmatrix} = r\sin\theta\sin\phi\cos\phi = 0 \qquad \Rightarrow \frac{\frac{\partial z}{\partial \phi}}{\frac{\partial x}{\partial \phi}} = \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}}.$$

At r=0, even if we assume: $\frac{\frac{\partial \theta_{23}}{\partial y}}{\frac{\partial \theta_{23}}{\partial x}} \neq \frac{\frac{\partial \theta_{13}}{\partial y}}{\frac{\partial \theta_{13}}{\partial x}}$ and $\frac{\frac{\partial \theta_{23}}{\partial z}}{\frac{\partial \theta_{23}}{\partial x}} \neq \frac{\frac{\partial \theta_{13}}{\partial z}}{\frac{\partial \theta_{13}}{\partial x}}$,

the ratios (*A1* and *A2*) turns into unity, i. e.,

$$\frac{\frac{\partial \theta_{23}}{\partial \theta}}{\frac{\partial \theta_{23}}{\partial r}} = \frac{\frac{\partial \theta_{13}}{\partial \theta}}{\frac{\partial \theta_{13}}{\partial r}} \qquad \Rightarrow \frac{\partial \theta_{23}}{\partial r}\frac{\partial \theta_{13}}{\partial \theta} - \frac{\partial \theta_{23}}{\partial \theta}\frac{\partial \theta_{13}}{\partial r} = 0$$

$$\frac{\frac{\partial \theta_{23}}{\partial \phi}}{\frac{\partial \theta_{23}}{\partial r}} = \frac{\frac{\partial \theta_{13}}{\partial \phi}}{\frac{\partial \theta_{13}}{\partial r}} \qquad \Rightarrow \frac{\partial \theta_{23}}{\partial r}\frac{\partial \theta_{13}}{\partial \phi} - \frac{\partial \theta_{23}}{\partial \phi}\frac{\partial \theta_{13}}{\partial r} = 0.$$

At $r \neq 0$, with the assumptions:

(a) $$\frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{23}}{\partial x}} \neq \frac{\frac{\partial\theta_{13}}{\partial y}}{\frac{\partial\theta_{13}}{\partial x}} \quad \text{and} \quad \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x}} \neq \frac{\frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{13}}{\partial x}},$$

(b) chosen value of r is theoretically non - zero but numerically negligible.

The Jacobian relations translate as:

$$\frac{\partial(x,y)}{\partial(r,\theta)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial y}{\partial \theta} \end{vmatrix} = 0 \qquad \Rightarrow \frac{\frac{\partial y}{\partial \theta}}{\frac{\partial x}{\partial \theta}} = \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}},$$

$$\frac{\partial(x,z)}{\partial(r,\theta)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial z}{\partial \theta} \end{vmatrix} = -r\cos\theta \simeq \epsilon \simeq 0 \qquad \Rightarrow \frac{\frac{\partial z}{\partial \theta}}{\frac{\partial x}{\partial \theta}} \simeq \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}},$$

$$\frac{\partial(x,y)}{\partial(r,\phi)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} \\ \frac{\partial x}{\partial \phi} & \frac{\partial y}{\partial \phi} \end{vmatrix} = r\sin^2\theta \simeq \epsilon \simeq 0 \qquad \Rightarrow \frac{\frac{\partial y}{\partial \phi}}{\frac{\partial x}{\partial \phi}} \simeq \frac{\frac{\partial y}{\partial r}}{\frac{\partial x}{\partial r}},$$

$$\frac{\partial(x,z)}{\partial(r,\phi)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \phi} & \frac{\partial z}{\partial \phi} \end{vmatrix} = r\sin\theta\sin\phi\cos\phi \simeq \epsilon \simeq 0 \qquad \Rightarrow \frac{\frac{\partial z}{\partial \phi}}{\frac{\partial x}{\partial \phi}} \simeq \frac{\frac{\partial z}{\partial r}}{\frac{\partial x}{\partial r}},$$

and thereby, the ratios *A1* and *A2* become:

$$
\begin{aligned}
A1 &\simeq 1 \qquad \Rightarrow \frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{23}}{\partial r}} \simeq \frac{\frac{\partial\theta_{13}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial r}} \qquad \Rightarrow \frac{\partial\theta_{23}}{\partial r}\frac{\partial\theta_{13}}{\partial\theta} - \frac{\partial\theta_{23}}{\partial\theta}\frac{\partial\theta_{13}}{\partial r} \simeq 0,\\
A2 &\simeq 1 \qquad \Rightarrow \frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{23}}{\partial r}} \simeq \frac{\frac{\partial\theta_{13}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial r}} \qquad \Rightarrow \frac{\partial\theta_{23}}{\partial r}\frac{\partial\theta_{13}}{\partial\phi} - \frac{\partial\theta_{23}}{\partial\phi}\frac{\partial\theta_{13}}{\partial r} \simeq 0.
\end{aligned}
$$

To analyze the first assumption we define the following ratios,

$$
B1 = \frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{13}}{\partial y}} \cdot \frac{\frac{\partial\theta_{13}}{\partial x}}{\frac{\partial\theta_{23}}{\partial x}} \qquad\qquad B2 = \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{13}}{\partial z}} \cdot \frac{\frac{\partial\theta_{13}}{\partial x}}{\frac{\partial\theta_{23}}{\partial x}}
$$

express in terms of polar coordinate by using the chain rule of differentiation

$$
B1 = \frac{\frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{13}}{\partial y}}}{\frac{\frac{\partial\theta_{23}}{\partial x}}{\frac{\partial\theta_{13}}{\partial x}}} = \frac{\left(1 + \frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial y}}{\frac{\partial r}{\partial y}} + \frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial y}}{\frac{\partial r}{\partial y}}\right)\left(1 + \frac{\frac{\partial\theta_{13}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial x}}{\frac{\partial r}{\partial x}} + \frac{\frac{\partial\theta_{13}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial x}}{\frac{\partial r}{\partial x}}\right)}{\left(1 + \frac{\frac{\partial\theta_{13}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial y}}{\frac{\partial r}{\partial y}} + \frac{\frac{\partial\theta_{13}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial y}}{\frac{\partial r}{\partial y}}\right)\left(1 + \frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial x}}{\frac{\partial r}{\partial x}} + \frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial x}}{\frac{\partial r}{\partial x}}\right)}
$$

and

$$B2 = \frac{\frac{\partial\theta_{23}}{\partial z} \Big/ \frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x} \Big/ \frac{\partial\theta_{13}}{\partial x}} = \frac{\left(1 + \frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial z}}{\frac{\partial r}{\partial z}} + \frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial z}}{\frac{\partial r}{\partial z}}\right)\left(1 + \frac{\frac{\partial\theta_{13}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial x}}{\frac{\partial r}{\partial x}} + \frac{\frac{\partial\theta_{13}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial x}}{\frac{\partial r}{\partial x}}\right)}{\left(1 + \frac{\frac{\partial\theta_{13}}{\partial\theta}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial z}}{\frac{\partial r}{\partial z}} + \frac{\frac{\partial\theta_{13}}{\partial\phi}}{\frac{\partial\theta_{13}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial z}}{\frac{\partial r}{\partial z}}\right)\left(1 + \frac{\frac{\partial\theta_{23}}{\partial\theta}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\theta}{\partial x}}{\frac{\partial r}{\partial x}} + \frac{\frac{\partial\theta_{23}}{\partial\phi}}{\frac{\partial\theta_{23}}{\partial r}} \cdot \frac{\frac{\partial\phi}{\partial x}}{\frac{\partial r}{\partial x}}\right)}$$

When Jacobian relations are substituted in B1 and B2, we obtain:

$$\frac{\frac{\partial\theta_{23}}{\partial y}}{\frac{\partial\theta_{23}}{\partial x}} \simeq \frac{\frac{\partial\theta_{13}}{\partial y}}{\frac{\partial\theta_{13}}{\partial x}} \quad \text{and} \quad \frac{\frac{\partial\theta_{23}}{\partial z}}{\frac{\partial\theta_{23}}{\partial x}} \simeq \frac{\frac{\partial\theta_{13}}{\partial z}}{\frac{\partial\theta_{13}}{\partial x}}.$$

Therefore:

$$\left(\frac{\partial\theta_{23}}{\partial y}\frac{\partial\theta_{13}}{\partial x} - \frac{\partial\theta_{23}}{\partial x}\frac{\partial\theta_{13}}{\partial y}\right), \left(\frac{\partial\theta_{23}}{\partial z}\frac{\partial\theta_{13}}{\partial x} - \frac{\partial\theta_{23}}{\partial x}\frac{\partial\theta_{13}}{\partial z}\right) \text{ and } \left(\frac{\partial\theta_{23}}{\partial y}\frac{\partial\theta_{13}}{\partial z} - \frac{\partial\theta_{23}}{\partial z}\frac{\partial\theta_{13}}{\partial y}\right) \text{ or}$$

$$\left(\frac{\partial\theta_{23}}{\partial\theta}\frac{\partial\theta_{13}}{\partial r} - \frac{\partial\theta_{23}}{\partial r}\frac{\partial\theta_{13}}{\partial\theta}\right) \left(\frac{\partial\theta_{23}}{\partial\phi}\frac{\partial\theta_{13}}{\partial r} - \frac{\partial\theta_{23}}{\partial r}\frac{\partial\theta_{13}}{\partial\phi}\right) \text{ and } \left(\frac{\partial\theta_{23}}{\partial\theta}\frac{\partial\theta_{13}}{\partial\phi} - \frac{\partial\theta_{23}}{\partial\phi}\frac{\partial\theta_{13}}{\partial\theta}\right) \text{ vis -a-vis}$$

$$Curl\,\tau_{ij}^{pq}\ (p,q \equiv x,y,z \quad \text{or} \quad r,\theta,\phi)$$

are either identically or approximately zero around the conical intersection.

Appendix 2

Parametric representation of a conical surface:

A surface with a parametric representation of the form $\mathbf{r}(u, v)$ can be described by the vector equation,

$$\mathrm{r}(u, v) = \vec{i}\; X(u, v) + \vec{j}\; Y(u, v) + \vec{k}\; Z(u, v), \qquad (u, v) \in T, \tag{C1}$$

where $X(u, v)$, $Y(u, v)$, and $Z(u, v)$ are the three equations expressing x, y, and z in terms of two parameters u and v:

$$x = X(u, v), \qquad y = Y(u, v), \qquad z = Z(u, v). \tag{C2}$$

The point (u, v) can vary over a two - dimensional connected set T in the uv-plane, and the corresponding points (x, y, z) trace out a surface in xyz-plane.

If X, Y, and Z are differentiable on T, we consider the two vectors,

$$\frac{\partial \mathrm{r}}{\partial u} = \vec{i}\,\frac{\partial X}{\partial u} + \vec{j}\,\frac{\partial Y}{\partial u} + \vec{k}\,\frac{\partial Z}{\partial u}$$

and

$$\frac{\partial \mathrm{r}}{\partial v} = \vec{i}\,\frac{\partial X}{\partial v} + \vec{j}\,\frac{\partial Y}{\partial v} + \vec{k}\,\frac{\partial Z}{\partial v}$$

The cross product of these two vectors $\frac{\partial \mathrm{r}}{\partial u} \times \frac{\partial \mathrm{r}}{\partial v}$ is the *fundamental vector product* of the representation r. Its components can be expressed as Jacobian determinants as follows,

$$\frac{\partial \mathrm{r}}{\partial u} \times \frac{\partial \mathrm{r}}{\partial v} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial X}{\partial u} & \frac{\partial Y}{\partial u} & \frac{\partial Z}{\partial u} \\ \frac{\partial X}{\partial v} & \frac{\partial Y}{\partial v} & \frac{\partial Z}{\partial v} \end{vmatrix} = \vec{i}\begin{vmatrix} \frac{\partial Y}{\partial u} & \frac{\partial Z}{\partial u} \\ \frac{\partial Y}{\partial v} & \frac{\partial Z}{\partial v} \end{vmatrix} + \vec{j}\begin{vmatrix} \frac{\partial Z}{\partial u} & \frac{\partial X}{\partial u} \\ \frac{\partial Z}{\partial v} & \frac{\partial X}{\partial v} \end{vmatrix} + \vec{k}\begin{vmatrix} \frac{\partial X}{\partial u} & \frac{\partial Y}{\partial u} \\ \frac{\partial X}{\partial v} & \frac{\partial Y}{\partial v} \end{vmatrix} \tag{C3}$$

$$= \vec{i}\,\frac{\partial(Y,Z)}{\partial(u,v)} + \vec{j}\,\frac{\partial(Z,X)}{\partial(u,v)} + \vec{k}\,\frac{\partial(X,Y)}{\partial(u,v)}. \tag{C4}$$

If (u, v) is a point in T at which $\frac{\partial \mathbf{r}}{\partial u}$ and $\frac{\partial \mathbf{r}}{\partial v}$ are continuous and the fundamental vector product is nonzero, then the image point $\mathbf{r}(u, v)$ is a regular point of $\mathbf{r}$. Points at which $\frac{\partial \mathbf{r}}{\partial u}$ or $\frac{\partial \mathbf{r}}{\partial v}$ fails to be continuous or $\frac{\partial \mathbf{r}}{\partial u} \times \frac{\partial \mathbf{r}}{\partial v} = 0$ are the *singular points* of r.

We consider the surface of a cone (see Fig.1) as the image of the rectangle $T = [0, 2\pi] \times [0, h]$ under the mapping,

$$\mathrm{R}(r, \theta) = \vec{i}\ (\rho \cos\delta + r \sin\alpha \cos\theta) + \vec{j}\ (\rho \sin\delta + r \sin\alpha \sin\theta) + \vec{k}\ (z_0 - r\cos\alpha) \tag{C5}$$

The vectors $\frac{\partial \mathrm{R}}{\partial r}$ and $\frac{\partial \mathrm{R}}{\partial \theta}$ are given by,

$$\frac{\partial \mathrm{R}}{\partial r} = \vec{i}\ \sin\alpha\cos\theta + \vec{j}\ \sin\alpha\sin\theta - \vec{k}\ \cos\alpha \tag{C6}$$

$$\frac{\partial \mathrm{R}}{\partial \theta} = -\vec{i}\ r\sin\alpha\sin\theta + \vec{j}\ r\sin\alpha\cos\theta \tag{C7}$$

Their cross product is:

$$\frac{\partial \mathrm{R}}{\partial r} \times \frac{\partial \mathrm{R}}{\partial \theta} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \sin\alpha\cos\theta & \sin\alpha\sin\theta & -\cos\alpha \\ -r\sin\alpha\sin\theta & r\sin\alpha\cos\theta & 0 \end{vmatrix}$$

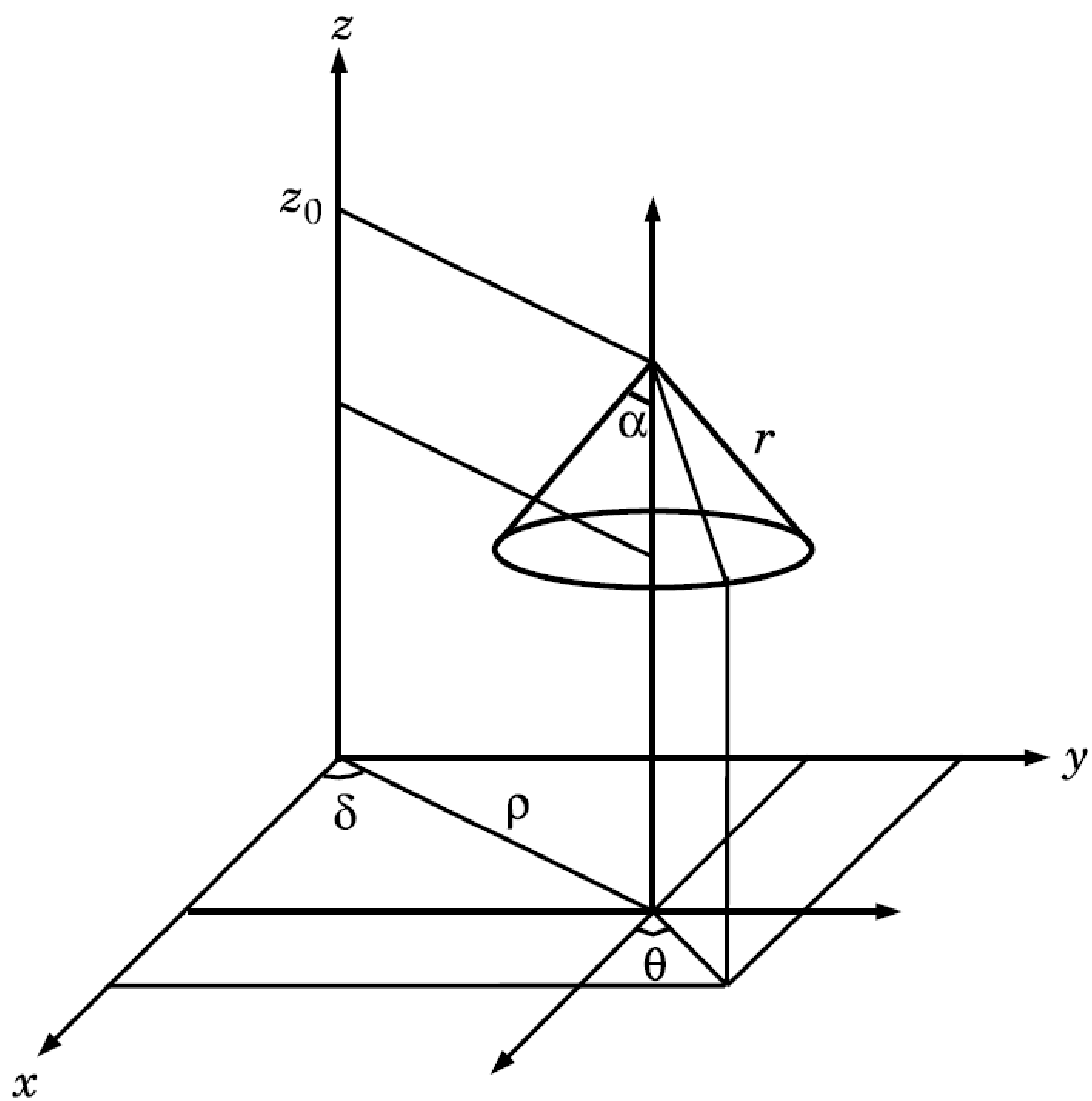
$$= \vec{i}\ r\sin\alpha\cos\alpha\cos\theta + \vec{j}\ r\sin\alpha\cos\alpha\sin\theta + \vec{k}\ r\sin^2\alpha \tag{C8}$$

Since $||\frac{\partial \mathrm{R}}{\partial r} \times \frac{\partial \mathrm{R}}{\partial \theta}|| = r^2 \sin^2 \alpha$, the only singular point of this representation occurs when $r = 0$, which is the vertex of the cone.

The Jacobian determinant as defined in the cross product [Eqs. (C3) and (C8)] vanishes when $r = 0$, but this does not affect the validity of the transformation formula because the set of points with $r = 0$ has content zero. As for example, the Jacobian determinant along the unit vector $\vec{k}$ for $r = 0$ is given by:

$$\begin{vmatrix} \frac{\partial X}{\partial r} & \frac{\partial Y}{\partial r} \\ \frac{\partial X}{\partial \theta} & \frac{\partial Y}{\partial \theta} \end{vmatrix} = r \sin^2 \alpha = 0 \tag{C9}$$

Geometry of a cone in Cartesian coordinate



Appendix 3

(a) Since the matrix representation of the ADT ($\mathbf{\Phi}=G^{\dagger}\mathbf{\Psi}$) is given by

$$\begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} \frac{g_3}{\eta} & -\frac{g_2}{\eta} & \frac{g_1}{\eta} \\ -\frac{g_1 g_3 + i\eta g_2}{\sqrt{2}\lambda\eta} & \frac{g_1 g_2 - i\eta g_3}{\sqrt{2}\lambda\eta} & \frac{\lambda}{\sqrt{2}\eta} \\ \frac{-g_1 g_3 + i\eta g_2}{\sqrt{2}\lambda\eta} & \frac{g_1 g_2 + i\eta g_3}{\sqrt{2}\lambda\eta} & \frac{\eta}{\sqrt{2}\eta} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix}$$

with

$$\begin{aligned} g_1 &= -1 - \sin\theta_{23}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right), \\ g_2 &= -\sin\theta_{12}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) - \cos\theta_{12}\cos\theta_{23}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right), \\ g_3 &= -\cos\theta_{12}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + \sin\theta_{12}\cos\theta_{23}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right), \\ \lambda &= \sqrt{g_2^2 + g_3^2} = \left[\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \cos^2\theta_{23}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2\right]^{\frac{1}{2}}, \\ \eta &= \sqrt{g_1^2 + g_2^2 + g_3^2} = \left[1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + 2\sin\theta_{23}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\right]^{\frac{1}{2}}, \end{aligned}$$

one can have the general identity

$$\psi_k = \frac{1}{G^d_{kk}}\phi_k - \sum_{l\neq k}\frac{G^d_{kl}}{G^d_{kk}}\psi_l \qquad\qquad k,l = 1,2,3;$$

(b) The product, V$\mathbf{\Phi}$, for the i th equation can be rearranged as below,

$$(V\Phi)_i = u_1\Phi_i + \sum_{j=2}^{3} G^d_{ij}(u_j - u_1)\psi_j, \qquad\qquad i = 1,2,3.$$

The i th BO equation can be written from the matrix equation as:

$$\begin{aligned} - \quad & \frac{\hbar^2}{2m}\Big[(\vec{\nabla} + i\vec{\omega})^2\Phi\Big]_i - \frac{\hbar^2}{2m}\Big[\sum_k G^d_{ik}\nabla^2\psi_k - \sum_k \nabla^2(G^d_{ik}\psi_k) + \sum_k i\vec{\omega}_i G^d_{ik}\vec{\nabla}\psi_k \\ - \quad & \sum_k i\vec{\omega}_i\vec{\nabla}(G^d_{ik}\psi_k) + \sum_{km} G^d_{ik}\vec{\nabla}(\vec{\tau}_{km}\psi_m) - \sum_{km}\vec{\nabla}(G^d_{ik}\vec{\tau}_{km}\psi_m)\Big] + \Big[(\mathbf{V} - E)\Phi\Big]_i = 0. \end{aligned}$$

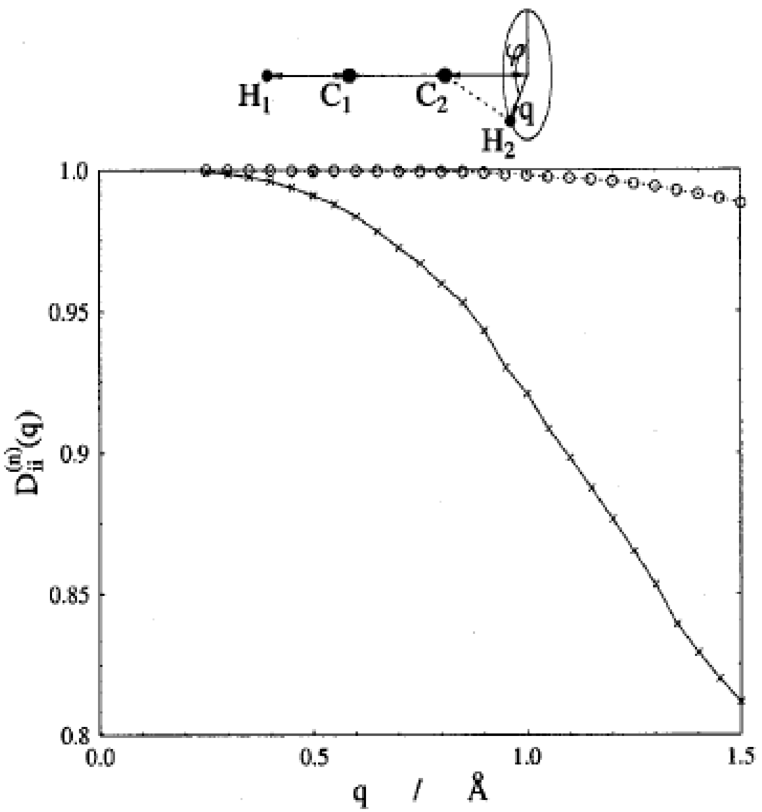
Appendix 4

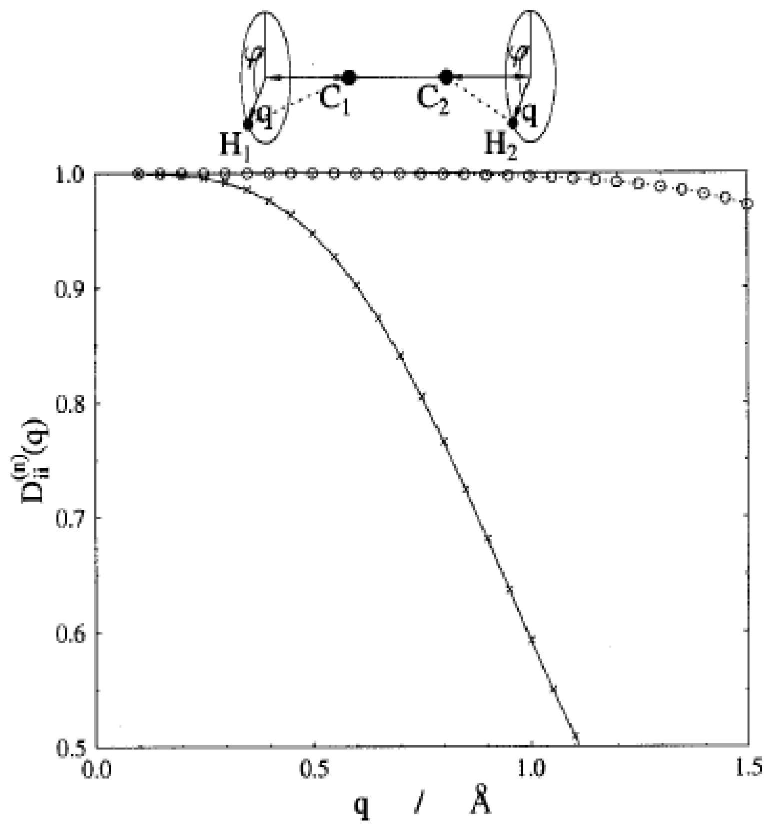
eigenvalue of τ matrix when $\mathit{Curl}\ \tau_{ij}^{pq} = [\tau^p, \tau^q] = 0$

$$
\begin{aligned}
\vec{\omega}_i \;=\;& \pm\vec{\nabla}\theta_{12}\Bigg[-\frac{1}{2}\Bigg\{ 1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2 \\
&+ 2\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{23}\sin\theta_{14}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) \\
&+ 2\sin\theta_{24}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + 2\cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) \\
&+ 2\big(\sin\theta_{13}\sin\theta_{23} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24}\big)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\Bigg\} \\
&\pm \frac{1}{2}\Bigg\{\Bigg[1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2 \\
&+ 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + 2\big(\cos\theta_{13}\cos\theta_{23}\sin\theta_{14} + \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\big)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) \\
&+ 2\big(\sin\theta_{13}\sin\theta_{23} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24} + \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\big)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) \\
&+ 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2\big(\cos\theta_{23}\sin\theta_{14}\cos\theta_{24} + \sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\big)\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) \\
&+ 2\big(\sin\theta_{23}\sin\theta_{14} - \cos\theta_{23}\cos\theta_{14}\big)\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{14}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) \\
&+ 2\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{24}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\Bigg]
\end{aligned}
$$

$$
\begin{aligned}
\times & \Bigg[1+\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2+\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2+\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2+\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2+\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2 \\
+ & 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)+2\big(\cos\theta_{13}\cos\theta_{23}\sin\theta_{14}-\cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\big)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) \\
+ & 2\big(\sin\theta_{13}\sin\theta_{23}-\cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24}-\cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\big)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) \\
- & 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)+2\big(\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}-\sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\big)\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) \\
+ & 2\big(\sin\theta_{23}\sin\theta_{14}+\cos\theta_{23}\cos\theta_{14}\big)\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)+2\sin\theta_{14}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) \\
- & 2\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)-2\sin\theta_{24}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\Bigg]\Bigg\}^{\frac{1}{2}}\Bigg]^{\frac{1}{2}}
\end{aligned}
$$

⇨ The study on the tetra atomic system, $C_2H_2^+$, distinguish between the case where τ is of 2x2 ($1^2A'$ and $1^2A''$) dimension and the case where it is of the 3x3 dimension ($1^2A'$, $1^2A''$ and $2^2A''$)[9]





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