MWQC - 2022 Tutorial

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1. NO_3 radical (D_{3h} symmetry) has 6 normal modes :

   - Totally symmetric (Q_1); Umbrella (Q_2)
   - Degenerate asymmetric stretching (Q_{3x} and Q_{3y})
   - Degenerate asymmetric bending (Q_{4x} and Q_{4y})

   If the electronic states are coupled through nuclear coordinates as, $V_{ij} = \sum_k Q_k \langle \phi_i^{(0)} | \hat{V}_k | \phi_j^{(0)} \rangle$ [$\hat{V}_k \left(= \frac{\partial H}{\partial Q_k} \right)$ is the first order perturbations w.r.t normal modes, $\{Q_k\}s$], apply the JT condition ($\Gamma(\phi_i^{(0)}) \otimes \Gamma(\hat{V}_k) \otimes \Gamma(\phi_j^{(0)}) \notin \Gamma^0$) to explore the JT activity of Q_{3x}, Q_{3y}, Q_{4x} and Q_{4y} modes. Γ s are irreducible representations.

   The character table of D_{3h} point group :

D_{3h}	E	$2C_3(z)$	$3C_2'$	$\sigma_h(xy)$	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions	normal modes of NO_3
A_1'	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	$x(x^2-3y^2)$	Q_1
A_2'	+1	+1	-1	+1	+1	-1	R_z	-	$y(3x^2-y^2)$	
E'	+2	-1	0	+2	-1	0	(x, y)	(x^2-y^2, xy)	(xz^2, yz^2), $[x(x^2+y^2), y(x^2+y^2)]$	Q_{3x}, Q_{3y}, Q_{4x}, Q_{4y}
A_1''	+1	+1	+1	-1	-1	-1	-	-	-	
A_2''	+1	+1	-1	-1	-1	+1	z	-	$z^3, z(x^2+y^2)$	Q_2
E''	+2	-1	0	-2	+1	0	(R_x, R_y)	(xz, yz)	$[xyz, z(x^2-y^2)]$	

   [Hint: One needs to know the direct product of irreducible representation and within symmetric interval, totally symmetric irreducible representation of the integrand defines the existence of integral.]

2. A model Hamiltonian describing the molecular system within a degenerate manifold is:

$$\hat{H} = \hat{T}_n + \hat{H}_{el}$$

$$\begin{aligned} \hat{H} &= \hat{T}_n + \left(-\frac{1}{2} E_{el} \frac{\partial^2}{\partial \theta^2} + \frac{1}{2} q^2 - q \cos(2\theta - \phi) \right), \\ \hat{T}_n &= -\frac{1}{2\mu} \nabla^2 = -\frac{1}{2\mu} \Big[\frac{d^2}{dq^2} + \frac{1}{q^2} \frac{d^2}{d\phi^2} \Big] \end{aligned}$$

where $\hat{T}_n, \hat{H}_{el}$ are the nuclear kinetic energy operator and electronic Hamiltonian, respectively. θ is the electronic phase angle and q, ϕ are the nuclear coordinates. On the other hand, electronic eigenfunctions obey the following equation:

$$\left(-\frac{1}{2} E_{el} \frac{\partial^2}{\partial \theta^2} - q \cos(2\theta - \phi) + \frac{1}{2} q^2 - u(q, \phi) \right) \xi(\theta, q, \phi) = 0 \tag{2.1}$$

(a) Considering the trial function $\xi = a(q, \phi) \cos\theta + b(q, \phi) \sin\theta$ in terms of basis functions ($\cos\theta$ and $\sin\theta$), find the eigenvalues (u_1 and u_2) and eigenfunctions (ξ_1 and ξ_2) of the above equation.

(b) Find the non adiabatic coupling terms:

$$\begin{aligned} \tau_q(q, \phi) &= \langle \xi_1(\theta, q, \phi) | \frac{d}{dq} | \xi_2(\theta, q, \phi) \rangle \\ \tau_\phi(q, \phi) &= \frac{1}{q} \langle \xi_1(\theta, q, \phi) | \frac{d}{d\phi} | \xi_2(\theta, q, \phi) \rangle \end{aligned}$$

and show that the integration of τ_ϕ along a closed contour leads to π.

[Hint: The basic idea for the solution of Schrödinger equation (Eq. 2.1) in the matrix representation with the given trial function is enough. Since the trial function ($\xi = a(q, \phi) \cos\theta + b(q, \phi) \sin\theta$) has two basis, the matrix will be 2 X 2 and thereby, two eigenvalues and two eigenfunctions. Those eigenfunctions on substitution in coupling terms will provide the functional forms of those terms.]

3. For a three electronic state sub-Hilbert space, the matrix representation of adiabatic nuclear Schrödinger equation is given by

$$\sum_{j=1}^{3} (H_{ij} - E\delta_{ij}) \psi_j(\vec{n}) = 0, \qquad i = 1, 2, 3,$$

where

$$\begin{aligned}
H_{ii} &= -\frac{\hbar^2}{2m}(\nabla^2 + 2\vec{\tau}_{ii}^{(1)} \cdot \vec{\nabla} + \tau_{ii}^{(2)}) + u_i(n) \\
H_{ij} &= -\frac{\hbar^2}{2m}(2\vec{\tau}_{ij}^{(1)} \cdot \vec{\nabla} + \tau_{ij}^{(2)}) = H_{ji}^{\dagger} \\
\vec{\tau}_{ij}^{(1)} &= \langle \xi_i(\vec{e},\vec{n})|\vec{\nabla}|\xi_j(\vec{e},\vec{n})\rangle \\
\tau_{ij}^{(2)} &= \langle \xi_i(\vec{e},\vec{n})|\nabla^2|\xi_j(\vec{e},\vec{n})\rangle \\
\langle \xi_i(\vec{e},\vec{n})|\xi_j(\vec{e},\vec{n})\rangle &= \delta_{ij},
\end{aligned}$$

where $\vec{n}$ and $\vec{e}$ are the sets of nuclear and electronic coordinates, respectively. If $\xi_i(\vec{e},\vec{n})$ s are the electronic basis functions defined as below:

$$\begin{aligned}
\xi_1 &= \begin{pmatrix} \cos\alpha\cos\beta \\ \sin\alpha\cos\beta \\ \sin\beta \end{pmatrix} \\
\xi_2 &= \begin{pmatrix} -\cos\alpha\sin\beta\sin\gamma - \sin\alpha\cos\gamma \\ -\sin\alpha\sin\beta\sin\gamma + \cos\alpha\cos\gamma \\ \cos\beta\sin\gamma \end{pmatrix}, \\
\xi_3 &= \begin{pmatrix} -\cos\alpha\sin\beta\cos\gamma + \sin\alpha\sin\gamma \\ -\sin\alpha\sin\beta\cos\gamma + \cos\alpha\sin\gamma \\ \cos\beta\cos\gamma \end{pmatrix},
\end{aligned}$$

and $\alpha(\vec{n})$, $\beta(\vec{n})$, and $\gamma(\vec{n})$ are the mixing angles between "1-2", "1-3", and "2-3" electronic states, find the explicit forms of non adiabatic coupling matrix elements ($\vec{\tau}_{ij}^{(1)}(\vec{n}) = \langle \xi_i(\vec{e},\vec{n})|\vec{\nabla}_n|\xi_j(\vec{e},\vec{n})\rangle$).

The z-components of the mathematical curl ($Curl\ \tau_{xy}^{ij}$) and the commutator curl (C_{xy}^{ij}) of NACTs are given by

$$Curl\ \tau_{xy}^{ij} = \frac{\partial}{\partial y}\tau_x^{ij} - \frac{\partial}{\partial x}\tau_y^{ij} \tag{3.1}$$

$$C_{xy}^{ij} = (\tau_x\tau_y)^{ij} - (\tau_y\tau_x)^{ij} \tag{3.2}$$

Show that mathematical and commutator curls are equal (Yang-Mill Field) if the (3×3) $\vec{\tau}$ matrix strictly form a three state sub-Hilbert space.

[Hint: One requires to know how to take symbolic derivative and that will provide the functional forms of τ_{ij}. If there are two nuclear coordinates x and y, cross-derivative needs to be taken on the corresponding scalar components (x and y) of explicit forms of τ_{ij} to calculate mathematical curl (Eq. 3.1), whereas the commutator between the explicit forms of those scalar components of τ_{ij} will provide the commutator curl (Eq. 3.2).]

4. Given the model diabatic Hamiltonian matrix expanded in terms of the active modes [complex linear combination of two normal modes, bending (Q_x) and asymmetric stretching (Q_y)] for the two $2\,^2E'$ states of Na_3 cluster:

$$\hat{H}_e(\rho,\phi) = \begin{pmatrix} \frac{\rho^2}{2} & K\rho e^{i\phi} + \frac{1}{2}g\rho^2 e^{-2i\phi} \\ K\rho e^{-i\phi} + \frac{1}{2}g\rho^2 e^{2i\phi} & \frac{\rho^2}{2} \end{pmatrix} \tag{4.1}$$

find the eigenvalues and eigenfunctions of the above Hamiltonian. Also formulate the analytic forms of ρ ($\tau_\rho = \langle\xi_i(\rho,\phi)|\frac{d}{d\rho}|\xi_j(\rho,\phi)\rangle$) and ϕ ($\tau_\phi = \langle\xi_i(\rho,\phi)|\frac{1}{\rho}\frac{d}{d\phi}|\xi_j(\rho,\phi)\rangle$) components of non adiabatic coupling elements.

[Hint: One needs to know how to diagonalize a 2 X 2 matrix. Column vectors of the diagonalizing matrix are the eigenfunctions, which can be used to find out τ_ρ and τ_ϕ by taking simple derivatives on those functions. Here two coordinates are necessary, particularly, in polar form to get the angular nonadiabatic coupling term (τ_ϕ), which on integration over circular coordinate (ϕ) provides π.]

5. For a tri-atomic system ABC, the reactant coordinates in collinear arrangement are given by:

$$(r_{BC}, r_{BA}) \Leftrightarrow (r, \rho)$$

$$\vec{r}_R = \vec{r}_{BC} \qquad \vec{\rho}_R = \vec{r}_{BA} - \left(\frac{m_C}{m_B+m_C}\right)\vec{r}_{BC}$$

$$\mu_{BC} = \frac{m_B m_C}{m_B+m_C} \qquad \mu_{A,BC} = \frac{m_A(m_B+m_C)}{M},$$

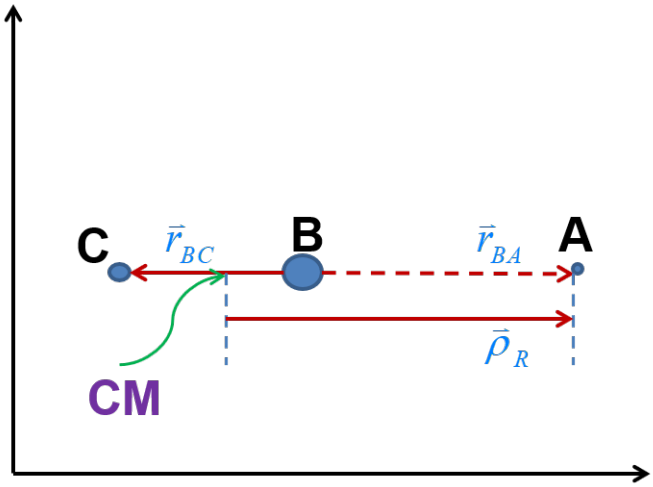

Figure 1: Reactant coordinates in collinear arrangement

whereas the product coordinate in collinear arrangement:

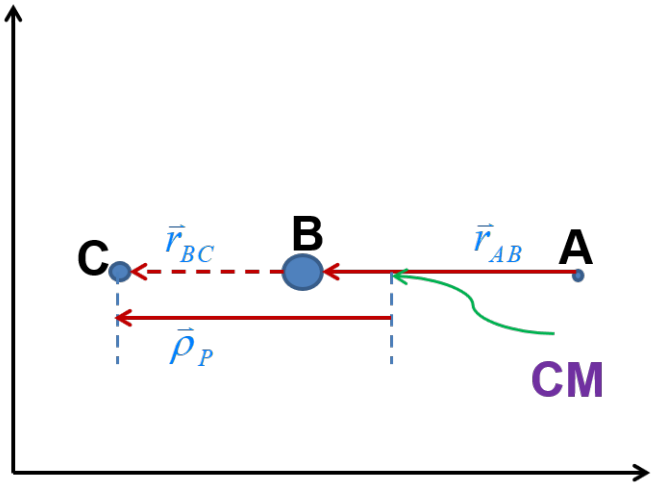

Figure 2: Product coordinates in collinear arrangement

$$\vec{r}_P = \vec{r}_{AB} \qquad \vec{\rho}_P = \vec{r}_{BC} + \left(\frac{m_A}{m_A+m_B}\right)\vec{r}_{AB}$$
$$\mu_{AB} = \frac{m_A m_B}{m_A+m_B} \qquad \mu_{C,AB} = \frac{m_C(m_A+m_B)}{M}$$

The scaling factors λ_I and λ_{II} are defined as:

$$\lambda_I = \left(\frac{\mu_{BC}}{\mu_{A,BC}}\right)^{\frac{1}{4}} \qquad \text{and} \qquad \lambda_{II} = \left(\frac{\mu_{AB}}{\mu_{C,AB}}\right)^{\frac{1}{4}},$$

Thus, the new sets of rescaled coordinates become:

$$\vec{r}_I = r_R \vec{\lambda}_I \qquad \vec{\rho}_I = \vec{\rho}_R \lambda_I^{-1}$$
$$\vec{r}_{II} = \vec{r}_P \lambda_{II} \qquad \vec{\rho}_{II} = \vec{\rho}_P \lambda_{II}^{-1}$$

which are related through the following transformation:

$$\begin{bmatrix} \vec{\rho}_{II} \\ \vec{r}_{II} \end{bmatrix} = \begin{bmatrix} \cos\beta & \sin\beta \\ -\sin\beta & \cos\beta \end{bmatrix} \begin{bmatrix} \vec{\rho}_I \\ \vec{r}_I \end{bmatrix} \tag{5.1}$$

Find the transformation matrix in terms of masses of the atoms.

[Hint: The working habit on algebraic manipulation is enough.]

6. If the amplitudes of the wave packet on the θ grid ($0 \leq \theta \leq 2\pi$) are given by

$$\chi(\theta_1), \chi(\theta_2), \ldots, \chi(\theta_{N-1}), \chi(\theta_N)$$

[$\theta_1, \theta_2, \ldots \theta_N$ are N number of grid points], the amplitudes can be written as linear combination of plane waves forming a complete basis set:

$$\chi(\theta) = \sum_{n=1}^{2M} C_n \exp\left(-i\kappa_n \theta\right) \tag{6.1}$$

Such basis functions are continuous and their amplitudes match exactly at $\theta = 0$ and 2π.

Therefore, we obtain the following equations:

$$\begin{aligned} \chi(\theta_1) &= \sum_{n=1}^{2M} C_n \exp\left(-i\kappa_n \theta_1\right), \\ \chi(\theta_2) &= \sum_{n=1}^{2M} C_n \exp\left(-i\kappa_n \theta_2\right), \\ &\vdots \\ \chi(\theta_k) &= \sum_{n=1}^{2M} C_n \exp\left(-i\kappa_n \theta_k\right), \end{aligned}$$

where

$$\begin{aligned} \kappa_n &= \tfrac{2\pi}{L} n, \qquad \text{when} \quad n \leq M \\ &= \tfrac{2\pi}{L}(n - 1 - 2M), \qquad \text{when} \quad n > M \end{aligned}$$

Thus

$$\begin{aligned}\int_\theta \chi(\theta)\exp(i\kappa_m\theta)\,d\theta &= \sum_{n=1}^{2M} C_n\left[\int_\theta \exp(-i\kappa_n\theta)\exp(i\kappa_m\theta)\,d\theta\right]\\ &= \sum_{n=1}^{2M} C_n\delta_{nm} = C_m\end{aligned}$$

In general, the Fourier coefficients can be written as:

$$\begin{aligned}&C_m = \int_\theta \chi(\theta)\exp(i\kappa_m\theta)\,d\theta\\ &\Rightarrow\ C_m\ = \sum_{l=1}^{2N}\chi(\theta_l)\exp(i\kappa_m\theta_l)\,\Delta\theta\end{aligned} \tag{6.2}$$

If we back substitute those C_ms into Eq. 6.1, we can regenerate the original wave function.

If the wave packet on the θ-grid is defined within the domain 0 and $\pi/2$, the amplitudes of the Fourier basis at θ=0 do not match at $\theta = \pi/2$ for continuity and thereby, one can avoid the problem by performing sine transformation.

If the amplitudes of the wave packet on the grid ($0 \le \theta \le \pi/2$) are represented as,

$$\chi(\theta_1), \chi(\theta_2), \ldots, \chi(\theta_{N-1}), \chi(\theta_N),$$

then show that doubling the grid in the following fashion

$$\begin{aligned}\theta = \ & 0 \qquad \cdots\cdots \qquad \pi/2 \qquad \cdots\cdots \qquad \pi\\ & \chi(\theta_1), \chi(\theta_2), \ldots, \chi(\theta_{N-1}), \chi(\theta_N), -\chi(\theta_N), -\chi(\theta_{N-1}), \ldots, -\chi(\theta_2), -\chi(\theta_1),\end{aligned} \tag{6.3}$$

would lead to sine transformation:

$$C_m = \sum_{l=1}^{N} 2i\chi(\theta_l)\sin(\kappa_m\theta_l)\,\Delta\theta \tag{6.4}$$

[Hint: Only the rule of complex exponential functions using Euler's formula is needed.]

7. Time dependent Schrödinger equation can be written as:

$$i\hbar\frac{\partial\Phi}{\partial t} = H\Phi, \tag{7.1}$$

where in matrix representation, Φ is a vector of length N and H is a $N \times N$ matrix.

The matrix (Q) that transform the Hamiltonian matrix (H) into a tri-diagonal form (T) is:

$$Q^\dagger H Q = T \qquad\qquad Q^\dagger Q = 1, \tag{7.2}$$

where Q is defined as:

$$Q = [q_1\, q_2 \ldots q_j \ldots q_l]_{1\times l}, \qquad q_i \text{ is vector of length } N$$

and T is of the following form,

$$T = \begin{bmatrix}
\alpha_1 & \beta_1 & 0 & \ldots & & & \ldots & & & 0 \\
\beta_1 & \alpha_2 & \beta_2 & & & & & & & \vdots \\
0 & \beta_2 & \alpha_3 & \beta_3 & & & & & & \\
\vdots & & & \ddots & & & & & & \\
& & & & & \beta_{j-1} & & & & \\
& & & & \beta_{j-1} & \alpha_j & \beta_j & & & \\
\vdots & & & & & \beta_j & \alpha_{j+1} & & & \vdots \\
& & & & & & & & & \\
& & & & & & & & & \beta_{l-1} \\
0 & \ldots & & & & & \ldots & 0 & \beta_{l-1} & \alpha_l
\end{bmatrix}_{l\times l}.$$

Considering,

$$\begin{gathered} HQ = QT \\ \Rightarrow H \begin{bmatrix} q_1 & q_2 & \ldots & q_j & \ldots & q_l \end{bmatrix} = \begin{bmatrix} q_1 & q_2 & \ldots & q_j & \ldots & q_l \end{bmatrix} T, \end{gathered} \tag{7.3}$$

derive the relations ($\alpha_j = q_j^\dagger H q_j$, $\beta_{j-1} = q_{j-1}^\dagger H q_j$) to obtain the elements of tri-diagonal matrix T.

[Hint: The knowledge on the multiplication of matrix and understanding on the orthogonal properties of vectors are only required.]