

33-780 Nuclear and Particle Physics II

Note 5 Tensor Method in $SU(n)$

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1 Molecular Vibration

Molecules consists of many atoms can execute vibrational motions. In these motions we can treat the atoms as point particles moving slightly away from their equilibrium positions. Let $\vec{x} = (x_1, x_2, \dots, x_n)$ be the generalized coordinates for describing the atoms in the molecule. Then the small deviations from the equilibrium position can be described by expanding their potential energy V around the equilibrium position,

$$V(\vec{x}) = V(\vec{x}_0) + (x_i - x_{i0}) \left. \frac{\partial V}{\partial x_i} \right|_{x=x_0} + \frac{1}{2} (x_i - x_{i0}) (x_j - x_{j0}) \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_{x=x_0} + \dots$$

Here \vec{x}_0 is the equilibrium position and $\left. \frac{\partial V}{\partial x_i} \right|_{x=x_0} = 0$. We can write the potential energy as

$$V = V_0 + \frac{1}{2} u_{ij} q_i q_j$$

where

$$V_0 = V(\vec{x}_0), \quad q_i = (x_i - x_{i0}), \quad u_{ij} = \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_{x=x_0}$$

Write the kinatic energy as

$$T = \frac{1}{2} M_{ij} \dot{q}_i \dot{q}_j, \quad \text{where} \quad M_{ij} = m_i \delta_{ij} \quad (\text{no sum over } i)$$

The Lagrangian is then

$$L = T - V$$

From Euler-Lagrange equation we get,

$$M_{ij} \ddot{q}_j = -u_{ij} q_j$$

We are interested in the normal mode solution of the form, $q_i = \eta_i \exp(-i\omega t)$. Equation of motion then gives

$$\omega^2 M_{ij} \eta_j = u_{ij} \eta_j \tag{1}$$

Or in matrix notation,

$$\omega^2 M \eta = U \eta \tag{2}$$

where

$$(M)_{ij} = M_{ij}, \quad (U)_{ij} = u_{ij}, \quad \eta = \begin{pmatrix} \eta_1 \\ \vdots \\ \eta_n \end{pmatrix}$$

This is very similar to the eigenvalue equation except for the presence of the mass matrix M . Non-trivial solution exists only if

$$\det |\omega^2 M - U| = 0$$

whose solutions give normal mode frequencies, $\omega^{(1)}, \omega^{(2)}, \dots, \omega^{(n)}$. For each normal mode frequency, we get normal mode configuration, $\eta^{(1)}, \eta^{(2)}, \dots, \eta^{(n)}$.

1.1 Orthogonality of normal modes

From

$$\begin{aligned}\omega^{(\alpha)2} M_{ij} \eta_j^{(\alpha)} &= u_{ij} \eta_j^{(\alpha)} \\ \omega^{(\beta)2} M_{ij} \eta_j^{(\beta)} &= u_{ij} \eta_j^{(\beta)}\end{aligned}$$

we get

$$\left(\omega^{(\alpha)2} - \omega^{(\beta)2} \right) \eta^{(\beta)} M_{ij} \eta_j^{(\alpha)} = 0$$

Thus, normal modes are orthogonal with respect to M ,

$$\eta^{(\beta)} M_{ij} \eta_j^{(\alpha)} = \delta_{\alpha\beta}$$

General solution

$$q = \sum_{i=1}^n c^{(i)} \eta^{(i)} \cos \left[\omega^{(i)} t + \phi^{(i)} \right]$$

1.2 Normal model coordinates

Define $R_{j\alpha} = \eta_j^{(\alpha)}$ then

$$\begin{aligned}(R^t M R)_{\alpha\beta} &= R_{\alpha i}^T M_{ij} R_{j\beta} = \eta_i^{(\alpha)} M_{ij} \eta_j^{(\beta)} = \delta_{\alpha\beta} \\ (R^t u R)_{\alpha\beta} &= R_{\alpha i}^T u_{ij} R_{j\beta} = \omega^{(\beta)2} \eta_i^{(\alpha)} M_{ij} \eta_j^{(\beta)} = \delta_{\alpha\beta} \omega^{(\beta)2}\end{aligned}$$

This means that in the new coordinates defined by

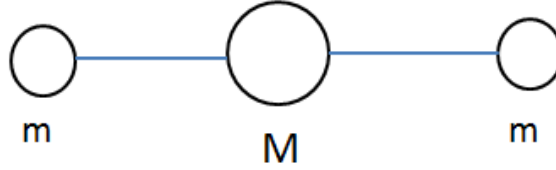
$$x_j = R_{j\alpha} z_\alpha$$

the kinetic and potential energies are all diagonal

$$T = \frac{1}{2} \dot{x}_i M_{ij} \dot{x}_j = \frac{1}{2} \dot{z}_\alpha \dot{z}_\alpha, \quad V = \frac{1}{2} x_i u_{ij} x_j = \frac{1}{2} \omega^{(\alpha)2} z_\alpha^2$$

Thus in terms of z_α , the normal mode coordinates, the oscillators decouple.

Example 1: Linear triatomic molecule



$$\begin{aligned}T &= \frac{1}{2} \left[m \dot{x}_1^2 + M \dot{x}_2^2 + m \dot{x}_3^2 \right] \\ V &= \frac{k}{2} \left[(x_1 - x_2)^2 + (x_2 - x_3)^2 \right]\end{aligned}$$

The corresponding mass matrix and potential matrix are

$$M = \begin{pmatrix} m & & \\ & M & \\ & & m \end{pmatrix}, \quad u = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

Normal mode frequencies

$$\begin{vmatrix} k - m\omega^2 & -k & 0 \\ -k & 2k - m\omega^2 & -k \\ 0 & -k & k - m\omega^2 \end{vmatrix} = 0$$

or

$$\omega^2 (k - m\omega^2) [mM\omega^2 - km(2m + M)] = 0$$

1. $\omega = 0$, translational mode

$$\eta^{(1)} = \frac{1}{\sqrt{2m + M}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

2. $\omega = \sqrt{\frac{k}{m}}$, spring frequency

$$\eta^{(2)} = \frac{1}{\sqrt{2m}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

3. $\omega = \sqrt{\frac{k}{M} \left(2 + \frac{M}{m}\right)}$

$$\eta^{(3)} = \frac{1}{\sqrt{2m \left(1 + 2\frac{m}{M}\right)}} \begin{pmatrix} 1 \\ -2\left(\frac{m}{M}\right) \\ 1 \end{pmatrix}$$

1.3 Symmetries and Normal modes

This system is symmetric under the interchange, $x_1 \leftrightarrow x_3$, which can be represented by the operator with matrix,

$$\sigma = \begin{pmatrix} & & 1 \\ & 1 & \\ 1 & & \end{pmatrix}$$

The eigenvectors are

$$v_1 = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \quad v_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \text{with eigenvalue } 1$$

$$v_3 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \quad \text{with eigenvalue } -1$$

By inspection, v_3 is a normal mode. Since the zero mode of translation is proportional to $v_1 + v_2$, the remaining mode can be obtained by orthogonality.

Example: 4-chain



$$T = \frac{m}{2} \left[\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2 + \dot{x}_4^2 \right]$$

$$V = \frac{k}{2} \left[(x_1 - x_2)^2 + (x_2 - x_3)^2 + (x_3 - x_4)^2 \right] = \frac{1}{2} (x_i u_{ij} x_j)$$

where

$$u = k \begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -1 & 1 \end{pmatrix}$$

The translational zero mode is clearly of the form,

$$\eta^{(1)} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

Note that the system is symmetric under $x_1 \leftrightarrow x_4$, $x_3 \leftrightarrow x_4$ which can be represented by the matrix

$$\sigma = \begin{pmatrix} & & & 1 \\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix}$$

The eigenvectors are

$$\eta^{(1)} = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}, \quad \eta^{(2)} = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} \quad \text{with eigenvalue } 1$$

and

$$\eta^{(3)} = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix}, \quad \eta^{(4)} = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} \quad \text{with eigenvalue } -1$$

By inspection, we see that

$$u\eta^{(2)} = 2k\eta^{(2)}$$

Thus $\eta^{(2)}$ is a normal mode with frequency $\omega^2 = \frac{2k}{m}$. Now in the space expanded by $\eta^{(3)}$, and $\eta^{(4)}$, we get

$$u\eta^{(3)} = k(\eta^{(3)} - \eta^{(4)})$$

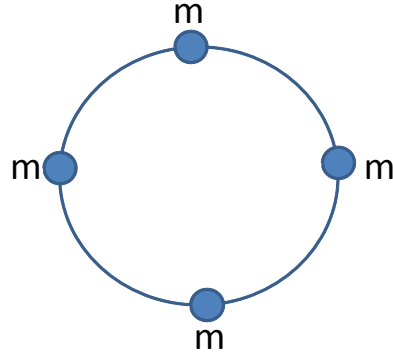
$$u\eta^{(4)} = k(-\eta^{(3)} + 3\eta^{(4)})$$

or

$$u' = k \begin{pmatrix} 1 & -1 \\ -1 & 3 \end{pmatrix}$$

It is straightforward to diagonalize this matrix. The eigenvalues are $k(2 \pm \sqrt{2})$ and the eigenvectors are $\eta^{(3)} - (1 + \sqrt{2})\eta^{(4)}$, and $(1 + \sqrt{2})\eta^{(3)} + \eta^{(4)}$.

Example: 4-ring



The potential energy is given by,

$$u = k \begin{pmatrix} 2 & -1 & 0 & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ -1 & 0 & -1 & 2 \end{pmatrix}$$

Clearly the zero mode is of the form

$$\eta^{(1)} = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

Symmetry: $x_1 \leftrightarrow x_3$, $x_2 \leftrightarrow x_4$. The latter one can be represented by

$$\sigma_y = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

The eigenvectors are

$$\begin{aligned}\eta^{(1)} &= \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}, & \eta^{(2)} &= \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}, & \lambda &= 1 \\ \eta^{(3)} &= \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix}, & \eta^{(4)} &= \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix}, & \lambda &= -1\end{aligned}$$

It can be checked that these are all normal modes.

1.4 Group Theory and Molecular Vibration

For a molecule with symmetry G , both the kinetic energy and potential energy are invariant under the group transformation,^b

$$[T, M] = 0, \quad [T, U] = 0$$

Then from eigenvalue equation in Eq(2) we get

$$TU\eta = U(T\eta) = T\omega^2 M\eta = \omega^2 M(T\eta)$$

This means η and $T\eta$ have the same frequency ω . If we run the transformation T over the whole group and select a linear independent set, $\phi_1, \phi_2, \dots, \phi_r$, then this set will form a basis for the transformation $T_i \in G$. It is then clear that if we put together all these linear independent sets, we will get a representation matrix in the block diagonal form with each block representing an irrep.

As we have discussed before, coordinate vector, $\vec{x} = (x_1, x_2, \dots, x_n)$, will give a reducible representation of group G ,

$$T_i x_a = x_b X_{ba}(T_i), \quad \text{and} \quad X(T_j) X(T_i) = X(T_j T_i)$$

Therefore if we can find out how the representation of coordinate vector, $\vec{x} = (x_1, x_2, \dots, x_n)$, reduces in terms of irrep we can find the degeneracies and structure of the normal modes,

$$X = \sum_i k_i D^{(i)}$$

where $D^{(i)}$ are the irrep and the coefficient k_i is the number of time each irrep $D^{(i)}$ appears in this reduction. The coefficient n_i can be calculated in terms of the characters of the representations,

$$k_i = \frac{1}{g} \sum_i n_P \chi_p^{(i)*} \chi_p^{(X)}$$

In this formula, we only need to know the trace of each group element. Thus the only contributions to $\chi_p^{(X)}$ come from those atoms which are unmoved by transformation of the symmetry group G because each atom which is moved to some other site will not have diagonal elements in the representation matrix. For a proper rotation of angle θ , $R(\theta)$, a unmoved atom will contribute $(1 + 2 \cos \theta)$ to the trace and the total trace is

$$\chi^{(X)}(R(\theta)) = N_{R(\theta)} (1 + 2 \cos \theta)$$

where $N_{R(\theta)}$ is the number of atoms which are not moved by the rotation $R(\theta)$. Similarly, for an improper rotation of angle θ , $S(\theta)$, a rotation of angle θ followed by a reflection on a plan perpendicular to the axis of rotation, the trace is,

$$\chi^{(X)}(S(\theta)) = N_{S(\theta)} (-1 + 2 \cos \theta)$$

where $N_{S(\theta)}$ is the number of atoms which are not moved by the rotation $S(\theta)$. However, for any molecular vibration, there are always 6 zero modes, 3 for translation of molecule as a whole and 3 for rotation. We need to remove these zero modes to get the real vibrational mode. We can use center of mass coordinates \vec{R} to describe these motions. So under proper rotation, and improper rotation we have,

$$\chi_{trans}^{(X)}(R(\theta)) = (1 + 2 \cos \theta), \quad \chi_{trans}^{(X)}(S(\theta)) = (-1 + 2 \cos \theta)$$

For the rotational modes, we can describe it in terms of an axial vector

$$\chi_{rot}^{(X)}(R(\theta)) = (1 + 2 \cos \theta), \quad \chi_{rot}^{(X)}(S(\theta)) = -(-1 + 2 \cos \theta)$$

Thus if we subtract the translational and rotational zero modes, we get the trace for the pure vibrational modes,

$$\begin{aligned}\chi_{vib}^{(X)}(R(\theta)) &= (N_{R(\theta)} - 2)(1 + 2 \cos \theta) \\ \chi_{vib}^{(X)}(S(\theta)) &= N_{S(\theta)}(-1 + 2 \cos \theta)\end{aligned}$$

As an illustration, we will study the water molecule H_2O , which has C_{2v} symmetry. The vibrational characters are

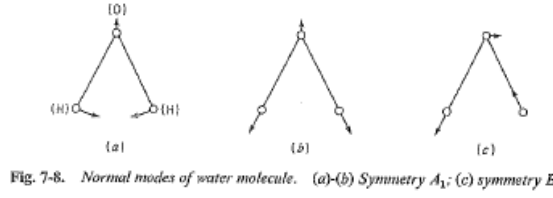
$$\begin{array}{ll} E(\text{proper}, \theta = 0, N_E = 3) & \chi_{vib}(E) = 3 \\ C_2(\text{proper}, \theta = \pi, N_{C_2} = 1) & \chi_{vib}(C_2) = 1 \\ \sigma_v(\text{improper}, \theta = 0, N_{\sigma_v} = 3) & \chi_{vib}(\sigma_v) = 3 \\ \sigma'_v(\text{improper}, \theta = 0, N_{\sigma'_v} = 1) & \chi_{vib}(\sigma'_v) = 1 \end{array}$$

We can use the character table for C_{2v} to see how the vibrational modes reduced in terms of irrep of C_{2v} .

C_{2v}	E	C_2	σ_v	σ'_v
$A_1(z)$	1	1	1	1
$A_2(R_z)$	1	1	-1	-1
$B_1(x)$	1	-1	1	-1
$B_2(y)$	1	-1	-1	1
χ_{vib}	3	1	3	1

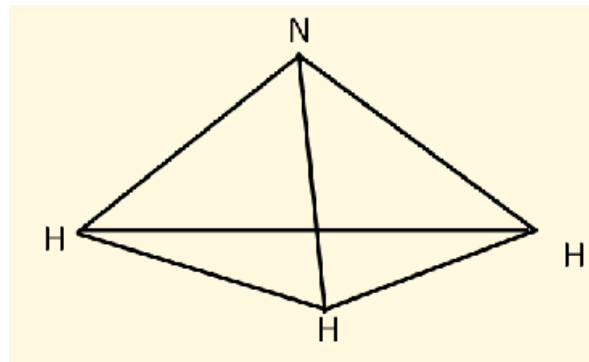
We take σ_v to be the reflection in the plane of the molecule and σ'_v to be reflection in the perpendicular plane bisecting the HOH bond angle. The C_2 axis is z and y axis. We see that the reduction is

$$\chi_{vib} = 2A_1 + B_1$$



Thus the vibrational modes are given by 2 A_1 modes which are invariant under C_{2v} and 1 B_1 mode which is invariant under C_2 rotation and change sign under σ_v .

Another example : NH_3 molecule



This molecule has D_3 symmetry. The characters for vibrational modes are

D_3	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
χ_{vib}	6	0	2

We see that the reduction of vibrational modes are

$$\chi_{vib} = 2A_1 + 2E$$

Thus there are 2 non-degenerate and 2 doubly degenerate modes.