Fundamentals of Molecular Symmetry

An internet lecture course
Now:

Application to molecules

- Electronic wavefunctions
- Vibrational wavefunctions
- Rotational wavefunctions
Cl electronic wavefunction

\[ \Psi_e^{(\text{CI})}(R_e, R_n) = \sum_p c_p \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots) \]

\[ \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(r_1)\alpha(\xi_1) & \chi_1(r_1)\beta(\xi_1) & \chi_2(r_1)\alpha(\xi_1) & \ldots & \chi_m(r_1)\beta(\xi_1) \\ \chi_1(r_2)\alpha(\xi_2) & \chi_1(r_2)\beta(\xi_2) & \chi_2(r_2)\alpha(\xi_2) & \ldots & \chi_m(r_2)\beta(\xi_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \chi_1(r_n)\alpha(\xi_n) & \chi_1(r_n)\beta(\xi_n) & \chi_2(r_n)\alpha(\xi_n) & \ldots & \chi_m(r_n)\beta(\xi_n) \end{vmatrix} \]

Slater determinant
Electron spin functions
Molecular orbital, „space function“
Expansion coefficients
Cl electronic wavefunction

\[ \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots) \]

\[ = \frac{1}{\sqrt{n!}} \begin{vmatrix} 
\chi_1(r_1)\alpha(\xi_1) & \chi_1(r_1)\beta(\xi_1) & \chi_2(r_1)\alpha(\xi_1) & \ldots & \chi_m(r_1)\beta(\xi_1) \\
\chi_1(r_2)\alpha(\xi_2) & \chi_1(r_2)\beta(\xi_2) & \chi_2(r_2)\alpha(\xi_2) & \ldots & \chi_m(r_2)\beta(\xi_2) \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\chi_1(r_n)\alpha(\xi_n) & \chi_1(r_n)\beta(\xi_n) & \chi_2(r_n)\alpha(\xi_n) & \ldots & \chi_m(r_n)\beta(\xi_n) 
\end{vmatrix} \]

Each Slater determinant satisfies Fermi-Dirac statistics for the electrons

\[ \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, \ldots, r_i, \xi_i, \ldots, r_k, \xi_k, \ldots, r_n, \xi_n) \]

\[ = -\Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, \ldots, r_k, \xi_k, \ldots, r_i, \xi_i, \ldots, r_n, \xi_n) \]
CI electronic wavefunction

Symmetry in the MS group

\[ \Psi_{e}^{(CI)}(R_e, R_n) = \sum_{p} c_p \Phi_{\det}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, ...) \]

Owing to the vanishing integral rule, only \( \Phi_{\det}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, ...) \) of the same MS group symmetry mix.

How do we find the MS group symmetry of \( \Phi_{\det}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, ...) \)?
The Slater determinant

$$\Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots)$$

$$= \frac{1}{\sqrt{n!}} \begin{vmatrix}
\chi_1(r_1)\alpha(\xi_1) & \chi_1(r_1)\beta(\xi_1) & \chi_2(r_1)\alpha(\xi_1) & \ldots & \chi_m(r_1)\beta(\xi_1) \\
\chi_1(r_2)\alpha(\xi_2) & \chi_1(r_2)\beta(\xi_2) & \chi_2(r_2)\alpha(\xi_2) & \ldots & \chi_m(r_2)\beta(\xi_2) \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\chi_1(r_n)\alpha(\xi_n) & \chi_1(r_n)\beta(\xi_n) & \chi_2(r_n)\alpha(\xi_n) & \ldots & \chi_m(r_n)\beta(\xi_n)
\end{vmatrix}$$

is made of

- electron spin functions $\alpha(\xi_k)$ and $\beta(\xi_k)$
- molecular orbitals (MO's) $\chi_j(r_k)$
Electron spin functions $\alpha(\xi_k)$ and $\beta(\xi_k)$

Any electron has two spin functions

- $\alpha(\xi_k) = |s, m_s\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$
- $\beta(\xi_k) = |1/2, -1/2\rangle$

$s = \frac{1}{2}$ is the quantum number for the spin angular momentum, $m_s = \pm \frac{1}{2}$ is the projection on the space-fixed Z axis.

Electron spin functions are unaffected by MS group operations
Molecular orbitals (MO's) $\chi_j(r_k)$

Atomic orbitals (AO's) $\varphi_\mu(r_k)$: s, p, d, ..... orbitals localized on specific nuclei

Molecular orbitals (MO's) $\chi_j(r_k)$ expressed as

$$\chi_j(r_k) = \sum_\mu c_{\mu j} \varphi_\mu(r_k)$$

Linear Combinations of Atomic Orbitals, LCAO
MS group symmetry of the electronic (CI) wavefunction

1. Determine MS group symmetry of the AO’s $\varphi_\mu(\mathbf{r}_k)$

2. Then you also know the symmetry of the MO’s $\chi_j(\mathbf{r}_k)$ (vanishing integral rule)

3. Then you know the symmetry of the Slater determinant $\Phi_{\text{det}}^{(p)}$ (MO products)

4. Then you know the symmetry of the CI wavefunction $\Psi_e^{(CI)}$ (vanishing integral rule)

$$\Psi_e^{(CI)}(\mathbf{R}_e, \mathbf{R}_n) = \sum_p c_p \Phi_{\text{det}}^{(p)}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \mathbf{r}_3, \xi_3, \ldots)$$
Electronic wavefunction for $\text{H}_2\text{O}$

Atomic orbitals (AO’s) $\varphi_\mu(\mathbf{r}_k)$ considered here for water:

$1s(\text{O}), 2s(\text{O}), 2p_x(\text{O}), 2p_y(\text{O}), 2p_z(\text{O})$

$1s(\text{H}_1), 1s(\text{H}_2)$

$2p_y(\text{O})$
Transformation under (12)

\[ 2p_z(O) \]

\[ \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ -z \end{pmatrix} \]

Initial:

- \( x_i \), \( y_i \), \( z_i \)

„No axis change“:

- \( x_i \), \( y_i \), \( z_i \)

„Axis change“:

- \( x_i \), \(-y_i\), \(-z_i\)

(12) \( 2p_z(O) = -2p_z(O) \)
Electronic wavefunction for $\text{H}_2\text{O}$

Symmetrized atomic orbitals (SO’s) for water

$A_1$: $1\text{s}(\text{O}), 2\text{s}(\text{O}), 2\text{p}_x(\text{O}), \frac{1}{\sqrt{2}} [1\text{s}(\text{H}_2) + 1\text{s}(\text{H}_1)]$

$B_1$: $2\text{p}_y(\text{O})$

$B_2$: $2\text{p}_z(\text{O}), \frac{1}{\sqrt{2}} [1\text{s}(\text{H}_2) - 1\text{s}(\text{H}_1)]$

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MS group symmetry of the electronic (CI) wavefunction

1. Determine MS group symmetry of the AO's $\varphi_\mu(r_k)$

2. Then you also know the symmetry of the MO's $\chi_j(r_k)$ (vanishing integral rule)

3. Then you know the symmetry of the Slater determinant $\Phi_{\text{det}}^{(p)}$ (MO products)

4. Then you know the symmetry of the CI wavefunction $\Psi_e^{(CI)}$ (vanishing integral rule)
Electronic wavefunction for H$_2$O 

LCAO calculation 

\[
\chi_j(r_k) = \sum \mu c_{\mu j} \varphi_\mu(r_k)
\]

MO’s for water, in order of increasing energy

A$_1$:

1a$_1$ = 1s(O) 2e

2a$_1$ = $\frac{1}{\sqrt{2}} \left\{ 2s(O) + \frac{1}{\sqrt{2}} \left[ 1s(H_2) + 1s(H_1) \right] \right\}$ 2e

B$_2$:

1b$_2$ = $\frac{1}{\sqrt{2}} \left\{ 2p_z(O) + \frac{1}{\sqrt{2}} \left[ 1s(H_2) - 1s(H_1) \right] \right\}$ 2e

A$_1$:

3a$_1$ = $\frac{1}{\sqrt{2}} \left\{ 2p_x(O) + \frac{1}{\sqrt{2}} \left[ 1s(H_2) + 1s(H_1) \right] \right\}$ 2e

B$_1$:

1b$_1$ = 2p$_y$(O) 2e

10e

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3. Then you know the symmetry of the Slater determinant $\Phi_{\text{det}}^{(p)}$ (MO products)

4. Then you know the symmetry of the CI wavefunction $\Psi^{(CI)}_e$ (vanishing integral rule)

$$\Psi^{(CI)}_e(R_e, R_n) = \sum_p c_p \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots)$$
Electronic wavefunction for H₂O
Ground state Slater determinant

Each term in the determinant has the form

\[ \chi_{1a_1}(\mathbf{r}_1) \chi_{1a_1}(\mathbf{r}_2) \chi_{2a_1}(\mathbf{r}_3) \chi_{2a_1}(\mathbf{r}_4) \chi_{1b_2}(\mathbf{r}_5) \chi_{1b_2}(\mathbf{r}_6) \]
\[ \times \chi_{3a_1}(\mathbf{r}_7) \chi_{3a_1}(\mathbf{r}_8) \chi_{1b_1}(\mathbf{r}_9) \chi_{1b_1}(\mathbf{r}_{10}) \times \text{spin functions} \]

and the symmetry

\[ \Gamma_{\text{elec}} = (A_1)^2 \otimes (A_1)^2 \otimes (B_2)^2 \otimes (A_1)^2 \otimes (B_1)^2 = A_1 \]

Ground state Slater determinant has \( A_1 \) symmetry
**MS group symmetry of the electronic (CI) wavefunction**

1. Determine MS group symmetry of the AO's \( \varphi_\mu(r_k) \)

2. Then you also know the symmetry of the MO's \( \chi_j(r_k) \) (vanishing integral rule)

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4. Then you know the symmetry of the CI wavefunction \( \Psi_e^{(\text{CI})} \) (vanishing integral rule)

\[
\Psi_e^{(\text{CI})}(R_e, R_n) = \sum_p c_p \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots)
\]
CI electronic wavefunction
/ Symmetry in the MS group

\[ \Psi^{(\text{CI})}(R_e, R_n) = \sum_p c_p \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots) \]

Owing to the vanishing integral rule, only \( \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots) \) of the same MS group symmetry mix.

Ground state CI wavefunction has \( A_1 \) symmetry
MS group symmetry of the electronic (CI) wavefunction

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$$\Psi_e^{(CI)}(R_e, R_n) = \sum_p c_p \Phi_{\text{det}}^{(p)}(r_1, \xi_1, r_2, \xi_2, r_3, \xi_3, \ldots)$$
Electronic wavefunction for H$_2$O Configurations

The electronic ground state of water, with $A_1$ symmetry, has the configuration

$$(1a_1)^2 \ (2a_1)^2 \ (1b_2)^2 \ (3a_1)^2 \ (1b_1)^2$$

The first excited state, called the $\tilde{A}$ state, has the configuration

$$(1a_1)^2 \ (2a_1)^2 \ (1b_2)^2 \ (3a_1)^2 \ (1b_1)^1 \ (3sa_1)^1$$

$\tilde{A}$-state CI wavefunction has $B_1$ symmetry
Now:

Application to molecules

- Electronic wavefunctions
- Vibrational wavefunctions
- Rotational wavefunctions
Vibrational symmetry

Simplest approximation for vibrational wavefunction

\[ \Psi_{\text{vib}} (Q_1, Q_2, Q_3, \ldots, Q_{3N-6}) = \Phi_{v_1} (Q_1) \Phi_{v_2} (Q_2) \Phi_{v_3} (Q_3) \ldots \Phi_{v_{N-6}} (Q_{3N-6}) \]

The \( Q_i \) are normal coordinates

The \( \Phi_{v_i} (Q_i) \) are harmonic oscillator eigenfunctions, characterized by the quantum number \( v_i = 0, 1, 2, \ldots \)
Vibrational wavefunction?

Simplest approximation

$$\Psi_{\text{vib}} (Q_1, Q_2, Q_3, \ldots, Q_{3N-6}) = \prod_{i=1}^{3N-6} \Phi_{v_i}(Q_i)$$

Better approximation

$$\Psi_{\text{vib}} (Q_1, Q_2, Q_3, \ldots, Q_{3N-6}) = \sum v_1 \sum v_2 \sum v_3 \ldots \sum v_{3N-6} c_{v_1 v_2 v_3 \ldots v_{3N-6}} \prod_{i=1}^{3N-6} \Phi_{v_i}(Q_i)$$

Anharmonic vibrations

Matrix diagonalization, vanishing integral rule

But first: Symmetry of the normal coordinates $Q_i$?
Method I:

We consider the vibration of H$_2$O as an example

Internal coordinates are $r_1$, $r_2$, and $\gamma$

The normal coordinates $Q_1$, $Q_2$, $Q_3$ have the same symmetries as $r_1$, $r_2$, and $\gamma$

$\Gamma_Q = 2 A_1 \oplus B_2$
Method II:

Cartesian displacement coordinates in the molecule-fixed axis

Nine nuclear coordinates in total:

\[(\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3)\]
Transformation under (12)

Initial:

„No axis change“:

Δx₁  Δy₁  Δz₁  Δx₂  Δy₂  Δz₂  Δx₃  Δy₃  Δz₃

Δx₂  Δy₂  Δz₂  Δx₁  Δy₁  Δz₁  Δx₃  Δy₃  Δz₃

„Axis change“:

Δx₂  −Δy₂  −Δz₂  Δx₁  −Δy₁  −Δz₁  Δx₃  −Δy₃  −Δz₃

χ_{Car}[(12)] = −1
Transformation under $E^*$

Initial:

\[
\begin{align*}
\Delta x_1 & \quad \Delta y_1 & \quad \Delta z_1 & \quad \Delta x_2 & \quad \Delta y_2 & \quad \Delta z_2 & \quad \Delta x_3 & \quad \Delta y_3 & \quad \Delta z_3 \\
\end{align*}
\]

„No axis change“:

\[
\begin{align*}
-\Delta x_1 & \quad -\Delta y_1 & \quad -\Delta z_1 & \quad -\Delta x_2 & \quad -\Delta y_2 & \quad -\Delta z_2 & \quad -\Delta x_3 & \quad -\Delta y_3 & \quad -\Delta z_3 \\
\end{align*}
\]

„Axis change“:

\[
\begin{align*}
\Delta x_1 & \quad -\Delta y_1 & \quad \Delta z_1 & \quad \Delta x_2 & \quad -\Delta y_2 & \quad \Delta z_2 & \quad \Delta x_3 & \quad -\Delta y_3 & \quad \Delta z_3 \\
\end{align*}
\]

$\chi_{\text{Car}}[E^*] = 3 \quad \chi_{\text{Car}}[(12)^*] = +1$
Reduction of $\Gamma_{\text{Car}}$

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<td>$\Gamma_{\text{Car}}$</td>
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<td>$-1$</td>
<td>3</td>
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$$a_i = \frac{1}{h} \sum_{R} \chi^\Gamma[R] \chi^{\Gamma_i}[R]^*$$

$$\Gamma_{\text{Car}} = 3 \ A_1 \oplus A_2 \oplus 2 \ B_1 \oplus 3 \ B_2$$

There are nine displacement coordinates but only three vibrational coordinates .......?
Redundancies

The molecule-fixed coordinates of the displacement vectors satisfy six conditions

Center-of-mass conditions

\[ T_\alpha = \sum_{i=1}^{N} m_i \Delta \alpha_i = 0, \quad \alpha = x, y, z \]

Eckart conditions

\[ R_z = \sum_{i=1}^{N} m_i \left( x_i^e \Delta y_i - y_i^e \Delta x_i \right) = 0 \]

\[ R_x = \sum_{i=1}^{N} m_i \left( y_i^e \Delta z_i - z_i^e \Delta y_i \right) = 0 \]

\[ R_y = \sum_{i=1}^{N} m_i \left( z_i^e \Delta x_i - x_i^e \Delta z_i \right) = 0 \]
Think first of $T$ and $R$ as vectors in the space-fixed axis system

\[
T_\alpha = \sum_{i=1}^{N} m_i \Delta \alpha_i = 0, \quad \alpha = x, y, z
\]

\[
R = \sum_{i=1}^{N} m_i (x_i^e \Delta y_i - y_i^e \Delta x_i) = 0
\]

\[
R_x = \sum_{i=1}^{N} m_i (y_i^e \Delta z_i - z_i^e \Delta y_i) = 0
\]

\[
R_y = \sum_{i=1}^{N} m_i (z_i^e \Delta x_i - x_i^e \Delta z_i) = 0
\]

$P^T = T$;

$P^R = R$;

$P^* T = -T$;

$P^* R = R$;

$P$ „pure“ permutation

$P^*$ permutation-inversion
Transformation under (12)

\[ \begin{align*}
\mathbf{P} \mathbf{T} &= \mathbf{T}, \\
\mathbf{P} \mathbf{R} &= \mathbf{R}; \\
\end{align*} \]

Initial:

\[
\begin{bmatrix}
T_x & T_y & T_z & R_x & R_y & R_z \\
\end{bmatrix}
\]

„No axis change“:

\[
\begin{bmatrix}
T_x & T_y & T_z & R_x & R_y & R_z \\
\end{bmatrix}
\]

„Axis change“:

\[
\begin{bmatrix}
T_x & -T_y & -T_z & R_x & -R_y & -R_z \\
\end{bmatrix}
\]

\[\chi_{\text{TR}}[(12)] = -2\]
Transformation under $E^*$

\[
P^* T = -T; \\
P^* R = R; \\
E^* \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ -z \end{pmatrix}
\]

Initial:

\[
\begin{pmatrix} T_x & T_y & T_z & R_x & R_y & R_z \\
-T_x & -T_y & -T_z & R_x & R_y & R_z \\
T_x & -T_y & T_z & -R_x & R_y & -R_z
\end{pmatrix}
\]

‟No axis change“:

\[
\begin{pmatrix} T_x & T_y & T_z & R_x & R_y & R_z \\
-T_x & -T_y & -T_z & R_x & R_y & R_z \\
T_x & -T_y & T_z & -R_x & R_y & -R_z
\end{pmatrix}
\]

‟Axis change“:

\[
\chi_{TR}[E^*] = 0 \\
\chi_{TR}[(12)^*] = 0
\]
### Reduction of $\Gamma_{TR}$

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\[
a_i = \frac{1}{\hbar} \sum_R \chi^\Gamma[R] \chi^{\Gamma_i}[R]^*
\]

\[
\Gamma_{TR} = A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2
\]
Determination of $\Gamma_Q$

All nine displacement coordinates generate

$$\Gamma_{\text{Car}} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2$$

The six coordinates of $T$ and $R$ generate

$$\Gamma_{\text{TR}} = A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2$$

Since $\Gamma_{\text{Car}} = \Gamma_{\text{TR}} \oplus \Gamma_Q$:

$$\Gamma_Q = 2A_1 \oplus B_2$$
Summary: Determination of $\Gamma_Q$

Method I:

We consider the vibration of H$_2$O as an example.

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Internal coordinates are $r_1$, $r_2$, and $\gamma$.

The normal coordinates $Q_1$, $Q_2$, $Q_3$ have the same symmetry as $r_1$, $r_2$, and $\gamma$.

$\Gamma_Q = 2A_1 \oplus B_2$

Method II:

Determination of $\Gamma_Q$

All nine displacement coordinates generate

$\Gamma_{\text{Car}} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2$

The six coordinates of $T$ and $R$ generate

$\Gamma_{\text{TR}} = A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2$

Since $\Gamma_{\text{Car}} = \Gamma_{\text{TR}} \oplus \Gamma_Q$:

$\Gamma_Q = 2A_1 \oplus B_2$
Vibrational symmetry for \( \text{H}_2\text{O} \)

Simplest approximation for vibrational wavefunction

\[
\Psi_{\text{vib}}(Q_1, Q_2, Q_3) = \Phi_{v_1}(Q_1) \Phi_{v_2}(Q_2) \Phi_{v_3}(Q_3)
\]

\[
A_1 \quad A_1 \quad B_2
\]

\[
\Phi_{v_i}(Q_i) \sim Q_i^{v_i} \exp(-\alpha_i Q_i^2)
\]

\[
\Gamma_{v_1v_2v_3} = (A_1)^{v_1} \otimes (A_1)^{v_2} \otimes (B_2)^{v_3}
\]

\[
= \begin{cases} 
A_1 & \text{for } v_3 \text{ even} \\
B_2 & \text{for } v_3 \text{ odd}
\end{cases}
\]
Vibrational symmetry for $\text{CH}_3\text{F}$

$C_{3v}(M) = \{E, (123), (132), (12)^*, (13)^*, (23)^*\}$

$\Gamma_Q = 3A_1 \oplus 3E$

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>(123)</th>
<th>(12)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

$Q_1, Q_2, Q_3, (Q_{4a}, Q_{4b}), (Q_{5a}, Q_{5b}), (Q_{6a}, Q_{6b})$
Vibrational symmetry for CH$_3$F

Simplest approximation for vibrational wavefunction

\[ \Psi_{\text{vib}} (Q_1, Q_2, Q_3, Q_{4a}, Q_{4b}, Q_{5a}, Q_{5b}, Q_{6a}, Q_{6b}) = \Phi_{v_1} (Q_1) \Phi_{v_2} (Q_2) \Phi_{v_3} (Q_3) \]

\[ \times \Phi_{v_4, l_4} (Q_{4a}, Q_{4b}) \Phi_{v_5, l_5} (Q_{5a}, Q_{5b}) \Phi_{v_6, l_6} (Q_{6a}, Q_{6b}) \]

\[
\begin{array}{c|ccc}
E & (123) & (12)^* \\
--- & --- & --- & --- \\
1 & 2 & 3 & \\
A_1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 \\
E & 2 & -1 & 0 \\
\end{array}
\]

\[ v_i = 0, 1, 2, 3, \ldots \]

\[ l_i = -v_i, -v_i + 2, -v_i + 4, \ldots, v_i - 2, v_i \]

\[ v_i + 1 \text{ values} \]
Symmetry of a $\Phi_{\nu_i, l_i}(Q_{i_a}, Q_{i_b})$ function

\[ \nu_i = l_i = 0 \]

\[ \Phi_{0,0}(Q_{i_a}, Q_{i_b}) \sim \exp(-\alpha_i [Q_{i_a}^2 + Q_{i_b}^2]) \]

$A_1$ symmetry

\[ \nu_i = 1, l_i = \pm 1 \]

\[ \Phi_{1,\pm1}(Q_{i_a}, Q_{i_b}) \sim \begin{cases} Q_{i_a} & \text{if } \nu_i = 1, l_i = 1 \\ Q_{i_b} & \text{if } \nu_i = 1, l_i = -1 \end{cases} \exp(-\alpha_i [Q_{i_a}^2 + Q_{i_b}^2]) \]

$E$ symmetry

\[ \nu_i = 2, l_i = 0, \pm 2 \]

\[ \Phi_{2,l_i}(Q_{i_a}, Q_{i_b}) \sim \begin{cases} Q_{i_a}^2 & \text{if } \nu_i = 2, l_i = 2 \\ Q_{i_b}^2 & \text{if } \nu_i = 2, l_i = -2 \\ Q_{i_a} Q_{i_b} & \text{if } \nu_i = 2, l_i = 0 \end{cases} \exp(-\alpha_i [Q_{i_a}^2 + Q_{i_b}^2]) \]

Symmetric product

\[ [E \otimes E] = A_1 \oplus E \]

$E = \begin{cases} l_i = 0 & \nu_i = 2, l_i = 0 \\ l_i = \pm 2 & \nu_i = 2, l_i = \pm 2 \end{cases}$
Remember the symmetric product?

$\Phi_{n_1}, \Phi_{n_2}$ have $E$ symmetry in $C_{3v}(M)$

Which representation is generated by the three products $\Phi_{n_1}\Phi_{n_1}, \Phi_{n_2}\Phi_{n_2}, \Phi_{n_1}\Phi_{n_2} = \Phi_{n_2}\Phi_{n_1}$?

Symmetric product representation:

$$[E]^2 = [E \otimes E] = A_1 \oplus E$$

with characters:

$$\chi^{[E \otimes E]}[R] = \frac{1}{2}((\chi^E[R])^2 + \chi^E[R^2])$$
Special case:

Characters:

\[ \chi^{[E \otimes E]}[R] = \frac{1}{2} \left( (\chi^{E}[R])^2 + \chi^{E}[R^2] \right) \]

\[
\begin{array}{cccc}
\text{C}_{3v}(M): & E & (123) & (23)^* \\
1 & 2 & 3 \\
\text{C}_{3v}: & E & 2C_3 & 3\sigma_v \\
\text{Equiv. rot.}: & R^0 & R^{2\pi/3} & R^{\pi/2} \\
A_1: & 1 & 1 & 1 \\
A_2: & 1 & 1 & -1 \\
E: & 2 & -1 & 0 \\
\end{array}
\]

\[ E^2 = E \]
\[ (123)^2 = (132) \]
\[ ((12)^*)^2 = E \]

\[ [E]^2 = [E \otimes E] = A_1 \oplus E \]
Symmetry of a $\Phi_{v_i, l_i} (Q_{ia}, Q_{ib})$ function

General $v_i$

The $v_i + 1$ wavefunctions generate the same representation as the $v_i + 1$ products

$$Q_{ia} v_i, Q_{ia} v_i^{-1} Q_{ib}, Q_{ia} v_i^{-2} Q_{ib}^2, Q_{ia} v_i^{-3} Q_{ib}^3, \ldots, Q_{ia}^2 Q_{ib} v_i^{-2}, Q_{ia} Q_{ib} v_i^{-1}, Q_{ib} v_i$$

This representation is $n$th order symmetric product representation $[E]^n$ with characters

$$\chi^{[E]^n}[R] = \frac{1}{2} (\chi^E[R] \chi^{[E]^{n-1}}[R] + \chi^E[R^n])$$
\[ \chi^{[E]^n}[R] = \frac{1}{2} (\chi^E[R] \chi^{[E]^{n-1}}[R] + \chi^E[R^n]). \]

**Characters:**

<table>
<thead>
<tr>
<th>( C_{3v}(M) )</th>
<th>( E )</th>
<th>(123)</th>
<th>(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( C_{3v} )</th>
<th>( E )</th>
<th>2C_3</th>
<th>3\sigma_v</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Equiv. rot.:</th>
<th>( R^0 )</th>
<th>( R^2_{\pi/3} )</th>
<th>( R^{\pi/2} )</th>
</tr>
</thead>
</table>

| \( A_1 \) | 1 | 1 | 1 |
| \( A_2 \) | 1 | 1 | -1 |
| \( E \)   | 2 | -1 | 0 |

\[ [E]^3 = A_1 \oplus A_2 \oplus E \]

\[ l_i = \pm 3 \quad l_i = \pm 1 \]
General symmetric top

$Q_1, Q_2, \ldots, Q_t$ transform as the non-degenerate irreps $\Gamma_1, \Gamma_2, \ldots, \Gamma_t$, respectively.

Each of the coordinate pairs $(Q_{t+1,a}, Q_{t+1,b}), (Q_{t+2,a}, Q_{t+2,b}), \ldots, (Q_{n,a}, Q_{n,b})$ transforms as a doubly degenerate irrep called $\Gamma_{t+1}, \Gamma_{t+2}, \ldots, \Gamma_n$, respectively.

Symmetry of vibrational wavefunction

$$\Gamma_{\text{vib}} = (\Gamma_1)^{v_1} \otimes (\Gamma_2)^{v_2} \otimes (\Gamma_3)^{v_3} \otimes \ldots \otimes (\Gamma_t)^{v_t} \otimes [\Gamma_{t+1}]^{v_{t+1}} \otimes [\Gamma_{t+2}]^{v_{t+2}} \ldots \otimes [\Gamma_n]^{v_n}$$

Symmetric products