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Lecture 5/11
Fundamentals of Molecular Symmetry
An internet lecture course
Symmetry: Formal definition

$S$ is an operation (operator), such as $(12), E^*, (12)^*$

$H_{rve}$ is the molecular rovibronic Hamiltonian

$S$ is a symmetry operation when

$$[S, H_{rve}] = S H_{rve} - H_{rve} S = 0$$

i.e., when $S$ commutes with the Hamiltonian
Symmetry example: H$_2$O

$E, (12), E^*, (12)^*$ are symmetry operations for H$_2$O

For example, the electrostatic H$_2$O Hamiltonian is

$$\hat{H}^0 = \frac{1}{2 m_H} \left( \hat{P}_1^2 + \hat{P}_2^2 \right) + \frac{1}{2 m_O} \hat{P}_3^2 + \frac{1}{2 m_e} \sum_{r=4}^{13} \hat{P}_r^2$$

$$+ \frac{e^2}{4\pi\epsilon_0 R_{12}} + \frac{8e^2}{4\pi\epsilon_0} \left( \frac{1}{R_{13}} + \frac{1}{R_{23}} \right) - \frac{e^2}{4\pi\epsilon_0} \sum_{r=4}^{13} \left( \frac{1}{R_{1r}} + \frac{1}{R_{2r}} \right)$$

$$- \frac{8e^2}{4\pi\epsilon_0} \sum_{r=4}^{13} \frac{1}{R_{3r}} + \sum_{r<s=4}^{13} \frac{e^2}{4\pi\epsilon_0 R_{rs}}$$

$$\hat{P}_r^2 = -\hbar^2 \left( \frac{\partial^2}{\partial X_r^2} + \frac{\partial^2}{\partial Y_r^2} + \frac{\partial^2}{\partial Z_r^2} \right)$$

$E, (12), E^*, (12)^*$ leave this Hamiltonian unchanged, i.e. commute with it.
Symmetry example: $H_2O$

$\psi_{rve}$ is a non-degenerate wavefunction for $H_2O$

\[ H_{rve} \psi_{rve} = E_{rve} \psi_{rve} \]

$S$ is a symmetry operation:
\[ [ S, H_{rve} ] = S H_{rve} - H_{rve} S = 0, \]
\[ S H_{rve} \psi_{rve} = S E_{rve} \psi_{rve} \]

\[ H_{rve} (S \psi_{rve}) = E_{rve} (S \psi_{rve}) \]

so $S \psi_{rve}$ is a solution of the Schrödinger equation with eigenvalue $E_{rve}$

but then we must have \[ S \psi_{rve} = c_S \psi_{rve} \]
Symmetry example: $\text{H}_2\text{O}$

\[ E\psi_{\text{rve}} = \psi_{\text{rve}} = c_E \psi_{\text{rve}} \text{ so } c_E = 1 \]

For $S = (12), E^*, (12)^*$ we have \( S^2 = E \) so

\[ S^2\psi_{\text{rve}} = c_{S^2} \psi_{\text{rve}} = \psi_{\text{rve}} \]

thus \( c_{S^2} = 1 \implies c_S = \pm 1 \)

Also, because, for example, $\displaystyle (12)^* = E^* (12)$

\( (12)^* \psi_{\text{rve}} = c_{(12)^*} \psi_{\text{rve}} = E^* (12) \psi_{\text{rve}} = c_{E^*} c_{(12)} \psi_{\text{rve}} \)

so that

\[ c_{(12)^*} = c_{E^*} c_{(12)} \]
Only these combinations of $c_S$ values are allowed:

<table>
<thead>
<tr>
<th>$C_{2v}$ (M):</th>
<th>$E$</th>
<th>(12)</th>
<th>$E^*$</th>
<th>(12)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$ (M):</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$E$</td>
<td>$C_{2b}$</td>
<td>$\sigma_{ab}$</td>
<td>$\sigma_{bc}$</td>
</tr>
<tr>
<td>Equiv. rot.:</td>
<td>$R^0$</td>
<td>$R_{b}^{\Pi}$</td>
<td>$R_{c}^{\Pi}$</td>
<td>$R_{a}^{\Pi}$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>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>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The wavefunctions of H$_2$O generate the irreducible representations of $C_{2v}$(M)
Symmetry labels for H\textsubscript{2}O

<table>
<thead>
<tr>
<th>\text{C}_{2v} (M):</th>
<th>E</th>
<th>(12)</th>
<th>E*</th>
<th>(12)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>\text{C}_{2v}:</th>
<th>E</th>
<th>C_{2b}</th>
<th>\sigma_{ab}</th>
<th>\sigma_{bc}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>C_{2b}</td>
<td>\sigma_{ab}</td>
<td>\sigma_{bc}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Equiv. rot.:</th>
<th>\text{R}^0</th>
<th>\text{R}_b^\pi</th>
<th>\text{R}_c^\pi</th>
<th>\text{R}_a^\pi</th>
</tr>
</thead>
</table>

$\begin{array}{cccc}
A_1: & 1 & 1 & 1 & 1 \\
A_2: & 1 & 1 & -1 & -1 \\
B_1: & 1 & -1 & -1 & 1 \\
B_2: & 1 & -1 & 1 & -1 \\
\end{array}$

<table>
<thead>
<tr>
<th>$E/(\hbar c \text{ cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{para-H}_2\text{O}</td>
</tr>
<tr>
<td>\text{ortho-H}_2\text{O}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>\text{A}_1</th>
<th>\text{A}_2</th>
<th>\text{B}_1</th>
<th>\text{B}_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>8_{26}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7_{44}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6_{42}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8_{08}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6_{24}</td>
<td>7_{17}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5_{42}</td>
<td>6_{33}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4_{40}</td>
<td>5_{33}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6_{06}</td>
<td>4_{31}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5_{24}</td>
<td>3_{13}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2_{20}</td>
<td>3_{12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2_{02}</td>
<td>2_{11}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0_{00}</td>
<td>1_{11}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\begin{align*}
\text{para-H}_2\text{O} & : 8_{26}, 7_{44}, 6_{42}, 8_{08}, 6_{24}, 5_{42}, 4_{40}, 6_{06}, 5_{24}, 2_{20}, 2_{02}, 0_{00} \\
\text{ortho-H}_2\text{O} & : 7_{43}, 9_{09}, 7_{25}, 8_{18}, 6_{43}, 5_{50}, 7_{16}, 6_{34}, 5_{32}, 6_{16}, 5_{14}, 4_{32} \\
\end{align*}
Summary $\text{H}_2\text{O}$

Geometrical symmetry at equilibrium

$$C_{2v} = \{E, C_2, \sigma_{xy}, \sigma_{yz}\}$$

CNPI (Complete Nuclear Permutation Inversion)

Group $C_{2v}(M) = \{E, (12), E^*, (12)^*\}$

The two groups $C_{2v}(M)$ and $C_{2v}$ are isomorphic

The rovibronic states of $\text{H}_2\text{O}$ are labeled by the irreducible representations $A_1, A_2, B_1, B_2$ of $C_{2v}(M)$
Nondegenerate state generally

\[ H \psi_n = E_n \psi_n \]

\[ S H \psi_n = S E_n \psi_n \]

\[ H(S \psi_n) = E_n (S \psi_n) \]

\( S \) is a symmetry operation:  
\[ [ S, H] = S H - H S = 0 \]

\( S \psi_n \) is a solution of the Schrödinger equation
with eigenvalue \( E_n \) but the state is non-degenerate
and then we must have

\[ S \psi_n = c_S \psi_n \]

where \( c_S \) is a constant.
With two symmetry operations, \( R \) and \( S \), and their product \( T = RS \) we have

\[
\begin{align*}
R \psi_n &= c_R \psi_n \\
S \psi_n &= c_S \psi_n \\
T \psi_n &= c_T \psi_n
\end{align*}
\]

\[
RS \psi_n = R(c_S \psi_n) = c_S R \psi_n = c_S c_R \psi_n
\]

Since \( T = RS \) we deduce that \( c_T = c_R c_S \)

The constants \( c_T, c_R, c_S \ldots \) form a 1D representation

\( \psi_n \) transforms according to this representation
Degenerate state (\(\ell\)-fold) generally

\[ H \psi_{nk} = E_n \psi_{nk} \]

\(\ell\) degenerate functions \(\psi_{n1}, \psi_{n2}, \psi_{n3}, \ldots, \psi_{n\ell}\)

\[ S H \psi_{nk} = S E_n \psi_{nk} \]

\[ H(S\psi_{nk}) = E_n(S\psi_{nk}) \]

\(S\) is a symmetry operation: \([S, H] = SH - HS = 0\)

\(S\psi_{nk}\) is a solution of the Schrödinger equation with eigenvalue \(E_n\). For an \(\ell\)-fold degenerate state

\[ S\psi_{nk} = D[S]_{k1} \psi_{n1} + D[S]_{k2} \psi_{n2} + D[S]_{k3} \psi_{n3} + \ldots + D[S]_{kl} \psi_{nl} \]
Degenerate state (\(\ell\)-fold) generally

For the \(\ell\) degenerate wavefunctions \(\psi_{n1}, \psi_{n2}, \psi_{n3}, \ldots, \psi_{n\ell}\) with eigenvalue \(E_n\), the effect of the symmetry operation \(S\) is

\[
S \psi_{nk} = D[S]_{k1} \psi_{n1} + D[S]_{k2} \psi_{n2} + D[S]_{k3} \psi_{n3} + \ldots + D[S]_{kl} \psi_{n\ell}
\]

For each relevant symmetry operation \(S\), the constants \(D[S]_{kp}\) form the elements of an \(\ell \times \ell\) matrix \(D[S]\).

\[
T = RS \Rightarrow D[T] = D[R] D[S]
\]

The matrices \(D[T], D[R], D[S]\) ….. form an \(\ell\)-dimensional representation

The \(\ell\) \(\psi_{nk}\) functions \textit{transform} according to this representation
Degenerate state (ℓ-fold) generally

The matrices $D[T], D[R], D[S] \ldots$ form an $\ell$-dimensional representation.

The $\ell \, \Psi_{nk}$ functions *transform* according to this representation.

In all known cases, the representation is irreducible.

If we would ever find a reducible representation in this way, we would call this *an accidental degeneracy*.

Normally the degeneracy would not be accidental, but would suggest that we had forgotten some symmetry operations.
Imagine that we had a molecule with $S_3$ symmetry, but that we had forgotten about (12), (23), and (13)

\[ \varepsilon = e^{i2\pi/3} \]

<table>
<thead>
<tr>
<th>$S_3$</th>
<th>$E$</th>
<th>(123)</th>
<th>(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<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>

<table>
<thead>
<tr>
<th>$C_3(M)$</th>
<th>$E$</th>
<th>(123)</th>
<th>(132)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_a$</td>
<td>1</td>
<td>$\varepsilon$</td>
<td>$\varepsilon^*$</td>
</tr>
<tr>
<td>$E_b$</td>
<td>1</td>
<td>$\varepsilon^*$</td>
<td>$\varepsilon$</td>
</tr>
</tbody>
</table>

Correlation:

<table>
<thead>
<tr>
<th>$S_3$</th>
<th>$C_3(M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A$</td>
</tr>
<tr>
<td>$E$</td>
<td>$E_a \oplus E_b$</td>
</tr>
</tbody>
</table>

In $C_3(M)$, all $E_a, E_b$ pairs are exactly degenerate. They must be because they are $E$ states of $S_3$. 
Degenerate state ($\ell$-fold) generally

Imagine a molecule for which $C_3(M)$ is the complete MS group (triphenylphosphine)

$$\varepsilon = e^{i2\pi/3}$$

For such a molecule, all $E_a, E_b$ pairs are exactly degenerate due to time reversal symmetry.

<table>
<thead>
<tr>
<th>$C_3(M)$</th>
<th>$E$</th>
<th>(123)</th>
<th>(132)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_a$</td>
<td>1</td>
<td>$\varepsilon$</td>
<td>$\varepsilon^*$</td>
</tr>
<tr>
<td>$E_b$</td>
<td>1</td>
<td>$\varepsilon^*$</td>
<td>$\varepsilon$</td>
</tr>
</tbody>
</table>

Generally, for a group with two irreps like $E_a, E_b$

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$E$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$\ldots$</th>
<th>$P_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ell$</td>
<td>$\chi_2$</td>
<td>$\chi_3$</td>
<td>$\ldots$</td>
<td>$\chi_h$</td>
<td></td>
</tr>
<tr>
<td>$\ell$</td>
<td>$\chi_2^*$</td>
<td>$\chi_3^*$</td>
<td>$\ldots$</td>
<td>$\chi_h^*$</td>
<td></td>
</tr>
</tbody>
</table>

Levels with symmetry $\Gamma, \Gamma^*$ are exactly degenerate due to time reversal symmetry.
Degenerate state (ℓ-fold) generally

A final bureaucratic question:

What happens if we change the basis set

\[ \Psi_{n1}, \Psi_{n2}, \Psi_{n3}, \ldots, \Psi_{nl} \quad \text{to} \quad \phi_{n1}, \phi_{n2}, \phi_{n3}, \ldots, \phi_{nl} \]

where

\[ \phi_{nk} = a_{k1} \Psi_{n1} + a_{k2} \Psi_{n2} + a_{k3} \Psi_{n3} + \ldots + a_{kl} \Psi_{nl} \]

The \( a_{ki} \) elements define a matrix A
Degenerate state ($\ell$-fold) generally

$$\varphi_{nk} = a_{k1} \psi_{n1} + a_{k2} \psi_{n2} + a_{k3} \psi_{n3} + \ldots + a_{kl} \psi_{nl}$$

$$\begin{pmatrix}
\varphi_{n1} \\
\varphi_{n2} \\
\varphi_{n3} \\
\vdots \\
\varphi_{nl}
\end{pmatrix} =
\begin{pmatrix}
\psi_{n1} \\
\psi_{n2} \\
\psi_{n3} \\
\vdots \\
\psi_{nl}
\end{pmatrix} =
\begin{pmatrix}
\psi_{n1} \\
\psi_{n2} \\
\psi_{n3} \\
\vdots \\
\psi_{nl}
\end{pmatrix}$$

$$\begin{pmatrix}
\varphi_{n1} \\
\varphi_{n2} \\
\varphi_{n3} \\
\vdots \\
\varphi_{nl}
\end{pmatrix} =
\begin{pmatrix}
R\psi_{n1} \\
R\psi_{n2} \\
R\psi_{n3} \\
\vdots \\
R\psi_{nl}
\end{pmatrix} =
\begin{pmatrix}
\psi_{n1} \\
\psi_{n2} \\
\psi_{n3} \\
\vdots \\
\psi_{nl}
\end{pmatrix}$$
The new basis set \( \phi_{n1}, \phi_{n2}, \phi_{n3}, \ldots, \phi_{nl} \) generates a representation of \( D'[R] \) matrices equivalent to the \( D[R] \) representation – that is, the two representations have the same characters and consist of the same irreps.
Symmetry example: PH$_3$

$G_{\text{CNPI}} = \{ E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^* \}$

The CNPI group has 12 elements
\[ G_{\text{CNPI}} = \{ E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^* \} \]

Irreducible representations

<table>
<thead>
<tr>
<th>( D_{3h}(M) )</th>
<th>( E )</th>
<th>( (123) )</th>
<th>( (23) )</th>
<th>( E^* )</th>
<th>( (123)^* )</th>
<th>( (23)^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{3h} )</td>
<td>( E )</td>
<td>( 2C_3 )</td>
<td>( 3C_2 )</td>
<td>( \sigma_h )</td>
<td>( 2S_3 )</td>
<td>( 3\sigma_v )</td>
</tr>
</tbody>
</table>

Equiv. rot.: \( R^0 \), \( R_{z \frac{2\pi}{3}} \), \( R_{\frac{\pi}{2} \pi} \), \( R_{\pi \pi} \), \( R_z \frac{5\pi}{3} \), \( R_0 \pi \)

| \( A_1' \) | 1 | 1 | 1 | 1 | 1 | 1 |
| \( A_1'' \) | 1 | 1 | 1 | -1 | -1 | -1 |
| \( A_2' \) | 1 | 1 | -1 | 1 | 1 | -1 |
| \( A_2'' \) | 1 | 1 | -1 | -1 | -1 | 1 |
| \( E' \) | 2 | -1 | 0 | 2 | -1 | 0 |
| \( E'' \) | 2 | -1 | 0 | -2 | 1 | 0 |
Symmetry example: $\text{PH}_3$

Geometrical symmetry at equilibrium

$C_{3v} = \{E, C_3, C_3^2, \sigma_1, \sigma_2, \sigma_3 \}$

The point group has 6 elements – so it is not isomorphic to the 12-element CNPI group here?
Irreducible representations

\[ C_{3v} = \{ E, C_3, C_3^2, \sigma_1, \sigma_2, \sigma_3 \} \]

<table>
<thead>
<tr>
<th></th>
<th>( C_{3v} ):</th>
<th>( E )</th>
<th>( 2C_3 )</th>
<th>( 3\sigma_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiv. rot.:</td>
<td>( R^0 )</td>
<td>( R_z^{2\pi/3} )</td>
<td>( R_{\pi/2}^{\pi} )</td>
<td></td>
</tr>
<tr>
<td>( A_1 ):</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>( A_2 ):</td>
<td>1</td>
<td>1</td>
<td>(-1)</td>
<td></td>
</tr>
<tr>
<td>( E ):</td>
<td>2</td>
<td>(-1)</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
The CNPI group is a „true“ symmetry group — but can we use it in practice?

Number of elements in the CNPI groups of various molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CNPI Group</th>
<th>Point Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2! × 2 = 4</td>
<td>C₂H₆</td>
</tr>
<tr>
<td>H₂O</td>
<td>2! × 2 = 4</td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>BF₃</td>
<td>3! × 2 = 12</td>
<td>C₆H₆</td>
</tr>
<tr>
<td>CH₃F</td>
<td>3! × 2 = 12</td>
<td>CH₃COCH₂CH₂OH</td>
</tr>
<tr>
<td>CH₄</td>
<td>4! × 2 = 48</td>
<td>C₆H₅CH₃</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>2! × 4! × 2 = 96</td>
<td>(C₆H₆)(H₂O)₂</td>
</tr>
<tr>
<td>SF₆</td>
<td>6! × 2 = 1440</td>
<td>C₆₀</td>
</tr>
</tbody>
</table>

C₆H₆, for example, has a 1036800-element CNPI group, but a 24-element point group at equilibrium, D₆h

PH₃ has a 12-element CNPI group, but a 6-element point group at equilibrium, C₃v
Back to PH$_3$

Very, very high potential barrier

No tunneling through barrier – energies doubly degenerate
We cannot see any effects of the tunneling through the barrier.

We do not really need the symmetry operations accompanied by this tunneling.

They are unfeasible!

**PH$_3$:**

\[
G_{\text{CNPI}} = \{ E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^* \}
\]

The six feasible elements are

\[
G_{\text{MS}} = \{ E, (123), (132), (12)^*, (13)^*, (23)^* \}
\]
The feasible elements form a group called

THE MOLECULAR SYMMETRY GROUP

(MS GROUP)
Symmetry example: PH$_3$

Geometrical symmetry at equilibrium (point group)

\[
C_{3v} = \{ E, C_3, C_3^2, \sigma_1, \sigma_2, \sigma_3 \}
\]

MS group

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

The point group and the MS group are isomorphic!

(\text{so were the point group and the CNPI group of H}_2\text{O})
If we only have to consider one minimum of the potential energy surface in describing the rotation and vibration of the molecule (i.e., there is negligible tunneling to neighbouring minima) we say that the molecule is rigid.

For a rigid molecule, the MS group is isomorphic to the point group of the equilibrium configuration.