Summary: Molecular vibrations.

\[ L = \sum_{\alpha=1}^{N} \frac{1}{2} \sum_{\mu=1}^{3N} \left( \ddot{x}_{\alpha}^{\mu} \right)^2 - V(x_{1},...,x_{N}) = T - V \]

\[ \sum_{\alpha=1}^{N} \frac{1}{m_{\alpha}} \dot{\bar{x}}_{\alpha}^{2} = \text{mass-weighted coordinates}. \]

\[ T = \frac{1}{2} \sum_{\alpha=1}^{N} \sum_{\mu=1}^{3N} \ddot{\bar{x}}_{\alpha}^{\mu} \]

\[ V(x_{1},...,x_{N}) = W(\bar{x}_{1},...,\bar{x}_{N}) \]

Let \( \bar{x}_{\alpha 0} \) or \( \bar{s}_{\alpha 0} \) be equilibrium position.

Let \( \delta \bar{x}_{\alpha} = \bar{x}_{\alpha} - \bar{x}_{\alpha 0} \)
\[ \delta \bar{s}_{\alpha} = \bar{s}_{\alpha} - \bar{s}_{\alpha 0} \]

Let \( q_{\mu} = (\delta \bar{s}_{1},...,\delta \bar{s}_{N}) \), \( \mu = 1,...,3N \)

\[ L = T - V = \frac{1}{2} \sum_{\mu=1}^{3N} \ddot{q}_{\mu}^{2} - \frac{1}{2} \sum_{\mu,\nu=1}^{N} W_{\mu \nu}^{''} q_{\mu} q_{\nu} \]

after expanding \W.

where \( W_{\mu \nu}^{''} = \frac{\partial^{2} W}{\partial q_{\mu} \partial q_{\nu}} \).

→ Want to diagonalize this Lagrangian (that is, the matrix \( W_{\mu \nu}^{''} \)) to find the normal modes of vibration.

Suppose the molecular equilibrium has symmetry. This means the molecular point group is nontrivial. This in turn means the following.

Def. The molecular point group is the subgroup of \( O(3) \),

\[ \{ R \in O(3) \mid R \text{ permutes equilibrium positions of identical atoms when molecule rotated about C.O.M.} \} \]

We write \( R_{n} \), \( n = \) index of M.P.G. group element. Thus the set \( \{ R_{n} \} \) forms a \( 3 \times 3 \) rep. of the M.P.G.
The MPG has a 3N x 3N rep which acts on the config. space of the molecule (3N-space) and leaves the potential invariant. Call this rep \( \{ R_n^{(3N)} \} \). That is, \( R_n \) without the superscript is understood to be the 3D rep.

Define of 3N-dim. rep of MPG:

\[
R_n^{(3N)} \begin{pmatrix} \dot{x}_1^N \\ \vdots \\ \dot{x}_N^N \end{pmatrix} = \begin{pmatrix} \dot{x}_1^N \\ \vdots \\ \dot{x}_N^N \end{pmatrix} \text{,}
\]

Then rule is,

\[
\dot{x}_\alpha^N (\text{new}) = R_n \cdot \dot{x}_\beta^N (\text{old})
\]

where \( \dot{x}_\alpha^N = R_n \cdot \dot{x}_\beta^N \).

In words: if \( R_n \) takes equilibrium \( \beta \) to equil. \( \alpha \), then its action on \( \dot{x}_\beta^N \) (attached to equil. \( \beta \)) is to transport the base of this vector over to equil. \( \alpha \), then rotate it by \( R_n \).

Notice that \( R_n \cdot \dot{x}_\alpha^N = \dot{x}_\alpha^N \), \( \dot{\vec{M}}_\beta = \dot{\vec{M}}_\beta \). But if \( R_n \cdot \dot{x}_\beta^N = \dot{x}_\alpha^N \), then \( \vec{M}_\beta = \vec{M}_\alpha \) (\( R_n \) permutes only identical atoms). So, the action of \( R_n \) may be stated in terms of mass-weighted poses,

\[
\dot{\vec{S}}_\alpha^N (\text{new}) = R_n \cdot \dot{\vec{S}}_\beta^N (\text{old})
\]

where \( \dot{\vec{S}}_\alpha^N = R_n \cdot \dot{\vec{S}}_\beta^N \).

Since the MPG leaves the potential invariant, the \( \{ R_n^{(3N)} \} \) are reducible.

In general, both \( \{ R_n \} \) as \( \{ R_n^{(3N)} \} \) are reducible.
About the 3N-dim. config. space. Think of coordinates \( q_\mu \), \( \mu = 1, ..., 3N \).

A single point in the 3N-dim. config. space represents a set of N points (the locations of the masses) in 3D space. For example, \( q_\mu = 0, \mu = 1, ..., 3N \) (the origin in 3N-dim. space) is the equilibrium, \( \delta S_\alpha = 0 \) or \( \mathbf{v}_\alpha = \mathbf{v}_{\alpha_0} \), \( \alpha = 1, ..., N \). So the potential \( V \) (or \( W \)) is a minimum at \( q_\mu = 0 \).

But it is not an isolated minimum (previously called "absolute"
minimum—it poor terminology) because the directions corresponding
to overall translation of the molecule do not change the potential
(because overall translations don't change the distances between atoms).
These are 3 directions in the 3N-dim. config. space corresponding to
overall translations. They are

\[
(\delta S_1', ..., \delta S_N') = (\mathbf{e}_i) (\mathbf{v}_i, \mathbf{v}_i, ..., \mathbf{v}_i)
\]

where \( \mathbf{e}_i = \hat{x}, \hat{y}, \hat{z} \)

for \( i = 1, 2, 3 \)

\( \delta S = \) small displaced.

Define the scalar product in 3N-dim. config. space by

\[
(\delta S_1', ..., \delta S_N') \cdot (\delta S_1', ..., \delta S_N') = \sum_{\alpha=1}^{N} \delta S_\alpha' \cdot \delta S_\alpha'
\]

or \( (q_1', ..., q_{3N'}) \cdot (q_1', ..., q_{3N'}) = \sum_{\mu=1}^{3N} q_\mu q_\mu' \).

This is the metric that appears in the kinetic energy.

Then the vectors \( (\mathbf{e}_i, \mathbf{e}_j, ..., \mathbf{e}_i) \), \( i = 1, 2, 3 \), are orthogonal:

\[
(\mathbf{e}_i, \mathbf{e}_i, ..., \mathbf{e}_i) \cdot (\mathbf{e}_j, \mathbf{e}_j, ..., \mathbf{e}_j) = N \delta_{ij}
\]
They also span a 3D subspace of the \(3N\)-dim. config. space that is invariant under the action of the group. That's because...

\[ R^{(3N)}_n (\hat{e}_i, \hat{e}_i, \ldots, \hat{e}_i) = (R_n \hat{e}_i, R_n \hat{e}_i, \ldots, R_n \hat{e}_i) \]

But \( R_n \hat{e}_i = \sum_j \hat{e}_j (R_n)_{ji} \), where \((R_n)_{ji}\) are the components of the 3x3 matrices \(R_n\). So,

\[ = \sum_j (\hat{e}_j, \hat{e}_j, \ldots, \hat{e}_j) (R_n)_{ji}. \]

Thus, these vectors are mapped into linear combinations of themselves under the action of \(R^{(3N)}_n\), so the rep \(\{R^{(3N)}_n\}\) has a 3D invariant subspace. Recall, if a unitary rep. of a group has an invariant subspace, then the orthog. subspace is also invariant. Thus if we choose the 3 vectors \((\hat{e}_i, \hat{e}_i, \ldots, \hat{e}_i)\) as a basis in the translational subspace, then \(3N-3\) more vectors orthogonal to these, the matrices \(R^{(3N)}_n\) have a block diagonal form,

\[
\begin{bmatrix}
R_n & 0 \\
0 & X
\end{bmatrix}
\]

where \(X\) is a \((3N-3)\times(3N-3)\) rep. of the M.P.G. When we take \(\hat{e}_i\) traces, the total trace (character) is the sum of the translational part plus all the rest. The translational character is the same
as the character of the 3D rep. of the MPG, which can be
determined by the rules on pp. 7-8, 9/2/03, and in prob. 18, HW9.
We will write,
\[ \chi^{(3)}_n = \chi^{(3)}_n = \tau_i (R_n). \]

The 3N-dim rep \{R^{(2n)}_n\} of the MPG has another 3D invariant
subspace, corresponding to overall rotations of the molecule. Overall rotations
of the whole molecule (about any axis by any angle) do not change the
distances betw. the atoms, therefore they do not change the potential energy,
therefore an infinitesimal rotation applied to the molecule in equilibrium
(minimum of V) must sweep out a neutral direction.

Look at what an infinitesimal roti does to an arb. vector in 3D:

\[ \delta \hat{\vec{x}} = \delta \theta \hat{\vec{n}} \times \vec{x}. \]

That is,
\[ R(\hat{\vec{n}}, \delta \theta) \vec{x} = \delta \theta \hat{\vec{n}} \times \vec{x} \]
when \( \delta \theta = \) small.

So if we apply \( R(\hat{\vec{n}}, \delta \theta) \) to the equilibrium forces \( \delta \hat{\vec{x}}_{x0} \), we get
\[ \delta \hat{\vec{x}}_x = \delta \theta \hat{\vec{n}} \times \delta \hat{\vec{x}}_{x0}. \]
or
\[ \delta \hat{\vec{s}}_x = \delta \theta \hat{\vec{n}} \times \delta \hat{\vec{s}}_{x0}. \]

See picture (b), p. 14, 4/19/03
Thus there are 3 indep. directions in the 3N-D config. space that are produced by infinitesimal, overall rotations:

\[
(\vec{S}_1, \ldots, \vec{S}_N) = 8N (\hat{e}_i \times \vec{S}_0, \hat{e}_i \times \vec{S}_0, \ldots, \hat{e}_i \times \vec{S}_N), \quad i = 1, 2, 3
\]

The subspace of infin. overall roto's in 3D. It is also an invariant subspace under the group action, because

\[
R^{(3N)}_{\alpha} (\hat{e}_i \times \vec{S}_0, \ldots, \hat{e}_i \times \vec{S}_N)
\]

To compute it, take the \(\beta\)-th vector in the list, \(\hat{e}_i \times \vec{S}_0\).

According to the rules, we must transport it to position \(\beta\), where \(R_\alpha \vec{S}_0 = \vec{S}_\beta\), then rotate it. But when we rotate it, we get

\[
R_\alpha (\hat{e}_i \times \vec{S}_0) = (\det R_\alpha) (R_\alpha \hat{e}_i) \times (R_\alpha \vec{S}_0).
\]

Here we use the rule,

\[
R (\vec{a} \times \vec{b}) = (\det R) (R \vec{a}) \times (R \vec{b}).
\]

If \(\det R = +1\) (proper rotations), the cross product transforms as a vector; if \(\det R = -1\) (improper rotations), it changes sign.

But, \(R_\alpha \vec{S}_0 = \vec{S}_\beta\), so,

\[
\Rightarrow = (\det R_\alpha) (R_\alpha \hat{e}_i) \times \vec{S}_\beta
\]

\[
= (\det R_\alpha) \sum_j \hat{e}_j \times \vec{S}_\beta (R_\alpha)_{ji}
\]

So, ...

\[
\Rightarrow = (\det R_\alpha) \sum_j (\hat{e}_j \times \vec{S}_0, \ldots, \hat{e}_j \times \vec{S}_N) (R_\alpha)_{ji}.
\]
Thus the 3 vectors \((\hat{c}_i \times \hat{s}_{i0}, ... , \hat{c}_i \times \hat{s}_{3N})\), \(i=1,2,3\), in the 3N dim'l. space are mapped into lin. combs. of themselves under the action of \(\{R_n^{(3N)}\}\), and thus they span a 3D covariant subspace of the 3N-D config. space. This is the subspace of overall rotations. It is orthogonal to the subspace of overall translations, since (omit proof.)

The vectors of this rotational subspace transform as

\[(\det R_n) R_n\]

that is, the 3x3 rep. of the M.P.G. times the determinant rep. This is another rep. of the M.P.G. (another 3D rep.). It has certain characters,

\[\chi^{(\text{rot})}_{m} = \text{tr}((\det R_n) R_n) = (\det R_n) \chi_{m}^{(3)}\]

The 6 directions for overall translations and overall rotations are the neutral directions at the minimum of the potential energy. The remaining 3N-6 directions are the vibrational directions.

Thus the 3N dimensions break up,

\[3N = 3 + 3 + (3N-6)\]

\[\uparrow \uparrow \uparrow \text{trans. rot vib.}\]

And,

\[\chi^{(3N)} = \chi^{(\text{trans})} + \chi^{(\text{rot})} + \chi^{(\text{vib})}\]
For example, $\text{NH}_3$ with $C_{3v} = \text{M.P.G.}$, we found previously, $(3N = 3 \times 4 = 12)$

<table>
<thead>
<tr>
<th>$\chi^{(6N)}$</th>
<th>E</th>
<th>2$C_3$</th>
<th>3$\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
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But we also have

<table>
<thead>
<tr>
<th>$\chi^{(6M)}$</th>
<th>E</th>
<th>2$C_3$</th>
<th>3$\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^{(3)}$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$\chi^{(1M)}$</td>
<td>3</td>
<td>0</td>
<td>+1</td>
</tr>
</tbody>
</table>

So, $\chi^{(\text{vib})}$

<table>
<thead>
<tr>
<th>E</th>
<th>2$C_3$</th>
<th>3$\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

This implies that the irreps content of the vibrational modes is

$$\text{vib. modes} = 2A_2 \oplus 2E.$$ 

There are 2 singlets ($2A_2$) and 2 doublets ($2E$) in the vibrational frequencies of $\text{NH}_3$.

Similarly if you analyze $\text{CH}_4$, you find triple degeneracies in the frequencies.

(Must use tetrahedral group.)