Setting: We are given a rep. \( g \rightarrow T(g) \) of a group \( G \) acting on a vector space \( V \) by means of unitary ops \( T(g): V \rightarrow V \).

\( M(g) \) means the matrix of \( T(g) \) in some basis.

\( \{ e^r \} \) or \( \{ 1 \alpha i \} \) means the symmetry adapted basis

\( r = \) irrep label
\( \alpha = \) copy of irrep \( = 1, \ldots, \mu_r \)
\( i = \) row or col. of individual irrep copy of \( \alpha \) = copy of irrep \( = 1, \ldots, d_r \).

\[
< \alpha i | T(g) | \beta j > = \delta_{rs} \delta_{\alpha \beta} \ M^{(r)}_{ji}(g)
\]

Block diag. form of \( T(g) \) in symm. adapted basis.

\[
T(g) | \alpha i > = \sum_j M^{(r)}_{ji} | \alpha j >
\]

set \( \{ 1 \alpha i \} , \ i = 1, \ldots, d_r \) "transforms as" irrep \( r \).

Today we study projection operators that can be used to construct the S.A.B. We define

\[
P^{(r)} = \frac{d_r}{(\# G)} \sum_g \chi^{(r)}(g)^* \ T(g).
\]

We claim \( P^{(r)} \) is a projector onto the \( r \)-subspace of \( V \), i.e., onto the subspace spanned by \( \{ 1 \alpha i \} , \ \alpha = 1, \ldots, \mu_r ; \ i = 1, \ldots, d_r \), that is, all basis vectors with \( r \) label. We claim \( P^{(r)} \) has the following properties,

1. \( P^{(r)} P^{(r)} = P^{(r)} \)
2. \( P^{(r)} P^{(s)} = \delta_{rs} P^{(r)} \)
3. \( P^{(r)} = \sum_{\alpha i} | 1 \alpha i > < 1 \alpha i | \)
4. \( \sum_r P^{(r)} = 1. \)

Go to p. 15, 4/2/03, then resume with next page.
Note, \[ \chi^{(r)}(g)^* = \sum_i M^{(r)}_{ii}(g)^* \]
\[ \chi^{(s)}(g^{-1}a)^* = \sum_{jk} M^{(s)}_{jk}(g)^* M^{(s)}_{kj}(a)^* \]
\[ \Rightarrow M^{(r)}_{kj}(g). \]

So \[ P^{(r)} P^{(s)} = \frac{dr ds}{(\# G)^2} \sum_{g,a} \sum_{ijk} M^{(r)}_{ii}(g)^* M^{(s)}_{kj}(g) M^{(s)}_{kj}(a)^* T(a) \]

use G.O.T.

\[ \Rightarrow = \sum_a \sum_{ijk} \delta_{rs} \delta_{lk} \delta_{ij} M^{(s)}_{kj}(a)^* T(a) \]

\[ = \delta_{rs} \frac{dr}{(\# G)} \sum_a \chi^{(r)}(a)^* T(a) \]

or \[ P^{(r)} P^{(s)} = \delta_{rs} P^{(r)} \]

The case \( r=s \) means \( P^{(r)} = P^{(r)} \), so along with \( P^{(r)^*} = P^{(r)} \)
proven above, this proves that \( P^{(r)} \) is a projection op.

The case \( r+s \) gives \( P^{(r)} P^{(s)} = 0 \), which means that the spaces
upon which \( P^{(r)} \) and \( P^{(s)} \) project (the \( r \)- and \( s \)-subspaces
let's call them) are orthogonal.

Let's note another useful fact about these proj. ops:
\[ \sum_{\text{all } r \text{ ops}} P^{(r)} = 1 \quad \text{(the identity)} \]
This means that the space \( V \) is decomposed into a set of orthogonal subspaces, the \( r \)-subspaces for \( r = 1, 2, \ldots \), and the \( P^{(r)} \) project onto these subspaces. (It's a completeness relation.)

\[
\sum_r P^{(r)} = \frac{1}{(\# G)} \sum_r \sum_{g \in G} \chi^{(r)}(g)^* T(g). 
\]

Consider \( \sum_r d_r \chi^{(r)}(g)^* = \sum_r \chi^{(r)}(c) \chi^{(r)}(g)^* \) since \( d_r = \chi^{(r)}(c) \)

\( = (\# G) \delta_{cg} \) by the column orthogonality relation for characters.

So...

\( = \sum_{g \in G} \delta_{cg} T(g) = T(c) = 1 = \text{identity}. \) QED.

Now the question remains, what is this \( r \)-subspace upon which \( P^{(r)} \) projects? Can answer by looking at what \( P^{(r)} \) does to the S.A.B.

\[
P^{(r)} |s\alpha_j\rangle = \sum \frac{d_r}{(\# G)} \sum_g \chi^{(r)}(g)^* T(g) |s\alpha_j\rangle \sum_i |s\alpha_i\rangle M^{(c)}_{ij}(g) \sum_k \delta_{k(i)} \delta_{k(j)} |s\alpha_i\rangle = \delta_{rs} |s\alpha_j\rangle.
\]
In other words, \( P^{(r)} \) annihilates \( |s\alpha i\rangle \) if \( r \neq s \), otherwise it leaves it invariant. Thus the space upon which \( P^{(r)} \) projects is spanned by the S.A.B. basis vectors,

\[
\{ |\alpha i\rangle, \alpha = 1, \ldots, \mu r, i = 1, \ldots, dr \}
\]

in other words, all those vectors labelled by \( r \). Thus,

\[
P^{(r)} = \sum_{\alpha i} |\alpha i\rangle \langle \alpha i|.
\]

Let's look at an example in the 6-spring problem. We have a 6D reducible rep of \( C_{6v} \), what we called \( R^{(6)}_{m,5} \), \( m = 0, \ldots, 5 \), see p. 13, 3/19/03. And we found

\[
R^{(6)}_{m,5} = A_1 \oplus A_2 \oplus 2E.
\]

Thus the \( r = A_1 \) and \( r = A_2 \) subspaces are 1D, and the \( r = E \) subspace is 4D. Let's write out the proj. op. onto the \( r = A_1 \) subspace. This is the trivial irrep for which \( \chi^{A_1}(g) = 1 \), all \( g \in G \), so

\[
P^{(A_1)} = \frac{1}{(\#G)} \sum_{g} T(g)
\]

or with the matrices on p. 13, 3/19/03,

\[
P^{(A_1)} = \frac{1}{6} \begin{pmatrix}
E + R_3 & R_2 + R_5 & R_1 + R_4 \\
R_1 + R_5 & E + R_4 & R_2 + R_3 \\
R_2 + R_4 & R_1 + R_3 & E + R_5
\end{pmatrix}
\]

partitioned into 9 2x2 matrices \( E, R_1, \ldots, R_5 \). These are the 2D irrep of \( C_{6v} \), see p. 1, 3/5/03.
Write this out explicitly as a $6 \times 6$ matrix.

$$\mathbf{P}^{(A_1)} = \frac{1}{6} \begin{pmatrix}
  0 & 0 & 0 & 0 & 0 & 0 \\
  0 & 2 & -\sqrt{3} & -1 & \sqrt{3} & -1 \\
  0 & -\sqrt{3} & 3/2 & \sqrt{3}/2 & -3/2 & \sqrt{3}/2 \\
  0 & -1 & \sqrt{3}/2 & 1/2 & -\sqrt{3}/2 & 1/2 \\
  0 & \sqrt{3} & -3/2 & -\sqrt{3}/2 & 3/2 & -\sqrt{3}/2 \\
  0 & -1 & \sqrt{3}/2 & 1/2 & -\sqrt{3}/2 & 1/2 \\
\end{pmatrix}$$

According to our decomposition $A_0 \oplus A_1 \oplus 2\mathbf{E}$,

This should project onto a 1D subspace. This means if $x$ is any vector, then $\mathbf{P}^{(A_1)}x$ should lie in this subspace and span it (unless $\mathbf{P}^{(A_1)}x = 0$). Let $x$ run over the 6 "unit vectors". Then $\mathbf{P}^{(A_1)}x$ will give the 6 columns of the matrix above. If the theory is right, all these columns should be proportional. Indeed they are.

Any non-zero column can be taken as a basis vector (the basis vector) in the $A_1$-subspace. We can normalize if we wish.

Let's take the 2nd column $x + \frac{1}{2}$. This is

$$\begin{pmatrix}
  0 \\
  1 \\
  -\sqrt{3}/2 \\
  -1/2 \\
  \sqrt{3}/2 \\
  -1/2 \\
\end{pmatrix} = \begin{pmatrix}
  8x_1 \\
  8y_1 \\
  8x_2 \\
  8y_2 \\
  8x_3 \\
  8y_3 \\
\end{pmatrix}$$

for the normal mode in the $A_1$ symmetry class (trivial or scalar class).

This is the basis vector $|x_0\rangle$ for $\tau = A_1$, $\alpha = 1, i = 1$. 

5
Geometrically this is

\[ \delta x_1 = (0) \]

(not drawn are 3 other springs).

\[ \delta x_2 = (-\frac{\sqrt{2}}{2}, \frac{1}{2}) \]

\[ \delta x_3 = (+\frac{\sqrt{2}}{2}, -\frac{1}{2}) \]

This is the "breather mode" which we could have guessed physically. Similarly you can work out the normal mode for the A_2 (pseudoscalar) mode.

The E modes are more complicated since they come in 2 copies and each copy is 2D.

To handle the case of multiple copies of irreps and/or multidimensional irreps, we introduce more projection and other operators.

The operator \( \Pi^{(r)} \) projects onto subspace \( r \), which may be multidimensional. Can we find operators that project onto subspaces of these subspaces?

Recall, \( \Pi^{(r)} = \frac{1}{\#G} \sum_{g \in G} \chi^{(r)}(g)^* T(g) \).

Now define \( B^{(r)}_{ij} = \frac{1}{\#G} \sum_{g \in G} M^{(r)}_{ij}(g)^* T(g) \).
I use symbol $B$ instead of $P$ because there are not projection operators (not always, anyway). The parentheses around $(i,j)$ is to remind you that $i,j$ are labels of the operator, not components. (If we want components of the operator we could write something like $B(i,j)_{\mu\nu}$.)

These operators have the following properties. The proofs are very similar to what we had before for the operators $P^{(r)}$, and will be omitted.

1. $B(i,j)^\dagger = B(j,i)$.
   Thus, if $i \neq j$, $B(i,j)$ is not Hermitian and cannot be a projection operator.

2. $B(i,j)B(k,l) = \delta_{rs}\delta_{jk}B(r,k)$.

3. The operators $B(i,i)$ are projection operators. This follows from 1. and 2. They project onto the subspace of $V$ given by indices $r,i$, that is, in the S.A.B.,

   $$B(i,i)\left\{\psi_{ij}\right\} = \delta_{rs}\delta_{ij}\left\{\psi_{ai}\right\},$$

   or, $B(i,i) = \sum_{\alpha} \left\{\psi_{ai}\right\}\left\langle\psi_{ai}\right\rangle$.

4. $P^{(r)} = \sum_{i} B(i,i) = \sum_{\alpha} \left\{\psi_{ai}\right\}\left\langle\psi_{ai}\right\rangle$.
   This means the $r$-subspace is the direct sum of orthogonal subspaces labelled by $V_i$. Each has dimensionality $\mu_r$. 

7
5. The operators $B(i,j)$ can be used to construct the SAB. Details will be omitted for now, we'll come back to it if we need it.

Now let's think about molecular vibrations. We'll take NH$_3$ as a first example. Here's a picture (as good as I can draw it).

![Diagram of NH$_3$ molecule]

The plane of the H atoms is below the x-y plane, if we want the origin to be the center of mass. Actually the picture is exaggerated, the NH$_3$ molecule is flatter than drawn.

There are 3 features that make a molecular vibration problem harder than the spring problems we have been discussing.

1. The motion is in 3D
2. The masses are not all the same
3. The molecule is not attached to an inertial frame

Items 1 and 2 are relatively simple. 3 is harder.
Begin with classical Lagrangian for molecule. Let

\[ N = \text{# of atoms}, \]
\[ \dot{x}_\alpha = \text{position of atom } \alpha, \quad \alpha = 1, \ldots, N \]
\[ m_\alpha = \text{mass} \]

Then

\[ L = T - V \]
\[ T = \sum_{\alpha=1}^{N} \frac{m_\alpha}{2} \dot{x}_\alpha^2 \]
\[ V = V(x_1^{\alpha}, \ldots, x_N^{\alpha}) \]

Idea is same as before, we want to expand \( V \) about an equilibrium, and then diagonalize both \( T \) and \( V \). Let \( \overrightarrow{x}_\alpha^{eq} \) = equal posn. of atom \( \alpha \).

Unlike spring problems, masses are not identical, so kinetic energy, while diagonal, is not a multiple of identity. So introduce

\[ \overrightarrow{s}_\alpha = \sqrt{M_\alpha} \overrightarrow{x}_\alpha \]

call the \( \{\overrightarrow{s}_\alpha\} \) \underline{mass-weighted coordinate}, so that

\[ T = \frac{1}{2} \sum_{\alpha=1}^{N} \dot{s}_\alpha^2 \]

Then express pot. energy as fn. of the \( \{\overrightarrow{s}_\alpha\} \),

\[ V(x_1, \ldots, x_N) = V(s_1, \ldots, s_N) \]

using a new symbol \( V \) since it is a new function.
Now write

$$\delta \mathbf{S}_\alpha = \mathbf{S}_\alpha - \mathbf{S}_{\alpha 0}$$

for the small displacements about equil., and expand the potential,

$$W = W(0) + \frac{1}{2} \sum_{\alpha \beta = 1}^{N} \sum_{i,j=1}^{3} \frac{\partial^2 W(0)}{\partial S_{\alpha i} \partial S_{\beta j}} \delta S_{\alpha i} \delta S_{\beta j}$$

\text{ const, drop it} \quad \text{Here (0) means eval. @ equil.}

Now write

$$q_{\mu} = (\delta S_{x1}, \delta S_{y1}, \delta S_{z1}, \ldots, \delta S_{xN}) \quad \text{a 3N-vector of small displacements}$$

Then in terms of the \( q \)'s we have

$$T = \frac{1}{2} \sum_{\mu = 1}^{3N} \dot{q}_{\mu}^2$$

$$V = \frac{1}{2} \sum_{\mu, \nu = 1}^{3N} W^{\nu \mu} q_{\mu} q_{\nu}$$

where

$$W^{\nu \mu} = \frac{\partial^2 W(0)}{\partial q_{\mu} \partial q_{\nu}}$$

so this gives us a Lagrangian just like we had in the vibrating spring problems, only difference (so far) is that we're using mass-weighted coordinates.

Now suppose we have a group \( G \), a subgroup of \( O(3) \), such that when the center of mass of the molecule is at the origin, the group elements (the 3x3 rotations) map the equilibrium
positions of the atoms into themselves. This means that the rotations \( R_n \) in the group bring about a permutation of the equilibrium positions of identical atoms.

In the example of \( \text{NH}_3 \), the rotations \( R_n \) are the six \( 3 \times 3 \) matrices belonging to \( C_3 \), which permute the equilibrium positions of the \( H \) atoms while leaving the equilibrium position of the \( N \) atom alone. (If we had a molecule with two or more \( N \) atoms, it would be permissible to permute them, too.)

This group is called the molecular point group.

Now we define an action of the molecular point group on the \( 3N \)-dimensional configuration space of the molecule, most conveniently expressed in terms of the coordinates \( \{ S_{\alpha} \} \) or \( \{ S_{\beta} \} \) or \( \{ \phi_\mu \} \). In terms of the \( S_{\alpha} \), the rule is

\[
S_{\alpha}^{\text{(new)}} = R_n S_{\alpha}^{\text{(old)}}
\]

That is,
\[
R_n \vec{z}_\alpha = \vec{z}_\mu.
\]

where \( R_n \) maps equilibrium \( \beta \) to equilibrium \( \alpha \). This is the same rule used in the spring problems, and it gives a representation of the group on the \( 3N \)-dimensional configuration space. The rule can be equivalently stated

\[
S_{\beta}^{\text{(new)}} = R_n S_{\beta}^{\text{(old)}},
\]

since \( \alpha \rightarrow \beta \) if equilibrium \( \alpha, \beta \) are permuted (we only permute identical atoms). This \( 3N \)-dim. action of the molecular point group leaves the potential invariant.
The character of the $3N$-dimensional rep. of the molec. pt. gp. is given by rule,

\[ \chi^{(3N)}_n = \left( \frac{\# \text{ atoms left}}{\text{invariant under } R_n} \right) \times \chi^{(3)}_n \]

as a $3 \times 3$ matrix.

where $\chi^{(3)}_n$ means the character of group element $R_n$. For example, with $C_{3v}$ and NH$_3$, we have the character table

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>2C$_3$</th>
<th>3σv</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>

and the calculation of $\chi^{(12)}$ (since $N=4$ for ammonia)

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>2C$_3$</th>
<th>3σv</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^{(12)}$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$\chi^{(12)}$</td>
<td>12</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

Then decomposing $\chi^{(12)}$ we find the irrep content,

\[
\begin{pmatrix}
12 \text{D rep. of } C_{3v}
\end{pmatrix} = A_1 \oplus 3A_2 \oplus 4E.
\]

This is essentially the solution to HW prob. 2 for this week.
However, it is not the right answer for describing the normal modes of vibration of NH$_3$.

The reason is that the potential energy for a molecule is not an absolute minimum at the equilibrium configuration. An absolute minimum means that $V_{ij}$ is positive definite, so for example with $V(x_1, x_2)$ (a 2D config. space) the graph of the potential looks like

\[ V \]

\[ \begin{array}{c}
\text{x}_2 \\
\text{x}_1 \\
\end{array} \]

\[ (x_{10}, x_{20}) = \text{equil.} \]

The potentials we had in the spring problems were like this, except instead of a 2D config. space we had dimensions 2, 3, 6, or 9, depending on the problem we looked at.

On the other hand, in the molecular problem, we have neutral directions, so that the potential looks like

\[ V \]

\[ \begin{array}{c}
\text{x}_2 \\
\text{x}_1 \\
\end{array} \]

neutral direction.
For potentials like this, the neutral directions are ones in which the potential is constant. There is no vibration in the neutral directions, only in the directions orthogonal to them.

The potential in the molecular problem is like this, except there are 6 neutral directions and 3N-6 directions orthogonal to the neutral directions. Thus there are only 3N-6 vibrational modes (not 3N).

The neutral directions correspond to overall translations and overall rotations (6 = 3+3) of the molecule. To visualize these directions we need to think in terms of the 3N-dimensional configuration space. We use coordinates \{Sx\} or \{S_3x\} or \{y\} in this space, so the origin is an equilibrium position. To visualize a 3N-dim. displacement in the 3N-dim. configuration space, we may think of N 3-dimensional, small displacements from equil. in 3D space, for example in the H₂O molecule.

\[ \text{(a)} \] \[ \text{(b)} \] \[ \text{(c)} \]

Here \(N=3\) so configuration space is 9D. Case (a) illustrates a small, overall translation in the x-direction. This represents a certain vector in the 9D config. space which is a neutral direction. Similarly for small displacements in the y- and z-directions.
Case (b) represents a small rotation about the z-axis, with the origin at the center of mass (X in the figure). This is also a neutral direction in the 9D space. Similarly for rotations about the x- or y-axes. Case (c) represents a dilational vibrational mode. This direction in the 9D space is orthogonal to the 6 neutral directions. (Or it would be if I draw the picture right).

3N-dimensional

So the configuration space of a molecule, with an equilibrium at the origin (δX = 0 or δZ = 0 or qμ = 0) breaks up into subspaces of dimensions 6 and 3N - 6:

\[ \text{6 neutral directions} = 3 \text{trans} + 3 \text{rot.} \]

\[ \text{3N-6 vibrational directions.} \]

The vibrational directions are defined to be those 1 to the 6 neutral directions. The orthogonality is defined with respect to the scalar product

\[ \sum_{\mu} \delta q_{\mu}^2 \quad \text{or} \quad \sum_{\alpha} |\delta X_{\alpha}|^2 \quad \text{or} \quad \sum_{\alpha} m_{\alpha} |\delta X_{\alpha}|^2. \]

This is a mass-weighted scalar product (the same one that occurs in the kinetic energy).

It's best to think of the picture above as applying only to small displacements about equilibrium. (What is called the tangent space in mathematics.)
let us explore the neutral directions (subspaces). First look at overall translations. A small displacement (from equilbrium) in the $x$-direction is described by

$$(\delta \vec{s}_1, ..., \delta \vec{s}_N) = (\delta \vec{e})(\hat{x}, \hat{x}, ..., \hat{x})$$

where $(\delta \vec{e})$ is the small distance. This specifies a vector in the $3N$ dimensional config. space (the LHS). Since there are $3$ directions of displacement, we get $3$ vectors in the $3N$-dim'l. config. space,

$$(\delta \vec{s}_1, \delta \vec{s}_2, ..., \delta \vec{s}_N) = 8 \delta (\hat{e}_i, \hat{e}_i, ..., \hat{e}_i),$$

$\hat{e}_i = \hat{x}, \hat{y}$ or $\hat{z}$,  $i = 1, 2, 3.$

Look at the action of one of the $3N$-dimensional rotations on this vector. Recall the rule is $\delta \vec{s}_x \xrightarrow{\text{new}} R_n \delta \vec{s}_x (\text{rot})$, where $R_n \delta \vec{s}_0 = \delta \vec{s}_0$.

So,

$$R_n^{(\mathbf{\hat{e}_i}, ..., \mathbf{\hat{e}_i})} = (\delta \vec{e})(R_n \hat{e}_i, R_n \hat{e}_i, ..., R_n \hat{e}_i).$$

But $R_n \hat{e}_i = \sum_j \delta \vec{e}_j (R_n)_{ji}$

$$\text{a 3x3 matrix for } R_n \text{ at molecular point } \text{gp.}$$

Thus the vectors $(\hat{e}_i, ..., \hat{e}_i), \ i = 1, 2, 3,$ span a $3$-dim'l. invariant subspace of the $3N$-dim'l action of the molecular pt. gp. The basis vectors in this subspace "transform as" the $3D$ rep. of the molec. pt. gp.

Reminder: If a unitary rep. of a group possesses an invariant subspace, then the orthogonal subspace is also invariant.