Degenerate Representations

- degenerate representations cannot be described by a single representation they necessarily have two components
- in non-degenerate representations (A and B symmetry labels), under a symmetry operation each of the orbitals maps exactly (within a phase difference of ±1) onto one of the others so that the starting and finishing shapes are identical.
- in a degenerate representation (E and T symmetry labels), the individual components do NOT necessarily map onto each other, in this case the characters in the character table refer to the transformation of both components!
- in this document we will illustrate how the \( p_x \) and \( p_y \) are components form a degenerate representation (E for the \( C_{3v} \) point group), we will also examine how these orbitals behave under the symmetry operations of the \( C_{3v} \) point group

\[
\begin{array}{c|ccc|}
C_{3v} & E & 2C_3 & 3\sigma_v \\
\hline
A_1 & 1 & 1 & 1 & T_z \\
A_2 & 1 & 1 & -1 \\
E & 2 & -1 & 0 & (T_x, T_y) \\
\end{array}
\]

\( C_{3v} \) character table

- start by taking a point on the tip of the orbitals under consideration and determining it's position in terms of the x and y axes, ie it's coordinates \((x, y)\) or in our case we will use the vector notation: \( \begin{pmatrix} x \\ y \end{pmatrix} \)
- the \( p_x \) orbital "point" has coordinates \( \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \)
- the \( p_y \) orbital "point" has coordinates \( \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \)
- one way to think of this is as a set of unit vectors
- if the two vectors are positioned side by side a 2 by 2 matrix is generated formed

\[
\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

- consider the transformation of each orbital (unit vector) under \( E \)
  - \( p_x \) and \( p_y \) remain the same
  - the equation for this (\( E \) operating on the points) is given below:
    \[
    E \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
    \]
  - the character is the sum of the diagonal terms of the matrix which is just 1+1=2
  - hence the character for \( E \) is 2
  - check this against your character table!
• consider the transformation under $\sigma_v$
  o the equation for this is given below:
    \[
    \sigma_v \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
    \]
  o the character is the sum of the diagonal terms of the matrix which is just $1 + (-1) = 0$
  o hence the character for $\sigma_v$ is 0
  o check this against your character table for $C_{3v}$

• consider the transformation under $C_3$
  o the $p_x$ and $p_y$ orbitals are rotated 120º
  o the start point and finish points for the $p_x$ diagram are shown in more detail on the next page
  o simple trigonometry is required to determine the x and y coordinates for the final point
  o the key trigonometric identities are:

\[
\cos \theta = \frac{\text{adjacent}}{\text{hypotenuse}} \quad \sin \theta = \frac{\text{opposite}}{\text{hypotenuse}}
\]

o consider the $p_z$ point, the triangle generated by the rotation is shown to the left
o a more detailed representation is also given below:
we find that the coordinates for the final point are: \[
\begin{pmatrix}
-\sin 30^\circ \\
-\cos 30^\circ
\end{pmatrix}
\]
if the procedure is repeated for the p_y orbital we find that the coordinates are: \[
\begin{pmatrix}
\cos 30^\circ \\
-\sin 30^\circ
\end{pmatrix}
\]
but from the simple triangle shown earlier we know that \( \sin 30^\circ = \frac{1}{2} \) and \( \cos 30^\circ = \frac{\sqrt{3}}{2} \).

the equation for the \( C_3 \) is given below:
\[
C_3 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \rightarrow \begin{pmatrix}
-\sin 30^\circ & \cos 30^\circ \\
-\cos 30^\circ & -\sin 30^\circ
\end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix}
-\frac{1}{2} & \frac{\sqrt{3}}{2} \\
-\frac{\sqrt{3}}{2} & -\frac{1}{2}
\end{pmatrix}
\]
the character is the sum of the diagonal terms of this final matrix which is just \(-\frac{1}{2} + (-\frac{1}{2}) = -1\).

hence the character for \( C_3 \) is -1.
check this against your character table!

thus we now know where the characters for the E irreducible representation in \( C_3 \), originate from.

so far we have just used degenerate orbitals, but where do they come from?

any two (or more!) wavefunctions that have the same energy are degenerate.
this just means that the \( H\Psi = E\Psi \) for \( \Psi = \Psi_1 \) or \( \Psi = \Psi_2 \) gives the same energy.
wavefunctions can be accidentally degenerate or degenerate by symmetry.

put another way: wavefunctions that are related by a symmetry operation are degenerate.
the equations below tell us than any (normalised) wavefunction composed of a linear combination of degenerate functions also has the same energy.
sometimes we say that degenerate functions can “rotate among themselves” this just means that the values of \( C_i \) can change without changing the energy of the linear combination.

\[
H\psi_i = E_i \psi_i, \quad \forall \ i E_i = E
\]
\[
\Phi = c_1 \psi_1 + c_2 \psi_2 + \cdots = \sum_i c_i \psi_i
\]
\[
H\Phi = H \sum_i c_i \psi_i = \sum_i c_i H\psi_i = \sum_i c_i E\psi_i = E \sum_i c_i \psi_i = E\Phi
\]
we normally choose our degenerate wavefunctions to be orthogonal (ie they do not overlap!)