iv) Second orthogonality theorem for characters

$$\frac{1}{h}\sum_{j=1}^{N_{ir}} \sqrt{c_k}\,\chi^j(\mathcal{C}_k)\,\sqrt{c_\ell}\,\chi^j(\mathcal{C}_\ell)^* = \delta_{k\ell}$$

this relation describes the orthogonality of the columns of the character table.

$$Q_{ik} = \sqrt{\frac{c_k}{h}}\,\chi^i(\mathcal{C}_k) \Rightarrow (Q^+)_{kj} = Q_{jk}^* = \sqrt{\frac{c_k}{h}}\,\chi^j(\mathcal{C}_k)^*$$

$k \in$ Classes
$i \in$ irrepresentations

$$(QQ^+)_{ij} = \sum_k Q_{ik}(Q^+)_{kj} = \sum_k \sqrt{\frac{c_k}{h}}\,\chi^i(\mathcal{C}_k)\,\chi^j(\mathcal{C}_k)^*\sqrt{\frac{c_k}{h}}$$

$$\frac{1}{h}\sum_k c_k\,\chi^i(\mathcal{C}_k)\,\chi^j(\mathcal{C}_k)^* \overset{(ii)}{=} \delta_{ij}$$

In matrix form $QQ^+ = \mathbb{1}_{N_2}$ $\quad N_2$ = Number of irreducible representations = Nclasses

$Q$ is unitary $\Rightarrow$ also $Q^+Q = \mathbb{1}$

$$(Q^+Q)_{k\ell} = \sum_i (Q^+)_{ki}\,Q_{i\ell} = \delta_{k\ell}$$

$$= \sum_i \sqrt{\frac{c_k}{h}}\,\chi^i(\mathcal{C}_k)^*\,\sqrt{\frac{c_\ell}{h}}\,\chi^i(\mathcal{C}_\ell) = \delta_{k\ell}$$

And, by taking the complex conjugation.

$$\frac{1}{h}\sum_{i=1}^{N_{ir}} \sqrt{c_k}\,\chi^i(\mathcal{C}_k)\,\sqrt{c_\ell}\,\chi^i(\mathcal{C}_\ell)^* = \delta_{k\ell}$$

$\Rightarrow k=\ell \quad \sum_i c_k|\chi^i(\mathcal{C}_k)|^2 = h \quad$ and, if $\mathcal{C}_k = E \quad c_k = 1 \quad \chi^i(E) = \ell_i$

$$\sum_i \ell_i^2 = h \;.$$

There are a number of important consequences of the orthogonality relations that we have just proven.

* Characters tell us if a representation is irreducible or not. Reducible representations do not respect the orthogonality relations we just proved.

* Characters tells us whether or not we have found ALL the irreducible representations.

  $D_3$ for example has order 6 $\Rightarrow$ it cannot have an irreducible representation of dimension 3.

* A necessary and sufficient condition that 2 irreducible representations are equivalent is that the characters are the same

$$\chi^i = \chi^j \quad \Rightarrow \quad v^i_k \equiv \frac{\sqrt{c_k}}{\sqrt{g}}\chi^i(\mathcal{C}_k) = v^j_k \equiv \frac{\sqrt{c_k}}{\sqrt{g}}\chi^j(\mathcal{C}_k)$$

but 2 non equivalent irreducible representations would generate $\vec{v}^i \perp \vec{v}^j$. The other way is trivial.

* The reduction of any reducible representation into its irreducible constituents is unique.

* The number of irreducible representations for Abelian groups (e.g. $C_n$) <u>is</u> the number of elements of the group.

$$\sum_j l_j^2 = h \quad \Rightarrow \quad l_j = 1 \quad \forall j$$

The irreducible representations have all dimension 1.

# SETTING UP CHARACTER TABLES

The character tables for all common groups are listed in books and articles. Nevertheless, as an application of the theorems that we have just proven we will now construct the character tables of 2 small groups: $D_3$ and $C_3$.

Before starting let us set up a certain number of rules derived from the orthogonality theorems:

$\boxed{A}$ # irr. repr. = # classes

$\boxed{B}$ $\sum_i l_i^2 = h$ — $l_i$ is the dimensionality of $\Gamma_i$; $h$ is the order of the group.

$\boxed{C}$ There is always a row of ones in the character table for the "identity" representation. For point groups think to the isomorphism to the transformation of (wave) functions and then take the 1-dimensional Hilbert space generated by a spherically symmetrical function.

$\boxed{D}$ The first column of the character table is $l_i$ since it is the trace of $\mathbb{1}_{l_i}$.

$\boxed{E}$ $\forall i : \Gamma_i \neq$ identity $\quad \sum_k c_k \chi^i(\mathcal{C}_k) = 0$

$\boxed{F}$ Normalization or Orthogonalization of rows $\quad \sum_k \chi^i(\mathcal{C}_k)\chi^{j*}(\mathcal{C}_k)\, c_k = h\,\delta_{ij}$

$\boxed{G}$ Normalization or Orthogonalization of columns $\quad \sum_i \chi^i(\mathcal{C}_k)\chi^i(\mathcal{C}_l) = \frac{h}{c_k}\delta_{kl}$

$\boxed{H}$ $\forall k : \mathcal{C}_k \neq E \quad \sum_i l_i \chi^i(\mathcal{C}_k) = 0$

$\boxed{D_3}$ $\quad E \quad 2C_3 \quad 3C_2'$ ← These are the 3 classes. 6 elements in total

- ⇒ 3 irreducible representations
- $6 = 1^2 + ?^2 + ?^2$ solution $1^2 + 1^2 + 2^2$.

Both notation of IR. Only specifies the dimensionality

| | $E$ | $2C_3$ | $3C_2'$ |
|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 |
| $\Gamma_1'$ | 1 | | |
| $\Gamma_2$ | 2 | | |

- Orthogonalization rows: $1 \cdot 1 + 2 \cdot ? + 3 \cdot ? = 0$

Remember that $|?| = 1$ since we are speaking of simmetry operations for a 1 dimensional representation.

| | $E$ | $2C_3$ | $3C_2'$ |
|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 |
| $\Gamma_1'$ | 1 | 1 | -1 |
| $\Gamma_2$ | 2 | .. | |

- Orthogonalization columns: $1 \cdot 2\times1 + 1 \cdot 2\times1 + 2 \cdot 2\times? = 0$

$? = -1$

| | $E$ | $2C_3$ | $3C_2'$ |
|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 |
| $\Gamma_1'$ | 1 | 1 | -1 |
| $\Gamma_2$ | 2 | -1 | 0 |

$1 \cdot 3\times1 + 1 \cdot 3\times-1 + 2 \cdot 3\times? = 0$

$? = 0$

$\boxed{C_3}$ $E \quad C_3^+ \quad C_3^-$ ← these are the 3 classes

=> 3 irreducible representations all 1 dimensional.

$3 = 1^2 + ?^2 + ?^2$ solution $1^2 + 1^2 + 1^2$

| | $E$ | $C_3^+$ | $C_3^-$ |
|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 |
| $\Gamma_1'$ | 1 | $a$ | $b$ |
| $\Gamma_1''$ | 1 | $c$ | $d$ |

$$\left.\begin{array}{l} 1 + a + b = 0 \\ 1 + c + d = 0 \end{array}\right\} \text{row orth}$$

$$\left.\begin{array}{l} 1 + a + c = 0 \\ 1 + b + d = 0 \end{array}\right\} \text{column orth}$$

$$\underbrace{\begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix}}_{\det = 0} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = \begin{pmatrix} -1 \\ -1 \\ -1 \\ -1 \end{pmatrix}$$

We can use another information coming from the multiplication table.

$(C_3^+)^2 = C_3^-$ and $(C_3^+)^3 = E$

$\Downarrow$

$a^2 = b$ $\qquad a^3 = 1 \Rightarrow a = \exp\left[i\frac{2\pi}{3}\right]$

$b = \exp\left[i\frac{4\pi}{3}\right]$

| | $E$ | $C_3^+$ | $C_3^-$ |
|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 |
| $\Gamma_1'$ | 1 | $\omega$ | $\omega^2$ |
| $\Gamma_1''$ | 1 | $c$ | $d$ |

$\omega + c = -1 \Rightarrow c = \omega^2$

$\omega^2 + d = -1 \Rightarrow d = \omega$

Since $\sum_{i=1}^{N} \omega^i = 0$ if $\omega^N = 1$.

| | $E$ | $C_3^+$ | $C_3^-$ |
|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 |
| $\Gamma_1'$ | 1 | $\omega$ | $\omega^2$ |
| $\Gamma_1''$ | 1 | $\omega^2$ | $\omega$ |

# Mulliken Notation for irreducible representations

| $l$ | Notation IR | $\chi(C_n)$ or $\chi(S_n)$ | $\chi(C_2')$ or $\chi(\sigma_v)$ | $\chi(\sigma_h)$ | $\chi(i)$ |
|---|---|---|---|---|---|
| 1 | A | +1 | | | |
| | B | -1 | | | |
| 1, (2, 3) | subscript 1 | | +1 | | |
| | subscript 2 | | -1 | | |
| 2 | E | | | | |
| 3 | T | | | | |
| 1, 2 or 3 | superscript ' | | | + | |
| | superscript " | | | − | |
| | subscript g | | | | + |
| | subscript u | | | | − |

example $D_3$

| | $E$ | $2C_3$ | $3C_2'$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 |
| $E_{(2)}$ | 2 | -1 | 0 |

How can we reduce a reducible representation? The basic idea is to use the orthogonality theorems for the characters.

Let's take a generic representation $\Gamma$. We know that by definition of irreducible representation

$$\Gamma = \bigoplus_{i=1}^{N_{ir}} c_i \Gamma^i$$

Correspondingly

$$\chi^{\Gamma}(R) = \sum_{i=1}^{N_{ir}} c_i \chi^{\Gamma^i}(R) \quad (*) \qquad \forall R \text{ in the group.}$$

N.B. $c_i$ has nothing to do with the order of the classes.

The relation (*) in page 78 can also be written for classes

$$(**) \qquad \chi^{\Gamma}(\mathcal{C}_k) = \sum_{i=1}^{N_{ir}} c_i \, \chi^{\Gamma^i}(\mathcal{C}_k) \qquad \forall\, k = 1, \dots, N_{classes}$$

But now we can use the I orthogonality theorem for characters

$$\sum_{k=1}^{N} \sqrt{\frac{c_k}{h}}\, \chi^{\Gamma^i}(\mathcal{C}_k) \sqrt{\frac{c_k}{h}}\, \chi^{\Gamma^j}(\mathcal{C}_k)^* = \delta_{ij} \qquad N = N_{ir} = N_{classes}$$

We take then (**), multiply by $c_k/h \, \chi^{\Gamma^j}(\mathcal{C}_k)^*$ and sum over k

$$\sum_{k=1}^{N} \frac{c_k}{h} \chi^{\Gamma^j}(\mathcal{C}_k)^* \chi^{\Gamma}(\mathcal{C}_k) = \sum_{i,k=1}^{N} \frac{c_i c_k}{h} \chi^{\Gamma^j}(\mathcal{C}_k)^* \chi^{\Gamma^i}(\mathcal{C}_k)$$

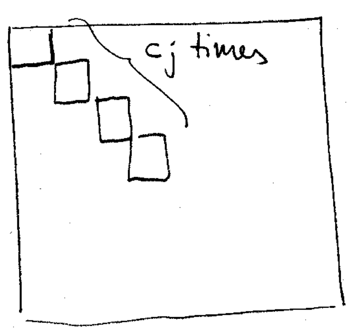
$$= \sum_{i=1}^{N} c_i \, \delta_{ij} = c_j$$

$$\boxed{c_j = \sum_{k=1}^{N_{cl}} \frac{c_k}{h} \chi^{\Gamma^j}(\mathcal{C}_k)^* \chi^{\Gamma}(\mathcal{C}_k)}$$

This is called REDUCTION FORMULA. It gives the coefficients of the expansion of a reducible representation in terms of its irreducible components.

the sizes of the blocks is $l_j$.

$\Gamma(R) =$



## Projection operator technique

Given a certain point group $\mathcal{G}$ we know that we can construct an isomorphism between this group and a group of operators $\hat{R}$ : $\hat{R}f(x) = f(R^{-1}x)$ $\forall\, x \in \mathbb{R}^3$. If $\mathcal{G}$ is the symmetry group for the Hamiltonian $\hat{H}$ we also know that $[\hat{H}, \hat{R}] = 0$ $\forall\, R \in \mathcal{G}$. $\Rightarrow$ $\hat{H}$ and each of the $\hat{R}$ have a common eigenvector basis. (N.B. In general this basis is not at the same time an eigenbasis for all $\hat{R}$.). Finding an eigenbasis for one of the operators $\hat{R}$ is as difficult as finding one for $\hat{H}$. On the other hand

① we know that all $\{\hat{R}\}$ are block diagonal with the same diagonal form in a specific basis (the IR-basis)

② In the IR-basis, as in all others $[\hat{H}, \hat{R}] = 0$
$\Rightarrow$ $\hat{H}$ has the same block diagonal structure
$\Rightarrow$ (Schur's lemma 1) Each block of $\hat{H}$ is just proportional to the identity matrix which imply that the size of the blocks gives the size of the symmetry induced degeneracies.

The technique used to construct the IR-basis is called projector operator technique.

Let's take a generic function belonging to the Hilbert space for our system. Since it can be written in terms of the eigenbasis for $\hat{H}$ $\Rightarrow$ it can be also written in the IR-basis

$$\phi(x) = \sum_j \sum_{\mu=1}^{l_j} \phi_\mu^j(x)\, b_\mu^j$$

where $j$ label the irreducible representations (N.B. in general they can appear more than once) and $l_j$ is the dimensionality of the $j$th representation. If $\hat{T}$ is the operator that correspond to the point symmetry $T$ $\Rightarrow$ by construction:

$$\hat{T}\,\phi_\mu^j(x) = \sum_{\nu=1}^{l_j} \Gamma^j(T)_{\nu\mu}\,\phi_\nu^j(x)$$

$$\Rightarrow \left(\frac{l_i}{h}\right) \sum_T \Gamma_{\sigma\sigma}^i(\hat{T})^* \,\hat{T}(\phi) = \left(\frac{l_i}{h}\right) \sum_T \Gamma_{\sigma\sigma}^i(T)^* \sum_{j\nu\mu} b_\mu^j \Gamma_{\nu\mu}^j(T)\,\phi_\nu^j$$

$$= \frac{l_i}{h} \sum_{j\mu\nu} \left[\sum_T \Gamma_{\sigma\sigma}^i(T)^* \Gamma_{\nu\mu}^j(T)\right] \phi_\nu^j\, b_\mu^j \quad \Big\downarrow \text{WOT}$$

$$= \sum_{j\mu\nu} \delta_{ij}\,\delta_{\sigma\nu}\,\delta_{\sigma\mu}\,\phi_\nu^j\, b_\mu^j = \phi_\sigma^i\, k_\sigma^i \qquad (*)$$

We have already found a way of extracting, from a generic vector $\phi$, the component in the subspace that "generates" the irreducible representation $j$. With abuse of notation the subspace that "generates" a certain representation is also called a representation.

$(*)$ is still not so practical since one should know all the $\Gamma_{\sigma\sigma}^i(T)$. But, if we sum also over $\sigma$ the elements of the matrix representation are not needed: the characters are enough.

$$\frac{l_i}{h} \sum_T \chi^i(T)^* \hat{T} \phi = \sum_\sigma \phi_\sigma^i b_\sigma^i \equiv \phi^i$$

It is clear that the coefficients $b_\sigma^i$ are not known a priori (the problem would be already solved!!) but it is also clear that, apart from normalization, $\phi^i$ is a good basis vector for the irreducible representation $\Gamma^i$. Since the normalization is (at this point) not relevant we can also get rid of the antiesthetic prefactor $l_i/h$ and define the <u>projection operator</u> relative to the irreducible representation $i$:

$$\boxed{\hat{P}^i = \sum_T \chi^i(T)^* \hat{T}}$$

<u>A practical note:</u>

* If the representation is one-dimensional and it appears only once in the reducible representation corresponding to the Hilbert space => $\phi^i$ is already an eigenstate for the Hamiltonian

* In case the representation has dimensionality > 1 or/and it appears more than once in the reducible representation associated to the Hilbert space ->

  A - the projection operator technique must be repeated until we find $c_i \cdot l_i$ linearly independent vectors.

  B - we cannot construct directly the eigenstates of $\hat{H}$

In summary, with what concerns the diagonalization problem Group Theory represents a clear help:

-1- Given the decomposition of the "Hilbert space" into irreducible representations

$$\Gamma^H = \bigoplus_{i=1}^{N_{IR}} c_i \, \Gamma^i \quad (*)$$

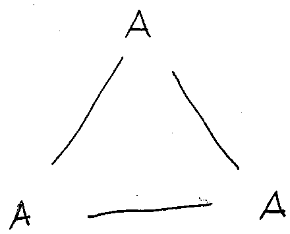
we know how to find a basis in H such that H is block diagonal with blocks of size $c_i \cdot l_i$ where $c_i$ appears in (*) and $l_i$ is the dimensionality of the $i^{th}$ irreducible representation. This defines the size of the problem: $S = \max_i (c_i \cdot l_i)$. If $S > 5$ the problem is not analytically solvable (in general). Numerically one can go much beyond.

-2- From (*) we already know, with the help of Schur's Lemma I that the spectrum of H contains many degeneracies. Each irreducible representation of tipe E or T contains 2 or 3 degenerate states.

We did not consider yet many aspects of group theory concerning spin (and the so called double groups), phonons (or better vibrons) with the associated "direct product representations" or crystal field theory which predicts the lifting of degeneracies due to lowering of the symmetry or the prediction of transition rates with symmetry arguments... But these topics would leads us to far from the scope of this course.

## An instructive (not so realistic) example:

Let's assume to have a molecule composed of 3 equal atoms which are at the vertices of an equilateral triangle.




The full symmetry point group for this "molecule" is $D_{3h}$.
For simplicity we will analyze the diagonalization of an Hamiltonian for this molecule with respect to the 2 subgroups:

$$C_3 \quad \text{and} \quad D_3$$

The character tables for these 2 groups have been constructed at pages 77 and 76 respectively.

| $C_3$ | | $E$ | $C_3^+$ | $C_3^-$ |
|---|---|---|---|---|
| $\Gamma_1$ | $A_1$ | 1 | 1 | 1 |
| $\Gamma_2$ | $E$ | 1 | $\omega$ | $\omega^2$ |
| $\Gamma_3$ | | 1 | $\omega^2$ | $\omega$ |

$$\omega = e^{2\pi i/3}$$

| $D_3$ | $E$ | $2C_3$ | $3C_2'$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 |
| $E$ | 2 | -1 | 0 |

In order to continue we have now to specify an hamiltonian for the system and an Hilbert space. Again for simplicity we assume that the molecular orbital for our molecule can be written as linear combination of atomic orbitals and we take a 1S orbital per atom.

We define the Hamiltonian in II quantization

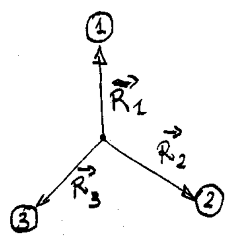
$$H = \sum_{\alpha\sigma} \varepsilon_1 \, c^{+}_{\alpha\sigma} c_{\alpha\sigma} + b\left(c^{+}_{\alpha\sigma} c_{\alpha+1\sigma} + c^{+}_{\alpha+1\sigma} c_{\alpha\sigma}\right) + U \, c^{+}_{\alpha\uparrow} c^{+}_{\alpha\downarrow} c_{\alpha\downarrow} c_{\alpha\uparrow}$$

$\alpha = 1,2,3$

Where $c^{+}_{\alpha\sigma}$ create an electron in the 1s orbital close to atom $\alpha$ and spin $\sigma$. This orbital is the $\psi_{1s}(\vec{r} - \vec{R}_\alpha)$. It is important to notice that in reality $\psi_{1s}(\vec{r})$ is just a function of $|\vec{r}|$.

The Hilbert space that we want to consider is the one of the states with one electron and spin $\uparrow$. (since $[S_z^{TOT}, H] = 0$ we know that the case with $\sigma = \downarrow$ will be equal).

$$\mathcal{H} = \mathrm{span}\left\{ \psi_{1s}(\vec{r} - \vec{R}_1), \psi_{1s}(\vec{r} - \vec{R}_2), \psi_{1s}(\vec{r} - \vec{R}_3) \right\}$$




The symmetry operators in $C_3$ and $D_3$ have an intuitive operator mapping: namely

$$C_3^{+} \longrightarrow \hat{C}_3^{+} : \quad \hat{C}_3^{+} f(\vec{r}) = f(R_{-2\pi/3, \hat{z}} \vec{r})$$

- in particular we can then construct a $3\times 3$ matrix representative for $\hat{C}_3^{+}$:

$$\hat{C}_3^{+} \psi_{1s}(\vec{r} - \vec{R}_1) = \psi_{1s}(R_{-2\pi/3, \hat{z}} \vec{r} - \vec{R}_1) = \psi_{1s}\left(R_{-2\pi/3, \hat{z}}\left(\vec{r} - R_{2\pi/3, \hat{z}} \vec{R}_1\right)\right)$$

$$= \psi_{1s}\left(\vec{r} - R_{2\pi/3, \hat{z}} \vec{R}_1\right) = \psi_{1s}(\vec{r} - \vec{R}_3)$$

And analogously

$$\hat{C}_3^{+} \psi_{1s}(\vec{r} - \vec{R}_2) = \psi_{1s}(\vec{r} - \vec{R}_1)$$
$$\hat{C}_3^{+} \psi_{1s}(\vec{r} - \vec{R}_3) = \psi_{1s}(\vec{r} - \vec{R}_2)$$

The matrix representative of $\hat{C}_3^+$ in $\mathcal{H}$ is thus:

$$\Gamma^{\mathcal{H}}(\hat{C}_3^+) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

Consequently $\Gamma^{\mathcal{H}}(\hat{C}_3^-) = \Gamma^{\mathcal{H}}[(\hat{C}_3^+)^{-1}] = [\Gamma^{\mathcal{H}}(C_3^+)]^{-1} = [\Gamma^{\mathcal{H}}(C_3^+)]^T$

$$\Gamma^{\mathcal{H}}(\hat{C}_3^-) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

Analolously we could also construct the matrix representations for the $\hat{C}_2'$ operators originated from $C_2'$ in $D_3$. But, since we are interested only in the characters of these matrix representatives, we can simply count for each transformation how many orbitals are transformed into themselves. This will give ones in the diagonal of the matrix representatives and thus influence the characters.

$C_3 \rightarrow \Gamma^{\mathcal{H}}: \quad 3 \quad 0 \quad 0 \quad \leftarrow$ set of characters

$D_3 \rightarrow \Gamma^{\mathcal{H}}: \quad 3 \quad 0 \quad 1$

At this point we can use the reduction formula in order to reduce the $\Gamma^{\mathcal{H}}$ of $C_3$ and $D_3$ in terms of irreducible representations:

$\boxed{C_3}$

$$c_{\Gamma_1} = \frac{1}{3}\left[(1\cdot 3) + (1\cdot 0) + (1\cdot 0)\right] = 1$$

$$c_{\Gamma_2} = \frac{1}{3}\left[(1\cdot 3) + (\omega\cdot 0) + (\omega^2\cdot 0)\right] = 1$$

$$c_{\Gamma_3} = \frac{1}{3}\left[(1\cdot 3) + (\omega^2\cdot 0) + (\omega\cdot 0)\right] = 1$$

$$\Gamma^{\mathcal{H}} = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \quad \text{with respect of } C_3$$

N.B. since $\omega + \omega^2 = -1$ also the check in terms of characters is easily done.

$\boxed{D_3}$

$$C_{A_1} = \frac{1}{6}\left[1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot 1\cdot 1\right] = 1$$

$$C_{A_2} = \frac{1}{6}\left[1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot(-1)\cdot 1\right] = 0$$

$$C_E = \frac{1}{6}\left[1\cdot 2\cdot 3 + 2\cdot(-1)\cdot 0 + 3\cdot 0\cdot 1\right] = 1$$

$$\Gamma^{\mathcal{H}} = A_1 \oplus E \quad \text{with respect of } D_3$$

As a last step, by means of the projection operator technique, we can now construct the IR-basis both for $C_3$ and $D_3$. I will take as "seed" for the projector $\varphi_{1s}(\vec{r} - \vec{R}_1) = \varphi_1$

$\boxed{C_3}$

$$\hat{P}^{\Gamma_1}\varphi_1 = 1\cdot\hat{E}\varphi_1 + 1\cdot\hat{C}_3^+\varphi_1 + 1\cdot\hat{C}_3^-\varphi_1 =$$
$$= \varphi_1 + \varphi_3 + \varphi_2 = \varphi_{\Gamma_1}$$

$$\hat{P}^{\Gamma_2}\varphi_1 = 1\cdot\hat{E}\varphi_1 + \omega\cdot\hat{C}_3^+\varphi_1 + \omega^2\cdot\hat{C}_3^-\varphi_1 =$$
$$= \varphi_1 + \exp\left(\frac{2\pi i}{3}\right)\varphi_3 + \exp\left(\frac{4\pi i}{3}\right)\varphi_2 = \varphi_{\Gamma_2}$$

$$\hat{P}^{\Gamma_3}\varphi_1 = 1\cdot\hat{E}\varphi_1 + \omega^2\cdot\hat{C}_3^+\varphi_1 + \omega\cdot\hat{C}_3^-\varphi_1 =$$
$$= \varphi_1 + \exp\left(\frac{4\pi i}{3}\right)\varphi_3 + \exp\left(\frac{2\pi i}{3}\right)\varphi_2 = \varphi_{\Gamma_3}$$

Since the irreducible representations are all of dimension 1, the set $(\varphi_{\Gamma_1}, \varphi_{\Gamma_2}, \varphi_{\Gamma_3})$ with a $\frac{1}{\sqrt{3}}$ normalization factor gives the eigenfunctions for the system.

In fact $\psi_{\Gamma_i} = \psi_\ell = \sum_{\alpha=1}^{3} \frac{1}{\sqrt{3}} e^{i\frac{2\pi}{3}\alpha\ell} \psi_\alpha$ $_{\ell=0,\pm1}$. The change of basis can be translated in terms of creation and annihilation operators as:

$$c^+_{\ell\sigma}|0\rangle = |\psi_{\ell\sigma}\rangle = \frac{1}{\sqrt{3}} \sum_{\alpha=1}^{3} e^{i\frac{2\pi}{3}\alpha\ell} |\psi_{\alpha\sigma}\rangle = \frac{1}{\sqrt{3}} \sum_{\alpha=1}^{3} e^{i\frac{2\pi}{3}\alpha\ell} c^+_{\alpha\sigma}|0\rangle$$

$$\Rightarrow \quad c^+_{\alpha\sigma} = \frac{1}{\sqrt{3}} \sum_{\ell} e^{-i\frac{2\pi}{3}\alpha\ell} c^+_{\ell\sigma} .$$

We are not interested into the interaction part of the Hamiltonian (at the moment) since it vanishes on the single particle Hilbert space.

$$H = \frac{1}{3} \sum_{\alpha\ell\ell'\sigma} \varepsilon\, e^{i\frac{2\pi}{3}\alpha(\ell-\ell')} c^+_{\ell\sigma} c_{\ell'\sigma} + b\,\frac{1}{3} \sum_{\alpha\ell\ell'\sigma} \left(e^{i\frac{2\pi}{3}[\alpha\ell-(\alpha+1)\ell']} + e^{i\frac{2\pi}{3}[(\alpha+1)\ell-\alpha\ell']}\right) c^+_{\ell} c_{\ell''}$$

$$= \sum_{\ell\ell'\sigma} \varepsilon\, \delta_{\ell\ell'} c^+_{\ell\sigma} c_{\ell'\sigma} + b \sum_{\ell\ell'\sigma} \left(e^{-i\frac{2\pi}{3}\ell''} + e^{+i\frac{2\pi}{3}\ell}\right) \delta_{\ell\ell'} c^+_{\ell} c_{\ell'}$$

$$= \sum_{\ell\sigma} \left[\varepsilon + 2b\cos\left(\frac{2\pi}{3}\ell\right)\right] c^+_{\ell\sigma} c_{\ell\sigma} .$$

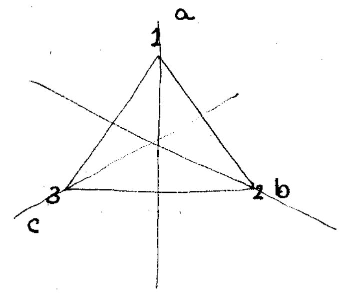
The eigenvalues are $\varepsilon + 2b\cos\left(\frac{2\pi}{3}\ell\right)$.

We notice already at this level that the eigenvalues with $\ell=1$ and $\ell=-1$ are degenerate. The theory nevertheless seems not to predict it. The answer comes from the analysis of the larger group $D_3$.

$\boxed{D_3}$ The projection operator technique for the $D_3$ group gives the following results:

$$\hat{P}^{A_1}\psi_1 = 1\cdot\hat{E}\,\psi_1 + 1\cdot\hat{C}_3^{+}\psi_1 + 1\cdot\hat{C}_3^{-}\psi_1 + 1\cdot\hat{C}'_{2a}\psi_1 + 1\cdot\hat{C}'_{2b}\psi_1 + 1\cdot\hat{C}'_{2c}\psi_1$$

$$= 2\psi_1 + 2\psi_2 + 2\psi_3 .$$




$\hat{C}'_{2a}\psi_1 = \psi_1 \qquad \hat{C}'_{2a}\psi_2 = \psi_3 \qquad \hat{C}'_{2a}\psi_3 = \psi_2$ etc.

$$\hat{P}^{E}\psi_1 = 2\hat{E}\cdot\psi_1 - 1\,\hat{C}_3^{+}\psi_1 - 1\,\hat{C}_3^{-}\psi_1 =$$

$$= 2\psi_1 - \psi_2 - \psi_3 = \psi_{E_1}$$

Notice that by using the $D_3$ group we have "a priori" informations about the degeneracy and we know that the E representation is bidimensional and degenerate. We look for the 2 basis vector by starting with the new seed $\psi_2$

$$\hat{P}^{E}\psi_2 = 2\hat{E}\,\psi_2 - 1\,\hat{C}_3^{+}\psi_2 - 1\,\hat{C}_3^{-}\psi_2 =$$

$$= 2\psi_2 - \psi_1 - \psi_3 = \psi_{E_2}$$

Now we can check that $\psi_{E_1}$ and $\psi_{E_2}$ are eigenvectors of H with the same eigenenergy:

$$\begin{vmatrix} \varepsilon & b & b \\ b & \varepsilon & b \\ b & b & \varepsilon \end{vmatrix}\begin{vmatrix} 2 \\ -1 \\ -1 \end{vmatrix} = \begin{vmatrix} 2\varepsilon - 2b \\ b - \varepsilon \\ b - \varepsilon \end{vmatrix} = (\varepsilon - b)\begin{vmatrix} 2 \\ -1 \\ -1 \end{vmatrix} \qquad \varepsilon - b = \varepsilon + 2b\cos\left(\frac{2\pi}{3}l\right) \quad l = \pm 1.$$

$$\begin{vmatrix} \varepsilon & b & b \\ b & \varepsilon & b \\ b & b & \varepsilon \end{vmatrix}\begin{vmatrix} -1 \\ 2 \\ -1 \end{vmatrix} = \begin{vmatrix} -\varepsilon + b \\ \varepsilon - 2b \\ -\varepsilon + b \end{vmatrix} = (\varepsilon - b)\begin{vmatrix} -1 \\ 2 \\ -1 \end{vmatrix}$$

Since $\psi_{E_1}$ and $\psi_{E_2}$ are linearly independent and $\psi_{A_1} = \psi_{T_1}$, the $C_3$ and $D_3$ diagonalizations coincide.