4. Basis functions

Consider a group $\mathcal{G}$ with symmetry operations R and symmetry operators $\hat{R}$. Moreover $\Gamma^j(\hat{R})$ is the irrep labelled by the index j.

Def: BASIS VECTORS are the vectors which span the vector space associated to a irreducible representation Γ^j. Each of the basis vectors is also called component or partner of the representation.

BASIS VECTOR = COMPONENT = PARTNER

Notation $|\Gamma^j, \mu\rangle$ $\mu = 1, \dots, l_j$ l_j is the dimension of the IR

$$\hat{R}\, |\Gamma^j, \mu\rangle = \sum_{\mu'} \Gamma^j_{\mu'\mu}(\hat{R})\, |\Gamma^j, \mu'\rangle$$

By definition of basis vector and of matrix representative $\Gamma^j(\hat{R})$.

Def. BASIS FUNCTIONS are basis vectors explicitly written in coordinate space

Notation $\phi^j_\mu(x,y,z)$ or $\phi^j_\mu(x)$ in a more compact form.

Wave functions are important examples of basis functions.

Example

D_3	E	$2C_3$	$3C_2'$	Basis functions	
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z	
E	2	-1	0	(x,y)	(xz, yz), (x^2-y^2, xy)

All polynomial of order n are vector spaces of dimension 3^n in which one can identify partners of irreducible representations.

<u>Theorem</u> Basis functions which are either partners of different irreducible unitary representations or are different partners of the same unitary irrep. are orthogonal.

<u>proof</u>:
Let's take $\phi^i_\mu(x)$ and $\phi^j_\nu(x)$ two different basis functions associated to $\mathcal{G}$

By definition, if $R \in \mathcal{G}$

$$\hat{R}\,\phi^i_\mu(x) = \sum_{\mu'} \Gamma^i_{\mu'\mu}(\hat{R})\,\phi^i_{\mu'}(x)$$

$$\hat{R}\,\phi^j_\nu(x) = \sum_{\nu'} \Gamma^j_{\nu'\nu}(\hat{R})\,\phi^j_{\nu'}(x)$$

Now let's consider the scalar product $(\phi^i_\mu, \phi^j_\nu) = \int dx\, \phi^{i*}_\mu(x)\,\phi^j_\nu(x)$

Due to the definition of symmetry operator $\hat{R} f(x) = f(R^{-1}x)$ we have

$$(\phi^i_\mu, \phi^j_\nu) = (\hat{R}\phi^i_\mu, \hat{R}\phi^j_\nu) = \sum_{\mu'\nu'} \Gamma^{i*}_{\mu'\mu}(\hat{R})\,\Gamma^j_{\nu'\nu}(\hat{R})\,(\phi^i_{\mu'}, \phi^j_{\nu'}) \quad \forall R \in \mathcal{G}$$

$$= \frac{1}{h}\sum_{R\in\mathcal{G}} \sum_{\mu'\nu'} \Gamma^{i}_{\mu'\mu}(\hat{R})\,\Gamma^j_{\nu'\nu}(\hat{R})\,(\phi^i_{\mu'}, \phi^j_{\nu'}) = \text{WOT}$$

$$= \sum_{\mu'\nu'} \frac{1}{l_i}\,\delta_{ij}\,\delta_{\mu'\nu'}\,\delta_{\mu\nu}\,(\phi^i_{\mu'}, \phi^j_{\nu'}) = \frac{1}{l_i}\,\delta_{ij}\,\delta_{\mu\nu} \sum_{\mu'} (\phi^i_{\mu'}, \phi^i_{\mu'}) \qquad \blacksquare$$

The determination of of the basis functions is particularly important in quantum mechanics. If $\mathcal{G}$ is a symmetry group for the system or even the group of the Hamiltonian $\Rightarrow$ $[\hat{H}, \hat{R}] = 0$ $\forall R \in \mathcal{G}$. In the vector space associated to a irrep of $\mathcal{G}$ $[H, \Gamma(\hat{R})] = 0 \Rightarrow H = \lambda \mathbb{1}_{l_j}$.
The irrep. basis $\Rightarrow$ allows to identify <u>SYMMETRY protected degeneracies</u> of the system.

4.1 | Projector operator technique

The projector operator technique allows to extract, known the characters of an irrep. basis functions for that irrep from a generic function. If the matrix representatives are known, it allows to extract all the partners of a irrep.

Def: PROJECTION OPERATORS are operators which transform a partner of an irrep. into another one:

$$\hat{P}^j_{\mu\nu} : \quad \hat{P}^j_{\mu\nu} | \Gamma^j, \nu \rangle = | \Gamma^j, \mu \rangle$$

Clearly, projection operator can operate on basis functions $\hat{P}^j_{\mu\nu} \phi^j_\nu(x) = \phi^j_\mu(x)$.

Theorem Projection operators can be expressed explicitly in terms of symmetry operators $\hat{R}$ and matrix representatives $\Gamma^j(\hat{R})$ of a specific irreducible representation j.

$$\hat{P}^j_{\mu\nu} = \frac{l_j}{h} \sum_R \Gamma^j_{\mu\nu}(\hat{R})^* \hat{R}$$

proof:

$$\frac{l_j}{h} \sum_R \Gamma^j_{\mu\nu}(\hat{R})^* \hat{R} | \Gamma^j, \nu \rangle \overset{\text{def of } \Gamma}{=} \frac{l_j}{h} \sum_R \Gamma^j_{\mu\nu}(\hat{R})^* \sum_{\mu'} \Gamma^j_{\mu'\nu}(\hat{R}) | \Gamma^j, \mu' \rangle$$

$$\overset{\text{WOT}}{=} \sum_{\mu'} \delta_{\mu\mu'} | \Gamma^j, \mu' \rangle = | \Gamma^j, \mu \rangle$$

■

We can now consider the effect of the projection operator as obtained by the previous theorem on a generic wave function $\phi(x)$. The latter, since it belongs to an Hilbert space left invariant by $\hat{R}$ $\forall R \in \mathcal{G}$ can be written as:

$$\phi(x) = \sum_{j'\mu'} b^{j'}_{\mu'} \phi^{j'}_{\mu'}(x)$$

The question on how to extract a basis function set of the irrep Γ^j is answered by the following theorem:

Theorem Let $\phi(x)$ a generic function $\phi : \mathbb{R}^3 \to \mathbb{C}$ belonging to a vector space invariant under the group $\mathcal{G} = \{\hat{R}\}$ where $\hat{R}$ is a functional associated to the point symmetry operation R. The projector operator

$$\boxed{\hat{P}^j = \sum_R \chi^{j*}(R)\,\hat{R}}$$

where $\chi^j(R)$ are the characters of the irrep Γ^j extracts the jth component of ϕ.

proof:

$$\hat{P}^j \phi(x) = \sum_R \chi^{j*}(R)\,\hat{R} \sum_{j'\mu'} b^{j'}_{\mu'} \phi^{j'}_{\mu'}(x) =$$

$$= \sum_{R\mu\nu} \Gamma^{j*}_{\mu\mu}(R)\, \Gamma^{j'}_{\nu\mu'}(R) \sum_{j'\mu'} b^{j'}_{\mu'} \phi^{j'}_{\mu'}(x) = \quad \text{(WOT)}$$

$$\frac{h}{\ell_j} \sum_{j'\mu'} \sum_{\mu\nu} \delta_{\mu\nu}\, \delta_{\mu\mu'}\, \delta_{jj'}\, b^{j'}_{\mu'} \phi^{j}_{\mu'}(x) = \sum_\mu \frac{h}{\ell_j}\, b^j_\mu \phi^j_\mu(x).$$

The coefficients b^j_μ are not known, but, apart from normalization $\hat{P}^j\phi(x)$ is a good basis vector for Γ^j, being a linear combination of $\{\phi^j_\mu\}$.

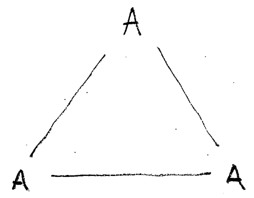
Notice:
+ If the irrep. is 1-dimensional and it appears only once in the reducible representation corresponding to the Hilbert space $\hat{P}^j$ delivers an eigenstate of the Hamiltonian.
+ If the representation has dimension >1 or it appears more than once in the reducible representation associated to the Hilbert space

A - the projection $\hat{P}^j \phi$ should be repeated until we find $\alpha_i \cdot l_i$ linearly independent vectors

B - We construct $\Gamma^j_{\mu\nu}$ and proceed with the projectors $\hat{P}^j_{\mu\nu}$

4.2 An instructive (not so realistic) example

Let's assume to have a "molecule" composed of 3 equal atoms sitting at the vertices of an equilateral triangle:



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

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

The character tables for these groups have been explicity constructed

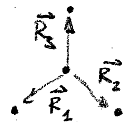
	C_3	E	C_3^+	C_3^-
Γ_1	A_1	1	1	1
Γ_2	E	1	ω	ω^2
Γ_3		1	ω^2	ω

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

$\omega = e^{-i 2\pi/3}$ (phase sign taken negative for convenience)

The nomenclature E for the set of 2 complex irreps of C_3 stems from the level degeneracy in presence of time reversal symmetry.

We fix for simplicity a Hilbert space of spherically symmetric (s type) orbitals centered around the 3 atomic positions:



$$\mathcal{H} = \operatorname{span}\{\psi_s(\vec r - \vec R_1),\ \psi_s(\vec r - \vec R_2),\ \psi_s(\vec r - \vec R_3)\}$$

We approach the problem from the point of view of the linear combination of atomic orbitals LCAO.

The symmetry operations in C_3 and D_3 have an intuitive operator mapping

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

We can construct the 3x3 matrix representative for $\hat C_3^+$ in $\mathcal{H}$:

$$\hat{C}_3^+ \psi_s(\vec r - \vec R_1) = \psi_s(R_{-2\pi/3\,\hat z}\,\vec r - \vec R_1) = \psi_s(\cancel{R_{-2\pi/3\,\hat z}}(\vec r - R_{2\pi/3,\hat z}\vec R_1))$$

$$= \psi_s(\vec r - \vec R_2). \qquad \psi_s(\vec r) = \psi_s(|\vec r|)$$

And, analogously:

$$\hat{C}_3^+ \psi_s(\vec r - \vec R_2) = \psi_s(\vec r - \vec R_3)$$
$$\hat{C}_3^+ \psi_s(\vec r - \vec R_3) = \psi_s(\vec r - \vec R_1)$$

The matrix representative of $\hat C_3^+$ in $\mathcal{H}$ reads, thus:

$$\Gamma^{\mathcal{H}}(\hat C_3^+) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

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

$$\Gamma^{\mathcal{H}}(\hat C_3^-) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

We could construct all the matrix representatives for C_3' operations in D_3. Instead, we concentrate on the characters, i.e. the diagonal element and count how many orbitals are transformed into themselves by the corresponding operator. We readily obtain the character sets:

$$C_3 \to \Gamma^{\#}: \quad 3 \quad 0 \quad 0$$

$$D_3 \to \Gamma^{\#}: \quad 3 \quad 0 \quad 1$$

At this point we can use the reduction formula in order to split $\Gamma^{\#}$ of C_3 and D_3 in terms of irrep.

$\boxed{C_3}$

$$\left.\begin{aligned} \alpha_{\Gamma_1} &= \frac{1}{3}\left[(1\cdot 3) + (1\cdot 0) + (1\cdot 0)\right] = 1 \\ \alpha_{\Gamma_2} &= \frac{1}{3}\left[(1\cdot 3) + (\omega^{*}\cdot 0) + (\omega^{2*}\cdot 0)\right] = 1 \\ \alpha_{\Gamma_3} &= \frac{1}{3}\left[(1\cdot 3) + (\omega^{2*}\cdot 0) + (\omega^{*}\cdot 0)\right] = 1 \end{aligned}\right\} \Rightarrow \Gamma^{\#} = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3$$

$\boxed{D_3}$

$$\left.\begin{aligned} \alpha_{A_1} &= \frac{1}{6}\left(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot 1\cdot 1\right) = 1 \\ \alpha_{A_2} &= \frac{1}{6}\left(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot(-1)\cdot 1\right) = 0 \\ \alpha_{E} &= \frac{1}{6}\left(1\cdot 2\cdot 3 + 2(-1)\cdot 0 + 3\cdot 0\cdot 1\right) = 1 \end{aligned}\right\} \quad \Gamma^{\#} = A_1 \oplus \underset{\text{degeneracy!}}{\underset{\uparrow}{E}}$$

As a last step, by means of the projector operator technique, we construct the irrep basis both for C_3 and D_3.

As "seed" for the projectors we take $\varphi_s(\vec{r}-\vec{R}_1) \equiv \varphi_1$ and we introduce the notation $\varphi_\alpha := \varphi_s(\vec{r}-\vec{R}_\alpha)$.

$\boxed{C_3}$

$$\hat{P}^{\Gamma_1}\,\psi_1 = 1\cdot\hat{E}(\psi_1) + 1\cdot\hat{C}_3^+(\psi_1) + 1\,\hat{C}_3^-(\psi_1) =$$
$$= \psi_1 + \psi_2 + \psi_3 = \psi^{\Gamma_1}$$

$$\hat{P}^{\Gamma_2}\,\psi_1 = 1\cdot\hat{E}(\psi_1) + \omega^*\cdot\hat{C}_3^+(\psi_1) + \omega^{2*}\hat{C}_3^-(\psi_1) =$$
$$= \psi_1 + e^{+i2\pi/3}\,\psi_2 + e^{+i4\pi/3}\,\psi_3 = \psi^{\Gamma_2}$$

$$\hat{P}^{\Gamma_3}\,\psi_1 = 1\cdot\hat{E}(\psi_1) + \omega^{2*}\,C_3^+(\psi_1) + \omega^*\hat{C}_3^-(\psi_1) =$$
$$= \psi_1 + e^{+i4\pi/3}\,\psi_2 + e^{+i2\pi/3}\,\psi_3 = \psi^{\Gamma_3}$$

Since the irreps are all of dimension 1, the set $\{\psi^{\Gamma_1}, \psi^{\Gamma_2}, \psi^{\Gamma_3}\}$ gives the eigenfunctions of the system. We are here concentrating on the single particle wavefunctions. Similarly we could consider the two particle Hilbert space spanned by the vectors:

$$\psi_{12} := \langle \vec{r}_1, \vec{r}_2 | c_1^+ c_2^+ | \phi \rangle = \psi_s(\vec{r}_1 - \vec{R}_1)\,\psi_s(\vec{r}_2 - \vec{R}_2) - \psi_s(\vec{r}_1 - \vec{R}_2)\,\psi_s(\vec{r}_2 - \vec{R}_1)$$
$$\psi_{23} := \langle \vec{r}_1, \vec{r}_2 | c_2^+ c_3^+ | \phi \rangle = \psi_s(\vec{r}_1 - \vec{R}_2)\,\psi_s(\vec{r}_2 - \vec{R}_3) - \psi_s(\vec{r}_1 - \vec{R}_3)\,\psi_s(\vec{r}_2 - \vec{R}_2)$$
$$\psi_{31} := \langle \vec{r}_1, \vec{r}_2 | c_3^+ c_1^+ | \phi \rangle = \psi_s(\vec{r}_1 - \vec{R}_3)\,\psi_s(\vec{r}_2 - \vec{R}_1) - \psi_s(\vec{r}_1 - \vec{R}_1)\,\psi_s(\vec{r}_2 - \vec{R}_3)$$

with analogous results, since $\Gamma^{\mathcal{H}_2}$: 3 0 0.

$$\hat{P}^{\Gamma_1}\,\psi_{12} = \psi_{12} + \psi_{23} + \psi_{31} = \varphi_0\sqrt{3}$$
$$\hat{P}^{\Gamma_2}\,\psi_{12} = \psi_{12} + \omega^*\psi_{23} + \omega^{2*}\psi_{31} = \varphi_1\sqrt{3}$$
$$\hat{P}^{\Gamma_3}\,\psi_{12} = \psi_{12} + \omega^{2*}\psi_{23} + \omega^*\psi_{31} = \varphi_2\sqrt{3}$$

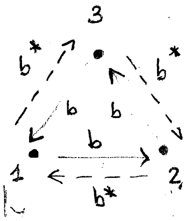
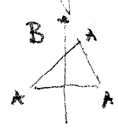
We can now verify the predictions above on a specific model.

Notice: for the moment we do not consider the spin degree of freedom. We will return to it at a later point.

We now consider the Hamiltonian, in II quantization:

$$H = \sum_{\alpha=1}^{3}\left(\varepsilon\, c^+_\alpha c_\alpha + b\, c^+_{\alpha+1} c_\alpha + b^* c^+_\alpha c_{\alpha+1} + V\, c^+_\alpha c_\alpha c^+_{\alpha+1} c_{\alpha+1}\right)$$

with the condition $c^+_4 \equiv c^+_1$.

Graphically we have  which shows that, if $b \neq b^*$ the symmetry is really lowered to C_3 and it returns to Δ_3 for $b = b^*$. A different hopping parameter depending on the direction of the tunnelling arises due to a threading magnetic flux, which also explains the reduction of symmetry. 

Let's introduce the shorthand notation

$l = 1, \dots 3$ $\quad \psi^{\Gamma_l} =: \psi_{l-1}$ $\quad$ where $\psi_l = \frac{1}{\sqrt{3}} \sum_\alpha e^{+i\frac{2\pi}{3} l\alpha} \psi_\alpha$, in terms of creator operators $c^+_l = \frac{1}{\sqrt{3}} \sum_\alpha e^{+i\frac{2\pi}{3} l\alpha} c^+_\alpha$. This equation can be inverted to obtain $c^+_\alpha = \frac{1}{\sqrt{3}} \sum_{l=0}^{2} e^{-i\frac{2\pi}{3} l\alpha} c^+_l$.

$$H = \sum_{\alpha=1}^{3}\left[\frac{1}{3}\sum_{ll'} e^{-i\frac{2\pi}{3}(l-l')\alpha}\left(\varepsilon + b e^{-i\frac{2\pi}{3}l} + b^* e^{+i\frac{2\pi}{3}l'}\right)\right] c^+_l c_{l'} + V \sum_{\alpha=1}^{3} c^+_\alpha c^+_{\alpha+1} c_{\alpha+1} c_\alpha$$

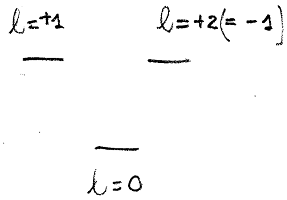
$$= \sum_l \left[\varepsilon + 2|b| \cos\left(\frac{2\pi}{3} l - \pi - \phi\right)\right] c^+_l c_l + V \sum_{\alpha=1}^{3} c^+_\alpha c^+_{\alpha+1} c_{\alpha+1} c_\alpha \qquad b = |b| e^{i(\pi+\phi)}$$

For the subspace with 1 particle the interaction vanishes and we obtain

$\varepsilon_0 = \varepsilon_{\Gamma_1} = \varepsilon - 2|b| \cos(\phi)$ $\qquad \phi = 0$ corresponds to no magnetic field

$\varepsilon_{+1} = \varepsilon_{\Gamma_2} = \varepsilon - 2|b| \cos\left(\frac{2\pi}{3} - \phi\right)$

$\varepsilon_{-1} = \varepsilon_{\Gamma_3} = \varepsilon - 2|b| \cos\left(\frac{2\pi}{3} - \phi\right)$



The degeneracy is lifted for $\phi \neq n\frac{2\pi}{3}$ $\quad n \in \mathbb{Z}$.

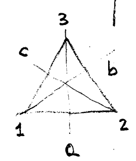
The two particles sector works similarly (for $\phi = 0$)

$$\varphi_0 = c^+_{l=1} c^+_{l=-1} |0\rangle \qquad \mathcal{E}_0 = 2\varepsilon + 2|b| + V$$

$$\varphi_1 = c^+_{l=1} c^+_{l=0} |0\rangle \qquad \mathcal{E}_1 = 2\varepsilon - |b| + V$$

$$\varphi_2 = c^+_{l=-1} c^+_{l=0} |0\rangle \qquad \mathcal{E}_2 = 2\varepsilon - |b| + V$$

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



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

$$= \psi_1 + \psi_2 + \psi_3 + \psi_2 + \psi_1 + \psi_3 = 2(\psi_1 + \psi_2 + \psi_3)$$

$$\hat{P}^{E} \psi_1 = 2\hat{E}(\psi_1) - 1\,\hat{C}_3^+ \psi_1 - 1\,\hat{C}_3^- \psi_1 = 2\psi_1 - \psi_2 - \psi_3 = \psi_1^E$$

By using the D_3 group we know "a priori" about the degeneracy of the E representation. We look for the second basis vector by starting with a new "seed".

$$\hat{P}^{E} \psi_2 = 2\psi_2 - \psi_3 - \psi_1 = \psi_2^E .$$

We can check that ψ_1^E and ψ_2^E are both eigenvectors of H with the same eigenenergy:

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

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