4. Basis functions

Suppose to have a group G with symmetry elements R and symmetry operators $\hat{P}_R$. $\Gamma^{(n)}$ is the irreducible representation labelled by the index n. Each irreducible representation is associated to a set of basis vectors

Def: COMPONENT or PARTNER: each of the basis vectors associated to an irreducible representation is called component or partner of the representation

Def: Basis function is simply a basis vector expressed explicitly in coordinate space.

example: D_3

			E	$2C_3$	$3C_2'$
x^2+y^2, z^2		A_1	1	1	1
	R_z, z	A_2	1	1	-1
(xz, yz)	(x,y)	E	2	-1	0
(x^2-y^2, xy)	(R_x, R_y)				

all polinomial of order 1 can be written as linear combination of x, y, z.

all polinomial of order 2 can be written as a linear combination of x^2, y^2, z^2, xy, yz, xz.

Notice that no polynomial of order 1 is a partner of A_1.
2 " " 2 are possible partners of A_1

Projection operator technique

Given a certain point group G we know that we can construct an isomorphism between this group and a group of operator $\hat{R}$: $\hat{R}f(x) = f(R^{-1}x) \quad \forall x \in \mathbb{R}^3$. If G is the symmetry group for the Hamiltonian $\hat{H}$ we also know that $[\hat{H}, \hat{R}] = 0 \quad \forall R \in G$. $\Rightarrow$ $\hat{H}$ 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 $\hat{H}$ => it can be also written in the IR-basis

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

where j labels the inequivalent 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 corresponds to the point symmetry T => by construction:

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

$$\Rightarrow \left(\frac{\ell_i}{h}\right) \sum_T \Gamma^i_{\sigma\sigma}(\hat{T})^* \hat{T}(\phi) = \left(\frac{\ell_i}{h}\right) \sum_T \Gamma^i_{\sigma\sigma}(T)^* \sum_{j\nu\mu} b_\mu^j \Gamma^j_{\nu\mu}(T)\, \phi_\nu^j$$

$$= \frac{\ell_i}{h} \sum_{j\mu\nu} \left[\sum_T \Gamma^i_{\sigma\sigma}(T)^* \Gamma^j_{\nu\mu}(T)\right] \phi_\nu^j\, b_\mu^j \qquad \downarrow \text{WOT}$$

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

We have already found a way of extracting, from a generic vector ϕ, the component in the subspace that "generates" the inequivalent 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 $\Gamma^i_{\sigma\sigma}(T)$. But, if we sum also over σ 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_σ^i are not known a priori (the problem would be already solved!!) but it is also clear that, apart from normalization, ϕ^i is a good basis vector for the irreducible representation Γ^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 $\Rightarrow$ ϕ^i is already an eigenstate for the Hamiltonian

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

  A - the projection operator technique must be repeated until we find $\phi_i \cdot e_i$ 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

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

we know how to find a basis in H such that H is block diagonal with blocks of size $\alpha_i \cdot \ell_i$ where α_i appears in (*) and ℓ_i is the dimensionality of the i^{th} irreducible representation. This defines the size of the problem: $S = \max_i (\alpha_i \cdot \ell_i)$. 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 type $\tilde{t}$ or T contains 2 or 3 degenerate states.

Projection operators $\hat{P}_{kl}^{(\Gamma_n)}$ (following Dresselhaus)

The projection operators $\hat{P}_{kl}^{(\Gamma_n)}$ are defined by the relation

$$\hat{P}_{kl}^{(\Gamma_n)} \, | \Gamma_n l \rangle \equiv | \Gamma_n k \rangle$$

where $|\Gamma_n l\rangle$ and $|\Gamma_n k\rangle$ are partners of the irreducible representation Γ_n.

Theorem: The projection operators $\hat{P}_{kl}^{(\Gamma_n)}$ are given explicitly by the relation

$$\hat{P}_{kl}^{(\Gamma_n)} = \sum_R A_{kl}(R) \, \hat{R}$$

where $A_{kl}(R) = \frac{l_n}{h} \, D^{(\Gamma_n)}(R)^*_{kl}$ and $D^{(\Gamma_n)}(R)^*_{kl}$ is the complex conjugate of the matrix element kl for the matrix representative of the group element R in the irreducible representation Γ_n.

proof

$$| \Gamma_n k \rangle = \hat{P}_{kl}^{(\Gamma_n)} \, | \Gamma_n l \rangle = \sum_R A_{kl}(R) \, \hat{R} \, | \Gamma_n l \rangle$$

project on $\langle \Gamma_n k |$

$$1 = \sum_R A_{kl}(R) \underbrace{\langle \Gamma_n k | \hat{R} | \Gamma_n l \rangle}_{D^{(\Gamma_n)}(R)_{kl}}$$

WOT

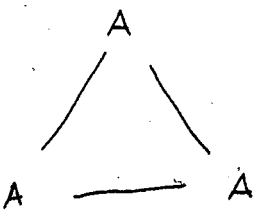
$$\sum_R D^{(\Gamma_n)}(R)^*_{kl} \, D^{(\Gamma_n)}(R)_{kl} = \frac{h}{l_n}$$

$\Rightarrow$ we can identify $A_{kl}(R) = \frac{l_n}{h} \, D^{(\Gamma_n)}(R)^*_{kl}$.

■

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

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

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

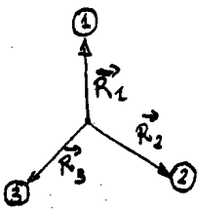
$$H = \sum_{\alpha\sigma} \varepsilon_1 \, c^{+}_{\alpha\sigma} c_{\alpha\sigma} + b\left(c^{+}_{\alpha\sigma} c_{\alpha+1\sigma} + c^{+}_{\alpha+1\sigma} c_{\alpha\sigma} \right) + U \, c^{+}_{\alpha\uparrow} c^{+}_{\alpha\downarrow} c_{\alpha\downarrow} c_{\alpha\uparrow}$$

$\alpha = 1,2,3$

Where $c^{+}_{\alpha\sigma}$ create an electron in the 1s orbital close to atom α and spin σ. 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 $[S^{Tot}_z, H] = 0$ we know that the case with $\sigma = \downarrow$ will be equal).

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



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

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

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

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

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

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

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

Analogously 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.

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

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

C_3

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

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

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

$$\Gamma^{HP} = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \qquad \text{with respect of } C_3$$

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

D_3

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

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

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

$$\Gamma^{HP} = A_1 \oplus E \qquad \text{with respect of } D_3$$

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 $\psi_{1s}(|\vec{r} - \vec{R}_1|) = \psi_1$

C_3

$$\hat{P}^{\Gamma_1}\psi_1 = 1\cdot \hat{E}\psi_1 + 1\cdot \hat{C}_3^{+}\psi_1 + 1\cdot \hat{C}_3^{-}\psi_1 =$$

$$= \psi_1 + \psi_3 + \psi_2 = \psi_{\Gamma_1}$$

$$\hat{P}^{\Gamma_2}\psi_1 = 1\cdot \hat{E}\psi_1 + \omega\cdot \hat{C}_3^{+}\psi_1 + \omega^2\cdot \hat{C}_3^{-}\psi_1 =$$

$$= \psi_1 + \exp\left(\frac{2\pi i}{3}\right)\psi_3 + \exp\left(\frac{4\pi i}{3}\right)\psi_2 = \psi_{\Gamma_2}$$

$$\hat{P}^{\Gamma_3}\psi_1 = 1\cdot \hat{E}\psi_1 + \omega^2\cdot \hat{C}_3^{+}\psi_1 + \omega\cdot \hat{C}_3^{-}\psi_1 =$$

$$= \psi_1 + \exp\left(\frac{4\pi i}{3}\right)\psi_3 + \exp\left(\frac{2\pi i}{3}\right)\psi_2 = \psi_{\Gamma_3}$$

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

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

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

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

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

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

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

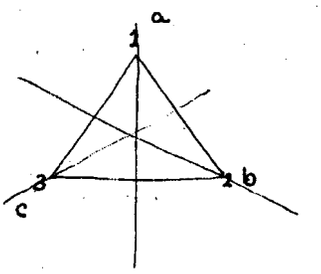
$$= \sum_{\ell\sigma} \left[\varepsilon + 2b \cos\left(\tfrac{2\pi}{3}\ell\right) \right] c^\dagger_{\ell\sigma} c_{\ell\sigma} .$$

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.

D_3 The projection operator technique for the D_3 group gives the following results.

$$\hat{P}^{A_1}\psi_1 = 1\cdot\hat{E}\,\psi_1 + 1\cdot\hat{C}_3^{+}\psi_1 + 1\cdot\hat{C}_3^{-}\psi_1$$
$$+ 1\cdot\hat{C}'_{2a}\psi_1 + 1\cdot\hat{C}'_{2b}\psi_1 + 1\cdot\hat{C}'_{2c}\psi_1$$
$$= 2\psi_1 + 2\psi_2 + 2\psi_3 .$$



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

$$\hat{P}^{E}\psi_1 = 2\hat{E}\cdot\psi_1 - 1\hat{C}_3^{+}\psi_1 - 1\hat{C}_3^{-}\psi_1 =$$
$$= 2\psi_1 - \psi_2 - \psi_3 = \psi_{E_1}$$

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