As a last argument of the course we take the 9th chapter which fits more naturally into the discussion.

9. Transition between electronic states

In this section we deal with selection rules. Given an interaction Hamiltonian H' we ask the question whether

$$\langle \psi_\alpha | H' | \psi_\beta \rangle$$

vanishes or not, where ψ_α and ψ_β are eigenstates of the Hamiltonian H_0.

In principle the answer is easy: $\langle \psi_\alpha | H' | \psi_\beta \rangle$ is a number and if it does not transform as a number it must vanish.

9.1 Electromagnetic interaction as a perturbation.

The canonical way to insert electromagnetic fields into an Hamiltonian is

$$H = \frac{1}{2m} \left(p - \frac{e}{c} A \right)^2 + V$$

Expanding up to first order in $\frac{eA}{c}$

$$H = \frac{p^2}{2m} + V - \frac{e}{mc} \vec{p} \cdot \vec{A} = H_0 + H'_{em}$$

The symmetry (properties) of H'_{em} is in general lower than the one of H_0. This ensures that transitions between eigenstates of H_0 are possible due to perturbations.

9.2 Orthogonality of basis functions

H_0 defines a group: the group of the Hamiltonian of of the Schrödinger equation.

The first point is to determine selection rules for H_0, namely the orthogonality of basis functions

$$H_0 \longmapsto \text{Group of } H_0 \longmapsto \underset{\substack{\uparrow \\ \text{IR}}}{\Gamma^j} \longrightarrow \underset{\substack{\uparrow \\ \text{basis functions.}}}{\boxed{\varphi_\alpha^{(j)}}}$$

Theorem Two basis functions which belong either to different irreducible representations or to different columns (rows) of the same representation are orthogonal.

proof $\phi_\alpha^{(i)}$ and $\varphi_{\alpha'}^{(i')}$ two basis functions for IR (i) and (i') and associated to the columns α and α' of their representation

$$\hat{P}_R \phi_\alpha^{(i)} = \sum_{j=1}^{l_i} D^{(i)}(R)_{\alpha j}\, \phi_j^{(i)}$$

$$\hat{P}_R \phi_{\alpha'}^{(i')} = \sum_{j'=1}^{l_{i'}} D^{(i')}(R)_{\alpha' j'}\, \varphi_{j'}^{(i')}$$

For the scalar product

$$\left(\phi_\alpha^{(i)}, \varphi_{\alpha'}^{(i')}\right) = \left(\hat{P}_R \phi_\alpha^{(i)}, \hat{P}_R \varphi_{\alpha'}^{(i')}\right) =$$ ← the scalar product is independent of the coordinate system!

$$= \sum_{jj'} D^{(i)}(R)^*_{\alpha j}\, D^{(i')}(R)_{\alpha' j'} \left(\phi_j^{(i)}, \varphi_{j'}^{(i')}\right)$$

$$= \frac{1}{h} \sum_R \sum_{jj'} D^{(i)}(R)^*_{\alpha j}\, D^{(i')}(R)_{\alpha' j'} \left(\phi_j^{(i)}, \varphi_{j'}^{(i')}\right)$$ ← The same argument is valid for all transformation R

$$\overset{\text{WOT}}{=} \frac{1}{l_i} \delta_{ii'} \delta_{\alpha\alpha'} \sum_{j=1}^{l_i} \left(\phi_j^{(i)}, \phi_j^{(i)}\right) = \delta_{ii'} \delta_{\alpha\alpha'}$$ if the basis functions are normalized.

$H_0 \varphi^{(i')}_{\alpha'} = E^{(i')}_{\alpha'} \varphi^{(i')}_{\alpha'}$ due to Schur's lemma => the orthogonality relation is a selection rule for H_0. In general, though, $H'\varphi$ does NOT transform like φ.

9.3 Direct product of two groups

$$G_A = \{E, A_2, \dots, A_{h_a}\}$$
$$G_B = \{E, B_2, \dots, B_{h_b}\}$$

are two groups of order h_a and h_b

=> Def: The direct product $G_A \otimes G_B$ is defined as

$$G_A \otimes G_B = E, A_2, \dots, A_{h_a}, B_2, A_2 B_2, \dots, A_{h_a} B_2, \dots, A_{h_a} B_{h_b}$$

and has $(h_a \times h_b)$ elements. It is easy to prove that $G_A \otimes G_B$ is also a group. Examples $D_{6h} = D_6 \otimes \{E, \sigma_h\} = D_6 \otimes \{E, i\}$.

9.4 Direct product of two irreducible representations

The solution to the problem comes from algebra. The direct product of matrices has the following definition

$$C = A \otimes B \qquad A_{ij} B_{kl} = C_{ik,jl}$$

C has simply double indices and if A is (2×2) and B (3×3) then C is (6×6).

Theorem: The direct product of the representations of the groups A and B forms a representation of the direct product group proof: We need to prove that

$$D^{(a)}_{ij}(A_i)\otimes D^{(b)}_{pq}(B_j) \stackrel{?}{=} \left(D^{(a\otimes b)}(A_iB_j)\right)_{ip,jq} \quad \text{is a good representation}$$

We know how to make the direct product of two matrices. But a representation is such if it respects the composition.

$$D^{(a\otimes b)}(A_kB_\ell)\, D^{(a\otimes b)}(A_{k'}B_{\ell'}) = D^{(a\otimes b)}(A_iB_j)$$

where $A_kA_{k'} = A_i$ and $B_\ell B_{\ell'} = B_j$

$$D^{(a\otimes b)}(A_kB_\ell)\, D^{(a\otimes b)}(A_{k'}B_{\ell'}) = \left[D^{(a)}(A_k)\otimes D^{(b)}(B_\ell)\right]\left[D^{(a)}(A_{k'})\otimes D^{(b)}(B_{\ell'})\right]$$

now in elements

$$\left[D^{(a\otimes b)}(A_kB_\ell)\, D^{(a\otimes b)}(A_{k'}B_{\ell'})\right]_{ip,jq} =$$

$$= \sum_{sr}\left[D^{(a)}(A_k)\otimes D^{(b)}(B_\ell)\right]_{ip,sr}\left[D^{(a)}(A_{k'})\otimes D^{(b)}(B_{\ell'})\right]_{sr,jq}$$

$$= \sum_{sr} D^{(a)}(A_k)_{is}\, D^{(b)}(B_\ell)_{pr}\, D^{(a)}(A_{k'})_{sj}\, D^{(b)}(B_{\ell'})_{rq} =$$

$$= \sum_{s} D^{(a)}(A_k)_{is}\, D^{(a)}(A_{k'})_{sj} \sum_{r} D^{(b)}(B_\ell)_{pr}\, D^{(b)}(B_{\ell'})_{rq} =$$

$$= D^{(a)}(A_kA_{k'})_{ij}\, D^{(b)}(B_\ell B_{\ell'})_{pq} = D^{(a)}(A_i)_{ij}\, D^{(b)}(B_j)_{pq} = D^{(a\otimes b)}(A_iB_j)_{ip,jq}.$$

Further one can prove that: if A and B are different groups ∎
$\Rightarrow D^{(a\otimes b)}$ is irreducible if (a) and (b) have this property. Further notice that in the proof we never assumed that A_iB_j could not be performed.

If A and B belong to the same group

$$\left[D^{(\ell_1\otimes\ell_2)}(A)\right]_{ip,jq} := D^{(\ell_1)}(A)_{ij}\, D^{(\ell_2)}(A)_{pq}$$

$$\left[D^{(\ell_1\otimes\ell_2)}(B)\right]_{ip,jq} := D^{(\ell_1)}(B)_{ij}\, D^{(\ell_2)}(B)_{pq}$$

one has to prove that the composition is respected

$$D^{(\ell_1\otimes\ell_2)}(AB) = D^{(\ell_1\otimes\ell_2)}(A)\, D^{(\ell_1\otimes\ell_2)}(B).$$

In components

$$\left[D^{(\ell_1\otimes\ell_2)}(AB)\right]_{ip,jq} = D^{(\ell_1)}(AB)_{ij}\, D^{(\ell_2)}(AB)_{pq} =$$

$$= \sum_{rs} D^{(\ell_1)}(A)_{ir}\, D^{(\ell_1)}(B)_{rj}\, D^{(\ell_2)}(A)_{ps}\, D^{(\ell_2)}(B)_{sq} =$$

$$= \sum_{rs} D^{(\ell_1\otimes\ell_2)}(A)_{ip,rs}\, D^{(\ell_1\otimes\ell_2)}(B)_{rs,jq}$$

end of the proof ∎

Nevertheless if ℓ_1 and ℓ_2 are irreducible $\ell_1\otimes\ell_2$ is, in general, REDUCIBLE.

9.5 Characters for the direct product

Theorem

- $\chi^{(a\otimes b)}(A_k B_\ell) = \chi^{(a)}(A_k)\, \chi^{(b)}(B_\ell)$

- $\chi^{(\ell_1\otimes\ell_2)}(R) = \chi^{(\ell_1)}(R)\, \chi^{(\ell_2)}(R)$

proof – $\chi^{(a\otimes b)}(A_k B_\ell) = \sum_{ip}\left[D^{(a\otimes b)}(A_k B_\ell)\right]_{ip,ip} = \sum_i D^{(a)}(A_k)_{ii} \sum_p D^{(b)}(B_\ell)_{pp} =$

$$= \chi^{(a)}(A_k)\, \chi^{(b)}(B_\ell)$$

$$\chi^{(l_1\otimes l_2)}(R) = \sum_{ip}\left[D^{(l_1\otimes l_2)}(R)\right]_{ip,ip} =$$

$$= \sum_i D^{(l_1)}(R)_{ii} \sum_p D^{(l_2)}(R)_{pp} = \chi^{(l_1)}(R)\,\chi^{(l_2)}(R)$$

Since for both (l_1) and (l_2) χ is a class function $\Rightarrow R \to \mathbb{C}$. ■

As we have already applied many times. We can check the reducibility of the character system for $(l_1 \otimes l_2)$ using the reduction formula

$$\chi^{(\lambda)}(R)\,\chi^{(\mu)}(R) = \sum_\nu a_{\lambda\mu,\nu}\,\chi^{(\nu)}(R)$$

$$a_{\lambda\mu,\nu} = \frac{1}{h}\sum_{\mathcal{C}_\alpha} N_{\mathcal{C}_\alpha}\,\chi^{(\nu)}(\mathcal{C}_\alpha)^*\left[\chi^{(\lambda)}(\mathcal{C}_\alpha)\,\chi^{(\mu)}(\mathcal{C}_\alpha)\right]$$

for the simple examples like $D_{4h} = D_4 \otimes \{E, i\}$ we have already used this property for constructing character tables with associated gerade and ungerade representations.

9.6 Selection rules in group theoretical terms

$$\left(\psi_\alpha^{(i)},\, H'\,\phi_{\alpha'}^{(i')}\right)$$

$$\downarrow \qquad \downarrow \qquad \downarrow$$

$$\Gamma^i \otimes \sum_j \Gamma^j \otimes \Gamma^{i'}$$

If this product of representations of the Schrödinger eq. group does NOT contain $A_1 \Rightarrow (\ ,\ ) = 0$!

Simpler $\sum_j \Gamma^j \otimes \Gamma^{i'}$ should contain Γ^i.

9.7 Examples of selection rules

$$H'_{em} = -\frac{e}{mc}\,\vec{p}\cdot\vec{A}$$

$\vec{A}$ → invariant under

$\vec{p}$ → transforms like a vector

Let us consider the cubic group O_h. The vector $\vec{p}$ transforms in O_h like T_{1u}. Now, if we assume a starting wave function of type T_{2g}

$$\begin{array}{cccccccccccc} & & E & 8C_3 & 3C_2 & 6C_2 & 6C_4 & i & 8iC_3 & 3iC_2 & 6iC_2 & 6iC_4 \\ \chi(T_{1u}\otimes T_{2g}) & = & [\,9 & 0 & 1 & -1 & -1 & -9 & 0 & -1 & 1 & 1\,] \end{array}$$

The reduction formula finally implies:

$$T_{1u}\otimes T_{2g} = A_{2u}\oplus E_u \oplus T_{1u}\oplus T_{2u}$$

which sets the selection rules. If the system symmetry is lowered to D_{4h}

$$z \to A_{2u}$$
$$(x,y) \to E_u$$

$\Rightarrow$ H_{em} transforms like $A_{2u}\oplus E_u$ in D_{4h}. A state with symmetry T_{2g} goes to states with $E_g \oplus B_{2g}$ in D_{4h} (see chrystal field discussion)

$$E_g \otimes (A_{2u}\oplus E_u) = E_u \oplus (A_{1u}+A_{2u}+B_{1u}+B_{2u})$$

and analogously for the other term. In general one sees that the lower the symmetry the less restrictive the selection rules.