Crystal and Symmetries

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1 Introduction

Take1 a lattice with point group symmetry operations {G} leaving it invariant. The group elements are 3×3 unitary matrices. Unlike Bloch translation symmetry which simplifies our problem significantly, these point group symmetries can reduce computations by a factor of 3 or 24. Major significance is in getting the selection rules, as in which transitions are allowed in presence of external potentials (which can cause transition between electron states).

2 Mathematics Preliminary

What we want to study is how functions (can be wavefunctions) transform under action of the group, i.e.,

$$\psi_i(G\mathbf{r}) = \sum_j A(G)_{ij}\psi_j(\mathbf{r}). \tag{1}$$

This way we can find the matrices A(G). The set of matrices {A} is called a **representation of the group**. The matrices A and the group elements can all be taken to be unitary ($A^\dagger = A^{-1}$ and $G^\dagger = G^{-1}$).
Two representations $\{A^{(n)}\}$ and $\{A^{(m)}\}$ are **equivalent** if there exists a single matrix N such that the below holds for all elements of the group.

$$N^{-1}A^{(n)}(G)N = A^{(m)}(G) \tag{2}$$

Also, if we can decompose all matrices of our representation in some basis to Block diagonal form, then our representation is called **reducible**. To derive the main results like the great orthogonality theorem, we consider a matrix M, which is defined by a matrix X (choice of X could be arbitrary)

$$M = \sum_G A^{(m)}(G)XA^{(n)}(G^\dagger). \tag{3}$$

Then we see that

$$\begin{aligned}
A^{(m)}(G)M &= \sum_{G'} A^{(m)}(G)A^{(m)}(G')XA^{(n)}(G'^{\dagger}) \\
&= \sum_{G'} A^{(m)}(GG')XA^{(n)}(G'^{\dagger}) \\
&= \sum_{G'} A^{(m)}(G')XA^{(n)}(G'^{\dagger}G) \quad \text{(replace } G' \to G^{\dagger}G') \\
&= \sum_{G'} A^{(m)}(G')XA^{(n)}(G'^{\dagger})A^{(n)}(G) = MA^{(n)}.
\end{aligned} \tag{4}$$

So, for $\{A^{(n)}\}$ and $\{A^{(m)}\}$ representations to not be equivalent; the matrix M must be non-invertible. In the same way we can take a conjugate transpose of this to get a relation for matrix $M^{\dagger}$. We define a matrix, now $P = M + M^{\dagger}$, this matrix P now also satisfies

$$A^{(m)}(G)P = PA^{(n)}(G) \tag{5}$$

where P is now a hermitian matrix (as $P^{\dagger} = P$). Since, P is Hermitian, we can now diagonalize it and find the orthonormal basis. Then we write all the matrices $\{A^{(n)}\}, \{A^{(m)}\}$ and P in this basis.

Q. How do we know if our representations are irreducible?
If even a single off diagonal term (for all elements in group) in our representation (in the basis defined previously) is 0, then it's reducible. We can see that by taking $n = m$ in the equation above in our diagonal basis, that implies

$$A(G)_{ij}P_{jj} = P_{ii}A(G)_{ij}, \tag{6}$$

so, either $P_{ii} = P_{jj}$ or $A(G)_{ij} = 0$. If for any ij, let's say $A(G)_{12}$ is 0, then that means no transformation can take $G\psi_1$ to ψ_2 and vice versa. Hence, the wavefunctions generated by $G\psi_1$ and $G\psi_2$ are disjoint. So, if our **representation is irreducible then all the eigenvalues of P must be same**. If the representation is reducible we get irreducible blocks in this basis. If eigenvalues of a 10-dimensional representation are let's say $P_{11} = P_{22} = P_{33} = 1.2, P_{44} = P_{55} = 1.6$ and other eigenvalues are all distinct. Then we have reduced our representation to one 3-dimensional, one 2-dimensional and five 1-dimensional representation.

For different non-equivalent $\{A^{(n)}\}$ and $\{A^{(m)}\}$ representations which are irreducible, it turns out that the Hermitian matrix P has all eigenvalues which are zero.

Schur's Lemma: For two irreps $\{A^{(n)}\}$ and $\{A^{(m)}\}$ if $SA^{(n)}(G) = A^{(m)}S$ for all G in the group $\{G\}$, then either the two representations are equivalent or $S = 0$. If $m = n$ and again we have a S, for which the previous relation holds true for an irrep; then $S \propto 1$.

If we take our matrix X with only a single non-zero element at position $\beta\gamma$ ($X_{ij} = \delta_{i\beta}\delta_{j\gamma}$), then using Eqn. (3)

$$M_{\alpha\delta} = \sum_{G,i,j} A^{(m)}(G)_{\alpha i}\delta_{i\beta}\delta_{j\gamma}A^{(n)}(G^{\dagger})_{j\delta} = \sum_{G} A^{(m)}(G)_{\alpha\beta}A^{(n)}(G^{\dagger})_{\gamma\delta}. \tag{7}$$

For the matrix M, we know it satisfies Eqn. (4). hence, by Schur's lemma, we can say that all elements of matrix M should be zero, unless $m = n$, in which case the matrix should be a multiple of identity matrix.

$$\sum_{G} A^{(m)}(G)_{\alpha\beta}A^{(n)}(G^{\dagger})_{\gamma\delta} = \delta_{mn}\delta_{\alpha\delta}C_{\beta\gamma} \tag{8}$$

The precise multiple depends only on what matrix X we start with or in other words only on $\beta\gamma$. To find that constant we sum over *alpha* and set $\delta = \alpha$ and $n = m$. This simplifies our relation as

$$\begin{aligned} \implies \sum_{\alpha}\sum_{G} A^{(m)}(G)_{\alpha\beta}A^{(m)}(G^{\dagger})_{\gamma\alpha} &= \sum_{G} A^{(m)}(G^{\dagger}G)_{\gamma\beta} = \ell C_{\beta\gamma} \\ = \sum_{G} A^{(m)}(G^{\dagger}G)_{\gamma\beta} = |G|\delta_{\gamma\beta} &\implies C_{\beta\gamma}\frac{|G|}{\ell}\delta_{\gamma\beta} \end{aligned} \tag{9}$$

where ℓ is the dimension of the representation $\{A^{(m)}\}$. This gives us our **grand orthogonality theorem**:

$$\sum_{G} A^{(m)}(G)_{\alpha\beta}A^{(n)}(G^{\dagger})_{\gamma\delta} = \frac{|G|}{\ell}\delta_{mn}\delta_{\alpha\delta}\delta_{\gamma\beta} \tag{10}$$

Now, we can divide the elements in a group into classes (these classes are all disjoint) and elements i and j are in the same class if $gg_ig^{-1} = g_j$ for any $g \in G$. We define a quantity called character of a representation

$$\chi(G) = \mathrm{Tr}[A(G)]. \tag{11}$$

All the group elements in the same class will have the same character (by trace cyclicity property). So, now we write our orthogonality theorem in terms of characters as

$$\sum_{G,\alpha,\gamma} A^{(m)}(G)_{\alpha\alpha}A^{(n)}(G^{\dagger})_{\gamma\gamma} = \frac{|G|}{\ell}\sum_{\alpha,\gamma}\delta_{mn}\delta_{\alpha\gamma} = |G|\delta_{nm} \tag{12}$$

$$\implies \sum_{k} N_k\chi^{(m)}(C_k)\chi^{(n)*}(C_k) = |G|\delta_{nm} \tag{13}$$

where the sum over k is over distinct classes C_k. This equation provides a **sure-shot test whether a representation is irreducible or not**, i.e., if the sum of trace squared over all matrices of a representation is $|G|$ then and only then the representation is irreducible otherwise it will be greater than $|G|$.another important result (proof in Murnaghan 1938) is that **the number of classes equals the number of irreps**. With this result we can write the trace orthogonality relation in another form as

$$\sum_k N_n \chi^{(k)}(C_n)\chi^{(k)*}(C_m) = |G|\delta_{nm}. \tag{14}$$

This can be proved by making the matrices $Q_{mk} = \sqrt{N_k/|G|}\chi^{(m)}(C_k)$ and $Q'_{km} = \sqrt{N_k/|G|}\chi^{(m)}(C_k)$ which now satisfy

$$\sum_k Q_{mk}Q'_{km} = \delta_{nm}. \tag{15}$$

Hence, the matrix Q' is inverse of matrix Q, so they should multiply to identity as $\sum_k Q'_{mk}Q_{km} = \delta_{nm}$, from which Eqn (14) follows. The characters of irreps can be written in a table, with the class in the rows and the irrep in the column. This representation is called the **character table**. We know that identity will be a class with only one element, and in all the representations of the element identity it will be represented as the identity matrix. Hence, from Eq. (14) it follows

$$\sum_m d_m^2 = |G|, \tag{16}$$

where $\chi^{(m)}(E) = d_m$, is the dimension of the representation and the sum over m is over all irreps of the group. Note: It is often possible to find the character table from just the trace orthogonality relations. See Marder (CMP 2010) for an example of finding the character table of the group D_{3d} (crystallographic point group, naming in Schönflies notation).