SYMMETRY

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Point-group symmetry operations. The action of a crystal symmetry operation $\hat{S}$ on coordinates is given by:

$$(\hat{S}\mathbf{r}) \equiv \mathbf{r}' = O^{-1}\mathbf{r} - \mathbf{f} \longrightarrow \mathbf{r}'_\alpha = O^{-1}_{\alpha\beta} r_\beta - f_\alpha = O_{\beta\alpha} r_\beta - f_\alpha$$

where O is a real unitary matrix generating a rotation ($O^{-1} = O^\dagger$), $\mathbf{f}$ is a fractional translation. Let us transform to crystal coordinates:

$$\mathbf{r} = s_1\mathbf{a}_1 + s_2\mathbf{a}_2 + s_3\mathbf{a}_3, \qquad s_i = \mathbf{b}_i \cdot \mathbf{r}, \quad \text{and} \quad t_i = \mathbf{b}_i \cdot \mathbf{f}$$

where $\mathbf{a}_i$ and $\mathbf{b}_j$ are the primitive vectors for the direct and reciprocal lattice, respectively. Since $\mathbf{a}_i$ are in a_0 units and $\mathbf{b}_j$ in $2\pi/a_0$ units, $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$ holds. Then, in crystal coordinates:

$$s'_i = \mathbf{b}_i \cdot \mathbf{r}' = b_{i\alpha} O_{\beta\alpha} s_j a_{j\beta} - \mathbf{b}_i \cdot \mathbf{f}$$

that is,

$$s'_i = S_{ji} s_j - t_i, \quad S_{ji} = a_{j\beta} O_{\beta\alpha} b_{i\alpha}.$$

The reverse transformation from crystal to cartesian coordinates is:

$$O_{\beta\alpha} = a_{i\alpha} S_{ji} b_{j\beta}.$$

The product of two symmetry operations $S^{(1)}$ and $S^{(2)}$:

$$s'_i = S^{(1)}_{ji} s_j - t^{(1)}_i, \quad s''_l = S^{(2)}_{il} s'_i - t^{(2)}_l = S^{(2)}_{il} S^{(1)}_{ji} s_j - S^{(2)}_{il} t^{(1)}_i - t^{(2)}_l$$

so

$$S_{jl} = S^{(1)}_{ji} S^{(2)}_{il}, \quad t_l = S^{(2)}_{il} t^{(1)}_i + t^{(2)}_l.$$

Symmetrization in G-space. Effect of symmetry on Kohn-Sham orbitals:

$$\hat{S}\psi(\mathbf{r}) = \psi(O^{-1}\mathbf{r} - \mathbf{f}).$$

Orbitals are Bloch states with wavevector $\mathbf{k}$, expanded into a plane-wave basis set:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}},$$

thus:

$$\begin{aligned}
\hat{S}\psi_k(\mathbf{r}) &= \sum_{\mathbf{G}} c_{\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot(O^{-1}\mathbf{r}-\mathbf{f})} \\
&= \sum_{\mathbf{G}} c_{\mathbf{k}}(\mathbf{G}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{f}} e^{iO(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\
&= \sum_{\mathbf{G}} \left(c_{\mathbf{k}}(O^{-1}\mathbf{G}) e^{-i(\mathbf{k}+O^{-1}\mathbf{G})\cdot\mathbf{f}} \right) e^{i(O\mathbf{k}+\mathbf{G})\cdot\mathbf{r}},
\end{aligned}$$

that is:

$$\hat{S}\psi_{\mathbf{k}}(\mathbf{r}) \equiv \psi_{O\mathbf{k}}(\mathbf{r}), \qquad c_{O\mathbf{k}}(\mathbf{G}) = c_{\mathbf{k}}(O^{-1}\mathbf{G})e^{-i(\mathbf{k}+O^{-1}\mathbf{G})\cdot\mathbf{f}}.$$

Let us move to crystal coordinates. For **G**-vectors and **k**-points:

$$\mathbf{G} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3, \qquad h_i = \mathbf{a}_i \cdot \mathbf{G}, \quad \text{and} \quad \chi_i = \mathbf{a}_i \cdot \mathbf{k},$$

and (note the reversed indices wrt the real-space case)

$$h'_i = a_{i\alpha}O_{\beta\alpha}h_j b_{j\beta} = a_{i\alpha}\left(a_{k\beta}S_{lk}b_{l\alpha}\right)b_{j\beta}h_j = S_{ij}h_j.$$

Symmetrization of the charge density. Let us introduce the non-symmetrized charge density

$$\rho^{ns}(\mathbf{r}) = \sum_{\mathbf{k}\in IBZ} w_{\mathbf{k}}|\psi_{\mathbf{k}}(\mathbf{r})|^2,$$

where the sum is over the Irreducible Brillouin Zone and $w_{\mathbf{k}}$ are the weights of the **k**-points (i.e. how many independent k-points there are in the star of **k**). The true charge density is given by

$$\rho(\mathbf{r}) = \frac{1}{N_s}\sum_{\hat{S}}(\hat{S}\rho^{ns}(\mathbf{r})) = \frac{1}{N_s}\sum_{n=1}^{N_s}\rho^{ns}(O_n^{-1}\mathbf{r} - \mathbf{f}_n),$$

where N_s is the number of symmetry operations in the group. Since the charge density is symmetric, $\hat{S}\rho(\mathbf{r}) = \rho(O_n^{-1}\mathbf{r} - \mathbf{f}_n) = \rho(\mathbf{r})$ holds.

In **G**-space, one has

$$\hat{S}\rho^{ns}(\mathbf{r}) = \sum_{\mathbf{G}}\rho^{ns}(\mathbf{G})e^{i\mathbf{G}\cdot(O^{-1}\mathbf{r}-\mathbf{f})} = \sum_{\mathbf{G}}\left(\rho^{ns}(O^{-1}\mathbf{G})e^{-iO^{-1}\mathbf{G}\cdot\mathbf{f}}\right)e^{i\mathbf{G}\cdot\mathbf{r}}$$

that is:

$$\rho(\mathbf{G}) = \frac{1}{N_s}\sum_{n=1}^{N_s}\rho^{ns}(O_n^{-1}\mathbf{G})e^{-iO_n^{-1}\mathbf{G}\cdot\mathbf{f}_n}.$$

Since the charge density is symmetric,

$$\hat{S}\rho(\mathbf{r}) = \sum_{\mathbf{G}}\rho(\mathbf{G})e^{i\mathbf{G}\cdot(O^{-1}\mathbf{r}-\mathbf{f})} = \sum_{\mathbf{G}}\rho(O^{-1}\mathbf{G})e^{-iO^{-1}\mathbf{G}\cdot\mathbf{f}}e^{i\mathbf{G}\cdot\mathbf{r}},$$

that is, $\rho(O^{-1}\mathbf{G}) = \rho(\mathbf{G})e^{iO^{-1}\mathbf{G}\cdot\mathbf{f}}$.