Here we extend the formalism of inversion parity as treated in [1] to our group theory needs.

Let us denote the representations equivalent to Wigner D-matrices under proper rotations as Γ_j^W. Semiconductor point groups can typically be direct products of proper point groups with C_i or semi-direct products with C_s. In both cases, we have the notion of inversion parity–an angular momentum eigenstate can behave one of two ways under inversion ($\vec{r} \to -\vec{r}$):

1. $\hat{i}\,|\Psi\rangle = |\Psi\rangle$, the state is invariant under inversion. We say this state is *gerade.*
2. $\hat{i}\,|\Psi\rangle = -\,|\Psi\rangle$, the state is invariant under inversion. We say this state is *ungerade.*

Under the assumption that every improper point group can be constructed as a direct or semi-direct product of a proper point group with one of the two improper groups isomorphic to Z_2, there always exists a parity irrep Γ_P, which is defined as

$$\chi^{(\Gamma_P)}\,(\text{rotation}) = 1, \chi^{(\Gamma_P)}\,(\text{rotoinversion}) = -1$$

Atomic band orbitals, eigenstates of angular momentum operators, are integer-l spherical harmonics in spatial representations. We know the parity of these:

$$\hat{i}Y_{lm} = (-1)^l Y_{lm}$$

Hence, the representation of a basis $|l, m\rangle\,, m = -l, \ldots l$ becomes

$$\Gamma_l^{\text{ang}} = \begin{cases} \Gamma_{j=l}^W & l \text{ is even} \\ \Gamma_{j=l}^W \otimes \Gamma_P & l \text{ is odd} \end{cases}$$

Or, defining direct exponention as $\Gamma^n \equiv \bigotimes_{i=1}^n \Gamma$, we can write this more neatly as

$$\Gamma_l^{\text{ang}} = \Gamma_{j=l}^W \otimes {\Gamma_P}^l$$

From standard results, we know that angular momentum coupling can be represented as a direct sum of angular representations:

$$\Gamma_l^{\text{ang}} \otimes \Gamma_{l'}^{\text{ang}} = \bigoplus_{l''=|l-l'|}^{l''=l+l'} \Gamma_{l''}^{\text{ang}}$$

We can characterise this expression for a group element g:

$$\chi^{\left(\Gamma_l^{\text{ang}}\right)}(g)\chi^{\left(\Gamma_{l'}^{\text{ang}}\right)}(g) = \sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^{\text{ang}}\right)}(g)$$

Expanding this into a direct product of the proper representations Γ_j^W, which are always gerade, we obtain

$$\chi^{\left(\Gamma_l^W\right)}(g)\chi^{\left(\Gamma_{l'}^W\right)}(g)\left[\chi^{(\Gamma_P)}(g)\right]^{l+l'} = \sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g)\left[\chi^{(\Gamma_P)}(g)\right]^{l''}$$

However, this is obviously wrong, since the left side of the equation possesses an inversion parity, but the right side doesn't. To illustrate, consider G to be a direct product of a proper point group H with the group $C_i = \hat{E}, \hat{\imath}$. Then each element $g \in G$ can be written as $g = (h \in H, c \in C_i)$. From the definition of the parity representation, we have

$$\chi^{(\Gamma_P)}(g = (h \in H, c \in C_i)) = \begin{cases} 1 & c = \hat{E} \\ -1 & c = \hat{\imath} \end{cases}$$

And, consequently

$$\chi^{(\Gamma_P)}((h \in H, c \in C_i) \cdot (\hat{E}, \hat{\imath})) = -\chi^{(\Gamma_P)}((h \in H, c \in C_i))$$

Consider two elements in G: a rotation g and its corresponding rotoinversion $g' = g \cdot (\hat{E}, \hat{\imath})$. Then find the characters of g, g' in the angular momentum coupling representation for $l + l'$ odd:

$$\begin{aligned}
\chi^{\left(\Gamma_{\text{coupling}}\right)}(g) &= \chi^{\left(\Gamma_l^W\right)}(g)\chi^{\left(\Gamma_{l'}^W\right)}(g)\left[\chi^{(\Gamma_P)}(g)\right]^{l+l'} \\
&= \chi^{\left(\Gamma_l^W\right)}(g)\chi^{\left(\Gamma_{l'}^W\right)}(g) \\
\chi^{\left(\Gamma_{\text{coupling}}\right)}(g') &= \chi^{\left(\Gamma_l^W\right)}(g')\chi^{\left(\Gamma_{l'}^W\right)}(g')\left[\chi^{(\Gamma_P)}(g')\right]^{l+l'} \\
&= -\chi^{\left(\Gamma_l^W\right)}(g')\chi^{\left(\Gamma_{l'}^W\right)}(g') \\
\chi^{\left(\Gamma_{\text{coupling}}\right)}(g') &= -\chi^{\left(\Gamma_{\text{coupling}}\right)}(g)
\end{aligned}$$

Applying this relation to the right sides of the coupling equation:

$$\begin{aligned}
\sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g')\left[\chi^{(\Gamma_P)}(g')\right]^{l''} &= -\sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g)\left[\chi^{(\Gamma_P)}(g)\right]^{l''} \\
\sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g')(-1)^{l''} &= -\sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g)
\end{aligned}$$

Since Γ_j^W is defined on proper rotations, we have $\chi^{\left(\Gamma_j^W\right)}(g) = \chi^{\left(\Gamma_j^W\right)}(g')$. Hence

$$\sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g)(-1)^{l''} = -\sum_{l''=|l-l'|}^{l''=l+l'} \chi^{\left(\Gamma_{l''}^W\right)}(g)$$

This obviously isn't true for a general element g and values of l, l', since on the left side each other term of the sum has a different sign than its corresponding term on the right side.

Possible resolution? My conjecture: the decomposition of a direct product of two angular momentum eigenstate basis representations cannot be simply equated to a direct sum of similar representations when rotoinversions are introduced, since inversion parity needs to be preserved. Therefore the terms in the sum should pick up factors of Γ_P depending on the parities of l, l', and l''.

$$\text{My proposed solution: } \Gamma_l^{\text{ang}} \otimes \Gamma_{l'}^{\text{ang}} = \bigoplus_{l''=|l-l'|}^{l''=l+l'} \Gamma_{l''}^{\text{ang}} \otimes [\Gamma_P]^{l+l'-l''}$$

To truly prove this proposal, the fundamental nature of angular momentum coupling must be carried out.

References

[1] Shiau, S.-Y., Combescot, M. (2021), Missing understanding of the phase factor between valence-electron and hole operators. SEMICONDUCTORS, Vol. **55**, No. 9, pp. 1068