Notes on symmetrization of PAW equations

Notation:

- $R^a$, $R^b$: Atomic positions
- $\mathcal{R}$: Rotation (characterized by angles $\alpha$, $\beta$, and $\gamma$)
- $\sigma$: Non-primitive translation
- $\mathcal{R}r + \sigma$: Space group operation on a general position $r$

Suppose that a given space group operation $(\mathcal{R}, \sigma)$ transforms a lattice position “a” → “b”:

$$R^b = \mathcal{R}R^a + \sigma.$$  (1)

Then, we can write:

$$R^a = \mathcal{R}^{-1}(R^b - \sigma).$$  (2)

Transformation of the spherical harmonic functions:

$$Y_{lm}(\mathcal{R}r) = \sum_{m'} Y_{lm'}(\hat{r}) D^l_{m'm}(\mathcal{R})$$  (3)

Here,

$$D^l_{m'm}(\mathcal{R}) \equiv D^l_{m'm}(\alpha, \beta, \gamma) = e^{-i\alpha m'} d^l_{m'm}(\cos \beta)e^{-i\gamma m'},$$  (4)

according to the convention of M. E. Rose, *Elementary Theory of Angular Momentum*, John Wiley & Sons, Inc. 1957. For $m' \geq m$,

$$d^l_{m'm}(\cos \beta) = \frac{\Gamma((l-m)!(l+m')!)}{\Gamma((l+m)!(m'-m)!)^{\frac{1}{2}}} \left(\cos \frac{\beta}{2}\right)^{2l-(m'-m)} \left(-\sin \frac{\beta}{2}\right)^{m'-m}$$

$$\times \sqrt{\Gamma((m'-m+m+1)!)} F_1(m' - l; -m - l; m' - m + 1; -\tan^2 \frac{\beta}{2})$$

(5)

This equation can generate all the rotation matrices needed by use of some of the following identities:

$$d^l_{m'm}(\cos \beta) = d^l_{m'm'}(-\cos \beta)$$  (6)

$$D^l_{m'm}(\mathcal{R}) = (-1)^l D^l_{m'm}(\mathcal{R})^{-1},$$  (7)

where $\mathcal{R}^{-1}$ is the inversion of $\mathcal{R}$.

We can determine the Euler angles $\alpha$, $\beta$, and $\gamma$ for a given rotation matrix $\mathcal{R}$ by noting that the nine components of the rotation matrix are given by (in Rose’s convention):

$$\mathcal{R}_{xx} = \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma$$

$$\mathcal{R}_{xy} = \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma$$
\[
\mathcal{R}_{xz} = -\sin \beta \cos \gamma \\
\mathcal{R}_{yx} = -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma \\
\mathcal{R}_{yy} = -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma \\
\mathcal{R}_{yz} = \sin \beta \\
\mathcal{R}_{zx} = \cos \alpha \sin \beta \\
\mathcal{R}_{zy} = \sin \alpha \sin \beta \\
\mathcal{R}_{zz} = \cos \beta
\]

Therefore, given the rotation matrix \( \mathcal{R} \), we can determine the Euler angles using

\[
\cos \beta = \mathcal{R}_{zz}
\]

\[
\sin \beta = \sqrt{1 - \mathcal{R}_{zz}^2}
\]

If \( \sin \beta \neq 0 \), then

\[
e^{-i\alpha} = \frac{\mathcal{R}_{xx} - i\mathcal{R}_{xy}}{\sin \beta}
\]

and

\[
e^{-i\gamma} = \frac{\mathcal{R}_{xz} + i\mathcal{R}_{yz}}{-\sin \beta}
\]

If \( \sin \beta = 0 \), then we can choose \( \gamma = 0 \), and

\[
e^{-i\alpha} = \frac{\mathcal{R}_{xx} - i\mathcal{R}_{xy}}{\mathcal{R}_{zz}}
\]

When there is inversion symmetry, we can treat one of the inversion pairs using the above equations, while the other is obtained using Eq. 7.

Once these matrices are determined we can symmetrize the \( W_{ij}^a \) coefficients by suming over the \( N_R \) symmetry operations denoted by \( \mathcal{R} \). Here we will use the notation \( i \) implies \( n_i l_i m_i \) while \( i' \) implies \( n_i' l_i' m_i' \):

\[
\langle W_{ij}^a \rangle_{\text{symmetrized}} = \frac{1}{N_R} \sum_{\mathcal{R}} \sum_{m_i' m_j'} W_{ij}^{a \mathcal{R}} \mathcal{D}_{m_i' m_i}^{l_i} (\mathcal{R}) \mathcal{D}_{m_j' m_j}^{l_j} (\mathcal{R})
\]