Notes on symmetrization of PAW equations

Notation:

$\mathbf{R}^a$, $\mathbf{R}^b$	Atomic positions
$\mathcal{R}$	rotation (characterized by angles α, β, and γ)
σ	non-primitive translation
$\mathcal{R}\mathbf{r} + \sigma$	space group operation on a general position $\mathbf{r}$

Suppose that a given space group operation $(\mathcal{R}, \sigma)$ transforms a lattice position "a" $\rightarrow$ "b':

$$\mathbf{R}^b = \mathcal{R}\mathbf{R}^a + \sigma. \tag{1}$$

Then, we can write:

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

Transformation of the spherical harmonic functions:

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

Here,

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

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

$$\begin{aligned} d^l_{m'm}(\cos\beta) \;&= \sqrt{\tfrac{(l-m)!(l+m')!}{(l+m)!(l-m')!}}\tfrac{1}{(m'-m)!}\left(\cos\tfrac{\beta}{2}\right)^{2l-(m'-m)}\left(-\sin\tfrac{\beta}{2}\right)^{m'-m} \\ &\times\ {}_2F_1(m'-l; -m-l; m'-m+1; -\tan^2\tfrac{\beta}{2}) \end{aligned} \tag{5}$$

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

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

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

where $\bar{\mathcal{R}} \equiv$ (inversion) $\times\mathcal{R}$.

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

$$\mathcal{R}_{xx} = \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma \tag{8}$$

$$\mathcal{R}_{xy} = \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma \tag{9}$$

$$\mathcal{R}_{xz} = -\sin\beta\cos\gamma \tag{10}$$

$$\mathcal{R}_{yx} = -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma \tag{11}$$

$$\mathcal{R}_{yy} = -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma \tag{12}$$

$$\mathcal{R}_{yz} = \sin\beta\sin\gamma \tag{13}$$

$$\mathcal{R}_{zx} = \cos\alpha\sin\beta \tag{14}$$

$$\mathcal{R}_{zy} = \sin\alpha\sin\beta \tag{15}$$

$$\mathcal{R}_{zz} = \cos\beta \tag{16}$$

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

$$\cos\beta = \mathcal{R}_{zz} \tag{17}$$

$$\sin\beta = \sqrt{1 - \mathcal{R}_{zz}^2} \tag{18}$$

If $\sin\beta \neq 0$, then

$$e^{-i\alpha} = \frac{\mathcal{R}_{zx} - i\mathcal{R}_{zy}}{\sin\beta} \tag{19}$$

and

$$e^{-i\gamma} = \frac{\mathcal{R}_{xz} + i\mathcal{R}_{yz}}{-\sin\beta} \tag{20}$$

. If $\sin\beta = 0$, then we can choose $\gamma = 0$, and

$$e^{-i\alpha} = \frac{\mathcal{R}_{xx} - i\mathcal{R}_{xy}}{\mathcal{R}_{zz}} \tag{21}$$

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 $N_\mathcal{R}$ symmetry operations denoted by $\mathcal{R}$. Here we will use the notation i implies $n_i l_i m_i$ while i' implies $n_i l_i m_i'$:

$$\left\langle W_{ij}^a \right\rangle_{\text{symmetrized}} = \frac{1}{N_\mathcal{R}} \sum_{\mathcal{R}} \sum_{m_i' m_j'} W_{i'j'}^{\mathcal{R}^{-1}(\mathbf{R}^a - \sigma)} \mathcal{D}^{l_i}_{m_i' m_i}(\mathcal{R}) {\mathcal{D}^{l_j}}^*_{m_j' m_j}(\mathcal{R}) \tag{22}$$