# Angular basis for PES interpolation 

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## 1 Wigner D-matrix conventions

We start from functions of the form

$$
\begin{equation*}
D_{m k}^{j}(\alpha, \beta, \gamma)=\exp (-\imath m \alpha) d_{m k}^{j}(\beta) \exp (-\imath k \gamma) \tag{1}
\end{equation*}
$$

where the d -matrices are real functions of $\beta$ with the following index symmetries

$$
\begin{gather*}
d_{m k}^{j}=(-1)^{m-k} d_{k m}^{j} \\
d_{m k}^{j}=(-1)^{m-k} d_{-m-k}^{j}  \tag{2}\\
d_{m k}^{j}=d_{-k-m}^{j}
\end{gather*}
$$

## 2 Real combinations of Wigner D-matrices

We consider a $\alpha, \beta, \gamma$ trigonometric polynomial such as

$$
\begin{equation*}
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N} \sum_{m=-j}^{+j} \sum_{k=-j}^{+k} c_{j}^{m k} D_{m k}^{j}(\alpha, \beta, \gamma) \tag{3}
\end{equation*}
$$

We require the polynomial to be real, i.e.

$$
\begin{equation*}
f(\alpha, \beta, \gamma)=(f(\alpha, \beta, \gamma))^{\star} \tag{4}
\end{equation*}
$$

this conditions implies that

$$
\begin{gathered}
\sum_{j, m, k} c_{j}^{m k} D_{m k}^{j}=\sum_{j, m, k}\left(c_{j}^{m k}\right)^{\star}\left(D_{m k}^{j}\right)^{\star} \\
\sum_{j, m, k} c_{j}^{m k} D_{m k}^{j}=\sum_{j, m, k}\left(c_{j}^{m k}\right)^{\star} \exp (+i m \alpha) d_{m k}^{j}(\beta) \exp (+i k \gamma)
\end{gathered}
$$

renaming the $m, k$ indices in the r.h.s

$$
\begin{gathered}
\sum_{j, m, k} c_{j}^{m k} D_{m k}^{j}=\sum_{j, m, k}\left(c_{j}^{-m-k}\right)^{\star} \exp (-\imath m \alpha) d_{-m-k}^{j}(\beta) \exp (-\imath k \gamma) \\
\sum_{j, m, k} c_{j}^{m k} D_{m k}^{j}=\sum_{j, m, k}\left(c_{j}^{-m-k}\right)^{\star}(-1)^{m-k} D_{m k}^{j}
\end{gathered}
$$

which for the orthonormality of the Wigner D-matrices implies

$$
\begin{equation*}
c_{j}^{m k}=\left(c_{j}^{-m-k}\right)^{\star}(-1)^{m-k} \tag{5}
\end{equation*}
$$

If we explicitely write the imaginary part and the real part of the coefficients as

$$
\begin{equation*}
c_{j}^{m k}=\frac{a_{j}^{m k}}{2}+\imath \frac{b_{j}^{m k}}{2} \tag{6}
\end{equation*}
$$

the condition Eq. 5 becomes

$$
\begin{equation*}
c_{j}^{m k}=\left(c_{j}^{-m-k}\right)^{\star}(-1)^{m-k}=(-1)^{m-k}\left(\frac{a_{j}^{-m-k}}{2}-\imath \frac{b_{j}^{-m-k}}{2}\right) \tag{7}
\end{equation*}
$$

which will be useful in the following.
Now we get back to expression 3. For later convenience, we split the sum as

$$
\begin{equation*}
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N}\{\underbrace{c_{j}^{00} D_{00}^{j}}_{(A)}+\underbrace{\sum_{m \neq 0} c_{j}^{m 0} D_{m 0}^{j}}_{\left(B_{1}\right)}+\underbrace{\sum_{k \neq 0} c_{j}^{0 k} D_{0 k}^{j}}_{\left(B_{2}\right)}+\underbrace{\sum_{m \neq 0} \sum_{k \neq 0} c_{j}^{m k} D_{m k}^{j}}_{(C)}\} \tag{8}
\end{equation*}
$$

and consider each term separately.
(A) Let's start from (A). The condition expressed in Eq. 5 implies that

$$
\begin{equation*}
c_{j}^{00}=\left(c_{j}^{00}\right)^{\star} \tag{9}
\end{equation*}
$$

i.e. the coefficient is real. For later convenience we call it $a_{j}^{00}$. The Wigner function $D_{00}^{j}=d_{00}^{j}$ itself is real, and we can keep this term in the expansion as it is.
( $\mathbf{B}_{1}$ ) Now we focus on term $\left(\mathbf{B}_{1}\right)$. Dividing the $m>0$ part of the sum from the $m<0$, and using Eq. 7 . we get

$$
\begin{gathered}
\sum_{m \neq 0} c_{j}^{m 0} D_{m 0}^{j}=\sum_{m>0}\left(\frac{a_{j}^{m 0}}{2}+\imath \frac{b_{j}^{m 0}}{2}\right) D_{m 0}^{j}+\sum_{m<0}(-1)^{m}\left(\frac{a_{j}^{-m 0}}{2}-\imath \frac{b_{j}^{-m 0}}{2}\right) D_{m 0}^{j}= \\
=\sum_{m>0}\left(\frac{a_{j}^{m 0}}{2}+\imath \frac{b_{j}^{m 0}}{2}\right) D_{m 0}^{j}+(-1)^{m}\left(\frac{a_{j}^{m 0}}{2}-\imath \frac{b_{j}^{m 0}}{2}\right) D_{-m 0}^{j}= \\
=\sum_{m>0} \frac{a_{j}^{m 0}}{2}\left(D_{m 0}^{j}+(-1)^{m} D_{-m 0}^{j}\right)+\imath \frac{b_{j}^{m 0}}{2}\left(D_{m 0}^{j}-(-1)^{m} D_{-m 0}^{j}\right)
\end{gathered}
$$

We note that

$$
\begin{align*}
D_{m k}^{j} & +(-1)^{m} D_{-m-k}^{j}=\exp (-\imath m \alpha-\imath k \gamma) d_{m k}^{j}(\beta)+(-1)^{m} \exp (\imath m \alpha+\imath k \gamma) d_{-m-k}^{j}(\beta)= \\
& =d_{m k}^{j}(\beta)(\exp (-\imath m \alpha-\imath k \gamma)+\exp (\imath m \alpha+\imath k \gamma))=2 d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma) \tag{10}
\end{align*}
$$

and analogously

$$
\begin{equation*}
D_{m 0}^{j}-(-1)^{m} D_{-m 0}^{j}=-2 \imath d_{m k}^{j}(\beta) \sin (m \alpha+k \gamma) \tag{11}
\end{equation*}
$$

So the term $\left(B_{1}\right)$ becomes

$$
\begin{equation*}
\sum_{m \neq 0}^{-j \ldots+j} c_{j}^{m 0} D_{m 0}^{j}=\sum_{m=1}^{j} a_{j}^{m 0}\left(d_{m 0}^{j}(\beta) \cos (m \alpha)\right)+b_{j}^{m 0}\left(d_{m 0}^{j}(\beta) \sin (m \alpha)\right) \tag{12}
\end{equation*}
$$

which is a linear combination of real functions with real coefficients.
$\left(\mathbf{B}_{2}\right)$ In a completely analogous way, the term $\left(\mathrm{B}_{2}\right)$ can be rewritten as

$$
\begin{equation*}
\sum_{k \neq 0}^{-j \ldots+j} c_{j}^{0 k} D_{0 k}^{j}=\sum_{k=1}^{j} a_{j}^{0 k}\left(d_{0 k}^{j}(\beta) \cos (k \gamma)\right)+b_{j}^{0 k}\left(d_{0 k}^{j}(\beta) \sin (k \gamma)\right) \tag{13}
\end{equation*}
$$

(C) Now let's turn our attention to the term (C). The only difficulty here is that we have to pay attention to split the sum over $m$ and $k$, so that for each term $m, k$ in one sum there is one term $-m,-j$ in the other sum. There is no unique way to to this (and different choices result in different sign conventions). We set

$$
\begin{gathered}
\sum_{m \neq 0} \sum_{k \neq 0} c_{j}^{m k} D_{m k}^{j}=\left(\sum_{m>0} \sum_{k>0} c_{j}^{m k} D_{m k}^{j}+\sum_{m<0} \sum_{k<0} c_{j}^{m k} D_{m k}^{j}\right)+\left(\sum_{m>0} \sum_{k<0} c_{j}^{m k} D_{m k}^{j}+\sum_{m<0} \sum_{k>0} c_{j}^{m k} D_{m k}^{j}\right)= \\
=\left(\sum_{m>0} \sum_{k>0}\left(\frac{a_{j}^{m k}}{2}+\imath \frac{b_{j}^{m k}}{2}\right) D_{m k}^{j}+\sum_{m<0} \sum_{k<0}(-1)^{m-k}\left(\frac{a_{j}^{-m-k}}{2}-\imath \frac{b_{j}^{-m-k}}{2}\right) D_{m k}^{j}\right)+ \\
+\left(\sum_{m>0} \sum_{k<0}\left(\frac{a_{j}^{m k}}{2}+\imath \frac{b_{j}^{m k}}{2}\right) D_{m k}^{j}+\sum_{m<0} \sum_{k>0}(-1)^{m-k}\left(\frac{a_{j}^{-m-k}}{2}-\imath \frac{b_{j}^{-m-k}}{2}\right) D_{m k}^{j}\right)= \\
=\sum_{m>0} \sum_{k \neq 0}\left(\left(\frac{a_{j}^{m k}}{2}+\imath \frac{b_{j}^{m k}}{2}\right) D_{m k}^{j}+(-1)^{m-k}\left(\frac{a_{j}^{m k}}{2}-\imath \frac{b_{j}^{m k}}{2}\right) D_{-m-k}^{j}\right)= \\
=\sum_{m>0} \sum_{k \neq 0}\left(\frac{a_{j}^{m k}}{2}\left(D_{m k}^{j}+(-1)^{m-k} D_{-m-k}^{j}\right)+\imath \frac{b_{j}^{m k}}{2}\left(D_{m k}^{j}-(-1)^{m-k} D_{-m-k}^{j}\right)\right)
\end{gathered}
$$

Using Eq. 10 and 11, we get

$$
\begin{equation*}
\sum_{m \neq 0} \sum_{k \neq 0} c_{j}^{m k} D_{m k}^{j}=\sum_{m=1}^{j} \sum_{k \neq 0}^{-j \ldots+j} a_{j}^{m k}\left(d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma)\right)+b_{j}^{m k}\left(d_{m k}^{j}(\beta) \sin (m \alpha+k \gamma)\right) \tag{14}
\end{equation*}
$$

which is again a linear combination of real functions with real coefficients.
(conclusion) If we collect all the cosine expressions for a single $j$ of the different terms we have:

$$
\begin{aligned}
& a_{j}^{00} d_{00}^{j}+\sum_{m=1}^{j} a_{j}^{m 0}\left(d_{m 0}^{j}(\beta) \cos (m \alpha)\right)+\sum_{k=1}^{j} a_{j}^{0 k}\left(d_{0 k}^{j}(\beta) \cos (k \gamma)\right)+\sum_{m=1}^{j} \sum_{k \neq 0}^{-j \ldots+j} a_{j}^{m k}\left(d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma)\right)= \\
& =\sum_{k=0}^{j} a_{j}^{0 k}\left(d_{0 k}^{j}(\beta) \cos (k \gamma)\right)+\sum_{m=1}^{j} \sum_{k=-j}^{+j} a_{j}^{m k}\left(d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma)\right)=\sum_{m=0}^{j} \sum_{k=-j}^{+j} a_{j}^{m k}\left(d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma)\right)
\end{aligned}
$$

where the prime symbol over the sum in $k$ indicates that for $m=0$, only non-negative values of $k$ should be considered.

In a similar fashion, we can collect the sine terms as

$$
\sum_{m=0}^{j} \sum_{k=-j}^{+j} b_{j}^{\prime \prime}\left(d_{m k}^{j}(\beta) \sin (m \alpha+k \gamma)\right)
$$

and the double prime here means that for $m=0$, only positive values of $k$ should be considered (we could equivalently include a $m=0, k=0$ term, since it is identically zero). So in conclusion the real Wigner D-matrix expansion can be written as

$$
\begin{equation*}
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N} \sum_{m=0}^{j} \sum_{k=-j}^{+j} a_{j}^{m k}\left(d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma)\right)+b_{j}^{m k}\left(d_{m k}^{j}(\beta) \sin (m \alpha+k \gamma)\right) \tag{15}
\end{equation*}
$$

## 3 Symmetry operators

Now we want to characterize the rotational and reflection operations which should be taken into account in the construction of the PES.

In our potential, the coordinates of the molecule are parametrized with seven coordinates: the C-H bond length $r$, the angles $\alpha, \beta, \gamma$ and the $X, Y, Z$ position of the carbon atom. We have then to characterize how the symmetry operations of the PES operate on our parametrization of the potential.

Parametrization of the potential We start from reviewing the definitions of our coordinates. We define the geometry of the molecule starting from a fixed geometry, which is given by the following set of 5 cartesian vectors: $\mathbf{r}_{C}, \mathbf{r}_{H}, \mathbf{r}_{D_{1}}, \mathbf{r}_{D_{2}}, \mathbf{r}_{D_{3}}$ This initial geometry is function of $r$ only (more precisely, only the geometry of the $\mathbf{r}_{H}$ vector is function of $r$ ). In detail the initial vectors are

$$
\mathbf{r}_{C}=\left(\begin{array}{l}
0  \tag{16}\\
0 \\
0
\end{array}\right) \mathbf{r}_{H}=\left(\begin{array}{l}
0 \\
0 \\
r
\end{array}\right), \mathbf{r}_{D_{1}}=\left(\begin{array}{c}
1.952333 \\
0 \\
-0.68805
\end{array}\right) \mathbf{r}_{D_{2}}=\left(\begin{array}{c}
-0.976214 \\
-1.690814 \\
-0.68805
\end{array}\right) \mathbf{r}_{D_{3}}=\left(\begin{array}{c}
-0.976214 \\
1.690814 \\
-0.68805
\end{array}\right)
$$

Then the cartesian coordinates of the atoms in the final geometry of the molecule are obtained as

$$
\left\{\begin{array}{l}
\mathbf{r}_{C}^{\prime}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{r}_{C} \\
\mathbf{r}_{H}^{\prime}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{r}_{H} \\
\mathbf{r}_{D_{1}}^{\prime}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{r}_{D_{1}} \\
\mathbf{r}_{D_{2}^{\prime}}^{\prime}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{r}_{D_{2}} \\
\mathbf{r}_{D_{3}}^{\prime}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{r}_{D_{3}}
\end{array}\right.
$$

where $\mathcal{T}_{X Y Z}$ is a 3D rigid translation of vector $(X, Y, Z)$,

$$
\mathcal{T}_{X Y Z}\left(\begin{array}{l}
x  \tag{17}\\
y \\
z
\end{array}\right)=\left(\begin{array}{l}
x+X \\
y+Y \\
z+Z
\end{array}\right)
$$

while $\mathcal{R}_{\alpha \beta \gamma}$ is a 3D rigid rotation of Euler angles $\alpha, \beta$ and $\gamma$

$$
\mathcal{R}_{\alpha \beta \gamma}=R_{\alpha}^{z} R_{\beta}^{y} R_{\gamma}^{z}=\left[\begin{array}{ccc}
c \alpha c \beta c \gamma-s \alpha s \gamma & -c \alpha c \beta s \gamma-s \alpha c \gamma & c \alpha s \beta  \tag{18}\\
s \alpha c \beta c \gamma-c \alpha s \gamma & -s \alpha c \beta s \gamma+c \alpha c \gamma & s \alpha s \beta \\
-s \beta c \gamma & s \alpha s \gamma & c \beta
\end{array}\right]
$$

(ZYZ convention, counterclockwise rotations)

Umbrella rotational symmetry Let's consider first the symmetry of the $\mathrm{CHD}_{3}$ molecule. The molecule has $C_{3}$ symmetry, hence its geometry is invariant for rotations of $\frac{2 \pi}{3}$ and $\frac{4 \pi}{3}$ around the umbrella axis of the molecule. This kind of operation can be easily applied when the molecule is in the initial orienation, in the molecule frame. If we generally indicate the geometry of the methane in its molecular frame as $\mathbf{X}_{r}$, we have that

$$
\begin{equation*}
\mathbf{X}_{r}=R_{2 n \pi / 3}^{z} \mathbf{X}_{r} \quad n=1,2 \tag{19}
\end{equation*}
$$

and hence

$$
\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} R_{2 n \pi / 3}^{z} \mathbf{X}_{r}
$$

But we can rewrite the two rotations matrices as a single one

$$
\mathcal{R}_{\alpha \beta \gamma} R_{2 n \pi / 3}^{z}=R_{\alpha}^{z} R_{\beta}^{y} R_{\gamma}^{z} R_{2 n \pi / 3}^{z}=\mathcal{R}_{\alpha \beta \gamma+2 n \pi / 3}
$$

In conclusion in our parametrization of the methane coordinates, the action of the umbrella rotations can be expressed as

$$
\begin{equation*}
R_{2 n \pi / 3}(r, X, Y, Z, \alpha, \beta, \gamma) \rightarrow(r, X, Y, Z, \alpha, \beta, \gamma+2 n \pi / 3) \tag{20}
\end{equation*}
$$

Surface rotational symmetry Now let's consider the rotations of the molecule with respect to the space axis (i.e. with respect to the surface). This symmetry depends on the site of the surface in which the molecule is located. When we fix the $X, Y$ coordinates of the carbon atom to the coordinates of one of the high symmetry sites, we can then see that

$$
\begin{equation*}
\mathcal{T}_{X Y Z} R_{\omega_{n}}^{z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r}=\mathcal{T}_{X Y Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r} \tag{21}
\end{equation*}
$$

where $\omega_{n}$ are a series of values which depends on the symmetry of the site (e.g. $\omega_{n}=n \frac{\pi}{3} n=1 \ldots 5$ for the TOP site, which has $C_{6}$ symmetry).

Again, the action of the operator $R_{\omega_{n}}^{z}$ can be easily expressed in our parametrization of the potential as

$$
\begin{gather*}
R_{\omega_{n}}^{z} \mathcal{R}_{\alpha \beta \gamma}=R_{\omega_{n}}^{z} R_{\alpha}^{z} R_{\beta}^{y} R_{\gamma}^{z}=\mathcal{R}_{\alpha+\omega_{n} \beta \gamma} \\
R_{\omega_{n}}^{z}(r, X, Y, Z, \alpha, \beta, \gamma) \rightarrow\left(r, X, Y, Z, \alpha+\omega_{n}, \beta, \gamma\right) \tag{22}
\end{gather*}
$$

Reflection symmetry Now let's consider the reflection symmetry of the potential. We limit ourself to considering the potential in some high symmetry points, and we take into account a symmetry plane which passes through the high symmetry point and is given by $x=0$ (otherwise the basis functions have to be rotated along $\alpha$ so that $\alpha=0$ coincides with the symmetry plane).

In cartesian coordinate, this symmetry operations can be written as

$$
\sigma:\left\{\begin{array}{l}
x=x \\
y=-y \\
z=z
\end{array}\right.
$$

Note that the the potential is invariant for this symmetry operation acting both on the initial geometry of the methane

$$
\begin{equation*}
\mathbf{X}_{r}=\sigma \mathbf{X}_{r} \tag{23}
\end{equation*}
$$

(because of the symmetry of the molecule in its reference frame) and on the rotated geometry of the methane, then translated in the appropriate high symmetry site of the surface

$$
\mathcal{T}_{\bar{X} \bar{Y} Z} \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r}=\mathcal{T}_{\bar{X} \bar{Y} Z} \sigma \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r}
$$

(because of the symmetry of the surface in the high symmetry sites).
To evaluate the action of the symmetry operator on the geometry, we can use the fact that $\sigma \sigma=1$ (a reflection coincides with its inverse)

$$
\sigma \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r}=\sigma \mathcal{R}_{\alpha \beta \gamma} \sigma \sigma \mathbf{X}_{r}=\left(\sigma \mathcal{R}_{\alpha \beta \gamma} \sigma\right)\left(\sigma \mathbf{X}_{r}\right)
$$

we can use the fact that $\mathbf{X}_{r}=\sigma \mathbf{X}_{r}$ and obtain

$$
\sigma \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r}=\left(\sigma \mathcal{R}_{\alpha \beta \gamma} \sigma\right) \mathbf{X}_{r}
$$

By expliciting the operators as matrices acting on the cartesian components of the atom positions, we can easily obtain that

$$
\left(\sigma \mathcal{R}_{\alpha \beta \gamma} \sigma\right)=\mathcal{R}_{-\alpha \beta-\gamma}
$$

In conclusion

$$
\begin{align*}
\mathcal{T}_{\bar{X} \bar{Y} Z} \sigma \mathcal{R}_{\alpha \beta \gamma} \mathbf{X}_{r} & =\mathcal{T}_{\bar{X} \bar{Y} Z} \mathcal{R}_{-\alpha \beta-\gamma} \mathbf{X}_{r} \\
\sigma(r, \bar{X}, \bar{Y}, Z, \alpha, \beta, \gamma) & \rightarrow(r, \bar{X}, \bar{Y}, Z,-\alpha, \beta,-\gamma) \tag{24}
\end{align*}
$$

## 4 Symmetrization of the basis set

We assume that we expand our potential in terms of a generic complex polynomial, which is a sum of product of trigonometric functions in $\alpha, \beta, \gamma$. It can easily see that both Eq. 1 and 15 can be cast in a form such as

$$
\begin{equation*}
f(\alpha, \beta, \gamma)=\sum_{n_{1} n_{2} n_{3}} c_{n_{1} n_{2} n_{3}} \exp \left(\imath n_{1} \alpha\right) \exp \left(2 n_{2} \beta\right) \exp \left(2 n_{3} \gamma\right) \tag{25}
\end{equation*}
$$

Umbrella rotational symmetry Now, let's see the implications of the rotational symmetry with respect to the operations expressed by Eq. 20

$$
\begin{gather*}
R_{2 n \pi / 3} f(\alpha, \beta, \gamma)=f(\alpha, \beta, \gamma)  \tag{26}\\
f(\alpha, \beta, \gamma+2 n \pi / 3)=f(\alpha, \beta, \gamma)
\end{gather*}
$$

If we substitute the expression of $f(\alpha, \beta, \gamma)$, we get

$$
\sum_{n_{1} n_{2} n_{3}} c_{n_{1} n_{2} n_{3}} \exp \left(\imath n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(2 n_{3}(\gamma+2 n \pi / 3)\right)=\sum_{n_{1} n_{2} n_{3}} c_{n_{1} n_{2} n_{3}} \exp \left(\imath n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(\imath n_{3} \gamma\right)
$$

Because of the orthonormality of the complex exponentials, last equation implies that the coefficients $c_{n_{1} n_{2} n_{3}}$ are nonzero if and only if

$$
\exp \left(2 i \pi n_{3} n / 3\right)=1 n=1,2
$$

This is true only for those $n_{3}$ which are multiples of 3 , i.e.

$$
n_{3}=3 i i \in \mathbb{Z}
$$

If we consider the way that sine and cosine functions are obtained from complex exponentials, it is evident that from a sum of exponentials which contains only $n_{3}=3 i$ terms we can obtain trigonometric functions which are functions of $3 i \gamma$ only. Hence, the condition of Eq. 26 is satisfied by the real expansion Eq. 15 when we consider terms of the form

$$
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N} \sum_{m=0}^{j} \sum_{k=-j}^{+j} a_{j}^{m k}\left(d_{m 3 k}^{j}(\beta) \cos (m \alpha+3 k \gamma)\right)+b_{j}^{m k}\left(d_{m 3 k}^{j}(\beta) \sin (m \alpha+3 k \gamma)\right)
$$

Surface rotational symmetry This case is completely analogous the the previous one. We want to impose the condition

$$
R_{\omega_{n}}^{z} f(\alpha, \beta, \gamma)=f(\alpha, \beta, \gamma)
$$

which can be expressed as

$$
f\left(\alpha+\omega_{n}, \beta, \gamma\right)=f(\alpha, \beta, \gamma) \quad \omega_{n}=2 \pi n / N \quad n=1 \ldots N-1
$$

where N is the order of the rotation symmetry.
We can show that this condition implies that the coefficients $c_{n_{1} n_{2} n_{3}}$ of Eq. 25 are nonzero if and only if

$$
\exp \left(2 i \pi n_{1} n / N\right)=1
$$

which is true only for those $n_{1}$ which are multiples of $N$, i.e.

$$
n_{1}=N j j \in \mathbb{Z}
$$

Again, this limit the sum of Eq 15 only to the terms in which $n_{1}$ is multiple of N

$$
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N} \sum_{m=0}^{j} \sum_{k=-j}^{+j} a_{j}^{m k}\left(d_{N m k}^{j}(\beta) \cos (N m \alpha+3 k \gamma)\right)+b_{j}^{m k}\left(d_{N m k}^{j}(\beta) \sin (N m \alpha+3 k \gamma)\right)
$$

Reflection symmetry Now we want to consider the effect of the invariance expressed by Eq. 23. In this case the condition

$$
\sigma f(\alpha, \beta, \gamma)=f(-\alpha, \beta,-\gamma)=f(\alpha, \beta, \gamma)
$$

becomes

$$
\sum_{n_{1} n_{2} n_{3}} c_{n_{1} n_{2} n_{3}} \exp \left(-i n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(-i n_{3} \gamma\right)=\sum_{n_{1} n_{2} n_{3}} c_{n_{1} n_{2} n_{3}} \exp \left(i n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(i n_{3} \gamma\right)
$$

we can change the order of summation and transform the dummy integers $n_{1}$ to $-n_{1}$ and $n_{3}$ to $-n_{3}$. In this way the equation becomes

$$
\sum_{n_{1} n_{2} n_{3}} c_{-n_{1} n_{2}-n_{3}} \exp \left(i n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(i n_{3} \gamma\right)=\sum_{n_{1} n_{2} n_{3}} c_{n_{1} n_{2} n_{3}} \exp \left(i n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(i n_{3} \gamma\right)
$$

because of the orthonormality of the complex exponentials, last equation implies that the coefficients $c_{n_{1} n_{2} n_{3}}$ satisfy

$$
\begin{equation*}
c_{-n_{1} n_{2}-n_{3}}=c_{n_{1} n_{2} n_{3}} \tag{27}
\end{equation*}
$$

To see what this condition implies for the expansion of Eq. 25, we first split the summation in three pieces

$$
\begin{aligned}
f(\alpha, \beta, \gamma)= & \sum_{n_{2}} c_{0 n_{2} 0} \exp \left(\imath n_{2} \beta\right)+\sum_{n_{1}>0, n_{2} n_{3}>0} c_{n_{1} n_{2} n_{3}} \exp \left(\imath n_{1} \alpha\right) \exp \left(\imath n_{2} \beta\right) \exp \left(\imath n_{3} \gamma\right)+ \\
& +\sum_{n_{1}>0, n_{2} n_{3}>0} c_{-n_{1} n_{2}-n_{3}} \exp \left(-\imath n_{1} \alpha\right) \exp \left(i n_{2} \beta\right) \exp \left(-\imath n_{3} \gamma\right)
\end{aligned}
$$

substituting Eq. 27, we get

$$
f(\alpha, \beta, \gamma)=\sum_{n_{2}} c_{0 n_{2} 0} \exp \left(\imath n_{2} \beta\right)+\sum_{n_{1}>0, n_{2} n_{3}>0} c_{n_{1} n_{2} n_{3}} \exp \left(\imath n_{2} \beta\right)\left[\exp \left(\imath n_{1} \alpha\right) \exp \left(\imath n_{3} \gamma\right)+\exp \left(-\imath n_{1} \alpha\right) \exp \left(-\imath n_{3} \gamma\right)\right]
$$

the term in square brackets can be recognized as

$$
\begin{gathered}
\exp \left(i n_{1} \alpha\right) \exp \left(i n_{3} \gamma\right)+\exp \left(-i n_{1} \alpha\right) \exp \left(-i n_{3} \gamma\right)=2 \cos \left(i n_{1} \alpha+i n_{3} \gamma\right)= \\
=2 \cos \left(n_{1} \alpha\right) \cos \left(i n_{3} \gamma\right)+2 \sin \left(2 n_{1} \alpha\right) \sin \left(\imath n_{3} \gamma\right)
\end{gathered}
$$

With respect to Eq. 15 , it is immidiate to realize that the reflection symmetry implies that only cosine terms should be included in the expansion

$$
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N} \sum_{m=0}^{j} \sum_{k=-j}^{+j} a_{j}^{m k} d_{m k}^{j}(\beta) \cos (m \alpha+k \gamma)
$$

In conclusion Imposing all the symmetry invariances, implies that our real D-matrix expansion (Eq. 15) becomes

$$
f(\alpha, \beta, \gamma)=\sum_{j=1}^{N} \sum_{m=0}^{j} \sum_{k=-j}^{+j} a_{j}^{m k} d_{N m, 3 k}^{j}(\beta) \cos (N m \alpha+3 k \gamma)
$$

