

# Crystal Symmetry Matrix at Special k-points in Nonorthogonal Tight Binding Theory

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This document describes the formalism and practical way to calculate the crystal symmetry operation matrix of Bloch wave functions  $\langle \Psi_{n\mathbf{k}} | g | \Psi_{m\mathbf{k}} \rangle$  within the non-orthogonal tight binding or linear combination of (pseudo) atomic orbital(LC(P)AO) formalism.

Let's describe the Bloch wave function in the following form.

$$\begin{aligned} |\Psi_{n\mathbf{k}}(\mathbf{r})\rangle &= \sum_{i\alpha} C_{i\alpha}^{n\mathbf{k}} |\phi_{i\alpha}^{\mathbf{k}}\rangle \\ &= \sum_{i\alpha} C_{i\alpha}^{n\mathbf{k}} \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{i\alpha}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i)\rangle \end{aligned} \quad (1)$$

where  $i$  is index for atoms, and  $\alpha$  is index for atomic orbitals belonging to the atom  $i$ . The index of the matrix for tight binding Hamiltonian is denoted by combined index ( $i\alpha$ ). the atomic orbital  $|\phi\rangle$  is expressed as,

$$|\phi_{i\alpha}(\mathbf{r})\rangle = |R_{n_\alpha l_\alpha}(|\mathbf{r}|\rangle) |Y_{l_\alpha m_\alpha}(\theta, \phi)\rangle$$

and satisfying the orthogonality condition within the same atomic species.

$$\langle \phi_{i\alpha} | \phi_{i\beta} \rangle = \langle R_{n_\alpha l_\alpha} | R_{n_\beta l_\beta} \rangle \langle Y_{l_\alpha m_\alpha} | Y_{l_\beta m_\beta} \rangle = \delta_{\alpha\beta}$$

In here, it is assumed that all the atomic orbitals share the same coordinate system. For example,  $p_z$  orbital of the atom 1 has the same direction with that of  $p_z$  orbital of atom 2, etc. And it is also assumed that atoms in each set of atoms that related by symmetry operation have the identical set of atomic orbitals.

The crystal symmetry operation  $g$  is expressed as  $g = \{O|\mathbf{t}\}$ .  $O$  is rotation or roto-inversion(mirror or rotation+mirror) operation matrix, and  $\mathbf{t}$  is translation vector by fraction of lattice vector. It moves the atom at site  $\mathbf{r}$  into  $g\mathbf{r}$ .

$$g\mathbf{r} = O\mathbf{r} + \mathbf{t}$$

Additionally, let's introduce the center of rotation or mirror reflection  $\mathbf{c}$ . Then, the crystal symmetry operation  $g$  acts as follows.

$$g\mathbf{r} = \mathbf{c} + O(\mathbf{r} - \mathbf{c}) + \mathbf{t} = O\mathbf{r} + (I - O)\mathbf{c} + \mathbf{t}$$

For the function  $f(\mathbf{r})$ , crystal symmetry operation  $g$  acts as the inverse operation to  $\mathbf{r}$

$$gf(\mathbf{r}) = f(g^{-1}\mathbf{r})$$

As a first step, for the atom  $i$ , find the crystal symmetry pair  $i_g$  and define the corresponding lattice translation vector  $\mathbf{R}_i$  satisfying

$$g\boldsymbol{\tau}_i = O\boldsymbol{\tau}_i + (I - O)\mathbf{c} + \mathbf{t} \equiv \mathbf{R}_i + \boldsymbol{\tau}_{i_g}$$

Then, the operation of  $g$  for the atom  $i$  in the cell  $\mathbf{R}$  is expressed as,

$$g(\mathbf{R} + \boldsymbol{\tau}_i) = O\mathbf{R} + O\boldsymbol{\tau}_i + (I - O)\mathbf{c} + \mathbf{t} = O\mathbf{R} + \mathbf{R}_i + \boldsymbol{\tau}_{i_g}$$

Now, operate the crystal symmetry operator  $g$  to the tight binding basis  $|\phi_{i\alpha}^{\mathbf{k}}\rangle$

$$\begin{aligned} g|\phi_{i\alpha}^{\mathbf{k}}\rangle &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} g|\phi_{i\alpha}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i)\rangle \\ &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{i\alpha}(g^{-1}\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i)\rangle \\ &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}\beta} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{i\beta}(\mathbf{r} - g(\mathbf{R} + \boldsymbol{\tau}_i))\rangle \delta_{n_\beta n_\alpha} \delta_{l_\beta l_\alpha} R_{m_\beta m_\alpha}^{l_\alpha} \\ &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}\beta} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{i\beta}(\mathbf{r} - O\mathbf{R} - \mathbf{R}_i - \boldsymbol{\tau}_{i_g})\rangle \delta_{n_\beta n_\alpha} \delta_{l_\beta l_\alpha} R_{m_\beta m_\alpha}^{l_\alpha} \end{aligned} \quad (2)$$

The property of spherical harmonics is used and the rotation matrix for (real) spherical harmonics  $R_{m'm}^l$  is defined as follows. We can easily obtain the matrix  $R_{m'm}^l$  in the recursive method shown in the ref.[1] with appropriate permutation.

$$|Y_{lm}(O^{-1}\mathbf{r})\rangle = \sum_{m'} |Y_{lm'}(\mathbf{r})\rangle \langle Y_{lm'}(\mathbf{r}) | Y_{lm}(O^{-1}\mathbf{r}) \rangle \equiv \sum_{m'} |Y_{lm'}(\mathbf{r})\rangle R_{m'm}^l$$

Finally, calculate the crystal symmetry matrix of the Bloch eigenstate.

$$\begin{aligned} &\langle \Psi_{n\mathbf{k}} | g | \Psi_{m\mathbf{k}} \rangle \\ &= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'(i\alpha)(j\beta)} C_{i\alpha}^{n\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}' - \mathbf{R})} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i) | g | \phi_{j\beta}(\mathbf{r} - \mathbf{R}' - \boldsymbol{\tau}_j) \rangle \\ &= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'(i\alpha)(j\beta)\gamma} C_{i\alpha}^{n\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}' - \mathbf{R})} \\ &\quad \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r} - O\mathbf{R}' - \mathbf{R}_j - \boldsymbol{\tau}_{j_g}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \end{aligned} \quad (3)$$

Translate the  $\mathbf{r}$  into  $\mathbf{r} + \mathbf{R}$ . The value of overlap matrix does not change by this

translation.

$$\begin{aligned}
&= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'(i\alpha)(j\beta)\gamma} C_{i\alpha}^{m\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r}+\mathbf{R}-O\mathbf{R}'-\mathbf{R}_j-\boldsymbol{\tau}_{j_g}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \\
&= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'(i\alpha)(j\beta)\gamma} C_{i\alpha}^{m\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r}-(\mathbf{R}'-\mathbf{R})+(I-O)\mathbf{R}'-\mathbf{R}_j-\boldsymbol{\tau}_{j_g}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta}
\end{aligned} \tag{4}$$

Redefine the  $\mathbf{R}$  within the summation over  $\mathbf{R}'$  so that  $\mathbf{R}'-\mathbf{R}$  becomes  $\mathbf{R}$ .

$$\begin{aligned}
&= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'(i\alpha)(j\beta)\gamma} C_{i\alpha}^{m\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r}-\mathbf{R}+(I-O)\mathbf{R}'-\mathbf{R}_j-\boldsymbol{\tau}_{j_g}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta}
\end{aligned} \tag{5}$$

Then, translate  $\mathbf{R} \rightarrow \mathbf{R} + (I-O)\mathbf{R}'-\mathbf{R}_j$  within  $j$ -summation.

$$\begin{aligned}
&= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'(i\alpha)(j\beta)\gamma} C_{i\alpha}^{m\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} e^{i\mathbf{k}\cdot(I-O)\mathbf{R}'} e^{-i\mathbf{k}\cdot\mathbf{R}_j} \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r}-\mathbf{R}-\boldsymbol{\tau}_{j_g}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta}
\end{aligned} \tag{6}$$

Up to above expression, due to the unit cell number  $N$  and summation over two different lattice vector  $\mathbf{R}$  and  $\mathbf{R}'$ , it is not well-defined expression. But if  $e^{i\mathbf{k}\cdot(I-O)\mathbf{R}'} = 1$  for arbitrary  $\mathbf{R}'$ , only  $\mathbf{R}$  terms remain. Then, by the common logic of the tight binding model, summation over  $\mathbf{R}'$  is nothing but the multiplication by  $N$  which is canceled with the  $N$  in the denominator. Finally, it becomes well-defined expression. This condition is equivalent to

$$O^{-1}\mathbf{k} = \mathbf{k} + \mathbf{G}$$

or

$$O\mathbf{k} = \mathbf{k} + \mathbf{G}, \text{ where } \mathbf{G} \text{ is the reciprocal lattice vector}$$

Crystal momentum  $\mathbf{k}$  which satisfy this condition is the special  $\mathbf{k}$  point.

As a result, at the special  $\mathbf{k}$  point defined by the orthogonal transformation part  $O$  in the crystal symmetry operation  $g$ , The matrix element of  $g$  in the Bloch eigenstate is expressed as follows.

$$\begin{aligned}
\langle \Psi_{n\mathbf{k}} | g | \Psi_{m\mathbf{k}} \rangle &= \sum_{\mathbf{R}(i\alpha)(j\beta)\gamma} C_{i\alpha}^{m\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}_j} \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r}-\mathbf{R}-\boldsymbol{\tau}_{j_g}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta}
\end{aligned} \tag{7}$$

Let's denote the overlap matrices as follows.

$$\begin{aligned}
S_{(i\alpha)(j\beta)}(\mathbf{R}) &\equiv \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\beta}(\mathbf{r}-\mathbf{R}-\boldsymbol{\tau}_{j_g}) \rangle \\
S_{(i\alpha)(j\beta)}(\mathbf{k}) &\equiv \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} S_{(i\alpha)(j\beta)}(\mathbf{R})
\end{aligned} \tag{8}$$

Then,

$$\begin{aligned}
\langle \Psi_{n\mathbf{k}} | g | \Psi_{m\mathbf{k}} \rangle &= \sum_{(i\alpha)(j\beta)\gamma} C_{i\alpha}^{n\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_j} S_{(i\alpha)(j\beta)\gamma}(\mathbf{k}) \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \\
&= \sum_{(i\alpha)(j\beta)(k\gamma)} C_{i\alpha}^{n\mathbf{k}*} C_{j\beta}^{m\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_j} S_{(i\alpha)(k\gamma)}(\mathbf{k}) \delta_{kjg} \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \\
&= \mathbf{C}^{n\mathbf{k}\dagger} S(\mathbf{k}) \tilde{M}_g(\mathbf{k}) \mathbf{C}^{m\mathbf{k}} \\
&= \mathbf{C}^{n\mathbf{k}\dagger} M_g(\mathbf{k}) \mathbf{C}^{m\mathbf{k}}
\end{aligned} \tag{9}$$

where,  $\mathbf{C}^{m\mathbf{k}}$  is a column vector of which the  $(j\beta)$ -th element is  $C_{j\beta}^{m\mathbf{k}}$ .  $M_g(\mathbf{k}) = S(\mathbf{k}) \tilde{M}_g(\mathbf{k})$  is the matrix.  $S(\mathbf{k})$  is the overlap matrix.  $\tilde{M}_g(\mathbf{k})$  is a matrix of which the  $(k\gamma)(j\beta)$  element is  $e^{-i\mathbf{k}\cdot\mathbf{R}_j} \delta_{kjg} \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta}$ . Due to the phase factor  $e^{-i\mathbf{k}\cdot\mathbf{R}_j}$ , the crystal symmetry matrix for the tight binding theory depends on the crystal momentum  $\mathbf{k}$  in general. This  $\mathbf{k}$ -dependency in the symmetry operation matrix is consistent with other references[2-6] up to phase due to the convention issue(see Appendix C).

This formula can be practically implemented for the post processing tools for the first principle calculation code using the local basis or the LC(P)AO formalism.

## References

references

- [1] Joseph Ivanic and Klaus Ruedenberg, Rotation Matrices for Real Spherical Harmonics. Direct Determination by Recursion, J. Phys. Chem. 1996, 100, 6342-6347 (notice: this paper has minor error in Table 2)
- [2] R.F.Egorov, B.I.Reser, and V. P. Shirokovskii, Consistent Treatment of Symmetry in the Tight Binding Approximation. phys. stat. sol. 26, 391 (1968)
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- [7] Tahir Yusufaly, David Vanderbilt, and Sinisa Coh, Tight-Binding Formalism in the Context of the PythTB Package, <http://www.physics.rutgers.edu/pythtb/formalism.html> (2018)

## Appendix A

Summary Of Ref.[1] : Rotation Matrices Of Real Spherical Harmonics

Joseph Ivanic and Klaus Ruedenberg found the recursive formula for the rotation/roto-inversion matrix for the real spherical harmonics  $R^l$ [1]. This appendix is the summary of the ref.[1] with the error correction and the redescription for our purpose.

Let's consider the rotation/roto-inversion matrix  $R_{\text{carte}}$  which transforms the cartesian coordinate vector  $\mathbf{r}$  as follows.

$$R_{\text{carte}}\mathbf{r} = \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

The rotation/roto-inversion matrix for the real spherical harmonics is defined as  $R_{mm'}^l \equiv \langle Y_{lm}(\mathbf{r}) | Y_{lm'}(R_{\text{carte}}^{-1}\mathbf{r}) \rangle$ , where the  $|Y_{lm}(\mathbf{r})\rangle$  is the real spherical harmonics of the angular momentum quantum number  $l$  and the azimuthal quantum number  $m$ .  $m$  runs from  $-l$  to  $l$  (totally  $2l+1$  values).  $R^0 = 1$  and  $R^1$  is the permutation of  $R_{\text{carte}}$  into the order of real spherical harmonics. In general, orders of mathematically defined real spherical harmonics does not coincide with the orders of the cartesian coordinate and the atomic orbitals. For example,  $|Y_{1,-1}(\mathbf{r})\rangle \propto y/r$ ,  $|Y_{1,0}(\mathbf{r})\rangle \propto z/r$  and  $|Y_{1,1}(\mathbf{r})\rangle \propto x/r$ . Permutations of  $R^l$  to the atomic orbital orders for other  $l$  values will be shown in Appendix B according to the orders used in 'OpenMX' code. In this appendix, define

$$R \equiv R^1 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} R_{\text{carte}} \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

In the ref.[1],  $R^l$  for arbitrary values of  $l > 1$  can be obtained from  $R^1$  and  $R^{l-1}$  by the recursive method.

Real spherical harmonics is defined as follows.

$$Y_{lm}(\theta, \phi) = P_l^{|m|}(\cos \theta) \Phi_m(\phi)$$

where

$$\begin{aligned} \Phi_0 &= (2\pi)^{-1/2} \\ \Phi_m &= \pi^{-1/2} \cos(m\phi) \quad \text{for } m > 0 \\ &= \pi^{-1/2} \sin(m\phi) \quad \text{for } m < 0 \end{aligned}$$

and

$$\begin{aligned} P_l^m(t) &= \left[ \frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right]^{\frac{1}{2}} \tilde{P}_l^m(t) \\ \tilde{P}_l^m(t) &= (2^l l!)^{-1} (1-t^2)^{1/2} (\partial/\partial t)^{l+m} (t^2-1)^l \quad \text{with } t = \cos \theta \end{aligned}$$

The recurrence relation of the Legendre functions are

$$\cos \theta P_l^m = A_l^m P_{l-1}^m + A_{l+1}^m P_{l+1}^m$$

with

$$A_l^m = [(l+m)(l-m)/(2l+1)(2l-1)]^{1/2}$$

and

$$\begin{aligned} \sin \theta P_l^m &= B_l^m P_{l-1}^{m-1} - B_{l+1}^{-m+1} P_{l+1}^{m-1} \\ \sin \theta P_l^m &= -B_l^{-m} P_{l-1}^{m+1} + B_{l+1}^{m+1} P_{l+1}^{m+1} \end{aligned}$$

with

$$B_l^m = [(l+m)(l+m-1)/(2l+1)(2l-1)]^{1/2}$$

By multiplying  $\Phi_0$  or  $\Phi_{\pm 1}$  to these recurrence relations, we can get the recurrence relation for the real spherical harmonics.  $Y_{l+1,m}$ 's can be obtained from  $Y_{l,m}$ 's,  $Y_{l,m}$ 's and  $Y_{l-1,m}$ 's. Then let's consider the coordinate transformation. Because  $Y_{l,1} \propto x/r$ ,  $Y_{l,-1} \propto y/r$  and  $Y_{l,0} \propto z/r$ , transformation of  $Y_{l,m}$ 's is nothing but the transformation of coordinate system. And transformation of  $Y_{l,m}$ 's is expressed as  $|Y_{lm}(R_{\text{carte}}^{-1} \mathbf{r})\rangle = \sum_{m'} |Y_{lm'}(\mathbf{r})\rangle R_{m'm}^l$ . Finally, combining the recurrence relations and the transformation rules with some calculations and algebras, the transformation matrix for real spherical harmonics is obtained as following formula.

$$R_{mm'}^l = u_{mm'}^l U_{mm'}^l + v_{mm'}^l V_{mm'}^l + w_{mm'}^l W_{mm'}^l$$

where each of  $u, U, v, V, w$  and  $W$  are defined as following tables.

	$ m'  < l$	$ m'  = l$
$u_{mm'}^l$	$\left[ \frac{(l+m)(l-m)}{(l+m')(l-m')} \right]^{1/2}$	$\left[ \frac{(l+m)(l-m)}{(2l)(2l-1)} \right]^{1/2}$
$v_{mm'}^l$	$\frac{1}{2} \left[ \frac{(1+\delta_{m0})(l+ m -1)(l+ m )}{(l+m')(l-m')} \right]^{1/2} (1 - 2\delta_{m0})$	$\frac{1}{2} \left[ \frac{(1+\delta_{m0})(l+ m -1)(l+ m )}{(2l)(2l-1)} \right]^{1/2} (1 - 2\delta_{m0})$
$w_{mm'}^l$	$-\frac{1}{2} \left[ \frac{(l- m -1)(l- m )}{(l+m')(l-m')} \right]^{1/2} (1 - \delta_{m0})$	$-\frac{1}{2} \left[ \frac{(l- m -1)(l- m )}{(2l)(2l-1)} \right]^{1/2} (1 - \delta_{m0})$

	$m = 0$	$m > 0$	$m < 0$
$U_{mm'}^l$	${}_0P_{0m'}^l$	${}_0P_{mm'}^l$	${}_0P_{mm'}^l$
$V_{mm'}^l$	${}_1P_{1m'}^l + {}_{-1}P_{-1m'}^l$	${}_1P_{m-1,m'}^l (1 + \delta_{m1})^{\frac{1}{2}} - {}_{-1}P_{-m+1,m'}^l (1 - \delta_{m1})$	${}_1P_{m+1,m'}^l (1 - \delta_{m,-1}) + {}_{-1}P_{-m-1,m'}^l (1 + \delta_{m,-1})^{\frac{1}{2}}$
$W_{mm'}^l$	-	${}_1P_{m+1,m'}^l + {}_{-1}P_{-m-1,m'}^l$	${}_1P_{m-1,m'}^l - {}_{-1}P_{-m+1,m'}^l$

	$ m'  < l$	$m' = l$	$m' = -l$
${}_iP_{\mu m'}^l$	$R_{i,0} R_{\mu,m'}^{l-1}$	$R_{i,1} R_{\mu,l-1}^{l-1} - R_{i,-1} R_{\mu,-l+1}^{l-1}$	$R_{i,1} R_{\mu,-l+1}^{l-1} + R_{i,-1} R_{\mu,l-1}^{l-1}$

## Appendix B

### Permutation Matrices For The Rotation Matrices

In general, in the specific first principle code, the order of atomic orbitals having the same angular momentum quantum number  $l$  can be different from the order of real spherical harmonics defined in ref.[1]. In this appendix, the permutation matrix which permutes the order of the rotation/roto-inversion matrix  $R^l$  from the order of the ref.[1] to the order used in 'OpenMX' code[8] will be shown.

At first, let's look at which real spherical harmonics corresponds to which orbitals.

For  $l=1$ ,

$$\begin{aligned} |Y_{1,-1}\rangle &\approx p_y \propto y/r \\ |Y_{1,0}\rangle &\approx p_z \propto z/r \\ |Y_{1,1}\rangle &\approx p_x \propto x/r \end{aligned}$$

For  $l=2$ ,

$$\begin{aligned} |Y_{2,-2}\rangle &\approx d_{xy} \propto (xy)/r^2 \\ |Y_{2,-1}\rangle &\approx d_{yz} \propto (yz)/r^2 \\ |Y_{2,0}\rangle &\approx d_{z^2} \propto (3z^2 - r^2)/r^2 \\ |Y_{2,1}\rangle &\approx d_{xz} \propto (zx)/r^2 \\ |Y_{2,2}\rangle &\approx d_{x^2-y^2} \propto (x^2 - y^2)/r^2 \end{aligned}$$

For  $l=3$ ,

$$\begin{aligned} |Y_{3,-3}\rangle &\approx f_{y(3x^2-y^2)} \propto y(3x^2 - y^2)/r^3 \\ |Y_{3,-2}\rangle &\approx f_{xyz} \propto (xyz)/r^3 \\ |Y_{3,-1}\rangle &\approx f_{yz^2} \propto y(4z^2 - x^2 - y^2)/r^3 \\ |Y_{3,0}\rangle &\approx f_{z^3} \propto z(2z^2 - 3x^2 - 3y^2)/r^3 \\ |Y_{3,1}\rangle &\approx f_{xz^2} \propto x(4z^2 - x^2 - y^2)/r^3 \\ |Y_{3,2}\rangle &\approx f_{z(x^2-y^2)} \propto z(x^2 - y^2)/r^3 \\ |Y_{3,3}\rangle &\approx f_{x(x^2-3y^2)} \propto x(x^2 - 3y^2)/r^3 \end{aligned}$$

In the OpenMX, the orders of the orbitals are as following.

For  $l = 1$ ,

$$\{p_x, p_y, p_z\} = \{|Y_{1,1}\rangle, |Y_{1,-1}\rangle, |Y_{1,0}\rangle\}$$

For  $l = 2$ ,

$$\{d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}\} = \{|Y_{2,0}\rangle, |Y_{2,2}\rangle, |Y_{2,-2}\rangle, |Y_{2,1}\rangle, |Y_{2,-1}\rangle\}$$

For  $l = 3$ ,

$$\begin{aligned} &\{f_{z^3}, f_{xz^2}, f_{yz^2}, f_{z(x^2-y^2)}, f_{xyz}, f_{x(x^2-3y^2)}, f_{y(3x^2-y^2)}\} \\ &= \{|Y_{3,0}\rangle, |Y_{3,1}\rangle, |Y_{3,-1}\rangle, |Y_{3,2}\rangle, |Y_{3,-2}\rangle, |Y_{3,3}\rangle, |Y_{3,-3}\rangle\} \end{aligned}$$

We can define the permutation matrix  $P^l$  for each  $l$ .

$$P^1 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

$$P^2 = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$$P^3 = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Let's denote the rotation/roto-inversion matrix with  $l$  in the order of real spherical harmonics like ref.[1] as  $R_{\text{rsh}}^l$  and that in the order of atomic orbitals in OpenMX code as  $R_o^l$ . Then,

$$R_o^l = P^l R_{\text{rsh}}^l (P^l)^T$$

## Appendix C

### The Convention Issue In The Tight Binding Theory

For the tight binding method, there are 2 kinds of conventions for the phase factor in the tight binding basis. In the main text, convention only using the lattice vector  $\mathbf{R}$  is adopted, i.e.  $e^{i\mathbf{k}\cdot\mathbf{R}}$ . This convention is so called 'unitcell convention'. On the other hand, convention using the atomic site(basis or sometimes denoted as Wyckoff position)  $\boldsymbol{\tau}$  in addition to the lattice vector for the phase factor is also commonly used. This is so called 'cell-periodic convention'. The basis function is written as follows.

$$|\phi_{i\alpha}^{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\tau}_i)} |\phi_{i\alpha}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i)\rangle$$

These 2 conventions are related by the unitary transformation which only multiply the phase factor to the coefficients. So they give us the physically identical result. But, the details of the formula are different.

Let's denote the coefficient from the 'cell-periodic' convention by the primed notation, i.e.  $C'_{i\alpha}{}^{n\mathbf{k}}$ . The overlap matrix also redefined in this convention.

$$S'_{(i\alpha)(j\beta)}(\mathbf{k}) \equiv \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\tau}_j-\boldsymbol{\tau}_i)} S_{(i\alpha)(j\beta)}(\mathbf{R})$$

Then the crystal symmetry matrix in the 'cell-periodic' convention is as fol-



lows.

$$\begin{aligned}
\langle \Psi_{n\mathbf{k}} | g | \Psi_{m\mathbf{k}} \rangle &= \sum_{\mathbf{R}(i\alpha)(j\beta)\gamma} C'_{i\alpha}{}^{n\mathbf{k}*} C'_{j\beta}{}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\tau}_j-\boldsymbol{\tau}_i)} e^{-i\mathbf{k}\cdot\mathbf{R}_j} \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}-\boldsymbol{\tau}_i) | \phi_{j\gamma}(\mathbf{r}-\mathbf{R}-\boldsymbol{\tau}_{jg}) \rangle \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \\
&= \sum_{(i\alpha)(j\beta)\gamma} C'_{i\alpha}{}^{n\mathbf{k}*} C'_{j\beta}{}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}_j-\boldsymbol{\tau}_{jg}-\mathbf{R}_j)} S'_{(i\alpha)(j\beta)\gamma}(\mathbf{k}) \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \\
&= \sum_{(i\alpha)(j\beta)(k\gamma)} C'_{i\alpha}{}^{n\mathbf{k}*} C'_{j\beta}{}^{m\mathbf{k}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}_j-\boldsymbol{\tau}_{jg}-\mathbf{R}_j)} S'_{(i\alpha)(k\gamma)}(\mathbf{k}) \delta_{kjg} \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta} \\
&= \mathbf{C}'^{n\mathbf{k}\dagger} S'(\mathbf{k}) \tilde{M}'_g(\mathbf{k}) \mathbf{C}'^{m\mathbf{k}} \\
&= \mathbf{C}'^{n\mathbf{k}\dagger} M'_g(\mathbf{k}) \mathbf{C}'^{m\mathbf{k}}
\end{aligned} \tag{10}$$

where

$$(\tilde{M}'_g(\mathbf{k}))_{(k\gamma)(j\beta)} = e^{i\mathbf{k}\cdot(\boldsymbol{\tau}_j-\boldsymbol{\tau}_{jg}-\mathbf{R}_j)} \delta_{kjg} \delta_{n_\gamma n_\beta} \delta_{l_\gamma l_\beta} R_{m_\gamma m_\beta}^{l_\beta}$$

note that by definition,  $\boldsymbol{\tau}_j - \boldsymbol{\tau}_{jg} - \mathbf{R}_j = \boldsymbol{\tau}_j - g\boldsymbol{\tau}_j$ .

If we need to explicitly describe the model, 'cell-periodic' convention may be more convenient. But in the automated calculations such as the post processing step of first-principle codes, the additional phase factor is redundant. In that case, the 'unitcell' convention in the main text will be appropriate.

The convention issue is discussed in ref.[7] in detail. In fact, the convention issue occurs when we treat the coefficient vector as the Bloch states. Because the basis in the tight binding formalism is Fourier transformed basis, we can't do so in general. If we describe the states in fully explicit form, the convention issue is avoided naturally.

## Appendix D

### Transformation Property Of The Crystal Momentum

In the main text, the special  $\mathbf{k}$ -point condition  $O\mathbf{k} = \mathbf{k} + \mathbf{G}$  are introduced. Considering the orthogonality of Bloch wave function, this is natural. Let's apply the lattice translation  $T_{\mathbf{R}'}$  which translate the coordinate in the function as  $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}'$  to the tight binding basis transformed by crystal symmetry

operation  $g$ .

$$\begin{aligned}
T_{\mathbf{R}'} g |\phi_{i\alpha}^{\mathbf{k}}\rangle &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}\beta} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{i\beta}(\mathbf{r} + \mathbf{R}' - O\mathbf{R} - \mathbf{R}_i - \boldsymbol{\tau}_{i_g})\rangle \delta_{n_\beta n_\alpha} \delta_{l_\beta l_\alpha} R_{m_\beta m_\alpha}^{l_\alpha} \\
&= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}\beta} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{i\beta}(\mathbf{r} + O(O^{-1}\mathbf{R}' - \mathbf{R}) - \mathbf{R}_i - \boldsymbol{\tau}_{i_g})\rangle \delta_{n_\beta n_\alpha} \delta_{l_\beta l_\alpha} R_{m_\beta m_\alpha}^{l_\alpha} \\
&= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}\beta} e^{i\mathbf{k}\cdot(\mathbf{R} + O^{-1}\mathbf{R}')} |\phi_{i\beta}(\mathbf{r} - O\mathbf{R} - \mathbf{R}_i - \boldsymbol{\tau}_{i_g})\rangle \delta_{n_\beta n_\alpha} \delta_{l_\beta l_\alpha} R_{m_\beta m_\alpha}^{l_\alpha} \\
&= e^{i\mathbf{k}\cdot O^{-1}\mathbf{R}'} g |\phi_{i\alpha}^{\mathbf{k}}\rangle = e^{iO\mathbf{k}\cdot\mathbf{R}'} g |\phi_{i\alpha}^{\mathbf{k}}\rangle
\end{aligned} \tag{11}$$

This is consistent with the general properties of Bloch wave function.

$$\begin{aligned}
T_{\mathbf{R}'}(g\Psi_{\mathbf{k}}(\mathbf{r})) &= T_{\mathbf{R}'} g(e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})) = T_{\mathbf{R}'}(e^{i\mathbf{k}\cdot g^{-1}\mathbf{r}} u_{\mathbf{k}}(g^{-1}\mathbf{r})) \\
&= T_{\mathbf{R}'}(e^{i\mathbf{k}\cdot(O^{-1}\mathbf{r} - O^{-1}\mathbf{t})} u_{\mathbf{k}}(O^{-1}\mathbf{r} - O^{-1}\mathbf{t})) \\
&= e^{i\mathbf{k}\cdot(O^{-1}\mathbf{r} + O^{-1}\mathbf{R}' - O^{-1}\mathbf{t})} u_{\mathbf{k}}(O^{-1}\mathbf{r} + O^{-1}\mathbf{R}' - O^{-1}\mathbf{t}) \\
&= e^{i\mathbf{k}\cdot O^{-1}\mathbf{R}'} e^{i\mathbf{k}\cdot(O^{-1}\mathbf{r} - O^{-1}\mathbf{t})} u_{\mathbf{k}}(O^{-1}\mathbf{r} + \mathbf{R}'' - O^{-1}\mathbf{t}) \\
&= e^{iO\mathbf{k}\cdot\mathbf{R}'} (g\Psi_{\mathbf{k}}(\mathbf{r}))
\end{aligned} \tag{12}$$

From this result and the Bloch theorem, we can confirm that  $g\Psi_{n\mathbf{k}}$  is a Bloch eigenstate of the crystal momentum  $O\mathbf{k}$ . So, for the crystal momentum which does not satisfy the special  $\mathbf{k}$  point condition above, the matrix element should vanish.