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NOTE

General Formulas for the Slater–Koster Tables

The recent development in the *tight-binding linear muffin thin orbital* method [1] of bandstructure calculations made it necessary to extend the Slater–Koster tables [2] of two-center overlap integrals for higher angular momenta. Several attempts have been made in this field, e.g., by Sharma [3] and Lendi [4]; nevertheless, a complete listing of the s–f, p–f, d–f, f–f and higher elements of the Slater–Koster transformation matrix is not available in the literature. In this note, first, we briefly describe the theory and obtain a completely general equation for the Slater–Koster transformation. Furthermore, instead of providing pages for formulas which cannot be treated properly, we give a listing of a simple MATHEMATICA program which is able to do all the required calculations symbolically.

Let us assume that we have two functions $\Psi^A(\mathbf{r})$ centered at the origin and $\Psi^B(\mathbf{r}-\mathbf{R})$ centered at $\mathbf{R}$. We wish to calculate a scalar product $\sigma^{AB}=\langle\Psi^A(\mathbf{r})\,\Psi^B(\mathbf{r}-\mathbf{R})\rangle$. Assume that the angular-dependence of the Ψ functions are given by

$$\begin{aligned}\Psi^A_{l'm'}(\mathbf{r})&=\phi^A_{l'}(r)\,Y_{l'm'}(\hat{r})\\ \Psi^B_{lm}(\mathbf{r}-\mathbf{R})&=\phi^B_l(|\mathbf{r}-\mathbf{R}|)\,Y_{lm}(\widehat{\mathbf{r}-\mathbf{R}}).\end{aligned} \tag{1}$$

Let us rotate the coordinate system (x, y, z) according to Fig. 1 into (x', y', z'). Then in the new system

$$\begin{aligned}\Psi^A_{l'm'}&=\sum_{\mu'} D^{l'}_{\mu'm'}(\Theta,\phi)\,\Psi^A_{l'\mu'}\\ \Psi^B_{lm}&=\sum_{\mu} D^{l}_{\mu,m}(\Theta,\phi)\,\Psi^B_{l\mu}.\end{aligned} \tag{2}$$

Here $D^l_{\mu m}$ stands for the irreducible matrix representation of the rotational group (see [5])

$$D^l_{\mu,m}(\Theta,\phi)=d^l_{\mu,m}(\Theta)\,e^{\imath m\phi}. \tag{3}$$

(Here we assumed that we have chosen the coordinate system in such a way that $\gamma=0$, see Fig. 1). The formulae for $d^l_{\mu,m}(\Theta)$ is given, e.g., in [5]. Thus

$$\begin{aligned}\sigma^{AB}_{l'm',lm}(\mathbf{R})&=\sum_{\mu\mu'} D^{l'*}_{\mu'm'}(\Theta,\phi)\,D^l_{\mu m}(\Theta,\phi)\langle\Psi^A_{l'\mu'}\,\Psi^B_{l\mu}\rangle\\ &=\sum_{\mu} Z^{m',m}_{l',l,\mu}(\Theta,\phi)\,I_{l',l,\mu},\end{aligned} \tag{4}$$

where we used that $\langle\Psi^A_{l'\mu'}\,\Psi^B_{l\mu}\rangle=\delta_{\mu\mu'}I_{l',l,\mu}$ and

$$Z^{m',m}_{l',l,\mu}(\Theta,\phi)=D^{l'*}_{\mu m'}(\Theta,\phi)\,D^l_{\mu m}(\Theta,\phi). \tag{5}$$

This product can be written [5] as

$$\begin{aligned}&D^{l'*}_{\mu m'}(\Theta,\phi)\,D^l_{\mu m}(\Theta,\phi)\\ &\quad=(-1)^{\mu-m'}D^{l'*}_{-\mu-m'}(\Theta,\phi)\,D^l_{\mu m}(\Theta,\phi)\\ &\quad=(-1)^{\mu-m'}\sum_\lambda{}'(2\lambda+1)\begin{pmatrix} l' & l & \lambda\\ -\mu & \mu & 0\end{pmatrix}\\ &\qquad\times\begin{pmatrix} l' & l & \lambda\\ -m' & m & m'-m\end{pmatrix}D^{\lambda*}_{0,m'-m}.\end{aligned} \tag{6}$$

Furthermore,

$$D^{\lambda*}_{0,m'-m}=\sqrt{4\pi/(2\lambda+1)}\;Y^*_{\lambda,m'-m}(\Theta,\phi).$$

In the λ summation the prime means that we have to satisfy the vector addition rules, i.e.,

$$|l'-l|\leqslant\lambda\leqslant l'+l$$

and

$$|m'-m|\leqslant\lambda.$$

After some manipulations, using the expressions for the spherical harmonics, we obtain

$$\begin{aligned}Z^{m'm}_{l'l\mu}&=[c_l+\imath\,\mathrm{sign}(m-m')\,c_m]^{|m-m'|}\\ &\quad\times\sum_{\lambda=|l'-l|}^{l'+l}{}'A_\lambda\sum_{k=[\lambda+|m-m'|+1]/2}^{\lambda}R^k_\lambda c_n^{2k-\lambda+1}.\end{aligned} \tag{7}$$

Here c_l, c_m, c_n are the direction cosines of the vector $\mathbf{R}$:

$$\begin{aligned}c_l&=\sin\Theta\cos\phi\\ c_m&=\sin\Theta\sin\phi\\ c_n&=\cos\Theta\end{aligned} \tag{8}$$

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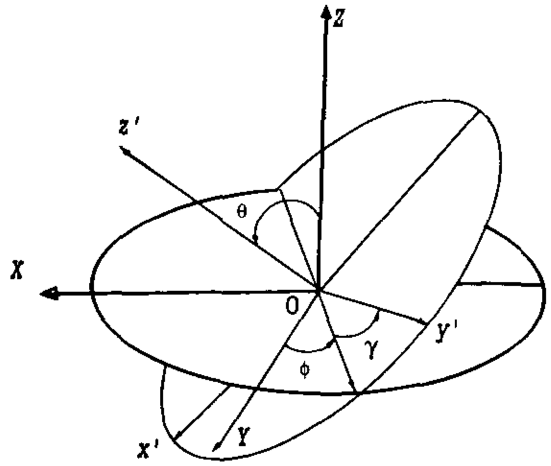

FIG. 1. Relative positions of the x, y, z and the x', y', z' coordinate systems.

and

$$A_\lambda = (-1)^{m+\mu+(m-m'+|m-m'|)/2} \times \sqrt{(\lambda-|m-m'|)!/(\lambda+|m-m'|)!\,(2\lambda+1)} \times \begin{pmatrix} l' & l & \lambda \\ -\mu & \mu & 0 \end{pmatrix} \begin{pmatrix} l' & l & \lambda \\ -m' & m & m'-m \end{pmatrix} \quad (9)$$

$$R_\lambda^k = \frac{(-1)^{\lambda-k}}{2^\lambda} \frac{(2k)!}{k!\,(\lambda-k)!\,(2k-\lambda-|m-m'|)!}.$$

If in (4) we restrict ourself to $\mu \geqslant 0$ only, then it is easy to show that

$$\sigma^{AB}_{l'm',lm} = \sum_{\mu \geqslant 0} \beta(\mu)\, Z^{m'm}_{l'l\mu} I_{l'l\mu}$$

$$\beta(\mu) = \begin{cases} 1 & \text{if } \mu = 0 \\ 2 & \text{otherwise} \end{cases}$$

and Z is defined exactly the same way as in (7); but in the λ-summation, apart from satisfying the vector addition rules, only those terms should be included for which $l' + l + \lambda$ is even.

Now, instead of using spherical harmonics Y_{lm}, we introduce the real harmonics in the following way:

$$\bar{Y}_{l0} = Y_{l0}$$

$$\bar{Y}_{lm-} = \frac{(-1)^m}{\imath\sqrt{2}} (Y_{lm} - Y^*_{lm}) \quad (10)$$

$$\bar{Y}_{lm+} = \frac{(-1)^m}{\sqrt{2}} (Y_{lm} + Y^*_{lm}),$$

$$m = 1, ..., l.$$

Explicit expressions for the real harmonics for s, p, d, and f are

$$\bar{Y}_{00} = C_s$$
$$\bar{Y}_{10} = C_p z$$
$$\bar{Y}_{11+} = C_p x$$
$$\bar{Y}_{11-} = C_p y$$
$$\bar{Y}_{20} = C_d(3z^2 - 1)$$
$$\bar{Y}_{21+} = \sqrt{12}\, C_d zx$$
$$\bar{Y}_{21-} = \sqrt{12}\, C_d zy$$
$$\bar{Y}_{22+} = \sqrt{3}\, C_d(x^2 - y^2)$$
$$\bar{Y}_{22-} = \sqrt{12}\, xy$$
$$\bar{Y}_{30} = C_f(5z^2 - 3)\, z$$
$$\bar{Y}_{31+} = \sqrt{3/2}\, C_f(5z^2 - 1)\, x$$
$$\bar{Y}_{31-} = \sqrt{3/2}\, C_f(5z^2 - 1)\, y$$
$$\bar{Y}_{32+} = \sqrt{15}\, C_f(x^2 - y^2)\, z$$
$$\bar{Y}_{32-} = 2\sqrt{15}\, C_f xyz$$
$$\bar{Y}_{33+} = \sqrt{5/2}\, C_f(x^2 - 3y^2)\, x$$
$$\bar{Y}_{33-} = \sqrt{5/2}\, C_f(3x^2 - y^2)\, y$$
$$C_s = \sqrt{1/4\pi}$$
$$C_p = \sqrt{3}\sqrt{1/4\pi}$$
$$C_d = \frac{\sqrt{5}}{2}\sqrt{1/4\pi}.$$
$$C_f = \frac{\sqrt{7}}{2}\sqrt{1/4\pi}.$$

Using this basis set, i.e., $\Psi = \phi \bar{Y}_{lm}$,

$$S^{m'm}_{l'l}(\mathbf{R}) = \sum_{\mu=0}^{\min(l'l)} \beta(\mu)\, \bar{Z}^{m'm}_{l'l\mu} I_{l'l\mu}, \quad (12)$$

where $\bar{Z}$ is connected to Z defined in (7) as

$$\bar{Z}^{m'+m+}_{l'l\mu} = (-1)^{m+m'}\,[\mathrm{Re}(Z^{m'm}_{l'l\mu}) + (-1)^{m'}\,\mathrm{Re}(Z^{-m'm}_{l'l\mu})]$$
$$\bar{Z}^{m'-m-}_{l'l\mu} = (-1)^{m+m'}\,[\mathrm{Re}(Z^{m'm}_{l'l\mu}) - (-1)^{m'}\,\mathrm{Re}(Z^{-m'm}_{l'l\mu})]$$
$$\bar{Z}^{m'-m+}_{l'l\mu} = (-1)^{m+m'}\,[-\mathrm{Im}(Z^{m'm}_{l'l\mu}) + (-1)^{m'}\,\mathrm{Im}(Z^{-m'm}_{l'l\mu})]$$
$$\bar{Z}^{m'+m-}_{l'l\mu} = (-1)^{m+m'}\,[\mathrm{Im}(Z^{m'm}_{l'l\mu}) + (-1)^{m'}\,\mathrm{Im}(Z^{-m'm}_{l'l\mu})]$$
$$\bar{Z}^{m'+0}_{l'l\mu} = \sqrt{2}\,(-1)^{m'}\,\mathrm{Re}(Z^{m'0}_{l'l\mu})$$
$$\bar{Z}^{m'-0}_{l'l\mu} = \sqrt{2}\,(-1)^{m'}\,\mathrm{Im}(Z^{m'0}_{l'l\mu}). \quad (13)$$

Finally, we give the listing of a MATHEMATICA [6] code, which is able to calculate the elements of $\bar{Z}$. It is necessary to use the "factor" package provided with the MATHEMATICA distribution. The package "wigner" is essentially the same as the one in the "discrete" distribution package except that it is using a modified function to calculate the square root of an integer number. In the code, the six $\bar{Z}$ matrixes in (13) are defined as integer functions zbpp, zbmm, zbmp, zbpm, zb0p, zbm0. A sample session to calculate $\bar{Z}^{1-2+}_{333}$:

```
In[1]:=<<factor.m

In[2]:=<<wigner.m

In[3]:=<<zbar.m

In[4]:=Simp[zbmp[3,1,3,2,3]]

        15cm(-1+cn)cn(1+cn)(3+3cl^2-cm^2+cn^2)
Out[4]= --------------------------------------
                  32Sqrt[2]Sqrt[5]
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