ARTICLES

Two-center *s-f* Slater-Koster integrals

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Two-center Slater-Koster integrals may be expressed as linear combinations of simpler polynomials that can either be factored or are of lower power in the direction cosines. This structure facilitates their tabulation and manipulation, as illustrated here by providing the complete set of *s-f* two-center integrals in this manner, as well as values of their m,m'-matrix dot products. The latter provide useful constraints for testing analytic or coded forms of these functions. These dot products also define a transformed two-center expansion which provides more convenient treatment of crystal-field terms. [S0163-1829(98)02032-3]

I. INTRODUCTION

Two-center Slater-Koster integrals[1] are an important component of tight-binding total-energy representations, which are increasingly used to provide realistic forces for molecular-dynamics simulations.[2] They also remain useful for providing an efficient parametrization of one-electron band structure.[3] These integrals describe the way that certain one-electron matrix elements vary as a function of the direction between two different sites about which the real atomic orbitals or potentials involved are centered. Slater and Koster first tabulated these functions for an *s-d* basis.[1,4] Subsequently, Lendi[5] gave tables for the *sf*, *pf*, and *df* cases; Sharma[6] provided selected integrals involving *f* and *g* orbitals; while Takegahara, Aoki, and Yanase[7] gave the complete set of *lf* integrals, $l \leqslant f$, although for a basis of cubic harmonics rather than the more usual real spherical harmonics [$\mathrm{Re}(Y_{lm})$, $\mathrm{Im}(Y_{lm})$, $m \geqslant 0$] used by Lendi and Sharma. The values of the two-center integrals can also be calculated numerically from general formulas;[5–9] however, especially for molecular-dynamics applications, it is essential to have a very efficient evaluation which favors coding of the individual polynomial forms for each integral. A difficulty associated with adding *f* states to the standard *s-d* tabulation[1,4] is the fact that the number and complexity of the functions increases significantly.

The purpose of the present paper is to note the internal structure of the Slater-Koster integrals which facilitates their tabulation and manipulation by expressing them as linear combinations of simpler polynomials that can either be factored or are of lower power in the direction cosines. To illustrate these features, the complete set of *s-f* two-center integrals are presented in this manner, using the more customary real spherical-harmonic basis [$\mathrm{Re}(Y_{lm})$, $\mathrm{Im}(Y_{lm})$, $m \geqslant 0$], which is more apt to be used by band-structure codes than cubic harmonics. Values are also given for the m,m'-matrix dot products between the Slater-Koster functions which provide important basis-independent constraints that are useful for testing either the analytic or coded functions. These dot products also define a transformed two-center expansion that greatly facilitates treatment of site-energy and crystal-field terms.

The two-center Slater-Koster integrals will be denoted by $g_\mu(lm,l'm',\hat{\mathbf{R}})$ in this paper, and also referred to more descriptively as geometric functions given their fundamental structural nature. They are most simply understood in terms of a diatomic molecule, where

$$\langle 0lm|H|\mathbf{R}l'm'\rangle = \sum_\mu g_\mu(lm,l'm',\hat{\mathbf{R}})\langle 0l\mu|H|\mathbf{R}l'\mu\rangle, \tag{1}$$

$$= \sum_\mu g_\mu(lm,l'm',\hat{\mathbf{R}})t_{ll'\mu}(R), \tag{2}$$

with $\mu = 0,\ldots,l_{\min}$, $l_{\min} \equiv \min(l,l')$, and $R \equiv |\mathbf{R}|$, $\hat{\mathbf{R}} \equiv \mathbf{R}/R$. Here $|0lm\rangle$ is an atomic orbital centered about one atom at the origin, characterized by angular momentum l and a magnetic quantum number m quantized as usual about the $\mathbf{z}$ axis; and similarly for $|\mathbf{R}l'm'\rangle$ at the other atom at $\mathbf{R}$. H is an operator such as the one-electron Hamiltonian. Equation (1) represents an expansion of these orbitals in terms of atomic orbitals $|0l\mu\rangle$ and $|\mathbf{R}l'\mu'\rangle$, quantized about the bond axis $\mathbf{R}$. Given axial symmetry, $\langle 0l\mu|H|\mathbf{R}l'\mu'\rangle$ is nonzero only for $\mu = \mu'$, and independent of the sign of μ. With appropriate definition of the $g_\mu(lm,l'm',\hat{\mathbf{R}})$, the expansion in Eq. (1) need therefore only involve non-negative values of μ, customarily denoted $\mu = \sigma,\pi,\delta,\phi,\ldots$. The matrix element $\langle 0l\mu|H|\mathbf{R}l'\mu\rangle = t_{ll'\mu}(R)$ is also a function only of the distance between the atoms and not their relative orientation. Thus Eq. (2) serves to separate structural and material-specific dependencies of the matrix elements, $\langle 0lm|H|\mathbf{R}l'm'\rangle$, into the geometric functions $g_\mu(lm,l'm',\hat{\mathbf{R}})$ and what in the solid are called hopping parameters $t_{ll'\mu}(R)$, respectively. The former are products of rotation group matrix elements when the two orbitals are defined in terms of spherical harmonics and the full μ range is used. This simple structure is spoiled except for $\mu = \sigma$

when real orbitals and the non-negative μ range are desired. This is the case considered by Slater and Koster,[1] and is of interest here.

The two-center expansion becomes an approximation in the solid,

$$\langle 0lm|H|\mathbf{R}l'm'\rangle \approx \sum_{\mu} g_{\mu}(lm,l'm',\hat{\mathbf{R}})t_{ll'\mu}(R), \qquad (3)$$

where infinitesimal rotation symmetry about the bond axis is lost and the orbitals $|\mathbf{R}lm\rangle$ may be Wannier functions which are no longer exact eigenfunctions of the angular momentum about the site at $\mathbf{R}$. A more formal interpretation[10,11] of this approximation is provided by noting that the geometric matrices $\mathbf{g}_{\mu}(l,l',\hat{\mathbf{R}}) \equiv [g_{\mu}(lm,l'm',\hat{\mathbf{R}})]$ for $\mu=\sigma,\ldots,l_{\min}$ provide an orthogonal matrix basis for $[(2l+1)\times(2l'+1)]$-dimensional m,m' matrices. The two-center expansion [Eq. (3)] is then just a decomposition of a given m,m' matrix into components ''along'' these orthogonal ''directions,'' just as a vector is expressed as a sum of its x, y, and z components. Equation (3) is an approximation only because this matrix basis is in general incomplete. Nonetheless, the hopping parameters $t_{ll'\mu}(R)$ are precisely defined by projection of $\langle 0lm|H|\mathbf{R}l'm'\rangle$ onto the existing basis matrices,

$$t_{ll'\mu}(R) = (2-\delta_{\mu\sigma})^{-1} \sum_{m,m'} g_{\mu}(lm,l'm',\hat{\mathbf{R}}) \times \langle 0lm|H|\mathbf{R}l'm'\rangle, \qquad (4)$$

where use has been made of the orthogonality relations[10]

$$\mathbf{g}_{\mu}(l,l',\hat{\mathbf{R}})\cdot\mathbf{g}_{\nu}(l,l',\hat{\mathbf{R}}) \equiv \sum_{m,m'} g_{\mu}(lm,l'm',\hat{\mathbf{R}})g_{\nu}(lm,l'm',\hat{\mathbf{R}}) = (2-\delta_{\mu\sigma})\delta_{\mu\nu}. \qquad (5)$$

In the remainder of this paper, definitions and conventions associated with presentation of the geometric functions $g_{\mu}(lm,l'm',\hat{\mathbf{R}})$ are noted in Sec. II. Section III then gives these s-f functions as linear combinations of simpler polynomials, denoted $\Delta_i(lm,l'm',\hat{\mathbf{R}})$, which are tabulated. This simplification also facilitates calculation of the matrix dot products, $\mathbf{g}_{\mu}(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_{\nu}(l,l',\hat{\mathbf{R}}_2)$, which are polynomials in $\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$, and are given for all s-f cases. These dot products provide powerful constraints which are useful for testing coded Slater-Koster integrals. They also define a transformation of the two-center expansion which offers a more convenient treatment of site-energy and crystal-field terms. This transformation is given for the s-f case in Sec. IV. Finally, a brief summary is given in Sec. V.

II. DEFINITIONS AND CONVENTIONS

The usual real linear combinations of spherical harmonics, $\overline{Y}_{lm}$, are used in this paper,

$$\overline{Y}_{l0} = Y_{l0},$$

TABLE I. Column vectors $\mathbf{g}_{\sigma}(l,s,\hat{\mathbf{R}}) \equiv [g_{\sigma}(lm,s,\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$. Row vectors $\mathbf{g}_{\sigma}(s,l,\hat{\mathbf{R}})$ are given by the transpose. Note that the customary real linear combinations of spherical harmonics are just $\overline{Y}_{lm}(\hat{\mathbf{R}}) = \sqrt{(2l+1)/4\pi}\, g_{\sigma}(lm,s,\hat{\mathbf{R}})$.

m,l	0	1	2	3
0	1	z	$\frac{1}{2}(3z^2-1)$	$\frac{1}{2}(5z^2-3)\,z$
1		x	$\sqrt{3}\,xz$	$\sqrt{\frac{3}{8}}\,(5z^2-1)\,x$
2		y	$\sqrt{3}\,yz$	$\sqrt{\frac{3}{8}}\,(5z^2-1)\,y$
3			$\frac{\sqrt{3}}{2}(x^2-y^2)$	$\frac{\sqrt{15}}{2}(x^2-y^2)\,z$
4			$\sqrt{3}\,xy$	$\sqrt{15}\,xyz$
5				$\sqrt{\frac{5}{8}}\,(x^2-3y^2)\,x$
6				$\sqrt{\frac{5}{8}}\,(3x^2-y^2)\,y$

$$\overline{Y}_{l,2m-1} = \frac{(-1)^m}{\sqrt{2}}(Y_{lm}+Y_{lm}^*), \qquad (6)$$

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

for $0\leqslant m\leqslant l$. Except for these three equations, the magnetic quantum number m is taken elsewhere in this work over the larger range $0\leqslant m\leqslant 2l$ to describe $\overline{Y}_{lm}$ and their associated geometric functions. In particular the l-s geometric functions are just

$$g_{\sigma}(lm,s,\hat{\mathbf{R}}) = \sqrt{\frac{4\pi}{2l+1}}\,\overline{Y}_{lm}(\hat{\mathbf{R}}), \qquad (7)$$

as listed in Table I. While it has also been customary to write the direction cosines as (l,m,n), this creates confusion with the frequent use of l and m as angular and magnetic quantum numbers in this work. Therefore, throughout this paper, the notation $\hat{\mathbf{R}}=(x,y,z)$ is used for the direction cosines where this triple is normalized to unity, $x^2+y^2+z^2=1$.

Tables of the polynomials $\Delta_i(lm,l'm',\hat{\mathbf{R}})$, used to define $g_{\mu}(lm,l'm',\hat{\mathbf{R}})$, are presented here for $l\geqslant l'$, rather than the more standard $l\leqslant l'$ limit, in order to provide a consistent tabulation while avoiding the need to split up the p-f and d-f matrices due to the practical limitations of column and page width. Note, however, that the matrices $\mathbf{g}_{\mu}(l,l',\hat{\mathbf{R}})$ and $\mathbf{g}_{\mu}(l',l,\hat{\mathbf{R}})$ are transposes of one another in this paper, i.e.,

$$g_{\mu}(lm,l'm',\hat{\mathbf{R}}) = g_{\mu}(l'm',lm,\hat{\mathbf{R}}), \qquad (8)$$

and similarly for Δ_i. The sign change for odd $l+l'$ in the overall matrix element,

$$\langle 0l'm'|H|\mathbf{R}lm\rangle=(-1)^{l+l'}\langle 0lm|H|\mathbf{R}l'm'\rangle, \quad (9)$$

must then come from $t_{l'l\mu}=(-1)^{l+l'}t_{ll'\mu}$, which is consistent with the interpretation of $t_{ll'\mu}(R)\sim\langle 0l\mu|H|\mathbf{R}l'\mu\rangle$. It may be more convenient in computer codes to include this sign factor as part of the $g_\mu(lm,l'm',\hat{\mathbf{R}})$, so as to not worry about the index order in the hopping parameters. Even so, note that the present matrix elements $g_\mu(lm,l'm',\hat{\mathbf{R}})$ for $l\leqslant l'$, obtained via Eq. (8), are in agreement with those of Slater and Koster,[1,4] Lendi,[5] and Ref. 7 and are appropriate for use with $t_{ll'\mu}$'s of customary sign conventions.

III. TABULATED GEOMETRIC MATRICES

The two-center Slater-Koster geometric matrices $\mathbf{g}_\mu(l,l',\hat{\mathbf{R}})$, $\mu=\sigma,\ldots,l_{\min}$ may be conveniently given as linear combinations of an equal number of $[(2l+1)\times(2l'+1)]$-dimensional matrices, $\mathbf{\Delta}_i(l,l',\hat{\mathbf{R}})$:

$$\mathbf{g}_\mu(l,l',\hat{\mathbf{R}})=\sum_{k=0}^{l_{\min}} c_{\mu k}(l,l')\mathbf{\Delta}_{l+l'-2k}(l,l',\hat{\mathbf{R}}). \quad (10)$$

Here the index $i=l+l'-2k$ also indicates the highest power of the direction cosines which appears in the matrix elements of $\mathbf{\Delta}_i(l,l',\hat{\mathbf{R}})$. Furthermore,

$$\mathbf{\Delta}_{l+l'}(l,l',\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(l,l',\hat{\mathbf{R}})=\mathbf{g}_\sigma(l,s,\hat{\mathbf{R}})\ \mathbf{g}_\sigma(s,l',\hat{\mathbf{R}}); \quad (11)$$

that is,

$$\Delta_{l+l'}(lm,l'm',\hat{\mathbf{R}})\equiv g_\sigma(lm,l'm',\hat{\mathbf{R}}) = g_\sigma(lm,s,\hat{\mathbf{R}})g_\sigma(s,l'm',\hat{\mathbf{R}}), \quad (12)$$

noting that $\mathbf{g}_\sigma(l,l',\hat{\mathbf{R}})$ may be factored into the product of the column vector $\mathbf{g}_\sigma(l,s,\hat{\mathbf{R}})$ multiplied by the row vector $\mathbf{g}_\sigma(s,l',\hat{\mathbf{R}})$. Thus, given the simple structure of $\mathbf{\Delta}_{l+l'}$, one need only tabulate matrices $\mathbf{\Delta}_i$ which involve lower powers of the direction cosines, by 2, 4, and so on. Moreover, for $l=l'$, one of the $l+1$ matrices $\mathbf{\Delta}_i$ is $\mathbf{\Delta}_0=\mathbf{1}$, i.e., just the identity.

The matrices $\Delta_i(l,l',\hat{\mathbf{R}})$ were calculated analytically in this work using the tabulations of Slater and Koster[1,4] for s-d states, and those of Refs. 5 and 7 for the lf cases, with the last appropriately transformed to correspond to the present basis. While a recent paper by Kollár and Ujfalussy[9] provides a MATHEMATICA (Ref. 12) code for obtaining the polynomial forms of the Slater-Koster integrals, a more crude but effective approach was used here to obtain the polynomials $\Delta_i(l,l',\hat{\mathbf{R}})$ in a numerical fashion as a test of the analytic derivations. All Slater-Koster geometric functions as well as the linear combinations defining Δ_i were numerically calculated using general formulas[13] on a $\sim$800-point mesh on the direction cosine surface $x^2+y^2+z^2=1$, and the results fit by least squares to polynomials in $x^iy^jz^k$ with $k\leqslant 1$. The root-mean-square deviations in these fits were in all cases of the order of the machine round-off error demonstrating the completeness of the representation. The resultant coefficients and powers were easily converted to analytic forms, with factors of x^2+y^2 generally replaced by $1-z^2$. There was complete agreement among all analytic and numerically derived polynomials except for two of Lendi's df expressions, as noted in Ref. 5, which are also inconsistent with Ref. 7. As an additional test, the polynomials Δ_i tabulated here, as well as the associated geometric functions g_μ, were coded, and numerical calculations then performed of the matrix dot products $\mathbf{\Delta}_i(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(l,l',\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)$. A random direction was taken for $\hat{\mathbf{R}}_1$, while $\hat{\mathbf{R}}_2$ was sampled over the above-mentioned mesh, and a least-squares fit made to the results as a function of $\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$. These numerical polynomials also agreed with the analytically derived dot product functions. As an indication of the power of these dot-product constraints, a single sign error in one of the Slater-Koster integrals can change the root-mean-square deviation of such a fit from machine round-off error, 10^{-13}–10^{-15} for the workstation used here, to $O(10^{-1})$, for example.

TABLE II. Matrix dot products $\mathbf{\Delta}_i(p,p,\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(p,p,\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(p,p,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(p,p,\hat{\mathbf{R}}_2)$, where $\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$.

i j	$\mathbf{\Delta}_i\cdot\mathbf{\Delta}_j$	μ ν	$\mathbf{g}_\mu\cdot\mathbf{g}_\nu$
0 0	3	σ σ	χ^2
0 2	1	σ π	$1-\chi^2$
2 2	χ^2	π π	$1+\chi^2$

In the remainder of this section, $\mathbf{g}_\mu$ are defined in terms of the polynomials $\mathbf{\Delta}_i$, which are tabulated. The method used here was briefly outlined at the end of the Appendix in Ref. 10 for just the s-d case; however, no polynomials were tabulated. Matrix dot products are given for both $\mathbf{\Delta}_i(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(l,l',\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)$, which are functions of $\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$. The latter reduce to the orthogonality relations [Eq. (5)] for $\hat{\mathbf{R}}_1=\hat{\mathbf{R}}_2$. Note that the abbreviation

$$\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2=x_1x_2+y_1y_2+z_1z_2, \quad (13)$$

is used throughout this section, where each direction triplet (x,y,z) is normalized to unity.

A. l-s matrices

The two-center l-s geometric matrices are given in Table I, with dot products for different directions given by

$$\mathbf{g}_\sigma(l,s,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\sigma(l,s,\hat{\mathbf{R}}_2)=\begin{cases}1, & l=s\\ \chi, & l=p\\ \frac{1}{2}(3\chi^2-1), & l=d\\ \frac{1}{2}(5\chi^2-3)\chi, & l=f.\end{cases} \quad (14)$$

B. p-p matrices

The two-center p-p geometric matrices may be written

$$\mathbf{g}_\sigma(p,p,\hat{\mathbf{R}})=\mathbf{\Delta}_2(p,p,\hat{\mathbf{R}}),$$
$$\mathbf{g}_\pi(p,p,\hat{\mathbf{R}})=-\mathbf{\Delta}_2(p,p,\hat{\mathbf{R}})+\mathbf{\Delta}_0(p,p,\hat{\mathbf{R}}), \quad (15)$$

TABLE III. The matrix $\mathbf{\Delta}_1(d,p,\hat{\mathbf{R}})\equiv[\Delta_1(dm,pm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$. $\mathbf{\Delta}_1(p,d,\hat{\mathbf{R}})$ is given by the transpose.

m,m'	0	1	2
0	$\frac{2}{\sqrt{3}}z$	$-\frac{1}{\sqrt{3}}x$	$-\frac{1}{\sqrt{3}}y$
1	x	z	0
2	y	0	z
3	0	x	$-y$
4	0	y	x

where

$$\mathbf{\Delta}_2(p,p,\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(p,s,\hat{\mathbf{R}})\mathbf{g}_\sigma(s,p,\hat{\mathbf{R}}), \tag{16}$$

$$\mathbf{\Delta}_0(p,p,\hat{\mathbf{R}})\equiv\mathbf{1}. \tag{17}$$

The matrix dot products for different directions are given in Table II.

C. *d-p* matrices

The two-center *d-p* geometric matrices may be written

$$\begin{aligned}\mathbf{g}_\sigma(d,p,\hat{\mathbf{R}})&=\mathbf{\Delta}_3(d,p,\hat{\mathbf{R}}),\\ \mathbf{g}_\pi(d,p,\hat{\mathbf{R}})&=-\frac{2}{\sqrt{3}}\mathbf{\Delta}_3(d,p,\hat{\mathbf{R}})+\mathbf{\Delta}_1(d,p,\hat{\mathbf{R}}),\end{aligned} \tag{18}$$

where

$$\mathbf{\Delta}_3(d,p,\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(d,s,\hat{\mathbf{R}})\mathbf{g}_\sigma(s,p,\hat{\mathbf{R}}), \tag{19}$$

and $\mathbf{\Delta}_1(d,p,\hat{\mathbf{R}})$ is defined in Table III. The matrix dot products for different directions are given in Table IV.

D. *d-d* matrices

The two-center *d-d* geometric matrices may be written

$$\begin{aligned}\mathbf{g}_\sigma(d,d,\hat{\mathbf{R}})&=\mathbf{\Delta}_4(d,d,\hat{\mathbf{R}}),\\ \mathbf{g}_\pi(d,d,\hat{\mathbf{R}})&=-\tfrac{4}{3}\mathbf{\Delta}_4(d,d,\hat{\mathbf{R}})+\mathbf{\Delta}_2(d,d,\hat{\mathbf{R}})+\mathbf{\Delta}_0(d,d,\hat{\mathbf{R}}),\\ \mathbf{g}_\delta(d,d,\hat{\mathbf{R}})&=\tfrac{1}{3}\mathbf{\Delta}_4(d,d,\hat{\mathbf{R}})-\mathbf{\Delta}_2(d,d,\hat{\mathbf{R}}),\end{aligned} \tag{20}$$

TABLE IV. Dot products $\mathbf{\Delta}_i(d,p,\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(d,p,\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(d,p,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(d,p,\hat{\mathbf{R}}_2)$, where $\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$.

i j	$\mathbf{\Delta}_i\cdot\mathbf{\Delta}_j$	μ ν	$\mathbf{g}_\mu\cdot\mathbf{g}_\nu$
1 1	$\frac{10}{3}\chi$	σ σ	$\frac{1}{2}\chi(3\chi^2-1)$
1 3	$\frac{2}{\sqrt{3}}\chi$	σ π	$-\sqrt{3}\,\chi(\chi^2-1)$
3 3	$\frac{1}{2}(3\chi^2-1)\chi$	π π	$2\chi^3$

TABLE V. The matrix $\mathbf{\Delta}_2(d,d,\hat{\mathbf{R}})\equiv[\Delta_2(dm,dm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$.

m,m'	0	1	2	3	4
0	$z^2-\frac{2}{3}$	$\frac{1}{\sqrt{3}}xz$	$\frac{1}{\sqrt{3}}yz$	$-\frac{1}{\sqrt{3}}(x^2-y^2)$	$-\frac{2}{\sqrt{3}}xy$
1	$\frac{1}{\sqrt{3}}xz$	$-y^2$	xy	xz	yz
2	$\frac{1}{\sqrt{3}}yz$	xy	$-x^2$	$-yz$	xz
3	$-\frac{1}{\sqrt{3}}(x^2-y^2)$	xz	$-yz$	$-z^2$	0
4	$-\frac{2}{\sqrt{3}}xy$	yz	xz	0	$-z^2$

where

$$\mathbf{\Delta}_4(d,d,\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(d,s,\hat{\mathbf{R}})\mathbf{g}_\sigma(s,d,\hat{\mathbf{R}}), \tag{21}$$

$\mathbf{\Delta}_2(d,d,\hat{\mathbf{R}})$ is defined in Table V, and

$$\mathbf{\Delta}_0(d,d,\hat{\mathbf{R}})\equiv\mathbf{1}. \tag{22}$$

The matrix dot products for different directions are given in Table VI.

E. *f-p* matrices

The two-center *f-p* geometric matrices may be written

$$\begin{aligned}\mathbf{g}_\sigma(f,p,\hat{\mathbf{R}})&=\mathbf{\Delta}_4(f,p,\hat{\mathbf{R}}),\\ \mathbf{g}_\pi(f,p,\hat{\mathbf{R}})&=-\sqrt{\tfrac{3}{2}}\mathbf{\Delta}_4(f,p,\hat{\mathbf{R}})+\tfrac{1}{2}\mathbf{\Delta}_2(f,p,\hat{\mathbf{R}}),\end{aligned} \tag{23}$$

where

$$\mathbf{\Delta}_4(f,p,\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(f,s,\hat{\mathbf{R}})\mathbf{g}_\sigma(s,p,\hat{\mathbf{R}}), \tag{24}$$

and $\mathbf{\Delta}_2(f,p,\hat{\mathbf{R}})$ is given in Table VII. The matrix dot products for different directions are given in Table VIII.

TABLE VI. Dot products $\mathbf{\Delta}_i(d,d,\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(d,d,\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(d,d,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(d,d,\hat{\mathbf{R}}_2)$, where $\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$.

i j	$\mathbf{\Delta}_i\cdot\mathbf{\Delta}_j$	μ ν	$\mathbf{g}_\mu\cdot\mathbf{g}_\nu$
0 0	5	σ σ	$\frac{1}{4}(3\chi^2-1)^2$
0 2	$-\frac{5}{3}$	σ π	$-3\chi^2(\chi^2-1)$
0 4	1	σ δ	$\frac{3}{4}(\chi^2-1)^2$
2 2	$\frac{1}{9}(21\chi^2-2)$	π π	$4\chi^4-3\chi^2+1$
2 4	$\frac{1}{3}(3\chi^2-2)$	π δ	$-\chi^4+1$
4 4	$\frac{1}{4}(3\chi^2-1)^2$	δ δ	$\frac{1}{4}(\chi^4+6\chi^2+1)$

TABLE VII. The matrix $\mathbf{\Delta}_2(f,p,\hat{\mathbf{R}})\equiv[\Delta_2(fm,pm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$. $\mathbf{\Delta}_2(p,f,\hat{\mathbf{R}})$ is given by the transpose.

m,m'	0	1	2
0	$\sqrt{\frac{3}{2}}(3z^2-1)$	$-\sqrt{6}\,xz$	$-\sqrt{6}\,yz$
1	$4xz$	$\frac{1}{2}(5z^2-2x^2-1)$	$-xy$
2	$4yz$	$-xy$	$\frac{1}{2}(5z^2-2y^2-1)$
3	$\sqrt{\frac{5}{2}}(x^2-y^2)$	$\sqrt{10}\,xz$	$-\sqrt{10}\,yz$
4	$\sqrt{10}\,xy$	$\sqrt{10}\,yz$	$\sqrt{10}\,xz$
5	0	$\frac{\sqrt{15}}{2}(x^2-y^2)$	$-\sqrt{15}\,xy$
6	0	$\sqrt{15}\,xy$	$\frac{\sqrt{15}}{2}(x^2-y^2)$

F. f-d matrices

The two-center f-d geometric matrices may be written

$$\mathbf{g}_\sigma(f,d,\hat{\mathbf{R}})=\mathbf{\Delta}_5(f,d,\hat{\mathbf{R}}),$$

$$\mathbf{g}_\pi(f,d,\hat{\mathbf{R}})=-\sqrt{2}\;\mathbf{\Delta}_5(f,d,\hat{\mathbf{R}})+\frac{1}{2}\mathbf{\Delta}_3(f,d,\hat{\mathbf{R}})+\frac{1}{2}\mathbf{\Delta}_1(f,d,\hat{\mathbf{R}}),\tag{25}$$

$$\mathbf{g}_\delta(f,d,\hat{\mathbf{R}})=\frac{1}{\sqrt{5}}\,\mathbf{\Delta}_5(f,d,\hat{\mathbf{R}})-\sqrt{\tfrac{2}{5}}\mathbf{\Delta}_3(f,d,\hat{\mathbf{R}}),$$

TABLE VIII. Dot products $\mathbf{\Delta}_i(f,p,\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(f,p,\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(f,p,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(f,p,\hat{\mathbf{R}}_2)$, where $\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$.

i j	$\mathbf{\Delta}_i\cdot\mathbf{\Delta}_j$	μ ν	$\mathbf{g}_\mu\cdot\mathbf{g}_\nu$
2 2	$7(3\chi^2-1)$	σ σ	$\frac{1}{2}(5\chi^2-3)\chi^2$
2 4	$\sqrt{\frac{3}{2}}(3\chi^2-1)$	σ π	$-\sqrt{\frac{3}{8}}(5\chi^2-1)(\chi^2-1)$
4 4	$\frac{1}{2}(5\chi^2-3)\chi^2$	π π	$\frac{1}{4}(15\chi^4-6\chi^2-1)$

where

$$\mathbf{\Delta}_5(f,d,\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(f,s,\hat{\mathbf{R}})\mathbf{g}_\sigma(s,d,\hat{\mathbf{R}}),\tag{26}$$

and $\mathbf{\Delta}_3(f,d,\hat{\mathbf{R}})$ and $\mathbf{\Delta}_1(f,d,\hat{\mathbf{R}})$ are defined in Tables IX and X, respectively. The matrix dot products for different directions are given in Table XI.

G. f-f matrices

The two-center f-f geometric matrices may be written

$$\mathbf{g}_\sigma(f,f,\hat{\mathbf{R}})=\mathbf{\Delta}_6(f,f,\hat{\mathbf{R}}),\tag{27}$$

$$\mathbf{g}_\pi(f,f,\hat{\mathbf{R}})=-\tfrac{3}{2}\mathbf{\Delta}_6(f,f,\hat{\mathbf{R}})+\tfrac{5}{8}\mathbf{\Delta}_4(f,f,\hat{\mathbf{R}})+\tfrac{5}{8}\mathbf{\Delta}_2(f,f,\hat{\mathbf{R}})+\tfrac{5}{8}\mathbf{\Delta}_0(f,f,\hat{\mathbf{R}}),$$

$$\mathbf{g}_\delta(f,f,\hat{\mathbf{R}})=\tfrac{3}{5}\mathbf{\Delta}_6(f,f,\hat{\mathbf{R}})-\mathbf{\Delta}_4(f,f,\hat{\mathbf{R}}),$$

$$\mathbf{g}_\phi(f,f,\hat{\mathbf{R}})=-\tfrac{1}{10}\mathbf{\Delta}_6(f,f,\hat{\mathbf{R}})+\tfrac{3}{8}\mathbf{\Delta}_4(f,f,\hat{\mathbf{R}})-\tfrac{5}{8}\mathbf{\Delta}_2(f,f,\hat{\mathbf{R}})+\tfrac{3}{8}\mathbf{\Delta}_0(f,f,\hat{\mathbf{R}}),$$

where

$$\mathbf{\Delta}_6(f,f,\hat{\mathbf{R}})\equiv\mathbf{g}_\sigma(f,s,\hat{\mathbf{R}})\mathbf{g}_\sigma(s,f,\hat{\mathbf{R}});\tag{28}$$

TABLE IX. The matrix $\mathbf{\Delta}_3(f,d,\hat{\mathbf{R}})\equiv[\Delta_3(fm,dm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$. $\mathbf{\Delta}_3(d,f,\hat{\mathbf{R}})$ is given by the transpose.

m,m'	0	1	2	3	4
0	$\frac{1}{\sqrt{2}}(4z^2-3)z$	$\sqrt{\frac{3}{2}}\,xz^2$	$\sqrt{\frac{3}{2}}\,yz^2$	$-\sqrt{6}\,(x^2-y^2)z$	$-2\sqrt{6}\,xyz$
1	$\frac{\sqrt{3}}{2}(3z^2-1)x$	$\frac{1}{2}(x^2-5y^2)z$	$3xyz$	$(\frac{5}{2}z^2-x^2+y^2)x$	$\frac{1}{2}(5z^2-4x^2)y$
2	$\frac{\sqrt{3}}{2}(3z^2-1)y$	$3xyz$	$\frac{1}{2}(y^2-5x^2)z$	$-(\frac{5}{2}z^2+x^2-y^2)y$	$\frac{1}{2}(5z^2-4y^2)x$
3	0	$\sqrt{\frac{5}{2}}(z^2-2y^2)x$	$-\sqrt{\frac{5}{2}}(z^2-2x^2)y$	$\sqrt{\frac{5}{2}}(1-2z^2)z$	0
4	0	$\sqrt{\frac{5}{2}}(1-2y^2)y$	$\sqrt{\frac{5}{2}}(1-2x^2)x$	0	$\sqrt{\frac{5}{2}}(1-2z^2)z$
5	$\frac{\sqrt{5}}{2}(3y^2-x^2)x$	$\frac{\sqrt{15}}{2}(x^2-y^2)z$	$-\sqrt{15}\,xyz$	$-\frac{\sqrt{15}}{2}\,xz^2$	$\frac{\sqrt{15}}{2}\,yz^2$
6	$-\frac{\sqrt{5}}{2}(3x^2-y^2)y$	$\sqrt{15}\,xyz$	$\frac{\sqrt{15}}{2}(x^2-y^2)z$	$-\frac{\sqrt{15}}{2}\,yz^2$	$-\frac{\sqrt{15}}{2}\,xz^2$

TABLE X. The matrix $\mathbf{\Delta}_1(f,d,\hat{\mathbf{R}})\equiv[\Delta_1(fm,dm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$. $\mathbf{\Delta}_1(d,f,\hat{\mathbf{R}})$ is given by the transpose.

m,m'	0	1	2	3	4
0	$\frac{3}{\sqrt{2}}z$	$-\sqrt{\frac{3}{2}}x$	$-\sqrt{\frac{3}{2}}y$	0	0
1	$\sqrt{3}x$	$2z$	0	$-\frac{1}{2}x$	$-\frac{1}{2}y$
2	$\sqrt{3}y$	0	$2z$	$\frac{1}{2}y$	$-\frac{1}{2}x$
3	0	$\sqrt{\frac{5}{2}}x$	$-\sqrt{\frac{5}{2}}y$	$\sqrt{\frac{5}{2}}z$	0
4	0	$\sqrt{\frac{5}{2}}y$	$\sqrt{\frac{5}{2}}x$	0	$\sqrt{\frac{5}{2}}z$
5	0	0	0	$\frac{\sqrt{15}}{2}x$	$-\frac{\sqrt{15}}{2}y$
6	0	0	0	$\frac{\sqrt{15}}{2}y$	$\frac{\sqrt{15}}{2}x$

$\mathbf{\Delta}_4(f,f,\hat{\mathbf{R}})$ and $\mathbf{\Delta}_2(f,f,\hat{\mathbf{R}})$ are defined in Tables XII and XIII, respectively, and

$$\mathbf{\Delta}_0(f,f,\hat{\mathbf{R}})\equiv\mathbf{1}. \tag{29}$$

The matrix dot products for different directions are given in Table XIV.

IV. TRANSFORMED GEOMETRIC MATRICES

A transformation of the geometric matrices and their associated two-center expansion greatly simplifies treatment of site-energy and crystal-field contributions to the one-electron Hamiltonian. This transformation has been given elsewhere for an s-d basis, as has a detailed discussion of its benefits.[10] Here, it is presented for the extended s-f basis, and related to the matrix dot products given in Sec. III.

TABLE XI. Dot products $\mathbf{\Delta}_i(f,d,\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(f,d,\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(f,d,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(f,d,\hat{\mathbf{R}}_2)$, where $\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$.

i j	$\mathbf{\Delta}_i\cdot\mathbf{\Delta}_j$	μ ν	$\mathbf{g}_\mu\cdot\mathbf{g}_\nu$
1 1	$\frac{35}{2}\chi$	σ σ	$\frac{1}{4}(5\chi^2-3)(3\chi^2-1)\chi$
1 3	$-\frac{7}{2}\chi$	σ π	$-\frac{3}{\sqrt{8}}(5\chi^2-1)(\chi^2-1)\chi$
1 5	$\frac{3}{\sqrt{2}}\chi$	σ δ	$\frac{\sqrt{45}}{4}(\chi^2-1)^2\chi$
3 3	$\frac{1}{2}(24\chi^2-13)\chi$	π π	$\frac{1}{2}(15\chi^4-16\chi^2+5)\chi$
3 5	$\frac{1}{\sqrt{2}}(4\chi^2-3)\chi$	π δ	$-\sqrt{\frac{5}{8}}(3\chi^2+1)(\chi^2-1)\chi$
5 5	$\frac{1}{4}(5\chi^2-3)(3\chi^2-1)\chi$	δ δ	$\frac{1}{4}(3\chi^4+10\chi^2-5)\chi$

To review the motivation for the transformation, consider the intrasite matrix element

$$\langle 0lm|H|0l'm'\rangle\approx\varepsilon_l\delta_{ll'}\delta_{mm'}+\sum_{\mathbf{R}\neq0,\mu}^{\mathbf{R}\neq0}g_\mu(lm,l'm',\hat{\mathbf{R}})\chi_{ll'\mu}(R), \tag{30}$$

where H is the one-electron Hamiltonian, ε_l is a site energy, and $\chi_{ll'\mu}(R)$ are crystal-field parameters which arise from two-center expansion of one-electron potential terms at sites $\mathbf{R}\neq0$. In contrast to the intersite matrix elements, Eq. (30) involves geometric matrices for different directions, $\hat{\mathbf{R}}$, which spoils the orthogonality relations [Eq. (5)]. That is, projection of $\langle 0lm|H|0l'm'\rangle$ onto $\mathbf{g}_\mu(l,l',\hat{\mathbf{R}})$ for some μ and $\hat{\mathbf{R}}$ will in general still yield terms involving all values of μ. Moreover, for $l=l'$, $\mathbf{g}_\mu(l,l,\hat{\mathbf{R}})$ are not orthogonal to $[\delta_{mm'}]$, so that crystal-field and site-energy terms mix in a complex manner. Both shortcomings may be rectified by what is in effect a ''rotation'' of the set of geometric basis matrices, $\mathbf{g}_\mu$, $\mu=\sigma,\ldots,l_{\min}$, to use the language of the discussion below Eq. (3). In the $l=l'$ case, for example, the transformed two-center expansion based on the rotated matrices exhibits a clean separation between crystal-field terms which contribute to $\langle 0lm|H|0l'm'\rangle$ as coefficients of $[\delta_{mm'}]$, and those which serve as coefficients of orthogonal matrices. The former are responsible for environmental dependence of what are really the effective site energies, ε_l plus crystal-field contributions, that are customarily obtained from fits to band structure.[10]

The transformation is defined by diagonalizing a scaled dot-product matrix

$$[M_{\mu\nu}]\equiv[c_\mu\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)c_\nu],$$

where the scaling factors $c_\mu\equiv(2-\delta_{\mu\sigma})^{-1/2}$ are related to the normalization of $\mathbf{g}_\mu$, and serve to make the remaining part of the transformation unitary. The dot products $\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)$ are the polynomials in $\chi\equiv\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$ given in Sec. III. Viewed as functions of χ, each linearly independent term in

$$f_{\mu\nu}(\chi)\equiv c_\mu\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)c_\nu$$

defines a separate μ,ν matrix, the set of which can be shown to all mutually commute for a given l,l'. This means that a single fixed unitary transformation can diagonalize $[M_{\mu\nu}]$ *for all* directions $\hat{\mathbf{R}}_1$ and $\hat{\mathbf{R}}_2$. If the transformed quantities are indicated by tildes and indices α,β in place of μ,ν, then

$$\tilde{\mathbf{g}}_\alpha(l,l',\hat{\mathbf{R}})=\sum_\mu U_{\alpha\mu}c_\mu\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}), \tag{31}$$

$$\tilde{\mathbf{g}}_\alpha(l,l',\hat{\mathbf{R}}_1)\cdot\tilde{\mathbf{g}}_\beta(l,l',\hat{\mathbf{R}}_2)=\sum_{\mu,\nu}U_{\alpha\mu}c_\mu\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)c_\nu U_{\beta\nu}\propto\delta_{\alpha\beta}, \tag{32}$$

TABLE XII. The matrix $\mathbf{\Delta}_4(f,f,\hat{\mathbf{R}})\equiv[\Delta_4(fm,fm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$.

m,m'	0	1	2
0	$\frac{3}{5}(5z^2-4)z^2$	$\frac{\sqrt{6}}{5}(5z^2-2)xz$	$\frac{\sqrt{6}}{5}(5z^2-2)yz$
1	$\frac{\sqrt{6}}{5}(5z^2-2)xz$	$-\frac{2}{5}x^2-\frac{1}{2}(5y^2-3x^2)z^2$	$\frac{2}{5}(10z^2-1)xy$
2	$\frac{\sqrt{6}}{5}(5z^2-2)yz$	$\frac{2}{5}(10z^2-1)xy$	$-\frac{2}{5}y^2-\frac{1}{2}(5x^2-3y^2)z^2$
3	$-\sqrt{\frac{3}{5}}(x^2-y^2)z^2$	$\frac{1}{\sqrt{10}}(6z^2-8y^2-1)xz$	$-\frac{1}{\sqrt{10}}(6z^2-8x^2-1)yz$
4	$-\sqrt{\frac{12}{5}}\,xyz^2$	$\frac{1}{\sqrt{10}}(2z^2-8y^2+3)yz$	$\frac{1}{\sqrt{10}}(2z^2-8x^2+3)xz$
5	$\sqrt{\frac{18}{5}}(3y^2-x^2)xz$	$\frac{\sqrt{15}}{2}(x^2-y^2-\frac{7}{5}\,x^4+\frac{6}{5}\,x^2y^2+y^4)$	$\sqrt{\frac{3}{5}}(4y^2-4z^2-1)xy$
6	$\sqrt{\frac{18}{5}}(y^2-3x^2)yz$	$\sqrt{\frac{3}{5}}(4z^2-4x^2+1)xy$	$\frac{\sqrt{15}}{2}(x^2-y^2-x^4-\frac{6}{5}\,x^2y^2+\frac{7}{5}\,y^4)$

m,m'	3	4
0	$-\sqrt{\frac{3}{5}}(x^2-y^2)z^2$	$-\sqrt{\frac{12}{5}}\,xyz^2$
1	$\frac{1}{\sqrt{10}}(6z^2-8y^2-1)xz$	$\frac{1}{\sqrt{10}}(2z^2-8y^2+3)yz$
2	$-\frac{1}{\sqrt{10}}(6z^2-8x^2-1)yz$	$\frac{1}{\sqrt{10}}(2z^2-8x^2+3)xz$
3	$(2-3z^2)z^2-4x^2y^2$	$2(x^2-y^2)xy$
4	$2(x^2-y^2)xy$	$-(2z^2-1)^2+4x^2y^2$
5	$-\sqrt{\frac{3}{2}}(2z^2-1)xz$	$\sqrt{\frac{3}{2}}(2z^2-1)yz$
6	$-\sqrt{\frac{3}{2}}(2z^2-1)yz$	$-\sqrt{\frac{3}{2}}(2z^2-1)xz$

m,m'	5	6
0	$\sqrt{\frac{18}{5}}(3y^2-x^2)xz$	$\sqrt{\frac{18}{5}}(y^2-3x^2)yz$
1	$\frac{\sqrt{15}}{2}(x^2-y^2-\frac{7}{5}\,x^4+\frac{6}{5}x^2y^2+y^4)$	$\sqrt{\frac{3}{5}}(4z^2-4x^2+1)xy$
2	$\sqrt{\frac{3}{5}}(4y^2-4z^2-1)xy$	$\frac{\sqrt{15}}{2}(x^2-y^2-x^4-\frac{6}{5}\,x^2y^2+\frac{7}{5}\,y^4)$
3	$-\sqrt{\frac{3}{2}}(2z^2-1)xz$	$-\sqrt{\frac{3}{2}}(2z^2-1)yz$
4	$\sqrt{\frac{3}{2}}(2z^2-1)yz$	$-\sqrt{\frac{3}{2}}(2z^2-1)xz$
5	$\frac{3}{2}(z^2-1)z^2$	0
6	0	$\frac{3}{2}(z^2-1)z^2$

TABLE XIII. The matrix $\mathbf{\Delta}_2(f,f,\hat{\mathbf{R}})\equiv[\Delta_2(fm,fm',\hat{\mathbf{R}})]$ in terms of the direction cosines $\hat{\mathbf{R}}=(x,y,z)$, where $x^2+y^2+z^2=1$.

m,m'	0	1	2
0	$\frac{2}{5}(3z^2-1)$	$\frac{\sqrt{6}}{5}xz$	$\frac{\sqrt{6}}{5}yz$
1	$\frac{\sqrt{6}}{5}xz$	$\frac{3}{10}(1-4y^2+z^2)$	$\frac{6}{5}xy$
2	$\frac{\sqrt{6}}{5}yz$	$\frac{6}{5}xy$	$\frac{3}{10}(1-4x^2+z^2)$
3	$-\sqrt{\frac{3}{5}}(x^2-y^2)$	$\frac{3}{\sqrt{10}}xz$	$-\frac{3}{\sqrt{10}}yz$
4	$-\sqrt{\frac{12}{5}}xy$	$\frac{3}{\sqrt{10}}yz$	$\frac{3}{\sqrt{10}}xz$
5	0	$-\sqrt{\frac{3}{20}}(x^2-y^2)$	$\sqrt{\frac{3}{5}}xy$
6	0	$-\sqrt{\frac{3}{5}}xy$	$-\sqrt{\frac{3}{20}}(x^2-y^2)$

m,m'	3	4	5	6
0	$-\sqrt{\frac{3}{5}}(x^2-y^2)$	$-\sqrt{\frac{12}{5}}xy$	0	0
1	$\frac{3}{\sqrt{10}}xz$	$\frac{3}{\sqrt{10}}yz$	$-\sqrt{\frac{3}{20}}(x^2-y^2)$	$-\sqrt{\frac{3}{5}}xy$
2	$-\frac{3}{\sqrt{10}}yz$	$\frac{3}{\sqrt{10}}xz$	$\sqrt{\frac{3}{5}}xy$	$-\sqrt{\frac{3}{20}}(x^2-y^2)$
3	0	0	$\sqrt{\frac{3}{2}}xz$	$\sqrt{\frac{3}{2}}yz$
4	0	0	$-\sqrt{\frac{3}{2}}yz$	$\sqrt{\frac{3}{2}}xz$
5	$\sqrt{\frac{3}{2}}xz$	$-\sqrt{\frac{3}{2}}yz$	$-\frac{1}{2}(3z^2-1)$	0
6	$\sqrt{\frac{3}{2}}yz$	$\sqrt{\frac{3}{2}}xz$	0	$-\frac{1}{2}(3z^2-1)$

where $c_\mu\equiv(2-\delta_{\mu\sigma})^{-1/2}$ and $U_{\alpha\mu}$ is the (real) unitary transformation that insures Eq. (32). Note that in spite of this mutual orthogonality for $\alpha\neq\beta$, the matrices $\tilde{\mathbf{g}}_\alpha(l,l',\hat{\mathbf{R}}_1)$ and $\tilde{\mathbf{g}}_\beta(l,l',\hat{\mathbf{R}}_2)$ are not in general identical for $\alpha=\beta$. Rather, the transformation partitions the space of $[(2l+1)\times(2l'+1)]$-dimensional matrices into orthogonal subspaces, in one of which lie all the $\tilde{\mathbf{g}}_0(l,l',\hat{\mathbf{R}})$ for different directions, $\mathbf{R}$, and in another all of the $\alpha=1$ matrices, and so on.

For $l\leqslant l'\leqslant f$, relation (31) between the transformed and original geometric functions is

$$\tilde{g}_{pp0}=(g_{pp\sigma}+g_{pp\pi})/\sqrt{3}, \tag{33}$$

$$\tilde{g}_{pp1}=(2g_{pp\sigma}-g_{pp\pi})/\sqrt{6},$$

$$\tilde{g}_{pd0}=(\sqrt{3}\,g_{pd\sigma}-g_{pd\pi})/\sqrt{5},$$

$$\tilde{g}_{pd1}=(2g_{pd\sigma}+\sqrt{3}\,g_{pd\pi})/\sqrt{10},$$

$$\tilde{g}_{dd0}=(g_{dd\sigma}+g_{dd\pi}+g_{dd\delta})/\sqrt{5},$$

$$\tilde{g}_{dd1}=(6g_{dd\sigma}-4g_{dd\pi}+g_{dd\delta})/\sqrt{70},$$

$$\tilde{g}_{dd2}=(2g_{dd\sigma}+g_{dd\pi}-2g_{dd\delta})/\sqrt{14},$$

$$\tilde{g}_{pf0}=(2\sqrt{2}\,g_{pf\sigma}-\sqrt{3}\,g_{pf\pi})/\sqrt{14},$$

$$\tilde{g}_{pf1}=(\sqrt{3}\,g_{pf\sigma}+\sqrt{2}\,g_{pf\pi})/\sqrt{7},$$

TABLE XIV. Matrix dot products $\mathbf{\Delta}_i(f,f,\hat{\mathbf{R}}_1)\cdot\mathbf{\Delta}_j(f,f,\hat{\mathbf{R}}_2)$ and $\mathbf{g}_\mu(f,f,\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(f,f,\hat{\mathbf{R}}_2)$, where $\chi \equiv \hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$.

i j	$\mathbf{\Delta}_i\cdot\mathbf{\Delta}_j$	μ ν	$\mathbf{g}_\mu\cdot\mathbf{g}_\nu$
0 0	7	σ σ	$\frac{1}{4}(5\chi^2-3)^2\chi^2$
0 2	0	σ π	$-\frac{3}{8}(5\chi^2-1)^2(\chi^2-1)$
0 4	$-\frac{7}{5}$	σ δ	$\frac{15}{4}\chi^2(\chi^2-1)^2$
0 6	1	σ ϕ	$-\frac{5}{8}(\chi^2-1)^3$
2 2	$\frac{42}{25}(3\chi^2-1)$	π π	$\frac{1}{16}(225\chi^6-305\chi^4+111\chi^2+1)$
2 4	$\frac{6}{25}(3\chi^2-1)$	π δ	$-\frac{5}{8}(9\chi^4-2\chi^2+1)(\chi^2-1)$
2 6	$\frac{2}{5}(3\chi^2-1)$	π ϕ	$\frac{15}{16}(\chi^2+1)(\chi^2-1)^2$
4 4	$\frac{1}{25}(220\chi^4-186\chi^2+25)$	δ δ	$\frac{1}{4}(9\chi^6+10\chi^4-15\chi^2+4)$
4 6	$\frac{3}{5}(5\chi^2-4)\chi^2$	δ ϕ	$-\frac{3}{8}(\chi^4+6\chi^2+1)(\chi^2-1)$
6 6	$\frac{1}{4}(5\chi^2-3)^2\chi^2$	ϕ ϕ	$\frac{1}{16}(\chi^4+14\chi^2+1)(\chi^2+1)$

$$\tilde{g}_{df0}=(2\sqrt{5}\ g_{df\sigma}-\sqrt{10}\ g_{df\pi}+g_{df\delta})/\sqrt{42},$$

$$\tilde{g}_{df1}=(2\sqrt{2}\ g_{df\sigma}+g_{df\pi}-\sqrt{10}\ g_{df\delta})/\sqrt{30},$$

$$\tilde{g}_{df2}=(3g_{df\sigma}+2\sqrt{2}\ g_{df\pi}+\sqrt{5}\ g_{df\delta})/\sqrt{35},$$

$$\tilde{g}_{ff0}=(g_{ff\sigma}+g_{ff\pi}+g_{ff\delta}+g_{ff\phi})/\sqrt{7},$$

$$\tilde{g}_{ff1}=(20g_{ff\sigma}-15g_{ff\pi}+6g_{ff\delta}-g_{ff\phi})/\sqrt{924},$$

$$\tilde{g}_{ff2}=(6g_{ff\sigma}+g_{ff\pi}-7g_{ff\delta}+3g_{ff\phi})/\sqrt{154},$$

$$\tilde{g}_{ff3}=(4g_{ff\sigma}+3g_{ff\pi}-5g_{ff\phi})/\sqrt{84},$$

where we have abbreviated $\tilde{g}_{ll'\alpha}\equiv\tilde{g}_\alpha(lm,l'm',\hat{\mathbf{R}})$, and similarly $g_{ll'\mu}\equiv g_\mu(lm,l'm',\hat{\mathbf{R}})$. It is straightforward to verify the orthogonality of these functions for different directions [Eq. (32)], using the matrix dot products of Sec. III. For the *same* direction, these matrices are orthonormal, $\tilde{g}_\alpha(lm,l'm',\hat{\mathbf{R}})\cdot\tilde{g}_\beta(lm,l'm',\hat{\mathbf{R}})=\delta_{\alpha\beta}$. For $l=l'$, note also that

$$\tilde{g}_0(lm,lm',\hat{\mathbf{R}})=\frac{1}{\sqrt{2l+1}}\,\Delta_0(lm,lm',\hat{\mathbf{R}})=\frac{1}{\sqrt{2l+1}}\,\delta_{mm'}, \tag{34}$$

which uniquely identifies those crystal-field parameters, denoted below by $\tilde{\chi}_{ll0}(R)$, which contribute to the one-electron Hamiltonian in the same way as the site energies.[10,11]

If the transformed crystal-field parameters $\tilde{\chi}_{ll'\alpha}(R)$ are defined as projections onto the new geometric matrices, then

$$\tilde{\chi}_{ll'\alpha}(R)=\sum_\mu U_{\alpha\mu}\,c_\mu^{-1}\,\chi_{ll'\mu}(R), \tag{35}$$

and the two-center expansion is automatically preserved,

$$\sum_\alpha \tilde{g}_\alpha(lm,l'm',\hat{\mathbf{R}})\tilde{\chi}_{ll'\alpha}(R) = \sum_\mu g_\mu(lm,l'm',\hat{\mathbf{R}})\chi_{ll'\mu}(R). \tag{36}$$

The transformed crystal-field parameters are given by

$$\tilde{\chi}_{pp0}=(\chi_{pp\sigma}+2\,\chi_{pp\pi})/\sqrt{3}, \tag{37}$$

$$\tilde{\chi}_{pp1}=(\chi_{pp\sigma}-\chi_{pp\pi})\sqrt{2/3},$$

$$\tilde{\chi}_{pd0}=(\sqrt{3}\ \chi_{pd\sigma}-2\,\chi_{pd\pi})/\sqrt{5},$$

$$\tilde{\chi}_{pd1}=(\chi_{pd\sigma}+\sqrt{3}\ \chi_{pd\pi})\sqrt{2/5},$$

$$\tilde{\chi}_{dd0}=(\chi_{dd\sigma}+2\,\chi_{dd\pi}+2\,\chi_{dd\delta})/\sqrt{5},$$

$$\tilde{\chi}_{dd1}=(3\,\chi_{dd\sigma}-4\,\chi_{dd\pi}+\chi_{dd\delta})\sqrt{2/35},$$

$$\tilde{\chi}_{dd2}=(\chi_{dd\sigma}+\chi_{dd\pi}-2\,\chi_{dd\delta})\sqrt{2/7},$$

$$\tilde{\chi}_{pf0}=(2\,\chi_{pf\sigma}-\sqrt{6}\ \chi_{pf\pi})/\sqrt{7},$$

$$\tilde{\chi}_{pf1}=(\sqrt{3}\ \chi_{pf\sigma}+2\sqrt{2}\ \chi_{pf\pi})/\sqrt{7},$$

$$\tilde{\chi}_{df0}=(\sqrt{5}\ \chi_{df\sigma}-\sqrt{10}\ \chi_{df\pi}+\chi_{df\delta})\sqrt{2/21},$$

$$\tilde{\chi}_{df1}=(\sqrt{2}\ \chi_{df\sigma}+\chi_{df\pi}-\sqrt{10}\ \chi_{df\delta})\sqrt{2/15},$$

$$\tilde{\chi}_{df2}=(3\,\chi_{df\sigma}+4\sqrt{2}\ \chi_{df\pi}+2\sqrt{5}\ \chi_{df\delta})/\sqrt{35},$$

$$\tilde{\chi}_{ff0}=(\chi_{ff\sigma}+2\,\chi_{ff\pi}+2\,\chi_{ff\delta}+2\,\chi_{ff\phi})/\sqrt{7},$$

$$\tilde{\chi}_{ff1}=(10\,\chi_{ff\sigma}-15\,\chi_{ff\pi}+6\,\chi_{ff\delta}-\chi_{ff\phi})/\sqrt{231},$$

$$\tilde{\chi}_{ff2}=(3\,\chi_{ff\sigma}+\chi_{ff\pi}-7\,\chi_{ff\delta}+3\,\chi_{ff\phi})\sqrt{2/77},$$

$$\tilde{\chi}_{ff3}=(2\,\chi_{ff\sigma}+3\,\chi_{ff\pi}-5\,\chi_{ff\phi})/\sqrt{21},$$

where we have suppressed the R dependence of these functions.

While the discussion in this section has focused on the site-energy and crystal-field terms, the transformation presented here also has some relevance to the intersite hoping terms. In particular, it is interesting to note that the $\sigma:\pi:\delta$ ratios among the bare canonical structure constants in the linear muffin-tin orbital method[14] are the same as the ratios of coefficients in Eq. (33) for one particular value of α or another; e.g., in the dd case, $6:-4:1$ corresponds to $\alpha=1$. The significance of this fact is clear at least for $l=l'$, where there is a direct mapping of Andersen's canonical band theory onto a nonorthogonal tight-binding problem, with the bare canonical structure constant ratios implying similar ratios of the hopping parameters.[11] This in turn implies that the pp and dd hopping parameters in canonical band theory are of *pure* $\alpha=1$ character according to the transformation of this section. Given the success of canonical band theory, e.g., for structural trends in the transition metals,[15] this raises the possibility that the transformation discussed here may more naturally segregate the hopping parameters $\tilde{t}_{ll'\alpha}(R)$ in terms of relative importance than is the case for the conventional $t_{ll'\mu}(R)$.

V. SUMMARY

The two-center Slater-Koster integrals, denoted here by $g_\mu(lm,l'm',\hat{\mathbf{R}})$, are important components of tight-binding total-energy representations routinely used now with s-d bases. Extension to s-f bases has been hindered in part by the increased number and complexity of the resultant analytic functions of the direction $\hat{\mathbf{R}}$. This paper has shown that these and all of the s-f integrals may be represented as linear combinations of simpler and more manageable polynomials in the direction cosines, and by this means provided a full listing of the Slater-Koster integrals in polynomial form for an s-f basis.

This treatment has also facilitated calculation of the matrix dot products,

$$\mathbf{g}_\mu(l,l',\hat{\mathbf{R}}_1)\cdot\mathbf{g}_\nu(l,l',\hat{\mathbf{R}}_2)$$

$$=\sum_{m,m'} g_\mu(lm,l'm',\hat{\mathbf{R}}_1)g_\nu(lm,l'm',\hat{\mathbf{R}}_2),$$

which are functions of $\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2$ and provide rather strong constraints useful for testing tabulated or coded Slater-Koster integrals. Moreover, the dependence of these dot products on μ and ν points to a transformation of the Slater-Koster integrals and the associated two-center expansion which greatly simplifies the treatment of crystal-field terms in tight-binding representations.

Underlying both this and earlier work[10,11] is the perspective that the matrices $\mathbf{g}_\mu(l,l',\hat{\mathbf{R}})$ for $\mu=\sigma,\ldots,l_{\min}$ are in general an incomplete, orthogonal basis for the space of $[(2l+1)\times(2l'+1)]$-dimensional m,m' matrices. This perspective and the kind of dot products calculated here offer obvious possibilities for improving the two-center approximation without losing its existing virtues, by simply expanding this basis beyond $\mu=l_{\min}$ with matrices orthogonalized to the existing set. Values for the additional tight-binding parameters could be easily obtained from projections such as Eq. (4). The critical question is whether or not such parameters would exhibit a useful degree of transferability, which along with the choice of the expanded geometric basis matrices is a natural area for future research.

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