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Extension of the Slater-Koster tables for tight-binding calculations to f electrons

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In order to make tight-binding calculations possible for substances with f electrons, the overlap (or energy) integrals for (s-f), (p-f), and (d-f) interactions have been calculated. Using the two-center approximation and considering first- and second-nearest-neighbor contributions the results have been applied to the fcc lattice.

I. INTRODUCTION

In recent years there has been growing interest in the investigation of rare-earth elements and compounds.[1,2] For the metals many band-structure calculations[2,3] are available for comparison with experiments related to the electronic structure. In the case of compounds, in particular of magnetic semiconductors, the situation is less satisfactory for several reasons. First of all, there exist only a few calculations.[4-7] Furthermore, the high-lying $4f$-electron states cause serious troubles, apart from general difficulties met with in any band calculation for heavy elements.

Recent experiments on photoemission of spin-polarized electrons from magnetic materials seem to indicate that the usual assumptions of band theory could be in error,[8] at least in the case of d-electron magnetism. Since the magnetic-interaction mechanism for f-electron systems is different,[1,2] we expect it to be particularly fruitful and interesting to analyze the position and dispersion of f-like and neighboring bands by means of a tight-binding calculation, especially in view of recent substantial improvements of this method,[9] and in order to see how the results compare with the above-mentioned discrepancies.

The inconveniences of unreliable molecular integrals, due to hybridization of almost flat with strongly dispersive bands, arising in the case of transition metals[9] should greatly be reduced, especially in an application to rare-earth magnetic semiconductors where the $4f$ states lie in the energy gap and completely separate valence from conduction bands. Since the $4f$-electron density is sharply localized close to the nucleus[10,11] it should be sufficient to consider only two-center and first- or at most second-nearest-neighbor contributions as well as (s-f), (p-f), and (d-f) interactions; the (f-f) interaction is out of the question because of too big lattice spacings in the materials considered.[2]

To this extent we are going to extend the well-known Slater-Koster tables[12] which did not include any results for f electrons.

II. TRANSFORMATION OF WAVE FUNCTIONS

Let us denote any atomic wave function of angular momentum j and z-projection k by $\phi_j^k(\vec{x})$, not exhibiting explicitly the main or any other quantum numbers because they will not be important in the present discussion. The problem consists of expressing in an appropriate way the overlap integrals between such functions centered at different lattice sites. If, for instance, an atom B is situated with respect to A as in Fig. 1, it is most convenient to rotate the original coordinate system (x', y', z') with its z' axis into the line $(AB) \equiv \vec{R}$, because in this way the integrations over the azimuthal angle will become trivial.[13] It would be more elegant to analyze the transformation by means of the irreducible representations of the rotation group whose matrix elements in terms of the Euler angles are known. However, in order to keep the agreement with the original method and notation of Slater and Koster, which has become familiar to workers in this field, we will instead follow their procedure.

Denoting the unitary operator corresponding to the above-mentioned transformation by U_{lmn} where $l = \cos\chi_1$, $m = \cos\chi_2$, and $n = \cos\chi_3$, we can write[13]

$$(U_{lmn}\phi_j^k)(\vec{x}) = \sum_i C_{ik}^j(lmn)\phi_j^i(\vec{x}), \quad -j \leq i, k \leq +j \qquad (1)$$

or transforming to real functions called $\mathcal{R}_j^\lambda(\vec{x})$, ($\lambda = 0, 1, \ldots, 2j$), by taking combinations like $(1/\sqrt{2})(\phi_j^{+|k|} \pm \phi_j^{-|k|})$, we can also write

$$(U_{lmn}\mathcal{R}_j^\lambda)(\vec{x}) = \sum_i b_{i\lambda}^j(lmn)\,\phi_j^i(\vec{x}) \quad , \qquad (2)$$

where the $b_{j\lambda}^i(lmn)$'s are appropriately symmetrized C elements. Since the ϕ_j^k's (or $\mathcal{R}_j^\lambda$'s) are basis functions of irreducible representations of the rotation group, only functions with the same j appear on the right-hand side of Eq. (1).

For tight-binding calculations one needs quantities[12,14] like

$$(\mathcal{R}_j^\lambda(\vec{x}' + \vec{R}'), \ \mathcal{R}_k^\nu(\vec{x}'))$$

or, equally well,

$$(\mathcal{R}_j^\lambda(\vec{x}' + \vec{R}'), \ V_{ext}(\vec{x}' + \vec{R}')\,\mathcal{R}_k^\nu(\vec{x}')) \quad ,$$

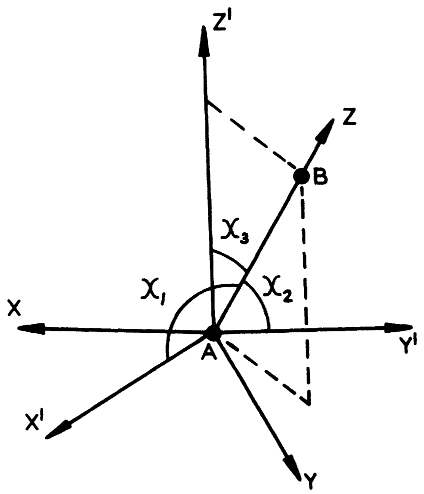

FIG. 1. Original (x', y', z') and rotated (x, y, z) coordinate system for two-center integrals.

where $V_{ext}(\vec{x}' + \vec{R}')$ is the contribution to the crystal potential by the atoms surrounding the one at $\vec{R}$. (The prime refers to the original coordinate system.) The last formula implies restriction to the two-center approximation.

Inserting (2) we get

$$(\mathcal{R}_j^\lambda(\vec{x}' + \vec{R}'),\ V_{ext}(\vec{x}' + \vec{R}')\mathcal{R}_k^\nu(\vec{x}'))$$
$$= \sum_{i,h} \bar{b}_{i\lambda}^j(lmn) b_{h\nu}^k(lmn)\, (\phi_j^i(\vec{x} + \vec{R}),\ V_{ext}(\vec{x} + \vec{R})\phi_k^h(\vec{x})). \tag{3}$$

This expression is further reduced by noting that our special choice of coordinate system yields

$$(\phi_j^i(\vec{x} + \vec{R}),\ V_{ext}(\vec{x} + \vec{R})\phi_k^h(\vec{x})) = \delta_{ih} O_{jk}^h, \quad O_{jk}^h = O_{jk}^{-h} \tag{4}$$

where $O_{jk}^{\pm h}$ denotes the well-known $(\sigma, \pi, \delta, \ldots)$ two-center integrals (see Appendix), and we are left with the real quantities

$$(\mathcal{R}_j^\lambda(\vec{x}' + \vec{R}'),\ V_{ext}(\vec{x}' + \vec{R}')\mathcal{R}_k^\nu(\vec{x}'))$$
$$= 2 \sum_{(p \geq 0)}^{\min(j,k)} O_{jk}^p \{\mathrm{Re}[\bar{b}_{p\lambda}^j(lmn) b_{p\nu}^k(lmn)]\}\ . \tag{5}$$

The final problem consists of the somewhat tedious calculation of the coefficients $b_{p\lambda}^j(lmn)$ and evaluation of the above matrix elements. For this purpose we introduce the real three-dimensional representation of U_{lmn} through the orthogonal matrix $A = \{a_{ik}\}$, where $A^T = A^{-1}$ and $\det A = +1$. Since A transforms $\{x', y', x'\} \to \{x, y, z\}$, we must have $a_{13} = l$, $a_{23} = m$, $a_{33} = n$. The coefficients $b_{p\lambda}^j(lmn)$ are polynomials of the a_{ik}'s, and in order to express them as far as possible in terms of the parameters l, m, and n, we use the following theorem for the cofactors $\mathfrak{a}_{ik}$ of A.

Theorem:

$$\mathfrak{a}_{ik} = a_{ik}, \quad i, k = 1, 2, 3$$

Proof:

Let $\vec{v}^k = (a_{1k}, a_{2k}, a_{3k})$ and $\vec{w}^k = (\mathfrak{a}_{1k}, \mathfrak{a}_{2k}, \mathfrak{a}_{3k})$.

It follows from $A^T = A^{-1}$ that $(\vec{v}^k, \vec{v}^k) = 1\ (\forall k)$.

Since $\det(A) = (\vec{v}^k, \vec{w}^k) = +1$,

$\vec{v}^k = \vec{w}^k$ must hold.

We specify finally to $k = 3$ getting

$$\mathfrak{a}_{13} = l, \quad \mathfrak{a}_{23} = m, \quad \text{and} \quad \mathfrak{a}_{33} = n.$$

Apart from this remark we do not go into details of the calculation.

The definitions of s, p, d, and f functions are given in the Appendix. We actually transform to the real functions $\mathcal{R}_j^\lambda$, which for clarity will be denoted by S, P, D, and F from now on and which, for instance, in the case of $j = 3$ are obtained as follows:

$$F_0 = f_0,$$
$$F_{(2\lambda - 1/2) \mp 1/2} = [(-i)^{\lambda+1}/\sqrt{2}]$$
$$\times [f_{+\lambda} + (-1)^{(\lambda - 1/2) \pm 1/2} f_{-\lambda}], \quad 1 \leq \lambda \leq 3$$

and similarly for P and D.

In particular we define S $(= s)$ as

$$S = (4\pi)^{-1/2}.$$

For $C_p = (3/4\pi)^{1/2}$,

$$P_0 = C_p z\ ,$$
$$P_1 = C_p x\ ,$$
$$P_2 = C_p y\ ;$$

for $C_d = (5/16\pi)^{1/2}$,

$$D_0 = C_d(3z^2 - r^2)\ ,$$
$$D_1 = \sqrt{12}\, C_d xz\ ,$$
$$D_2 = \sqrt{12}\, C_d yz\ ,$$
$$D_3 = \sqrt{3}\, C_d (x^2 - y^2)\ ,$$
$$D_4 = \sqrt{12}\, C_d xy\ ;$$

and for $C_f = (7/16\pi)^{1/2}$,

$$F_0 = C_f(5z^2 - 3r^2) z\ ,$$
$$F_1 = \sqrt{\tfrac{3}{2}}\, C_f(5z^2 - r^2) x\ ,$$
$$F_2 = \sqrt{\tfrac{3}{2}}\, C_f(5z^2 - r^2) y\ ,$$
$$F_3 = \sqrt{15}\, C_f(x^2 - y^2) z\ ,$$
$$F_4 = \sqrt{15}\, C_f(2xyz)\ ,$$
$$F_5 = \sqrt{\tfrac{5}{2}}\, C_f(x^2 - 3y^2) x\ ,$$
$$F_6 = \sqrt{\tfrac{5}{2}}\, C_f(3x^2 - y^2) y\ .$$

The coefficients expressing the transformed real functions in terms of spherical harmonics are given in Table I.

III. ENERGY INTEGRALS

For convenience we change the notation of Slater and Koster[12] and write for instance E_{D_1,F_0} in place of $E_{xz,(5z^2-3r^2)z}$ for (*d-f*) integrals; and according to our earlier notation, $E_{D_1,F_0}=(\mathcal{R}_2^1,\ V_{ext}\mathcal{R}_3^0)$. Using the results of Table I all the expressions (5) have been worked out and are given below.

TABLE I. The coefficients $b_{i\lambda}^j(lmn)$. The terms for $i=3$ ($j=3$) are omitted because they are not needed for the calculation.

j	λ	$i=0$	$i=+1$	$i=+2$
0	0	1		
	0	n	$-(1/\sqrt{2})(a_{31}-ia_{32})$	
1	1	l	$-(1/\sqrt{2})(a_{11}-ia_{12})$	
	2	m	$-(1/\sqrt{2})(a_{21}-ia_{22})$	
	0	$\frac{1}{2}(3n^2-1)$	$-\sqrt{\frac{3}{2}}\,n(a_{31}-ia_{32})$	$\sqrt{\frac{3}{8}}\,(a_{31}-ia_{32})^2$
	1	$\sqrt{3}\,ln$	$-(1/\sqrt{2})\,[n(a_{11}-ia_{12})+l(a_{31}-ia_{32})]$	$(1/\sqrt{2})(a_{11}-ia_{12})(a_{31}-ia_{32})$
2	2	$\sqrt{3}\,mn$	$-(1/\sqrt{2})\,[n(a_{21}-ia_{22})+m(a_{31}-ia_{32})]$	$(1/\sqrt{2})(a_{21}-ia_{22})(a_{31}-ia_{32})$
	3	$\frac{\sqrt{3}}{2}\,(l^2-m^2)$	$-(1/\sqrt{2})\,[l(a_{11}-ia_{12})-m(a_{21}-ia_{22})]$	$(1/\sqrt{8})[(a_{11}-ia_{12})^2-(a_{21}-ia_{22})^2]$
	4	$\sqrt{3}\,lm$	$-(1/\sqrt{2})[m(a_{11}-ia_{12})+l(a_{21}-ia_{22})]$	$(1/\sqrt{2})(a_{11}-ia_{12})(a_{21}-ia_{22})$

$j=3$		
λ	i	
	0	$\frac{1}{2}n\ [5n^2-3]$
0	1	$-(1/\sqrt{48})\ [15n^2-3]\ (a_{31}-ia_{32})$
	2	$\sqrt{\frac{15}{8}}\,n(a_{31}-ia_{32})^2$
	0	$\sqrt{\frac{3}{8}}\,l[5n^2-1]$
1	1	$-(1/\sqrt{32})\ \{2(a_{11}-ia_{12})[5n^2-3]+5(ln-im)(a_{31}-ia_{32})\}$
	2	$\sqrt{\frac{5}{16}}\ \{2n(a_{11}-ia_{12})(a_{31}-ia_{32})+(a_{31}-ia_{32})^2 l\}$
	0	$\sqrt{\frac{3}{8}}\,m\ [5n^2-1]$
2	1	$-(1/\sqrt{32})\ \{[10n^2-6]\ (a_{21}-ia_{22})+5(mn+il)\ (a_{31}-ia_{32})\}$
	2	$\sqrt{\frac{5}{16}}\{2n(a_{21}-ia_{22})(a_{31}-ia_{32})+m(a_{31}-ia_{32})^2\}$
	0	$\sqrt{\frac{15}{4}}\,n\ [l^2-m^2]$
3	1	$-\sqrt{\frac{5}{16}}\ \{2[l^2-m^2]\ (a_{31}-ia_{32})+(ln+im)(a_{11}-ia_{12})-(mn-il)(a_{21}-ia_{22})\}$
	2	$(1/\sqrt{8})\ \{2(a_{31}-ia_{32})[l(a_{11}-ia_{12})-m(a_{21}-ia_{22})]+n[(a_{11}-ia_{12})^2-(a_{21}-ia_{22})^2]\}$
	0	$\sqrt{15}\ lmn$
4	1	$-\frac{1}{2}\sqrt{5}\ \{2lm(a_{31}-ia_{32})+(mn-il)(a_{11}-ia_{12})\}$
	2	$(1/\sqrt{2})\ \{(a_{31}-ia_{32})[m(a_{11}-ia_{12})+l(a_{21}-ia_{22})]+n(a_{11}-ia_{12})(a_{21}-ia_{22})\}$
	0	$\sqrt{\frac{5}{8}}\ l[l^2-3m^2]$
5	1	$-\sqrt{\frac{15}{32}}\ \{[l^2-2m^2+1](a_{11}-ia_{12})-(lm+in)(a_{21}-ia_{22})\}$
	2	$\sqrt{\frac{3}{16}}\ \{l(a_{11}-ia_{12})^2-l(a_{21}-ia_{22})^2-2m(a_{11}-ia_{12})(a_{21}-ia_{22})\}$
	0	$\sqrt{\frac{5}{8}}\ m\ [3l^2-m^2]$
6	1	$\sqrt{\frac{15}{32}}\ \{(a_{21}-ia_{22})[m^2-2l^2+1]-(lm-in)(a_{11}-ia_{12})\}$
	2	$\sqrt{\frac{3}{16}}\ \{m(a_{11}-ia_{12})^2-m(a_{21}-ia_{22})^2+2l(a_{11}-ia_{12})(a_{21}-ia_{22})\}$

(s-f) integrals.

$$E_{S,F_0}=\tfrac{1}{2}n\,(5n^2-3)\,(sf\sigma),\qquad E_{S,F_1}=\sqrt{\tfrac{3}{2}}\,\tfrac{1}{2}l\,(5n^2-1)\,(sf\sigma),\qquad E_{S,F_2}=\sqrt{\tfrac{3}{2}}\,\tfrac{1}{2}m\,(5n^2-1)\,(sf\sigma),$$
$$E_{S,F_3}=\sqrt{15}\,\tfrac{1}{2}n\,(l^2-m^2)\,(sf\sigma),\quad E_{S,F_4}=\sqrt{15}\,lmn\,(sf\sigma),$$
$$E_{S,F_5}=\sqrt{\tfrac{5}{2}}\,\tfrac{1}{2}l\,(l^2-3m^2)\,(sf\sigma),\quad E_{S,F_6}=\sqrt{\tfrac{5}{2}}\,\tfrac{1}{2}m\,(3l^2-m^2)\,(sf\sigma)\quad .$$

(p-f) integrals.

$$E_{P_0,F_0}=\tfrac{1}{2}n^2(5n^2-3)\,(pf\sigma)-\sqrt{\tfrac{3}{8}}\,(5n^2-1)\,(n^2-1)\,(pf\pi),$$
$$E_{P_1,F_0}=\tfrac{1}{2}ln\,(5n^2-3)\,(pf\sigma)-\sqrt{\tfrac{3}{8}}\,ln(5n^2-1)\,(pf\pi),$$
$$E_{P_2,F_0}=\tfrac{1}{2}mn\,(5n^2-3)\,(pf\sigma)-\sqrt{\tfrac{3}{8}}\,mn\,(5n^2-1)\,(pf\pi);$$

$$E_{P_0,F_1}=\sqrt{\tfrac{3}{8}}\,ln\,(5n^2-1)\,(pf\sigma)-\tfrac{1}{4}ln\,(15n^2-11)\,(pf\pi)\ ,$$
$$E_{P_1,F_1}=\sqrt{\tfrac{3}{8}}\,l^2(5n^2-1)\,(pf\sigma)-\tfrac{1}{4}\left[(5n^2-1)\,(3l^2-1)+2l^2\right](pf\pi)\ ,$$
$$E_{P_2,F_1}=\sqrt{\tfrac{3}{8}}\,lm\,(5n^2-1)\,(pf\sigma)-\tfrac{1}{4}lm\,(15n^2-1)\,(pf\pi);$$

$$E_{P_0,F_2}=\sqrt{\tfrac{3}{8}}\,mn\,(5n^2-1)\,(pf\sigma)-\tfrac{1}{4}mn\,(15n^2-11)\,(pf\pi),$$
$$E_{P_1,F_2}=\sqrt{\tfrac{3}{8}}\,lm\,(5n^2-1)\,(pf\sigma)-\tfrac{1}{4}lm\,(15n^2-1)\,(pf\pi),$$
$$E_{P_2,F_2}=\sqrt{\tfrac{3}{8}}\,m^2\,(5n^2-1)\,(pf\sigma)-\tfrac{1}{4}\left[(5n^2-1)\,(3m^2-1)+2m^2\right](pf\pi);$$

$$E_{P_0,F_3}=\tfrac{1}{2}\sqrt{15}\,n^2(l^2-m^2)\,(pf\sigma)-\sqrt{\tfrac{5}{8}}\,(3n^2-1)\,(l^2-m^2)\,(pf\pi),$$
$$E_{P_1,F_3}=\tfrac{1}{2}\sqrt{15}\,ln(l^2-m^2)\,(pf\sigma)-\sqrt{\tfrac{5}{8}}\,ln\left[3(l^2-m^2)-2\right](pf\pi),$$
$$E_{P_2,F_3}=\tfrac{1}{2}\sqrt{15}\,mn(l^2-m^2)\,(pf\sigma)-\sqrt{\tfrac{5}{8}}\,mn\left[3(l^2-m^2)+2\right](pf\pi);$$

$$E_{P_0,F_4}=\sqrt{15}\,lmn^2\,(pf\sigma)-\sqrt{\tfrac{5}{2}}\,lm\,(3n^2-1)\,(pf\pi),$$
$$E_{P_1,F_4}=\sqrt{15}\,l^2mn\,(pf\sigma)-\sqrt{\tfrac{5}{2}}\,mn\,(3l^2-1)\,(pf\pi),$$
$$E_{P_2,F_4}=\sqrt{15}\,lm^2n\,(pf\sigma)-\sqrt{\tfrac{5}{2}}\,ln\,(3m^2-1)\,(pf\pi);$$

$$E_{P_0,F_5}=\sqrt{\tfrac{5}{8}}\,ln(l^2-3m^2)\,(pf\sigma)-\tfrac{1}{4}\sqrt{15}\,ln(l^2-3m^2)\,(pf\pi),$$
$$E_{P_1,F_5}=\sqrt{\tfrac{5}{8}}\,l^2(l^2-3m^2)\,(pf\sigma)-\tfrac{1}{4}\sqrt{15}\left[l^2(l^2-3m^2)+m^2-l^2\right](pf\pi),$$
$$E_{P_2,F_5}=\sqrt{\tfrac{5}{8}}\,ml(l^2-3m^2)\,(pf\sigma)-\tfrac{1}{4}\sqrt{15}\,lm(l^2-3m^2+2)\,(pf\pi);$$

$$E_{P_0,F_6}=\sqrt{\tfrac{5}{8}}\,mn(3l^2-m^2)\,(pf\sigma)-\tfrac{1}{4}\sqrt{15}\,mn(3l^2-m^2)\,(pf\pi),$$
$$E_{P_1,F_6}=\sqrt{\tfrac{5}{8}}\,lm(3l^2-m^2)\,(pf\sigma)-\tfrac{1}{4}\sqrt{15}\,lm\,(3l^2-m^2-2)\,(pf\pi),$$
$$E_{P_2,F_6}=\sqrt{\tfrac{5}{8}}\,m^2(3l^2-m^2)\,(pf\sigma)-\tfrac{1}{4}\sqrt{15}\left[m^2(3l^2-m^2)+m^2-l^2\right](pf\pi)\ .$$

(d-f) integrals.

$$E_{D_0,F_0}=\tfrac{1}{4}n\,(3n^2-1)\,(5n^2-3)\,(df\sigma)-(3/\sqrt{8})\,n(5n^2-1)\,(n^2-1)\,(df\pi)+\tfrac{1}{4}\sqrt{45}\,n(n^2-1)^2(df\delta),$$
$$E_{D_1,F_0}=\tfrac{1}{2}\sqrt{3}\,ln^2\,(5n^2-3)\,(df\sigma)-\sqrt{\tfrac{3}{8}}\,l(5n^2-1)\,(2n^2-1)\,(df\pi)+\tfrac{1}{2}\sqrt{15}\,ln^2(n^2-1)\,(df\delta),$$
$$E_{D_2,F_0}=\tfrac{1}{2}\sqrt{3}\,mn^2\,(5n^2-3)\,(df\sigma)-\sqrt{\tfrac{3}{8}}\,m\,(5n^2-1)\,(2n^2-1)\,(df\pi)+\tfrac{1}{2}\sqrt{15}\,mn^2(n^2-1)\,(df\delta),$$
$$E_{D_3,F_0}=\tfrac{1}{4}\sqrt{3}\,n\,(5n^2-3)\,(l^2-m^2)\,(df\sigma)-\sqrt{\tfrac{3}{8}}\,n(5n^2-1)\,(l^2-m^2)\,(df\pi)+\tfrac{1}{4}\sqrt{15}\,n(n^2+1)\,(l^2-m^2)\,(df\delta),$$

$$E_{D_4,F_0}=\tfrac{1}{2}\sqrt{3}\,lmn\,(5n^2-3)\,(df\sigma)-\sqrt{\tfrac{3}{2}}\,lmn(5n^2-1)\,(df\pi)+\tfrac{1}{2}\sqrt{15}\,lmn\,(n^2+1)\,(df\delta);$$

$$E_{D_0,F_1}=\sqrt{\tfrac{3}{32}}\,l\,(3n^2-1)\,(5n^2-1)\,(df\sigma)-\tfrac{1}{4}\sqrt{3}\,ln^2\,(15n^2-11)\,(df\pi)+\sqrt{\tfrac{15}{32}}\,l\,(n^2-1)\,(3n^2-1)\,(df\delta)\,,$$

$$E_{D_1,F_1}=(3/\sqrt{8}\,)\,l^2n\,(5n^2-1)\,(df\sigma)-\tfrac{1}{4}n\,[l^2(30n^2-11)-4n^2+m^2]\,(df\pi)+\sqrt{\tfrac{5}{8}}\,n(n^2-1)\,(3l^2-2)\,(df\delta),$$

$$E_{D_2,F_1}=(3/\sqrt{8}\,)\,lmn\,(5n^2-1)\,(df\sigma)-\tfrac{3}{2}lmn\,(5n^2-2)\,(df\pi)+\sqrt{\tfrac{45}{8}}\,lmn(n^2-1)\,(df\delta),$$

$$E_{D_3,F_1}=(3/\sqrt{32})\,l(5n^2-1)\,(l^2-m^2)\,(df\sigma)-\tfrac{1}{4}l\,[15n^2(l^2-m^2)+2m^2-4n^2]\,(df\pi)$$
$$+\sqrt{\tfrac{5}{32}}\,l[(l^2-m^2)\,(3n^2+1)-4n^2]\,(df\delta),$$

$$E_{D_4,F_1}=(3/\sqrt{8}\,)\,l^2m(5n^2-1)\,(df\sigma)-\tfrac{1}{4}m\,[(6l^2-1)\,(5n^2-1)+4l^2]\,(df\pi)+\sqrt{\tfrac{5}{8}}\,m\,[l^2(3n^2+1)-2n^2]\,(df\delta);$$

$$E_{D_0,F_2}=\sqrt{\tfrac{3}{32}}\,m(3n^2-1)\,(5n^2-1)\,(df\sigma)-\tfrac{1}{4}\sqrt{3}\,mn^2(15n^2-11)\,(df\pi)+\sqrt{\tfrac{15}{32}}\,m(n^2-1)\,(3n^2-1)\,(df\delta),$$

$$E_{D_1,F_2}=(3/\sqrt{8}\,)\,lmn\,(5n^2-1)\,(df\sigma)-\tfrac{3}{2}lmn\,(5n^2-2)\,(df\pi)+\sqrt{\tfrac{45}{8}}\,lmn\,(n^2-1)\,(df\delta),$$

$$E_{D_2,F_2}=(3/\sqrt{8}\,)\,m^2n\,(5n^2-1)\,(df\sigma)-\tfrac{1}{4}n\,[m^2(30n^2-11)-4n^2+l^2]\,(df\pi)+\sqrt{\tfrac{5}{8}}\,n(n^2-1)\,(3m^2-2)\,(df\delta),$$

$$E_{D_3,F_2}=\frac{3}{\sqrt{32}}\,m(l^2-m^2)\,(5n^2-1)\,(df\sigma)-\tfrac{1}{4}m\,[15n^2(l^2-m^2)+4n^2-2l^2]\,(df\pi)$$
$$+\sqrt{\tfrac{5}{32}}\,m\,[(l^2-m^2)\,(3n^2+1)+4n^2]\,(df\delta),$$

$$E_{D_4,F_2}=(3/\sqrt{8}\,)\,lm^2\,(5n^2-1)\,(df\sigma)-\tfrac{1}{4}l\,[(6m^2-1)\,(5n^2-1)+4m^2]\,(df\pi)+\sqrt{\tfrac{5}{8}}\,l\,[m^2(3n^2+1)-2n^2]\,(df\delta);$$

$$E_{D_0,F_3}=\tfrac{1}{4}\sqrt{15}\,n\,(3n^2-1)\,(l^2-m^2)\,(df\sigma)-\sqrt{\tfrac{15}{8}}\,n(3n^2-1)\,(l^2-m^2)\,(df\pi)+\tfrac{1}{4}\sqrt{3}\,n\,(3n^2-1)\,(l^2-m^2)\,(df\delta),$$

$$E_{D_1,F_3}=\tfrac{1}{2}\sqrt{45}\,ln^2(l^2-m^2)\,(df\sigma)-\sqrt{\tfrac{5}{8}}\,l\,[(6n^2-1)\,(l^2-m^2)-2n^2]\,(df\pi)+\tfrac{1}{2}l\,[3n^2(l^2-m^2)+4m^2-2n^2]\,(df\delta),$$

$$E_{D_2,F_3}=\tfrac{1}{2}\sqrt{45}\,mn^2\,(l^2-m^2)\,(df\sigma)-\sqrt{\tfrac{5}{8}}\,m\,[(6n^2-1)\,(l^2-m^2)+2n^2]\,(df\pi)+\tfrac{1}{2}m\,[3n^2(l^2-m^2)-4l^2+2n^2]\,(df\delta),$$

$$E_{D_3,F_3}=\tfrac{1}{4}\sqrt{45}\,n\,(l^2-m^2)^2\,(df\sigma)-\sqrt{\tfrac{5}{8}}\,n\,[3(l^2-m^2)^2+2n^2-2]\,(df\pi)+\tfrac{1}{4}n\,[3(l^2-m^2)^2+8n^2-4]\,(df\delta),$$

$$E_{D_4,F_3}=\tfrac{1}{2}\sqrt{45}\,lmn\,(l^2-m^2)\,(df\sigma)-\sqrt{\tfrac{45}{2}}\,lmn\,(l^2-m^2)\,(df\pi)+\tfrac{3}{2}lmn\,(l^2-m^2)\,(df\delta);$$

$$E_{D_0,F_4}=\tfrac{1}{2}\sqrt{15}\,lmn\,(3n^2-1)\,(df\sigma)-\sqrt{\tfrac{15}{2}}\,lmn\,(3n^2-1)\,(df\pi)+\tfrac{1}{2}\sqrt{3}\,lmn\,(3n^2-1)\,(df\delta),$$

$$E_{D_1,F_4}=\sqrt{45}\,l^2mn^2\,(df\sigma)-\sqrt{\tfrac{5}{2}}\,m\,(6l^2n^2+m^2-1)\,(df\pi)+m\,(3l^2n^2+2m^2-1)\,(df\delta),$$

$$E_{D_2,F_4}=\sqrt{45}\,lm^2n^2\,(df\sigma)-\sqrt{\tfrac{5}{2}}\,l(6m^2n^2+l^2-1)(df\pi)+l\,(3m^2n^2+2l^2-1)\,(df\delta),$$

$$E_{D_3,F_4}=\tfrac{1}{2}\sqrt{45}\,lmn\,(l^2-m^2)\,(df\sigma)-\sqrt{\tfrac{45}{2}}\,lmn\,(l^2-m^2)\,(df\pi)+\tfrac{3}{2}lmn\,(l^2-m^2)\,(df\delta),$$

$$E_{D_4,F_4}=\sqrt{45}\,l^2m^2n\,(df\sigma)-\sqrt{\tfrac{5}{2}}\,n\,(6l^2m^2+n^2-1)\,(df\pi)+n\,(3l^2m^2+2n^2-1)\,(df\delta);$$

$$E_{D_0,F_5}=\sqrt{\tfrac{5}{32}}\,l\,(3n^2-1)\,(l^2-3m^2)\,(df\sigma)-\tfrac{1}{4}\sqrt{45}\,ln^2\,(l^2-3m^2)\,(df\pi)+(3/\sqrt{32})\,l\,(n^2+1)\,(l^2-3m^2)\,(df\delta),$$

$$E_{D_1,F_5}=\sqrt{\tfrac{15}{8}}\,l^2n\,(l^2-3m^2)\,(df\sigma)-\tfrac{1}{4}\sqrt{15}\,n\,[2l^2(l^2-3m^2)-l^2+m^2]\,(df\pi)+\sqrt{\tfrac{3}{8}}\,n\,[l^2\,(l^2-3m^2)-2l^2+2m^2]\,(df\delta)\,,$$

$$E_{D_2,F_5}=\sqrt{\tfrac{15}{8}}\,lmn\,(l^2-3m^2)\,(df\sigma)-\tfrac{1}{2}\sqrt{15}\,lmn\,(l^2-3m^2+1)\,(df\pi)+\sqrt{\tfrac{3}{8}}\,lmn\,(l^2-3m^2+4)\,(df\delta),$$

$$E_{D_3,F_5}=\sqrt{\tfrac{15}{32}}\,l\,(l^2-m^2)\,(l^2-3m^2)\,(df\sigma)-\tfrac{1}{4}\sqrt{15}\,l\,[(l^2-m^2)\,(l^2-3m^2)-n^2+1]\,(df\pi)$$
$$+\sqrt{\tfrac{3}{32}}\,l\,[(l^2-m^2)\,(l^2-3m^2)+4n^2]\,(df\delta),$$

$$E_{D_4,F_5}=\sqrt{\tfrac{15}{8}}\,l^2m\,(l^2-3m^2)\,(df\sigma)-\tfrac{1}{4}\sqrt{15}\,m\,[2l^2\,(l^2-3m^2)-n^2+1]\,(df\pi)+\sqrt{\tfrac{3}{8}}\,m\,[l^2(l^2-3m^2)-2n^2](df\delta);$$

$$E_{D_0,F_6}=\sqrt{\tfrac{5}{32}}\,m\,(3n^2-1)\,(3l^2-m^2)\,(df\sigma)-\tfrac{1}{4}\sqrt{45}\,mn^2(3l^2-m^2)\,(df\pi)+(3/\sqrt{32})m(n^2+1)(3l^2-m^2)(df\delta),$$

$$E_{D_1,F_6}=\sqrt{\tfrac{15}{8}}\,lmn\,(3l^2-m^2)\,(df\sigma)-\tfrac{1}{2}\sqrt{15}\,lmn\,(3l^2-m^2-1)\,(df\pi)+\sqrt{\tfrac{3}{8}}\,lmn\,(3l^2-m^2-4)\,(df\delta),$$

$$E_{D_2,F_6}=\sqrt{\tfrac{15}{8}}\,m^2n\,(3l^2-m^2)\,(df\sigma)-\tfrac{1}{4}\sqrt{15}\,n\,[2m^2(3l^2-m^2)-l^2+m^2]\,(df\pi)+\sqrt{\tfrac{3}{8}}\,n\,[m^2(3l^2-m^2)-2l^2+2m^2]\,(df\delta),$$

$$E_{D_3,F_6}=\sqrt{\tfrac{15}{32}}\, m\,(l^2-m^2)(3l^2-m^2)(df\sigma)-\tfrac{1}{4}\sqrt{15}\, m\,[(l^2-m^2)(3l^2-m^2)+n^2-1](df\pi)$$
$$+\sqrt{\tfrac{3}{32}}\, m\,[(l^2-m^2)(3l^2-m^2)+4n^2](df\delta),$$
$$E_{D_4,F_6}=\sqrt{\tfrac{15}{8}}\, lm^2(3l^2-m^2)(df\sigma)-\tfrac{1}{4}\sqrt{15}\, l\,[2m^2(3l^2-m^2)+n^2-1](df\pi)+\sqrt{\tfrac{3}{8}}\, l\,[m^2(3l^2-m^2)-2n^2](df\delta)\ .$$

IV. APPLICATION TO A FACE-CENTERED-CUBIC LATTICE

According to tight-binding theory[14] one has to find superpositions of the energy (or overlap) integrals appropriate to the local coordination of neighboring atoms, as, for instance,

$$(D_1/F_0)=\sum_{\nu}\sum_{\{\vec{R}^{(\nu)}\}} e^{i(\vec{k}\cdot\vec{R}^{(\nu)})}E^{(\nu)}_{D_1,F_0}\quad ,$$

where $\{\vec{R}^{(\nu)}\}$ is the set of (ν)th nearest neighbors.

For reasons mentioned in the introduction we only consider first- and second-nearest neighbor interactions in terms of two-center integrals. The corresponding molecular integrals will be denoted by $(\cdots)_1$ and $(\cdots)_2$, respectively, and we use the abbreviations

$$\xi=k_x a,\quad \eta=k_y a,\quad \zeta=k_z a,$$

where $\vec{k}=(k_x, k_y, k_z)$ and a is the lattice constant.

(s-f) contributions.

$$(S/F_0)=-(i/\sqrt{2})\sin\zeta[\cos\xi+\cos\eta](sf\sigma)_1+2i\sin\zeta(sf\sigma)_2,$$
$$(S/F_1)=\sqrt{3}\, i\sin\xi[-\cos\eta+\tfrac{3}{2}\cos\zeta](sf\sigma)_1-\sqrt{\tfrac{3}{2}}\, i\sin\xi(sf\sigma)_2,$$
$$(S/F_3)=\sqrt{\tfrac{15}{2}}\, i\sin\zeta[\cos\xi-\cos\eta](sf\sigma)_1\ ,$$
$$(S/F_4)=0\ ,$$
$$(S/F_5)=-\tfrac{1}{2}\sqrt{5}\, i\sin\xi\,[2\cos\eta-\cos\zeta](sf\sigma)_1+\sqrt{\tfrac{5}{2}}\, i\sin\xi\,(sf\sigma)_2\ .$$

(p-f) contributions.

$$(P_0/F_0)=-\tfrac{1}{2}\cos\zeta\,[\cos\xi+\cos\eta](pf\sigma)_1+2\cos\zeta\,(pf\sigma)_2+\tfrac{1}{2}\sqrt{\tfrac{3}{2}}\,[3\cos\xi\,\cos\zeta+3\cos\eta\,\cos\zeta-4\cos\xi\,\cos\eta](pf\pi)_1$$
$$-\sqrt{\tfrac{3}{2}}\,[\cos\xi+\cos\eta](pf\pi)_2\ ,$$
$$(P_1/F_0)=\tfrac{1}{2}\sin\xi\,\sin\zeta\,[(pf\sigma)_1+3\sqrt{\tfrac{3}{2}}\,(pf\pi)_1]\ ;$$

$$(P_0/F_1)=-\tfrac{1}{2}\sin\xi\,\sin\zeta\,[3\sqrt{\tfrac{3}{2}}\,(pf\sigma)_1+\tfrac{7}{2}(pf\pi)_1]\ ,$$
$$(P_1/F_1)=\tfrac{1}{2}\sqrt{\tfrac{3}{2}}\cos\xi\,[-2\cos\eta+3\cos\zeta](pf\sigma)_1-\sqrt{\tfrac{3}{2}}\cos\xi\,(pf\sigma)_2-[\tfrac{1}{2}\cos\xi\,\cos\eta+\tfrac{7}{4}\cos\xi\,\cos\zeta-\tfrac{3}{2}\cos\eta\,\cos\zeta](pf\pi)_1$$
$$+[-\tfrac{1}{2}\cos\eta+2\cos\zeta](pf\pi)_2\ ,$$
$$(P_2/F_1)=\sin\xi\,\sin\eta\,[\sqrt{\tfrac{3}{2}}\,(pf\sigma)_1-\tfrac{1}{2}(pf\pi)_1]\ ;$$

$$(P_0/F_3)=\tfrac{1}{2}\cos\zeta\,(\cos\xi-\cos\eta)\,[\sqrt{15}\,(pf\sigma)_1-\sqrt{\tfrac{5}{2}}(pf\pi)_1]+\sqrt{\tfrac{5}{2}}\,[\cos\xi-\cos\eta](pf\pi)_2\ ,$$
$$(P_1/F_3)=-\tfrac{1}{2}\sin\xi\,\sin\zeta\,[\sqrt{15}\,(pf\sigma)_1+\sqrt{\tfrac{5}{2}}\,(pf\pi)_1]\ ;$$

$$(P_0/F_4)=-\sqrt{10}\,\sin\xi\,\sin\eta\,(pf\pi)_1\ ;$$

$$(P_0/F_5)=-\tfrac{1}{2}\sin\xi\,\sin\zeta\,[\sqrt{\tfrac{5}{2}}\,(pf\sigma)_1-\tfrac{1}{2}\sqrt{15}\,(pf\pi)_1]\ ,$$
$$(P_1/F_5)=-\tfrac{1}{2}\cos\xi\,(2\cos\eta-\cos\zeta)\,[\sqrt{\tfrac{5}{2}}\,(pf\sigma)_1+\tfrac{1}{2}\sqrt{15}\,(pf\pi)_1]+\sqrt{\tfrac{5}{2}}\cos\xi\,(pf\sigma)_2-\tfrac{1}{2}\sqrt{15}\cos\eta\,(pf\pi)_2\ ,$$
$$(P_2/F_5)=\sin\xi\,\sin\eta\,[\sqrt{\tfrac{5}{2}}\,(pf\sigma)_1-\tfrac{1}{2}\sqrt{15}\,(pf\pi)_1]\ .$$

(d-f) contributions.

$$(D_0/F_0)=-\tfrac{1}{4}i\sin\zeta\,(\cos\xi+\cos\eta)\,[(1/\sqrt{2})\,(df\sigma)_1-9(df\pi)_1-3\sqrt{\tfrac{5}{2}}\,(df\delta)_1]+2i\sin\zeta\,(df\sigma)_2\ ,$$
$$(D_1/F_0)=-\tfrac{1}{2}\sqrt{\tfrac{3}{2}}\, i\sin\xi\,\cos\zeta\,[(df\sigma)_1+\sqrt{5}\,(df\delta)_1]+\sqrt{3}\, i\sin\xi\,\cos\eta\,(df\pi)_1+\sqrt{\tfrac{3}{2}}\, i\sin\xi\,(df\pi)_2\ ,$$

$$(D_3/F_0) = -\tfrac{1}{4}\sqrt{3}\, i \sin\zeta\, (\cos\xi - \cos\eta)\, [(1/\sqrt{2})\, (df\sigma)_1 + 3(df\pi)_1 - 3\sqrt{\tfrac{5}{2}}\, (df\delta)_1] ,$$

$$(D_4/F_0) = 0 \;;$$

$$(D_0/F_1) = \tfrac{1}{8}\sqrt{3}\, i \sin\xi\, (4\cos\eta + 3\cos\zeta)\, [(df\sigma)_1 + \sqrt{5}\, (df\delta)_1] + \tfrac{7}{4}\sqrt{\tfrac{3}{2}}\, i \sin\xi \cos\zeta\, (df\pi)_1$$
$$+ \tfrac{1}{2}\sqrt{\tfrac{3}{2}}\, i \sin\xi\, [(df\sigma)_2 + \sqrt{5}\, (df\delta)_2] ,$$

$$(D_1/F_1) = \tfrac{9}{4}\, i \cos\xi \sin\zeta\, (df\sigma)_1 + \tfrac{3}{4}\sqrt{2}\, i \cos\eta \sin\zeta\, (df\pi)_1 + 2i \sin\zeta\, (df\pi)_2 + \tfrac{1}{4}\sqrt{5}\, i \sin\zeta\, [\cos\xi + 4\cos\eta]\, (df\delta)_1 ,$$

$$(D_2/F_1) = 0 ,$$

$$(D_3/F_1) = \tfrac{3}{8} i \sin\xi \cos\zeta\, [3(df\sigma)_1 - \sqrt{5}\, (df\delta)_1] - \tfrac{1}{8}\sqrt{2}\, i \sin\xi\, [4\cos\eta + 7\cos\zeta]\, (df\pi)_1$$
$$- (i/\sqrt{8})\, \sin\xi\, [3\, (df\sigma)_2 - \sqrt{5}\, (df\delta)_2] ,$$

$$(D_4/F_1) = -\tfrac{3}{2} i \cos\xi \sin\eta\, (df\sigma)_1 + \tfrac{3}{4}\sqrt{2}\, i \sin\eta \cos\zeta\, (df\pi)_1 - \tfrac{1}{2} i \sin\eta (df\pi)_2 + \tfrac{1}{2}\sqrt{5}\, i \sin\eta\, [\cos\xi - 2\cos\zeta]\, (df\delta)_1 \;;$$

$$(D_0/F_3) = \tfrac{1}{4}\sqrt{3}\, i \sin\zeta\, (\cos\xi - \cos\eta)\, [\sqrt{\tfrac{5}{2}}\, (df\sigma)_1 - \sqrt{5}\, (df\pi)_1 + (1/\sqrt{2})\, (df\delta)_1] ,$$

$$(D_1/F_3) = \tfrac{3}{2}\sqrt{\tfrac{5}{2}}\, i \sin\zeta \cos\zeta\, (df\sigma)_1 + \sqrt{\tfrac{5}{2}}\, i \sin\xi\, (df\pi)_2 + \tfrac{1}{4}\sqrt{2}\, i \sin\xi\, [8\cos\eta - \cos\zeta]\, (df\delta)_1 ,$$

$$(D_3/F_3) = \tfrac{1}{4} i \sin\zeta\, (\cos\xi + \cos\eta)\, [3\sqrt{\tfrac{5}{2}}\, (df\sigma)_1 + \sqrt{5}\, (df\pi)_1 + (3/\sqrt{2})\, (df\delta)_1] + 2i \sin\zeta\, (df\delta)_2 ,$$

$$(D_4/F_3) = 0 \;;$$

$$(D_0/F_4) = 0 ,$$

$$(D_1/F_4) = \sqrt{5}\, i \sin\eta\, [\cos\xi + \cos\zeta]\, (df\pi)_1 + 2i \sin\eta\, (df\delta)_2 ,$$

$$(D_3/F_4) = 0 \;;$$

$$(D_0/F_5) = \tfrac{1}{8}\sqrt{5}\, i \sin\xi\, [4\cos\eta + \cos\zeta]\, (df\sigma)_1 - (i/\sqrt{8})\, \sin\xi\, [\sqrt{5}\, (df\sigma)_2 - 3\, (df\delta)_2]$$
$$- \tfrac{3}{4}\sqrt{\tfrac{5}{2}}\, i \sin\xi \cos\zeta\, (df\pi)_1 - \tfrac{3}{8} i \sin\xi\, [4\cos\eta - 3\cos\zeta]\, (df\delta)_1 ,$$

$$(D_1/F_5) = \tfrac{1}{4}\sqrt{15}\, i \cos\xi \sin\zeta\, (df\sigma)_1 - \tfrac{1}{2}\sqrt{\tfrac{15}{2}}\, i \cos\eta \sin\zeta\, (df\pi)_1 - \tfrac{1}{4}\sqrt{3}\, i \sin\zeta\, [3\cos\xi - 4\cos\eta]\, (df\delta)_1 ,$$

$$(D_2/F_5) = 0 ,$$

$$(D_3/F_5) = \tfrac{1}{8}\sqrt{3}\, i \sin\xi \cos\zeta\, [\sqrt{5}\, (df\sigma)_1 + 9\, (df\delta)_1] - \tfrac{1}{4} i \sqrt{\tfrac{15}{2}}\, \sin\xi\, [4\cos\eta + 3\cos\zeta]\, (df\pi)_1$$
$$+ \sqrt{3}\, i \sin\xi\, [\tfrac{1}{2}\sqrt{\tfrac{5}{2}}\, (df\sigma)_2 - \sqrt{5}\, (df\pi)_2 + (1/\sqrt{8})\, (df\delta)_2] ,$$

$$(D_4/F_5) = -\tfrac{1}{2}\sqrt{15}\, i \cos\xi \sin\eta\, (df\sigma)_1 - \tfrac{1}{2}\sqrt{\tfrac{15}{2}}\, i \sin\eta \cos\zeta\, (df\pi)_1 - \tfrac{1}{2}\sqrt{15}\, i \sin\eta\, (df\pi)_2$$
$$- \tfrac{1}{2}\sqrt{3}\, i \sin\eta\, [\cos\xi + 2\cos\zeta]\, (df\delta)_1 .$$

All the missing quantities among the foregoing expressions can be obtained by interchanging variables, e.g., (D_2/F_3) from (D_1/F_3) by the interchange $\xi \leftrightarrow \eta$ and reversing the sign, etc. The rules for this procedure are easily found from the representation of E integrals in Sec. III.

V. CONCLUDING REMARKS

For calculations including only spin-exchange splitting of the energy bands the generalization of the results presented is trivial.

In principle, the two-center integrals can be evaluated according to methods discussed, for instance, in Refs. 15 and 16. However, experience in applications of the tight-binding method made it clear that these quantities should be looked at instead as disposable parameters, as was suggested already in the original paper by Slater and Koster.[12] On the other hand, the sharp localization of f electrons close to the nucleus provides a situation quite different from the case of d electrons and therefore the calculated integrals are expected to be more reliable. This point, we hope, is going to be clarified by future applications of our analytical results in tight-binding calculations.

Note added in manuscript. All the data presented in this article are available upon request in form of a FORTRAN-IV card deck from the author.

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APPENDIX

Using the ordinary definition of spherical harmonics,[17]

$$Y_l^m(\theta,\phi)=\frac{1}{2^l l!}\left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-m)!}{(l+m)!}\right]^{1/2}$$

$$\times e^{im\phi}(-\sin\theta)^m\left[\left(\frac{d}{d\cos\theta}\right)^{l+m}(\cos^2\theta-1)^l\right] \quad ,$$

with the property

$$Y_l^{-m}(\theta,\phi)=(-1)^m Y_l^{m*}(\theta,\phi) \quad ,$$

we introduce after conversion to Cartesian coordinates (disregarding radial factors)

$$s=(1/\sqrt{4\pi}) \quad (l=0) \;;$$

$$\left.\begin{aligned} p_0&=C_p z\\ p_{\pm1}&=\mp(1/\sqrt{2})C_p(x\pm iy)\end{aligned}\right\}(l=1),$$

where $C_p=(3/4\pi)^{1/2}$;

$$d_0=C_d(3z^2-r^2) \qquad (l=2),$$

$$\left.\begin{aligned} d_{\pm1}&=\mp\sqrt{6}\,C_d(x\pm iy)z\\ d_{\pm2}&=\sqrt{\tfrac{3}{2}}\,C_d(x\pm iy)^2\end{aligned}\right\}\qquad (l=2),$$

where $C_d=(5/16\pi)^{1/2}$;

$$\left.\begin{aligned} f_0&=C_f(5z^2-3r^2)z\\ f_{\pm1}&=\mp\tfrac{1}{2}\sqrt{3}\,C_f(5z^2-r^2)(x\pm iy)\\ f_{\pm2}&=\sqrt{\tfrac{15}{2}}\,C_f(x\pm iy)^2 z\\ f_{\pm3}&=\mp\tfrac{1}{2}\sqrt{5}\,C_f(x\pm iy)^3\end{aligned}\right\}(l=3),$$

where $C_f=(7/16\pi)^{1/2}$.

The definition of the molecular two-center integrals in terms of these quantities is then as follows:

$$(s(\vec{x}+\vec{R}),\ V_{ext}(\vec{x}+\vec{R})f_0(\vec{x}))\equiv(sf\sigma),$$

$$(p_k(\vec{x}+\vec{R}),\ V_{ext}(\vec{x}+\vec{R})f_k(\vec{x}))\equiv\begin{cases}(pf\sigma), & k=0\\ (pf\pi), & k=\pm1\end{cases}$$

$$(d_k(\vec{x}+\vec{R}),\ V_{ext}(\vec{x}+\vec{R})f_k(\vec{x}))\equiv\begin{cases}(df\sigma), & k=0\\ (df\pi), & k=\pm1\\ (df\delta), & k=\pm2\end{cases} \quad .$$

The simple overlap integrals are defined in the same way, but without V_{ext}.

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