THE APPLICATION OF THE TIGHT BINDING METHOD TO THE INVESTIGATION OF ENERGY BANDS IN HEXAGONAL CLOSE-PACKED STRUCTURE. I.

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Tables for reduction of the matrix components of energy in the tight binding method have been prepared for hexagonal close-packed lattices.

The tight binding or LCAO method originally proposed by Bloch (1928) can be applied satisfactorily to the investigation of the symmetry properties of energy bands in crystals. Slater and Koster (1954) worked out this method in detail, discussed the possible approximations and the validity of the application of this method to real cases.

A rigorous application of this method is hardly possible on account of the enormous amount of numerical work. Taking into account the approximations discussed by Slater and Koster, this method can be applied to crystals, in which the electrons are tightly bound. The LCAO method can be applied also in the case, when the electrons are not tightly bound, but then only as an interpolation method. The energy integrals are then not computed analytically but they are used as disposable constants which can be found using the energy values calculated by other methods at restricted symmetry points in the Brillouin zone.

The calculations of Slater and Koster have been performed for simple cubic structures, namely for a simple cubic lattice; for face- and body-centered cubic lattices and for a cubic structure with basis, in particular for the diamond lattice.

In the present work the LCAO method is used to investigate the properties of energy bands in hexagonal close-packed structure. The calculations for hexagonal close-packed structure are more laborious bacause the unit cell has two non-equivalent atoms and the geometry of this lattice is more complicated, the directions along the axes of rectangular co-ordinate system being non-equivalent.

There are in literature a few papers on energy bands in hexagonal structure. Herring and Hill (1940) have applied to beryllium the method of orthogonalized

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plane waves. Schiff (1955) investigated the symmetry properties of energy bands in titanium by the cellular method.

The metal to which the LCAO method could be applied is the hexagonal form of cobalt; α — Co. Cobalt belongs to the group of transition elements, as Ni and Fe, the d states of which can be treated with the tight binding approximation. For instance Fletcher and Wohlfarth (1951) and Fletcher (1952) investigated with the help of this method the energy bands in face-centered Ni. Suffczyński (1956) calculated two-center integrals for body-centered Fe.

The hexagonal close-packed lattice can be described as a simple hexagonal lattice with two non-equivalent atoms in the unit cell. The primitive translation vectors in rectangular co-ordinate system are: $\boldsymbol{A}_1 = (a/2, -\sqrt{3}\,a/2, 0)$, $\boldsymbol{A}_2 = (a/2, \sqrt{3}\,a/2, 0)$, $\boldsymbol{A}_3 = (0, 0, c)$, where a is lattice constant in the horizontal plane. The basis vectors are: $\boldsymbol{t}_1 = (0, 0, 0)$, $\boldsymbol{t}_2 = (a/2, \sqrt{3}\,a/6, c/2)$, when the origin of the co-ordinate system coincide with the position of an atom of the lattice. The simple lattice with an atom at $(0, 0, 0)$ is denoted by the index 1, and the lattice with an atom at $(a/2, \sqrt{3}\,a/6, c/2)$ by the index 2.

For convenience we use different length units along different axes of the rectangular co-ordinate system, namely $\alpha = a/2$, $\beta = \sqrt{3}\,a/2$, $\gamma = c/2$ in the x, y, z directions respectively.

In our calculations we use the model of the hexagonal ideal close-packed lattice, i. e., we put the distance between two nearest non-equivalent atoms equal to a; $|\boldsymbol{t}_2| = a$. Then $c/a = \sqrt{\frac{8}{3}} = 1.63$. This is approximately fulfilled for many crystals with hexagonal structure, for instance for α — Co we have $c/a = 1.62$.

The energy dependence on the wave vector $\boldsymbol{k}$ will be obtained by solving the secular equation

$$\det|\,(m/n)_{\omega\omega'} - \delta_{mn}\,\delta_{\omega\omega'}\,E\,| = 0,$$

where $(m/n)_{\omega\omega'}$ are the matrix components of the Hamiltonian (energy) between corresponding Bloch sums. In the present work these components are computed using firstly the general three-center integrals and subsequently the two-center integrals.

The general formula for the matrix components of energy is given by

$$(m/n)_{\omega\omega'} = \exp\left[i\boldsymbol{k}\,(\boldsymbol{t}_\omega - \boldsymbol{t}_{\omega'})\right] \sum_l \exp\,(i\boldsymbol{k}\boldsymbol{r}_l) \int \varphi_m^{\star}\,(\boldsymbol{r} - \boldsymbol{t}_{\omega'})\, H\, \varphi_n\,(\boldsymbol{r} - \boldsymbol{r}_l - \boldsymbol{t}_\omega)\, d\boldsymbol{r}.$$

m, n denote here atomic states, φ_n are the atomic functions, $\boldsymbol{r}_l = l_1\,\boldsymbol{A}_1 + l_2\,\boldsymbol{A}_2 + l_3\,\boldsymbol{A}_3$ — translation vectors (l_1, l_2, l_3 are integers), $\boldsymbol{t}_\omega$ — basis vectors. The Hamiltonian $H = -\Delta + V(\boldsymbol{r})$ is an Hermitian operator. $V(\boldsymbol{r}) = \sum_l [U(\boldsymbol{r} - \boldsymbol{r}_l) + U(\boldsymbol{r} - \boldsymbol{r}_l - \boldsymbol{t}_2)]$ is the periodic potential of the whole crystal, thus $V(\boldsymbol{r} + \boldsymbol{r}_l) = V(\boldsymbol{r})$. $U(\boldsymbol{r} - \boldsymbol{r}_l)$ is the potential of an isolated ion located at the point $\boldsymbol{r}_l$. The energy integrals (E-integrals)

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have the form

$$E_{m,n}(\mathbf{t}_{\omega'}, \mathbf{r}_l + \mathbf{t}_\omega) = \int \varphi^*_m (\mathbf{r} - \mathbf{t}_{\omega'})\, H\, \varphi_n (\mathbf{r} - \mathbf{r}_l - \mathbf{t}_\omega)\, d\mathbf{r}.$$

The matrix components are calculated for the following states: *s*, *p* (3 functions of the type *x*, *y*, *z* times $f_1(r)$, denoted by p_j), *d* (5 functions of the type *xy*, *yz*, *xz*, x^2-y^2, $3z^2-r^2$ times $f_2(r)$, denoted by d_q). Since we have nine such states and a unit cell contains two non-equivalent atoms, we construct 18 Bloch sums. The general matrix of energy has $18 \times 18 = 324$ components.

Using symmetry properties of the Hamiltonian and of atomic functions we can perform the reduction of these matrix components. It is convenient at this moment to put the origin of the co-ordinate system in the middle point of the line joining two non-equivalent atoms in the unit cell. In such a system the basis vectors are $\mathbf{t}'_1$ and $\mathbf{t}'_2 = -\mathbf{t}'_1 = \frac{1}{2}\mathbf{t}_2$.

The periodic potential takes the form

$$V(\mathbf{r}) = \sum_l \left[U\left(\mathbf{r} - \mathbf{r}_l - \frac{1}{2}\mathbf{t}_2\right) + U\left(\mathbf{r} - \mathbf{r}_l + \frac{1}{2}\mathbf{t}_2\right)\right] \quad \text{and therefore}$$

$V(\mathbf{r}) = V(-\mathbf{r})$. We also use the fact, that to every vector $\mathbf{r}_l$ corresponds the vector $\mathbf{r}'_l = -\mathbf{r}_l$.

We notice the following general relation

$$(m/n)_{\omega'\omega} = [(n/m)_{\omega\omega'}]^*$$

Further relations are given in Table I.

TABLE I

$(s/s)_{11} = (s/s)_{22}$	$(s/s)_{12} = (s/s)_{21}^*$	
$(s/p_j)_{11} = -(s/p_j)_{22}^*$	$(s/p_j)_{12} = -(s/p_i)_{21}^*$	
$(s/d_q)_{11} = (s/d_q)_{22}^*$	$(s/d_q)_{12} = (s/d_q)_{21}^*$	
$(p_j/p_j)_{11} = (p_j/p_j)_{22}$	$(p_j/p_j)_{12} = (p_j/p_j)_{21}^*$	
$(p_j/p_i)_{11} = (p_j/p_i)_{22}$	$(p_j/p_i)_{12} = (p_j/p_i)_{21}^*$	$i \neq j$
$(p_j/d_q)_{11} = -(p_j/d_q)_{22}^*$	$(p_j/d_q)_{12} = -(p_j/d_q)_{21}^*$	
$(d_q/d_q)_{11} = (d_q/d_q)_{22}$	$(d_q/d_q)_{12} = (d_q/d_q)_{21}^*$	
$(d_q/d_r)_{11} = (d_q/d_r)_{22}^*$	$(d_q/d_r)_{12} = (d_q/d_r)_{21}^*$	$q \neq r$

From the total of 324 components only 90 components must now be considered: 45 components of the type

$$(m/n)_{11} = \sum_l \exp(i\mathbf{k}\mathbf{r}_l) \int \varphi^*_m(\mathbf{r})\, H\, \varphi_n(\mathbf{r} - \mathbf{r}_l)\, d\mathbf{r}$$

and 45 components of the type

$$(m/n)_{12} = \sum \exp[i\mathbf{k}(\mathbf{r}_l + \mathbf{t}_2)] \int \varphi^*_m)\mathbf{r})\, H\, \varphi_n(\mathbf{r} - \mathbf{r}_l - \mathbf{t}_2)\, d\mathbf{r}.$$

In the above integrals the origin of the co-ordinate system is again located at the position of an atom. This system will be used exclusively in the following.

We make now the nearest-neighbours approximation. Every atom in a hexagonal ideal close-packed lattice has 12 nearest neighbours: six neighbours in lattice 1 and six in lattice 2. Therefore, in the matrix components (m/n_{11}) there remain only seven E-integrals corresponding to the lattice sites $\boldsymbol{r}_l$ (0, 0, 0); (1, — 1, 0), (2, 0, 0), (1, 1, 0), (—1, — 1, 0), (—2, 0, 0), (—1, 1, 0) in terms of α, β, γ and in $(m/n)_{12}$ six E-integrals corresponding to $\boldsymbol{r}_l + \boldsymbol{t}_2$: (1, 1/3, 1), (—1, 1/3, 1), (0, — 2/3, 1) (1, 1/3, — 1), (0, — 2/3, — 1). So $7 \times 45 + 6 \times 45 = 585$ E-integrals remain to be calculated. Not all of them are independent. The reduction of these integrals must be performed. Here we use more particular symmetries of the Hamiltonian and atomic functions. We perform the orthogonal transformations which carry the hexagonal close-packed lattice into itself. Under these symmetry transformations the Hamiltonian is invariant.

We take into account the following transformations: 1) reflections in three vertical planes, the normals to which make the angles $\frac{2}{3}\pi$ among themselves; one of these planes is the plane $x = 0$, 2) reflection in the horizontal plane $z = 0$. From these transformations we can obtain all other necessary transformations.

Under these transformations the atomic functions transform in some definite way. If we take for instance one of the d functions located on the atom $\boldsymbol{r}_l$, then after any one of the above transformations we obtain a linear combination of the d functions all located on some other atom, say $\boldsymbol{r}_k$.

In the first step of the reduction of E-integrals we use only these symmetry transformations after which in a given matrix component, say (m_0/n_0), only E-integrals remain with the same index m_0 and n_0. By this treatment the non-vanishing matrix components can be divided into ten sets. Every set has different relations between the E-integrals. Therefore the $\boldsymbol{k}$ dependence of all components in one set is the same.

First we write down all the copmonents which belong to every set, secondly the relations between E-integrals in this set and lastly the $\boldsymbol{k}$ dependence. We use here the following abbreviations: $\xi = \alpha k_x = ak_x/2$, $\eta = \beta k_y = \sqrt{3}\, a\, k_y/2$, $\zeta = \gamma k_z = c\, k_z/2 = ak_z \sqrt{(2/3)}$.

1. $(s/s)_{11}$, $(s/3z^2 - r^2)_{11}$, $(z/z)_{11}$, $(3z^2 - r^2/3z^2 - r^2)_{11}$

$E_{m,n}$ (0, 0, 0) $\neq 0$

$E_{m,n}(\boldsymbol{r}_l)$ — identical for six vectors $\boldsymbol{r}_l$ corresponding to nearest neighbours in lattice 1.

$(m/n)_{11} = E_{m,n}(0, 0, 0) + 2E_{m,n}(2, 0, 0)\,(2 \cos \xi \cos \eta + \cos 2\,\xi)$

2. $(s/s)_{12}$, $(s/3z^2 - r^2)_{12}$, $(z/z)_{12}$, $(3z^2 - r^2/3z^2 - r^2)_{12}$

$E_{m,n}(\boldsymbol{r}_1 + \boldsymbol{t}_2)$ — identical for six vectors $(\boldsymbol{r}_1 + \boldsymbol{t}_2)$ corresponding to nearest neighbours in lattice 2.

$$(m/n)_{12} = 2E_{m,n}\left(0, -\frac{2}{3}, 1\right) \cos\zeta \left[\left(2\cos\xi\cos\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right) + \right.$$
$$\left. + i\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right)\right]$$

3. $(s/x)_{11}$, $(s/xy)_{11}$, $(x/y)_{11}$, $(x/x^2-y^2)_{11}$, $(x/3z^2-r^2)_{11}$
$(y/xy)_{11}$, $(z/xz)_{11}$, $(xy/x^2-y^2)_{11}$, $(xy/z^2-r^2)_{11}$, $(yx/xz)_{11}$

$$E_{m,n}(0,0,0) = 0$$
$$E_{m,n}(1,-1,0) = -E_{m,n}(-1,-1,0)$$
$$E_{m,n}(1,1,0) = -E_{m,n}(-1,1,0)$$
$$E_{m,n}(2,0\,0) = -E_{m,n}(-2,0,0)$$
$$(m/n)_{11} = 2\,[E_{m,n}(1,-1,0) - E_{m,n}(1,1,0)]\sin\xi\sin\eta + 2i\,\{[E_{m,n}(1,-1,0) +$$
$$+ E_{m,n}(1,1,0)]\sin\xi\cos\eta + E_{m,n}(2,0,0)\sin 2\xi\}$$

4. $(s/x)_{12}$, $(s/xy)_{12}$, $(x/y)_{12}$, $(x/x^2-y^2)_{12}$, $(x/3z^2-r^2)_{12}$ $(y/xy)_{12}$, $(z/xz)_{12}$, $(xy/x^2-y^2)_{12}$, $(xy/3z^2-r^2)_{12}$; $(yz/xz)_{12}$

$$E_{m,n}\left(1,\frac{1}{3},1\right) = E_{m,n}\left(1,\frac{1}{3},-1\right) = -E_{m,n}\left(-1,\frac{1}{3},1\right)$$
$$= -E_{m,n}\left(-1,\frac{1}{3},-1\right)$$
$$E_{m,n}\left(0,-\frac{2}{3},1\right) = E_{m,n}\left(0,-\frac{2}{3},-1\right) = 0$$
$$(m/n)_{12} = -4\,E_{m,n}\left(1,\frac{1}{3},1\right)\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

5. $(s/y)_{11}$, $(s/x^2-y^2)_{11}$, $(x/xy)_{11}$, $(y/x^2-y^2)_{11}$, $(y/3z^2-r^2)_{11}$, $(z/yz)_{11}$ $(x^2-y^2/3z^2-r^2)_{11}$,

$$E_{m,n}(0,0,0) \neq 0$$
$$E_{m,n}(1,-1,0) = E_{m,n}(-1,-1,0)$$
$$E_{m,n}(1,1,0) = E_{m,n}(-1,1,0)$$
$$E_{m,n}(2,0,0) = E_{m,n}(-2,0,0)$$
$$(m/n)_{11} = E_{m,n}(0,0,0) + 2\,[E_{m,n}(1,-1,0) + E_{m,n}(1,1,0)]\cos\xi\cos\eta +$$
$$+ 2E_{m,n}(2,0,0)\cos 2\xi + 2i\,[E_{m,n}(1,1,0) - E_{m,n}(1,-1,0)]\cos\xi\sin\eta$$

6. $(s/y)_{12}$, $(s/x^2-y^2)_{12}$; $(x/x)_{12}$, $(y/y]_{12}$, $(x/xy)^6{}_{12}$ $(y/x^2-y^2)_{12}$, $(y/3z^2-r^2)_{12}$,
$(z/yz)_{12}$, $(xy/xy)_{12}$, $(xz/xz)_{12}$, $(yz/yz)_{12}$, $(x^2-y^2/x^2-y^2)_{12}$, $(x^2-y^2/3z^2-r^2)_{12}$

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$$E_{m,n}\left(1,\frac{1}{3},1\right)=E_{m,n}\left(1,\frac{1}{3},-1\right)=E_{m,n}\left(-1,\frac{1}{3},1\right)=E_{m,n}\left(-1,\frac{1}{3},-1\right)$$

$$E_{m,n}\left(0,-\frac{2}{3},1\right)=E_{m,n}\left(0,-\frac{2}{3},-1\right)$$

$$(m/n)_{12}=2\cos\zeta\left[2E_{m,n}\left(1,\frac{1}{3},1\right)\cos\xi\cos\frac{1}{3}\eta+E_{m,n}\left(0,-\frac{2}{3},1\right)\cos\frac{2}{3}\eta\right]+$$

$$+2i\cos\zeta\left[2E_{m,n}\left(1,\frac{1}{3},1\right)\cos\xi\sin\frac{1}{3}\eta-E_{m,n}\left(0,-\frac{2}{3},1\right)\sin\frac{2}{3}\eta\right]$$

7. $(s/z)_{12}$, $(z/3z^2-r^2)_{12}$

$$E_{m,n}\left(1,\frac{1}{3},1\right)=E_{m,n}\left(-1,\frac{1}{3},1\right)=E_{m,n}\left(0,-\frac{2}{3},1\right)$$

$$=-E_{m,n}\left(1,\frac{1}{3},-1\right)=-E_{m,n}\left(-1,\frac{1}{3},-1\right)=-E_{m,n}\left(0,-\frac{2}{3},-1\right)$$

$$(m/n)_{12}=-2E_{m,n}\left(1,\frac{1}{3},1\right)\sin\zeta\left[\left(2\cos\xi\sin\frac{1}{3}\eta-\sin\frac{2}{3}\eta\right)-\right.$$

$$\left.-i\left(2\cos\xi\cos\frac{1}{3}\eta+\cos\frac{2}{3}\eta\right)\right]$$

8. $(s/xz)_{12}$, $(z/z)_{12}$, $(y/xz)_{12}$, $(x/yz)_{12}$, $(z/xy)_{12}$ $(xy/yz)_{12}$, $(xz/x^2-y^2)_{12}$, $(xz/3z^2-r^2)_{12}$

$$E_{m,n}\left(1,\frac{1}{3},1\right)=-E_{m,n}\left(1,\frac{1}{3},-1\right)=-E_{m,n}\left(-1,\frac{1}{3},1\right)$$

$$=E_{m,n}\left(-1,\frac{1}{3},-1\right)$$

$$E_{m,n}\left(0,-\frac{2}{3},1\right)=E_{m,n}\left(0,-\frac{2}{3},-1\right)=0$$

$$(m/n)_{12}=-4\mathrm{E}_{m,n}\left(1,\frac{1}{3},1\right)\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta+i\sin\frac{1}{3}\eta\right)$$

9. $(s/yz)_{12}$, $(y/z)_{12}$, $(x/xz)_{12}$, $(y/yz)_{12}$, $(z/x^2-y^2)_{12}$, $(xy/xz)_{12}$, $(yz/x^2-y^2)_{12}$, $(yz/3z^2-r^2)_{12}$

$$E_{m,n}\left(1,\frac{1}{3},1\right)=-E_{m,n}\left(1,\frac{1}{3},-1\right)=E_{m,n}\left(-1,\frac{1}{3},1\right)$$

$$=-E_{m,n}\left(-1,\frac{1}{3},-1\right)$$

$$E_{m,n}\left(0,-\frac{2}{3},1\right)=-E_{m,n}\left(0,-\frac{2}{3},1\right)$$

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$$(m/n)_{12} = 2 \sin \zeta \left[-2\, E_{m,n} \left(1, \frac{1}{3}, 1 \right) \cos \xi \sin \frac{1}{3} \eta + \right.$$

$$\left. + E_{m,n} \left(0, -\frac{2}{3}, 1 \right) \sin \frac{2}{3} \eta \right] + 2\, i \sin \zeta \left[2 E_{m,n} \left(1, \frac{1}{3}, 1 \right) \cos \xi \cos \frac{1}{3} \eta \right.$$

$$\left. + E_{m,n} \left(0, -\frac{2}{3}, 1 \right) \cos \frac{2}{3} \eta \right]$$

10. $(x/x)_{11}$, $(y/y)_{11}$, $(xy/xy)_{11}$, $(xz/xz)_{211}$, $(yz/yz)_{11}$, $(x^2 - y^2/x^2 - y^2)_{11}$

$E_{m,n}(1, -1, 0) = E_{m,n}(-1, -1, 0) = E_{m,n}(-1, 1, 0) = E_{m,n}(1, 1, 0)$

$E_{m,n}(2, 0, 0) = E_{m,n}(-2, 0, 0)$

$(m/n)_{11} = E_{m,n}(0, 0, 0) + 4E_{m,n}(1, -1, 0) \cos \xi \cos \eta + 2E_{m,n}(2, 0, 0) \cos 2\xi$

E-integrals for remaining matrix components vanish for all $\boldsymbol{r}_l$, therefore these matrix components disappear:

$$(s/z)_{11} = (s/xz)_{11} = (s/yz)_{11} = (x/z)_{11} = (y/z)_{11} = (x/xz)_{11}$$
$$= (x/yz)_{11} = (y/xz)_{11} = (y/yz)_{11} = (z/xy)_{11} = (z/x^2 - y^2)_{11} = (z/3z^2 - r^2)_{11}$$
$$= (xy/xz)_{11} = (xy/yz)_{11} = (xz/x^2 - y^2)_{11} = (xz/3z^2 - r^2)_{11}$$
$$= (yz/x^2 - y^2)_{11} = (yz/3z^2 - r^2)_{11} = 0.$$

Now among all the non-vanishing E-integrals only E-integrals for $\boldsymbol{r}_l = \boldsymbol{R} = (2, 0, 0)$ and $\boldsymbol{r}_l + \boldsymbol{t}_2 = \boldsymbol{T} = (0, -2/3, 1)$ are independent. Therefore, in the second step of the reduction, we express all integrals $E_{m,n}(1, -1, 0)$ and $E_{m,n}(1, 1, 0)$ in terms of $E_{m,n}(\boldsymbol{R})$ and the integrals $E_{m,n}(1, 1/3, 1)$ in terms of $E_{m,n}(\boldsymbol{T})$. Here we use the symmetry transformations, which were not taken into account previously. The component (m_0/n_0) will now contain the integrals with m and n not necessarily equal to m_0 and n_0. We have only 71 independent E-integrals. The expressions for the remaining integrals are given in Table II.

TABLE II

$$E_{s,x}(1, \pm 1, 0) = \frac{1}{2} \left[E_{s,x}(\boldsymbol{R}) \pm \sqrt{3}\, E_{s,y}(\boldsymbol{R}) \right]$$

$$E_{s,x}\left(1, \frac{1}{3}, 1\right) = \sqrt{3}\, E_{s,y}\left(1, \frac{1}{3}, 1\right) = -\frac{1}{2} \sqrt{3}\, E_{s,y}(\boldsymbol{T})$$

$$E_{s,y}(1, \pm 1, 0) = \frac{1}{2} \left[\pm \sqrt{3}\, E_{s,x}(\boldsymbol{R}) - E_{s,y}(\boldsymbol{R}) \right]$$

$$E_{s,xy}(1, \pm 1, 0) = \frac{1}{2} \left[\pm \sqrt{3}\, E_{s,x^2-y^2}(\boldsymbol{R}) + E_{s,xy}(\boldsymbol{R}) \right]$$

$$E_{s,xy}\left(1,\frac{1}{3},1\right)=\sqrt{3}\,E_{s,x^2-y^2}\left(1,\frac{1}{3},1\right)=-\frac{1}{2}\sqrt{3}\,E_{s,x^2-y^2}(\boldsymbol{T})$$

$$E_{s,xz}\left(1,\frac{1}{3},1\right)=\sqrt{3}\,E_{s,yz}\left(1,\frac{1}{3},1\right)=-\frac{1}{2}\sqrt{3}\,E_{s,yz}(\boldsymbol{T})$$

$$E_{s,x^2-y^2}(1,\pm 1,0)=\frac{1}{2}\left[-E_{s,x^2-y^2}(\boldsymbol{R})\pm\sqrt{3}\,E_{s,xy}(\boldsymbol{R})\right]$$

$$E_{x,x}(1,-1,0)=\frac{1}{4}\left[E_{x,x}(\boldsymbol{R})+3\,E_{y,y}(\boldsymbol{R})\right]$$

$$E_{x,x}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\left[E_{x,x}(\boldsymbol{T})+3\,E_{y,y}(\boldsymbol{T})\right]$$

$$E_{y,y}(1,-1,0)=\frac{1}{4}\left[3\,E_{x,x}(\boldsymbol{R})+E_{y,y}(\boldsymbol{R})\right]$$

$$E_{y,y}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\left[3\,E_{x,x}(\boldsymbol{T})+E_{y,y}(\boldsymbol{T})\right]$$

$$E_{x,y}(1,\pm 1,0)=\pm\frac{1}{4}\sqrt{3}\,E_{x,x}(\boldsymbol{R})-E_{x,y}(\boldsymbol{R})\mp\frac{1}{4}\sqrt{3}\,E_{y,y}(\boldsymbol{R})$$

$$E_{x,y}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\sqrt{3}\left[-E_{x,x}(\boldsymbol{T})+E_{y,y}(\boldsymbol{T})\right]$$

$$E_{x,z}\left(1,\frac{1}{3},1\right)=\sqrt{3}\,E_{y,z}\left(1,\frac{1}{3},1\right)=-\frac{1}{2}\sqrt{3}\,E_{y,z}(\boldsymbol{T})$$

$$E_{x,xy}(1,\pm 1,0)=\frac{1}{4}\left[\pm\sqrt{3}\,E_{x,x^2-y^2}(\boldsymbol{R})+E_{x,xy}(\boldsymbol{R})+3E_{y,x^2-y^2}(\boldsymbol{R})\pm\sqrt{3}\,E_{y,xy}(\boldsymbol{R})\right]$$

$$E_{x,xy}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\left[E_{x,xy}(\boldsymbol{T})+3E_{y,x^2-y^2}(\boldsymbol{T})\right]$$

$$E_{x,xy}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\left[E_{x,xz}(\boldsymbol{T})+3E_{y,yz}(\boldsymbol{T})\right]$$

$$E_{x,yz}\left(1,\frac{1}{3},1\right)=E_{y,xz}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\sqrt{3}\left[-E_{x,xz}(\boldsymbol{T})+E_{y,yz}(\boldsymbol{T})\right]$$

$$E_{x,x^2-y^2}(1,\pm 1,0)=\frac{1}{4}\left[-E_{x,x^2-y^2}(\boldsymbol{R})\pm\sqrt{3}\,E_{x,xy}(\boldsymbol{R})\pm\sqrt{3}E_{y,x^2-y^2}(\boldsymbol{R})+3E_{y,xy}(\boldsymbol{R})\right]$$

$$E_{x,x^2-y^2}\left(1,\frac{1}{3},1\right)=E_{y,xy}\left(1,\frac{1}{3},1\right)=\frac{1}{4}\sqrt{3}\left[-E_{x,xy}(\boldsymbol{T})+E_{y,x^2-y^2}(\boldsymbol{T})\right]$$

$$E_{x,3z^2-r^2}(1,\pm 1,0)=\frac{1}{2}\left[E_{x,3z^2-r^2}(\boldsymbol{R})\pm\sqrt{3}\,E_{y,3z^2-r^2}(\boldsymbol{R})\right]$$

$$E_{x,3z^2-r^2}\left(1,\frac{1}{2},1\right) = \sqrt{3}\,E_{y,3z^2-r^2}\left(1,\frac{1}{3},1\right) = -\frac{1}{2}\sqrt{3}\,E_{y,3z^2-r^2}(\boldsymbol{T})$$

$$E_{y,xy}(1,\pm 1,0) = \frac{1}{4}\left[3E_{x,x^2-y^2}(\boldsymbol{R}) \pm \sqrt{3}\,E_{x,xy}(\boldsymbol{R}) \mp \sqrt{3}\,E_{y,x^2-y^2}(\boldsymbol{R}) - E_{y,xy}(\boldsymbol{R})\right]$$

$$E_{y,yz}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\left[3\,E_{x,xz}(\boldsymbol{T}) + E_{y,yz}(\boldsymbol{T})\right]$$

$$E_{y,x^2-y^2}(1,\pm 1,0) = \frac{1}{4}\left[\mp\sqrt{3}\,E_{x,x^2-y^2}(\boldsymbol{R}) + 3\,E_{x,xy}(\boldsymbol{R}) + E_{y,x^2-y^2}(\boldsymbol{R}) \mp \sqrt{3}\,E_{y,xy}(\boldsymbol{R})\right]$$

$$E_{y,x^2-y^2}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\left[3\,E_{x,xy}(\boldsymbol{T}) + E_{y,x^2-y^2}(\boldsymbol{T})\right]$$

$$E_{y,3z^2-r^2}(1,\pm 1,0) = \frac{1}{2}\left[\pm\sqrt{3}\,E_{x,3z^2-r^2}(\boldsymbol{R}) - E_{y,3z^2-r^2}(\boldsymbol{R})\right]$$

$$E_{z,xy}\left(1,\frac{1}{3},1\right) = \sqrt{3}\,E_{z,x^2-y^2}\left(1,\frac{1}{3},1\right) = -\frac{1}{2}\sqrt{3}\,E_{z,x^2-y^2}(\boldsymbol{T})$$

$$E_{z,xz}(1,\pm 1,0) = \frac{1}{2}\left[E_{z,xz}(\boldsymbol{R}) \pm \sqrt{3}\,E_{z,yz}(\boldsymbol{R})\right]$$

$$E_{z,xz}\left(1,\frac{1}{3},1\right) = \sqrt{3}\,E_{z,yz}\left(1,\frac{1}{3},1\right) = -\frac{1}{2}\sqrt{3}\,E_{z,yz}(\boldsymbol{T})$$

$$E_{z,yz}(1,\pm 1,0) = \frac{1}{2}\left[\pm\sqrt{3}\,E_{z,xz}(\boldsymbol{R}) - E_{z,yz}(\boldsymbol{R})\right]$$

$$E_{xy,xy}(1,-1,0) = \frac{1}{4}\left[E_{xy,xy}(\boldsymbol{R}) + 3\,E_{x^2-y^2,x^2-y^2}(\boldsymbol{R})\right]$$

$$E_{xy,xy}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\left[E_{xy,xy}(\boldsymbol{T}) + 3E_{x^2-y^2,x^2-y^2}(\boldsymbol{T})\right]$$

$$E_{xz,xz}(1,-1,0) = \frac{1}{4}\left[E_{xz,xz}(\boldsymbol{R}) + 3E_{yz,yz}(\boldsymbol{R})\right]$$

$$E_{xz,xz}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\left[E_{xz,xz}(\boldsymbol{T}) + 3E_{yz,yz}(\boldsymbol{T})\right]$$

$$E_{yz,yz}(1,-1,0) = \frac{1}{4}\left[E_{yz,yz}(\boldsymbol{R}) + 3E_{xz,xz}(\boldsymbol{R})\right]$$

$$E_{yz,yz}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\left[E_{yz,yz}(\boldsymbol{T}) + 3E_{xz,xz}(\boldsymbol{T})\right]$$

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$$E_{x^2-y^2,x^2-y^2}\,(1,\,-\,1,0) = \frac{1}{4}\,[E_{x^2-y^2,x^2-y^2}\,(\boldsymbol{R}) + 3E_{xy,xy}\,(\boldsymbol{R})]$$

$$E_{x^2-y^2,x^2-y^2}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\,]E_{x^2-y^2,x^2-y^2}\,(\boldsymbol{T}) + 3E_{xy,xy}\,(\boldsymbol{T})]$$

$$E_{xy,xz}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\,[E_{xy,xz}\,(\boldsymbol{T}) + 3E_{yz,x^2-y^2}\,(\boldsymbol{T})]$$

$$E_{xy,yz}\left(1,\frac{1}{3},1\right) = E_{xz,x^2-y^2}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\sqrt{3}\,[E_{yz,x^2-y^2}\,(\boldsymbol{T}) - E_{xy,xz}\,(\boldsymbol{T})]$$

$$E_{xy,x^2-y^2}\,(1,\pm\,1,0) = \mp\frac{1}{4}\sqrt{3}\,E_{x^2-y^2,x^2-y^2}\,(\boldsymbol{R}) - E_{xy,x^2-y^2}\,(\boldsymbol{R}) \pm \frac{1}{4}\sqrt{3}\,E_{xy,xy}\,(\boldsymbol{R})$$

$$E_{xy,x^2-y^2}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\sqrt{3}\,[E_{x^2-y^2,x^2-y^2}\,(\boldsymbol{T}) - E_{xy.xy}\,(\boldsymbol{T})]$$

$$E_{xy,3z^2-r^2}\,(1,\pm\,1,0) = \frac{1}{2}\,[E_{xy,3z^2-r^2}\,(\boldsymbol{R}) \pm \sqrt{3}\,E_{x^2-y^2,3z^2-r^2}\,(\boldsymbol{R})]$$

$$E_{xy,3z^2-r^2}\left(1,\frac{1}{3},1\right) = \sqrt{3}E_{x^2-y^2,3z^2-r^2}\left(1,\frac{1}{3},1\right) = -\frac{1}{2}\sqrt{3}\,E_{x^2-y^2,3z^2-r^2}\,(\boldsymbol{T})$$

$$E_{yz,xz}\,(1,\pm\,1,0) = \pm\frac{1}{4}\sqrt{3}\,E_{xz,xz}\,(\boldsymbol{R}) - E_{yz,xz}\,(\boldsymbol{R}) \mp \frac{1}{4}\sqrt{3}\,E_{yz,yz}\,(\boldsymbol{R})$$

$$E_{yz,xz}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\sqrt{3}\,[E_{yz.yz}\,(\boldsymbol{T}) - E_{xz,xz}\,(\boldsymbol{T})]$$

$$E_{yz,x^2-y^2}\left(1,\frac{1}{3},1\right) = \frac{1}{4}\,[E_{yz,x^2-y^2}\,(\boldsymbol{T}) + 3E_{xy.xz}\,(\boldsymbol{T})]$$

$$E_{xz,3z^2-r^2}\left(1,\frac{1}{3},1\right) = \sqrt{3}\,E_{yz,3z^2-r^2}\left(1,\frac{1}{3},1\right) = -\frac{1}{2}\sqrt{3}\,E_{yz,3z^2-r^2}\,(\boldsymbol{T})$$

$$E_{x^2-y^2,3z^2-r^2}\,(1,\pm\,1,0) = \frac{1}{2}\,[-E_{x^2-y^2,3z^2-r^2}\,(\boldsymbol{R}) \pm \sqrt{3}\,E_{xy,3z^2-r^2}\,(\boldsymbol{R})]$$

We could use for $\boldsymbol{R}$ and $\boldsymbol{T}$ instead of (2, 0, 0) and (0, — 2/3, 1) some other $\boldsymbol{r}_l$ and $\boldsymbol{r}_l + \boldsymbol{t}_2$ given above. We choose these particular $\boldsymbol{R}$ and $\boldsymbol{T}$ because the direction cosines (l, m, n) of these vectors are given by the most simple numbers possible. The matrix components expressed in terms of the three-center E-integrals in the nearest-neighbours approximation are summarized in Table III.

TABLE III

$(s/s)_{11}$	$E_{s,s}(0) + 2E_{s,s}(\boldsymbol{R})(2\cos\xi\cos\eta + \cos 2\xi)$
$(s/s)_{12}$	$2E_{s,s}(\boldsymbol{T})\cos\zeta\left[\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right) + i\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right)\right]$
$s/x)_{11}$	$-2\sqrt{3}E_{s,y}(\boldsymbol{R})\sin\xi\sin\eta + 2iE_{s,x}(\boldsymbol{R})(\sin\xi\cos\eta + \sin 2\xi)$
$(s/x)_{12}$	$2\sqrt{3}E_{s,y}(\boldsymbol{T})\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$
$(s/y)_{11}$	$E_{s,y}(0) - 2E_{s,y}(\boldsymbol{R})(\cos\xi\cos\eta - \cos 2\xi) + 2\sqrt{3}\,iE_{s,x}(\boldsymbol{R})\cos\xi\sin\eta$
$(s/y)_{12}$	$-2E_{s,y}(\boldsymbol{T})\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) + i\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\right)\right]$
$(s/z)_{12}$	$-2E_{s,z}(\boldsymbol{T})\sin\zeta\left[\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right) - i\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right)\right]$
$(s/xy)_{11}$	$-2\sqrt{3}E_{s,x^2-y^2}(\boldsymbol{R})\sin\xi\sin\eta + 2iE_{s,xy}(\boldsymbol{R})(\sin\xi\cos\eta + \sin 2\xi)$
$(s/xy)_{12}$	$2\sqrt{3}E_{s,x^2-y^2}(\boldsymbol{T})\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$
$(s/yz)_{12}$	$2E_{s,yz}(\boldsymbol{T})\sin\zeta\left[\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right) - i\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right)\right]$
$(s/xz)_{12}$	$2\sqrt{3}E_{s,yz}(\boldsymbol{T})\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta + i\sin\frac{1}{3}\eta\right)$
$(s/x^2-y^2)_{11}$	$E_{s,x^2-y^2}(0) - 2E_{s,x^2-y^2}(\boldsymbol{R})(\cos\xi\cos\eta - \cos 2\xi) + 2\sqrt{3}\,iE_{s,xy}(\boldsymbol{R})\cos\xi\sin\eta$
$(s/x^2-y^2)_{12}$	$-2E_{s,x^2-y^2}(\boldsymbol{T})\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) + i\left(\cos\zeta\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right)\right]$
$(s/3z^2-r^2)_{11}$	$E_{s,3z^2-r^2}(0) + 2E_{s,3z^2-r^2}(\boldsymbol{R})(2\cos\xi\cos\eta + \cos 2\xi)$
$(s/3z^2-r^2)_{12}$	$2E_{s,3z^2-r^2}(\boldsymbol{T})\cos\zeta\left[\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right) + i\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right)\right]$
$(x/x)_{11}$	$E_{x,x}(0) + [E_{x,x}(\boldsymbol{R}) + 3E_{y,y}(\boldsymbol{R})]\cos\xi\cos\eta + 2E_{x,x}(\mathbf{R})\cos 2\xi$
$(x/x)_{12}$	$\cos\zeta\left\{[E_{x,x}(\boldsymbol{T}) + 3E_{y,y}(\boldsymbol{T})]\cos\xi\cos\frac{1}{2}\eta + 2E_{x,x}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\} + i\cos\zeta\left\{[E_{x,x}(\boldsymbol{T}) + 3E_{y,y}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta - 2E_{x,x}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\}$

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$(x/y)_{11}$ $\sqrt{3}\,[E_{y,y}(\boldsymbol{R}) - E_{x,x}(\boldsymbol{R})] \sin\xi \sin\eta - 2\,i\,E_{x,y}(\boldsymbol{R})\,(2\sin\xi\cos\eta - \sin 2\xi)$

$(x/y)_{12}$ $\sqrt{3}\,[E_{x,x}(\boldsymbol{T}) - E_{y,y}(\boldsymbol{T})] \sin\xi\cos\zeta \left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$

$(x/z)_{12}$ $2\sqrt{3}\,E_{y,z}(\boldsymbol{T})\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta + i\sin\frac{1}{3}\eta\right)$

$(x/xy)_{11}$ $E_{x,xy}(0) + [E_{x,xy}(\boldsymbol{R}) + 3\,E_{y,x^2-y^2}(\boldsymbol{R})]\cos\xi\cos\eta + 2\,E_{x,xy}(\boldsymbol{R})\cos 2\xi +$
$\sqrt{3}\,i\,[E_{x,x^2-y^2}(\boldsymbol{R}) + E_{y,xy}(\boldsymbol{R})]\cos\xi\sin\eta$

$(x/xy)_{12}$ $\cos\zeta\left\{[E_{x,xy}(\boldsymbol{T}) + 3\,E_{y,x^2-y^2}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + 2\,E_{x,xy}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\} +$
$+\,i\cos\zeta\left\{[E_{x,xy}(\boldsymbol{T}) + 3\,E_{y,x^2-y^2}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta - 2\,E_{x,xy}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\}$

$(x/yz)_{12} = (y/xz)_{12}$ $\sqrt{3}\,[E_{x,xz}(\boldsymbol{T}) - E_{y,yz}(\boldsymbol{T})]\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta + i\sin\frac{1}{3}\eta\right)$

$(x/xz)_{12}$ $\sin\zeta\left\{-[E_{x,xz}(\boldsymbol{T}) + 3\,E_{y,yz}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta + 2\,E_{x,xz}(\boldsymbol{T})\sin\frac{2}{3}\right\}\eta +$
$+\,i\sin\zeta\left\{[E_{x,xz}(\boldsymbol{T}) + 3\,E_{y,yz}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + 2\,E_{x,xz}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\}$

$(x/x^2-y^2)_{11}$ $\sqrt{3}\,[E_{y,x^2-y^2}(\boldsymbol{R}) - E_{x,xy}(\boldsymbol{R})]\sin\xi\sin\eta - i\,\{[E_{x,x^2-y^2}(\boldsymbol{R}) -$
$-\,3\,E_{y,xy}(\boldsymbol{R})]\sin\xi\cos\eta - 2\,E_{x,x^2-y^2}(\boldsymbol{R})\sin 2\xi\}$

$(x/x^2-y^2)_{12}$
$= (y/xy)_{12}$ $\sqrt{3}\,[E_{x,xy}(\boldsymbol{T}) - E_{y,x^2}(\boldsymbol{T})]\sin\xi\cos\zeta\times\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$

$(x/3z^2-r^2)_{11}$ $-2\sqrt{3}\,E_{y,3z^2-r^2}(\boldsymbol{R})\sin\xi\sin\eta + 2\,i\,E_{x,3z^2-r^2}(\boldsymbol{R})\,(\sin\xi\cos\eta + \sin 2\xi)$

$(x/3z^2-r^2)_{12}$ $2\sqrt{3}\,E_{y,3z^2-r^2}(\boldsymbol{T})\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$

$(y/y)_{11}$ $E_{y,y}(0) + [E_{y,y}(\boldsymbol{R}) + 3\,E_{x,x}(\boldsymbol{R})]\cos\xi\cos\eta + 2\,E_{y,y}(\boldsymbol{R})\cos 2\xi$

$(y/y)_{12}$ $\cos\zeta\left\{[E_{y,y}(\boldsymbol{T}) + 3\,E_{x.x}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + 2\,E_{y,y}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\} +$
$+\,i\cos\zeta\left\{[E_{y,y}(\boldsymbol{T}) + 3\,E_{x,x}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta - 2\,E_{y,y}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\}$

$(y/z)_{12}$ $2\,E_{y,z}(\boldsymbol{T})\sin\zeta\left[\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right) -\right.$
$\left.-\,i\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right)\right]$

$(y/xy)_{11}$

$$\sqrt{3}\,[E_{y,x^2-y^2}(\boldsymbol{R}) - E_{x,xy}(\boldsymbol{R})]\sin\xi\sin\eta - i\{[E_{y,xy}(\boldsymbol{R}) - 3E_{x,x^2-y^2}(\boldsymbol{R})]\sin\xi\cos\eta - 2E_{y,xy}(\boldsymbol{R})\sin 2\xi\}$$

$(y/yz)_{12}$

$$\sin\zeta\left\{-[E_{y,yz}(\boldsymbol{T}) + 3E_{x,xz}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta + 2E_{y,yz}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\} + i\sin\zeta\left\{[E_{y,yz}(\boldsymbol{T}) + 3E_{x,xz}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + 2E_{y,yz}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\}$$

$(y/x^2-y^2)_{11}$

$$E_{y,x^2-y^2}(0) + [E_{y,x^2-y^2}(\boldsymbol{R}) + 3E_{x,xy}(\boldsymbol{R})]\cos\xi\cos\eta + 2E_{y,x^2-y^2}(\boldsymbol{R})\cos 2\xi - \sqrt{3}\,i\,[E_{x,x^2-y^2}(\boldsymbol{R}) + E_{y,xy}(\boldsymbol{R})]\cos\xi\sin\eta$$

$(y/x^2-y^2)_{12}$

$$\cos\zeta\left\{[E_{y,x^2-y^2}(\boldsymbol{T}) + 3E_{x,xy}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + 2E_{y,x^2-y^2}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\} + i\cos\zeta\left\{[E_{y,x^2-y^2}(\boldsymbol{T}) + 3E_{x,xy}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta - 2E_{y,x^2-y^2}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\}$$

$(y/3z^2-r^2)_{11}$

$$E_{y,3z^2-r^2}(0) - 2E_{y,3z^2-r^2}(\boldsymbol{R})(\cos\xi\cos\eta - \cos 2\xi) + 2\sqrt{3}\,i\,E_{x,3z^2-r^2}(\boldsymbol{R})\cos\xi\sin\eta$$

$(y/3z^2-r^2)_{12}$

$$-2E_{y,3z^2-r^2}(\boldsymbol{T})\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) + i\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right)\right]$$

$(z/z)_{11}$

$$E_{z,z}(0) + 2E_{z,z}(\boldsymbol{R})(2\cos\xi\cos\eta + \cos 2\xi)$$

$(z/z)_{12}$

$$2E_{z,z}(\boldsymbol{T})\cos\zeta\left[\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right) + i\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right)\right]$$

$(z/xy)_{12}$

$$2\sqrt{3}\,E_{z,x^2-y^2}(\boldsymbol{T})\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta + i\sin\frac{1}{3}\eta\right)$$

$(z/yz)_{11}$

$$E_{z,yz}(0) - 2E_{z,yz}(\boldsymbol{R})(\cos\xi\cos\eta - \cos 2\xi) + 2\sqrt{3}\,i\,E_{z,xz}(\boldsymbol{R})\cos\xi\sin\eta$$

$(z/yz)_{12}$

$$-2E_{z,yz}(\boldsymbol{T})\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) + i\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right)\right]$$

$(z/xz)_{11}$

$$-2\sqrt{3}\,E_{z,yz}(\boldsymbol{R})\sin\xi\sin\eta + 2\,i\,E_{z,xz}(\boldsymbol{R})\times(\sin\xi\cos\eta + \sin 2\xi)$$

$(z/xz)_{12}$

$$2\sqrt{3}\,E_{z,yz}(\boldsymbol{T})\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

$(z/x^2-y^2)_{12}$

$$2E_{z,x^2-y^2}(\boldsymbol{T})\sin\zeta\left[\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right) - i\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right)\right]$$

$(z/3z^2-r^2)_{12}$

$$-2E_{z,3z^2-y^2}(\boldsymbol{T})\sin\zeta\left[\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right) - i\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right)\right]$$

$(xy/xy)_{11}$ $\quad E_{xy,xy}(0) + [E_{xy,xy}(\boldsymbol{R}) + 3E_{x^2-y^2,x^2-y^2}(\boldsymbol{R})] \times \cos\xi\cos\eta + 2E_{xy,xy}(\boldsymbol{R})\cos 2\xi$

$(xy/xy)_{12}$

$$\cos\zeta\left\{[E_{xy,xy}(\boldsymbol{T}) + 3\,E_{x^2-y^2,x^2-y^2}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + \right.$$

$$\left. + 2\,E_{xy,xy}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\} +$$

$$+ i\cos\zeta\left\{[E_{xy,xy}(\boldsymbol{T}) + 3\,E_{x^2-y^2,x^2-y^2}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta - \right.$$

$$\left. - 2\,E_{xy,xy}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\}$$

$(xy/yz)_{12} = (xz/x^2-y^2)_{12}$

$$\sqrt{3}\,[E_{xy,xz}(\boldsymbol{T}) - E_{yz,x^2-y^2}(\boldsymbol{T})]\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta + i\sin\frac{1}{3}\eta\right)$$

$(xy/xz)_{12}$

$$\sin\zeta\left\{-[E_{xy,xz}(\boldsymbol{T}) + 3\,E_{yz,x^2-y^2}(\boldsymbol{T})]\cos\xi\sin\frac{1}{3}\eta + \right.$$

$$\left. + 2\,E_{xy,xz}(\boldsymbol{T})\sin\frac{2}{3}\eta\right\} +$$

$$+ i\sin\zeta\left\{[E_{xy,xz}(\boldsymbol{T}) + 3\,E_{yz,x^2-y^2}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + \right.$$

$$\left. + 2E_{xy,xz}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\}$$

$(xy/x^2-y^2)_{11}$

$$\sqrt{3}\,[E_{x^2-y^2,x^2-y^2}(\boldsymbol{R}) - E_{xy,xy}(\boldsymbol{R})]\sin\xi\sin\eta -$$

$$- 2\,i\,E_{xy,x^2-y^2}(\boldsymbol{R})\,(2\sin\xi\cos\eta - \sin 2\xi)$$

$(xy/x^2-y^2)_{12}$

$$\sqrt{3}\,[E_{xy,xy}(\boldsymbol{T}) - E_{x^2-y^2,x^2-y^2}(\boldsymbol{T})]\sin\xi\cos\zeta\,\times$$

$$\times\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

$(xy/3z^2-r^2)_{11}$

$$- 2\sqrt{3}\,E_{x^2-y^2,3z^2-r^2}(\boldsymbol{R})\sin\xi\sin\eta + 2\,i\,E_{xy,3z^2-r^2}(\boldsymbol{R})\,(\sin\xi\cos\eta + \sin 2\xi)$$

$(xy/3z^2-r^2)_{12}$

$$2\sqrt{3}\,E_{x^2-y^2,3z^2-r^2}(\boldsymbol{T})\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

$(yz/yz)_{11}$

$$E_{yz,yz}(0) + [E_{yz,yz}(\boldsymbol{R}) + 3E_{xz,xz}(\boldsymbol{R})]\cos\xi\cos\eta + 2E_{yz,yz}(\boldsymbol{R})\cos 2\xi$$

$(yz/yz)_{12}$

$$\cos\zeta\left\{[E_{yz,yz}(\boldsymbol{T}) + 3E_{xz,xz}(\boldsymbol{T})]\cos\xi\cos\frac{1}{3}\eta + \right.$$

$$\left. + 2E_{yz,yz}(\boldsymbol{T})\cos\frac{2}{3}\eta\right\} +$$

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$$+ i \cos\zeta \left\{ [E_{yz,yz}(\boldsymbol{T}) + 3E_{xz,xz}(\boldsymbol{T})] \cos\xi \sin\frac{1}{3}\eta - \right.$$

$$\left. - 2E_{yz,yz}(\boldsymbol{T}) \sin\frac{2}{3}\eta \right\}$$

$yz/xz)_{11}$

$$\sqrt{3}\,[E_{yz,yz}(\boldsymbol{R}) - E_{xz,xz}(\boldsymbol{R})] \sin\xi \sin\eta -$$

$$- 2\,i\,E_{yz,xz}(\boldsymbol{R})\,(2 \sin\xi \cos\eta - \sin 2\,\xi)$$

$(yz/xz)_{12}$

$$\sqrt{3}\,[E_{xz,xz}(\boldsymbol{T}) - E_{yz,yz}(\boldsymbol{T})] \sin\xi \cos\zeta \left(\sin\frac{1}{3}\eta - i \cos\frac{1}{3}\eta \right)$$

$(yz/x^2 - y^2)_{12}$

$$\sin\zeta \left\{ - [E_{yz,x^2-y^2}(\boldsymbol{T}) + 3E_{xy,xz}(\boldsymbol{T})] \cos\xi \sin\frac{1}{3}\eta + \right.$$

$$\left. + 2E_{yz,x^2-y^2}(\boldsymbol{T}) \sin\frac{2}{3} \right\} +$$

$$i \sin\zeta \left\{ [E_{yz,x^2-y^2}(\boldsymbol{T}) + 3E_{xy,xz}(\boldsymbol{T})] \cos\xi \cos\frac{1}{3}\eta + \right.$$

$$\left. + 2E_{yz,x^2-y^2}(\boldsymbol{T}) \cos\frac{2}{3}\eta \right\}$$

$(yz/3z^2 - r^2)_{12}$

$$2E_{yz,3z^2-r^2}(\boldsymbol{T}) \sin\zeta \left[\left(\cos\xi \sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta \right) - \right.$$

$$\left. - i \left(\cos\xi \cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta \right) \right]$$

$xz/xz)_{11}$

$$E_{xz,xz}(0) + [E_{xz,xz}(\boldsymbol{R}) + 3E_{yz,yz}(\boldsymbol{R})] \cos\xi \cos\eta + 2E_{xz,xz}(\boldsymbol{R}) \cos 2\,\xi$$

$(xz/xz)_{12}$

$$\cos\zeta \left\{ [E_{xz,xz}(\boldsymbol{T}) + 3E_{yz,yz}(\boldsymbol{T})] \cos\xi \cos\frac{1}{3}\eta + \right.$$

$$\left. + 2E_{xz,xz}(\boldsymbol{T}) \cos\frac{2}{3}\eta \right\} +$$

$$+ i \cos\zeta \left\{ [E_{xz,xz}(\boldsymbol{T}) + 3E_{yz,yz}(\boldsymbol{T})] \cos\xi \sin\frac{1}{3}\eta - \right.$$

$$\left. - 2E_{xz,xz}(\boldsymbol{T}) \sin\frac{2}{3}\eta \right\}$$

$xz/3z^2 - r^2)_{12}$

$$2\sqrt{3}\,E_{yz,3z^2-r^2}(\boldsymbol{T}) \sin\xi \sin\zeta \left(\cos\frac{1}{3}\eta + i \sin\frac{1}{3}\eta \right)$$

$(x^2 - y^2/x^2 - y^2)_{11}$

$$E_{x^2-y^2,x^2-y^2}(0) + [E_{x^2-y^2,x^2-y^2}(\boldsymbol{R}) + 3\,E_{xy,xy}(\boldsymbol{R})] \times$$

$$\times \cos\xi \cos\eta + 2\,E_{x^2-y^2,x^2-y^2}(\boldsymbol{R}) \cos 2\,\xi$$

$$(x^2 - y^2/x^2 - y^2)_{12} \quad \cos\zeta \left\{ [E_{x^2-y^2,x^2-y^2}(\boldsymbol{T}) + 3\,E_{xy,xy}(\boldsymbol{T})] \cos\xi \cos\frac{1}{3}\eta + \right.$$

$$\left. + 2\,E_{x^2-y^2,x^2-y^2}(\boldsymbol{T}) \cos\frac{2}{3}\eta \right\} +$$

$$+ i\cos\zeta \left\{ [E_{x^2-y^2,x^2-y^2}(\boldsymbol{T}) + 3\,E_{xy,xy}(\boldsymbol{T})] \cos\xi \sin\frac{1}{3}\eta - \right.$$

$$\left. - 2\,E_{x^2-y^2,x^2-y^2}(\boldsymbol{T}) \sin\frac{2}{3}\eta \right\}$$

$$(x^2 - y^2/3z^2 - r^2)_{11} \quad E_{x^2-y^2,3z^2-r^2}(0) - 2\,E_{x^2-y^2,3z^2-r^2}(\boldsymbol{R})\,(\cos\xi\cos\eta - \cos 2\xi) +$$

$$+ 2\sqrt{3}\,i\,E_{xy,3z^2-r^2}(\boldsymbol{R}) \cos\xi \sin\eta$$

$$(x^2 - y^2/3z^2 - r^2)_{12} \quad -2\,E_{x^2-y^2,3z^2-r^2}(\boldsymbol{T}) \cos\zeta \left[\left(\cos\xi \cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta \right) + \right.$$

$$\left. + i \left(\cos\xi \sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta \right) \right]$$

$$(3z^2 - r^2/3z^2 - r^2)_{11} \quad E_{3z^2-r^2,3z^2-r^2}(0) + 2\,E_{3z^2-r^2,3z^2-r^2}(\boldsymbol{R})\,(2\cos\zeta\cos\eta + \cos 3\xi)$$

$$(3z^2 - r^2/3z^2 - r^2)_{12} \quad 2\,E_{3z^2-r^2,3z^2-r^2}(\boldsymbol{T}) \cos\zeta \left[\left(2\cos\xi \cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta \right) + \right.$$

$$\left. + i \left(2\cos\xi \sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta \right) \right]$$

The E-integrals for $\boldsymbol{r}_l \neq 0$ can be written in the following form:

$$E_{m,n}(\boldsymbol{r}_l) = \int \varphi_m^\star(\boldsymbol{r})\, H\, \varphi_n(\boldsymbol{r} - \boldsymbol{r}_l)\, d\boldsymbol{r}$$

$$= \int \varphi_m^\star(\boldsymbol{r})\,[-\Delta + U(\boldsymbol{r}) + U(\boldsymbol{r} - \boldsymbol{r}_l)]\,\varphi_n(\boldsymbol{r} - \boldsymbol{r}_l)\, d\boldsymbol{r} +$$

$$+ \sum_{i \neq l,0} \int \varphi_m^\star(\boldsymbol{r})\, U(\boldsymbol{r} - \boldsymbol{r}_j)\, \varphi_n(\boldsymbol{r} - \boldsymbol{r}_l)\, d\boldsymbol{r} +$$

$$+ \sum_i \int \varphi_m^\star(\boldsymbol{r})\, U(\boldsymbol{r} - \boldsymbol{r}_j - \boldsymbol{t}_2)\, \varphi_n(\boldsymbol{r} - \boldsymbol{r}_l)\, d\boldsymbol{r},$$

in which the second and third term contain only three-center integrals. We now make the approximation of neglecting all three-center integrals. The E-integrals for $\boldsymbol{r} = 0$ in the two-center approximation can be written

$$E_{m,n}(0) = \int \varphi_m^\star(\boldsymbol{r})\,[-\Delta + U(\boldsymbol{r}) + \sum U(\boldsymbol{r} - \boldsymbol{r}_j) + \sum_j U(\boldsymbol{r} - \boldsymbol{r}^j - \boldsymbol{t}_2)]\,\varphi_n(\boldsymbol{r})\, d\boldsymbol{r},$$

where $\boldsymbol{r}_j$ and $\boldsymbol{r}_j + \boldsymbol{t}_2$ are here the position vectors of the 12 nearest neighbours.

Slater and Koster have given a table for the reduction of E-integrals to two-center integrals calculated for functions with σ-, π-, δ-symmetry. In the two-center

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approximation only 16 independent integrals remain: $s_0, p_0, d_0, d_1, d_2, (pd)_0, (ss\sigma)_1, (sp\sigma)_1, (sd\sigma)_1, (pp\sigma)_1, (pp\pi)_1, (pd\sigma)_1, (pd\pi)_1, (dd\sigma)_1, (dd\pi)_1, (dd\delta)_1$. Using Table I of Slater and Koster we must know only the directions cosines of the vectors $\boldsymbol{R}$ and $\boldsymbol{T}$. We have for $\boldsymbol{R}$: $l = 1$, $m = 0$, $n = 0$ and for $\boldsymbol{T}$: $l = 0$, $m = -\sqrt{3}/3$, $n = \sqrt{2/3}$

The E-integrals in terms of the two-center integrals are given in Table IV.

TABLE IV

$$E_{s,y}(O) = E_{s,x^2-y^2}(0) = E_{s,3z^2-r^2}(0) = E_{z,yz}(0) = E_{y,3z^2-r^2}(0) = E_{x^2-y^2,3z^2-r^2}(0) = 0$$

$$E_{s,y}(\boldsymbol{R}) = E_{s,xy}(\boldsymbol{R}) = E_{x,y}(\boldsymbol{R}) = E_{x,xy}(\boldsymbol{R}) = E_{y,x^2-y^2}(\boldsymbol{R}) = E_{y,3z^2-r^2}(\boldsymbol{R}) = E_{z,yz}(\boldsymbol{R})$$
$$= E_{xy,x^2-y^2}(\boldsymbol{R}) = E_{xy,3z^2-r^2}(\boldsymbol{R}) = E_{yz,xz}(\boldsymbol{R}) = 0$$

$$E_{s.s}(\boldsymbol{R}) = s_0$$

$$E_{x,x}(0) = E_{y,y}(0) = E_{z,z}(0) = p_0$$

$$E_{xy,xy}(0) = E_{x^2-y^2,x^2-y^2}(0) = d_0$$

$$E_{xz,xz}(0) = E_{yz,yz}(0) = d_1$$

$$E_{3z_3-r^2,3z^2-r^2}(0) = d_2$$

$$E_{x,xy}(0) = E_{y,x^2-y^2}(0) = (pd)_0$$

$$E_{s.s}(\boldsymbol{R}) = E_{s,s}(\boldsymbol{T}) = (ss\sigma)_1$$

$$E_{s,x}(\boldsymbol{R}) = -\sqrt{3}\,E_{s,y}(\mathbf{T}) = \sqrt{\frac{3}{2}}\,E_{s,z}(\boldsymbol{T}) = (sp\sigma)_1$$

$$E_{s,3z^2-r^2}(\boldsymbol{T}) = -E_{s,3z^2-r^2}(\boldsymbol{R}) = -\sqrt{3}\,E_{s,x^2-y^2}(\boldsymbol{T}) = \frac{1}{3}\sqrt{3}\,E_{s,x^2-y^2}(\boldsymbol{R}) =$$
$$= -\frac{1}{2}\sqrt{\frac{3}{2}}\,E_{s,yz}(\boldsymbol{T}) = \frac{1}{2}(sd\sigma)_1$$

$$E_{x,x}(\boldsymbol{R}) = (pp\sigma)_1$$

$$E_{x,x}(\boldsymbol{T}) = E_{y,y}(\boldsymbol{R}) = E_{z,z}(\mathbf{R}) = (pp\pi)_1$$

$$E_{y,y}(\boldsymbol{T}) = \frac{1}{3}(pp\sigma)_1 + \frac{2}{3}(pp\pi)_1$$

$$E_{z,z}(\boldsymbol{T}) = \frac{2}{3}(pp\sigma)_1 + \frac{1}{3}(pp\pi)_1$$

$$E_{y,z}(\boldsymbol{T}) = -\frac{1}{3}\sqrt{2}\,(pp\sigma)_1 + \frac{1}{3}\sqrt{2}\,(pp\pi)_1$$

$$E_{z,xz}(\boldsymbol{R}) = -\sqrt{3}\,E_{x,xy}(\boldsymbol{T}) = \sqrt{\frac{3}{2}}\,E_{x,xz}(\boldsymbol{T}) = E_{y,xy}(\boldsymbol{R}) = (pd\pi)_1$$

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$$E_{x,3z^2-r^2}(\boldsymbol{R}) = -\frac{1}{3}\sqrt{3}\,E_{x,x^2-y^2}(\boldsymbol{R}) = -\frac{1}{2}(pd\sigma)_1$$

$$E_{y,yz}(\boldsymbol{T}) = \frac{1}{3}\sqrt{2}\,(pd\sigma)_1 + \frac{1}{3}\sqrt{\frac{2}{3}}\,(pd\pi)_1$$

$$E_{y,x^2-y^2}(\boldsymbol{T}) = \frac{1}{6}(pd\sigma)_1 + \frac{2}{9}\sqrt{3}\,(pd\pi)_1$$

$$E_{y,3z^2-r^2}(\boldsymbol{T}) = -\frac{1}{6}\sqrt{3}\,(pd\sigma)_1 + \frac{2}{3}(pd\pi)_1$$

$$E_{z,yz}(\boldsymbol{T}) = -\frac{2}{3}(pd\sigma)_1 + \frac{1}{9}\sqrt{3}\,(pd\pi)_1$$

$$E_{z,x^2-y^2}(\boldsymbol{T}) = -\frac{1}{6}\sqrt{2}\,(pd\sigma)_1 + \frac{1}{3}\sqrt{\frac{2}{3}}\,(pd\pi)_1$$

$$E_{z,3z^2-r^2}(\boldsymbol{T}) = \frac{1}{2}\sqrt{\frac{2}{3}}\,(pd\sigma)_1 + \frac{1}{3}\sqrt{2}\,(pd\pi)_1$$

$$E_{xy,xy}(\boldsymbol{R}) = E_{xz,xz}(\boldsymbol{R}) = (dd\pi)_1$$

$$E_{yz,yz}(\boldsymbol{R}) = (dd\delta)_1$$

$$E_{xy,xy}(\boldsymbol{T}) = \frac{1}{3}(dd\pi)_1 + \frac{2}{3}(dd\delta)_1$$

$$E_{xz,xz}(\boldsymbol{T}) = \frac{2}{3}(dd\pi)_1 + \frac{1}{3}(dd\delta)_1$$

$$E_{yz,yz}(\boldsymbol{T}) = \frac{2}{3}(dd\sigma)_1 + \frac{1}{9}(dd\pi)_1 + \frac{2}{9}(dd\delta)_1$$

$$E_{x^2-y^2,x^2-y^2}(\boldsymbol{R}) = \frac{3}{4}(dd\sigma)_1 + \frac{1}{4}(dd\delta)_1$$

$$E_{x^2-y^2,x^2-y^2}(\boldsymbol{T}) = \frac{1}{12}(dd\sigma)_1 + \frac{2}{9}(dd\pi)_1 + \frac{25}{36}(dd\delta)_1$$

$$E_{3z^2-r^2,3z^2-r^2}(\boldsymbol{R}) = \frac{1}{4}(dd\sigma)_1 + \frac{3}{4}(dd\delta)_1$$

$$E_{3z^2-r^2,3z^2-r^2}(\boldsymbol{T}) = \frac{1}{4}(dd\sigma)_1 + \frac{2}{3}(dd\pi)_{21} + \frac{1}{12}(dd\delta)_1$$

$$E_{xy,xz}(\boldsymbol{T}) = -\frac{1}{3}\sqrt{2}\,(dd\pi)_1 + \frac{1}{3}\sqrt{2}\,(dd\delta)_1$$

$$E_{yz,x^2-y^2}(\boldsymbol{T}) = \frac{1}{6}\sqrt{2}\,(dd\sigma)_1 + \frac{1}{9}\sqrt{2}\,(dd\pi)_1 - \frac{5}{18}\sqrt{2}\,(dd\delta)_1$$

$$E_{yz,3z^2-r^2}(\boldsymbol{T}) = -\frac{1}{2}\sqrt{\frac{2}{3}}\,(dd\sigma)_1 + \frac{1}{3}\sqrt{\frac{2}{3}}\,(dd\pi)_1 + \frac{1}{6}\sqrt{\frac{2}{3}}\,(dd\delta)_1$$

$$E_{x^2-y^2,3z^2-r^2}(\boldsymbol{R}) = -\frac{1}{4}\sqrt{3}\,(dd\sigma)_1 = \frac{1}{4}\sqrt{3}\,(dd\delta)_1$$

$$E_{x^2-y^2,3z^2-r^2}(\boldsymbol{T}) = -\frac{1}{12}\sqrt{3}\,(dd\sigma)_1 + \frac{2}{9}\sqrt{3}\,(dd\pi)_1 - \frac{5}{56}\sqrt{3}\,(dd\delta)_1$$

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The table given by Slater and Koster simplifies also considerably the calculations of the overlap integrals:

$$\int \varphi_m^{\star}(\boldsymbol{r}-\boldsymbol{r}_i)\,\varphi_n(\boldsymbol{r}-\boldsymbol{r}_j)\,d\boldsymbol{r}.$$

We summarize finally in Tably V the matrix components of energy in the two-center approximation.

TABLE V

$(s/s)_{11}$	$s_0 + 2(ss\sigma)_1\,(2\cos\xi\cos\eta + \cos 2\xi)$
$(s/s)_{12}$	$2(ss\sigma)_1\cos\zeta\left[\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right) + i\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right)\right]$
$(s/x)_{11}$	$2\,i\,(sp\sigma)_1\,(\sin\xi\cos\eta + \sin 2\xi)$
$(s/x)_{12}$	$-2\,(sp\sigma)_1\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$
$(s/y)_{11}$	$2\sqrt{3}\,i\,(sp\sigma)_1\cos\xi\sin\eta$
$(s/y)_{12}$	$\frac{2}{3}\sqrt{3}\,(sp\sigma)_1\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) + i\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right)\right]$
$(s/z)_{12}$	$-2\sqrt{\frac{2}{3}}\,(sp\sigma)_1\sin\zeta\left[\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right) - i\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right)\right]$
$(s/xy)_{11}$	$-3\,(sd\sigma)_1\sin\xi\sin\eta$
$(s/xy)_{12}$	$-(sd\sigma)_1\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$

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$(s/yz)_{12}$

$$-2\sqrt{\frac{2}{3}}\,(sd\sigma)_1\,\sin\zeta\left[\left(\cos\xi\sin\frac{1}{3}\eta+\sin\frac{2}{3}\eta\right)-\right.$$
$$\left.-\,i\left(\cos\xi\cos\frac{1}{3}\eta-\cos\frac{2}{3}\eta\right)\right]$$

$(s/xz)_{12}$

$$-\,2\sqrt{2}\,(sd\sigma)_1\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta+i\sin\frac{1}{3}\eta\right)$$

$(s/x^2-y^2)_{11}$

$$-\sqrt{3}\,(sd\sigma)_2\,(\cos\xi\cos\eta-\cos 2\,\xi)$$

$(s/x^2-y^2)_{12}$

$$\frac{1}{3}\sqrt{3}\,(sd\sigma)_1\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta-\cos\frac{2}{3}\eta\right)+\right.$$
$$\left.+\,i\left(\cos\xi\sin\frac{1}{3}\eta+\sin\frac{2}{3}\eta\right)\right]$$

$(s/3z^2-r^2)_{11}$

$$-\,(sd\sigma)_1\,(2\cos\xi\cos\eta+\cos 2\,\xi)$$

$(s/3z^2-r^2)_{12}$

$$(sd\sigma)_1\cos\zeta\left[\left(2\cos\xi\cos\frac{1}{3}\eta+\cos\frac{2}{3}\eta\right)+\right.$$
$$\left.+\,i\left(2\cos\xi\sin\frac{1}{3}\eta-\sin\frac{2}{3}\eta\right)\right]$$

$(x/x)_{11}$

$$p_0+[(pp\sigma)_1+3\,(pp\pi)_1]\cos\xi\cos\eta+2\,(pp\,\sigma)_1\cos 2\,\xi$$

$(x/x)_{12}$

$$\cos\zeta\left\{[(pp\sigma)_1+3\,(pp\pi)_1]\cos\xi\cos\frac{1}{3}\eta+2\,(pp\,\pi)_1\cos\frac{2}{3}\eta\right\}+$$
$$+\,i\cos\zeta\left\{[(pp\sigma)_1+3\,(pp\pi)_1]\cos\xi\sin\frac{1}{3}\eta-2\,(pp\,\pi)_1\sin\frac{2}{3}\eta\right\}$$

$(x/y)_{11}$

$$-\sqrt{3}\,[(pp\sigma)_1-(pp\pi)_1]\sin\xi\sin\eta$$

$(x/y)_{12}$

$$-\frac{1}{3}\sqrt{3}\,[(pp\sigma)_1-(pp\pi)_1]\,\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta-i\cos\frac{1}{3}\eta\right)$$

$(x/z)_{12}$

$$-2\sqrt{\frac{2}{3}}\,[(pp\sigma)_1-(pp\pi)_1]\,\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta+i\sin\frac{1}{3}\eta\right)$$

$(x/xy)_{11}$

$$(pd)_0+i\left[\frac{2}{3}\,(pd\sigma)_1+\sqrt{3}\,(pd\pi)_1\right]\cos\xi\sin\eta$$

$(x/xy)_{12}$

$$\cos\zeta\left\{\left[\frac{1}{2}\,(pd\sigma)_1+\frac{1}{3}\sqrt{3}\,(pd\pi)_1\right]\cos\xi\cos\frac{1}{3}\eta-\right.$$
$$\left.-\,\frac{2}{3}\sqrt{3}\,(pd\pi)_1\cos\frac{2}{3}\eta\right\}+$$
$$+\,i\cos\zeta\left\{\left[\frac{1}{2}\,(pd\sigma)_1+\frac{1}{3}\sqrt{3}\,(pd\pi)_1\right]\cos\xi\sin\frac{1}{3}\eta+\right.$$
$$\left.+\,\frac{2}{3}\sqrt{3}\,(pd\pi)_1\,\sin\frac{2}{3}\eta\right\}$$

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$(x/yz)_{12} = (y/xz)_{12} = (z/xy)_{12}$	$-\left[\sqrt{\frac{2}{3}}\,(pd\sigma)_1 - \frac{2}{3}\sqrt{2}\,(pd\pi)_1\right]\sin\xi\sin\zeta\left(\cos\frac{1}{3}\eta + i\sin\frac{1}{3}\eta\right)$
$(x/xz)_{12}$	$\sin\zeta\left\{-\left[\sqrt{2}\,(pd\sigma)_1 + 2\sqrt{\frac{2}{3}}\,(pd\pi)_1\right]\cos\xi\sin\frac{1}{3}\eta + 2\sqrt{\frac{2}{3}}\,(pd\pi)_1\sin\frac{2}{3}\eta\right\} + i\sin\zeta\left\{\left[\sqrt{2}\,(pd\sigma)_1 + 2\sqrt{\frac{2}{3}}\,(pd\pi)_1\right]\cos\xi\cos\frac{1}{3}\eta + 2\sqrt{\frac{2}{3}}\,(pd\pi)_1\cos\frac{2}{3}\eta\right\}$
$(x/x^2-y^2)_{11}$	$i\left\{-\left[\frac{1}{2}\sqrt{3}\,(pd\sigma)_1 - 3\,(pd\pi)_1\right]\sin\xi\cos\eta + \sqrt{3}\,(pd\sigma)_1\sin 2\xi\right\}$
$(x/x^2-y^2)_{12} = (y/xy)_{12}$	$-\frac{1}{3}\left[\frac{1}{2}\sqrt{3}\,(pd\sigma)_1 + 5\,(pd\pi)_1\right]\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$
$(x/3z^2-r^2)_{11}$	$-i\,(pd\sigma)_1\,(\sin\xi\cos\eta + \sin 2\xi)$
$(x/3z^2-r^2)_{12}$	$-\left[(pd\sigma)_1 - \frac{4}{3}\sqrt{3}\,(pd\pi)_1\right]\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$
$(y/y)_{11}$	$p_0 + [3\,(pp\sigma)_1 + (pp\pi)_1]\cos\xi\cos\eta + 2\,(pp\pi)_1\cos 2\xi$
$(y/y)_{12}$	$\frac{1}{3}\cos\zeta\left\{[(pp\sigma)_1 + 11\,(pp\pi)_1]\cos\xi\cos\frac{1}{3}\eta + 2\,[(pp\sigma)_1 + 2\,(pp\pi)_1]\cos\frac{2}{3}\eta\right\} + \frac{1}{3}\,i\cos\zeta\left\{[(pp\sigma)_1 + 11\,(pp\pi)_1]\cos\xi\sin\frac{1}{3}\eta - 2\,[(pp\sigma)_1 + 2\,(pp\pi)_1]\sin\frac{2}{3}\eta\right\}$
$(y/z)_{12}$	$-\frac{2}{3}\sqrt{2}\,[(pp\sigma)_1 - (pp\pi)_1]\sin\zeta\left[\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right) - i\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{1}{3}\eta\right)\right]$
$(y/xy)_{11}$	$i\left\{\left[\frac{3}{2}\sqrt{3}\,(pd\sigma)_1 - (pd\pi)_1\right]\sin\xi\cos\eta + 2\,(pd\pi)_1\sin 2\xi\right\}$
$(y/yz)_{12}$	$\frac{1}{3}\sin\zeta\left\{-\left[\sqrt{2}\,(pd\sigma)_1 + 10\sqrt{\frac{2}{3}}\,(pd\pi)_1\right]\cos\xi\sin\frac{1}{3}\eta +\right.$

$$+ 2\left[\sqrt{2}\,(pd\sigma)_1 + \sqrt{\frac{2}{3}}\,(pd\pi)_1\right]\sin\frac{2}{3}\eta\Big\} +$$

$$+\frac{1}{3}\,i\sin\zeta\left\{\left[\sqrt{2}\,(pd\sigma)_1 + 10\sqrt{\frac{2}{3}}\,(pd\,\pi)_1\right]\cos\xi\cos\frac{1}{3}\eta +\right.$$

$$\left.+ 2\left[\sqrt{2}\,(pd\sigma)_1 + \frac{2}{3}\,(pd\pi)_1\right]\cos\frac{2}{3}\eta\right\}$$

$(y/x^2 - y^2)_{11}$

$$(pd)_0 - i\left[\frac{3}{2}\,(pd\sigma)_1 + \sqrt{3}\;pd\pi)_1\right]\cos\xi\sin\eta$$

$(y/x^2 - y^2)_{12}$

$$\frac{1}{3}\cos\zeta\left\{\left[\frac{1}{2}\,(pd\sigma)_1 - \frac{7}{3}\sqrt{3}\,(pd\pi)_1\right]\cos\xi\cos\frac{1}{3}\eta +\right.$$

$$\left.+\; 2\left[\frac{1}{2}\,(pd\sigma)_1 + \frac{2}{3}\sqrt{3}\,(pd\pi)_1\right]\cos\frac{2}{3}\eta\right\} +$$

$$+\;\frac{1}{3}\,i\cos\zeta\left\{\left[\frac{1}{2}\,(pd\sigma)_1 - \frac{7}{3}\sqrt{3}\,(pd\pi)_1\right]\cos\xi\sin\frac{1}{3}\eta -\right.$$

$$\left.-\; 2\left[\frac{1}{2}\,(pd\sigma)_1 + \frac{2}{3}\sqrt{3}\,(pd\pi)_1\right]\sin\frac{2}{3}\eta\right\}$$

$(y/3z^2 - r^2)_{11}$

$$-\sqrt{3}\,i\,(pd\sigma)_2\cos\xi\sin\eta$$

$(y/3z^2 - r^2)_{12}$

$$\frac{1}{3}\left[\sqrt{3}\,(pd\,\sigma)_1 - 4\,(pd\,\pi)_1\right]\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) +\right.$$

$$\left.+\; i\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right)\right]$$

$(z/z)_{11}$

$$p_0 + 2\,(pp\,\pi)_1\,(2\cos\xi\cos\eta + \cos 2\,\xi)$$

$(z/z)_{12}$

$$\frac{2}{3}\left[2\,(pp\,\sigma)_2 + (pp\,\pi)_1\right]\cos\zeta\left[\left(2\cos\xi\cos\frac{1}{3}\eta + \cos\frac{2}{3}\eta\right) +\right.$$

$$\left.+\; i\left(2\cos\xi\sin\frac{1}{3}\eta - \sin\frac{2}{3}\eta\right)\right].$$

$(z/yz)_{11}$

$$2\sqrt{3}\,i\,(pd\pi)_1\cos\xi\sin\eta$$

$(z/yz)_{12}$

$$\frac{2}{3}\left[2\,(pd\sigma)_1 - \frac{1}{3}\sqrt{3}\,(pd\pi)_1\right]\cos\zeta\left[\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right) +\right.$$

$$\left.+\; i\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right)\right]$$

$(z/xz)_{11}$

$$2\,i\,(pd\pi)_1\,(\sin\xi\cos\eta + \sin 2\,\xi)$$

$(z/xz)_{12}$

$$-\frac{2}{3}\left[2\sqrt{3}\,(pd\sigma)_1 - (pd\pi)_1\right]\sin\xi\cos\zeta\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

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$(z/x^2-y^2)_{12}$
$$-\frac{1}{3}\left[\sqrt{2}\,(pd\sigma)_1-2\sqrt{\frac{2}{3}}\,(pd\pi)_1\right]\sin\zeta\left[\left(\cos\xi\sin\frac{1}{3}\eta+\sin\frac{2}{3}\eta\right)-\right.$$
$$\left.-i\left((\cos\xi\cos\frac{1}{3}\eta-\cos\frac{2}{3}\eta\right)\right]$$

$(z/3z^2-r^2)_{12}$
$$-\left[\sqrt{\frac{2}{3}}\,(pd\sigma)_1+\frac{2}{3}\sqrt{2}\,(pd\pi)_1\right]\sin\zeta\left[\left(2\cos\xi\sin\frac{1}{3}\eta+\sin\frac{2}{3}\eta\right)-\right.$$
$$\left.-i\left(2\cos\xi\cos\frac{1}{3}\eta+\cos\frac{2}{3}\eta\right)\right]$$

$(xy/xy)_{11}$
$$d_0+\left[\frac{9}{4}(dd\sigma)_1+(dd\pi)_1+\frac{3}{4}(dd\delta)_1\right]\cos\xi\cos\eta+2\,(dd\pi)_1\cos 2\xi$$

$(xy/xy)_{12}$
$$\cos\zeta\left\{\frac{1}{4}\left[(dd\sigma)_1+4\,(dd\pi)_1+11\,(dd\delta)_1\right]\cos\xi\cos\frac{1}{3}\eta+\right.$$
$$\left.+\frac{2}{3}\left[(dd\pi)_1+2\,(dd\delta)_1\right]\cos\frac{2}{3}\eta\right\}+$$
$$+i\cos\zeta\left\{\frac{1}{4}\left[(dd\sigma)_1+4\,(dd\pi)_1+11\,(dd\delta)_1\right]\cos\xi\sin\frac{1}{3}\eta-\right.$$
$$\left.-\frac{2}{3}\left[(dd\pi)_1+2\,(dd\delta)_1\right]\sin\frac{2}{3}\eta\right\}$$

$(xy/yz)_{12}$
$=(xz/x^2-y^2)_{12}$
$$-\sqrt{\frac{2}{3}}\left[\frac{1}{2}(dd\sigma)_1+\frac{4}{3}(dd\pi)_1-\frac{11}{6}(dd\delta)_1\right]\sin\xi\sin\zeta\times$$
$$\times\left(\cos\frac{1}{3}\eta+i\sin\frac{1}{3}\eta\right)$$

$(xy/xz)_{12}$
$$-\sqrt{2}\sin\zeta\left\{\frac{1}{2}\left[(dd\sigma)_1-(dd\delta)_1\right]\cos\xi\sin\frac{1}{3}\eta+\right.$$
$$\left.+\frac{2}{3}\left[(dd\pi)_1-(dd\delta)_1\right]\sin\frac{2}{3}\eta\right\}+$$
$$+\sqrt{2}\,i\sin\zeta\left\{\frac{1}{2}\left[(dd\sigma)_1-(dd\delta)_1\right]\cos\xi\cos\frac{1}{3}\eta-\right.$$
$$\left.-\frac{2}{3}\left[(dd\pi)_1-(dd\delta)_1\right]\cos\frac{2}{3}\eta\right\}$$

$(xy/x^2-y^2)_{11}$
$$\frac{1}{4}\sqrt{3}\left[3\,(dd\sigma)_1-4\,(dd\pi)_1+(dd\delta)_1\right]\sin\xi\sin\eta$$

$(xy/x^2-y^2)_{12}$
$$-\frac{1}{3}\sqrt{3}\left[\frac{1}{4}(dd\sigma)_1-\frac{1}{3}(dd\pi)_1+\frac{1}{12}(dd\delta)_1\right]\sin\xi\cos\zeta\times$$
$$\times\left(\sin\frac{1}{3}\eta-i\cos\frac{1}{3}\eta\right)$$

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$(xy/3z^2 - r^2)_{11}$

$$\frac{3}{2}\left[(dd\sigma)_1 - (dd\delta)_1\right] \sin\xi \sin\eta$$

$(xy/3z^2 - r^2)_{12}$

$$-\left[\frac{1}{2}(dd\sigma)_1 - \frac{4}{3}(dd\pi)_1 + \frac{5}{6}(dd\delta)_1\right] \sin\xi \cos\zeta \times$$
$$\times\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

$(yz/yz)_{11}$

$$d_1 + \left[3\,(dd\pi)_1 + (dd\delta)_1\right]\cos\xi\cos\eta + 2\,(dd\delta)_1\cos 2\xi$$

$(yz/yz)_{12}$

$$\frac{1}{3}\cos\zeta\left\{\left[2\,(dd\sigma)_1 + \frac{19}{3}(dd\pi)_1 + \frac{11}{3}(dd\delta)_1\right]\cos\xi\cos\frac{1}{3}\eta +\right.$$
$$\left.+\,2\left[2\,(dd\sigma)_1 + \frac{1}{3}(dd\pi)_1 + \frac{2}{3}(dd\delta)_1\right]\cos\frac{2}{3}\eta\right\} +$$
$$+\frac{1}{3}\,i\cos\zeta\left\{\left[2\,(dd\sigma)_1 + \frac{19}{3}(dd\pi)_1 + \frac{11}{3}(dd\sigma)_1\right]\times\cos\xi\,\sin\frac{1}{3}\eta -\right.$$
$$\left.-\,2\left[2\,(dd\sigma)_1 + \frac{1}{3}(dd\pi)_1 + \frac{2}{3}(dd\delta)_1\right]\sin\frac{2}{3}\eta\right\}$$

$(yz/xz)_{11}$

$$-\sqrt{3}\left[(dd\pi)_1 - (dd\delta)_1\right]\sin\xi\sin\eta$$

$(yz/xz)_{12}$

$$-\frac{1}{3}\sqrt{3}\left[2\,(dd\sigma)_1 - \frac{5}{3}(dd\pi)_1 - \frac{1}{3}(dd\delta)_1\right]\sin\xi\cos\zeta\times$$
$$\times\left(\sin\frac{1}{3}\eta - i\cos\frac{1}{3}\eta\right)$$

$(yz/x^2 - y^2)_{12}$

$$-\frac{1}{3}\sqrt{2}\sin\zeta\left\{\left[\frac{1}{2}(dd\sigma)_1 - \frac{8}{3}(dd\pi)_1 + \frac{13}{6}(dd\delta)_1\right]\cos\xi\sin\frac{1}{3}\eta -\right.$$
$$\left.-\left[(dd\sigma)_1 + \frac{2}{3}(dd\pi)_1 - \frac{5}{3}(dd\delta)_1\right]\sin\frac{2}{3}\eta\right] +$$
$$+\frac{1}{3}\sqrt{2}\,i\sin\zeta\left\{\left[\frac{1}{2}(dd\sigma)_1 - \frac{8}{3}(dd\pi)_1 + \frac{13}{6}(dd\delta)_1\right]\cos\xi\cos\frac{1}{3}\eta +\right.$$
$$\left.+\left[(dd\sigma)_1 + \frac{2}{3}(dd\pi)_1 - \frac{5}{3}(dd\delta)_1\right]\cos\frac{2}{3}\eta\right\}$$

$(yz/3z - r^2)_{12}$

$$-2\sqrt{\frac{2}{3}}\left[\frac{1}{2}(dd\sigma)_1 - \frac{1}{3}(dd\pi)_1 - \frac{1}{6}(dd\delta)_1\right]\sin\zeta\times$$
$$\times\left[\left(\cos\xi\sin\frac{1}{3}\eta + \sin\frac{2}{3}\eta\right) + i\left(\cos\xi\cos\frac{1}{3}\eta - \cos\frac{2}{3}\eta\right)\right]$$

$(xz/xz)_{11}$

$$d_1 + \left[(dd\pi)_1 + 3\,(dd\delta)_1\right]\cos\xi\cos\eta + 2\,(dd\,\pi)_1\cos 2\xi$$

$(xz/xz)_{12}$

$$\cos\zeta\left\{[2(dd\sigma)_1+(dd\pi)_1+(dd\delta)_1]\cos\xi\cos\frac{1}{3}\eta+\frac{2}{3}[2(dd\pi)_1+(dd\delta)_1]\cos\frac{2}{3}\eta\right\}+$$
$$+i\cos\zeta\left\{[2(dd\sigma)_1+(dd\pi)_1+(dd\delta)_1]\cos\xi\sin\frac{1}{3}\eta-\frac{2}{3}[2(dd\pi)_1+(dd\delta)_1]\sin\frac{2}{3}\eta\right\}$$

$(xz/3z^2-r^2)_{12}$

$$-2\sqrt{2}\left[\frac{1}{2}(dd\sigma)_1-\frac{1}{3}(dd\pi)_1-\frac{1}{6}(dd\delta)_1\right]\sin\xi\sin\zeta\times\left(\cos\frac{1}{3}\eta+i\sin\frac{1}{3}\eta\right)$$

$(x^2-y^2/x^2-y^2)_{11}$

$$d_\delta+\left[\frac{3}{4}(dd\sigma)_1+3(dd\pi)_1+\frac{1}{4}(dd\delta)_1\right]\cos\xi\cos\eta+\frac{1}{2}[3(dd\sigma)_1+(dd\delta)_1]\cos 2\xi$$

$(x^2-y^2/x^2-y^2)_{12}$

$$\frac{1}{3}\cos\zeta\left\{\left[\frac{1}{4}(dd\delta)_1+\frac{11}{3}(dd\pi)_1+\frac{97}{12}(dd\delta)_1\right]\cos\xi\cos\frac{1}{3}\eta+2\left[\frac{1}{4}(dd\sigma)_1+\frac{2}{3}(dd\pi)_1+\frac{25}{12}(dd\delta)_1\right]\cos\frac{2}{3}\eta\right\}+$$
$$+\frac{1}{3}i\cos\zeta\left\{\left[\frac{1}{4}(dd\sigma)_1+\frac{11}{13}(dd\pi)_1+\frac{97}{12}(dd\delta)_1\right]\times\cos\xi\sin\frac{1}{3}\eta-2\left[\frac{1}{4}(dd\sigma)_1+\frac{2}{3}(dd\pi)_1+\frac{25}{12}(dd\delta)_1\right]\sin\frac{2}{3}\eta\right\}$$

$(x^2-y^2/3z^2-r^2)_{11}$

$$\frac{1}{2}\sqrt{3}\,][(dd\sigma)_1-(dd\delta)_1](\cos\xi\cos\eta-\cos 2\xi)$$

$(x^2-y^2/3z^2-r^2)_{12}$

$$\frac{2}{3}\sqrt{3}\left[\frac{1}{4}(dd\sigma)_1-\frac{2}{3}(dd\pi)_1+\frac{5}{12}(dd\delta)_1\right]\cos\zeta\times\left[\left(\cos\xi\cos\frac{1}{3}\eta-\cos\frac{2}{3}\eta\right)+i\left(\cos\xi\sin\frac{1}{3}\eta+\sin\frac{2}{3}\eta\right)\right]$$

$(3z^2-r^2/3z^2-r^2)_{11}$

$$d_2+\frac{1}{2}[(dd\sigma)_1+3(dd\delta)_1](2\cos\xi\cos\eta+\cos 2\xi)$$

$(3z^2-r^2/3z^2-r^2)_{12}$

$$\left[\frac{1}{2}(dd\sigma)_1+\frac{4}{3}(dd\pi)_1+\frac{1}{6}(dd\delta)_1\right]\cos\zeta\times\left[\left(2\cos\xi\cos\frac{1}{3}\eta+\cos\frac{2}{3}\eta\right)+i\left(2\cos\zeta\sin\frac{1}{3}\eta-\sin\frac{2}{3}\eta\right)\right]$$

It should hardly be emphasized that all the above tables can be also used for the reduction of general overlap integrals of Bloch sums.

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КРАТКОЕ СОДЕРЖАНИЕ

М. Мьонсек, *Применение метода тесной связи для исследования своиств симметрии энергетических полос в компактной гексагональной структуре*.

В работе высчитано элементы матриц энергии сперва при применении интегралов трицентровых а после при приближении двуцентровом. В расчетах было принято во внимание только первых соседей сетки.

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