BSc Thesis Applied Mathematics & Physics

Slater-Koster energy integrals of simple and facecentered cubic crystals

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Abstract

Electronic band structures are the primary component used to calculate electrical, optical and even magnetic properties of crystals. For this reason physicists, chemists, and material scientists want to develop methods to accurately compute these band structures. Accurate calculations will help directly in for example the development of more efficient solar cells. Several of these methods exist, for example Density Functional Theory (DFT) or the GW-approach. The downside of these methods are that although very accurate they are often too computationally expensive or require too much working memory. This thesis investigates an alternative method, first proposed by J.C. Slater and G.F. Koster in 1954, a variation on the method called the LCAO or tight binding method. Energy contributions of electrons beyond a certain distance from the origin are neglected by assuming these are sufficient tightly bound to their nucleus. We will derive the energy contributions or matrix elements for s, p and d orbitals on a simple cubic and FCC lattice. These formulas contain several integrals, which we cannot solve without reverting back to DFT or GW calculations. These formulas can still be used however, using the integrals as fitting parameters to fit to bandstructure data from DFT or GW calculations. The method proposed in this thesis, and by Slater & Koster therefore functions as an interpolation method for more expensive and accurate calculations. This reduces the computational complexity of these algorithms.

Contents

1 Introduction

We make use of materials every day. From the polymer in our phone cases to the concrete that we use to build our buildings. As our society becomes more technologically advanced, the demand for complex materials with incrementally better material properties increases. In 1866, by mixing two substances, a chemist discovered a highly unstable compound. By mixing these substances, dynamite was discovered[4]. This approach to material science was the main method used until the end of the 19th century. But the time for guessing has readily passed. In the modern era we do not simply want a strong material, we want the strongest. We do not want light materials (low density), we want the lightest. This is why physicists have been tasked to develop more and more accurate and complex models to improve our understanding of these solid materials. By merging ideas from Electrodynamics, Statistical Physics, Quantum Physics, Classical Mechanics, Chemistry and many other fields of study we have obtained an accurate description of the microscopic and macroscopic properties of materials. This branch of study is called "condensed matter" or "solid state" physics. One of the material properties currently receiving a lot of attention are optical properties; how does light get absorbed or reflected by materials. Optical properties have obvious applications in calculating the efficiency of solar panel materials and therefore requires a lot of research. We already have accurate theories that determine optical properties from other material properties [11], but these theories have their limitations. The main limitations of these theories are that they all rely on a material property called the **band structure**. In layman's terms the band structure describes the allowed energy values an electron in a material's crystal is allowed to have. This band structure can be calculated by means of a branch of electronic structure theory called Density Functional Theory. "Density functional theory is a successful branch of numerical simulations of quantum systems. While the foundations are rigorously defined, it uses an universal functional that must be approximated. The search for improved functionals has resulted in hundreds of different functionals, remaining an active research area."[3] A downside to DFT is its computational complexity as well as its memory intensivity, scaling rapidly as the number of electrons in the simulation increases. DFT's computational complexity scales so rapidly with the number of electrons, that when calculating full band structures of materials the simulation can take several hours to compute. When doing DFT calculations, it is faster to only calculate the band structure in a few points instead of computing the whole graph. A question is how to connect these points. One naive approach would be to just draw a line between each of the points, but this is not physically accurate if we lack a large number of points. This thesis attempts to derive a method to connect the dots that is both physically accurate, as well as computationally cheap. We are going to rely on an approximate method called the LCAO or tight binding method. The tight binding method takes only electronic contributions into consideration of a limited set of electrons, making it an approximate method. The tight binding method yields parametric formulas that can be used to fit to DFT data, speeding up DFT calculations considerably. Another benefit in using tight binding models is that the results obtained from these give results that are easier to interpret than the results from methods such as DFT. The fitting value of the integrals can give direct insight to what sites contribute to the band structure, whereas this is very hard to retrieve from DFT data.

2 Introduction to the LCAO method for solids

A standard methods of solving periodic potential problems in the theory of electron transport is the LCAO (Linear combination of atomic orbitals), Bloch or Tight binding method. It was first proposed by F. Bloch in 1928 [5]. The general approach of the method is making linear combinations of atomic orbitals with coefficients $\exp(i\mathbf{k} \cdot \mathbf{R})$ where $\mathbf{R}$ is the lattice site on which the atom is located. The equations obtained from this contain various energy integrals that cannot be solved without reverting back to the algorithms we are trying to avoid. To still use the equations obtained, the integrals are used as fitting parameters to data calculated from first principle calculations, albeit DFT or GW data. So in a sense the LCAO method can be seen as an interpolation method to DFT calculations, reducing its computational complexity.

2.1 Bloch's theorem

We are investigating the periodic potential problem, trying to solve the following Schrödinger equation:

$$\hat{H}(\mathbf{r})\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + U(\mathbf{r})\psi = \epsilon\psi$$

Where $U(\mathbf{r})$ is periodic in the general Bravais lattice vectors $\mathbf{R}_i$. Because of this periodicity it is natural to assume that the wave function is periodic due to the periodicity of the potential:

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}_i)$$

But this is clearly incorrect since $U(\mathbf{r}) = 0$ has plane wave solutions (non periodic). The following theorem does give insight in the form of the solutions in such a periodic potential (called Bloch's theorem [2]):

Theorem 1 *The eigenstates ψ of the one-electron Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})$, where $U(\boldsymbol{r} - \boldsymbol{R}) = U(\boldsymbol{r})$ for all $\boldsymbol{R}$ in a Bravais lattice, can be chosen to have the form of a plane wave times a function with periodicity of the Bravais lattice:*

$$\psi_k = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{R})$$

Proof:
We define a translation operator $\hat{T}_{\mathbf{R}}$, that shifts any function by $\mathbf{R}$:

$$\hat{T}_{\mathbf{R}} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$$

Since addition of vectors is commutative, it is easy to see that:

$$\hat{T}_{\mathbf{R}}\hat{T}_{\mathbf{R}'} = \hat{T}_{\mathbf{R}'}\hat{T}_{\mathbf{R}} = \hat{T}_{\mathbf{R}+\mathbf{R}'} \tag{1}$$

Because of the periodicity in the Hamiltonian we have:

$$\hat{T}_{\mathbf{R}}\left(\hat{H}(\mathbf{r})\psi(\mathbf{r})\right) = \hat{H}(\mathbf{r} + \mathbf{R})\psi(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})\psi(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})\hat{T}_{\mathbf{R}}\psi(\mathbf{r})$$

Or in other words: $\hat{H}\hat{T}_{\mathbf{R}} = \hat{T}_{\mathbf{R}}\hat{H}$.

Because this translation operator commutes with the Hamiltonian we know that the eigenstates of $\hat{H}$ are simultaneous eigenstates of the translation operator:

$$\hat{H}\psi = \epsilon\psi$$

$$T_{\mathbf{R}}\psi = c(\mathbf{R})\psi$$

The eigenvalues of the translation operator can be obtained through equation 1:

$$\hat{T}_{\mathbf{R}'}\hat{T}_{\mathbf{R}}\psi = c(\mathbf{R}')c(\mathbf{R})\psi$$

$$\hat{T}_{\mathbf{R}'}\hat{T}_{\mathbf{R}}\psi = \hat{T}_{\mathbf{R}'+\mathbf{R}}\psi = C(\mathbf{R}' + \mathbf{R})\psi$$

Or in other words: $c(\mathbf{R}')c(\mathbf{R}) = C(\mathbf{R}' + \mathbf{R})$. Let $\mathbf{a}_i$ denote the three primitive (basis) vectors for the Bravais lattice. Because $\hat{T}_{\mathbf{R}}$ is a unitary operator, $|c| = 1$:

$$c(\mathbf{a}_i) = e^{2\pi i x_i}$$

It then follows for a general Bravais lattice vector $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$:

$$C(\mathbf{R}) = c(\mathbf{a}_1)^{n_1}c(\mathbf{a}_2)^{n_2}c(\mathbf{a}_3)^{n_3} = e^{2\pi i(x_1n_1+x_2n_2+x_3n_3)} = e^{i\mathbf{k}\cdot\mathbf{R}}$$

Where $\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3$, and the $\mathbf{b}_i$ are reciprocal lattice vectors satisfying $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$. This shows that for a spatially periodic Hamiltonian we can solve for eigenstates ψ such that:

$$\psi_k = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{R})$$

2.2 Derivation of the LCAO method

To derive the matrix components of energy we start with atomic orbitals located on an atom at the position $\mathbf{R}_i$, and quantum number n ($\phi_n(\mathbf{r} - \mathbf{R}_i)$, we can form a Bloch sum:

$$\psi_n(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}_i}\exp(i\mathbf{k}\cdot\mathbf{R}_i)\phi_n(\mathbf{r} - \mathbf{R}_i)$$

- $\psi_n(\mathbf{r})$: atomic orbital (radial part multiplied with angular part)
- N: number of electrons in the crystal
- $\mathbf{R}_i$: vector pointing towards lattice site i
- $\mathbf{k}$: wave vector

Where the sum runs over all electrons of all atoms in the crystal, and ϕ_n denotes a Lowdin function[10]. Where a Lowdin function is a linear combination of atomic orbitals such that the symmetry properties of orbitals are conserved but orbitals on different atoms are mutually orthogonal. Using this relation for the wave function we find for the matrix components of energy:

$$(n/m) = \frac{1}{N}\sum_{\mathbf{R}_i}\sum_{\mathbf{R}_j}\exp(i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i))\cdot\int\phi_n^*(\mathbf{r} - \mathbf{R}_i)\hat{H}\phi_m(\mathbf{r} - \mathbf{R}_j)d\mathbf{v}$$

Here we integrate over all space ($\mathbf{v}$), over coordinate $\mathbf{r}$, and abbreviate the full braket $\langle\psi_n|\hat{H}|\psi_m\rangle$ as (n/m). Substituting $\mathbf{x} = \mathbf{r} - \mathbf{R}_i$:

$$(n/m) = \frac{1}{N}\sum_{\mathbf{R}_i}\sum_{\mathbf{R}_j}\exp(i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i))\cdot\int\phi_n^*(\mathbf{x})\hat{H}\phi_m(\mathbf{x} - (\mathbf{R}_j - \mathbf{R}_i))d\mathbf{v}$$

For a fixed $\mathbf{R}_i$ the summation over $\mathbf{R}_j$ might as well go over the translated vector $\mathbf{R}' = \mathbf{R}_j - \mathbf{R}_i$. We can do this because $\mathbf{R}'$ is a lattice site, and the summation over $\mathbf{R}_j$ goes over all lattice sites. This leaves us with a redundant summation over $\mathbf{R}_i$ that cancels with the factor of $1/N$ giving us:

$$(n/m) = \sum_{\mathbf{R}'} \exp(i\mathbf{k} \cdot \mathbf{R}') \cdot \int \phi_n^*(\mathbf{r}) \hat{H} \phi_m(\mathbf{r} - \mathbf{R}') d\mathbf{v}$$

The Hamiltonian $\hat{H}$ can be written as a sum of a kinetic term and a sum of spherically symmetric potentials centered at the atoms of our crystal. The sum of spherical potential leaves us with integrals over a product of two atomic orbitals (centered on R_i, and R_j) and a potential centered at a third atomic coordinate. These integrals are called three center integrals. We assume that these three center integrals are negligible compared to two-center integrals (the potential is centered on one of the two atomic orbitals). This is motivated by the fact that all three functions decay rapidly over space, if two of these functions were centered at the same site, the integral will be much larger. This reasoning is supported by other research [6]. Neglecting three center integrals leaves us with the final form ($\hat{H} = -\frac{\hbar^2}{2m} + U(\mathbf{r})$, where $U(\mathbf{r})$ is a spherically symmetric potential):

$$(n/m) = \sum_{\mathbf{R}'} \exp(i\mathbf{k} \cdot \mathbf{R}') \cdot \int \phi_n^*(\mathbf{r}) \hat{H} \phi_m(\mathbf{r} - \mathbf{R}') d\mathbf{v} \tag{2}$$

At first glance it seems like we have hit a solid brick wall, a summation of integrals running over all electrons the entire crystal. To get an exact result, we would have to solve an amount of integrals in the order of 10^{23}. This is not feasible, even by numerical approximation, but we can progress by invoking the tight-binding approximation. We assume that orbitals are sufficient closely (tightly) bound to their nucleus so that contributions to an orbitals energy from "faraway" orbitals can be neglected. What constitutes "faraway" is dependent on the accuracy needed but often the first three neighbours of an orbital suffices. There is one thing to be noticed about the integrals in equation 2. Many of them are related or can without calculations be found to give zero contribution. This can be done through demands of crystal and orbital symmetry. We shall see examples of this in section 2.3. Rules like this can be studied by inspection or group theory, and will greatly decrease the number of integrals we need to carry out.

2.3 Orbital Symmetry

As discussed before, inspecting the symmetry of atomic orbitals can greatly reduce the number of integrals we need to calculate in equation 2. In this thesis we shall only consider s, p, and d orbitals, but could easily be extended to include f, or higher order orbitals as well [8]. In order to further analyse our integrals we first need to look at the symmetries of the orbitals considered. The notation used for orbitals in this thesis are the same as in Figure 1.

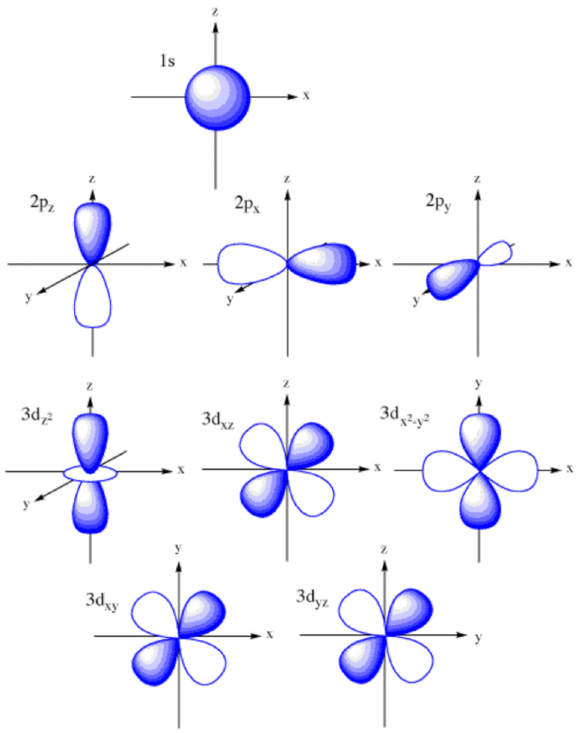

FIGURE 1: visualization of s,p, and d orbitals centered at $R_i = \vec{0}$. The orbital here denoted as d_{z^2} is the same as $d_{3z^2-r^2}$ used in this thesis. [12]

2.3.1 Symmetries of the s orbital

The s-orbital has constant angular dependence, hence it is symmetric along every axis or plane one can think of.

2.3.2 Symmetries of p orbitals

For p_x, p_y, and p_z orbitals we have more interesting symmetries, they are symmetric when reflected across the (xy, and xz), (xy, yz), and (xz, yz) planes respectively. p_x, p_y, and p_z orbitals undergo a sign change when reflected across the yz, xz, and xy planes respectively. Finally we can notice that by rotation we can morph one p-orbital into another. Specifically p_x rotated 90 degrees along the y axis is p_z, p_z rotated 90 degrees along the x axis is p_y, and p_y rotated 90 degrees along the z axis is p_x

2.3.3 Symmetries of the d orbital

The $d_{3z^2-r^2}$ orbital is symmetric when reflected across the xy, xz, yz planes.

The $d_{x^2-y^2}$ orbital is symmetric when reflected across the xy, xz, yz planes. Apart from this it also undergoes a sign change when reflected across the $x = y$, and $x = -y$ planes.

The d_{xz} orbital is symmetric when reflected across the $x = z$, $x = -z$, and xz planes. Apart from this it also undergoes a sign change when reflected across the xy, and yz planes.

The d_{xy} orbital is symmetric when reflected across the $x = y$, $x = -y$, and xy planes. Apart from this it also undergoes a sign change when reflected across the xz, and yz planes.

The d_{yz} orbital is symmetric when reflected across the $y = z$, $y = -z$, and yz planes. Apart from this it also undergoes a sign change when reflected across the xy, and xz planes.
Finally by rotating 45 or 90 degrees along various axes we can rotate xy,xz,yz, and $x^2 - y^2$ into one and other.

2.4 Motivating the use of symmetries

How do the above symmetry properties help us in analyzing our problem? Firstly, since the potential is spherically symmetric we can sometimes find an rotational axis along which rotation morphs one integral into another, or a reflective plane to mirror one into another, see for example Figure 2.

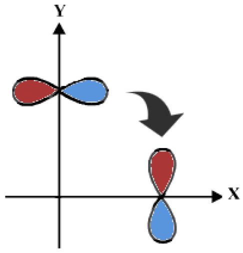

FIGURE 2: By rotating a p_x orbital centered at (010) by -90 degrees along the z axis we obtain a y orbital centered at (100)

By looking at Figure 2 we see that if the orbital at the origin is invariant under this rotation the following holds:

$$\int \psi_n^*(r)\hat{H}\psi_{p_x}(r - a\hat{y})dv = \int \psi_n^*(r)\hat{H}\psi_{p_y}(r - a\hat{x})dv$$

Secondly, we are looking at integrals of the following form:

$$\int_{\mathbb{R}^3} \psi_n^*(\mathbf{r})\hat{H}(\mathbf{r})\psi_m(\mathbf{r} - \mathbf{R}_j)dv$$

If we were able to find a plane going through the origin, across which the multiplication of the two orbitals is an odd function we can set the integral to zero. The only way for a multiplication of two functions to be odd is that one is odd and the other even.

Take as an example for this the integral between an s orbital (constant) centered at the origin and a p_x orbital centered at (010) (see Figure 3).

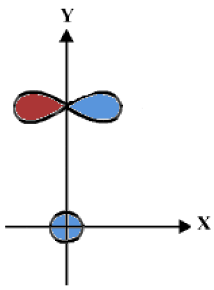

FIGURE 3: A p_x orbital centered at (010), and an s orbital centered at (000)

In this case, p_x undergoes a sign change when mirrored across the yz plane, while the s orbital remains unchanged. This leaves us with an odd function across this plane, which immediately tells us the integral between these functions is zero.

2.5 π, σ, and δ bonding

At some point we are going to run out of symmetry considerations to further reduce the number of integrals we have to solve. There is still a way to slightly reduce the number of integrals further. Two atomic orbitals ψ_n, ψ_m form π, σ, and δ bonds. The integration between two orbitals can be approximated as a sum of these π, σ, and δ bonds. We are looking at the following quantities [8]:

$$\langle \psi_n(r)|\hat{H}|\psi_m(r-\mathbf{R}_j)\rangle$$

If it were the case that the z axis is parallel to the $\mathbf{R}_j$ vector, we obtain the following formula[9]:

$$\langle \psi_{l_1}^{m_1}(r)|\hat{H}|\psi_{l_2}^{m_2}(r-\mathbf{R}_j)\rangle = (l_1 l_2 m_1)\delta_{m_1 m_2}$$

Where ψ_l^m is an full atomic orbital and $(l_1 l_2 m_1)$ an integral between two orbitals like $(sp\sigma)$:

$$\psi_l^m = R_l(r) Y_l^m(\theta, \phi)$$

To make use of the above identity, we need to rotate our coordinate system such that the z axis points in the direction of the lattice site. This rotation is carried out using Euler angles (α, β). In our new coordinate system we have:

$$\psi_l^{m_1} = \sum_{k=-l}^{l} R_{m_1 k}^{l*}(\alpha, \beta)\psi_l^k(r')$$

Where the $R_{m_1 k}^{l*}(\alpha, \beta)$ are elements of the Wigner-D matrix. Substitution of the new representation and the delta function gives us:

$$\langle \psi_{l_1}^{m_1}(r)|\hat{H}|\psi_{l_2}^{m_2}(r-\mathbf{R}_j)\rangle = \sum_{k_1=-l_1}^{l_1}\sum_{k_2=-l_2}^{l_2} R_{m_1 k_1}^{l_1}(\alpha, \beta) R_{m_1 k_2}^{l_2 *}(\alpha, \beta)\, \langle \psi_{l_1}^{k_1}(r')|\hat{H}|\psi_{l_2}^{k_2}(r'-\mathbf{R}_j)\rangle$$

$$\langle \psi_{l_1}^{m_1}(r)|\hat{H}|\psi_{l_2}^{m_2}(r-\mathbf{R}_j)\rangle = \sum_{k_1=-\min(l_1,l_2)}^{\min(l_1,l_2)} R_{m_1 k_1}^{l_1}(\alpha, \beta) R_{m_1 k_1}^{l_2 *}(\alpha, \beta)(l_1 l_2 k_1)$$

Using the above formula, Slater and Koster have calculated all two-center integrals for s, p, and d orbitals [6] (see Figure 4). A more indepth derivation is done by Takegahara et al, including f orbitals [8]. By use of Slater Koster table 1, we can approximate these integrals to further reduce the number of integrals we have to carry out. It however turns out that for our applications this is a too large approximation [7]. In some cases however, the number of integrals like $(pd\sigma)$ are equal to the number of E integrals we have, in this case the representation is exact [6]. We shall see in later examples that this can help us reduce the number of integrals by a small amount.

$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

FIGURE 4: Energy integrals for crystals in terms of two-center integrals. Derived by Slater & Koster. [6]

3 The simple cubic lattice

With our full integral reduction framework at the ready we can tackle some real examples. A good starting point to get a grip on the tight binding approximation, symmetry properties and (π,σ, δ)-bonding is by looking at the simple cubic crystal. We consider this example because it is the most simple, while still beneficial to our main goal; deriving tight binding formulas for a FCC lattice (as we will see in section 4).

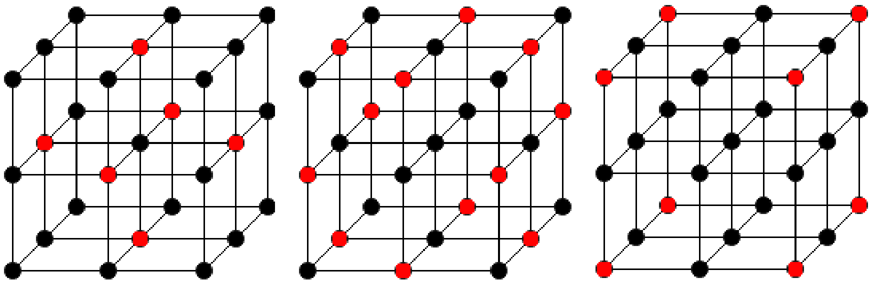

FIGURE 5: Three neareast neighbours of an atomic site in a simple cubic lattice

As we can see in Figure 5, the three nearest neighbours of an atom in a simple cubic lattice lie on a 3x3x3 grid. To begin our derivation we start of with equation 2:

$$\sum_{\mathbf{R}_j} \exp(i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)) \cdot \int \psi_n^*(\mathbf{r}-\mathbf{R}_i)\hat{H}(\mathbf{r}-\mathbf{R}_i)\psi_m(\mathbf{r}-\mathbf{R}_j)dv$$

We shall denote our integrals as follows:

$$E_{n,m}(p,q,r) = \int \psi_n^* \hat{H} \psi_m(r - pa\hat{i} - qa\hat{j} - ra\hat{k})dv \tag{3}$$

Neglecting contributions from all but the three nearest neighbours of the atom located at $R_i = 0$, we can split up the summation in onsite, first, second, and third nearest neighbours:

$$(n/m) = E_{n,m}(0,0,0) \tag{4}$$

$$+e^{iak_x}E_{n,m}(1,0,0) + e^{-iak_x}E_{n,m}(-1,0,0) + e^{iak_y}E_{n,m}(0,1,0)$$
$$+e^{-iak_y}E_{n,m}(0,-1,0) + e^{iak_z}E_{n,m}(0,0,1) + e^{-iak_z}E_{n,m}(0,0,-1)$$

$$+e^{ia\cdot(k_x+k_y)}E_{n,m}(1,1,0)+e^{ia\cdot(-k_x+k_y)}E_{n,m}(-1,1,0)+e^{ia\cdot(k_x-k_y)}E_{n,m}(1,-1,0)+e^{ia\cdot(-k_x-k_y)}E_{n,m}(-1,-1,0)$$
$$+e^{ia\cdot(k_x+k_z)}E_{n,m}(1,0,1)+e^{ia\cdot(-k_x+k_z)}E_{n,m}(-1,0,1)+e^{ia\cdot(k_x-k_z)}E_{n,m}(1,0,-1)+e^{ia\cdot(-k_x-k_z)}E_{n,m}(-1,0,-1)$$
$$+e^{ia\cdot(k_y+k_z)}E_{n,m}(0,1,1)+e^{ia\cdot(-k_y+k_z)}E_{n,m}(0,-1,1)+e^{ia\cdot(k_y-k_z)}E_{n,m}(0,1,-1)+e^{ia\cdot(-k_y-k_z)}E_{n,m}(0,-1,-1)$$

$$+e^{ia\cdot(k_x+k_y+k_z)}E_{n,m}(1,1,1) + e^{ia\cdot(-k_x+k_y+k_z)}E_{n,m}(-1,1,1) + e^{ia\cdot(k_x-k_y+k_z)}E_{n,m}(1,-1,1)$$
$$+e^{ia\cdot(k_x+k_y-k_z)}E_{n,m}(1,1,-1)+e^{ia\cdot(-k_x-k_y+k_z)}E_{n,m}(-1,-1,1)+e^{ia\cdot(-k_x+k_y-k_z)}E_{n,m}(-1,1,-1)$$
$$+e^{ia\cdot(k_x-k_y-k_z)}E_{n,m}(1,-1,-1) + e^{ia\cdot(-k_x-k_y-k_z)}E_{n,m}(-1,-1,-1)$$

As we mentioned before, dependent on the orbitals under consideration many of these integrals can be set to zero or equal to each other (up to $\pm$ sign).

3.1 Symmetry examples

Before we work out a full example of a matrix component, we will first look at some simple geometric examples. For our examples we will look at three first nearest neighbour examples, but the general arguments extend to higher order neighbours.

3.1.1 Symmetry example 1

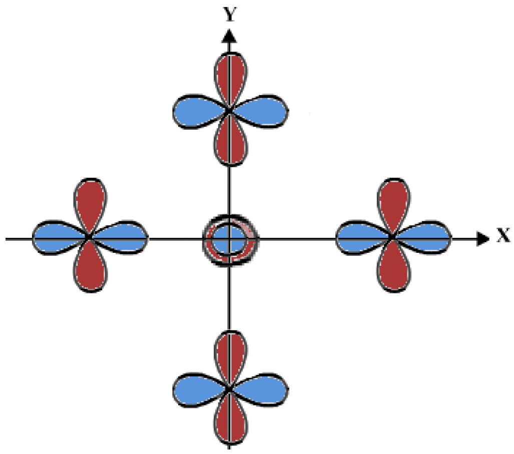

FIGURE 6: An $d_{3z^2-r^2}$ orbital centered at the origin and $d_{x^2-y^2}$ orbitals centered at first nearest neighbour locations in the xy plane.

In Figure 6 we can see that when rotating the $d_{x^2-y^2}(100)$ orbital 90 degrees along the z-axis we obtain an $-d_{x^2-y^2}(010)$ orbital (notice the sign change), further rotating by 90 degree increments we get an $d_{x^2-y^2}(-100)$, and an $-d_{x^2-y^2}(0-10)$ orbital. Since the $d_{3z^2-r^2}$ orbital is invariant under this rotation we obtain:

$$E_{3z^2-r^2,x^2-y^2}(100) = -E_{3z^2-r^2,x^2-y^2}(010) = E_{3z^2-r^2,x^2-y^2}(-100) = -E_{3z^2-r^2,x^2-y^2}(0-10)$$

3.1.2 Symmetry example 2

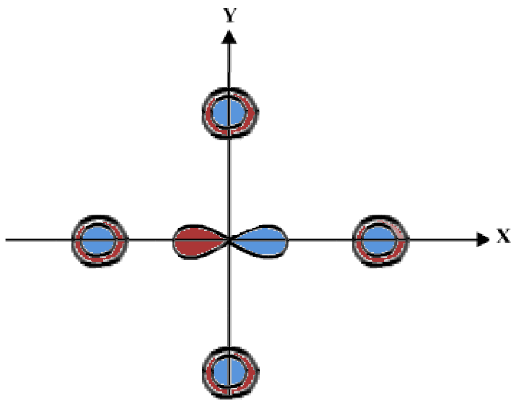

FIGURE 7: An yz orbital centered at the origin and x^2-y^2 orbitals centered at first nearest neighbour locations in the xy plane.

In Figure 7 we see that there is no way to compose reflections and rotations so that the orbital at the origin remains the same (up to sign change), and the orbital at (100) morphs into (010) at the same time. Hence we have at least two distinct integrals in this example.
By reflection across the yz plane we find that d_{yz} undergoes a sign change and $d_{x^2-y^2}(100) = -d_{x^2-y^2}(-100)$.
By reflection across the xz plane we find that both d_{yz} remains the same and that $d_{x^2-y^2}(010)$ maps to $d_{x^2-y^2}(0-10)$, giving us the final relations:

$$E_{yz,x^2-y^2}(100) = -E_{yz,x^2-y^2}(-100)$$

$$E_{yz,x^2-y^2}(010) = E_{yz,x^2-y^2}(0-10)$$

3.1.3 Symmetry example 3

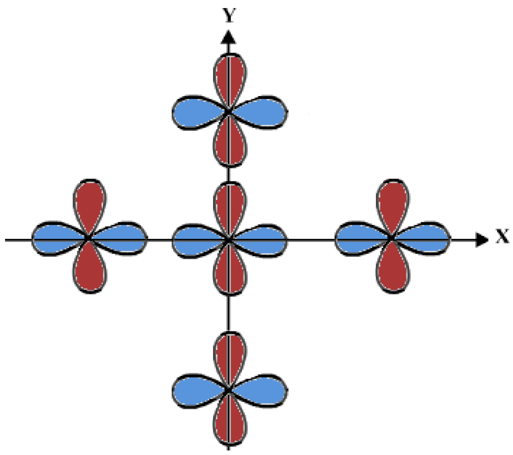

FIGURE 8: $x^2 - y^2$ orbitals centered at both the origin as well as first nearest neighbour locations in the xy plane.

For every 90-degree rotation along the z-axis the center orbital undergoes a sign change, for this same rotation the first nearest neighbour also undergoes a sign change (morphing into each-other like 6). Since double sign changes cancel we obtain:

$$E_{x^2-y^2,x^2-y^2}(100) = E_{x^2-y^2,x^2-y^2}(-100) = E_{x^2-y^2,x^2-y^2}(010) = E_{x^2-y^2,x^2-y^2}(0-10)$$

3.2 Simple cubic crystal $p_x/d_{3z^2-r^2}$ orbital

With these short examples out of the way we shall work out an example of a matrix component for the simple cubic crystal. We shall investigate the coupling between an p_x orbital centered at the origin with an $d_{3z^2-r^2}$ orbital at the other lattice sites. We examine this example in more detail because it shows the use of symmetry properties as well as σ, π, δ bonding.

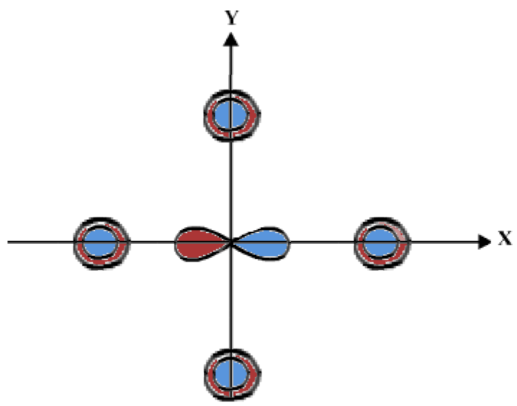

FIGURE 9: A p_x orbital centered at the origin as well as $3z^2 - r^2$ orbitals as first nearest neighbours in the xy plane.

First we will investigate this problem by using the symmetry properties at our disposal. Looking first at the first nearest neighbours. We can see by examining Figure 9 that the p_x orbital is an odd function across the yz plane. This in combination with the fact that the $d_{3z^2-r^2}$ orbital is an even function across this plane gives us:

$$E_{x,3z^2-r^2}(0,0,0) = E_{x,3z^2-r^2}(0,1,0) = E_{x,3z^2-r^2}(0,-1,0) = E_{x,3z^2-r^2}(0,0,1) = E_{x,3z^2-r^2}(0,0,-1) = 0$$

The remaining nearest neighbour is a nonzero integral, p_x being an odd function gives us:

$$E_{x,3z^2-r^2}(1,0,0) = -E_{x,3z^2-r^2}(-1,0,0)$$

We then investigate the second nearest neighbours. By similar reasoning as with the first nearest neighbours we can set all combinations that reside in the yz plane to zero. Visual inspection then gives us two families of integrals: One that resides in the xz plane and one in the xy plane. Since p_x is an odd function across the yz plane, the x-coordinate determines the sign of the integral giving us:

$$E_{x,3z^2-r^2}(1,1,0) = E_{x,3z^2-r^2}(1,-1,0) = -E_{x,3z^2-r^2}(-1,1,0) = -E_{x,3z^2-r^2}(-1,-1,0)$$

$$E_{x,3z^2-r^2}(1,0,1) = E_{x,3z^2-r^2}(1,0,-1) = -E_{x,3z^2-r^2}(-1,0,1) = -E_{x,3z^2-r^2}(-1,0,-1)$$

$$E_{x,3z^2-r^2}(0,1,1) = E_{x,3z^2-r^2}(0,1,-1) = E_{x,3z^2-r^2}(0,-1,1) = E_{x,3z^2-r^2}(0,-1,-1) = 0$$

An inspection of the third nearest neighbour tells you that this is one group of integrals, all nonzero, where the x-coordinate once again determines the sign. All this information is summarized in Table 1.

TABLE 1: All energy integral relations for interactions between p_x and $3z^2-r^2$ orbitals on a simple cubic lattice. Neglecting all contributions above third nearest neighbours.

$E_{x,3z^2-r^2}(0,0,0)$	0	$E_{x,3z^2-r^2}(-1,0,-1)$	$-E_{x,3z^2-r^2}(1,0,1)$
$E_{x,3z^2-r^2}(1,0,0)$	$E_{x,3z^2-r^2}(1,0,0)$	$E_{x,3z^2-r^2}(0,1,-1)$	0
$E_{x,3z^2-r^2}(-1,0,0)$	$-E_{x,3z^2-r^2}(1,0,0)$	$E_{x,3z^2-r^2}(0,-1,1)$	0
$E_{x,3z^2-r^2}(0,1,0)$	0	$E_{x,3z^2-r^2}(0,1,-1)$	0
$E_{x,3z^2-r^2}(0,-1,0)$	0	$E_{x,3z^2-r^2}(0,1,-1)$	0
$E_{x,3z^2-r^2}(0,0,1)$	0	$E_{x,3z^2-r^2}(1,1,1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(0,0,-1)$	0	$E_{x,3z^2-r^2}(-1,1,1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,1,0)$	$E_{x,3z^2-r^2}(1,1,0)$	$E_{x,3z^2-r^2}(1,-1,1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,-1,0)$	$E_{x,3z^2-r^2}(1,1,0)$	$E_{x,3z^2-r^2}(1,1,-1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,1,0)$	$-E_{x,3z^2-r^2}(1,1,0)$	$E_{x,3z^2-r^2}(-1,1,-1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,-1,0)$	$-E_{x,3z^2-r^2}(1,1,0)$	$E_{x,3z^2-r^2}(-1,-1,1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,0,1)$	$E_{x,3z^2-r^2}(1,0,1)$	$E_{x,3z^2-r^2}(1,-1,-1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,0,-1)$	$E_{x,3z^2-r^2}(1,0,1)$	$E_{x,3z^2-r^2}(-1,-1,-1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,0,1)$	$-E_{x,3z^2-r^2}(1,0,1)$		

The relations from Table 1 can be substituted in equation 4, obtaining:

$$(x/3z^2-r^2) = E_{x,3z^2-r^2}(1,0,0)\left(e^{iak_x}-e^{-iak_x}\right)$$
$$+E_{x,3z^2-r^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)}+e^{ia\cdot(k_x-k_y)}-e^{ia\cdot(-k_x+k_y)}-e^{ia\cdot(-k_x-k_y)}\right)$$
$$+E_{x,3z^2-r^2}(1,0,1)\left(e^{ia\cdot(k_x+k_z)}+e^{ia\cdot(k_x-k_z)}-e^{ia\cdot(-k_x+k_z)}-e^{ia\cdot(-k_x-k_z)}\right)$$
$$+E_{x,3z^2-r^2}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)}-e^{ia\cdot(-k_x+k_y+k_z)}+e^{ia\cdot(k_x-k_y+k_z)}+e^{ia\cdot(k_x+k_y-k_z)}$$
$$-e^{ia\cdot(-k_x-k_y+k_z)}-e^{ia\cdot(-k_x+k_y-k_z)}+e^{ia\cdot(k_x-k_y-k_z)}-e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x/3z^2-r^2) = 2iE_{x,3z^2-r^2}(1,0,0)\sin(ak_x)$$
$$+2E_{x,3z^2-r^2}(1,1,0)\left(\cos(ak_y)e^{iak_x}-\cos(ak_y)e^{-iak_x}\right)$$
$$+2E_{x,3z^2-r^2}(1,0,1)\left(\cos(ak_z)e^{iak_x}-\cos(ak_z)e^{-iak_x}\right)$$
$$+2iE_{x,3z^2-r^2}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)}+\sin(ak_x)e^{ia\cdot(-k_y+k_z)}+\sin(ak_x)e^{ia\cdot(k_y-k_z)}+\sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(x/3z^2-r^2) = 2iE_{x,3z^2-r^2}(1,0,0)\sin(ak_x)$$
$$+4iE_{x,3z^2-r^2}(1,1,0)\sin(ak_x)\cos(ak_y) + 4iE_{x,3z^2-r^2}(1,0,1)\sin(ak_x)\cos(ak_z)$$
$$+4iE_{x,3z^2-r^2}(1,1,1)\left(\sin(ak_x)\cos(ak_y)e^{iak_z} + \sin(ak_x)\cos(ak_y)e^{-iak_z)}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x/3z^2-r^2) = 2iE_{x,3z^2-r^2}(1,0,0)\sin(\xi)$$
$$+4iE_{x,3z^2-r^2}(1,1,0)\sin(\xi)\cos(\eta)+4iE_{x,3z^2-r^2}(1,0,1)\sin(\xi)\cos(\zeta)+8iE_{x,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$$

Slater & Koster [6] derived forms for integrals, see Figure 4 (where l, m, n denote the directional cosine of the respective coordinate):

$$E_{x,3z^2-r^2}(110) = l[n^2 - \frac{1}{2}(l^2+m^2)](pd\sigma) - \sqrt{3}ln^2(pd\pi) = -\frac{\sqrt{2}}{4}(pd\sigma)$$
$$E_{z,x^2-y^2}(011) = \frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma) - n(l^2-m^2)(pd\pi) = -\frac{\sqrt{2}\sqrt{3}}{8}(pd\sigma) - \frac{\sqrt{2}}{4}(pd\pi)$$
$$E_{z,3z^2-r^2}(011) = n[n^2 - \frac{1}{2}(l^2+m^2)](pd\sigma) + \sqrt{3}n(l^2+m^2)(pd\pi) = \frac{\sqrt{2}}{8}(pd\sigma) + \frac{\sqrt{2}\sqrt{3}}{4}(pd\pi)$$

These relations can also be obtained for other energy integrals. We then obtain 4 systems of equations. Solving these gives us:

$$E_{x,3z^2-r^2}(1,0,0) = -\frac{1}{2}E_{z,3z^2-r^2}(0,0,1)$$
$$E_{x,3z^2-r^2}(110) = \frac{\sqrt{3}}{2}E_{z,x^2-y^2}(011) - \frac{1}{2}E_{z,3z^2-r^2}(011)$$
$$E_{x,3z^2-r^2}(101) = -\frac{\sqrt{3}}{2}E_{z,x^2-y^2}(011) - \frac{1}{2}E_{z,3z^2-r^2}(011)$$
$$E_{x,3z^2-r^2}(1,1,1) = \frac{i}{\sqrt{3}}E_{x,x^2-y^2}(111)$$

These relations are exact, since number of energy symbols $(pd\sigma)$ and$(pd\pi)$ of a given order are exactly the number of energy integrals of that order. We can therefore insert these in our found equation giving us the final form:

$$(x/3z^2-r^2) = -iE_{z,3z^2-r^2}(0,0,1)\sin(\xi) + 2\sqrt{3}iE_{z,3z^2-r^2}(1,1,0)\left(\sin(\xi)\cos(\eta) - \sin(\xi)\cos(\zeta)\right)$$
$$-2iE_{z,3z^2-r^2}(0,1,1)\left(\sin(\xi)\cos(\eta) + \sin(\xi)\cos(\zeta)\right) - \frac{8}{\sqrt{3}}E_{x,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$$

3.3 Simple Cubic matrix components

The example from section 3.2 is but one of 81 combinations of orbitals. Luckily for us, a lot of these are one and the same. (p_x, p_y) and (p_y, p_z) are an example where the energy integral is the same up to cyclic permutation of the coordinates. This reduces the problem down to 21 configurations of orbitals [6]. These were all analyzed. For a full derivation we invite the reader to look at the appendix (section 10). A summary of the result is listed in Table 2. This table was first derived by J.C. Slater and G.F. Koster in 1954 [6]. In the next sections (4), we will calculate this table for an FCC lattice and apply this theory to a single Perovskite bandstructure.

3.3.1 Simple Cubic matrix components table

TABLE 2: Matrix components of energy for simple cubic crystals

(s/s)	$E_{s,s}(0,0,0) + 2E_{s,s}(1,0,0)\left(\cos(\xi)+\cos(\eta)+\cos(\zeta)\right)$ $+4E_{s,s}(1,1,0)(\cos(\xi))\cos(\eta)+\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta))$ $+8E_{s,s}(1,1,1)(\cos(\xi)\cos(\eta)\cos(\zeta$
(s/x)	$2iE_{s,x}(1,0,0)\sin(\xi) + 4iE_{s,y}(1,1,0)\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$ $+8iE_{s,x}(1,1,1)(\sin(\xi)\cos(\eta)\cos(\zeta$
(s/xy)	$-4E_{s,xy}(1,1,0)\sin(\xi)\sin(\eta) - 8E_{s,y}(1,1,1)\left(\sin(\xi)\sin(\eta)\cos(\zeta)\right)$
(s/x^2-y^2)	$\sqrt{3}E_{s,x^2-y^2}(1,0,0)\left(\cos(\xi)-\cos(\eta)\right)$ $+2\sqrt{3}E_{s,3z^2-r^2}(0,1,1)\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$
$(s/3z^2-r^2)$	$E_{s,3z^2-r^2}(0,0,1)\left(-\cos(\xi)-\cos(\eta)+2\cos(\zeta)\right)$ $-2E_{s,3z^2-r^2}(1,1,0)\left(-2\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$
(x/x)	$E_{x,x}(0,0,0) + 2E_{x,x}(1,0,0)\cos(\xi) + 2E_{y,y}(1,0,0)\left(\cos(\eta)+\cos(\zeta)\right)$ $+4E_{x,x}(1,1,0)\left(\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)\right) + 4E_{x,x}(0,1,1)\cos(\eta)\cos(\zeta)$ $+8E_{x,x}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$
(x/y)	$-4E_{x,y}(110)\sin(\xi)\sin(\eta) - 8E_{x,y}(111)\sin(\xi)\sin(\eta)\cos(\zeta)$
(x/xy)	$2iE_{x,xy}(0,1,0)\sin(\eta)$ $+4iE_{x,xy}(1,1,0)\cos(\xi)\sin(ak_y) + 4iE_{x,xy}(0,1,1)\sin(\eta)\cos(\zeta)$ $+8iE_{x,xy}(1,1,1)\cos(\xi)\sin(\eta)\cos(\zeta)$
(x/yz)	$-8iE_{x,yz}(1,1,1)\sin(\xi)\sin(\eta)\sin(\zeta)$
(x/x^2-y^2)	$\sqrt{3}iE_{z,3z^2-r^2}(0,0,1)\sin(\xi) + 2\sqrt{3}iE_{z,3z^2-r^2}(011)\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$ $+2iE_{z,x^2-y^2}(011)\left(\sin(\xi)\cos(\eta)-\sin(\xi)\cos(\zeta)\right)$ $+8iE_{x,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$
$(x/3z^2-r^2)$	$-iE_{z,3z^2-r^2}(0,0,1)\sin(\xi) + 2\sqrt{3}iE_{z,3z^2-r^2}(1,1,0)\left(\sin(\xi)\cos(\eta)-\sin(\xi)\cos(\zeta)\right)$ $-2iE_{z,3z^2-r^2}(0,1,1)\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$ $-\frac{8}{\sqrt{3}}E_{x,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$
$(z/3z^2-r^2)$	$2iE_{z,3z^2-r^2}(0,0,1)\sin(\zeta) + 4iE_{z,3z^2-r^2}(0,1,1)\left(\cos(\xi)\sin(\zeta)+\sin(\eta)\cos(\zeta)\right)$ $+\frac{16}{\sqrt{3}}iE_{x,x^2-y^2}(1,1,1)\cos(\xi)\cos(\eta)\sin(\zeta)$
(xy/xy)	$E_{xy,xy}(0,0,0) + 2E_{xy,xy}(1,0,0)\left(\cos(\xi)+\cos(\eta)+\cos(\zeta)\right)$ $+4E_{xy,xy}(1,1,0)\cos(\eta)\cos(\zeta) + 4E_{xy,xy}(0,1,1)\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$ $+E_{xy,xys}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$
(xy/xz)	$-4E_{xy,xz}(0,1,1)\sin(\eta)\sin(\zeta) - 8E_{xy,xz}(1,1,1)\cos(\xi)\sin(\eta)\sin(\zeta)$
(xy/x^2-y^2)	0
$(xy/3z^2-r^2)$	$-4E_{xy,3z^2-r^2}(1,1,0)\sin(\xi)\sin(\eta) - 8E_{xy,3z^2-r^2}(1,1,1)\sin(\xi)\sin(\eta)\cos(\zeta)$
(xz/x^2-y^2)	$2\sqrt{3}E_{xy,3z^2-r^2}(1,1,0)\sin(\xi)\cos(\zeta) + 4\sqrt{3}E_{xy,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\sin(\zeta)$
$(xz/3z^2-r^2)$	$2E_{xy,3z^2-r^2}(1,1,0)\sin(\xi)\sin(\zeta) + 4E_{xy,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\sin(\zeta)$
(x^2-y^2/x^2-y^2)	$E_{x^2-y^2,x^2-y^2}(0,0,0) + \frac{3}{2}E_{x^2-y^2,x^2-y^2}(001)\left(\cos(\xi)+\cos(\eta)\right)$ $+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\left(\frac{1}{4}\cos(\xi)+\frac{1}{4}\cos(\eta)+\cos(\zeta)\right)$ $+4E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\frac{1}{4}\cos(\xi)\cos(\zeta)+\frac{1}{4}\cos(\eta)\cos(\zeta)+\cos(\xi)\cos(\eta)\right)$ $+3E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$ $+8E_{3z^2-r^2,3z^2-r^2}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$
$(3z^2-r^2/3z^2-r^2)$	$E_{3z^2-r^2,3z^2-r^2}(0,0,0) + \frac{3}{2}E_{x^2-y^2,x^2-y^2}(001)\left(\cos(\xi)+\cos(\eta)\right)$ $+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\left(\frac{1}{4}\cos(\xi)+\frac{1}{4}\cos(\eta)+\cos(\zeta)\right)$ $+4E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\frac{1}{4}\cos(\xi)\cos(\zeta)+\frac{1}{4}\cos(\eta)\cos(\zeta)+\cos(\xi)\cos(\eta)\right)$ $+3E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$ $+8E_{3z^2-r^2,3z^2-r^2}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$
$(x^2-y^2/3z^2-r^2)$	$\frac{\sqrt{3}}{2}E_{x^2-y^2,x^2-y^2}(1,0,0)\left(\cos(\xi)-\sin(\eta)\right)$ $-\frac{\sqrt{3}}{2}E_{3z^2-r^2,3z^2-r^2}(1,0,0)\left(\cos(\xi)-\sin(\eta)\right)$ $+4E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\cos(\xi)\cos(\zeta)-\cos(\eta)\cos(\zeta)\right)$ $-4E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\cos(\xi)\cos(\zeta)-\cos(\eta)\cos(\zeta)\right)$

4 The face cubic lattice

As mentioned earlier in this thesis, the main goal is to apply our theory to perovskites, specifically single perovskite laticces. For this we need to derive Table 1 again, this time for an FCC lattice.

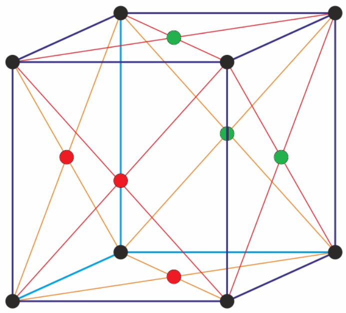

FIGURE 10: The unit cell of a FCC lattice. Compared to a simple cubic we have two new neighbour groups within the 3x3x3 grid, labelled in red and green.

As we see in Figure 10, compared to the simple cubic crystal considered previously we now have two more neighbours included in our analysis. They are labelled in red and green in Figure 10. The symmetry of the red group we have already analyzed. This being just the second nearest neighbours considered in the simple cubic crystal but scaled down by a factor of 2. Because of the radial dependence of the potential these integrals differ. The form of these integrals can be copied from the previous section (replacing (110) by (1/2,1/2,0) etc.). The two center approximation will have to be recalculated for these examples. The green group in figure 10 must be analyzed separately since it is a new group of neighbours. For a full derivation we again invite the reader to look at the appendix (section 11). A summary of the results are listed in table 3 and 4, note that this table only includes the matrix elements not present in the simple cubic, for the full matrix elements these should be summed.

4.1 Face Cubic matrix components table

TABLE 3: Part of the matrix components of energy for face centered cubic crystals, excluding terms already present in simple cubic crystals, sum these for full matrix elements.

(s/s)	$4E_{s,s}(\frac{1}{2},\frac{1}{2},0)(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})+\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2}))$ $+8E_{s,s}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
(s/x)	$4iE_{s,y}(\frac{1}{2},\frac{1}{2},0)\left((\frac{\xi}{2})\cos(\frac{\eta}{2})+\sin(\frac{\xi}{2})\cos(\frac{\zeta}{2})\right)$ $+8iE_{s,x}(\frac{1}{2},\frac{1}{2},1)\left(2\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+2\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
(s/xy)	$-4E_{s,xy}(\frac{1}{2},\frac{1}{2},0)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})$ $+8E_{s,xy}(1,\frac{1}{2},\frac{1}{2})\left(\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\zeta)+2\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2})+2\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
(s/x^2-y^2)	$-2\sqrt{3}E_{s,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(-\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+\frac{16}{\sqrt{3}}E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})-\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
$(s/3z^2-r^2)$	$4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})-\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})-\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+8E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(-2\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
(x/x)	$2E_{x,x}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})+\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+8E_{x,x}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})\right)$ $+8E_{x,x}(1,\frac{1}{2},\frac{1}{2})\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$
(x/y)	$-4E_{x,y}(\frac{1}{2},\frac{1}{2},0)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})-8E_{x,y}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\zeta)$ $-8E_{x,y}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})-8E_{x,y}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2})$
(x/xy)	$4iE_{x,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\frac{\xi}{2})\sin(\frac{\eta}{2})+4iE_{x,xy}(0,\frac{1}{2},\frac{1}{2})\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})$ $+8iE_{x,xy}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+8iE_{x,xy}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$ $+8iE_{x,xy}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$
(x/yz)	$-8E_{x,yz}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})$ $-8E_{x,yz}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2})-8E_{x,yz}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})$
(x/x^2-y^2)	$\frac{8i}{5}\sqrt{3}E_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})+\sin(\frac{\xi}{2})\cos(\frac{\zeta}{2})\right)$ $+\frac{4i}{5}E_{z,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(4\sin(\xi)\cos(\frac{\eta}{2})-\sin(\xi)\cos(\frac{\zeta}{2})\right)+8iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$ $+8iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+8iE_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$
$(x/3z^2-r^2)$	$4iE_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(-5\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})+2\sin(\frac{\xi}{2})\cos(\zeta)\right)$ $+8\sqrt{3}iE_{z,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(2\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})-\sin(\frac{\xi}{2})\cos(\frac{\zeta}{2})\right)$ $+8iE_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$ $+8iE_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$ $+8iE_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$

Table 4: Part of the matrix components of energy for face cubic crystals, excluding terms already present in simple cubic crystals, sum these for full matrix elements.

$(z/3z^2-r^2)$	$4iE_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\sin(\zeta)+\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+8iE_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\sin(\zeta)$ $+8iE_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\sin(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})\right)$
(xy/xy)	$4E_{xy,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})+4E_{xy,xy}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+8E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$ $+8E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})-\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
(xy/xz)	$-4E_{xy,xz}(0,\frac{1}{2},\frac{1}{2})\sin(\frac{\eta}{2})\sin(\frac{\zeta}{2})$ $-8E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})-8E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\sin(\frac{\zeta}{2})$ $-8E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})$
(xy/x^2-y^2)	$8E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2})+\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
$(xy/3z^2-r^2)$	$-4E_{xy,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})$ $-8E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})$ $-8E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2})+\sin(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})\right)$
(xz/x^2-y^2)	$2\sqrt{3}E_{xz,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\sin(\frac{\xi}{2})\cos(\frac{\zeta}{2})$ $+8iE_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})+8iE_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$ $+8iE_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$
$(xz/3z^2-r^2)$	$-4E_{xz,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\frac{\xi}{2})\sin(\zeta)$ $-8E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\sin(\zeta)-8E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\sin(\frac{\zeta}{2})$ $-8E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})$
(x^2-y^2/x^2-y^2)	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\left(4\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})+\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+3E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\eta)\cos(\frac{\zeta}{2})\right)$ $+8E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$ $+8E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})-\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
$(3z^2-r^2/3z^2-r^2)$	$E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(4\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})+\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+3E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+8E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$ $+8E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$
$(x^2-y^2/3z^2-r^2)$	$\sqrt{3}E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\left(-\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+\sqrt{3}E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(-\cos(\frac{\xi}{2})\cos(\frac{\zeta}{2})+\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$ $+8E_{x^2-y^2,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(-\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$

5 Fitting & results

We have now reduced our problem to a few dozen integrals. These integrals, while innocent looking are actually impossible to solve without referring back to DFT calculations (or similar). This is because the radial part of both the wave functions and that of the potential are unknown without these calculations. Slater and Koster [6] propose ridding ourselves of these integrals all together. Proposing instead to take the required orbitals that belong to the valance and conduction band, taking these contributions and using the integrals as fitting parameters. These formulas can then be fitted to parts of accurate calculations of band structures preformed by a DFT algorithm or other schemes. In this way we can use our tight binding model to interpolate DFT results, reducing the computation time considerably. An excellent code has been written by J. Schiphorst [7], making use of the two-center approximation. A similar approach can be used for our purposes.

5.1 Fitting

In the previous section, energy contributions of s, p, and d orbitals were derived. We take symbols like $E_{\phi_n,\phi_m}(klm)$ as fitting parameters to DFT data obtained from [7]. The main purpose for the methods derived in this thesis were to study single and double perovskites. These materials are receiving a lot of attention lately for the efficiency they have when used in solar panels. As a proof of concept we will use our theory to fit to the band structure of $CsPbI_3$ (a single ABX_3 perovskite). Experiments have shown that in both single and double perovskites, the A site does not alter the band structure. By inspecting the periodic table, we can by looking at the valence band of each of both Pb and I see that orbitals contributing to the band edges of Pb are the s, and p orbitals. The orbitals contributing to the band edges of of I are only the p orbitals.

The matrix elements of energy can then be fitted to the bands calculated by DFT. We have three separate matrix components (and cyclic permutations of these) to fit to. Interactions between (s, p) orbitals, (p_x, p_x) orbitals, and (p_x, p_y) orbitals. We can then use various global optimizing techniques to fit the energy integrals to DFT data. As a proof of concept, I chose to use a Basin-hopping algorithm. "Basin-hopping is a local optimization technique that iterates by performing random perturbation of coordinates, performing local optimization, and accepting or rejecting new coordinates based on a minimized function value."[1] It does not guarantee a true global minimum, but it is sufficient as a proof of concept.

As a minimization function I chose the sum of the absolute square errors in the energy values, more elaborate minimization functions can be found. The absolute square error suffices for a proof of concept.

5.2 Results

With the method outlined above, a fit was done on the band structure of $CsPbI_3$, along directions MR, $R\Gamma$, and ΓX as well as all these paths together.

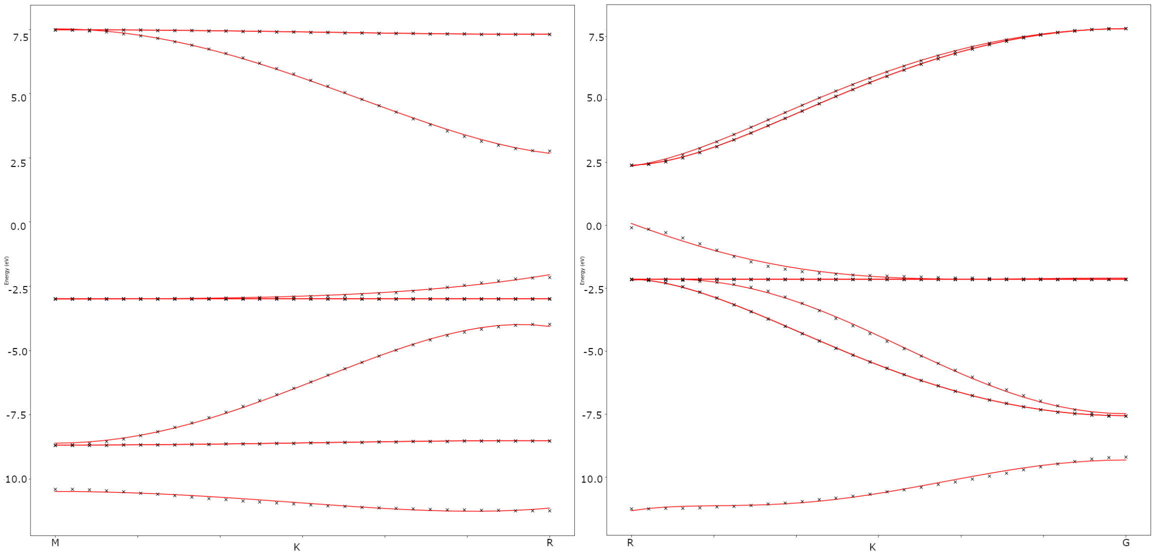

FIGURE 11: A fit to DFT data of CsPbI3 in directions MR and RG. The fit was done taking neighbours up to distance $\sqrt{3}$ atomic units into account. The red line shows the fit, the black crosses show DFT data.

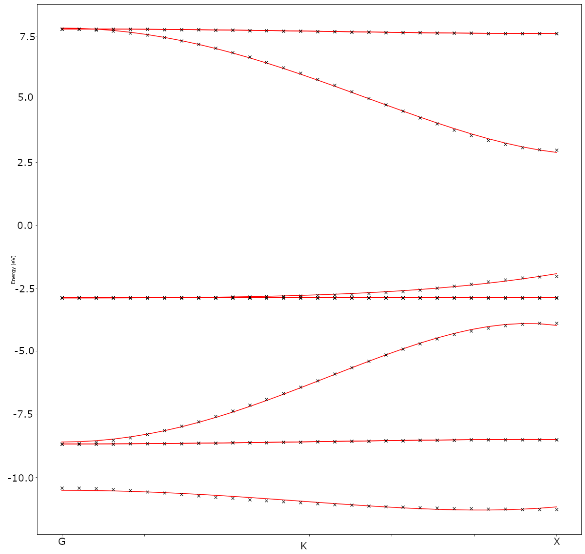

FIGURE 12: A fit to DFT data of CsPbI3 in direction GX. The fit was done taking neighbours up to distance $\sqrt{3}$ atomic units into account. The red line shows the fit, the black crosses show DFT data.

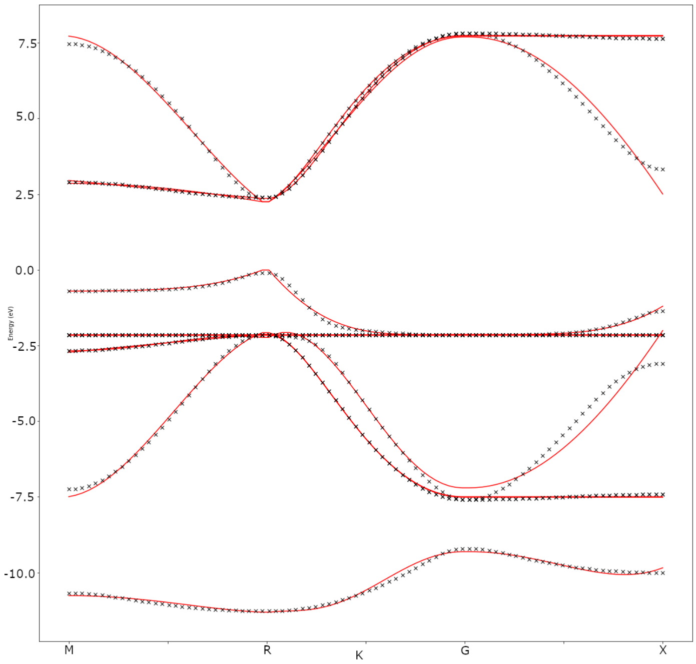

FIGURE 13: A fit to DFT data of CsPbI3, taking neighbours up to distance $\sqrt{3}$ atomic units into account. The fit was done to data of all three directions simultaneously. The red line shows the fit, the black crosses show DFT data.

6 Conclusion

We have succesfully derived the energy matrix elements for single cubic and face centered cubic crystals. This was the main goal of the thesis. Moreover I was able to show that the method proposed is accurate when used in fitting to DFT data. As we can see in Figures 11, 12, and 13, the fit obtained is quite accurate. It is lacking accuracy when fitted to multiple k paths at the same time. As a proof of concept our derived method works and is able to fit band structures accurately.

7 Discussion

Our goal has been achieved, resulting in a good fit of $CsPbI_3$. The code used to fit to the data however was very crude, using the most basic fitting method that exists (to save time in implementation).

For future research I recommend making a more robust code, also taking spin orbit coupling into account (the fit was made to DFT data without spin orbit coupling removed).

A second suggestion is to apply the theory to double perovskites, for which previous fitting formulas did not work.

A secondary point of concern is the accuracy of the fit. The fit uses a Basin-hopping algorithm. While accurate to a certain extent, more global methods must be used in future applications to ensure the quality of the fit. Taking for example boundary conditions, periodicity, continutity etc. into account.

If readers of this thesis would want to use the process outlined in this thesis to rare earth metals, the tables will have to be extended to include f orbitals as well.

8 Acknowledgements

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A special thank you goes out to Lyonne de Wit, who is always there for me and has always supported me, especially through the personal hardships I went through in the process of writing this thesis.

Lastly, I would like to thank everyone who has supported me, both family and friends.

9 References

References

[1] ? *Basin Hopping*. URL: https://en.wikipedia.org/wiki?curid=57184342. (accessed: 25.06.2022).

[2] Ashcroft/Mermin. *Solid State Physics*. Cengage, 2019. ISBN: 978-0-03-083993-1.

[3] Volker Bach. *Many-Electron Approaches in Physics, Chemistry and Mathematics*. springer, 2014. ISBN: 978-3-319-06379-9.

[4] M. Bellis. *Alfred Nobel and the History of Dynamite*. URL: https://www.thoughtco.com/history-of-dynamite-1991564#:~:text=Nitroglycerin%20was%20first%20invented%20by,a%20malleable%20paste%20called%20dynamite.. (accessed: 25.06.2022).

[5] F. Bloch. In: *Physik* 52 (1928), p. 555.

[6] G.F. Koster J.C. Slater. "Simplified LCAO method for the Periodic Potential Problem". In: *Physical review* 94.6 (1954), pp. 1–27. DOI: https://doi.org/10.1103/PhysRev.94.1498.

[7] J.Schiphorst. "Calculating optoelectronic properties of halide double perovskites using a tight-binding model". In: *master thesis Utwente* ().

[8] A Yanase K Takegahara Y Aoki. "Slater-Koster tables for f electrons". In: *J. Phys. C: Solid State Phys* 13.4 (1980), p. 583. DOI: https://doi.org/10.1088/0022-3719/13/4/016.

[9] Nussbaum. "Solid St. Phys." In: 18 (1966), pp. 165–272.

[10] P.O.Lowdin. In: *J. Chem. Phys.* 18 (1950), p. 365.

[11] Joy Sarkar, Rajat Biswas, and Suman Chatterjee. "THE ELECTRONIC BAND STRUCTURE AND DENSITY OF STATES ANALYSIS OF ELECTRON TRANSPORT MATERIALS FOR PEROVSKITE SOLAR CELLS". In: 1 (Jan. 2021).

[12] T Squire. *Orbitals shapes and sizes*. URL: https://chembam.com/definitions/orbitals/. (accessed: 16.05.2022).

10 Appendix A, Simple cubic matrix elements

10.1 Simple cubic crystal s/s orbital

$E_{s,s}(0,0,0)$	$E_{s,s}(0,0,0)$	$E_{s,s}(-1,0,-1)$	$E_{s,s}(1,1,0)$
$E_{s,s}(1,0,0)$	$E_{s,s}(1,0,0)$	$E_{s,s}(0,1,1)$	$E_{s,s}(1,1,0)$
$E_{s,s}(-1,0,0)$	$E_{s,s}(1,0,0)$	$E_{s,s}(0,-1,1)$	$E_{s,s}(1,1,0)$
$E_{s,s}(0,1,0)$	$E_{s,s}(1,0,0)$	$E_{s,s}(0,1,-1)$	$E_{s,s}(1,1,0)$
$E_{s,s}(0,-1,0)$	$E_{s,s}(1,0,0)$	$E_{s,s}(0,-1,-1)$	$E_{s,s}(1,1,0)$
$E_{s,s}(0,0,1)$	$E_{s,s}(1,0,0)$	$E_{s,s}(1,1,1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(0,0,-1)$	$E_{s,s}(1,0,0)$	$E_{s,s}(-1,1,1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(1,1,0)$	$E_{s,s}(1,1,0)$	$E_{s,s}(1,-1,1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(1,-1,0)$	$E_{s,s}(1,1,0)$	$E_{s,s}(1,1,-1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(-1,1,0)$	$E_{s,s}(1,1,0)$	$E_{s,s}(-1,1,-1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(-1,-1,0)$	$E_{s,s}(1,1,0)$	$E_{s,s}(-1,-1,1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(1,0,1)$	$E_{s,s}(1,1,0)$	$E_{s,s}(1,-1,-1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(1,0,-1)$	$E_{s,s}(1,1,0)$	$E_{s,s}(-1,-1,-1)$	$E_{s,s}(1,1,1)$
$E_{s,s}(-1,0,1)$	$E_{s,s}(1,1,0)$		

We substitute these, obtaining:

$$
\begin{gathered}
(s/s) = E_{s,s}(0,0,0) \\
+E_{s,s}(1,0,0)\left(e^{iak_x} + e^{-iak_x} + e^{iak_y} + e^{-iak_y} + e^{iak_z} + e^{-iak_z}\right) \\
+E_{s,s}(1,1,0)\Big(e^{ia\cdot(k_x+k_y)} + e^{ia\cdot(-k_x+k_y)} + e^{ia\cdot(k_x-k_y)} + e^{ia\cdot(-k_x-k_y)} + e^{ia\cdot(k_x+k_z)} \\
+e^{ia\cdot(k_x-k_z)} + e^{ia\cdot(-k_x+k_z)} + e^{ia\cdot(-k_x-k_z)} + e^{ia\cdot(k_y+k_z)} + e^{ia\cdot(k_y-k_z)} + e^{ia\cdot(-k_y+k_z)} + e^{ia\cdot(-k_y-k_z)}\Big) \\
+E_{s,s}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} + e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)} \\
+e^{ia\cdot(-k_x-k_y+k_z)} + e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\Big)
\end{gathered}
$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$
\begin{gathered}
(s/s) = E_{s,s}(0,0,0) \\
+2E_{s,s}(1,0,0)\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right) \\
+2E_{s,s}(1,1,0)\left(\cos(ak_x)e^{iak_y} + \cos(ak_x)e^{-iak_y} + \cos(ak_z)e^{iak_x}\right. \\
\left. + \cos(ak_z)e^{-iak_x} + \cos(ak_z)e^{iak_y} + \cos(ak_z)e^{-iak_y}\right) \\
+2E_{s,s}(1,1,1)\Big(\cos(ak_x)e^{ia\cdot(k_y+k_z)} + \cos(ak_x)e^{ia\cdot(-k_y+k_z)} + \cos(ak_x)e^{ia\cdot(-k_y-k_z)} + \cos(ak_x)e^{ia\cdot(k_y-k_z)}\Big)
\end{gathered}
$$

Further factoring yields:

$$(s,s) = E_{s,s}(0,0,0) + 2E_{s,s}(1,0,0)\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right)$$
$$+4E_{s,s}(1,1,0)(\cos(ak_x))\cos(ak_y) + \cos(ak_x)\cos(ak_z) + \cos(ak_y)\cos(ak_z)$$
$$+4E_{s,s}(1,1,1)(\cos(ak_x)\cos(ak_y)e^{iakz} + \cos(ak_x)\cos(ak_y)e^{-iakz})$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s,s) = E_{s,s}(0,0,0) + 2E_{s,s}(1,0,0)\left(\cos(\xi) + \cos(\eta) + \cos(\zeta)\right)$$

$$+4E_{s,s}(1,1,0)(\cos(\xi))\cos(\eta) + \cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)) + 8E_{s,s}(1,1,1)(\cos(\xi)\cos(\eta)\cos(\zeta)$$

10.2 Simple cubic crystal s/x orbital

$E_{s,x}(0,0,0)$	0	$E_{s,x}(-1,0,-1)$	$-E_{s,x}(1,1,0)$
$E_{s,x}(1,0,0)$	$E_{s,x}(1,0,0)$	$E_{s,x}(0,1,1)$	0
$E_{s,x}(-1,0,0)$	$-E_{s,x}(1,0,0)$	$E_{s,x}(0,-1,1)$	0
$E_{s,x}(0,1,0)$	0	$E_{s,x}(0,1,-1)$	0
$E_{s,x}(0,-1,0)$	0	$E_{s,x}(0,-1,-1)$	0
$E_{s,x}(0,0,1)$	0	$E_{s,x}(1,1,1)$	$E_{s,x}(1,1,1$
$E_{s,x}(0,0,-1)$	0	$E_{s,x}(-1,1,1)$	$-E_{s,x}(1,1,1)$
$E_{s,x}(1,1,0)$	$E_{s,x}(1,1,0)$	$E_{s,x}(1,-1,1)$	$E_{s,x}(1,1,1)$
$E_{s,x}(1,-1,0)$	$E_{s,x}(1,1,0)$	$E_{s,x}(1,1,-1)$	$E_{s,x}(1,1,1)$
$E_{s,x}(-1,1,0)$	$-E_{s,x}(1,1,0)$	$E_{s,x}(-1,1,-1)$	$-E_{s,x}(1,1,1)$
$E_{s,x}(-1,-1,0)$	$-E_{s,x}(1,1,0)$	$E_{s,x}(-1,-1,1)$	$-E_{s,x}(1,1,1)$
$E_{s,x}(1,0,1)$	$E_{s,x}(1,1,0)$	$E_{s,x}(1,-1,-1)$	$E_{s,x}(1,1,1)$
$E_{s,x}(1,0,-1)$	$E_{s,x}(1,1,0)$	$E_{s,x}(-1,-1,-1)$	$-E_{s,x}(1,1,1)$
$E_{s,x}(-1,0,1)$	$-E_{s,x}(1,1,0)$		

We substitute these, obtaining:

$$(s/x) = E_{s,x}(1,0,0)\left(e^{iak_x} - e^{-iak_x}\right)$$

$$+E_{s,x}(1,1,0)\Big(e^{ia\cdot(k_x+k_y)} - e^{ia\cdot(-k_x+k_y)} + e^{ia\cdot(k_x-k_y)} - e^{ia\cdot(-k_x-k_y)} + e^{ia\cdot(k_x+k_z)}$$

$$-e^{ia\cdot(k_x-k_z)} + e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(-k_x-k_z)} + e^{ia\cdot(k_y+k_z)} - e^{ia\cdot(k_y-k_z)} + e^{ia\cdot(-k_y+k_z)} - e^{ia\cdot(-k_y-k_z)}\Big)$$

$$+E_{s,x}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}$$

$$-e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} - e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of sines:

$$(s/x) = 2iE_{s,x}(1,0,0)\sin(ak_x)$$

$$+2iE_{s,x}(1,1,0)\left(\sin(ak_x)e^{iak_y} + \sin(ak_x)e^{-iak_y} + \cos(ak_z)e^{iak_x} - \cos(ak_z)e^{-iak_x}\right)$$

$$+2iE_{s,x}(1,1,1)\Big(\sin(ak_x)e^{ia\cdot(k_y+k_z)} + \sin(ak_x)e^{ia\cdot(-k_y+k_z)} + \sin(ak_x)e^{ia\cdot(-k_y-k_z)} + \sin(ak_x)e^{ia\cdot(k_y-k_z)}\Big)$$

Further factoring yields:

$$(s/x) = 2iE_{s,x}(1,0,0)\sin(ak_x)$$

$$+4iE_{s,x}(1,1,0)\left(\sin(ak_x)\cos(ak_y) + \cos(ak_z)\sin(ak_x)\right)$$

$$+4iE_{s,x}(1,1,1)\left(\sin(ak_x)\sin(ak_y)e^{iak_z} + \sin(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s/x) = 2iE_{s,x}(1,0,0)\sin(\xi) + 4iE_{s,y}(1,1,0)\left(\sin(\xi)\cos(\eta) + \sin(\xi)\cos(\zeta)\right) + 8iE_{s,x}(1,1,1)(\sin(\xi)\cos(\eta)\cos(\zeta)$$

10.3 Simple cubic crystal s/xy orbital

$E_{s,xy}(0,0,0)$	0	$E_{s,xy}(-1,0,-1)$	0
$E_{s,xy}(1,0,0)$	0	$E_{s,xy}(0,1,1)$	0
$E_{s,xy}(-1,0,0)$	0	$E_{s,xy}(0,-1,1)$	0
$E_{s,xy}(0,1,0)$	0	$E_{s,xy}(0,1,-1)$	0
$E_{s,xy}(0,-1,0)$	0	$E_{s,xy}(0,-1,-1)$	0
$E_{s,xy}(0,0,1)$	0	$E_{s,xy}(1,1,1)$	$E_{s,xy}(1,1,0)$
$E_{s,xy}(0,0,-1)$	0	$E_{s,xy}(-1,1,1)$	$E_{s,xy}(1,1,0)$
$E_{s,xy}(1,1,0)$	$E_{s,xy}(1,1,0)$	$E_{s,xy}(1,-1,1)$	$-E_{s,xy}(1,1,1)$
$E_{s,xy}(1,-1,0)$	$-E_{s,xy}(1,1,0)$	$E_{s,xy}(1,1,-1)$	$E_{s,xy}(1,1,1)$
$E_{s,xy}(-1,1,0)$	$-E_{s,xy}(1,1,0)$	$E_{s,xy}(-1,1,-1)$	$E_{s,xy}(1,1,1)$
$E_{s,xy}(-1,-1,0)$	$E_{s,xy}(1,1,0)$	$E_{s,xy}(-1,-1,1)$	$-E_{s,xy}(1,1,1)$
$E_{s,xy}(1,0,1)$	0	$E_{s,xy}(1,-1,-1)$	$-E_{s,xy}(1,1,1)$
$E_{s,xy}(1,0,-1)$	0	$E_{s,xy}(-1,-1,-1)$	$-E_{s,xy}(1,1,1)$
$E_{s,xy}(-1,0,1)$	0		

We substitute these, obtaining:

$$(s/xy) = E_{s,xy}(1,1,0)\left(e^{ia\cdot(k_x+k_y)} - e^{ia\cdot(-k_x+k_y)} - e^{ia\cdot(k_x-k_y)} + e^{ia\cdot(-k_x-k_y)}\right)$$

$$+E_{s,xy}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} - e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}\right.$$

$$\left.+e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} - e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of sines:

$$(s/xy) = 2iE_{s,xy}(1,1,0)\left(\sin(ak_x)e^{iak_y} - \sin(ak_x)e^{-iak_y}\right)$$

$$+2iE_{s,y}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)} - \sin(k_x)e^{ia\cdot(-k_y+k_z)} + \sin(ak_x)e^{ia\cdot(k_y-k_z)} - \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(s/xy) = -4E_{s,xy}(1,1,0)\sin(ak_x)\sin(ak_y) - 4E_{s,y}(1,1,1)\left(\sin(ak_x)\sin(ak_y)e^{iak_z} + \sin(ak_x)\sin(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s/xy) = -4E_{s,xy}(1,1,0)\sin(\xi)\sin(\eta) - 8E_{s,y}(1,1,1)\left(\sin(\xi)\sin(\eta)\cos(\zeta)\right)$$

10.4 Simple cubic crystal s/$x^2 - y^2$ orbital

$E_{s,x^2-y^2}(0,0,0)$	0	$E_{s,x^2-y^2}(-1,0,-1)$	$-E_{s,x^2-y^2}(0,1,1)$
$E_{s,x^2-y^2}(1,0,0)$	$E_{s,x^2-y^2}(1,0,0)$	$E_{s,x^2-y^2}(0,1,1)$	$E_{s,x^2-y^2}(0,1,1)$
$E_{s,x^2-y^2}(-1,0,0)$	$E_{s,x^2-y^2}(1,0,0)$	$E_{s,x^2-y^2}(0,-1,1)$	$E_{s,x^2-y^2}(0,1,1)$
$E_{s,x^2-y^2}(0,1,0)$	$-E_{s,x^2-y^2}(1,0,0)$	$E_{s,x^2-y^2}(0,-1,-1)$	$E_{s,x^2-y^2}(0,1,1)$
$E_{s,x^2-y^2}(0,-1,0)$	$-E_{s,x^2-y^2}(1,0,0)$	$E_{s,x^2-y^2}(0,1,-1)$	$E_{s,x^2-y^2}(0,1,1)$
$E_{s,x^2-y^2}(0,0,1)$	0	$E_{s,x^2-y^2}(1,1,1)$	0
$E_{s,x^2-y^2}(0,0,-1)$	0	$E_{s,x^2-y^2}(-1,1,1)$	0
$E_{s,x^2-y^2}(1,1,0)$	0	$E_{s,x^2-y^2}(1,-1,1)$	0
$E_{s,x^2-y^2}(1,-1,0)$	0	$E_{s,x^2-y^2}(1,1,-1)$	0
$E_{s,x^2-y^2}(-1,1,0)$	0	$E_{s,x^2-y^2}(-1,1,-1)$	0
$E_{s,x^2-y^2}(-1,-1,0)$	0	$E_{s,x^2-y^2}(-1,-1,1)$	0
$E_{s,x^2-y^2}(1,0,1)$	$-E_{s,x^2-y^2}(0,1,1)$	$E_{s,x^2-y^2}(1,-1,-1)$	0
$E_{s,x^2-y^2}(1,0,-1)$	$-E_{s,x^2-y^2}(0,1,1)$	$E_{s,x^2-y^2}(-1,-1,-1)$	0
$E_{s,x^2-y^2}(-1,0,1)$	$-E_{s,x^2-y^2}(0,1,1)$		

We substitute these, obtaining:

$$(s/x^2 - y^2) = E_{s,x^2-y^2}(1,0,0)\left(e^{iak_x} + e^{-iak_x} - e^{iak_y} - e^{-iak_y}\right)$$

$$+E_{s,x^2-y^2}(0,1,1)\Big(-e^{ia\cdot(k_x+k_z)} - e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(k_x-k_z)} - e^{ia\cdot(-k_x-k_z)}$$

$$+e^{ia\cdot(k_y+k_z)} + e^{ia\cdot(-k_y+k_z)} + e^{ia\cdot(k_y-k_z)} + e^{ia\cdot(-k_y-k_z)}\Big)$$

Factorizing gives us:

$$(s/x^2 - y^2) = 2E_{s,x^2-y^2}(1,0,0)\left(\cos(ak_x) - \cos(ak_y)\right)$$

$$+2E_{s,x^2-y^2}(0,1,1)\left(-\cos(ak_x)e^{iak_z} - \cos(ak_x)e^{-iak_z} + \cos(ak_y)e^{iak_z} + \cos(ak_y)e^{-iak_z}\right)$$

Further factorizing:

$$(s/x^2 - y^2) = 2E_{s,x^2-y^2}(1,0,0)\left(\cos(ak_x) - \cos(ak_y)\right)$$

$$+4E_{s,x^2-y^2}(0,1,1)\left(-\cos(ak_x)\cos(ak_z) + \cos(ak_y)\cos(ak_z)\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s/x^2 - y^2) = 2E_{s,x^2-y^2}(1,0,0)\left(\cos(\xi) - \cos(\eta)\right) + 4E_{s,x^2-y^2}(0,1,1)\left(-\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right)$$

We can find using Slater Koster table I two relations that will reduce the parameters further: $2E_{s,x^2-y^2}(1,0,0) = \sqrt{3}2E_{s,3z^2-r^2}(0,0,1)$ and $4E_{s,x^2-y^2}(0,1,1) = 2\sqrt{3}E_{s,3z^2-r^2}(1,1,0)$ giving us the final result:

$$(s/x^2 - y^2) = \sqrt{3}E_{s,x^2-y^2}(1,0,0)\left(\cos(\xi) - \cos(\eta)\right) + 2\sqrt{3}E_{s,3z^2-r^2}(0,1,1)\left(-\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right)$$

10.5 Simple cubic crystal s/$3z^2-r^2$ orbital

$E_{s,3z^2-r^2}(0,0,0)$	0	$E_{x,x}(-1,0,-1)$	$E_{s,3z^2-r^2}(1,0,1)$
$E_{s,3z^2-r^2}(1,0,0)$	$E_{s,3z^2-r^2}(1,0,0)$	$E_{s,3z^2-r^2}(0,1,1)$	$E_{s,3z^2-r^2}(1,0,1)$
$E_{s,3z^2-r^2}(-1,0,0)$	$E_{s,3z^2-r^2}(1,0,0)$	$E_{s,3z^2-r^2}(0,-1,1)$	$E_{s,3z^2-r^2}(1,0,1)$
$E_{s,3z^2-r^2}(0,1,0)$	$E_{s,3z^2-r^2}(1,0,0)$	$E_{s,3z^2-r^2}(0,1,-1)$	$E_{s,3z^2-r^2}(1,0,1)$
$E_{s,3z^2-r^2}(0,-1,0)$	$E_{s,3z^2-r^2}(1,0,0)$	$E_{s,3z^2-r^2}(0,-1,-1)$	$E_{s,3z^2-r^2}(1,0,1)$
$E_{s,3z^2-r^2}(0,0,1)$	$E_{s,3z^2-r^2}(0,0,1)$	$E_{s,3z^2-r^2}(1,1,1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(0,0,-1)$	$E_{s,3z^2-r^2}(0,0,1)$	$E_{s,3z^2-r^2}(-1,1,1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(1,1,0)$	$E_{s,3z^2-r^2}(1,1,0)$	$E_{s,3z^2-r^2}(1,-1,1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(1,-1,0)$	$E_{s,3z^2-r^2}(1,1,0)$	$E_{s,3z^2-r^2}(1,1,-1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(-1,1,0)$	$E_{s,3z^2-r^2}(1,1,0)$	$E_{s,3z^2-r^2}(-1,1,-1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(-1,-1,0)$	$E_{s,3z^2-r^2}(1,1,0)$	$E_{s,3z^2-r^2}(-1,-1,1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(1,0,1)$	$E_{s,3z^2-r^2}(1,0,1)$	$E_{s,3z^2-r^2}(1,-1,-1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(1,0,-1)$	$E_{s,3z^2-r^2}(1,0,1)$	$E_{s,3z^2-r^2}(-1,-1,-1)$	$E_{s,3z^2-r^2}(1,1,1)$
$E_{s,3z^2-r^2}(-1,0,1)$	$E_{s,3z^2-r^2}(1,0,1)$		

We substitute these, obtaining:

$$(s/3z^2-r^2) = E_{s,3z^2-r^2}(1,0,0)\left(e^{iak_x}+e^{-iak_x}+e^{iak_y}+e^{-iak_y}\right)+E_{s,3z^2-r^2}(0,0,1)\left(e^{iak_z}+e^{-iak_z}\right)$$
$$+E_{s,3z^2-r^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)}+e^{ia\cdot(k_x-k_y)}+e^{ia\cdot(-k_x+k_y)}+e^{ia\cdot(-k_x-k_y)}\right)$$
$$+E_{s,3z^2-r^2}(1,0,1)\Big(e^{ia\cdot(k_x+k_z)}-e^{ia\cdot(k_x-k_z)}+e^{ia\cdot(-k_x+k_z)}-e^{ia\cdot(-k_x-k_z)}$$
$$e^{ia\cdot(k_y+k_z)}+e^{ia\cdot(-k_y+k_z)}+e^{ia\cdot(k_y-k_z)}+e^{ia\cdot(-k_y-k_z)}\Big)$$
$$+E_{s,3z^2-r^2}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)}+e^{ia\cdot(-k_x+k_y+k_z)}+e^{ia\cdot(k_x-k_y+k_z)}+e^{ia\cdot(k_x+k_y-k_z)}$$
$$+e^{ia\cdot(-k_x+k_y-k_z)}+e^{ia\cdot(-k_x-k_y+k_z)}+e^{ia\cdot(k_x-k_y-k_z)}+e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

Factorizing:

$$(s/3z^2-r^2) = 2E_{s,3z^2-r^2}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)\right)+2E_{s,3z^2-r^2}(0,0,1)\cos(ak_z)$$
$$+2E_{s,3z^2-r^2}(1,1,0)\left(\cos(ak_y)e^{iak_x}+\cos(ak_y)e^{-iak_x}\right)$$
$$+2E_{s,3z^2-r^2}(1,0,1)\left(\cos(ak_z)e^{iak_x}+\cos(ak_z)e^{-iak_x}+\cos(ak_y)e^{iak_z}+\cos(ak_y)e^{-iak_z}\right)$$
$$+2E_{s,3z^2-r^2}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)}+\cos(ak_x)e^{ia\cdot(-k_y+k_z)}+\cos(ak_x)e^{ia\cdot(k_y-k_z)}+\cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factorizing:

$$(s/3z^2-r^2) = 2E_{s,3z^2-r^2}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)\right)+2E_{s,3z^2-r^2}(0,0,1)\cos(ak_z)$$
$$4E_{s,3z^2-r^2}(1,1,0)\cos(ak_x)\cos(ak_y)+4E_{s,3z^2-r^2}(1,0,1)\left(\cos(ak_x)\cos(ak_z)+\cos(ak_y)\cos(ak_z)\right)$$
$$+4E_{s,3z^2-r^2}(1,1,1)\left(\cos(ak_x)\cos(ak_y)e^{iak_z}+\cos(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

We now use Slater Koster table 1 to find the following relations: $2E_{s,3z^2-r^2}(1,0,0)=-E_{s,3z^2-r^2}(0,0,1)$, $4E_{s,3z^2-r^2}(1,0,1)=-2E_{s,3z^2-r^2}(1,1,0)$, and $4E_{s,3z^2-r^2}(1,1,1)=0$ We substitute these, preform a Final factorization and substitute $ak_x=\xi$, $ak_y=\eta$, and $ak_z=\zeta$ (standard literature form):

$$(s/3z^2-r^2) = E_{s,3z^2-r^2}(0,0,1)\left(-\cos(\xi)-\cos(\eta)+2\cos(\zeta)\right)$$
$$-2E_{s,3z^2-r^2}(1,1,0)\left(-2\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

10.6 Simple cubic crystal x/x orbital

$E_{x,x}(0,0,0)$	$E_{x,x}(0,0,0)$	$E_{x,x}(-1,0,-1)$	$E_{x,x}(1,1,0)$
$E_{x,x}(1,0,0)$	$E_{x,x}(1,0,0)$	$E_{x,x}(0,1,1)$	$E_{x,x}(0,1,1)$
$E_{x,x}(-1,0,0)$	$E_{x,x}(1,0,0)$	$E_{x,x}(0,-1,1)$	$E_{x,x}(0,1,1)$
$E_{x,x}(0,1,0)$	$E_{y,y}(1,0,0)$	$E_{x,x}(0,1,-1)$	$E_{x,x}(0,1,1)$
$E_{x,x}(0,-1,0)$	$E_{y,y}(1,0,0)$	$E_{x,x}(0,-1,-1)$	$E_{x,x}(0,1,1)$
$E_{x,x}(0,0,1)$	$E_{y,y}(1,0,0)$	$E_{x,x}(1,1,1)$	$E_{x,x}(1,1,0)$
$E_{x,x}(0,0,-1)$	$E_{y,y}(1,0,0)$	$E_{x,x}(-1,1,1)$	$-E_{x,x}(1,1,0)$
$E_{x,x}(1,1,0)$	$E_{x,x}(1,1,0)$	$E_{x,x}(1,-1,1)$	$E_{x,x}(1,1,1)$
$E_{x,x}(1,-1,0)$	$E_{x,x}(1,1,0)$	$E_{x,x}(1,1,-1)$	$E_{x,x}(1,1,1)$
$E_{x,x}(-1,1,0)$	$E_{x,x}(1,1,0)$	$E_{x,x}(-1,1,-1)$	$-E_{x,x}(1,1,1)$
$E_{x,x}(-1,-1,0)$	$E_{x,x}(1,1,0)$	$E_{x,x}(-1,-1,1)$	$-E_{x,x}(1,1,1)$
$E_{x,x}(1,0,1)$	$E_{x,x}(1,1,0)$	$E_{x,x}(1,-1,-1)$	$E_{x,x}(1,1,1)$
$E_{x,x}(1,0,-1)$	$E_{x,x}(1,1,0)$	$E_{x,x}(-1,-1,-1)$	$-E_{x,x}(1,1,1)$
$E_{x,x}(-1,0,1)$	$E_{x,x}(1,1,0)$		

We substitute these, obtaining:

$$(x/x) = E_{x,x}(0,0,0) + E_{x,x}(1,0,0)\left(e^{iak_x} + e^{-iak_x}\right)$$

$$+E_{y,y}(1,0,0)\left(e^{iak_y} + e^{-iak_y} + e^{iak_z} + e^{-iak_z}\right)$$

$$+E_{x,x}(1,1,0)\Big(e^{ia\cdot(k_x+k_y)} + e^{ia\cdot(-k_x+k_y)} + e^{ia\cdot(k_x-k_y)} + e^{ia\cdot(-k_x-k_y)}$$

$$+ e^{ia\cdot(k_x+k_z)} + e^{ia\cdot(-k_x+k_z)} + e^{ia\cdot(k_x-k_z)} + e^{ia\cdot(-k_x-k_z)}\Big)$$

$$+E_{x,x}(0,1,1)\left(e^{ia\cdot(k_y+k_z)} + e^{ia\cdot(-k_y+k_z)} + e^{ia\cdot(k_y-k_z)} + e^{ia\cdot(-k_y-k_z)}\right)$$

$$+E_{x,x}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} + e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}$$

$$+e^{ia\cdot(-k_x-k_y+k_z)} + e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

Factorizing out exponentials and insertion the exponential forms of (co)sines:

$$(x/x) = E_{x,x}(0,0,0) + 2E_{x,x}(1,0,0)\cos(ak_x)$$

$$+2E_{y,y}(1,0,0)\left(\cos(ak_y) + \cos(ak_z)\right)$$

$$+2E_{x,x}(1,1,0)\left(\cos(ak_x)e^{ak_y} + \cos(ak_x)e^{-ak_y} + \cos(ak_x)e^{ak_z} + \cos(ak_x)e^{-ak_z}\right)$$

$$+2E_{x,x}(0,1,1)\left(\cos(ak_y)e^{iak_z} + \cos(ak_y)e^{-iak_z}\right)$$

$$+2E_{x,x}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)} + \cos(ak_x)e^{ia\cdot(-k_y+k_z)} + \cos(ak_x)e^{ia\cdot(k_y-k_z)} + \cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Factorizing further:

$$
\begin{aligned}
(x/x) = E_{x,x}(0,0,0) + 2E_{x,x}(1,0,0)\cos(ak_x) \\
+2E_{y,y}(1,0,0)\left(\cos(ak_y) + \cos(ak_z)\right) \\
+2E_{x,x}(1,1,0)\left(\cos(ak_x)\cos(ak_y) + \cos(ak_x)\cos(ak_z)\right) \\
+2E_{x,x}(0,1,1)\cos(ak_y)\cos(ak_z) \\
+4E_{x,x}(1,1,1)\left(\cos(ak_x)\cos(ak_y)e^{iak_z} + \cos(ak_x)\cos(ak_y)e^{-iak_z}\right)
\end{aligned}
$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$
\begin{aligned}
(x/x) = E_{x,x}(0,0,0) + 2E_{x,x}(1,0,0)\cos(\xi) + 2E_{y,y}(1,0,0)\left(\cos(\eta) + \cos(\zeta)\right) \\
+4E_{x,x}(1,1,0)\left(\cos(\xi)\cos(\eta) + \cos(\xi)\cos(\zeta)\right) + 4E_{x,x}(0,1,1)\cos(\eta)\cos(\zeta) \\
+8E_{x,x}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)
\end{aligned}
$$

10.7 Simple cubic crystal x/y orbital

$E_{x,y}(0,0,0)$	0	$E_{x,y}(-1,0,-1)$	0
$E_{x,y}(1,0,0)$	0	$E_{x,y}(0,1,1)$	0
$E_{x,y}(-1,0,0)$	0	$E_{x,y}(0,-1,1)$	0
$E_{x,y}(0,1,0)$	0	$E_{x,y}(0,1,-1)$	0
$E_{x,y}(0,-1,0)$	0	$E_{x,y}(0,-1,-1)$	0
$E_{x,y}(0,0,1)$	0	$E_{x,y}(1,1,1)$	$E_{x,y}(1,1,1)$
$E_{x,y}(0,0,-1)$	0	$E_{x,y}(-1,1,1)$	$-E_{x,y}(1,1,1)$
$E_{x,y}(1,1,0)$	$E_{x,y}(1,1,0)$	$E_{x,y}(1,-1,1)$	$-E_{x,y}(1,1,1)$
$E_{x,y}(1,-1,0)$	$-E_{x,y}(1,1,0)$	$E_{x,y}(1,1,-1)$	$E_{x,y}(1,1,1)$
$E_{x,y}(-1,1,0)$	$-E_{x,y}(1,1,0)$	$E_{x,y}(-1,1,-1)$	$-E_{x,y}(1,1,1)$
$E_{x,y}(-1,-1,0)$	$E_{x,y}(1,1,0)$	$E_{x,y}(-1,-1,1)$	$-E_{x,y}(1,1,1)$
$E_{x,y}(1,0,1)$	0	$E_{x,y}(1,-1,-1)$	$-E_{x,y}(1,1,1)$
$E_{x,y}(1,0,-1)$	0	$E_{x,y}(-1,-1,-1)$	$-E_{x,y}(1,1,1)$
$E_{x,y}(-1,0,1)$	0		

We substitute these, obtaining:

$$(x/y) = E_{x,y}(110)\left(e^{ia(k_x+k_y)} - e^{ia(k_x-k_y)} - e^{ia(-k_x+k_y)} + e^{ia(-k_x-k_y)}\right)$$

$$E_{x,y}(111)\left(e^{ia(k_x+k_y+k_z)} - e^{ia(-k_x+k_y+k_z)} - e^{ia(k_x-k_y+k_z)} + e^{ia(k_x+k_y-k_z)}\right.$$

$$\left.-e^{ia(-k_x+k_y-k_z)} - e^{ia(-k_x-k_y+k_z)} - e^{ia(k_x-k_y-k_z)} - e^{ia(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x/y) = 2iE_{x,y}(110)\left(\sin(ak_y)e^{iak_x} - \sin(ak_y)e^{-iak_x}\right)$$

$$2iE_{x,y}(111)\left(\sin(ak_x)e^{ia(k_y+k_z)} - \sin(ak_x)e^{ia(-k_y+k_z)} + \sin(ak_x)e^{ia(k_y-k_z)} - \sin(ak_x)e^{ia(-k_y-k_z)}\right)$$

Further factoring yields:

$$(x/y) = -4E_{x,y}(110)\sin(ak_x)\sin(ak_y)$$

$$-4E_{x,y}(111)\left(\sin(ak_x)\sin(ak_y)e^{iak_z} + \sin(ak_x)\sin(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x/y) = -4E_{x,y}(110)\sin(\xi)\sin(\eta) - 8E_{x,y}(111)\sin(\xi)\sin(\eta)\cos(\zeta)$$

10.8 Simple cubic crystal x/xy orbital

$E_{x,xy}(0,0,0)$	0	$E_{x,xy}(-1,0,-1)$	0
$E_{x,xy}(1,0,0)$	0	$E_{x,xy}(0,1,1)$	$E_{x,xy}(0,1,1)$
$E_{x,xy}(-1,0,0)$	0	$E_{x,xy}(0,-1,1)$	$-E_{x,xy}(0,1,1)$
$E_{x,xy}(0,1,0)$	$E_{x,xy}(0,1,0)$	$E_{x,xy}(0,1,-1)$	$E_{x,xy}(0,1,1)$
$E_{x,xy}(0,-1,0)$	$-E_{x,xy}(0,1,0)$	$E_{x,xy}(0,-1,-1)$	$-E_{x,xy}(0,1,1)$
$E_{x,xy}(0,0,1)$	0	$E_{x,xy}(1,1,1)$	$E_{x,xy}(1,1,1)$
$E_{x,xy}(0,0,-1)$	0	$E_{x,xy}(-1,1,1)$	$E_{x,xy}(1,1,1)$
$E_{x,xy}(1,1,0)$	$E_{x,xy}(1,1,0)$	$E_{x,xy}(1,-1,1)$	$E_{x,xy}(1,1,1)$
$E_{x,xy}(1,-1,0)$	$-E_{x,xy}(1,1,0)$	$E_{x,xy}(1,1,-1)$	$E_{x,xy}(1,1,1)$
$E_{x,xy}(-1,1,0)$	$E_{x,xy}(1,1,0)$	$E_{x,xy}(-1,1,-1)$	$-E_{x,xy}(1,1,1)$
$E_{x,xy}(-1,-1,0)$	$-E_{x,xy}(1,1,0)$	$E_{x,xy}(-1,-1,1)$	$-E_{x,xy}(1,1,1)$
$E_{x,xy}(1,0,1)$	0	$E_{x,xy}(1,-1,-1)$	$-E_{x,xy}(1,1,1)$
$E_{x,xy}(1,0,-1)$	0	$E_{x,xy}(-1,-1,-1)$	$-E_{x,xy}(1,1,1)$
$E_{x,xy}(-1,0,1)$	0		

We substitute these, obtaining:

$$(x/xy) = E_{x,xy}(0,1,0)\left(e^{iak_y} - e^{-iak_y}\right)$$

$$+E_{x,xy}(1,1,0)\left(e^{ia\cdot(k_x+k_y)} - e^{ia\cdot(k_x-k_y)} + e^{ia\cdot(-k_x+k_y)} - e^{ia\cdot(-k_x-k_y)}\right)$$

$$+E_{x,xy}(0,1,1)\left(e^{ia\cdot(k_y+k_z)} - e^{ia\cdot(-k_y+k_z)} + e^{ia\cdot(k_y-k_z)} - e^{ia\cdot(-k_y-k_z)}\right)$$

$$+E_{x,xy}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)} + e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}\right.$$

$$\left.-e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} - e^{ia\cdot(k_x-k_y-k_z)} - e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x/xy) = 2iE_{x,xy}(0,1,0)\sin(ak_y)$$

$$+2iE_{x,xy}(1,1,0)\left(\sin(ak_y)e^{iak_x} + \sin(ak_y)e^{-iak_x}\right) + 2iE_{x,xy}(0,1,1)\left(\sin(ak_y)e^{iak_z} + \sin(ak_y)e^{-iak_z}\right)$$

$$+2E_{x,xy}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)} - \cos(ak_x)e^{ia\cdot(-k_y+k_z)} + \cos(ak_x)e^{ia\cdot(k_y-k_z)} - \cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(x/xy) = 2iE_{x,xy}(0,1,0)\sin(ak_y) + 4iE_{x,xy}(1,1,0)\cos(ak_x)\sin(ak_y) + 2iE_{x,xy}(0,1,1)\sin(ak_y)\cos(ak_z)$$

$$+4iE_{x,xy}(1,1,1)\left(\cos(ak_x)\sin(ak_y)e^{iak_z} + \cos(ak_x)\sin(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x/xy) = 2iE_{x,xy}(0,1,0)\sin(\eta) + 4iE_{x,xy}(1,1,0)\cos(\xi)\sin(ak_y) + 4iE_{x,xy}(0,1,1)\sin(\eta)\cos(\zeta)$$

$$+8iE_{x,xy}(1,1,1)\cos(\xi)\sin(\eta)\cos(\zeta)$$

10.9 Simple cubic crystal x/yz orbital

$E_{x,yz}(0,0,0)$	0	$E_{x,yz}(-1,0,-1)$	0
$E_{x,yz}(1,0,0)$	0	$E_{x,yz}(0,1,-1)$	0
$E_{x,yz}(-1,0,0)$	0	$E_{x,yz}(0,-1,1)$	0
$E_{x,yz}(0,1,0)$	0	$E_{x,yz}(0,1,-1)$	0
$E_{x,yz}(0,-1,0)$	0	$E_{x,yz}(0,-1,-1)$	0
$E_{x,yz}(0,0,1)$	0	$E_{x,yz}(1,1,1)$	$E_{x,yz}(1,1,1)$
$E_{x,yz}(0,0,-1)$	0	$E_{x,yz}(-1,1,1)$	$-E_{x,yz}(1,1,1)$
$E_{x,yz}(1,1,0)$	0	$E_{x,yz}(1,-1,1)$	$-E_{x,yz}(1,1,1)$
$E_{x,yz}(1,-1,0)$	0	$E_{x,yz}(1,1,-1)$	$-E_{x,yz}(1,1,1)$
$E_{x,yz}(-1,1,0)$	0	$E_{x,yz}(-1,1,-1)$	$E_{x,yz}(1,1,1)$
$E_{x,yz}(-1,-1,0)$	0	$E_{x,yz}(-1,-1,1)$	$E_{x,yz}(1,1,1)$
$E_{x,yz}(1,0,1)$	0	$E_{x,yz}(1,-1,-1)$	$E_{x,yz}(1,1,1)$
$E_{x,yz}(1,0,-1)$	0	$E_{x,yz}(-1,-1,-1)$	$-E_{x,yz}(1,1,1)$
$E_{x,yz}(-1,0,1)$	0		

We substitute these, obtaining:

$$(x/yz) = E_{x,yz}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} - e^{ia\cdot(k_x-k_y+k_z)} - e^{ia\cdot(k_x+k_y-k_z)}$$

$$+e^{ia\cdot(-k_x-k_y+k_z)} + e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} - e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x/yz) = 2iE_{x,yz}(1,1,1)\Big(\sin(ak_x)e^{ia\cdot(k_y+k_z)} - \sin(ak_x)e^{ia\cdot(-k_y+k_z)}$$

$$-\sin(ak_x)e^{ia\cdot(k_y-k_z)} + \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\Big)$$

Further factoring yields:

$$(x/yz) = -4E_{x,yz}(1,1,1)\left(\sin(ak_x)\sin(ak_y)e^{iak_z} - \sin(ak_x)\sin(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x/yz) = -8iE_{x,yz}(1,1,1)\sin(\xi)\sin(\eta)\sin(\zeta)$$

10.10 Simple cubic crystal x/$x^2 - y^2$ orbital

$E_{x,x^2-y^2}(0,0,0)$	0	$E_{x,x^2-y^2}(-1,0,-1)$	$-E_{x,x^2-y^2}(1,0,1)$
$E_{x,x^2-y^2}(1,0,0)$	$E_{x,x^2-y^2}(1,0,0)$	$E_{x,x^2-y^2}(0,1,-1)$	0
$E_{x,x^2-y^2}(-1,0,0)$	$-E_{x,x^2-y^2}(1,0,0)$	$E_{x,x^2-y^2}(0,-1,1)$	0
$E_{x,x^2-y^2}(0,1,0)$	0	$E_{x,x^2-y^2}(0,-1,-1)$	0
$E_{x,x^2-y^2}(0,-1,0)$	0	$E_{x,x^2-y^2}(0,1,-1)$	0
$E_{x,x^2-y^2}(0,0,1)$	0	$E_{x,x^2-y^2}(1,1,1)$	$E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(0,0,-1)$	0	$E_{x,x^2-y^2}(-1,1,1)$	$-E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(1,1,0)$	$E_{x,x^2-y^2}(1,1,0)$	$E_{x,x^2-y^2}(1,-1,1)$	$E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(1,-1,0)$	$E_{x,x^2-y^2}(1,1,0)$	$E_{x,x^2-y^2}(1,1,-1)$	$E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(-1,1,0)$	$-E_{x,x^2-y^2}(1,1,0)$	$E_{x,x^2-y^2}(-1,1,-1)$	$-E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(-1,-1,0)$	$-E_{x,x^2-y^2}(1,1,0)$	$E_{x,x^2-y^2}(-1,-1,1)$	$E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(1,0,1)$	$E_{x,x^2-y^2}(1,0,1)$	$E_{x,x^2-y^2}(1,-1,-1)$	$E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(1,0,-1)$	$E_{x,x^2-y^2}(1,0,1)$	$E_{x,x^2-y^2}(-1,-1,-1)$	$E_{x,x^2-y^2}(1,1,1)$
$E_{x,x^2-y^2}(-1,0,1)$	$-E_{x,x^2-y^2}(1,0,1)$		

We substitute these, obtaining:

$$(x/x^2-y^2) = E_{x,x^2-y^2}(1,0,0)\left(e^{iak_x} - e^{-iak_x}\right)$$

$$+E_{x,x^2-y^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)} - e^{ia\cdot(-k_x+k_y)} + e^{ia\cdot(k_x-k_y)} - e^{ia\cdot(-k_x-k_y)}\right)$$

$$+E_{x,x^2-y^2}(1,0,1)\left(e^{ia\cdot(k_x+k_z)} - e^{ia\cdot(-k_x+k_z)} + e^{ia\cdot(k_x-k_z)} - e^{ia\cdot(-k_x-k_z)}\right)$$

$$E_{x,x^2-y^2}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}\right.$$

$$\left.+e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x/x^2-y^2) = 2iE_{x,x^2-y^2}(1,0,0)\sin(ak_x) + 2iE_{x,x^2-y^2}(1,1,0)\left(\sin(ak_x)e^{iak_y} + \sin(ak_x)e^{-iak_y}\right)$$

$$+E_{x,x^2-y^2}(1,1,0)\left(\sin(ak_x)e^{iak_z} + \sin(ak_x)e^{-iak_z}\right)$$

$$+2iE_{x,x^2-y^2}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)} + \sin(ak_x)e^{ia\cdot(-k_y+k_z)} + \sin(ak_x)e^{ia\cdot(k_y-k_z)} + \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(x/x^2-y^2) = 2iE_{x,x^2-y^2}(1,0,0)\sin(ak_x) + 4iE_{x,x^2-y^2}(1,1,0)\sin(ak_x)\cos(ak_y)$$

$$+4iE_{x,x^2-y^2}(1,0,1)\sin(ak_x)\cos(ak_z) + 4iE_{x,x^2-y^2}(1,1,1)\left(\sin(ak_x)\cos(ak_y)e^{iak_z} + \sin(ak_x)\sin(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x/x^2-y^2) = 2iE_{x,x^2-y^2}(1,0,0)\sin(\xi) + 4iE_{x,x^2-y^2}(1,1,0)\sin(\xi)\cos(\eta)$$

$$+4iE_{x,x^2-y^2}(1,0,1)\sin(\xi)\cos(\zeta) + 8iE_{x,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$$

Using Slater Koster table 1 we can find the following relations:

$$2iE_{x,x^2-y^2}(1,0,0) = \sqrt{3}iE_{z,3z^2-r^2}(0,0,1)$$

$$4iE_{x,x^2-y^2}(1,1,0) = 2\sqrt{3}iE_{z,3z^2-r^2}(011) + 2iE_{z,x^2-y^2}(011)$$

$$4iE_{x,x^2-y^2}(1,0,1) = 2\sqrt{3}iE_{z,3z^2-r^2}(011) - 2iE_{z,x^2-y^2}(011)$$

Which gives us the final result:

$$(x/x^2-y^2) = \sqrt{3}iE_{z,3z^2-r^2}(0,0,1)\sin(\xi) + 2\sqrt{3}iE_{z,3z^2-r^2}(011)\left(\sin(\xi)\cos(\eta) + \sin(\xi)\cos(\zeta)\right)$$

$$+2iE_{z,x^2-y^2}(011)\left(\sin(\xi)\cos(\eta) - \sin(\xi)\cos(\zeta)\right) + 8iE_{x,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$$

10.11 Simple cubic crystal x/$3z^2 - r^2$ orbital

$E_{x,3z^2-r^2}(0,0,0)$	0
$E_{x,3z^2-r^2}(1,0,0)$	$E_{x,3z^2-r^2}(1,0,0)$
$E_{x,3z^2-r^2}(-1,0,0)$	$-E_{x,3z^2-r^2}(1,0,0)$
$E_{x,3z^2-r^2}(0,1,0)$	0
$E_{x,3z^2-r^2}(0,-1,0)$	0
$E_{x,3z^2-r^2}(0,0,1)$	0
$E_{x,3z^2-r^2}(0,0,-1)$	0
$E_{x,3z^2-r^2}(1,1,0)$	$E_{x,3z^2-r^2}(1,1,0)$
$E_{x,3z^2-r^2}(1,-1,0)$	$E_{x,3z^2-r^2}(1,1,0)$
$E_{x,3z^2-r^2}(-1,1,0)$	$-E_{x,3z^2-r^2}(1,1,0)$
$E_{x,3z^2-r^2}(-1,-1,0)$	$-E_{x,3z^2-r^2}(1,1,0)$
$E_{x,3z^2-r^2}(1,0,1)$	$E_{x,3z^2-r^2}(1,0,1)$
$E_{x,3z^2-r^2}(1,0,-1)$	$E_{x,3z^2-r^2}(1,0,1)$
$E_{x,3z^2-r^2}(-1,0,1)$	$-E_{x,3z^2-r^2}(1,0,1)$

$E_{x,3z^2-r^2}(-1,0,-1)$	$-E_{x,3z^2-r^2}(1,0,1)$
$E_{x,3z^2-r^2}(0,1,-1)$	0
$E_{x,3z^2-r^2}(0,-1,1)$	0
$E_{x,3z^2-r^2}(0,1,-1)$	0
$E_{x,3z^2-r^2}(0,-1,-1)$	0
$E_{x,3z^2-r^2}(1,1,1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,1,1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,-1,1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,1,-1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,1,-1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,-1,1)$	$-E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(1,-1,-1)$	$E_{x,3z^2-r^2}(1,1,1)$
$E_{x,3z^2-r^2}(-1,-1,-1)$	$-E_{x,3z^2-r^2}(1,1,1)$

We substitute these, obtaining:

$$(x/3z^2 - r^2) = E_{x,3z^2-r^2}(1,0,0)\left(e^{iak_x} - e^{-iak_x}\right)$$
$$+E_{x,3z^2-r^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)} + e^{ia\cdot(k_x-k_y)} - e^{ia\cdot(-k_x+k_y)} - e^{ia\cdot(-k_x-k_y)}\right)$$
$$+E_{x,3z^2-r^2}(1,0,1)\left(e^{ia\cdot(k_x+k_z)} + e^{ia\cdot(k_x-k_z)} - e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(-k_x-k_z)}\right)$$
$$+E_{x,3z^2-r^2}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}$$
$$-e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} - e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x/3z^2 - r^2) = 2iE_{x,3z^2-r^2}(1,0,0)\sin(ak_x)$$
$$+2E_{x,3z^2-r^2}(1,1,0)\left(\cos(ak_y)e^{iak_x} - \cos(ak_y)e^{-iak_x}\right)$$
$$+2E_{x,3z^2-r^2}(1,0,1)\left(\cos(ak_z)e^{iak_x} - \cos(ak_z)e^{-iak_x}\right)$$
$$+2iE_{x,3z^2-r^2}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)} + \sin(ak_x)e^{ia\cdot(-k_y+k_z)} + \sin(ak_x)e^{ia\cdot(k_y-k_z)} + \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(x/3z^2 - r^2) = 2iE_{x,3z^2-r^2}(1,0,0)\sin(ak_x)$$
$$+4iE_{x,3z^2-r^2}(1,1,0)\sin(ak_x)\cos(ak_y) + 4iE_{x,3z^2-r^2}(1,0,1)\sin(ak_x)\cos(ak_z)$$
$$+4iE_{x,3z^2-r^2}(1,1,1)\left(\sin(ak_x)\cos(ak_y)e^{iak_z} + \sin(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x/3z^2 - r^2) = 2iE_{x,3z^2-r^2}(1,0,0)\sin(\xi)$$
$$+4iE_{x,3z^2-r^2}(1,1,0)\sin(\xi)\cos(\eta)+4iE_{x,3z^2-r^2}(1,0,1)\sin(\xi)\cos(\zeta)+8iE_{x,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$$

Using Slater Koster table 1 we find the following relations:

$$E_{x,3z^2-r^2}(1,0,0) = -\frac{1}{2}E_{z,3z^2-r^2}(0,0,1)$$

$$E_{x,3z^2-r^2}(110) = \frac{\sqrt{3}}{2}E_{z,x^2-y^2}(011) - \frac{1}{2}E_{z,3z^2-r^2}(011)$$

$$E_{x,3z^2-r^2}(101) = -\frac{\sqrt{3}}{2}E_{z,x^2-y^2}(011) - \frac{1}{2}E_{z,3z^2-r^2}(011)$$

$$E_{x,3z^2-r^2}(1,1,1) = \frac{i}{\sqrt{3}}E_{x,x^2-y^2}(111)$$

Inserting gives us the final form:

$$(x/3z^2-r^2) = -iE_{z,3z^2-r^2}(0,0,1)\sin(\xi) + 2\sqrt{3}iE_{z,3z^2-r^2}(1,1,0)\left(\sin(\xi)\cos(\eta) - \sin(\xi)\cos(\zeta)\right)$$

$$-2iE_{z,3z^2-r^2}(0,1,1)\left(\sin(\xi)\cos(\eta) + \sin(\xi)\cos(\zeta)\right) - \frac{8}{\sqrt{3}}E_{x,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\cos(\zeta)$$

10.12 Simple cubic crystal $z/3z^2 - r^2$ orbital

$E_{z,3z^2-r^2}(0,0,0)$	0
$E_{z,3z^2-r^2}(1,0,0)$	0
$E_{z,3z^2-r^2}(-1,0,0)$	0
$E_{z,3z^2-r^2}(0,1,0)$	0
$E_{z,3z^2-r^2}(0,-1,0)$	0
$E_{z,3z^2-r^2}(0,0,1)$	$E_{z,3z^2-r^2}(0,0,1)$
$E_{z,3z^2-r^2}(0,0,-1)$	$-E_{z,3z^2-r^2}(0,0,1)$
$E_{z,3z^2-r^2}(1,1,0)$	0
$E_{z,3z^2-r^2}(1,-1,0)$	0
$E_{z,3z^2-r^2}(-1,1,0)$	0
$E_{z,3z^2-r^2}(-1,-1,0)$	0
$E_{z,3z^2-r^2}(1,0,1)$	$E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(1,0,-1)$	$-E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(-1,0,1)$	$E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(-1,0,-1)$	$-E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(0,1,1)$	$E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(0,-1,1)$	$E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(0,-1,-1)$	$-E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(0,-1,-1)$	$-E_{z,3z^2-r^2}(0,1,1)$
$E_{z,3z^2-r^2}(1,1,1)$	$E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(-1,1,1)$	$E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(1,-1,1)$	$E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(1,1,-1)$	$-E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(-1,1,-1)$	$-E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(-1,-1,1)$	$E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(1,-1,-1)$	$-E_{z,3z^2-r^2}(1,1,1)$
$E_{z,3z^2-r^2}(-1,-1,-1)$	$-E_{z,3z^2-r^2}(1,1,1)$

We substitute these, obtaining:

$$(z/3z^2-r^2) = E_{z,3z^2-r^2}(0,0,1)\left(e^{aik_z} - e^{-iak_z}\right)$$
$$+E_{z,3z^2-r^2}(0,1,1)\Big(e^{ia\cdot(k_x+k_z)} - e^{ia\cdot(k_x-k_z)} + e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(-k_x-k_z)}$$
$$+e^{ia\cdot(k_y+k_z)} + e^{ia\cdot(-k_y+k_z)} - e^{ia\cdot(k_y-k_z)} - e^{ia\cdot(-k_y-k_z)}\Big)$$
$$+E_{z,3z^2-r^2}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} + e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} - e^{ia\cdot(k_x+k_y-k_z)}$$
$$+e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(k_x-k_y-k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} - e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(z/3z^2-r^2) = 2iE_{z,3z^2-r^2}(0,0,1)\sin(ak_z)$$
$$+2iE_{z,3z^2-r^2}(0,1,1)\left(\sin(ak_z)e^{iak_x} + \sin(ak_z)e^{-iak_x} + \sin(ak_y)e^{iak_z} + \sin(ak_y)e^{-iak_z}\right)$$
$$+2E_{z,3z^2-r^2}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)} + \cos(ak_x)e^{ia\cdot(-k_y+k_z)} - \cos(ak_x)e^{ia\cdot(k_y-k_z)} - \cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(z/3z^2-r^2) = 2iE_{z,3z^2-r^2}(0,0,1)\sin(ak_z) + 4iE_{z,3z^2-r^2}(0,1,1)\left(\cos(ak_x)\sin(ak_z) + \sin(ak_y)\cos(ak_z)\right)$$
$$+4E_{z,3z^2-r^2}(1,1,1)\left(\cos(ak_x)\cos(ak_y)e^{iak_z} - \cos(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(z/3z^2-r^2) = 2iE_{z,3z^2-r^2}(0,0,1)\sin(\zeta) + 4iE_{z,3z^2-r^2}(0,1,1)\left(\cos(\xi)\sin(\zeta) + \sin(\eta)\cos(\zeta)\right)$$
$$+8iE_{z,3z^2-r^2}(1,1,1)\cos(\xi)\cos(\eta)\sin(\zeta)$$

Using Slater Koster table 1 we find the following relation:$E_{z,3z^2-r^2}(1,1,1) = \frac{2}{\sqrt{3}}E_{x,x^2-y^2}(1,1,1)$
Giving us the final result:

$$(z/3z^2-r^2) = 2iE_{z,3z^2-r^2}(0,0,1)\sin(\zeta) + 4iE_{z,3z^2-r^2}(0,1,1)\left(\cos(\xi)\sin(\zeta) + \sin(\eta)\cos(\zeta)\right)$$
$$+\frac{16}{\sqrt{3}}iE_{x,x^2-y^2}(1,1,1)\cos(\xi)\cos(\eta)\sin(\zeta)$$

10.13 Simple cubic crystal xy/xy orbital

$E_{xy,xy}(0,0,0)$	$E_{xy,xy}(0,0,0)$	$E_{xy,xy}(-1,0,-1)$	$E_{xy,xy}(0,1,1)$
$E_{xy,xy}(1,0,0)$	$E_{xy,xy}(1,0,0)$	$E_{xy,xy}(0,1,-1)$	$E_{xy,xy}(0,1,1)$
$E_{xy,xy}(-1,0,0)$	$E_{xy,xy}(1,0,0)$	$E_{xy,xy}(0,-1,1)$	$E_{xy,xy}(0,1,1)$
$E_{xy,xy}(0,1,0)$	$E_{xy,xy}(1,0,0)$	$E_{xy,xy}(0,-1,-1)$	$E_{xy,xy}(0,1,1)$
$E_{xy,xy}(0,-1,0)$	$E_{xy,xy}(1,0,0)$	$E_{xy,xy}(0,-1,-1)$	$E_{xy,xy}(0,1,1)$
$E_{xy,xy}(0,0,1)$	$E_{xy,xy}(0,0,1)$	$E_{xy,xy}(1,1,1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(0,0,-1)$	$E_{xy,xy}(0,0,1)$	$E_{xy,xy}(-1,1,1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(1,1,0)$	$E_{xy,xy}(1,1,0)$	$E_{xy,xy}(1,-1,1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(1,-1,0)$	$E_{xy,xy}(1,1,0)$	$E_{xy,xy}(1,1,-1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(-1,1,0)$	$E_{xy,xy}(1,1,0)$	$E_{xy,xy}(-1,1,-1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(-1,-1,0)$	$E_{xy,xy}(1,1,0)$	$E_{xy,xy}(-1,-1,1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(1,0,1)$	$E_{xy,xy}(0,1,1)$	$E_{xy,xy}(1,-1,-1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(1,0,-1)$	$E_{xy,xy}(0,1,1)$	$E_{xy,xy}(-1,-1,-1)$	$E_{xy,xy}(1,1,1)$
$E_{xy,xy}(-1,0,1)$	$E_{xy,xy}(0,1,1)$		

We substitute these, obtaining:

$$(xy/xy) = E_{xy,xy}(0,0,0)$$
$$+E_{xy,xy}(1,0,0)\left(e^{iak_x}+e^{-iak_x}+e^{iak_y}+e^{-iak_y}+e^{iak_z}+e^{-iak_z}\right)$$
$$+E_{xy,xy}(1,1,0)\left(e^{ia\cdot(k_x+k_y)}+e^{ia\cdot(-k_x+k_y)}+e^{ia\cdot(k_x-k_y)}+e^{ia\cdot(-k_x-k_y)}\right)$$
$$+E_{xy,xy}(0,1,1)\Big(+e^{ia\cdot(k_x+k_z)}+e^{ia\cdot(k_x-k_z)}+e^{ia\cdot(-k_x+k_z)}+e^{ia\cdot(-k_x-k_z)}$$
$$+e^{ia\cdot(k_y+k_z)}+e^{ia\cdot(k_y-k_z)}+e^{ia\cdot(-k_y+k_z)}+e^{ia\cdot(-k_y-k_z)}\Big)$$
$$+E_{xy,xy}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)}+e^{ia\cdot(-k_x+k_y+k_z)}+e^{ia\cdot(k_x-k_y+k_z)}+e^{ia\cdot(k_x+k_y-k_z)}$$
$$+e^{ia\cdot(-k_x-k_y+k_z)}+e^{ia\cdot(-k_x+k_y-k_z)}+e^{ia\cdot(k_x-k_y-k_z)}+e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(s/s) = E_{xy,xy}(0,0,0) + 2E_{xy,xy}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)+\cos(ak_z)\right)$$
$$+2E_{xy,xy}(1,1,0)\left(\cos(ak_y)e^{iak_y}+\cos(ak_x)e^{-iak_y}\right)$$
$$+2E_{xy,xy}(0,1,1)\left(\cos(ak_z)e^{iak_x}+\cos(ak_z)e^{-iak_x}+\cos(ak_z)e^{iak_y}+\cos(ak_z)e^{-iak_y}\right)$$
$$+E_{xy,xy}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)}+\cos(ak_x)e^{ia\cdot(-k_y+k_z)}+\cos(ak_x)e^{ia\cdot(k_y-k_z)}+\cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(s/s) = E_{xy,xy}(0,0,0) + 2E_{xy,xy}(1,0,0)\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right)$$
$$+4E_{xy,xy}(1,1,0)\cos(ak_y)\cos(ak_z) + 4E_{xy,xy}(0,1,1)\left(\cos(ak_x)\cos(ak_z) + \cos(ak_y)\cos(ak_z)\right)$$
$$+E_{xy,xy}(1,1,1)\left(\cos(ak_x)\cos(ak_y)e^{iak_z} + \cos(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xy/xy) = E_{xy,xy}(0,0,0) + 2E_{xy,xy}(1,0,0)\left(\cos(\xi) + \cos(\eta) + \cos(\zeta)\right)$$
$$+4E_{xy,xy}(1,1,0)\cos(\eta)\cos(\zeta) + 4E_{xy,xy}(0,1,1)\left(\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right)$$
$$+E_{xy,xy}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$$

10.14 Simple cubic crystal xy/xz orbital

$E_{xy,xz}(0,0,0)$	0	$E_{xy,xz}(-1,0,-1)$	0
$E_{xy,xz}(1,0,0)$	0	$E_{xy,xz}(0,1,1)$	$E_{xy,xz}(0,1,1)$
$E_{xy,xz}(-1,0,0)$	0	$E_{xy,xz}(0,-1,1)$	$-E_{xy,xz}(0,1,1)$
$E_{xy,xz}(0,1,0)$	0	$E_{xy,xz}(0,1,-1)$	$-E_{xy,xz}(0,1,1)$
$E_{xy,xz}(0,-1,0)$	0	$E_{xy,xz}(0,-1,-1)$	$E_{xy,xz}(0,1,1)$
$E_{xy,xz}(0,0,1)$	0	$E_{xy,xz}(1,1,1)$	$E_{xy,xz}(1,1,1)$
$E_{xy,xz}(0,0,-1)$	0	$E_{xy,xz}(-1,1,1)$	$E_{xy,xz}(1,1,1)$
$E_{xy,xz}(1,1,0)$	0	$E_{xy,xz}(1,-1,1)$	$-E_{xy,xz}(1,1,1)$
$E_{xy,xz}(1,-1,0)$	0	$E_{xy,xz}(1,1,-1)$	$-E_{xy,xz}(1,1,1)$
$E_{xy,xz}(-1,1,0)$	0	$E_{xy,xz}(-1,1,-1)$	$-E_{xy,xz}(1,1,1)$
$E_{xy,xz}(-1,-1,0)$	0	$E_{xy,xz}(-1,-1,1)$	$-E_{xy,xz}(1,1,1)$
$E_{xy,xz}(1,0,1)$	0	$E_{xy,xz}(1,-1,-1)$	$E_{xy,xz}(1,1,1)$
$E_{xy,xz}(1,0,-1)$	0	$E_{xy,xz}(-1,-1,-1)$	$E_{xy,xz}(1,1,1)$
$E_{xy,xz}(-1,0,1)$	0		

We substitute these, obtaining:

$$(xy/xz) = E_{xy,xz}(0,1,1)\left(e^{ia\cdot(k_y+k_z)} - e^{ia\cdot(-k_y+k_z)} - e^{ia\cdot(k_y-k_z)} + e^{ia\cdot(-k_y-k_z)}\right)$$

$$+E_{xy,xz}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)} + e^{ia\cdot(-k_x+k_y+k_z)} - e^{ia\cdot(k_x-k_y+k_z)} - e^{ia\cdot(k_x+k_y-k_z)}\right.$$

$$\left.-e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(xy/xz) = 2iE_{xy,xz}(0,1,1)\left(\sin(ak_y)e^{iak_z} - \sin(ak_y)e^{-iak_z}\right)$$

$$+2E_{xy,xz}(1,1,1)\left(-\cos(ak_x)e^{ia\cdot(k_y+k_z)} + \cos(ak_x)e^{ia\cdot(-k_y+k_z)} - \cos(ak_x)e^{ia\cdot(k_y-k_z)} + \cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(xy/xz) = -4E_{xy,xz}(0,1,1)\sin(ak_y)\sin(ak_z)$$

$$+4iE_{xy,xz}(1,1,1)\left(\cos(ak_x)\sin(ak_z)e^{iak_y} - \sin(ak_x)\cos(ak_z)e^{-iak_y}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xy/xz) = -4E_{xy,xz}(0,1,1)\sin(\eta)\sin(\zeta) - 8E_{xy,xz}(1,1,1)\cos(\xi)\sin(\eta)\sin(\zeta)$$

10.15 Simple cubic crystal $xy/x^2 - y^2$ orbital

$E_{xy,x^2-y^2}(0,0,0)$	0	$E_{xy,x^2-y^2}(-1,0,-1)$	0
$E_{xy,x^2-y^2}(1,0,0)$	0	$E_{xy,x^2-y^2}(0,1,-1)$	0
$E_{xy,x^2-y^2}(-1,0,0)$	0	$E_{xy,x^2-y^2}(0,-1,1)$	0
$E_{xy,x^2-y^2}(0,1,0)$	0	$E_{xy,x^2-y^2}(0,-1,-1)$	0
$E_{xy,x^2-y^2}(0,-1,0)$	0	$E_{xy,x^2-y^2}(0,1,-1)$	0
$E_{xy,x^2-y^2}(0,0,1)$	0	$E_{xy,x^2-y^2}(1,1,1)$	0
$E_{xy,x^2-y^2}(0,0,-1)$	0	$E_{xy,x^2-y^2}(-1,1,1)$	0
$E_{xy,x^2-y^2}(1,1,0)$	0	$E_{xy,x^2-y^2}(1,-1,1)$	0
$E_{xy,x^2-y^2}(1,-1,0)$	0	$E_{xy,x^2-y^2}(1,1,-1)$	0
$E_{xy,x^2-y^2}(-1,1,0)$	0	$E_{xy,x^2-y^2}(-1,1,-1)$	0
$E_{xy,x^2-y^2}(-1,-1,0)$	0	$E_{xy,x^2-y^2}(-1,-1,1)$	0
$E_{xy,x^2-y^2}(1,0,1)$	0	$E_{xy,x^2-y^2}(1,-1,-1)$	0
$E_{xy,x^2-y^2}(1,0,-1)$	0	$E_{xy,x^2-y^2}(-1,-1,-1)$	0
$E_{xy,x^2-y^2}(-1,0,1)$	0		

This just gives zero contribution i.e.

$$(xy/x^2 - y^2) = 0$$

10.16 Simple cubic crystal xy/$3z^2-r^2$ orbital

$E_{xy,3z^2-r^2}(0,0,0)$	0	$E_{xy,3z^2-r^2}(-1,0,-1)$	0
$E_{xy,3z^2-r^2}(1,0,0)$	0	$E_{xy,3z^2-r^2}(0,1,1)$	0
$E_{xy,3z^2-r^2}(-1,0,0)$	0	$E_{xy,3z^2-r^2}(0,-1,1)$	0
$E_{xy,3z^2-r^2}(0,1,0)$	0	$E_{xy,3z^2-r^2}(0,1,-1)$	0
$E_{xy,3z^2-r^2}(0,-1,0)$	0	$E_{xy,3z^2-r^2}(0,-1,-1)$	0
$E_{xy,3z^2-r^2}(0,0,1)$	0	$E_{xy,3z^2-r^2}(1,1,1)$	$E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(0,0,-1)$	0	$E_{xy,3z^2-r^2}(-1,1,1)$	$-E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(1,1,0)$	$E_{xy,3z^2-r^2}(1,1,0)$	$E_{xy,3z^2-r^2}(1,-1,1)$	$-E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(1,-1,0)$	$-E_{xy,3z^2-r^2}(1,1,0)$	$E_{xy,3z^2-r^2}(1,1,-1)$	$E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(-1,1,0)$	$-E_{xy,3z^2-r^2}(1,1,0)$	$E_{xy,3z^2-r^2}(-1,1,-1)$	$-E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(-1,-1,0)$	$E_{xy,3z^2-r^2}(1,1,0)$	$E_{xy,3z^2-r^2}(-1,-1,1)$	$E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(1,0,1)$	0	$E_{xy,3z^2-r^2}(1,-1,-1)$	$-E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(1,0,-1)$	0	$E_{xy,3z^2-r^2}(-1,-1,-1)$	$E_{xy,3z^2-r^2}(1,1,1)$
$E_{xy,3z^2-r^2}(-1,0,1)$	0		

We substitute these, obtaining:

$$(xy/3z^2-r^2) = E_{xy,3z^2-r^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)} - e^{ia\cdot(-k_x+k_y)} - e^{ia\cdot(k_x-k_y)} + e^{ia\cdot(-k_x-k_y)}\right)$$

$$E_{xy,3z^2-r^2}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} - e^{ia\cdot(k_x-k_y+k_z)} + e^{ia\cdot(k_x+k_y-k_z)}$$

$$-e^{ia\cdot(-k_x+k_y-k_z)} + e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(xy/3z^2-r^2) = 2iE_{xy,3z^2-r^2}(1,1,0)\left(\sin(ak_x)e^{iak_y} - \sin(ak_x)e^{-iak_y}\right)$$

$$+2iE_{xy,3z^2-r^2}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)} - \sin(ak_x)e^{ia\cdot(-k_y+k_z)} + \sin(ak_x)e^{ia\cdot(k_y-k_z)} - \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(xy/3z^2-r^2) = -4E_{xy,3z^2-r^2}(1,1,0)\sin(ak_x)\sin(ak_y)$$

$$-4E_{xy,3z^2-r^2}(1,1,1)\left(\sin(ak_x)\sin(ak_y)e^{iak_z} + \sin(ak_x)\sin(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x=\xi$, $ak_y=\eta$, and $ak_z=\zeta$ (standard literature form):

$$(xy/3z^2-r^2) = -4E_{xy,3z^2-r^2}(1,1,0)\sin(\xi)\sin(\eta) - 8E_{xy,3z^2-r^2}(1,1,1)\sin(\xi)\sin(\eta)\cos(\zeta)$$

10.17 Simple cubic crystal $xz/x^2 - y^2$ orbital

$E_{xz,x^2-y^2}(0,0,0)$	0	$E_{xz,x^2-y^2}(-1,0,-1)$	$E_{xz,x^2-y^2}(1,0,1)$
$E_{xz,x^2-y^2}(1,0,0)$	0	$E_{xz,x^2-y^2}(0,1,1)$	0
$E_{xz,x^2-y^2}(-1,0,0)$	0	$E_{xz,x^2-y^2}(0,-1,1)$	0
$E_{xz,x^2-y^2}(0,1,0)$	0	$E_{xz,x^2-y^2}(0,1,-1)$	0
$E_{xz,x^2-y^2}(0,-1,0)$	0	$E_{xz,x^2-y^2}(0,-1,-1)$	0
$E_{xz,x^2-y^2}(0,0,1)$	0	$E_{xz,x^2-y^2}(1,1,1)$	$E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(0,0,-1)$	0	$E_{xz,x^2-y^2}(-1,1,1)$	$-E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(1,1,0)$	0	$E_{xz,x^2-y^2}(1,-1,1)$	$E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(1,-1,0)$	0	$E_{xz,x^2-y^2}(1,1,-1)$	$-E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(-1,1,0)$	0	$E_{xz,x^2-y^2}(-1,1,-1)$	$E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(-1,-1,0)$	0	$E_{xz,x^2-y^2}(-1,-1,1)$	$-E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(1,0,1)$	$E_{xz,x^2-y^2}(1,0,1)$	$E_{xz,x^2-y^2}(1,-1,-1)$	$-E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(1,0,-1)$	$-E_{xz,x^2-y^2}(1,0,1)$	$E_{xz,x^2-y^2}(-1,-1,-1)$	$E_{xz,x^2-y^2}(1,1,1)$
$E_{xz,x^2-y^2}(-1,0,1)$	$-E_{xz,x^2-y^2}(1,0,1)$		

We substitute these, obtaining:

$$(xz/x^2 - y^2) = E_{xz,x^2-y^2}(1,0,1)\left(e^{ia\cdot(k_x+k_z)} - e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(k_x-k_z)} + e^{ia\cdot(-k_x-k_z)}\right)$$

$$+E_{xz,x^2-y^2}(1,1,1)\Big(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} - e^{ia\cdot(k_x+k_y-k_z)}$$

$$+e^{ia\cdot(-k_x+k_y-k_z)} - e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(xz/x^2 - y^2) = 2iE_{xz,x^2-y^2}(1,0,1)\left(\sin(ak_x)e^{iak_z} - \sin(ak_x)e^{-iak_z}\right)$$

$$+2iE_{xz,x^2-y^2}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)} + \sin(ak_x)e^{ia\cdot(-k_y+k_z)} + \sin(ak_x)e^{ia\cdot(k_y-k_z)} + \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(xz/x^2 - y^2) = -4E_{xz,x^2-y^2}(1,0,1)\sin(ak_x)\cos(ak_z)$$

$$+4iE_{xz,x^2-y^2}(1,1,1)\left(\sin(ak_x)\cos(ak_y)e^{iak_z} - \sin(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xz/x^2 - y^2) = -4E_{xz,x^2-y^2}(1,0,1)\sin(\xi)\cos(\zeta) - 8E_{xz,x^2-y^2}(1,1,1)\sin(\xi)\cos(\eta)\sin(\zeta)$$

Using Slater-Koster table 1 we find the following relations:

$$E_{xz,x^2-y^2}(1,0,1) = -\frac{\sqrt{3}}{2}E_{xy,3z^2-r^2}(1,1,0)$$

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

Substituting gives us the final answer:

$$(xz/x^2 - y^2) = 2\sqrt{3}E_{xy,3z^2-r^2}(1,1,0)\sin(\xi)\cos(\zeta) + 4\sqrt{3}E_{xy,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\sin(\zeta)$$

10.18 Simple cubic crystal $xz/3z^2 - r^2$ orbital

$E_{xz,3z^2-r^2}(0,0,0)$	0	$E_{xz,3z^2-r^2}(-1,0,-1)$	$E_{xz,3z^2-r^2}(1,0,1)$
$E_{xz,3z^2-r^2}(1,0,0)$	0	$E_{xz,3z^2-r^2}(0,1,1)$	0
$E_{xz,3z^2-r^2}(-1,0,0)$	0	$E_{xz,3z^2-r^2}(0,-1,1)$	0
$E_{xz,3z^2-r^2}(0,1,0)$	0	$E_{xz,3z^2-r^2}(0,1,-1)$	0
$E_{xz,3z^2-r^2}(0,-1,0)$	0	$E_{xz,3z^2-r^2}(0,-1,-1)$	0
$E_{xz,3z^2-r^2}(0,0,1)$	0	$E_{xz,3z^2-r^2}(1,1,1)$	$E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(0,0,-1)$	0	$E_{xz,3z^2-r^2}(-1,1,1)$	$-E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(1,1,0)$	0	$E_{xz,3z^2-r^2}(1,-1,1)$	$E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(1,-1,0)$	0	$E_{xz,3z^2-r^2}(1,1,-1)$	$-E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(-1,1,0)$	0	$E_{xz,3z^2-r^2}(-1,1,-1)$	$E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(-1,-1,0)$	0	$E_{xz,3z^2-r^2}(-1,-1,1)$	$-E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(1,0,1)$	$E_{xz,3z^2-r^2}(1,0,1)$	$E_{xz,3z^2-r^2}(1,-1,-1)$	$-E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(1,0,-1)$	$-E_{xz,3z^2-r^2}(1,0,1)$	$E_{xz,3z^2-r^2}(-1,-1,-1)$	$E_{xz,3z^2-r^2}(1,1,1)$
$E_{xz,3z^2-r^2}(-1,0,1)$	$-E_{xz,3z^2-r^2}(1,0,1)$		

We substitute these, obtaining:

$$(xz/3z^2 - r^2) = E_{xz,3z^2-r^2}(1,0,1)\left(e^{ia\cdot(k_x+k_z)} - e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(k_x-k_z)} + e^{ia\cdot(-k_x-k_z)}\right)$$

$$E_{xz,3z^2-r^2}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)} - e^{ia\cdot(-k_x+k_y+k_z)} + e^{ia\cdot(k_x-k_y+k_z)} - e^{ia\cdot(k_x+k_y-k_z)}\right.$$

$$\left.+e^{ia\cdot(-k_x+k_y-k_z)} - e^{ia\cdot(-k_x-k_y+k_z)} - e^{ia\cdot(k_x-k_y-k_z)} + e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(xz/3z^2 - r^2) = 2iE_{xz,3z^2-r^2}(1,0,1)\left(\sin(ak_x)e^{iak_z} - \sin(ak_x)e^{-iak_z}\right)$$

$$+2iE_{xz,3z^2-r^2}(1,1,1)\left(\sin(ak_x)e^{ia\cdot(k_y+k_z)} + \sin(ak_x)e^{ia\cdot(-k_y+k_z)} - \sin(ak_x)e^{ia\cdot(k_y-k_z)} - \sin(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(xz/3z^2 - r^2) = -4E_{xz,3z^2-r^2}(1,0,1)\sin(ak_x)\sin(ak_z)$$

$$+4iE_{xz,3z^2-r^2}(1,1,1)\left(\sin(ak_x)\cos(ak_y)e^{iak_z} - \sin(ak_x)\cos(ak_y)e^{-iak_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xz/3z^2 - r^2) = -4E_{xz,3z^2-r^2}(1,0,1)\sin(\xi)\sin(\zeta) - 8E_{xz,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\sin(\zeta)$$

Using Slater-Koster table 1 we find the following relations:

$$E_{xz,3z^2-r^2}(1,0,1) = -\frac{1}{2}E_{xy,3z^2-r^2}(1,1,0)$$

$$E_{xz,3z^2-r^2}(1,1,1) = -\frac{1}{2}E_{xy,3z^2-r^2}(1,1,1)$$

Substituting these we get the final answer:

$$(xz/3z^2 - r^2) = 2E_{xy,3z^2-r^2}(1,1,0)\sin(\xi)\sin(\zeta) + 4E_{xy,3z^2-r^2}(1,1,1)\sin(\xi)\cos(\eta)\sin(\zeta)$$

10.19 Simple cubic crystal x^2-y^2/x^2-y^2 orbital

$E_{x^2-y^2,x^2-y^2}(0,0,0)$	$E_{x^2-y^2,x^2-y^2}(0,0,0)$	$E_{x^2-y^2,x^2-y^2}(-1,0,-1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$
$E_{x^2-y^2,x^2-y^2}(1,0,0)$	$E_{x^2-y^2,x^2-y^2}(1,0,0)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$
$E_{x^2-y^2,x^2-y^2}(-1,0,0)$	$E_{x^2-y^2,x^2-y^2}(1,0,0)$	$E_{x^2-y^2,x^2-y^2}(0,-1,1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$
$E_{x^2-y^2,x^2-y^2}(0,1,0)$	$E_{x^2-y^2,x^2-y^2}(1,0,0)$	$E_{x^2-y^2,x^2-y^2}(0,1,-1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$
$E_{x^2-y^2,x^2-y^2}(0,-1,0)$	$E_{x^2-y^2,x^2-y^2}(1,0,0)$	$E_{x^2-y^2,x^2-y^2}(0,-1,-1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$
$E_{x^2-y^2,x^2-y^2}(0,0,1)$	$E_{x^2-y^2,x^2-y^2}(0,0,1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(0,0,-1)$	$E_{x^2-y^2,x^2-y^2}(0,0,1)$	$E_{x^2-y^2,x^2-y^2}(-1,1,1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(1,1,0)$	$E_{x^2-y^2,x^2-y^2}(1,1,0)$	$E_{x^2-y^2,x^2-y^2}(1,-1,1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(1,-1,0)$	$E_{x^2-y^2,x^2-y^2}(1,1,0)$	$E_{x^2-y^2,x^2-y^2}(1,1,-1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(-1,1,0)$	$E_{x^2-y^2,x^2-y^2}(1,1,0)$	$E_{x^2-y^2,x^2-y^2}(-1,1,-1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(-1,-1,0)$	$E_{x^2-y^2,x^2-y^2}(1,1,0)$	$E_{x^2-y^2,x^2-y^2}(-1,-1,1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(1,0,1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$	$E_{x^2-y^2,x^2-y^2}(1,-1,-1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(1,0,-1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$	$E_{x^2-y^2,x^2-y^2}(-1,-1,-1)$	$E_{x^2-y^2,x^2-y^2}(1,1,1)$
$E_{x^2-y^2,x^2-y^2}(-1,0,1)$	$E_{x^2-y^2,x^2-y^2}(0,1,1)$		

We substitute these, obtaining:

$$(x^2-y^2,x^2-y^2)=E_{x^2-y^2,x^2-y^2}(0,0,0)$$
$$+E_{x^2-y^2,x^2-y^2}(1,0,0)\left(e^{iak_x}+e^{-iak_x}+e^{iak_y}+e^{-iak_y}\right)+E_{x^2-y^2,x^2-y^2}(0,0,1)\left(e^{iak_z}+e^{-iak_z}\right)$$
$$+E_{x^2-y^2,x^2-y^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)}+e^{ia\cdot(k_x-k_y)}+e^{ia\cdot(-k_x+k_y)}+e^{ia\cdot(-k_x-k_y)}\right)$$
$$+E_{x^2-y^2,x^2-y^2}(0,1,1)\left(e^{ia\cdot(k_x+k_z)}+e^{ia\cdot(-k_x+k_z)}+e^{ia\cdot(k_x-k_z)}+e^{ia\cdot(-k_x-k_z)}\right.$$
$$\left.e^{ia\cdot(k_y+k_z)}+e^{ia\cdot(k_y-k_z)}+e^{ia\cdot(-k_y+k_z)}+e^{ia\cdot(-k_y-k_z)}\right)$$
$$+E_{x^2-y^2,x^2-y^2}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)}+e^{ia\cdot(-k_x+k_y+k_z)}+e^{ia\cdot(k_x-k_y+k_z)}+e^{ia\cdot(k_x+k_y-k_z)}\right.$$
$$\left.+e^{ia\cdot(-k_x-k_y+k_z)}+e^{ia\cdot(-k_x+k_y-k_z)}+e^{ia\cdot(k_x-k_y-k_z)}+e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x^2-y^2,x^2-y^2)=E_{x^2-y^2,x^2-y^2}(0,0,0)$$
$$+2E_{x^2-y^2,x^2-y^2}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)\right)+2E_{x^2-y^2,x^2-y^2}(0,0,1)\cos(ak_z)$$
$$+2E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\cos(ak_y)e^{iak_x}+\cos(ak_y)e^{-iak_x}\right)$$
$$+2E_{x^2-y^2,x^2-y^2}(0,1,1)\left(\cos(ak_x)e^{iak_z}+\cos(ak_x)e^{-iak_z}+\cos(ak_z)e^{iak_y}+\cos(ak_z)e^{-iak_y}\right)$$
$$+2E_{x^2-y^2,x^2-y^2}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)}+\cos(ak_x)e^{ia\cdot(-k_y+k_z)}+\cos(ak_x)e^{ia\cdot(+k_y-k_z)}+\cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(x^2-y^2,x^2-y^2)=E_{x^2-y^2,x^2-y^2}(0,0,0)+2E_{x^2-y^2,x^2-y^2}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)\right)$$
$$+2E_{x^2-y^2,x^2-y^2}(0,0,1)\cos(ak_z)+2E_{x^2-y^2,x^2-y^2}(1,1,0)\cos(ak_x)\cos(ak_y)$$
$$+4E_{x^2-y^2,x^2-y^2}(0,1,1)\left(\cos(ak_x)\cos(ak_z)+\cos(ak_y)\cos(ak_z)\right)$$
$$+4E_{x^2-y^2,x^2-y^2}(1,1,1)\left(\cos(ak_x)\cos(ak_y)e^{iak_z}+\cos(ak_x)\cos(ak_y)e^{-k_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x^2 - y^2, x^2 - y^2) = E_{x^2-y^2,x^2-y^2}(0,0,0) + 2E_{x^2-y^2,x^2-y^2}(1,0,0)\left(\cos(\xi) + \cos(\eta)\right)$$
$$+2E_{x^2-y^2,x^2-y^2}(0,0,1)\cos(\zeta) + 4E_{x^2-y^2,x^2-y^2}(1,1,0)\cos(\xi)\cos(\eta)$$
$$+4E_{x^2-y^2,x^2-y^2}(0,1,1)\left(\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right) + 8E_{x^2-y^2,x^2-y^2}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$$

Using Slater-Koster table 1 we find the following relations:

$$E_{x^2-y^2,x^2-y^2}(100) = \frac{3}{4}E_{x^2-y^2,x^2-y^2}(001) + \frac{1}{4}E_{3z^2-r^2,3z^2-r^2}(001)$$
$$E_{x^2-y^2,x^2-y^2}(011) = \frac{1}{4}E_{x^2-y^2,x^2-y^2}(110) + \frac{3}{4}E_{3z^2-r^2,3z^2-r^2}(110)$$
$$E_{x^2-y^2,x^2-y^2}(1,1,1) = E_{3z^2-r^2,3z^2-r^2}(1,1,1)$$

Substituting gives us the final answer:

$$(x^2 - y^2, x^2 - y^2) = E_{x^2-y^2,x^2-y^2}(0,0,0) + \frac{3}{2}E_{x^2-y^2,x^2-y^2}(001)\left(\cos(\xi) + \cos(\eta)\right)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\left(\frac{1}{4}\cos(\xi) + \frac{1}{4}\cos(\eta) + \cos(\zeta)\right)$$
$$+4E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\frac{1}{4}\cos(\xi)\cos(\zeta) + \frac{1}{4}\cos(\eta)\cos(\zeta) + \cos(\xi)\cos(\eta)\right)$$
$$+3E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right) + 8E_{3z^2-r^2,3z^2-r^2}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$$

10.20 Simple cubic crystal $3z^2-r^2/3z^2-r^2$ orbital

$E_{3z^2-r^2,3z^2-r^2}(0,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(0,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(-1,0,-1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(1,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(-1,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(0,-1,1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(0,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,-1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(0,-1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,0,0)$	$E_{3z^2-r^2,3z^2-r^2}(0,-1,-1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(0,0,1)$	$E_{3z^2-r^2,3z^2-r^2}(0,0,1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(0,0,-1)$	$E_{3z^2-r^2,3z^2-r^2}(0,0,1)$	$E_{3z^2-r^2,3z^2-r^2}(-1,1,1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(1,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,-1,1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(1,-1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,-1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(-1,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(-1,1,-1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(-1,-1,0)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,0)$	$E_{3z^2-r^2,3z^2-r^2}(-1,-1,1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(1,0,1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$	$E_{3z^2-r^2,3z^2-r^2}(1,-1,-1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(1,0,-1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$	$E_{3z^2-r^2,3z^2-r^2}(-1,-1,-1)$	$E_{3z^2-r^2,3z^2-r^2}(1,1,1)$
$E_{3z^2-r^2,3z^2-r^2}(-1,0,1)$	$E_{3z^2-r^2,3z^2-r^2}(0,1,1)$		

We substitute these, obtaining:

$$(3z^2-r^2,3z^2-r^2)=E_{3z^2-r^2,3z^2-r^2}(0,0,0)$$
$$+E_{3z^2-r^2,3z^2-r^2}(1,0,0)\left(e^{iak_x}+e^{-iak_x}+e^{iak_y}+e^{-iak_y}\right)+E_{3z^2-r^2,3z^2-r^2}(0,0,1)\left(e^{iak_z}+e^{-iak_z}\right)$$
$$+E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(e^{ia\cdot(k_x+k_y)}+e^{ia\cdot(k_x-k_y)}+e^{ia\cdot(-k_x+k_y)}+e^{ia\cdot(-k_x-k_y)}\right)$$
$$+E_{3z^2-r^2,3z^2-r^2}(0,1,1)\left(e^{ia\cdot(k_x+k_z)}+e^{ia\cdot(-k_x+k_z)}+e^{ia\cdot(k_x-k_z)}+e^{ia\cdot(-k_x-k_z)}\right.$$
$$\left.e^{ia\cdot(k_y+k_z)}+e^{ia\cdot(k_y-k_z)}+e^{ia\cdot(-k_y+k_z)}+e^{ia\cdot(-k_y-k_z)}\right)$$
$$+E_{3z^2-r^2,3z^2-r^2}(1,1,1)\left(e^{ia\cdot(k_x+k_y+k_z)}+e^{ia\cdot(-k_x+k_y+k_z)}+e^{ia\cdot(k_x-k_y+k_z)}+e^{ia\cdot(k_x+k_y-k_z)}\right.$$
$$\left.+e^{ia\cdot(-k_x-k_y+k_z)}+e^{ia\cdot(-k_x+k_y-k_z)}+e^{ia\cdot(k_x-k_y-k_z)}+e^{ia\cdot(-k_x-k_y-k_z)}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(3z^2-r^2,3z^2-r^2)=E_{3z^2-r^2,3z^2-r^2}(0,0,0)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)\right)+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\cos(ak_z)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\cos(ak_y)e^{iak_x}+\cos(ak_y)e^{-iak_x}\right)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(0,1,1)\left(\cos(ak_x)e^{iak_z}+\cos(ak_x)e^{-iak_z}+\cos(ak_z)e^{iak_y}+\cos(ak_z)e^{-iak_y}\right)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(1,1,1)\left(\cos(ak_x)e^{ia\cdot(k_y+k_z)}+\cos(ak_x)e^{ia\cdot(-k_y+k_z)}+\cos(ak_x)e^{ia\cdot(+k_y-k_z)}+\cos(ak_x)e^{ia\cdot(-k_y-k_z)}\right)$$

Further factoring yields:

$$(3z^2-r^2,3z^2-r^2)=E_{3z^2-r^2,3z^2-r^2}(0,0,0)+2E_{3z^2-r^2,3z^2-r^2}(1,0,0)\left(\cos(ak_x)+\cos(ak_y)\right)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\cos(ak_z)+2E_{3z^2-r^2,3z^2-r^2}(1,1,0)\cos(ak_x)\cos(ak_y)$$
$$+4E_{3z^2-r^2,3z^2-r^2}(0,1,1)\left(\cos(ak_x)\cos(ak_z)+\cos(ak_y)\cos(ak_z)\right)$$
$$+4E_{3z^2-r^2,3z^2-r^2}(1,1,1)\left(\cos(ak_x)\cos(ak_y)e^{iak_z}+\cos(ak_x)\cos(ak_y)e^{-k_z}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(3z^2 - r^2, 3z^2 - r^2) = E_{3z^2-r^2,3z^2-r^2}(0,0,0) + 2E_{3z^2-r^2,3z^2-r^2}(1,0,0)\left(\cos(\xi) + \cos(\eta)\right)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\cos(\zeta) + 4E_{3z^2-r^2,3z^2-r^2}(1,1,0)\cos(\xi)\cos(\eta)$$
$$+4E_{3z^2-r^2,3z^2-r^2}(0,1,1)\left(\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right) + 8E_{3z^2-r^2,3z^2-r^2}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$$

Using Slater-Koster table 1 we find the following relations:

$$E_{3z^2-r^2,3z^2-r^2}(100) = \frac{3}{4}E_{x^2-y^2,x^2-y^2}(001) + \frac{1}{4}E_{3z^2-r^2,3z^2-r^2}(001)$$
$$E_{3z^2-r^2,3z^2-r^2}(011) = \frac{1}{4}E_{x^2-y^2,x^2-y^2}(110) + \frac{3}{4}E_{3z^2-r^2,3z^2-r^2}(110)$$

Substituting gives us the final answer:

$$(3z^2 - r^2, 3z^2 - r^2) = E_{3z^2-r^2,3z^2-r^2}(0,0,0) + \frac{3}{2}E_{x^2-y^2,x^2-y^2}(001)\left(\cos(\xi) + \cos(\eta)\right)$$
$$+2E_{3z^2-r^2,3z^2-r^2}(0,0,1)\left(\frac{1}{4}\cos(\xi) + \frac{1}{4}\cos(\eta) + \cos(\zeta)\right)$$
$$+4E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\frac{1}{4}\cos(\xi)\cos(\zeta) + \frac{1}{4}\cos(\eta)\cos(\zeta) + \cos(\xi)\cos(\eta)\right)$$
$$+3E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right) + 8E_{3z^2-r^2,3z^2-r^2}(1,1,1)\cos(\xi)\cos(\eta)\cos(\zeta)$$

10.21 Simple cubic crystal $x^2 - y^2/3z^2 - r^2$ orbital

$E_{x^2-y^2,3z^2-r^2}(0,0,0)$	0	$E_{x^2-y^2,3z^2-r^2}(-1,0,-1)$	$-E_{x^2-y^2,3z^2-r^2}(0,1,1)$
$E_{x^2-y^2,3z^2-r^2}(1,0,0)$	$E_{x^2-y^2,3z^2-r^2}(1,0,0)$	$E_{x^2-y^2,3z^2-r^2}(0,1,1)$	$E_{x^2-y^2,3z^2-r^2}(0,1,1)$
$E_{x^2-y^2,3z^2-r^2}(-1,0,0)$	$E_{x^2-y^2,3z^2-r^2}(1,0,0)$	$E_{x^2-y^2,3z^2-r^2}(0,-1,1)$	$E_{x^2-y^2,3z^2-r^2}(0,1,1)$
$E_{x^2-y^2,3z^2-r^2}(0,1,0)$	$-E_{x^2-y^2,3z^2-r^2}(1,0,0)$	$E_{x^2-y^2,3z^2-r^2}(0,1,-1)$	$E_{x^2-y^2,3z^2-r^2}(0,1,1)$
$E_{x^2-y^2,3z^2-r^2}(0,-1,0)$	$-E_{x^2-y^2,3z^2-r^2}(1,0,0)$	$E_{x^2-y^2,3z^2-r^2}(0,-1,-1)$	$E_{x^2-y^2,3z^2-r^2}(0,1,1)$
$E_{x^2-y^2,3z^2-r^2}(0,0,1)$	0	$E_{x^2-y^2,3z^2-r^2}(1,1,1)$	0
$E_{x^2-y^2,3z^2-r^2}(0,0,-1)$	0	$E_{x^2-y^2,3z^2-r^2}(-1,1,1)$	0
$E_{x^2-y^2,3z^2-r^2}(1,1,0)$	0	$E_{x^2-y^2,3z^2-r^2}(1,-1,1)$	0
$E_{x^2-y^2,3z^2-r^2}(1,-1,0)$	0	$E_{x^2-y^2,3z^2-r^2}(1,1,-1)$	0
$E_{x^2-y^2,3z^2-r^2}(-1,1,0)$	0	$E_{x^2-y^2,3z^2-r^2}(-1,1,-1)$	0
$E_{x^2-y^2,3z^2-r^2}(-1,-1,0)$	0	$E_{x^2-y^2,3z^2-r^2}(-1,-1,1)$	0
$E_{x^2-y^2,3z^2-r^2}(1,0,1)$	$-E_{x^2-y^2,3z^2-r^2}(0,1,1)$	$E_{x^2-y^2,3z^2-r^2}(1,-1,-1)$	0
$E_{x^2-y^2,3z^2-r^2}(1,0,-1)$	$-E_{x^2-y^2,3z^2-r^2}(0,1,1)$	$E_{x^2-y^2,3z^2-r^2}(-1,-1,-1)$	0
$E_{x^2-y^2,3z^2-r^2}(-1,0,1)$	$-E_{x^2-y^2,3z^2-r^2}(0,1,1)$		

We substitute these, obtaining:

$$(x^2 - y^2/3z^2 - r^2) = E_{x^2-y^2,3z^2-r^2}(1,0,0)\left(e^{iak_x} + e^{-iak_x} - e^{iak_y} - e^{-iak_y}\right)$$

$$+E_{x^2-y^2,3z^2-r^2}(0,1,1)\Big(-e^{ia\cdot(k_x+k_z)} - e^{ia\cdot(-k_x+k_z)} - e^{ia\cdot(k_x-k_z)} - e^{ia\cdot(-k_x-k_z)}$$

$$+e^{ia\cdot(k_y+k_z)} + e^{ia\cdot(-k_y+k_z)} + e^{ia\cdot(k_y-k_z)} + e^{ia\cdot(-k_y-k_z)}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of (co)sines:

$$(x^2 - y^2/3z^2 - r^2) = 2E_{x^2-y^2,3z^2-r^2}(1,0,0)\left(\cos(ak_x) - \sin(ak_y)\right)$$

$$+2E_{x^2-y^2,3z^2-r^2}(0,1,1)\left(-\cos(ak_x)e^{iak_z} - \cos(ak_x)e^{-iak_z} + \cos(ak_y)e^{iak_z} + \cos(ak_y)e^{-iak_z}\right)$$

Further factoring yields and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x^2 - y^2/3z^2 - r^2) = 2E_{x^2-y^2,3z^2-r^2}(1,0,0)\left(\cos(\xi) - \sin(\eta)\right)$$

$$+4E_{x^2-y^2,3z^2-r^2}(0,1,1)\left(-\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right)$$

Using Slater-Koster table 1 we find the following relations:

$$E_{x^2-y^2,3z^2-r^2}(1,0,0) = \frac{\sqrt{3}}{4}E_{x^2-y^2,x^2-y^2}(1,0,0) - \frac{\sqrt{3}}{4}E_{3z^2-r^2,3z^2-r^2}(1,0,0)$$

$$E_{x^2-y^2,3z^2-r^2}(0,1,1) = \frac{\sqrt{3}}{4}E_{x^2-y^2,x^2-y^2}(1,1,0) - \frac{\sqrt{3}}{4}E_{3z^2-r^2,3z^2-r^2}(1,1,0)$$

Substituting gives us the final answer:

$$(x^2-y^2/3z^2-r^2) = \frac{\sqrt{3}}{2}E_{x^2-y^2,x^2-y^2}(1,0,0)\left(\cos(\xi) - \sin(\eta)\right) - \frac{\sqrt{3}}{2}E_{3z^2-r^2,3z^2-r^2}(1,0,0)\left(\cos(\xi) - \sin(\eta)\right)$$

$$+4E_{3z^2-r^2,3z^2-r^2}(1,1,0)\left(\cos(\xi)\cos(\zeta) - \cos(\eta)\cos(\zeta)\right) - 4E_{x^2-y^2,x^2-y^2}(1,1,0)\left(\cos(\xi)\cos(\zeta) - \cos(\eta)\cos(\zeta)\right)$$

11 Appendix B, Face cubic matrix elements

11.1 Face cubic crystal s/s orbital

$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},1,\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(-\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-\frac{1}{2},1,\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(\frac{1}{2},-\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},1,-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(\frac{1}{2},\frac{1}{2},-1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},-1,\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-1,\frac{1}{2},\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(1,-\frac{1}{2},\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(1,\frac{1}{2},-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,s}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,s}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,s}(\frac{1}{2},\frac{1}{2},1)$

We substitute these, obtaining:

$$(s,s) = 4E_{s,s}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta) + \cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta))$$
$$+E_{s,s}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$
$$+ e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}$$
$$+ e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$
$$+ e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$
$$+ e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$
$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(s,s) = 4E_{s,s}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta) + \cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta))$$
$$+2E_{s,s}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}$$
$$+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$
$$+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(s,s) = 4E_{s,s}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta) + \cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta))$$
$$+4E_{s,s}(\frac{1}{2},\frac{1}{2},1)\Bigg(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}$$
$$+\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} + \cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}} + \cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\Bigg)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s,s) = 4E_{s,s}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta) + \cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta))$$

$$+8E_{s,s}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + \cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) + \cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.2 Face cubic crystal s/x orbital

$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(\frac{1}{2},1,\frac{1}{2})$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(\frac{1}{2},-\frac{1}{2},1)$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(\frac{1}{2},1,-\frac{1}{2})$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(\frac{1}{2},\frac{1}{2},-1)$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(\frac{1}{2},-1,\frac{1}{2})$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,x}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{s,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{s,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{s,x}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x}(1,-\frac{1}{2},\frac{1}{2})$	$E_{s,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{s,x}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x}(1,\frac{1}{2},-\frac{1}{2})$	$E_{s,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{s,x}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{s,x}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(s,x) = 4iE_{s,y}(\frac{1}{2},\frac{1}{2},0)\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$$

$$+E_{s,x}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$+E_{s,x}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(s,x) = 4iE_{s,y}(\frac{1}{2},\frac{1}{2},0)\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$$

$$+2E_{s,x}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}$$

$$+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$+2iE_{s,x}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(s,x) = 4iE_{s,y}(\frac{1}{2},\frac{1}{2},0)\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$$

$$+4iE_{s,x}(\frac{1}{2},\frac{1}{2},1)\Big(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}$$

$$+\sin(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}} + \sin(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\Big)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s,x) = 4iE_{s,y}(\frac{1}{2},\frac{1}{2},0)\left(\sin(\xi)\cos(\eta) + \sin(\xi)\cos(\zeta)\right)$$

$$+8iE_{s,x}(\frac{1}{2},\frac{1}{2},1)\left(\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + \sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})\right) + 8iE_{s,x}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

Using Slater Koster table 1 we find:

$$E_{s,x}(1,\frac{1}{2},\frac{1}{2}) = 2E_{s,x}(\frac{1}{2},\frac{1}{2},1) =$$

Substituting:

$$(s,x) = 4iE_{s,y}(\frac{1}{2},\frac{1}{2},0)\left(\sin(\xi)\cos(\eta) + \sin(\xi)\cos(\zeta)\right)$$

$$+8iE_{s,x}(\frac{1}{2},\frac{1}{2},1)\left(2\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + 2\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) + \sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.3 Face cubic crystal s/xy orbital

$$
\begin{array}{c|c|}
E_{s,xy}(\frac{1}{2},\frac{1}{2},1) & E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(-\frac{1}{2},\frac{1}{2},1) & -E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(\frac{1}{2},-\frac{1}{2},1) & -E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(-\frac{1}{2},-\frac{1}{2},1) & E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(\frac{1}{2},\frac{1}{2},-1) & E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(-\frac{1}{2},\frac{1}{2},-1) & -E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(\frac{1}{2},-\frac{1}{2},-1) & -E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(-\frac{1}{2},-\frac{1}{2},-1) & E_{s,xy}(\frac{1}{2},\frac{1}{2},1) \\
E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(1,-\frac{1}{2},\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(1,\frac{1}{2},-\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(1,-\frac{1}{2},-\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2})
\end{array}
\qquad
\begin{array}{|c|c}
E_{s,xy}(\frac{1}{2},1,\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-\frac{1}{2},1,\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(\frac{1}{2},1,-\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-\frac{1}{2},1,-\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
-E_{s,xy}(\frac{1}{2},-1,\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-\frac{1}{2},-1,\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(\frac{1}{2},-1,-\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-\frac{1}{2},-1,-\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-1,\frac{1}{2},\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-1,-\frac{1}{2},\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-1,\frac{1}{2},-\frac{1}{2}) & -E_{s,xy}(1,\frac{1}{2},\frac{1}{2}) \\
E_{s,xy}(-1,-\frac{1}{2},-\frac{1}{2}) & E_{s,xy}(1,\frac{1}{2},\frac{1}{2})
\end{array}
$$

We substitute these, obtaining:

$$
\begin{aligned}
(s,xy) = -4E_{s,xy}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta) \\
+E_{s,xy}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)} \\
+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big) \\
+E_{s,xy}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})} \\
-e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})} \\
+e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})} \\
-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)
\end{aligned}
$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$
\begin{aligned}
(s,xy) = -4E_{s,xy}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta) \\
+2E_{s,xy}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big) \\
+2iE_{s,xy}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})} \\
+\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)
\end{aligned}
$$

Further factoring yields:

$$
\begin{aligned}
(s,xy) = -4E_{s,xy}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta) + 4iE_{s,xy}(\frac{1}{2},\frac{1}{2},1)\Big(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\Big) \\
-4E_{s,xy}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(\frac{k_x}{2})\sin(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\sin(k_y)e^{-ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\Big)
\end{aligned}
$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s, xy) = -4E_{s,xy}(\frac{1}{2}, \frac{1}{2}, 0)\sin(\xi)\sin(\eta) - 8E_{s,xy}(\frac{1}{2}, \frac{1}{2}, 1)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\zeta)$$

$$+8E_{s,xy}(1, \frac{1}{2}, \frac{1}{2})\left(\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2}) + \sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

Using Slater Koster table 1 we find:

$$E_{s,xy}(1, \frac{1}{2}, \frac{1}{2}) = 2E_{s,xy}(\frac{1}{2}, \frac{1}{2}, 1)$$

Substituting:

$$(s, xy) = -4E_{s,xy}(\frac{1}{2}, \frac{1}{2}, 0)\sin(\xi)\sin(\eta)$$

$$-8E_{s,xy}(1, \frac{1}{2}, \frac{1}{2})\left(\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\zeta) + 2\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2}) + 2\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.4 Face cubic crystal $s/x^2 - y^2$ orbital

$E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	0	$E_{s,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(-\frac{1}{2},\frac{1}{2},1)$	0	$E_{s,x^2-y^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(\frac{1}{2},-\frac{1}{2},1)$	0	$-E_{s,x^2-y^2}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},1)$	0	$E_{s,x^2-y^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},-1)$	0	$E_{s,x^2-y^2}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(-\frac{1}{2},\frac{1}{2},-1)$	0	$E_{s,x^2-y^2}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(\frac{1}{2},-\frac{1}{2},-1)$	0	$E_{s,x^2-y^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},-1)$	0	$E_{s,x^2-y^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(-1,\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,x^2-y^2}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,x^2-y^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(s,x^2-y^2) = 4E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta)+\cos(\eta)\cos(\zeta))$$

$$+E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\left(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}\right.$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$-\left(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}\right.$$

$$\left.\left.+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\right)\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(s,x^2-y^2) = 4E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta)+\cos(\eta)\cos(\zeta))$$

$$+2E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\left(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\right.$$

$$\left.-\left(\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\right)\right)$$

Further factoring yields:

$$(s,x^2-y^2) = 4E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)(\cos(\xi))\cos(\eta)+\cos(\eta)\cos(\zeta))$$

$$+4E_{s,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}+\cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}-\cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}\right.$$

$$\left.-\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s, x^2 - y^2) = 4E_{s,x^2-y^2}(0, \frac{1}{2}, \frac{1}{2}) \left(-\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right)$$

$$+8E_{s,x^2-y^2}(\frac{1}{2}, \frac{1}{2}, 1) \left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) - \cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

Using Slater Koster table 1 we find:

$$E_{s,x^2-y^2}(0, \frac{1}{2}, \frac{1}{2}) = -\frac{\sqrt{3}}{2}E_{s,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2})$$

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

Substituting:

$$(s, x^2 - y^2) = -2\sqrt{3}E_{s,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2}) \left(-\cos(\xi)\cos(\zeta) + \cos(\eta)\cos(\zeta)\right)$$

$$+\frac{16}{\sqrt{3}}E_{s,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2}) \left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) - \cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.5 Face cubic crystal $s/3z^2 - r^2$ orbital

$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(-\frac{1}{2},1,\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},1,-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},-1,\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{s,3z^2-r^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(-1,\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{s,3z^2-r^2}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{s,3z^2-r^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(s,3z^2-r^2) = 4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta) + 4E_{s,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(s,3z^2-r^2) = 4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta) + 4E_{s,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+2E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(s,3z^2-r^2) = 4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta) + 4E_{s,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(+\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} + \cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}} + \cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}\right.$$

$$\left.+\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(s,3z^2-r^2) = 4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta) + 4E_{s,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + 8E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) + \cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

Using Slater Koster table 1 we find:

$$E_{s,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2}) - E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)$$

$$E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1) = -2E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$$

Substituting:

$$(s,3z^2-r^2) = 4E_{s,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\eta) - \cos(\xi)\cos(\zeta) - \cos(\eta)\cos(\zeta)\right)$$

$$+8E_{s,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(-2\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + \cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) + \cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.6 Face cubic crystal x/x orbital

$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},1,\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(-\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(-\frac{1}{2},1,\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(\frac{1}{2},-\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},1,-\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(\frac{1}{2},\frac{1}{2},-1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},-1,\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,x}(\frac{1}{2},\frac{1}{2},1)$
$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x}(-1,\frac{1}{2},\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,x}(1,-\frac{1}{2},\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,x}(1,\frac{1}{2},-\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,x}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,x}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(x,x) = 4E_{x,x}(1,1,0)\left(\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)\right) + 4E_{x,x}(0,1,1)\cos(\eta)\cos(\zeta)$$

$$+E_{x,x}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big)$$

$$+E_{x,x}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(x,x) = 2E_{x,x}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)\right) + 2E_{x,x}(0,\frac{1}{2},\frac{1}{2})\cos(\eta)\cos(\zeta)$$

$$+2E_{x,x}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}$$

$$+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big)$$

$$+E_{x,x}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(x,x) = 2E_{x,x}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)\right) + 2E_{x,x}(0,\frac{1}{2},\frac{1}{2})\cos(\eta)\cos(\zeta)$$

$$+4E_{x,x}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}}+\cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}+\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}+\cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+E_{x,x}(1,\frac{1}{2},\frac{1}{2})\left(\cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}+\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x,x) = 2E_{x,x}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)\right) + 2E_{x,x}(0,\frac{1}{2},\frac{1}{2})\cos(\eta)\cos(\zeta)$$

$$+8E_{x,x}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})\right)+8E_{x,x}(1,\frac{1}{2},\frac{1}{2})\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

Using Slater Koster table 1 we find:

$$E_{x,x}(\frac{1}{2},\frac{1}{2},0) = E_{x,x}(0,\frac{1}{2},\frac{1}{2})\cos(\eta)\cos(\zeta)$$

Substituting:

$$(x,x) = 2E_{x,x}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{x,x}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})\right)+8E_{x,x}(1,\frac{1}{2},\frac{1}{2})\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

11.7 Face cubic crystal x/y orbital

$E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(\frac{1}{2},1,\frac{1}{2})$	$E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(\frac{1}{2},-\frac{1}{2},1)$	$-E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(\frac{1}{2},1,-\frac{1}{2})$	$E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(\frac{1}{2},\frac{1}{2},-1)$	$E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(\frac{1}{2},-\frac{1}{2},-1)$	$-E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,y}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,y}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,y}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,y}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,y}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,y}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{x,y}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,y}(1,-\frac{1}{2},\frac{1}{2})$	$-E_{x,y}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,y}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{x,y}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,y}(1,\frac{1}{2},-\frac{1}{2})$	$E_{x,y}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,y}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{x,y}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,y}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{x,y}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,y}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,y}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(x,y) = -4E_{x,y}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta)$$

$$+E_{x,y}(\frac{1}{2},\frac{1}{2},1)\left(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}\right.$$

$$\left.+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\right)$$

$$+E_{x,y}(1,\frac{1}{2},\frac{1}{2})\left(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}\right.$$

$$\left.-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\right)$$

$$+E_{x,y}(\frac{1}{2},1,\frac{1}{2})\left(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}\right.$$

$$\left.- e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(x,y) = -4E_{x,y}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta)$$

$$+2E_{x,y}(\frac{1}{2},\frac{1}{2},1)\left(-\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\right)$$

$$+2iE_{x,y}(1,\frac{1}{2},\frac{1}{2})\left(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\right)$$

$$+2iE_{x,y}(\frac{1}{2},1,\frac{1}{2})\left(\sin(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\right)$$

Further factoring yields:

$$(x,y) = -4E_{x,y}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta)$$

$$+4iE_{x,y}(\frac{1}{2},\frac{1}{2},1)\left(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} - \sin(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$-4E_{x,y}(1,\frac{1}{2},\frac{1}{2})\left(\sin(k_x)\sin(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$-4E_{x,y}(\frac{1}{2},1,\frac{1}{2})\left(\sin(\frac{k_x}{2})\sin(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\sin(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x,y) = -4E_{x,y}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\sin(\eta) - 8E_{x,y}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\zeta)$$

$$-8E_{x,y}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2}) - 8E_{x,y}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2})$$

11.8 Face cubic crystal x/xy orbital

$E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$	$E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(\frac{1}{2},-\frac{1}{2},1)$	$E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(\frac{1}{2},1,-\frac{1}{2})$	$E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(\frac{1}{2},\frac{1}{2},-1)$	$E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(\frac{1}{2},-1,\frac{1}{2})$	$E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{x,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,xy}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x,xy}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,xy}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,xy}(1,-\frac{1}{2},\frac{1}{2})$	$E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,xy}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,xy}(1,\frac{1}{2},-\frac{1}{2})$	$E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,xy}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,xy}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,xy}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{x,xy}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(x,xy) = 4iE_{x,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\sin(ak_y) + 4iE_{x,xy}(0,\frac{1}{2},\frac{1}{2})\sin(\eta)\cos(\zeta)$$

$$+E_{x,xy}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{x,xy}(\frac{1}{2},1,\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big)$$

$$+E_{x,xy}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(x,xy) = 4iE_{x,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\sin(ak_y) + 4iE_{x,xy}(0,\frac{1}{2},\frac{1}{2})\sin(\eta)\cos(\zeta)$$

$$+2E_{x,xy}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+2E_{x,xy}(\frac{1}{2},1,\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big)$$

$$+2iE_{x,xy}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(x,xy) = 4iE_{x,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\sin(ak_y) + 4iE_{x,xy}(0,\frac{1}{2},\frac{1}{2})\sin(\eta)\cos(\zeta)$$

$$+4iE_{x,xy}(\frac{1}{2},\frac{1}{2},1)\left(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+4iE_{x,xy}(\frac{1}{2},1,\frac{1}{2})\left(\sin(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} + \cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+4iE_{x,xy}(1,\frac{1}{2},\frac{1}{2})\left(\sin(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x,xy) = 4iE_{x,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\sin(ak_y) + 4iE_{x,xy}(0,\frac{1}{2},\frac{1}{2})\sin(\eta)\cos(\zeta)$$

$$+8iE_{x,xy}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+8iE_{x,xy}(\frac{1}{2},1,\frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+8iE_{x,xy}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

11.9 Face cubic crystal x/yz orbital

$E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$	$E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(\frac{1}{2},-\frac{1}{2},1)$	$-E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(\frac{1}{2},\frac{1}{2},-1)$	$-E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{x,yz}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,yz}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x,yz}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,yz}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,yz}(1,-\frac{1}{2},\frac{1}{2})$	$-E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,yz}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,yz}(1,\frac{1}{2},-\frac{1}{2})$	$-E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,yz}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,yz}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,yz}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{x,yz}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$
\begin{aligned}
(x,yz) = E_{x,yz}(\frac{1}{2},\frac{1}{2},1)\Big(&e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)} \\
&-e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big) \\
+E_{x,yz}(\frac{1}{2},1,\frac{1}{2})\Big(&e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})} \\
&-e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big) \\
+E_{x,yz}(1,\frac{1}{2},\frac{1}{2})\Big(&e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})} \\
&-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)
\end{aligned}
$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$
\begin{aligned}
&(x,yz) = 2iE_{x,yz}(\frac{1}{2},\frac{1}{2},1)\Big(\sin(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \sin(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} - \sin(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \sin(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})} \\
&+2iE_{x,yz}(\frac{1}{2},1,\frac{1}{2})\Big(\sin(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big) \\
&+2iE_{x,yz}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)
\end{aligned}
$$

Further factoring yields:

$$
\begin{aligned}
(x,yz) = -4E_{x,yz}(\frac{1}{2},\frac{1}{2},1)&\left(\sin(\frac{k_x}{2})\sin(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\sin(k_z)e^{-ia\frac{k_y}{2}}\right) \\
-4E_{x,yz}(\frac{1}{2},1,\frac{1}{2})&\left(\sin(\frac{k_x}{2})\sin(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\sin(k_y)e^{-ia\cdot\frac{k_z}{2}}\right) \\
-4E_{x,yz}(1,\frac{1}{2},\frac{1}{2})&\left(\sin(k_x)\sin(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)
\end{aligned}
$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x, yz) = -8E_{x,yz}(\frac{1}{2}, \frac{1}{2}, 1)\sin(\frac{\xi}{2})\sin(\frac{\eta}{2})\cos(\zeta)$$

$$-8E_{x,yz}(\frac{1}{2}, 1, \frac{1}{2})\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2}) - 8E_{x,yz}(1, \frac{1}{2}, \frac{1}{2})\sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

11.10 Face cubic crystal $x/x^2 - y^2$ orbital

$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(\frac{1}{2},1,-\frac{1}{2})$	$E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(\frac{1}{2},-1,\frac{1}{2})$	$E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,x^2-y^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x^2-y^2}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,x^2-y^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x^2-y^2}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,x^2-y^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x^2-y^2}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,x^2-y^2}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,x^2-y^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(x,x^2-y^2) = +4iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\cos(\eta) + 4iE_{x,x^2-y^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+ e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{x,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+ e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big)$$

$$+E_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(x,x^2-y^2) = +4iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\cos(\eta) + 4iE_{x,x^2-y^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+2E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}$$

$$+2E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big)$$

$$+2iE_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(x,x^2-y^2) = +4iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\cos(\eta) + 4iE_{x,x^2-y^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+4iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}$$

$$+4iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\left(\sin(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}+\sin(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+4iE_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\sin(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}+\sin(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x,x^2-y^2) = 4iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\cos(\eta) + 4iE_{x,x^2-y^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+8iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + 8iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$$

$$+8iE_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

Using Slater Koster table 1 we find:

$$E_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},0) = \frac{2}{5}\sqrt{3}E_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2}) + \frac{4}{5}E_{z,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})$$

$$E_{x,x^2-y^2}(\frac{1}{2},0,\frac{1}{2}) = \frac{2}{5}\sqrt{3}E_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2}) - \frac{1}{5}E_{z,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})$$

Substituting:

$$(x,x^2-y^2) = \frac{8i}{5}\sqrt{3}E_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\sin(\xi)\cos(\eta)+\sin(\xi)\cos(\zeta)\right)$$

$$+\frac{4i}{5}E_{z,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(4\sin(\xi)\cos(\eta)-\sin(\xi)\cos(\zeta)\right. + 8iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$$

$$+8iE_{x,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) + 8iE_{x,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

11.11 Face cubic crystal $x/3z^2 - r^2$ orbital

$E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(\frac{1}{2},1,-\frac{1}{2})$	$E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(\frac{1}{2},-1,\frac{1}{2})$	$E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x,3z^2-r^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,3z^2-r^2}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,3z^2-r^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,3z^2-r^2}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,3z^2-r^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,3z^2-r^2}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x,3z^2-r^2}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x,3z^2-r^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(x,3z^2-r^2) = 4iE_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\cos(\eta) + 4iE_{x,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+ e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+ e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big)$$

$$+E_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(x,3z^2-r^2) = 4iE_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\sin(\xi)\cos(\eta) + 4iE_{x,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+2E_{x,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} - \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+2E_{x,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big)$$

$$+2iE_{x,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(x, 3z^2 - r^2) = 4iE_{x,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 0)\sin(\xi)\cos(\eta) + 4iE_{x,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+4iE_{x,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1)\left(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right.$$

$$+4iE_{x,3z^2-r^2}(\frac{1}{2}, 1, \frac{1}{2})\left(\sin(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+4iE_{x,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2})\left(\sin(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x, 3z^2 - r^2) = 4iE_{x,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 0)\sin(\xi)\cos(\eta) + 4iE_{x,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+8iE_{x,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + 8iE_{x,3z^2-r^2}(\frac{1}{2}, 1, \frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$$

$$+8iE_{x,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

Using Slater Koster table 1 we find:

$$E_{x,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 0) = -5E_{z,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2}) + 4\sqrt{3}E_{z,x^2-y^2}(0, \frac{1}{2}, \frac{1}{2})$$

$$E_{x,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2}) = 2E_{z,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2}) - 2\sqrt{3}E_{z,x^2-y^2}(0, \frac{1}{2}, \frac{1}{2})$$

Substituting:

$$(x, 3z^2 - r^2) = 4iE_{z,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2})\left(-5\sin(\xi)\cos(\eta) + 2\sin(\xi)\cos(\zeta)\right)$$

$$+8\sqrt{3}iE_{z,x^2-y^2}(0, \frac{1}{2}, \frac{1}{2})\left(2\sin(\xi)\cos(\eta) - \sin(\xi)\cos(\zeta)\right) + 8iE_{x,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$$

$$+8iE_{x,3z^2-r^2}(\frac{1}{2}, 1, \frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2}) + 8iE_{x,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

11.12 Face cubic crystal $z/3z^2 - r^2$ orbital

$E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(-\frac{1}{2},1,\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},-1)$	$-E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},-1,\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},-1)$	$-E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{z,3z^2-r^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(-1,\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(1,\frac{1}{2},-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{z,3z^2-r^2}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{z,3z^2-r^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(z,3z^2-r^2) = 4iE_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\sin(\zeta)+\sin(\eta)\cos(\zeta)\right)$$

$$+E_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$-e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)}-e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)}-e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)}-e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}-e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}-e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}-e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}-e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}-e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}-e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(z,3z^2-r^2) = 4iE_{z,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\sin(\zeta)+\sin(\eta)\cos(\zeta)\right)$$

$$+2iE_{z,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(\sin(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})}+\sin(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})}+\sin(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})}+\sin(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+2E_{z,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}-\cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}-\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}-\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}-\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(z, 3z^2 - r^2) = 4iE_{z,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2}) \left(\cos(\xi)\sin(\zeta) + \sin(\eta)\cos(\zeta)\right)$$

$$+4iE_{z,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1) \left(\cos(\frac{k_x}{2})\sin(k_z)e^{ia\frac{k_y}{2}} + \cos(\frac{k_x}{2})\sin(k_z)e^{-ia\frac{k_y}{2}}\right.$$

$$+4E_{z,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2}) \left(\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} - \cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right.$$

$$\left. + \cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} - \cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(z, 3z^2 - r^2) = 4iE_{z,3z^2-r^2}(0, \frac{1}{2}, \frac{1}{2}) \left(\cos(\xi)\sin(\zeta) + \sin(\eta)\cos(\zeta)\right)$$

$$+8iE_{z,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\sin(\zeta)$$

$$+8iE_{z,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2}) \left(\cos(\frac{\xi}{2})\cos(\eta)\sin(\frac{\zeta}{2}) + \cos(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})\right)$$

11.13 Face cubic crystal xy/xy orbital

$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},1,\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(-\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(\frac{1}{2},-\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(\frac{1}{2},\frac{1}{2},-1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,xy}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(-1,\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(1,-\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(1,\frac{1}{2},-\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,xy}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,xy}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$
\begin{aligned}
(xy,xy) &= 4E_{xy,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\eta)\cos(\zeta) + 4E_{xy,xy}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right) \\
&+E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)} \\
&\quad + e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big) \\
&+E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})} \\
&\quad + e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})} \\
&\quad - \Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})} \\
&\quad +e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)\Big)
\end{aligned}
$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$
\begin{aligned}
(xy,xy) &= 4E_{xy,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\eta)\cos(\zeta) + 4E_{xy,xy}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right) \\
&+2E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big) \\
&+2E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})} \\
&\quad - \Big(\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)\Big)
\end{aligned}
$$

Further factoring yields:

$$
\begin{aligned}
(xy,xy) &= 4E_{xy,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\eta)\cos(\zeta) + 4E_{xy,xy}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right) \\
&+4E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)
\end{aligned}
$$

$$+4E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}+\cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}-\cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}-\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xy,xy) = 4E_{xy,xy}(\frac{1}{2},\frac{1}{2},0)\cos(\eta)\cos(\zeta) + 4E_{xy,xy}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{xy,xy}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+8E_{xy,xy}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})-\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.14 Face cubic crystal xy/zx orbital

$E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$	$E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(\frac{1}{2},-\frac{1}{2},1)$	$E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(\frac{1}{2},1,-\frac{1}{2})$	$E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(\frac{1}{2},\frac{1}{2},-1)$	$-E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(\frac{1}{2},-\frac{1}{2},-1)$	$-E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,zx}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})$
$E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,zx}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,zx}(1,-\frac{1}{2},\frac{1}{2})$	$E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,zx}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,zx}(1,\frac{1}{2},-\frac{1}{2})$	$-E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,zx}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,zx}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,zx}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(xy,zx) = -4E_{xy,xz}(0,\frac{1}{2},\frac{1}{2})\sin(\eta)\sin(\zeta)$$

$$+E_{xy,zx}(\frac{1}{2},\frac{1}{2},1)\left(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}\right.$$

$$\left. + e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\right)$$

$$+E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})\left(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}\right.$$

$$\left. +e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\right)$$

$$+E_{xy,zx}(1,\frac{1}{2},\frac{1}{2})\left(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}\right.$$

$$\left. -e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\right)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(xy,zx) = -4E_{xy,xz}(0,\frac{1}{2},\frac{1}{2})\sin(\eta)\sin(\zeta)$$

$$+2iE_{xy,zx}(\frac{1}{2},\frac{1}{2},1)\left(\sin(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \sin(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \sin(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} - \sin(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\right)$$

$$+2E_{xy,zx}(\frac{1}{2},1,\frac{1}{2})\left(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\right)$$

$$+2iE_{xy,zx}(1,\frac{1}{2},\frac{1}{2})\left(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\right)$$

Further factoring yields:

$$(xy, zx) = -4E_{xy,xz}(0, \frac{1}{2}, \frac{1}{2})\sin(\eta)\sin(\zeta)$$

$$+4E_{xy,zx}(\frac{1}{2}, \frac{1}{2}, 1)\left(\sin(\frac{k_x}{2})\sin(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\sin(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+4iE_{xy,zx}(\frac{1}{2}, 1, \frac{1}{2})\left(\sin(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+4iE_{xy,zx}(1, \frac{1}{2}, \frac{1}{2})\left(\sin(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xy, zx) = -4E_{xy,xz}(0, \frac{1}{2}, \frac{1}{2})\sin(\eta)\sin(\zeta)$$

$$-8E_{xy,zx}(\frac{1}{2}, \frac{1}{2}, 1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\sin(\zeta) - 8E_{xy,zx}(\frac{1}{2}, 1, \frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\sin(\frac{\zeta}{2})$$

$$-8E_{xy,zx}(1, \frac{1}{2}, \frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})$$

11.15 Face cubic crystal $xy/x^2 - y^2$ orbital

$E_{xy,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	0	$E_{xy,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(-\frac{1}{2},\frac{1}{2},1)$	0	$E_{xy,x^2-y^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(\frac{1}{2},-\frac{1}{2},1)$	0	$E_{xy,x^2-y^2}(\frac{1}{2},1,-\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},1)$	0	$E_{xy,x^2-y^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(\frac{1}{2},\frac{1}{2},-1)$	0	$E_{xy,x^2-y^2}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(-\frac{1}{2},\frac{1}{2},-1)$	0	$E_{xy,x^2-y^2}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(\frac{1}{2},-\frac{1}{2},-1)$	0	$E_{xy,x^2-y^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},-1)$	0	$E_{xy,x^2-y^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,x^2-y^2}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(1,-\frac{1}{2},\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,x^2-y^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,x^2-y^2}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,x^2-y^2}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,x^2-y^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(xy, x^2-y^2) =$$

$$+E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$-e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(xy, x^2-y^2) =$$

$$+2iE_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} - \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$+\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(xy, x^2-y^2) =$$

$$4iE_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\sin(\frac{k_x}{2})\sin(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\sin(k_y)e^{-ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xy, x^2-y^2) = 8E_{xy,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\sin(\frac{\xi}{2})\sin(\eta)\cos(\frac{\zeta}{2}) + \sin(\xi)\sin(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.16 Face cubic crystal $xy/3z^2 - r^2$ orbital

$E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},1)$	$-E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},-1)$	$-E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},-1)$	$-E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xy,3z^2-r^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,3z^2-r^2}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(1,-\frac{1}{2},\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,3z^2-r^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,3z^2-r^2}(-1,\frac{1}{2},-\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xy,3z^2-r^2}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xy,3z^2-r^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(xy,3z^2-r^2) = -4E_{xy,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\sin(\eta)$$

$$+E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} + e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$-e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$+ e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(xy,3z^2-r^2) = -4E_{xy,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\sin(\eta)$$

$$+2E_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} + \cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+2iE_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \sin(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$+\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(xy,3z^2-r^2) = -4E_{xy,3z^2-r^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\sin(\eta)$$

$$+4iE_{xy,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\left(\sin(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$-4E_{xy,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(\frac{k_x}{2})\sin(k_y)e^{ia\cdot\frac{k_z}{2}} + \sin(\frac{k_x}{2})\sin(k_y)e^{-ia\cdot\frac{k_z}{2}} + \sin(k_x)\sin(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \sin(k_x)\cos(\sin k_y 2)e^{-ia}$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xy, 3z^2 - r^2) = -4E_{xy,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2}) \sin(\xi) \sin(\eta)$$

$$-8E_{xy,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1) \sin(\frac{\xi}{2}) \sin(\frac{\eta}{2}) \cos(\zeta) - 8E_{xy,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2}) \left(\sin(\frac{\xi}{2}) \sin(\eta) \cos(\frac{\zeta}{2}) + \sin(\xi) \cos(\frac{\eta}{2}) \sin(\frac{\zeta}{2}) \right)$$

11.17 Face cubic crystal xz/x^2-y^2 orbital

$E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(-\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(-\frac{1}{2},1,\frac{1}{2})$	$E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(\frac{1}{2},-\frac{1}{2},1)$	$-E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(\frac{1}{2},1,-\frac{1}{2})$	$E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(\frac{1}{2},-\frac{1}{2},-1)$	$-E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$-E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{xz,x^2-y^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xz,x^2-y^2}(-1,\frac{1}{2},\frac{1}{2})$	$E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xz,x^2-y^2}(1,-\frac{1}{2},\frac{1}{2})$	$-E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xz,x^2-y^2}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xz,x^2-y^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xz,x^2-y^2}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{xz,x^2-y^2}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{xz,x^2-y^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$-E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(xz,x^2-y^2) = -4E_{xz,x^2-y^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)}-e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)}-e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)}-e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)}-e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}-e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big)$$

$$+E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}-e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}-e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}-e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}-e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(xz,x^2-y^2) = -4E_{xz,x^2-y^2}(\frac{1}{2},0,\frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+2E_{xz,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})}-\cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})}-\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+2iE_{xz,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})\Big(\sin(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}+\sin(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}+\sin(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}+\sin(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big)$$

$$+2E_{xz,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}-\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}-\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(xz, x^2 - y^2) = -4E_{xz,x^2-y^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+4E_{xz,x^2-y^2}(\frac{1}{2}, \frac{1}{2}, 1)\left(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}} - \cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+4iE_{xz,x^2-y^2}(\frac{1}{2}, 1, \frac{1}{2})\left(\cos(\frac{k_x}{2})\sin(k_y)e^{ia\cdot\frac{k_z}{2}} + \cos(\frac{k_x}{2})\sin(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+4iE_{xz,x^2-y^2}(1, \frac{1}{2}, \frac{1}{2})\left(\cos(k_x)\sin(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} + \cos(k_x)\sin(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(xz, x^2 - y^2) = -4E_{xz,x^2-y^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\cos(\zeta)$$

$$+8iE_{xz,x^2-y^2}(\frac{1}{2}, \frac{1}{2}, 1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + 8iE_{xz,x^2-y^2}(\frac{1}{2}, 1, \frac{1}{2})\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$$

$$+8iE_{xz,x^2-y^2}(1, \frac{1}{2}, \frac{1}{2})\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

Using Slater Koster table 1 we find:

$$E_{xz,x^2-y^2}(\frac{1}{2}, 0, \frac{1}{2}) = -\frac{\sqrt{3}}{2}E_{xz,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 0$$

Substituting:

$$(xz, x^2 - y^2) = 2\sqrt{3}E_{xz,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 0)\sin(\xi)\cos(\zeta)$$

$$+8iE_{xz,x^2-y^2}(\frac{1}{2}, \frac{1}{2}, 1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta) + 8iE_{xz,x^2-y^2}(\frac{1}{2}, 1, \frac{1}{2})\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})$$

$$+8iE_{xz,x^2-y^2}(1, \frac{1}{2}, \frac{1}{2})\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})$$

11.18 Face cubic crystal $zx/3z^2 - r^2$ orbital

$E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},1)$	$-E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},1)$	$-E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},-1)$	$-E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},-1,\frac{1}{2})$	$E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(\frac{1}{2},-\frac{1}{2},-1)$	$-E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{zx,3z^2-r^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})$
$E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{zx,3z^2-r^2}(-1,\frac{1}{2},\frac{1}{2})$	$-E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{zx,3z^2-r^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{zx,3z^2-r^2}(-1,-\frac{1}{2},\frac{1}{2})$	$-E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{zx,3z^2-r^2}(1,\frac{1}{2},-\frac{1}{2})$	$-E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{zx,3z^2-r^2}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{zx,3z^2-r^2}(1,-\frac{1}{2},-\frac{1}{2})$	$-E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{zx,3z^2-r^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(zx, 3z^2 - r^2) = -4E_{xz,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\sin(\zeta)$$

$$+E_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)} + e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)} - e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$- e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)} - e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)} + e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+ e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})} - e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})} + e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}\Big)$$

$$+E_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big)e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})} - e^{ia\cdot(k_x-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$-e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})} - e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})} + e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})} + e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(zx, 3z^2 - r^2) = -4E_{xz,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\sin(\zeta)$$

$$+2iE_{zx,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(\sin(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})} - \sin(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})} + \sin(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})} - \sin(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\Big)$$

$$+2E_{zx,3z^2-r^2}(\frac{1}{2},1,\frac{1}{2})\Big(-\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})} - \cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})} + \cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}\Big)$$

$$+2iE_{zx,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(\sin(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})} + \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})} - \sin(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(zx, 3z^2 - r^2) = -4E_{xz,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\sin(\zeta)$$

$$-4E_{zx,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1)\left(\sin(\frac{k_x}{2})\sin(k_z)e^{ia\frac{k_y}{2}} + \sin(\frac{k_x}{2})\sin(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+4iE_{zx,3z^2-r^2}(\frac{1}{2}, 1, \frac{1}{2})\left(\sin(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}} - \sin(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right)$$

$$+4iE_{zx,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2})\left(\sin(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}} - \sin(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(zx, 3z^2 - r^2) = -4E_{xz,3z^2-r^2}(\frac{1}{2}, 0, \frac{1}{2})\sin(\xi)\sin(\zeta)$$

$$-8E_{zx,3z^2-r^2}(\frac{1}{2}, \frac{1}{2}, 1)\sin(\frac{\xi}{2})\cos(\frac{\eta}{2})\sin(\zeta) - 8E_{zx,3z^2-r^2}(\frac{1}{2}, 1, \frac{1}{2})\sin(\frac{\xi}{2})\cos(\eta)\sin(\frac{\zeta}{2})$$

$$-8E_{zx,3z^2-r^2}(1, \frac{1}{2}, \frac{1}{2})\sin(\xi)\cos(\frac{\eta}{2})\sin(\frac{\zeta}{2})$$

11.19 Face cubic crystal $x^2 - y^2/x^2 - y^2$ orbital

$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},1,\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},1,\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},1,-\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},1,-\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},-1,\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},-1,\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{x^2-y^2,x^2-y^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$-E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(-1,\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{x^2-y^2,x^2-y^2}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(x^2-y^2,x^2-y^2) = 4E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{x^2-y^2,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}\Big)$$

$$+E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$-\Big(e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(x^2-y^2,x^2-y^2) = 4E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{x^2-y^2,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+2E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\left(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}\right)$$

$$+2E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$-\Big(\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)\Big)$$

Further factoring yields:

$$(x^2-y^2, x^2-y^2) = 4E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{x^2-y^2,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+4E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}}+\cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+4E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}+\cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}\right.$$

$$\left.-\cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}-\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\right)$$

Final factorization and substituting $ak_x = \xi$, $ak_y = \eta$, and $ak_z = \zeta$ (standard literature form):

$$(x^2-y^2, x^2-y^2) = 4E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{x^2-y^2,x^2-y^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+8E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})-\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

Using Slater Koster table 1 we find:

$$E_{x^2-y^2,x^2-y^2}(0,\frac{1}{2},\frac{1}{2}) = \frac{1}{4}E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)+\frac{3}{4}E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)$$

Substituting:

$$(x^2-y^2, x^2-y^2) = E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\left(4\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+3E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)+8E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$$

$$+8E_{x^2-y^2,x^2-y^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})-\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.20 Face cubic crystal $3z^2 - r^2/3z^2 - r^2$ orbital

$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},1,\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(-\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(-\frac{1}{2},1,\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(\frac{1}{2},-\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},1,-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(-\frac{1}{2},-\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(-\frac{1}{2},1,-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},-1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},-1,\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(-\frac{1}{2},\frac{1}{2},-1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(-\frac{1}{2},-1,\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(\frac{1}{2},-\frac{1}{2},-1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(\frac{1}{2},-1,-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(-\frac{1}{2},-\frac{1}{2},-1)$	$E_{3z^2,3z^2}(\frac{1}{2},\frac{1}{2},1)$	$E_{3z^2,3z^2}(-\frac{1}{2},-1,-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(-1,\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(1,-\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(-1,-\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(1,\frac{1}{2},-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(-1,\frac{1}{2},-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$
$E_{3z^2,3z^2}(1,-\frac{1}{2},-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$	$E_{3z^2,3z^2}(-1,-\frac{1}{2},-\frac{1}{2})$	$E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})$

We substitute these, obtaining:

$$(3z^2-r^2,3z^2-r^2) = 4E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{3z^2-r^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}+k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}+k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}+k_z)}$$

$$+e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2}-k_z)}+e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2}-k_z)}+e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2}-k_z)}$$

$$+E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})\Big(e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}+e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}+e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})}$$

$$+e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})}$$

$$+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$(3z^2-r^2,3z^2-r^2) = 4E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{3z^2-r^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+2E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\Big(\cos(k_z)e^{ia\cdot(\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(\frac{k_x}{2}-\frac{k_y}{2})}+\cos(k_z)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_y}{2})}$$

$$+2E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})\Big(\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}+\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})}$$

$$+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)$$

Further factoring yields:

$$(3z^2-r^2,3z^2-r^2) = 4E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{3z^2-r^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+4E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\left(\cos(\frac{k_x}{2})\cos(k_z)e^{ia\frac{k_y}{2}}+\cos(\frac{k_x}{2})\cos(k_z)e^{-ia\frac{k_y}{2}}\right)$$

$$+4E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})\Bigg((\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}+\cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}$$

$$+\cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}+\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\Bigg)$$

Final factorization and substituting $ak_x=\xi$, $ak_y=\eta$, and $ak_z=\zeta$ (standard literature form):

$$(3z^2-r^2,3z^2-r^2) = 4E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\cos(\xi)\cos(\eta)+4E_{3z^2-r^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)+8E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

Using Slater Koster table 1 we find:

$$E_{3z^2-r^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})=\frac{3}{4}E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)+\frac{1}{4}E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)$$

Substituting:

$$(3z^2-r^2,3z^2-r^2)=E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(4\cos(\xi)\cos(\eta)+\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+3E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\left(\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)+8E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},1)\cos(\frac{\xi}{2})\cos(\frac{\eta}{2})\cos(\zeta)$$

$$+8E_{3z^2,3z^2}(1,\frac{1}{2},\frac{1}{2})\left(\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

11.21 Face cubic crystal $x^2 - y^2/3z^2 - r^2$ orbital

$$
\begin{array}{c|c|c|c|c}
E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) & 0 & & E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},1,\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},\tfrac{1}{2},1) & 0 & & E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},1,\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},-\tfrac{1}{2},1) & 0 & & E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},1,-\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},-\tfrac{1}{2},1) & 0 & & E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},1,-\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},\tfrac{1}{2},-1) & 0 & & E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},-1,\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},\tfrac{1}{2},-1) & 0 & & E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},-1,\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},-\tfrac{1}{2},-1) & 0 & & E_{x^2-y^2,3z^2-r^2}(\tfrac{1}{2},-1,-\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},-\tfrac{1}{2},-1) & 0 & & E_{x^2-y^2,3z^2-r^2}(-\tfrac{1}{2},-1,-\tfrac{1}{2}) & -E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) & & E_{x^2-y^2,3z^2-r^2}(-1,\tfrac{1}{2},\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(1,-\tfrac{1}{2},\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) & & E_{x^2-y^2,3z^2-r^2}(-1,-\tfrac{1}{2},\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},-\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) & & E_{x^2-y^2,3z^2-r^2}(-1,\tfrac{1}{2},-\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) \\
E_{x^2-y^2,3z^2-r^2}(1,-\tfrac{1}{2},-\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2}) & & E_{x^2-y^2,3z^2-r^2}(-1,-\tfrac{1}{2},-\tfrac{1}{2}) & E_{x^2-y^2,3z^2-r^2}(1,\tfrac{1}{2},\tfrac{1}{2})
\end{array}
$$

We substitute these, obtaining:

$$
\begin{aligned}
(x^2-y^2,3z^2-r^2) &= 4E_{x^2-y^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right) \\
&+E_{x^2-y^2,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(-e^{ia\cdot(\frac{k_x}{2}+k_y+\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}+k_y+\frac{k_z}{2})}-e^{ia\cdot(\frac{k_x}{2}+k_y-\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}+k_y-\frac{k_z}{2})} \\
&-e^{ia\cdot(\frac{k_x}{2}-k_y+\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}-k_y+\frac{k_z}{2})}-e^{ia\cdot(\frac{k_x}{2}-k_y-\frac{k_z}{2})}-e^{ia\cdot(-\frac{k_x}{2}-k_y-\frac{k_z}{2})} \\
&+e^{ia\cdot(k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(1-\frac{k_y}{2}-\frac{k_z}{2})} \\
&+e^{ia\cdot(-k_x+\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}+\frac{k_z}{2})}+e^{ia\cdot(-k_x+\frac{k_y}{2}-\frac{k_z}{2})}+e^{ia\cdot(-k_x-\frac{k_y}{2}-\frac{k_z}{2})}\Big)
\end{aligned}
$$

We can factor some of the exponential parts out, leaving us with exponential forms of cosines:

$$
(x^2-y^2,3z^2-r^2) = 4E_{x^2-y^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)
$$

$$
\begin{aligned}
&+2E_{x^2-y^2,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Big(-\cos(k_y)e^{ia\cdot(\frac{k_x}{2}+\frac{k_z}{2})}-\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}+\frac{k_z}{2})}-\cos(k_y)e^{ia\cdot(\frac{k_x}{2}-\frac{k_z}{2})}-\cos(k_y)e^{ia\cdot(-\frac{k_x}{2}-\frac{k_z}{2})} \\
&+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}+\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(\frac{k_y}{2}-\frac{k_z}{2})}+\cos(k_x)e^{ia\cdot(-\frac{k_y}{2}-\frac{k_z}{2})}\Big)
\end{aligned}
$$

Further factoring yields:

$$(x^2-y^2,3z^2-r^2) = 4E_{x^2-y^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+4E_{x^2-y^2,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\Bigg(-\cos(\frac{k_x}{2})\cos(k_y)e^{ia\cdot\frac{k_z}{2}}-\cos(\frac{k_x}{2})\cos(k_y)e^{-ia\cdot\frac{k_z}{2}}$$

$$+\cos(k_x)\cos(\frac{k_y}{2})e^{ia\cdot\frac{k_z}{2}}+\cos(k_x)\cos(\frac{k_y}{2})e^{-ia\cdot\frac{k_z}{2}}\Bigg)$$

Final factorization and substituting $ak_x=\xi$, $ak_y=\eta$, and $ak_z=\zeta$ (standard literature form):

$$(x^2-y^2,3z^2-r^2) = 4E_{x^2-y^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2})\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{x^2-y^2,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(-\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$

Using Slater Koster table 1 we find:

$$E_{x^2-y^2,3z^2-r^2}(0,\frac{1}{2},\frac{1}{2}) = \frac{\sqrt{3}}{4}E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)+\frac{\sqrt{3}}{4}E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)$$

Substituting:

$$(x^2-y^2,3z^2-r^2) = \sqrt{3}E_{x^2-y^2,x^2-y^2}(\frac{1}{2},\frac{1}{2},0)\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+\sqrt{3}E_{3z^2-r^2,3z^2-r^2}(\frac{1}{2},\frac{1}{2},0)\left(-\cos(\xi)\cos(\zeta)+\cos(\eta)\cos(\zeta)\right)$$

$$+8E_{x^2-y^2,3z^2-r^2}(1,\frac{1}{2},\frac{1}{2})\left(-\cos(\frac{\xi}{2})\cos(\eta)\cos(\frac{\zeta}{2})+\cos(\xi)\cos(\frac{\eta}{2})\cos(\frac{\zeta}{2})\right)$$