Solid State Theory
Solution Sheet 2

Exercise 2.1 Energy bands of almost free electrons on the fcc lattice

The Bloch equation is written in Fourier space as [see Eq. (1.21) of lecture notes]

$$\left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 - \varepsilon_{n,\vec{k}}\right] c_{\vec{G}} + \sum_{\vec{G}'} V_{\vec{G}-\vec{G}'} c_{\vec{G}'} = 0. \tag{1}$$

For $V \equiv 0$ the dispersion along the Δ-line is shown in Fig. 1 for the few lowest bands. The numbers indicate the degeneracy of the bands. The different lines stem from different

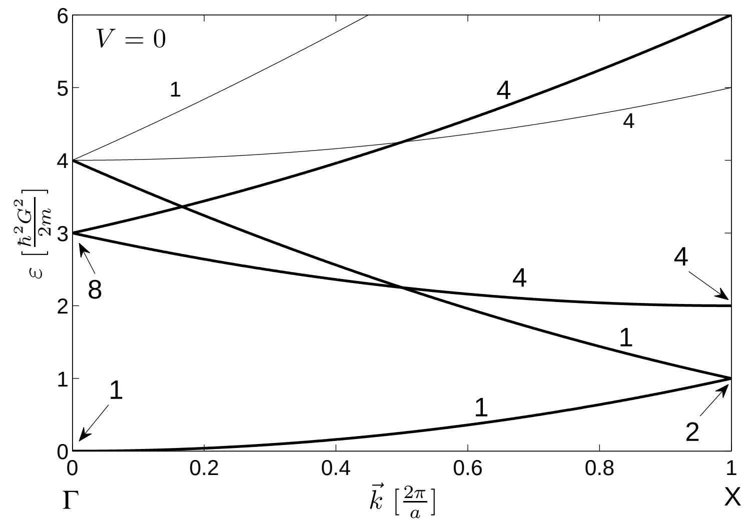

Figure 1: The dispersion along the Δ-line for free electrons on a fcc lattice. The numbers indicate the degeneracy of the eigenstates.

energy parabolas centered at different but equivalent points in reciprocal space. Figure 2 shows the part of the reciprocal lattice which is relevant for the lowest energy bands.

a) For $V = 0$ the second energy level, $E_0 = 3\frac{\hbar^2 G^2}{2m}$, is 8-fold degenerate. It stems from parabolas centered at the 8 points connected to Γ by the following reciprocal lattice vectors:

$$\begin{array}{ll} \vec{G}_1 = G(1,1,1), & \vec{G}_2 = G(-1,1,1), \\ \vec{G}_3 = G(-1,-1,1), & \vec{G}_4 = G(1,-1,1), \\ \vec{G}_5 = G(1,1,-1), & \vec{G}_6 = G(-1,1,-1), \\ \vec{G}_7 = G(-1,-1,-1), & \vec{G}_8 = G(1,-1,-1), \end{array} \tag{2}$$

where $G = \frac{2\pi}{a}$. The eigenfunctions are given by

$$\psi_j(\vec{r}) = \langle \vec{r}|\vec{G}_j\rangle = \frac{e^{i\vec{G}_j\cdot\vec{r}}}{\sqrt{V}} \tag{3}$$

and form an 8 dimensional Hilbertspace. The representation Γ of O_h on this subspace is defined as

$$\hat{\Gamma}(g)|\vec{G}_j\rangle = |g\vec{G}_j\rangle \tag{4}$$

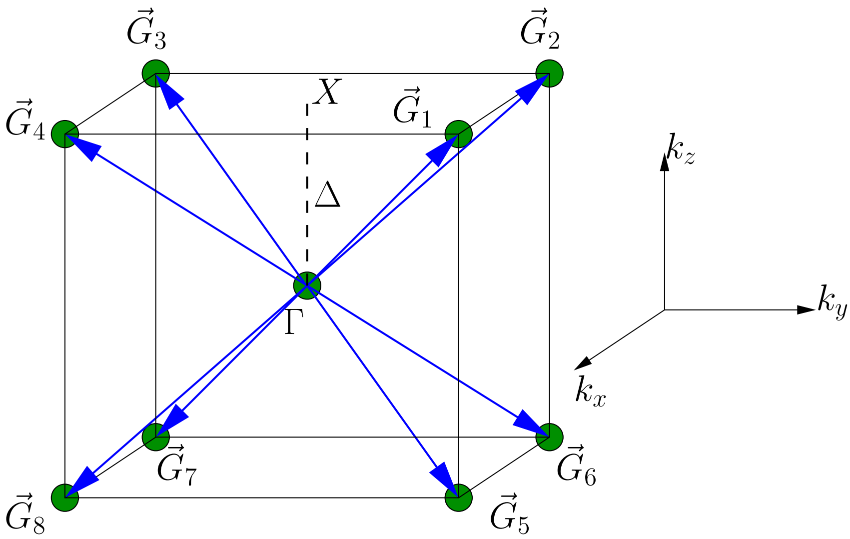

Figure 2: Section of the reciprocal lattice. The length of the cube is $\frac{4\pi}{a}$.

where $g \in O_h$. It is easy to see that each element of the cubic point group simply permutes the $\vec{G}_j$'s. For example, a rotation by $\pi/2$ around the z-axis is represented as

$$R^z_{\pi/2} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}.$$

The character of this transformation is $\chi_\Gamma(R^z_{\pi/2}) = \mathrm{tr}(R^z_{\pi/2}) = 0$. Clearly, in order to find all the characters of the representation Γ defined by Eq. (4) we don't have to compute all the matrices. Instead, we simply have to know how many of the $\vec{G}_i$'s are invariant under a certain element. For this purpose, it is sufficient to consider one element of each conjugacy class. In the following, J will denote the inversion, $C_3(8)$ the conjugacy class of rotations by $2\pi/3$ around one of the diagonals of the cube, $C_4(6)$ the conjugacy class of the rotations by $\pi/2$, $C_2(6)$ the conjugacy class of rotations by π around an axis through the edges of the cube and $C_4^2(3)$ the conjugacy class of the rotations by π around an axis through surface of the cube. (The number in brackets denotes the number of elements in the corresponding conjugacy class.) One finds the following group character

	E	$C_3(8)$	$C_4^2(3)$	$C_2(6)$	$C_4(6)$	J	$JC_3(8)$	$JC_4^2(3)$	$JC_2(6)$	$JC_4(6)$
χ_Γ	8	2	0	0	0	0	0	0	4	0

Using the orthogonality of the characters we can compute how many times the irreducible representation $\Gamma_i^\pm$ is contained in Γ:

$$n_{\Gamma_i^\pm} = \left\langle \chi_\Gamma, \chi_{\Gamma_i^\pm} \right\rangle := \frac{1}{|O_h|} \sum_{g \in O_h} \overline{\chi_\Gamma(g)} \chi_{\Gamma_i^\pm}(g) = \frac{1}{|O_h|} \sum_{C_n} \overline{\chi_\Gamma(C_n)} \chi_{\Gamma_i^\pm}(C_n) \, |C_n|$$

where C_n denotes the conjugacy classes of O_h, $|C_n|$ the order of the conjugacy class (e.g. $C_3(8)$ has 8 elements) and $|O_h| = 48$ the order of the group. One computes

$$
\begin{aligned}
n_{\Gamma_1^+} &= \frac{1}{48}(8 + 2\times 8 + 4\times 6) = 1,\\
n_{\Gamma_1^-} &= \frac{1}{48}(8 + 2\times 8 - 4\times 6) = 0,\\
n_{\Gamma_2^+} &= \frac{1}{48}(8 + 2\times 8 - 4\times 6) = 0,\\
n_{\Gamma_2^-} &= \frac{1}{48}(8 + 2\times 8 + 4\times 6) = 1,\\
n_{\Gamma_{12}^+} &= \frac{1}{48}(2\times 8 - 2\times 8) = 0,\\
n_{\Gamma_{12}^-} &= \frac{1}{48}(2\times 8 - 2\times 8) = 0,\\
n_{\Gamma_{15}^+} &= \frac{1}{48}(3\times 8 - 4\times 6) = 0,\\
n_{\Gamma_{15}^-} &= \frac{1}{48}(3\times 8 + 4\times 6) = 1,\\
n_{\Gamma_{25}^+} &= \frac{1}{48}(3\times 8 + 4\times 6) = 1,\\
n_{\Gamma_{25}^-} &= \frac{1}{48}(3\times 8 - 4\times 6) = 0.
\end{aligned}
$$

Therefore,

$$\Gamma = \Gamma_1^+ \oplus \Gamma_2^- \oplus \Gamma_{15}^- \oplus \Gamma_{25}^+. \tag{5}$$

b) For $V \neq 0$ the wave functions $\psi_j(\vec{r})$ mix. We define the following quantities: $E_0 = \frac{\hbar^2}{2m}3(\frac{2\pi}{a})^2$, $u = V_{\frac{4\pi}{a}\left(\begin{smallmatrix} 1 & 1 & 1 \end{smallmatrix}\right)}$, $v = V_{\frac{4\pi}{a}\left(\begin{smallmatrix} 1 & 0 & 0 \end{smallmatrix}\right)}$ and $w = V_{\frac{4\pi}{a}\left(\begin{smallmatrix} 1 & 1 & 0 \end{smallmatrix}\right)}$. Applying degenerate perturbation theory to Eq. (1) leads to the secular equation

$$\det\begin{pmatrix}
E_0-\varepsilon & v & w & v & v & w & u & w\\
v & E_0-\varepsilon & v & w & w & v & w & u\\
w & v & E_0-\varepsilon & v & u & w & v & w\\
v & w & v & E_0-\varepsilon & w & u & w & v\\
v & w & u & w & E_0-\varepsilon & v & w & v\\
w & v & w & u & v & E_0-\varepsilon & v & w\\
u & w & v & w & w & v & E_0-\varepsilon & v\\
w & u & w & v & v & w & v & E_0-\varepsilon
\end{pmatrix} = 0$$

which has to be solved for ε. By projecting suitable vectors onto the symmetry subspaces found in a) one can systematically construct an eigenbasis and with it find the energies.

However, for relatively small systems it is often possible to guess the correct eigenfunctions using some symmetry properties of the basis functions of the irreducible representations. Since the physical eigenfunctions have to be periodic in real space it is natural to use combinations of $\cos(Gx)$ and $\sin(Gx)$ etc. (Instead of the polynomials given on page 15 of the lecture notes.)

1. The eigenfunction belonging to the subset Γ_1^+ has to be totally symmetric under all the operations. Therefore, $e_1 = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$ is an eigenvector with energy $\varepsilon_1 = E_0 + u + 3v + 3w$. The physical eigenfunction can be found as $f_1(\vec{r}) \sim \sum_j e^{i\vec{G}_j\vec{r}} \sim \cos(Gx)\cos(Gy)\cos(Gz)$.

2. The eigenfunction belonging to the subset Γ_2^- has to be symmetric under interchange of x, y and z but has to change sign if an odd number of the coordinates changes sign (see character table). The function $f_2(\vec{r}) \sim \sin(Gx)\sin(Gy)\sin(Gz)$ fulfills these conditions. Writing it as a linear combination of the $e^{i\vec{G}_j\cdot\vec{r}}$ we find the eigenvector $e_2 = \begin{pmatrix} 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \end{pmatrix}$. The energy is $\varepsilon_2 = E_0 - u - 3v + 3w$

3. For Γ_{15}^- we need three functions which are odd under the inversion operation $\vec{r} \to -\vec{r}$. We therefore need an odd number of sin's. What is left are the combinations $f_3(\vec{r}) \sim \sin(Gx)\cos(Gy)\cos(Gz)$, $f_4(\vec{r}) \sim \cos(Gx)\sin(Gy)\cos(Gz)$ and $f_5(\vec{r}) \sim \cos(Gx)\cos(Gy)\sin(Gz)$. They correspond to the following vectors

$$\begin{aligned}
e_3 &= \begin{pmatrix} 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \end{pmatrix} \\
e_4 &= \begin{pmatrix} 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \end{pmatrix} \\
e_5 &= \begin{pmatrix} 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \end{pmatrix}
\end{aligned}$$

with energy $\varepsilon_{3-5} = E_0 - u + v - w$.

4. The eigenfunctions belonging to the subspace Γ_{25}^+ are even under inversion $\vec{r} \to -\vec{r}$. Therefore, the functions $f_6(\vec{r}) \sim \cos(Gx)\sin(Gy)\sin(Gz)$, $f_7(\vec{r}) \sim \sin(Gx)\cos(Gy)\sin(Gz)$ and $f_8(\vec{r}) \sim \sin(Gx)\sin(Gy)\cos(Gz)$ are good candidates. The corresponding vectors are

$$\begin{aligned}
e_6 &= \begin{pmatrix} 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \end{pmatrix} \\
e_7 &= \begin{pmatrix} 1 & -1 & -1 & 1 & -1 & 1 & 1 & -1 \end{pmatrix} \\
e_8 &= \begin{pmatrix} 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \end{pmatrix}
\end{aligned}$$

and are indeed eigenvectors with energy $\varepsilon_{6-8} = E_0 + u - v - w$.

c) On the Δ-line the number of symmetry operations which leave the $\vec{k}$-vector invariant is reduced. Only the rotations around the z-axis or the reflections on mirror planes containing the z-axis leaves the $\vec{k}$-vector invariant. The "small group" is now C_{4v}, the symmetry group of a square. Under these reduced operations, the irreducible representation of O_h will in general split into irreducible representations of C_{4v}.

(i) Of course, the trivial representation of O_h changes to the trivial representation of C_{4v}: $\Gamma_1^+ \mapsto \Delta_1$.

(ii) Under the operations of C_{4v} the group character of Γ_2^- is easily found using the properties of the basis function $f_2(\vec{r})$:

C_{4v}	E	C_4^2	C_4	σ_v	σ_d
$\chi_{\Gamma_2^-}$	1	1	-1	-1	1

(6)

This is the character of Δ_4 and therefore $\Gamma_2^- \mapsto \Delta_4$.

(iii) Using the basis functions $\{f_3(\vec{r}), f_4(\vec{r}), f_5(\vec{r})\}$ we find the following matrices belonging to different conjugacy classes

$$C_4^2([\bar{x}\bar{y}z]) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_4([y\bar{x}z]) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\sigma_v([\bar{x}yz]) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_d([yxz]) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The group character is then found to be

$$\begin{array}{c|ccccc} C_{4v} & E & C_4^2 & C_4 & \sigma_v & \sigma_d \\ \hline \chi_{\Gamma_4^-} & 3 & -1 & 1 & 1 & 1 \end{array} \tag{7}$$

Again we use the orthogonality of the characters and compute

$$\begin{aligned} n_{\Delta_1} &= \frac{1}{8}(3-1+2+2+2) = 1, \\ n_{\Delta_2} &= \frac{1}{8}(3-1+2-2-2) = 0, \\ n_{\Delta_3} &= \frac{1}{8}(3-1-2+2-2) = 0, \\ n_{\Delta_4} &= \frac{1}{8}(3-1-2-2+2) = 0, \\ n_{\Delta_5} &= \frac{1}{8}(6+2) = 1. \end{aligned}$$

Therefore, $\Gamma_{15}^- \mapsto \Delta_1 \oplus \Delta_5$.

(iv) For Γ_{25}^+ we find in an analogous way

$$\begin{array}{c|ccccc} C_{4v} & E & C_4^2 & C_4 & \sigma_v & \sigma_d \\ \hline \chi_{\Gamma_{25}^+} & 3 & -1 & -1 & -1 & 1 \end{array} \tag{8}$$

and therefore $\Gamma_5^+ \mapsto \Delta_4 \oplus \Delta_5$.

d) At the point $X = \frac{2\pi}{a} \begin{pmatrix} 0 & 0 & 1 \end{pmatrix}$ the small group is again bigger. It contains all the elements of O_h which map z to z or to $-z$. This group is called D_{4h}. In order to compute the lifting of the degeneracy of the lowest two levels we can simply diagonalize the corresponding matrices.

Lowest level: The $\vec{G}$-vectors entering the Bloch equation in lowest order in the periodic potential are $\vec{G}_0 = 0$ and $\vec{G}_9 = 2G(0,0,1)$. Furthermore, $v = V_{\vec{G}_0 - \vec{G}_9}$ enters and we have to solve

$$\det \begin{pmatrix} \frac{\hbar^2 G^2}{2m} - E & v \\ v & \frac{\hbar^2 G^2}{2m} - E \end{pmatrix} = 0.$$

The solution is $E_1 = E_0 + v$ with $e_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $E_2 = E_0 - v$ with $e_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$. The eigenfunctions are $\cos Gz$ and $\sin Gz$, respectively. In the lecture notes one finds the irreducible representations of D_{4h} and it is clear that e_1 corresponds to X_1^+ and e_2 to X_2^-.

Second-lowest level: The $\vec{G}$-vectors entering the Bloch equation in lowest order in the periodic potential are $\vec{G}_1$ to $\vec{G}_4$ and we have to diagonalize the matrix

$$\begin{pmatrix} 2\frac{\hbar^2 G^2}{2m} & v & w & v \\ v & 2\frac{\hbar^2 G^2}{2m} & v & w \\ w & v & 2\frac{\hbar^2 G^2}{2m} & v \\ v & w & v & 2\frac{\hbar^2 G^2}{2m} \end{pmatrix}.$$

Here, v and w have the same meaning as above. From the symmetry of the matrix it is clear that the eigenvectors are of the form (a, b, b, a) and $(a, b, -b, -a)$. One then finds

$$\begin{aligned}
e_1 &= \begin{pmatrix} 1 & 1 & 1 & 1 \end{pmatrix} \text{ and } E_1 = 2\frac{\hbar^2 G^2}{2m} + 2v + w, \\
e_2 &= \begin{pmatrix} 1 & 1 & -1 & -1 \end{pmatrix} \text{ and } E_2 = 2\frac{\hbar^2 G^2}{2m} - w, \\
e_3 &= \begin{pmatrix} 1 & -1 & -1 & 1 \end{pmatrix} \text{ and } E_3 = 2\frac{\hbar^2 G^2}{2m} - w, \\
e_4 &= \begin{pmatrix} 1 & -1 & 1 & -1 \end{pmatrix} \text{ and } E_4 = 2\frac{\hbar^2 G^2}{2m} - 2v + w.
\end{aligned}$$

Again, comparing the eigenfunctions with page 16 of the lecture notes we see that e_1 corresponds to X_1^+ and e_4 to X_2^+. Furthermore, e_2 and e_3 have to span the only two-dimensional irreducible representation X_5^- of D_{4h}.

e) The dispersion along the Δ-line can now be sketched. Assuming that the only non-vanishing components of the potential are u, v and w we can diagonalize the matrices also for $0 < \delta < 1$ in order to get the dispersion along the Δ-line. The result is shown in Fig. 3. One can see that the degeneracy is partially lifted when going away from the Γ point. In general, other components of the potential will lead to a hybridization of the bands at the places where they cross. In this respect, the plot shown in Fig. 3 is incomplete.

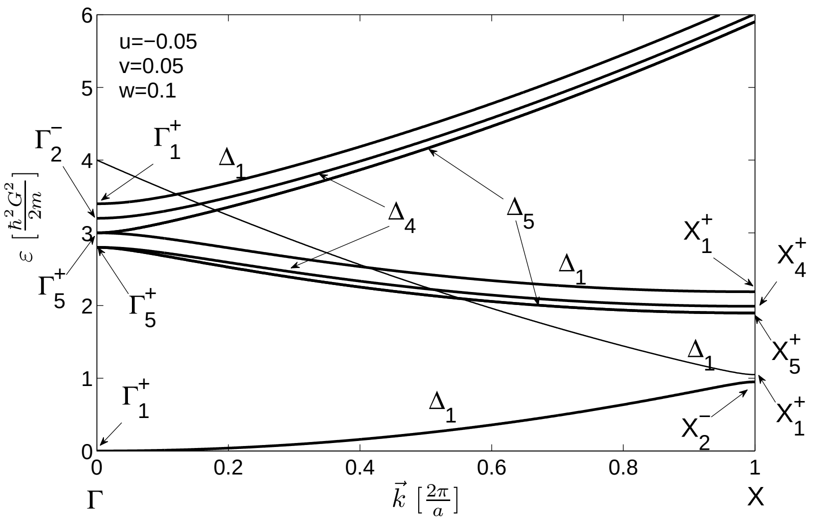

Figure 3: The dispersion along the Δ-line for almost free electrons on a fcc lattice for a potential which is characterized by u, v and w.

Exercise 2.2 Lifting the degeneracy of the atomic states

The continuous group $O(3)$ has irreducible representations in each odd dimension $2l+1$. The spherical harmonics $Y_{lm}(\theta, \phi)$, $m = -l, \ldots, l$ form a basis for the $(2l+1)$ dimensional representations. Within the group $O(3)$, each element which describes a rotation by the same angle belongs to the same conjugacy class. Therefore, we can focus on the rotations around the z-axis. A rotation around the z axis transforms the spherical harmonics according to

$$Y_{lm}(\theta,\phi) \mapsto Y_{lm}(\theta,\phi+\alpha) = e^{im\alpha} Y_{lm}(\theta,\phi).$$

The matrix for such a rotation is diagonal in the basis of the spherical harmonics:

$$D^{(l)}(\alpha) = \mathrm{diag}(e^{-il\alpha},\ldots,e^{il\alpha}). \tag{9}$$

The trace is given by

$$\begin{aligned}
\chi_l(\alpha) &= \sum_{m=-l}^{l} e^{im\alpha} = 1 + \sum_{m=1}^{l} e^{im\alpha} + \sum_{m=1}^{l} e^{-im\alpha} \\
&= 1 + \frac{e^{i\alpha} - e^{i\alpha(l+1)}}{1-e^{i\alpha}} + \frac{e^{-i\alpha} - e^{-i\alpha(l+1)}}{1-e^{-i\alpha}} = \ldots \\
&= \frac{\cos(\alpha l) - \cos\left[\alpha(l+1)\right]}{1-\cos(\alpha)} = \frac{\sin\left[\alpha(l+\frac{1}{2})\right]}{\sin(\frac{\alpha}{2})}
\end{aligned} \tag{10}$$

Now we assume that the atom belongs to a crystal with a crystal field of cubic symmetry. Due to the reduced symmetry the representations will in general split into irreducible representations of O_h.

***p*-orbitals, l=1** From Eq. (10) we obtaine for $l = 1$ the following group character

O_h	E	$C_3(8)$	$C_4^2(3)$	$C_2(6)$	$C_4(6)$
χ_p	3	0	-1	-1	1

There is no need to worry about the inversion, because the parity of the spherical harmonics is known to be $(-1)^l$. Using the orthogonality relation we find

$$\begin{aligned}
n_{\Gamma_1} &= \frac{1}{24}(3-3-6+6) = 0, \\
n_{\Gamma_2} &= \frac{1}{24}(3-3+6-6) = 0, \\
n_{\Gamma_{12}} &= \frac{1}{24}(6-6) = 0, \\
n_{\Gamma_{15}} &= \frac{1}{24}(9+3+6+6) = 1, \\
n_{\Gamma_{25}} &= \frac{1}{24}(3-3+6-6) = 0.
\end{aligned}$$

Because the parity for $l = 1$ is -1 it follows that $D_1 \mapsto \Gamma_{15}^-$.

***d*-orbitals, l=2** In the same way we find for $l = 2$

O_h	E	$C_3(8)$	$C_4^2(3)$	$C_2(6)$	$C_4(6)$
χ_d	5	-1	1	1	-1

and

$$\begin{aligned}
n_{\Gamma_1} &= \frac{1}{24}(5-8+3+6-6) = 0, \\
n_{\Gamma_2} &= \frac{1}{24}(5-8+3-6+6) = 0, \\
n_{\Gamma_{12}} &= \frac{1}{24}(10+8+6) = 1, \\
n_{\Gamma_{15}} &= \frac{1}{24}(15-3-6-6) = 0, \\
n_{\Gamma_{25}} &= \frac{1}{24}(15-3+6+6) = 1.
\end{aligned}$$

Since the parity is now positive it follows that $D_2 \mapsto \Gamma_{12}^+ \oplus \Gamma_{25}^+$.

f-orbitals, l=3

O_h	E	$C_3(8)$	$C_4^2(3)$	$C_2(6)$	$C_4(6)$
χ_f	7	1	-1	-1	-1

This yields

$$\begin{aligned}
n_{\Gamma_1} &= \frac{1}{24}(7+8-3-6-6) = 0, \\
n_{\Gamma_2} &= \frac{1}{24}(7+8-3+6+6) = 1, \\
n_{\Gamma_{12}} &= \frac{1}{24}(14-8-6) = 0, \\
n_{\Gamma_{15}} &= \frac{1}{24}(21+3+6-6) = 1, \\
n_{\Gamma_{25}} &= \frac{1}{24}(21+3-6+6) = 1.
\end{aligned}$$

Because of the negative parity we obtain $D_3 \mapsto \Gamma_2^- \oplus \Gamma_{15}^- \oplus \Gamma_{25}^-$.

Eigenfunctions of the d-orbitals We know that $D_2 \mapsto \Gamma_{12}^+ \oplus \Gamma_{25}^+$ where Γ_{12}^+, Γ_{25}^+ are two and three dimensional representations, respectively. It is also known that the spherical harmonics for $l = 2$ form a basis for the harmonic, homogeneous polynomials of order 2. Such a polynomial can be written as

$$P = c_1 xz + c_2 xy + c_3 yz + c_4(x^2 - z^2) + c_5(y^2 - z^2) \tag{11}$$

where it is implicitly assumed that $x^2 + y^2 + z^2 = 1$. Now let us consider a rotation around the z axis by $\pi/2$. Thus, $z \mapsto z$, $x \mapsto y$ and $y \mapsto -x$. This yields

$$\begin{aligned}
xz \mapsto yz \;\; xy \mapsto -xy \;\; yz \mapsto -xz, \\
x^2 \mapsto y^2 \;\; y^2 \mapsto x^2 \;\; z^2 \mapsto z^2.
\end{aligned}$$

We see that the triple $\{xz, xy, yz\}$ and the duple $\{x^2 - z^2, y^2 - z^2\}$ do not mix under this transformation. Therefore,
$\{xz, xy, yz\} = \left\{\cos\phi \sin\theta \cos\theta, \cos\phi \sin\phi \sin^2\theta, \sin\phi \sin\theta \cos\theta\right\}$ is a basis for Γ_{25}^+ and $\{x^2 - z^2, y^2 - z^2\} = \{\cos\phi^2 \sin\theta^2 - \cos\theta^2, \sin\phi^2 \sin\theta^2 - \cos\theta^2\}$ is a basis for Γ_{12}^+. Often, the two dimensional subspace of Γ_{12}^+ is called the e_g subspace and the three dimensional subspace of Γ_{25}^+ is called the t_{2g} subspace.