Solid State Theory
Exercise 2

Point groups and their representations: Energy bands of nearly free electrons on the fcc lattice

Let us consider almost free electrons on a face-centered cubic (fcc) lattice. The goal of this exercise is to compute the lowest energy bands along the Δ-line using degenerate perturbation theory and the machinery of *group theory*.

- What does the first Brillouin zone of the fcc look like? Include a sketch and label the Γ and X points. The line connecting them is the above mentioned Δ-line.

The Bloch equation is written in Fourier space as

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

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

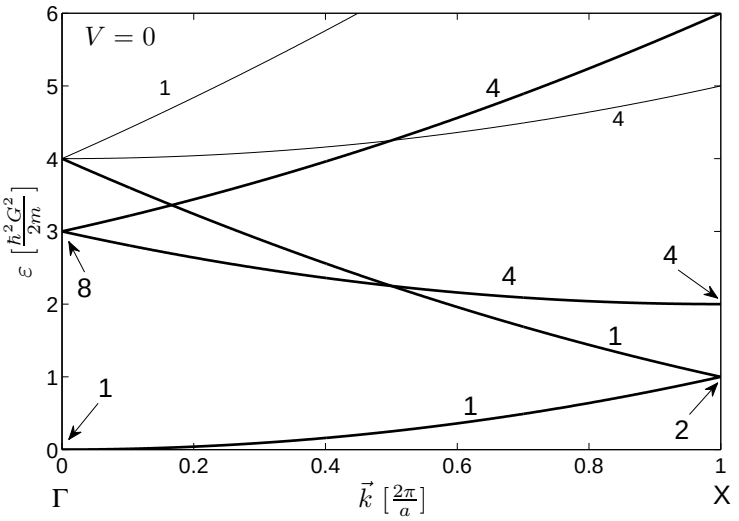

Figure 1: The dispersion along the Δ-line for free electrons on a fcc lattice. The numbers indicate the degeneracy of the eigenstates.

energy parabolas centered at different but equivalent points in reciprocal space.

- Relate the different curves and their degeneracies to the different contributions from points in the reciprocal space. Draw the nearest and next nearest neighbour reciprocal vectors and label them. Use the same labels to label the curves in Fig. 1.

We first study the Γ point. For *free* electrons ($V = 0$) the lowest energy level is non-degenerate and the second one has an eight fold degeneracy. From here on we focus on

the second energy level.

As you found in the previous part, the 8-fold degeneracy 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 $G = \frac{2\pi}{a}$. These vectors form an 8 dimensional Hilbertspace, and the eigenfunctions are given by

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

The point group of the cubic Bravais lattices (simple cubic, fcc, bcc) is denoted by O_h (symmetry group of a cube). Its character table is given in Tab. 1.

O_h	E $[xyz]$	$C_3(8)$ $[zxy]$	$C_4^2(3)$ $[\bar{x}\bar{y}z]$	$C_2(6)$ $[yx\bar{z}]$	$C_4(6)$ $[\bar{y}xz]$	J $[\bar{x}\bar{y}\bar{z}]$	$JC_3(8)$ $[\bar{z}\bar{x}\bar{y}]$	$JC_4^2(3)$ $[xy\bar{z}]$	$JC_2(6)$ $[\bar{y}\bar{x}z]$	$JC_4(6)$ $[y\bar{x}\bar{z}]$
$\chi_{\Gamma_1^+}$	1	1	1	1	1	1	1	1	1	1
$\chi_{\Gamma_1^-}$	1	1	1	1	1	−1	−1	−1	−1	−1
$\chi_{\Gamma_2^+}$	1	1	1	−1	−1	1	1	1	−1	−1
$\chi_{\Gamma_2^-}$	1	1	1	−1	−1	−1	−1	−1	1	1
$\chi_{\Gamma_{12}^+}$	2	−1	2	0	0	2	−1	2	0	0
$\chi_{\Gamma_{12}^-}$	2	−1	2	0	0	2	1	−2	0	0
$\chi_{\Gamma_{15}^+}$	3	0	−1	−1	1	3	0	−1	−1	1
$\chi_{\Gamma_{15}^-}$	3	0	−1	−1	1	−3	0	1	1	−1
$\chi_{\Gamma_{25}^+}$	3	0	−1	1	−1	3	0	−1	1	−1
$\chi_{\Gamma_{25}^-}$	3	0	−1	1	−1	−3	0	1	−1	1

Table 1: The character table of the cubic point group O_h.

We will denote the eight-dimensional representation of O_h defined on this subspace by Γ. Find the irreducible representations contained in Γ. To this end, we compute the group character χ_Γ and use the character table of O_h to show that

$$\Gamma = \Gamma_1^+ \oplus \Gamma_2^- \oplus \Gamma_{15}^- \oplus \Gamma_{25}^+. \tag{4}$$

The representation Γ of O_h on this subspace is defined as

$$\hat{\Gamma}(g)|\vec{G}_j\rangle = |g\vec{G}_j\rangle \tag{5}$$

where $g \in O_h$.

- How does a real space vector $\vec{r}$ change under the action of such a symmetry operation?

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. (5) 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.

- Explain shortly why one obtains the character in this case simply by counting the invariant $\vec{G}_i$'s.

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 $C^2_4(3)$ 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.)

- Complete the following character table

	E	$C_3(8)$	$C^2_4(3)$	$C_2(6)$	$C_4(6)$	J	$JC_3(8)$	$JC^2_4(3)$	$JC_2(6)$	$JC_4(6)$
χ_Γ	.	.	.	.	0	.	.	.	.	.

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

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

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

$$n_{\Gamma^+_1} = \frac{1}{48}(8 + 2 \times 8 + 4 \times 6) = 1 \tag{6}$$

Similarly, one finds $n_{\Gamma^-_2} = n_{\Gamma^-_{15}} = n_{\Gamma^+_{25}} = 1$, while all the others are 0. Therefore,

$$\Gamma = \Gamma^+_1 \oplus \Gamma^-_2 \oplus \Gamma^-_{15} \oplus \Gamma^+_{25}. \tag{7}$$

A finite periodic potential will in general split the second energy level at the Γ point. Applying degenerate perturbation theory to the Bloch equation [Eq. (1.27) in the lecture notes] leads to an 8×8 matrix with off-diagonal elements $u = V_{\frac{4\pi}{a}(1,1,1)}$, $v = V_{\frac{4\pi}{a}(1,0,0)}$ and $w = V_{\frac{4\pi}{a}(1,1,0)}$.

- Check for yourself that this matrix is given by

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

This matrix can be diagonalized by going into the symmetry subspaces. We will show that for the energies and the wave functions one finds

$$\begin{array}{lll} \Gamma_1^+: & E_0+u+3v+3w & \cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right); \\ \Gamma_2^-: & E_0-u-3v+3w & \sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right)\sin\left(\frac{2\pi}{a}z\right); \\ \Gamma_{15}^-: & E_0-u+v-w & \left\{\sin\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right), \text{cyclic}\right\}; \\ \Gamma_{25}^+: & E_0+u-v-w & \left\{\cos\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right)\sin\left(\frac{2\pi}{a}z\right), \text{cyclic}\right\}; \end{array} \tag{8}$$

where $E_0 = \frac{\hbar^2}{2m}3(\frac{2\pi}{a})^2$.

For $V \neq 0$ the wave functions $\psi_j(\vec{r})$ mix. Applying degenerate perturbation theory means we have to solve the secular equation:

$$\det A = 0$$

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.

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

- Using the character table, repeat the above steps to find the eigenfunction $f_2(\vec{r})$ belonging to the subset Γ_2^-. Also compute its energy.

- Again, repeat the above for the eigenfunctions and energy belonging to the subspace Γ_{25}^{+}.

How do the irreducible representations split on the Δ-line? The Δ-line is defined by the points $\vec{k} = \frac{2\pi}{a}(0, 0, \delta)$, $0 \leq \delta \leq 1$ (i.e. we choose the z-axis going through X). Use the character table of C_{4v}.

C_{4v}	E $[xyz]$	$C_2(1)$ $[\bar{x}\bar{y}z]$	$C_4(2)$ $[y\bar{x}z]$	$\sigma_v(2)$ $[\bar{x}yz]$	$\sigma_d(2)$ $[yxz]$
χ_{Δ_1}	1	1	1	1	1
χ_{Δ_2}	1	1	1	-1	-1
χ_{Δ_3}	1	1	-1	1	-1
χ_{Δ_4}	1	1	-1	-1	1
χ_{Δ_5}	2	-2	0	0	0

Table 2: The character table of C_{4v}.

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 representations 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

(9)

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

- Using the basis functions $\{f_3(\vec{r}), f_4(\vec{r}), f_5(\vec{r})\}$, find the matrix belonging to the different conjugacy classes. For example, a matrix belonging to the conjugacy class $C_4([y\bar{x}z])$ would be computed as follows. Consider the function $f_3(x, y, z)$; then performing a C_4 rotation, this function becomes $f_3(y, -x, z)$. Inspection of this latter function shows that it is identical to $f_4(x, y, z)$, explaining the first row of the following matrix:

$$C_4([y\bar{x}z]) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{10}$$

  It is imporant to realize that this transformation acts on the basis functions (imagine a vector (f_3, f_4, f_5) on which this matrix acts). In this case, the matrix can also be found by considering simply the vector $(x, y, z) \to (y, -x, z)$).

  Then compute the group character and extract the irreducible representations by using the orthogonality of the characters (as in the first part of this exercise).

$$\begin{array}{c|ccccc} C_{4v} & E & C_4^2 & C_4 & \sigma_v & \sigma_d \\ \hline \chi_{\Gamma_4^-} & \cdot & \cdot & \cdot & \cdot & \cdot \end{array} \tag{11}$$

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

$$\begin{array}{c|ccccc} C_{4v} & E & C_4^2 & C_4 & \sigma_v & \sigma_d \\ \hline \chi_{\Gamma_{25}^+} & 3 & -1 & -1 & -1 & 1 \end{array} \tag{12}$$

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

Let us now consider the point $X = \frac{2\pi}{a}(0,0,1)$. The lowest level is two fold and the second four fold degenerate for $V = 0$. Compute the energies and the wave functions for these two levels.

At the point $X = \frac{2\pi}{a}\begin{pmatrix} 0 & 0 & 1 \end{pmatrix}$ the symmetry is larger than along the Δ-line, but smaller than the full group O_h. 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. The irreducible representation of D_{4h} are given in Table 3.

even	basis function	d_X	odd	basis function	d_X
X_1^+	1	1	X_1^-	$xyz(x^2-y^2)$	1
X_2^+	$xy(x^2-y^2)$	1	X_2^-	z	1
X_3^+	x^2-y^2	1	X_3^-	xyz	1
X_4^+	xy	1	X_4^-	$z(x^2-y^2)$	1
X_5^+	zx, zy	2	X_5^-	x, y	1

Table 3: Irreducible representations of D_{4h}, split according to their parity ($z \to z$ or $z \to -z$. The dimension of the irreducible representation is indicated in the column labeled d_X.

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 as well.

- Construct the secular equation, and find the eigenvectors.

The eigenfunctions you find from the vectors are $\cos Gz$ and $\sin Gz$, respectively. Comparing this to the irreducible representations of D_{4h} we find 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

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

- Compare these results again to the eigenfunctions given in Table 3, and identify the irreducible representations they belong to.

- Finally, sketch the energy bands between the Γ and the X point and compare it to the free electron ($V = 0$ case). For an actual numerical calculation use the values $u = -0.05$, $v = 0.05$ and $w = 0.1$ (in units of $\frac{(2\pi\hbar)^2}{2ma^2}$).

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