Lecture 4 — Symmetry in the solid state -

Part IV: Brillouin zones and the symmetry of the band structure.

1 Symmetry in Reciprocal Space — the Wigner-Seitz construction and the Brillouin zones

Non-periodic phenomena in the crystal (elastic or inelastic) are described in terms of generic (non-RL) reciprocal-space vectors and give rise to scattering outside the RL nodes.

In describing these phenomena, however, one encounters a problem: as one moves away from the RL origin, symmetry-related “portions” of reciprocal space will become very distant from each other. In order to take full advantage of the reciprocal-space symmetry, it is therefore advantageous to bring symmetry-related parts of the reciprocal space together in a compact form. This is exactly what the Wigner-Seitz (W-S) constructions accomplish very cleverly. "Brillouin zones" is the name that is given to the portions of the extended W-S contructions that are “brought back together”. A very good description of the Wigner-Seitz and Brillouin constructions can be found in [3].

1.1 The Wigner-Seitz construction

The W-S construction is essentially a method to construct, for every Bravais lattice, a fully-symmetric unit cell that has the same volume of a primitive cell. As such, it can be applied to both real and reciprocal spaces, but it is essentially employed only for the latter.

For a given lattice node \( \tau \), the W-S unit cell containing \( \tau \) is the set of points that are closer to \( \tau \) than to any other lattice node.

It is quite apparent that:

- Each W-S unit cell contains one and only one lattice node.
- Every point in space belongs to at least one W-S unit cell. Points belonging to more than one cell are boundary points between cells.
- From the previous two points, it is clear that the W-S unit cell has the same volume of a primitive unit cell. In fact, it “tiles” the whole space completely with identical cells, each containing only one lattice node.
Figure 1: Construction of the W-S unit cell for the case of a \( C \)-centered rectangular lattice in 2D. 

A: bisecting lines are drawn to the segments connecting the origin with the neighbouring points (marked “1”). B: these lines define a polygon — the W-S unit cell. C: the W-S unit cell is shown together with lines bisecting segments to more distant lattice points.

- The W-S unit cell containing the origin has the full point-group symmetry of the lattice (holohedry). In real space, the origin is arbitrary, and all the W-S unit cells are the same. In the “weighed” reciprocal space the W-S at \( q = 0 \) is unique in having the full point-group symmetry. As we shall see shortly, the Brillouin zone scheme is used to project fully-symmetric portions of reciprocal space away from the origin into the first W-S unit cell.
A dummies’ guide to the W-S construction (fig. 1)

- Draw segments connecting the origin with the neighbouring points. The first “ring” of points (marked with “1” in fig. 1 A) should be sufficient, although these points may not all be symmetry-equivalent.

- Draw orthogonal lines bisecting the segments you just drew. These lines define a polygon containing the origin (fig. 1 B)—this is the W-S unit cell. In 3D, one would need to draw orthogonal bisecting planes, yielding W-S polyhedra.

- Fig. 1 C shows an extended construction (to be used later) including lines bisecting the segments to the second and third “rings”. As you can see, the new lines do not intersect the original W-S unit cell.

- The whole space can be “tiled” with W-S cells (fig. 2).

1.1.1 “Reduction” to the first Wigner-Seitz unit cell (first Brillouin zone).

As anticipated, the main use of the W-S unit cell is in reciprocal space:

Every vector \( q \) in reciprocal space can be written as

\[
q = k + \tau
\]  

(1)

where \( \tau \) is a \( RL \) vector and \( k \) is within the first W-S unit cell. (i.e., the one containing the origin). We more often say that \( k \) is the “equivalent” of \( q \) reduced to the first Brillouin zone (see here below).

The repeated W-S scheme shown in fig. 2 is used to determine which \( \tau \) should be used for a given \( q \) — clearly, the one corresponding to the lattice node closer to it.

1.2 The extended W-S construction: higher Brillouin zones

We have just learned how to “reduce” every reciprocal-space point to the first W-S unit cell (or first Brillouin zone). But the question is: which “bits” of reciprocal space should be “reduced” together? One may be tempted to think that an entire W-S unit cell around a \( RL \) point should be “reduced” together — after all, one would only need a single \( RL \) vector to accomplish this. It is readily seen, however, that this is not a good idea. As we mentioned before, higher W-S unit cells (i.e., other than the first) do not possess any symmetry, and we are specifically interested in “reducing” together symmetry-related parts of reciprocal space. Therefore, a different construction, known as the extended W-S construction—is required to reduce symmetry-related
Figure 2: Repeated W-S cell scheme, showing how the entire space can be tiled with these cells. Each cell can be “reduced” to the first W-S cell with a single $RL$ vector.

portions of reciprocal space simultaneously.

The first Brillouin zone coincides with the first W-S unit cell. Higher W-S unit cells are emphatically not Brillouin zones.
Figure 3: The extended W-S construction. The starting point is fig. 1 C. A A number is given to each polygon, according to how many lines are crossed to reach the origin. Polygons with the same number belong to the same Brillouin zone. The figure shows the scheme for the first three Brillouin zones. B Portions of a higher Brillouin zone can be reduced to the first Brillouin zone in the normal way, i.e., by using the repeated W-S construction (here, the reduction procedure is shown for the third zone). C When reduced, higher zones “tile” perfectly within the first W-S cell.
A dummies’ guide to the extended W-S construction (fig. 3)

- Start off in the same way as for the “normal” W-S construction, but with lines bisecting the segments to higher-order “rings” of points, as per fig. 1 C.

- Many polygons of different shapes (polyhedra in 3D) will be obtained. Each of these will be given a number according to how many lines (planes in 3D) are crossed to reach the origin with a straight path. If m lines (planes) are crossed, the order of the Brillouin zone will be \(m + 1\).

- A Brillouin zone is formed by polygons (polyhedra) having the same number (fig. 3 A).

- As anticipated, the first Brillouin zone is also the first W-S cell (no line is crossed).

- The different portions of a Brillouin zone are “reduced” to the first Brillouin zone in the normal way, i.e., using the repeated W-S construction (fig. 3 B).

- All the portions of a higher Brillouin zone will tile perfectly within the first Brillouin zone (fig. 3 C).

2 Symmetry of the electronic band structure

We will now apply the concepts introduced here above to describe a number of important properties of all wave-like excitations in crystals that can be determined purely based on symmetry considerations. We will only consider the case of electronic wavefunctions, but it is important to state that almost identical considerations can be applied to other wave-like excitations in crystals, such as phonons and spin waves (magnons).

The starting point of this discussion is the Bloch theorem, which you have already encountered in previous courses. Later in the course we will present a general symmetry prospective of this theorem, but here we will just quote the main results: the electronic eigenstates of a Hamiltonian with a periodic potential are of the Bloch form:

\[
\psi_k(r) = e^{i \mathbf{k} \cdot \mathbf{r}} u_k(r) \tag{2}
\]

where \(u_k(r)\) has the periodicity of the crystal. We also recall that the crystal wavevector \(k\) can be limited to the first Brillouin zone (BZ). In fact, a function \(\psi_k'(r) = e^{i \mathbf{k}' \cdot \mathbf{r}} u_k'(r)\) with \(k'\) outside the first BZ can be rewritten as

\[
\psi_k'(r) = e^{i \mathbf{k} \cdot \mathbf{r}} \left[ e^{i \mathbf{r} \cdot \mathbf{r}} u_k(r) \right] \tag{3}
\]
Figure 4: A set of typical 1-dimensional electronic dispersion curves in the reduced zone scheme.

where $k' = \tau + k$, $k$ is within the 1\textsuperscript{st} BZ and $\tau$ is a reciprocal lattice vector ($RLV$). Note that the function in square brackets has the periodicity of the crystal, so that eq. 3 is in the Bloch form.

The application of the Bloch theorem to 1-dimensional (1D) electronic wavefunctions, using either the nearly-free electron approximation or the tight-binding approximation leads to the typical set of electronic dispersion curves ($E$ vs. $k$ relations) shown in fig. 4. We draw attention to three important features of these curves:

\textbf{Properties of the electronic dispersions in 1D}

- They are symmetrical (i.e., even) around the origin.
- The left and right zone boundary points differ by the $RLV$ $2\pi/a$, and are also related by symmetry.
- The slope of the dispersions is zero both at the zone centre and at the zone boundary. We recall that the slope (or more generally the gradient of the dispersion is related to the group velocity of the wavefunctions in band $n$ by:

$$v_n(k) = \frac{1}{\hbar} \frac{\partial E_n(k)}{\partial k}$$

As we shall see shortly, these 1D properties do not give much of a clue of what goes on in 2D and 3D. We will just state the corresponding properties in 2D and 3D, and proceed to give some justification of these statements.
Properties of the electronic dispersions in 2D and 3D

- They have the full Laue (point-group) symmetry of the crystal. This applies to both energies (scalar quantities) and velocities (vector quantities).

- Zone edge centre (2D) or face centre (3D) points on opposite sides of the origin differ by a RLV and are also related by inversion symmetry.

- Zone boundary points that are related by symmetry do not necessarily differ by a RLV.

- Zone boundary points that differ by a RLV are not necessarily related by symmetry.

- Group velocities are zero at zone centre, edge centre (2D) or face centre (3D) points.

- Some components of the group velocities are (usually) zero at zone boundary points.

- Group velocities directions are constrained by symmetry on symmetry elements such as mirror planes and rotation axes.

2.1 The band structure has the Laue symmetry of the crystal

Any "macroscopic" observable property of the crystal must have at least the point-group symmetry of the crystal \(^1\) In addition, it is easy to show that if the Bloch wavefunction \(\psi_k = e^{ik \cdot r} u_k(r)\) is an eigenstate of the Schroedinger equation

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + U(r) \right] \psi_k = E_k \psi_k
\]

then \(\psi_k^\dagger = e^{-ik \cdot r} u_k^\dagger(r)\) is a solution of the same Schroedinger equation with the same eigenvalue (this is always the case if the potential is a real function). \(\psi_k^\dagger\) has crystal momentum \(-k\). Therefore, the energy dispersion surfaces (and the group velocities) must be inversion-symmetric even if the crystal is not. This can also be explained as being a consequence of time-reversal symmetry, since the time reversal operator acts on any time-dependent wavefunction as:

\[
t \to -t, \psi(x, t) \to \psi^\ast(x, -t)
\]

\(^1\)As we shall see later, Neumann’s principle states: “The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal. It is applicable to any physical observable measured with a probe that is insensitive to lattice periodicity. The energy dispersion surfaces are observable by non-atomic probes such as photoemission, so Neumann’s principle applies to them.

The Laue symmetry of the electronic constant-energy surfaces, including of course the Fermi surface, can be seen beautifully using an experimental techniques called Angle-Resolved Photoemission Spectroscopy (ARPES). Very briefly, in ARPES the energy-momentum relations for electrons in metals and semiconductors can be determined experimentally by illuminating a crystal with UV or soft-X-ray radiation of precisely known energy and direction and measuring the energy and momentum of the photo-electrons ejected from the surface. Fig. 5 provides two graphical illustration of ARPES data for crystals with different symmetries.

### 2.2 The group velocity is zero at zone-centre points and has additional constraints at the zone boundary and on high-symmetry directions

The following conditions are a straightforward consequence of symmetry and the fact that velocity is an ordinary (polar) vector.

- The group velocity at two points related by inversion in the BZ must be opposite.
- For points related by a mirror plane or a 2-fold axis, the components of the group velocity parallel and perpendicular to the plane or axis must be equal or opposite, respectively.
- Similar constraints apply to points related by higher-order axes — in particular, the components of the group velocity parallel to the axis must be equal.
Since $e^{i k \cdot r} u_k(r) = e^{i (k + \tau) \cdot r} \{ e^{-\tau \cdot r} u_k(r) \}$ and the latter has crystal momentum $k + \tau$, $E_k$ and its gradient (and therefore $v_n(k)$) must be the same across Brillouin zone (BZ) faces (opposite faces are separated by $\tau$).

2.2.1 The oblique lattice: a low symmetry case

We will first illustrate these points by considering the lowest possible lattice symmetry in 2D: that of the oblique lattice. The point-group symmetry of this lattice is 2, and so is the Laue class of any 2D crystal with this symmetry (remember that the inversion and the 2-fold rotation coincide in 2D).

Fig. 6 shows the usual Wigner-Seitz construction on an oblique lattice. It is clear by inspection that points on opposite zone-boundary edge centres (A-A and B-B) are related by 2-fold rotation–inversion (so their group velocities must be opposite) and are also related by a RLV (so their group velocities must be the same). Follows that at points A and B, as well as at the $\Gamma$ point (which is on the centre of inversion) the group velocity is zero. For the other points, symmetry does not lead to a cancelation of the group velocities: in fact, for example, points $a_1$ and $b_1$ are related by a RLV but not by inversion, so their group velocities are the same but non-zero. Similarly, points $c_1$ and $c_2$ are related by inversion but not by a RLV, so their group velocities are opposite but not zero. For this reason points $a_1$, $a_2$, $b_1$ etc. do not have any special significance. It is therefore customary for this type of lattice (and for the related monoclinic and triclinic lattices...
in 3D) to use as the first Brillouin zone not the Wigner-Seitz cell, but the conventional reciprocal-lattice unit cell, which has a simpler parallelogram shape. The relation between these two cells is shown in fig. 7.

2.2.2 The square lattice: a high symmetry case

A more symmetrical situation is shown in fig. 8 for the square lattice (Laue symmetry $4mm$). A tight-binding potential has been used to calculate constant-energy surfaces, and the group velocity field has been plotted using arrows. By applying similar symmetry and $RLV$ relations, one can easily show that the group velocity is zero at the $\Gamma$ point, and the BZ edge centres and at the BZ corners. On the BZ edge the group velocity is parallel to the edge. Furthermore, inside the BZ, the group velocity of points lying on the mirror planes is parallel to those planes.

3 Symmetry in the nearly-free electron model: degenerate wavefunctions

The considerations in the previous section are completely general, and are valid regardless of the shape and strength of the potential, provided that it has the required symmetry. However, one important class of problems you have already encountered involves the application of degenerate perturbation theory to the free-electron Hamiltonian, perturbed by a weak periodic potential $U(\mathbf{r})$: 
Figure 8: Constant-energy surfaces and group velocity field on a square lattice, shown in the repeated zone scheme. The energy surfaces have been calculated using a tight-binding potential.
\[ H = -\frac{\hbar^2}{2m} \nabla^2 + U(r) \]  \hspace{1cm} (7)

Since the potential is periodic, only degenerate points related by a RLV are allowed to “interact” in degenerate perturbation theory and give rise to non-zero matrix elements. The 1D case you have already encountered is very simple: points inside the BZ have a degeneracy of one and correspond to travelling waves. Points at the zone boundary have a degeneracy of two, since \( k = \pi/a \) and therefore \( k - (-k) = 2\pi/a \) is a RLV. The perturbed solutions are standing wave, and have a null group velocity, as we have seen (fig. 4). The situation is 2D and 3D is rather different, and this is where symmetry can help.

In a typical problem, one would be asked to calculate the energy gaps and the level structure at a particular point, usually but not necessarily at the first Brillouin zone boundary. The first step in the solution involves determining which and how many degenerate free-electron wavefunctions with momenta differing by a RLV have a crystal wavevector at that particular point of the BZ. As we will see here below, symmetry can be very helpful in setting up this initial step, particularly if the symmetry is sufficiently high. For the detailed calculation of the gaps, we will defer to the “band structure” part of the C3 course.

A dummies’ guide to nearly-free electron degenerate wavefunctions

- Draw a circle centred at the \( \Gamma \) point and passing through the BZ point you are asked to consider (either in the first or in higher BZ — see fig. 9). Points on this circle correspond to free-electron wavefunctions having the same energy.
- Mark all the points on the circle that are symmetry-equivalent to your BZ point.
- Among these, group together the points that are related by a RLV. These points represent the degenerate multiplet you need to apply degenerate perturbation theory.
- Write the free-electron wavefunctions of your degenerate multiplet in Bloch form. You will find that all the wavefunctions in each multiplet have the same crystal momentum. Functions in different multiplets have symmetry-related crystal momenta.

This construction is shown in fig. 9 in the case of the square lattice (point group \( 4mm \)) for boundary points between different Brillouin zones. One can see that:

- The degeneracy of points in the interior of the first BZ is always one, since no two points can differ by a RLV. This is not so for higher zones though (see lecture).
- X-points: there are 4 such points, and are related in pairs by a RLV. Therefore, there are two symmetry-equivalent doublets of free-electron wavefunctions (which will be split by the
Figure 9: Construction of nearly-free electron degenerate wavefunctions for the square lattice (point group $4mm$). Some special symmetry point are labelled. Relevant $RLV$s are also indicated.
periodic potential in two singlets).

- **Y-points**: there are 8 such points, and are related in pairs by a RLV. Therefore, there are four symmetry-equivalent doublets of free-electron wavefunctions (which will be split by the periodic potential in two singlets).

- **M-points**: there are 4 such points, all related by RLVs. Therefore, there is a single symmetry-equivalent quadruplet of free-electron wavefunctions (which will be split by the periodic potential in two singlets and a doublet).

- **X\_2-points**: these are X-point in a higher Brillouin zone. There are 8 such points, related by RLVs in groups of four. Therefore, there are two symmetry-equivalent quadruplets of free-electron wavefunctions (each will be split by the periodic potential in two singlets and a doublet). These two quadruplets will be brought back above (in energy) the previous two doublets in the reduced-zone scheme.

4 Bibliography

Ashcroft & Mermin [3] is now a rather old book, but, sadly, it is probably still the best solid-state physics book around. It is a graduate-level book, but it is accessible to the interested undergraduate.

References

