Solid State Theory
(Theorie der kondensierten Materie)

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Martin Eckstein
Max-Planck Research Departement for Structural Dynamics, CFEL
Desy, Bldg. 99, Rm. 02.001
Luruper Chaussee 149
22761 Hamburg, Germany
Tel: +49 (0)40 8998 6270
email: martin.eckstein@mpsd.cfel.de

Lecture Website:

Literature:


Topics:
Electrons in the periodic crystal (band-structure calculations); Interacting electrons: Screening, Landau’s Theory of Fermi Liquids; Phonons; Superconductivity; Magnetism;
Introduction

In solid state physics, we aim to understand

- structure of solids
- phases of condensed matter systems, like metallic or insulating behavior, magnetism, superconductivity, ...
- elementary excitations (↔ spectroscopical measurements, transport properties)

For the understanding of many phenomena, quantum mechanics is essential. Examples: chemical binding and stability of matter explained by quantum effect. Our non-relativistic theory of everything would be given by the Hamiltonian

$$H = \sum_i \frac{P_i^2}{2m} + \sum_{i<j} \frac{e^2}{r_i - r_j} + \sum_i \frac{P_i^2}{2m} + \sum_{i<j} \frac{e^2 Z_i Z_j}{|R_i - R_j|} - \sum_{i,k} \frac{e^2 Z_k}{|r_i - R_k|} \quad (1)$$

The typical binding energy of an electron to a nucleus is of the order of several electron volts (H-atom: $13.6eV = 1Ry$). With the basic energy-temperature conversion

$$1eV = k_B 11600 \text{ Kelvin} \Rightarrow 300K \approx 30meV \ll 1Ry, \quad (2)$$

one can see that thermal fluctuations $k_B T$ are negligible compared to atomic energies at room temperature. The Hamiltonian (1) is thus useful for the understanding of properties of matter at 100000K (this would be a plasma), but it is usually not a good starting point to learn about a solid at room temperature.

Not even fundamental phenomena such as the formation of a crystal can be predicted fully “ab-initio”, although it should be contained in the formulation. The Hamiltonian can be vied as the high-energy theory for condensed matter physics, from which low-energy effective theories for condensed matter phases emerge. The situation in low energy physics is opposite to high-energy physics, where one tries to uncover the high-energy theories from which the physical laws for atoms and nuclei emerge:
Examples for effective theories for the solid:

- Harmonic crystal
- Spin models (→ magnetism of localized moments)
- Electronic quasiparticles
Periodic structures

Most solids have crystalline order on the atomic scale (although, macroscopically they can form crystallites on the \( \mu m \) scale.) Exceptions are glasses (amorphous structures), liquid crystals, etc., see Fig. 1. Crystalline symmetries are essential for a theoretical description of solids, hence we will deal almost exclusively with crystalline structures in this lecture.

![Figure 1: Left: Translational, but no orientational symmetry (e.g., Spin glass). Middle: Orien-
tational, but no translational symmetry (e.g., nematic order). Right: Perfect crystalline order.](image)

Classification of crystalline structures

**Bravais lattice**: Infinite set of points generated via translations of one point by integer linear combinations of a set of given vectors \( \mathbf{a}_i \)

\[
\{ \mathbf{R} \} = \{ n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 | n_i \in \mathbb{Z} \},
\]

\( \mathbf{a}_i \) primitive lattice vectors, linearly independent.

\( \Leftrightarrow \) Lattice “looks identical” from every of its points.

Example: The vectors

\[
\mathbf{a}_1 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{a}_2 = \begin{pmatrix} 0 \\ a \\ 0 \end{pmatrix}, \quad \mathbf{a}_3 = \begin{pmatrix} 0 \\ 0 \\ a \end{pmatrix}
\]

generate the perfect cubic lattice with lattice spacing \( a \).
Note: The choice of the primitive lattice vectors is not unique: If \( \vec{a}_i \) is a set of primitive vectors, \( \vec{a}'_i \) generates the same lattice iff \( \vec{a}_i = \sum_j M_{ij} \vec{a}'_j \) with an integer matrix \( M \) of determinant \( \pm 1 \).

**Primitive unit cell:** The volume spanned by the primitive unit vectors is called the primitive unit cell. It has volume

\[
V = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|. \tag{4}
\]

In general, a unit cell can be any volume that covers full space without overlaps when it is translated by every vector of the Bravais lattice. A special (uniquely defined) choice is the Wigner-Seitz cell, which is chosen to be the set of all points closer to a point \( \vec{R} \) of the Bravais lattice than any other point (see Fig. 2)

![Figure 2: Left: A primitive unit cell of the square lattice (which has not the full point group symmetry of the lattice) Right: The Wigner-Seitz cell. The Wigner-Seitz cell around a lattice point \( \vec{R} \) is geometrically constructed by drawing the line from \( \vec{R} \) to any other point of the lattice, and the plane perpendicular to the line half-way between the points. All these planes “cut out” the Wigner-Seitz cell.](image)

**Crystal Structure:** A Bravais lattice is only the set of points generated by the translation operations. The full crystal structure is obtained by placing objects of typically lower symmetry (atoms, molecules) in the lattice. The objects within one unit cell is called the **basis**. Example: The honey-comb lattice is not a Bravais lattice, but a Bravais lattice with a basis of two atoms (Fig. 3)

![Figure 3: The honey-comb lattice.](image)
**Crystal Symmetries**: A crystal symmetry is a linear transformation of space
\[ \vec{r} \rightarrow \vec{r}' = D\vec{r} + \vec{a} \] (5)

which maps the structure onto itself.

\( \vec{a} \): Translation. \( D \): orthogonal transformation (rotation, reflection, inversion). All operations \( D \) define the **point group** of the crystal (\( D \) is a transformation which leaves one point of the lattice invariant). All symmetry operations (point group + translations) define the **space group** of the crystal.

**Note**: The operations \( D \) do not necessarily form a sub-group of the space group; there can be rotations/reflections that are symmetries of the crystal only in combination with a translation:

- **screw axis**: rotation + translation along rotation axis
- **glide plane**: reflection + translation along reflection plane

![Diagram showing a crystal structure with a glide plane](image)

**How many crystal symmetries are there?**

Important restriction:

|only 2,3,4,6 fold rotation axis is compatible with translational symmetry|

**(Algebraic proof)**:

Consider rotation matrix around \( z \):

\[ D_z(\varphi) = \begin{pmatrix} \cos(\varphi) & \sin(\varphi) & 0 \\ 0 \sin(\varphi) & \cos(\varphi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

Trace of this matrix is invariant under transformation into a different basis, because \( \text{Tr}[U^{-1}DU] = \text{Tr}D \) for any invertible matrix \( U \). Transforming to the basis defined by the primitive vectors (note...
that the matrix $U$ above need not be orthogonal), the rotation must be a matrix with integer entries (it maps primitive vectors on primitive vectors). Hence $D_z$ must satisfy

$$\text{Tr} \, D_z(\varphi) = 2\cos(\varphi) + 1 \in \mathbb{Z}.$$ 

The only solutions to this equation are $\varphi = 0, \frac{\pi}{3}, \frac{2\pi}{3}, \pi$.

**Note:** There are structures with apparent 5-fold coordination in reciprocal space (Bragg-peaks in X-ray diffraction, see below). These *quasi-crystals* are not periodic in space, but may be obtained by projecting a periodic structure in higher dimensional space onto a subspace along a direction not commensurate with the primitive vectors.

The crystallographic restriction finally restricts the number of Bravais lattices and crystal structures (i.e., Bravais lattice + basis):

<table>
<thead>
<tr>
<th>number of point groups</th>
<th>Bravais lattice</th>
<th>crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 (4)</td>
<td></td>
<td>32 (13)</td>
</tr>
<tr>
<td>14 (5)</td>
<td></td>
<td>230 (17)</td>
</tr>
</tbody>
</table>

The number in brackets corresponds to spatial dimension $d = 2$. The space groups in $d = 2$ are called wallpaper groups. The correspond to a symmetries of mosaic tilings of the plane. There are many good illustrations in the internet, e.g.,


For a more detailed discussion of symmetries and Bravais lattices in 3d, see Ashcroft & Mermin, Chapter 6.

**Importance of symmetry for the description of solids:**

- Quantum numbers, degeneracies in the spectrum (see band structure lectures).

- Symmetry determines the response coefficients of a solid. In general, the physical observables must be symmetric under all crystal symmetries.

  Example: In general, the conductivity $\sigma$ is given by the linear response relation

  $$j_\alpha = \sum_{\alpha'} \sigma_{\alpha\alpha'} E_{\alpha'}, \quad \alpha, \alpha' = x, y, z.$$ 

  ($j$ and $E$ are current and electric field, respectively). The matrix $\sigma$ must be invariant under the point-group operations of the crystal,

  $$D \sigma D^{-1} = \sigma.$$
For cubic symmetry, this implies already that the matrix \( \sigma \) is a scalar (proportional to the identity matrix): Rotations by 180° around the \( z \) axis, with \( D = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \), imply

\[
D \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} D^{-1} = \begin{pmatrix} \sigma_{11} & -\sigma_{12} & -\sigma_{13} \\ -\sigma_{21} & \sigma_{22} & \sigma_{23} \\ -\sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix},
\]

hence \( \sigma_{12} = \sigma_{13} = \sigma_{21} = \sigma_{31} = 0 \). Similar rotations around the \( y \) and \( z \) axis require the matrix to be diagonal. Rotations by 120° around the body-diagonal (which permute \( x,y,z \)) imply that \( \sigma_{11} = \sigma_{22} = \sigma_{33} \).

**The reciprocal lattice**

**Definition:** For a Bravais lattice \( G = \{ \vec{R} \} \), the reciprocal lattice is defined by the points

\[
G^* = \{ \vec{G} \mid \vec{G} \cdot \vec{R} = 2\pi n \text{ with } n \in \mathbb{Z} \text{ for all } \vec{R} \in G \}.
\]

(6)

The reciprocal lattice is a Bravais lattice itself, with primitive vectors

\[
\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}, \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}, \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}.
\]

**Note:** The reciprocal lattice need not be of the same lattice type (fcc ↔ bcc). **Example:** If \( \vec{a}_i \) are orthogonal, \( \vec{a}_1 = a_x \hat{e}_x, \vec{a}_2 = a_y \hat{e}_y, \vec{a}_3 = a_z \hat{e}_z \), then \( \vec{b}_1 = \frac{2\pi}{a_x} \hat{e}_x, \vec{b}_2 = \frac{2\pi}{a_y} \hat{e}_y, \vec{b}_3 = \frac{2\pi}{a_z} \hat{e}_z \).

Figure 4: Reciprocal lattice of an orthogonal lattice in dimensions \( d = 2 \).

The reciprocal lattice is important in three aspects, which are described below:
1) **Fourier-transformation of space periodic functions** If \( f(\vec{r}) \) is a function which has the lattice periodicity, i.e.,

\[
    f(\vec{r} + \vec{R}) = f(\vec{r}) \quad \text{for all} \quad \vec{R} \in \mathcal{G},
\]

then the only non-zero Fourier coefficients of \( f \) appear at the points of the reciprocal lattice. In short,

\[
    f_{\vec{k}} = \int d^3r f(\vec{r}) e^{i\vec{k} \cdot \vec{r}} = \int d^3r f(\vec{r} + \vec{R}) e^{i\vec{k} \cdot \vec{r}} = \int d^3r f(\vec{r}) e^{i\vec{k} (\vec{r} - \vec{R})} = e^{-i\vec{k} \cdot \vec{R}} f_{\vec{k}},
\]

(where in the first equality we used translational invariance of \( f \), the second equality is a variable transform), i.e., \( \vec{k} \) must satisfy \( e^{-i\vec{k} \cdot \vec{R}} = 1 \) for all \( \vec{R} \in \mathcal{G} \), which is equivalent to \( \vec{k} \in \mathcal{G}^* \) by the definition (6). In general, the fourier series representation of \( f \) and its inverse is given by (\( V \) is the volume of the unit cell)

\[
    f(\vec{r}) = \sum_{\vec{G} \in \mathcal{G}^*} f_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \quad (7)
\]

\[
    f_{\vec{G}} = \frac{1}{V} \int_{\text{unit-cell}} d^3r \ f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} \quad (8)
\]
• momentum conservation on the lattice

In a periodic crystal, \( H \) commutes with all translation operators,

\[
[H, T \mathbf{R}] = 0 \quad \forall \mathbf{R} \in \mathbb{G}
\]

\[
(C(T_{\mathbf{R}} \psi)(\mathbf{r})) = \psi(\mathbf{r} - \mathbf{R})
\]

⇒ we can choose eigenfunctions of \( H \) to be simultaneous eigenfunctions of \( T_{\mathbf{R}} \)

\[
T_{\mathbf{R}} \left| \psi \right> = c(\mathbf{R}) \left| \psi \right> \quad \forall \mathbf{R}
\]

\[
\left| \psi \right> \rightarrow \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]

\[
T_{n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3} \left| \psi \right> = (T_{\mathbf{a}_1})^{n_1} (T_{\mathbf{a}_2})^{n_2} (T_{\mathbf{a}_3})^{n_3} \left| \psi \right>
\]

translational commutes (Abelian group)

\[
= c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3} \left| \psi \right>
\]

\[
\forall n_1, n_2, n_3 \in \mathbb{Z}
\]
Furthermore, we know that $|c(R)| = 1$, because $\|1\rangle \| = \| Tr1\rangle \|$

$\Rightarrow$ we can implicitly define a vector $\tilde{k}$, such that

$c(\hat{a}_i) = e^{i\tilde{k} \cdot \hat{a}_i} \quad i = 1, 2, 3$

$\Rightarrow c(\tilde{R}) = e^{i\tilde{k} \cdot \hat{a}_1} e^{i\tilde{k} \cdot \hat{a}_2} e^{i\tilde{k} \cdot \hat{a}_3} = e^{i\tilde{k} \cdot \tilde{R}}$

$\tilde{k}$: Quantum number which characterizes transformation of wave function under translation:

"$|\psi\rangle$ has quasi-momentum $\tilde{k}$" $\Leftrightarrow$ $Tr |\psi\rangle = e^{i\tilde{k} \cdot \tilde{R}} |\psi\rangle \quad \forall \tilde{R}$

- compare: $L^2, L_z$: Quantum numbers which characterize transformation of wave function $\Psi_{L, L_z}(\theta, \phi)$ under rotations.

- Note: $\tilde{k}$ only defined up to arbitrary shift by a reciprocal lattice vector.

$\tilde{k} \equiv \tilde{k} + \tilde{G}$

both are the same quasi-momentum!
without loss of generality, \( \mathbf{k} \) can be chosen in the first Wigner-Seitz cell of the reciprocal lattice, which is called the 1st Brillouin zone.

**Conservation of quasi-momentum**

If \([H, \mathbf{R}] = 0 \) \( \forall \mathbf{R} \), this implies that if \( |\Psi\rangle \) has quasi-momentum \( \mathbf{k} \), then \( |\Psi(t)\rangle = e^{-i\mathbf{k} \cdot \mathbf{R}} |\Psi\rangle \) has quasi-momentum \( \mathbf{k} \) for all times, i.e., "\( \mathbf{k} \) is conserved".

Note: this is different from momentum conservation!

- **Scattering of an electron with quasi-momentum \( \mathbf{k} \) with something else (phonon, another e-\) with quasi-momentum \( \mathbf{q} \).**

- **Umklapp scattering**
Illustration: X-ray scattering.

\[ t \rightarrow -\infty \]
\[ \tilde{q} \text{ X-rays} \]
\[ \Phi \rightarrow \Phi' \]

Wave function of solid with good quasi momentum

\[ t \rightarrow +\infty \]
\[ \tilde{q}' \]

Assume elastic scattering, i.e. wave function of crystal is not changed

\[ \tilde{q}, \tilde{q}' \text{ correspond to same quasi momentum} \]

\[ \tilde{q} - \tilde{q}' = \tilde{\alpha} \text{ mit } \tilde{\alpha} \in \tilde{q}^* \]

\[ \Rightarrow \text{ you save condition (see above) } \]