

Theory of condensed matter

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1 Crystal structure and group-theoretical classification

1.1 Introduction

The theoretical description of the physics of solids and other condensed materials (liquids and soft matter) is a longstanding issue, which nowadays covers a large fraction of theoretical physics. The key point of traditional solid state theory is, of course, the crystal symmetry, which facilitates the solution of the electronic band structure problem – as well as the phonon problem – enormously. Most of the solid state theory literature up to the 70's or so was therefore devoted to the application and refinement of band structures.

The description of non-crystalline materials such as liquids and polymers was (and is until now) almost entirely based on statistical and thermodynamic concepts. This part of condensed matter science was more at home in chemistry than in the physical community. Nowadays these parts have merged into a wealth of descriptions of condensed matter making use both of (eventually present) crystal symmetry and (eventually present) disorder statistics.

Solid state theory, however does not only deal with approximate one-particle theories in a crystalline or disordered environment but also with the physics which results from interactions. The most prominent interaction phenomena are magnetism and superconductivity.

The focus of the present, somewhat unusual introductory lecture is on mean-field concepts, which help to approximately solve the Schrödinger equation (and other fundamental equations) in the presence of interactions and disorder. These mean-field concepts are the random-phase approximation (RPA) for interacting many-body systems, the coherent potential (CPA) and self-consistent Born (SCBA) approximations for disorder, the Weiss theory for magnetism, the Bardeen-Cooper-Schrieffer (BCS) theory for superconductivity and the Landau theory for a general phase transition.

From a mathematical point of view we shall make use of the concept of Green's functions and – to a certain extent – of functional integrals. These concepts will be introduced within the lectures.

The starting point of the lecture is the structure of crystals and their group-theoretical classification. The second chapter deals with the statistical description of liquids and polymers. The following chapters are devoted to the electronic and vibrational structures of solids with and without crystalline symmetry. The three chapters on transport deal with the distinction between metals and semiconductors, the disorder-induced metal-nonmetal transition and then with the description of transport in the presence of weak (Boltzmann equation) and strong disorder (hopping and diffusion equation). The two final chapters are on magnetism and superconductivity.

1.2 Groups and representations

We here give a *very* brief review of the theory of groups and their representations.

A set g with a composition " \circ " is called *group* if

- \circ does not lead out of g $a \circ b = c \quad a \in g, b \in g \Rightarrow c \in g$
- \circ is associative $a \circ (b \circ c) = (a \circ b) \circ c$
- there exists a neutral element e with $e \circ a = a \circ e = a$ for all $a \in g$
- for each $a \in g$ there exists an inverse a^{-1} with $a \circ a^{-1} = e$

If, in addition, \circ is commutative (i.e. $a \circ b = b \circ a$ for all $a, b \in g$) the group is called *Abelian*.

If there is a finite number h of group elements, h is called the *order* of the group g .

A group of finite order is completely characterized by its *multiplication table*.

Most simple example: Turning of an object

$t = \text{turn}$

$e = \text{no action}$

Multiplication table:

	e	t
e	e	t
t	t	e

So we see that all the group axioms are fulfilled. g is trivially Abelian, because for all groups of order 2 $e \circ t = t \circ e$ must hold, and the above is the simplest nontrivial multiplication table. (A trivial group is just $\{e\}$.)

For any group element one can form a sequence

$$a, \quad a \circ a, \quad a^3, \dots, a^{n-1}, a^n = e$$

n is the *order* of the group element a . If the n powers of a exhaust the group, the group is called *cyclic*.

Example:

The solutions of the equation

$$z^n = 1 \quad z \in \mathbb{C} \quad n \in \mathbb{N}$$

("roots of unity"). We put

$$z_1 = e^{i\frac{2\pi}{n}} \quad \text{and} \quad z_\nu = z_1^\nu$$

Obviously for all z_n the equation is fulfilled, and they form a cyclic group of order n .

All cyclic groups are Abelian.

A *subgroup* is a subset of g , which forms a group. If the powers of an element $a \in g$ do *not* exhaust g , these powers form a *cyclic subgroup* of g .

A mapping between two groups

$$g \xrightarrow{f} g'$$

with compositions \circ and \circ' , resp. is called *homomorphic* if

$$f(a \circ b) = f(a) \circ' f(b)$$

If this mapping is *injective*, i.e. $a \neq b \Rightarrow f(a) \neq f(b)$ the groups are called *isomorphic* and f is an *isomorphism*.

The elements a, b are *conjugate* if they can be *transformed* into each other by

$$b = c^{-1}ac \quad a, b, c \in g$$

All mutually conjugate elements form a *class*. e forms always its own class.

A subgroup s of g , composed entirely of classes is called an *invariant subgroup* or *normal divisor*.

If $s = \{a_1, \dots, a_f\}$ is a normal divisor then $s = \{ca_1, \dots, ca_f\} = s = \{a_1c, \dots, a_fc\}$ ($c \in g$) is called a *co-set*. The normal divisor together with its cosets is a set of sets. This "set-set" forms a group, which is called *factor group* or *quotient group* g/s .

1.3 Representations of groups

Let g be a group and G a set of *non-singular unitary quadratic matrices*, which forms a group with respect to matrix multiplication. If there exists a homomorphic mapping f

$$g \xrightarrow{f} G$$

G is called a *representation* of g . If f is an isomorphism G is called a *true* or *faithful* representation¹.

Example: the two matrices

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad T = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

form a true representation of the group (e, t) , introduced above.

The dimension of the matrices is called the *dimension* of the representation. A one-dimensional matrix is just a complex number. If this number has to be unitary it must be of the form $z = e^{i\phi}$. The n -th unit roots form a one-dimensional representation of any cyclic group of order n . If one can perform a transformation

$$A'_1 = S^{-1}AS$$

$$\begin{array}{c} | \\ | \end{array}$$

$$A'_h = S^{-1}A_hS$$

between $G = \{A_1, \dots, A_h\}$ and $G' = \{A'_1, \dots, A'_h\}$ the two matrix groups (or representations) are *equivalent* and one writes $G' \cong G$.

A representation G is called *reducible*, if it is *equivalent* to a matrix G' , which has *block form*, i.e. all elements A of G' have the form

$$\begin{pmatrix} \boxed{A^{(1)}} & 0 & 0 \\ 0 & \boxed{A^{(2)}} & 0 \\ 0 & 0 & \boxed{A^{(n)}} \end{pmatrix}$$

Representations for which such a decomposition is not possible are called *irreducible*. The irreducible representations of symmetry groups play a key role in quantum mechanics, and hence in the quantum theory of crystalline solids.

Theorems on representations:

- Any representation is either irreducible or *completely reducible*.

¹Deutsch: treue Darstellung

- Let d_i be the dimension of representation i . Then we have for the order h of g

$$\sum_{i=1}^{i_{\max}} d_i^2 = h \quad (1)$$

- The number of irreducible representations of a group is equal to the number of classes

Example The group $\{T, E\}$ introduced above is a true representation of $\{t, e\}$, but it is *reducible*. An irreducible nontrivial representation of $\{t, e\}$ is $\{1, -1\}$.

Abelian groups

Consider an abelian group $g = \{a_1, a_2, \dots, a_h\}$.

If we try to form conjugate elements

$$a_2^{-1} a_1 a_2 = a_1 \quad \text{or} \quad a_1^{-1} a_2 a_1 = a_2$$

we see that each element is only conjugate to itself, i.e. it forms a class on its own. From this follows that the number of classes is equal to the order h of the group. Therefore the number of irreducible representations must also be equal to h . The relation (1) can in this case only be fulfilled if all d_i are equal to 1. Therefore we state the important theorem

The irreducible representations of an Abelian group are all one-dimensional.

1.4 The role of the irreducible representations of symmetry groups in quantum mechanics

Let $s = \{s_1, \dots, s_h\}$ be a group of symmetry operations, where s_r are operators in Hilbert space, then a state vector $|\psi\rangle$ is transformed under s into other vectors:

$$\begin{aligned} |\psi_{s_1}\rangle &= s_1 |\psi\rangle \\ &| & | \\ &| & | \\ |\psi_{s_h}\rangle &= s_h |\psi\rangle \end{aligned}$$

This set is not necessarily linearly independent. Let's assume there are d linearly independent vectors, which are transformed under s into each other. Then we have

$$s_r |\psi_\alpha\rangle = \sum_{\beta=1}^d \Gamma_{\alpha\beta}(s_r) |\psi_\beta\rangle$$

where Γ is a d -dimensional representation of s . $\langle \mathbf{r} | \psi_\alpha \rangle = \psi_\alpha(\mathbf{r})$ is called *basis function*.

If $\{|\psi_1\rangle, \dots, |\psi_d\rangle\}$ is an orthonormal basis, the Γ are *unitary*, and we have

$$\Gamma_{\alpha\beta}(s_r) = \langle \psi_\alpha | s_r | \psi_\beta \rangle$$

By definition if s is the symmetry group of the Hamiltonian \mathcal{H} , the elements of s must commute with \mathcal{H} .

\Rightarrow All observables, which can be represented as operator function of elements of s are invariants

\Rightarrow All eigenvectors of elements of s are also eigenvectors of \mathcal{H} with respect to the same eigenvalue of \mathcal{H} .

The group of symmetry operations that commute with \mathcal{H} is called *group of the Schrödinger equation*, because it leaves the Schrödinger equation

$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

invariant. Let E_i be a particular eigenvalue and Let's assume that E_i is d_i -fold degenerate, i.e. there exist d_i linearly independent eigenvectors of E_i . If s is a symmetry group, these vectors must transform among each other according to

$$s_r |\psi_\alpha^{(i)}\rangle = \sum_{\beta=1}^d \Gamma_{\alpha\beta}^{(i)}(s_r) |\psi_\beta^{(i)}\rangle$$

$\langle \mathbf{r} | \psi_\alpha^{(i)} \rangle = \psi_\alpha(\mathbf{r})^{(i)}$ is called the α th basis function of the i th irreducible representation of s .

- To each eigenvalue E_i there corresponds an irreducible representation $\Gamma^{(i)}$ of s .
- The label i is the *quantum number*.
- The dimension of $\Gamma^{(i)}$ is equal to the degeneracy of E_i .

<u>Atom</u>	<u>Quantum numbers</u>	<u>Solid (crystal)</u>
$s = \text{continuous rotation group}$		$s = \text{crystal covering group (space group)}$
n, l, m		n, k_x, k_y, k_z

1.5 Crystal symmetry operations

A crystal is a regular arrangement of atoms, groups of atoms or molecules within a *unit cell*, which is repeated by the *translation operator*

$$T = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad n_i \in \mathbb{Z}, \quad \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \text{ linearly independent}$$

The set of points generated by T is called *Bravais lattice*.

The translations are not the only covering operations of a crystal. The other symmetry operations are found as those, which leave a particular point (origin) unchanged. These operations form the *point group* of the crystal. The total symmetry group is called *space group*.

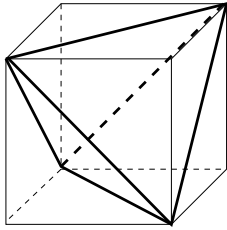
Symmetry operations, which build up the point group:

1. Rotations about axes through the origin;
2. Reflections in planes containing the origin.

Notations (Schoenflies):

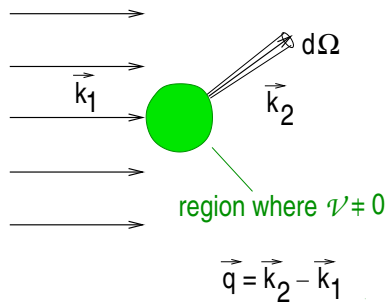
E	= Identity
C_n	= Rotation through $2\pi/n$
σ	= Reflection in a plane
σ_h	= " " rectangular to the axis of highest symmetry (horizontal plane)
σ_v	= " " passing through the axis of highest symmetry (vertical plane)
S_n	= Improper rotation = rotation, followed by a reflection in a plane rectangular to the rotation axis
$i = S_2$	= Inversion, takes \mathbf{r} into $-\mathbf{r}$

List of point groups



C_n		Only one n -fold symmetry about one axis
C_{nv}		In addition to the C_n symmetry there are n σ_v planes
C_{nh}	$= C_n \times \{E, i\}$	There is a σ_h plane
S_{2n}		Improper rotations about an angle $2\pi/2n$, contains C_n as subgroup
D_n		In addition to C_n the group contains n two-fold axes perpendicular to the main axis
D_{nh}	$= D_n \times \{E, i\}$	D_n plus horizontal reflection plane
D_{nd}		D_n plus n vertical reflection planes that <i>bisect</i> the angle of the 2-fold axes
T	Tetrahedral group	C_n 's, which take a regular tetrahedron into itself: E 3 C_2 's about x, y, z axes, 8 C_3 's about body diagonals 12
T_d		Including all reflections which take the tetrahedron onto itself
T_h	$= T_d \times \{E, i\}$	
O	Octahedral group	All proper rotations, which take an <i>octahedron</i> or a <i>cube</i> into itself E 8 C_3 's about body diagonals 6 C_2 's around axes \parallel face diagonals 6 C_4 's around axes \perp face midpoints 3 C_2 's around axes \perp face midpoints 24
O_h	$= O_d \times \{E, i\}$	

1.6 Scattering theory



We want to describe the scattering of X-rays or neutrons from a simple liquid sample. We study an ingoing plane wave (1st term) and an outgoing scattered spherical wave (2nd term) of the following asymptotic form

$$\psi(\mathbf{r}) \stackrel{|\mathbf{r}| \rightarrow \infty}{\approx} e^{i\mathbf{k}_1 \cdot \mathbf{r}} + f(\theta) \frac{1}{r} e^{ik_2 r} \quad (2)$$

The scattering cross-section into the solid angle element $d\Omega$ in the direction of \mathbf{k}_2 is then given by the modulus-square of the scattering amplitude

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \quad (3)$$

If the scattering potential (the potential between the scattered rays and the particles) can be decomposed as

$$\mathcal{V}(\mathbf{r}) = \sum_{\alpha=1}^N v(\mathbf{r} - \mathbf{r}_\alpha) \quad (4)$$

the scattering amplitude is given in 2nd approximation (*Born approximation*)

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \langle \mathbf{k}_2 | \mathcal{V} | \mathbf{k}_1 \rangle = -\frac{m}{2\pi\hbar^2} \mathcal{V}(\mathbf{q}) = -\frac{m}{2\pi\hbar^2} \sum_{\alpha=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_\alpha} v(\mathbf{q}) \equiv \sum_{\alpha=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_\alpha} f(\mathbf{q}), \quad (5)$$

$f(\mathbf{q})$ is called *form factor* and has the unit of length. In the case of *energy unresolved* neutron or X-ray diffraction there is no net energy exchange with the sample, i.e. $|\mathbf{k}_1| = |\mathbf{k}_2|$. In an isotropic material the

form factor depends only on the modulus of the exchanged momentum, which is given by

$$q = |\mathbf{k}_1 - \mathbf{k}_2| = k_1 \sqrt{2[1 - \cos(\theta)]} = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right), \quad (6)$$

where θ is the angle between \mathbf{k}_1 and \mathbf{k}_2 and $\lambda = \frac{2\pi}{|k_1|}$ is the wavelength.

In the case of neutrons, which scatter from the nuclei, whose potential $v(\mathbf{r})$ is extremely short-ranged, $f(q)$ does not depend on q (in the range of interest $q < 20 \text{ \AA}^{-1}$) and is called *scattering length* and is denoted by the letter b .

Let us look at the scattering amplitude in the case of a crystal. Max von Laue's condition for constructive interference of incoming and scattered waves gives

$$e^{i\mathbf{q}\mathbf{R}_\ell} = 1 \quad (7)$$

where \mathbf{R}_ℓ are lattice points. One can show that the vectors \mathbf{q} that fulfil (7) form a three-dimensional lattice. This lattice is called the *reciprocal lattice*. The reciprocal lattice has a fundamental significance for band structure and phonon dispersion calculations for a crystal. Its unit cell is called *first Brillouin zone*. The reciprocal lattice is formed by the normal vectors corresponding to all lattice planes, i.e. all planes that contain two-dimensional sublattices of the 3d lattice.

The unit vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are given in terms of the unit vectors of the real-space lattice as

$$\mathbf{b}_1 = \frac{2\pi}{V_E} \mathbf{a}_2 \times \mathbf{a}_3 \quad (8a)$$

$$\mathbf{b}_2 = \frac{2\pi}{V_E} \mathbf{a}_3 \times \mathbf{a}_1 \quad (8b)$$

$$\mathbf{b}_3 = \frac{2\pi}{V_E} \mathbf{a}_1 \times \mathbf{a}_2, \quad (8c)$$

$$(8d)$$

where $V_E = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ is the volume of the unit cell.