Solid State Physics

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Chapter 1

Crystal Structure

1.1 Direct lattice

Lattice + **Basis** = **Crystal**
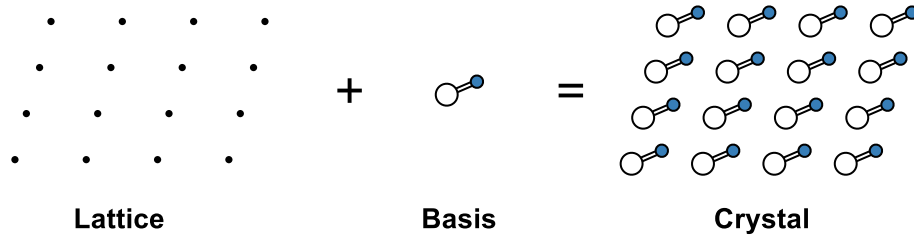
The mathematical description of the crystal consists of two parts: the *lattice* which is a periodic grid of points extending over space and the *basis* which in this context is the set of ions repeating at every lattice point.

The lattice can be described by the set of so called *lattice vectors* $\{\mathbf{R}\}$ given by

$$\mathbf{R} \equiv \mathbf{R}_{n_1 n_2 n_3} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \tag{1.1}$$

where $n_i \in \mathbb{Z}$ and $\mathbf{a}_i$ are linearly independent vectors in the real space called the *primitive vectors*. The primitive vectors have the dimensions of length owing to which the lattice spanned by them is referred to as the *direct lattice*. It should be noted the choice of the primitive vectors is not unique; any non-collinear set of the lattice vectors can be used.

The lattice can be infinite or finite depending on the allowed values of n_i. Quite often it is convenient to deal with infinite lattice which extends over all spatial dimensions. In such case the lattice is known as the *Bravais lattice*.

An important concept of *unit cell* builds upon the lattice. A unit cell is a volume of space that can fill the entire space without overlaps or leaving gaps behind when translated by a suitable set of Bravais lattice vectors. A *primitive unit cell* is a special set of unit cells which enclose precisely one lattice point. Therefore, if the number density of lattice points is n, the primitive unit cell volume v is

$$v = \frac{1}{n} \tag{1.2}$$

regardless the shape of the cell. Sometimes it is, however, easier to work with a *conventional unit cell* instead. For example, a primitive unit cells of a BCC (body-centered cubic) lattice can be difficult to work with since their angles are not orthogonal. The usual choice is to

use a cubical cell containing two lattice points instead. Note that whereas primitive unit cells can be translated by all the lattice vectors without any overlaps, the same is not true for the conventional ones.

There is, however, a common used way to choose a primitive unit cell that has the full symmetry of the lattice. Consider a single lattice point and take all the points in its vicinity that are nearer to it than any other point in the lattice. The volume covered by those points leads to a unique primitive unit cell which is known as the *Wigner-Seitz cell*. The concept is worth remembering as it has an important role in the subsequent discussion.
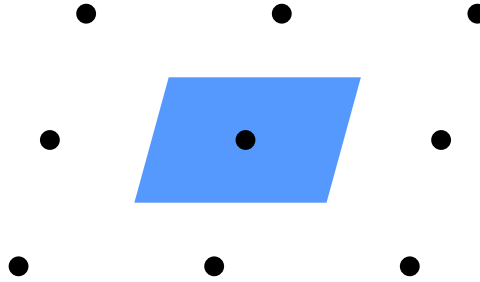

Figure 1.1: Wigner-Seitz cell of an oblique 2D-lattice. The blue area covers the points closest to the lattice point in the center.

1.2   Reciprocal lattice

Chapter 2

Magnetism

2.1 Pauli equation

A suitable starting point to investigate magnetism in atomic systems is the Pauli equation, which describes the dynamics of a non-relativistic spin-1/2 particle in an electromagnetic field. A single electron with the mass m and the charge $-e$ the standard form of the time-independent equation is

$$\left[\frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + \frac{e\hbar}{m}\mathbf{s} \cdot \mathbf{B} - e\phi \right] |\psi\rangle = E|\psi\rangle, \tag{2.1}$$

where ϕ is the electric scalar potential, $\mathbf{A}$ is the (unquantized) vector potential, the magnetic field $B = \nabla \times \mathbf{A}$ and $\mathbf{s} = (s_x, s_y, s_z)$ are the components of the (unitless) spin-1/2 operator. Quite often s_i are given in terms of Pauli matrices:

$$s_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad s_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad s_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{2.2}$$

In such a representation the state $|\psi\rangle$ is represented by a two-component spinor

$$|\psi\rangle = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \psi_+|\uparrow\rangle + \psi_-|\downarrow\rangle. \tag{2.3}$$

Let us consider an ion with N electrons. The Pauli equation now reads

$$\sum_{i=1}^{N} \left[\frac{(\mathbf{p}_i + e\mathbf{A}_i)^2}{2m} + \frac{e\hbar}{m}\mathbf{s}_i \cdot \mathbf{B}_i - e\phi_i \right] |\psi\rangle = E|\psi\rangle, \tag{2.4}$$

where

$$\phi_i = \frac{1}{4\pi\epsilon_0} \left(\frac{Z_n e}{|\mathbf{r}_i|} - \frac{1}{2}\sum_{j \neq i} \frac{e}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \tag{2.5}$$

is the electrostatic potential due to the nuclear charge and other electrons[1]. $\mathbf{r}_i$ is the position vector of ith electron. Assuming that $\mathbf{A}_i$ are in Coulomb gauge $i.e.$ $\nabla \cdot \mathbf{A}_i = 0$, we may expand[2]

$$(\mathbf{p}_i + e\mathbf{A}_i)^2 = \mathbf{p}_i^2 + \underbrace{e\mathbf{p}_i \cdot \mathbf{A}_i}_{=0} + 2e\mathbf{A}_i \cdot \mathbf{p}_i + e^2\mathbf{A}_i^2 = \mathbf{p}_i^2 + 2e\mathbf{A}_i \cdot \mathbf{p}_i + e^2\mathbf{A}_i^2. \tag{2.6}$$

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[1] Factor of $\frac{1}{2}$ is added to avoid double counting

[2] Note that $\mathbf{p}_i$ and $\mathbf{A}_i$ are operators that do not commute. The obtained result was derived using a test function.

Therefore the total Hamiltonian can be written as $\hat{H} = \hat{H}_0 + \hat{H}_M$, where

$$\hat{H}_0 = \sum_i \frac{\mathbf{p}_i^2}{2m} - e\phi_i, \tag{2.7}$$

is the electronic part without magnetic interactions and

$$\hat{H}_M = \sum_i \frac{e}{m}\mathbf{A}_i \cdot \mathbf{p}_i + \frac{e^2 \mathbf{A}_i^2}{2m} + \frac{e\hbar}{m}\mathbf{s}_i \cdot \mathbf{B}_i, \tag{2.8}$$

describes the contribution of the magnetic field.

2.2   Magnetic energy

Omitting the spin-orbit interaction, consider an ion which is put into a homogeneous magnetic field $\mathbf{B}_i = \mathbf{B}_0$. In this case the vector potential can be chosen so that

$$\mathbf{A}_i = -\frac{1}{2}\mathbf{r}_i \times \mathbf{B}_0 \tag{2.9}$$

Therefore[3]

$$\mathbf{A}_i \cdot \mathbf{p}_i = -\frac{1}{2}\left(\mathbf{r}_i \times \mathbf{B}_0\right) \cdot \mathbf{p}_i = \frac{1}{2}\mathbf{B}_0 \cdot \left(\mathbf{r}_i \times \mathbf{p}_i\right) = \frac{\hbar}{2}\mathbf{B}_0 \cdot \mathbf{l}_i, \tag{2.10}$$

where in the last step we have defined a unitless orbital angular momentum operator $\hbar\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i$. Without the loss of generality, we may choose z-axis to be parallel with $\mathbf{B}_0$. Thus

$$\mathbf{A}_i \cdot \mathbf{p}_i = \frac{\hbar B_0}{2}l_{z,i}, \tag{2.11}$$

where $l_{z,i}$ is the z-component of $\mathbf{l}_i$. Similarly

$$\mathbf{A}_i^2 = \frac{1}{4}(\mathbf{r}_i \times \mathbf{B}_0)^2 = \frac{1}{4}(y_i B_0 \hat{\mathbf{x}} - x_i B_0 \hat{\mathbf{y}})^2 = \frac{B_0^2}{4}(x_i^2 + y_i^2) \tag{2.12}$$

Substituting the derived expressions for $\mathbf{A}_i \cdot \mathbf{p}_i$ and $\mathbf{A}_i^2$, and $\mathbf{s}_i \cdot \mathbf{B}_i = B_0 s_{z,i}$ into Eq. (2.8), we obtain

$$\hat{H}_M = \sum_i \frac{e\hbar B_0}{2m}l_{z,i} + \frac{e^2 B_0^2}{8m}(x_i^2 + y_i^2) + \frac{e\hbar B_0}{m}s_{z,i}. \tag{2.13}$$

We may simplify the result by defining Bohr magneton

$$\mu_B = \frac{e\hbar}{2m} = 5.788 \cdot 10^{-5}\ \frac{\text{eV}}{\text{T}} = 9.274 \cdot 10^{-24}\ \frac{\text{J}}{\text{T}}. \tag{2.14}$$

Thus

$$\hat{H}_M = \mu_B B_0 (L_z + 2S_z) + \frac{e^2 B_0^2}{8m}\sum_i (x_i^2 + y_i^2), \tag{2.15}$$

where $L_z = \sum_i l_{z,i}$ and $S_z = \sum_i s_{z,i}$ are the z-components of the total orbital angular momentum and spin angular momentum operators $\mathbf{L}$ and $\mathbf{S}$, respectively.

Since magnetic energy is rather small compared to the energy of an unperturbed atom, we may obtain it by using the perturbation theory. Up to the first order the magnetic energy is

$$\Delta E_M = \mu_B B_0 \langle\psi|L_z + 2S_z|\psi\rangle + \frac{e^2 B_0^2}{8m}\sum_i \langle\psi|x_i^2 + y_i^2|\psi\rangle \tag{2.16}$$

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[3]Again, the derivation using a test function.

If we deal with ions with a one electron short being half filled shell, or molecules that do not have an axis of symmetry parallel to the magnetic field, we have to include also the second order contribution

$$\sum_{\psi' \neq \psi} \frac{|\langle \psi | L_z + 2 S_z | \psi' \rangle|^2}{E_\psi - E_{\psi'}}, \tag{2.17}$$

where the sum goes over all the exited states. This term is the source of so called *Van Vleck paramagnetism* which will not be consider further in these notes.

2.3 Magnetization and thermodynamics

The magnetization $\mathbf{M}$ connects the magnetic flux density $\mathbf{B}$ and the magnetic field strength $\mathbf{H}$ as follows

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}), \tag{2.18}$$

where $\mu_0 = 4\pi \cdot 10^{-7}$ H/m is the permeability of the vacuum. The quantity which is the measure of "magnitisability" of the material as a response to an external field is known as the magnetic susceptibility χ, which can be defined as[4]

$$\chi = \frac{\partial M}{\partial H} \tag{2.19}$$

We now take a brief tour into thermodynamics because it is a necessary tool for calculating the magnetic properties. The partition function Z is defined as

$$Z = \sum_n e^{-E_n / k_B T}. \tag{2.20}$$

Since the magnetic energy is given by $E = -\mathbf{m} \cdot \mathbf{B} = -m_z B_0$, we find that

$$\frac{\partial Z}{\partial B_0} = \sum_n -\frac{1}{k_B T} e^{-E_n / k_B T} \frac{\partial E_n}{\partial B_0} = \frac{1}{k_B T} \sum_n m_{z,n} e^{-E_n / k_B T}. \tag{2.21}$$

Thus the magnetization of the system is

$$M = \frac{\langle m_z \rangle}{V} = \frac{1}{V} \frac{k_B T}{Z} \frac{\partial Z}{\partial B_0} \tag{2.22}$$

Since the Helmholtz energy $A = -k_B T \ln Z$, the former can be simplified to

$$M = \frac{\langle m_z \rangle}{V} = -\frac{1}{V} \frac{\partial A}{\partial B_0}. \tag{2.23}$$

Thus the magnetic susceptibility can be obtain from A as follows

$$\chi = \frac{\partial M}{\partial H} = -\frac{1}{V} \frac{\partial^2 A}{\partial H \partial B_0}. \tag{2.24}$$

If χ is small, then $\mathbf{B} \approx \mu_0 \mathbf{H}$ and we get

$$\chi = \frac{\partial M}{\partial H} = -\frac{\mu_0}{V} \frac{\partial^2 A}{\partial B_0^2} \tag{2.25}$$

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[4]Here χ is a scalar quantity but in general it can be a tensor $\chi_{ij} = \partial M_i / \partial H_j$

2.4   Diamagnetism

Consider an ion which contains only filled shells. For such an ion $L^2|\psi\rangle = S^2|\psi\rangle = 0$ and thus the magnetic energy (2.16) becomes

$$\Delta E_M = \frac{e^2 B_0^2}{8m} \sum_i \langle\psi|x_i^2 + y_i^2|\psi\rangle. \tag{2.26}$$

In low temperatures, only the ground state of the system is populated: the Helmholtz energy of N ions is simply $A = N\Delta E_M$. Therefore the susceptibility of such ions in the volume V is

$$\chi = -\frac{\mu_0 N}{V}\frac{\partial^2 \Delta E_M}{\partial B_0^2} = -\frac{N}{V}\frac{\mu_0 e^2}{4m}\sum_i \langle\psi|x_i^2 + y_i^2|\psi\rangle. \tag{2.27}$$

Since the shells are filled, we may assume that the ion is spherically symmetric, thus $\langle\psi|x_i^2|\psi\rangle = \langle\psi|y_i^2|\psi\rangle = \frac{1}{3}\langle\psi|r_i^2|\psi\rangle$. Furthermore, we may write $\sum_i\langle\psi|r_i^2|\psi\rangle = Z_e r^2$, where Z_e is the number of electrons and r is the effective ionic radius. Thus the susceptibility becomes

$$\chi_{dia} = -\frac{N}{V}\frac{\mu_0 e^2}{12m}Z_e r^2. \tag{2.28}$$

The susceptibility caused by this term is negative, so it goes against the applied magnetic field. Thus it is fitting to call the macroscopic magnetic response *diamagnetic*[5]. More specifically, the derived term is known as the *Larmor diamagnetism.*

2.5   Total angular momentum J

Consider a system where orbital and spin angular momenta are decoupled from each other. The states of such a system are consequently the eigenstates of operators $\mathbf{L}^2$, $\mathbf{S}^2$, L_z, and S_z. Thus the states can be characterised by the quantum numbers L, S, m_L, and m_S or $|LSm_Lm_S\rangle$. However, the situation changes if we add in spin-orbit interaction. Let the Hamiltonian be

$$\hat{H} = \hat{H}_0 + \lambda\mathbf{L}\cdot\mathbf{S}, \tag{2.29}$$

where $\hat{H}_0$ is the part of the Hamiltonian in which $\mathbf{L}$ and $\mathbf{S}$ are disconnected. Since $\mathbf{L}$ and $\mathbf{S}$ commute, we may write $\mathbf{L}\cdot\mathbf{S} = L_x S_x + L_y S_y + L_z S_z$. This is where the problem arises. Whereas $|LSm_Lm_S\rangle$ is an eigenstate for L_z and S_z operators, it not so for x- and y-components. Thus the magnetic quantum numbers m_L and m_S are not good quantum numbers for describing the eigenstates of LS-coupled system.

For that we define the total angular momentum operator

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{2.30}$$

Since $\mathbf{L}$ and $\mathbf{S}$ commute, also $\mathbf{J}$ commutes with them. This means that an eigenstate of $\mathbf{L}^2$ and $\mathbf{S}^2$ is also an eigenstate of $\mathbf{J}^2$. It can also be shown that such an eigenstate is also an eigenstate of J_z labelled by m_J. Since $J_z = L_z + S_z$ it is easy to see that the state $|LSm_Lm_S\rangle$ is also an eigenstate of J_z. However, *the converse is not true.*

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[5] *dia* = against, across

Now since $\mathbf{J}^2 = \mathbf{L}^2 + 2\mathbf{L} \cdot \mathbf{S} + \mathbf{S}^2$, we find that

$$\lambda \mathbf{L} \cdot \mathbf{S} = \frac{\lambda}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) \tag{2.31}$$

Therefore we arrive at the conclusion that the good quantum numbers describing the LS-coupled system are J, L, S, and m_J.

Bibliography

[1] N. W. Ashcroft and N. D. Mermin. *Solid State Physics.* Saunders College Publishing, 1976.

[2] S. Blundell. *Magnetism in Condensed Matter.* Oxford University Press, 2001.