

Chapter 1

Introduction to Magnetism

Magnetic properties originate in the spin degrees of freedom of electrons and their associated motion in solids. We first describe the microscopic magnetic moments of electrons, and the formation of atomic magnetic moments due to strong Coulomb interactions in an atom with unfilled shell. Atomic magnetic moments change their nature when the atoms form a solid. The key to understanding the behavior of magnetic moments in solids is the degree of electron localization. We briefly introduce the concept of the metal and the insulator (i.e., the Mott insulator). Electrons in the latter are localized on each atom, so that their magnetic properties are described by the atomic magnetic moments and the magnetic interactions between them. We present in this chapter only a minimal discussion on the magnetism in insulators. On the other hand, electrons move from site to site over the entire crystal in metals, so that the magnetic properties are connected to the whole degrees of freedom of correlated electrons. Needless to say, the main theme of this book is the magnetism of metals and alloys. In the last section, we elucidate various magnetic structures in solids to provide a basic knowledge on magnetism.

1.1 Magnetic Moments

Magnetic moment $\mathbf{M}$ in the electromagnetics is defined by the torque $\mathbf{N}$ on a magnet under the magnetic field $\mathbf{H}$ as

$$\mathbf{N} \equiv \mathbf{M} \times \mathbf{H}. \quad (1.1)$$

It originates in electrons in the magnet. According to the classical electromagnetics, the coil-type local current $\mathbf{i}(\mathbf{r})$ due to electron motion causes a magnetic moment. It is given in the CGS-Gauss unit as [1]

$$\mathbf{M}_L = \frac{1}{2c} \int \mathbf{r} \times \mathbf{i}(\mathbf{r}) d^3x. \quad (1.2)$$

Here c is the speed of light. $\mathbf{i}(\mathbf{r})$ is the current density of electrons, given by $\mathbf{i}(\mathbf{r}) = -\sum_i e \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i)$ with $\mathbf{v}_i$ being the velocity of the electron and $-e$ the charge of the electron at $\mathbf{r}_i$. Substituting the expressions into (1.2), we obtain

$$\mathbf{M}_L = -\sum_i \frac{e}{2m_e c} \mathbf{l}_i. \quad (1.3)$$

Here m_e is the mass of an electron and $\mathbf{l}_i$ denotes the angular momentum of electron i . Equation (1.3) indicates that an electron with angular momentum $\mathbf{l}$ generates a magnetic moment,

$$\mathbf{m}_l = -\frac{e}{2m_e c} \mathbf{l}. \quad (1.4)$$

This is called the orbital magnetic moment for an electron.

According to the quantum mechanics, an electron has its own magnetic moment called the spin magnetic moment [2]. It is given by

$$\mathbf{m}_s = -g_e \frac{e}{2m_e c} \mathbf{s}. \quad (1.5)$$

Here s is the spin angular momentum of an electron with spin $s = 1/2$. The constant $g_e = 2.0023$ is referred as the g -value of electron. The deviation from 2 is caused by the interaction with electro-magnetic fields. The spin magnetic moment was found first experimentally by Stern and Gerlach in 1922, and was established theoretically in 1928 by Dirac in his relativistic theory of electrons [3]. In the following we assume that $g_e = 2$ for simplicity.

As seen from (1.5), the spin of an electron leads to the magnetic moment

$$\mu_B = \frac{e\hbar}{2m_e c} = 0.9274 \times 10^{-20} \text{ emu}. \quad (1.6)$$

Here $\hbar$ is the Planck constant divided by 2π . The magnetic moment μ_B denotes the Bohr magneton, and is often used as a unit of the magnetic moment in atomic scale.

Equations (1.4) and (1.5) indicate that an electron has the following magnetic moment in the atomic scale.

$$\mathbf{m} = \mathbf{m}_l + \mathbf{m}_s = -(\mathbf{l} + 2\mathbf{s})\mu_B, \quad (1.7)$$

and the total magnetic moment is given by

$$\mathbf{M} = -\left\langle \sum_i (\mathbf{l}_i + 2\mathbf{s}_i) \mu_B \right\rangle. \quad (1.8)$$

Here the angular momenta $\mathbf{l}$ and $\mathbf{s}$ are measured in units of $\hbar = 1$. The $\mathbf{l}_i$ and $\mathbf{s}_i$ at the right-hand-side (r.h.s.) of the above equation should be regarded as quantum mechanical operators, and $\langle \sim \rangle$ means a quantum mechanical expectation value. In the following, we omit the minus sign at the r.h.s. of (1.8) for convenience bearing in mind that the real magnetic moments are opposite in direction.

It should be noted that the nuclei in the magnet also have magnetic moments because they have their own spins. The size of their magnetic moments is however characterized by the nuclear magneton μ_N , which is defined by

$$\mu_N = \frac{e\hbar}{2m_p c}. \quad (1.9)$$

Here m_p denotes the mass of proton. The nuclear magneton μ_N is only $1/1800$ of the Bohr magneton μ_B because $\mu_N/\mu_B = m_e/m_p$. Therefore the magnetism in solids is dominated by the magnetic moments of electrons. In the following equations, we adopt a unit of $\mu_B = 1$ for simplicity.

1.2 Basic Hamiltonian

Magnetic moments and magnetic properties are governed by the Hamiltonian of the system. The basic Hamiltonian of electrons in solids is given as follows in the second quantization.

$$\begin{aligned} H = & \int \psi^\dagger(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + v_N(\mathbf{r}) \right) \psi(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \int \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi(\mathbf{r}') \psi(\mathbf{r}) d\mathbf{r} d\mathbf{r}' \\ & + \int \psi^\dagger(\mathbf{r}) \left[\frac{1}{2} \nabla v_N(\mathbf{r}) \times (-i\nabla) \cdot \frac{1}{2} \boldsymbol{\sigma} \right] \psi(\mathbf{r}) d\mathbf{r} \\ & - \int \psi^\dagger(\mathbf{r}) (\mathbf{l} + 2\mathbf{s}) \psi(\mathbf{r}) d\mathbf{r} \cdot \mathbf{H}. \end{aligned} \quad (1.10)$$

Here we have adopted the units $m_e = 1$, $\hbar = 1$, and $e = 1$ for simplicity. $\psi(\mathbf{r}) = (\psi_\uparrow(\mathbf{r}), \psi_\downarrow(\mathbf{r}))$ is the electron field operator. $v_N(\mathbf{r})$ is the one electron potential energy due to nuclei, and is given by $v_N(\mathbf{r}) = -\sum_i Z_i/|\mathbf{r} - \mathbf{R}_i|$. Z_i is the atomic number of the atom at position $\mathbf{R}_i$. $\mathbf{H}$ denotes the magnetic field, and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ denote the Pauli spin matrices given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (1.11)$$

The first term in the Hamiltonian (1.10) consists of the kinetic energy and the attractive potential due to nuclei, and describes the independent motion of electrons.

The second term denotes the electron–electron interaction, the third term denotes the spin–orbit interaction, and the last term is the Zeeman interaction due to magnetic field. Note that in the above expression we have omitted the diamagnetic term which is proportional to the square of the magnetic field [2], because we do not consider the diamagnetism in this book.

In solids, we may express the field operators by means of a basis set of wave-functions $\{\varphi_i(\mathbf{r})\}$ as follows.

$$\psi_\sigma(\mathbf{r}) = \sum_i a_{i\sigma} \varphi_i(\mathbf{r}). \quad (1.12)$$

Here $\varphi_i(\mathbf{r})$ are orthonormal basis functions. The suffix i stands for a set of the atomic position i (quantum number n) and orbital L (momentum $\mathbf{k}$) when we adopt atomic orbitals (one-electron eigen functions in solids) as the basis functions.

Using the orthonormal basis set, we can express the Hamiltonian (1.10) as follows.

$$H = \sum_{ij\sigma} \varepsilon_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{k\sigma'} a_{l\sigma} + H_{\text{SO}} + H_{\text{Zeeman}}. \quad (1.13)$$

Here ε_{ij} (V_{ijkl}) are the matrix elements for the independent electron (the Coulomb interaction) part of the Hamiltonian (1.10). They are given by

$$\varepsilon_{ij} = \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + v_{\text{N}}(\mathbf{r}) \right) \varphi_j(\mathbf{r}), \quad (1.14)$$

$$V_{ijkl} = \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}') \varphi_l(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.15)$$

The third and last terms at the r.h.s. of (1.13) are the spin–orbit interaction term and the Zeeman term, respectively.

$$H_{\text{SO}} = \sum_{i\alpha j\gamma} \zeta_{i\alpha j\gamma} a_{i\alpha}^\dagger a_{j\gamma}, \quad (1.16)$$

$$H_{\text{Zeeman}} = - \sum_{i\alpha j\gamma} (\mathbf{l} + 2\mathbf{s})_{i\alpha j\gamma} a_{i\alpha}^\dagger a_{j\gamma} \cdot \mathbf{H}. \quad (1.17)$$

Here the spin–orbit interaction matrix elements $\zeta_{i\alpha j\gamma}$ are given by

$$\zeta_{i\alpha j\gamma} = \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \left[\frac{1}{2} \nabla v(\mathbf{r}) \times (-i\nabla) \right] \varphi_j(\mathbf{r}) \cdot (\mathbf{s})_{\alpha\gamma}. \quad (1.18)$$

In molecules and solids, atomic orbitals are often useful as the basis functions.

$$\varphi_i^{(\text{atom})}(\mathbf{r}) = \phi_{inl}(|\mathbf{r} - \mathbf{R}_i|) Y_{lm}(\mathbf{r} - \mathbf{R}_i). \quad (1.19)$$

Here $\phi_{inl}(|\mathbf{r} - \mathbf{R}_i|)$ is a radial wave function for an atom located at $\mathbf{R}_i$, the subscripts n and l denote the principal quantum number and the azimuthal quantum number,

respectively. $Y_{lm}(\mathbf{r} - \mathbf{R}_i)$ is the spherical harmonics located at atom $\mathbf{R}_i$, and m denotes the magnetic quantum number.

In the application to solids, it is convenient to make use of real functions $\{P_{lv}\}$ instead of complex basis functions $\{Y_{lm}\}$. The former called the cubic harmonics are constructed by linear combinations of spherical harmonics. Defining the orbital $L = (l, v)$, the atomic functions for solids are written as follows.

$$\varphi_{inL}(\mathbf{r}) = \phi_{inl}(|\mathbf{r} - \mathbf{R}_i|) P_{lv}(\mathbf{r} - \mathbf{R}_i). \quad (1.20)$$

The cubic harmonics are constructed to yield the irreducible representation for the cubic symmetry of the point group in crystal. The s ($l = 0$) function belonging to the A_{1g} representation for the cubic point symmetry is a constant function.

$$P_{a_{1g}}(\mathbf{r}) = Y_{00} = \frac{1}{\sqrt{4\pi}}. \quad (1.21)$$

The p ($l = 1$) functions belonging to the T_{1u} representation are defined as follows.

$$P_{t_{1u}\alpha}(\mathbf{r}) = \frac{1}{\sqrt{2}}(-Y_{11} + Y_{1,-1}) = \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \quad (1.22)$$

$$P_{t_{1u}\beta}(\mathbf{r}) = \frac{i}{\sqrt{2}}(Y_{11} + Y_{1,-1}) = \sqrt{\frac{3}{4\pi}} \frac{y}{r}, \quad (1.23)$$

$$P_{t_{1u}\gamma}(\mathbf{r}) = Y_{10} = \sqrt{\frac{3}{4\pi}} \frac{z}{r}. \quad (1.24)$$

The d ($l = 2$) orbitals form the E_g ($d\gamma$) and T_{2g} ($d\varepsilon$) representations. The d functions belonging to the E_g representation are given by

$$P_{e_{gu}}(\mathbf{r}) = Y_{20} = \sqrt{\frac{5}{4\pi}} \frac{1}{2} \frac{3z^2 - r^2}{r^2}, \quad (1.25)$$

$$P_{e_{gv}}(\mathbf{r}) = \frac{1}{\sqrt{2}}(Y_{22} + Y_{2,-2}) = \sqrt{\frac{5}{4\pi}} \frac{\sqrt{3}}{2} \frac{x^2 - y^2}{r^2}. \quad (1.26)$$

The remaining d ($l = 2$) functions belonging to the T_{2g} representation are given by

$$P_{t_{2g\xi}}(\mathbf{r}) = \frac{i}{\sqrt{2}}(Y_{21} + Y_{2,-1}) = \sqrt{\frac{5}{4\pi}} \sqrt{3} \frac{yz}{r^2}, \quad (1.27)$$

$$P_{t_{2g\eta}}(\mathbf{r}) = \frac{1}{\sqrt{2}}(-Y_{21} + Y_{2,-1}) = \sqrt{\frac{5}{4\pi}} \sqrt{3} \frac{zx}{r^2}, \quad (1.28)$$

$$P_{t_{2g\zeta}}(\mathbf{r}) = \frac{i}{\sqrt{2}}(-Y_{22} + Y_{2,-2}) = \sqrt{\frac{5}{4\pi}} \sqrt{3} \frac{xy}{r^2}. \quad (1.29)$$

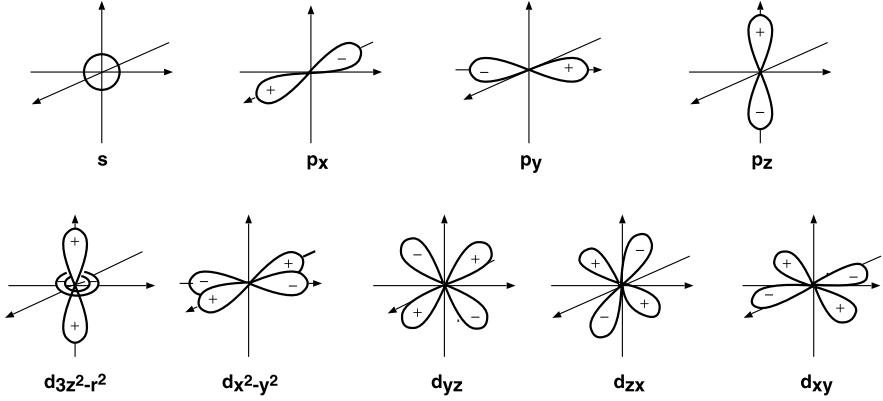


Fig. 1.1 Atomic orbitals from s to d symmetry. The sign of wave functions is shown by + and – in the figure

The angular dependence of the cubic harmonics is shown in Fig. 1.1. The spatial distribution of the atomic wave functions governs the electron hoppings in solids, thus determining the electronic and magnetic properties of solids.

1.3 Formation of Atomic Moments

The electronic structure and related properties of an atom may be understood by an independent-electron picture. The spin–orbit interaction in the Hamiltonian (1.13) is smaller than the Coulomb interaction in the ‘light’ elements such as the 3d transition metals. We first neglect the former, and treat the latter by means of the following approximation.

$$\begin{aligned}
 a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{k\sigma'} a_{l\sigma} &= \langle a_{i\sigma}^\dagger a_{l\sigma} \rangle a_{j\sigma'}^\dagger a_{k\sigma'} + a_{i\sigma}^\dagger a_{l\sigma} \langle a_{j\sigma'}^\dagger a_{k\sigma'} \rangle \\
 &\quad - \langle a_{i\sigma}^\dagger a_{k\sigma'} \rangle a_{j\sigma'}^\dagger a_{l\sigma} - a_{i\sigma}^\dagger a_{k\sigma'} \langle a_{j\sigma'}^\dagger a_{l\sigma} \rangle \\
 &\quad - \langle a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{k\sigma'} a_{l\sigma} \rangle.
 \end{aligned} \tag{1.30}$$

Here the average $\langle \rangle$ is taken with respect to an independent particle system which will be chosen later. Note that the two particle operator has been decoupled so that (1.30) exactly holds true when we take the average. This is called the Hartree–Fock approximation.

In the Hartree–Fock approximation, the Hamiltonian (1.13) is reduced to

$$H = \sum_{ij\sigma} h_{ij\sigma} a_{i\sigma}^\dagger a_{j\sigma} - \frac{1}{2} \sum_{ijkl\sigma\sigma'} (V_{ijkl} - V_{ijkl}\delta_{\sigma\sigma'}) \langle a_{i\sigma}^\dagger a_{l\sigma} \rangle \langle a_{j\sigma'}^\dagger a_{k\sigma'} \rangle. \tag{1.31}$$

Here $h_{ij\sigma}$ is given as follows.

$$h_{ij\sigma} = \int \varphi_{i\sigma}^\dagger(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + v_N(\mathbf{r}) + \int d\mathbf{r}' \frac{\langle n(\mathbf{r}') \rangle}{|\mathbf{r} - \mathbf{r}'|} \right) \varphi_{j\sigma}(\mathbf{r}) \\ - \int d\mathbf{r} d\mathbf{r}' \varphi_{i\sigma}^\dagger(\mathbf{r}) \frac{\langle \psi_\sigma^\dagger(\mathbf{r}') \psi_\sigma(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|} \varphi_{j\sigma}(\mathbf{r}'). \quad (1.32)$$

The Hartree–Fock one-electron wave functions $\{\varphi_{i\sigma}(\mathbf{r})\}$ are determined by solving the following self-consistent equations.

$$\left(-\frac{1}{2} \nabla^2 + v_N(\mathbf{r}) + \int d\mathbf{r}' \frac{\langle n(\mathbf{r}') \rangle}{|\mathbf{r} - \mathbf{r}'|} \right) \varphi_{i\sigma}(\mathbf{r}) \\ - \sum_j \langle n_{j\sigma} \rangle \int d\mathbf{r}' \frac{\varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_{j\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r}). \quad (1.33)$$

Here $\varepsilon_{i\sigma}$ is the Hartree–Fock energy eigen value. When we apply the Hartree–Fock independent particle Hamiltonian in the average $\langle \rangle$, $\langle n_{j\sigma} \rangle$ is given by the Fermi distribution function $f(\varepsilon_{j\sigma})$ and $\langle n(\mathbf{r}) \rangle = \sum_{j\sigma} f(\varepsilon_{j\sigma}) \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})$ denotes a charge density in the Hartree–Fock approximation. The third term at the l.h.s. of (1.33) gives the electrostatic potential due to electrons. The last term also originates in the Coulomb interaction, but the wave functions have been exchanged due to the anti-symmetric property of the Slater determinant. It is referred as the exchange potential. The Hartree–Fock wave function is the best Slater determinant at the ground state according to the variational principle [4].

Taking the Hartree–Fock wavefunctions as the basis functions, one can express the Hartree–Fock Hamiltonian (1.31) as follows.

$$H = \sum_{i\sigma} \varepsilon_{i\sigma} n_{i\sigma} - \frac{1}{2} \sum_{ij\sigma\sigma'} (V_{ijji} - V_{ijij} \delta_{\sigma\sigma'}) \langle n_{i\sigma} \rangle \langle n_{j\sigma'} \rangle. \quad (1.34)$$

Here V_{ijji} (V_{ijij}) is known as the Coulomb integral (exchange integral). (Note that V_{ijkl} should more precisely be $V_{i\sigma j\sigma' k\sigma' l\sigma}$.) The second term at the r.h.s. is to eliminate the double counting of Coulomb interaction in the Hartree–Fock one-electron energy.

The exchange potential in the Hartree–Fock equation (1.33) is nonlocal. Slater proposed an approximate local exchange potential, using the free-electron wave functions. It is given as follows [4].

$$v_{\text{ex}\sigma}(\mathbf{r}) = -3 \left(\frac{3}{4\pi} \right)^{1/3} n_\sigma(\mathbf{r})^{1/3}, \quad (1.35)$$

where $n_\sigma(\mathbf{r})$ is the electron density with spin σ .

The effective potential in the Hartree–Fock self-consistent equation is spherical in the atomic system when we apply the potential (1.35). We can express the atomic

wave function for an electron as

$$\varphi_{nlm\sigma}(\mathbf{r}) = \phi_{nl\sigma}(r)Y_{lm}(\hat{\mathbf{r}}). \quad (1.36)$$

Here $\phi_{nl\sigma}(r)$ is the radial wave function, and $Y_{lm}(\hat{\mathbf{r}})$ is the spherical harmonics. n , l , and m denote the principal quantum number, the azimuthal quantum number, and the magnetic quantum number, respectively. Orbitals $l = 0, 1, 2, 3, \dots$ are called s, p, d, f, $\dots$, respectively. The nl shells are therefore written as ns , np , nd , nf , etc. In each shell, there are $2l + 1$ degenerate orbitals.

With the use of the Hartree–Fock atomic orbitals, a many electron state of an atom is expressed in the form of the Slater determinant. The ground-state electronic structure of an atom is constructed according to the Pauli principle. For example, in the case of Ar, we have the ground state $1s^2 2s^2 2p^6 3s^2 3p^6$. Since the outermost electron shell of Ar is closed, the magnetic moment of Ar vanishes.

For an atom with an unfilled shell, the magnetic moment may appear. Since the total number of electrons (N), the total spin (S), and the total orbital moment (L) of an atom commute with the Hamiltonian, the eigen function Ψ should be specified by the set $(N L M S M_S)$: $\Psi(N L M S M_S)$, where L (S) and M (M_S) denote the magnitude and z component of orbital moment L (spin S), respectively. The eigen energy, on the other hand, should depend only on N , L , and S because of the rotational symmetry: $E_A(N L S)$.

The ground state of electrons in an atom should be obtained by minimizing the Coulomb energy. The Coulomb interaction of the Hamiltonian for the unfilled shell is written as follows according to (1.13).

$$H_{\text{Coulomb}} = \sum_{\nu} U_{\nu\nu} n_{\nu\uparrow} n_{\nu\downarrow} + \sum_{\nu > \nu'} \left(U_{\nu\nu'} - \frac{1}{2} J_{\nu\nu'} \right) n_{\nu} n_{\nu'} - 2 \sum_{\nu > \nu'} J_{\nu\nu'} \mathbf{s}_{\nu} \cdot \mathbf{s}_{\nu'}. \quad (1.37)$$

Here ν denotes an orbital lm ($m = -l \dots l$). n_{ν} ($\mathbf{s}_{\nu}$) denotes the charge (spin) density operator for electrons in the orbital ν . We have taken into account the Hartree–Fock Coulomb and exchange interactions, $U_{\nu\nu'} = V_{\nu\nu'\nu\nu}$ and $J_{\nu\nu'} = V_{\nu\nu'\nu'\nu}$, and omitted the other types of interactions. The first term at the r.h.s. of (1.37) denotes the intra-orbital Coulomb interaction, the second term expresses the inter-orbital interaction, and the third term the exchange interaction between the spins on different orbitals. Note that $U_{\nu\nu} > U_{\nu\nu'} (\nu \neq \nu') > J_{\nu\nu'} > 0$. Typical values of Coulomb interactions are $U_{\nu\nu} \approx 20$ eV, $U_{\nu\nu} - U_{\nu\nu'} \approx 2$ eV, and $J_{\nu\nu'} \approx 0.9$ eV for 3d transition-metal elements [5]. Note that N stands for the total number of electrons in the unfilled shell when the Hamiltonian (1.37) is applied.

The intra-orbital Coulomb interaction (i.e., the first term at the r.h.s. of (1.37)) acts to reduce the doubly occupied states on the same orbital so that it creates active spins on the orbitals of an unfilled shell. The third term in (1.37) aligns the active spins on the orbitals because $J_{\nu\nu'} > 0$. These effects suggest that the magnitude of the total spin S is maximized at the ground state. This is known as Hund’s first rule, and therefore $J_{\nu\nu'}$ are often called the Hund-rule couplings. On the other hand, the

second term in (1.37) is the energy associated with the configuration of electrons on different orbitals. One might expect that such an interaction energy is reduced when electrons move around the nucleus in the same direction avoiding each other. Thus we expect that the magnitude of the total angular momentum L should be maximized at the ground state under the maximum magnitude of total spin. This is referred as Hund's second rule. The first and second Hund rules are verified by the full Hartree–Fock numerical calculations.

The maximum S and L at the ground state are obtained by using the Pauli principle and the Hund rule, especially from the conditions $S = M_s(\text{Max})$ and $L = M(\text{Max})$ under the maximum S that corresponds to the state $\Psi(NLLSS)$:

$$S = \begin{cases} \frac{N}{2} & \text{for } N \leq 2l + 1, \\ \frac{4l + 2 - N}{2} & \text{for } N > 2l + 1, \end{cases} \quad (1.38)$$

$$L = \begin{cases} \frac{1}{2}N(2l + 1 - N) & \text{for } N \leq 2l + 1, \\ \frac{1}{2}(N - 2l - 1)(4l + 2 - N) & \text{for } N > 2l + 1. \end{cases} \quad (1.39)$$

The ground state $\Psi(NLMSM_s)$ is $(2L + 1)(2S + 1)$ -fold degenerate. The multiplet is written as $^{2S+1}L_J$ where L takes S, P, D, F, G, H, ... according to $L = 0, 1, 2, 3, 4, 5, \dots$, and $J (= |L \pm S|)$ is the total angular momentum. These properties are summarized in Fig. 1.2 for 3d transition metal atoms.

The value of J at the ground state is determined by the spin–orbit interaction. The spin–orbit interaction (1.16) in the atomic system can be written as

$$H_{SO} = \sum_{\nu\alpha\nu'\gamma} \zeta_{nl} (\mathbf{l})_{\nu\nu'} \cdot (\mathbf{s})_{\alpha\gamma} a_{\nu\alpha}^\dagger a_{\nu'\gamma}. \quad (1.40)$$

Here

$$\zeta_{nl} = \frac{1}{2} \int_0^\infty |\phi_{nl}(r)|^2 \frac{dV}{dr} r dr > 0. \quad (1.41)$$

Assume that the ground state is determined by the Hund rule, and the temperature is such that the corresponding thermal energy is much lower than that of the first excited state of the Coulomb interaction, i.e., the Hund-rule coupling J_H : $k_B T \ll J_H$. Here J_H is an average value of $\{J_{\nu\nu'}\}$, and k_B denotes Boltzmann's constant. Moreover the spin–orbit interaction energy is much smaller than J_H in 3d transition metals. In this case, we can neglect all the excited state of the Coulomb interactions, and limit the states to the $(2L + 1)(2S + 1)$ dimensional Hund-rule subspace: $\{\Psi(NLMSM_s)\}$. We can then verify the following relation in the subspace.

$$\begin{aligned} & \langle \Psi(NLMSM_s) | H_{SO} | \Psi(NLM'SM'_s) \rangle \\ &= \lambda(NLS) \langle \Psi(NLMSM_s) | \mathbf{L} \cdot \mathbf{S} | \Psi(NLM'SM'_s) \rangle. \end{aligned} \quad (1.42)$$

$\begin{smallmatrix} \diagup & N \\ m_z & \diagdown \end{smallmatrix}$	1	2	3	4	5	6	7	8	9	10
2										
1	—									
0	—	—								
-1	—	—	—							
-2	—	—	—	—						
S	1/2	1	3/2	2	5/2	2	3/2	1	1/2	0
L	2	3	3	2	0	2	3	3	2	0
$J = L \mp S $	3/2	2	3/2	0	5/2	4	9/2	4	5/2	0
G S	$^2D_{3/2}$	3F_2	$^4F_{3/2}$	5D_0	$^6S_{5/2}$	5D_4	$^4F_{9/2}$	3F_4	$^2D_{5/2}$	1S_0
λ (eV)	0.014	0.013	0.011	0.007	0.00	-0.012	-0.022	-0.042	-0.105	0.00
Ions	Sc ²⁺ Ti ³⁺ V ⁴⁺	Ti ²⁺ V ³⁺ Cr ⁴⁺	V ²⁺ Cr ³⁺ Mn ⁴⁺	Cr ²⁺ Mn ³⁺	Mn ²⁺ Fe ³⁺	Fe ²⁺ Co ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺

Fig. 1.2 The ground state of atoms with 3d unfilled shell. N and m_z denote the d electron number and the orbital magnetic quantum number, respectively. Electron configuration for each N in the upper row of the figure shows the state $\Psi(NLLSS)$ leading to the total spin S and the orbital angular momentum L at the ground state. J denotes the total angular momentum. The ground state multiplets (GS) are expressed as $^{2S+1}L_J$. The experimental values of the spin–orbit coupling constant λ are given. Examples of the 3d transition metal ions are also given in the bottom row

Thus we have an effective Hamiltonian for the spin–orbit interaction in the Hund-rule subspace as follows.

$$H_{SO} = \lambda(NLS)L \cdot S. \quad (1.43)$$

The coefficient $\lambda(NLS)$ is obtained by comparing the diagonal matrix element of H_{SO} for the state $\Psi(NLLSS)$ obtained from (1.40) with that of the r.h.s. of (1.43).

$$\lambda(NLS) = \begin{cases} \frac{\zeta_{nl}}{N} & \text{for } N \leq 2l + 1, \\ -\frac{\zeta_{nl}}{4l + 2 - N} & \text{for } N > 2l + 1. \end{cases} \quad (1.44)$$

Because $\zeta_{nl} > 0$, $\lambda(NLS) > 0$ for $N \leq 2l + 1$ and $\lambda(NLS) < 0$ for $N > 2l + 1$. Thus, $J = |L - S|$ is realized for $N \leq 2l + 1$, and $J = |L + S|$ for $N > 2l + 1$ at the ground state among possible states $J = |L + S|, |L + S - 1|, \dots, |L - S|$. Therefore $J = |L - S|$ is the ground-state in the light transition-metal elements and the light

rare-earth elements, and $J = |L + S|$ is the ground state in the heavy transition-metal elements and the heavy rare-earth elements. Note that the typical value of the spin-orbit coupling is only one tenth of the Hund rule coupling ($J_H \sim 1$ eV) in the case of 3d transition metal ions as shown in Fig. 1.2. When the spin-orbit coupling is significant as in the rare-earth atoms, the ground-state should be $(2J + 1)$ -fold degenerate instead of $(2S + 1)(2L + 1)$ fold.

Ions such as Ti^{2+} , V^{3+} , and Cr^{4+} , for example, have two electrons in the d shell (see the $N = 2$ column in Fig. 1.2). The Hund rule tells us that the total spin and orbital angular momenta at the ground state are $S = 1$ and $L = 3$, respectively. Because the spin-orbit coupling $\lambda > 0$ in the light atoms, the total angular momentum at the ground state is given by $J = 3 - 1$. Thus we have the ground-state multiplet 3F_2 according to the notation $^{2S+1}L_J$. In the same way, the ion Co^{2+} has 7 electrons in the d shell. According to the Hund rule, we find the ground-state spin and orbital momenta $S = 3/2$ and $L = 3$, respectively. Because the spin-orbit coupling $\lambda < 0$ in the heavy atoms, the total angular momentum is given by $J = 9/2$. Thus we obtain the ground-state multiplet $^4F_{9/2}$ for Co^{2+} ion.

When the external magnetic field H is applied to the atoms, the energy due to the magnetic field is given by $-g_J \mu_B J_z H$. Here g_J is Landé's g factor and is given by $g_J = 3/2 + [S(S + 1) - L(L + 1)]/2J(J + 1)$. The susceptibility which is defined by the induced magnetization divided by H is then given by

$$\chi = \frac{g_J^2 \mu_B^2 J(J + 1)}{3k_B T}. \quad (1.45)$$

The above temperature dependence is referred as the Curie law, and $C \equiv g_J^2 \mu_B^2 J(J + 1)/3k_B$ is called the Curie constant. The observation of the Curie law in the susceptibility measurement is regarded as an indication of the existence of local magnetic moments.

1.4 Metal and Insulator in Solids

When atoms form a solid, electrons in the outermost shell of atoms start to hop from atom to atom via overlap between atomic orbitals. The question then is whether electrons tend to remain in each atom or to itinerate in the solid. In the case of the former, atomic magnetic moments are well defined in solids and their properties are expected to be explained from the atomic point of view. In the case of the latter, magnetic properties may be quite different from those expected from atomic ones and one has to start from the itinerant limit in order to explain their magnetism.

Whether electrons in solids are movable or not is governed by the detailed balance between the energy gain due to electron hopping and the loss of Coulomb interaction. The simplest example may be the case of the hydrogen molecule H_2 . According to the molecular orbital picture, the 1s atomic orbitals split into the bonding state with energy $\varepsilon_0 - |t|$ and the anti-bonding state with energy $\varepsilon_0 + |t|$ when hydrogen atoms form a molecule. Here ε_0 denotes the atomic ground state, and t is the

electron hopping integral which is defined by atomic potential $v(\mathbf{r})$ and wave function $\varphi(\mathbf{r})$ as $t = \int \varphi(\mathbf{r} - \mathbf{R})v(\mathbf{r} - \mathbf{R})\varphi(\mathbf{r}) d\mathbf{r}$. The bonding orbital is occupied by two electrons according to the Pauli principle. It leads to the total energy gain $2|t|$. This is the covalent bond in the hydrogen molecule. In this state, electrons hop from one atom to another, and thus they are movable. The covalent bond is stabilized by the kinetic energy gain of independent electrons. It consists of the polarized state in which the 1s orbital of an atom is doubly occupied and the orbital of another atom is unoccupied, and the neutral state in which each atomic orbital is occupied by an electron.

When the Coulomb interaction between electrons are taken into account, the covalent bonding state is not necessarily stable because it contains the polarization state with double occupancy on an atomic orbital. Assume that the loss of the intraatomic Coulomb interaction energy in the covalent bonding state is given by U , and consider the neutral-atom state as the state in which each electron is localized on an atom. The total energy in the covalent bonding state is given by $E(\text{covalent}) = 2\varepsilon_0 - 2|t| + U$, while the energy in the neutral atom state is given by $E(\text{neutral}) = 2\varepsilon_0$. Thus, the neutral atom state is realized when the following condition is satisfied.

$$2|t| < U. \quad (1.46)$$

This condition is satisfied when the interatomic distance goes to infinity because $|t|$ goes to zero. Thus the neutral atom state in which electrons are localized on each atom and each atom has a well defined local magnetic moment $s = 1/2$ is realized in the atomic limit.

In solids, we expect the same behavior as found in the hydrogen molecule. Let us consider the behavior of electrons when atoms form a solid. Electrons in solids move in a potential obtained by a superposition of the atomic potentials $\sum_i v(\mathbf{r} - \mathbf{R}_i)$. Here $v(\mathbf{r} - \mathbf{R}_i)$ denotes the atomic potential on site i . When we adopt the atomic orbitals $\{\varphi_{i\nu}(\mathbf{r} - \mathbf{R}_i)\}$ as the basis functions and assume the orthogonality between the orbitals, the Hamiltonian for electrons on the outermost shells in solids may be obtained from (1.13) as

$$H = H_0 + H_{\text{Coulomb}}, \quad (1.47)$$

$$H_0 = \sum_{i\nu} \varepsilon_{i\nu} n_{i\nu} + \sum_{ij\nu\nu'} t_{ij\nu\nu'} a_{i\nu\sigma}^\dagger a_{j\nu'\sigma}, \quad (1.48)$$

$$\begin{aligned} H_{\text{Coulomb}} = & \sum_{i\nu} U_{i\nu\nu} n_{i\nu\uparrow} n_{i\nu\downarrow} + \sum_i \sum_{\nu>\nu'} \left(U_{i\nu\nu'} - \frac{1}{2} J_{i\nu\nu'} \right) n_{i\nu} n_{i\nu'} \\ & - 2 \sum_i \sum_{\nu>\nu'} J_{i\nu\nu'} \mathbf{s}_{i\nu} \cdot \mathbf{s}_{i\nu'}. \end{aligned} \quad (1.49)$$

Here $\varepsilon_{i\nu}$ is the atomic level for the orbital ν of site i , and $t_{ij\nu\nu'}$ the transfer integral between the orbital ν at site i and the orbital ν' at site j . The latter is expressed in

the two-center approximation as

$$t_{ivjv'} = \int \varphi_{iv}^*(\mathbf{r} - \mathbf{R}_i) v(\mathbf{r} - \mathbf{R}_i) \varphi_{jv'}(\mathbf{r} - \mathbf{R}_j) d\mathbf{r}. \quad (1.50)$$

Note that we have taken into account in H_{Coulomb} only the intra-atomic Coulomb interactions and omitted the inter-site Coulomb interaction contributions for simplicity.

It is not easy to treat the electrons in solids described by the Hamiltonian (1.47) because both the electron hoppings and the Coulomb repulsions have to be taken into consideration. In order to discuss both the itinerant and localized behaviors of electrons in solids, we can consider a simpler Hamiltonian consisting of one orbital per site as follows.

$$H = \sum_{i\sigma} \varepsilon_0 n_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow}. \quad (1.51)$$

Here ε_0 , t_{ij} , and U denote the atomic level, the transfer integral between sites i and j , and the intra-atomic Coulomb interaction energy, respectively. The Hamiltonian (1.51) is known as the Hubbard model, and was proposed by Gutzwiller and Hubbard independently [6–10].

The Hubbard model (1.51) is the simplest Hamiltonian which describes the motion of interacting electrons in solids. Nevertheless it describes the localization of electrons as well as their itinerant behavior in solids. Let us consider the atomic limit of the model. For an atom, we have 4 atomic states: the empty state ($n_\uparrow = 0, n_\downarrow = 0$), the single electron states ($n_\uparrow = 1, n_\downarrow = 0$) and ($n_\uparrow = 0, n_\downarrow = 1$), and the doubly occupied state ($n_\uparrow = 1, n_\downarrow = 1$). Associated energies are given as 0, ε_0 , ε_0 , and $2\varepsilon_0 + U$, respectively. An unfilled shell with spin $S = 1/2$ appears only for the $n = 1$ state. Note that there is no Hund's rule arrangement for spin in this case.

In the atomic limit for a solid where $t_{ij} = 0$, electron number n_i on each atom is no longer constant, though the total number of electrons N is given; $N = \sum_{i\sigma} n_{i\sigma}$. The eigenstates are given by $|\Psi\rangle = |\{n_{i\sigma}\}\rangle$, i.e., a set of the electron numbers with spin σ on site i . The eigenenergy for the state is given by

$$E(\{n_{i\sigma}\}) = \sum_i (\varepsilon_0 n_i + U n_{i\uparrow} n_{i\downarrow}). \quad (1.52)$$

It should be noted that the energy of the system increases by U when the number of doubly occupied states D is increased by one. The ground-state energy E_0 of the atomic limit is obtained by minimizing the energy with respect to the number of double occupancy in solid. Assume that the number of lattice points is given by L . When $N < L$, the ground-state energy is obtained as $E_0 = \varepsilon_0 N$ by choosing $D = 0$. Magnetic moments on the sites with an electron are active in this case as shown in Fig. 1.3. Because there are $L!/N!(L - N)!$ electron configurations on the L lattice points, the ground state is $[2^N L!/N!(L - N)!]$ -fold degenerate.

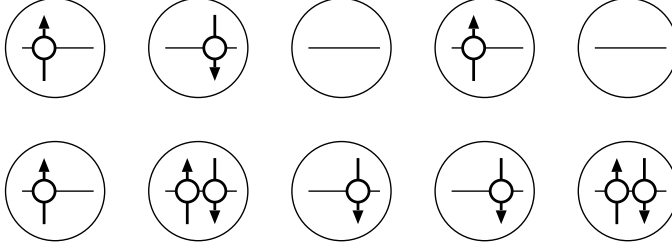


Fig. 1.3 Electron configurations for less than half filling (*upper figure*) and for more than half filling (*lower figure*) in the atomic limit

At half filling, all the atoms are occupied by an electron so that spin degrees of freedom by 2^N remain; the degenerated wave functions are given by $|1s_{1z}1s_{2z}1s_{3z}\dots\rangle$ when the wave function $|\{n_{i\sigma}\}\rangle$ is written as $|n_1s_{1z}n_2s_{2z}n_3s_{3z}\dots\rangle$ by using the charge $n_i = n_{i\uparrow} + n_{i\downarrow}$ and the spin $s_{iz} = (n_{i\uparrow} - n_{i\downarrow})/2$.

When the electron number N is larger than L , it is no longer possible to keep $D = 0$; the minimum value of D is given by $D = N - L$. The ground state energy is then given by $E_0 = \varepsilon_0 N + U(N - L)$. The ground state is $[2^{2L-N} L! / (2L - N)!(N - L)!]$ -fold degenerate because there are $L! / (2L - N)!(N - L)!$ configurations for choosing $2L - N (< L)$ sites with the single electron from L lattice sites and there are 2^{2L-N} spin degrees of freedom for each configuration. Note that the spins on $2L - N$ sites are active in this case.

Let us consider the case that electron hopping t_{ij} is small but finite. When $N \neq L$, electrons are mobile at $T = 0$ because electrons can move from site to site without increasing the double occupation number D . Thus the system is a metal. However, at half-filling, electron hopping creates a doubly occupied state, thus creating a finite excitation energy by the amount of Coulomb interaction energy U . Therefore electrons cannot move under the infinitesimal electric field. We have then an insulator with local magnetic moments at each site in this case.

When there is no Coulomb interaction ($U = 0$), on the other hand, electrons are generally itinerant. The Hamiltonian is given as

$$H = \sum_{ij\sigma} (\mathbf{H}_0)_{ij} a_{i\sigma}^\dagger a_{j\sigma}. \quad (1.53)$$

Here $(\mathbf{H}_0)_{ij} = \varepsilon_0 \delta_{ij} + t_{ij}(1 - \delta_{ij})$. The noninteracting Hamiltonian is diagonalized by a unitary transformation $a_{i\sigma} = \sum_k a_{k\sigma} \langle i|k \rangle$ ($a_{i\sigma}^\dagger = \sum_k a_{k\sigma}^\dagger \langle i|k \rangle^*$) so that

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma}, \quad (1.54)$$

where $\varepsilon_k = \sum_{ij} \langle k|i \rangle (\mathbf{H}_0)_{ij} \langle j|k \rangle$ is an eigen value for the tight-binding one-electron Hamiltonian matrix $\mathbf{H}_0$, and the set $\{\langle j|k \rangle\}$ ($j = 1, \dots, L$) is the eigen vector for ε_k .

The eigen states for noninteracting Hamiltonian H are given by $|\Psi\rangle = |\{n_{k\sigma}\}\rangle$, i.e., a set of electrons with momentum $\mathbf{k}$ and spin σ . The eigenenergy is given by

$$E(\{n_{k\sigma}\}) = \sum_{k\sigma} \varepsilon_k n_{k\sigma}, \quad (1.55)$$

where the c-number $n_{k\sigma}$ takes on the value of 0 or 1. The ground state is obtained by putting electrons on the energy levels from the bottom to the Fermi level ε_F according to the Pauli principle,

$$|\phi_0\rangle = \left[\prod_{k\sigma}^{\varepsilon_k < \varepsilon_F} a_{k\sigma}^\dagger \right] |0\rangle, \quad (1.56)$$

so that the ground-state energy is given by

$$E_0(\{n_{k\sigma}\}) = \sum_{k\sigma}^{\varepsilon_k < \varepsilon_F} \varepsilon_k. \quad (1.57)$$

Alternatively, defining the density of states per atom per spin as

$$\rho(\varepsilon) = \frac{1}{L} \sum_k \delta(\varepsilon - \varepsilon_k), \quad (1.58)$$

we can express the ground-state energy per atom as

$$E_0 = 2 \int_{-\infty}^{\varepsilon_F} \varepsilon \rho(\varepsilon) d\varepsilon. \quad (1.59)$$

A non-interacting electron system is in general metallic unless the electrons in the atom form a closed shell. The electrons in such systems are mobile. This is because one can add an electron at the energy level just above the Fermi level by applying infinitesimal electric field. Note that spins of itinerant electrons are also mobile. We may expect that there is a transition from metal to insulator at half filling when the intra-atomic Coulomb interaction is increased. Assume that there is a band for a non-interacting system whose band width is W . The center of the gravity of the noninteracting band is assumed to be located at ε_0 . When the Coulomb interaction U is increased, each atom tends to be occupied by one electron, and electron hopping to neighboring sites tends to be suppressed in order to reduce the on-site Coulomb interaction energy. In the strongly correlated region, an electron should have a potential $\varepsilon_0 + U$ on a site having an opposite-spin electron because of the increment of the Coulomb interaction energy due to double occupation, while an electron has a potential ε_0 on an empty site. We then expect one more band with the band width of order of W around $\varepsilon_0 + U$. The density of states as excitation spectrum is expected to split into two bands at $U_c \sim W$ (see Fig. 1.4). The formation

Fig. 1.4 The upper and lower Hubbard bands created by on-site Coulomb interaction U

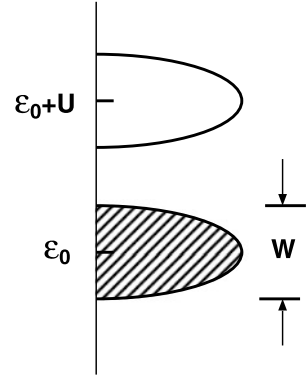
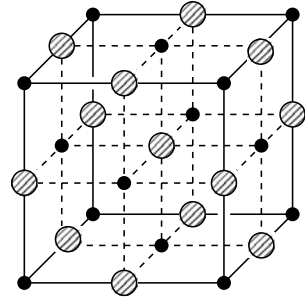


Fig. 1.5 NaCl type structure in NiO

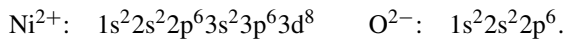


of a gap at the Fermi level implies the existence of an insulator. The insulating state therefore may be realized by the electron correlations when

$$U > W. \quad (1.60)$$

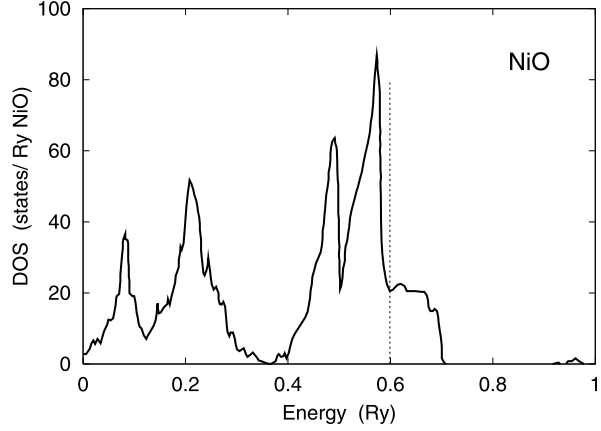
This is Hubbard's alloy analogy picture to the metal–insulator transition [9, 10]. The metal–insulator transition due to electron correlations as mentioned above is commonly known as the Mott transition. The split bands are named the upper and lower Hubbard bands, respectively. The insulator caused by the electron correlations is referred as the Mott insulator.

The concept of the Mott insulator was first proposed by Mott [11]. He considered the case of NiO. NiO has the NaCl structure in which Ni–O chain network is formed along [100] direction (see Fig. 1.5). The electronic configuration of the Ni^{28} (O^8) atom is given by $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ ($1s^2 2s^2 2p^4$). The oxygen atoms are considered to form a closed shell in the compound taking electrons from Ni atoms, so that we have

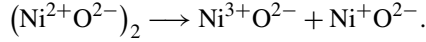


In this case, the Fermi level should be on the d bands in the crystalline system, and we can expect a metal because the 5-fold d bands overlap each other in general (see Fig. 1.6).

Fig. 1.6 Density of states for NiO in the paramagnetic state obtained by the band calculation [12]. The vertical dashed line shows the Fermi level



Experimental results however indicate that NiO is an insulator. To clarify the insulating behavior, Mott considered the electron hopping on the NiO network. Let us estimate an excitation energy ΔE_g when an electron moves to the neighboring Ni^{2+} site. This process is similar to an excitation of the H_2 molecule to a polarized state.



Assume that the intra-atomic Coulomb interaction is given by $\sum_i \sum_{(v\sigma, v'\sigma')} U \cdot n_{iv\sigma} n_{iv'\sigma'}$ for simplicity. There an electron is coupled to the remaining 7 electrons via the on-site Coulomb interaction. After the hopping, the electron is coupled to 8 electrons at the neighboring site, so that the Coulomb interaction is increased by U . On the other hand, the kinetic energy gain due to electron hopping at Ni^{3+} and Ni^{2+} sites may be given by

$$2z|t| \sim W, \quad (1.61)$$

because electrons in surrounding Ni sites can enter into the Ni^{3+} ions and the electrons in Ni^{2+} ions can jump to the surrounding Ni sites. Here z is the number of Ni nearest neighbors, and t is an effective electron hopping between Ni atoms. Note that $|t|$ corresponds to an energy gain for the formation of the bonding state due to electron hopping in the H_2 molecule, while U corresponds to the Coulomb energy loss in the polarized state. The excitation energy of an electron hopping is therefore given by

$$\Delta E_g \sim U - W. \quad (1.62)$$

Thus, we again have the same criterion for the formation of the Mott insulator (1.60) from the condition $\Delta E_g > 0$.

The magnetic materials in the insulator are considered to be the Mott-type insulator in which the atomic magnetic moments are built up in the unfilled shell. CrO_2 and CrBr_2 are typical ferromagnetic insulators, while MnO , FeO , CoO , and NiO

are known as antiferromagnetic insulators in which the atomic magnetic moments change their direction alternatively from site to site.

On the other hand, there are many magnetic metals where the polarized electrons are mobile. These materials are referred as the metallic magnets or itinerant electron magnets. The magnetic properties of these systems are known as the metallic magnetism or itinerant magnetism. Fe, Co, and Ni are typical examples of the metallic ferromagnet, while Cr and Mn alloys show the antiferromagnetism. We describe in this book the itinerant magnetism of metals and alloys.

1.5 Quenching of Orbital Magnetic Moments

The expectation value of the total orbital magnetic moment $\langle \mathbf{M}_L \rangle = \langle \mathbf{L} \rangle$ is usually quenched in the crystalline system due to the crystalline potential of electrons. Let us consider the case where the spin-orbit interactions are negligible as in the 3d transition metals, and that the magnetic field is not applied. Moreover we may assume in solids that the ground state is nondegenerate. One can then choose the ground-state wave function to be real; $\Psi^* = \Psi$.

The angular momentum $\langle \mathbf{L} \rangle$ is real because it is a physical quantity:

$$\langle \mathbf{L} \rangle = \langle \mathbf{L} \rangle^*. \quad (1.63)$$

Using the relation $\Psi^* = \Psi$, the r.h.s. of the above equation is written as

$$\langle \mathbf{L} \rangle^* = -\langle \Psi | \mathbf{L} | \Psi \rangle. \quad (1.64)$$

Therefore (1.63) indicates that

$$\langle \mathbf{L} \rangle = \mathbf{0}. \quad (1.65)$$

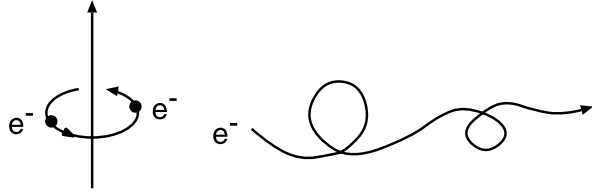
Thus, one can expect in metals with sufficiently small spin-orbit interactions that only spin magnetic moments contribute to the magnetization.

$$\langle \mathbf{M} \rangle = \langle 2\mathbf{S} \rangle. \quad (1.66)$$

This is referred as the quenching of orbital magnetic moments.

In the atomic system, electrons are bound by the nuclei, and the orbital angular momentum is finite in general according to Hund's second rule. In the crystalline system, the Coulomb energy gain leading to Hund's second rule is not expected because electrons can hop to the neighboring sites to reduce the Coulomb energy, and electrons can move turning around to right and left (see Fig. 1.7). It may lead to $\langle \mathbf{L} \rangle = \mathbf{0}$. This is a physical reason for the quenching of orbital moments in solids. In the 3d transition metals and alloys which we will discuss, the orbital magnetic moments are usually quenched. In the system with a large spin-orbit coupling such as the rare-earth metals or the system with a strong magnetic field, the orbital moments remain.

Fig. 1.7 Concept of orbital magnetic moments in atom ($L \neq 0$: left) and solids ($L = 0$: right)



1.6 Heisenberg Model

In the insulator, magnetic behaviors are often described by a simple Hamiltonian known as the Heisenberg model. We briefly discuss the Hamiltonian and related properties of the insulator magnetism in this section.

Let us consider the hydrogen molecule. We assume one orbital for each hydrogen atom, φ_1 for atom 1 and φ_2 for atom 2, and neglect the overlap integrals for simplicity, i.e., $\langle \varphi_1 | \varphi_2 \rangle = 0$. The Hamiltonian for the hydrogen molecule is obtained from (1.13) as we derived (1.47).

$$H = \sum_{i\sigma} \varepsilon_0 n_{i\sigma} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} + \left(K - \frac{1}{2} J \right) n_1 n_2 - 2J \mathbf{s}_1 \cdot \mathbf{s}_2. \quad (1.67)$$

Here K and J denote the intersite Coulomb and exchange integrals given by

$$K = \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_1^*(\mathbf{r}) \varphi_2^*(\mathbf{r}') \varphi_2(\mathbf{r}') \varphi_1(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (1.68)$$

$$J = \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_1^*(\mathbf{r}) \varphi_2^*(\mathbf{r}') \varphi_1(\mathbf{r}') \varphi_2(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.69)$$

In the atomic subspace where $n_1 = n_2 = 1$ and the electron hopping is suppressed, the Hamiltonian (1.67) reduces as follows.

$$H = 2\varepsilon_0 + K - \frac{1}{2} J - 2J \mathbf{s}_1 \cdot \mathbf{s}_2. \quad (1.70)$$

It is diagonalized with the use of the total spin S (in the representation of S and S_z) as

$$H = 2\varepsilon_0 + K - J[S(S+1) - 1]. \quad (1.71)$$

Therefore the hydrogen molecule has the energy $2\varepsilon_0 + K - J$ for the triplet state and $2\varepsilon_0 + K + J$ for the singlet state when the inter-site atomic distance is large. This is the Heitler–London theory for the hydrogen molecule.

The last term in (1.70) denotes an interaction between the atomic spins $\mathbf{s}_1$ and $\mathbf{s}_2$. In general, the following Hamiltonian showing the interactions between atomic

spins $\{\mathbf{S}_i\}$ is known as the Heisenberg model.

$$H = - \sum_{(i,j)} J_{ij} \mathbf{S}_1 \cdot \mathbf{S}_2. \quad (1.72)$$

The interaction $J_{ij} = 2J$ in the Heitler–London theory is the inter-site exchange integral due to the Coulomb interaction. This coupling in the Heisenberg model is referred as the direct exchange interaction. The direct exchange interaction is generally positive in sign (i.e., ferromagnetic).

Another type of the Heisenberg model with effective exchange coupling is possible in the insulator. In order to derive the effective Hamiltonian, we first derive the perturbative effective Hamiltonian from a more general point of view [13]. The effective Hamiltonian is constructed such that it yields the same energy eigen values in a subspace as in the original Hamiltonian acting on the full Hilbert space.

Let us consider a subspace $\mathcal{P}$ spanned by a set of states $\{|s\rangle\}$, and introduce a projection operator $P = \sum_s |s\rangle\langle s|$ which projects any state onto subspace $\mathcal{P}$. The projection operator which chooses the complementary subspace $\mathcal{Q}$ is defined by $Q = 1 - P$. Note that $P^2 = P$, $Q^2 = Q$, and $PQ = QP = 0$.

The eigen value problem of the original Hamiltonian H is written as

$$(H - E)\psi = 0. \quad (1.73)$$

Inserting the identity $1 = P + Q$ into the above equation as $(P + Q)(H - E)(P + Q)\psi = 0$ and multiplying P from the l.h.s. of the equation, we obtain

$$[(PHP - E)P + PHQ]\psi = 0. \quad (1.74)$$

In the same way, we can derive the following equation

$$[QHP + (QHQ - E)Q]\psi = 0. \quad (1.75)$$

In (1.74) and (1.75), the wave function ψ is separated into two components belonging to different subspaces, $P\psi$ and $Q\psi$. From both equations, one can eliminate the wave function $Q\psi$ that leads to the eigenvalue equation in subspace $\mathcal{P}$, namely,

$$[PHP - PHQ(QHQ - E)^{-1}QHP]P\psi = EP\psi. \quad (1.76)$$

The above equation indicates that the following Hamiltonian $H_p(E)$ acting on the wave function $P\psi$ in the subspace $\mathcal{P}$ is regarded as an effective Hamiltonian which yields the same eigen value E as in the original Hamiltonian H , where

$$H_p(E) = PHP - PHQ(QHQ - E)^{-1}QHP. \quad (1.77)$$

The effective Hamiltonian depends on the energy which should be obtained self-consistently. Taking the subspace spanned by a subset of the eigenfunctions of an

unperturbed Hamiltonian, one can derive the effective Hamiltonian which is correct up to the second order of the interaction Hamiltonian. Assume that the Hamiltonian consists of a noninteracting part H_0 and an interaction part H_1 such that $H = H_0 + H_1$. The eigenvalues $\{E_k^0\}$ and eigenfunctions $\{\phi_k\}$ for H_0 are assumed to be known. We define the subspace $\mathcal{P}$ spanned by a part of $\{|\phi_k\rangle\}$. The projection operator is then defined by $P = \sum_{\mu}^{\mathcal{P}} |\phi_{\mu}\rangle\langle\phi_{\mu}|$. We have the relation $QHP = QH_1P$, and thus obtain the effective Hamiltonian which is correct up to the second order in interaction, after having replaced the Hamiltonian H and the energy E in the denominator of (1.77) with the zeroth-order ones, H_0 and E_k^0 , i.e.,

$$H_p = PHP - PH_1Q(QH_0Q - E_k^0)^{-1}QH_1P. \quad (1.78)$$

The effective Hamiltonian depends on the eigen state k explicitly. Therefore we rewrite the second term as follows.

$$(QH_0Q - E_k^0)^{-1}QH_1P\phi_k = \sum_{\mu}^{\mathcal{P}} \sum_{\nu}^{\mathcal{Q}} (E_{\nu}^0 - E_{\mu}^0)^{-1} |\phi_{\nu}\rangle\langle\phi_{\nu}|H_1|\phi_{\mu}\rangle\langle\phi_{\mu}|\phi_k\rangle. \quad (1.79)$$

Thus the perturbative Hamiltonian (1.78) is expressed as follows.

$$H_p = PHP - PH_1Q(E_Q^0 - E_P^0)^{-1}QH_1P. \quad (1.80)$$

Here E_P^0 (E_Q^0) denotes the eigenvalues belonging to subspace $\mathcal{P}$ ($\mathcal{Q}$). The eigenvalue equation for the perturbative effective Hamiltonian is then given by

$$H_p P\psi_k = E_k P\psi_k. \quad (1.81)$$

We can derive the effective Heisenberg model in the strong Coulomb interaction regime at half-filling using the formula (1.80). Let us consider the Hubbard model (1.51). As found in Sect. 1.4, the ground state of the atomic limit at half-filling is specified by $\{n_i = 1\}$ states. The ground state is 2^L -fold degenerate, L being the number of sites. We start from the ground state in the atomic limit at half filling, i.e., the $\{n_i = 1\}$ states, and define the subspace $\mathcal{P}$ from them. The complementary subspace $\mathcal{Q}$ consists of the subspace containing empty states and the subspace containing the doubly occupied states. In the strongly correlated region, the electron hopping rate $|t_{ij}|$ is much smaller than the Coulomb interaction strength U , so that the Hamiltonian H is separated into the atomic state $H_0 = \sum_{i\sigma} \varepsilon_0 n_{i\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow}$ and the ‘interaction’ term $H_1 = \sum_{ij\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma}$. The first term at the r.h.s. of (1.80) is given by $PL\varepsilon_0P$. In the calculations of the second term, we have $QH_1P = \sum_{ij\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} P$ because $a_{i\sigma}^{\dagger} a_{j\sigma} P$ belong to the space $\mathcal{Q}$. Moreover, $E_Q^0 - E_P^0 = U$ when it is operated on the single doubly-occupied state QH_1P . Thus we obtain the expression for the second term at the r.h.s.

of (1.80) as follows.

$$P H_1 Q (E_Q^0 - E_P^0)^{-1} Q H_1 P = \sum_{ijkl\sigma\sigma'} \frac{t_{lk} t_{ij}}{U} P a_{l\sigma'}^\dagger a_{k\sigma'} a_{i\sigma}^\dagger a_{j\sigma} P. \quad (1.82)$$

Among the summation at the r.h.s. of (1.82) only the $k = i$ and $l = j$ terms remain. Rearranging the creation and annihilation operators, we obtain the relation.

$$\sum_{\sigma\sigma'} a_{j\sigma'}^\dagger a_{i\sigma'} a_{i\sigma}^\dagger a_{j\sigma} = n_j - \frac{1}{2} n_i n_j - 2 s_i \cdot s_j. \quad (1.83)$$

Substituting the above relation into (1.82), we obtain the following effective Hamiltonian.

$$H_p = P \left[L \left(\varepsilon_0 - \frac{1}{2} \sum_j \frac{|t_{ij}|^2}{U} \right) + \sum_{(i,j)} \frac{4|t_{ij}|^2}{U} s_i \cdot s_j \right] P. \quad (1.84)$$

Apart from the constant term, we arrive at the following effective Heisenberg model in the strong Coulomb interaction regime at half filling, which operates on the subspace $\mathcal{P}$.

$$H = - \sum_{(i,j)} J_{ij} s_i \cdot s_j. \quad (1.85)$$

Here

$$J_{ij} = - \frac{4|t_{ij}|^2}{U}. \quad (1.86)$$

The effective exchange integral (1.86) is known as the super exchange interaction because it is caused by a virtual exchange of electrons belonging to different atoms via transfer integrals. The super exchange interaction is antiferromagnetic, while the direct exchange interaction (1.69) is ferromagnetic. Note that the subspace on which the Hamiltonian (1.85) acts is given by $\{P|n_1 s_{1z}, n_2 s_{2z}, \dots\rangle\} = \{|1 s_{1z}, 1 s_{2z}, \dots\rangle\}$. This can be simplified as $\{|s_{1z}, s_{2z}, \dots\rangle\}$. In many magnetic insulators, anions are often located between the magnetic ions. In such a case, the super exchange interaction becomes dominant. The Heisenberg model (1.85) is not justified in the metallic system where the band width $W \sim U$. Nevertheless, we often find the same type of the intersite magnetic interactions, which are useful for qualitative understanding of the magnetism (see Sects. 6.4 and 8.3 for examples).

1.7 Magnetic Structure

Magnetic materials have their microscopic structure for arrangement of atomic magnetic moments. This is called the magnetic structure. The structure characterizes the

magnetic property as well as the electronic structure. In this section, we introduce the Fourier representation of the magnetic structure and explain briefly the magnetic structures in solids.

The magnetic structure is characterized by the magnetic moment density which is given by

$$\mathbf{M}(\mathbf{r}) = \langle \psi^\dagger(\mathbf{r}) \mathbf{m} \psi(\mathbf{r}) \rangle. \quad (1.87)$$

Here $\psi(\mathbf{r}) = (\psi_\uparrow(\mathbf{r}), \psi_\downarrow(\mathbf{r}))$ is the field operator of electrons. $\mathbf{m}$ denotes the magnetic moment for an electron as given by (1.7).

In a crystalline system, we may divide the space into the Wigner–Seitz cells for each atom. Then we can define a magnetic moment of atom i as follows.

$$\mathbf{m}_i = \int_i \mathbf{M}(\mathbf{r}) d^3x. \quad (1.88)$$

Here the integration is over the Wigner–Seitz cell belonging to atom i . In a non-crystalline system we may adopt the Voronoi polyhedra instead of the Wigner–Seitz cells.

In the case of the crystalline system, the atomic position $\mathbf{R}_l$ is expressed by using the primitive translational vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ as

$$\mathbf{R}_l = l_1 \mathbf{a} + l_2 \mathbf{b} + l_3 \mathbf{c}. \quad (1.89)$$

The atomic magnetic moment is expanded with use of the Fourier lattice series as follows.

$$\mathbf{m}_l = \sum_{\mathbf{q}} \mathbf{m}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_l}. \quad (1.90)$$

Here $\mathbf{q}$ is the wave vector in the first Brillouin zone. The Fourier components of the magnetic moments are given as

$$\mathbf{m}(\mathbf{q}) = \frac{1}{L} \sum_l \mathbf{m}_l e^{-i\mathbf{q} \cdot \mathbf{R}_l}, \quad (1.91)$$

L being the number of lattice points. Note that $\mathbf{m}(-\mathbf{q}) = \mathbf{m}(\mathbf{q})^*$ because $\mathbf{m}_l$ are real. Moreover we assumed that there is only one atom per unit cell. When there are more than one atom per unit cell, we have to add the atomic position in a unit cell η_λ to (1.89). Accordingly, the magnetic moments (1.90) and (1.91) are specified by the type of atom λ as $\mathbf{m}_l^{(\lambda)}$ ($\mathbf{m}^{(\lambda)}(\mathbf{q})$). Hereafter we consider the crystalline system with one magnetic atom per unit cell.

The microscopic magnetic structure of magnetic materials is specified by a set of $\{\mathbf{m}_l\}$ or $\{\mathbf{m}(\mathbf{q})\}$. The simplest structure is that all of the atomic magnetic moments have the same direction. It is realized when all the Fourier components vanish except $\mathbf{m}(\mathbf{q} = \mathbf{0}) = \mathbf{m}$, and is known as the ferromagnetic structure (see Fig. 1.8). Typical transition metals such as Fe, Co, and Ni exhibit the ferromagnetism.

Fig. 1.8 Ferromagnetic arrangement



Fig. 1.9 Antiferromagnetic arrangement



The antiferromagnetic structure (AF) is defined by alternative arrangement of the atomic magnetic moments along a direction, e.g., the z direction (see Fig. 1.9). It is specified by a set, $\mathbf{m}(\pm \mathbf{Q}) = m\mathbf{k} \exp(\pm i\alpha)$ and $\mathbf{m}(\mathbf{q} \neq \pm \mathbf{Q}) = \mathbf{0}$, where $\mathbf{Q}$ consists of half a reciprocal lattice vectors, and $\mathbf{k}$ denotes a unit vector along the z axis, and α denotes a phase of the structure. In the case $\alpha = 0$, we have

$$\mathbf{m}_l = m\mathbf{k} \cos(\mathbf{Q} \cdot \mathbf{R}_l). \quad (1.92)$$

When the position $\mathbf{R}_l$ moves along $\mathbf{Q}$ vector, $\mathbf{Q} \cdot \mathbf{R}_l$ changes by π . Accordingly, the magnetic moment $\mathbf{m}_l$ changes its sign.

The AF structure on the simple cubic lattice as shown in Fig. 1.10(a) is expressed by the wave vector $\mathbf{Q} = (\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3)/2 = (1, 1, 1)\pi/a$, a being the lattice constant. The AF structure on the body-centered cubic lattice as shown in Fig. 1.10(b) is expressed by the wave vector $\mathbf{Q} = (-\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3)/2 = (0, 0, 1)2\pi/a$. In the case of the face-centered cubic lattice (fcc) structure, two kinds of AF structures are known. The AF structure of the first-kind as shown in Fig. 1.10(c) is described by a wave vector $\mathbf{Q} = (\mathbf{K}_2 + \mathbf{K}_3)/2 = (0, 0, 1)2\pi/a$. The atomic moment alternatively changes the direction with a translation by $(0, 0, 1)a/2$. It is also possible to change direction alternatively along $\langle 1\ 1\ 1 \rangle$ axis. This is referred as the AF structure of the second-kind, and is characterized by $\mathbf{Q} = (\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3)/2 = (1, 1, 1)\pi/a$ (see Fig. 1.11). Cr with 1 at% Mn on the bcc lattice shows the AF structure, and γ -Mn on the fcc lattice shows the AF structure of the first-kind according to the neutron diffraction experiments.

It should be noted that the network consisting of the up-spin atoms (or the down-spin atoms) forms a lattice referred as the sublattice. There are two sublattices in the antiferromagnetic structures shown in Fig. 1.10. Each sublattice forms the fcc lattice with the lattice constant $2a$ in the case of the sc structure (Fig. 1.10(a)), the sc lattice with the lattice constant a in the case of the bcc structure (Fig. 1.10(b)), and the simple tetragonal structure with the lattice constants $a/\sqrt{2}$ and a in the case of the fcc structure (Fig. 1.10(c)), respectively.

The sinusoidal spin density wave (SDW) structure is expressed by

$$\mathbf{m}_l = m\mathbf{k} \sin(\mathbf{Q} \cdot \mathbf{R}_l + \alpha), \quad (1.93)$$

where $\mathbf{Q}$ vector is neither equal to $\mathbf{0}$ nor to the AF wave vectors. The magnetic moment sinusoidally changes with a period $\lambda = 2\pi/|\mathbf{Q}|$ along the $\mathbf{Q}$ direction (see

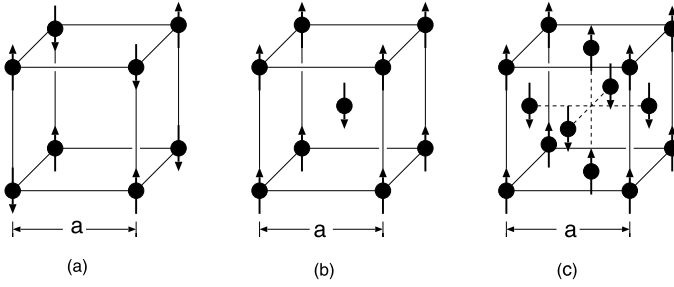


Fig. 1.10 Antiferromagnetic arrangements on the simple cubic lattice (a), body-centered cubic lattice (b), and face-centered cubic lattice (c). The lattice constants are shown by a

Fig. 1.11 The antiferromagnetic structure of the second-kind on the face-centered cubic lattice

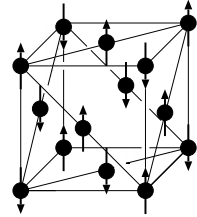


Fig. 1.12 Spin density wave structure

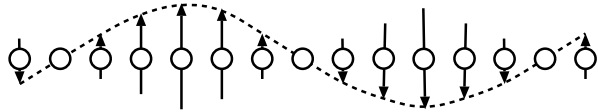


Fig. 1.12). Note that the period is not necessarily commensurate with the lattice spacing in general. Cr is a well-known example of the SDW.

It is also possible that the magnetic moment rotates with a translation (see Fig. 1.13). This is known as the helical structure, and is expressed as

$$\mathbf{m}_l = m[\mathbf{e}_1 \cos(\mathbf{Q} \cdot \mathbf{R}_l + \alpha) + \mathbf{e}_2 \sin(\mathbf{Q} \cdot \mathbf{R}_l + \alpha)]. \quad (1.94)$$

Here $\mathbf{e}_1$ and $\mathbf{e}_2$ are the unit vectors being orthogonal to each other. The magnetic moment with amplitude m rotates on the $\mathbf{e}_1$ – $\mathbf{e}_2$ plane with the translation along the $\mathbf{Q}$ vector.

The above expression (1.94) can also be written as

$$\mathbf{m}_l = m(\mathbf{Q})e^{i\mathbf{Q} \cdot \mathbf{R}_l} + m(\mathbf{Q})^*e^{-i\mathbf{Q} \cdot \mathbf{R}_l}, \quad (1.95)$$

with

$$\mathbf{m}(\mathbf{Q}) = \frac{m}{2}(\mathbf{e}_1 - i\mathbf{e}_2)e^{i\alpha}. \quad (1.96)$$

It indicates that the helical structure is specified by the $\mathbf{Q}$ vector and the condition

$$m(\mathbf{Q})^2 = 0. \quad (1.97)$$

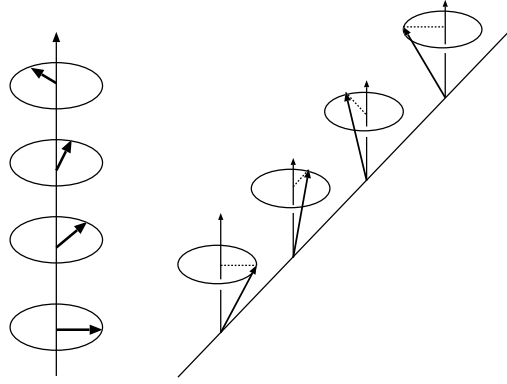
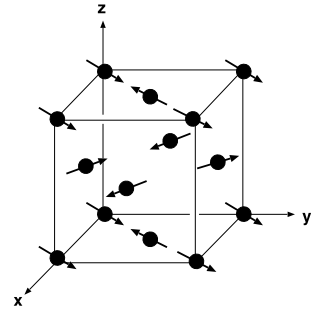


Fig. 1.13 Helical structure (*left*) and conical structure (*right*)

Fig. 1.14 $2Q$ multiple-spin-density wave structure



It is known from the neutron experiments that Au_2Mn , MnO_2 , CrO_2 , Eu , Tb , Dy , Ho etc. show the helical structure.

So far the magnetic structures are characterized by only one $\mathbf{Q}$ vector. One can also consider the helical type structure with the bulk magnetization as follows.

$$\mathbf{m}_l = m_z \mathbf{k} + m(i \cos(\mathbf{Q} \cdot \mathbf{R}_l + \alpha) + j \sin(\mathbf{Q} \cdot \mathbf{R}_l + \alpha)). \quad (1.98)$$

The above expression is alternatively written as

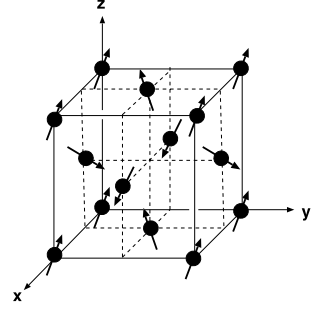
$$\mathbf{m}_l = m_z \mathbf{k} + \mathbf{m}(\mathbf{Q})e^{i\mathbf{Q} \cdot \mathbf{R}_l} + \mathbf{m}(\mathbf{Q})^*e^{-i\mathbf{Q} \cdot \mathbf{R}_l}, \quad (1.99)$$

with

$$\mathbf{m}(\mathbf{Q})^2 = 0. \quad (1.100)$$

This is referred as the conical magnetic structure (see Fig. 1.13). The magnetic moment rotates for example on the x - y plane when the moment translates along the direction of $\mathbf{Q}$.

Fig. 1.15 $3Q$ multiple-spin-density wave structure



One can also consider a magnetic structure consisting of two wave vectors, $\mathbf{Q}_1$ and $\mathbf{Q}_2$. For example, we can consider a structure such as

$$\mathbf{m}_l = \mathbf{m}(\mathbf{Q}_1)e^{i\mathbf{Q}_1 \cdot \mathbf{R}_l} + \mathbf{m}(\mathbf{Q}_2)e^{i\mathbf{Q}_2 \cdot \mathbf{R}_l} + \text{c. c.} \quad (1.101)$$

Assuming that $\mathbf{m}(\mathbf{Q}_1) = m_x \mathbf{i}/2$ and $\mathbf{m}(\mathbf{Q}_2) = m_x \mathbf{j}/2$, we have

$$\mathbf{m}_l = m_x \mathbf{i} \cos(\mathbf{Q}_1 \cdot \mathbf{R}_l) + m_y \mathbf{j} \cos(\mathbf{Q}_2 \cdot \mathbf{R}_l). \quad (1.102)$$

This is known as a double $\mathbf{Q}$ multiple SDW ($2Q$ -MSDW) (see Fig. 1.14). In the case of the fcc lattice, we may consider the wave vectors $\mathbf{Q}_1 = (1, 0, 0)2\pi/a$ and $\mathbf{Q}_2 = (0, 1, 0)2\pi/a$. Then the $x(y)$ component changes the sign with a translation $\mathbf{R}_l = (1, 0, 0)a/2$ ($\mathbf{R}_2 = (0, 1, 0)a/2$) as shown in Fig. 1.14.

We can also consider the magnetic structure consisting of three wave vectors $\mathbf{Q}_1$, $\mathbf{Q}_2$ and $\mathbf{Q}_3$, which is the so-called triple $\mathbf{Q}$ multiple SDW ($3Q$ -MSDW). For example, we have a $3Q$ -MSDW such that

$$\mathbf{m}_l = m_x \mathbf{i} \cos(\mathbf{Q}_1 \cdot \mathbf{R}_l) + m_y \mathbf{j} \cos(\mathbf{Q}_2 \cdot \mathbf{R}_l) + m_z \mathbf{k} \cos(\mathbf{Q}_3 \cdot \mathbf{R}_l), \quad (1.103)$$

with $\mathbf{Q}_1 = (1, 0, 0)2\pi/a$, $\mathbf{Q}_2 = (0, 1, 0)2\pi/a$, and $\mathbf{Q}_3 = (0, 0, 1)2\pi/a$. Each component changes sign after the translation by $a/2$ along the same direction as shown in Fig. 1.15.

In the substitutional disordered alloys, we have more complicated structures which cannot be described by a small number of wave vectors. When we take a configurational average of the atomic magnetic moments, we can define the average magnetization $[\mathbf{m}_l]_c$. Here $[\sim]_c$ denotes the configurational average. In some

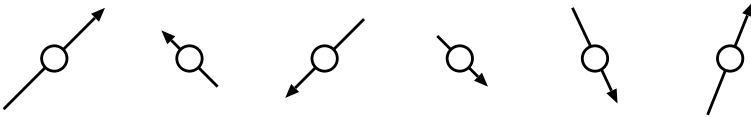


Fig. 1.16 Spin glass arrangement

cases, an ordered state with randomly oriented magnetic moments referred as the spin glass (SG) appears (see Fig. 1.16). The SG is considered to be characterized by the condition such that

$$[\mathbf{m}_l]_c = \mathbf{0} \quad \text{and} \quad [m_l^2]_c = 0. \quad (1.104)$$

The disordered dilute alloys such as $\text{Cu}_{1-x}\text{Mn}_x$ ($x \lesssim 0.1$) and $\text{Au}_{1-x}\text{Fe}_x$ ($x \lesssim 0.1$) are known to show a SG at low temperatures (see Sect. 7.1).

Experimentally most magnetic structures of crystalline systems are determined by the neutron elastic scattering experiments. The readers who are interested in the experimental determination of the magnetic structure are recommended to refer to the books by Marshall and Lovesey [14, 15].

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