Chapter 1

MAGNETIC HAMILTONIANS

1.1. Hydrogen Molecule Hamiltonian

The magnetism is a typical quantum effect due to the Pauli "exclusion princi-ple". To understand this, let us consider one of the most simple quantum system: the hydrogen molecule containing two protons (nuclei) and two electrons. In the non-relativistic approximation and neglecting the nuclear kinetic energy (adiabatic approximation), the Hamiltonian of a hydrogen molecule reads

$$\mathcal{H} = -\frac{\hbar^2}{2m}\bigtriangledown_1^2 - \frac{\hbar^2}{2m}\bigtriangledown_2^2 + e^2\left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2b}}\right) \quad (1.1.1)$$

where R is the distance between the nuclei; $r_{i\alpha}$ (with $i = 1, 2$ and $\alpha = a, b$) is the distance between the i-th electron and the α-th nucleus, r_{12} is the distance between the two electrons; $\bigtriangledown_i^2$ (with $i = 1, 2$) is the Laplacian corresponding to the i-electron; $e = -4.803 \times 10^{-10}$ statCoulomb is the charge of the electron and $m = 9.11 \times 10^{-28}$ g is its mass. Note that any magnetic interaction has been neglected in the Hamiltonian (1.1.1). The wave function ψ of the two electrons is given by the product of a spatial function times a spin function like

$$\psi(\boldsymbol{r}_1\sigma_1, \boldsymbol{r}_2\sigma_2) = \phi(\boldsymbol{r}_1, \boldsymbol{r}_2)\chi(\sigma_1, \sigma_2) \quad (1.1.2)$$

where σ_1 and σ_2 are the components of the electronic spin along the (arbitrary) quantization axis. The wave function (1.1.2) has to be chosen antisymmetric under the simultaneous exchange of the coordinates and spin variables of the two electrons. This means that a spatial antisymmetric function $\phi_\mathrm{A}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ has to be associated with a symmetric spin function $\chi_\mathrm{S}(\sigma_1, \sigma_2)$ and a symmetric space function $\phi_\mathrm{S}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ has to be associated with an antisymmetric spin function $\chi_\mathrm{A}(\sigma_1, \sigma_2)$. The spin function χ will be chosen symmetric (χ_S) when the total spin of the two electons $\boldsymbol{S} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2$ is characterized by a quantum number $S = 1$ (triplet) and it will be chosen antisymmetric (χ_A) when the total spin quantum number is $S = 0$ (singlet). As a consequence, the spatial wave function has to be antisymmetric (ϕ_A) for $S = 1$ and symmetric (ϕ_S) for $S = 0$. Assuming that the interaction between the hydrogen atoms making up the molecule is weak and that both hydrogen atoms are in the

ground state, the space functions ϕ_S and ϕ_A can be written in terms of the spatial wave functions of each electron in the Coulomb field of each nucleus, that is

$$\phi_A(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2(1-\Delta^2)}}[\phi_{1s}(r_{1a})\phi_{1s}(r_{2b}) - \phi_{1s}(r_{2a})\phi_{1s}(r_{1b})] \qquad (1.1.3)$$

and

$$\phi_S(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2(1+\Delta^2)}}[\phi_{1s}(r_{1a})\phi_{1s}(r_{2b}) + \phi_{1s}(r_{2a})\phi_{1s}(r_{1b})] \qquad (1.1.4)$$

where $\phi_{1s}(r_{i\alpha})$ is the normalized wave function of the ground state of the hydrogen atom consisting on an electron i orbiting around a nucleus α, that is

$$\phi_{1s}(r_{1a}) = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r_{1a}}{a_0}}, \quad \phi_{1s}(r_{2a}) = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r_{2a}}{a_0}},$$

$$\phi_{1s}(r_{1b}) = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r_{1b}}{a_0}}, \quad \phi_{1s}(r_{2b}) = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r_{2b}}{a_0}} \qquad (1.1.5)$$

where $a_0 = \hbar^2/(me^2) = 0.5292$ Å is the atomic unit length. The "overlap integral" Δ in Eqs. (1.1.3) and (1.1.4) assures the normalization of the wavefunctions ϕ_A and ϕ_S and it is given by

$$\Delta = \int d^3\boldsymbol{r}_1 \; \phi_{1s}(r_{1a})\phi_{1s}(r_{1b}) = \frac{1}{\pi a_0^3} \int d^3\boldsymbol{r}_1 \; e^{-\frac{r_{1a}+r_{1b}}{a_0}} = e^{-\rho}\left(1 + \rho + \frac{1}{3}\rho^2\right) \qquad (1.1.6)$$

with $\rho = R/a_0$. The explicit calculations may be found in the original papers.[1,2]

The mean values of the energy of the hydrogen molecule in the states corresponding to $S = 1$ (ϕ_A) and $S = 0$ (ϕ_S) are given by

$$E_{\uparrow\uparrow} = \int d\boldsymbol{r}_1 \; d\boldsymbol{r}_2 \; \phi_A(\boldsymbol{r}_1, \boldsymbol{r}_2) \; \mathcal{H} \; \phi_A(\boldsymbol{r}_1, \boldsymbol{r}_2) = 2E_{1s} + \frac{Q-A}{1-\Delta^2} \qquad (1.1.7)$$

and

$$E_{\uparrow\downarrow} = \int d\boldsymbol{r}_1 \; d\boldsymbol{r}_1 \; \phi_S(\boldsymbol{r}_1, \boldsymbol{r}_2) \; \mathcal{H} \; \phi_S(\boldsymbol{r}_1, \boldsymbol{r}_2) = 2E_{1s} + \frac{Q+A}{1+\Delta^2} \qquad (1.1.8)$$

where $E_{1s} = -\frac{e^2}{2a_0}$ is the ground state energy of a hydrogen atom consisting of electron 1 orbiting around the nucleus a satisfying the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_{1a}}\right)\phi_{1s}(r_{1a}) = E_{1s}\phi_{1s}(r_{1a}) \qquad (1.1.9)$$

or electron 2 orbiting around the nucleus b satisfying the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_{2b}}\right)\phi_{1s}(r_{2b}) = E_{1s}\phi_{1s}(r_{2b}). \qquad (1.1.10)$$

Obviously, $2E_{1s}$ is the energy of the system when the two hydrogen atoms are far away ($R \to \infty$). The quantity Q appearing in Eqs. (1.1.7) and (1.1.8) is called the

Coulomb integral and it is given by

$$Q = e^2 \int d^3\boldsymbol{r}_1 \int d^3\boldsymbol{r}_2 \; \phi_{1s}^2(r_{1a})\phi_{1s}^2(r_{2b}) \left(\frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right)$$

$$+ \frac{e^2}{R} = I_{12} + 2I_1 + \frac{e^2}{R} \tag{1.1.11}$$

where

$$I_{12} = \int d^3\boldsymbol{r}_1 \int d^3\boldsymbol{r}_2 \; \phi_{1s}^2(r_{1a})\phi_{1s}^2(r_{2b})\frac{e^2}{r_{12}}$$

$$= \frac{e^2}{a_0\rho} \left[1 - e^{-2\rho}\left(1 + \frac{11}{8}\rho + \frac{3}{4}\rho^2 + \frac{1}{6}\rho^3 \right) \right] \tag{1.1.12}$$

is the average Coulomb repulsion between the two electrons;

$$I_1 = -\int d^3\boldsymbol{r}_1 \; \phi_{1s}^2(r_{1a})\frac{e^2}{r_{1b}} = -\frac{e^2}{a_0\rho}[1 - e^{-2\rho}(1 + \rho)] \tag{1.1.13}$$

is the average Coulomb attraction between the electron 1 and the nucleus b; an indentical contribution comes from the Coulomb interaction between electron 2 and the nucleus a: this explains the factor 2 in Eq. (1.1.11). The last term of Eq. (1.1.11) represents the Coulomb repulsion between the two nuclei. The quantity A appearing in Eqs. (1.1.7) and (1.1.8) is called *exchange integral* and it is given by

$$A = e^2 \int d^3\boldsymbol{r}_1 \int d^3\boldsymbol{r}_2 \; \phi_{1s}(r_{1a}) \, \phi_{1s}(r_{2a}) \, \phi_{1s}(r_{1b}) \, \phi_{1s}(r_{2b}) \left(\frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right)$$

$$+ \frac{e^2}{R} \, \Delta^2 = J_{12} + 2 \, J_1 \, \Delta + \frac{e^2}{R} \, \Delta^2 \tag{1.1.14}$$

where

$$J_{12} = \int d^3\boldsymbol{r}_1 \int d^3\boldsymbol{r}_2 \; \phi_{1s}(r_{1a}) \, \phi_{1s}(r_{2a}) \, \phi_{1s}(r_{1b}) \, \phi_{1s}(r_{2b})\frac{e^2}{r_{12}}$$

$$= \frac{e^2}{a_0} \left\{ e^{-2\rho}\left(\frac{5}{8} - \frac{23}{20}\rho - \frac{3}{5}\rho^2 - \frac{1}{15}\rho^3 \right) \right.$$

$$\left. + \frac{6}{5\rho} \left[\Delta^2 \, (C + \ln\rho) + M^2 \, \mathrm{Ei}(-4\rho) - 2 \, M \, \Delta \, \mathrm{Ei}(-2\rho) \right] \right\} \tag{1.1.15}$$

with

$$M = e^\rho \left(1 - \rho + \frac{1}{3}\rho^2 \right), \tag{1.1.16}$$

$C = 0.57722$ is the Euler's constant[3] and

$$\mathrm{Ei}(x) = -\int_{-x}^{\infty} dt \, \frac{e^{-t}}{t} \tag{1.1.17}$$

is the exponential integral function;[4]

$$J_1 = -\int d^3\boldsymbol{r}_1 \; \phi_{1s}(r_{1a}) \, \phi_{1s}(r_{1b})\frac{e^2}{r_{1b}} = -\frac{e^2}{a_0}e^{-\rho}\,(1 + \rho). \tag{1.1.18}$$

An identical contribution comes from the integral in Eq. (1.1.14) containing $\frac{1}{r_{2a}}$ that justifies the factor 2 in the last side of Eq. (1.1.14), the last term of which comes

from the repulsion between the nuclei. Notice that in each term of the exchange integral, the wave function of the same electron 1 or 2 centered on both nuclei simultaneously appears so that, in view of the structure of the ground state wave functions (1.1.5), one expects an exponential decay of the exchange contribution as the distance between the nuclei increases. Replacing Eqs. (1.1.11) and (1.1.14) into Eqs. (1.1.7) and (1.1.8), one obtains

$$E_{\uparrow\uparrow} = \frac{e^2}{a_0} \left[-1 + \frac{q(\rho) - a(\rho)}{1 - \Delta^2} \right] \tag{1.1.19}$$

and

$$E_{\uparrow\downarrow} = \frac{e^2}{a_0} \left[-1 + \frac{q(\rho) + a(\rho)}{1 + \Delta^2} \right] \tag{1.1.20}$$

with

$$q(\rho) \equiv \frac{a_0}{e^2} Q = \frac{1}{\rho} e^{-2\rho} \left(1 + \frac{5}{8}\rho - \frac{3}{4}\rho^2 - \frac{1}{6}\rho^3 \right) \tag{1.1.21}$$

and

$$a(\rho) \equiv \frac{a_0}{e^2} A = \frac{1}{\rho} \Delta^2 \left[1 + \frac{6}{5} \left(C + \ln \rho \right) \right] - e^{-2\rho} \left(\frac{11}{8} + \frac{103}{20}\rho + \frac{49}{15}\rho^2 + \frac{11}{15}\rho^3 \right)$$
$$+ \frac{6}{5\rho} M \left[M \, \mathrm{Ei}(-4\rho) - 2\Delta \, \mathrm{Ei}(-2\rho) \right]. \tag{1.1.22}$$

Note that each term forming the Coulomb integral $q(\rho)$ decays as $\frac{1}{\rho}$ when the distance between the nuclei increases as one can see from Eqs. (1.1.12) and (1.1.13) according to the electrostatic Coulomb interaction. Their sum, however, leads to exponential decaying as shown by (1.1.21). On the contrary, each term forming the exchange energy $a(\rho)$ decays exponentially with the distance as one can see directly by Eq. (1.1.18) and Eq. (1.1.15), recalling the asymptotic expansion of the exponential integral function[3]

$$\mathrm{Ei}(-x) = -\frac{e^{-x}}{x} \left(1 - \frac{1}{x} + \frac{2}{x^2} - \frac{6}{x^3} + \dots \right). \tag{1.1.23}$$

In Fig. 1.1, the energy of the triplet $E_{\uparrow\uparrow}$ and of the singlet $E_{\uparrow\downarrow}$ are shown as function of the distance between the nuclei. It is evident from Fig. 1.1 that two hydrogen atoms in their ground state are able to form a molecule only if the spins of the electrons are antiparallel (singlet): this "bonding state" shows a minimum for $\rho_{\mathrm{eq}} = 1.6425$ corresponding to the equilibrium distance between nuclei in the hydrogen molecule ground state $R_{\mathrm{eq}} = 0.87$ Å, to be compared with the experimental value $R_{\mathrm{exp}} = 0.74$ Å. The value of the binding energy is given by the difference between the energy of two far-away hydrogen atoms and the minimum of the singlet energy that is $2E_{1s} - E_{\uparrow\downarrow}(\rho_{\mathrm{eq}}) = 0.11597\frac{e^2}{a_0} = 3.15$ eV that to be compared with the experimental value 4.45 eV. The state with parallel spins (triplet) is an "antibonding state" and cannot form a molecule.
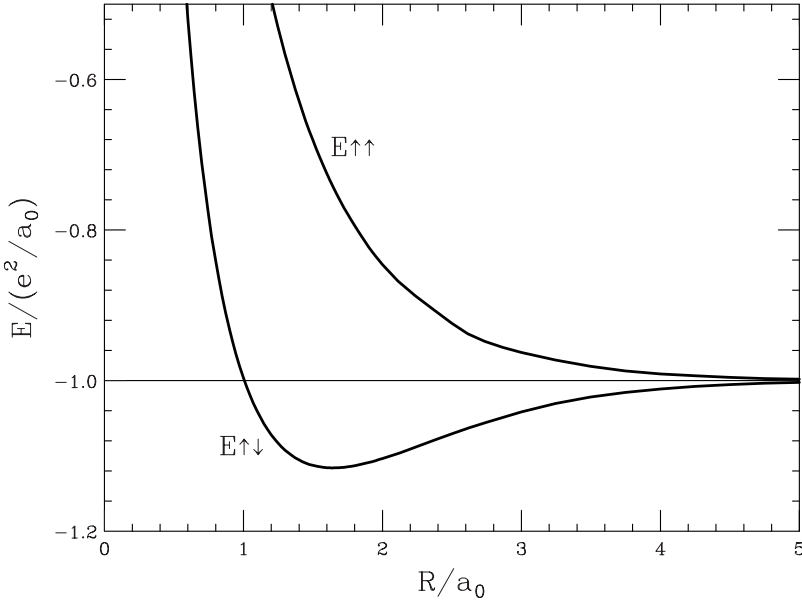
Fig. 1.1.   Lowest energy levels (in units of e^2/a_0) of a hydrogen molecule for a triplet state ($E_{\uparrow\uparrow}$) and for a singlet state ($E_{\uparrow\downarrow}$) as function of the distance between the nuclei $\rho = R/a_0$.

1.2. Heisenberg Hamiltonian

The simple example of the hydrogen molecule in its ground state illustrates how the pure quantum effect of the electronic exchange leads to an effective interaction between the hydrogen atoms which is strongly dependent on the total spin of the two electrons even if the spin variables of the electrons do not appear explicitly in the Hamiltonian. Another way to write the Hamiltonian of a hydrogen molecule in its ground state is

$$\mathcal{H} = -J(r)\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 + E(r) \tag{1.2.1}$$

where $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are the electron spin operators and $J(r)$ and $E(r)$ are functions of r chosen so that the eigenvalues of the operator $\mathcal{H}$ given by Eq. (1.2.1) are the same as $E_{\uparrow\uparrow}$ and $E_{\uparrow\downarrow}$ given by Eqs. (1.1.19) and (1.1.20), respectively. The eigenvalues of Hamiltonian (1.2.1) are easily obtained from the identity

$$\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = \frac{1}{2}\left(\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2\right)^2 - \frac{1}{2}\left(\boldsymbol{\sigma}_1^2 + \boldsymbol{\sigma}_2^2\right) = \frac{1}{2}\boldsymbol{S}^2 - \frac{3}{4} \tag{1.2.2}$$

where the eigenvalues of $\boldsymbol{S}^2$ are $S(S+1)$ with $S = 0, 1$. Since the eigenvalues of the scalar product in Eq. (1.2.2) are $-\frac{3}{4}$ and $\frac{1}{4}$ for $S = 0$ and $S = 1$, respectively, the eigenvalues of Hamiltonian (1.2.1) coincide with $E_{\uparrow\uparrow}$ and $E_{\uparrow\downarrow}$ if $J(r)$ and $E(r)$ are

chosen as

$$J(r) = E_{\uparrow\downarrow}(r) - E_{\uparrow\uparrow}(r) = 2\,\frac{e^2}{a_0}\,\frac{a(\rho) - q(\rho)\Delta^2}{1 - \Delta^4} \tag{1.2.3}$$

and

$$E(r) = \frac{3}{4}E_{\uparrow\uparrow}(r) + \frac{1}{4}E_{\uparrow\downarrow}(r) = -\frac{e^2}{a_0}$$
$$+ \frac{e^2}{2a_0}\,\frac{(2 + \Delta^2)q(\rho) - (1 + 2\Delta^2)a(\rho)}{1 - \Delta^4}. \tag{1.2.4}$$

The function $E(r)$ is the mean energy of the two hydrogen atoms since the statistical weights $\frac{3}{4}$ and $\frac{1}{4}$ correspond to weights of the triplet and singlet state, respectively. The function $J(r)$ reduces to the exchange integral $a(\rho)$ when the overlap integral Δ is small. This fact explains why the first term of Eq. (1.2.1) is called *exchange Hamiltonian*. Note that the exchange integral $J(r)$ is considered a short-range interaction because it decays exponentially with the distance.

A generalization of the exchange Hamiltonian (1.2.1) leads to the Heisenberg Hamiltonian

$$\mathcal{H} = -\sum_{i,j} J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j - h\sum_i S_i^z \tag{1.2.5}$$

where i, j label the lattice sites; $2J_{ij} = 2J(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$ is the exchange integral between the spins at i and j depending only on the distance between the spins; $\boldsymbol{S}_i$ is the spin associated to the site i and $h = g\mu_B H$ where g is the Landé factor, $\mu_B = 9.27 \times 10^{-20}$ erg $\times$ gauss^{-1} is the Bohr magneton and H the applied external magnetic field assumed to be directed along the z-axis. The simplest approximation neglects any interaction between the spins that are not nearest neighbour (NN) spins.

Let us give some examples of spin clusters for which the eigenvalues and eigenvectors of the Heisenberg Hamiltonian can be obtained exactly. Assuming that the spin quantum number is $\sigma = \frac{1}{2}$ let us consider the Hamiltonian given in Eq. (1.2.1) ignoring the term $E(r)$. Replacing $J(r)$ by $2J$ and adding the interaction with an external magnetic field, we obtain:

$$\mathcal{H} = -2J\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - h(\sigma_1^z + \sigma_2^z) = -J\left(\boldsymbol{S}^2 - \frac{3}{2}\right) - hS^z \tag{1.2.6}$$

where $\boldsymbol{S} = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2$ is the total spin of the complex and S^z is the z-component of the total spin. The complete set of eigenvalues and eigenvectors of Hamiltonian (1.2.6) is easily obtained recalling the composition rule of the angular momenta $\boldsymbol{S}^2 = S(S + 1)$ with $S = 1$ (triplet) and $S = 0$ (singlet). The result is illustrated in Fig. 1.2. For $J > 0$ the lowest energy level (ground state) and the corresponding eigenstate are given by

$$E_{\mathrm{GS}} = -\frac{J}{2} - h, \quad |\uparrow\uparrow\rangle, \tag{1.2.7}$$
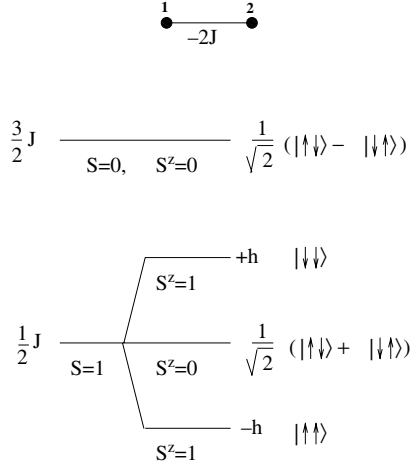
Fig. 1.2. Energy levels of a couple of spin interacting by an exchange integral $-2J$. The total spin number and its z-component associated to each state is shown.

respectively. The eigenstate $|\uparrow\uparrow\rangle$ is a contracted form of the state $|\sigma_1^z = \frac{1}{2}, \sigma_2^z = \frac{1}{2}\rangle$ where the symbols $\uparrow$ and $\downarrow$ mean $\sigma^z = \frac{1}{2}$ and $\sigma^z = -\frac{1}{2}$, respectively. The energies of the excited states and the corresponding eigenstates are given by

$$E_1 = -\frac{J}{2}, \quad \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \tag{1.2.8}$$

$$E_2 = -\frac{J}{2} + h, \quad |\downarrow\downarrow\rangle \tag{1.2.9}$$

and

$$E_3 = \frac{3}{2}J, \quad \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \tag{1.2.10}$$

In Fig. 1.3, we give the eigenvalues and eigenstates of a cluster of 3 spins forming a triangle described by the Heisenberg Hamiltonian

$$\mathcal{H} = -2J(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_3 \cdot \boldsymbol{\sigma}_1) - hS^z$$

$$= -J\left(\boldsymbol{S}^2 - \frac{9}{4}\right) - hS^z \tag{1.2.11}$$

where the last step is obtained from the identity

$$\boldsymbol{S}^2 = \sum_{i=1}^{3}\sum_{j=1}^{3} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j = \frac{9}{4} + 2(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_3 \cdot \boldsymbol{\sigma}_1). \tag{1.2.12}$$

From Eq. (1.2.11), it is direct to write the complete set of eigenvalues and eigenstates ($2^3 = 8$) of the Hamiltonian using the composition rules of the angular momenta. In this case, $S = \frac{3}{2}$ and $S = \frac{1}{2}$ (twice degenerate). The result is shown in Fig. 1.3. Four eigenvalues belong to the quartet corresponding to $S = \frac{3}{2}$ and two eigenvalues (each of which twice degenerate) belong to the doublet corresponding to $S = \frac{1}{2}$.
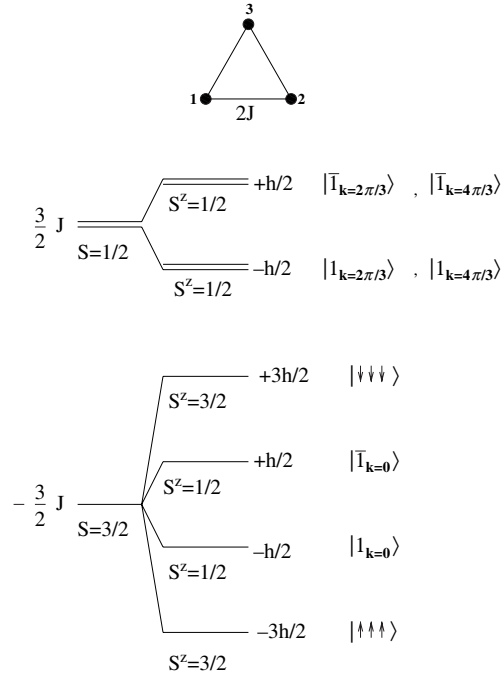
Fig. 1.3. Energy levels of a cluster of 3 spins forming a triangle. Each couple of spins interacts by an exchange integral $-2J$. The total spin number and its z-component associated to each state is shown. The double line in the highest doublet means that eigenvalue is twice degenerate.

There is no way to determine univocally the 2 states belonging to the eigenvalues $\frac{3}{2}J - \frac{h}{2}$ or $\frac{3}{2}J + \frac{h}{2}$. For a reason that will be clear later, we choose the two eigenstates belonging to the degenerate eigenvalue $\frac{3}{2}J - \frac{h}{2}$ as

$$|1_k> = \frac{1}{\sqrt{3}}(e^{ik}|\downarrow\uparrow\uparrow\rangle + e^{2ik}|\uparrow\downarrow\uparrow\rangle + |\uparrow\uparrow\downarrow\rangle) \qquad (1.2.13)$$

with $k = \frac{2}{3}\pi$ and $k = \frac{4}{3}\pi$. The notation $|1_k\rangle$ is motivated by the fact that the state is a linear combination of states each containing 1 spin reversal with respect to the ground state $|0\rangle = |\uparrow\uparrow\uparrow\rangle$ localized in the different vertices of the triangle; the label k reflects the k-dependence of the coefficients of the linear combination. Analogously, the two eigenstates belonging to the degenerate eigenvalue $\frac{3}{2}J + \frac{h}{2}$ are choosen as

$$|\overline{1}_k\rangle = \frac{1}{\sqrt{3}}(e^{ik}|\uparrow\downarrow\downarrow\rangle + e^{2ik}|\downarrow\uparrow\downarrow\rangle + |\downarrow\downarrow\uparrow\rangle) \qquad (1.2.14)$$

with $k = \frac{2}{3}\pi$ and $k = \frac{4}{3}\pi$. Notice that the states of Eq. (1.2.14) are obtained by reversing the spins of the states of Eq. (1.2.13). They are a linear combination of states with a spin reversal with respect to the state $|\overline{0}\rangle = |\downarrow\downarrow\downarrow\rangle$. Note that the states given by Eq. (1.2.13) and the state belonging to the eigenvalue $-\frac{3}{2} - \frac{1}{2}h$ may

be written in the more general form

$$|1_k\rangle = \frac{1}{\sqrt{3}} \sum_{n=1}^{3} e^{ikn}|1_n\rangle \tag{1.2.15}$$

with $k = \frac{2}{3}\pi$, $\frac{4}{3}\pi$ and 0, respectively, where $|1_n\rangle$ means a state characterized by a single deviation located at the site n. The three discrete values of k reflect the periodic boundary conditions (PBC) of a periodic structure of 3 spins: $kN = 2\pi l$ with $N = 3$.

More work is required to obtain the complete set of eigenvalues and eigenstates of a cluster of 4 spins located on the vertices of a square as shown in Fig. 1.4. Assuming that the NN spins interact via an exchange integral $-2J_1$ and the next-nearest-neighbour (NNN) spins interact via an exchange integral $-2J_2$, the Hamiltonian reads

$$\mathcal{H} = -2J_1(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_3 \cdot \boldsymbol{\sigma}_4 + \boldsymbol{\sigma}_4 \cdot \boldsymbol{\sigma}_1)$$
$$- 2J_2(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_4) - hS^z$$
$$= -J_1(\boldsymbol{S}^2 - 3) + 2(J_1 - J_2)(\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_4) - hS^z. \tag{1.2.16}$$

The most direct way to obtain the eigenvalues of Hamiltonian (1.2.16) is to give the matrix elements of such Hamiltonian between the $2^4 = 16$ states $|\sigma_1^z \, \sigma_2^z \, \sigma_3^z \, \sigma_4^z\rangle$
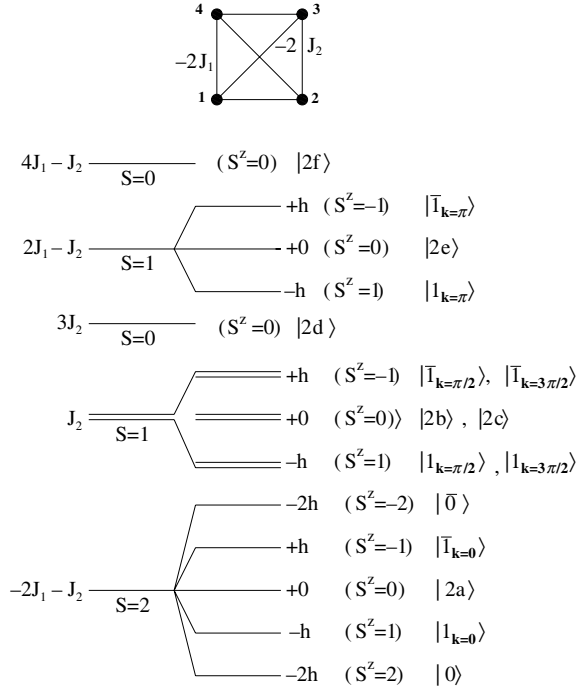

Fig. 1.4. Energy levels of a cluster of 4 spins forming a square with exchange interaction $-2J_1$ between spins along the edges of the square and $-2J_2$ between spins belonging to the diagonals of the square. The total spin number and its z-component associated to each state is shown.

with $\sigma_i^z = \pm\frac{1}{2}$ ($\uparrow$, $\downarrow$). The 16×16 matrix can be reduced to a matrix with blocks along the principal diagonal grouping the states according to S^z. Indeed, for $S^z = 2$ ($|\uparrow\uparrow\uparrow\uparrow\rangle$), the only matrix element is given by

$$\mathcal{H}^{(2)} = -2J_1 - J_2 - 2h. \tag{1.2.17}$$

For $S^z = 1$ ($|\downarrow\uparrow\uparrow\uparrow\rangle$, $|\uparrow\downarrow\uparrow\uparrow\rangle$, $|\uparrow\downarrow\downarrow\uparrow\rangle$ and $|\uparrow\uparrow\uparrow\downarrow\rangle$), the 4×4 matrix is given by

$$\mathcal{H}^{(1)} = \begin{pmatrix} -h & -J_1 & -J_2 & -J_1 \\ -J_1 & -h & -J_1 & -J_2 \\ -J_2 & -J_1 & -h & -J_1 \\ -J_1 & -J_2 & -J_1 & -h \end{pmatrix}. \tag{1.2.18}$$

For $S^z = 0$ ($|\downarrow\downarrow\uparrow\uparrow\rangle$, $|\downarrow\uparrow\downarrow\uparrow\rangle$, $|\downarrow\uparrow\uparrow\downarrow\rangle$, $|\uparrow\downarrow\downarrow\uparrow\rangle$, $|\uparrow\downarrow\uparrow\downarrow\rangle$, $|\uparrow\uparrow\downarrow\downarrow\rangle$), the 6×6 matrix is given by

$$\mathcal{H}^{(0)} = \begin{pmatrix} J_2 & -J_1 & -J_2 & -J_2 & -J_1 & 0 \\ -J_1 & (2J_1 - J_2) & -J_1 & -J_1 & 0 & -J_1 \\ -J_2 & -J_1 & J_2 & 0 & -J_1 & -J_2 \\ -J_2 & -J_1 & 0 & J_2 & -J_1 & -J_2 \\ -J_1 & 0 & -J_1 & -J_1 & (2J_1 - J_2) & -J_1 \\ 0 & -J_1 & -J_2 & -J_2 & -J_1 & J_2 \end{pmatrix}. \tag{1.2.19}$$

The blocks for $S^z = -1$ and $S^z = -2$ can be obtained directly from Eqs. (1.2.18) and (1.2.17) respectively, simply by changing the sign in front of h. The eigenvalues and eigenvectors of Hamiltonian (1.2.16) are shown in Fig. 1.4. Their ordering in increasing energies is related to the assumption $J_1 > J_2 > h > 0$.

The ground state is characterized by

$$E_{\text{GS}} = -2J_1 - J_2 - 2h, \quad |0\rangle = |\uparrow\uparrow\uparrow\uparrow\rangle. \tag{1.2.20}$$

The other 4 states of the quintuplet $S = 2$ are given by

$$E_1 = -2J_1 - J_2 - h, \quad |1_{k=0}\rangle = \frac{1}{2}\sum_{n=1}^{4} |1_n\rangle \tag{1.2.21}$$

$$E_2 = -2J_1 - J_2, \quad |2a\rangle = \frac{1}{\sqrt{6}}(|\downarrow\downarrow\uparrow\uparrow\rangle + |\downarrow\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\downarrow\rangle$$

$$+ |\uparrow\downarrow\downarrow\uparrow\rangle + |\uparrow\downarrow\uparrow\downarrow\rangle + |\uparrow\uparrow\downarrow\downarrow\rangle), \tag{1.2.22}$$

$$E_3 = -2J_1 - J_2 + h, \quad |\bar{1}_{k=0}\rangle = \frac{1}{2}\sum_{n=1}^{4} |\bar{1}_n\rangle \tag{1.2.23}$$

where $|\bar{1}_n\rangle$ is obtained from $|1_n\rangle$ reversing all spins; and

$$E_4 = -2J_1 - J_2 + 2h, \quad |\bar{0}\rangle = |\downarrow\downarrow\downarrow\downarrow\rangle. \tag{1.2.24}$$

The states of the lowest triplet ($S = 1$) corresponding to eigenvalues with degeneracy 2 can be chosen as follows

$$E_5 = E_6 = J_2 - h, \quad |1_k\rangle = \frac{1}{2}\sum_{n=1}^{4} e^{ikn}|1_n\rangle \tag{1.2.25}$$

with $k = \frac{1}{2}\pi$ and $k = \frac{3}{2}\pi$;

$$E_7 = E_8 = J_2, \quad |2b\rangle = \frac{1}{\sqrt{2}}(|\downarrow\downarrow\uparrow\uparrow\rangle + |\uparrow\uparrow\downarrow\downarrow\rangle), \quad |2c\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\uparrow\rangle) \tag{1.2.26}$$

and

$$E_9 = E_{10} = J_2 + h, \quad |\overline{1}_k\rangle = \frac{1}{2}\sum_{n=1}^{4} e^{ikn}|\overline{1}_n\rangle \tag{1.2.27}$$

with $k = \frac{1}{2}\pi$ and $k = \frac{3}{2}\pi$. The lowest singlet ($S = 0$) is characterized by

$$E_{11} = 3J_2, \quad |2d\rangle = \frac{1}{2}(|\downarrow\downarrow\uparrow\uparrow\rangle + |\uparrow\uparrow\downarrow\downarrow\rangle - |\downarrow\uparrow\uparrow\downarrow\rangle - |\uparrow\downarrow\downarrow\uparrow\rangle). \tag{1.2.28}$$

The next triplet ($S = 1$) is characterized by

$$E_{12} = 2J_1 - J_2 - h, \quad |1_\pi\rangle = \frac{1}{2}\sum_{n=1}^{4} e^{i\pi n}|1_n\rangle, \tag{1.2.29}$$

$$E_{13} = 2J_1 - J_2, \quad |2e\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\downarrow\uparrow\rangle + |\uparrow\downarrow\uparrow\downarrow\rangle) \tag{1.2.30}$$

and

$$E_{14} = 2J_1 - J_2 + h, \quad |\overline{1}_\pi\rangle = \frac{1}{2}\sum_{n=1}^{4} e^{i\pi n}|\overline{1}_n\rangle. \tag{1.2.31}$$

Finally, the highest singlet ($S = 0$) is characterized by

$$E_{15} = 4J_1 - J_2,$$

$$|2f\rangle = \frac{1}{3\sqrt{3}}[|\downarrow\downarrow\uparrow\uparrow\rangle + |\uparrow\uparrow\downarrow\downarrow\rangle + |\downarrow\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\uparrow\rangle$$

$$- 2(|\downarrow\uparrow\downarrow\uparrow\rangle + |\uparrow\downarrow\uparrow\downarrow\rangle)]. \tag{1.2.32}$$

Some general remarks can be deduced from the spectra of these small clusters. For $J > 0$, the ground state is the eigenstate corresponding to the saturated state with all spins up $|\uparrow \ldots \uparrow\rangle$ and it belongs to the maximum eigenvalue $NS(NS + 1)$ of $\boldsymbol{S}^2$ and to the maximum eigenvalue NS of S^z. The states with one deviation with respect to the ground state are given by the general equation

$$|1_k\rangle = \frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{ikn}|1_n\rangle \tag{1.2.33}$$

with $k = \frac{2\pi}{N}l$ and $l = 0, 1, 2, \ldots, N - 1$. The state with $k = 0$, when acted upon by operators S^z and $\boldsymbol{S}^2$, has eigenvalues $(NS - 1)$ and $NS(NS + 1)$, respectively. In contrast, the states with $k \neq 0$, when acted upon by operators S^z and $\boldsymbol{S}^2$, have eigenvalues $(NS - 1)$ and $NS(NS - 1)$, respectively. The energy of the states (1.2.33) for $J_2 = 0$ can be written

$$E_k = E_{\text{GS}} + h + 2J_1(1 - \cos k). \tag{1.2.34}$$

As we will see in the next section, $E_k - E_{\text{GS}}$ is the spin wave energy with wavevector k in 1D with PBC.

1.3. Spin Wave Excitations

If we restrict the exchange interaction to NN spins, the Hamiltonian (1.2.5) becomes

$$\mathcal{H} = -J \sum_{i,\boldsymbol{\delta}} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+\boldsymbol{\delta}} - h \sum_i S_i^z. \tag{1.3.1}$$

The spins $\boldsymbol{S}_i$ occurring in (1.3.1) are angular momentum operators defined by the commutation rules[5]

$$[S_i^x, S_j^y] = i S_i^z \delta_{i,j}, \quad [S_i^z, S_j^x] = i S_i^y \delta_{i,j}, \quad [S_i^y, S_j^z] = i S_i^x \delta_{i,j}. \tag{1.3.2}$$

The commutation rules (1.3.2) imply that the components of the spins located at different lattice sites commute with each other so that the spins belonging to different lattice sites are treated as "distinguishable" particles. This is certainly true for the magnetic insulators in which the magnetic moments are localized on the lattice sites. It is useful to define the *raising* and *lowering* operators S_i^+ and S_i^- as

$$S_i^+ = S_i^x + i S_i^y, \quad S_i^- = S_i^x - i S_i^y \tag{1.3.3}$$

whose commutation rules are obtained directly from Eq. (1.3.2)

$$[S_i^z, S_j^+] = S_i^+ \delta_{i,j}, \quad [S_i^z, S_j^-] = -S_i^- \delta_{i,j}, \quad [S_i^+, S_j^-] = 2 S_i^z \delta_{i,j}. \tag{1.3.4}$$

From the commutation rules (1.3.4), it follows that in the representation where $\boldsymbol{S}_i^2 \equiv (S_i^x)^2 + (S_i^y)^2 + (S_i^z)^2$ and S_i^z are diagonal, one has

$$\langle S'm' | \boldsymbol{S}_i^2 | Sm \rangle = S(S+1)\, \delta_{S,S'}\, \delta_{m,m'}, \quad \langle S'm' | S_i^z | Sm \rangle = m\, \delta_{S,S'}\, \delta_{m,m'} \tag{1.3.5}$$

with $-S \le m \le S$. The matrix elements of the raising and lowering operators are

$$\langle S'm' | S_i^+ | Sm \rangle = \sqrt{(S-m)(S+m+1)}\, \delta_{S,S'}\, \delta_{m',m+1} \tag{1.3.6}$$

and

$$\langle S'm' | S_i^- | Sm \rangle = \sqrt{(S+m)(S-m+1)}\, \delta_{S,S'}\, \delta_{m',m-1}. \tag{1.3.7}$$

By the use of the raising and lowering spin operators of Eq. (1.3.3), the Hamiltonian (1.3.1) becomes

$$\mathcal{H} = -J \sum_{i,\boldsymbol{\delta}} \left[S_i^z S_{i+\boldsymbol{\delta}}^z + \frac{1}{2}(S_i^+ S_{i+\boldsymbol{\delta}}^- + S_i^- S_{i+\boldsymbol{\delta}}^+) \right] - h \sum_i S_i^z. \tag{1.3.8}$$

The constants of motion of the Hamiltonian (1.3.8), that is the operators that commute with it, are the square of the total spin of the system

$$\boldsymbol{S}_{\text{tot}}^2 = \left[\sum_l \boldsymbol{S}_l \right]^2 = \sum_{l,m} \left[S_l^z S_m^z + \frac{1}{2}(S_l^+ S_m^- + S_l^- S_m^+) \right] \tag{1.3.9}$$

and its z-component

$$S_{\text{tot}}^z = \sum_l S_l^z. \tag{1.3.10}$$

Note that the magnetization of the whole system is proportional to the total spin vector through the relationship $\boldsymbol{M}_{\text{tot}} = g\mu_B \boldsymbol{S}_{\text{tot}}$. The existence of constants of

motion like those given in Eqs. (1.3.9) and (1.3.10) means that the Hamiltonian (1.3.8) cannot change the magnetization of the system or its z-component acting on a state of assigned S_{tot} and S_{tot}^z. We have seen in the previous section that in the ground state $|0\rangle$, all spins are directed along the field assuming their maximum value. Acting with the operators (1.3.8)–(1.3.10) on the ground state, one obtains

$$\mathcal{H}|0\rangle = E_{\text{GS}}|0\rangle, \quad E_{\text{GS}} = -zJS^2N - hSN \tag{1.3.11}$$

and

$$\boldsymbol{S}_{\text{tot}}{}^2|0\rangle = NS(NS+1)|0\rangle, \ S_{\text{tot}}^z|0\rangle = NS|0\rangle \tag{1.3.12}$$

where z is the number of NN (coordination number), S is the spin quantum number of the magnetic moment located on each lattice site and N is the number of lattice sites. As we have seen in the previous section, the lowest excitation energy levels are expected to correspond to states with only one spin deviation from the ground state. For this reason, we consider the state $S_j^-|0\rangle = \sqrt{2S}|1_j\rangle$ with a single spin deviation localized at the lattice site $\boldsymbol{r}_j$. The action of the operators (1.3.8)–(1.3.10) on the normalized state $|1_j\rangle$ gives

$$\mathcal{H}|1_j\rangle = (E_{\text{GS}} + h + 2zJS)|1_j\rangle - 2JS\sum_{\boldsymbol{\delta}} |1_{j+\boldsymbol{\delta}}\rangle, \tag{1.3.14}$$

$$\boldsymbol{S}_{\text{tot}}{}^2|1_j\rangle = NS(NS-1)|1_j\rangle + 2S\sum_{m} |1_m\rangle \tag{1.3.15}$$

and

$$S_{\text{tot}}^z|1_j\rangle = (NS-1)|1_j\rangle, \tag{1.3.16}$$

showing that the state with one *localized* deviation is neither an eigenstate of the Hamiltonian (1.3.8) nor an eigenstate of the total spin operator $\boldsymbol{S}_{\text{tot}}^2$ (1.3.9) even though it is an eigenstate of S_{tot}^z (1.3.10). In analogy with what we have seen in the case of small clusters, we define a *delocalized* state

$$|1_{\boldsymbol{k}}\rangle = \frac{1}{\sqrt{N}}\sum_{j} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_j}|1_j\rangle \tag{1.3.17}$$

consisting of a linear combination of the "localized" states $|1_j\rangle$. The action of the operators (1.3.8)–(1.3.10) on the state (1.3.17) gives

$$\mathcal{H}|1_{\boldsymbol{k}}\rangle = \left[E_{\text{GS}} + h + 2JS\sum_{\boldsymbol{\delta}}(1 - \cos\boldsymbol{k}\cdot\boldsymbol{\delta})\right]|1_{\boldsymbol{k}}\rangle, \tag{1.3.18}$$

$$\boldsymbol{S}_{\text{tot}}{}^2|1_{\boldsymbol{k}}\rangle = [NS(NS-1) + 2NS\,\delta_{\boldsymbol{k},0}]|1_{\boldsymbol{k}}\rangle \tag{1.3.19}$$

and

$$S_{\text{tot}}^z|1_{\boldsymbol{k}}\rangle = (NS-1)|1_{\boldsymbol{k}}\rangle. \tag{1.3.20}$$

Eqs. (1.3.18)–(1.3.20) prove that $|1_{\boldsymbol{k}}\rangle$ is an eigenstate of the Hamiltonian, of the total spin operator and of the z-component of the total spin simultaneously. The cost of

energy to create a delocalized spin deviation in the system is obtained by subtracting the ground-state energy (1.3.11) from Eq. (1.3.18), that is

$$\hbar\omega_{\boldsymbol{k}} = h + 2JS\sum_{\boldsymbol{\delta}}(1 - \cos\boldsymbol{k}\cdot\boldsymbol{\delta}). \tag{1.3.21}$$

For a ring of N spins $S = \frac{1}{2}$ with NN exchange interaction ($\delta = \pm 1$ in units of lattice spacing), we recover the spin wave energy of small cluster given by Eq. (1.2.34). The energy (1.3.21) corresponding to a single spin deviation delocalized over the whole lattice is the *spin wave* energy and it is the lowest excited state of the Heisenberg Hamiltonian. Note that the mean value of the local spin operator S_j^z on the localized state $|1_j\rangle$ is $S-1$ while its mean value on the delocalized state $|1_{\boldsymbol{k}}\rangle$ is $S-\frac{1}{N}$. Indeed, the single deviation is no more localized on a particular lattice site but distributed over the whole lattice, each spin component being reduced by $\frac{1}{N}$ on the average. Equation (1.3.19) shows that only the state corresponding to a spin wave with $\boldsymbol{k}=0$ belongs to the maximum eigenvalue of $\boldsymbol{S}_{\text{tot}}^2$ that is $NS(NS+1)$. On the contrary, the eigenstates of the spin waves with $\boldsymbol{k}\neq 0$ belong to the eigenvalue $(NS-1)NS$. In other words, the total spin quantum number is NS for $|1_0\rangle$ and $NS-1$ for $|1_{\boldsymbol{k}}\rangle$, while the quantum number of the z-component of the total spin S_{tot}^z is $NS-1$ for any $|1_{\boldsymbol{k}}\rangle$ as shown by Eq. (1.3.20). This result is in agreement with the results obtained for small clusters in Section 1.2.

1.4. Two-Spin Deviation Excitations

In analogy with the choice done in the previous section for the states with a single spin deviation, we introduce the state with two spin deviations localized at the sites $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ $S_i^- S_j^-|0\rangle = 2S|1_i, 1_j\rangle$ for $i \neq j$ and $(S_i^-)^2|0\rangle = \sqrt{4S(2S-1)}|2_i\rangle$ for $i = j$. The states $|1_i, 1_j\rangle$ and $|2_i\rangle$ are normalized states and the coefficients in front of them are obtained from the matrix elements (1.3.7). The most general state with two spin deviations is given by

$$|\psi\rangle = \sum_{i,j} f_{ij} S_i^- S_j^-|0\rangle = \sum_{i\neq j} 2S f_{ij}|1_i, 1_j\rangle + \sum_i \sqrt{4S(2S-1)} f_{ii}|2_i\rangle \tag{1.4.1}$$

with the symmetry rules $f_{ij} = f_{ji}$ coming from the property $[S_i^-, S_j^-] = 0$. Notice that for $i = j$, the state $(S_i^-)^2|0\rangle$ is zero for $S = 1/2$. Using the commutation rules (1.3.4), the ground-state property $S_i^+|0\rangle = 0$ and the Heisenberg Hamiltonian (1.2.5)

$$\mathcal{H} = -\sum_{l,m} J_{lm}\left[S_l^z S_m^z + \frac{1}{2}(S_l^+ S_m^- + S_l^- S_m^+)\right] - h\sum_m S_m^z \tag{1.4.2}$$

where $J_{lm} = J_{ml}$, the Schrödinger equation can be written as

$$\mathcal{H}|\psi\rangle = E_{\text{GS}}|\psi\rangle + \sum_{i,j} f_{ij}[\mathcal{H}, S_i^- S_j^-]|0\rangle = E|\psi\rangle \tag{1.4.3}$$

where $E_{\mathrm{GS}} = -\sum_{l,m} J_{lm} S^2 - hSN$ is the ground-state energy. Defining the two-spin wave excitation energy as $\hbar\omega = E - E_{\mathrm{GS}}$, Eq. (1.4.3) becomes

$$\hbar\omega \sum_{i,j} f_{ij} S_i^- S_j^- |0\rangle = \sum_{i,j} f_{ij} [\mathcal{H}, S_i^- S_j^-]|0\rangle. \qquad (1.4.4)$$

The commutation rules (1.3.4) lead to the relationship

$$[\mathcal{H}, S_i^- S_j^-] = -2\sum_m [J_{jm}(S_i^- S_m^- S_j^z - S_i^- S_j^- S_m^z)$$

$$+ J_{im}(S_m^- S_j^- S_i^z - S_i^- S_j^- S_m^z)$$

$$- J_{im} S_m^- S_j^- \delta_{i,j}] - 2J_{ij} S_i^- S_j^- + 2h S_i^- S_j^-. \qquad (1.4.5)$$

Using the identity $S_i^z |0\rangle = S|0\rangle$ from Eqs. (1.4.4) and (1.4.5), one obtains

$$\hbar\omega \sum_{i,j} f_{ij} S_i^- S_j^- |0\rangle$$

$$= \sum_{i,j} \left\{ \left[2h + 2S \sum_m (J_{im} + J_{jm}) - 2J_{ij} \right] f_{ij} \right.$$

$$\left. - 2S \sum_m (J_{jm} f_{im} + J_{im} f_{jm}) + J_{ij}(f_{ii} + f_{jj}) \right\} S_i^- S_j^- |0\rangle \qquad (1.4.6)$$

or

$$\left(\hbar\omega - 2h - 4S \sum_m J_{im} \right) f_{ij} + 2S \sum_m (J_{jm} f_{im} + J_{im} f_{jm})$$

$$= J_{ij}(f_{ii} + f_{jj} - 2f_{ij}). \qquad (1.4.7)$$

Let us introduce the Fourier transform[6]

$$f_{ij} = \frac{1}{N} \sum_{\boldsymbol{K}} e^{i\frac{\boldsymbol{K}}{2}\cdot(\boldsymbol{r}_i + \boldsymbol{r}_j)} F_{\boldsymbol{K}}(\boldsymbol{r}_{ij}) \qquad (1.4.8)$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ and $\boldsymbol{K} = 2\pi(\frac{l_x}{L_x}, \frac{l_y}{L_y}, \frac{l_z}{L_z})$ with $l_\alpha = 0, 1, 2, \ldots, L_\alpha - 1$ and $L_x L_y L_z = N$. Because of the symmetry rules $f_{ij} = f_{ji}$, one obtains the relationship $F_{\boldsymbol{K}}(\boldsymbol{r}_{ij}) = F_{\boldsymbol{K}}(\boldsymbol{r}_{ji})$ from Eq. (1.4.8). By replacing Eq. (1.4.8) into Eq. (1.4.7), one has

$$\left(\hbar\omega - 2h - 4S \sum_m J_{im} \right) F_{\boldsymbol{K}}(\boldsymbol{r}_{ij})$$

$$+ 2S \sum_m [J_{jm} e^{i\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{r}_{mj}} F_{\boldsymbol{K}}(\boldsymbol{r}_{ij} + \boldsymbol{r}_{jm}) + J_{im} e^{i\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{r}_{mi}} F_{\boldsymbol{K}}(\boldsymbol{r}_{ij} + \boldsymbol{r}_{mi})]$$

$$= 2J_{ij} \left[\cos\left(\frac{\boldsymbol{K}}{2} \cdot \boldsymbol{r}_{ij} \right) F_{\boldsymbol{K}}(0) - F_{\boldsymbol{K}}(\boldsymbol{r}_{ij}) \right]. \qquad (1.4.9)$$

If we restrict the exchange interaction to NN, that is, $J_{ij} = J$ if i and j are NN sites and $J = 0$ otherwise, Eq. (1.4.9) becomes

$$(\hbar\omega - 2h - 4JzS)F_{\boldsymbol{K}}(\boldsymbol{r}) + 4JS\sum_{\boldsymbol{\delta}} e^{i\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{\delta}}F_{\boldsymbol{K}}(\boldsymbol{r} + \boldsymbol{\delta})$$

$$= 2J(\boldsymbol{r})\left[\cos\left(\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{r}\right)F_{\boldsymbol{K}}(0) - F_{\boldsymbol{K}}(\boldsymbol{r})\right] \tag{1.4.10}$$

where $\boldsymbol{\delta}$ is a vector connecting a spin with its z NN. Let us introduce[6] the finite Fourier transforms

$$F_{\boldsymbol{K}}(\boldsymbol{r}) = \frac{1}{N}\sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}f_{\boldsymbol{K}}(\boldsymbol{q}) \tag{1.4.11}$$

and

$$f_{\boldsymbol{K}}(\boldsymbol{q}) = \sum_{\boldsymbol{r}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}F_{\boldsymbol{K}}(\boldsymbol{r}). \tag{1.4.12}$$

After multiplication of both sides of Eq. (1.4.10) by $e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}$ and summation over $\boldsymbol{r}$, we obtain

$$[\hbar\omega - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q})]f_{\boldsymbol{K}}(\boldsymbol{q}) = 2J\sum_{\boldsymbol{\delta}}\cos\boldsymbol{q}\cdot\boldsymbol{\delta}\frac{1}{N}\sum_{\boldsymbol{q}'}\left(\cos\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{\delta} - \cos\boldsymbol{q}'\cdot\boldsymbol{\delta}\right)f_{\boldsymbol{K}}(\boldsymbol{q}') \tag{1.4.13}$$

where

$$\hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}) = 2h + 4JS\sum_{\boldsymbol{\delta}}\left(1 - \cos\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{\delta}\,\cos\boldsymbol{q}\cdot\boldsymbol{\delta}\right) \tag{1.4.14}$$

is the energy of two *free* spin waves of momenta $\boldsymbol{k}_1 = \frac{\boldsymbol{K}}{2} + \boldsymbol{q}$ and $\boldsymbol{k}_2 = \frac{\boldsymbol{K}}{2} - \boldsymbol{q}$. As one can see from Eq. (1.4.13), the state corresponding to two *free* spin waves is *never* an eigenstate of the Heisenberg Hamiltonian because of the occurrence of the right-hand side of Eq. (1.4.13) that comes from the interaction potential between the spin waves. Let us write Eq. (1.4.13) for the "cubic lattices" and assume the lattice spacing $a = 1$:

$$[\hbar\omega - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q})]f_{\boldsymbol{K}}(\boldsymbol{q}) = 4J\sum_{\alpha}\cos q_\alpha\frac{1}{N}\sum_{\boldsymbol{q}'}\left(\cos\frac{K_\alpha}{2} - \cos q'_\alpha\right)f_{\boldsymbol{K}}(\boldsymbol{q}') \tag{1.4.15}$$

where $\alpha = x, y, z$ for a simple cubic (SC) lattice, $\alpha = x, y$ for a square (SQ) lattice and $\alpha = x$ for a linear chain (LC). We are able to prove that Eq. (1.4.15) has two kinds of solutions according to

i) the frequency ω is inside the two-spin wave band that is $\omega_{\text{bottom}} < \omega < \omega_{\text{top}}$ where $\hbar\omega_{\text{bottom}} = 8JS(d - \sum_\alpha \cos\frac{K_\alpha}{2})$ and $\hbar\omega_{\text{top}} = 8JS(d + \sum_\alpha \cos\frac{K_\alpha}{2})$ with $d = 1, 2, 3$ for LC, SQ and SC, respectively, or

ii) the frequency is below ($\omega < \omega_{\text{bottom}}$) or above ($\omega > \omega_{\text{top}}$) the two-spin wave band.

Let us begin considering the case i): we focus on a wavevector $\boldsymbol{q}_0$ and assume[7] that $f_{\boldsymbol{K}}(\pm\boldsymbol{q}_0) = N/2$. Then for $\boldsymbol{q} = \pm\boldsymbol{q}_0$, Eq. (1.4.15) becomes

$$\hbar\omega = \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}_0) + \frac{\Delta_{\boldsymbol{K}}}{N} \tag{1.4.16}$$

where

$$\Delta_{\boldsymbol{K}} = 8J \sum_\alpha \cos q_0^\alpha \left(\cos \frac{K_\alpha}{2} - \cos q_0^\alpha + V_{\boldsymbol{K}}^\alpha \right) \tag{1.4.17}$$

with

$$V_{\boldsymbol{K}}^\alpha = \frac{1}{N} \sum_{\boldsymbol{q} \neq \pm\boldsymbol{q}_0} \left(\cos \frac{K_\alpha}{2} - \cos q_\alpha \right) f_{\boldsymbol{K}}(\boldsymbol{q}). \tag{1.4.18}$$

For $\boldsymbol{q} \neq \pm\boldsymbol{q}_0$, Eq. (1.4.15) becomes

$$[\hbar\omega - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q})]f_{\boldsymbol{K}}(\boldsymbol{q}) = 4J \sum_\alpha \cos q_\alpha \left(\cos \frac{K_\alpha}{2} - \cos q_0^\alpha + V_{\boldsymbol{K}}^\alpha \right) \tag{1.4.19}$$

and using Eq. (1.4.16), one obtains

$$f_{\boldsymbol{K}}(\boldsymbol{q}) = 4J \sum_\alpha \frac{\cos q_\alpha \left(\cos \frac{K_\alpha}{2} - \cos q_0^\alpha + V_{\boldsymbol{K}}^\alpha \right)}{\hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}_0) - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}) + \frac{\Delta_{\boldsymbol{K}}}{N}}. \tag{1.4.20}$$

Multiplying both sides of Eq. (1.4.20) by $(\cos \frac{K_\beta}{2} - \cos q_\beta)$ with $\beta = x, y, z$ and summing over $\boldsymbol{q}$ with the restriction $\boldsymbol{q} \neq \pm\boldsymbol{q}_0$, we obtain

$$V_{\boldsymbol{K}}^\beta = \sum_\alpha \left(\cos \frac{K_\alpha}{2} - \cos q_0^\alpha + V_{\boldsymbol{K}}^\alpha \right) M_{\alpha\beta}(\boldsymbol{K}, \boldsymbol{q}_0) \tag{1.4.21}$$

where

$$M_{\alpha\beta}(\boldsymbol{K}, \boldsymbol{q}_0) = \frac{4J}{N} \sum_{\boldsymbol{q} \neq \pm\boldsymbol{q}_0} \frac{\cos q_\alpha \left(\cos \frac{K_\beta}{2} - \cos q_\beta \right)}{\hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}_0) - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}) + \frac{\Delta_{\boldsymbol{K}}}{N}}. \tag{1.4.22}$$

By the use of the matrix algebra, Eq. (1.4.21) becomes

$$V_{\boldsymbol{K}}^\alpha = \sum_{\beta\gamma} \left(\cos \frac{K_\beta}{2} - \cos q_0^\beta \right) M_{\beta\gamma} [\mathbf{1} - \mathbf{M}]_{\gamma\alpha}^{-1}. \tag{1.4.23}$$

with α, β, γ running over x, y, z. Replacing Eq. (1.4.23) into Eqs. (1.4.17) and (1.4.20), after some elementary matrix algebra, one obtains the complete solution of Eq. (1.4.15) in the case i), that is for $\omega_{\text{bottom}} < \omega < \omega_{\text{top}}$. We have

$$\hbar\omega = \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}_0) + \frac{8J}{N} \sum_{\alpha,\beta} \left(\cos \frac{K_\alpha}{2} - \cos q_0^\alpha \right) [\mathbf{1} - \mathbf{M}]_{\alpha\beta}^{-1} \cos q_0^\beta, \tag{1.4.24}$$

$$f_{\boldsymbol{K}}(\boldsymbol{q}) = 4J \sum_{\alpha\beta} \frac{\cos \frac{K_\alpha}{2} - \cos q_\alpha}{\hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}_0) - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}) + \frac{\Delta_{\boldsymbol{K}}}{N}} [\mathbf{1} - \mathbf{M}]_{\alpha\beta}^{-1} \cos q_\beta \tag{1.4.25}$$

for $\boldsymbol{q} \neq \pm\boldsymbol{q}_0$ and $f_{\boldsymbol{K}}(\pm\boldsymbol{q}_0) = N/2$ as assumed from the beginning. Strictly speaking, Eq. (1.4.24) is a self-consistent equation since $\mathbf{M}$ is function of $\Delta_{\boldsymbol{K}}/N$ as shown by Eq. (1.4.22). However, a good approximation for large N neglects $\Delta_{\boldsymbol{K}}/N$ in Eqs. (1.4.22) and (1.4.25). From Eq. (1.4.24), one sees that the energy eigenvalue of the two-spin wave complex never coincides with the sum of the energies of the two *free* spin waves as anticipated during the discussion of Eq. (1.4.15). However, the interaction energy between the two spin waves given by the second term on the right-hand side of Eq. (1.4.24) decreases as N increases and vanishes in the thermodynamic limit ($N \to \infty$) where the energy of the two-spin wave complex coincides with the sum of the energies of the two individual spin waves.

Now, we investigate the energy eigenvalue in the case ii) where the energy of the couple is outside the two-magnon band: in this case, since $\omega \neq \omega_{\boldsymbol{K}}(\boldsymbol{q})$, Equation (1.4.15) may be written as

$$f_{\boldsymbol{K}}(\boldsymbol{q}) = 4J \sum_\alpha \frac{\cos q_\alpha}{\hbar\omega - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q})} G_{\boldsymbol{K}}^\alpha \qquad (1.4.26)$$

where

$$G_{\boldsymbol{K}}^\alpha = \frac{1}{N} \sum_{\boldsymbol{q}} \left(\cos \frac{K_\alpha}{2} - \cos q_\alpha \right) f_{\boldsymbol{K}}(\boldsymbol{q}). \qquad (1.4.27)$$

Then multiplying both sides of Eq. (1.4.26) by $(\cos \frac{K_\beta}{2} - \cos q_\beta)$ and summing over $\boldsymbol{q}$, we obtain

$$G_{\boldsymbol{K}}^\beta = \sum_\alpha G_{\boldsymbol{K}}^\alpha M_{\alpha\beta}(\boldsymbol{K}, \omega) \qquad (1.4.28)$$

where

$$M_{\alpha\beta}(\boldsymbol{K}, \omega) \equiv \frac{1}{2S} B_{\alpha\beta}(\boldsymbol{K}, \omega) = \frac{4J}{N} \sum_{\boldsymbol{q}} \frac{\cos q_\alpha \left(\cos \frac{K_\beta}{2} - \cos q_\beta \right)}{\hbar\omega - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q})}. \qquad (1.4.29)$$

Equation (1.4.28) has a non-trivial solution for $G_{\boldsymbol{K}}^\alpha$ only if

$$\det\left[\mathbf{1} - \frac{1}{2S}\mathbf{B}(\boldsymbol{K}, \omega) \right] = 0. \qquad (1.4.30)$$

The roots ω_{BS} of Eq. (1.4.30) are the bound states of two spin waves and they will be discussed in detail in Chapter 5.

For a two-magnon bound state of momentum $\boldsymbol{K}$, the probability of finding two spin deviations on sites apart from a lattice vector $\boldsymbol{r} \neq 0$ is

$$\frac{1}{2} \sum_l \frac{|\langle 1_l, 1_{l+r}|\psi\rangle|^2}{\langle\psi|\psi\rangle} = 8S^2 \sum_l \frac{|f_{l,l+r}|^2}{\langle\psi|\psi\rangle} = 8S^2 F_{\boldsymbol{K}}^2(\boldsymbol{r}) \frac{N}{\langle\psi|\psi\rangle} \qquad (1.4.31)$$

and the probability of finding two spin deviations on the same site is

$$\sum_l \frac{|\langle 2_l|\psi\rangle|^2}{\langle\psi|\psi\rangle} = 4S(2S-1)\sum_l \frac{|f_{l,l}|^2}{\langle\psi|\psi\rangle} = 8S^2\left(1 - \frac{1}{2S}\right)F_{\boldsymbol{K}}^2(0)\frac{N}{\langle\psi|\psi\rangle} \qquad (1.4.32)$$

where

$$\langle\psi|\psi\rangle = 8S^2\left(1 - \frac{1}{2S}\right)F_{\boldsymbol{K}}^2(0)N + N\sum_{\boldsymbol{r}\neq 0}8S^2 F_{\boldsymbol{K}}^2(\boldsymbol{r}). \qquad (1.4.33)$$

Equations (1.4.31) and (1.4.32) are obtained from Eqs. (1.4.1) and (1.4.8) in which the sum is restricted to the selected wavevector of the bound state $\boldsymbol{K}$. The factor N comes from the sum over l and from the property that in a lattice with PBC, the functions $|f_{l,l+r}|$ depend on r but not on l, that is, they depend on the separation between the spin deviations but they are independent of the choice of the first deviation. The probability of finding two spin deviations on the same site in a bound state of momentum $\boldsymbol{K}$ is then

$$P_{\boldsymbol{K}}(0) = \frac{\left(1 - \frac{1}{2S}\right)F_{\boldsymbol{K}}^2(0)}{\left(1 - \frac{1}{2S}\right)F_{\boldsymbol{K}}^2(0) + \sum_{\boldsymbol{r}\neq 0}F_{\boldsymbol{K}}^2(\boldsymbol{r})} \qquad (1.4.34)$$

and the probability of finding two spin deviations localized at distance $\boldsymbol{r}$ with $\boldsymbol{r}\neq 0$ is

$$P_{\boldsymbol{K}}(\boldsymbol{r}) = \frac{F_{\boldsymbol{K}}^2(\boldsymbol{r})}{\left(1 - \frac{1}{2S}\right)F_{\boldsymbol{K}}^2(0) + \sum_{\boldsymbol{r}\neq 0}F_{\boldsymbol{K}}^2(\boldsymbol{r})}. \qquad (1.4.35)$$

Note that $P_{\boldsymbol{K}}(0)$ vanishes for $S = 1/2$, as expected, since for $S = 1/2$ one spin deviation corresponds to a spin reversal so that any further deviation on the same site is excluded.

1.5. Two-Spin Deviation States in a Ring

In this section, we consider a ring of N spins ($S = 1/2$) with the exchange interaction restricted to NN which is topologically equivalent to a LC with PBC. The aim of this section is to investigate the approach to thermodynamic limit ($N \to \infty$) starting from the exact solutions for finite clusters of Section 1.2. For a ring of N spins Eq. (1.4.10) becomes

$$(\hbar\omega - 2h - 4J)F_K(r) + 2J\cos\frac{K}{2}[F_K(r+1) + F_K(r-1)]$$

$$= 2J(r)\left[\cos\frac{K}{2}F_K(0) - F_K(r)\right] \qquad (1.5.1)$$

where $K = \frac{2\pi}{N}l$ with $l = 0, 1, \ldots, N-1$. The symmetry rules ($f_{ij} = f_{ji}$) and the PBC ($f_{i,j+N} = f_{ij}$) lead to the relations $F_K(r) = F_K(-r)$ and $F_K(N-r) = e^{-i\frac{K}{2}N}F_K(r)$, respectively. For $r = 0$, Eq. (1.5.1) becomes

$$(2h + 4J - \hbar\omega)F_K(0) - 4J\cos\frac{K}{2}\ F_K(1) = 0. \qquad (1.5.2)$$

For $r = 1$, Equation (1.5.1) becomes

$$(2h + 2J - \hbar\omega)F_K(1) - 2J\cos\frac{K}{2} F_K(2) = 0. \tag{1.5.3}$$

Assuming N is even, Eq. (1.5.1) becomes

$$(2h + 4J - \hbar\omega)F_K(r) - 2J\cos\frac{K}{2}[F_K(r-1) + F_K(r+1)] = 0 \tag{1.5.4}$$

for $2 \le r \le \frac{N}{2} - 1$ and

$$(2h + 4J - \hbar\omega)F_K\left(\frac{N}{2}\right) - 2J\cos\frac{K}{2}\left(1 + e^{i\frac{K}{2}N}\right) F_K\left(\frac{N}{2} - 1\right) = 0 \tag{1.5.5}$$

for $r = \frac{N}{2}$. The equations obtained from Eq. (1.5.1) for $r = \frac{N}{2} + 1, \ldots, N - 1$ can be reduced to Eqs. (1.5.3) and (1.5.4) by making use of the PBC. Equation (1.5.2) is of no physical interest because it simply gives the function $F(0)$ in terms of $F(1)$ but the probability of finding a doubly occupied site is zero when $S = 1/2$ as confirmed by Eq. (1.4.34). Notice that Eqs. (1.5.3)–(1.5.5) do not contain the unphysical amplitude $F(0)$. Then Eq. (1.5.5) gives

$$(2h + 4J - \hbar\omega)F_K\left(\frac{N}{2}\right) - 4J\cos\frac{K}{2}F_K\left(\frac{N}{2} - 1\right) = 0 \tag{1.5.6}$$

for $K = \frac{4\pi s}{N}$ with $s = 0, \pm 1, \ldots \pm (\frac{N}{4} - 1), \frac{N}{4}$ supposing N is a multiple of 4 and $F_K(\frac{N}{2}) = 0$ for $K = \pm\frac{2\pi}{N}(2s + 1)$ with $s = 0, 1, \ldots, \frac{N}{4} - 1$. Eqs. (1.5.3)-(1.5.5) can be grouped in two matrix equations given by

$$\begin{pmatrix} 2h + 2J - \hbar\omega & -2J\cos\dfrac{K}{2} & \cdots & 0 \\ -2J\cos\dfrac{K}{2} & 2h + 4J - \hbar\omega & \cdots & 0 \\ 0 & -2J\cos\dfrac{K}{2} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 2h + 4J - \hbar\omega & -2J\cos\dfrac{K}{2} \\ 0 & \cdots & -4J\cos\dfrac{K}{2} & 2h + 4J - \hbar\omega \end{pmatrix}$$

$$\times \begin{pmatrix} F_K(1) \\ F_K(2) \\ F_K(3) \\ \vdots \\ F_K\left(\dfrac{N}{2} - 1\right) \\ F_K\left(\dfrac{N}{2}\right) \end{pmatrix} = 0 \tag{1.5.7}$$

with $F_K(\frac{N}{2} + r) = F_K(\frac{N}{2} - r)$ for $K = \frac{4\pi s}{N}$ and

$$
\begin{pmatrix}
2h + 2J - \hbar\omega & -2J\cos\dfrac{K}{2} & \cdots & 0 \\[2ex]
-2J\cos\dfrac{K}{2} & 2h + 4J - \hbar\omega & \cdots & 0 \\[2ex]
0 & -2J\cos\dfrac{K}{2} & \cdots & 0 \\[2ex]
\vdots & \vdots & \ddots & \vdots \\[2ex]
0 & \cdots & -2J\cos\dfrac{K}{2} & 2h + 4J - \hbar\omega
\end{pmatrix}
$$

$$
\times \begin{pmatrix}
F_K(1) \\
F_K(2) \\
F_K(3) \\
\vdots \\
F_K\left(\dfrac{N}{2} - 1\right)
\end{pmatrix} = 0 \tag{1.5.8}
$$

with $F_K(\frac{N}{2} + r) = -F_K(\frac{N}{2} - r)$ for $K = \frac{2\pi}{N}(2s + 1)$. Note that the square matrix occurring in Eq. (1.5.7) has dimension $\frac{N}{2}$ so that it has $\frac{N}{2}$ eigenvalues while the square matrix occurring in Eq. (1.5.8) has dimension $\frac{N}{2} - 1$ so that it has $\frac{N}{2} - 1$ eigenvalues. Since the wavevector K can assume $\frac{N}{2}$ values in both Eqs. (1.5.7) and (1.5.8), the total number of eigenvalues for two-magnon excitations is $(\frac{N}{2})^2 + \frac{N}{2}(\frac{N}{2} - 1) = \frac{N(N-1)}{2}$ corresponding to the number of states with two spin deviations. For comparison, let us recall that the ground state is unique, the one-magnon states are N and the total number of states of the ring is 2^N. We find explicitly the eigenvalues of (1.5.7) and (1.5.8) for $N = 8$ and 16. For $N = 8$, we give the 28 eigenvalues in Table 1.1. As one can see, the number of eigenvalues of the two-spin wave energy is 4 for $K = 0, \pm\frac{\pi}{2}$ and π since the dimension of the square matrix occurring in Eq. (1.5.7) is 4 while the number of eigenvalues for $\pm\frac{\pi}{4}$ and $\pm\frac{3\pi}{4}$ is 3 since the dimension of the square matrix occurring in Eq. (1.5.8) is 3. The

Table 1.1.   Two-spin deviation eigenvalues for $N = 8$ spins $S = 1/2$ on a ring.

K/π	$\hbar\omega/J$
0	0, 1.50604, 4.89008, 7.60388
$\pm\dfrac{1}{4}$	0.58579, 3.12597, 6.28825
$\pm\dfrac{1}{2}$	0.94863, 2, 4.51730, 6.53407
$\pm\dfrac{3}{4}$	1.71175, 3.41421, 4.87403
1	2, 4, 4, 4

Table 1.2.   Two-spin deviation eigenvalues for $N = 16$ spins $S = 1/2$ on a ring.

K/π	$\hbar\omega/J$
0	0, 0.34582, 1.32348, 2.76393, 4.41811, 6, 7.23607, 7.91259
$\pm\dfrac{1}{8}$	0.15224, 0.81690, 2.03080, 3.58431, 5.20881, 6.62341, 7.58353
$\pm\dfrac{1}{4}$	0.28039, 0.58579, 1.49441, 2.83236, 4.36875, 5.83797, 6.98600, 7.61433
$\pm\dfrac{3}{8}$	0.63739, 1.23463, 2.27524, 3.60685, 4.99929, 6.21182, 7.03478
$\pm\dfrac{1}{2}$	0.99626, 1.30412, 2, 3.04050, 4.23691, 5.38134, 6.27568, 6.76518
$\pm\dfrac{5}{8}$	1.38294, 2.06999, 2.76537, 3.67369, 4.62711, 5.45827, 6.02263
$\pm\dfrac{3}{4}$	1.70710, 2.51511, 2.85111, 3.41421, 4.07839, 4.71858, 5.22029, 5.49520
$\pm\dfrac{7}{8}$	1.92388, 3.30209, 3.52881, 3.84776, 4.19298, 4.49803, 4.70645
1	2, 4, 4, 4, 4, 4, 4, 4

double degeneracy of the eigenvalues belonging to $\pm K \neq 0$ or π is a consequence of the parity of the cosine function. At the zone boundary $K = \pi$, all eigenvalues are degenerate except one: indeed for $K = \pi$, the matrix occurring in Eq. (1.5.7) becomes diagonal with all elements equal to $2h + 4J - \hbar\omega$ except one that is $2h + 2J - \hbar\omega$. For N=16, we give the 120 eigenvalues in Table 1.2. As one can see for $K = \frac{\pi}{4}s$ with $s = 0, \pm1, \pm2, \pm3, 4$, one has 8 eigenvalues while for $K = \pm\frac{\pi}{8}(2s + 1)$ with $s = 0, 1, 2, 3$, one has 7 eigenvalues. One can compare the eigenvalues of Table 1.2 for an assigned wavevector K with the energy of two *free* spin waves of momenta $k_1 = \frac{K}{2} + q_0$ and $k_2 = \frac{K}{2} - q_0$, given by

$$\hbar\omega_K(q_0) = 4J\left(1 - \cos\frac{K}{2}\cos q_0\right) \tag{1.5.9}$$

in which K is the momentum of the couple of the non-interacting magnons and $q_0 = \frac{2\pi}{16}l$ with $l = 0, \pm1, \pm2, \ldots, \pm7, 8$. The values $q_0 = 0$ and $q_0 = \pi$ correspond to the bottom and to the top of the two-magnon band, respectively. One can see that the energy of the two free spin waves differs from the exact eigenvalues given in Table 1.2 for two interacting spin waves except for $q_0 = \frac{K}{2}$ that occurs only for $K = \frac{\pi}{4}s$. This result is not surprising since we have seen that the interaction between spin waves prevents the states with two free spin waves to be eigenstates of the Heisenberg Hamiltonian.

   The thermodynamic limit can be easily obtained from Eqs. (1.5.3) and (1.5.4). In the limit $N \to \infty$, Eq. (1.5.4) becomes an infinite set of equations with $r \geq 2$. Two kinds of solutions can be found that satisfy this infinite set. One is of the type

$$F_K(r) = f^{r-1}F_K(1) \tag{1.5.10}$$

with $r \geq 1$ and f is a function of $\cos \frac{K}{2}$ to be determined. Note that the choice (1.5.10) reduces the infinite set (1.5.4) to the unique equation

$$\hbar\omega = 2h + 4J \left[1 - \frac{1 + f^2}{2f} \cos \frac{K}{2} \right]. \tag{1.5.11}$$

Replacing Eq. (1.5.10) into the remaining Eq. (1.5.3), one obtains

$$\hbar\omega = 2h + 2J \left[1 - f \cos \frac{K}{2} \right]. \tag{1.5.12}$$

From Eqs. (1.5.11) and (1.5.12), one finds $f = \cos \frac{K}{2}$ and the complete solution of the infinite system (1.5.3) and (1.5.4) is

$$\hbar\omega = 2h + 2J \sin^2 \frac{K}{2}, \tag{1.5.13}$$

$$F_K(r) = F_K(1) \left(\cos \frac{K}{2} \right)^{r-1} \tag{1.5.14}$$

and the probability of finding the two spin reversals at a distance r becomes

$$P_K(r) = \sin^2 \frac{K}{2} \left(\cos^2 \frac{K}{2} \right)^{r-1} = \sin^2 \frac{K}{2} \, e^{-\frac{r-1}{\xi}} \tag{1.5.15}$$

where $\xi = [-\ln(\cos^2 \frac{K}{2})]^{-1}$. The probability (1.5.15) decays exponentially with the distance r so that the maximum of probability corresponds to the case in which the two spin reversals are on NN sites. For $K \to 0$, the probability (1.5.15) reduces to $P_K(r) = \frac{1}{4}K^2 e^{-\frac{1}{4}(r-1)}$ that means the probability is spread over the whole ring. On the contrary, at the zone boundary ($K = \pi$), the probability is $P_K(1) = 1$ and $P_K(r) = 0$ for any $r \neq 1$, meaning that the spin reversals are located on NN sites.

The second solution is of the type

$$F_K(r) = A \cos(q_0 r) F_K(1) \tag{1.5.16}$$

with $r \geq 2$, where A and and q_0 are functions to be determined. Once again, the choice (1.5.16) reduces the infinite set (1.5.4) to the unique equation

$$\hbar\omega = 2h + 4J \left(1 - \cos \frac{K}{2} \cos q_0 \right) \tag{1.5.17}$$

that coincides with the energy of the two non-interacting spin waves given in Eq. (1.5.9). Replacing Eqs. (1.5.16) and (1.5.17) into the remaining Eq. (1.5.3), one obtains

$$A = \frac{2 \cos \frac{K}{2} \cos q_0 - 1}{\cos \frac{K}{2} \cos 2q_0}. \tag{1.5.18}$$

The probability of finding two spin deviations at a distance r is then

$$P_K(1) = \frac{1}{1 + A^2 \sum_{r=2}^{\infty} \cos^2(q_0 r)} \to \frac{2}{A^2 N} \quad \text{for } N \to \infty \tag{1.5.19}$$

and

$$P_K(r) = \frac{A^2 \cos^2(q_0 r)}{1 + A^2 \sum_{r=2}^{\infty} \cos^2(q_0 r)} \rightarrow \frac{2}{N} \cos^2(q_0 r) \quad \text{for} \quad N \rightarrow \infty \tag{1.5.20}$$

with $r \geq 2$. The limit for $N \rightarrow \infty$ is obtained from the relationship

$$\frac{1}{N} \sum_{r=2}^{N} \cos^2(q_0 r) = \frac{1}{2} - \frac{1}{N} \cos^2 q_0. \tag{1.5.21}$$

As one can see from Eq. (1.5.20), the probability is ocsillating and no longer undergoes exponential decay like the first solution. It decreases as N increases, indicating that the two deviations may be found at any distance with very small probability, in agremeent with a couple of delocalized deviations. The set of eigenvalues given in Eq. (1.5.17) with arbitrary q_0 confirms that this state corresponds to free spin wave whose energy is inside the two-magnon band $0 < q_0 < \pi$, in agreement with the expectation that in the thermodynamic limit, the eigenvalues with energy inside the two-magnon band are just the eigenvalues of two free spin waves.

In Fig. 1.5, we show the energy eigenvalues of a ring with $N = 8$ (crosses) corresponding to the numerical values of Table 1.1 and a ring with $N = 16$ (full circles) corresponding to the numerical values of 1.2. The continuous curve is the thermodynamic limit result given by Eq. (1.5.13) with $h = 0$. The scenario is clearer for K near the zone boundary where the two-magnon band becomes narrower and reduces to a point at $K = \pi$. Indeed for a finite system, the eigenvalues belonging to a fixed wavevector K group together within the two-magnon band delimited
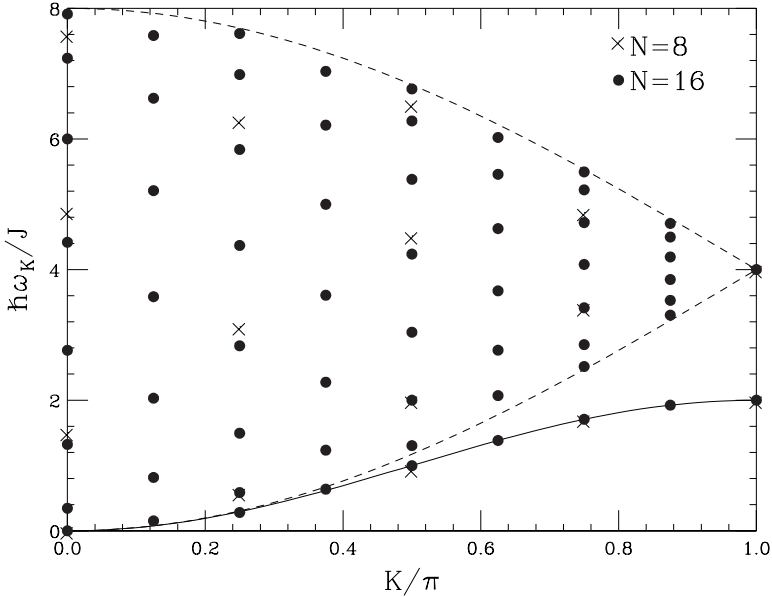

Fig. 1.5. Two spin wave energy $\hbar\omega/J$ versus K/π for a ring of 8 (crosses) and 16 (full circle) spins $S = 1/2$. Dashed curves are the top and the bottom of the two-magnon band. Continuous curve is the bound state in the thermodynamic limit.

by the dashed lines shown in Fig. 1.5 except one eigenvalue that remains well below the band: this "isolated" eigenvalue approaches the two-magnon "bound state" in the thermodynamic limit (continuous curve).

It may be interesting to obtain the results shown in Fig. 1.5 which are given numerically in Tables 1.1 and 1.2 in a different way. Let us come back to Eq. (1.5.1): multiply both sides by e^{-iqr} (with $q = \frac{2\pi}{N}l$ and $l = 0, 1, \ldots, N-1$) and sum over r (with $r = 1, 2, \ldots, N-1$). We obtain

$$\left[\hbar\omega - 2h - 4J\left(1 - \cos\frac{K}{2}\cos q\right)\right]\sum_{r=1}^{N-1}F_K(r)e^{-iqr}$$

$$= 2J\left[\cos\frac{K}{2}\left(1 + e^{-i\frac{K}{2}N}\right) - \left(e^{-iq} + e^{iq}e^{-i\frac{K}{2}N}\right)\right]F_K(1). \quad (1.5.22)$$

The Fourier transforms (1.4.11) and (1.4.12) for the present 1D case reduce to

$$F_K(r) = \frac{1}{N}\sum_q e^{iqr}f_K(q) \quad (1.5.23)$$

and

$$f_K(q) = \sum_r e^{-iqr}F_K(r). \quad (1.5.24)$$

Equation (1.5.22) becomes

$$\left[\hbar\omega - 2h - 4J\left(1 - \cos\frac{K}{2}\cos q\right)\right]f_K(q)$$

$$= 4J\left(\cos\frac{K}{2} - \cos q\right)\frac{1}{N}\sum_{q'}e^{iq'}f_K(q') \quad (1.5.25)$$

for $K = \frac{4\pi}{N}s$ and

$$\left[\hbar\omega - 2h - 4J\left(1 - \cos\frac{K}{2}\cos q\right)\right]f_K(q) = 4iJ\sin q\frac{1}{N}\sum_{q'}e^{iq'}f_K(q') \quad (1.5.26)$$

for $K = \frac{2\pi}{N}(2s+1)$.

For $K = \frac{4\pi}{N}s$, one has the symmetry properties $F_K(N-r) = F_K(r)$ and $f_K(q) = f_K(2\pi - q)$ so that Eq. (1.5.25) becomes

$$\left(x + \cos\frac{K}{2}\cos\frac{2\pi}{N}l\right)f_K\left(\frac{2\pi}{N}l\right) = 4J\left(\cos\frac{K}{2} - \cos\frac{2\pi}{N}l\right)V_K \quad (1.5.27)$$

where

$$\hbar\omega = 2h + 4J(1+x) \quad (1.5.28)$$

and

$$V_K = \frac{1}{N}\left[f_K(0) - f_K(\pi) + 2\sum_{l=1}^{\frac{N}{2}-1}f_K\left(\frac{2\pi}{N}l\right)\cos\frac{2\pi}{N}l\right]. \quad (1.5.29)$$

For $K = \frac{2\pi}{N}(2s+1)$, one has the symmetry properties $F_K(N-r) = -F_K(r)$ and $f_K(q) = -f_K(2\pi - q)$ so that Eq. (1.5.26) becomes

$$\left(x + \cos\frac{K}{2} \cos\frac{2\pi}{N} l \right) f_K\left(\frac{2\pi}{N} l \right) = 4J\, W_K \sin\frac{2\pi}{N} l \qquad (1.5.30)$$

where

$$W_K = \frac{2}{N} \sum_{l=1}^{\frac{N}{2}-1} f_K\left(\frac{2\pi}{N} l \right) \sin\frac{2\pi}{N} l. \qquad (1.5.31)$$

A "trivial" solution of Eq. (1.5.27) is obtained for $\frac{K}{2} = \frac{4\pi}{N} l$, that is, for $l = s$; the solution is

$$x = -\cos^2\frac{K}{2}. \qquad (1.5.32)$$

Note that Eq. (1.5.32) leads to the energy (1.5.9) of two non interacting spin waves with $q_0 = \frac{K}{2}$. This is a direct consequence of Eq. (1.5.25) where the interaction between the spin waves vanishes for $q = \frac{K}{2}$.

All the other solutions of Eq. (1.5.27) may be obtained as follows: for $x \neq -\cos\frac{K}{2} \cos\frac{2\pi}{N} l$, Equation (1.5.27) may be written as

$$f_K\left(\frac{2\pi}{N} l \right) = \frac{\cos\frac{K}{2} - \cos\frac{2\pi}{N} l}{x + \cos\frac{K}{2} \cos\frac{2\pi}{N} l} V_K. \qquad (1.5.33)$$

After having multiplied both sides of Eq. (1.5.33) by $\cos\frac{2\pi}{N} l$, performing the summation over l and using the relationship (1.5.29), one obtains

$$[1 - M(K,x)]V_K = 0 \qquad (1.5.34)$$

where

$$M(K,x) = \frac{2}{N}\left[\frac{\cos^2\frac{K}{2} + x}{\cos^2\frac{K}{2} - x^2} + \sum_{l=1}^{\frac{N}{2}-1} \frac{\cos\frac{2\pi}{N} l \left(\cos\frac{K}{2} - \cos\frac{2\pi}{N} l \right)}{\cos\frac{K}{2} \cos\frac{2\pi}{N} l + x} \right]. \qquad (1.5.35)$$

The solutions of Eq. (1.5.34) are the zeros of the function $[1 - M(K,x)]$. For $K = \pi$ ($s = N/2$), the solution (1.5.32) gives $x = 0$ while Eq. (1.5.35) reduces to $M(\pi, x) = -\frac{1}{2x}$ when making use of the identity[3] $\sum_{l=1}^{N/2-1} \cos^2\frac{2\pi}{N} l = \frac{N}{4} - 1$ so that Eq. (1.5.34) has only one zero for $x = -\frac{1}{2}$. Then, from Eq. (1.5.28) one has $\hbar\omega = 2h + 4J$ and $2h + 2J$ for $x = 0$ and $x = -\frac{1}{2}$, respectively, reflecting the property that at zone boundary, a bound state exists below the two-magnon band, the width of which is reduced to a single point as shown in Fig. 1.5. For $K \neq \pi$, the function $[1 - M(K,x)]$ is characterized by vertical asymptotes at $x = -\cos\frac{K}{2} \cos\frac{2\pi}{N} l$ for $l = 0, 1, \ldots, \frac{N}{2}$ with exclusion of $\frac{2\pi}{N} l = \frac{K}{2}$ and $l = \frac{N}{4}$ for which the vanishing of the numerators in the sum of Eq. (1.5.35) prevents any divergence. Fig. 1.6 shows the function $(1 - M)$ for $N = 16$ and $K = \frac{\pi}{4}$. Qualitatively, similar plots are obtained for $K = \frac{\pi}{4}s$ with $s = 0, 1, 2, 3$. On the contrary, for $s = 4$ ($K = \pi$), the function $[1 - M(\pi, x)]$ reduces to the hyperbola $1 + \frac{1}{2x}$. To recover all the solutions of Eq. (1.5.27), the solution
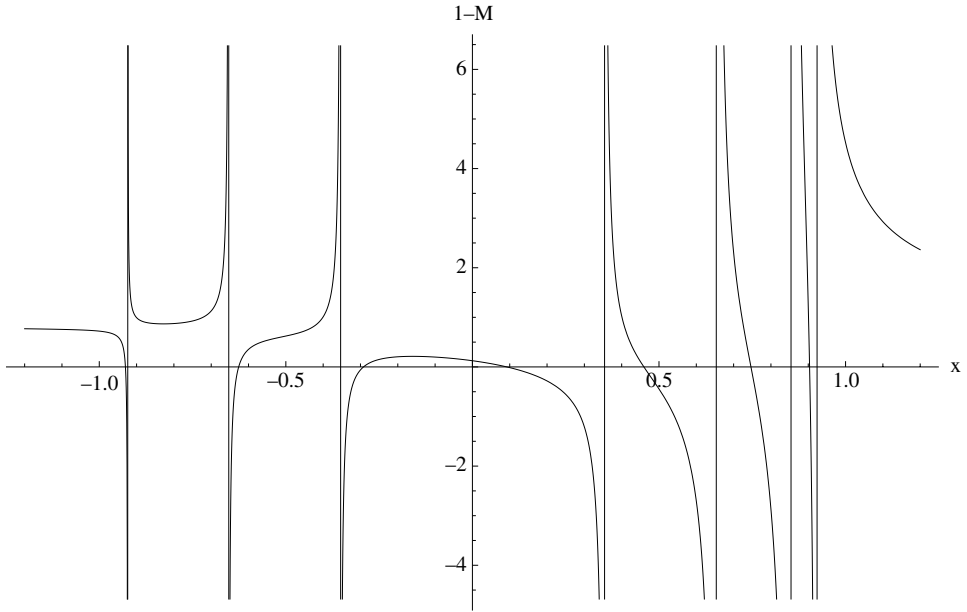
Fig. 1.6. $[1 - M(K, x)]$ vs x for $N = 16$ and $K = \frac{\pi}{4}$.

$x = -\cos^2 \frac{\pi}{8}$ obtained from Eq. (1.5.32) has to be taken into account. By means of similar steps, Eq. (1.5.30) leads to the equation

$$[1 + R(K, x)]W_K = 0 \tag{1.5.36}$$

where

$$R(K, x) = \frac{2}{N} \sum_{l=1}^{\frac{N}{2}-1} \frac{\sin^2 \frac{2\pi}{N}l}{\cos \frac{K}{2} \cos \frac{2\pi}{N}l + x}. \tag{1.5.37}$$

The solutions of Eq. (1.5.36) are the zeros of the function $[1 + R(K, x)]$ shown in Fig. 1.7 for $N = 16$ and $K = \frac{3\pi}{8}$. Like $(1 - M)$ also $(1 + R)$ is characterized by vertical asymptotes at $x = -\cos \frac{K}{2} \cos \frac{\pi}{8}l$ with $l = 1, \ldots, 7$ and goes to 1 for $x \to \pm\infty$. The zeros of the function $(1 - M)$ shown in Fig. 1.6 and those of the function $(1 + R)$ shown in Fig. 1.7 lead to energies that coincide with the third $(K = \pm\frac{\pi}{4})$ and fourth line $(K = \pm\frac{3\pi}{8})$ of Table 1.2 for $h = 0$. Obviously, all the energy eigenvalues of Table 1.2 are recovered by evaluating the solutions of the equation $[1 - M(K, x)] = 0$ for $K = \frac{\pi}{4}s$ with $s = 0, 1, 2, 3, 4$ and of the equation $[1 + R(K, x)] = 0$ for $K = \frac{\pi}{8}(2s + 1)$ with $s = 0, 1, 2, 3$ and using the relationship $\hbar\omega = 4J(1 + x)$. Of course, for $K = \frac{\pi}{4}s$, one more solution given by $x = -\cos^2 \frac{K}{2}$ has to be accounted for.

One can see that the number of zeros of Eqs. (1.5.34) and (1.5.36) increases as N increases. Even though a numerical evaluation of the zeros is in order, we can deduce some important restrictions about the locations of the zeros of the functions
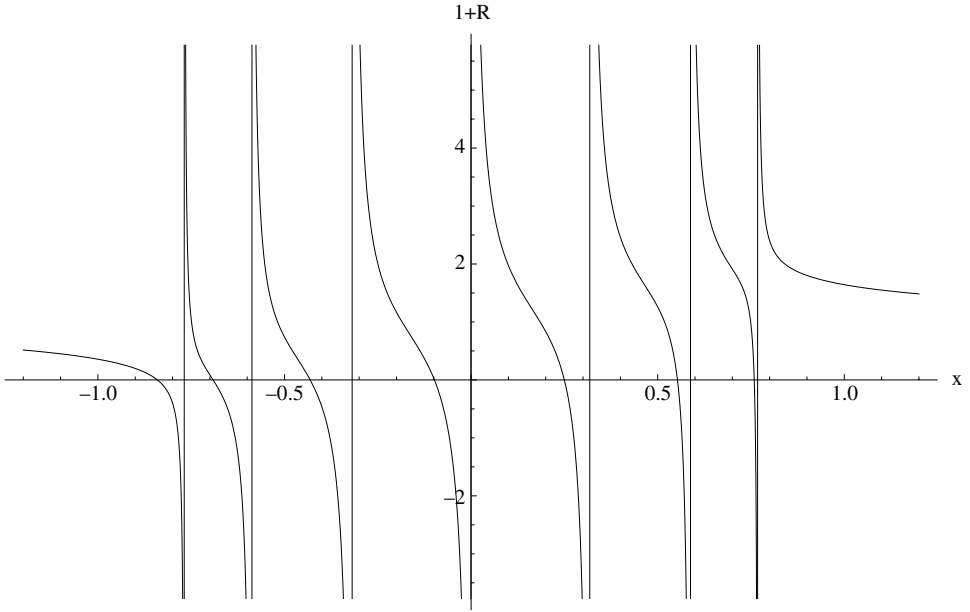
Fig. 1.7. $[1 + R(K, x)]$ vs x for $N = 16$ and $K = \frac{3\pi}{8}$.

$(1 - M)$ and $(1 + R)$. For a fixed value of $K = \frac{4\pi}{N}s$, the solutions of Eq. (1.5.27) are subject to the following unequalities

$$x_0 \leq -\cos \frac{2\pi}{N}s, \tag{1.5.38}$$

$$-\cos\left(\frac{2\pi}{N}s\right)\cos\frac{2\pi}{N}(l-1) < x_l < -\cos\left(\frac{2\pi}{N}s\right)\cos\frac{2\pi}{N}l \tag{1.5.39}$$

for $0 < l < s$,

$$x_s = -\cos^2\frac{2\pi}{N}s \tag{1.5.40}$$

for $l = s$ and

$$-\cos\left(\frac{2\pi}{N}s\right)\cos\frac{2\pi}{N}l < x_l < -\cos\left(\frac{2\pi}{N}s\right)\cos\frac{2\pi}{N}(l+1) \tag{1.5.41}$$

for $s < l \leq \frac{N}{2} - 1$.

Analogously, for a fixed value of $K = \frac{2\pi}{N}(2s + 1)$, the solutions of Eq. (1.5.30) are subject to the following unequalities

$$x_0 \leq -\cos\frac{2\pi}{N}(2s+1), \tag{1.5.42}$$

$$-\cos\left[\frac{2\pi}{N}(2s+1)\right]\cos\frac{2\pi}{N}l < x_l < \cos\left[\frac{2\pi}{N}(2s+1)\right]\cos\frac{2\pi}{N}(l+1) \tag{1.5.43}$$

for $0 < l \leq \frac{N}{2} - 2$.

The inequalities (1.5.38) and (1.5.42) show that the lowest solution (x_0) is always on the left of the first asymptote since $x_0 < -\cos\frac{K}{2}$ and corresponds to the bound state: $x_0 = x_{\mathrm{BS}}$. The location of x_0 is approximately independent of N and it remains well apart from all the other zeros that accumulate as N increases within the two-magnon band $-\cos\frac{K}{2} < x_l < \cos\frac{K}{2}$. More specifically, the inequalities (1.5.39), (1.5.41) and (1.5.43) imply that for large N,

$$x_l \to -\cos\frac{K}{2}\cos\frac{2\pi}{N}l \qquad (1.5.44)$$

leading to the energy (1.5.17) corresponding to the energy of two free spin waves.

For comparison with the exact results obtained by solving Eqs. (1.5.34) and (1.5.36), we give the first-order results obtained by strictly following the steps of Section 1.4. The first-order solutions of Eqs. (1.5.27) and (1.5.30) are obtained after replacing x by $-\cos q_0 \cos\frac{K}{2} + \frac{\Delta_K}{N}$ and neglecting $\frac{\Delta_K}{N}$ in the denominators of $f_K(q)$, $M(K, q_0)$ and $R(K, q_0)$. For $K = \frac{4\pi}{N}s$, one has $f_K(q_0) = \frac{N}{2}$ and

$$f_K^{(1)}(q) = \frac{\cos\frac{K}{2} - \cos q}{\cos\frac{K}{2}(\cos q - \cos q_0)}\frac{\cos q_0}{1 - M^{(1)}(K, q_0)} \qquad (1.5.45)$$

for $q \neq q_0$, where

$$M^{(1)}(K, q_0) = \frac{2}{N}\left[\frac{\cos\frac{K}{2} - \cos q_0}{\cos\frac{K}{2}\sin^2 q_0} + \sum_{q \neq q_0}\frac{\cos q\left(\cos\frac{K}{2} - \cos q\right)}{\cos\frac{K}{2}(\cos q - \cos q_0)}\right]. \qquad (1.5.46)$$

The first-order correction to the energy of the two free spin waves becomes

$$\Delta_K^{(1)} = 8J\left(\cos\frac{K}{2} - \cos q_0\right)\frac{\cos q_0}{1 - M^{(1)}(K, q_0)}. \qquad (1.5.47)$$

For $K = \frac{2\pi}{N}(2s + 1)$, one has $f_K(q_0) = \frac{N}{2}$ and

$$f_K^{(1)}(q) = -\frac{\sin q \sin q_0}{\cos\frac{K}{2}(\cos q - \cos q_0)}\frac{\cos q_0}{1 + R^{(1)}(K, q_0)} \qquad (1.5.48)$$

for $q \neq q_0$, where

$$R^{(1)}(K, q_0) = \frac{2}{N}\sum_{q \neq q_0}\frac{\sin^2 q}{\cos\frac{K}{2}(\cos q - \cos q_0)}. \qquad (1.5.49)$$

The first-order correction to the energy becomes

$$\Delta_K^{(1)} = -8J\frac{\sin^2 q_0}{1 + R^{(1)}(K, q_0)}. \qquad (1.5.50)$$

Let us perform the sums over q in Eqs. (1.5.46) and (1.5.49) for large N. Let us begin with the sum of Eq. (1.5.46). The first term on the right hand-side can be neglected because it is multiplied by a factor $\frac{2}{N}$ and the sum over q with $q \neq q_0$

reduces to the principal value of the corresponding integral. Indeed, for large N, defining $\epsilon = \frac{2\pi}{N}$ and noticing that $\Delta q = \frac{2\pi}{N}$, Eq. (1.5.46) becomes

$$
\begin{aligned}
M^{(1)}(K, q_0) &= \frac{1}{\pi} \int_0^{q_0 - \epsilon} dq \frac{\cos q \left(\cos \frac{K}{2} - \cos q\right)}{\cos \frac{K}{2}(\cos q - \cos q_0)} \\
&\quad + \frac{1}{\pi} \int_{q_0 + \epsilon}^{\pi} dq \frac{\cos q \left(\cos \frac{K}{2} - \cos q\right)}{\cos \frac{K}{2}(\cos q - \cos q_0)} \\
&\equiv \frac{P}{\pi} \int_0^{\pi} dq \frac{\cos q \left(\cos \frac{K}{2} - \cos q\right)}{\cos \frac{K}{2}(\cos q - \cos q_0)} = 1 - \frac{\cos q_0}{\cos \frac{K}{2}}
\end{aligned}
\qquad (1.5.51)
$$

where P (principal value) makes the integral in Eq. (1.5.51) convergent.[3] In a similar way, for large N, Eq. (1.5.49) reduces to

$$
R^{(1)}(K, q_0) = \frac{P}{\pi} \int_0^{\pi} dq \frac{\sin^2 q}{\cos \frac{K}{2}(\cos q - \cos q_0)} = -\frac{\cos q_0}{\cos \frac{K}{2}}. \qquad (1.5.52)
$$

Replacing Eqs. (1.5.51) and (1.5.52) into Eqs. (1.5.47) and (1.5.50) respectively, the first-order energy of the two interacting spin waves of momenta $k_1 = \frac{K}{2} + q_0$ and $k_2 = \frac{K}{2} - q_0$ is given by

$$
\hbar\omega = 4J \left(1 - \cos \frac{K}{2} \cos q_0\right) + \frac{8J}{N} \cos \frac{K}{2} \left(\cos \frac{K}{2} - \cos q_0\right) \qquad (1.5.53)
$$

for $K = \frac{4\pi}{N}s$ and

$$
\hbar\omega = 4J \left(1 - \cos \frac{K}{2} \cos q_0\right) - \frac{8J}{N} \frac{\cos \frac{K}{2} \sin^2 q_0}{\cos \frac{K}{2} - \cos q_0} \qquad (1.5.54)
$$

for $K = \frac{2\pi}{N}(2s+1)$. Note that Eq. (1.5.53) can be obtained directly from Eq. (1.4.24) while Eq. (1.5.54) has no analogous in Section 1.4. This comes from the finite nature of the ring: indeed, from Eq. (1.4.10), one obtains the two equations (1.5.25) and (1.5.26) according to $K = \frac{4\pi}{N}s$ or $K = \frac{2\pi}{N}(2s+1)$. In the same way, from Eq. (1.4.10), one should obtain different equations for finite N according to $K_\alpha = \frac{4\pi}{L_\alpha}s_\alpha$ or $K_\alpha = \frac{2\pi}{L_\alpha}(2s_\alpha + 1)$ with $\alpha = x, y, z$ and $L_x L_y L_z = N$. However, in view of the thermodynamic limit, the effect of the distinction between the different choice of $\boldsymbol{K}$ becomes irrelevant so that in Section 1.4, we have performed the calculation for a generic $\boldsymbol{K} = 2\pi(\frac{l_x}{L_x}, \frac{l_y}{L_y}, \frac{l_z}{L_z})$ that for $l_\alpha = 0, 1, \ldots, L_\alpha - 1$, recovers all possible wavevectors leading to Eq. (1.4.15).

Another discrepancy appears when the first-order results given by Eqs. (1.5.53) and (1.5.54) are compared to the exact results obtained from the equations $[1 - M(\frac{4\pi}{N}s, x)] = 0$ and $[1 + R(\frac{2\pi}{N}(2s+1), x)] = 0$: we have seen that the number of the exact energy eigenvalues is $\frac{N(N-1)}{2}$ which correspond to the number of ways of putting a couple of spin deviations on two different sites. On the contrary, the first-order result leads to $\frac{N^2}{2}$ possible solutions. Also, this discrepancy disappears in the thermodynamic limit.

To conclude, in the study of the ring, we evaluate explicitly the bound state solution $x_0 < -\cos\frac{K}{2}$ for large N where the sums can be replaced by integrals. For $K = \frac{4\pi}{N}s$, the bound state is obtained from the solution of the equation $[1 - M(K, x)] = 0$ where

$$M(K, x) = \frac{1}{\pi} \int_0^\pi \frac{\cos q \left(\cos\frac{K}{2} - \cos q\right)}{x + \cos\frac{K}{2}\cos q} = \left(1 + \frac{x}{\cos^2\frac{K}{2}}\right)[1 - xI_0(K, x)] \quad (1.5.55)$$

with

$$I_0(K, x) = \frac{1}{\pi} \int_0^\pi \frac{1}{x + \cos\frac{K}{2}\cos q}. \quad (1.5.56)$$

For $K = \frac{2\pi}{N}(2s + 1)$, the bound state is obtained from the solution of the equation $[1 + R(K, x)] = 0$ where

$$R(K, x) = \frac{1}{\pi} \int_0^\pi \frac{\sin^2 q}{x + \cos\frac{K}{2}\cos q} = \left(1 - \frac{x^2}{\cos^2\frac{K}{2}}\right)I_0(K, x) + \frac{x}{\cos^2\frac{K}{2}}. \quad (1.5.57)$$

Replacing Eq. (1.5.55) into the equation $[1 - M(K, x)] = 0$ and Eq. (1.5.57) into the equation $[1 + R(K, x)] = 0$ and making use of the relationship[3]

$$I_0(K, x) = -\frac{1}{\sqrt{x^2 - \cos^2\frac{K}{2}}} \quad (1.5.58)$$

which is true for $x < -\cos\frac{K}{2}$, one finds the same solution for both equations, that is

$$x = -\frac{1}{2}\left(1 + \cos^2\frac{K}{2}\right) \quad (1.5.59)$$

leading to

$$\hbar\omega_{\mathrm{BS}} = 2h + 2J\sin^2\frac{K}{2} \quad (1.5.60)$$

that coincides with the bound state energy given by Eq. (1.5.13).

1.6. Spin Waves in Classical Mechanics

In this section, we will study the classical version of the spin waves that is the classical counterpart of the quantum spin waves obtained in the previous section. As for the theory of small oscillations in solids that leads to the classical normal modes or phonons in quantum mechanics, the classical spin waves may be seen as rotations of the spin vectors around the direction of the external magnetic field with a frequency which is the spin wave frequency. The spin vector at each lattice site sweeps the surface of a cone with a small apex angle with the same frequency and a phase difference constant, depending on the distance between the spins considered. These collective excitations are named spin waves or magnons and represent the magnetic normal modes of a ferromagnet while the phonons represent the vibrational normal modes of an elastic medium. First of all, let us replace the spin operators by usual

angular momentum vectors $\hbar \boldsymbol{S}_j$ and assume that the magnetic moment localized on site j is proportional to the angular momentum on that site, that is $\boldsymbol{\mu}_j = g\mu_B \boldsymbol{S}_j$. The effective magnetic field experienced by the magnetic moment on the site j is the sum of the external magnetic field and the effective field due to the exchange interaction with the NN magnetic moments

$$\boldsymbol{H}_{\text{tot}} = \boldsymbol{H} + \boldsymbol{H}_j = \boldsymbol{H} + \frac{2J}{g\mu_B} \sum_{\delta} \boldsymbol{S}_{j+\delta}. \tag{1.6.1}$$

The Hamiltonian of a magnetic moment in the presence of a magnetic field is given by $-\boldsymbol{\mu}_j \cdot \boldsymbol{H}_{\text{tot}}$. If we extend the sum over all the lattice sites, we obtain

$$\mathcal{H} = -\sum_j \boldsymbol{\mu}_j \cdot \left[\boldsymbol{H} + \frac{1}{2}\boldsymbol{H}_j \right] = -g\mu_B \boldsymbol{H} \cdot \sum_j \boldsymbol{S}_j - J \sum_{i,\delta} \boldsymbol{S}_j \cdot \boldsymbol{S}_{i+\delta} \tag{1.6.2}$$

where the factor $\frac{1}{2}$ is necessary to avoid a double counting of the interaction with the effective field due to the NN moments. The torque equation of the classical mechanics is then

$$\frac{d}{dt} \left(\hbar \boldsymbol{S}_j \right) = \boldsymbol{\mu}_j \times \boldsymbol{H}_{\text{tot}}. \tag{1.6.3}$$

Using Eq. (1.6.1), the torque equation becomes

$$\frac{d\boldsymbol{S}_j}{dt} = \frac{g\mu_B}{\hbar} \boldsymbol{S}_j \times \boldsymbol{H} + \frac{2J}{\hbar} \sum_{\delta} \boldsymbol{S}_j \times \boldsymbol{S}_{j+\delta}. \tag{1.6.4}$$

Supposing that the external magnetic field is directed along the z-axis, the vector equation (1.6.4) reduces the three scalar equations

$$\frac{dS_j^x}{dt} = \frac{g\mu_B}{\hbar} S_j^y H + \frac{2J}{\hbar} \left[S_j^y \sum_{\delta} S_{j+\delta}^z - S_j^z \sum_{\delta} S_{j+\delta}^y \right], \tag{1.6.5}$$

$$\frac{dS_j^y}{dt} = -\frac{g\mu_B}{\hbar} S_j^x H - \frac{2J}{\hbar} \left[S_j^x \sum_{\delta} S_{j+\delta}^z - S_j^z \sum_{\delta} S_{j+\delta}^x \right], \tag{1.6.6}$$

$$\frac{dS_j^z}{dt} = \frac{2J}{\hbar} \left[S_j^x \sum_{\delta} S_{j+\delta}^y - S_j^y \sum_{\delta} S_{j+\delta}^x \right]. \tag{1.6.7}$$

Assuming that each spin makes a precession motion around the direction of the external magnetic field, one may writes its components as follows

$$S_j^x = u \, \cos(\boldsymbol{k} \cdot \boldsymbol{r}_j - \omega t), \tag{1.6.8}$$

$$S_j^y = u \, \sin(\boldsymbol{k} \cdot \boldsymbol{r}_j - \omega t) \tag{1.6.9}$$

and

$$S_j^z = \sqrt{S^2 - u^2}. \tag{1.6.10}$$

It is direct to prove that Eqs. (1.6.8)–(1.6.10) are solutions of Eqs. (1.6.5)–(1.6.7) for any u, provided that

$$\hbar\omega = g\mu_B H + 2J\sqrt{S^2 - u^2} \sum_{\delta} (1 - \cos \boldsymbol{k} \cdot \boldsymbol{\delta}). \tag{1.6.11}$$

The solution (1.6.8)–(1.6.11) corresponds to a precession of each magnetic moment about the z-axis sweeping the surface of a cone of height $\sqrt{S^2 - u^2}$ and apex angle $\alpha = \arctan \frac{u}{S}$. The point of the vector $\boldsymbol{S}_i$ describes a uniform circular motion along the circumference of radius u in a period $T = \frac{2\pi}{\omega}$. The magnetic moments located on the sites $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ have a constant phase difference given by $\theta = \boldsymbol{k} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j)$. The wavevectors $\boldsymbol{k}$ are determined by the PBC and by the lattice structure: their domain is extended over the first Brillouin zone (BZ) of the reciprocal lattice. In classical mechanics, the arbitrary value of u is fixed by the initial conditions. As one can see from Eq. (1.6.11), the precession frequency coincides with the quantum spin wave frequency given in Eq. (1.3.21) if u is small compared to S. A complete solution of the system of differential equations (1.6.5)–(1.6.7) may be obtained, neglecting terms proportional to u^2. This approximation implies that $S_i^z \simeq S$ and Eq. (1.6.7) is identically satisfied; Eqs. (1.6.5) and (1.6.6) become

$$\frac{dS_j^x}{dt} = \frac{g\mu_B}{\hbar} S_j^y H + \frac{2JS}{\hbar} \sum_{\boldsymbol{\delta}} (S_j^y - S_{j+\boldsymbol{\delta}}^y) \tag{1.6.12}$$

and

$$\frac{dS_j^y}{dt} = -\frac{g\mu_B}{\hbar} S_j^x H - \frac{2JS}{\hbar} \sum_{\boldsymbol{\delta}} (S_j^x - S_{j+\boldsymbol{\delta}}^x), \tag{1.6.13}$$

respectively. The general solution of Eqs. (1.6.12)–(1.6.13) is a superposition of normal modes given by

$$S_j^x = \sum_{\boldsymbol{k}} u_{\boldsymbol{k}} \cos(\boldsymbol{k} \cdot \boldsymbol{r}_j - \omega_{\boldsymbol{k}} t) \tag{1.6.14}$$

and

$$S_j^y = \sum_{\boldsymbol{k}} u_{\boldsymbol{k}} \sin(\boldsymbol{k} \cdot \boldsymbol{r}_j - \omega_{\boldsymbol{k}} t) \tag{1.6.15}$$

that looks like the superposition of the normal modes of a vibrating crystal in harmonic approximation.

1.7. Heisenberg Hamiltonian for Actual Compounds

The Hamiltonian (1.2.5) is the simplest Hamiltonian for an isotropic insulating ferromagnet. The most part of the theory of magnetism is based on the Hamiltonian (1.2.5) even though actual compounds cannot be described by a so simple Hamiltonian. For instance, in the transition metals like iron (Fe), cobalt (Co) or nikel (Ni) which are characterized by ions having an incomplete $3d$-shell, the effect of the conduction electrons is non-negligible. The interaction between the conduction electrons and the magnetic moments of the localized ions may be described by an effective exchange interaction not restricted to NN spins known as RKKY interaction[8] from the initials of the names of the proposers: Ruderman, Kittel, Kasuya, Yosida. These

authors used a second-order perturbation theory to describe the "indirect exchange coupling". The mechanism consists of the polarization by a localized magnetic ion of the conduction electrons which in their turn, interact with other magnetic ions of the lattice, leading to an effective long-range interaction between the localized magnetic moments. An analogous approach is used to obtain the spin waves in rare earths like europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho) and erbium (Er) where the magnetic ions are characterized by an incomplete $4f$-shell. For such elements, the Hamiltonian (1.2.5) is used with exchange integrals not restricted to NN but chosen to fit experimental data.[9]

The low temperature behaviour of some actual compounds is successfully described, adding anisotropic terms to the isotropic Hamiltonian (1.2.5). Typical anisotropic contributions to the spin Hamiltonian of a ferromagnet are the single-ion and exchange terms. The single-ion anisotropy due to the effect of a crystal field is described by the Hamiltonian

$$\mathcal{H}_D = -D \sum_i (S_i^z)^2. \tag{1.7.1}$$

This type of anisotropy forces the spins along the z "easy-axis" for $D > 0$ or into the xy "easy-plane" for $D < 0$. The simplest two-ion anisotropy is the exchange anisotropy described by the Hamiltonian

$$\mathcal{H}_K = -\sum_{i,\boldsymbol{\delta}} K \; S_i^z S_{i+\boldsymbol{\delta}}^z \tag{1.7.2}$$

that favours an alignement of the spins along z for $K > 0$ (Ising-like symmetry) or a planar configuration for $K < 0$ (XY-like symmetry). The anisotropy contributions (1.7.1) and (1.7.2) may be grouped together into the anisotropic Hamiltonian

$$\mathcal{H} = -\sum_{i,\boldsymbol{\delta}} \left[J^z \; S_i^z S_{i+\boldsymbol{\delta}}^z + \frac{1}{2} J^\perp (S_i^+ S_{i+\boldsymbol{\delta}}^- S_i^- S_{i+\boldsymbol{\delta}}^+) \right]$$
$$- D \sum_i (S_i^z)^2 - h \sum_i S_i^z \tag{1.7.3}$$

where $h = g\mu_B H$, $J^z = J + K$ and $J^\perp = J$. For easy-axis ferromagnets ($D > 0$ and $J^z > J^\perp > 0$), the spin wave spectrum (1.3.21) becomes

$$\hbar\omega_{\boldsymbol{k}} = h + D(2S - 1) + 2J^z S \sum_{\boldsymbol{\delta}} \left(1 - \frac{J^\perp}{J^z} \cos \boldsymbol{k} \cdot \boldsymbol{\delta} \right). \tag{1.7.4}$$

As one can see from Eq. (1.7.4), the external magnetic field and the easy-axis single-ion anisotropy shift the spin wave spectrum upwards by an amount which is the same for any wavevector. On the contrary, the upwards shift caused by the exchange anisotropy is $\boldsymbol{k}$-dependent: its amount goes from a minimum $2J^z S \sum_{\boldsymbol{\delta}} (1 - J^\perp/J^z)$ at the zone centre to a maximum $2J^z S \sum_{\boldsymbol{\delta}} (1 + J^\perp/J^z)$ at the zone corner (ZC) $\boldsymbol{k} \cdot \boldsymbol{\delta} = \pi$. Replacing the Hamiltonian (1.3.8) by the anisotropic Hamiltonian (1.7.3),

Equation (1.4.10) for the two-spin waves energy, becomes

$$[\hbar\omega - 2h - 2D(2S-1) - 4zJ^z S]F_{\boldsymbol{K}}(\boldsymbol{r}) + 4J^{\perp}S\sum_{\boldsymbol{\delta}} e^{i\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{\delta}}F_{\boldsymbol{K}}(\boldsymbol{r}+\boldsymbol{\delta})$$

$$= \left[2J^{\perp}(\boldsymbol{r})\cos\left(\frac{\boldsymbol{K}}{2}\cdot\boldsymbol{r}\right) - 2D\delta_{\boldsymbol{r},0}\right]F_{\boldsymbol{K}}(0) - 2J^z(\boldsymbol{r})F_{\boldsymbol{K}}(\boldsymbol{r}) \tag{1.7.5}$$

and Eq. (1.4.15) for the "cubic lattices" becomes

$$[\hbar\omega - \hbar\omega_{\boldsymbol{K}}(\boldsymbol{q})]f_{\boldsymbol{K}}(\boldsymbol{q}) = 2D\frac{1}{N}\sum_{\boldsymbol{q}'} f_{\boldsymbol{K}}(\boldsymbol{q}')$$

$$+4J^z\sum_{\alpha}\cos q_{\alpha}\frac{1}{N}\sum_{\boldsymbol{q}'}\left(\cos\frac{K_{\alpha}}{2} - \frac{J^{\perp}}{J^z}\cos q_{\alpha}'\right)f_{\boldsymbol{K}}(\boldsymbol{q}') \tag{1.7.6}$$

where

$$\hbar\omega_{\boldsymbol{K}}(\boldsymbol{q}) = 2h + 2D(2S-1) + 8J^z Sd - 8J^{\perp}S\sum_{\alpha}\cos\frac{K_{\alpha}}{2}\cos q_{\alpha} \tag{1.7.7}$$

with $d = 1, 2, 3$ for LC, SQ, SC lattices, respectively. Using the definitions

$$G_{\boldsymbol{K}}^{\alpha} = \frac{1}{N}\sum_{\boldsymbol{q}}\left(\cos\frac{K_{\alpha}}{2} - \frac{J^{\perp}}{J^z}\cos q_{\alpha}\right)f_{\boldsymbol{K}}(\boldsymbol{q}) \tag{1.7.8}$$

with $\alpha = x, y, z$ and

$$G_{\boldsymbol{K}}^0 = \frac{1}{N}\sum_{\boldsymbol{q}} f_{\boldsymbol{K}}(\boldsymbol{q}), \tag{1.7.9}$$

Equation (1.7.6) becomes

$$f_{\boldsymbol{K}}(\boldsymbol{q}) = -\left(\frac{D}{4J^{\perp}S}G_{\boldsymbol{K}}^0 + \frac{J^z}{2J^{\perp}S}\sum_{\alpha}G_{\boldsymbol{K}}^{\alpha}\cos q_{\alpha}\right)\frac{1}{x + \sum_{\sigma}\cos\frac{K_{\sigma}}{2}\cos q_{\sigma}} \tag{1.7.10}$$

where $\sigma = x, y, z$ and

$$x = \frac{\hbar\omega}{8J^{\perp}S} - \frac{h}{4J^{\perp}S} - \frac{D}{4J^{\perp}S} - d\frac{J^z}{J^{\perp}}. \tag{1.7.11}$$

Multiplying both sides of Eq. (1.7.10) by $(\cos q_{\beta} - \frac{J^{\perp}}{J^z}\cos\frac{K_{\beta}}{2})$ where $\beta = x, y, z$ and summing over $\boldsymbol{q}$, one obtains the d equations

$$\frac{D}{4J^{\perp}S}G_{\boldsymbol{K}}^0\left(I_{\beta} - \frac{J^{\perp}}{J^z}I_0\cos\frac{K_{\beta}}{2}\right) + \frac{J^z}{2J^{\perp}S}\sum_{\alpha}G_{\boldsymbol{K}}^{\alpha}\left(I_{\alpha\beta} - \frac{J^{\perp}}{J^z}I_{\alpha}\cos\frac{K_{\beta}}{2}\right) = 0 \tag{1.7.12}$$

where

$$I_0 = \frac{1}{N}\sum_{\boldsymbol{q}}\frac{1}{x + \sum_{\sigma}\cos\frac{K_{\sigma}}{2}\cos q_{\sigma}}, \tag{1.7.13}$$

$$I_{\alpha} = \frac{1}{N}\sum_{\boldsymbol{q}}\frac{\cos q_{\alpha}}{x + \sum_{\sigma}\cos\frac{K_{\sigma}}{2}\cos q_{\sigma}}. \tag{1.7.14}$$

$$I_{\alpha\beta} = \frac{1}{N}\sum_{\boldsymbol{q}}\frac{\cos q_{\alpha}\cos q_{\beta}}{x + \sum_{\sigma}\cos\frac{K_{\sigma}}{2}\cos q_{\sigma}}. \tag{1.7.15}$$

Moreover, summing over $\boldsymbol{q}$ on both sides of Eq. (1.7.10) one obtains

$$\left(1 + \frac{D}{4J^\perp S}I_0\right)G_{\boldsymbol{K}}^0 + \frac{J^z}{2J^\perp S}\sum_\alpha I_\alpha G_{\boldsymbol{K}}^\alpha = 0. \tag{1.7.16}$$

The system made up of the d equations (1.7.12) and the single equation (1.7.16) has non trivial solutions only if

$$\det \begin{pmatrix} 1 + \dfrac{D}{4J^\perp S}I_0 & \dfrac{J^z}{2J^\perp S}I_x & \dfrac{J^z}{2J^\perp S}I_y & \dfrac{J^z}{2J^\perp S}I_z \\[2ex] \dfrac{D}{4J^\perp S}A_x & 1 - \dfrac{1}{2S}B_{xx} & -\dfrac{1}{2S}B_{xy} & -\dfrac{1}{2S}B_{xz} \\[2ex] \dfrac{D}{4J^\perp S}A_y & -\dfrac{1}{2S}B_{yx} & 1 - \dfrac{1}{2S}B_{yy} & -\dfrac{1}{2S}B_{yz} \\[2ex] \dfrac{D}{4J^\perp S}A_z & -\dfrac{1}{2S}B_{zx} & -\dfrac{1}{2S}B_{zy} & 1 - \dfrac{1}{2S}B_{zz} \end{pmatrix} = 0 \tag{1.7.17}$$

where

$$A_\alpha = I_\alpha - \frac{J^\perp}{J^z}I_0 \cos\frac{K_\alpha}{2} \tag{1.7.18}$$

and

$$B_{\alpha\beta} = I_\alpha \cos\frac{K_\beta}{2} - \frac{J^z}{J^\perp}I_{\alpha\beta}. \tag{1.7.19}$$

The roots x_{BS} of the determinant equation (1.7.17) give the bound states of the anisotropic ferromagnet that we will study in more detail in Chapter 5. The probability of finding the two spin deviations at a distance r is given by Eq. (1.4.34) and (1.4.35) with

$$F_{\boldsymbol{K}}(\boldsymbol{r}) = \frac{1}{N}\sum_{\boldsymbol{q}} f_{\boldsymbol{K}}(\boldsymbol{q})\cos\boldsymbol{q}\cdot\boldsymbol{r} \tag{1.7.20}$$

where $f_{\boldsymbol{K}}(\boldsymbol{q})$ is given by Eq. (1.7.10).

For magnetic insulators like EuS, EuO, BX$_2$ and ABX$_3$, where A is an alkali metal like potassium (K), sodium (Na), cesium (Ce) or rubidium (Rb), B is a transition metal like vanadium (V), manganese (Mn) or copper (Cu) and X is a halogen like fluorine (F), chlorine (Cl), bromine (Br) or iodine (I), the anisotropic Hamiltonian (1.7.3) can be assumed to fit well with the magnetic excitations at low temperature.

In order to describe the ground state configuration of some heavy rare earths or some compounds of the family BX$_2$ or ABX$_3$, the extension of the exchange integral occurring in the Hamiltonian (1.2.5) to more distant neighbours with alternating sign can be used. In particular, the choice of an alternating sign of the exchange interactions moving from NN to more distant spins can give rise to non-collinear configurations like spiral or helix configurations that will be discussed in Chapter 7.

The sign of the exchange integral in Eq. (1.2.5) determines the kind of magnetic order in the ground state: for $J > 0$, the ferromagnetic order is established and the

ground state is characterized by an assembly of magnetic ions with all their angular momenta (spins) assuming the maximum value (S) and aligned in the same direction. For $J < 0$, an exact calculation of the ground state[10,11] and of the elementary excitations[12] is restricted to the LC with $S = 1/2$. Otherwise, approximate calculations are used: a reasonable approximation for the ground state is the "Neél state" in which all the magnetic moments point in the same direction but the spins located on the NN sites of a given spin are antiparallel to the spin in that site. Note that for $J < 0$, the order of the levels in Figs. 1.2–1.4 has to be reversed. For instance, the antiferromagnetic ground state of the cluster with 4 spins is given by Eq. (1.2.32): while the corresponding Neél state is given by the last two terms of Eq. (1.2.32). In any case, for an even number of spins, the antiferromagnetic ground state is always a singlet $(S_{\text{tot}} = 0)$.

Note that the spin operators appearing in Hamiltonian (1.2.5) are "effective spin" operators that account for both the orbital and the spin contribution of the multi-electron ion. To determine the effective spin quantum number S of the magnetic ion, one must evaluate the lowest energy levels of the ground-state multiplet of the "free" magnetic ion split by the crystalline field due to the NN non-magnetic ions by a perturbative method. The energy shift between the lowest levels so obtained, is of the order of the magnetic excitations, usually 0.01-0.1 eV. An example of such a calculation will be given in Chapter 9.