

Solutions to the problems in Chapter 25 and 26

25.2 Classical electrons in a magnetic field

The spin degree-of-freedom does not occur in classical physics. The elementary particles do neither exist, but accepting their existence, they only interact with the electromagnetic fields because of their charges, and with the gravitational field because of their masses. The classical Hamiltonian \mathcal{H} of a many-body system (see for instance Goldstein) is a function of the independent canonical variables (\vec{r}_i, \vec{p}_i) of all the particles. The canonical impulse \vec{p}_i , independent of \vec{r}_i , is defined in terms of the Lagrangian $\mathcal{L} = \mathcal{L}(\vec{r}_i, \dot{\vec{r}}_i, \dots)$ as $\vec{p}_i = \partial\mathcal{L}/\partial\dot{\vec{r}}_i$ (or, in terms of the Hamiltonian theory, as the generator of an infinitesimal translation $\vec{r}_i \rightarrow \vec{r}_i + \delta\vec{r}_i$).

(a) If the external constraints (fields) are independent of time, the Hamiltonian is equal the total (kinetic plus potential) energy of the system. In this case the classical partition function is

$$Z = e^{-\beta\mathcal{F}} = \frac{1}{h^n} \int d\vec{r}_1 d\vec{p}_1 \cdots d\vec{r}_n d\vec{p}_n e^{-\beta\mathcal{H}(\vec{r}_1, \vec{p}_1, \dots, \vec{r}_n, \vec{p}_n)} \quad (1)$$

(b) In the presence of a time-independent electromagnetic field, \vec{E} only contributes to the potential energy as determined by the scalar potential. The magnetic field \vec{B} only affects the velocities of the particles via the vector potential $\vec{A} = \vec{A}(\vec{r})$, where $\vec{B} = \nabla \times \vec{A}$. For the i th particle with mass m_i and charge q_i , the canonical impulse is

$$\vec{p}_i = m_i \dot{\vec{r}}_i + \frac{q_i}{c} \vec{A} \quad \Rightarrow \quad T_i = \frac{1}{2} m_i (\dot{\vec{r}}_i)^2 = \frac{1}{2m_i} \left(\vec{p}_i - \frac{q_i}{c} \vec{A} \right)^2 \quad (2)$$

[The magnetic field needs not to be uniform in space, but only to be constant in time – the case of a spatial uniform field is discussed in the next problem 25.4].

(c) The canonical impulse \vec{p}_i appears in the Hamiltonian only via the kinetic energy T_i . Assuming \mathcal{H} in (1) to be the Hamiltonian function of the system, when the magnetic field is zero (but including the potential energy contributions of the electric field), then the introduction of the magnetic field implies that

$$\mathcal{H}(\vec{r}_1, \vec{p}_1, \dots, \vec{r}_n, \vec{p}_n) \rightarrow \mathcal{H}\left(\vec{r}_1, \vec{p}_1 - \frac{q_1}{c} \vec{A}(\vec{r}_1), \dots, \vec{r}_n, \vec{p}_n - \frac{q_n}{c} \vec{A}(\vec{r}_n)\right) \quad (3)$$

The partition function Z in the presence of the magnetic field is then

$$\begin{aligned} Z(\vec{B}) &= \frac{1}{h^n} \int d\vec{r}_1 d\vec{p}_1 \cdots d\vec{r}_n d\vec{p}_n e^{-\beta\mathcal{H}(\vec{r}_1, \vec{p}_1 - \frac{q_1}{c} \vec{A}(\vec{r}_1), \dots, \vec{r}_n, \vec{p}_n - \frac{q_n}{c} \vec{A}(\vec{r}_n))} \\ &= \frac{1}{h^n} \int d\vec{r}_1 d\vec{p}_1' \cdots d\vec{r}_n d\vec{p}_n' e^{-\beta\mathcal{H}(\vec{r}_1, \vec{p}_1', \dots, \vec{r}_n, \vec{p}_n')} = Z(\vec{0}) \end{aligned} \quad (4)$$

The integration with respect to the canonical impulse \vec{p}_i may be performed before the \vec{r}_i -integrations. Introducing the following change of variables $\vec{p}_i' = \vec{p}_i - \frac{q_i}{c} \vec{A}(\vec{r}_i)$, then $d\vec{p}_i' = d\vec{p}_i$, since $\vec{A}(\vec{r}_i)$ is independent of \vec{p}_i . This transformation of variables therefore leads to the same integral as in (1). The elimination of \vec{B} in the partition function means, for instance, that the magnetic susceptibility of a classical equilibrium system is zero. This result is called the *Bohr–van Leeuwen theorem*. Notice, that it is important for the argumentation that the system is in equilibrium (the basis for the use of the partition function).

25.4 Quantum electrons in a magnetic field

The Hamiltonian of an electron with charge $-e$ in a magnetic field \vec{B} is

$$\mathcal{H} = \frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A} \right)^2 \quad (1)$$

The choice of the “Landau gauge”

$$\vec{A} = (0, Bx, 0) \quad \Rightarrow \quad \vec{B} = \nabla \times \vec{A} = (0, 0, B), \quad \nabla \cdot \vec{A} = 0 \quad (2)$$

i.e. this vector potential corresponds to a spatial uniform field \vec{B} in the z direction. Since the divergence of \vec{A} is zero, the two quantum mechanical operators \vec{A} and \vec{p} commute, $\vec{p} = (\hbar/i)\nabla$ in the \vec{r} -representation. Introducing this choice of gauge in (1), we get

$$\mathcal{H} = \frac{1}{2m} \left[p_x^2 + \left(p_y + \frac{eB}{c} x \right)^2 + p_z^2 \right] \quad (3)$$

The wave function of the electron is assumed to be

$$\psi(\vec{r}) = u(x) e^{i(yk_y + zk_z)} \quad (4)$$

and the eigenvalue equation is

$$\mathcal{H} \psi = e^{i(yk_y + zk_z)} \frac{1}{2m} \left[p_x^2 + \left(\hbar k_y + \frac{eB}{c} x \right)^2 + (\hbar k_z)^2 \right] u(x) \quad (5)$$

When the common phase factor is deleted, this eigenvalue equation is reduced to one, which only involves a determination of $u(x)$, and the equation may be written:

$$\mathcal{H} u(x) = \left[\frac{p_x^2}{2m} + \frac{1}{2} m \omega_c^2 (x - x_0)^2 + \varepsilon_z \right] u(x) \quad (6)$$

where

$$\omega_c = \frac{eB}{mc}, \quad x_0 = -\frac{\hbar k_y}{m\omega_c}, \quad \varepsilon_z = \frac{\hbar^2 k_z^2}{2m} \quad (7)$$

Equation (6) is the eigenvalue equation for the one-dimensional harmonic oscillator, displaced to be centered around $x = x_0$ and shifted in energy by the constant (with respect to x) energy ε_z . Hence, the final eigenstates are classified by (k_y, k_z) and the occupation number ν , and the energy eigenvalues are

$$\varepsilon_{\nu, k_y, k_z} = \left(\nu + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m}, \quad \nu = 0, 1, 2, \dots \quad (8)$$

This is the result (25.48) utilized in the analysis of the Landau diamagnetism.

26.2 Ferromagnetic ground state

We are going to discuss the ferromagnetic ground state of the Heisenberg model for an arbitrary integer/half-integer value of S . The Heisenberg Hamiltonian is

$$\mathcal{H} = - \sum_{\langle ll' \rangle} J_{ll'} \vec{S}_l \cdot \vec{S}_{l'} = -\frac{1}{2} \sum_{l \neq l'} J_{ll'} \vec{S}_l \cdot \vec{S}_{l'} \quad (1)$$

according to (26.21) in Marder. The possibility of $J_{ll} \neq 0$ may be excluded, since such a term would contribute only by a constant term $J_{ll}S(S+1)$ to the energy. The components of \vec{S}_l fulfill the usual spin-commutator relations

$$[S_{lx}, S_{ly}] = i \delta_{ll'} S_{lz}, \quad [S_{ly}, S_{lz}] = i \delta_{ll'} S_{lx}, \quad [S_{lz}, S_{lx}] = i \delta_{ll'} S_{ly} \quad (2)$$

(a) Defining the following operator:
$$\mathcal{S}_z = \sum_l S_{lz} \quad (3)$$

then the commutator of this operator with a single term $\vec{S}_l \cdot \vec{S}_{l'}$ in (1) is

$$\begin{aligned} [\mathcal{S}_z, \vec{S}_l \cdot \vec{S}_{l'}] &= [\mathcal{S}_z, \vec{S}_l] \cdot \vec{S}_{l'} + \vec{S}_l \cdot [\mathcal{S}_z, \vec{S}_{l'}] \\ &= [S_{lz}, S_{lx}] S_{l'x} + [S_{lz}, S_{ly}] S_{l'y} + S_{lx} [S_{l'z}, S_{l'x}] + S_{ly} [S_{l'z}, S_{l'y}] \\ &= i S_{ly} S_{l'x} - i S_{lx} S_{l'y} + i S_{lx} S_{l'y} - i S_{ly} S_{l'x} = 0 \end{aligned} \quad (4)$$

showing that $[\mathcal{S}_z, \mathcal{H}] = 0$. The S_z -representation for each site is defined by $S_{lz}|m_l\rangle = m_l|m_l\rangle$, where $m_l = -S, -S+1, \dots, S$, and $\mathcal{S}_z \prod_l |m_l\rangle = (\sum_l m_l) \prod_l |m_l\rangle$. Most of these eigenstates are highly degenerated except for the two “singlets”, $\prod_l |m_l = \pm S\rangle = \prod_l | + S \rangle$ or $\prod_l | - S \rangle$. Because \mathcal{S}_z and \mathcal{H} commute the two non-degenerate eigenstates of \mathcal{S}_z are also eigenstates to \mathcal{H} , and

$$\mathcal{H} \prod_l |m_l = \pm S\rangle = -\frac{1}{2} N J(\vec{0}) S^2 \prod_l |m_l = \pm S\rangle, \quad J(\vec{k}) = \sum_{l'} J_{ll'} e^{-i\vec{k} \cdot (\vec{r}_l - \vec{r}_{l'})} \quad (5)$$

(b) Defining $\vec{\mathbb{S}} = \vec{S}_{\vec{R}} + \vec{S}_{\vec{R}'}$ and using $\vec{\mathbb{S}}^2 = (\vec{S}_{\vec{R}} + \vec{S}_{\vec{R}'})^2 = \vec{S}_{\vec{R}}^2 + \vec{S}_{\vec{R}'}^2 + 2\vec{S}_{\vec{R}} \cdot \vec{S}_{\vec{R}'}$

$$\langle \Psi | \vec{\mathbb{S}}^2 | \Psi \rangle = \begin{cases} S(S+1) + S(S+1) + 2\langle \Psi | \vec{S}_{\vec{R}} \cdot \vec{S}_{\vec{R}'} | \Psi \rangle \\ \mathbb{S}(\mathbb{S}+1), & \mathbb{S} = 0, 1, \dots, 2S \end{cases} \quad (6)$$

which shows that $\langle \Psi | \vec{S}_{\vec{R}} \cdot \vec{S}_{\vec{R}'} | \Psi \rangle$ attains its maximum value, when $\mathbb{S} = 2S$, and

$$\text{Max}\{\langle \Psi | \vec{S}_{\vec{R}} \cdot \vec{S}_{\vec{R}'} | \Psi \rangle\} = \frac{1}{2}[2S(2S+1) - 2S(S+1)] = S^2 \quad (7)$$

(c) The eigenvalue of \mathcal{H} in (5) for the fully polarized states requires that each pair of operators in (1) contributes by their maximum. Hence, if all exchange constants $J_{ll'} \geq 0$, then the eigenvalue in (5) is the lowest possible value, i.e. the two fully polarized states are the two degenerate ground states.

The lowest excited states are linear combination of the states, where all $m_l = S$ except that $m_l = S-1$ for one particular site. Naming the product of these states for $|l\rangle$, where l is the site at which $m_l = S-1$, then it is straightforward to show that the eigenstates of \mathcal{H} constructed from these states are the Fourier transforms of $|l\rangle$. These excited states are characterized by the wave vector \vec{k} of the Fourier transformation, and the energy difference between one excited \vec{k} -state and the ground state is the spin wave energy, $S[J(\vec{0}) - J(\vec{k})]$. Hence, these lowest excited states, the one-magnon states, are exact solutions to the Heisenberg Hamiltonian – but this is no longer the case if proceeding to the two-magnon states, where the eigenvalue of \mathcal{S}_z is $NS-2$.

26.4 Diagonalizing spin waves

The result derived in (26.62) may be written in a reduced form:

$$\begin{aligned}\hat{h} &= \frac{1}{2z|J|S} \left(\mathcal{H} + Nz|J|S^2 \right) = \frac{1}{2z} \sum_{\vec{\delta}} \left[2a_{\vec{k}}^+ a_{\vec{k}} + \left(a_{\vec{k}}^+ a_{-\vec{k}}^+ + a_{\vec{k}} a_{-\vec{k}} \right) \cos(\vec{k} \cdot \vec{\delta}) \right] \\ &= \sum_{\vec{k}} \left[a_{\vec{k}}^+ a_{\vec{k}} + \frac{1}{2} \left(a_{\vec{k}}^+ a_{-\vec{k}}^+ + a_{\vec{k}} a_{-\vec{k}} \right) B_{\vec{k}} \right], \quad B_{\vec{k}} = \frac{1}{z} \sum_{\vec{\delta}} \cos(\vec{k} \cdot \vec{\delta})\end{aligned}\quad (1)$$

The operators are defined by (26.51) in terms of a_l and its hermitean conjugate a_l^+ , which are the annihilation and creation operators, also named Bose operators, of a harmonic oscillator at the site l . These operators obey the Bose commutator relations $[a_l, a_{l'}^+] = \delta_{ll'}$ and $[a_l^+, a_{l'}^+] = [a_l, a_{l'}] = 0$, which imply

$$[a_{\vec{k}}, a_{\vec{k}'}^+] = \frac{1}{N} \sum_{l'} \left[a_l e^{i\vec{k} \cdot \vec{r}_l}, a_{l'}^+ e^{-i\vec{k}' \cdot \vec{r}_{l'}} \right] = \frac{1}{N} \sum_{l'} \delta_{ll'} e^{i\vec{k} \cdot \vec{r}_l - i\vec{k}' \cdot \vec{r}_{l'}} = \frac{1}{N} \sum_l e^{i(\vec{k} - \vec{k}') \cdot \vec{r}_l} \quad (2)$$

or that the Fourier transforms of the Bose operators, diagonal with respect to the site index, are Bose operators in reciprocal space

$$[a_{\vec{k}}, a_{\vec{k}'}^+] = \delta_{\vec{k}\vec{k}'}, \quad [a_{\vec{k}}, a_{\vec{k}'}] = 0, \quad [a_{\vec{k}}^+, a_{\vec{k}'}^+] = 0 \quad (3)$$

which are diagonal with respect to the wave vector index (notice that the wave vector \vec{k} is assumed to be a discrete variable). The Hamiltonian (1) is not diagonal in the number representations of the harmonic oscillators, since it involves $a_{\vec{k}}^+ a_{-\vec{k}}^+ + a_{\vec{k}} a_{-\vec{k}}$. One way to solve an eigenvalue problem is to make a canonical transformation of the Hamiltonian to one for which the eigenvalue equations have been solved. In the present case, we want to find a new Bose operator $\gamma_{\vec{k}}$, in terms of which \hat{h} only depends on the number operators $\gamma_{\vec{k}}^+ \gamma_{\vec{k}}$, in which case \hat{h} is “diagonal”. This procedure is called *the Bogoliubov transformation*:

$$a_{\vec{k}} = u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}}^+, \quad a_{\vec{k}}^+ = u_{\vec{k}}^* \gamma_{\vec{k}}^+ + v_{\vec{k}}^* \gamma_{-\vec{k}} = u_{\vec{k}} \gamma_{\vec{k}}^+ + v_{\vec{k}} \gamma_{-\vec{k}} \quad (4)$$

The last equation indicates that $u_{\vec{k}}$ and $v_{\vec{k}}$ are assumed to be real functions. This is a valid simplification in the present case, but it is not a general requirement. The demand that the new operators should also be Bose operators implies

$$[a_{\vec{k}}, a_{\vec{k}'}^+] = [u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}}^+, u_{\vec{k}'} \gamma_{\vec{k}'}^+ + v_{\vec{k}'} \gamma_{-\vec{k}'}] = u_{\vec{k}} u_{\vec{k}'} \delta_{\vec{k}\vec{k}'} - v_{\vec{k}} v_{\vec{k}'} \delta_{-\vec{k}-\vec{k}'} = \delta_{\vec{k}\vec{k}'} \quad (5)$$

and, similarly, $[a_{\vec{k}}, a_{\vec{k}'}] = u_{\vec{k}} v_{\vec{k}'} \delta_{\vec{k}-\vec{k}'} - v_{\vec{k}} u_{\vec{k}'} \delta_{-\vec{k}\vec{k}'} = 0$. Hence, the fulfillment of the Bose commutator relations for $\gamma_{\vec{k}}$ requires

$$u_{\vec{k}}^2 - v_{\vec{k}}^2 = 1, \quad u_{\vec{k}} v_{-\vec{k}} - v_{\vec{k}} u_{-\vec{k}} = 0 \quad (6)$$

Inserting (4) in (1) we get

$$\begin{aligned}\hat{h} &= \sum_{\vec{k}} \left[\left(u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}} \right) \left(u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}}^+ \right) + \frac{1}{2} B_{\vec{k}} \left\{ \left(u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}} \right) \right. \right. \\ &\quad \left. \left. \times \left(u_{-\vec{k}} \gamma_{-\vec{k}} + v_{-\vec{k}} \gamma_{\vec{k}}^+ \right) + \left(u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}}^+ \right) \left(u_{-\vec{k}} \gamma_{-\vec{k}} + v_{-\vec{k}} \gamma_{\vec{k}}^+ \right) \right\} \right] \quad (7)\end{aligned}$$

Collecting corresponding terms and replacing $-\vec{k}$ with \vec{k} in some of the terms (utilizing $B_{\vec{k}} = B_{-\vec{k}}$ and $\gamma_{\vec{k}}\gamma_{-\vec{k}} = \gamma_{-\vec{k}}\gamma_{\vec{k}}$), then (7) is reduced to

$$\hat{h} = \sum_{\vec{k}} \left[\left(u_{\vec{k}}^2 + B_{\vec{k}} u_{\vec{k}} v_{-\vec{k}} \right) \gamma_{\vec{k}}^+ \gamma_{\vec{k}} + \left(v_{-\vec{k}}^2 + B_{\vec{k}} u_{\vec{k}} v_{-\vec{k}} \right) \gamma_{\vec{k}} \gamma_{\vec{k}}^+ \right. \\ \left. + \left\{ 2u_{\vec{k}} v_{\vec{k}} + B_{\vec{k}} \left(u_{\vec{k}} u_{-\vec{k}} + v_{\vec{k}} v_{-\vec{k}} \right) \right\} \frac{1}{2} \left(\gamma_{\vec{k}}^+ \gamma_{-\vec{k}}^+ + \gamma_{\vec{k}} \gamma_{-\vec{k}} \right) \right] \quad (8)$$

In order to diagonalize this Hamiltonian we have to search for values of $u_{\vec{k}}$ and $v_{\vec{k}}$, where the last term in (8) vanishes and the requirements of (6) are fulfilled. In order to simplify the search, we make the *ansatz* $u_{-\vec{k}} = u_{\vec{k}}$, which is consistent with the different conditions only if $v_{-\vec{k}} = v_{\vec{k}}$. In this case the equations are

$$2u_{\vec{k}} v_{\vec{k}} = -B_{\vec{k}} \left(u_{\vec{k}}^2 + v_{\vec{k}}^2 \right), \quad u_{\vec{k}}^2 - v_{\vec{k}}^2 = 1 \quad (9)$$

Introducing $v_{\vec{k}}^2 = u_{\vec{k}}^2 - 1$ in the squared version of the first equation, we get an equation of second degree in $u_{\vec{k}}^2$. Determining the solution of this equation subject to the condition $v_{\vec{k}}^2 > 0$ or $u_{\vec{k}}^2 > 1$, we get

$$u_{\vec{k}}^2 = \frac{1 + \varepsilon_{\vec{k}}}{2\varepsilon_{\vec{k}}}, \quad v_{\vec{k}}^2 = \frac{1 - \varepsilon_{\vec{k}}}{2\varepsilon_{\vec{k}}}, \quad 2u_{\vec{k}} v_{\vec{k}} = -\frac{B_{\vec{k}}}{\varepsilon_{\vec{k}}}, \quad \varepsilon_{\vec{k}} = \sqrt{1 - B_{\vec{k}}^2} \quad (10)$$

According to the definition in (1), $|B_{\vec{k}}| \leq 1$ implying $0 \leq \varepsilon_{\vec{k}} \leq 1$. This is the same solution as given by equations (26.63) and (26.64) in Marder, since $u_{\vec{k}} = \cosh(\alpha_{\vec{k}})$ and $v_{\vec{k}} = \sinh(\alpha_{\vec{k}})$ imply $u_{\vec{k}}^2 - v_{\vec{k}}^2 = 1$ and $\tanh(2\alpha_{\vec{k}}) = 2u_{\vec{k}} v_{\vec{k}} / (u_{\vec{k}}^2 + v_{\vec{k}}^2) = -B_{\vec{k}}$. Introducing the solution (10) in (8) we finally get

$$\hat{h} = \sum_{\vec{k}} \left[\frac{1}{2} (\varepsilon_{\vec{k}} + 1) \gamma_{\vec{k}}^+ \gamma_{\vec{k}} + \frac{1}{2} (\varepsilon_{\vec{k}} - 1) \gamma_{\vec{k}} \gamma_{\vec{k}}^+ \right] = \sum_{\vec{k}} \left[\frac{1}{2} (\varepsilon_{\vec{k}} - 1) + \varepsilon_{\vec{k}} \gamma_{\vec{k}}^+ \gamma_{\vec{k}} \right] \\ \mathcal{H} = -Nz|J|S^2 - z|J|S \sum_{\vec{k}} (1 - \varepsilon_{\vec{k}}) + \sum_{\vec{k}} \mathcal{E}_{\vec{k}} \gamma_{\vec{k}}^+ \gamma_{\vec{k}} \quad (11) \\ \mathcal{E}_{\vec{k}} = 2z|J|S \varepsilon_{\vec{k}}, \quad \langle \gamma_{\vec{k}}^+ \gamma_{\vec{k}} \rangle = n_{\vec{k}} = [e^{\beta \mathcal{E}_{\vec{k}}} - 1]^{-1}$$

The antiferromagnetic Néel state, where the spins of the two sublattices are either $+S$ or $-S$ is not an eigenstate of the Hamiltonian. The second term of \mathcal{H} , discussed by Marder, shows that the ground state energy is smaller than that derived from the Néel state. Additionally, the magnitude $|\langle S_z(l) \rangle|$ is smaller than S at zero temperature. This “zero-point” reduction of the antiferromagnetic moment is determined by the site average of $|\langle 0|S_z(l)|0 \rangle| = S - \langle 0|a_l^+ a_l|0 \rangle$, where $|0 \rangle$ is the product ground state of the N independent harmonic oscillators, $\gamma_{\vec{k}}|0 \rangle = 0$,

$$\Delta S = \frac{1}{N} \sum_l \langle 0|a_l^+ a_l|0 \rangle = \frac{1}{N} \sum_{\vec{k}} \langle 0|a_{\vec{k}}^+ a_{\vec{k}}|0 \rangle = \\ \frac{1}{N} \sum_{\vec{k}} \langle 0| \left(u_{\vec{k}} \gamma_{\vec{k}}^+ + v_{\vec{k}} \gamma_{-\vec{k}} \right) \left(u_{\vec{k}} \gamma_{\vec{k}} + v_{\vec{k}} \gamma_{-\vec{k}}^+ \right) |0 \rangle = \frac{1}{N} \sum_{\vec{k}} v_{\vec{k}}^2 = \frac{1}{N} \sum_{\vec{k}} \frac{1 - \varepsilon_{\vec{k}}}{2\varepsilon_{\vec{k}}} \quad (13)$$

which number is calculated [P.W. Anderson, Phys. Rev. **86**, 694 (1952)] to be 0.078 in the case of a simple cubic lattice ($z = 6$).

Solution to HS's problem 4

Localized atoms: heat capacity and magnetic susceptibility

1) In the case of non-interacting atoms, the total energy is the sum of the contributions from each site $\mathcal{E} = \sum_l \mathcal{E}_l$. This implies that the partition function is the product of the partition functions determined for each site (see also the note "Magnetic energy and domains"), and when the atoms are identical:

$$\mathcal{Z} = \prod_{l=1}^N Z_l = Z^N, \quad Z_l = Z = \sum_i e^{-\beta \epsilon_i} = e^{\beta \Delta} + 1 + e^{-\beta \Delta} \quad (1)$$

The free energy is

$$F = -k_B T \ln \mathcal{Z} = -N k_B T \ln Z = -N k_B T \ln \left(e^{\beta \Delta} + 1 + e^{-\beta \Delta} \right) \quad (2)$$

The internal energy is $U = F + T\mathcal{S}$, where the entropy is

$$\begin{aligned} \mathcal{S} &= -\frac{\partial F}{\partial T} = N k_B \ln Z + N k_B T \frac{1}{Z} \frac{\partial Z}{\partial T} \Rightarrow \\ U &= F + T\mathcal{S} = N k_B T^2 \frac{1}{Z} \frac{\partial Z}{\partial T} = -N \frac{1}{Z} \frac{\partial Z}{\partial \beta} = N \frac{1}{Z} \sum_i \epsilon_i e^{-\beta \epsilon_i} \end{aligned} \quad (3)$$

Introducing the population factor for the i th level (the probability that this level is occupied):

$$p_i \equiv \frac{e^{-\beta \epsilon_i}}{Z} \Rightarrow U = N \sum_i \epsilon_i p_i = -N \Delta \frac{e^{\beta \Delta} - e^{-\beta \Delta}}{e^{\beta \Delta} + 1 + e^{-\beta \Delta}} \quad (4)$$

Notice, that $\sum_i p_i = 1$. In terms of the population factors, the thermal expectation value of any single site operator \hat{A} is $\langle \hat{A} \rangle = \sum_i \langle i | \hat{A} | i \rangle p_i$, and the entropy is $\mathcal{S} = -N k_B \sum_i p_i \ln p_i$.

2) In the limit $k_B T \gg \Delta$ or $\beta \Delta \ll 1$, we have from (1)

$$\begin{aligned} Z &\simeq 1 + \beta \Delta + \frac{1}{2}(\beta \Delta)^2 + 1 + 1 - \beta \Delta + \frac{1}{2}(\beta \Delta)^2 = 3 + (\beta \Delta)^2 \Rightarrow \\ F &\simeq -N k_B T \ln \left[3 + (\beta \Delta)^2 \right] = -N k_B T \ln 3 \left[1 + \frac{1}{3}(\beta \Delta)^2 \right] = -N k_B T \ln 3 - \frac{N \Delta^2}{3 k_B T} \\ \mathcal{S} &= -\frac{\partial F}{\partial T} = N k_B \ln 3 - \frac{N \Delta^2}{3 k_B T^2}, \quad U = F + T\mathcal{S} = -\frac{2 N \Delta^2}{3 k_B T} \end{aligned} \quad (5)$$

The heat capacity may be determined either as

$$C = \frac{\partial U}{\partial T} = \frac{2 N \Delta^2}{3 k_B T^2} \quad \text{or} \quad C = T \frac{\partial \mathcal{S}}{\partial T} = T(-2) \left(-\frac{N \Delta^2}{3 k_B T^3} \right) = \frac{2 N \Delta^2}{3 k_B T^2} \quad (6)$$

3) The derivative of F with respect to Δ is

$$\frac{\partial F}{\partial \Delta} = -N k_B T \frac{1}{Z} \frac{\partial Z}{\partial \Delta} = -N k_B T (\beta p_1 + 0 \cdot p_2 - \beta p_3) = N(p_3 - p_1) \simeq -\frac{2 N \Delta}{3 k_B T} \quad (7)$$

The last equality is most simply obtained from F derived in (5). In the presence of a magnetic field H , applied along the z axis, the Hamiltonian is specified in terms of the Zeeman interaction

$$\mathcal{H} = \sum_l \mathcal{H}_l = -g \mu_B H \sum_l S_{lz}, \quad S = 1 \quad (8)$$

The Hamiltonian of one of the sites is diagonal in the S_z -representation and the eigenenergies are

$$\begin{cases} |S_z = -1\rangle & \Rightarrow \epsilon_i = g\mu_B H = \Delta & (i = 3) \\ |S_z = 0\rangle & \Rightarrow \epsilon_i = 0 & (i = 2) \\ |S_z = 1\rangle & \Rightarrow \epsilon_i = -g\mu_B H = -\Delta & (i = 1) \end{cases} \quad (9)$$

Hence the Hamiltonian (8) leads to the case considered when $g\mu_B H = \Delta$, and the derivative of F with respect to Δ is proportional to the magnetization, or

$$M = -\frac{1}{V} \frac{\partial F}{\partial H} = -\frac{(g\mu_B)}{V} \frac{\partial F}{\partial \Delta} \simeq \frac{N}{V} \frac{2(g\mu_B)^2}{3k_B T} H, \quad \chi = \left. \frac{M}{H} \right|_{H \rightarrow 0} = \frac{N}{V} \frac{2(g\mu_B)^2}{3k_B T} \quad (10)$$

The susceptibility is calculated in the limit of H or $\Delta \rightarrow 0$, hence the expression derived is valid at all T . Notice, that M may also be obtained from

$$MV = g\mu_B \sum_l \langle S_{lz} \rangle = Ng\mu_B \sum_i \langle i | S_z | i \rangle p_i = Ng\mu_B (p_1 - p_3) \quad (11)$$

The result for χ in (10) is Curie’s law in the case of $S = 1$, see (25.31)-(25.32).

4) Defining $x = \beta\Delta$ the heat capacity derived from U in (4) is

$$\begin{aligned} C &= \frac{\partial U}{\partial T} = -\frac{\Delta}{k_B T^2} \frac{\partial U}{\partial x} = N \frac{\Delta^2}{k_B T^2} \frac{\partial}{\partial x} \left(\frac{e^x - e^{-x}}{e^x + 1 + e^{-x}} \right) = N \frac{\Delta^2}{k_B T^2} \frac{e^x + e^{-x} + 4}{(e^x + 1 + e^{-x})^2} \\ &= N \frac{\Delta^2}{k_B T^2} \frac{e^{\beta\Delta} + e^{-\beta\Delta} + 4}{(e^{\beta\Delta} + 1 + e^{-\beta\Delta})^2} \rightarrow N \frac{\Delta^2}{k_B T^2} e^{-\Delta/(k_B T)} \quad \text{for } T \rightarrow 0 \end{aligned} \quad (12)$$

The figure to the left shows the reduced heat capacity $c = C/(Nk_B)$ as a function of the reduced temperature $t = k_B T/\Delta$ – the thin lines are the results for $c(t)$ in the high- and low-temperature limits, (6) and (12). This characteristic behaviour of the heat capacity is called a *Schottky anomaly*. The number of levels involved in the anomaly for an arbitrary value of S is $(2S + 1)$, i.e. 3 levels in the present case of $S = 1$. This number may be determined from a heat capacity experiment by evaluating the entropy in the high temperature limit, since $\mathcal{S}_\infty = Nk_B \ln(2S + 1)$ for a general value of S . A measurement of $C = T(\partial\mathcal{S}/\partial T)$ determines \mathcal{S} , and

$$\mathcal{S} = \int_0^T \frac{C}{T} dT \Rightarrow s_\infty = \frac{\mathcal{S}_\infty}{Nk_B} = \int_0^\infty \frac{c}{t} dt = \ln(2S + 1) \quad (13)$$

