Quantum mechanics
Magnetization and susceptibility
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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I. Formulation of susceptibility in quantum mechanics

The partition function is given by

$$Z = Tr[e^{-\beta\hat{H}}]$$

We note that

$$\frac{\partial Z}{\partial B} = Tr[-\beta\frac{\partial\hat{H}}{\partial B}e^{-\beta\hat{H}}]$$
$$= \beta Tr[\hat{M}e^{-\beta\hat{H}}]$$

where $\hat{H}$ is the spin Hamiltonian and is defined by

$$\hat{H} = -\hat{M}\cdot B$$

$\hat{M}$ is the operator of magnetic moment. The average magnetization is given by

$$\langle\hat{M}\rangle = \frac{1}{\beta}\frac{\partial\ln Z}{\partial B} = \frac{1}{\beta}\frac{Z'}{Z}$$

where

$$Z' = \frac{\partial Z}{\partial B}, \qquad Z'' = \frac{\partial^2 Z}{\partial B^2} = \beta^2 Tr[\hat{M}^2 e^{-\beta\hat{H}}] = \beta^2 Z\langle\hat{M}^2\rangle$$

We also have

$$\left\langle \hat{M}^2 \right\rangle = \frac{1}{\beta^2} \frac{Z''}{Z}.$$

The fluctuation of magnetization is

$$\begin{aligned}
(\Delta M)^2 &= \left\langle \hat{M}^2 \right\rangle - \left\langle \hat{M} \right\rangle^2 \\
&= \frac{1}{\beta^2} \left(\frac{Z''Z - Z'^2}{Z^2} \right) \\
&= \frac{1}{\beta^2} \frac{d}{dB} \frac{Z'}{Z} \\
&= \frac{1}{\beta^2} \frac{d^2}{dB^2} \ln Z
\end{aligned}$$

The susceptibility is related to $(\Delta M)^2$ by

$$\chi = \frac{\partial \langle M \rangle}{\partial B} = \frac{1}{\beta} \frac{\partial^2 \ln Z}{\partial B^2} = \beta (\Delta M)^2$$

When $\left\langle \hat{M} \right\rangle = 0$, we get

$$(\Delta M)^2 = \left\langle \hat{M}^2 \right\rangle$$

leading to

$$\chi = \frac{1}{k_B T} \left\langle \hat{M}^2 \right\rangle$$

2. Quantum mechanics: General formula for Magnetic susceptibility of angular momentum *j*

We consider the magnetic susceptibility for the angular momentum *j*, where $\left| j, m \right\rangle$ is the eigenstate of the angular momentum $\hat{\boldsymbol{J}}$ with *m*=-*j*, -*j*+1,…, *j*-1, and *j*.

$$\left\langle \hat{M} \right\rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial B} = \frac{1}{\beta} \frac{Z'}{Z}$$

$$Z = Tr[e^{-\beta \hat{H}}].$$

with

$$\hat{H} = -(-g_J \mu_B \hat{J}_z) B = g_J \mu_B \hat{J}_z B$$

where $\hat{J}_z$ is the angular momentum $\hat{\boldsymbol{J}}$ (dimensionless) and the magnetic moment is given by

$$\hat{\boldsymbol{\mu}} = -g_J \mu_B \hat{\boldsymbol{J}}$$

Note that

$$\hat{J}_z \left| j, m \right\rangle = m \left| j, m \right\rangle. \qquad \hat{\boldsymbol{J}}^2 \left| j, m \right\rangle = j(j+1) \left| j, m \right\rangle.$$

The one-partition function can be evaluated as

$$
\begin{aligned}
Z_{C1} &= Tr[e^{-\beta\hat{H}}] \\
&= \sum_{m=-j}^{j} \langle jm | e^{-\beta\hat{H}} | jm \rangle \\
&= \sum_{m=-j}^{j} e^{-\beta g_J \mu_B m B} \\
&= \sum_{m=-j}^{j} e^{-\frac{m}{j}x}
\end{aligned}
$$

where we use the variable x as

$$x = \beta g_J j \mu_B B \, .$$

The partition function is obtained as

$$Z_{C1} = \cosh(x) + \sinh(x)\coth(\frac{x}{2j}) = \frac{\sinh(x + \frac{x}{2j})}{\sinh(\frac{x}{2j})}$$

The average magnetization is obtained as

$$\langle \hat{M} \rangle = N\frac{1}{\beta}\frac{\partial \ln Z_{C1}}{\partial B} = N\frac{1}{\beta}\frac{\partial x}{\partial B}\frac{\partial \ln Z_{C1}}{\partial x} = N g_J j \mu_B \frac{\partial \ln Z_{C1}}{\partial x}$$

Note that

$$\frac{\partial \ln Z_{C1}}{\partial x} = -\frac{1}{2j}\ \text{csch}\,(\frac{x}{2j})\,\text{csch}\,[(x+\frac{1}{2\text{j}})x][(1+j)\sinh(x) - j\sinh[(1+\frac{1}{j})x]$$

$$= -\frac{1}{2j}\ \text{csch}\,(\frac{x}{2j})\,\text{csch}\,[(1+\frac{1}{2\text{j}})x][(1+j)\sinh[(x+\frac{x}{2j}) - \frac{x}{2j}]$$

$$-j\sinh[(x+\frac{x}{2j}) + \frac{x}{2j}]$$

$$= \frac{2j+1}{2j}\coth[\frac{2j+1)x}{2j}] - \frac{1}{2j}\coth(\frac{x}{2j})$$

Then we have

$$\left\langle \hat{M} \right\rangle = N g_J j \mu_B B_j(x)$$

where $B_j(x)$ is the Brillouin function

$$B_j(x) = \frac{(2j+1)}{2j}\cot(x+\frac{x}{2j}) - \frac{1}{2j}\coth(\frac{x}{2j})$$

with

$$\text{csch}\,(x) = \frac{1}{\sinh(x)}$$

In the limit of $B \to 0$, we expand $\left\langle \hat{M} \right\rangle$ in a power of x as

$$\left\langle \hat{M} \right\rangle = \frac{1}{3} g_J (j+1)\mu_B x - \frac{1}{90 j^2} g_J \mu_B x^3 (j+1)[1+2j(j+1)] + ...$$

The magnetic susceptibility is

$$\chi = \frac{\partial < \hat{M} >}{\partial B} = \frac{\partial x}{\partial B}\frac{\partial < \hat{M} >}{\partial x} = \frac{g_J{}^2 \mu_B{}^2 j(j+1)}{3k_B T}$$

where

$$\left\langle \hat{M} \right\rangle = \frac{1}{3} g_J (j+1)\mu_B x = \frac{g_J{}^2 \mu_B{}^2 j(j+1)}{3k_B T} B$$

We use the Brillouin function

$$B_j(x) = \frac{2j+1}{2j}\coth(\frac{2j+1}{2j}x) - \frac{1}{2j}\coth(\frac{x}{2j}).$$

In the limit of $j \to \infty$, $B_j(x)$ becomes the Langevin function.

$$L(x) = \coth x - \frac{1}{x}$$

with

$$x = \frac{g_J \mu_B B}{k_B T}$$

$$\left\langle \hat{M} \right\rangle = g_J \mu_B L(x)$$

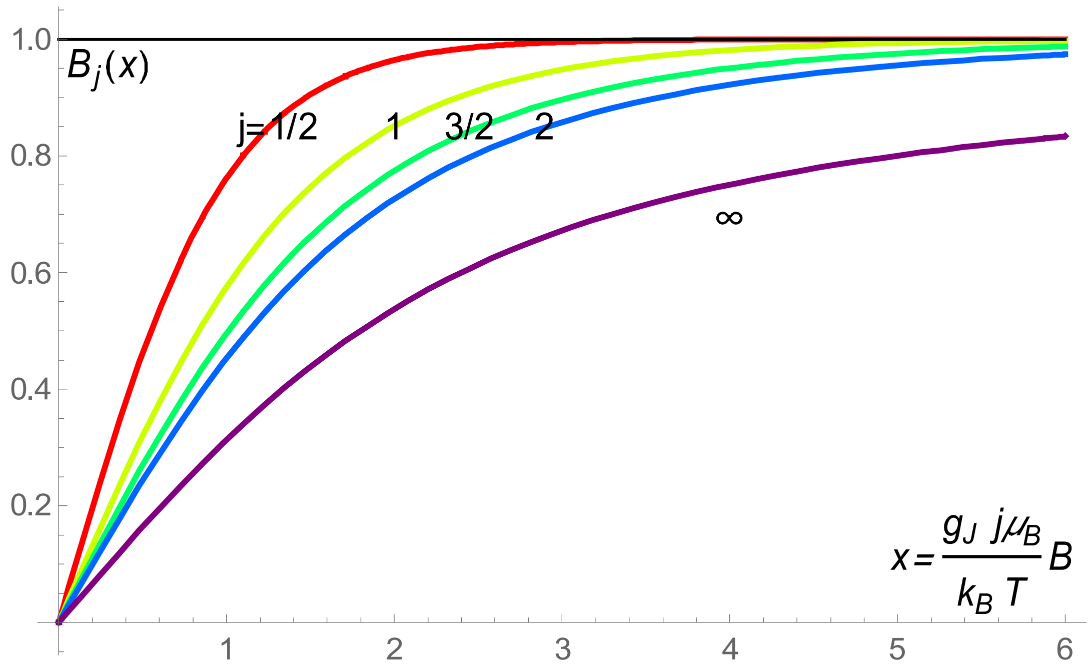
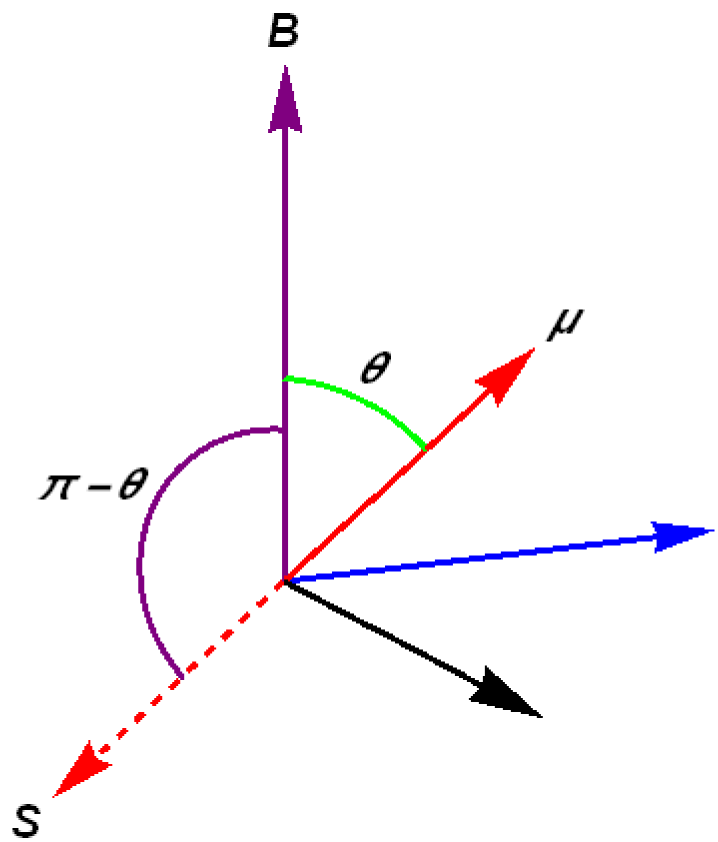


Fig. Brillouin function $B_j(x)$ as a function of x. j = 1/2, 1, 3/2, and 2. The Langevin function corresponds to $B_j(x)$ with $j = \infty$.

3. Classical theory for paramagnetic system

We discuss the magnetic susceptibility of paramagnet in the classical theory. The system can be regarded as a collection of N fixed magnetic moments with $\boldsymbol{\mu}$. The direction of the magnetic moments are randomly distributed. When the magnetic field is applied along the z direction, the Zeeman energy of each magnetic moment is given by

$$H = -\boldsymbol{\mu} \cdot \boldsymbol{B} = -\mu B \cos\theta$$



where θ is the angle between the magnetic moment (μ) and the magnetic field (z axis). Then the one-particle partition function for one magnetic moments is given by

$$Z_{C1} = \int d\Omega \exp(-\beta\mu B\cos\theta)$$
$$= \int_0^{\pi} 2\pi \sin\theta d\theta \exp(-\beta\mu B\cos\theta)$$
$$= 4\pi \frac{\sinh(\beta\mu B)}{\beta\mu B}$$

The partition function for N magnetic moments is

$$Z_{CN} = (Z_{C1})^N$$

The average magnetization is

$$
\begin{aligned}
M &= \frac{1}{\beta}\frac{\partial \ln Z_{CN}}{\partial B} \\
&= \frac{N}{\beta}\frac{\partial \ln Z_{C1}}{\partial B} \\
&= \frac{N}{\beta}(-\frac{1}{B} + \beta\mu \coth(\beta\mu B) \\
&= N\mu(-\frac{1}{\beta\mu B} + \coth(\beta\mu B)
\end{aligned}
$$

We use $x = \beta\mu B$

$$M = N\mu(\coth x - \frac{1}{x})$$

where $L(x)$ is the Langevin function

$$L(x) = \coth(x) - \frac{1}{x}$$

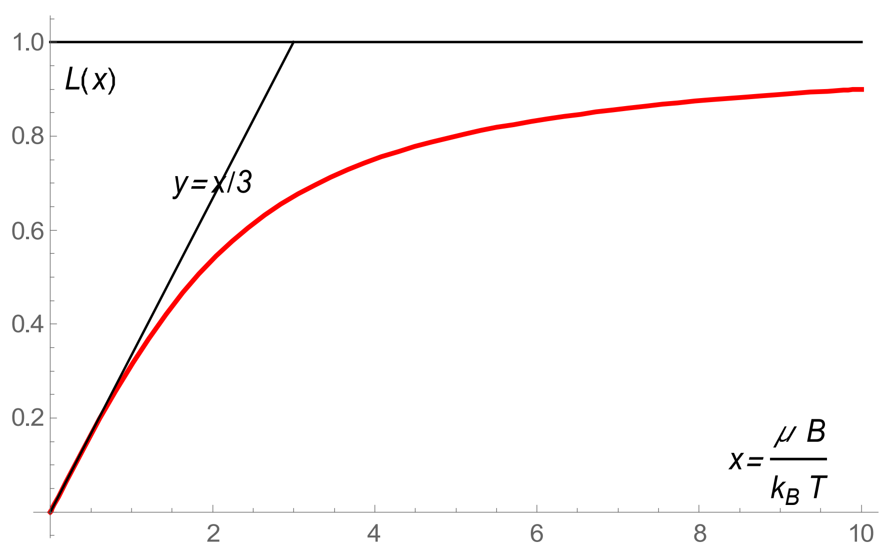


Fig. Langevin function $L(x)$.

In the small limit of x,

$$\coth x - \frac{1}{x} = \frac{x}{3} - \frac{x^3}{45} + \frac{2x^5}{945} - \frac{x^7}{4725} + \frac{2x^9}{93555} + ...$$

$$M \approx \frac{1}{3} N\mu x = \frac{N\mu^2 B}{3k_B T}$$

The magnetic susceptibility is

$$\chi = \frac{N\mu^2}{3k_B T}$$

The significant difference between the quantum and the classical model was that, in the classical system, the range of possible energy configurations was infinite while, in the quantum case, the range was discrete and finite.

4. Comparison between the Brillouin function and Langevin function

We note that the Brillouin function for $j \to \infty$ becomes the Langevin function. In the Brillouin function

$$B_j(x) = \frac{2j+1}{2j} \coth(\frac{2j+1}{2j} x) - \frac{1}{2j} \coth(\frac{x}{2j})$$

the first term tends to $\coth(x)$ in the limit of $j \to \infty$. The second term tends to

$$\frac{1}{2j} \coth(\frac{x}{2j}) = \varepsilon \coth(\varepsilon x) = \varepsilon \frac{e^{\varepsilon x} + e^{-\varepsilon x}}{e^{\varepsilon x} - e^{-\varepsilon x}} = \varepsilon \frac{1 + \varepsilon x + 1 - \varepsilon x}{1 + \varepsilon x - (1 - \varepsilon x)} = \frac{2\varepsilon}{2\varepsilon x} = \frac{1}{x}$$

where $\varepsilon = \frac{1}{2j}$ $(\varepsilon \to 0$ as $j \to \infty)$. Thus we get the Langevin function.

$$L(x) = \coth x - \frac{1}{x}$$

5. Magnetic susceptibility with S = 1/2

We consider a paramagnetic crystal, with non-interacting magnetic ions at $S = 1/2$. Evaluate the fluctuation $(\Delta M)^2$ of the magnetization and show that it is related to the susceptibility

$$\chi = \frac{\partial\langle\hat{M}\rangle}{\partial B}$$

by the relation $\chi = \frac{(\Delta M)^2}{k_B T}$ (particular case of the **fluctuation dissipation theorem**).

((**Solution**))

$$\hat{H} = -\hat{\boldsymbol{M}}\cdot\boldsymbol{B} = -\hat{M}_z B = \frac{g\mu_B B}{2}\hat{\sigma}_z$$

where

$$\hat{M}_z = -\frac{g\mu_B}{\hbar}\hat{S}_z = -\frac{g\mu_B}{2}\hat{\sigma}_z$$

The on-particle partition function

$$\begin{aligned}
Z_{C1} &= Tr[e^{-\beta\hat{H}}] = \langle +|e^{-\beta\hat{H}}|+\rangle + \langle -|e^{-\beta\hat{H}}|-\rangle \\
&= \exp(\frac{g\mu_B B}{2}) + \exp(-\frac{g\mu_B B}{2}) \\
&= 2\cosh(\frac{g\mu_B B}{2})
\end{aligned}$$

The density operator

$$\hat{\rho} = \frac{1}{Z} e^{-\beta\hat{H}} = \frac{1}{2\cosh(\frac{g\mu_B B}{2})} \begin{pmatrix} \exp(\frac{g\mu_B B}{2}) & 0 \\ 0 & \exp(-\frac{g\mu_B B}{2}) \end{pmatrix}$$

The magnetization

$$\begin{aligned} \langle \hat{M} \rangle &= Tr[\hat{M}\hat{\rho}] \\ &= -\frac{g\mu_B}{2} Tr[\hat{\sigma}_z \hat{\rho}] \\ &= -\frac{g\mu_B}{4\cosh(\frac{g\mu_B B}{2})} Tr[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \exp(\frac{\beta g\mu_B B}{2}) & 0 \\ 0 & \exp(-\frac{\beta g\mu_B B}{2}) \end{pmatrix}] \\ &= -\frac{g\mu_B}{4\cosh(\frac{g\mu_B B}{2})} Tr[\begin{pmatrix} \exp(\frac{\beta g\mu_B B}{2}) & 0 \\ 0 & -\exp(-\frac{\beta g\mu_B B}{2}) \end{pmatrix}] \\ &= -\frac{g\mu_B}{2} \tanh(\frac{\beta g\mu_B B}{2}) \end{aligned}$$

In the small limit of, $\frac{g\mu_B B}{2} << 1$

$$\langle \hat{M} \rangle \approx -\frac{\beta g^2 {\mu_B}^2 B}{4} = -\frac{g^2 {\mu_B}^2 B}{4 k_B T}$$

The susceptibility is

$$\chi = \beta Tr[\hat{M}_1{}^2 \hat{\rho}]$$
$$= \beta Tr[\frac{g^2 \mu_B{}^2}{4} \hat{\sigma}_z{}^2 \hat{\rho}]$$
$$= \beta \frac{g^2 \mu_B{}^2}{4} Tr[\hat{\rho}]$$
$$= \beta \frac{g^2 \mu_B{}^2}{4}$$

or

$$\chi = \frac{\beta g^2 \mu_B{}^2}{4} = \frac{g^2 \mu_B{}^2}{4 k_B T}$$

6. Magnetic susceptibility with spin *S*=1

((**Mathematica**)) We calculate the magnetic susceptibility of spin $S = 1$,using the density matrix.

$$\hat{H} = -\hat{\boldsymbol{M}} \cdot \boldsymbol{B} = -\hat{M}_z B$$

where

$$\hat{M}_z = -\frac{g\mu_B}{\hbar} \hat{S}_z = -g\mu_B \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The on-particle partition function

$$Z_{C1} = Tr[e^{-\beta \hat{H}}]$$

The density operator

$$\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$$

The susceptibility is

$$\chi = \beta Tr[\hat{M}_1{}^2 \hat{\rho}] = \frac{(1 + e^{2\beta g \mu_B B})}{1 + e^{\beta g \mu_B B} + e^{2\beta g \mu_B B}} \beta g^2 \mu_B{}^2$$

In the limit of $B \to 0$, we have

$$\chi = \frac{2}{3} \beta g^2 \mu_B{}^2 = \frac{2 g^2 \mu_B{}^2}{3 k_B T}$$

```
Clear["Global`*"]; M1 = -g μB {{1, 0, 0}, {0, 0, 0}, {0, 0, -1}};

H1 = -M1 B; Z = Tr[MatrixExp[-β H1]];

ρ1 = 1/Z MatrixExp[-β H1];

χ1 = β Tr[M1.M1.ρ1] // Simplify
```

$$\frac{\left(1 + e^{2\, B\, g\, \beta\, \mu B}\right) g^2\, \beta\, \mu B^2}{1 + e^{B\, g\, \beta\, \mu B} + e^{2\, B\, g\, \beta\, \mu B}}$$

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χ11 = χ1 /. B → 0
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$$\frac{2}{3} g^2\, \beta\, \mu B^2$$

7. Summary for the magnetic susceptibility with spin S

For spin *S*, the susceptibility is given by

$$\chi_S = \frac{g^2 \mu_B{}^2}{3k_B T} S(S+1)$$

Using the relation

$$\chi_S = \frac{(\Delta M)^2}{k_B T} = \frac{g^2 \mu_B{}^2}{3k_B T} S(S+1)$$

$$(\Delta M)^2 = \frac{g^2 \mu_B{}^2}{3} S(S+1)$$

where $g = 2$.

For $S = 1$, we have

$$\chi_{S=1} = \frac{2^2 \mu_B{}^2}{3k_B T} 2 = \frac{8\mu_B{}^2}{3k_B T}$$

For $S = 1/2$, we have

$$\chi_{S=1/2} = \frac{2^2 \mu_B{}^2}{3k_B T} \frac{1}{2} \frac{3}{2} = \frac{\mu_B{}^2}{k_B T}$$

and

$$(\Delta M)^2 = \mu_B{}^2$$

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8. p.163 Rigamonti example

Problem F.IV.9
A. Rigamonti and P. Carretta, Structure of Matter, An Introductory Course with Problems and Solutions (Springer, 2007).

Consider an ensemble of N/2 pairs of atoms at S = 1/2 interacting through a Heisenberg-like coupling K $\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_1$ with K>0. By neglecting the interactions among different pairs, derive the magnetic susceptibility. Express the density matrix and the operator $\hat{S}_z$ on the basis of the singlet and triplet states.

((**Solution**))

$$\hat{M}^z = -\frac{2\mu_B}{\hbar}(\hat{S}_1^z + \hat{S}_2^z) = -\mu_B(\hat{\sigma}_1^z + \hat{\sigma}_2^z)$$

$$\rightarrow \hat{M} = -\mu_B(\hat{\sigma}_1^z \otimes \hat{1}_2 + \hat{1}_2 \otimes \hat{\sigma}_2^z) = \begin{pmatrix} -2\mu_B & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\mu_B \end{pmatrix}$$

where

$$S_1^z \otimes \hat{1}_2 = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\hat{1}_1 \otimes S_2^z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

The density operator:

$$\hat{\rho} = \frac{1}{Z}\exp(-\beta\hat{H})$$

where Z is the partition function

$$Z = Tr[\exp(-\beta\hat{H})] = 3\exp(-\frac{K\beta\hbar^2}{4}) + \exp(\frac{3K\beta\hbar^2}{4})$$

The susceptibility is given by

$$\chi = \frac{1}{k_B T}\left\langle \hat{M}^2 \right\rangle = \frac{1}{k_B T} Tr[\hat{M}^2 \hat{\rho}] = \frac{8\mu_B{}^2}{k_B T}\frac{1}{3+e^{\hbar\omega\beta}}$$

For $N/2$ pairs, the total susceptibility is

$$\chi_{tot} = \frac{N}{2}\frac{8\mu_B{}^2}{k_B T}\frac{1}{3+e^{\hbar\omega\beta}} = \frac{4N\mu_B{}^2}{k_B T}\frac{1}{3+e^{\hbar\omega\beta}}$$

((**Mathematica**))

```
Clear["Global`*"];
rule1 = {a → K ħ^2/4};
σz = PauliMatrix[3];
I2 = IdentityMatrix[2];
H0 = a {{1, 0, 0, 0}, {0, -1, 2, 0}, {0, 2, -1, 0}, {0, 0, 0, 1}};
s1 = ħ/2 KroneckerProduct[σz, I2];
s2 = ħ/2 KroneckerProduct[I2, σz];
M1 = (-2 μB)/ħ (s1 + s2) // Simplify;
Z0 = Tr[MatrixExp[-β H0]];
ρ0 = 1/Z0 MatrixExp[-β H0] // FullSimplify;
Xav = β Tr[M1.M1.ρ0] /. rule1 /. {K → ω/ħ} // Simplify
```

$$\frac{8\, \beta\, \mu B^2}{3 + e^{\beta \omega \hbar}}$$

((**Another method**))

(a) Energy eigenvalue: $\frac{K\hbar^2}{4} = \frac{\hbar\omega}{4}$

$$|1\rangle = |++\rangle, \qquad |2\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle), \qquad |3\rangle = |--\rangle \qquad (S = 1 \text{ triplet state})$$

(b) Energy eigenvalue: $-\frac{3K\hbar^2}{4} = -\frac{3\hbar\omega}{4}$

$$|4\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \qquad (S = 0, \text{ singlet state})$$

For $S = 1$, the susceptibility is given by

$$\chi_1 = \frac{8}{3}\frac{\mu_B^{\ 2}}{k_B T}$$

For S = 0, $\chi_0 = 0$. The probability for the system in the triplet state is

$$P_1 = \frac{3e^{-\beta\hbar\omega}}{1+3e^{-\beta\hbar\omega}}$$

The probability for the system in the singlet state is

$$P_0 = \frac{1}{1+3e^{-\beta\hbar\omega}}$$

Then the total susceptibility is

$$
\begin{aligned}
\chi_{tot} &= \frac{N}{2}(p_0\chi_0 + p_1\chi_1) \\
&= \frac{N}{2} p_1\chi_1 \\
&= \frac{N}{2}\frac{3e^{-\beta\hbar\omega}}{1+3e^{-\beta\hbar\omega}}\frac{8}{3}\frac{\mu_B{}^2}{k_B T} \\
&= \frac{4N\mu_B{}^2}{k_B T}\frac{e^{-\beta\hbar\omega}}{1+3e^{-\beta\hbar\omega}} \\
&= \frac{4N\mu_B{}^2}{k_B T}\frac{1}{3+e^{\beta\hbar\omega}}
\end{aligned}
$$

where $\hbar\omega$ is the energy difference between the triplet state and the singlet state.