Problem and solution
Problem F.IV.9
A. Rigamonti and P. Carretta, Structure of Matter,
An Introductory Course with Problems and Solutions (Springer, 2007).
(Date: November 10, 2019)

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. Finally derive the time-dependence of the statistical ensemble average $\left\langle \hat{S}_1^{\ z}(t)\hat{S}_1^{\ z}(0)\right\rangle$, known as auto-correlation function.

((**Solution**))

$$\hat{H} = K\ \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_1 = \frac{K\hbar^2}{4}\hat{\sigma}_1 \cdot \hat{\sigma}_2$$

Dirac exchange operator:

$$P_{12} = \frac{1}{2}(1 + \hat{\sigma}_1 \cdot \hat{\sigma}_2)$$

Then $\hat{H}$ can be rewritten as

$$\hat{H} = \frac{K\hbar^2}{4}(2\hat{P}_{12} - \hat{1})$$

We consider the four states; $\left|++\right\rangle$, $\left|+-\right\rangle$, $\left|-+\right\rangle$, $\left|--\right\rangle$,

$$\begin{aligned}\hat{H}\left|++\right\rangle &= \frac{K\hbar^2}{4}(2\hat{P}_{12} - \hat{1})\left|++\right\rangle \\ &= \frac{K\hbar^2}{4}(2\left|++\right\rangle - \left|++\right\rangle) \\ &= \frac{K\hbar^2}{4}\left|++\right\rangle\end{aligned}$$

$$\hat{H}|--\rangle = \frac{K\hbar^2}{4}(2\hat{P}_{12} - \hat{1})|--\rangle$$
$$= \frac{K\hbar^2}{4}(2|--\rangle - |--\rangle)$$
$$= \frac{K\hbar^2}{4}|--\rangle$$

$$\hat{H}|+-\rangle = \frac{K\hbar^2}{4}(2\hat{P}_{12} - \hat{1})|+-\rangle$$
$$= \frac{K\hbar^2}{4}(2|-+\rangle - |+-\rangle)$$

$$\hat{H}|-+\rangle = \frac{K\hbar^2}{4}(2\hat{P}_{12} - \hat{1})|-+\rangle$$
$$= \frac{K\hbar^2}{4}(2|+-\rangle - |-+\rangle)$$

Under the basis of $\{|++\rangle, |+-\rangle, |-+\rangle, |++\rangle\}$, the matrix $\hat{H}$ can be given by

$$\hat{H} = \frac{K\hbar^2}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$|++\rangle$ is the eigenket of $\hat{H}$ with the eigenvalue $\frac{K\hbar^2}{4}$.

$|--\rangle$ is the eigenket of $\hat{H}$ with the eigenvalue $\frac{K\hbar^2}{4}$.

In the subspace of $|+-\rangle$ and $|-+\rangle$, the matrix $\hat{H}_{sub}$ is expressed by

$$\hat{H}_{sub} = \frac{K\hbar^2}{4}\begin{pmatrix} -1 & 2 \\ 2 & -1 \end{pmatrix} = \frac{K\hbar^2}{4}(-\hat{1} + 2\hat{\sigma}_x)$$

We note that

$$\hat{H}_{sub}|+x\rangle = \frac{K\hbar^2}{4}(-\hat{1}+2\hat{\sigma}_x)|+x\rangle = \frac{K\hbar^2}{4}|+x\rangle$$

$$\hat{H}_{sub}|-x\rangle = \frac{K\hbar^2}{4}(-\hat{1}+2\hat{\sigma}_x)|-x\rangle = -\frac{3K\hbar^2}{4}|-x\rangle$$

where

$$|+x\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle), \qquad \text{(eigenvalue } \frac{K\hbar^2}{4}\text{)}$$

$$|-x\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \qquad \text{(eigenvalue } -\frac{3K\hbar^2}{4}\text{)}$$

We define

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

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

We also define the unitary operator

$$|1\rangle = \hat{U}|++\rangle, \quad |2\rangle = \hat{U}|+-\rangle, \quad |3\rangle = \hat{U}|--\rangle, \quad |4\rangle = \hat{U}|-+\rangle$$

where

$$\hat{U} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\hat{U}^{+}\hat{H}\hat{U} = \begin{pmatrix} \frac{K\hbar^2}{4} & 0 & 0 & 0 \\ 0 & \frac{K\hbar^2}{4} & 0 & 0 \\ 0 & 0 & \frac{K\hbar^2}{4} & 0 \\ 0 & 0 & 0 & -\frac{3K\hbar^2}{4} \end{pmatrix}$$

The density operator is given by

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

where Z is the partition function

$$\begin{aligned} Z &= Tr[\exp(-\beta\hat{H})] \\ &= Tr[\hat{U}^{+}\exp(-\beta\hat{H})\hat{U}] \\ &= Tr[\exp(-\beta\hat{U}^{+}\hat{H}\hat{U})] \\ &= Tr\begin{pmatrix} \exp(-\frac{K\beta\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(-\frac{K\beta\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(-\frac{K\beta\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(\frac{3K\beta\hbar^2}{4}) \end{pmatrix} \\ &= 3\exp(-\frac{K\beta\hbar^2}{4}) + \exp(\frac{3K\beta\hbar^2}{4}) \end{aligned}$$

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

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

$$\begin{aligned}
\hat{U}^+ \hat{\rho} \hat{U} &= \frac{1}{Z} \hat{U}^+ \exp(-\beta \hat{H}) \hat{U} \\
&= \frac{1}{Z} \exp(-\beta \hat{U}^+ \hat{H} \hat{U}) \\
&= \frac{1}{Z} \begin{pmatrix} \exp(-\frac{K\beta\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(-\frac{K\beta\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(-\frac{K\beta\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(\frac{3K\beta\hbar^2}{4}) \end{pmatrix}
\end{aligned}$$

The autocorrelation function

$$\begin{aligned}
g(t) &= \left\langle \{\hat{S}_1^z(0)\hat{S}_1^z(t)\} \right\rangle \\
&= \frac{1}{2}\left\langle \hat{S}_1^z(0)\hat{S}_1^z(t) + \hat{S}_1^z(t)\hat{S}_1^z(t) \right\rangle \\
&= \mathrm{Re}[\left\langle \hat{S}_1^z(t)\hat{S}_1^z(0) \right\rangle]
\end{aligned}$$

where $\hat{S}_1^z(t)$ is the spin operator in the Heisenberg picture,

$$\hat{S}_1^z(t) = \exp(\frac{i}{\hbar}\hat{H}t)\hat{S}_1^z \exp(-\frac{i}{\hbar}\hat{H}t) .$$

Thus we get

$$\begin{aligned}
g(t) &= \mathrm{Re}[\left\langle \hat{S}_1^z(t)\hat{S}_1^z(0) \right\rangle] \\
&= \mathrm{Re}[Tr[\hat{\rho}\hat{S}_1^z(t)\hat{S}_1^z(0)] \\
&= \mathrm{Re}[Tr[\hat{\rho}\exp(\frac{i}{\hbar}\hat{H}t)\hat{S}_1^z \exp(-\frac{i}{\hbar}\hat{H}t)\hat{S}_1^z]
\end{aligned}$$

where $\hat{S}_1^z$ is the spin operator in the Schrödinger picture.

$$\hat{S}_1^z = \hat{S}_1^z(0)$$

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

$$\hat{U}^+ \exp(\frac{i}{\hbar}\hat{H}t)\hat{U} = \begin{pmatrix} \exp(\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(-\frac{it}{\hbar}\frac{3K\hbar^2}{4}) \end{pmatrix}$$

$$\hat{U}^+ \exp(-\frac{i}{\hbar}\hat{H}t)\hat{U}) = \begin{pmatrix} \exp(-\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(-\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(-\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(\frac{it}{\hbar}\frac{3K\hbar^2}{4}) \end{pmatrix}$$

Then we have

$$Tr[\hat{\rho}\exp(\frac{i}{\hbar}\hat{H}t)\hat{S}_1^{\,z}\exp(-\frac{i}{\hbar}\hat{H}t)\hat{S}_1^{\,z}]$$

$$= Tr[(\hat{U}^+\hat{\rho}\hat{U})(\hat{U}^+\exp(\frac{i}{\hbar}\hat{H}t)\hat{U})(\hat{U}^+\hat{S}_1^{\,z}\hat{U})(\hat{U}^+\exp(-\frac{i}{\hbar}\hat{H}t)\hat{U})(\hat{U}^+\hat{S}_1^{\,z}\hat{U})]$$

$$= \frac{1}{Z}Tr[\begin{pmatrix} \exp(-\frac{K\beta\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(-\frac{K\beta\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(-\frac{K\beta\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(\frac{3K\beta\hbar^2}{4}) \end{pmatrix}$$

$$\begin{pmatrix} \exp(\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(-\frac{it}{\hbar}\frac{3K\hbar^2}{4}) \end{pmatrix}$$

$$\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} \exp(-\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 & 0 \\ 0 & \exp(-\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 & 0 \\ 0 & 0 & \exp(-\frac{it}{\hbar}\frac{K\hbar^2}{4}) & 0 \\ 0 & 0 & 0 & \exp(\frac{it}{\hbar}\frac{3K\hbar^2}{4}) \end{pmatrix}$$

$$\frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}]$$

or

$$Tr[\hat{\rho}\exp(\frac{i}{\hbar}\hat{H}t)\hat{S}_1^{\,z}\exp(-\frac{i}{\hbar}\hat{H}t)\hat{S}_1^{\,z}] = \frac{\hbar^2(2+e^{iKt\hbar}+e^{-iKt\hbar}e^{K\beta\hbar^2})}{4(3+e^{K\beta\hbar^2})}$$

and

$$g(t) = \mathrm{Re}[\langle \hat{S}_1^{\,z}(t)\hat{S}_1^{\,z}(0)\rangle] = \frac{\hbar^2[2+\cos(\omega t)(1+e^{\hbar\omega\beta})]}{4(3+e^{\hbar\omega\beta})},$$

where

$$\omega = \hbar K .$$

((**Mathematica**))

Here we show a different approach by using Mathematica. In this calculation, we use "MatrixExp". In this case, we directly use the basis of $\{|++\rangle, |+-\rangle, |-+\rangle, |--\rangle\}$.

```
Clear["Global`*"]; H = a (1   0   0   0
                          0  -1   2   0
                          0   2  -1   0
                          0   0   0   1)

{{a, 0, 0, 0}, {0, -a, 2 a, 0},
 {0, 2 a, -a, 0}, {0, 0, 0, a}}

Z = Tr[MatrixExp[-β H]]

3 e^(-a β) + e^(3 a β)

ρ = 1/Z MatrixExp[-β H] // Simplify
```

$$\left\{\left\{\frac{1}{3+e^{4a\beta}}, 0, 0, 0\right\}, \left\{0, \frac{1+e^{4a\beta}}{6+2e^{4a\beta}}, \frac{1-e^{4a\beta}}{6+2e^{4a\beta}}, 0\right\}, \left\{0, \frac{1-e^{4a\beta}}{6+2e^{4a\beta}}, \frac{1+e^{4a\beta}}{6+2e^{4a\beta}}, 0\right\}, \left\{0, 0, 0, \frac{1}{3+e^{4a\beta}}\right\}\right\}$$

```
Eigensystem[H]
```

{{-3 a, a, a, a}, {{0, -1, 1, 0},
  {0, 0, 0, 1}, {0, 1, 1, 0}, {1, 0, 0, 0}}}

$$h1 = \text{MatrixExp}\left[\frac{i}{\hbar} H\, t\right];\; h2 = \text{MatrixExp}\left[\frac{-i}{\hbar} H\, t\right];$$

```
I2 = IdentityMatrix[2]; σz = PauliMatrix[3];
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$$s1 = \frac{\hbar}{2}\,\text{KroneckerProduct}[\sigma z, I2];$$

$$s2 = \frac{\hbar}{2}\,\text{KroneckerProduct}[I2, \sigma z];$$

```
p1 = Tr[ρ .h1.s1.h2.s1] // Simplify
```

$$\frac{\left(2 + e^{4 a \left(\beta - \frac{i t}{\hbar}\right)} + e^{\frac{4 i a t}{\hbar}}\right) \hbar^2}{4 \left(3 + e^{4 a \beta}\right)}$$

$$rule1 = \left\{a \to \frac{K}{4}\, \hbar^2\right\};\; p11 = p1 \,//.\, rule1$$

$$\frac{\left(2 + e^{i K t \hbar} + e^{K \left(\beta - \frac{i t}{\hbar}\right) \hbar^2}\right) \hbar^2}{4 \left(3 + e^{K \beta \hbar^2}\right)}$$