Hot Quantum Mechanics

Thus far we have been principally concerned with energy eigenstates in QM,

$$H|\psi\rangle = E|\psi\rangle . \qquad \underset{E_0 \text{ ground state},}{|\psi_0\rangle,} \quad \left\{ \begin{matrix} |\psi_n\rangle, \\ E_{n>0} \end{matrix} \right\} \text{excitations}$$

In nature one finds instead interacting systems that share some amount of mean energy, which they have received through interaction with other "external" systems. This implies a probability $p(E)$ of finding our system in a state of energy E. Since energy of subsystems is additive, for two weakly interacting subsystems that can be treated as independent

1: E_1	2: E_2

we have

$$p(E = E_1 + E_2) = p(E_1) \cdot p(E_2)$$

(no correlation, and E is additive)

The solution is an exponential, $e^{-E/E_{scale}}$.

This scale of "thermal" excitations is called the temperature T. For historical reasons it is quoted in non-energy units ($°K$), so we have a proportionality constant k_B

$$p(E) \propto e^{-\beta E} \qquad \beta = \frac{1}{k_B T}$$

$$\underbrace{k_B = 1.380\,6503(24) \cdot 10^{-16}\ [\mathrm{erg}\ °K^{-1}]}_{\text{Boltzmann constant}}$$

To less accuracy, other useful forms of k_B are implicit in

$$1\ [\mathrm{meV}] = 11.604\ [°K] \quad , \quad 1\ [°K] = 0.08618\ [\mathrm{meV}]$$

and if you are a chemist,

$$1\ [\mathrm{meV\ particle}^{-1}] = 23.06\ [\mathrm{cal\ mole}^{-1}]$$

Ashcroft & Mermin Solid State Physics

Thermal averages of quantities are often denoted by angle brackets, and are conventional QM matrix elements but weighted by the thermal probability distribution:

$$\underline{\langle \mathcal{O} \rangle} = \eta \sum_n \underbrace{p(E_n)}_{\underline{e^{-\beta E_n}}} \langle \psi_n | \mathcal{O} | \psi_n \rangle .$$

(up to normalization, which η will provide)

The normalization follows from the requirement that the thermal average of 1 is 1,

$$\langle 1 \rangle = \eta \sum_n p(E_n) \underbrace{\langle \psi_n | \psi_n \rangle}_{1} = 1 \ , \quad \therefore \ \eta = \frac{1}{\sum_n p(E_n)}$$

sum over energy eigenstates

This quantity $\sum_n p(E_n)$ is so central to quantum statistical mechanics that it has a special name, the "Zustandsumme" (sum over states),

$$\underline{Z = \sum_n p(E_n) = \sum_n e^{-\beta E_n}} \qquad \text{also} \quad \underline{e^{-\beta F} \equiv Z}$$

$F =$ "free energy"

so

$$\underline{\langle \mathcal{O} \rangle = \frac{1}{Z} \sum_n \langle \psi_n | \mathcal{O} | \psi_n \rangle e^{-\beta E_n}}$$

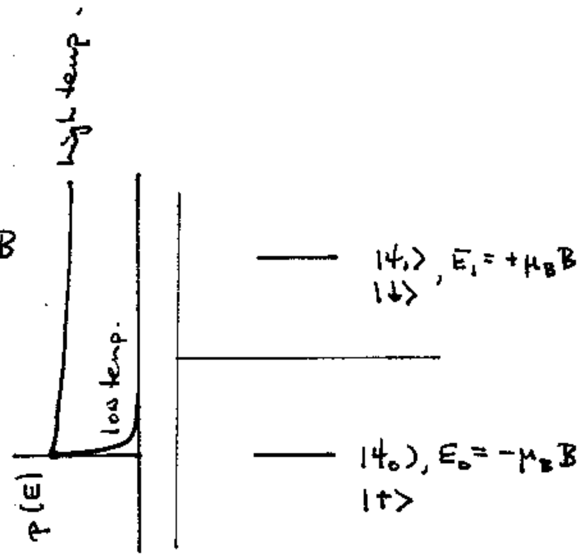
Let's do a quick example of this, with a particle in a magnetic field.

$$H = -\vec{\mu} \cdot \vec{B} = -\mu_B B \sigma_z \qquad \text{for } \vec{B} = B\hat{z}$$

the energy eigenstates and eigenvalues are

$$|\psi_0\rangle = |\uparrow\rangle = \begin{bmatrix}1\\0\end{bmatrix}, \qquad E_0 = -\mu_B B$$

$$|\psi_1\rangle = |\downarrow\rangle = \begin{bmatrix}0\\1\end{bmatrix}, \qquad E_1 = +\mu_B B$$



$$\underline{Z} = \sum_n e^{-\beta E_n} =$$

$$e^{\beta\mu_B B} + e^{-\beta\mu_B B}$$

$$= \underline{2\cosh(\beta\mu_B B)}$$

$$\frac{P_\downarrow}{P_\uparrow} = e^{-\beta\Delta E} = e^{-2\mu_B B/kT} = e^{-2\beta\mu_B B}$$

note trivially $\lim_{T\to 0} Z = n_0 e^{-\beta E_0}$ ← degeneracy of ψ_0

or more usefully $\lim_{T\to\infty} Z = \sum_n 1 = n_{\text{states}}$.
$(\beta \to 0)$

<u>e.g.s of expected values:</u>

$$\mathcal{O} = \vec{S} = \tfrac{1}{2}\hbar\vec{\sigma}$$

what is the thermal average of $\vec{S}$?

$$\langle \vec{S} \rangle = \frac{1}{Z}\sum_n \langle \psi_n | \vec{S} | \psi_n \rangle e^{-\beta E_n}$$

$$= \frac{1}{Z}\cdot\tfrac{1}{2}\hbar\hat{z}\left\{ e^{-\beta E_0} - e^{-\beta E_1}\right\}$$

$$= \tfrac{1}{2}\hbar\hat{z}\,\frac{(e^{\beta\mu_B B} - e^{-\beta\mu_B B})}{(e^{\beta\mu_B B} + e^{-\beta\mu_B B})} = \tfrac{1}{2}\hbar\hat{z}\tanh(\beta\mu_B B)$$

limits:

<u>very low temp</u> $T \to 0$, $\beta \to \infty$, $\tanh(\beta\mu_B B) \to 1$,

$$\langle \vec{S} \rangle = +\tfrac{1}{2}\hbar\hat{z}$$ (just the $|\psi_0\rangle$ expected value)

<u>high temp</u> $T \to \infty$, $\beta \to 0$, $\tanh(\beta\mu_B B) \to \beta\mu_B B$

$$\langle \vec{S} \rangle \to \underbrace{\tfrac{1}{2}\hbar\hat{z} \cdot \frac{\mu_B B}{k_B T}}\ \xrightarrow[T\to\infty]{} 0$$ (thermal disorder completely washes out any preferred spin orientation)

"Curie's law: high temp. magnetization (actually susceptibility, $\frac{\partial M}{\partial H}$) scales like $1/T$.
Characteristic of permanent magnetic moments.

n.b. <u>low temp leading corrections</u>

$$\langle \vec{S} \rangle \approx \tfrac{1}{2}\hbar\hat{z}\left\{1 - 2\underbrace{e^{-2\beta\mu_B B}}_{e^{-E_{gap}/kT}} + \mathcal{O}\big(\underbrace{e^{-4\beta\mu_B B}}_{e^{-2E_{gap}/kT}}\big)\right\}$$

$, \quad E_{gap} = E_1 - E_0$

<u>Very</u> characteristic low temperature behavior, $e^{-\beta E_{gap}}$, approach to $|\psi_0\rangle$ properties for a gapped system.

Typically you find power-law (T^p) corrections if gapless.

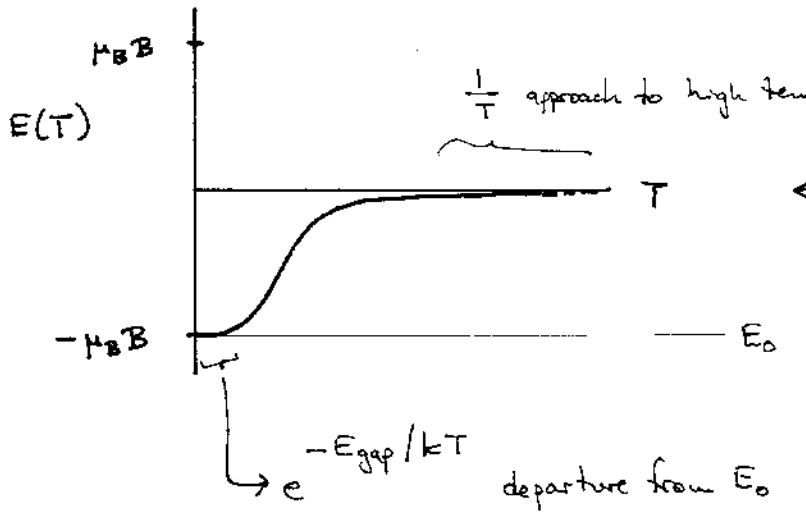
Another example : the <u>expected energy</u> "thermal energy"

$$\underline{E(T) \equiv \langle H \rangle} = \frac{1}{Z}\sum_n \langle \psi_n | H | \psi_n \rangle \, e^{-\beta E_n} = \underline{\frac{1}{Z}\sum_n E_n e^{-\beta E_n}}$$

in our example

$$E(T) = \langle H \rangle = \frac{1}{\left(e^{\beta\mu_B B} + e^{-\beta\mu_B B}\right)}\left\{ \underbrace{(-\mu_B B)}_{E_0}\cdot e^{\beta\mu_B B} + \underbrace{(+\mu_B B)}_{E_1}\cdot e^{-\beta\mu_B B} \right\}$$

$$= -\mu_B B \tanh(\beta\mu_B B)$$



$\left(E(T) \approx -\frac{(\mu_B B)^2}{k_B T} \right)$

← multiplicity-weighted mean energy [all states are equally likely as $T \to \infty$].

It stalls out because we have a finite set of states; we run out of new states to populate with increasing T.

$$E(T) \approx E_0 \cdot \left\{ 1 - 2\underbrace{e^{-2\beta\mu_B B}}_{e^{-E_{gap}/kT}} \right\}$$

Note we can get E(T) simply from Z :

$$\underline{-\frac{\partial}{\partial\beta}\ln Z} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_n e^{-\beta E_n} = +\frac{1}{Z}\sum_n E_n e^{-\beta E_n}$$

$$\underline{= E(T)}$$

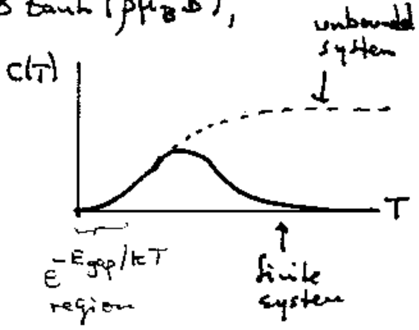
Specific heat

A frequent differential measurement is the specific heat $c(T)$, which is the change in thermal energy w.r.t. temperature T,

$$\underline{c(T) = \frac{dE(T)}{dT}} = -k_B \beta^2 \frac{d}{d\beta} E(T) = \underline{+k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z}$$

Again using our spin-½ example, with $E(T) = -\mu_B B \tanh(\beta \mu_B B)$, we find

$$\underline{c(T)} = \underline{k_B (\mu_B B)^2 \beta^2 \frac{1}{\cosh^2(\beta \mu_B B)}}$$



Limits:

low temp, $\cosh(\beta \mu_B B) \approx \frac{1}{2} e^{\beta \mu_B B}$, $\quad \lim_{T \to 0} \underline{c(T)} = 4(\mu_B B)^2 k_B^{-1} T^{-2} \underline{e^{-2\beta \mu_B B}}$

$T \to 0$, $\beta \to \infty$

$\propto e^{-E_{gap}/kT} \cdot T$ power

but with no $c(0)$.

high temp $\quad \lim_{\substack{T \to \infty \\ \beta \to 0}} \underline{c(T)} = (\mu_B B)^2 \cdot \underline{\frac{1}{k_B T^2}}$

It's saturating in this finite system because we have already populated all available states.

Susceptibility

This is a very important standard laboratory measurement for magnetic materials.

Put the system in an external field, say in the $\hat{z}$ direction,

$$H = H_0 - \mu\Big(\sum_i S_{zi}\Big) B_{ext} = H_0 - M_z B_{ext}$$

We can measure the induced expected magnetization

$$\langle M_z \rangle = \mu \langle \sum_i S_{zi} \rangle$$ versus temp. & external field.

The slope at small field per ion is the "zero-field susceptibility",

$$\chi(T) \equiv \frac{1}{N} \left. \frac{\partial \langle M_z \rangle}{\partial B_{ext}} \right|_{B_{ext}=0}$$

actually in general this is a tensor,

$$\chi_{ij}(T) \equiv \frac{1}{N} \left. \frac{\partial \langle M_i \rangle}{\partial B_{ext_j}} \right|_{B_{ext}=0}$$

but for the cases we will consider it's isotropic, $\chi_{ij} = \delta_{ij}\chi$.

From the Feynman-Hellman theorem,

$$\langle M_z \rangle = \left\{ - \frac{\partial}{\partial B_{ext}} \langle H \rangle \right\} \Big|_{B_{ext}=0}$$

and so

$$\chi(T) = \frac{1}{N} \left. \frac{\partial \langle M_z \rangle}{\partial B_{ext}} \right|_{B_{ext}=0} = - \left. \frac{\partial^2 e}{\partial B_{ext}^2} \right|_{B_{ext}=0} \qquad e \equiv \frac{\langle H \rangle}{N}$$

Density matrix form

We have expressed these thermodynamic quantities like Z in terms of a complete set of energy eigenvalues $\{E_n\}$ (and matrix elements $\langle \psi_n | \mathcal{O} | \psi_n \rangle$).

Usually we do not have a complete set of eigenvalues, but we do know what the hamiltonian matrix H is in some basis.
We can recast our results in terms of the "density matrix"

$$\underline{\rho \equiv e^{-\beta H}}$$

1st, note in a diagonal (eigenvector) basis

$$H = \begin{bmatrix} E_1 & & 0 \\ & E_2 & \\ 0 & & \ddots & \\ & & & E_N \end{bmatrix} \qquad \text{so} \quad \mathrm{Tr}(H) = \sum_n E_n$$

so

$$\rho = e^{-\beta H} = \begin{bmatrix} e^{-\beta E_1} & & \\ & e^{-\beta E_2} & \\ & & \ddots & \\ & & & e^{-\beta E_N} \end{bmatrix} \qquad \text{so} \quad \mathrm{Tr}(\rho) = \mathrm{Tr}(e^{-\beta H})$$

$$= \sum_n e^{-\beta E_n}$$

this is just the partition function Z:

$$Z = \mathrm{Tr}(\rho) = \mathrm{Tr}(e^{-\beta H}) = \sum_n e^{-\beta E_n}$$

We can similarly write the thermal averages as traces ...

Starting with the simplest, the "thermal energy" is

$$E(T) = \langle H \rangle = \frac{1}{Z} \sum_n E_n e^{-\beta E_n}$$

$$= \frac{1}{Z} \operatorname{Tr}\left\{ H e^{-\beta H} \right\}$$ (clearest in an eigenvalue basis) diagonal

$$= \frac{\operatorname{Tr}\left\{ H e^{-\beta H} \right\}}{\operatorname{Tr}\left\{ e^{-\beta H} \right\}} = \frac{\operatorname{Tr}\left\{ \rho H \right\}}{\operatorname{Tr}\left\{ \rho \right\}}$$

$\operatorname{Tr}(\rho H) = \operatorname{Tr}(H\rho)$ of course

Other quantities?

$$\underline{\langle \mathcal{O} \rangle} = \frac{1}{Z} \sum_n \langle \psi_n | \mathcal{O} | \psi_n \rangle e^{-\beta E_n}$$

$$= \frac{1}{Z} \sum_n \langle \psi_n | \mathcal{O} e^{-\beta H} | \psi_n \rangle = \frac{1}{Z} \operatorname{Tr}\left\{ \mathcal{O} \rho \right\},$$

$$= \underline{\frac{\operatorname{Tr}\left\{ \rho \mathcal{O} \right\}}{\operatorname{Tr}\left\{ \rho \right\}}}$$

This attractively simple form is useful if the Hilbert space is simple or relatively small, so we can evaluate $e^{-\beta H}$ and $\mathcal{O} e^{-\beta H}$ explicitly & take their traces.

Another use is in expansions, especially <u>high-temperature expansions</u> (power series in T^{-1}) that can often be evaluated to quite high order.

High temperature series

Simple thermodynamic properties can be determined from the partition function

$$Z = \mathrm{Tr}\{\rho\} = \mathrm{Tr}\{e^{-\beta H}\} \qquad \beta = \frac{1}{k_B T}$$

e.g. $$E(T) = -\frac{\partial}{\partial\beta}\ln Z$$

and
$$c(T) = k_B \beta^2 \frac{\partial^2}{\partial\beta^2}\ln Z \,.$$

If we cannot evaluate $\mathrm{Tr}\{e^{-\beta H}\}$ directly, we may nonetheless be able to evaluate $\mathrm{Tr}\{H\}$, $\mathrm{Tr}\{H^2\}$ ....

This leads to a high-temperature series for the partition function

$$Z = \sum_{m=0}^{\infty} \frac{(-\beta)^m}{m!} \mathrm{Tr}\{H^m\}$$

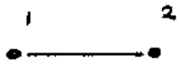
which may even converge rapidly.

and for any thermal average

$$\langle \mathcal{O} \rangle = \frac{\sum_{m=0}^{\infty} \frac{(-\beta)^m}{m!} \mathrm{Tr}\{\mathcal{O} H^m\}}{\sum_{m=0}^{\infty} \frac{(-\beta)^m}{m!} \mathrm{Tr}\{H^m\}}$$

This ratio of two series can of course lead to complicated coefficients.

Let's illustrate this with our simplest example of interacting spins, the spin dimer



$$H = J\vec{S}_1 \cdot \vec{S}_2$$

$$= J\left\{ S_1^z S_2^z + \tfrac{1}{2}\left(S_1^+ S_2^- + S_1^- S_2^+\right)\right\}$$

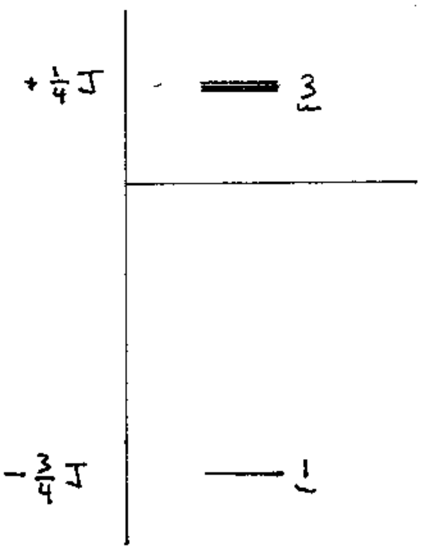
$$Z = \mathrm{Tr}\{\rho\} = \mathrm{Tr}\{e^{-\beta H}\} = \sum_n e^{-\beta E_n}$$

Actually we can easily write Z directly because we know the spectrum:

$$\vec{S}_{tot} = \vec{S}_1 + \vec{S}_2 \qquad \vec{S}_{tot}^{\,2} = \vec{S}_1^{\,2} + \vec{S}_2^{\,2} + 2\vec{S}_1 \cdot \vec{S}_2$$

$$H = \tfrac{1}{2}J\left\{ \vec{S}_{tot}^{\,2} - \vec{S}_1^{\,2} - \vec{S}_2^{\,2} \right\}$$

$S_{tot} = \frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$



eigenvalues

$$E_n = \tfrac{1}{2}J\left\{ S_{tot}(S_{tot}+1) \underbrace{- 2\cdot\tfrac{1}{2}\cdot\tfrac{3}{2}}_{-\frac{3}{2}} \right\}$$

$$= \begin{cases} +\frac{1}{4}J & S_{tot} = 1 \\ -\frac{3}{4}J & S_{tot} = 0 \end{cases}$$

so $\underline{\text{exact } Z} = \underbrace{e^{-\beta\cdot(-\frac{3}{4}J)}}_{\psi_0 \text{ contrib.}} + \underbrace{\underset{\uparrow \, 3 \text{ states}}{3} \cdot e^{-\beta\cdot(+\frac{1}{4}J)}}_{\psi_1 \text{ contrib.}} = \underline{e^{\frac{3}{4}\beta J} + 3e^{-\frac{1}{4}\beta J}}$

However, suppose we don't know that and want to evaluate the high-temp. series directly...

$$Z = \sum_{m=0}^{\infty} \frac{(-\beta)^m}{m!} \mathrm{Tr}\{H^m\}$$

$O(\beta^0)$ term $\quad \mathrm{Tr}\{H^0\} = \mathrm{Tr}\{I\} = N$ total number of states in Hilbert space.

e.g. $\underbrace{|{+}{+}\rangle, |{+}{-}\rangle, |{-}{+}\rangle, |{-}{-}\rangle}_{\underset{\sim}{4} \text{ basis states}}$

$\therefore$ $m=0$ term is

$$\frac{(-\beta)^0}{0!} \mathrm{Tr}\{I\} = 4$$

$$\overset{?}{=} e^{\frac{3}{4}\beta J} + 3e^{-\frac{1}{4}\beta J}$$

at $\beta = 0$? ✓

$O(T^{-1}) = O(\beta)$ term

$$\underbrace{\frac{(-\beta)^1}{1!}}_{-\beta} \underbrace{\mathrm{Tr}\{H\}}$$

we can evaluate this in any basis.
z-component spins is convenient, as we know the effect of H on these states

$$H|{+}{+}\rangle = J\left\{ S_1^z S_2^z + \tfrac{1}{2}(S_1^+ S_2^- + S_1^- S_2^+) \right\} |{+}{+}\rangle$$

$$= +\tfrac{1}{4} J |{+}{+}\rangle$$

$$H|{+}{-}\rangle = -\tfrac{1}{4} J |{+}{-}\rangle + \tfrac{1}{2} J |{-}{+}\rangle$$

$$H|{-}{+}\rangle = -\tfrac{1}{4} J |{-}{+}\rangle + \tfrac{1}{2} J |{+}{-}\rangle$$

$$H|{-}{-}\rangle = +\tfrac{1}{4} J |{-}{-}\rangle$$

So, $\mathrm{Tr}\{H\} = \sum_n \langle \phi_n | H | \phi_n \rangle$

<u>any</u> basis

$$\mathrm{Tr}\{H\} = \begin{array}{l} \langle ++|H|++\rangle \\ + \langle +-|H|+-\rangle \\ + \langle -+|H|-+\rangle \\ + \langle --|H|--\rangle \end{array} = \begin{array}{l} +\frac{1}{4}J \\ -\frac{1}{4}J \\ -\frac{1}{4}J \\ +\frac{1}{4}J \end{array} = 0$$

<u>H is traceless</u>

$\therefore\ \mathcal{O}(\beta)$ term $= -\beta\,\mathrm{Tr}\{H\} = 0$

exact
$$Z = e^{\frac{3}{4}\beta J} + 3e^{-\frac{1}{4}\beta J} = 1 + \frac{3}{4}\beta J + \frac{1}{2}\cdot\frac{3^2}{4^2}\beta^2 J^2 + \dots$$
$$+3\left[1 - \frac{1}{4}\beta J + \frac{1}{2}\cdot\frac{(-1)^2}{4^2}\beta^2 J^2 + \dots\right]$$
$$= \underbrace{4}_{\text{dim. of Hilbert space}} + 0\cdot\beta J + \frac{3}{8}\beta^2 J^2 + \mathcal{O}(\beta^3)$$

Can we check the $\mathcal{O}(\beta^2)$ term?

$H^2|++\rangle = \frac{1}{16}J^2|++\rangle \qquad H^2|--\rangle = \frac{1}{16}J^2|--\rangle$

$\langle +-|H^2|+-\rangle = \left|H|+-\rangle\right|^2 = \left(-\frac{1}{4}J\right)^2 + \left(\frac{1}{2}J\right)^2 = \frac{5}{16}J^2$

$= \langle -+|H^2|-+\rangle$

$\therefore\ \mathrm{Tr}\{H^2\} = \frac{3}{4}J^2$

$\mathcal{O}(\beta^2)$ term in Z is $\quad \frac{(-\beta)^2}{2!}\mathrm{Tr}\{H^2\} = +\frac{3}{8}\beta^2 J^2$ ✓

Given this Z series, we can obtain high-temperature series for the internal energy and specific heat. These are (adding terms to $O(\beta^5)$ to Z),

$$Z = 4 + \frac{3}{8}(\beta J)^2 + \frac{1}{16}(\beta J)^3 + \frac{7}{512}(\beta J)^4 + \frac{1}{512}(\beta J)^5 + O(\beta^6)$$

$$\therefore E(T) = -\frac{\partial}{\partial\beta}\ln(Z) = J\cdot\left\{ -\frac{3}{16}\beta J - \frac{3}{64}(\beta J)^2 + \frac{1}{256}(\beta J)^3 + \frac{5}{1024}(\beta J)^4 + \frac{13}{20480}(\beta J)^5 + \dots \right\}$$

$$c(T) = k_B\beta^2\frac{\partial^2}{\partial\beta^2}\ln(Z)$$

$$= k_B \cdot \left\{ \frac{3}{16}(\beta J)^2 - \frac{3}{32}(\beta J)^3 - \frac{3}{256}(\beta J)^4 + \frac{5}{256}(\beta J)^5 + \dots \right\}$$

Just for completeness, and as a reminder that the series may be worse than the exact result, they (the exact results) are

$$Z = e^{+\frac{3}{4}\beta J} + 3\cdot e^{-\frac{1}{4}\beta J}$$

$$E(T) = -\frac{3}{4}J\,\frac{(1 - e^{-\beta J})}{(1 + 3e^{-\beta J})}$$

$$c(T) = k_B\cdot\frac{3(\beta J)^2\, e^{-\beta J}}{(1 + 3e^{-\beta J})^2}$$

As a final example, what is the zero-field magnetic susceptibility of this spin-dimer?

$$\chi(T) = \frac{\beta}{Z}\, \mathrm{Tr}\{ M_z^2\, e^{-\beta H} \}$$

$$= \frac{\beta}{Z} \sum_n \langle \psi_n | M_z^2 | \psi_n \rangle e^{-\beta E_n}$$

(E eigenstates)

$$M_z = \mu_B \sum_i S_i^z = S^z_{tot}$$

$$\langle ++ | M_z^2 | ++ \rangle = \mu_B^2 \langle ++ | 1^2 | ++ \rangle = \mu_B^2$$

$$\langle -- | M_z^2 | -- \rangle = \mu_B^2$$

$$\langle 1,0 | M_z^2 | 1,0 \rangle = 0 = \langle 0,0 | M_z^2 | 0,0 \rangle$$

S^{tot} S_z^{tot}

$$\therefore\ \chi(T) = \frac{\beta \cdot 2\mu_B^2\, e^{-\frac{1}{4}\beta J}}{e^{+\frac{3}{4}\beta J} + 3e^{-\frac{1}{4}\beta J}} = 2\mu_B^2 \beta \frac{e^{-\beta J}}{\left(1 + 3e^{-\beta J}\right)}$$

high-temp series

$$\chi(T) = \underbrace{\frac{\mu_B^2}{2} \cdot \frac{1}{k_B T}}_{\text{Curie's law}} \cdot \left\{ 1 - \frac{1}{4}\beta J - \frac{1}{16}(\beta J)^2 + \frac{1}{192}(\beta J)^3 + \frac{5}{768}(\beta J)^4 + \dots \right\}$$

$E(T)$, $c(T)$, $\chi(T)$

Note, as promised, all three thermodynamic variables have the expected

$$e^{-E_{gap}/kT} = e^{-\beta E_{gap}} \quad (\text{here } = e^{-\beta J})$$

low-temperature approach to their thermodynamic exponential approaches to their low-temperature limits. (zero)