3. ***Doublet excited states*** Some organic molecules have a doublet ($S=\frac{1}{2}$) excited state at an energy Δ above a singlet (S=0) ground state. (a) Find an expression for the magnetic moment $<\mu>$ in a field B. (b) Show that the susceptibility for $k_B T >> \Delta$ is approximately independent of Δ. (c) Will this system be cooled by adiabatic magnetization, or demagnetization? Explain your answer.

(a)

When a magnetic field is applied, the state energy will become

$$\underbrace{0}_{\text{Singlet ground state}}, \quad \underbrace{\Delta - \vec{\mu}\cdot\vec{B},\ \Delta + \vec{\mu}\cdot\vec{B}}_{\text{Doublet}}$$

$\therefore$ the three states are

$0\ (j_z = 0),\ \Delta - \mu B\ (j_z = -\frac{1}{2}),\ \Delta + \mu B\ (j_z = +\frac{1}{2})$

$$\therefore \ <\mu> \ = \sum_{j_z} \mu \frac{N_{j_z}}{N} = \frac{+\mu e^{-(\Delta-\mu B)/k_B T} - \mu e^{-(\Delta+\mu B)/k_B T}}{1 + e^{-(\Delta-\mu B)/k_B T} + e^{-(\Delta+\mu B)/k_B T}}$$

$$= \frac{\mu e^{-(\Delta)/k_B T}\left[e^{\mu B/k_B T} - e^{-\mu B/k_B T}\right]}{1 + e^{-(\Delta)/k_B T}\left[e^{\mu B/k_B T} + e^{-\mu B/k_B T}\right]}$$

$$= \frac{2\mu \sinh[\mu B / k_B T]}{e^{\Delta/k_B T} + 2\cosh[\mu B / k_B T]}$$

(b)

For $T >> \Delta$,

$$<\mu> \ = \frac{2\mu \sinh[\mu B / k_B T]}{\exp[\Delta / k_B T] + 2\cosh[\mu B / k_B T]}$$

$$\approx \frac{2\mu \sinh[\mu B / k_B T]}{1 + 2\cosh[\mu B / k_B T]} \quad \text{which is independent of } \Delta.$$

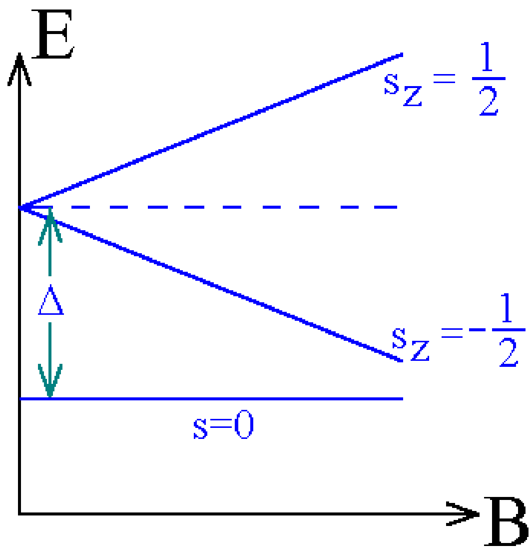
For small field,

$\sinh[\mu B / k_B T] \approx \mu B / k_B T, \ \cosh[\mu B / k_B T] \approx 1$

$$<\mu> \ \approx \frac{2\mu \cdot \mu B / k_B T}{1+2} = \frac{2\mu^2 B}{3k_B T}$$

$$\chi = \frac{\partial(N <\mu>)}{\partial B} \approx \frac{2\mu^2 N}{3k_B T}$$

(c)



In the case of demagnetization cooling, the energy levels in the paramagnetic salt is further and further apart as the magnetic field is increased. The present situation is just opposite, as can be seen from the figure, the s=0 and the lowest of s=1/2 (i.e. s_z=-1/2) get closer together as the magnetic field is increased. Hence we expect cooling resulted from magnetization for this system (i.e. cooling by adiabatic magnetization). We can make the argument as follow:

Assume B is large and T is low so that $\mu B \approx \Delta >> k_B T$, then we need only to consider the lowest two levels.

$$e^{-F/k_BT} = \sum e^{-E_n/k_BT} \approx e^0 + e^{-(\Delta-\mu B)/k_BT}$$

$$\Rightarrow \frac{F}{k_BT} = f\left(\frac{\Delta - \mu B}{k_BT}\right) \quad \text{(f is a functional form)}$$

$$\Rightarrow F = k_BT\, f\left(\frac{\Delta - \mu B}{k_BT}\right)$$

$$\Rightarrow S = -\frac{\partial F}{\partial T} = k_B\left[-f\left(\frac{\Delta - \mu B}{k_BT}\right) + T\cdot\left(\frac{\Delta - \mu B}{k_BT^2}\right) f'\left(\frac{\Delta - \mu B}{k_BT}\right)\right]$$

$$\Rightarrow S = g\left(\frac{\Delta - \mu B}{k_BT}\right) \quad \text{(g is another functional form)}$$

For adiabatic change, dS = 0. If B is increased, the numerator will become smaller. T has to be decreased also to mantain constant S.