DATE 2021/07/25/Sun

NO. 1.

Ce^{3+} の磁化.

Ce^{3+} : $S=\frac{1}{2}$. $L=3$. $J=\frac{5}{2}$. $J_z = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$

結晶場 Hamiltonian は

$$\hat{H}_{crys} = B_4\left(O_4^0 + 5O_4^4\right)$$

$$O_4^0 = 35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2$$

$$O_4^4 = \frac{1}{2}\left(J_+^4 + J_-^4\right)$$

$\begin{cases} O_4^0 \rightarrow J, J_z \text{ を代入すれば定数になる。} \\ O_4^4 \rightarrow J_z \text{ に応じて計算する.} \end{cases}$

固有値たち

$$H_{crys} = \begin{array}{c|cccccc} J_z & |\frac{5}{2}\rangle & |\frac{3}{2}\rangle & |\frac{1}{2}\rangle & |-\frac{1}{2}\rangle & |-\frac{3}{2}\rangle & |-\frac{5}{2}\rangle \\ \hline \langle\frac{5}{2}| & 60B_4 & 0 & 0 & 0 & 60\sqrt{5}B_4 & 0 \\ \langle\frac{3}{2}| & 0 & -180B_4 & 0 & 0 & 0 & 60\sqrt{5}B_4 \\ \langle\frac{1}{2}| & 0 & 0 & 120B_4 & 0 & 0 & 0 \\ \langle-\frac{1}{2}| & 0 & 0 & 0 & 120B_4 & 0 & 0 \\ \langle-\frac{3}{2}| & 60\sqrt{5}B_4 & 0 & 0 & 0 & -180B_4 & 0 \\ \langle-\frac{5}{2}| & 0 & 60\sqrt{5}B_4 & 0 & 0 & 0 & 60B_4 \end{array}$$

$$J_\pm|J, J_z\rangle = \sqrt{(J\mp J_z)(J\pm J_z+1)}\,|J, J_z \pm 1\rangle$$

(i) $J_z = \frac{5}{2}$ のとき

$$\hat{H}_{crys}|\tfrac{5}{2}\rangle = B_4\left(O_4^0 + 5O_4^4\right)|\tfrac{5}{2}\rangle$$
$$= B_4 O_4^0|\tfrac{5}{2}\rangle + 5B_4 O_4^4|\tfrac{5}{2}\rangle$$

$$B_4 O_4^0|\tfrac{5}{2}\rangle = 60B_4|\tfrac{5}{2}\rangle$$

$$5B_4 O_4^4|\tfrac{5}{2}\rangle = 5B_4 \times \frac{1}{2}\left(J_+^4 + J_-^4\right)|\tfrac{5}{2}\rangle$$

J_+ は $|\frac{5}{2}\rangle$ より大きくなるので不適

$$= \frac{5}{2}B_4 J_-^4|\tfrac{5}{2}\rangle$$

$J_-|J, J_z\rangle$ を4回やる.

$$= \frac{5}{2}B_4 \times 24\sqrt{5}\,|-\tfrac{3}{2}\rangle$$

$$= 60\underset{\sqrt{5}}{\wedge}B_4|-\tfrac{3}{2}\rangle$$

よって

$$\hat{H}_{crys}|\tfrac{5}{2}\rangle = 60B_4|\tfrac{5}{2}\rangle + 60\sqrt{5}B_4|-\tfrac{3}{2}\rangle$$

よって．

$\langle \frac{5}{2}|\hat{H}_{\mathrm{crys}}|\frac{5}{2}\rangle = 60B_4$

$\langle \frac{3}{2}|\hat{H}_{\mathrm{crys}}|\frac{5}{2}\rangle = 0$.

$\vdots$

$\langle -\frac{3}{2}|\hat{H}_{\mathrm{crys}}|\frac{5}{2}\rangle = 60\sqrt{5}B_4$

$\vdots$

$\langle -\frac{5}{2}|\hat{H}_{\mathrm{crys}}|\frac{5}{2}\rangle = 0$

となる．

(ii) $J_z = \frac{3}{2}$ のとき

$$\hat{H}_{\mathrm{crys}}|\tfrac{3}{2}\rangle = B_4(O_4^0 + 5O_4^4)|\tfrac{3}{2}\rangle$$
$$= -180B_4|\tfrac{3}{2}\rangle + 5\times\tfrac{1}{2}(J_+^4 + J_-^4)|\tfrac{3}{2}\rangle$$

$$\frac{5}{2}(J_+^4 + J_-^4)|\tfrac{3}{2}\rangle = \frac{5}{2}J_-^4|\tfrac{3}{2}\rangle$$

~~$\frac{5}{2}\times 60\sqrt{5}$~~

$$= 60\sqrt{5}\underset{B_4}{\wedge}|-\tfrac{5}{2}\rangle$$

よって

$$\hat{H}_{\mathrm{crys}}|\tfrac{3}{2}\rangle = -180B_4|\tfrac{3}{2}\rangle + 60\sqrt{5}B_4|-\tfrac{5}{2}\rangle$$

$\langle \frac{5}{2}|\hat{H}_{\mathrm{crys}}|\frac{3}{2}\rangle = 0$

$\langle \frac{3}{2}|\hat{H}_{\mathrm{crys}}|\frac{3}{2}\rangle = -180B_4$

$\vdots$

$\langle -\frac{5}{2}|\hat{H}_{\mathrm{crys}}|\frac{3}{2}\rangle = 60\sqrt{5}B_4$

(iii) $J_z = \frac{1}{2}$ のとき

$$\hat{H}_{\mathrm{crys}}|\tfrac{1}{2}\rangle = B_4(O_4^0 + 5O_4^4)|\tfrac{1}{2}\rangle$$
$$= B_4\times 120|\tfrac{1}{2}\rangle + 5O_4^4|\tfrac{1}{2}\rangle$$
$$= 120B_4|\tfrac{1}{2}\rangle$$

J_+^4, J_-^4 いずれも 4つ全部やると $\pm\frac{5}{2}$ こえる

よって

$\langle \frac{1}{2}|\hat{H}_{\mathrm{crys}}|\frac{1}{2}\rangle = 120B_4$, others $= 0$

(iv) $J_z = -\frac{1}{2}$ のとき

J_+^4, J_-^4 どちらも ×

$$\hat{H}_{\mathrm{crys}}|-\tfrac{1}{2}\rangle = B_4(O_4^0 + 5O_4^4)|-\tfrac{1}{2}\rangle$$
$$= 120B_4|-\tfrac{1}{2}\rangle$$

よって

$\langle -\frac{1}{2}|\hat{H}_{\mathrm{crys}}|-\frac{1}{2}\rangle = 120B_4$

others $= 0$

(v) $J_z = -\frac{3}{2}$ のとき

J_+^4 が上がれる.

$$\hat{H}_{\mathrm{crys}}|-\tfrac{3}{2}\rangle = B_4(O_4^0 + 5O_4^4)|-\tfrac{3}{2}\rangle$$
$$= -180B_4|-\tfrac{3}{2}\rangle + 5B_4O_4^4|-\tfrac{3}{2}\rangle$$
$$= -180B_4|-\tfrac{3}{2}\rangle + B_4\times 60\sqrt{5}|\tfrac{5}{2}\rangle$$
$$= -180B_4|-\tfrac{3}{2}\rangle + 60\sqrt{5}B_4|\tfrac{5}{2}\rangle$$

よって　省略(crys)

$\langle \frac{5}{2}|\hat{H}|\cancel{\frac{3}{2}}\,{-\frac{3}{2}}\rangle = 60\sqrt{5}B_4$

$\vdots$

$\langle -\frac{3}{2}|\hat{H}|-\frac{3}{2}\rangle = -180B_4$　　others $= 0$

(vi) $J_z = -\frac{5}{2}$ のとき.

$$\hat{H}_{crys}\left|-\tfrac{5}{2}\right\rangle = B_4\left(O_4^0 + 5O_4^4\right)\left|-\tfrac{5}{2}\right\rangle$$
$$= 60B_4\left|-\tfrac{5}{2}\right\rangle + 5B_4 O_4^4\left|-\tfrac{5}{2}\right\rangle$$
$$= 60B_4\left|-\tfrac{5}{2}\right\rangle + B_4\, 60\sqrt{5}\left|\tfrac{3}{2}\right\rangle$$
$$= 60B_4\left|-\tfrac{5}{2}\right\rangle + 60\sqrt{5}B_4\left|\tfrac{3}{2}\right\rangle$$

← J_+^4 は ok.

よって.

$\left\langle\tfrac{3}{2}\right|\hat{H}\left|-\tfrac{5}{2}\right\rangle = 60\sqrt{5}B_4$, $\left\langle-\tfrac{5}{2}\right|\hat{H}\left|-\tfrac{5}{2}\right\rangle = 60B_4$, others $=0$

H_{crys} を 並べかえると.

$$\hat{H}_{crys} = \begin{array}{c|cccccc} & |\frac{5}{2}\rangle & |-\frac{3}{2}\rangle & |\frac{3}{2}\rangle & |-\frac{5}{2}\rangle & |\frac{1}{2}\rangle & |-\frac{1}{2}\rangle \\ \hline \langle\frac{5}{2}| & 60B_4 & 60\sqrt{5}B_4 & & & & \\ \langle-\frac{3}{2}| & 60\sqrt{5}B_4 & -180B_4 & & & & \\ \langle\frac{3}{2}| & & & -180B_4 & 60\sqrt{5}B_4 & & \\ \langle-\frac{5}{2}| & & & 60\sqrt{5}B_4 & 60B_4 & & \\ \langle\frac{1}{2}| & & & & & 120B_4 & \\ \langle-\frac{1}{2}| & & & & & & 120B_4 \end{array}$$

→ 新しい固有状態は $|\pm\frac{3}{2}\rangle$ と $|\pm\frac{5}{2}\rangle$ の $\boxed{線形結合}$ でかかれる

→ $|\pm\frac{1}{2}\rangle$ も入れたら 6パターン ある.

$$|\alpha\rangle = \sqrt{\tfrac{5}{6}}\left|\tfrac{5}{2}\right\rangle + \sqrt{\tfrac{1}{6}}\left|-\tfrac{3}{2}\right\rangle$$
$$|\beta\rangle = \sqrt{5/6}\left|-\tfrac{5}{2}\right\rangle + \sqrt{1/6}\left|\tfrac{3}{2}\right\rangle$$
$$|\gamma\rangle = \left|\tfrac{1}{2}\right\rangle$$
$$|\delta\rangle = \left|-\tfrac{1}{2}\right\rangle$$
$$|\kappa\rangle = \sqrt{1/6}\left|\tfrac{5}{2}\right\rangle - \sqrt{5/6}\left|-\tfrac{3}{2}\right\rangle$$
$$|\lambda\rangle = \sqrt{1/6}\left|-\tfrac{5}{2}\right\rangle - \sqrt{5/6}\left|+\tfrac{3}{2}\right\rangle$$

を基底関数として再度計算.

固有値が求まる　対角化

$$\left(\hat{H}\right)\left(\psi_n\right) = \begin{pmatrix} E & & 0 \\ & \ddots & \\ 0 & & E \end{pmatrix}\left(\psi_n\right)$$

→ Eに関する行列が対角化された状態を目指す.

固有値の行列が対角化された!

$$\hat{H} = \begin{array}{c|cccccc} & |\alpha\rangle & |\beta\rangle & |\gamma\rangle & |\delta\rangle & |\kappa\rangle & |\lambda\rangle \\ \hline \langle\alpha| & 120B_4 & 0 & 0 & 0 & 0 & 0 \\ \langle\beta| & 0 & 120B_4 & 0 & 0 & 0 & 0 \\ \langle\gamma| & 0 & 0 & 120B_4 & 0 & 0 & 0 \\ \langle\delta| & 0 & 0 & 0 & 120B_4 & 0 & 0 \\ \langle\kappa| & 0 & 0 & 0 & 0 & -240B_4 & 0 \\ \langle\lambda| & 0 & 0 & 0 & 0 & 0 & -240B_4 \end{array}$$

Γ_8

Γ_7

$\langle\alpha| = (|\alpha\rangle)^{\dagger} = |\alpha\rangle$

⋮

より. $\langle\alpha|\hat{H}|\beta\rangle = \langle\beta|\hat{H}|\alpha\rangle$

←赤文字は この性質より導かれたAnswer

$$\hat{H}_{crys}|\alpha\rangle = B_4(O_4^0 + 5O_4^4)\left(\sqrt{\frac{5}{6}}\left|\frac{5}{2}\right\rangle + \sqrt{\frac{1}{6}}\left|-\frac{3}{2}\right\rangle\right)$$

$$\cancel{= B_4\sqrt{\frac{5}{6}}O_4}$$

$$= \sqrt{\frac{5}{6}}\underbrace{\left(B_4(O_4^0 + 5O_4^4)\right)\left|\frac{5}{2}\right\rangle} + \sqrt{\frac{1}{6}}\underbrace{B_4(O_4^0 + 5O_4^4)\left|-\frac{3}{2}\right\rangle}$$

$$= \sqrt{\frac{5}{6}}\left(60B_4\left|\frac{5}{2}\right\rangle + 60\sqrt{5}B_4\left|-\frac{3}{2}\right\rangle\right) + \sqrt{\frac{1}{6}}\left(-180B_4\left|-\frac{3}{2}\right\rangle + 60\sqrt{5}B_4\left|\frac{5}{2}\right\rangle\right)$$

$$= \underline{\left(\sqrt{\frac{5}{6}}(60B_4) + 60\sqrt{\frac{5}{6}}B_4\right)\left|\frac{5}{2}\right\rangle + \left(60\sqrt{5}B_4 \times \frac{\sqrt{5}}{\sqrt{6}} - 180 \times \sqrt{\frac{1}{6}}B_4\right)\left|-\frac{3}{2}\right\rangle}$$

$$\langle\alpha|\hat{H}_{crys}|\alpha\rangle = \left\langle\frac{5}{2}\right|\sqrt{\frac{5}{6}}\left\{\sqrt{\frac{5}{6}}(60B_4) + \sqrt{\frac{5}{6}}(60B_4)\right\}\left|\frac{5}{2}\right\rangle + \left\langle-\frac{3}{2}\right|\sqrt{\frac{1}{6}}\left(\sqrt{\frac{5}{6}}60\sqrt{5}B_4 - \sqrt{\frac{1}{6}}180B_4\right)\left|-\frac{3}{2}\right\rangle$$

$$= \frac{5}{6}\times 60B_4 + \frac{5}{6}\times 60B_4 + \frac{5}{6}\times 60B_4 - \frac{180}{6}B_4$$

$$= 150B_4 - 30B_4$$

$$= \underline{120B_4}$$

$\underline{\text{others} = 0}$ （$\hat{H}_{crys}|\alpha\rangle$ と基が同じ $\langle k|\hat{H}|\alpha\rangle = 0$ も確認済）

$$\hat{H}_{crys}|\beta\rangle = B_4(O_4^0 + 5O_4^4)\left(\sqrt{\frac{5}{6}}\left|-\frac{5}{2}\right\rangle + \sqrt{\frac{1}{6}}\left|\frac{3}{2}\right\rangle\right)$$

$$= \sqrt{\frac{5}{6}}\underbrace{B_4(O_4^0 + 5O_4^4)\left|-\frac{5}{2}\right\rangle} + \sqrt{\frac{1}{6}}\underbrace{B_4(O_4^0 + 5O_4^4)\left|\frac{3}{2}\right\rangle}$$

$$= \sqrt{\frac{5}{6}}\left(60B_4\left|-\frac{5}{2}\right\rangle + 60\sqrt{5}B_4\left|\frac{3}{2}\right\rangle\right) + \sqrt{\frac{1}{6}}\left(-180B_4\left|\frac{3}{2}\right\rangle + 60\sqrt{5}B_4\left|-\frac{5}{2}\right\rangle\right)$$

$$= \underline{\left(2\times 60\times\sqrt{\frac{5}{6}}B_4\right)\left|-\frac{5}{2}\right\rangle + \left(60\times\frac{5}{\sqrt{6}}B_4 - \frac{180}{\sqrt{6}}B_4\right)\left|\frac{3}{2}\right\rangle}$$

$$\langle\beta|\hat{H}_{crys}|\beta\rangle = \left\langle-\frac{5}{2}\right|\sqrt{\frac{5}{6}}\left(2\cdot 60\cdot\sqrt{\frac{5}{6}}\cdot B_4\right)\left|-\frac{5}{2}\right\rangle + \left\langle\frac{3}{2}\right|\sqrt{\frac{1}{6}}\left(\frac{300}{\sqrt{6}}B_4 - \frac{180}{\sqrt{6}}B_4\right)\left|\frac{3}{2}\right\rangle$$

$$= \left(\frac{5}{\cancel{6}}\times\overset{20}{\cancel{120}} + \frac{\overset{50}{\cancel{300}}}{\cancel{6}} - \frac{180}{6}\right)B_4$$

$$= (100 + 50 - 30)B_4$$

$$= \underline{120B_4}$$

基が同じ

$$\langle\lambda|\hat{H}_{crys}|\beta\rangle = \left\langle-\frac{5}{2}\right|\frac{1}{\sqrt{6}}\left(2\cdot 60\cdot\sqrt{\frac{5}{6}}\overset{\cdot B_4}{\,}\right)\left|-\frac{5}{2}\right\rangle + \left\langle\frac{3}{2}\right|\left(-\sqrt{\frac{5}{6}}\right)\left(60\cdot\frac{5}{\sqrt{6}}B_4 - \frac{180}{\sqrt{6}}B_4\right)\left|\frac{3}{2}\right\rangle$$

$$= 120\cdot\frac{\sqrt{5}}{6} - 60\cdot\frac{5\sqrt{5}}{6} + \frac{\sqrt{5}\cancel{60}\cdot 180}{6}B_4 \quad \underline{= 0}$$

$$= (20\sqrt{5} - 50\sqrt{5} + 30\sqrt{5})B_4$$

$$\hat{H}_{crys}|\gamma\rangle = B_4(O_4^0 + 5O_4^4)|\tfrac{1}{2}\rangle$$
$$= \underline{120B_4|\tfrac{1}{2}\rangle}$$

$$\langle\gamma|\hat{H}_{crys}|\gamma\rangle = \underline{120B_4}, \quad \underline{\text{others} = 0}$$

$$\hat{H}_{crys}|\delta\rangle = B_4(O_4^0 + 5O_4^4)|-\tfrac{1}{2}\rangle$$
$$= \underline{120B_4|-\tfrac{1}{2}\rangle}$$

$$\underline{\langle\delta|\hat{H}_{crys}|\delta\rangle = 120B_4, \quad \text{others} = 0}$$

$$\hat{H}_{crys}|R\rangle = B_4(O_4^0 + 5O_4^4)\left(\sqrt{\tfrac{1}{6}}|\tfrac{5}{2}\rangle - \sqrt{\tfrac{5}{6}}|-\tfrac{3}{2}\rangle\right)$$
$$= \underbrace{\sqrt{\tfrac{1}{6}}B_4(O_4^0 + 5O_4^4)|\tfrac{5}{2}\rangle} - \sqrt{\tfrac{5}{6}}\underbrace{B_4(O_4^0 + 5O_4^4)|-\tfrac{3}{2}\rangle}$$
$$= \sqrt{\tfrac{1}{6}}\left(60B_4|\tfrac{5}{2}\rangle + 60\sqrt{5}B_4|-\tfrac{3}{2}\rangle\right) - \sqrt{\tfrac{5}{6}}\left(-180B_4|-\tfrac{3}{2}\rangle + 60\sqrt{5}B_4|\tfrac{5}{2}\rangle\right)$$
$$= \underline{\left(60\sqrt{\tfrac{1}{6}}B_4 - \sqrt{\tfrac{5}{6}}\cdot 60\cdot\sqrt{5}\cdot B_4\right)|\tfrac{5}{2}\rangle + \left(\sqrt{\tfrac{1}{6}}\cdot 60\sqrt{5}B_4 + \sqrt{\tfrac{5}{6}}\,180\cdot B_4\right)|-\tfrac{3}{2}\rangle}$$

$$\langle R|\hat{H}_{crys}|R\rangle = \langle\tfrac{5}{2}|\sqrt{\tfrac{1}{6}}\left(\sqrt{\tfrac{1}{6}}60B_4 - \tfrac{5}{\sqrt{6}}60B_4\right)|\tfrac{5}{2}\rangle + \langle-\tfrac{3}{2}|\left(-\sqrt{\tfrac{5}{6}}\left(60\sqrt{\tfrac{5}{6}}B_4 + \sqrt{\tfrac{5}{6}}180B_4\right)|-\tfrac{3}{2}\rangle\right.$$
$$= (10 - 50)B_4 + \left(-\overset{10}{\cancel{60}}\times\tfrac{5}{6} - \tfrac{5}{6}\times\overset{30}{\cancel{180}}\right)B_4$$
$$= -40B_4 + (-50 - 150)B_4$$
$$= \underline{-240B_4}$$

$$\hat{H}_{crys}|\lambda\rangle = B_4(O_4^0 + 5O_4^4)\left(\sqrt{\tfrac{1}{6}}|-\tfrac{5}{2}\rangle - \sqrt{\tfrac{5}{6}}|\tfrac{3}{2}\rangle\right)$$
$$= \underbrace{\sqrt{\tfrac{1}{6}}B_4(O_4^0 + 5O_4^4)|-\tfrac{5}{2}\rangle} - \sqrt{\tfrac{5}{6}}\underbrace{B_4(O_4^0 + 5O_4^4)|\tfrac{3}{2}\rangle}$$
$$= \sqrt{\tfrac{1}{6}}\left(60B_4|-\tfrac{5}{2}\rangle + 60\sqrt{5}B_4|\tfrac{3}{2}\rangle\right) - \sqrt{\tfrac{5}{6}}\left(-180B_4|\tfrac{3}{2}\rangle + 60\sqrt{5}B_4|-\tfrac{5}{2}\rangle\right)$$
$$= \left(60\sqrt{\tfrac{1}{6}}B_4 \mp 60\cdot\tfrac{5}{\sqrt{6}}B_4\right)|-\tfrac{5}{2}\rangle + \left(60\sqrt{\tfrac{5}{6}}B_4 + 180\sqrt{\tfrac{5}{6}}B_4\right)|\tfrac{3}{2}\rangle$$

$$\langle\lambda|\hat{H}_{crys}|\lambda\rangle = \langle\overset{-\frac{5}{2}}{\cancel{\lambda}}|\sqrt{\tfrac{1}{6}}\left(\sqrt{\tfrac{1}{6}}\times 60\times B_4 \mp \tfrac{1}{\sqrt{6}}\cdot 5\cdot 60\,B_4\right)|-\tfrac{5}{2}\rangle + \langle\tfrac{3}{2}|\left(-\sqrt{\tfrac{5}{6}}\right)\left(60\sqrt{\tfrac{5}{6}}B_4 + 180\sqrt{\tfrac{5}{6}}B_4\right)|\tfrac{3}{2}\rangle$$

$$= \left(\tfrac{1}{6}\times 60 \mp \tfrac{300}{6}\right)B_4 - \left(\tfrac{5}{6}\times 60 + \tfrac{5}{6}\times 180\right)B_4$$
$$= (10 \mp 50)B_4 - (50 + 150)B_4$$
$$= (-40 - 200)B_4$$
$$= \underline{-240B_4}$$

よって

Γ_8 : 4重縮退

Γ_7 : 2 〃

$B_4 > 0$ のとき : $E_{\Gamma_7} = -240 B_4$

$E_{\Gamma_8} = 120 B_4$

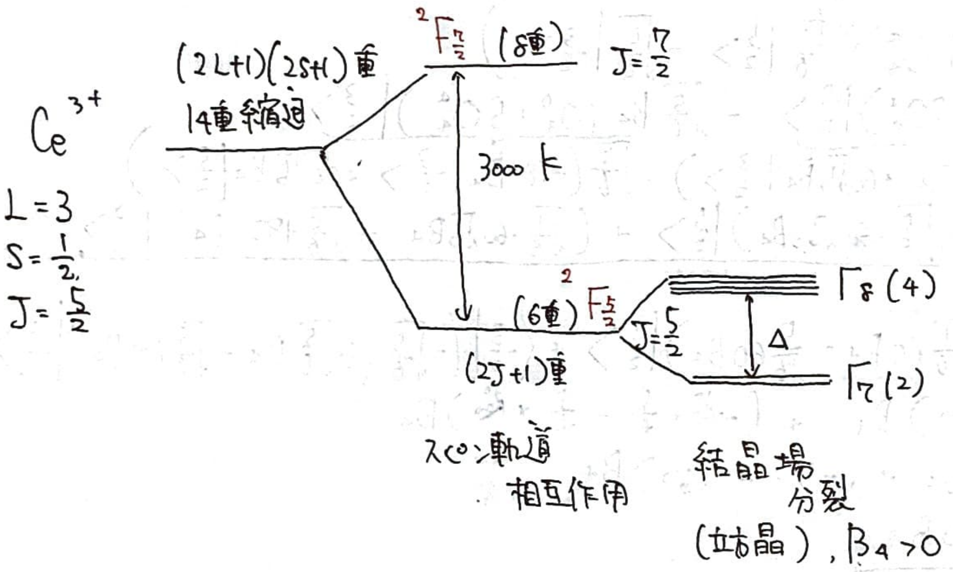
$\rightarrow E_{\Gamma_7} < E_{\Gamma_8}$

$\rightarrow \Gamma_7$ 基底状態

$B_4 < 0$ のとき

$E_{\Gamma_7} > E_{\Gamma_8}$

$\rightarrow \Gamma_8$ 基底状態



量子化軸をz軸にとっているので、磁場をz軸方向にかけたとき、上の固有状態は磁場中でも固有状態である。磁化は

$$\langle J_z \rangle_{av} = \frac{\sum_i \langle i|J_z|i\rangle \exp\left(-\frac{E_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{E_i}{k_B T}\right)}$$

を使って計算すれば良い。

$\hat{J}_z|J_z\rangle = J_z|J_z\rangle$

・磁場が小さい極限での磁化率の計算.

Γ_8

$$J_z = \begin{array}{c|cccccc} & |\alpha\rangle & |\beta\rangle & |\gamma\rangle & |\delta\rangle & |\kappa\rangle & |\lambda\rangle \\ \hline \langle\alpha| & \frac{11}{6} & 0 & 0 & 0 & \frac{2\sqrt{5}}{3} & 0 \\ \langle\beta| & 0 & -\frac{11}{6} & 0 & 0 & 0 & -\frac{2\sqrt{5}}{3} \\ \langle\gamma| & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 \\ \langle\delta| & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ \langle\kappa| & \frac{2\sqrt{5}}{3} & 0 & 0 & 0 & -\frac{5}{6} & 0 \\ \langle\lambda| & 0 & -\frac{2\sqrt{5}}{3} & 0 & 0 & 0 & \frac{5}{6} \end{array}$$

Γ_7

$$J_z|\alpha\rangle = J_z\left(\sqrt{\tfrac{5}{6}}\,|\tfrac{5}{2}\rangle + \sqrt{\tfrac{1}{6}}\,|-\tfrac{3}{2}\rangle\right)$$
$$= \underline{\tfrac{5}{2}\sqrt{\tfrac{5}{6}}\,|\tfrac{5}{2}\rangle + \left(-\tfrac{3}{2}\right)\sqrt{\tfrac{1}{6}}\,|-\tfrac{3}{2}\rangle}$$

$$\langle\alpha|J_z|\alpha\rangle = \frac{5}{2}\times\frac{5}{6} - \frac{1}{6}\times\frac{3}{2} = \frac{25}{12} - \frac{3}{12} = \frac{22}{12} = \frac{11}{6}$$
$$\langle\kappa|J_z|\alpha\rangle = \sqrt{\tfrac{1}{6}}\sqrt{\tfrac{5}{6}}\,\frac{5}{2} + \sqrt{\tfrac{5}{6}}\sqrt{\tfrac{1}{6}}\left(\frac{3}{2}\right) = \frac{\sqrt{5}}{6}\times\frac{5}{2} + \frac{\cancel{3}}{2}\times\frac{\sqrt{5}}{\cancel{6}\,2} = \frac{8\sqrt{5}}{12} = \frac{2\sqrt{5}}{3}$$

$$J_z|\beta\rangle = J_z\left(\sqrt{\tfrac{5}{6}}\,|-\tfrac{5}{2}\rangle + \sqrt{\tfrac{1}{6}}\,|\tfrac{3}{2}\rangle\right)$$
$$= \underline{\left(-\tfrac{5}{2}\right)\sqrt{\tfrac{5}{6}}\,|-\tfrac{5}{2}\rangle + \tfrac{3}{2}\sqrt{\tfrac{1}{6}}\,|\tfrac{3}{2}\rangle}$$

$$\langle\beta|J_z|\beta\rangle = -\frac{5}{2}\times\frac{5}{6} + \frac{1}{6}\times\frac{3}{2} = \frac{-25+3}{12} = -\frac{22}{12} = -\frac{11}{6}$$
$$\langle\lambda|J_z|\beta\rangle = \sqrt{\tfrac{1}{6}}\left(-\frac{5}{2}\right)\sqrt{\tfrac{5}{6}} - \sqrt{\tfrac{5}{6}}\sqrt{\tfrac{1}{6}}\,\frac{3}{2} = -\frac{5}{2}\cdot\frac{\sqrt{5}}{6} - \frac{\sqrt{5}}{6}\cdot\frac{3}{2} = -\frac{8\sqrt{5}}{12} = -\frac{\overset{2}{\cancel{8}}\sqrt{5}}{\cancel{12}\,3}$$

$$J_z|\gamma\rangle = J_z|\tfrac{1}{2}\rangle = \tfrac{1}{2}|\tfrac{1}{2}\rangle$$

$$J_z|\delta\rangle = J_z|-\tfrac{1}{2}\rangle = -\tfrac{1}{2}|-\tfrac{1}{2}\rangle$$

$$J_z|\kappa\rangle = J_z\left(\sqrt{\tfrac{1}{6}}\,|\tfrac{5}{2}\rangle - \sqrt{\tfrac{5}{6}}\,|-\tfrac{3}{2}\rangle\right)$$
$$= \tfrac{5}{2}\sqrt{\tfrac{1}{6}}\,|\tfrac{5}{2}\rangle + \tfrac{3}{2}\sqrt{\tfrac{5}{6}}\,|-\tfrac{3}{2}\rangle$$

$$\langle\kappa|J_z|\kappa\rangle = \frac{1}{6}\times\frac{5}{2} - \frac{3}{2}\times\frac{5}{6} = \frac{5-15}{12} = -\frac{10}{12} = -\frac{5}{6}$$

$$J_z|\lambda\rangle = J_z\left(\sqrt{\tfrac{1}{6}}\,|-\tfrac{5}{2}\rangle - \sqrt{\tfrac{5}{6}}\,|\tfrac{3}{2}\rangle\right) = -\tfrac{5}{2}\sqrt{\tfrac{1}{6}}\,|-\tfrac{5}{2}\rangle - \tfrac{3}{2}\sqrt{\tfrac{5}{6}}\,|\tfrac{3}{2}\rangle$$
$$\langle\lambda|J_z|\lambda\rangle = -\frac{5}{2}\times\frac{1}{6} + \frac{5}{6}\times\frac{3}{2} = \frac{-5+15}{12} = \frac{5}{6}$$

$H \to 0$ の極限における磁化率は

$$\chi = \frac{(g_J\mu_B)^2}{Z}\left[\underbrace{\sum_n\sum_m \frac{|\langle m|J_z|n\rangle|^2}{k_BT}e^{-\frac{E_m^0}{k_BT}}}_{m=n:\ \text{対角要素, Curie項}} + 2\underbrace{\sum_n\sum_m \frac{|\langle m|J_z|n\rangle|^2}{E_m^0-E_n^0}e^{-\frac{E_n}{k_BT}}}_{\text{非対角要素, Van Vleck項}}\right]$$

$$\equiv \frac{(g_J\mu_B)^2}{Z}\left[A+2B\right]$$

① Γ_7 基底状態のとき $(B_4>0)$

$$A = \frac{1}{k_BT}\left\{\underbrace{\langle \kappa|J_z|\kappa\rangle^2 e^{-\frac{E_\kappa^0}{k_BT}} + \langle\lambda|J_z|\lambda\rangle^2 e^{-\frac{\overset{0\ (\Gamma_7\text{基底なので})}{\boxed{E_\lambda^0}}}{k_BT}}}_{\Gamma_7\text{の関数}} + \overbrace{\left(\langle\alpha|J_z|\alpha\rangle^2+\langle\beta|J_z|\beta\rangle^2+\langle\gamma|J_z|\gamma\rangle^2+\langle\delta|J_z|\delta\rangle^2\right)}^{\Gamma_8}\times e^{-\frac{\overset{\Gamma_8\text{は上の準位}}{\boxed{\Delta}}}{k_BT}}\right\}$$

$$= \frac{1}{k_BT}\left[\left\{\left(-\frac{5}{6}\right)^2+\left(\frac{5}{6}\right)^2\right\}e^0 + \left\{\left(\frac{11}{6}\right)^2+\left(-\frac{11}{6}\right)^2+\left(\frac{1}{2}\right)^2+\left(-\frac{1}{2}\right)^2\right\}e^{-\frac{\cancel{k_B}\Delta}{\cancel{k_B}T}}\right]$$

$$= \frac{1}{k_BT}\left[\frac{25}{36}\times 2 + \left(\frac{121}{36}\times 2+\frac{1}{4}\times 2\right)e^{-\frac{\Delta}{\cancel{k_B}T}}\right]$$

$$= \frac{1}{k_BT}\left(\frac{50}{36}+\frac{242+18}{36}e^{-\frac{\Delta}{k_BT}}\right)$$

$$= \frac{1}{k_BT}\left(\frac{50}{36}+\frac{260}{36}e^{-\frac{\Delta}{k_BT}}\right)$$

エネルギーギャップが Δ(K) なので

$E = k_B\Delta$

[J] [J/K・K]

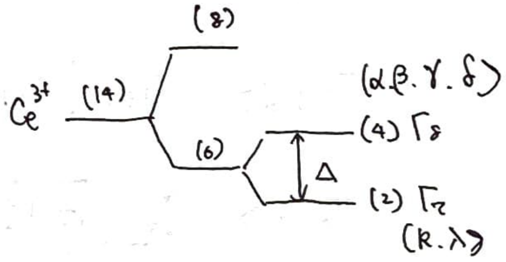
となり、k_Bは消える.

非対角要素

$\langle\alpha|J_z|\kappa\rangle = \langle\kappa|J_z|\alpha\rangle = \frac{2\sqrt{5}}{3}$

$\langle\beta|J_z|\lambda\rangle = \langle\lambda|J_z|\beta\rangle = -\frac{2\sqrt{5}}{3}$

の4つ.



$$B = \frac{|\langle\alpha|J_z|\kappa\rangle|^2}{E_\alpha^0-E_\kappa^0}e^{-\frac{E_\kappa}{k_BT}} + \frac{|\langle\kappa|J_z|\alpha\rangle|^2}{E_\kappa^0-E_\alpha^0}e^{-\frac{E_\alpha}{k_BT}}$$

$$+ \frac{|\langle\beta|J_z|\lambda\rangle|^2}{E_\beta^0-E_\lambda^0}e^{-\frac{E_\lambda}{k_BT}} + \frac{|\langle\lambda|J_z|\beta\rangle|^2}{E_\lambda^0-E_\beta^0}e^{-\frac{E_\beta}{k_BT}}$$

$$= \frac{\left(\frac{2\sqrt{5}}{3}\right)^2}{\Delta-0}e^{-\frac{0}{k_BT}} + \frac{\left(\frac{2\sqrt{5}}{3}\right)^2}{0-\Delta}e^{-\frac{\cancel{k_B}\Delta}{\cancel{k_B}T}}$$

$$+ \frac{\left(-\frac{2\sqrt{5}}{3}\right)^2}{\Delta-0}e^{-\frac{0}{k_BT}} + \frac{\left(-\frac{2\sqrt{5}}{3}\right)^2}{0-\Delta}e^{-\frac{\cancel{k_B}\Delta}{\cancel{k_B}T}}$$

$$= \frac{20}{9}\frac{1}{\Delta} + \left(-\frac{1}{\Delta}\right)\frac{20}{9}e^{-\frac{\Delta}{\cancel{k_B}T}} + \frac{1}{\Delta}\cdot\frac{20}{9} - \frac{1}{\Delta}\frac{20}{9}e^{-\frac{\Delta}{\cancel{k_B}T}}$$

$$= \frac{40}{9}\frac{1}{\Delta} - \frac{40}{9}\frac{1}{\Delta}e^{-\frac{\Delta}{k_BT}}$$

$$= \frac{160}{36}\left(\frac{1-e^{-\frac{\Delta}{\cancel{k_B}T}}}{\Delta}\right)$$

$$g_J = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)}$$

磁化率は

$$\chi = \frac{(g_J\mu_B)^2}{Z}\left[\frac{1}{k_BT}\left(\frac{50}{36}+\frac{260}{36}e^{-\frac{\Delta}{k_BT}}\right) + 2\times\frac{160}{36}\left(\frac{1-e^{-\frac{\Delta}{k_BT}}}{\Delta}\right)\right]$$

$$= \frac{(g_J\mu_B)^2}{k_BT}\frac{1}{Z}\left[\left(\frac{50}{36}+\frac{260}{36}e^{-\frac{\Delta}{k_BT}}\right)+\frac{2\times160}{36}\times\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right]$$

ここで イオンには の磁化率 χ_{free} は

$$\chi_{free} = (g_J\mu_B)^2\frac{J(J+1)}{3k_BT}$$

であり、Ce^{3+} では $J=\frac{5}{2}$ なので

$$\chi_{free} = \frac{(g_J\mu_B)^2}{k_BT}\,\frac{1}{3}\times\frac{5}{2}\times\frac{7}{2}$$

$$= \frac{35}{12}\frac{(g_J\mu_B)^2}{k_BT}$$

これを χ に代入して、

$$\chi = \frac{12}{35}\chi_{free}\,\frac{1}{Z}\left[\left(\frac{50}{36}+\frac{260}{36}e^{-\frac{\Delta}{k_BT}}\right)+\frac{320}{36}\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right]$$

$$= \frac{1}{Z}\chi_{free}\left[\underbrace{\frac{12}{35}\left(\frac{50}{36}+\frac{260}{36}e^{-\frac{\Delta}{k_BT}}\right)}_{①}+\underbrace{\frac{12}{35}\times\frac{320}{36}\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)}_{②}\right]$$

$$① = \frac{\cancel{12}}{\cancel{35}_7}\times\frac{\overset{2}{\cancel{10}}}{\cancel{36}_3}\left(5+26e^{-\frac{\Delta}{k_BT}}\right) = \frac{2}{21}\left(5+26e^{-\frac{\Delta}{k_BT}}\right)$$

$$② = \frac{\cancel{12}}{\cancel{35}_7}\times\frac{\overset{64}{\cancel{320}}}{\cancel{36}_3}\left(\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right) = \frac{64}{21}\left(\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right)$$

よって

$$\chi = \frac{1}{Z}\chi_{free}\left[\frac{2}{21}\left(5+26e^{-\frac{\Delta}{k_BT}}\right)+\frac{64}{21}\left(\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right)\right]$$

$$= \frac{2}{21}\frac{\chi_{free}}{Z}\left[5+26e^{-\frac{\Delta}{k_BT}}+32\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right]$$

さらに、

$$Z = \sum_i e^{-\frac{E_i}{k_BT}}$$

$$= e^{-\frac{E_R}{k_BT}}+e^{-\frac{E_\lambda}{k_BT}}+e^{-\frac{E_\alpha}{k_BT}}+e^{-\frac{E_\beta}{k_BT}}+e^{-\frac{E_\gamma}{k_BT}}+e^{-\frac{E_\delta}{k_BT}}$$

$$= 2+4e^{-\frac{\cancel{k_B}\Delta}{k_BT}}$$

$$= 2\left(1+2e^{-\frac{\Delta}{k_BT}}\right)$$

以上から、Γ_7 Ground State の磁化率は

$$\cancel{\chi}\quad \chi = \frac{5+26e^{-\frac{\Delta}{k_BT}}+32\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)}{21\left(1+2e^{-\frac{\Delta}{k_BT}}\right)}\cdot\chi_{free}$$

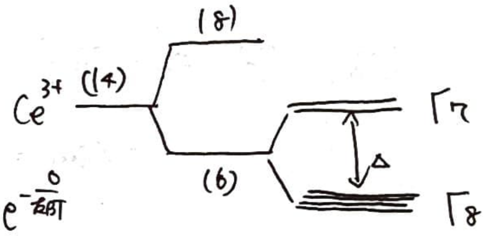
モル磁化率 は アボガドロ数 N_A をかければ良いので. 改めて モル磁化率 は

$$\chi = N_A \cdot \chi_{free} \cdot \frac{5 + 26e^{-\frac{\Delta}{k_BT}} + 32\frac{k_BT}{\Delta}\left(1 - e^{-\frac{\Delta}{k_BT}}\right)}{21\left(1 + 2e^{-\frac{\Delta}{k_BT}}\right)}$$

② Γ_8 基底状態 のとき

$$\chi = \frac{(g_J\mu_B)^2}{Z}\left[\sum_n\sum_m \frac{|\langle m|J_z|n\rangle|^2}{k_BT}e^{-\frac{E_n^0}{k_BT}} + 2\sum_n\sum_m \frac{|\langle m|J_z|n\rangle|^2}{E_m^0 - E_n^0}e^{-\frac{E_n}{k_BT}}\right]$$

$$= \frac{(g_J\mu_B)^2}{Z}(A + 2B)$$



$$A = \frac{1}{k_BT}\Big(\left(\langle\alpha|J_z|\alpha\rangle\right)^2 e^{-\frac{0}{k_BT}} + \left(\langle\beta|J_z|\beta\rangle\right)^2 e^{-\frac{0}{k_BT}} + \langle\gamma|J_z|\gamma\rangle^2 e^{-\frac{0}{k_BT}}$$
$$+ \langle\delta|J_z|\delta\rangle^2 e^{-\frac{0}{k_BT}} + e^{-\frac{\Delta}{k_BT}}\left\{\langle R|J_z|R\rangle^2 + \langle\lambda|J_z|\lambda\rangle^2\right\}\Big)$$

$\left(\begin{array}{l}\Gamma_8 : \alpha.\beta.\gamma.\delta \\ \Gamma_7 : R.\lambda\end{array}\right)$

$E = k_B\Delta$

$$= \frac{1}{k_BT}\left(\left(\frac{11}{6}\right)^2 + \left(-\frac{11}{6}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(-\frac{1}{2}\right)^2 + e^{-\frac{\Delta}{k_BT}}\left(\left(-\frac{5}{6}\right)^2 + \left(\frac{5}{6}\right)^2\right)\right)$$

$$= \frac{1}{k_BT}\left(\frac{121}{36}\times 2 + \frac{1}{4}\times 2 + \frac{25}{36}\times 2e^{-\frac{\Delta}{k_BT}}\right)$$

$$= \frac{1}{k_BT}\left(\frac{242+18}{36} + \frac{50}{36}e^{-\frac{\Delta}{k_BT}}\right)$$

$$= \frac{10}{36}\frac{1}{k_BT}\left(26 + 5e^{-\frac{\Delta}{k_BT}}\right)$$

$$B = \frac{\langle R|J_z|\alpha\rangle^2}{E_R - E_\alpha}e^{-\frac{E_\alpha}{k_BT}} + \frac{\langle\lambda|J_z|\beta\rangle^2}{E_\lambda - E_\beta}e^{-\frac{E_\beta}{k_BT}} + \frac{\langle\alpha|J_z|R\rangle^2}{E_\alpha - E_R}e^{-\frac{E_R}{k_BT}} + \frac{\langle\beta|J_z|\lambda\rangle^2}{E_\beta - E_\lambda}e^{-\frac{E_\lambda}{k_BT}}$$

$$= \frac{\left(\frac{2\sqrt{5}}{3}\right)^2}{\Delta - 0}e^{-\frac{0}{k_BT}} + \frac{\left(-\frac{2\sqrt{5}}{3}\right)^2}{\Delta - 0}e^{-\frac{0}{k_BT}} + \frac{\left(\frac{2\sqrt{5}}{3}\right)^2}{0 - \Delta}e^{-\frac{\cancel{k_B}\Delta}{k_BT}} + \frac{\left(-\frac{2\sqrt{5}}{3}\right)^2}{0 - \Delta}e^{-\frac{\cancel{k_B}\Delta}{k_BT}}$$

$$= \frac{1}{\Delta}\times\frac{20}{9} + \frac{1}{\Delta}\times\frac{20}{9} - \frac{1}{\Delta}\times\frac{20}{9}e^{-\frac{\Delta}{k_BT}} - \frac{1}{\Delta}\times\frac{20}{9}e^{-\frac{\Delta}{k_BT}}$$

$$= \frac{40}{9}\frac{1}{\Delta} - \frac{20}{9}\times 2e^{-\frac{\Delta}{k_BT}}\times\frac{1}{\Delta}$$

$$= \frac{40}{9}\left(\frac{1}{\cancel{\Delta}} - e^{-\frac{\Delta}{k_BT}}\right)$$

よって.

$$\chi = \frac{1}{Z}(g_J\mu_B)^2\left(\frac{10}{36}\frac{1}{k_BT}\left(26+5e^{-\frac{\Delta}{k_BT}}\right) + \frac{160.2}{36}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\frac{1}{\Delta}\right)$$

$$= \frac{1}{Z}(g_J\mu_B)^2\frac{1}{k_BT}\times\frac{10}{36}\left(26+5e^{-\frac{\Delta}{k_BT}} + \frac{\overset{32}{\cancel{20}}}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)k_BT\right)$$

ここで

$$\begin{cases} \chi_{free} = \frac{\cancel{12}}{\cancel{35}}\frac{35}{12}\frac{(g_J\mu_B)^2}{k_BT} \\ Z = \sum_i e^{-\beta E_i} = 4\times e^0 + 2\times e^{-\frac{\cancel{10}\Delta}{k_BT}} = 2\left(2+e^{-\frac{\Delta}{k_BT}}\right) \end{cases}$$

ゆえ

$$\chi = \frac{\cancel{12}}{\underset{7}{\cancel{35}}}\chi_{free}\times\frac{1}{2\left(2+e^{-\frac{\Delta}{k_BT}}\right)}\times\frac{\overset{2}{\cancel{10}}}{\underset{3}{\cancel{36}}}\left(26+5e^{-\frac{\Delta}{k_BT}} + \overset{32}{\cancel{20}}\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right)$$

$$= \frac{\chi_{free}}{2+e^{-\frac{\Delta}{k_BT}}}\times\frac{1}{21}\left(26+5e^{-\frac{\Delta}{k_BT}} + 32\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)\right)$$

$$= \chi_{free}\frac{26+5e^{-\frac{\Delta}{k_BT}} + 32\frac{k_BT}{\Delta}\left(1-e^{-\frac{\Delta}{k_BT}}\right)}{21\left(2+e^{-\frac{\Delta}{k_BT}}\right)} \quad //$$