one molecule partition function

$$z^{rot}_{QM} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta\frac{\hbar^2}{2I}\ell(\ell+1)}$$

high T, low β: sum $\to$ integral

$$z^{rot}_{QM} \to \int_{\ell=0}^{\infty} d\ell\,(2\ell+1)\, e^{-\beta\frac{\hbar^2}{2I}\ell(\ell+1)}$$

$x = \ell(\ell+1)$ $\qquad dx = (2\ell+1)\,d\ell$

$$z^{rot}_{QM} = \int_{x=0}^{\infty} dx\, e^{-\frac{\beta\hbar^2}{2I}x} = -\frac{2I}{\beta\hbar^2}\, e^{-\frac{\beta\hbar^2}{2I}x}\Big|_{x=0}^{\infty}$$

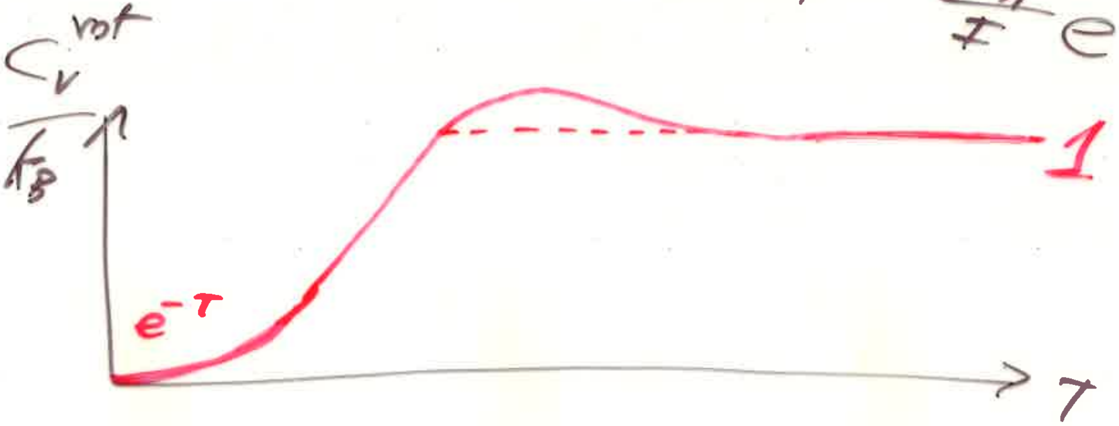
$$= \frac{2I}{\beta\hbar^2}$$ — reproduces classical z^{rot}_c

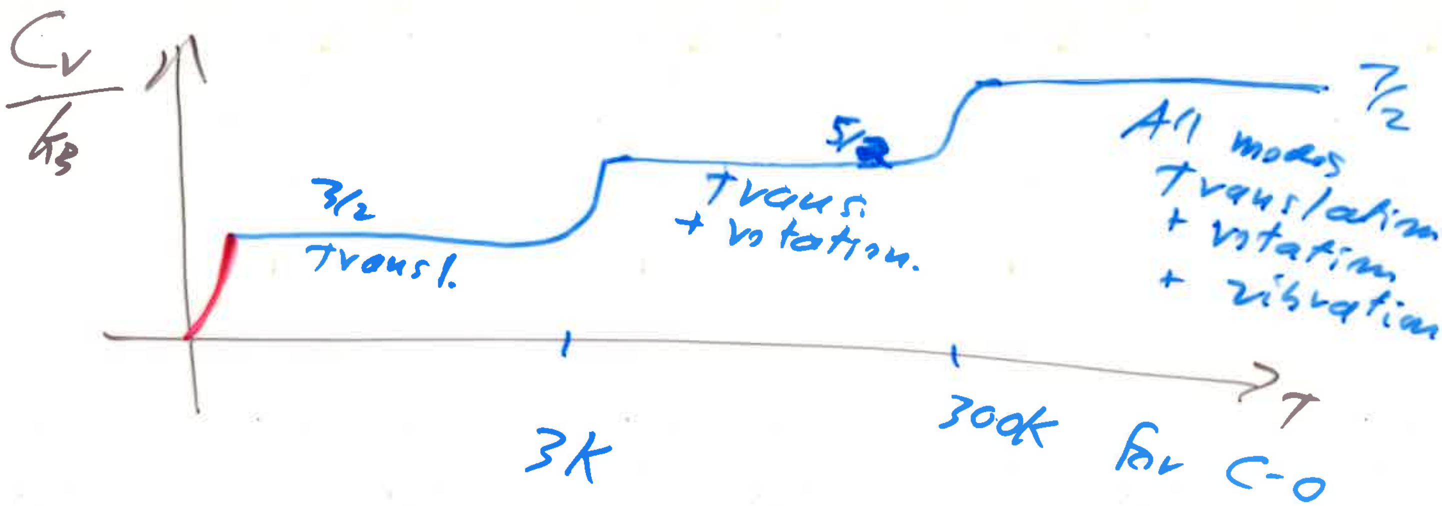
Low T, high β — non-identical atoms in molecule

e.g. C-O 

$$z^{rot}_{QM} = \underbrace{1}_{\ell=0} + \underbrace{3e^{-\frac{\beta\hbar^2}{2I}2}}_{\ell=1} + \dots$$

$$\epsilon_{rot} = \frac{-\partial \ln(z)^{rot}}{\partial \beta} \quad \begin{cases} \xrightarrow{\beta \ll 1} k_B T \\ \xrightarrow{\beta \gg 1} \frac{3\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}} + \dots \end{cases}$$





Complications for identical atoms

O_2 — spin-0 — bosons — rotation by π gives the same state back.

H_2 — spin-$\frac{1}{2}$ — fermions — high T, low β — $\frac{z^{rot}}{2!}$

D_2 — spin-1 — bosons — $\frac{-\partial}{\partial \beta}\left(\ln z^{rot} - \cancel{\ln(2)}\right)^0 = \epsilon^{rot}$

$C_v = \frac{d\epsilon}{dT}$ = same as w/o 2!

oxygen

O_2 – overall wavefunction is symmetric (even)

$$\Psi = \psi_{spin} \cdot \psi_{orbital}$$

$$+1 = \underbrace{\text{even}}_{+1} \cdot \underbrace{(-1)^{\ell}}_{+1}$$

$(-1)^{\ell} = +1 \rightarrow$ even ℓ only.

hydrogen

H_2 fermions

overall wavefunction is odd = antisymmetric

spins

ortho hydrogen

triplet: spin 1: $\underbrace{\uparrow\uparrow}_{m_s=+1}$ $\quad \overset{m_s=0}{\frac{(\uparrow\downarrow + \downarrow\uparrow)}{\sqrt{2}}}$ $\quad \underset{m_s=-1}{\downarrow\downarrow}$

singlet: $\frac{(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)}{\sqrt{2}}$ antisymmetric

para-hydrogen

spin 0

$$\psi_{overall} = \psi_{spin} \cdot \psi_{orbital}$$

$$(-1) = \begin{cases} (-1) \cdot (+1) \Rightarrow \text{even } \ell & \text{para} \\ (+1) \cdot (-1) \rightarrow \text{odd } \ell \text{ in sum} & \text{ortho} \end{cases}$$

D_2 deuterium — spin 1 - spin 1 bosons

$\psi_{overall}$ is symmetric (even)

$$\psi_{overall} = \psi_{spin} \cdot \psi_{orbital}$$

$$(+1) = \;?\;\;\; ?$$

9 spin states — 6 states ortho spin-symmetric orbital symm.

— 3 states para spin antisymm. orb. antisymm.