Quantum Mechanics for Rotations (1920s)

$$E_{QM\,\ell}^{rot} = \frac{\hbar^2}{2I}\ell(\ell+1)$$

$\ell = 0, 1, 2, 3, \ldots$ quantum number

$g_\ell = (2\ell+1)$ degeneracy

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

high T, low β: sum $\to$ integral

$$Z_{QM\,\text{high}\,T}^{rot} = \int_{\ell=0}^{\infty} \underline{d\ell\,(2\ell+1)}\, e^{-\beta\frac{\hbar^2}{2I}\underline{\ell(\ell+1)}}$$

$x = \ell(\ell+1)$

$dx = (2\ell+1)d\ell$

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

$$= \frac{2I}{\beta\hbar^2}$$ reproduces the classical result.

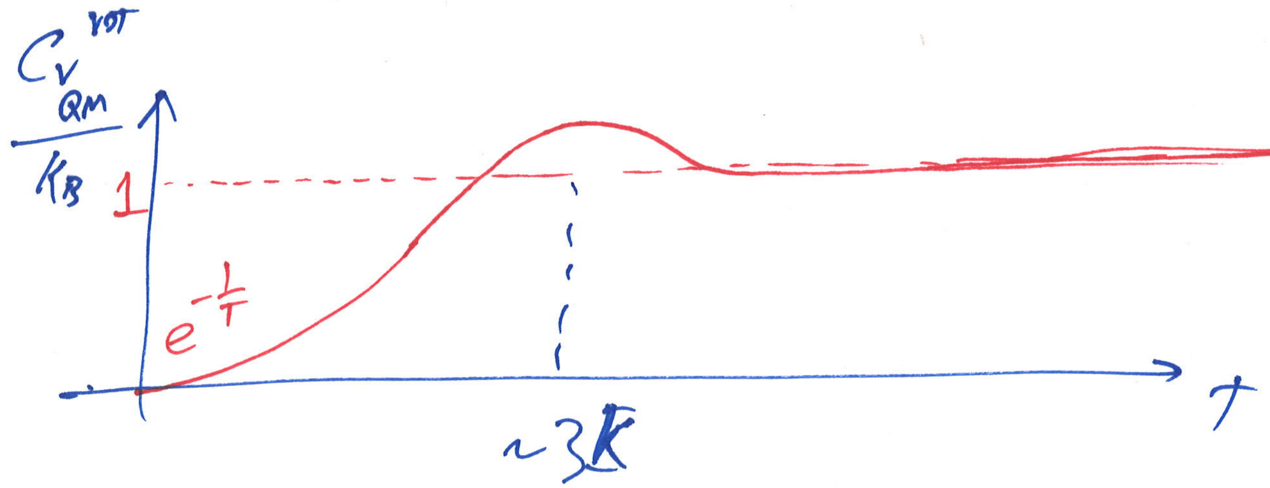
Low T, high β Non-identical nuclei, e.g. CO

$$z^{rot}_{QM} = \underbrace{1}_{l=0} + \underbrace{3e^{-\frac{\beta\hbar^2}{2I}2}}_{l=1} + \underbrace{5e^{-\frac{\beta\hbar^2}{2I}6}}_{l=2} + \dots \quad + \dots$$

$$\epsilon^{rot}_{QM} = \frac{-\partial \ln\left(z^{rot}_{QM}\right)}{\partial \beta}$$

high T, low β: $k_B T$

low T, high β: $\frac{3\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}} + \dots$



Complications for identical atoms

O_2 spin-0 bosons

H_2 spin-$\frac{1}{2}$ fermions

D_2 spin-1 bosons

rotation by π radians gives the same state back

got even or odd l terms in the sum.

oxygen O_2 spin-0 bosons $\Rightarrow$ total wavefunction is symmetric

$$\Psi = \psi_{spin}^{=1} \cdot \psi_{orbital}$$

total wavefunction sym

sym

$(-1)^{\ell}$

ℓ is quantum number

$$L^2 \psi_{orb} = \ell(\ell+1)\hbar^2 \psi_{orb}$$

$$\ell \in \{0, \cancel{1}, 2, \cancel{3} \dots\}$$

$\Rightarrow \psi_{orb}$ must be symmetric $\Rightarrow$

$\Rightarrow \ell$ is even

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hydrogen H_2 spin-$\frac{1}{2}$ fermions $\Rightarrow$ total wavefunction is antisymmetric

$$\Psi_{total} = \psi_{spin} \cdot \psi_{orbital}$$

$(-1)^{\ell}$

antisym

orthohydrogen

triplet spin-1 $(\uparrow_1\uparrow_2)$ or $\frac{(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)}{\sqrt{2}}$ or $(\downarrow_1\downarrow_2)$

spin symmetric

spins

parahydrogen

singlet spin-0 $\frac{(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)}{\sqrt{2}}$ spin antisymmetric

$$\Psi_{total} = \psi_{spin} \cdot \psi_{orbital}$$

antisym = triplet sym $\cdot$ antisym $\Rightarrow$ odd ℓ in sum

antisym $\cdot$ sym $\Rightarrow$ even ℓ in sum

singlet

deuterium D_2 spin-1 bosons $\Rightarrow$ total wavefunction is symmetric

$$\Psi_{total} = \Psi_{spin} \cdot \Psi_{orbital} (-1)^{\ell}$$

sym = sym — sym — even ℓ only

antisym — antisym — odd ℓ only

9 spin states

6 states ortho
spin-symmetric

3 states para
spin-antisymmetric