TOPIC
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q_{rot} of Diatomic Molecules (AB type)

Case-II : at very low temperature

General expression for q_{rot}

$$\boxed{q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-J(J+1)\Theta_r/T}}$$

For low T or molecules having large Θ_r,

e.g., HD molecule having $\Theta_r = 42.7\,°K$

$\Rightarrow$ $(\Theta_r/T) \rightarrow \infty$ or very high

$\Rightarrow$ Factor $(e^{-\Theta_r/T})^{J(J+1)}$ falls very fast to "0"

$\Rightarrow$ Majorly lowest excited states along with ground state

$$\Rightarrow \boxed{q_{rot} = 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + 7e^{-12\Theta_r/T} + \cdots + \infty}$$

Few term expansion

Case-III : At moderate temperature

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-J(J+1)\Theta_r/T}$$

Can not simply be written either Integral form or few term expansion form.

Requirement of Euler-Maclaurin series

$$\boxed{\sum_{n=a}^{b} f(n) = \int_a^b f(n)\,dn + \frac{1}{2}\left(f(a) + f(b)\right) + \sum_{j=1}^{\infty} (-1)^j \left(\frac{B_j}{(2j)!}\right)\left\{ f^{(2j-1)}(a) - f^{(2j-1)}(b) \right\}}$$

where $f^k(n) \equiv$ k-th derivative

$B_j \equiv$ Bernoulli's numbers

with $B_1 = 1/6$, $B_2 = \left(\frac{1}{30}\right)$, $B_3 = \left(\frac{1}{42}\right)$

$\therefore$ For $\boxed{q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-J(J+1)\theta r/T},}$

$f(J) = (2J+1)\, e^{-J(J+1)\theta r/T},$

$a = 0,$

$b = \infty,$

$\div$ K-th derivative, $f^k(x=J)$ to be evaluated at $J = 0$ & $J = \infty$

Now, let us evaluate, $f^k(J=\infty)$ and $f(J=\infty)$

$$\boxed{\lim_{J\to\infty} f(J) = e^{-\infty} = 0}$$

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($\forall \equiv$ For all)

Since, $\forall \left(\lim_{J\to\infty} f^{k}(J) \right)$ always carry a factor $f(J=\infty)$ and $\lim_{J\to\infty} f(J) = 0$

Hence; $\forall \; f^{k}(J=\infty) = 0$

Thus $$q_{rot} = \int_0^\infty f(J)\,dJ + \frac{1}{2} f(J=0) + \sum_{j=1}^{\infty} (-1)^{j} \left(\frac{B_j}{(2j)!}\right) f^{(2j-1)}(J=0)$$

Derivatives of $f(x) = (2x+1)\,e^{-cx(x+1)}$ (Supplimentary)

$$f(x) = \underbrace{(2x+1)}_{u}\, \underbrace{e^{-cx(x+1)}}_{v}$$

$$\Rightarrow f'(x) = (2x+1)\left(-(2x+1)c\right)e^{-cx(x+1)} + 2\,e^{-cx(x+1)}$$

$$\Rightarrow f^{(1)}(x) = f'(x) = \underbrace{\left(-c(2x+1)^2+2\right)}_{u}\, \underbrace{e^{-c(x(x+1))}}_{v}$$

$$\Rightarrow f''(x) = \left\{\left(-c(2x+1)^2+2\right)\left(-c(2x+1)\right) - 2c\times(2x+1)\times 2\right\} e^{-cx(x+1)}$$

$$\Rightarrow f''(x) = \left\{c(2x+1)\left(c(2x+1)^2 - 6\right)\right\} e^{-cx(x+1)}$$

$$\Rightarrow \boxed{f''(x) = f^{(2)}(x) = \underbrace{\left(\begin{matrix}-6c(2x+1) \\ +c^2(2x+1)^3\end{matrix}\right)}_{u} \underbrace{e^{-cx(x+1)}}_{v}}$$

$$\Rightarrow f'''(x) = f^{(3)}(x)$$

$$\left(-6c(2x+1) + c^2(2x+1)^3\right)\left(-c(2x+1)\right) e^{-cx(x+1)}$$

$$+ \left(-6c \cdot 2 + 3c^2(2x+1)^2 \times 2\right) e^{-cx(x+1)}$$

$$\Rightarrow f^{(3)}(x=0) = (-6c + c^2)(-c) + 6c^2 - 6c$$

$$\Rightarrow \boxed{f^{(3)}(0) = -c^3 + 12c^2 - 12c}$$

For q_{rot}, $f^{(1)}(0)$ and $f^{(3)}(0)$ are required

where $c = (\theta_r / T)$

$x = J$

$$f^{(1)}(J=0) = (-c+2)$$

& q_{rot} with $f^{(1)}(J=0)$ is <u>approximated expansion and higher terms are neglected</u>

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Hence

$$\boxed{q_{rot} = \int_0^\infty f(J)\,dJ + \frac{1}{2} f(J=0) + (-1)^1 \left(\frac{B_1}{(2\cdot 1)!}\right) f^{(1)}(J=0)}$$

$$\Rightarrow q_{rot} = \left(\frac{8\pi^2 I k_B T}{h^2}\right) + \frac{1}{2}\cdot 1 + (-1)^1 \frac{(1/6)}{2!}(-c+2) + \cdots +$$

$$q_{rot} = \left(\frac{T}{\theta_r}\right) + \left(\frac{1}{2} - \frac{1}{6}\right) + \left(\frac{\theta_r}{T}\right)\frac{1}{12} + \cdots - \cdots +$$

$$\Rightarrow q_{rot} = \left(\frac{T}{\theta_r}\right) + \frac{1}{3} + \left(\frac{\theta_r}{T}\right)\left(\frac{1}{12} - \cdots\right) + \cdots +$$

$$\boxed{q_{rot} = \left(\frac{T}{\theta_r}\right)\left(1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \cdots\right)},$$

For this exact value we need $f^{(3)}(J=0)$

Discussed in next Appendix

Appendix:

Considering $f^3(J=0)$ term

$$\Rightarrow q_{rot} = \left(\frac{T}{\theta_r}\right) + \frac{1}{2} \times 1$$

$$+ (-1)^1 \frac{B_1}{2!} f^{(1)}(0)$$

$$+ (-1)^2 \left(\frac{B_2}{(2,2)!}\right) f^{(3)}(0)$$

$$+ \ldots +$$

$$\Rightarrow q_{rot} = \left(\frac{T}{\theta_r}\right) + \frac{1}{2} + (-1)^1 \left(\frac{1/6}{2}\right)(-c+2)$$

$$+ \left\{\frac{(1/30)}{4!}\right\}\left(-c^3 + 12c^2 - 12c\right) + \ldots +$$

where $c = (\theta_r / T)$

Arranging in increasing order of "c"

$$q_{rot} = \left(\frac{T}{\theta_r}\right) + \frac{1}{3} + \left(\frac{1}{12} - \left(\frac{1}{30}\right) \times \left(\frac{12}{4 \times 3 \times 2 \times 1}\right)\right) c$$

$$+ \ldots + \ldots$$

$$\Rightarrow \boxed{q_{rot} = \left(\frac{T}{\theta_r}\right)\left\{1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \left(\frac{1}{15}\right)\left(\frac{\theta_r}{T}\right)^2 + \cdots + \right\}}$$