TOPIC:
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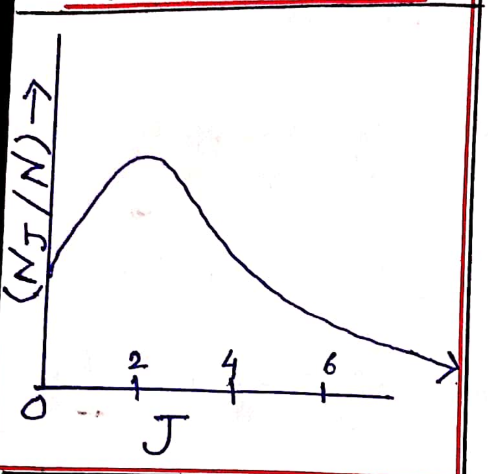
Symmetry and rotational Partition function of Polyatomic Molecules



Origin: Indistinguishable configurations due to exchange of all nuclei and electrons to sustain total or overall symmetry of Polyatomic Molecules, overcount energy levels appearing from composite of electrons and nuclei.

$\hat{A}_e$ = Symmetry Operator of e^-
$\hat{A}_N$ = Symmetry Operator of nuclei

$$\Rightarrow \boxed{\Psi_{total} = \hat{A}_e \hat{A}_N \left(\prod_{i=1}^{n} \Phi_e(\vec{r}_i)\right)\left(\prod_{I=1}^{N} \chi_{nuclei}(\vec{R}_I)\right)}$$

After transformation of coordinates of all particles around centre of Mass, along with Born-Oppenheimer Approximation,

$$\boxed{\Psi_{total} = \Psi_{trans}\Psi_{rot}\Psi_{vib}\Psi_{elec}\Psi_{nuclear}}$$

$$\Rightarrow \underbrace{\boxed{\Psi'_{total} = \Psi_{trans}\Psi_{rot}\Psi_{vib}\Psi_{elec}}}_{\text{After Born-Oppenheimer approximation}}$$

⇒ Ψ_{trans} doesn't depend on exchange of coordinates because it depends on Centre of Mass coordinate

$$\vec{R} = \sum m_i x_i / M$$

⇒ Ψ_{vib} depends on $|\vec{r}_i - \vec{r}_e|$, thus Ψ_{vib} remains unaffected due to exchange of coordinates of particles

⇒ Ψ'_{total} depends on symmetry operation of $\Psi_e \Psi_{rot}$

⇒ Since Ψ_e of ground state is generally symmetric,

⇒ Symmetry operation of Ψ_{rot} majorly decides symmetry property of total electronic wavefunctions of electrons (Ψ'_{total})

⇒ Symmetry of Molecular wavefunctions depends on choices of product of Ψ'_{total} and Ψ_N

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Symmetry & Rotational Partition Functions of Polyatomic Molecules

⇒ Symmetry of ψ_{rot} can be deided by rotational symmetry (σ)

⇒ Energy levels of molecules because of rotational symmetry σ be overcounted "σ" - times

⇒ Hence "σ" number of indistinguishable rotational Configuration should be taken care of rotational partition functions

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

⇒ $$E_{rot} = Nk_BT\left\{1 - \frac{\theta_r}{3T} - \frac{1}{45}\left(\frac{\theta_r}{T}\right)^2 + \cdots\right\}$$

⇒ $$C_{rot} = Nk_B\left\{1 + \frac{1}{45}\left(\frac{\theta_r}{T}\right)^2 + \; +\right\}$$

→ Since entropy "S" is directly related to Molecular Partition Function, "S" has dependence on σ

EXAMPLES

$\sigma(O_2) = \sigma(H_2) = \sigma(D_2) = 2$

$\sigma(HD) = 1$ (Heteroatomic Diatomic Molecules)

$\sigma(CO_2) = 2$

$\sigma(C_2H_2) = 2$

$\sigma(D\,{}^{12}C \equiv {}^{12}C\,D) = 2$