TOPIC

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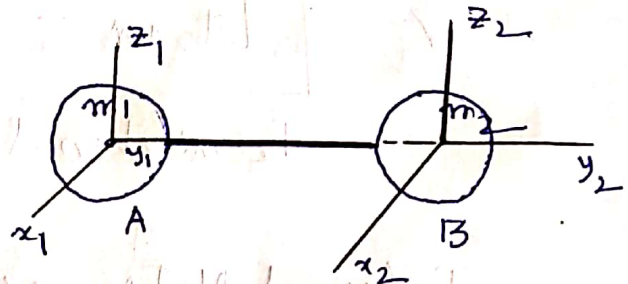
Partition functions of Diatomic Molecules



Hamiltonian (H) of Molecule AB can be segregated into Centre-of-mass (CM) and relative coordinates (Internal Motion) I.M.

$$\Rightarrow H = H_{CM} + H_{int}$$

$$\Rightarrow \text{Energy, } \varepsilon = \underset{(C.M.)}{\varepsilon_{trans}} + \underset{\text{(Internal Motion)}}{\varepsilon_{int}}$$

Total Partition fn (q_tot)

$$\Rightarrow q_{tot} = q_{trans} \cdot q_{int}$$

However, total mass concentrated at center of mass, $M = m_1 + m_2$ with Position vector

$$\vec{R}_{C.M.} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{(m_1 + m_2)}$$

Here motion of C.M., considered to be translational motion confined in 3-D box.

$$\Rightarrow \boxed{q_{trans} = \left(\frac{2\pi(m_1+m_2)K_BT}{h^2}\right)^{\frac{3}{2}} V}$$

Translational Partition fn. of diatomic Molecules

Internal Motion of diatomic molecules

I.M. of diatomic molecules can be classified as collection of radial motion (r) and azimuthal motion (θ, ϕ).

Since, atoms (A & B) are not flying off far away from each other ($r \neq \infty$) implies that there is an equilibrium distance or separation (r_e) around which atoms are oscillating along with rotational motions.

i.e., Non-rigid rotator
+
Harmonic Oscillator

Internuclear potential ($u(r)$) can be expanded as

$$u(r) = u(r_e) + (r-r_e)\left(\frac{du}{dr}\right)_{r=r_e} + (r-r_e)^2\frac{1}{2}\left(\frac{d^2u}{dr^2}\right)_{r=r_e} + \cdots$$

$$= u(r_e) + \frac{1}{2}K(r-r_e)^2 + \cdots$$

$\because \left(\frac{du}{dr}\right)_{r=r_e} = 0$ as it's potential minimum

Continued...