

Ideal Gas of Diatomic Molecules

diatomic molecule consists of two atoms

approximate atoms by point particles

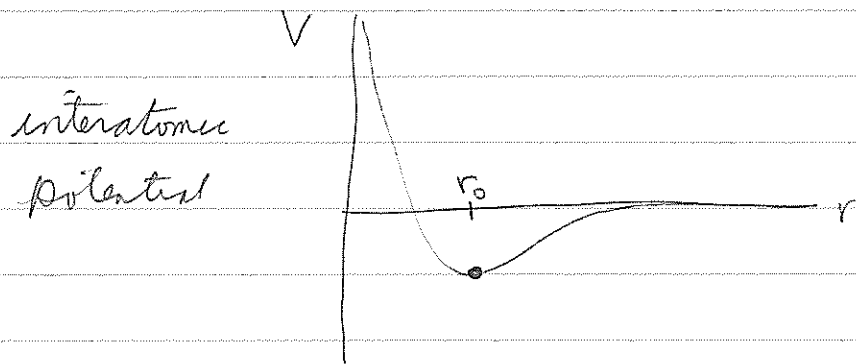
ignore spins

masses: m_1, m_2

positions: \vec{r}_1, \vec{r}_2

momenta: \vec{p}_1, \vec{p}_2

$$\text{Hamiltonian: } H = \frac{1}{2m_1} \vec{p}_1^2 + \frac{1}{2m_2} \vec{p}_2^2 + V(|\vec{r}_1 - \vec{r}_2|)$$



change to center-of-mass variable

and relative variable: $\vec{r} = \vec{r}_1 - \vec{r}_2$

$$\vec{p} = \frac{1}{2}(\vec{p}_1 - \vec{p}_2)$$

Hamiltonian for relative variable

$$H = \frac{1}{2\mu} \vec{p}^2 + V(r)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}$$

change to spherical coordinates: r, θ, ϕ

$$\begin{aligned} H &= \frac{1}{2\mu} \left[p_r^2 + \frac{1}{r^2} p_\theta^2 + \frac{1}{r^2 \sin^2 \theta} p_\phi^2 \right] + V(r) \\ &= \left[\frac{1}{2\mu} p_r^2 + V(r) \right] + \frac{1}{2\mu r^2} \underbrace{\left[p_\theta^2 + \frac{1}{\sin^2 \theta} p_\phi^2 \right]}_{\vec{L}^2} \end{aligned}$$

expand $V(r)$ around its minimum

$$V(r) = V(r_0) + \frac{1}{2} V''(r_0) (r-r_0)^2 + \frac{1}{6} V'''(r_0) (r-r_0)^3 + \dots$$

$$\begin{aligned} \frac{1}{2\mu r^2} &= \frac{1}{2\mu [r_0 + (r-r_0)]^2} \\ &= \frac{1}{2\mu r_0^2} \left[1 - 2 \frac{r-r_0}{r_0} + \dots \right] \end{aligned}$$

$$H = V(r_0) + H_{\text{vib}} + H_{\text{rot}} + H_{\text{pert}}$$

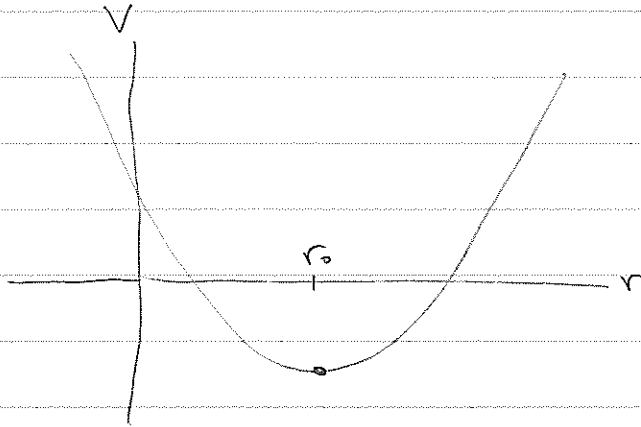
$$H_{\text{vib}} = \frac{1}{2\mu} p_r^2 + \frac{1}{2} \mu \omega^2 (r-r_0)^2 \quad \omega^2 = V''(r_0)/\mu$$

$$H_{\text{rot}} = \frac{1}{2I} \vec{L}^2 \quad I = \mu r_0^2$$

H_{pert} include $(r-r_0)^3$ term, $(r-r_0)\vec{L}^2$ term, etc.
treat as perturbation

Vibrational term

$$H_{\text{vib}} = \frac{1}{2\mu} P_r^2 + \frac{1}{2} \mu \omega^2 (r-r_0)^2$$



⇒ harmonic oscillation around minimum at r_0

extend range from $r > 0$ to $-\infty < r < \infty$
(treat difference as perturbation)

eigenfunctions: $\exp\left(-\frac{\mu\omega}{2\hbar}(r-r_0)^2\right) \times (\text{polynomial in } r-r_0)$

eigenvalues: $E_n = (n + \frac{1}{2})\hbar\omega$ $n = 0, 1, 2, \dots$

vibrational partition function

$$\begin{aligned} Z_{\text{vib}} &= \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \sinh(\frac{1}{2}\beta\hbar\omega)} \end{aligned}$$

high temperature limit: $Z_{\text{vib}} \rightarrow \frac{kT}{\hbar\omega}$

quantum effects freeze out for kT below energy scale $\hbar\omega$

Rotational term

$$H_{\text{rot}} = \frac{1}{2I} \vec{L}^2$$
$$= \frac{1}{2I} \left(p_\theta^2 + \frac{1}{\sin^2 \theta} p_\phi^2 \right)$$

eigenfunctions: $Y_{lm}(\theta, \phi)$ $l = 0, 1, 2, \dots$
 $m = -l, -l+1, \dots, +l$

eigenvalues: $E_l = \frac{1}{2I} l(l+1) \hbar^2$

degeneracy: $2l+1$

rotational partition function

$$Z_{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1) \hbar^2 / 2I}$$

low-temperature limit: keep $l=0, 1$

$$Z_{\text{rot}} \approx 1 + 3 e^{-\beta 2(\hbar^2/2I)}$$

high-temperature limit: approximate sum by integral

$$Z_{\text{rot}} \approx \int_0^{\infty} dl (2l+1) e^{-\beta l(l+1) \hbar^2 / 2I}$$
$$= \int_0^{\infty} dx e^{-\beta x \hbar^2 / 2I} = \frac{2I}{\beta \hbar^2}$$

internal partition function

$$Z_{\text{int}} \approx Z_{\text{vib}} Z_{\text{rot}} Z_{\text{nuc}}$$

unless two nuclei are identical bosons
or identical fermions
(same element, same isotope)

homonuclear diatomic molecules at room temperature
atmospheric pressure



identical $\begin{pmatrix} \text{bosons} \\ \text{fermions} \end{pmatrix}$:

wavefunction must be $\begin{pmatrix} \text{symmetric} \\ \text{antisymmetric} \end{pmatrix}$ under

$\begin{cases} \text{interchange of nuclei} \\ \text{parity transform of wavefunction: } \vec{r} \rightarrow -\vec{r} \end{cases}$

nuclear spin states: $|m_{i1}, m_{i2}\rangle \rightarrow |m_{i2}, m_{i1}\rangle$

wavefunction: $\psi(r, \theta, \phi) \rightarrow \psi(r, \pi - \theta, \phi + \pi)$

$(2i+1)^2$ spin states $|m_{i1}, m_{i2}\rangle$

total nuclear spin: $0, 1, 2, \dots, 2i-1, 2i$
A S A A S

symmetric states: $3 + 7 + \dots + (2i) = (i+1)(2i+1)$

antisymmetric states: $1 + 5 + \dots + (2i-1) = i(2i+1)$

rotational wavefunctions: $Y_{lm}(\theta, \phi)$ is even $l=0, 2, 4, \dots$
odd $l=1, 3, 5, \dots$

internal partition function:

$$Z_{\text{int}} = Z_{\text{rot}} \times Z_{\text{rot, nuclear}}$$

if nuclei are identical bosons

$$Z_{\text{rot, nuclear}} = (i+1)(2i+1) \sum_{l \text{ even}} e^{-\beta l(l+1) \hbar^2 / 2I} \\ + i(2i+1) \sum_{l \text{ odd}} e^{-\beta l(l+1) \hbar^2 / 2I}$$

if nuclei are identical fermions

$$Z_{\text{rot, nuclear}} = i(2i+1) \sum_{l \text{ even}} e^{-\beta l(l+1) \hbar^2 / 2I} \\ + (i+1)(2i+1) \sum_{l \text{ odd}} e^{-\beta l(l+1) \hbar^2 / 2I}$$