

Molecular para- and ortho-hydrogen

Hydrogen molecules (H_2) can exist in para- and ortho-states.

In para- H_2 , the protons form an anti-symmetric singlet state $\frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$

spin of first proton spin of second proton

To ensure that the wave function under the exchange of the two nuclei ($\hat{=}$ protons) is anti-symmetric, the orbital angular momentum quantum number l has to be even.

Let's model the rotational Hamiltonian \hat{H}_{rot} through

$$\hat{H}_{rot} = \frac{\hbar^2}{2J} \hat{L}^2$$

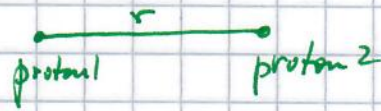
J : moment of inertia

\hat{L} : orbital angular momentum operator

Schrödinger equation $\hat{H}_{rot} \psi = E \psi$

From QM, we know: $\psi = Y_{lm}(\hat{r})$; $Y_{lm}(\hat{r}) = Y_{lm}(\theta, \phi)$

$Y_{lm}(\hat{r})$: spherical harmonics



\vec{r} vector is described by
 (r, θ, ϕ)

spherical coordinates

We are neglecting vibrations and electronic part of the problem. \rightarrow this is justified at room temperature

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

where $l = 0, 1, 2, \dots$

For each l , the projection quantum number m can take the values $-l, -l+1, \dots, l$ (degeneracy of $2l+1$).

Task: Calculate rotational partition function for para- H_2 (single molecule).

For para- H_2 , l must be even

Spin wave function is anti-symmetric.

So: need symmetric rotational wave fun.

$$Y_{lm}(-\hat{r}) = (-1)^l Y_{lm}(\hat{r})$$

if $l = \text{even}$, $(-1)^l = 1$
(symmetric rotational wave fun.)

$$\Rightarrow Q_{\text{rot}}^{\text{para}} = \sum_{l=0,2,\dots}^{\infty} (2l+1) e^{-\beta \frac{\hbar^2}{2I} l(l+1)}$$

working in canonical ensemble

degeneracy of each l -level due to m quantum number

Task: Consider the low and high temperature limits.

In the low- T limit: $T \rightarrow 0 \Rightarrow \beta \rightarrow \infty$

$$Q_{\text{rot}}^{\text{para}} \longrightarrow 1$$

keep only $l=0$ term

In the high- T limit, one can show

$$Q_{\text{rot}}^{\text{para}} \longrightarrow \frac{1}{2} \frac{2I}{\beta \hbar^2} = \frac{1}{2} \frac{2k_B T}{\frac{\hbar^2}{2I}}$$

Task: Calculate $Q_{\text{rot}}^{\text{ortho}}$.

$$Q_{\text{rot}}^{\text{ortho}} = \sum_{l=1,3,\dots}^{\infty} (2l+1) e^{-\beta \frac{\hbar^2}{2I} l(l+1)}$$

Task: Determine the rotational contributions to the internal energy for para- and ortho-hydrogen.

In general: $U = \langle \hat{H} \rangle$

$$= -\frac{\partial}{\partial \beta} \log Q$$

$$\Rightarrow U_{\text{rot}}^{\text{para}} = -\frac{\partial}{\partial \beta} \left(\log (Q_{\text{rot}}^{\text{para}}) \right)$$

$$U_{\text{rot}}^{\text{ortho}} = -\frac{\partial}{\partial \beta} \left(\log (Q_{\text{rot}}^{\text{ortho}}) \right)$$