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5.62 Physical Chemistry II
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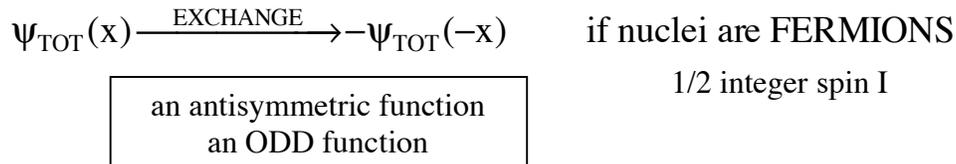
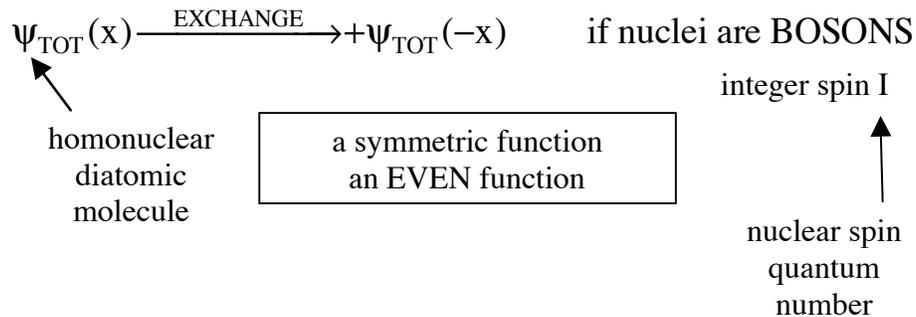
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5.62 Lecture #13: Nuclear Spin Statistics: Symmetry Number, σ . Low Temperature Limit for Rotational Partition Function

Readings: Hill, pp. 153-156, 153-159 [466-472]
 Maczek, pp. 54-57

ORIGIN OF σ — NUCLEAR SPIN STATISTICS

Quantum mechanics requires that the *total wavefunction* be either symmetric (does not change sign) or antisymmetric (changes sign) with respect to exchange of any two identical *nuclei*. Ψ_{TOT} must be symmetric if *nuclei* have integer spins (bosons) or antisymmetric if *nuclei* have 1/2 integer spins (fermions).



FOR EXAMPLE: O₂

The ¹⁶O nuclei have spin I = 0 ⇒ BOSONS

Therefore Ψ_{TOT} for O₂ must be symmetric or EVEN

$$\Psi_{TOT} = \Psi_{TRANS} \Psi_{VIB} \Psi_{ELEC} \Psi_{ROT} \Psi_{NUCL.SPIN}$$

Need to investigate symmetry of each one of these wavefunctions for O₂ upon exchange of two ¹⁶O nuclei. [NOTE: we are permuting nuclei, not atoms. The Na atom is a Boson, but the Na nucleus in Na₂ is a Fermion.]

- Ψ_{TRANS} — depends only on CM coordinate of the molecule so this function is not affected by exchange — we will no longer consider it
- Ψ_{VIB} — depends only on distance between the two nuclei so this coordinate is not affected by exchange — no longer consider it.
[Be careful. In a polyatomic molecule, internal rotation of a methyl group does permute identical nuclei and it is a vibration.]
- Ψ_{ELEC} — ground electronic state of O_2 is ${}^3\Sigma_g^-$. This term symbol tells us that the electronic wavefunction is antisymmetric or ODD with respect to exchange of the two nuclei. [The classification operator is $\sigma_v \times \mathbf{i}$ (both body-frame).]
- Σ_g^- and Σ_u^+ are both odd, Σ_g^+ and Σ_u^- are both even.
- Π, Δ etc. consist of one manifold of even states (like Σ_g^+) and one nearly identical manifold of odd states (like Σ_g^-).
- Ψ_{ROT} — rigid rotor rotational wavefunctions are spherical harmonics

$\Psi_{J=0,2,4,6} \dots$ are symmetric with respect to exchange
EVEN

$\Psi_{J=1,3,5,7} \dots$ are antisymmetric with respect to exchange
ODD

Ψ_{NUCLEAR} — ${}^{16}\text{O}$ nucleus has a nuclear spin $I = 0 \rightarrow$ a boson; there are

$(2I + 1)(I + 1)$ symmetric (EVEN) nuclear spin states: “ortho” (the states with larger nuclear spin degeneracy)

$(2I + 1)I$ antisymmetric (ODD) nuclear spin states: “para”

For $I = 0$

1 EVEN nuclear spin state

0 ODD nuclear spin state

<u>Ψ_{TOT}</u>	=	<u>Ψ_{ELEC}</u>	×	<u>Ψ_{ROT}</u>	×	<u>$\Psi_{\text{NUCL.SP}}$</u>
EVEN	=	ODD		$\Psi_{J=1,3}$ ODD		EVEN
EVEN	≠	ODD		$\Psi_{J=0,2}$ EVEN		EVEN

Therefore, O_2 molecules in the ground electronic state **cannot** exist in even rotational states!!! Because ODD * EVEN * EVEN does not result in an EVEN function as required by quantum mechanics!

[When $I = 1/2$, a homonuclear molecule has $I_{tot} = 1$ and 0

for $I_{tot} = 1$ there are 3 ortho substates

for $I_{tot} = 0$ there is 1 para substate.

When $I = 1$, $I_{tot} = 2, 1, 0$. $I_{tot} = 2$ and 0 are ortho: 6 substates

$I_{tot} = 1$ is para: 3 substates

When $I = 3/2$, $I_{tot} = 3, 2, 1, 0$. $I_{tot} = 3, 1$ are ortho: 10

$I_{tot} = 2, 0$ are para: 6.]

Therefore, for O_2

$$q_{\text{rot}} = \sum_{J=1,3,5,\dots}^{\infty} (2J+1)e^{-J(J+1)\theta_{\text{rot}}/T}$$

high temp. limit
integral approximation

$$= \frac{1}{2} \int_{J=0}^{\infty} (2J+1)e^{-J(J+1)\theta_{\text{rot}}/T} dJ = \frac{T}{2\theta_{\text{rot}}}$$

$\theta_{\text{rot}} = \frac{hcB}{k}$

↑
only 1/2 of the J's in this
integral contribute!!
the odd J's!

So $\sigma = 2!!$

Can use σ for high temp. limit only

[sounds like a fraud. Can you prove that $\frac{1}{2}$ is exactly the correct factor? It involves a simple change of variable for the integral.] Origin of σ : only 1/2 of the possible rotational states in the integral approximation contribute to the partition function because of symmetry restrictions imposed by quantum mechanics.

- not all homonuclear molecules have $I = 0$; other molecules have other symmetry restrictions that bring in the σ -factor (even when $I \neq 0$).

ORTHO-PARA HYDROGEN

another consequence of nuclear spin statistics

H_2 — hydrogen nuclei (protons) have $I = 1/2$
therefore, they are FERMIONS

so ψ_{TOT} must be ODD (antisymmetric)

ψ_{ELEC} is EVEN (symmetric) because ground electronic state of H_2 is $^1\Sigma_g^+$

ψ_{NUCL} has $(2I + 1) I = 1$ antisymmetric spin states (para) (nuclear spin singlet)

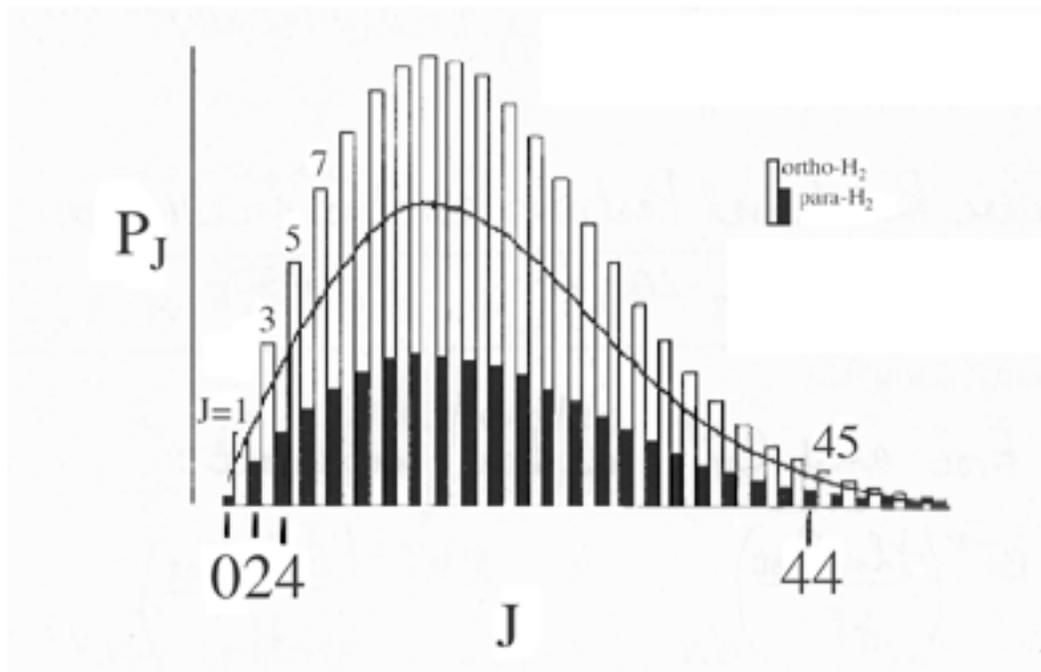
$$\alpha(1)\beta(2) - \alpha(2)\beta(1) \quad (\text{one state: called nuclear-spin "singlet"})$$

$$(2I+1)(I+1) = 3 \quad \text{symmetric spin states (ortho) (nuclear spin "triplet")}$$

$$\left. \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \end{array} \right\} \quad (\text{three states: called nuclear-spin "triplet"})$$

ψ_{TOT}	=	ψ_{ELEC}	*	ψ_{ROT}	*	$\psi_{NUCL.SP.}$
ODD	=	EVEN		$\psi_{J=0,2,4...}$ EVEN		1 ODD $\psi_{NUCL.SP}$
ODD	=	EVEN		$\psi_{J=1,3,5...}$ ODD		3 EVEN $\psi_{NUCL.SP}$

For ψ_{TOT} to be ODD, $\psi_{J=0,2,4...}$ EVEN-J have to be paired with ODD $\psi_{N.S.}$ and $\psi_{J=1,3,5...}$ ODD-J have to be paired with EVEN $\psi_{N.S.}$. But there are 3 times more EVEN nuclear spin states than ODD spin states. Therefore, there are 3 times more ODD rotational states available because each ODD rotational state can have three possible nuclear spin functions. In other words, the "degeneracy" of the ODD rotational levels is effectively three times that of the EVEN levels. Therefore, this leads to a probability distribution as a function of J that looks like:



H_2 with $J = 0, 2, 4 \dots$ is called PARA-hydrogen

H_2 with $J = 1, 3, 5 \dots$ is called ORTHO-hydrogen

We will not include nuclear spin statistics in our analysis of the rotational partition functions even though we are obviously making an error in calculating the probability of finding a homonuclear diatomic molecule in a particular J rotational state and in some macroscopic properties. We make no error in K_{eq} because the nuclear spin orientations are not altered (usually) in a chemical reaction and therefore nuclear spin degeneracy factors cancel.

Actually q_{rot} for H_2 may be shown to be exactly the same as the naïve prediction based on the $\sigma = 2$ symmetry number and neglecting nuclear spin altogether, except at very low T . [How low is "very low"?)

MOLECULAR ROTATIONAL PARTITION FUNCTION — LOW TEMP LIMIT

CASE 2: $\epsilon_{rot} > kT$ or $\theta_{rot} > T$

Cannot treat ϵ_{rot} as continuous. Must sum terms in q_{rot} . But terms in q_{rot} decrease rapidly with J . Sum series for first few terms. Stop sum when next term is "small enough".

$$q_{rot} = \sum_J (2J+1)e^{-\theta_{rot}J(J+1)/T}$$

Molecular Rotational Partition Function for Diatomics

$$q_{\text{rot}} = 1 + 3e^{-2\theta_r/T} + 5e^{-6\theta_r/T} + \dots$$

(For an electronic state that has lowest-J as $J = 0$)

Calculate \bar{E}_{rot} and C_V^{rot} in Low Temp Limit:

$$\bar{E}_{\text{rot}} = kT^2 \left(\frac{\partial \ln Q_{\text{rot}}}{\partial T} \right)_{N,V} = NkT^2 \left(\frac{\partial \ln q_{\text{rot}}}{\partial T} \right)_{N,V}$$

$$\begin{aligned} \ln q_{\text{rot}} &= \ln(1 + 3e^{-2\theta_r/T} + 5e^{-6\theta_r/T} + \dots) \\ &\approx \ln(1 + 3e^{-2\theta_r/T}) \end{aligned}$$

If $\theta_r > T$, then $3e^{-2\theta_r/T} \leq 1$. Set $x = 3e^{-2\theta_r/T}$

$$\ln(1+x) \approx x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots \text{ for } -1 < x \leq 1$$

SO $\ln q_{\text{rot}} \approx 3e^{-2\theta_r/T} + \dots$

SO $\bar{E}_{\text{rot}} = NkT^2 \left(\frac{\partial(3e^{-2\theta_r/T})}{\partial T} \right)_{N,V} = NkT^2 \frac{6\theta_r}{T^2} e^{-2\theta_r/T} = 6Nk\theta_r e^{-2\theta_r/T}$

Reasonable? Does it go to 0 as $T \rightarrow 0$?

$$C_V^{\text{rot}} = \frac{\partial E}{\partial T} = 6Nk\theta_r \frac{\partial(e^{-2\theta_r/T})}{\partial T} = \frac{12Nk\theta_r^2}{T^2} e^{-2\theta_r/T}$$

Reasonable? Does it go to 0 or ∞ as $T \rightarrow 0$?

A more honest approach to the symmetry number, not found in textbooks, appears here.

The factor of $\frac{1}{\sigma}$ in q_{rot} is of classical mechanical origin. But it must come out of QM. To see how this works, we must treat rotation and hyperfine together (not separately as two multiplicative factors) as q_{nucl} .

Homonuclear diatomic molecule: nuclear spin I_1
 hf-rot degeneracy is $(2I_1 + 1)(2I_1 + 1)(2J + 1)$

but half of the rotational levels “belong” to “ortho” and half belong to “para”

$$\left. \begin{array}{l} \text{ortho } (2I_1 + 1)(I_1 + 1) \\ \text{para } (2I_1 + 1)(I_1) \end{array} \right\} \text{sum is } (2I_1 + 1)^2$$

Evaluate contribution to partition function as two additive terms

$$\left. \begin{array}{l} \text{even-J } J = 2n \\ \text{odd-J } J = 2n + 1 \end{array} \right\} n = 0, 1, 2$$

$$\begin{aligned} q_{\text{rot,even-J}} &= \sum'_{J=0}^{\infty} (2J+1)e^{-hcBJ(J+1)/kT} \quad (' \text{ means } J \text{ even}) \\ &= \sum_{n=0}^{\infty} (4n+1)e^{-hcB[4n^2+2n]/kT} \\ &= \int_0^{\infty} dn(4n+1)e^{-hcB[4n^2+2n]/kT} + \frac{1}{2}[1+0] \end{aligned}$$

$$\omega = 4n^2 + 2n$$

$$\frac{d\omega}{dn} = 8n + 2 \quad n = 0 \rightarrow \omega = 0$$

$$\begin{aligned} q_{\text{rot,even-J}} &= \int_0^{\infty} \frac{1}{2} d\omega e^{-hcB\omega/kT} + \frac{1}{2} \\ &= \left(\frac{-kT}{2hcB} \right) [0 - 1] + \frac{1}{2} \\ &= \frac{1}{2} \frac{kT}{hcB} + \frac{1}{2} \end{aligned}$$

$$\begin{aligned} q_{\text{rot,odd}} &= \sum'_{J=0}^{\infty} (2J+1)e^{-hcBJ(J+1)/kT} \quad (' \text{ means } J \text{ odd}) \\ &= \sum_{n=0}^{\infty} (4n+3)e^{-hcB[4n^2+6n+2]/kT} + \frac{1}{2}[3e^{-2hcB/kT} + 0] \end{aligned}$$

$$\omega = 4n^2 + 6n + 2$$

$$\frac{d\omega}{dn} = 8n + 6$$

$$n = 0 \rightarrow \omega = 2$$

$$\begin{aligned}
 q_{\text{rot,odd}} &= \int_2^{\infty} \frac{1}{2} d\omega e^{-hcB\omega/kT} + \frac{3}{2} e^{-2hcB/kT} \\
 &= \frac{-kT}{2hcB} [0 - e^{-2hcB/kT}] + \frac{3}{2} e^{-2hcB/kT} \\
 &= e^{-2hcB/kT} \left[\frac{kT}{2hcB} + \frac{3}{2} \right]
 \end{aligned}$$

Now combine the two factors, multiplying each by the appropriate nuclear spin degeneracy factor

$$q_{\text{nucl}} = \frac{(2I_1+1)(I_1+1)}{2} \left[\frac{kT}{hcB} + 1 \right] + \frac{(2I_1+1)I_1}{2} \left[\frac{kT}{hcB} + 3 \right] e^{-2hcB/kT}$$

if $e^{-2hcB/kT} \approx 1$ (high T limit), we get

$$q_{\text{nucl}} = \underbrace{\frac{(2I_1+1)^2}{2} \frac{kT}{hcB}}_{\text{what we expect}} + \underbrace{\frac{(2I_1+1)}{2} [(I_1+1) + 3I_1]}_{\text{small correction term}}$$

correction
term

$$I = 0 \rightarrow \frac{1}{2}$$

$$I = \frac{1}{2} \rightarrow 3$$

$$I = 1 \rightarrow \frac{15}{2}$$

$$I = \frac{3}{2} \rightarrow 14$$

But do not forget the $e^{-2hcB/kT}$ factor that becomes important in the low-T limit. This term wipes out the contribution from all but the lowest-J level.

Non-Lecture

Paradox

Acetylene is a linear 4 atomic molecule, HCCH, consisting of a pair of $I = 1/2$ protons and a pair of $I = 0$ carbon nuclei. So will the rotational levels have *ortho/para* intensity ratios analogous to H_2 (3 : 1) or O_2 (1 : 0)? Or is this a built-in contradiction that is beyond human understanding?

The answer is in recognizing that our view of bonded networks is too simple. Suppose we put accounting labels 1,2 on the H nuclei and a,b on the C nuclei. Then we can build a wavefunction that is always even with respect to permutation of the two C atoms

$$\psi = 2^{-1/2}[1 ab_2 + 2 ab_1]$$

$$P_{ab}\psi = +\psi.$$

So now it is a simple matter to pair odd-J rotational levels with proton nuclear spin triplets ($I_{\text{tot}} = 1$) and even J rotational levels with proton nuclear spin singlets ($I_{\text{tot}} = 0$). This means that the rotational levels in the $\tilde{X}^1\Sigma_g^+$ electronic ground state of acetylene will exhibit exactly the same nuclear spin statistical weight pattern as the $\tilde{X}^1\Sigma_g^+$ state of H_2 : even-J are *para* (statistical weight 1), odd-J are *ortho* (statistical weight 3).