

## 6.3: Nuclear Spin Partition Function

### High-Temperature Limit

In the absence of a magnetic field, all nuclear spin states are degenerate,<sup>19</sup> except for the very tiny splittings that arise from  $J$  couplings between the nuclear spins themselves. Even if we consider the largest magnetic fields available, it is safe to assume that all nuclear spin states are equally populated down to temperatures of at least 1.5 K and that the contribution of nuclear spins to the total energy is negligibly small. Of course, NMR spectroscopy relies on the fact that these states are *not exactly* equally populated, but in the context of statistical thermodynamics, the contribution to internal energy and the population differences are negligible.

Hence, in this high-temperature limit all nuclear spin states are fully accessible and the number of accessible states equals the total number of nuclear spin states. This gives

$$Z_{\text{ns}} = \prod_i (2I_i + 1) , \quad (6.3.1)$$

where the  $I_i$  are the nuclear spin quantum numbers for nuclei in the molecule. Magnetic equivalence leads to degeneracy of nuclear spin levels, but does not influence the total number of nuclear spin states. Since the term  $u/T$  in Equation ???) is negligible and  $z_{\text{ns}} = Z_{\text{ns}}^N$ , we have

$$s = Nk_B \sum_i \ln(2I_i + 1) . \quad (6.3.2)$$

This contribution to entropy is not generally negligible. Still it is generally ignored in textbooks, which usually does not cause problems, as the contribution is constant under most conditions where experiments are conducted and does not change during chemical reactions.

### Symmetry Requirements

Nuclear spin states have another, more subtle effect that may prevent separation of state spaces. We consider this effect for  $\text{H}_2$ . In this molecule, the electron wavefunction arises from two electrons, which are fermions, and must thus be antisymmetric with respect to exchange of the two electrons. In quantum-chemical computations this is ensured by using a Slater determinant. Likewise, the nuclear wavefunction must be antisymmetric with respect to exchange of the two protons, which are also fermions. The spin part is antisymmetric for the singlet state with total nuclear spin quantum number  $F = 0$ ,

$$\psi_{\text{ns},S} = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle) , \quad (6.3.3)$$

and symmetric for the triplet state with  $F = 1$ , as can be seen by the wavefunctions of each of the three triplet substates:

$$\psi_{\text{ns},T_+} = |\alpha\alpha\rangle \quad (6.3.4)$$

$$\psi_{\text{ns},T_0} = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \quad (6.3.5)$$

$$\psi_{\text{ns},T_-} = |\beta\beta\rangle . \quad (6.3.6)$$

The translational, vibrational, and electron wavefunction are generally symmetric with respect to the exchange of the two nuclei. The rotational wavefunction is symmetric for even rotational quantum numbers  $J$  and antisymmetric for odd quantum numbers. Hence, to ensure that the generalized Pauli principle holds and the total wavefunction is antisymmetric with respect to exchange of indistinguishable nuclei, even  $J$  can only be combined with the antisymmetric nuclear spin singlet state and odd  $J$  only with the symmetric triplet state. The partition functions for these two cases must be considered separately. For  $\text{H}_2$  we have

$$Z_{\text{para}} = \sum_{J \text{ even}} (2J + 1) e^{-J(J+1)\hbar^2/2Ik_B T} , \quad (6.3.7)$$

where  $g_J = 2J + 1$  is the degeneracy of the rotational states and  $I$  is the moment of inertia, and

$$Z_{\text{ortho}} = 3 \sum_{J \text{ odd}} (2J + 1) e^{-J(J+1)\hbar^2/2Ik_B T} , \quad (6.3.8)$$

where  $g_I = 3$  is the degeneracy of the nuclear spin states.

For  $\text{H}_2$  the  $(J = 0, F = 0)$  state is called para-hydrogen and the  $(J = 1, F = 1)$  state ortho-hydrogen. At ambient temperature, both the  $(J = 0, F = 0)$  state and the  $(J = 1, F = 1)$  state are, approximately, fully populated and thus, the four nuclear spin substates described by Eqs. ([eq:singlet]-[eq:triplet\_m]) are equally populated. Statistics then dictates a para-hydrogen to ortho-hydrogen ratio of 1:3 and no macroscopic spin polarization in a magnetic field. The splitting between the two states is

$$\frac{\epsilon_{J=1, F=1} - \epsilon_{J=0, F=0}}{k_{\text{B}}} = 2\Theta_{\text{rot}} = \frac{\hbar^2}{k_{\text{B}}I} \approx 178.98 \text{ K}, \quad (6.3.9)$$

where we have introduced a characteristic rotational temperature analogous to the characteristic vibrational temperature for the harmonic oscillator in Equation ???). At temperatures well below this energy splitting, para-hydrogen is strongly enriched with respect to ortho-hydrogen. Equilibration in a reasonable time requires a catalyst. Still, no macroscopic spin polarization in a magnetic field is observed, as the two nuclear spins are magnetically equivalent and align antiparallel. If, however, para-hydrogen is reacted with a molecule featuring a multiple bond, magnetic equivalence of the two hydrogen atoms can be removed and in that case enhanced nuclear spin polarization is observable (para-hydrogen induced polarization, PHIP ). We note that for  $^2\text{H}_2$  the combination of nuclear spin states and rotational states to an allowed state reverses, as deuterons are bosons.

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