Nuclear Spin

In the absence of strong magnetic fields, nuclear spins are degenerate. Even at strong enough magnetic fields, extremely low temperatures are required to generate differences in the populations of different nuclear spins, which is the basis for magnetic resonance spectroscopy (*1*). Therefore, for most applications in statistical thermodynamics, all nuclear spins are considered degenerate and equally occupied (fully available). The partition function is therefore independent of the temperature and takes the value

$$q^{nspin} = \prod_i (2I_i + 1) \tag{1}$$

where I_i are the nuclear spin quantum numbers for all atoms in the molecule.

Due to the particular properties of particles with a specific spin statistics (fermions and bosons), the nuclear wavefunction must remain antisymmetric to the exchange of fermionic nuclei. The rotational wavefunction is symmetric with respect to even rotational numbers and antisymmetric for odd rotational quantum numbers. To ensure the antisymmetry of the total nuclear wavefunction, rotational states characterized by even quantum numbers can only be combined with antisymmetric singlet nuclear spin states and rotational states composed of odd quantum numbers can only be combined with symmetric triplet states of the nuclei. The former are known as ortho nuclear spin states, while the latter are known as para nuclear spin states. The two parts must also be considered separately. Due to this special type of coupling, the consideration of nuclear spin makes sense only when using the summations (not the classical limit) with the rigid rotor approximation. Furthermore, the σ parameter in the rotational partition function already takes the effects of nuclear spin in consideration. Therefore, nuclear spins should only be considered at extremely low temperatures (*2*).

Bibliography

1. G. Jeschke, *Lecture Notes: Advanced Physical Chemistry, Statistical Thermodynamics.* ETH, 2015.

2. A. Maczek and A. Meijer, *Statistical Thermodynamics.* Oxford, 2017.