

30.9 Spin-rotation coupling in homonuclear diatomic molecules

The total wave function of the diatomic molecule reads

$$\psi = \psi_e \psi_r \psi_v \psi_n, \quad (0.0.1)$$

where ψ_e is the electron wave function, ψ_r the rotational wave function, ψ_v the vibrational wave function, and ψ_n the nuclear spin wave function. Two nuclei cannot be distinguished, so under their permutation \mathcal{N} the total wave function ψ must be symmetric (bosonic nuclei) or anti-symmetric (fermionic nuclei) (see the [beginning](#) of this chapter). We know

$$\mathcal{N}\psi_e = \psi_e, \quad (0.0.2)$$

$$\mathcal{N}\psi_v = \psi_v, \quad (0.0.3)$$

$$\mathcal{N}\psi_r = (-1)^J \psi_r. \quad (0.0.4)$$

The first two are simply because the electron or phonon clouds are not affected at all. The last line follows from the property of the spherical harmonics Y_{Jm} (or recall s, p, d, f, \dots electrons). Thus ψ_n must also be an eigenstate of \mathcal{N} (i.e., it must have a definite parity). The parity of ψ_n depends on the nuclear spins: Let $\psi_A(s)$ be the spin state of nucleus A with the z -component s . Then, eigenstates of \mathcal{N} may be constructed as:

Symmetric case

$$\psi_n^{(+)} \propto \psi_A(s)\psi_B(s') + \psi_A(s')\psi_B(s). \quad (0.0.5)$$

Antisymmetric case

$$\psi_n^{(-)} \propto \psi_A(s)\psi_B(s') - \psi_A(s')\psi_B(s). \quad (0.0.6)$$

Suppose the nucleus has spin S . The total number of the distinguishable nuclear spin states is $(2S+1)^2$. If $s = s'$, only symmetric states are possible. There are $2S+1$ such ‘diagonal’ states. The remaining $2S(2S+1)$ states can have both symmetric and antisymmetric states. Therefore, there are $S(2S+1)$ distinct antisymmetric states,¹ and $(S+1)(2S+1)$ symmetric states.

Since the total symmetry of the wave function is constrained, we cannot consider rotational and nuclear wave functions independently.^q Suppose nucleons are fermions, then antisymmetric (resp., symmetric) ψ_n is possible only with even (resp., odd) J states. Therefore, the rotational and nuclear partition function for fermions reads

$$z_{nr} = (2S+1)(S+1)z_r^{(o)} + S(2S+1)z_r^{(e)}, \quad (0.0.7)$$

where

$$z_r^{(o)} = \sum_{J=\text{odd}} (2J+1)e^{-J(J+1)\Theta_r/T}, \quad (0.0.8)$$

$$z_r^{(e)} = \sum_{J=\text{even}} (2J+1)e^{-J(J+1)\Theta_r/T}. \quad (0.0.9)$$

It is clear that for bosonic homonuclear diatomic molecules

$$z_{nr} = (2S+1)(S+1)z_r^{(e)} + S(2S+1)z_r^{(o)}. \quad (0.0.10)$$

¹This is also ${}_{2S+1}C_2$.

In summary, the total partition function due to the internal degrees of freedom reads

$$z_i = z_e z_v z_{nr}. \quad (0.0.11)$$

At sufficiently high temperatures

$$z_r^{(e)} \simeq z_r^{(o)} \simeq \frac{1}{2} z_r. \quad (0.0.12)$$

Therefore, at sufficiently high temperatures

$$z_i = \frac{1}{2} z_e z_v z_r z_n. \quad (0.0.13)$$

The prefactor $1/2$ is the *symmetry factor* to avoid double counting of geometrically indistinguishable states.

The above homonuclear diatomic molecules may be a good elementary quantum mechanics topic, which is no more very interesting (except in exams). However, the topic played an important role in determining whether protons are fermions or not.

Is a proton a fermion?

Although it was known that the proton spin was $1/2$, before 1930 the spin-statistics relation was not known. For H_2 the rotational-nuclear partition function reads

$$z_{nr} = g_e z_r^{(e)} + g_o z_r^{(o)}. \quad (0.0.14)$$

If protons are fermions, $\beta = g_e/g_o = [(2S+1)S]/[(2S+1)(S+1)] = 1/3$, if bosons, its reciprocal, 3. In February 1927² Hund, analyzing the specific heat, found $\beta = 2$. Spectroscopically, Hori obtained $\beta = 1/3$. Dennison realized that there is no equilibrium between the singlet and triplet nuclear spin states in hydrogen gas (respectively called para hydrogen and ortho hydrogen) at low temperatures. Therefore, the nuclear-rotation partition function cannot be written as

$$Z_{nr} = z_{nr}^N = (g_e z_r^{(e)} + g_o z_r^{(o)})^N \quad (0.0.15)$$

but

$$Z_{nr} = (g_e z_r^{(e)})^{\rho N} (g_o z_r^{(o)})^{(1-\rho)N}, \quad (0.0.16)$$

where ρ is the fraction of the even rotational angular momentum states. Dennison found $\rho = 1/4$ from the specific heat data. This implies that at sufficiently high temperatures where two nuclear spin states can change into each other $\beta = 1/3$ (on June 3, 1927). Then, later he realized that this implies that protons are fermions (on June 16, 1927).³

Annealed and quenched systems

The difference between (0.0.15) and (0.0.16) is very important in the study of a system under the influence of external fields or randomness in the system. Suppose the system depends on a parameter (or a field) f , and f is a stochastic variable. For a fixed f , the partition function is given by $Z(f)$.

If f varies sufficiently rapidly so that within the observation time f samples its distribution almost evenly ('ergodically'), then the free energy we observe should be given by

$$A = -k_B T \log \langle Z(f) \rangle_f, \quad (0.0.17)$$

²[1927: This is the year Heisenberg proposed the uncertainty principle and matrix dynamics. Chiang Kai-shek set up a government in Nanjing; Mao moved to the Jinggang Mountains, Jiangxi]

³S. Tomonaga, *Spin the Spin* (World Scientific, 2004).

where $\langle \rangle_f$ is the average over f . However, if f is frozen for each sample, but is different from sample to sample, then the free energy we get should be

$$A = -k_B T \langle \log Z(f) \rangle_f. \quad (0.0.18)$$

The former is the *annealed case* and the latter *quenched case*. The low temperature hydrogen gas was a quenched system.

Can we study the intermediate case with the aid of equilibrium statistical mechanics? No. Recall that an equilibrium state is a state where all the fast events have occurred, but no slow events have occurred yet.

Let us conclude this section with a summary of *polyatomic gases*. As in the case of diatomic gases, we can write

$$z_i = z_r z_v. \quad (0.0.19)$$

The nuclear contribution can be treated as a mere multiplicative factor as is discussed. Let the principal moments of inertia of the molecule be I_1 , I_2 and I_3 . Then the rotational Hamiltonian reads

$$H_{rot} = \sum_i \frac{L_i^2}{2I_i}, \quad (0.0.20)$$

where L_i is the angular momentum around the i -th principal axis. We may treat the partition function classically, [q](#) so that

$$z_{rot} = \frac{(2k_B T)(\pi I_1 I_2 I_3)^{3/2}}{\hbar^3}. \quad (0.0.21)$$

Notice that $I_1 I_2 I_3$ is the determinant of the inertial tensor around the center of mass.

For a linear molecule $I_3 = 0$ and $I_1 = I_2 = I$, so that

$$z_{rot} = \frac{2Ik_B T}{\hbar^2}. \quad (0.0.22)$$

z_v is the product of contributions from each normal mode. Often, vibrational degrees of freedom are all frozen, so we may ignore them.