Chapter 8.   Nuclear Spin Statistics

Notes:
- *Most of the material presented in this chapter is taken from Bunker and Jensen (2005), Chap. 9, and Bunker and Jensen (1998), Chap. 8.*

8.1 The Complete Internal Wave Function Φ_{int}

In Chapter 2 when dealing with the spin of the electrons, we found that it was necessary to take into account the Pauli principle. Namely, we had to ensure that the wave function of the molecule be antisymmetric under the exchange of two identical fermions, in this case electrons. We accomplished this by breaking up molecular electronic wave function $\Phi_{\text{elec},n}$ (after the use of the Born-Oppenheimer approximation) into a product of electronic orbital and spin functions (see equation (2.29)).

In the case of the molecular nuclei, we are dealing with a slightly different problem in that not all of the nuclei have the same spin. In fact some nuclei will be bosons while others will be fermions. Again the Pauli principle will apply for any pair of identical fermion nuclei (i.e., the requirement of an antisymmetric wave function), but the wave function will remain unchanged under the exchange of any pair of identical bosons. Because of this potentially different nature of the nuclei, it has not been possible to formalize the treatment of nuclear spins in a manner exactly similar as was done for the electrons. In fact, we have so far avoided any discussion on the treatment of nuclear spins. Indeed, the rovibronic wave function $\Phi_{\text{rv},nj}$ derived in the previous chapters does not take into account the spins of the nuclei. To remedy this omission, we now define the complete internal wave function Φ_{int} as follows

$$
\begin{aligned}
\Phi_{\text{int}}\left(\mathbf{R}_{\text{N}},\sigma_{\text{N}},\mathbf{r}_{\text{e}},\sigma_{\text{e}}\right) &= \Phi_{\text{elec},n}\left(\mathbf{R}_{\text{N}},\mathbf{r}_{\text{e}},\sigma_{\text{e}}\right)\Phi_{\text{rv},nj}\left(\mathbf{R}_{\text{N}}\right)\Phi_{\text{ns},t}\left(\sigma_{\text{N}}\right) \\
&= \Phi_{\text{rve}}^{0}\left(\mathbf{R}_{\text{N}},\mathbf{r}_{\text{e}},\sigma_{\text{e}}\right)\Phi_{\text{ns},t}\left(\sigma_{\text{N}}\right),
\end{aligned}
\tag{8.1}
$$

where $\Phi_{\text{ns},t}$ is the nuclear spin function (t numbers the different spin functions), and $\mathbf{R}_{\text{N}}$, σ_{N}, $\mathbf{r}_{\text{e}}$, and σ_{e} stand for the nuclear and electronic coordinates and spins, respectively. We see that we can consider the product $\Phi_{\text{rv},nj}\Phi_{\text{ns},t}$ to be the nuclear equivalent to $\Phi_{\text{elec},n}$, which, as stated above, is the product of electronic orbital and spin functions. The important thing to remember is that it is Φ_{int}, and not Φ_{rve}^{0}, that is subjected to the Pauli principle.

8.1.1 The Classification of the Complete Internal Wave Function

We already know that the parity ($+$ or $-$) of an irreducible representation, and therefore of a wave function, is defined by its transformation under the inversion operator E^{*}. More precisely, given the effect of E^{*} in Φ_{int}

$$
E^{*}\Phi_{\text{int}} = \pm\Phi_{\text{int}},
\tag{8.2}
$$

we can classify the internal wave function with respect to whether it has positive or negative parity. Alternatively, we can also investigate the transformation of Φ_{int} under the odd or even permutations of fermions and bosons. That is, if we define P_{odd} and P_{even} as permutations of, respectively, odd and even number of pairs of fermions, then because of the Pauli principle we must have

$$
\begin{aligned}
P_{odd}\Phi_{int} &= -\Phi_{int} \\
P_{even}\Phi_{int} &= \Phi_{int},
\end{aligned}
\tag{8.3}
$$

irrespective of the details of the internal wave function. Permutations of any numbers of bosons will leave Φ_{int} unchanged. Equations (8.3) can be used to identify two non-degenerate irreducible representations from the MS group of a molecule, which will be in turn differentiated by the character of the inversion specified by equation (8.2), when it is an element of the group (see below). The representation with positive parity belongs to Γ^+, while the one with negative parity belongs to Γ^-.

For example, the MS group of water is $C_{2v}(M)$ has the character shown in Table 8-1. Since H_2O is composed, in part, of two fermions (labeled 1 and 2), then it is seen that $\Gamma^+ = B_2$ and $\Gamma^- = B_1$. If, on the other hand, we replace the hydrogen nuclei with deuterium nuclei, which are bosons, to get twice-deuterated water D_2O, then $\Gamma^+ = A_1$ and $\Gamma^- = A_2$, as Φ_{int} must now be left unchanged by the action of (12).

Table 8-1 – The character table for $C_{2v}(M)$, the MS group for water and twice-deuterated water.

$C_{2v}(M):$	E	(12)	E^*	$(12)^*$
$A_1:$	1	1	1	1
$A_2:$	1	1	−1	−1
$B_1:$	1	−1	−1	1
$B_2:$	1	−1	1	−1

It is often the case, however, that the inversion operator E^* is not a symmetry element of the MS group of a given molecule (it is always included in the CNPI group). Take for example the case of the methyl fluoride (CH_3F) molecule whose MS group is $C_{3v}(M)$ (the corresponding character table is shown in Table 8-2). Evidently the inversion E^* is not an element of this group. All is not lost however, since we can use the presence of the permutation-inversion $(12)^*$ operator in the group to our advantage. Indeed, if we consider the two internal wave functions $\Phi_{int}(A_1)$ and $\Phi_{int}(A_2)$ that respectively generate the two one-dimensional irreducible representations A_1 and A_2, then we can write

$$(12)^* \Phi_{\text{int}}(A_1) = E^*\left[(12)\Phi_{\text{int}}(A_1)\right] = E^*\left[-\Phi_{\text{int}}(A_1)\right] = \Phi_{\text{int}}(A_1)$$

$$(12)^* \Phi_{\text{int}}(A_2) = E^*\left[(12)\Phi_{\text{int}}(A_2)\right] = E^*\left[-\Phi_{\text{int}}(A_2)\right] = -\Phi_{\text{int}}(A_2).$$

(8.4)

Table 8-2 – The character table or $C_{3v}(M)$, the MS group for methyl fluoride; the three proton are labeled 1, 2, and 3.

$C_{3v}(M)$:	E	(123)	$(12)^*$
	1	2	3
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

But as is made explicit in equations (8.4), this operator consists of the combination of an odd permutation of fermions (i.e., (12)) and the inversion E^*. Because of the aforementioned definition of the parity of a wave function in relation to its transformation under E^*, and the demands of the Pauli principle concerning the permutation of pairs of fermions, we can generalize the results of equations (8.4) with

$$P_{\text{even}}^* \Phi_{\text{int}}\left(\Gamma^\pm\right) = \pm\Phi_{\text{int}}\left(\Gamma^\pm\right).$$

$$P_{\text{odd}}^* \Phi_{\text{int}}\left(\Gamma^\pm\right) = \mp\Phi_{\text{int}}\left(\Gamma^\pm\right)$$

(8.5)

That is, *the $\Gamma^\pm$ representation has the character ± 1 under any P_{even}^* operators and the character ∓ 1 under any P_{odd}^* operators.* Using this definition we find that

$$\Gamma^+ = A_2 \quad \text{and} \quad \Gamma^- = A_1$$

(8.6)

for the methyl fluoride molecule.

When the inversion and all permutation-inversion operators are unfeasible (i.e., none are part of the MS group), then the internal wave functions cannot be assigned a definite parity label and $\Gamma^+ = \Gamma^-$. Parity can be used to label the internal states of a molecule, but we prefer using the irreducible representations of the MS group for this purpose.

8.2 The Classification of the Nuclear Spin Wave Functions

The spin state of a nucleus is defined in the same way as that of an electron. That is, we have the operators $\hat{I}^2$ and $\hat{I}_Z$ for the square of the spin and its space-fixed Z-component, respectively, such that

$$\hat{I}^2|I,m_I\rangle = I(I+1)\hbar^2|I,m_I\rangle$$

$$\hat{I}_Z|I,m_I\rangle = m_I\hbar|I,m_I\rangle,$$

(8.7)

where $|I, m_I\rangle$ are the corresponding eigenvectors. For fermions the quantum numbers I and m_I are half-integer numbers (with $I > 0$ and $|m_I| = I-1, I-2, \ldots, 1/2$), while for bosons they are integers (with $I \geq 0$ and $|m_I| = I-1, I-2, \ldots, 0$).

For example, the two hydrogen nuclei of a water molecule have $I_1 = I_2 = 1/2$, and if, as usual, we define the two possible states for the spin of a given nucleus as

$$|\alpha\rangle = |1/2, 1/2\rangle \quad \text{and} \quad |\beta\rangle = |1/2, -1/2\rangle, \tag{8.8}$$

then the possible combined nuclei spin vectors for the molecule (the oxygen nucleus has $I_3 = 0$) are

$$
\begin{aligned}
m_I = -1: \quad & |\Phi_{ns,1}\rangle = |\beta_1\beta_2\rangle, \\
m_I = 0: \quad & |\Phi_{ns,2}\rangle = |\alpha_1\beta_2\rangle, \quad |\Phi_{ns,3}\rangle = |\beta_1\alpha_2\rangle, \\
m_I = 1: \quad & |\Phi_{ns,4}\rangle = |\alpha_1\alpha_2\rangle,
\end{aligned}
\tag{8.9}
$$

where m_I is for the total combined nuclear spin. If we investigate the transformation of the corresponding wave functions under the elements of the appropriate MS group (see Table 8-1) we find

$$
\begin{aligned}
&E\Phi_{ns,t} = \Phi_{ns,t} \\
&(12)\Phi_{ns,1} = \Phi_{ns,1} \quad (12)\Phi_{ns,2} = \Phi_{ns,3} \quad (12)\Phi_{ns,3} = \Phi_{ns,2} \quad (12)\Phi_{ns,4} = \Phi_{ns,4} \\
&E^*\Phi_{ns,t} = \Phi_{ns,t} \\
&(12)^*\Phi_{ns,1} = \Phi_{ns,1} \quad (12)^*\Phi_{ns,2} = \Phi_{ns,3} \quad (12)^*\Phi_{ns,3} = \Phi_{ns,2} \quad (12)^*\Phi_{ns,4} = \Phi_{ns,4},
\end{aligned}
\tag{8.10}
$$

where $t = 1, 2, 3,$ and 4. The corresponding character for the Γ_{nspin} representation generated by the combined wave functions is

$$\chi^{\Gamma_{nspin}}[E] = 4, \quad \chi^{\Gamma_{nspin}}[(12)] = 2, \quad \chi^{\Gamma_{nspin}}[E^*] = 4, \quad \chi^{\Gamma_{nspin}}[(12)^*] = 2. \tag{8.11}$$

Using equation (6.60) from Chapter 6

$$a_i = \frac{1}{h} \sum_R \chi^{\Gamma_{nspin}}[R] \chi^{\Gamma_i}[R]^*, \tag{8.12}$$

and Table 8-1 we find

$$\Gamma_{nspin} = 3A_1 \oplus B_2. \tag{8.13}$$

We can identify the four wave functions that correspondingly generate these four irreducible representations by using the projection operators (see equation (7.22) of Chapter 7)

$$P^{\Gamma_i} = \frac{1}{h}\sum_R \chi^{\Gamma_i}\left[R\right]^* R \tag{8.14}$$

to find

$$
\begin{aligned}
\psi_{ns,1}(A_1) &= \Phi_{ns,1} = \left|\beta_1\beta_2\right\rangle \\
\psi_{ns,2}(A_1) &= \Phi_{ns,4} = \left|\alpha_1\alpha_2\right\rangle \\
\psi_{ns,3}(A_1) &= \frac{1}{2}\left(\Phi_{ns,2} + \Phi_{ns,3}\right) = \frac{1}{2}\left(\left|\alpha_1\beta_2\right\rangle + \left|\beta_1\alpha_2\right\rangle\right) \\
\psi_{ns,4}(B_2) &= \frac{1}{2}\left(\Phi_{ns,2} - \Phi_{ns,3}\right) = \frac{1}{2}\left(\left|\alpha_1\beta_2\right\rangle - \left|\beta_1\alpha_2\right\rangle\right).
\end{aligned}
\tag{8.15}
$$

We therefore find that the three totally symmetric wave functions form the usual spin triplet state with $I = 1$ and $m_I = -1, 0$, and 1, while the antisymmetric state is the usual spin singlet state where $I = m_I = 0$; see equations (2.27) and (2.28) of Chapter 2.

For D_2O the situation is somewhat more complicated since both deuterium nuclei have a spin $I_1 = I_2 = 1$. There are therefore nine possible spin functions

$$
\begin{aligned}
m_I = 2: \quad & \left|\Phi_{ns,1}\right\rangle = \left|\alpha_1\alpha_2\right\rangle, \\
m_I = 1: \quad & \left|\Phi_{ns,2}\right\rangle = \left|\alpha_1\beta_2\right\rangle, \quad \left|\Phi_{ns,3}\right\rangle = \left|\beta_1\alpha_2\right\rangle, \\
m_I = 0: \quad & \left|\Phi_{ns,4}\right\rangle = \left|\alpha_1\gamma_2\right\rangle, \quad \left|\Phi_{ns,5}\right\rangle = \left|\gamma_1\alpha_2\right\rangle, \quad \left|\Phi_{ns,6}\right\rangle = \left|\beta_1\beta_2\right\rangle, \\
m_I = -1: \quad & \left|\Phi_{ns,7}\right\rangle = \left|\beta_1\gamma_2\right\rangle, \quad \left|\Phi_{ns,8}\right\rangle = \left|\gamma_1\beta_2\right\rangle, \\
m_I = -2: \quad & \left|\Phi_{ns,9}\right\rangle = \left|\gamma_1\gamma_2\right\rangle,
\end{aligned}
\tag{8.16}
$$

where this time we defined for a single spin i

$$\left|\alpha_i\right\rangle = \left|1,1\right\rangle, \quad \left|\beta_i\right\rangle = \left|1,0\right\rangle, \quad \text{and} \quad \left|\gamma_i\right\rangle = \left|1,-1\right\rangle . \tag{8.17}$$

Again we investigate the transformation of the combined spin functions taken as a whole to find

$$\chi^{\Gamma_{nspin}}\left[E\right] = 9, \quad \chi^{\Gamma_{nspin}}\left[(12)\right] = 3, \quad \chi^{\Gamma_{nspin}}\left[E^*\right] = 9, \quad \chi^{\Gamma_{nspin}}\left[(12)^*\right] = 3, \tag{8.18}$$

which through equation (8.12) yields

$$\Gamma_{\text{nspin}} = 6A_1 \oplus 3B_2. \tag{8.19}$$

The projection operators are then used, as is now custom, to give the corresponding symmetric and antisymmetric wave functions

$$\psi_{\text{ns},1}(A_1) = \Phi_{\text{ns},1} = |\alpha_1\alpha_2\rangle$$

$$\psi_{\text{ns},2}(A_1) = \Phi_{\text{ns},6} = |\beta_1\beta_2\rangle$$

$$\psi_{\text{ns},3}(A_1) = \Phi_{\text{ns},9} = |\gamma_1\gamma_2\rangle$$

$$\psi_{\text{ns},4}(A_1) = \frac{1}{2}\left(\Phi_{\text{ns},2} + \Phi_{\text{ns},3}\right) = \frac{1}{2}\left(|\alpha_1\beta_2\rangle + |\beta_1\alpha_2\rangle\right) \tag{8.20}$$

$$\psi_{\text{ns},5}(A_1) = \frac{1}{2}\left(\Phi_{\text{ns},4} + \Phi_{\text{ns},5}\right) = \frac{1}{2}\left(|\alpha_1\gamma_2\rangle + |\gamma_1\alpha_2\rangle\right)$$

$$\psi_{\text{ns},6}(A_1) = \frac{1}{2}\left(\Phi_{\text{ns},7} + \Phi_{\text{ns},8}\right) = \frac{1}{2}\left(|\beta_1\gamma_2\rangle + |\gamma_1\beta_2\rangle\right),$$

and

$$\psi_{\text{ns},7}(B_2) = \frac{1}{2}\left(\Phi_{\text{ns},2} - \Phi_{\text{ns},3}\right) = \frac{1}{2}\left(|\alpha_1\beta_2\rangle - |\beta_1\alpha_2\rangle\right)$$

$$\psi_{\text{ns},8}(B_2) = \frac{1}{2}\left(\Phi_{\text{ns},4} - \Phi_{\text{ns},5}\right) = \frac{1}{2}\left(|\alpha_1\gamma_2\rangle - |\gamma_1\alpha_2\rangle\right) \tag{8.21}$$

$$\psi_{\text{ns},9}(B_2) = \frac{1}{2}\left(\Phi_{\text{ns},7} - \Phi_{\text{ns},8}\right) = \frac{1}{2}\left(|\beta_1\gamma_2\rangle - |\gamma_1\beta_2\rangle\right).$$

8.3   The Determination of the Statistical Weights

As was shown in equation (8.1), a complete internal wave function Φ_{int} is a product of a rovibronic Φ_{rve}^0 and a spin $\Phi_{\text{ns},t}$ wave functions. It follows from this that the representation Γ_{int} thus generated is

$$\Gamma_{\text{int}} = \Gamma_{\text{rve}} \otimes \Gamma_{\text{ns},t}. \tag{8.22}$$

However, we also know from equations (8.3) that the only realized irreducible representations Γ_{int} are those that satisfy the Pauli principle. These representations are therefore easily determined with the character table of the MS group for the molecule under study. Moreover, we have just explored in the previous section how to determine the representations generated by the possible nuclear spin functions. These irreducible representations are also readily determined, at least in principle. So, given Γ_{int} and $\Gamma_{\text{ns},t}$ it will be possible to determine which are the rovibronic representations realized. Mathematically, the necessary condition can be written as

$$\Gamma_{\text{rve}} \otimes \Gamma_{\text{ns},t} \supset \Gamma_{\text{int}}. \tag{8.23}$$

For example, we already determine that for H_2O and D_2O the only possible representations Γ_{int} are

$$\Gamma_{int}\left(H_2O\right) = B_1 \text{ and } B_2$$
$$\Gamma_{int}\left(D_2O\right) = A_1 \text{ and } A_2,$$

(8.24)

respectively. Since we determined that for both molecules $\Gamma_{ns,t} = A_1$ and B_2, then the only possible rovibronic representations are

$$\Gamma_{rve} = A_1, A_2, B_1, \text{ and } B_2$$

(8.25)

for both molecules. This is because for H_2O

$$\frac{\Gamma_{rve} \otimes \Gamma_{ns,t} = \Gamma_{int}}{B_1 \otimes A_1 = B_1}$$
$$B_2 \otimes A_1 = B_2$$
$$A_1 \otimes B_2 = B_2$$
$$A_2 \otimes B_2 = B_1,$$

(8.26)

while for D_2O

$$\frac{\Gamma_{rve} \otimes \Gamma_{ns,t} = \Gamma_{int}}{A_1 \otimes A_1 = A_1}$$
$$A_2 \otimes A_1 = A_2$$
$$B_1 \otimes B_2 = A_2$$
$$B_2 \otimes B_2 = A_1.$$

(8.27)

Although every irreducible representations of the MS group are generated for both molecules, they are not realized with the same weight (i.e., the same number of times). That is, the presence of three H_2O nuclear spin functions with symmetry A_1 implies that there will be three different complete internal wave functions of symmetry B_1 or B_2 realized for every rovibronic wave functions (of similar symmetry) for that molecule. On the other hand, since there are six D_2O nuclear spin functions with symmetry A_1 then there will be six different complete internal wave functions of symmetry A_1 or A_2 realized for every rovibronic wave functions (of similar symmetry) for that molecule. The so-called **spin statistical weight** g_{ns} corresponds to the number of times that a complete internal wave function of symmetry Γ_{int} is realized. The results for water and twice-deuterated water are listed in Table 8-3.

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For molecules like H_2O and D_2O where we are in presence of different values of spin statistical weights, the states with higher and lower g_{ns} are called **ortho** and **para states**, respectively.

Table 8-3 – The spin statistical weights of H_2O and D_2O.

	H_2O				D_2O		
Γ_{rve}	$\Gamma_{ns,t}$	Γ_{int}	g_{ns}	Γ_{rve}	$\Gamma_{ns,t}$	Γ_{int}	g_{ns}
A_1	B_2	B_2	1	A_1	$6A_1$	A_1	6
A_2	B_2	B_1	1	A_2	$6A_1$	A_2	6
B_1	$3A_1$	B_1	3	B_1	$3B_2$	A_2	3
B_2	$3A_1$	B_2	3	B_2	$3B_2$	A_1	3

8.4 Intensity Alternations and Missing Levels

As we saw in the last section of Chapter 7, a perturbation term $\hat{H}'$ can be added to the Hamiltonian of an otherwise isolated molecule to model its interaction with an external agent (or alternatively some internal coupling such as for the hyperfine Hamiltonian). The representation Γ' generated by the perturbation Hamiltonian can be used to determine if a transition will occur between two states, according to the vanishing integral rule.

As will be seen in a subsequent chapter, the perturbation Hamiltonian due to the interaction of the molecular electric dipole and an external radiation field generates the A_2 representation for the H_2O and D_2O molecules. Therefore, radiative transitions between two states Γ_1 and Γ_2 will only be possible if

$$\Gamma_1 \otimes A_2 \otimes \Gamma_2 \supset \Gamma^{(s)} = A_1. \tag{8.28}$$

A quick study of the character table for these molecules (i.e., Table 8-1 for $C_{2v}(M)$) will reveal that $B_1 \leftrightarrow B_2$ and $A_1 \leftrightarrow A_2$ transitions are possible for the complete internal wave functions of H_2O and D_2O, respectively. Furthermore, an electric dipolar transition will not change the spin state of a molecule (since the electric dipole operator does not involve nuclear spins), but only the rovibronic state. So, for water there will respectively be three $B_1 \leftrightarrow B_2$ and one $A_1 \leftrightarrow A_2$ rovibronic transitions that satisfy these conditions. For D_2O there will be six $A_1 \leftrightarrow A_2$ and three $B_1 \leftrightarrow B_2$ allowed rovibronic transitions, respectively. In other words, for water the intensity of the effective $B_1 \leftrightarrow B_2$ rovibronic transition (resulting from the three individual transitions) will three times stronger than the single $A_1 \leftrightarrow A_2$ rovibronic transition because of their different associated spin statistical weights. For D_2O the effective $A_1 \leftrightarrow A_2$ rovibronic transition will be twice as strong as the corresponding $B_1 \leftrightarrow B_2$ rovibronic transition for the same reason. This phenomenon is referred to as **intensity alternations**.

It is also possible that the conditions imposed by the Pauli principle and the nuclear spin statistics will rule out the existence of some molecular states. An example of this is the

H_3^+ ion for which the MS group is $D_{3h}(M)$ (see Table B.8 of Bunker and Jansen (2005)) and

$$\Gamma_{\text{spin}} = 4A_1' \oplus 2E'. \tag{8.29}$$

Calculations such as the one performed above for H_2O and D_2O would yield the spin statistical weights shown in Table 8-4. As can be seen, the rovibronic A_1' and A_1'' representations are not realized because no spin representation can combine with them to yield the representations $\Gamma_{\text{int}} = A_2'$ and A_2'' corresponding to the only allowed internal wave functions. Unrealized rovibronic representations correspond to so-called **missing levels**.

Table 8-4 – Spin statistical weights for H_3^+

Γ_{rve}	Γ_{ns}	Γ_{int}	g_{ns}
A_1'	—	—	0
A_1''	—	—	0
A_2'	$4A_1'$	A_2'	4
A_2''	$4A_1'$	A_2''	4
E'	$2E'$	A_2'	2
E''	$2E'$	A_2''	2