

Nuclear spin selection rules in chemical reactions by angular momentum algebra

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Abstract

The detailed selection rules for reactive collisions reported by Quack using molecular symmetry group are derived by using angular momentum algebra. Instead of the representations of the permutation–inversion group for both nuclear spin and rovibronic coordinate wavefunctions, those of the rotation group for nuclear spin wavefunction only are used. The method allows more straightforward derivation of Quack’s results and further extension of the calculation for separating elementary reactions and application to higher proton systems.

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1. Introduction

The total nuclear spin quantum number I corresponding to the vector sum of kinetically equivalent identical nuclei, $I = \sum I_i$ is a robust quantum number which does not change easily because of the weakness of the nuclear magnetic interaction. It is well established that transitions between *ortho* ($I = 1$) and *para* ($I = 0$) spin modifications of two proton molecules such as H_2 , H_2O , and H_2CO are almost rigorously forbidden both in spectroscopy [1] and in collision [2]. Conversion between the two spin species is so slow that, for many applications, the two spin species may be regarded as independent molecules in the process of thermalization. This applies also to the *ortho* ($I = 3/2$) and *para* ($I = 1/2$) species of three proton molecules such as NH_3 , CH_3F , etc., and the *ortho* ($I = 1$), *meta* ($I = 2$), and *para* ($I = 0$) species of four proton molecules such as CH_4 .

The names *ortho* and *para* were initially introduced for the He spectrum empirically (parhelium and orthohelium) [3,4] and theoretically explained by Heisenberg [5] for the electron spins in the atom. Heisenberg later used them for the nuclear spins in the hydrogen molecule [6]. Maue [7] introduced *ortho*, *meta*, and *para* for CH_4 in the order of statistical weight.

In chemical reactions $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, protons are scrambled and nuclear spin species change. Nevertheless since the overall nuclear spin angular momentum of the reactants and the products conserves nearly rigorously, that is, $I_A + I_B = I_C + I_D$, there exist nearly rigorous branching ratios between different sets of $(I_A, I_B) \rightarrow (I_C, I_D)$. The theory of the relations was first formulated by Quack [8] based on the Hougen [9] Longuet-Higgins [10] molecular symmetry group and using Watson’s correlations of symmetry classifications [11]. Experimental supports of Quack’s theory have been reported for photodissociation of H_2CO [12] and ion-neutral reactions involving H_3^+ [13,14]. A more thorough discussion of selection rules in general and the literature can be found

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in [14]. The nuclear spin selection rules were also observed for reactions of CH_3 and CH_2 radicals in *para*- H_2 crystals [15].

In this paper, I present a different derivation of Quack's results using angular momentum algebra rather than group theory. Unlike Quack who considered both nuclear spin and rovibronic coordinate wavefunctions, we consider only the former since the latter is automatically taken care of by the requirement of the symmetry of the total wavefunctions with respect to permutation. Use of the angular momentum, that is, representations of the rotation group instead of the permutation inversion (PI) group, makes the treatment more general and straightforward. Also it is easier to extend the calculation for separating elementary reactions and to reactions with higher number of protons.

2. Nuclear spin modifications

The almighty formula for addition of angular momenta [16]

$$\mathcal{D}_{I_1} \otimes \mathcal{D}_{I_2} = \mathcal{D}_{I_1+I_2} \oplus \mathcal{D}_{I_1+I_2-1} \oplus \cdots \oplus \mathcal{D}_{|I_1-I_2|}, \quad (1)$$

is the only relation used in this paper. Using this relation repeatedly for $I_1 = I_2 = 1/2$ and calculating $(\mathcal{D}_{1/2})^n$ (where we use the notation $(\mathcal{D}_{1/2})^2 \equiv \mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}$), we obtain representations of nuclear spin modifications in the rotation group and their statistical weights as listed in Table 1. Representations using the PI group are also given for a comparison. Note that the dimension and the frequency of a representation are swapped between the rotation group and the PI group. Table 1 can be readily extended to molecules with larger number of protons although we run out of the *ortho*, *meta*, and *para* nomenclature for more than five protons. In general, we have

$$\begin{aligned} (\mathcal{D}_{1/2})^n &= \sum_{k=0}^{n/2, (n-1)/2} \frac{(n-2k+1)n!}{(n-k+1)!k!} \mathcal{D}_{n/2-k} \\ &= \sum_{I=n/2}^{0, 1/2} \frac{(2I+1)n!}{(n/2-I)!(n/2+I+1)!} \mathcal{D}_I, \end{aligned} \quad (2)$$

where the first and the second index above \sum apply for even and odd n , respectively. The first formula is

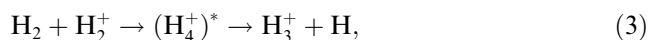
obtained from a straightforward enumeration and generalization, while the second from a more logical derivation [17].

3. Two examples

Like in many applications, a group theoretical enumeration is easier to carry out for specific simple examples rather than for the general case. Here, we first discuss two purely protonic ion-neutral reactions involving H_3^+ both of which play important roles in interstellar chemistry.

3.1. Production of H_3^+

The celebrated ion-neutral reaction with a high exothermicity of 1.7 eV which produces H_3^+ in hydrogen dominated plasmas can be written as a two step process



where $(\text{H}_4^+)^*$ represents the transient activated complex. For brevity, we sometimes use shorthand $(2,2) \rightarrow (4)^* \rightarrow (3,1)$ for reaction (3). Like Quack [8], we assume that the four protons on the activated complex scramble completely so that we can regard all of them as equivalent. This assumption is not valid if, for example, we regard (3) as a proton hop reaction from H_2^+ to H_2 . Experiments using deuterated species, however, have demonstrated that the four nuclei are completely scrambled [18,19].

Using total nuclear spin angular momenta, reaction (3) can be written as

$$\begin{aligned} (\mathcal{D}_1 \oplus \mathcal{D}_0)(\mathcal{D}_1 \oplus \mathcal{D}_0) &\rightarrow \mathcal{D}_2 \oplus 3\mathcal{D}_1 \oplus 2\mathcal{D}_0 \\ &\rightarrow (\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2})\mathcal{D}_{1/2}, \end{aligned}$$

where the notation $(\mathcal{D}_1 \oplus \mathcal{D}_0)(\mathcal{D}_1 \oplus \mathcal{D}_0) \equiv (\mathcal{D}_1 \oplus \mathcal{D}_0) \otimes (\mathcal{D}_1 \oplus \mathcal{D}_0)$, etc., are used. Finding the relations of nuclear spin species for the first half of the reaction $(2,2) \rightarrow (4)^*$ is trivial. For example, $\mathcal{D}_1 \otimes \mathcal{D}_1 \rightarrow \mathcal{D}_2 \oplus \mathcal{D}_1 \oplus \mathcal{D}_0$ demonstrates that the reaction of *o*- H_2 and *o*- H_2^+ , with the statistical weight of 9, produces *o*- $(\text{H}_4^+)^*$ ($I=1$), *m*- $(\text{H}_4^+)^*$ ($I=2$), and *p*- $(\text{H}_4^+)^*$ ($I=0$), with a ratio of 3:5:1. It is less trivial to find out how each spin species of $(\text{H}_4^+)^*$ decomposes into spin species of $(\text{H}_3^+)^*$ in the second half of the reaction $(4)^* \rightarrow (3,1)$.

Table 1
Representations and statistical weights of spin modifications

n	Examples	Rotation group	PI group	<i>ortho</i>	<i>meta</i>	<i>para</i>	Weight
2	$\text{H}_2, \text{H}_2\text{O}$	$\mathcal{D}_1 \oplus \mathcal{D}_0$	$3A \oplus B$	1		0	3:1
3	$\text{H}_3^+, \text{CH}_3$	$\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2}$	$4A_1 \oplus 2E$	3/2		1/2	4:4
4	$(\text{H}_4^+)^*, \text{CH}_4$	$\mathcal{D}_2 \oplus 3\mathcal{D}_1 \oplus 2\mathcal{D}_0$	$5A_1 \oplus 3F_1 \oplus E$	1	2	0	9:5:2
5	$(\text{H}_5^+)^*, \text{CH}_5^+$	$\mathcal{D}_{5/2} \oplus 4\mathcal{D}_{3/2} \oplus 5\mathcal{D}_{1/2}$	$6A_1 \oplus 4G_1 \oplus 2H_1$	3/2	1/2	5/2	16:10:6

Quack employed Watson's method [11] which traces the symmetry relation of the reverse reaction (4)* ← (3,1) and uses Frobenius' reciprocity. We do the same using angular momentum algebra.

For (4)* ← (3,1), we have

$$\begin{aligned} \mathcal{D}_2 \oplus \mathcal{D}_1 &\leftarrow \mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2} \\ 2\mathcal{D}_1 \oplus 2\mathcal{D}_0 &\leftarrow 2\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}. \end{aligned} \quad (4)$$

These equations show that \mathcal{D}_2 and \mathcal{D}_0 are produced only from $\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}$ and $\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}$, respectively. Reversing these, we learn that \mathcal{D}_2 and \mathcal{D}_0 dissociates only to $\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}$ and $\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}$, respectively. These agree with the intuitive picture that (H_4^+) with $I=2$ where all proton spins are parallel decomposes only to $o\text{-H}_3^+$, and (H_4^+) with $I=0$ where two pairs of spins are anti-parallel decomposes only to $p\text{-H}_3^+$. Balancing the dimensions, we obtain the first and third equations of Eqs. (5), shown below. Eqs. (4) show that \mathcal{D}_1 is produced from $\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}$ and $\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}$ and therefore decompose into both of them. We thus obtain the formula of \mathcal{D}_1 in Eqs. (5) from \mathcal{D}_2 and \mathcal{D}_0 in Eqs. (5) and the identity $\mathcal{D}_2 \oplus 3\mathcal{D}_1 \oplus 2\mathcal{D}_0 = (\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2})\mathcal{D}_{1/2}$.

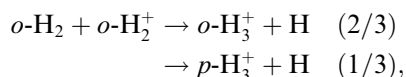
$$\begin{aligned} \mathcal{D}_2 &\rightarrow 5(\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}/8) \\ \mathcal{D}_1 &\rightarrow (\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}/8) + 2(\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}/4) \\ \mathcal{D}_0 &\rightarrow (\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}/4). \end{aligned} \quad (5)$$

In normalized forms ($\mathcal{D}_2/5 \equiv [2]$, $(\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}/8) \equiv [3/2, 1/2]$, etc., Eqs. (5) are written as

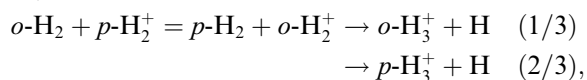
$$\begin{aligned} [2] &\rightarrow [3/2, 1/2], \\ 3[1] &\rightarrow [3/2, 1/2] + 2[1/2, 1/2], \\ 2[0] &\rightarrow 2[1/2, 1/2], \end{aligned}$$

which are more obviously the reciprocals of Eq. (4) in the sense of Frobenius' reciprocity [11].

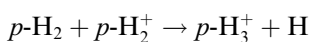
Using Eqs. (5), we have spin relations for the reaction (2,2) → (3,1) as $\mathcal{D}_1 \otimes \mathcal{D}_1 \rightarrow \mathcal{D}_2 \oplus \mathcal{D}_1 \oplus \mathcal{D}_0 \rightarrow 6(\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}/8) \oplus 3(\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}/4)$, corresponding to



$\mathcal{D}_1 \otimes \mathcal{D}_0 = \mathcal{D}_0 \otimes \mathcal{D}_1 \rightarrow \mathcal{D}_1 \rightarrow (\mathcal{D}_{3/2} \otimes \mathcal{D}_{1/2}/8) \oplus 2(\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}/4)$, corresponding to



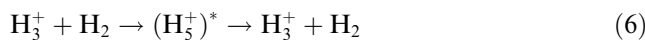
and $\mathcal{D}_0 \otimes \mathcal{D}_0 \rightarrow \mathcal{D}_0 \rightarrow (\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2}/4)$, corresponding to



that have been used in the analysis of our experiment [14]. Those relations are summarized in Table 2a where the more systematic I values rather than *ortho* and *para* notations are used to express spin modifications. We will call this relation a *branching ratio matrix*.

3.2. Reactive collision of H_3^+ with H_2

In H_2 -dominated plasmas such as those in interstellar molecular clouds, an H_3^+ ion collides with H_2 many times during its life undergoing the reaction



or (3,2) → (5)* → (3,2) in shorthand. Although the reactants and the products are the same, this is a chemical reaction in the sense that the five protons are scrambled and the spin species of H_3^+ may change. In fact this reaction is the major mechanism for thermalization of *o*- H_2 and *p*- H_2 in molecular clouds. Unlike for the highly exothermic reaction (3), this is a thermoneutral reaction and the activated complex $(\text{H}_5^+)^*$ has much smaller excess energy than $(\text{H}_4^+)^*$ of reaction (3). Therefore, the assumption of complete proton scrambling may not be valid. Indeed the experiment by Cordonnier et al. [14] has shown that proton hop reactions are faster than proton exchange reactions in their hollow cathode discharge at room temperature. So we need to separate reaction (6) into separate elementary reactions and calculate nuclear spin branching ratios separately for the proton hop reaction and proton exchange reaction.

To do this, we first calculate branching ratios assuming complete scrambling of the protons. With the angular momentum algebra, the reaction (6) is written as

$$\begin{aligned} (\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2})(\mathcal{D}_1 \oplus \mathcal{D}_0) &\rightarrow \mathcal{D}_{5/2} \oplus 4\mathcal{D}_{3/2} \oplus 5\mathcal{D}_{1/2} \\ &\rightarrow (\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2})(\mathcal{D}_1 \oplus \mathcal{D}_0). \end{aligned}$$

Proceeding as in Section 3.1, we have

$$\begin{aligned} \mathcal{D}_{5/2} \oplus \mathcal{D}_{3/2} \oplus \mathcal{D}_{1/2} &\leftarrow \mathcal{D}_{3/2} \otimes \mathcal{D}_1 \\ \mathcal{D}_{3/2} &\leftarrow \mathcal{D}_{3/2} \otimes \mathcal{D}_0 \\ 2\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2} &\leftarrow 2\mathcal{D}_{1/2} \otimes \mathcal{D}_1 \\ 2\mathcal{D}_{1/2} &\leftarrow 2\mathcal{D}_{1/2} \otimes \mathcal{D}_0 \end{aligned}$$

and their reciprocals

$$\begin{aligned} [5/2] &\rightarrow [3/2, 1] \\ 4[3/2] &\rightarrow [3/2, 1] \oplus [3/2, 0] \oplus 2[1/2, 1] \\ 5[1/2] &\rightarrow [3/2, 1] \oplus 2[1/2, 1] \oplus 2[1/2, 0] \end{aligned}$$

which give

$$\begin{aligned} \mathcal{D}_{5/2} &\rightarrow 6(\mathcal{D}_{3/2} \otimes \mathcal{D}_1/12) \\ \mathcal{D}_{3/2} &\rightarrow (\mathcal{D}_{3/2} \otimes \mathcal{D}_1/12) \oplus (\mathcal{D}_{3/2} \otimes \mathcal{D}_0/4) \\ &\oplus 2(\mathcal{D}_{1/2} \otimes \mathcal{D}_1/6) \\ \mathcal{D}_{1/2} &\rightarrow 2/5(\mathcal{D}_{3/2} \otimes \mathcal{D}_1/12) \oplus 4/5(\mathcal{D}_{1/2} \otimes \mathcal{D}_1/6) \\ &\oplus 4/5(\mathcal{D}_{1/2} \otimes \mathcal{D}_0/2) \end{aligned}$$

These lead to the branching ratio matrix listed in Table 2B that are also given in [13] and [14].

The complete scrambling of protons considered for reaction (6) contains $5!/3!2! = 10$ cases of proton partitions containing one identity, three proton hops that

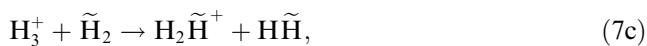
Table 2
Branching ratios of spin modifications in chemical reactions

A. (2,2) → (3,1) Ex. $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$							
Spin species	Weight	(3/2,1/2)	(1/2,1/2)				
(1,1)	9	6	3				
(1,0)	3	1	2				
(0,1)	3	1	2				
(0,0)	1	0	1				
B. (3,2) → (3,2) Ex. $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2$							
Spin species	Weight	(3/2,1)	(3/2,0)	(1/2,1)	(1/2,0)		
(3/2,1)	12	37/5	1	14/5	4/5		
(3/2,0)	4	1	1	2	0		
2(1/2,1)	12	14/5	2	28/5	8/5		
2(1/2,0)	4	4/5	0	8/5	8/5		
C. (3,3) → (4,2) Ex. $\text{H}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{H}_2$							
Spin species	Weight	(2,1)	(2,0)	(1,1)	(1,0)	(0,1)	(0,0)
(3/2,3/2)	16	25/3	1	23/5	1	2/3	2/5
2(3/2,1/2)	16	8/3	2	8	2	4/3	0
2(1/2,3/2)	16	8/3	2	8	2	4/3	0
4(1/2,1/2)	16	4/3	0	32/5	4	8/3	8/5
D. (4,3) → (5,2) Ex. $\text{CH}_4 + \text{H}_3^+ \rightarrow \text{CH}_5^+ + \text{H}_2$							
Spin species	Weight	(5/2,1)	(5/2,0)	(3/2,1)	(3/2,0)	(1/2,1)	(1/2,0)
(2,3/2)	20	65/7	1	40/7	8/7	15/7	5/7
2(2,1/2)	20	18/7	2	72/7	16/7	20/7	0
3(1,3/2)	36	27/7	3	120/7	24/7	45/7	15/7
6(1,1/2)	36	12/7	0	72/7	48/7	90/7	30/7
2(0,3/2)	8	4/7	0	16/7	16/7	20/7	0
4(0,1/2)	8	0	0	16/7	0	20/7	20/7
E. (4,4) → (5,3) Ex. $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$							
Spin species	Weight	(5/2,3/2)	(5/2,1/2)	(3/2,3/2)	(3/2,1/2)	(1/2,3/2)	(1/2,1/2)
(2,2)	25	145/14	5/2	40/7	20/7	25/14	25/14
3(2,1)	45	57/14	15/2	114/7	60/7	75/14	45/14
2(2,0)	10	1/2	1	2	4	5/2	0
3(1,2)	45	57/14	15/2	114/7	60/7	75/14	45/14
9(1,1)	81	45/14	9/2	108/7	180/7	225/14	225/14
6(1,0)	18	9/14	0	18/7	36/7	45/14	45/7
2(0,2)	10	1/2	1	2	4	5/2	0
6(0,1)	18	9/14	0	18/7	36/7	45/14	45/7
4(0,0)	4	0	0	8/7	0	0	20/7

are equivalent and six proton exchanges that are equivalent. They are expressed by



and



respectively, where $\tilde{\text{H}}$ represents protons that are originally in H_2 . The branching ratio matrix for identity (8a) is diagonal and is given by

$$\begin{pmatrix} 6/5 & 0 & 0 & 0 \\ 0 & 2/5 & 0 & 0 \\ 0 & 0 & 6/5 & 0 \\ 0 & 0 & 0 & 2/5 \end{pmatrix}, \quad (8a)$$

where the fractions are results of multiplying the probability of 1/10 to the identity matrix. The proton hop reaction (7b) is decomposed into a succession of reactions



i.e., (3) → (2, 1) and (1, 2) → (3).

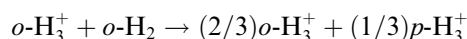
Using $\mathcal{D}_{3/2} \oplus 2\mathcal{D}_{1/2} \rightleftharpoons \mathcal{D}_{1/2}(\mathcal{D}_1 \oplus \mathcal{D}_0)$, the calculation is straightforward and we obtain the matrix for proton hop reactions as

$$\begin{pmatrix} 12/5 & 0 & 6/5 & 0 \\ 0 & 0 & 6/5 & 0 \\ 6/5 & 6/5 & 3/5 & 3/5 \\ 0 & 0 & 3/5 & 3/5 \end{pmatrix}. \quad (8b)$$

The branching ratio matrix for proton exchange reaction (7c) is obtained by subtracting (8a) and (8b) from the total matrix on Table 2B to be

$$\begin{pmatrix} 19/5 & 1 & 8/5 & 4/5 \\ 1 & 3/5 & 4/5 & 0 \\ 8/5 & 4/5 & 19/5 & 1 \\ 4/5 & 0 & 1 & 3/5 \end{pmatrix}. \quad (8c)$$

For many applications, the branching ratios of *ortho* and *para* H₂ are unimportant since H₂ is more abundant than H₃⁺ by many orders of magnitude (the ratio of the H₂ number density to the H₃⁺ number density is comparable or greater than 10⁶ both in laboratory and space plasmas). In this case we can add elements (3/2,1) and (3/2,0), and (1/2,1) and (1/2,0) in the same row of the branching ratio matrix. We thus have *ortho-para* branching ratios of H₃⁺



for both proton hop and proton exchange reactions, but $o\text{-H}_3^+ + p\text{-H}_2 \rightarrow p\text{-H}_3^+$, for proton hop reaction while $o\text{-H}_3^+ + p\text{-H}_2 \rightarrow (2/3)o\text{-H}_3^+ + (1/3)p\text{-H}_3^+$ for proton exchange reaction as listed in Table IV of [14]. Since the three proton hop reactions and the six proton exchange reactions are equivalent among themselves, the matrices (8b) and (8c) give nearly rigorous branching ratios of the elementary reactions. For analyzing experimental data, relative rates of the proton hop reaction and the proton exchange reaction should be multiplied to (8b) and (8c) to obtain the overall branching ratio matrix [14].

4. Extensions

The procedure given above can be readily extended to systems with larger numbers of protons if complete scrambling can be assumed. Results for (3,3) → (6)* → (4,2), for example, H₃⁺ + NH₃ → (NH₆⁺)* → NH₄⁺ + H₂, with a large exothermicity of 4.46 eV, (3,4) → (7)* → (5,2), for example, H₃⁺ + CH₄ → (CH₇⁺)* → CH₅⁺ + H₂, with an exothermicity of 1.33 eV and (4,4) → (8)* → (5,3), for example, CH₄⁺ + CH₄ → (C₂H₈⁺)* → CH₅⁺ + CH₃, with an exothermicity of 0.71 eV, are given in Table 2C–E. Elements of branching ratio matrices R_{ij} satisfy general sum rules

$$\sum_j R_{ij} = w_i, \quad \sum_i R_{ij} = [(2I_1 + 1)(2I_2 + 1)f_1 f_2],$$

$$\sum_{i,j} R_{ij} = \sum_i w_i = \sum_j [(2I_1 + 1)(2I_2 + 1)f_1 f_2]_j = 2^n, \quad (9)$$

where w_i represents the weight of combination i given in the table and $(2I + 1)$ and f represent the dimension and

the frequency, respectively, of \mathcal{D}_I in $(\mathcal{D}_{1/2})^n$ for combination $(I_1, I_2)_j$.

While we can enumerate branching ratios for systems of arbitrary numbers of protons following this procedure, such calculations may be academic for reactions involving a very large number of protons because the assumption of complete proton scrambling is not valid. Perhaps, the assumption is more valid for reactions with higher exothermicity. Separating those reactions into elementary reactions is more complicated than the case of Section 3.2.

Extension of this method for reactions with more than two product molecules is straightforward, although I cannot find a good example of such reactions. Extension of this method for nuclear species with spin higher than 1/2 is also straightforward.

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