

Unifying the rotational and permutation symmetry of nuclear spin states: Schur-Weyl duality in molecular physics

Hanno Schmiedt, Per Jensen', and Stephan Schlemmer

Citation: *J. Chem. Phys.* **145**, 074301 (2016); doi: 10.1063/1.4960956

View online: <http://dx.doi.org/10.1063/1.4960956>

View Table of Contents: <http://aip.scitation.org/toc/jcp/145/7>

Published by the [American Institute of Physics](#)

Unifying the rotational and permutation symmetry of nuclear spin states: Schur-Weyl duality in molecular physics

Hanno Schmiedt,¹ Per Jensen,^{2,a)} and Stephan Schlemmer¹

¹*I. Physikalisches Institut, Universität zu Köln, Zùlpicher StraÙe 77, 50937 Köln, Germany*

²*Physikalische und Theoretische Chemie, Fakultät für Mathematik und Naturwissenschaften, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany*

(Received 29 June 2016; accepted 2 August 2016; published online 15 August 2016)

In modern physics and chemistry concerned with many-body systems, one of the mainstays is identical-particle-permutation symmetry. In particular, both the intra-molecular dynamics of a single molecule and the inter-molecular dynamics associated, for example, with reactive molecular collisions are strongly affected by selection rules originating in nuclear-permutation symmetry operations being applied to the total internal wavefunctions, including nuclear spin, of the molecules involved. We propose here a general tool to determine coherently the permutation symmetry and the rotational symmetry (associated with the group of arbitrary rotations of the entire molecule in space) of molecular wavefunctions, in particular the nuclear-spin functions. Thus far, these two symmetries were believed to be mutually independent and it has even been argued that under certain circumstances, it is impossible to establish a one-to-one correspondence between them. However, using the Schur-Weyl duality theorem we show that the two types of symmetry are inherently coupled. In addition, we use the ingenious representation-theory technique of Young tableaux to represent the molecular nuclear-spin degrees of freedom in terms of well-defined mathematical objects. This simplifies the symmetry classification of the nuclear wavefunction even for large molecules. Also, the application to reactive collisions is very straightforward and provides a much simplified approach to obtaining selection rules. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4960956>]

Conventional molecular theory is based on the Born-Oppenheimer approximation, in which the full molecular dynamics can be treated in a two-step procedure: In the first step, the *ab initio* calculation, the electronic-motion Schrödinger problem is solved for a large number of fixed nuclear geometries and the effective Born-Oppenheimer potential energy function (PES) is obtained for the nuclei. In the second, subsequent step, the nuclear Schrödinger problem is solved with the nuclear motion being governed by the Born-Oppenheimer PES. The nuclear wavefunctions emerging in the second step describe the motion in space of the nuclei (i.e., the rotation and vibration) and the nuclear spin. In the present work, we make the common approximation of neglecting the exceedingly small nuclear-spin contribution to the energy (i.e., the *hyperfine* effects), and so the motional and nuclear-spin parts of the nuclear wavefunctions are independent. Analysis of the nuclear-spin wavefunctions is used, for example, to determine the motional states allowed by Fermi-Dirac or Bose-Einstein statistics, and it allows an initial description of the intensities for specific state-to-state transitions (cf., e.g., Ref. 1). This can be utilized for making the first, tentative assignments of experimental rovibrational spectra to obtain transition wavenumbers or frequencies, which are then fitted to yield values of effective rotation-vibration parameters. Moreover, spin statistics can be used to describe the kinetics of certain reactions, the primary example being reactions involving

hydrogen molecules where, for instance, the ortho-to-para conversion probability is determined by the rotation-vibration states occupied by the reaction partners and the intermediately formed complex.^{2–5} Such reactive collisions are currently of considerable astrophysical and chemical interest.

Following Longuet-Higgins,⁶ Quack² developed a method to determine symmetry selection rules for reactive collisions, considering in particular the identical-nuclei-permutation symmetry of the reactant molecules. Some thirty years later, Oka³ (see also Park and Light⁷) proposed a competing method with the selection rules derived in an approach making use of the angular momentum algebra of the nuclear spins. The two methods were applied to a number of cases with protons (spin $I = 1/2$) and, despite their fundamental conceptual differences, they produced the same results. Subsequently, the example cases considered became the gold standard for symmetry selection rules in reactive collisions (see, e.g., Refs. 4, 5, 8, and 9). It was realized a few years ago,¹⁰ however, that the one-to-one correspondence of the two methods breaks down in certain situations, where the identical nuclei considered in at least one reactant have a spin $I > 1/2$.

We show here that by using the mathematical concept of Schur-Weyl duality, we can combine the two approaches in a rather natural manner. The combined theory solves the problems encountered in Ref. 10. We will develop the new method step by step and apply it to example molecules of fundamental importance. Application to reactive collisions turns out to be straightforward and there are other potential applications which we discuss below. The simplicity—and

^{a)}Electronic mail: jensen@uni-wuppertal.de

the mathematical correctness—of the new method renders it a highly useful tool for determining the symmetry of nuclear spin wavefunctions for arbitrary molecules. In particular, the method is favorable for molecules that are very large and/or contain nuclei with spins $I > 1/2$.

To start, we recall the most natural way to find the nuclear spin functions and their symmetries for a given molecule (or molecular complex): Consider a system consisting only of N identical nuclei, each with spin I . With this information, one can set up all possible spin configurations of the N nuclei by hand; the total spin is given by the sum of the individual spin vectors. For N identical nuclei, any permutation is a symmetry operation,¹ and we can determine the behavior of the spin functions under these operations. This procedure is conventionally formulated in terms of the irreducible representations of the respective permutation group of the N identical particles: the symmetric group S_N (see, e.g., Ref. 1, where this group is called “the complete nuclear permutation group” for N identical nuclei).

For example, in the hydrogen molecule H_2 one finds four different nuclear spin states: $\uparrow\uparrow$, $\downarrow\downarrow$ and the antisymmetric/symmetric configurations $\uparrow\downarrow \mp \downarrow\uparrow$. The permutational symmetry in S_2 as well as the total spin I and component M_I ¹¹ are then simple to determine (Table I).

The table suggests a possible separation of the nuclear spin functions into two sets. Three of the four possible spin states share the same total spin of $I_{\text{tot}} = 1$ and the same total (A) symmetry under the nuclear permutation (12).¹ The fourth configuration has $I_{\text{tot}} = 0$ and is antisymmetric (B) under (12). Thus, there is a one-to-one correlation between the total spin and the permutation symmetry.

As the number of identical nuclei grows and the spin I of an individual nucleus increases to 1, $3/2$, ..., it is obvious that the pedestrian method described above becomes impracticable. Nevertheless, Quack² used this method to determine symmetry selection rules for reactive collisions with certain combinations of the molecular symmetry groups¹ (which describes the permutation symmetry) for reactants and products, respectively.

As mentioned above, Oka³ took an alternative approach to the problem of determining selection rules for reactive collisions. His method is based exclusively on the spin angular momenta and their rotational symmetries. Thus, the nuclear-spin functions for a given value of the total spin I_{tot} span an irreducible representation of the 3D rotation group called $K(\text{spatial})$ in Ref. 1 (see, explicitly, Sections 4.2 and 7.3.2 in Ref. 1). In the mathematical literature, this group is

commonly known as $SO(3)$, the special orthogonal group in three dimensions, and we will use this notation from now on.¹² The irreducible representations are usually labeled by $\mathcal{D}_{I_{\text{tot}}}$, where \mathcal{D} represents the Wigner-D-matrices. The main idea in Ref. 3 is based on the “almighty formula for addition of angular momentum,”³ where the product of two such representations is expressed as a direct sum of them (cf. Eqs. (7-44) of Ref. 1):

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

Using this rule recursively, one obtains the irreducible representations spanned by all possible spin states of a given molecule, consisting of N identical spin- I particles. Returning to the example of H_2 , the above rule gives $\mathcal{D}_{1/2} \otimes \mathcal{D}_{1/2} = \mathcal{D}_1 \oplus \mathcal{D}_0$ and we retrieve the result found by coupling the spin angular momenta in the pedestrian way. Just as Quack² before him, Oka³ dealt with reactive collisions, but he determined all selection rules from Equation (1) and did not consider permutation symmetry at all. Nevertheless, in this manner he recovered, for the chosen examples involving protons, the same selection rules previously determined by Quack.

Hugo¹⁰ noticed that in certain deuterated molecules, for example D_3 (where a deuteron has a spin of $I = 1$), the possible nuclear-spin functions generate irreducible representations of the permutation group that are not in an immediately recognizable, one-to-one correlation with those obtained in the rotational group. From Equation (1), we obtain that the spin functions of three particles, each with unit spin, generate the reducible representation $\mathcal{D}_0 \oplus 3\mathcal{D}_1 \oplus 2\mathcal{D}_2 \oplus \mathcal{D}_3$ so that the total spin $I_{\text{tot}} = 0, 1, 2$, or 3, and there are three separate three-fold degenerate states with $I_{\text{tot}} = 1$ and two five-fold degenerate states with $I_{\text{tot}} = 2$. By applying permutation symmetry, we find that the same 27 functions span the representation¹ $10A_1 \oplus A_2 \oplus 8E$ of S_3 (where A_1 and A_2 are non-degenerate whereas E is doubly degenerate), and we cannot match this directly to the rotational symmetry. However, closer inspection shows that each three-fold degenerate set of $I_{\text{tot}} = 1$ functions spans $A_1 \oplus E$ of S_3 , and so the rotational symmetry $\mathcal{D}_0 \oplus 2\mathcal{D}_2 \oplus \mathcal{D}_3$ must correspond to the S_3 -symmetry $7A_1 \oplus A_2 \oplus 5E$. Thus by inspection we realize that each of the seven \mathcal{D}_3 -functions with $I_{\text{tot}} = 3$ has the S_3 -symmetry A_1 , the one $I_{\text{tot}} = 0$ function has A_2 symmetry, and the 2×5 functions with $I_{\text{tot}} = 2$ give rise to five function pairs, each pair having E symmetry. It is obvious that the symmetry determination becomes increasingly more difficult for increasing values of N and I . In studies of reactions, the increasing number of states with the same symmetries can cause ambiguities, rendering impossible the symmetry correlation between reactant and product states.

In the following, we present a new, in our opinion more elegant and—more importantly—correct method that combines the angular-momentum and the permutation-symmetry approaches in a unique fashion. The main concept employed is the Schur-Weyl duality theorem;^{13,14} it straightforwardly correlates permutation and rotational symmetry. As a tool, we use the Young diagrammatic technique (cf. Ref. 15 and for modern reviews, e.g., Ref. 16

TABLE I. Permutation symmetry and total nuclear spin quantum numbers I_{tot} and M_I of the hydrogen molecule. The respective partition labels $\{\lambda_1, \lambda_2\}$ of the unitary group $U(2)$ are given in the right-most column. These labels, together with the definition of $U(2)$, will be explained later on in the paper.

Configuration	S_2 -symmetry	I_{tot}	M_I	$\{\lambda_1, \lambda_2\}$
$\uparrow\uparrow$	A	1	1	$\{2, 0\}$
$\downarrow\downarrow$	A	1	-1	$\{2, 0\}$
$\uparrow\downarrow + \downarrow\uparrow$	A	1	0	$\{2, 0\}$
$\uparrow\downarrow - \downarrow\uparrow$	B	0	0	$\{1, 1\}$

and Sec. 9.4.5 of Ref. 1); it simplifies the representation-theory description of both permutation groups and rotational groups.

Towards explaining the new method we initially consider a system consisting of N identical spin-1/2 particles taken to be nuclei here. We focus on the nuclear spin-dependent part of the total molecular Hamiltonian and we consider the individual nuclear spins to be independent both from the other spins and all other molecular degrees of freedom. Therefore the total nuclear spin Hamiltonian can be written as a sum of individual spin Hamiltonians. The eigenfunctions of each of these single-spin Hamiltonians span certain Hilbert space, \mathcal{H}_d say. The dimension d of the Hilbert space (for spin-1/2 nuclei $d = 2$) is defined by the number of possible spin configurations (here up and down) and in addition, the symmetry group of a single nuclear spin Hamiltonian is the unitary group $U(d)$. It includes all unitary transformations of a d -state system, which in this case is the most general symmetry group. These unitary transformations leave the spin I unchanged, while they possibly scramble the $2I + 1$ distinct M_I -states. The energy is taken to be independent of the nuclear spin and so all M_I -states are degenerate. Since the $U(d)$ group is very general, it includes, as a subgroup, the group $SO(3)$ of “usual” rotations in 3D space.

Considering now the N nuclear spins together, the eigenfunctions in general span the product space

$$\mathcal{H}_d^N := \mathcal{H}_d \otimes \mathcal{H}_d \otimes \cdots \otimes \mathcal{H}_d \quad (N \text{ copies}). \quad (2)$$

For example, the H_2 nuclear spin states span the $\mathcal{H}_2 \otimes \mathcal{H}_2$ Hilbert space, where all possible functions are shown in the left column of Table I. However, the nuclei themselves can be labelled by $i = 1, \dots, N$ and, since they are indistinguishable, they are subject to the symmetry imposed by any permutation of these N nuclei.

The eigenstates of the Hamiltonian of any quantum mechanical system generate irreducible representations of the appropriate symmetry group.¹ In general, a single particle Hilbert space is said to *carry* the so-called standard representation of the $U(d)$ symmetry group. This representation has d dimensions and is spanned by the d spin eigenfunctions. In the N particle case, the Hilbert space \mathcal{H}_d^N therefore carries a tensor product of this standard representation of $U(d)$, and since the eigenstates are also subject to the permutation symmetry, they must span simultaneously an irreducible representation of S_N . For the H_2 example, the tensor product of these standard representations is given by the functions in the left column of Table I. Indeed, the tensor product representation is in general reducible in the $U(d)$ symmetry group. The mathematical literature (for example, Refs. 14 and 16) uses the term *dual representations* of $U(d) \times S_N$ for such simultaneous irreducible representations.

As explained in Section 9.4.5 of Ref. 1 and in standard representation-theory textbooks such as Ref. 16, any irreducible representation of the permutation group S_N can be labeled by $(\lambda_1, \lambda_2, \dots, \lambda_p)$, where $\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_p$. The integers $(\lambda_1, \lambda_2, \dots, \lambda_p)$ define a *partition* of N , i.e., one way of writing N as the sum of integers in that $\lambda_1 + \lambda_2 + \dots + \lambda_p = N$. The partitions, and hence the irreducible representations, are represented graphically by the so-called Young diagrams and

the basis functions generating them by the so-called Young tableaux.

Any irreducible representation is represented by a Young diagram of p rows, the j th row having λ_j columns. To explain the Young diagrams and tableaux briefly, we use the S_5 symmetry group as an example for the labeling of irreducible representation in S_N . The irreducible representations and the character table of S_5 can be found in Table 9-1 of Ref. 1.

For example, the $(3, 2)$ irreducible representation of S_5 is represented by the Young diagram



In molecular theory,¹ this irreducible representation is customarily called H_1 . All the irreducible representations customarily used in connection with molecular symmetry groups¹ are “translatable” to Young tableaux since they originate in permutation groups. In particular, the molecular symmetry group is a subgroup of the complete nuclear permutation inversion group of the molecule, where potential energy barriers determine the feasible elements.⁶ Nuclear spin states are not influenced by the inversion operation E^* , so that only the pure permutations in the molecular symmetry group have to be considered. Indeed, the permutations form a subgroup of the complete nuclear permutation group, which is either the symmetric group of order N , if there are N identical nuclei, or a product of symmetric groups, if the molecule consists of distinct nuclei. In the following, we focus on the case where N identical nuclei build the molecule and no potential energy is restricting their permutations, so that the full S_N is the appropriate symmetry group. However, any subgroup is again (isomorphic to) a symmetric group or a product of symmetric groups, so that our arguments are fully valid also for more restricted molecular symmetry groups. In determining the molecular symmetry group appropriate for describing a chemical reaction, we must consider all molecules (reactants, products, and intermediates) involved as corresponding to different minima on one potential energy surface, and operations in the complete nuclear permutation-inversion group¹ that interconvert any of these minima must be considered feasible according to the principles discussed in Chapter 3 of Ref. 1. The resulting molecular symmetry group will normally be larger than the molecular symmetry groups of the individual molecules since it contains these as subgroups. However, depending on the details of the reaction mechanism, we may obtain a molecular symmetry group smaller than the complete nuclear permutation-inversion group and this would simplify the symmetry description of the reaction. The molecular symmetry group is the smallest group that provides an adequate symmetry labeling of all molecular states of interest and, as mentioned above, for labeling the spin states it is sufficient to employ the *permutation subgroup*¹ of the molecular symmetry group.

The translation of irreducible representations into Young tableaux is most easily determined by noticing that a Young diagram of a certain shape defines a set of functions characterized by so-called *standard* Young tableaux. In these, the boxes are labeled by the particle number $1, \dots, N$ strictly

increasing from left to right and from top to bottom. The number of different possible labeling schemes is then equivalent to the dimension of the respective irreducible representation, giving a first hint for the translation. For more details, we refer to Section 9.4.5 of Ref. 1. For example, the $(3,2)$, or H_1 , irreducible representation of S_5 is generated by five functions labeled as

$$\begin{array}{|c|c|c|} \hline 1 & 2 & 3 \\ \hline 4 & 5 & \\ \hline \end{array}, \begin{array}{|c|c|c|} \hline 1 & 2 & 5 \\ \hline 3 & 4 & \\ \hline \end{array}, \begin{array}{|c|c|c|} \hline 1 & 3 & 5 \\ \hline 2 & 4 & \\ \hline \end{array}, \begin{array}{|c|c|c|} \hline 1 & 3 & 4 \\ \hline 2 & 5 & \\ \hline \end{array}, \begin{array}{|c|c|c|} \hline 1 & 2 & 4 \\ \hline 3 & 5 & \\ \hline \end{array}.$$

By contrast, the other five-dimensional irreducible representation, H_2 , is generated by

$$\begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & 4 \\ \hline 5 & \\ \hline \end{array}, \begin{array}{|c|c|} \hline 1 & 2 \\ \hline 3 & 5 \\ \hline 4 & \\ \hline \end{array}, \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & 4 \\ \hline 5 & \\ \hline \end{array}, \begin{array}{|c|c|} \hline 1 & 3 \\ \hline 2 & 5 \\ \hline 4 & \\ \hline \end{array}, \begin{array}{|c|c|} \hline 1 & 4 \\ \hline 2 & 5 \\ \hline 3 & \\ \hline \end{array}.$$

The irreducible representations of $U(2)$ can also be labeled by partitions and Young tableaux (see, for example, Ref. 17), where the partition λ now represents a generalized spin quantum number unambiguously defining the respective irreducible representation. Again, a tableau like $\{3,2\}$ of the example above is labeled by the quantum number of the single particle wavefunctions, i.e., the spin configurations $1 = \uparrow$ and $2 = \downarrow$. Although the numbered tableaux are constructed in a manner similar to that described above, the rule of increasing quantum numbers is not strictly observed for the rows of the diagrams. As a consequence, the $\{3,2\}$ irreducible representation is associated with the following numbered Young tableaux:

$$\begin{array}{|c|c|c|} \hline 1 & 1 & 1 \\ \hline 2 & 2 & \\ \hline \end{array}, \begin{array}{|c|c|c|} \hline 1 & 1 & 2 \\ \hline 2 & 2 & \\ \hline \end{array}$$

In a standard view of 3D rotational symmetry, these functions represent the two of $I_{\text{tot}} = 1/2$. This can be generalized to the branching rule of $U(2) \downarrow SO(3)$, where an irreducible representation $\{\lambda_1, \lambda_2\}$ of $U(2)$ always corresponds to the usual spin label $I_{\text{tot}} = (\lambda_1 - \lambda_2)/2$ (see, for example, Ref. 16) and hence the distinct numbering reflects the $2I_{\text{tot}} + 1$ projections on a certain molecule-fixed z -axis. To understand this branching in more detail, recall that under rotations in conventional 3D space, the spin functions of any particle transform as the \mathcal{D}_I representation of $SO(3)$ or $SO(3)^2$, where $SO(3)^2$ is the group called K^2 in Chapter 18 of Ref. 1 and I denotes the common spin label. Irrespective of 3D space, particles with certain spin are subjected—if no coupling to any other degree of freedom exists—to the symmetry group $U(d)$, where d denotes the number of possible spin configurations. In particular, complex “rotations” in more than two dimensions can occur and the eigenstates of the respective Hamiltonian span irreducible representations of $U(d)$. Still, to relate the common spin label (I) to these states, we have to determine their 3D-rotational symmetry, which is technically done by using the branching rules of $U(d) \downarrow SO(3)$.

Combining both symmetry groups as described by Equation (2) is done according to the Schur-Weyl duality theorem.^{13,14} It states exactly how one has to combine the irreducible representations of the two groups $U(d)$ and S_N to form an irreducible representation of the product group. A “joint” irreducible representation is shown to be a direct

product combining the same Young tableaux (same partitions), where the partition λ divides N into $p \leq d$ parts. More formally, the irreducible representation of the product group $\Gamma_d^{(N)}$ is given by

$$\Gamma_d^{(N)} = \bigoplus_{\lambda \vdash N}^{l(\lambda) \leq d} ((\lambda), \{\lambda\}), \quad (3)$$

where $\lambda \vdash N$ signals the partition λ of N and $l(\lambda) = p$ is the number of integers in the partition. The $U(2)$ irreducible representations are denoted by curly braces $\{\}$, whereas those of the permutation group are written with parentheses $(\)$. In our example of spin $1/2$, $d = 2$.

To understand the concept of Equation (3), we treat the hydrogen molecule in somewhat more detail. According to the Schur-Weyl theorem, the two following combinations of Young diagrams exist:

$$(\square\square, \square\square) \oplus \left(\begin{array}{|c|c|} \hline \square & \square \\ \hline \square & \square \\ \hline \end{array} \right).$$

Now by labeling the boxes according to the rules stated above, we obtain four possible combinations, each one representing one of the four functions of Table I:

$$\begin{aligned} (\square 1 \square, \square 1 \square) &\sim \uparrow\uparrow \\ (\square 1 \square, \square 2 \square) &\sim \downarrow\downarrow \\ (\square 1 \square, \square 1 2) &\sim \uparrow\downarrow \\ \left(\begin{array}{|c|c|} \hline \square & \square \\ \hline 2 & 2 \end{array} \right) &\sim \uparrow\downarrow - \downarrow\uparrow. \end{aligned}$$

Combining rows of Young diagrams gives rise to symmetric combinations for the particle i , labeled by 1, 2 in the S_N Young tableau, with spin $1 = \uparrow$ or $2 = \downarrow$, in the $U(2)$ diagram. Combination of two columns produces the determinantal combination, i.e., for two particles with spin $1/2$ the antisymmetric combination. With these numbered Young tableaux we also can infer the multiplicities of the respective irreducible representation in the two groups. There are three A functions combined each with one spin $1/2$ function and a single one of B symmetry combined with a $I = 0$ total spin function. Hence, in the combined picture the nuclear spin wavefunctions span the following representation in the $S_2 \times U(2)$ group:

$$(3A, \mathcal{D}_1) \oplus (B, \mathcal{D}_0).$$

For convenience, we include the multiplicity of the irreducible representations in the combined representation. This indicates that the dimension of the combined representation is equal to both, the symmetric and the unitary group part, i.e., $\dim(X, \mathcal{D}_I) = \dim X = \dim \mathcal{D}_I$.

This concept generalizes to larger spin quantum numbers and larger particle numbers.¹⁷ The generalization to larger particle numbers is very straightforward, while for spins other than $1/2$, we have to use the unitary groups in appropriate higher dimensions to account for the larger number of spin projections $d = 2I + 1$. In the Young tableaux, this produces a larger number of possible rows defined by $p \leq d$. Still, to find the commonly used total spin quantum number, we can use well-known branching rules of $U(d) \downarrow SO(3)$, which are as simple as the $U(2) \downarrow SO(3)$ rule stated above.^{16,17}

In conclusion, the Schur-Weyl duality theorem provides us with a general method for determining the “joint” symmetry of the nuclear-spin states in the spin-angular-momentum symmetry group (here $U(d)$), and the permutation group of the N identical particles S_N .

The Schur-Weyl duality theorem provides a rather formal description of the problems discussed here, and to understand better how to apply it to molecules, especially when these become more complex, we consider the H_5^+ cation as an example. The ion consists of five protons, each with spin $1/2$, and this is all the information we need to work through the program developed above. We have $N = 5$ and $d = 2$. Hence, all partitions divide 5 into at most $p = 2$ parts. The shapes of the possible Young tableaux are therefore $(5,0)$, $(4,1)$, and $(3,2)$, and the resulting $U(2)$ and S_5 irreducible representations are shown together with their commonly used labels in Table II.

As explained for H_2 , it is simple to determine the multiplicities of the $SO(3)$ or S_5 representations involved. The Young tableau of shape, e.g., $\{5,0\}$ in $U(2)$ describes six $I = 5/2$ functions labeled by the possible values of M_I . Now the Schur-Weyl duality theorem states that each of these six functions has A_1 permutational symmetry, so the multiplicity of the A_1 state has to be six. Conversely, for instance, the H_1 state is five-fold degenerate and each of these five functions has $I = 1/2$. Thus, the multiplicity of the $I = 1/2$ representation must be five. Simultaneously, the degeneracy of a single $1/2$ state is two and hence there must be two H_1 states. As a consequence, the degeneracy of the $SO(3)$ state determines the multiplicity of the S_5 state and vice versa,¹⁸

$$(6A_1, \mathcal{D}_{5/2}) \oplus (4G_1, 4\mathcal{D}_{3/2}) \oplus (2H_1, 5\mathcal{D}_{1/2}). \quad (4)$$

We have here an example of an application of the main result of the present work: We have established unambiguously the possible joint representations of $SO(3)$ and S_N , linked by the Schur-Weyl duality theorem.

The five-proton result of Equation (4) is well established; it has been determined in the pedestrian manner described above. For other, in particular deuterated, systems such as D_5 the pedestrian approach becomes more involved. Even more so, as pointed out in Ref. 10 and mentioned above, there are certain ambiguities of total spin and permutation symmetry. Since the Schur-Weyl duality stipulates an exact correspondence, this problem disappears here. Deuterons carry a spin of 1, and so there are three possible spin configurations ($M_I = +1, 0, -1$) and the single-particle

TABLE II. Irreducible representations spanned by the eigenfunctions of the nuclear spin Hamiltonian for five identical protons. The Young diagrams in the left-most column are visualizations of the irreducible representations in the respective row.

Young diagram	$U(2)$	$SO(3)$	S_5	Label
	$\{5,0\}$	$5/2$	$(5,0)$	A_1
	$\{4,1\}$	$3/2$	$(4,1)$	G_1
	$\{3,2\}$	$1/2$	$(3,2)$	H_1

symmetry group has to be $U(3)$. The appropriate Young diagrams now have at most three rows and this affects the possible numbering schemes. However, usage of Equation (3) is still straightforward and we find the Young tableaux and correlated labels of S_5 and $U(3)$ as indicated in Table III. In the spin-1 deuteron case, we have to use the branching rule from $U(3)$ to $SO(3)$ to correlate the common spin labels. We now identify more than a single spin quantum number to one permutation symmetry. For instance, the A_1 permutation symmetry is correlated to spin $I_{\text{tot}} = 1, 3, 5$. Conversely, from the spin point of view the $I_{\text{tot}} = 1$ spans $3(A_1 \oplus G_1 \oplus H_1 \oplus H_2)$ in the permutation symmetry group.

We have now identified the reason for the ambiguity found in Ref. 10: The one-to-one correspondence is lost by correlation from the (larger) $U(3)$ symmetry group to $SO(3)$. Still, the Schur-Weyl duality theorem provides useful information now: we know the correlated spin species that are, in a sense, collected in one S_5 species and one $U(3)$ irreducible representation. As discussed above, one obvious application of angular-momentum-rotation/permutation symmetry is the derivation of selection rules in reactive collisions. For example, the famous $H_3^+ + H_2 \rightarrow (H_5^+)^* \rightarrow H_3^+ + H_2$ reaction is of much interest since it is thought to be the major mechanism for the thermalization procedure of hydrogen in interstellar molecular clouds. It is a primary example of a chemical reaction with identical reactants and products in which the spin species can change owing to the formation of the intermediate H_5^+ complex. With the use of Schur-Weyl duality, the symmetries of the product states are straightforwardly determined in the permutation symmetry group as well as in terms of spin angular momentum. With the enlargement to the $U(3)$ group for deuterated species, also reactions involving spin 1 particles are treatable in a very general manner. Even more astonishing, the use of Young tableaux makes it possible to multiply graphically the irreducible representations of the reactants, since rules exist as to how to construct the resulting Young tableaux.¹⁷

We find that the Schur-Weyl duality theorem, which is a rather formal mathematical result, can be used to define unambiguously the possible combinations of spin-angular-momentum states and permutation-symmetry states for any molecule consisting of N identical particles having general

TABLE III. Irreducible representations spanned by the eigenfunctions of the nuclear-spin Hamiltonian for five identical deuterons. The $SO(3)$ labels represent the usual angular momentum quantum numbers.

Young diagram	$U(3)$	$SO(3)$	S_5	Label
	$\{5,0,0\}$	$5,3,1$	$(5,0)$	A_1
	$\{4,1,0\}$	$4,3,2,1$	$(4,1)$	G_1
	$\{3,2,0\}$	$3,2,1$	$(3,2)$	H_1
	$\{3,1,1\}$	$2,0$	$(3,1^2)$	I
	$\{2,2,1\}$	1	$(2^2,1)$	H_2

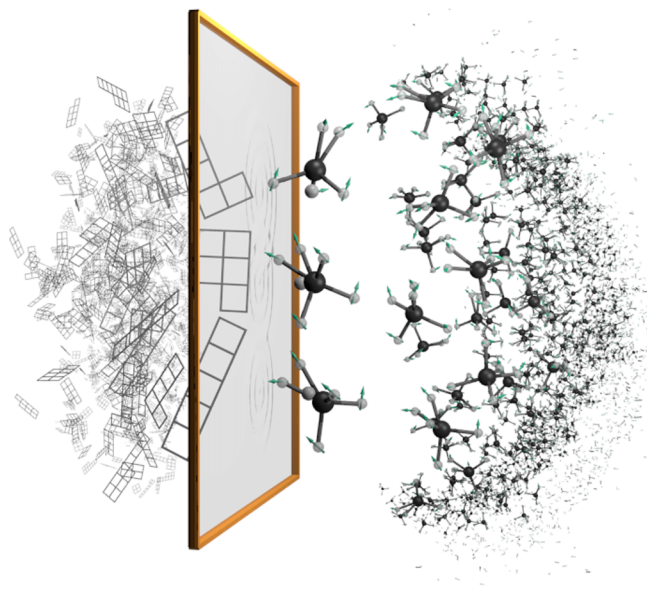


FIG. 1. Depiction of the nuclear spin degrees of freedom in molecules (right) being “mirrored” by the Young tableaux of representation theory (left). Each spin configuration unambiguously corresponds to a specific Young tableau, which can be used to describe mathematically the one-to-one correspondence of the nuclear-spin permutational and rotational symmetry.

(individual) spin degrees of freedom (Fig. 1). In conjunction with Young tableaux, the Schur-Weyl duality theorem is easy to use. It facilitates the application of Fermi-Dirac and Bose-Einstein statistics to the states of large molecules and/or molecules containing nuclei with large spin multiplicities. We expect it to be extremely useful in the treatment of reactions, where complexes are formed, since the (now) inherent correlation of spin and permutation symmetry of the reactants simplifies also that of the product states.

We realize that the nuclear spin states are reflected by their symmetry in the unitary group, which is expressed by Young tableaux, and use the Schur-Weyl theorem to show that the nuclear spin symmetry is inherently correlated to the permutation symmetry. This allows us to understand the close connection between the approaches of Quack² and Oka³ for determining selection rules in reactive collisions. Thus far, the two approaches were viewed as being distinct but the

Schur-Weyl duality theorem shows that they are, in fact, two formulations of the same underlying physics.

We thank Christoph Konietzko and Stefan Brackertz for critical discussion of the manuscript. The work of S.S. and H.S. is supported by Deutsche Forschungsgemeinschaft via the Collaborative Research Centre 956, sub project B3, and Grant No. SCHL 341/6-2. H.S. also thanks the Bonn-Cologne-Graduate School of Physics and Astronomy (BCGS) for support. The work of P.J. is supported in part by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

¹P. R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy*, 2nd ed. (NRC Research Press, 2006).

²M. Quack, *Mol. Phys.* **34**, 477 (1977).

³T. Oka, *J. Mol. Spectrosc.* **228**, 635 (2004).

⁴E. Hugo, O. Asvany, and S. Schlemmer, *J. Chem. Phys.* **130**, 164302 (2009).

⁵T. P. Grozdanov and R. McCarroll, *J. Phys. Chem. A* **116**, 4569 (2012).

⁶H. Longuet-Higgins, *Mol. Phys.* **6**, 445 (1963).

⁷K. Park and J. C. Light, *J. Chem. Phys.* **127**, 224101 (2007).

⁸S. Gómez-Carrasco, L. González-Sánchez, A. Aguado, C. Sanz-Sanz, A. Zanchet, and O. Roncero, *J. Chem. Phys.* **137**, 094303 (2012).

⁹O. Sipilä, J. Harju, P. Caselli, and S. Schlemmer, *Astron. Astrophys.* **581**, A122 (2015).

¹⁰E. Hugo, “The $\text{H}_3^+ + \text{H}_2$ isotopic system origin of deuterium astrochemistry,” Ph.D. thesis, Universität zu Köln, 2008.

¹¹The M_I quantum number is defined as the projection onto the z axis giving $2I + 1$ possible projections for certain I .

¹²H. Schmiedt, S. Schlemmer, and P. Jensen, *J. Chem. Phys.* **143**, 154302 (2015).

¹³I. Schur, “Ueber eine Klasse von Matrizen, die sich einer gegebenen Matrix zuordnen lassen,” Ph.D. thesis, Friedrichs-Wilhelms-Universität zu Berlin, 1901.

¹⁴H. Weyl, *The Classical Groups: Their Invariants and Representations*, Princeton Mathematical Series, 2nd ed. (Princeton University Press, Princeton, NJ, 1946), Vol. 1.

¹⁵A. Young, *The Collected Papers of Alfred Young: 1873–1940*, Mathematical Expositions (University of Toronto Press, Toronto [u.a.], 1977), Vol. 21.

¹⁶W. Fulton and J. Harris, *Representation Theory: A First Course*, Graduate Texts in Mathematics, 9th ed. (Springer Science + Business Media, New York, NY, 2004), Vol. 129.

¹⁷A pedagogical review for several different Young tableaux and for the Schur-Weyl duality theorem in general is given in, D. J. Rowe and J. L. Wood, *Foundational Models, Fundamentals of Nuclear Models* (World Scientific, Singapore [u.a.], 2010).

¹⁸Alternatively, one can work this out by determining the numbered Young diagrams as shown for H_2 .