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Testing the symmetrization postulate on molecules with three identical nuclei

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We propose an experiment to look for possible small violations of the symmetrization postulate of quantum mechanics, in systems composed of three identical particles. Such violations could be detected by investigating the population of particular rotovibrational states of symmetrical molecules containing three identical nuclei. We discuss the symmetry properties of such states, and the implications of the symmetrization postulate and the spin statistics connection. A high-sensitivity spectroscopic investigation of simple molecules such as SO_3, BH_3, and NH_3 could lead, to our knowledge, to *the first test of the symmetrization postulate* for spin-0 and spin-1/2 nuclei.

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I. INTRODUCTION

In recent years, the possibility of small violations of the symmetrization postulate (SP) and of the spin-statistics connection has been addressed from both experimental and theoretical points of view. The SP is at the basis of a quantum-mechanical description of systems composed of identical particles, asserting that only wave functions that are completely symmetric or antisymmetric in the permutation of the particles labels can describe physical states. In principle there would be no arguments against the existence of states with different symmetries, although they lack some of the properties which are peculiar to completely symmetric and antisymmetric states. The only strict requirement that can be derived in a formal way in quantum mechanics is the so-called *superselection rule*, which forbids transitions between different symmetry classes.

In addition, experimental observation so far seems to indicate a well-defined connection between the spin of the particles and the symmetry properties: half-integer spin particles can be described only by antisymmetric wave functions, and integer-spin particles by symmetric wave functions only. According to their behavior in a statistical ensemble, the two kinds of particles are indicated as fermions and bosons, respectively.

Although both the SP and the spin-statistics connection seem to hold in the physical world, there is great interest in investigating possible very small violations, not detected to date. In the case of two-particles systems, only symmetrical and antisymmetrical states can be defined, and therefore the SP is redundant. As a matter of fact, the experimental tests of symmetry reported so far have been limited to the investigation of states containing only two identical particles, looking for violations of the usual connection between spin and statistics. In particular the latest high-sensitivity experiments of this kind have been performed on both fermionic systems, namely electrons, and bosonic systems, such as photons and oxygen nuclei. In the case of electrons, the existence of totally symmetric states in the spectrum of atomic helium has been sought [1], and the negative result of such an investigation has led to the establishment of a bound to the degree of violation of the spin statistics, i.e., to the presence of exchange-symmetric electrons. A different experiment was performed on a metallic Cu sample [2], looking for the presence of any electrons in the conduction band, with no symmetry requirements with respect to electrons in the already filled shells. This can be considered a one-particle test of the identity of the electrons, which is even a more general property of the particles, but not a test of their symmetry. Results which are conceptually identical to the first case have been obtained for bosonic particles, by searching for an exchange-antisymmetric two-photon transition in atomic barium [3], and for rotational states in molecular oxygen [4–6] and carbon dioxide [7] which are antisymmetrical in the exchange of O nuclei. The principle of all these experiments was to look for particular atomic or molecular transitions, whose probability would be zero according to the usual spin statistics, by using high sensitivity spectroscopic detection techniques. The extrapolated bounds on the relative weight of the wrong statistics are almost at the level of 10^{-9} [7]. Reviews of different experiments which have been proposed, and interpretations of the results of various measurements as tests of the statistics, can be found in Refs. [8–10].

Theoretical studies of possible violations of the usual symmetry properties have focused on systems composed of a nonfixed number of particles, which can be treated within the quantum-field theory formalism. In such a context the spin-statistics connection is no longer a postulate dictated by experimental observation, but can be rigorously proved through the spin-statistics theorem [11,12], the main assumption being the validity of the SP. Several theories allowing for small violations of such a postulate have been proposed [13], and one of the most successful is based on the *q*-mutator algebra [14], in which deformed bilinear commutation relations are used in place of the ordinary ones. In this way it is possible to define exotic symmetries as a smooth interpolation between symmetric and antisymmetric ones, or statistics interpolating between the Bose and Fermi cases. By assuming the validity of this algebra it has also been possible to translate the bound on the spin statistics for oxygen nuclei [7] into a bound on the statistics of the nucleons composing the nuclei [15] or, more generally, to establish a relationship between constraints on different kinds of particles [16].

To summarize, so far experiments have been devoted to

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search for possible violations of the spin statistics in simple systems, while theories allowing for violations of the more fundamental SP focused on much more complex systems, which cannot be easily investigated experimentally. We note that no rigorous theoretical study of a simple quantum-mechanical system allowing for violations of the SP has been reported so far, although possible experiments on multiparticle molecular systems have been indicated [4,10].

In this paper we propose an experiment to be performed on molecular systems containing three identical nuclei, to search for possible violations of the SP in a system described within quantum-mechanical theory. For this purpose, in Sec. II we briefly recall the concept of the identity of particles, and the permutation properties of identical particles; we also recall that at least three particles are needed to define symmetries different from the usual ones. Then, in Sec. III, we discuss the properties of particular rotational states of symmetrical plane molecules with three spin-0 nuclei, which are forbidden by the SP, and with three spin-1/2 nuclei, which are forbidden by both the spin-statistics connection and the SP. We show that, nevertheless, such states have the proper symmetry to be defined consistently in a more general quantum-mechanical theory which does not include the SP. In Sec. IV we briefly discuss how to test the possible small symmetry violations. Finally, in Sec. V, we propose a high-sensitivity spectroscopic investigation to be performed on selected transitions of the SO_3 molecule, and of BH_3 and NH_3 molecules, which best represent the prototypal molecule respectively for the spin-0 and spin-1/2 cases treated above. In the latter case, such states could be investigated in a search for small violations of the statistics or of the symmetry of protons.

II. INDISTINGUISHABILITY OF IDENTICAL PARTICLES AND THE SYMMETRIZATION POSTULATE

A. General discussion

The indistinguishability of identical particles is one of the principles lying at the basis of quantum mechanics. It states that, given a system of particles belonging to the same species (i.e., which have the same physical properties, like mass, charge, spin, etc.), a permutation of such particles cannot affect any of the quantum observables of the system [17]. To discuss the implications of such a principle, here we briefly recall some properties of a system containing N identical particles (for a general discussion see, for example, Refs. [17–19]).

To each observable of the system we associate a Hermitian operator $\hat{A}$, which can be written as

$$\hat{A}=A(\{\hat{O}_1\},\ldots,\{\hat{O}_N\})\equiv\hat{A}(1,\ldots,N), \tag{2.1}$$

where $\{\hat{O}_j\}$ is a set of single-particle observables. In the same way, the vector

$$|1,2,\ldots,N\rangle \tag{2.2}$$

represents a state where the first particle is characterized by a set of quantum numbers $\{1\}$, the second by $\{2\}$, and so on. Moreover we can define the permutation operators as

$$\hat{P}_{j_1,j_2,\ldots,j_N}f(1,2,\ldots,N)=f(j_1,j_2,\ldots,j_N) \tag{2.3}$$

and these operators form the *symmetrization group* S_n. Therefore, since a permutation of identical particles cannot affect any quantum observable, all observables must be permutation invariant,

$$[\hat{P},\hat{A}]=0, \tag{2.4}$$

and, since the evolution operator $\hat{U}(t)$ is related to the Hamiltonian of system $\hat{H}$, which is a physical observable, the above condition is fulfilled at any instant of time

$$[\hat{P},\hat{H}]=0\Rightarrow[\hat{P},\hat{U}(t)]=0. \tag{2.5}$$

An important consequence of these relations is that the Hilbert space $\mathcal{H}$ can be written as a direct sum of hortogonal subspaces, each one invariant under the permutation group, the hortogonality being preserved along the evolution of the system, and following a physical measurement. This result can be stated as a *superselection rule* which forbids transitions between states transforming under inequivalent representations of the permutation group.

To investigate in detail the symmetry properties of a generic state of the system under permutation, it is convenient to introduce the operator of a *cyclic permutation*,

$$\hat{P}_{(k_1,k_2,\ldots,k_K)}f(k_1,k_2,\ldots,k_K)=f(k_2,\ldots,k_K,k_1), \tag{2.6}$$

and the exchange operators of two particles, $\hat{P}_{(j,k)}$ (they are a particular case of the former), which are Hermitian and unitary, with an eigenvalues $\epsilon_{j,k}=\pm1$.

Each generic permutation can be written either as the product of exchange between two particles, or of cyclic permutation of distinct elements, in the form

$$\hat{P}_{cyclic}\equiv\hat{P}_{(k_1,\ldots,k_p)(k_{p+1},\ldots,k_{p+q})(k_{p+q+1},\ldots,k_{p+q+r})\ldots}, \tag{2.7}$$

with the only condition that the sum of each cycle length must be equal to N:

$$p+q+r+\cdots=N \tag{2.8}$$

(here we adopt the convention $p\geqslant q\geqslant r\geqslant\cdots$). The properties of transformation of such operators under permutation do not change the length of the cycles, and therefore all the cyclic permutation with the same values of $p,q,r,\ldots$ are said to form a *class*. Obviously there are as many classes as there are possible decompositions of N as a sum of integer numbers.

From the properties of the exchange operators $\hat{P}_{(j,k)}$, it follows that the permutation operators admit only two common eigenstates, with the eigenvalues $\epsilon_{j,k}$ all equal to 1 or -1. In fact, the eigenvalue equation for the exchange operators $\hat{P}_{(j,k)}$ is ($\epsilon_{j,k}=\pm 1$)

$$\hat{P}_{(j,k)}f(1,2,\ldots,N)=\epsilon_{j,k}f(1,2,\ldots,N); \qquad (2.9)$$

then, from the relation

$$\hat{P}_{(j,k)}=\hat{P}_{(2,k)}\hat{P}_{(1,j)}\hat{P}_{(1,2)}\hat{P}_{(2,k)}\hat{P}_{(1,j)}, \qquad (2.10)$$

it follows that

$$\epsilon_{j,k}=\epsilon_{1,2}\epsilon_{2,k}^{2}\epsilon_{1,j}^{2}=\epsilon_{1,2}. \qquad (2.11)$$

These eigenvalues $\epsilon_{j,k}=\pm 1$ correspond to vectors of state completely symmetric or antisymmetric under the exchange of two particles, respectively, and we indicate the subspaces spanned by these vectors by $\mathcal{H}_{+}$ and $\mathcal{H}_{-}$, respectively. For $N=2$ the Hilbert space can be decomposed exactly as $\mathcal{H}=\mathcal{H}_{+}\oplus\mathcal{H}_{-}$, i.e., only symmetric or antisymmetric states are possible. For $N>2$ this is no longer true, and we have

$$\mathcal{H}=\mathcal{H}_{+}\oplus\mathcal{H}_{-}\oplus\mathcal{H}_{1}'\oplus\mathcal{H}_{2}'\oplus\cdots, \qquad (2.12)$$

where $\mathcal{H}_{j}'$ are permutation-invariant subspaces. Contrary to $\mathcal{H}_{+}$ and $\mathcal{H}_{-}$, which have a definite symmetry and are a one-dimensional representation of the permutation group (for a given set of quantum numbers $\{1,2,\ldots,N\}$, there exists only one possible combination which gives symmetric or antisymmetric states), the subspaces $\mathcal{H}_{j}'$ do not possess a definite symmetry and have a dimension greater than 1. This is the reason why one usually assumes the *symmetrization postulate* (SP), requiring physical states to be either symmetric or antisymmetric. Nevertheless, there is no stringent reason to exclude *a priori* the possibility of physical states not obeying the SP, since their presence does not violate any basic principle of quantum mechanics. The only difference that one has to take into account is the lack of a correspondence between physical states and vectors (modulo a phase factor), since the subspaces $\mathcal{H}_{j}'$ have a dimension greater than 1 and do not admit a complete set of mutually commutating physical observables. In fact, let us imagine to a common eigenvector $|u\rangle$ of a complete set of operators $\{O_i\}$ in $\mathcal{H}_{j}'$. Since $|u\rangle$ cannot be an eigenvector of all the permutation operators, there must exist some permutation such that $\hat{P}_{j_1,j_2,\ldots,j_N}|u\rangle$ is linearly independent of $|u\rangle$, and, therefore, $\mathcal{H}_{j}'$ must have dimension greater than 1, and the set of operators $\{O_i\}$ cannot be complete (i.e., the state of the system is not completely determined by the set of eigenvalues $\{o_i\}$). In the following we work out in more detail the permutation properties for the special case $n=3$ [20].

B. A system of three identical particles

The symmetrization group S_3 is a non-Abelian group of order 6, formed by the 3! cyclic permutations of the labels (1,2,3), which belong to three distinct classes

$$P_{(1)(2)(3)}=I, \qquad (2.13)$$

$$P_{(2,3)}, \quad P_{(1,3)}, \quad P_{(1,2)}, \qquad (2.14)$$

$$P_{(1,2,3)}, \quad P_{(3,2,1)}. \qquad (2.15)$$

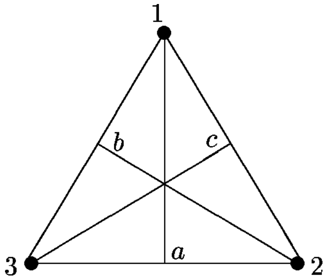

FIG. 1. The symmetry operation on this triangular configuration form the *dihedral group* D_3, and are (i) the identity transformation; (ii) the reflection about the axes *a*, *b*, and *c*, and (iii) the rotation around the center by angles $2\pi/3$ and $-2\pi/3$.

This group is isomorphic to the *dihedral group* D_3, generated by the symmetry transformation shown in Fig. 1. In fact, reflection about each axis (a,b,c) is equivalent to a two-label permutation $P_{(i,j)}$, while rotations around the center by angles $2\pi/3$ and $-2\pi/3$ lead to a cyclic permutation of all the three labels. The visualization of group S_3 by its association to the geometrical symmetries of D_3 is very helpful, since it is indeed this realization on a physical system (a molecule in our case) that we are looking for.

The permutation operators can be written explicitly in a matrix form, on the basis formed by the 3! permutations of the vector $|1,2,3\rangle$. For example, by defining

$$|1,2,3\rangle\equiv|1\rangle, \qquad (2.16)$$

$$|1,3,2\rangle\equiv|2\rangle, \qquad (2.17)$$

$$|2,1,3\rangle\equiv|3\rangle, \qquad (2.18)$$

$$|2,3,1\rangle\equiv|4\rangle, \qquad (2.19)$$

$$|3,1,2\rangle\equiv|5\rangle, \qquad (2.20)$$

$$|3,2,1\rangle\equiv|6\rangle, \qquad (2.21)$$

we obtain

$$P_{(1,2,3)}=\begin{pmatrix} 0&0&0&0&1&0\\ 0&0&1&0&0&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&0&0&1&0&0\\ 0&1&0&0&0&0 \end{pmatrix}, \qquad (2.22)$$

and

$$P_{(3,2,1)} = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}. \tag{2.23}$$

This matrix representation of group S_3 can be reduced, since it must contain a number of irreducible representations equal to the number n_c of distinct classes ($n_c = 3$). Moreover, since this is the so-called *regular representation*, each irreducible representation must appear a number of times equal to its dimensionality. From general results [20], we know that these representations are the symmetric and antisymmetric ones (which are one-dimensional), and that there must also be a two-dimensional representation occurring two times. A formal way to systematically reduce the regular representation of S_n into its irreducible components would be by using *Young diagrams* [20]. Here we work out the S_3 case with more heuristic arguments, as follows.

First of all, we can define the operators S and A, which are the projectors on the subspaces $\mathcal{H}_+$ and $\mathcal{H}_-$, respectively:

$$S = [I + P_{2,3} + P_{1,3} + P_{1,2} + P_{1,2,3} + P_{3,2,1}]/6, \tag{2.24}$$

$$A = [I - P_{2,3} - P_{1,3} - P_{1,2} + P_{1,2,3} + P_{3,2,1}]/6. \tag{2.25}$$

Each of them therefore has only one eigenvector associated with a nonzero eigenvalue, which are

$$|s\rangle \equiv [|1\rangle + |2\rangle + |3\rangle + |4\rangle + |5\rangle + |6\rangle]/\sqrt{6}, \tag{2.26}$$

$$|a\rangle \equiv [-|1\rangle + |2\rangle + |3\rangle - |4\rangle - |5\rangle + |6\rangle]/\sqrt{6}, \tag{2.27}$$

respectively, and are the standard symmetric and antisymmetric states.

Then, in order to generate the two two-dimensional irreducible representations of $\mathcal{H}'$, we can try to diagonalize the permutation operators $P_{(1,2,3)}$ and $P_{(3,2,1)}$. The eigenvectors of the former, and their corresponding eigenvalues λ, are

$$\begin{aligned} &|v_1\rangle \equiv \lambda_- |2\rangle + \lambda_+ |3\rangle + |6\rangle, \\ &|v_2\rangle \equiv \lambda_+ |1\rangle + \lambda_- |4\rangle + |5\rangle, \end{aligned} \quad \lambda_- = e^{-i(2\pi/3)}$$
$$\begin{aligned} &|v_3\rangle \equiv \lambda_+ |2\rangle + \lambda_- |3\rangle + |6\rangle, \\ &|v_4\rangle \equiv \lambda_- |1\rangle + \lambda_+ |4\rangle + |5\rangle. \end{aligned} \quad \lambda_+ = e^{+i(2\pi/3)} \tag{2.28}$$

The other cyclic permutation $P_{(3,2,1)}$ has the same eigenvectors, with the eigenvalues exchanged.

By looking at the behavior of such states under the exchange of two particles, it is easy to see that the two invariant subspaces $\mathcal{H}'_1$ and $\mathcal{H}'_2$ are generated by $\{v_1, v_4\}$ and $\{v_2, v_3\}$, respectively. Therefore, the effect of a generic exchange is a rotation of the vectors in $\mathcal{H}'_j$, with a change of the eigenvalues of $P_{(1,2,3)}$ and $P_{(3,2,1)}$. For example, the action of $P_{(2,3)}$ on v_1 gives

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ \mathrm{e}^{-i(2/3)\pi} \\ e^{+i(2/3)\pi} \\ 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} e^{-i(2/3)\pi} \\ 0 \\ 0 \\ e^{+i(2/3)\pi} \\ 1 \\ 0 \end{pmatrix}. \tag{2.29}$$

The resulting vector is v_4, which corresponds to different eigenvalues of both cyclic permutations. The same result applies for the other two exchanges. In Sec. III we investigate the consequences of these properties of the cyclic permutations for the specific case of three nuclei bound in a rigid molecule, and the possible physical implication of the existence of these states not obeying the SP.

III. SYMMETRY-FORBIDDEN STATES IN SYMMETRICAL THREE-NUCLEI MOLECULES

A. Three spin-0 identical nuclei

The prototypal molecule that we want to consider is composed of three identical spin-0 nuclei disposed at the vertices of an equilateral triangle, as sketched in Fig. 1, whose symmetries belong to the dihedral group D_3. The discussion below can be extended to any symmetrical molecule with additional nuclei in the plane (point group D_{3h}).

Within the Born-Oppenheimer approximation, the total wave function can be decomposed in the usual way as

$$\Psi = \Psi_e \Psi_n \Psi_v \Psi_r, \tag{3.1}$$

where the partial wave functions are electronic, nuclear spin, vibrational, and rotational components, respectively. To simplify our description, we can assume the molecule to be in the ground electronic and vibrational state, with species $^1\Sigma$ (which is the most common case), or, in other words, we assume the total electronic spin, electronic angular momentum, and vibrational angular momentum to be zero. Therefore, the electronic and vibrational wave functions Ψ_e and Ψ_v are completely symmetric under any permutations of the labels of the nuclei. In the case of spin-0 nuclei, the nuclear spin-wave function Ψ_n is also symmetric under permutations, and therefore we must consider the symmetry of the rotational wave-function alone.

For this purpose, we briefly recall the main properties of the rotational states of such a molecule, which are eigenstates of the rigid rotational Hamiltonian

$$H = B(\mathbf{J}/\hbar)^2 - (B - C)(\mathbf{K}/\hbar)^2, \tag{3.2}$$

where B and C are the two rotational constants, $\mathbf{J}$ is the total angular momentum, and $\mathbf{K}$ is its projection on the threefold-symmetry axis perpendicular to the molecule's plane. The eigenvalues of the Hamiltonian are of the form

$$E(J,K) = BJ(J+1) - (B - C)K^2, \tag{3.3}$$

with $K=-J,-J+1,\ldots,J$, and are strictly degenerate in the sign of K as far as the molecule is symmetric, even if nonrigidity and perturbations are considered (the degeneracy accounts for the undistiguishability of the two orientations of **K** with respect to the molecular axis). The eigenfunctions are somewhat complicated functions of J and K and of the Eulerian angles [22]; they also depend parametrically on the equilibrium positions of the three nuclei in the molecular potential. Here we are interested in their transformation properties under a generic rotation of the molecule. The general rule for such transformations is the usual

$$\Psi_r \rightarrow \Psi_r e^{i\alpha \mathbf{u}_\alpha \cdot \mathbf{J}}, \tag{3.4}$$

where α is the angle of rotation, and $\mathbf{u}_\alpha$ is the versor of the plane containing α. To find the symmetry character of the rotational states, we want to compare this transformation rule to those associated with the permutations of particles. For such purpose we write the generic rotational states in a formal way as a function of the coordinates of the three minima in the molecular potential:

$$|\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3\rangle. \tag{3.5}$$

These states are defined in the six-dimensional Hilbert space defined in Sec. II. We note that a permutation of the quantum labels corresponds to a classical permutation of the nuclei's mean positions, and therefore all the permutations are equivalent to rotations of the molecule.

We start by considering rotations in the plane of the molecule by angles $\theta=\epsilon 2\pi/3$, with $\epsilon=\pm 1$, which are equivalent to the cyclic permutations $P_{(1,2,3)}$ and $P_{(3,2,1)}$. Since the effect on the molecular wave function of these rotations must be the same of such cyclic permutations, we can compare the general transformation rules under rotations and under permutations. For the former, the appropriate phase shift is given by

$$\Psi_r \rightarrow \Psi_r \exp(i\epsilon 2\pi K/3), \tag{3.6}$$

since the rotation is in the molecule's plane, while for the permutations we have

$$\Psi_r \rightarrow \Psi_r \quad \text{and} \quad \Psi_r \rightarrow \Psi_r \exp(i\epsilon 2\pi/3), \tag{3.7}$$

respectively, for states in $\mathcal{H}_+$, $\mathcal{H}_-$, and $\mathcal{H}'$. Therefore, a state with $K=3q$, with q an integer, can be defined in $\mathcal{H}_+$ or $\mathcal{H}_-$, while states with $K=3q\pm 1$ can be defined only in $\mathcal{H}'$.

For the special case of a rotational state with $K=0$, we can also consider rotations about any of the three symmetry axes in the plane of the molecule by angles $\phi=\epsilon\pi$. Such rotations are equivalent to the three exchanges $P_{(1,2)}$, $P_{(2,3)}$, and $P_{(1,3)}$, and also the correspondent phase shifts in the wave function must be identical. This class of rotations transforms the wave function as

$$\Psi_r \rightarrow \Psi_r \exp(i\epsilon\pi J), \tag{3.8}$$

according to Eq. (3.4), since the angular momentum **J** lies in the molecule's plane. The exchanges are instead characterized by

$$\Psi_r \rightarrow \Psi_r \quad \text{and} \quad \Psi_r \rightarrow \Psi_r \exp(i\pi) \tag{3.9}$$

for states belonging to $\mathcal{H}_+$ and $\mathcal{H}_-$, respectively. As a result, the even-J states belong to $\mathcal{H}_+$, and the odd-J ones to $\mathcal{H}_-$, as summarized in Table I.

TABLE I. Appropriate Hilbert subspaces for rotational states of a D_{3h} molecule containing spin-0 identical nuclei, in the ground electronic and vibrational states. The states completely forbidden by the SP or by the spin-statistics (SS) are indicated.

K	J	Subspace	Forbidden by
$3q,\ q\neq 0$	any	$\mathcal{H}_+$, $\mathcal{H}_-$	-
$3q\pm 1$	any	$\mathcal{H}'$	SP
0	even	$\mathcal{H}_+$	-
0	odd	$\mathcal{H}_-$	SS

From the results obtained above, it appears that all the rotational states with $K=3q\pm 1$ are strictly forbidden by the SP, which requires any physical state to be defined in $\mathcal{H}_+$ or $\mathcal{H}_-$. Moreover, the odd-J states with $K=0$ are forbidden by the spin statistics, since the identical nuclei are spin-0 particles. The latter case is very similar to that of symmetrical molecules with two identical nuclei [4,5,7]. These consequences of both the SP and the spin statistics are well known in the field of molecular spectroscopy [22], since they lead to the absence of more than two thirds of the rotational states in molecules with the proper symmetry, as confirmed by the experimental investigation performed so far.

We now discuss a property of the SP-forbidden states, which can be defined in the unsymmetrical subspace $\mathcal{H}'$. Specifically, states with $K=3q-1$ could be described by the vectors v_1 and v_2, and those with $K=3q+1$ by vectors v_3 and v_4, to preserve the equality of the phase shifts reported in Eqs. (3.6) and (3.7). As we noted, such pairs of vectors do not define invariant subspaces, and therefore the physical states have to be defined in the two invariant subspaces $\mathcal{H}'_1$ and $\mathcal{H}'_2$. Although in each of these subspaces the sign of the rotational phase shift is not defined [see Eq. (2.28)], the sign of K is also not a physical observable, due to the degeneracy of the states with $\pm K$. In other words, even if in $\mathcal{H}'$ it is not possible to define a complete set of operators due to its multidimensionality, and in particular the sign of K is undefined, no paradox arises, since we have no means to measure such a sign.

B. Three spin-1/2 identical nuclei

In the case of a molecule containing three identical nuclei with nonzero spin, we should also consider the influence of the nuclear-spin-wave function; in the following we will discuss the special case of spin 1/2. Since the spin is nonzero, we can now define a nontrivial Hilbert space for the spin, in the same way as we defined it for the spatial coordinates. The total Hilbert space will be the direct product of the rotational and spin spaces:

$$\mathcal{H}=\mathcal{H}_S \otimes \mathcal{H}_R. \tag{3.10}$$

TABLE II. Decomposition of the direct product Hilbert space $\mathcal{H}_S \otimes \mathcal{H}_R$, into symmetry-inequivalent invariant subspaces (under S_3).

	$\mathcal{H}_+$	$\mathcal{H}_-$	$\mathcal{H}'$
$\mathcal{H}_+$	$\mathcal{H}_+$	$\mathcal{H}_-$	$\mathcal{H}'$
$\mathcal{H}_-$	$\mathcal{H}_-$	$\mathcal{H}_+$	$\mathcal{H}'$
$\mathcal{H}'$	$\mathcal{H}'$	$\mathcal{H}'$	$\mathcal{H}_+ \oplus \mathcal{H}_- \oplus \mathcal{H}'$

The general properties of the Hilbert space can easily be found, considering the discrete nature of the quantum labels associated with each particle. The generic three-particle state is now defined as

$$|S_{z1}, S_{z2}, S_{z3}\rangle, \tag{3.11}$$

and there are two states with total spin $I=1/2$ and one with $I=3/2$ (two doublet and one quartet). Using the formalism of Sec. II, it is possible to assign the quartet state to the symmetrical subspace $\mathcal{H}_+$, and the two doublets to the unsymmetrical $\mathcal{H}'$. We note that is not possible to build nonvanishing states completely antisymmetric under permutations of more than two spin-1/2 particles, since each quantum label can assume only two values.

Even in the absence of an electronic or vibrational angular momentum, the nuclear spin can couple to the rotational angular momentum, and give rise to a very small hyperfine splitting of the rotational states. The molecular states will therefore be eigenstates of the total angular momentum $\mathbf{F}=\mathbf{J}+\mathbf{I}$. We now want to assign each molecular state to a particular subspace of the overall Hilbert space, as we did in the previous case. For such a purpose we have to decompose the representation of the S_3 group on the direct product Hilbert space $\mathcal{H}_S \otimes \mathcal{H}_R$, into irreducible representations. By using general rules [21] we easily obtain the decomposition shown in Table II.

It is then straightforward to evaluate the appropriate Hilbert subspace for the overall rotational and nuclear-spin states, using the associations of Table I; the results are reported in Table III. If the hyperfine splitting of the rotational states is not resolved, as is usually the case, the states with $K \neq 0$ are no longer completely forbidden by the SP, while the even-J states with $K=0$ are forbidden by both the SP and the spin statistics. Specifically, states defined in $\mathcal{H}_+$ will have $I=3/2$, and those defined in $\mathcal{H}'$ will have $I=1/2$. As a consequence of the multidimensionality of $\mathcal{H}'$, it is impossible to distinguish between the two doublet states, but this is not a problem, since they are rigorously degenerate. In fact, the invariant subspaces of $\mathcal{H}'$ are eigenstates of I_z, and, therefore, in the presence of a magnetic field there is also no fundamental principle other than the SP to forbid the existence of these unsymmetrical states. We conclude by noting that in the case of a nuclear spin larger than 1/2 it is also possible to build antisymmetrical spin states in $\mathcal{H}_-$, and therefore none of the rotational states with $K=0$ is forbidden.

TABLE III. Appropriate Hilbert subspaces for the rotational and spin states of a D_{3h} molecule containing spin-1/2 identical nuclei.

K	J	I	Subspace	Forbidden by
$3q,\ q\neq 0$	any	1/2	$\mathcal{H}'$	SP
$3q,\ q\neq 0$	any	3/2	$\mathcal{H}_+$, $\mathcal{H}_-$	-
$3q\pm 1$	any	1/2	$\mathcal{H}_+$, $\mathcal{H}_-$, $\mathcal{H}'$	-
$3q\pm 1$	any	3/2	$\mathcal{H}'$	SP
0	even	1/2	$\mathcal{H}'$	SP
0	even	3/2	$\mathcal{H}_+$	SS
0	odd	1/2	$\mathcal{H}'$	SP
0	odd	3/2	$\mathcal{H}_-$	-

C. Nonplanar symmetrical molecules

We now extend the discussion to nonplanar symmetrical molecules containing three spin-0 or spin-1/2 identical nuclei (point group C_{3v}: the molecule has additional nonidentical nuclei out of the plane containing the identical nuclei). The main difference from the planar case stands in the transformation rule of the $K=0$ rotational states under rotations about a symmetry axis in the plane of the three identical nuclei. These rotations, by angles $\phi=\epsilon\pi$, are not identical to permutations of two identical nuclei, as was the case for a planar molecule, since also the additional nuclei out of the plane have also rotated. On the other hand, the combination of such a rotation with an inversion of the coordinates of all the nuclei with respect to the origin cannot be distinguished from a permutation of two nuclei.

The properties of the rotational states under space inversion are well known in the field of molecular spectroscopy [22], and here we give only the main result. If the nonrigidity of the molecule is taken into account, each rotational state is split into two states with definite symmetry under inversion (s and a species, respectively symmetric and antisymmetric under inversion). The splitting of the degeneracy of these pairs of states is indicated as inversion splitting. The analogous of the transformation rule of Eq. (3.8) for the rotation plus inversion is therefore

$$\Psi_r \rightarrow \pm \Psi_r \exp(i\epsilon\pi J), \tag{3.12}$$

where the positive (negative) sign refers to the s species (a species). If we compare this rule with the one for the exchange of two particles [Eq. (3.9)], we can assign each rotational state to the proper symmetry class, as summarized in Table IV for the cases of spin 0 and spin 1/2. In Sec. IV, we will indicate one molecular species in which the inversion splitting is sufficiently large to resolve the states forbidden by the SP from those allowed.

IV. TESTING SMALL SYMMETRY VIOLATIONS

As we noted above, those rotational states forbidden by the SP can be defined consistently in the unsymmetrical subspace $\mathcal{H}'$, since they are not violating any basic principle of quantum mechanics. The discussion can be extended to particular classes of rotational substates in excited vibrational

TABLE IV. Appropriate Hilbert subspaces for $K=0$ rotational states of a C_{3v} molecule. In the case of $S=1/2$, each rotational state is composed of two states with different total nuclear spin I, and the finer assignment of the Hilbert subspaces can be done following Table III.

Nuclear spin S	Inversion symmetry	J	Subspace	Forbidden by
0	s	even	$\mathcal{H}_+$	-
	s	odd	$\mathcal{H}_-$	SS
	a	even	$\mathcal{H}_-$	SS
	a	odd	$\mathcal{H}_+$	-
1/2	s	even	$\mathcal{H}_+$, $\mathcal{H}'$	SS, SP
	s	odd	$\mathcal{H}_-$, $\mathcal{H}'$	-
	a	even	$\mathcal{H}_-$, $\mathcal{H}'$	-
	a	odd	$\mathcal{H}_+$, $\mathcal{H}'$	SS, SP

and electronic states; due to the different symmetry of the vibrational and electronic wave functions, different classes of K and J levels can be forbidden by the SP. In any case, electromagnetic transitions between rotational levels are allowed only if the involved states belong to the same symmetry type, in accordance with the superselection rule.

Therefore, a violation of the SP can be thought of only in terms of the appearance of a population of nuclei identical between themselves, whose quantum states belong to $\mathcal{H}'$, and whose properties (mass, spin, charge) are the same as those of the normal nuclei. The presence of a nonzero population in SP-forbidden rotational states of the molecules formed by such nuclei could be detected by exciting electromagnetic transitions toward other forbidden states, in the same way as was done in previous experiments for testing the statistics. For a matter of sensitivity, the experimental investigation should focus on states *completely* forbidden by the SP alone, or by both the SP and the spin statistics, since we expect the violation, if present, to be very small. Therefore, the most interesting states to be probed in both D_{3h} and C_{3v} molecules are those with $K=3q\pm1$ in the case of $S=0$, and those with $K=0$ in the case of $S=1/2$.

We also note that all the statements above would not lose validity in the case of a breakdown of the Born-Oppenheimer approximation. Indeed, the symmetry character of the particles under permutation can only be assigned to a single class (i.e., a Hilbert subspace), as stated by the superselection rule, and no coherent superposition is allowed [18]. Therefore, if the total wave function appears to be correctly described as symmetrical (unsymmetrical) in the frame of the Born-Oppenheimer approximation, it would be so for any degree of violation of the approximation itself. The same argument applies in the case of the presence of external perturbations, such as electric or magnetic fields: even if they can change the molecular wave function to a large extent in a continuous way, the symmetry character of the wave function will be locked to a single class.

V. PROPOSAL FOR A HIGH-SENSITIVITY TEST OF THE SYMMETRY ON OXYGEN NUCLEI AND PROTONS

A simple tool to investigate for possible violations of the SP would be high-sensitivity spectroscopy of a thermal sample of gas, in search of a nonzero absorption of light by symmetry-violating molecules, as performed in previous experiments on statistics. It is possible to define a few general criteria to choose the proper molecule for such an experimental search. The first important parameter is the weight of the molecule, which determines the spacing between adjacent rotational transitions (the rotational constants B and C are inversely proportional to the mass), and therefore also the capability of resolving the forbidden transitions from the allowed ones [23]. This point is very important, since in nonlinear molecules the number of transitions which can possibly interfere in the detection of SP violations is increased with respect to linear molecules, due to the increased molteplicity of rotational states. Second, in order to have a high sensitivity in detecting a violation of the SP, one should probe strong transitions starting from low-lying rotational states in the ground electronic and vibrational states, which have the largest occupation probabilities. As usual, in these kinds of molecules the strong electronic transitions are confined to the UV, where laser sources are not easily available, and therefore one should rely on the fundamental vibrational transitions in the infrared, which are somewhat weaker. It is therefore important to find a near coincidence between a vibrational band and the emission of a coherent laser source suitable for high-sensitivity spectroscopy. Quantum-cascade semiconductor lasers are particularly interesting from this point of view, since they can be designed to emit almost everywhere in the midinfrared, they are widely tunable and have low-noise characteristics [24].

TABLE V. Vibrational energies (in cm^{-1}) and spin of the identical nuclei of selected molecules which present rotational states forbidden by the SP.

Molecule	Spin	ν_1	ν_2	ν_3	ν_4
SO_3	0	1065	498	1391	530
BH_3	1/2		1125	2828	1640
NH_3	1/2	3337	950	3444	1627

In the case of spin-0 nuclei, the lightest molecule with the proper symmetry is the plane SO_3 (group D_{3h}), whose vibrational energies [25] are reported in Table V. In principle the sensitivity for detection of SP-violating transitions can be expected to be comparable to those obtained in previous experiments on molecular systems. It could possibly be reduced by increased experimental difficulties (for example, SO_3 is not chemically stable in the presence of oxygen, and therefore it may not be easy to have the proper pressure and cell volume to optimize the sensitivity) or more fundamental limitations, such as the presence of weak hot transitions close to the SP-forbidden ones.

An alternative approach could be to perform a spectroscopic investigation on a supersonic beam of SO_3, instead of a thermal sample. With this technique, the problems connected with the high reactivity of SO_3 could possibly be solved, while the reduction in the density of the sample could be compensated for by the reduction of the rotational temperature and by an increase of the detection sensitivity. In addition, one would benefit from the accompanying increase in resolution, for a better identification of the detected spectrum of transitions.

As for the case of spin-1/2 nuclei, it is possible to find a relatively light plane molecule BH_3 (group D_{3h}), on which to search violations of the SP and of the spin statistics for $K=0$ rotational states. As we mentioned, the same symmetry properties can also be found for the corresponding rotational states of nonplanar symmetrical molecules (group C_{3v}) with inversion splitting. One of the most interesting species of this kind is NH_3, which is stable and particularly light, and has very strong vibrational absorption bands in the infrared spectral region covered by semiconductor lasers. Moreover, its spectrum has been the subject of extensive investigation, and therefore the assignment of observed lines can be performed in a relatively easy way. In addition, it is characterized by a very large inversion splitting of the rotational spectrum, and therefore the forbidden lines can be easily distinguished from the allowed ones. For such molecules, which are composed by spin-1/2 nuclei, we noted that for $K=0$ states different hyperfine components are forbidden by the SP and by the spin statistics. Since the hyperfine splitting of the rotational levels is usually negligible (at least for Σ electronic states [22]), we can expect to resolve the two classes of substates only thanks to Zeeman effects in strong magnetic fields.

To conclude, we note that in the case of BH_3 or NH_3, one would be testing the SP and the spin-statistics connection for *protons*. Such an experimental test would be particularly interesting to compare the present bound for violation of the statistics for composed nucleons [7] to a corresponding bound for fundamental nucleons, especially in view of the recent theoretical predictions [15].

VI. CONCLUSIONS

We have shown how to define consistently particular classes of rotational levels of symmetrical molecules containing three identical nuclei, by allowing for violations of the symmetrization postulate. This violation, if existing, must be small, according to the results of past experimental observations. However, it is possible to look with high sensitivity for the presence of tiny populations in SP-forbidden states, using spectroscopic tools in a scheme similar to those of previous experiments on O_2 and CO_2. If we allow for the presence of molecules composed of SP-violating nuclei in a sample of gas, which are identical to normal molecules in all but symmetry, then such a measurement can be interpreted as a test of the SP. This kind of experiment would represent a substantial improvement with respect to past investigations on possible violations of the spin-statistics connection. We propose a few simple molecules containing spin-0 nuclei (SO_3) or spin-1/2 nuclei (BH_3 and NH_3) as candidates for a high-sensitivity spectroscopic investigation to be performed on infrared vibrational transitions, with the help of semiconductor lasers. The latter species are particularly interesting, since they represent systems on which to test the SP for fundamental nucleons.

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