Spectroscopic Tests of Spin-Statistics Connection and Symmetrization Postulate of Quantum Mechanics

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Received September 12, 2000; accepted December 7, 2000

PACS ref: 05.30.Jp, 21.10.Hw, 33.20.-t, 42.62.Fi

Abstract

Recent experiments searching for violations of the spin-statistics connection and of the symmetrization postulate of quantum mechanics are reviewed. Spectroscopic tests on \( O_2 \) and \( CO_2 \) molecules are described in detail and it is shown that these should be considered as tests of the spin-statistics connection for the spin-0 oxygen nuclei. The possibility of new experiments to test the spin-statistics connection and the symmetrization postulate is discussed.

1. Introduction

Several experiments were performed to test the symmetrization postulate and/or the spin-statistics connection [1]. The symmetrization postulate and the spin-statistics connection are indeed amongst the fundamental tenets of quantum mechanics. The symmetrization postulate establishes that in a system containing identical particles the only possible states are either all symmetrical or all anti-symmetrical with respect to permutations of the particles. In the first case, the particles are called bosons and follow Bose–Einstein statistics; in the second case they are called fermions and follow Fermi–Dirac statistics. Experiments indicate that particles with integral values of spin are bosons, while particles with half-integral spin are fermions. The reason why only symmetric and antisymmetric states seem to occur in nature and the connection with the spin of the particles has been a puzzle since the early days of quantum mechanics [2,3]. The spin-statistics theorem, proved by W. Pauli [4] from the basic principles of quantum field theory and special relativity, states that given the choice between Bose and Fermi statistics, integral-spin particles must obey Bose statistics and half-integral-spin particles must obey Fermi statistics. Proofs of the spin-statistics theorem are discussed in [1,5]. Quantum mechanics would nevertheless allow also symmetries different from those imposed by the symmetrization postulate, and theories have been developed allowing for small deviations from conventional symmetry which might have been masked in the experiments performed so far. It is worth noting that no theory so far predicts the possibility of observing a violation in a particular system or in some specific condition. Consistent theories can be formulated, however, which would lead to different symmetry properties. Experiments are needed then to discriminate between these theories by imposing constraints which are the more stringent the higher is the experimental precision.

In this paper, after a brief account of the theoretical background, the experimental tests are presented with particular attention to recent spectroscopic tests on molecules including identical spin-0 nuclei. In the spectra of these molecules, some lines are missing. Their absence can be understood when the requirement of symmetry of the molecular wave function under exchange of the identical nuclei is considered, which prevents the occupation of some of the states. The basic idea of the experiments presented here is to search for molecules in such “wrong-symmetry” states. It is shown that the experiments performed so far should be considered as tests of the spin-statistics connection for \( ^{16}O \) nuclei. The possibility of experiments to search for violations of the symmetrization postulate for nuclei is also discussed.

2. Theoretical background

If a system includes \( N \) particles which have the same intrinsic properties (mass, charge, spin, ...), the states represented by vectors differing only by a permutation of identical particles cannot be distinguished by any observation. All the physical observables must be invariant under permutation of identical particles. The Hilbert space of the complete system can be decomposed into orthogonal sub-spaces which correspond to the irreducible representations of the permutation group. The irreducible eigensubspaces may have dimension greater than one. If a representation is of order one, the level is not degenerate; the consequence of a permutation of identical particles is only to multiply the eigenfunction by a phase factor. If the representation is of order \( h > 1 \), the associated eigenvalue is \( h \)-fold degenerate. Although it is not possible in this case to associate a single vector to a physical state, this degeneracy does not cause any difficulty: the measurable results on a state do not depend on which vector is chosen in the \( h \)-dimensional subspace to represent the state [6].

The symmetrization postulate admits only the representations of order one, that is only the completely symmetric and antisymmetric functions. The connection with the spin of the particles (taken as an experimental evidence or demonstrated from basic assumptions) completely defines the symmetry allowed for each type of particle.

Two important points must be noted to avoid confusion in the interpretation of experiments searching for violations of the symmetries dictated by the symmetrization postulate and by the spin-statistics connection. The first is that in a system including only two identical particles, the symmetric and antisymmetric representations are the only irreducible representations. Only two “entangled” states are then
possible:
\[
\Psi_S(1, 2) = \frac{1}{\sqrt{2}}[\psi_s(1)\psi_s(2) + \psi_s(1)\psi_s(2)]
\]
\[
\Psi_A(1, 2) = \frac{1}{\sqrt{2}}[\psi_s(2) - \psi_s(1)\psi_s(2)]
\]

(1)

where \( \psi_s \) and \( \psi_a \) are single-particle wave functions. In this case, the symmetrization postulate does not play a relevant role, the question being only the connection between the intrinsic spin of the particles and the symmetry of the two-particle state. This is not the case for systems including three or more identical particles. For three identical particles, for example, the state of the system could be represented by any of six vectors. The permutation group has two one-dimensional representations (the symmetric and the antisymmetric one) and two two-dimensional representations. In this case, the symmetrization postulate limits the possible states to the symmetric and antisymmetric ones and the connection to the particle spin determines which of the two states is occupied by each type of particle.

The second important remark is that if a system of \( N \) particles is in a particular state belonging to a given irreducible representation of the permutation group, it cannot be brought by any perturbation into another state belonging to a different representation. The perturbation operator must indeed be symmetric under particles exchange so that matrix elements between the initial state and states corresponding to a different representation vanish. The symmetry character of the wave function must then remain the same in time (the case of a variable number of particles requires special consideration). This “superselection rule” is a rigorous selection rule holding also in the presence of perturbations such as collisions or electric fields [2,7].

A consequence of the superselection rule is that it is not possible to consider states given by a coherent superposition of states with different permutation symmetries. Therefore symmetry violations in systems including identical particles can only be described in terms of an incoherent mixture which is represented by a density matrix. In the case of two integral-spin particles, for example, the density matrix taking into account small symmetry violations is:
\[
\rho_2 = (1 - \frac{1}{2}\beta^2)\rho_s + \frac{1}{2}\beta^2\rho_a
\]

(2)

where \( \rho_{\text{sym}} \) is the symmetric (antisymmetric) two-particle density matrix. A pair of particles will be found in the normal symmetric state with probability \((1 - \beta^2)/2\) and in the anomalous antisymmetric state with probability \(\beta^2/2\). In the case of particles with half-integral values of spin, \(\rho_s\) and \(\rho_a\) are exchanged.

Using the notation adopted in the literature, in the following \(\beta^2/2\) indicates the “symmetry-violation” parameter. Its real meaning needs to be specified, however, for the particular physical system and the theoretical model considered.

It is not the purpose of this paper to discuss in detail the theories allowing for symmetry properties different from the ones which are peculiar to bosons and fermions. A survey can be found in [1,8]. It is of interest, however, to put in evidence the possibility of theories allowing for small deviations from the usual symmetry relations, whose search is the subject of the experiments discussed in this paper. Such deviations can be expressed as a different symmetry of the state under particle exchange or, in Fock-space representation, as a deformation of the algebra of the creation and annihilation operators. A statistics intermediate between Bose and Fermi cases was first proposed in [9] considering the possibility that at most \( n \) identical particles could occupy the same quantum state. This idea led to a generalized field theory [10], called parastatistics, in which the field operators obey trilinear commutation relations instead of the usual bilinear relations. These theories predict, however, gross violations of statistics which are immediately excluded by experimental evidence. The possibility of a continuous interpolation between bosonic and fermionic behaviours is given by “quons” [11]. The commutation and anticommutation relations are replaced by generalized bilinear commutation relations depending on a parameter \( q \) (\( q \)-mutators):
\[
a_q a^\dagger_q - qa^\dagger_q a_q = \delta_{q1}, \quad -1 \leq q \leq 1
\]

(3)

with the vacuum condition \( a_q|0\rangle = 0 \). As \( q \) varies between \(-1\) and \( 1 \), the symmetry changes continuously from the completely antisymmetric case (fermions) to the completely symmetric case (bosons). In this frame, the value of \( \beta^2/2 \) can be related to the value of the \( q \) parameter: for small violations of Bose statistics, \( \beta^2 = 1 - q \); for small violations of Fermi statistics, \( \beta^2 = 1 + q \). It can be shown that this interpolation preserves positivity of norms and the non-relativistic form of locality [12]. Other aspects are still doubtful such as the possibility of accounting for local observables in a relativistic theory or for the existence of antiparticles. Statistics other than Fermi and Bose have also been investigated for one- and two-dimensional systems [13] and in connection with anyon high-temperature superconducting systems [14].

3. Experimental tests

In this section, experiments performed to search for violations of the symmetrization postulate and/or of the spin-statistics connection are discussed. After a brief review of experiments on electrons and photons, recent experiments on integral-spin nuclei in molecules are described in detail. In fact, no accurate test for integral-spin particles had been reported until recently. This is due to the fact that while there are several systems in which a violation of the Pauli exclusion principle would be detected as a signal on a zero background, the effect of a small violation for particles following Bose–Einstein statistics would usually manifest itself as a small change in the properties of a many-particle system. This obviously limits the achievable accuracy. In [15], a bound to a possible violation of the generalized Bose statistics for pions was inferred considering the \( K_2 \to \pi^+\pi^- \) decay, which is usually considered as due to CP violation (see also the contribution of I. Mannelli in [1]).

For a review of the experiments before 1989, the reader is referred to [15]. Some of the initial experiments suffered from a misunderstanding of the constraints imposed by the “superselection rule”. It is shown here that also the interpretation given for some recent experiments is questionable. In fact, although the papers published on this subject usually present their “null results” as a confirmation
of the validity of the symmetrization postulate, most of them should be considered as tests of the spin-statistics connection. An experiment that would allow a genuine test of the symmetrization postulate for nuclei is discussed in the following.

3.1. Experiments on electrons
A few experiments have been performed to test the validity of the Pauli principle for half-integer-spin particles. In particular, a high precision test on electrons was performed in [16] by running a current through a copper bar and searching for X-rays that would be emitted if some of the electrons introduced in the sample were captured by a copper atom and cascaded down to the 1S state, which is already filled with two electrons. No signal was found and this was interpreted as giving a limit $\beta^2/2 \leq 1.7 \times 10^{-26}$ to the probability that a new electron introduced into copper would form a mixed-symmetry state with respect to the other electrons already present in the copper sample. In this experiment, the large number of electrons in the system was important to reach such a high sensitivity but, on the other hand, makes the interpretation of the result more complicated. Conclusions may depend, for example, on whether we consider the symmetry of the system composed by the injected electron plus the electrons already present in the copper bar, or we consider a model in which the electron collides with a copper atom and is captured. A simpler two-electron system was investigated in [17]. A spectroscopic test was performed on helium atoms, searching for a transition involving the permutation symmetric 1s2s 1S0 state. An upper bound $\beta^2/2 \leq 5 \times 10^{-6}$ was set to a violation of the Pauli principle. In spite of the lower sensitivity, the interpretation of this result is simpler. Since only two identical particles are involved, this should be considered as a test of the spin-statistics connection for electrons. Doubts can be raised, however, about what would be the chemical stability of “paronic” atoms in ordinary samples. In [17], this was taken into account by having the atoms ionize and recombine in a discharge before entering the detection region.

3.2. Experiments on photons
Several papers have been published recently reporting or proposing experiments to set a limit to possible violations of Bose statistics for photons [18–23]. The fundamental nature of the photon and its peculiar properties make it very interesting to investigate this particle in this context. It is hard, however, to find an experiment that would give a direct evidence of a violation with a significant sensitivity. This is one case, in fact, in which a small deviation from normal statistics would usually produce only a small signal over a large background. An attempt to set a limit to a possible violation of Bose statistics was made in [18], based on light intensities attainable in laser systems. In [19], a possible dependence of the frequency of light on its intensity was searched for. This effect is expected if a $q$-nonlinearity is introduced in the description of the electromagnetic field. Since nonlinearities in the commutation relations give rise to mixed-symmetry states, this experiment could also be reinterpreted as a search for a violation of the symmetrization postulate for photons. The connection is not straightforward though and was not pursued in the paper. In [20], the experimental upper limit on the two-gamma decay of the Z-boson, $Z \rightarrow \gamma\gamma$, was used to establish an upper bound to a possible small violation of the exchange-symmetry for a system of two photons. The same idea, based on what is called Landau–Yang theorem, was exploited in [21] to improve the limit by searching for the forbidden $J = 0 \rightarrow J = 1$ transitions in atoms excited by two photons of the same energy. A limit of $\beta^2/2 \leq 10^{-7}$ was set on the probability that two photons are in an exchange-antisymmetric state. A different approach was followed in [23]. A very tight bound to a violation of statistics for photons was inferred considering photons and electrons as coupled “quons” and relating the bound for photons to that obtained in [16] for electrons. Although this argument is indirect and model-dependent, it is very interesting and it could also be extended to other particles.

3.3. Experiments on nuclei in molecules
Wigner [24] and Ehrenfest and Oppenheimer [25] showed that a composite system of fermions is a boson or a fermion depending on whether it is made of an even or an odd number of fermions (in fact, for this argument to be valid, it is necessary that the interaction between the composite particles is negligible compared to the internal excitation energy so that the internal structure can be neglected and the system can be considered as a single particle). Considering the total angular momentum resulting from the constituents angular momenta, an extension of the spin-statistics connection to composite systems, such as nuclei, is obtained.

The requirement of symmetry of the wave function under exchange of identical particles has a striking demonstration in the spectra of molecules including identical nuclei. Let us consider a molecule containing two identical spin-0 nuclei as, for example, $^{16}$O$_2$. According to the Born–Oppenheimer approximation and neglecting the coupling of the nuclear spin with the rest of the molecule (which is not important for these experiments since the spin of the nuclei is zero), the total wave function $\psi_t$ can be written in the form

$$\psi_t = \psi_e \psi_e \psi_e \psi_e \psi_n \psi_n$$ (4)

where $\psi_e$, $\psi_e$, $\psi_e$, $\psi_n$, and $\psi_n$ are the electronic, vibrational and $\psi_n$ rotational functions, respectively, and is the nuclear spin function. For integer-spin nuclei, the total wavefunction must be symmetric in the exchange of two nuclei. The $^{16}$O molecule represents a particularly simple case because the nuclear spin of $^{16}$O is zero and $\psi_n$ is therefore obviously symmetric. The vibrational wave function $\psi_e$ is also unaltered in the exchange of the nuclei because it depends only on the magnitude of the internuclear distance. Since the total wavefunction $\psi_t$ must be symmetric, only the states corresponding to even (odd) rotational quantum numbers are allowed if $\psi_e$ is symmetric (antisymmetric) [26]. In the case of the $^{16}$O$_2$ molecule, which is relevant for the experiments described in the following, the ground state is a $\Sigma^+_g$ state, which is antisymmetric under the exchange of the two nuclei. The rotational states corresponding to even values of the rotational number $K$ are therefore forbidden. Indeed, since the early work on $^{16}$O$_2$ spectra [27], it was observed that alternate lines are missing.

The other molecule investigated in this context, the $^{12}$C$^{16}$O$_2$ molecule, has the same symmetry properties. Both the ground electronic and vibrational wave functions are
in this case symmetric in the exchange of the two $^{16}$O nuclei. Therefore only rotational states corresponding to even values of the rotational quantum number are allowed.

The basic idea of the spectroscopic tests described in the following is to search with extremely high sensitivity for (weak) molecular lines involving the forbidden states. Indeed, the effect of a (small) violation of the expected symmetry would be that some molecules could be found in antisymmetric states corresponding to wrong-parity rotational numbers. The possibility of such a test was first suggested in [28] considering the CO$_2$ molecule. A specific experiment on O$_2$ was later proposed in [29]. The idea of these experiments is analogous to the one underlying the experiment on electrons in the helium atom [17]. This represents indeed a rare case in which a violation of the spin-statistics connection for integer-spin particles would be detected on a virtually zero background with a sensitivity comparable to the one achieved in experiments on fermions.

### 3.3.1. Experiments on $^{16}$O$_2$

In a first series of experiments [30–32], the spectrum of the $^{16}$O$_2$ molecule was investigated searching for transitions between states which are antisymmetric under the exchange of the two nuclei. The purpose of these experiments was to measure or to bound the relative abundance of molecules in “wrong-symmetry” states. I will first describe in some detail the experimental approach and results reported in [31] and then compare it with other experiments performed or planned on O$_2$.

The choice of the oxygen molecule was motivated by the simplicity of this system which makes the interpretation of the results easier. The 0–0 band of the $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ system of $^{16}$O$_2$ spectra around 762 nm was investigated. The observed transitions in this region are weak magnetic dipole transitions with an absorption coefficient of $10^{-6}$ cm$^{-1}$. However, the lines are narrow and well isolated, and high sensitivity laser spectroscopy detection methods can be used.

In [31], the laser source was a distributed-feedback (DFB) diode laser emitting 5 mW cw in a single mode. The emission wavelength could be varied between 760 nm and 762 nm by changing the temperature of the laser. A part of the light was sent to a 7-digits wavelength-meter and to a temperature-stabilized Fabry–Perot interferometer which provided a stable frequency marker. The change of the laser frequency was measured to be less than 20 MHz in a time of 100 s. The absorption cell was a White-type multipass cell. The absorption path was 100 m. A 10 cm focal-length lens focused the laser light emerging from the cell into a Si photodiode-preamplifier. In this experiment, a low-frequency wavelength-modulation detection technique was used. The laser frequency was modulated at a frequency $f = 40$ kHz by adding a modulation to the bias injection current of the diode. The output of the photodetector was sent to a lock-in amplifier and demodulated at a frequency of 2f in order to increase the detection sensitivity and to reduce a background signal due to the change of the laser intensity during the frequency scan. The output signal of the lock-in was sent to a digital oscilloscope and to a personal computer for the data acquisition. In order to improve the signal-to-noise ratio, the signal was averaged over several scans of the laser frequency.

The sensitivity achieved with the apparatus described above was high enough to observe, in addition to the lines of $^{16}$O$_2$, also those of the $^{16}$O$^{18}$O and $^{16}$O$^{17}$O molecules, with a total pressure in the cell as low as a few mbar. Historically, the detection of these weak lines in the atmospheric oxygen spectra led to the identification of the $^{16}$O and $^{17}$O isotopes of oxygen [27,33]. These spectra are interesting for two reasons. First, they provide a striking example of the effect of the distinguishability of nuclei: in $^{16}$O$^{17}$O spectra, for example, the lines starting from even rotational states can only be observed because the two nuclei in the molecule differ by one neutron. Second, because of the small natural abundance of these isotopes ($^{16}$O = 0.2%, $^{17}$O = 0.04%), their weak lines provided an accurate test of the sensitivity of the apparatus, which is particularly important in an experiment leading to a null result.

As discussed above, the purpose of this experiment was to set an upper limit to the intensity of possible absorption lines starting from exchange-antisymmetric states, with respect to the intensity of the normal transitions of $^{16}$O$_2$ involving symmetric states. The expected position of the missing transitions was calculated, with an uncertainty of less than 300 MHz, assuming the same Hamiltonian as for molecules in allowed states and using the data available in the literature for the relevant molecular parameters [34]. The following transitions were searched for: $^8$R(2) at 761.6740 nm, $^8$Q(2) at 761.5626 nm, $^8$R(4) at 761.3891 nm (vacuum wavelengths). The signal was recorded as the laser frequency was scanned across the expected position of the missing lines. The total O$_2$ pressure in the cell was 200 Torr. The absorption signal for the observed lines were recorded for comparison. In this case, the pressure in the cell was reduced to 5 Torr in order to avoid a broadening of the line due to the optical depth of the sample. The laser modulation width was adjusted in order to keep the same value of modulation index. The spectra recorded in this work showed no evidence of anomalous lines. By comparing the noise level with the intensity of the observed lines, an upper limit can then be deduced for the intensity of forbidden lines with respect to the intensity of observed lines. After scaling the recorded signals for the different values of the pressure in the cell, and taking into account the correction due to the pressure broadening of the lines, an upper bound of $\beta^2/2 \leq (5 \pm 2) \times 10^{-7}$ was set to a possible violation of the expected symmetry for $^{16}$O nuclei.

A similar result was obtained in [32]. Transitions in the same $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ band of $^{16}$O$_2$ were investigated. The apparatus was based on a tunable diode laser source and a 4 m long absorption path. A low-frequency wavelength modulation and a 2f demodulation detection scheme was used. The missing line searched for was $^8$Q(2) [35]. A limit $\beta^2/2 \leq 10^{-6}$ was obtained.

Experiments on $^{16}$O$_2$ were later reported in [36,37]. In [36], a cavity-ring-down spectroscopy method was used to perform a broad investigation of O$_2$ spectra including less abundant isotopes and detecting also electric quadrupole lines. Although the detection sensitivity was not high enough to improve the limit set in [31], this work provided a check of previous results. A significative improvement in sensitivity was obtained in [37] using a high-finesse optical cavity as absorption cell, with an equivalent absorption length of ~1 km, and a radio frequency...
detection scheme. This allowed to reach a very high detection sensitivity, comparable to that achieved in [38] in the investigation of electric quadrupole lines of O$_2$ in the sunset spectrum of the Earth’s atmosphere. A limit $\beta^2/2 \leq 5 \times 10^{-8}$ was set, which is the best value obtained so far with experiments on $^{16}$O$_2$. In this experiment, the sensitivity was mainly limited by technical factors and further improvements can be obtained with this method. A different method that would allow, in principle, to reach extremely high sensitivity in the detection of molecules in “wrong-symmetry” states is based on resonant ionization spectroscopy. An experiment is in progress [39]. The possibility of extending the experiments to a search of missing lines in the spectra of $^{18}$O$_2$ was discussed in [40].

3.3.2. Experiments on $^{12}$C-$^{16}$O$_2$. The most accurate test on $^{16}$O nuclei was performed by investigating the vibrational spectrum of the $^{13}$C$^{16}$O$_2$ molecule [41]. The CO$_2$ molecule has the same symmetry properties of O$_2$ but, since it is triatomic, it has strong active vibrational bands in the infrared which are lacking in O$_2$ spectra. In particular, the intensity of the 12$^1$–00 combination band around 2 $\mu$m, investigated in [41], is more than two orders of magnitude larger than the electronic transitions of oxygen previously investigated; the absorbance of a given population is correspondingly larger and this results in an increased detection sensitivity. Since the ground electronic wavefunction of the CO$_2$ molecule is symmetric in the exchange of the two $^{16}$O nuclei, the rotational wavefunction in the ground vibrational state must be symmetric and only even values for the rotational quantum number $J$ are allowed. The R-branch, for example, should then be composed only of $R(2J)$ transitions.

The position of the missing transitions was calculated from the molecular parameters [42] with an uncertainty smaller than 50 MHz. Only two lines were investigated, the others being too close to transitions belonging to hot bands or rare isotopes. The chosen transitions were the R(25) at 2.001790 $\mu$m and the R(33) at 2.000015 $\mu$m.

An InGaAsP distributed-feedback (DFB) diode laser was used as laser source, emitting on a single mode around 2 $\mu$m, with an output power of 7 mW. The intensity of the observed lines was preliminarily measured by a direct absorption scheme, on a relatively short pathlength (20–80 cm) in a single-pass cell. For each transition, the line profile was recorded for a set of CO$_2$ pressures and integrated, in order to extract the line intensity $S$. The following step consisted in the measurement of the intensity of selected weak transitions in the region of the missing lines; this provided an accurate scaling factor to compare the intensity of allowed and missing transitions. This intermediate measurement was performed with a 20 m Herriot-type multipass cell, by means of direct absorption and two-tone frequency modulation techniques.

The central part of the experiment was a high-sensitivity search for the missing lines, using a 130 m pathlength. A balanced two-tone frequency modulation technique was used. The modulation frequencies were (1300±3.5) MHz, and the detection was performed at 7 MHz. The effective detection bandwidth could be reduced by averaging a large number of scans. The maximum acquisition time was 10 minutes, corresponding to approximately 500 scans, limited by a slow drift of the laser emission frequency with respect to the absorption profiles. The CO$_2$ pressure in the cell was set to 30 Torr, corresponding to the maximum sensitivity for this apparatus. The two-tone frequency modulation signal consisted of various replicas of the absorption profile, spaced by 1300 MHz, with intensities scaling as a function of the modulation index. Such replicas were used to further scale the intensity measurement, down to the noise level. A bound of $\beta^2/2 \leq (2.1 \pm 0.7) \times 10^{-9}$ to the relative population of the forbidden states was deduced in this work. This experiment gives at present the most stringent test of the spin-statistics connection for $^{16}$O nuclei ([9] for very recent results, see contribution by G. Modugno et al. in [1]).

It is worth mentioning that in this experiment, several transitions of medium intensity ($S = 10^{-28} - 10^{-25}$) were observed which are not assigned in the literature. Most of them could be grouped in three different bands, and all the experimental observations about the Doppler width, pressure broadening coefficient and the spacing between the lines, seemed to assign them to a symmetric isotope of CO$_2$. A systematic investigation of the dependence of the intensity of these lines on the gas temperature allowed to exclude, however, any connection with symmetry-violating states.

3.3.3. Experiments on polyatomic molecules and test of the symmetrization postulate. An interesting prospect is the investigation of spectra of molecules containing more than two identical nuclei. Most of the experiments performed so far involve only two identical particles, therefore providing a test of the spin-statistics connection. In order to search for possible violations of the symmetrization postulate of quantum mechanics, systems including more than two identical particles should be considered. As discussed above, in this case possible symmetries do not reduce to the completely symmetric and antisymmetric cases. Molecules offer indeed the possibility of investigating more and more complex structures and, as for the experiments performed on O$_2$ and CO$_2$, high detection sensitivity can be achieved by laser spectroscopy methods. The interest of experiments on molecules including more than two identical nuclei as tests of the symmetrization postulate was first mentioned in [41] and discussed in [43]. A good candidate for this experiment is OsO$_4$, a highly symmetric molecule with up to four identical spin-0 nuclei. In spite of the higher complexity of the spectrum with respect to the simpler molecules investigated previously, high resolution and high sensitivity spectroscopy schemes have been developed, especially in the region around 10 $\mu$m which is of metrological interest. The good knowledge of molecular parameters makes it simpler to find the position of the relevant transitions and to separate them from spurious signals. In particular, transition frequencies can be singled out that would represent a signature of a violation of the symmetrization postulate. The expected detection sensitivity is expected to be comparable to that achieved in previous tests on molecules. Another possibility, based on the investigation of molecules with three identical nuclei such as SO$_2$ and NH$_3$, was studied in detail in [44]. An experiment on OsO$_4$ is in progress and preliminary results were presented by Ch. Borda and Ch. Chardonnet in [1].
4. Conclusions

Several experiments confirm the validity of the spin-statistics connection for various types of particles to a high level of accuracy. In particular, spectroscopic tests on molecules provide an upper bound to a possible violation of the expected symmetry for $^{16}$O nuclei. The best results published so far are $\beta^2/2 \leq 5 \times 10^{-8}$ from spectroscopy of O$_2$ and $\beta^2/2 \leq 2 \times 10^{-9}$ from spectroscopy of CO$_2$. This provides a proof of the general formalism of quantum mechanics and can be extended also to different particles. In a recent paper [45], the results obtained in [41] for nuclei were used to set a bound on possible violations of the Pauli exclusion principle for nucleons and for quarks.

Spectroscopic tests can be further improved and extended to new systems: the detection sensitivity can be increased, for example, by reducing the technical noise, by increasing the absorption pathlength, or by selecting stronger transitions. The fundamental vibrational band of CO$_2$ around 4.3 $\mu$m, which is about two thousand times stronger than the one at 2 $\mu$m investigated so far, can provide a significative increase of sensitivity. An increase in the detection sensitivity could also be obtained by a resonant- ionization-spectroscopy detection scheme. Similar tests can be performed on other nuclei as, for example, $^{18}$O.

On the other hand, not many experiments have really tested the validity of the symmetrization postulate with high precision. Experiments on molecules including more than two identical nuclei should allow to test the validity of this fundamental postulate of quantum mechanics with an accuracy comparable to that achieved in the spectroscopic tests of the spin-statistics connection reviewed in this paper.

References

35. See note in [36].