The "chain of symmetry groups" concept in the theory of molecular spectra

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I. INTRODUCTION

Because a molecule is a complex many-particle system, perturbation theory is the main working method used for seeking analytical solutions for the stationary states of molecules. One arrives at the zero order approximation by constructing a series of increasingly crude models, each embedded in the preceding one, until it becomes possible to obtain an exact solution of the model problem. Each model has certain symmetry properties which are specified by its symmetry group. For example, in the Born–Oppenheimer approximation the symmetry of the intramolecular motion at sufficiently small deviations from the equilibrium position is characterized by the geometric symmetry group of the equilibrium configuration of the molecule, while in the zero order approximation the symmetry of rotational motion of the molecule is determined by the symmetry of the rigid top, etc. As long as one is working in the framework of a single model there are no particular problems with the analysis of the symmetry properties. However, the situation is considerably more complicated if one attempts to analyze the evolution of the symmetry properties of the intramolecular motion (i.e., the evolution of the symmetry properties of the wave functions and the operators for the physical quantities) from one model to another. The latter analysis, as we shall see, is altogether indispensable for any kind of complete analysis. At present there is no generally accepted idea for solving this problem.

The most widespread approach is based on the use of the complete nuclear permutation–inversion (CNPI) group of the molecule. A detailed exposition of this approach is given in the monograph by Bunker.[1] The CNPI group is defined as the direct product of the group of permutations of identical nuclei of the molecule and the group of inversion of the spatial coordinates of all the particles of the molecule (i.e., all the nuclei and electrons) about its center of mass. Because of the limited accuracy of the experimental data and also to simplify the treatment, one ordinarily selects from the CNPI group only the so-called "feasible" elements (those relating to transformations of the molecule that correspond to a zero barrier or a barrier which is sufficiently small compared to the dissociation energy), which form the molecular symmetry (MS) group. It is assumed that: 1) the CNPI group (and, in the majority of cases, the MS group) includes all the symmetry elements necessary for characterizing the problem of stationary states of the molecule in a specified electronic state; 2) the action of the elements of the CNPI or MS group is specified in the configuration space of any approximate model and leaves invariant any model Hamiltonian; 3) to determine the correspondence between irreducible representations of the CNPI or MS group and the stationary states of the molecule it is necessary to write the zero order wave functions, to calculate the action of the elements of the CNPI or MS group on these functions, and to decompose the representation thus obtained into irreversible representations.

The chain of symmetry groups concept is actually a generalization of the approach to analysis of the symmetry properties of molecular states that was laid out in the book by Landau and Lifshitz.[2] The generalization concerns primarily the extension to the case of nonrigid molecules. Interestingly, the main reason for introducing the CNPI concept in the pioneering paper by Longuet–Higgins[3] was because of the impossibility of making this extension. The essential idea of the chain of symmetry groups approach is as follows. As we have said, in the analytical solution of the problem of the stationary states of a molecule by perturbation theory methods, a chain of embedded models arises. It is clear that in a quantitative calculation the transition between successive models must be continuous, as is expressed in the possibility of describing the difference between them in the form of an expansion in a small parameter. In spite of this requirement, the symmetry groups of the models used may be different, i.e., the symmetry can change abruptly. This is because the approximate model is based on a definite physical idea and can therefore carry additional qualitative information about the molecule under study. Since this information is contained in the symmetry group of the approximate model, this group plays a clear independent role in relation to the symmetry groups of the more rigorous models. All these groups are joined into a chain by the matching conditions, which identify in the symmetry groups of successive models the equivalent elements according to which the solutions of the Schrödinger equation must transform identically.

There are extremely significant philosophical differences between these two concepts for analysis of the symmetry properties in the theory of molecular spectra. This circumstance has even led to papers concerning the errors in Ref. 2 in regard to these questions (see Ref. 4, for example[1)]). In the present paper we discuss: 1) the present state of development of the chain of symmetry groups concept; 2) a number of advantages that this concept has in comparison with the CNPI-group approach for the analysis of both rigid and nonrigid molecules.

2. CLASSIFICATION OF THE STATIONARY STATES OF RIGID MOLECULES

In the analysis of the symmetry properties of a molecule an important factor is the number of its energetically

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equivalent equilibrium configurations, which are separated by a nonzero energy barrier. We will call these configurations independent. A molecule is rigid if it has only one independent configuration. For the sake of specificity, in this Section we will use the BF_3 molecule as an example.

In a rather rigorous formulation of the problem we can write the symmetry group as $\pi_3 \times C_i$, which coincides with the CNPI group[2)] (the use of the symmetry group C_i is associated with neglect of the weak interactions).[2] The fluorine nuclei are fermions, and the complete wave function, in neglect of the hyperfine interaction involving the nuclear spin, is represented in the form of a contraction of the coordinate and spin parts, which transform according to mutually dual Young diagrams.[3)] Since the spin of the fluorine nucleus is equal to 1/2, the dimension of the spin space is 2 and only the following spin Young diagrams are allowed:

$$[\tilde{\lambda}_{\text{spin}}]:[3],\ [21]. \tag{1}$$

$$3/2\ 1/2\,.$$

The numbers under the spin diagrams give the values of the total nuclear spin of the fluorine nuclei for each diagram. As a result, the allowed coordinate Young diagrams have the form

$$[\lambda_{\text{coord}}]:[1^3],\ [21]. \tag{2}$$

To solve the problem of the stationary states of the molecule we make a number of further approximations, the first of which is the Born–Oppenheimer (BO) approximation. Only in this approximation for a given electronic state does the concept of an interaction potential of the nuclei arise, and hence the concept of an equilibrium configuration of the molecule. Information about the symmetry of the spin field for sufficiently small deviations from the equilibrium position is carried by the geometry of the equilibrium configuration and is contained in the point (geometric) group of the molecule. This information is not contained in the group π_3. As a result, those configurations of the nuclei which are obtained by their small displacements from the equilibrium position and differ in relation to the force field coincide from the standpoint of permutations of identical nuclei. In the general case the point group of a molecule can be homomorphically mapped onto a subgroup of the group of permutations of identical nuclei.[7,8] Homomorphism arises and plays a fundamental role for linear and planar molecules. In this case the only allowed representations of the point group are those which behave identically with respect to its elements which are homomorphically mapped into the same one element of the permutation group. Representations excluded for this reason will be called geometrically forbidden, since their exclusion is based on the geometry of the equilibrium configuration of the molecule.

For the BF_3 molecule the equilibrium configuration is planar and corresponds to the point group[9]

$$D_{3h} = C_{3v} \times C_S\,.$$

The joining of the groups π_3 and D_{3h} is presented in Table I. Since the multiplet A_1' corresponds to a forbidden coordinate Young diagram, we obtain the following allowed multiplets:

TABLE I. Joining of the groups π_3 and $D_{3h} = C_{3v} \times C_S$ for finding the allowed multiplets of the BF_3 molecule.

Classes of π_3	$\{1^3\}$	$\{1^3\}$	$\{3\}$	$\{3\}$	$\{12\}$	$\{12\}$
Classes of D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3\sigma_v$	$3U_2$
Irreducible representations of π_3	[3]	$[1^3]$	...	...	[21]	...
Irreducible representations of D_{3h}	A_1'	A_2'	A_1''	A_2''	E'	E''

$$4A_2'^{(\pm)},\ 2E'^{(\pm)}. \tag{3}$$

The numbers in front of the multiplet notation give its nuclear statistical weight, and the signs ($\pm$) correspond to the behavior of the complete coordinate wave function under the inversion transformation i (group $D_{3h} \times C_i$).

In the next, zero order, approximation the motion of the nuclei is separated into independent vibrational and rotational motions, which we describe by the harmonic oscillator and rigid top models. The symmetry group of the vibrational problem is formally the same as the point group, but its elements act only on the vibrational coordinates, i.e., on small nuclear displacements. The symmetry group of the rotational problem is that of the rigid top. It has only purely rotational elements, which act on the Euler angles. In the present case it is the group D_∞. To construct a classification it is necessary to know from which of the electronic, vibrational, and rotational functions obtained in the zero order approximation that one can obtain the allowed multiplets. The joining of the symmetry groups in the BO approximation with the symmetry groups of the zero order approximation is of the form[8]

$$(\Gamma_{\text{mult}})_{D_{3h} \times C_i} = (\Gamma_{\text{el}})_{D_{3h}} \times (\Gamma_{\text{vib}})_{D_{3h}} \times (\Gamma_{\text{rot-in}})_{D_{3h} \times C_i}; \tag{4}$$

here Γ_{el} and Γ_{vib} are the irreducible representations of the group D_{3h} according to which the wave functions of the electronic and vibrational motions transform; $\Gamma_{\text{rot-in}}$ is the irreducible rotation–inversion group. The correlation between the rotational irreducible representations of the symmetry group of the symmetric top D_∞ and the rotation–inversion representations of the group $D_{3h} \times C_i$ (see Table II) is obtained by associating these groups according to their common rotation subgroup D_6. Here the representation D_{3h} pertains to the rotational function and the representation C_i pertains to the multiplet; this is indicated by the arrow in expression (4). The association of the groups $D_{3h} \times C_i$ and D_∞ is based on the following circumstances: 1) the behavior with respect to the electronic–nuclear operation i has physical meaning only for a multiplet, i.e., this symmetry element characterizes the total coordinate motion; 2) the difference in the use of the nuclear and electronic–nuclear symmetry operations takes into account the fact that only a portion of the total angular momentum, characterized by the coordinate motion in the BO

TABLE II. Correlation between the rotation representations of the group D_∞ and the rotation–inversion representations of the group $D_{3h}\times C_i$.

D_∞	D_6	$D_{3h}\times C_i$
A_1	A_1	$A_1'^{(+)}$, $A_2''^{(-)}$
A_2	A_2	$A_2'^{(+)}$, $A_1''^{(-)}$
E_1	E_1	$E''^{(+)}$, $E'^{(-)}$
E_2	E_2	$E'^{(+)}$, $E''^{(-)}$
E_3	B_1+B_2	$A_2''^{(+)}$, $A_1'^{(-)}+A_1''^{(+)}$, $A_2'^{(-)}$
E_4	E_2	$E'^{(+)}$, $E''^{(-)}$
E_5	E_1	$E''^{(+)}$, $E'^{(-)}$
E_6	A_1+A_2	$A_1'^{(+)}$, $A_2''^{(-)}+A_2'^{(+)}$, $A_1''^{(-)}$

approximation, goes over into the angular momentum of the rigid top. For a linear molecule this, in particular, leads to the automatic exclusion of states with $J<l$ (see Ref. 7), where J and l are the quantum numbers of the total and vibrational angular momenta.

Figure 1 gives a classification of the rotational levels in a completely symmetric vibronic state of the BF_3 molecule. Here we must emphasize the following. The spatial inversion element i plays a double role. First, it characterizes the symmetry of the space, and second, it can mix the independent configurations of the molecule among themselves. In the general case the presence of this mixing gives rise to the so-called inversion doubling of the levels. It is well known that such doubling is absent for linear and planar molecules. In the approach considered here this doubling is automatically forbidden for such molecules by virtue of the presence of a homomorphism of the point group to the group of permutations of identical nuclei. Nevertheless, all the states of these molecules have a completely determined behavior with respect to the operation i since the symmetry properties of the space are preserved.

Let us consider the selection rules for the example of electric dipole transitions. For the strongest transitions of this class, which go without a change in symmetry of the spin state, the dipole moment transforms according to the completely symmetric coordinate Young diagram of the group π_3. From Table I we find that in the BO approximation for the dipole moment, only the representation A_1' is allowed. When the behavior with respect to the operation i is taken into account, we have $A_1'^{(-)}$. As a result, the selection rules are written in the form

$$A_2'^{(+)}\leftrightarrow A_2'^{(-)},\ E'^{(+)}\leftrightarrow E'^{(-)}. \tag{5}$$

Let us conclude this Section with a brief discussion of the most salient features of the analysis of the symmetry properties of the stationary states of the BF_3 molecule when the CNPI concept is used. In this case it is necessary first of all to specify the action of the elements of the group $\pi_3\times C_i$ on the variables of the configuration space of the zero order approximation. Strictly speaking, this procedure is incorrect, since the symmetry transformations of the rigorous problem are not defined in the configuration space of the zero order approximation, and their formal definition is multivalued. The latter circumstance is due to the fact that this definition depends on the reconciliation of the behavior of the axes of the molecule coordinate system (MCS) under the action of the elements of the group $\pi_3\times C_i$, i.e., it is necessary to specify the relations

$$\vartheta'=g_k^{\vartheta},\ g_k\in\pi_3\times C_i, \tag{6}$$

where ϑ, ϑ' is the set of three Euler angles that determine the orientation of the MCS relative to the laboratory coordinate system (LCS) before and after the transformation g_k. The choice of operators g_k is not restricted in any way

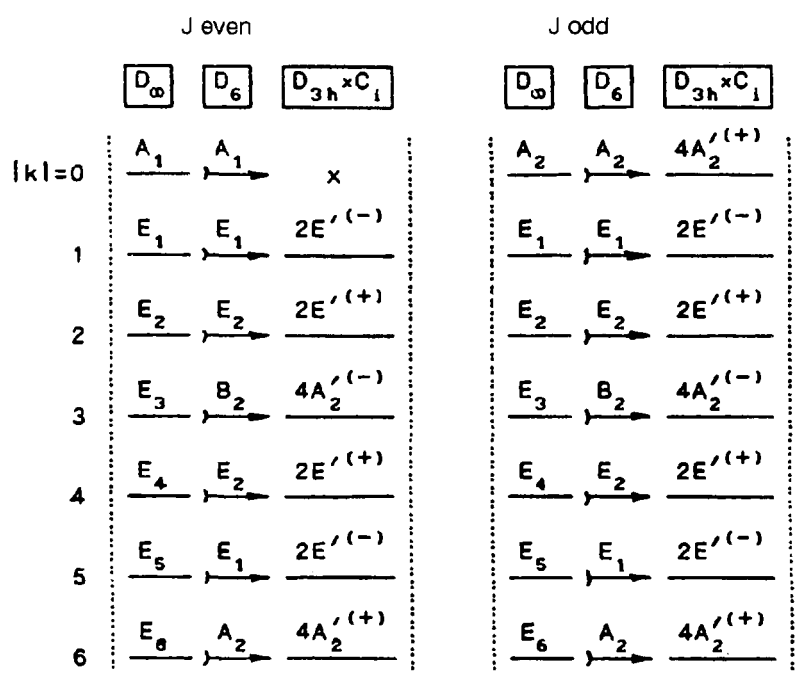

FIG. 1. Classification of the rotational levels of the BF_3 molecule in a completely symmetric vibronic state. The symbol × signifies that the state is forbidden. We note that there is no splitting of the levels with $|k|=3n$ because the multiplet A_1' is forbidden.

TABLE III. Rotations of the molecular coordinate system (MCS) corresponding to the choice made in Ref. 1 as to the action of the elements of the CNPI group on the Euler angles; here $\{...\}^* = \{...\} \times E^*$, where E^* is the analog of the operation i; R_n^α is a rotation through an angle α about the axis n (the z axis coincides with the threefold axis of the group D_{3h}); for each class of the CNPI group the rotation is given for just one element as an example; also indicated are the elements of the point group D_{3h} that represent, for the chosen rotations of the MCS, the action of the elements of the CNPI group on Φ_{vib} and Φ_{el}.

CNPI	$\{1^3\}$	$\{3\}$	$\{12\}$	$\{1^3\}^*$	$\{3\}^*$	$\{12\}^*$
Rotation of the MCS	R^0	$R_z^{2\pi/3}$	R_x^π	R_z^π	$R_z^{-\pi/3}$	R_y^π
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$

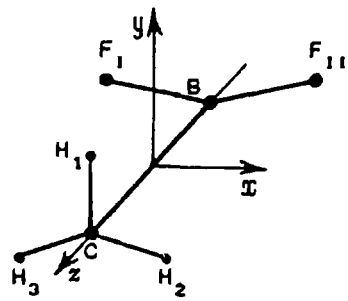

FIG. 2. Equilibrium configuration of the CH_3BF_2 molecule.

save for reasons of convenience. As an example, let us consider the inversion transformation i. In Ref. 10 it was proposed to use the relation[4)]

$$\vartheta' = \vartheta \text{ and , accordingly, } i\Phi_{rot} = \Phi_{rot}. \quad (7)$$

An idea that is often used is to perform a rotation of the MCS in order to compensate completely or partially the changes that occur in the equilibrium position of the nuclei in this coordinate system as a result of the inversion transformation. Complete compensation can be achieved only for molecules with a linear or planar equilibrium configuration. For linear molecules in this case we have the well-known relation[2]

$$i\Phi_{rot} = (-1)^J \Phi_{rot}. \quad (8)$$

It is the idea of complete compensation that underlies the use of reconciliation (6) in Ref. 1 in an analysis of the action of all the operations of the CNPI group for the BF_3 molecule. This allows one to represent all the symmetry transformations in the MCS as displacement transformations for small displacements from the equilibrium positions. The results are given in Table III, which also indicates the elements of the point group D_{3h} that act only on small displacements and represent the action of the elements of the CNPI group on Φ_{vib} and Φ_{el}. It should be emphasized that the element E^* (the analog of i) is used to describe reflection in the plane of the molecule. This is incorrect, since i is a symmetry element of the space and does not pertain to the symmetry of the equilibrium configuration. But when working in the CNPI group one does not have recourse to any other approach, since reflection in the plane of the molecule is impossible to describe even formally by a permutation of the nuclei lying in this plane.[5)]

Table III enables one to specify uniquely the action of the elements of the group $\pi_3 \times C_i$ on the variables of the configuration space of the zero order approximation. It is then necessary to evaluate their action on the wave functions of the zero order approximation and to decompose the representation thus obtained into irreducible representations. The result of this rather unwieldy scheme of construction is a classification of the stationary states of the molecule that is in the main equivalent to that which we obtained using the chain of symmetry groups concept. The most important difference between them is that the group $D_{3h} \times C_i$, which characterizes the symmetry in the BO approximation, is wider than the CNPI group, and one loses part of the information in working with the latter (there is no explicit information about the behavior of the wave functions under the operation of spatial inversion i).

Reviewing what was said in this section, we can reach the following important conclusion. In the chain of symmetry groups approach the concept of symmetry is "primary" in the sense that information about explicit form of the solutions of the Schrödinger equation is not used. In the CNPI-group approach, analysis of the explicit form of the solutions is an essential part, and therefore the concept of symmetry is "secondary."

3. CLASSIFICATION OF THE STATIONARY STATES OF NONRIGID MOLECULES

Classification of the molecular states on the basis of the CNPI group was first proposed in Ref. 3. The main reason for introducing this idea was the impossibility of extending the approach using the geometric symmetry group of the problem in the BO approximation to the case of nonrigid molecules. In this Section we discuss a different point of view, which was developed in Refs. 8, 11, and 12.

As a rather simple first step we analyze the molecule CH_3BF_2. If we neglect the internal rotation, the chain contains the following symmetry groups: 1) the group of permutations of identical nuclei, $\pi_3 \times \pi_2$; 2) the point group C_S (the proposed equilibrium configuration is shown in Fig. 2); 3) the rotation group D_2. Since the spin of the H and F nuclei is equal to 1/2, the dimension of the spin space is 2 for both kinds of nuclei. Determining the allowed coordinate Young diagrams of the group $\pi_3 \times \pi_2$ and joining it with the group C_S (all the correlation tables required for a rigid molecule are given in Table IV), we get the following allowed multiplets:

$$(12+6+2)A', \quad (6+4+2)A''. \quad (9)$$

These multiplets can be constructed from the zero order wave functions according to expression (4) with the group D_{3h} replaced by C_S. The correlation between the irreducible representations of the symmetry group of the asymmetric top D_2 and the rotation–inversion representations of the group $C_S \times C_i$ are obtained by associating these groups according to their common rotation subgroup C_2. Figure 3

TABLE IV. Correlation tables used in classifying the stationary states of a rigid CH_3BF_2 molecule.

$\pi_3 \times \pi_2$		C_S
$[1^3] \times [1^2]$		A'
$[21] \times [1^2]$		$A'+A''$
$[1^3] \times [2]$		A''
$[21] \times [2]$		$A'+A''$
D_2	C_2	$C_S \times C_i$
A	A	$A'^{(+)}$, $A''^{(-)}$
B_1	B	$A'^{(-)}$, $A''^{(+)}$
B_2	B	$A'^{(-)}$, $A''^{(+)}$
B_3	A	$A'^{(+)}$, $A''^{(-)}$

shows the classification of the rotational levels of the CH_3BF_2 molecule in a completely symmetric vibronic state. The electric dipole selection rules in the BO approximation are of the form

$$(\Gamma_{\text{mult}})_{C_S}{}^{(+)} \leftrightarrow (\Gamma_{\text{mult}})_{C_S}{}^{(-)}.$$

Table V shows how the class of the rotational electric dipole transitions for the ground vibrational state changes for different models. The symbol b denotes the "forbidden" transitions (forbidden in the zero order approximation) that arise for a rigid molecule in the BO approximation.[13]

We now take into account the presence of internal rotation about the chemical bond linking the carbon and boron atoms in the CH_3BF_2 molecule. It is clear that this circumstance is not reflected in the symmetry group of the rigorous problem. The situation is different for the geometric symmetry of the force field in the BO approximation: now the point group is insufficient for characterizing this symmetry. It is necessary to construct a wider geometric group in order to take into account the symmetry of the

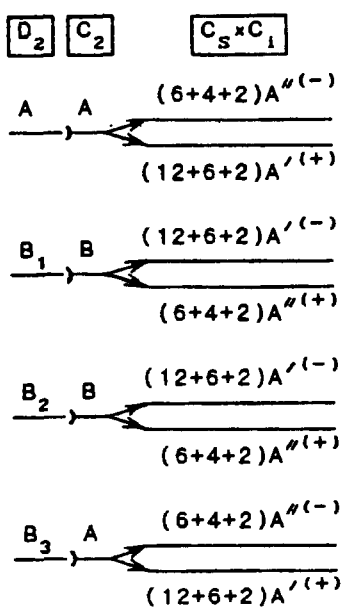

FIG. 3. Classification of the rotational levels of a rigid CH_3BF_2 molecule in a completely symmetric vibronic state.

TABLE V. Selection rules for the rotational electric dipole transitions of the CH_3BF_2 molecule. a represents transitions between rotational levels in the rigid top approximation; a,b are transitions in the BO approximation without allowance for the internal rotation; a,b,c are transitions in the BO approximation with allowance for the internal rotation.

	A	B_1	B_2	B_3
A	c	a	b	c
B_1	a	c	c	b
B_2	b	c	c	a
B_3	c	b	a	c

motion of the nuclei in transitions from one configuration to another. The expanded group must contain the point group of the molecule as a subgroup, and, in addition, we require that all of its elements as before leave one geometric point (the center of mass) invariant. This is because the position of the center of mass remains unchanged for any intramolecular motions. Following Ref. 8, where the concept of an expanded geometric group was first introduced, we shall call it the expanded point group. Thus there appears yet another symmetry group, which we must join on the one hand with the group of permutations of identical nuclei and on the other with the point group.

Specifically for the molecule CH_3BF_2 the expanded point group has the form $G_{24}=C_{3v}\times C_{2v}$, where the elements of the groups C_{3v} and C_{2v} act on the spatial coordinates of the nuclear structures of CH_3 and BF_2, respectively. For determining the allowed multiplets of the expanded point group one can separate the joining of the groups $\pi_3\times\pi_2$ and G_{24} into the joining of π_3 with C_{3v} and π_2 with C_{2v}. As a result, we have the following allowed multiplets for a nonrigid molecule:

$$4(A_2\times A_1),\ 2(E\times A_1),\ 12(A_2\times B_1),\ 6(E\times B_1). \tag{10}$$

Finally, by joining the groups G_{24} and C_S (all the additional correlation tables for the nonrigid molecule CH_3BF_2 are given in Table VI), we obtain a complete picture of the splittings with allowance for the internal rotation; this is

TABLE VI. Additional correlation tables used for taking into account the internal rotation in the CH_3BF_2 molecule.

C_S	$G_{24}=C_{3v}\times C_{2v}$
A'	$A_2\times B_1$, $E\times A_1$, $E\times B_1$
A''	$A_2\times A_1$, $E\times A_1$, $E\times B_1$
C_2	G_{12}
A	A_1, B_2, E_1, E_2
B	A_2, B_1, E_1, E_2
G_{12}	$G_{24}\times C_i$
A_1	$(A_2\times A_1)^{(-)}$
A_2	$(A_2\times A_1)^{(+)}$
B_1	$(A_2\times B_1)^{(-)}$
B_2	$(A_2\times B_1)^{(+)}$
E_1	$(E\times B_1)^{(\pm)}$
E_2	$(E\times A_1)^{(\pm)}$

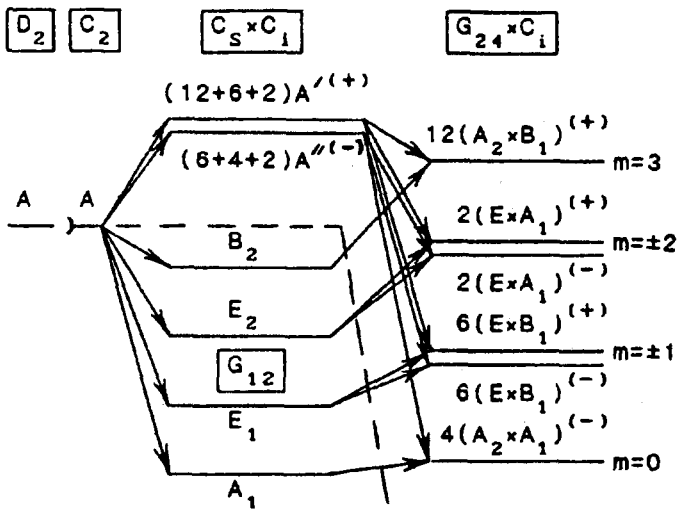

FIG. 4. Classification of the rotational levels of the CH_3BF_2 molecule in a completely symmetric vibronic state with allowance for internal rotation.

shown in Fig. 4 for a completely symmetric vibronic state. Also shown in Fig. 4 is a grouping of the splittings according to their order of magnitude. Here it was taken into account that the most strongly split levels are those which correspond to different representations of the purely rotation subgroups of the symmetry groups used in the constructing the classification. Therefore, the nuclear rotation subgroup of the group $G_{24}\times C_i$ was considered.[6] This subgroup, which is denoted G_{12}, is isomorphic with the group D_6. As a result, we separate out those level splittings to which there is a contribution from the internal rotation. Also given in Fig. 4 are the quantum numbers m corresponding to the torsional moment for the case of the free internal rotation of a rigid rotor. These quantum numbers are easily obtained from the joining of the group G_{12} with the symmetry group C_∞ of the free rigid rotor.

Analysis of the electric dipole selection rules leads to a new class of "forbidden" rotational transitions (see Table V). These transitions are due to mixing of different equilibrium configurations of the molecule as a result of the internal rotation. Therefore, in Ref. 8 it was proposed to call them configuration-forbidden transitions.

Significantly more interesting from a technical standpoint is the treatment of the ethane molecule $^{12}C_2H_6$ in Ref. 8. Here the point group $D_{3d}=C_{3v}\times C_I$ has an inversion element I, which mixes two structures of CH_3. This fact leads to an expanded point group $G_{72}=(C_{3v}\times C_{3v})\wedge C_I$, where C_{3v} is the point group of the CH_3 structure and the symbol $\wedge$ denotes the semidirect product.[14] The latter arises because the element I does not commute with the elements of the group $C_{3v}\times C_{3v}$. These two molecules are linked by the circumstance that the expanded point group includes elements that act only on the spatial nuclear coordinates. In general, transitions between energetically equivalent equilibrium configurations of a molecule can be divided into two types: 1) Transitions for which the spatial change in the position of the nuclei is an exchange of places of identical nuclei (exchange transitions). The corresponding symmetry transformations are purely nuclear. 2) Transitions for which the spatial change in the position of the nuclei can occur only with a spatial change of the electronic configuration (nonexchange transitions). The corresponding symmetry transformations are electronic–nuclear.

Thus for a nonrigid molecule the group of permutations of identical nuclei (together with the point group of the molecule) determines only the number of independent energetically equivalent configurations,[7] while classification of the stationary states of a nonrigid molecule depends substantially on the geometry of the transition between these equilibrium configurations, which is specified by the expanded point group. Naturally, the elements of this geometric group by no means always have even a formal analog among the elements of the CNPI group, owing to the possibility of transitions of the second type (nonexchange transitions). This is the main weakness of the CNPI concept for analyzing nonrigid molecules.

As an example of the analysis of nonrigid molecules with transitions of the second type between energetically equivalent configurations, let us consider the family of molecules of the type HAAH (where A=O for hydrogen peroxide and A=S for disulfane). If we neglect the nonrigid motion we have the following symmetry groups in the chain: 1) the group of permutations of identical nuclei $\pi_2\times\pi_2$; 2) the point group $C_2=(E,C_2^{(x)})$ (Ref. 9; the equilibrium configuration is shown in Fig. 5); 3) the rotation group $D_2=D_2^{(1)}=(E,C_2^{(3)},C_2^{(2)},C_2^{(x)})$, where the axes (3) and (2) do not coincide with the axes (z) and (y). In cases when nucleus A has zero spin ($A=^{16}O,^{32}S,^{34}S$) the permutation group can be replaced by π_2 without loss of generality in the subsequent discussion. Determining the allowed coordinate Young diagrams of the group π_2 and joining this group with the group C_2, we find that the allowed multiplets are $1A^{(\pm)}$, $3B^{(\pm)}$. These multiplets can be constructed from the zero order functions according to expression (4) with the group D_{3h} replaced by C_2. The correlation between the irreducible representations of the symmetry group D_2 of the asymmetric top and the rotation–inversion representations of the group $C_2\times C_i$ is obtained by associating these groups according to their

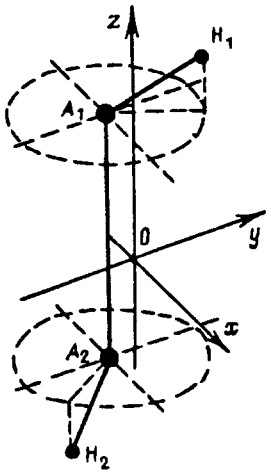

FIG. 5. Equilibrium configuration of the HAAH molecule.

common nuclear subgroup C_2 (all the necessary correlation tables are given in Table VII).

We now take into account the fact that the HAAH molecule has a nonrigid motion involving the tunneling of the AH structures between energetically equivalent positions. Since the center of mass of the molecule does not lie on the chemical bond AA, only a synchronous motion of the AH structures about the axis, toward each other or away from each other, is possible. We stress that in such a motion the nuclei do not exchange places with each other in space. The expanded point group can be represented in the form $G_4=C_2\times C_S$, where $C_S=(E,\sigma^{(x,y)})$, where: 1) the group C_S operates both on the coordinates of the nuclei and on the force field, i.e., on the electronic configuration (in this sense this group is similar to the group C_i); 2) the group G_4 contains elements that do not have analogs in π_2. Both of these features are due to the fact that the nonrigid motion is of the nonexchange type.[8] Joining the groups π_2 and G_4, we obtain the following allowed multiplets of the nonrigid molecule:

$$1(A\times A'),\ 1(A\times A''),\ 3(B\times A'),\ 3(B\times A''). \quad (11)$$

TABLE VII. Correlation of the symmetry groups for the HAAH molecule.

$D_2^{(1)}$	$C_2\times C_i$
A,B_3	$A^{(\pm)}$
B_1,B_2	$B^{(\pm)}$
$D_2^{(2)}$	$G_4\times C_i$
A	$(A\times A')^{(+)},\ (A\times A'')^{(-)}$
B_1	$(B\times A')^{(-)},\ (B\times A'')^{(+)}$
B_2	$(B\times A')^{(+)},\ (B\times A'')^{(-)}$
B_3	$(A\times A')^{(-)},\ (A\times A'')^{(+)}$

The symmetry of the purely rotational motion of the nonrigid HAAH molecule as a whole is characterized by the rotation subgroup of the group $G_4\times C_i$. This rotation subgroup is the same as the group $D_2=D_2^{(2)}=(E,C_2^{(z)},C_2^{(y)},C_2^{(x)})$. Interestingly, the rotation group $D_2^{(1)}$ is not preserved when the nonrigid motion is taken into account, since the ellipsoid of inversion of the rigid top changes its orientation during this motion. More precisely, only one element of the group $D_2^{(1)}$ remains, $C_2^{(x)}$, which then goes into the group $D_2^{(2)}$.

Since the behavior of the wave function with respect to the operations of the group C_S has physical meaning only for a multiplet, we have the following scheme of construction:

$$(\Gamma_{\text{mult}})_{C_2\times C_S\times C_i}=(\Gamma_{\text{el}})_{C_2}\times(\Gamma_{\text{vib}})_{C_2}\times(\Gamma_{\text{rot-conf}})_{C_2\times C_S\times C_i}. \quad (12)$$

The correlation between the rotation representations of the group $D_2^{(2)}$ and the rotation–configuration representations of the group $G_4\times C_i$ is obtained by associating these groups according to their common nuclear rotation subgroup $D_2^{(2)}$. Figure 6 shows the classification of the rotational levels of the nonrigid HAAH molecule in a completely symmetric vibronic state. We note the following. The configurations obtained from the initial configuration with the use of the electronic–nuclear operations i and $\sigma^{(xy)}$ are dependent. However, this does not lead to errors in the use of the group $G_4\times C_i$, since the joining of this group with the groups of the zero order approximation takes this pos-

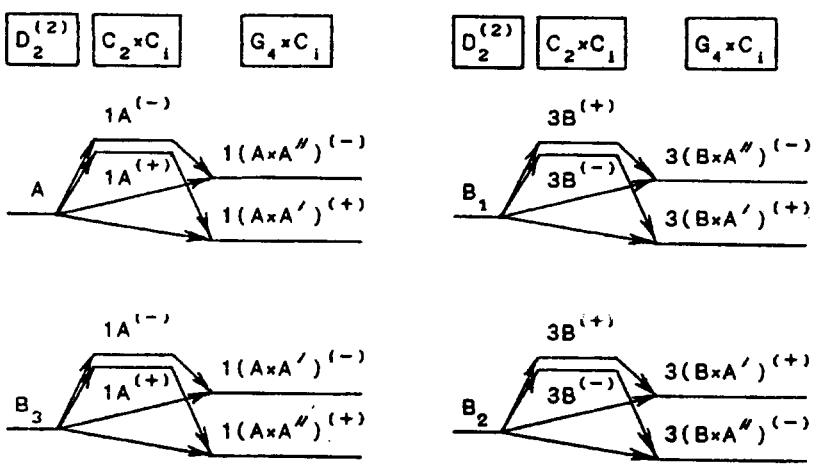

FIG. 6. Classification of the rotational levels of a nonrigid HAAH molecule in a completely symmetric vibronic state.

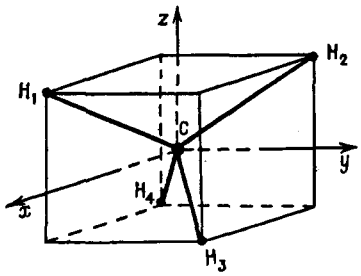

FIG. 7. Equilibrium configuration of the $^{12}CH_4$ molecule.

sibility into account. In Fig. 6 one can clearly see the rather nontrivial correlation between the indices +, − and ′, ″.

To retain the CNPI concept in the analysis of the nonrigid HAAH molecule, an expanded MS group is artificially introduced.[1] As in the case of a linear molecule, this is done for the purpose of obtaining at least formal analogs of all the necessary geometric symmetry elements in the BO approximation. This prescription is not the only possible one. For the nonrigid NH_3 molecule the symmetry operation corresponding to the tunneling of the N nucleus through the plane of the H nuclei is described with the aid of the element E* (the analog of i).[1] Attempts have been made to describe the symmetry element corresponding to nonrigid motion of the second type as some permutation of identical nuclei through an additional rotation of the molecule as a whole.[5] This rotation is to make the equilibrium configurations that are coupled by the nonrigid motion coincident in space. However, as was pointed out in Ref. 11, such a procedure leads to an incorrect additional requirement on the behavior of the wave function during nonrigid motion, stemming from the requirement of a definite transformation of the wave function under the permutation of identical nuclei that is used in describing this motion.

4. QUALITATIVE CONSTRUCTION OF THE OPERATORS FOR THE PHYSICAL QUANTITIES

The chain of symmetry groups concept enables one easily to construct in the required model the operator for any physical quantity characterizing the molecule. The construction of purely rotation operators for the physical quantities (i.e., operators characterizing the coordinate motion of a rigid molecule in a nondegenerate vibronic state) is discussed in Ref. 16, where, in particular, expressions are derived for the corrections to the rotation Hamiltonian due to the presence of interactions in the molecule that are noninvariant with respect to the operation of spatial inversion i. Here we examine the case of rigid molecules by considering as an example the construction of the spin–rotation Hamiltonian of the hyperfine interaction due to the nuclear spin for the methane molecule $^{12}CH_4$.

For the $^{12}CH_4$ molecule the chain has the following symmetry groups: 1) the group of permutations of identical nuclei π_4; 2) the point group T_d (Ref. 9; the equilibrium configuration is shown in Fig. 7); 3) the rotation group R_3. The dynamical variables in the Hamiltonian are the coordinate angular momentum (the coordinate part) and the spins of the H nuclei (the spin part). From the requirement that the spin–rotation Hamiltonian be invariant under transformations of the group π_4, it follows that its coordinate and spin parts must transform according to the same irreducible representation $[\lambda]$ of the group π_4. Then for each such representation in the case of the spin–rotation interaction of the lowest order[9] (with the mnemonic notation JI), one can write the following general expression:

$$H^{(JI)}=P^{[\lambda]}_{rik}J_i l_{k\alpha} \quad p^{[\lambda]}_{ra} I_{a\alpha}; \tag{13}$$

here J_i is a component of the coordinate angular momentum in the MCS, $l_{k\alpha}$ are the direction cosines specifying the orientation of the MCS relative to the LCS (the quantities $l_{k\alpha}$ permit one to represent in the MCS the nuclear spin components determined in the LCS, $I_{a\alpha}$ is a component of the spin of hydrogen nucleus a in the LCS, $P^{[\lambda]}$ and $p^{[\lambda]}$ are constant coefficients, and r is the index of the basis vector of the irreducible representation $[\lambda]$.

The spin part, which depends on the variables $\mathbf{I}_a$ ($a=1, 2, 3, 4$) in the LCS forms a representation of dimension 4, which decomposes into the direct sum of the irreducible representations [4] and [31]. Naturally, only these two representations are possible in expression (13). The interaction corresponding to the completely symmetric spin Young diagram will be called the scalar interaction, and that corresponding to the remaining possible spin diagrams, the tensor interaction. Joining the groups π_4 and T_d, we obtain for the total coordinate part of the Hamiltonian in the BO approximation the following allowed representations: $A_1^{(+)}$ and $F_2^{(+)}$. Here it has also been taken into account that the coordinate part must be invariant with respect to the operation i (the group $T_d \times C_i$). Thus the problem reduces to that of constructing a coordinate part with the required symmetry from purely rotational elements. The solution of this problem can be represented in the form

$$(\Gamma_{\text{coord}})_{T_d\times C_i}=(A_{1\text{el}})_{T_d}\times(A_{1\text{vib}})_{T_d} \times(\Gamma_{\text{rot-in}})_{T_d\times C_i}. \tag{14}$$

The electronic and vibrational parts of the Hamiltonian are absent in this case, and we use for them the representation A_1. The correlation between the rotation representations of the symmetry group R_3 of the spherical top and the rotation–inversion representations of the group $T_d \times C_i$ is obtained by associating these groups according to their common rotation subgroup O. Thus it is necessary to find purely rotational combinations in expression (13) that upon transition to the BO approximation evolve into solutions with symmetry $A_1^{(+)}$ and $F_2^{(+)}$. It is easily found[10] that these combinations must transform according to the representations A_1 and F_2, respectively, of the rotation subgroup O.

The combinations $J_i l_{k\alpha}$ transform according to the tensor representation $U_3 \times U_3$, where U_3 is the three-dimensional representation of the group of unitary

TABLE VIII. Coordinate and spin parts of the Hamiltonian of the spin–rotation interaction of the JI type for the $^{12}CH_4$ molecule in the ground state. The vectors are given for the laboratory coordinate system.

Coordinate part	Spin part
$A_1^{(+)}$: $\mathbf{T}=J_l\mathbf{I}_l$	[4]: $\mathbf{I}=\mathbf{I}_1+\mathbf{I}_2+\mathbf{I}_3+\mathbf{I}_4$
$F_2^{(+)}$: $\mathbf{T}^{(x)}=J_y\mathbf{I}_z+J_z\mathbf{I}_y$	[31]: $\mathbf{I}^{(x)}=\mathbf{I}_1-\mathbf{I}_2+\mathbf{I}_3-\mathbf{I}_4$
$\mathbf{T}^{(y)}=J_z\mathbf{I}_x+J_x\mathbf{I}_z$	$\mathbf{I}^{(y)}=-\mathbf{I}_1+\mathbf{I}_2+\mathbf{I}_3-\mathbf{I}_4$
$\mathbf{T}^{(z)}=J_x\mathbf{I}_y+J_y\mathbf{I}_x$	$\mathbf{I}^{(z)}=\mathbf{I}_1+\mathbf{I}_2-\mathbf{I}_3-\mathbf{I}_4$

transformations.[6] Performing the reduction to the group R_3, we obtain $U_3\times U_3=D^{(2)}+D^{(1)}+D^{(0)}$. Here we are interested in the representations $D^{(2)}$ and $D^{(0)}$, since only they contain the required combinations. The coordinate and spin parts thus constructed are given in Table VIII. The basis vectors of the spin part of the tensor interaction are chosen such that the matrices of the irreducible representation are the same as the transformation matrices of a polar vector for the group T_d. Such a basis was first introduced in Ref. 17. Finally, we have the following expressions for the scalar term

$$H_s^{(JI)}\sim J_i l_{i\alpha} I_\alpha \equiv J_i I_i \tag{15}$$

and tensor term

$$H_t^{(JI)}\sim T_\alpha^{(i)} I_\alpha^{i} \equiv \sum_{ikl=xyz,yzx,zxy} J_i(I_k^{(l)}+I_l^{(k)}) \tag{16}$$

of the spin–rotation Hamiltonian. It is straightforward to construct the terms of the spin–rotation Hamiltonian for the higher orders as well.[18]

Until now we have been considering the construction for a nondegenerate completely symmetric vibronic state. The generalization to the case of a nonsymmetric nondegenerate state is quite trivial. A more serious problem is to take degeneracy into account. Let us consider as an example vibrational degeneracy of type E for a rigid molecule with point symmetry group C_{3v}. To characterize the degeneracy it is necessary to introduce an additional dynamical variable, the vibrational "spin" **l**. In the case under discussion, the three components of **l** must represent the operators whose matrix elements describe the system of two degenerate sublevels.[11)] However, the operator **l** cannot be represented by a spinor operator with $l=1/2$ $(2l+1=2)$ because this spinor has unacceptable symmetry properties for describing the coordinate motion. In particular, its components change sign[2] upon a spatial rotation by 2π. Therefore, it is necessary to use an angular momentum operator **l** with $l=1$, but with the additional requirement that the state with zero eigenvalue of the operator l_z be suppressed (the z axis is coincident with the threefold symmetry axis of the group C_{3v}). As a result, the operators for the physical quantities can contain only the following combinations of the vibrational "spin" operator: l_+^2, l_-^2, and l_z, where $l_\pm=l_x\pm il_y$ are the raising and lowering operators. From this purely qualitative analysis we see immediately that the quantum number of the operator l_z can change only by 2. Thus, in constructing the operators for the physical quantities, one finds that the coordinate part contains vibrational terms which form a three-dimensional representation of the symmetry group C_{3v} of the vibrational problem. It is easy to show that this representation decomposes into the direct sum of the irreducible representations A_2 and E. The final results of the construction for the effective Hamiltonian can be found in Ref. 19.

In the case of nonrigid molecules there arises a degeneracy due to the presence of several equilibrium configurations (configurational degeneracy). The description of this type of degeneracy is a very important problem in the theory of molecular spectra. It is this problem that we will be discussing in the conclusion of this Section, using as an example the NH_3 molecule in a completely symmetric vibronic state. The nonrigid motion here is a tunneling of the N nucleus through the plane of the H nuclei (the so-called "inversion" motion, which is of the nonexchange type). As a result, the chain contains the following symmetry groups: 1) the group of permutations of identical nuclei π_3; 2) the point group C_{3v} (Ref. 9); 3) the rotation group D_∞; 4) the expanded point group $C_{3v}\times C_S=D_{3h}$, where C_S is the group of reflections in the plane orthogonal to the threefold axis of the group C_{3v}. We note that a classification of the stationary states of the NH_3 molecule by the chain of symmetry groups approach is constructed in Ref. 5.

The effective Hamiltonian describing the rotational motion with allowance for transitions between equilibrium configurations depends only on the spatial coordinates of the molecule. Therefore, it must transform according to the coordinate Young diagram [3] of the group π_3. It follows from the joining of the groups π_3 and $C_{3v}\times C_S$ that for the Hamiltonian in the B0 approximation the possible representations are A_{1s} and A_{1a} of the expanded point group. The indices s and a indicate symmetry and antisymmetry of the representation, respectively, with respect to reflection in the plane σ_h of the group C_S. The possibility of an asymmetric representation A_{1a} is due to the fact[12] that we are determining the contributions to the Hamiltonian to an accuracy up to a factor that does not depend on the dynamical variables under consideration. For contributions of the type A_{1a} this factor changes sign on reflection in the plane σ_h. Such a situation cannot occur for rigid molecules, since for them the factor in front of the allowed contributions always transforms according to a unitary representation of the geometric group. As we shall see, the presence of two possible symmetry types in the Hamiltonian automatically gives rise to the terms in it that are responsible for describing the existing twofold configurational degeneracy. In other words, we do not introduce *a priori* the corresponding dynamical variable, since there is no independent "inversion" degree of freedom.

To construct the effective Hamiltonian one must find combinations of the angular momentum components that on transition to the BO approximation evolve into solutions with symmetry $(A_{1s},A_{1a})^{(+)}$ with respect to the group $D_{3h}\times C_i$. We have a solution of this problem in the form

$$(\Gamma_{\text{coord}})_{C_{3v}\times C_S\times C_i}=(A_{1el})_{C_{3v}}\times(A_{1vib})_{C_{3v}}$$

$$\times(\Gamma_{\text{rot-conf}})_{C_{3v}\times C_S\times C_i}. \qquad (17)$$

The correlation between the rotation representations of the group D_∞ and the rotation–configuration representations of the group $C_{3v}\times C_S\times C_i$ is analogous to that given in Table II if one makes the replacements $'\to$s and $''\to$a. It follows from formula (17) that the desired rotational combinations must transform according to the representations A_1 and B_2 of the rotation subgroup D_6.

According to Ref. 6, the complete set of independent combinations, which are angular momentum components of total degree $2n$, transform[12] according to the symmetrized tensor representation $U_3^{[2n]}$. When the group of unitary transformations is reduced by the group of three-dimensional rotations R_3 we have $U_3^{[2n]} = D^{(2n)} + D^{(2n-2)} + \ldots + D^{(0)}$. By choosing the orientation of the Cartesian axes of the molecular coordinate system such that the z axis coincides with the threefold symmetry axis and the x, z plane coincides with one of the three reflection planes of the group C_{3v}, we obtain the following general expression for the terms of the effective configuration–rotation Hamiltonian with rotational combinations of total even degree:

$$H^{(s)}=\sum_{n=0}^{\infty}H_{2n}^{(s)}$$

$$=\sum_{n=0}^{\infty}\sum_{\substack{r,s,t\\(r+s+3t=n)}}c_{2r,2s,6t}\,J^{2r}J_z^{2s}(J_+^{6t}+J_-^{6t}), \qquad (18)$$

$$H_I^{(a)}=\sum_{n=2}^{\infty}H_{2n}^{(a)}$$

$$=\sum_{n=2}^{\infty}\sum_{\substack{r,s,t\\(r+s+3t=n-2)}}d_{2r,3s+1,6t+3}$$

$$\times J^{2r}J_z^{2s+1}(J_+^{6t+3}+J_-^{6t+3}). \qquad (19)$$

The coefficients c and d are operators in the space of states $|s\rangle$, $|a\rangle$ and have nonzero matrix elements only on and only off the diagonal, respectively. Further, we must take into account the fact that the terms of the type $A_{1a}^{(+)}$ in the effective Hamiltonian (which are off-diagonal terms in the space of states $|s\rangle$ and $|a\rangle$) can contain rotational combinations of total odd degree as well. Therefore, we have in addition

$$H_{II}^{(a)}=\sum_{n=1}^{\infty}H_{2n+1}^{(a)}$$

$$=\sum_{n=1}^{\infty}\sum_{\substack{r,s,t\\(r+s+3t=n-1)}}id_{2r,2s,6t+3}\,J^{2r}$$

$$\times J_z^{2s}(J_+^{6t+3}-J_-^{6t+3}). \qquad (20)$$

For a quantitative construction of the Hamiltonian (18)–(20) one must solve the rather complicated problem of taking into account the nonrigid motion even in the zero order approximation.[20]

5. CONCLUSION

In this paper we have demonstrated the rather rich possibilities of the chain of symmetry groups concept in the theory of the spectra of rigid and nonrigid molecules. The main advantages of this approach in comparison with the more widely used approach based on the CNPI group can be summarized as follows: 1) symmetry notions are "primary" in the sense that one does not use information about the explicit form of the solutions of the Schrödinger equation; 2) philosophical difficulties do not arise in the analysis of molecules whose essential symmetry elements cannot be represented as elements of the CNPI group; 3) the analysis of the symmetry properties is unambiguous; 4) no formal widening of the domain of applicability of physical concepts is incurred. At the same time, it must be emphasized that the construction of the expanded geometric group can be an extremely nontrivial problem. An interesting example of this is the PF_5 molecule.[21,22] The geometry of this molecule is such that apparently only with the use of a nonrigid motion (the Berry pseudorotation) can it be rotated in space by an arbitrary angle. In this case the expanded point group will have an infinite number of elements.

[1)]The specific reasons why the conclusions of Ref. 4 are mistaken are analyzed in Ref. 5.

[2)]The notation for all the symmetry groups used in this paper and for their classes and irreducible representations corresponds to Refs. 2 and 6. In the present case π_3 is the group of permutations of the identical fluorine nuclei and C_i is the group of inversion of the spatial coordinates of all the particles of the molecule. We also note that the complete symmetry group of the rigorous problem also has other transformations which are not important for our present purposes.

[3)]In working with the permutation group we will use the technique set forth in Ref. 6. As far as the results are concerned, it is completely equivalent to the technique used in Ref. 2, but it is more efficient.

[4)]We will use the same notation for the transformation operator acting in configuration space and in the functional space of states of the system.

[5)]A more dramatic situation arises when one is considering linear molecules. For a molecule without identical nuclei the CNPI group is $\pi_1\times C_i$. Naturally, this group cannot even formally describe the rich symmetry of the equilibrium configuration (point group $C_{\infty v}$). Therefore, an extremely artificial permutation group π_1^ε, which is continuous in the parameter ε, is introduced.[23,1] We note that in such an approach the exclusion of states with $J<l$ is imposed from without by proceeding from the specific solution of the Schrödinger equation.

[6)]The symmetry element i is related to the properties of the space and commutes with all the symmetry elements determined by the geometry of the molecule. We also note that the rotation group is equivalent to the MS group of the CH_3BF_2 molecule.

[7)]For example, the molecules NH_3 and BF_3 have the same group of permutations of identical nuclei, but for the molecule NH_3 (point group C_{3v}) there are two independent configurations, while for the BF_3 molecule (point group D_{3h}) there is only one.

[8)]One can also construct a wider geometric group $G_8=G_4\times C_S$, where $C_S=(E,\sigma^{(yz)})$. However, in the present case such an expansion of the group does not lead to any important new qualitative results.

[9)]The requirement that the Hamiltonian be invariant with respect to to time inversion implies that it must be of total even degree in the dynamical variables under discussion.

[10)]As in Ref. 2, we assume that the operation i is not defined in spin space.

This is contrary to the CNPI philosophy, where the invariance of the spin vector with respect to this operation is postulated and used in the analysis of the symmetry properties.[24–26] Furthermore, in the CNPI approach one makes use of the invariance of the rotational combinations with respect to transformations of the group T_d, which is isomorphic with the group O. For this, however, one must determine the behavior of the rotational combinations with respect to improper transformations of the group T_d.

11)This idea was used previously[2] to determine the principal contributions to the Coriolis interaction energy in a threefold degenerate vibrational state of a molecule of the spherical top type. The main advantage of this approach is that the discussion can immediately be restricted to only the required vibrational states.

12)The dynamical variable of the coordinate angular momentum has a classical analog. Therefore, following Refs. 16 and 27, in order to simplify the analysis we can go over to the classical analog of the Hamiltonian in this variable. The form of the Hamiltonian will not be changed from that for the consistent quantum mechanical treatment.

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