METHODOLOGICAL NOTES

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Symmetry of quantum intramolecular dynamics

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<u>Abstract.</u> The paper reviews the current progress in describing quantum intramolecular dynamics using merely symmetry principles as a basis. This closed qualitative approach is of particular interest because it is the only method currently available for a broad class of topical problems in the internal dynamics of molecules. Moreover, a molecule makes a physical system whose collective internal motions are geometrically structured, so that its description by perturbation methods requires a symmetry analysis of this structure. The nature of the geometrical symmetry groups crucial for the closed formulation of the qualitative approach is discussed. In particular, the point group of a molecule is of this type.

1. Introduction

A molecule is a complex multiparticle system, and in an isolated state its internal dynamics can, to a good approximation, be described with no regard for nuclear and electron spins in the Hamiltonian. The symmetry properties of a purely coordinate Hamiltonian are determined by the symmetry properties of space and time (external symmetry) and by the requirements specified to permutations of identical particles (internal symmetry). However, as soon as we try to solve the equations of motion with such a Hamiltonian by perturbation methods (at present this is the only feasible approach in the analytical or numerical treatment of the

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Received 17 April 2001, revised 26 December 2001 Uspekhi Fizicheskikh Nauk **172** (7) 813–836 (2002) Translated by E Yankovsky; edited by A Radzig problem), it emerges surprisingly that we have to introduce an additional intrinsic geometrical symmetry group that characterizes the molecule. This is a matter of principle in the approach, since otherwise there is no way in which we can write out the approximate equations of motion, with the Born–Oppenheimer (BO) approximation being the basic operative approximation here [1-3]. It is in this approximation that one introduces the concept of the effective interaction potential of nuclei in a given electronic state and, as a result, the concept of a set of equilibrium configurations corresponding to the minima of this potential.

From the qualitative point of view, molecules may be classified as rigid or nonrigid. The effective potential with a single minimum gives an adequate idea of nondegenerate electronic states for the first type of molecules, while the second one requires the presence of several such minima since internal motion incorporates transitions between such states. It has long been known that for rigid molecules one must select as the additional geometrical group the point group of their single equilibrium configuration, which, by definition, incorporates all the geometrical symmetry elements of the given structure as a whole [4, 5]. It is commonly assumed that this group and the inferences that follow from its presence are the corollaries of the BO approximation, i.e. only in this approximation we can speak of a certain geometrical structuring of the internal molecular motion. But even in this simple case there is no clear idea of the range of applicability of the point group, and the scientific literature contains two very different answers to this problem. According to Landau and Lifshitz [4] and Kaplan [5], this group characterizes the overall (electron-vibrational-rotational) internal molecular motion when deviations from equilibrium are small. However, the very definition of a sufficiently small deviation is ambiguous, to say the least. At the same time, Bunker [6] and Elliott and Dawber [7] have suggested that the point group describes the symmetry of only the vibrational A V Burenin

and electron motions in molecules but cannot be applied to rotational motion and hence to the overall internal motion. As a result, the analysis of the overall motion is done on the basis of what is known as the complete nuclear permutationinversion (CNPI) group. Such contradictions in the status of the empirically introduced geometrical groups that characterize the internal dynamics stem from the absence of a concrete viewpoint on their nature. Hence an important aspect of the present review is the statement that the empirically introduced geometrical groups are the dynamical groups of the rigorous problem of internal coordinate motion¹. In particular, the point groups of rigid molecules are dynamical invariant groups. Despite the fact that today we know of no method that would enable obtaining such a group through studies of the equations of rigorous coordinate dynamics, the latter statement can be logically substantiated by analyzing the observable properties of the molecular system. It is intriguing that one consequence of such a viewpoint is a change in our general ideas about a molecular system proper and about some other physical systems that also require a geometrical group to describe their internal dynamics by perturbation methods.

2. Why is it so important to analyze the symmetry properties of quantum intramolecular dynamics?

The point group of rigid molecules for a given electronic state emerged as a symmetry group of their single equilibrium configuration. It then became clear that this group must also be used in describing the internal excitation spectrum. However, bearing in mind its origin, it was inferred (see Ref. [4]) that the given procedure finds justification only when the deviations from the equilibrium position are small. Such a justification of the range within which the point group operates did not appear very convincing, since the existing asymmetric displacements of nuclei from the equilibrium position lower the geometrical symmetry of their configuration. A much more obvious (and yet largely ignored) fact is that the point group is subject to variation under changes in the electron excitation and is sure to vary in passing from the discrete spectrum to the continuous one. In other words, different isomeric forms of the molecule may be realized in various bound electronic states (see Section 7). As we pass from the discrete spectrum to the continuum, the finite degeneracy multiplicity of the levels changes to infinite one, which is possible only if the type of geometrical symmetry group changes, too. However, ordinary groups are independent of excitations in the system (e.g., the group of permutations of identical particles in a molecule is always the same). Such a change of symmetry is a clear indication of an implicit dynamical group. On the one hand, this group is specified by the dynamics of the system in question within a certain range of excitations, while on the other hand it itself determines the

qualitative properties of the molecular dynamics. When the limits of this range are surpassed, the dynamics of the system change dramatically, which leads to a sudden change in the dynamical group.

Let us assume that we are faced with a problem involving an implicit symmetry group and that the problem admits of a rigorous solution. Then there is no need for qualitative analysis subject to this group. It is only desirable to do such an analysis because on its basis one can explain the qualitative features of the system's behavior. A typical example is the problem of the stationary states of the hydrogen atom (see Section 3). The situation becomes quite a different if such an analysis is ignored, since, when employing the perturbation methods, we first must take care that all the correct symmetry properties of the internal dynamics are transferred to the approximate models. Hence, there emerges the problem of empirically finding the implicit group in relation to which we must correctly symmetrize the operators of physical quantities and the space of basis wave functions that allow for the types of motion in question, i.e. it becomes necessary to analyze the symmetry properties with allowance made for the implicit group. Such an analysis must precede the solution of the equations of motion (actually, without such an analysis we are left without approximate equations of motion).

The above conclusion is important in explaining a number of general qualitative properties of molecules but it changes almost nothing in the methods and results of an analysis that uses geometrical symmetry groups to characterize overall internal motion. A unified procedure of applying such methods to rigid molecules has been thoroughly developed [4, 5, 9]. Moreover, strange as it may seem, even the symmetry methods with what we believe to be a physically meaningless interpretation of the range of applicability of point groups produce equivalent results in the qualitative analysis touching the internal motions of rigid molecules [6]. The point is that in the case at hand we know a priori the qualitative properties of the basis wave functions and, leaning upon the freedom to select the procedure of applying symmetry groups, we can correctly fit the result to this answer. There is simply no place for error here. This, however, is a purely formal technique, which does not even allow us to study rigid molecules from a unified viewpoint, despite the fact that all such molecules have the same types of internal motions (electron, vibrational, and rotational). Even more importantly, this technique can hardly be extended to nonrigid molecules, since in most cases with such molecules the qualitative properties of the basis wave functions are not known a priori. Thus, the requirement that the symmetry methods be complete (or self-sufficient) is highly important. In this connection, the conceptual differences in the interpretation of the range of applicability of a geometrical symmetry group become quite important. Suffice it to notice that the main reason for the emergence of an analysis based on the CNPI group concept in Longuet-Higgins's pioneering work [10] was associated with the impossibility of extending the methods that use geometrical symmetry groups for describing overall internal molecular motion to the case of nonrigid molecules. However, later, as a result of developing the approach based on the concept of a chain of symmetry groups [9, 11], it was found that this is not true. Moreover, at present the given approach is the only one in which the description is built solely on symmetry principles, i.e. we can speak of a closed formulation of qualitative quantum intramolecular dynamics in which geometrical symmetry groups play a leading role.

¹ At present there are two definitions of dynamical symmetry [7, 8]. In the first definition, it is the presence of implicit (or hidden) symmetry in the Hamiltonian that suggests our dealing with dynamical symmetry, while in the second it is the presence of transformations that go beyond the scope of the symmetry of the Hamiltonian. We will call such groups dynamical invariant and dynamical noninvariant groups, respectively, thus emphasizing their relation to the Hamiltonian. Noninvariant groups play a crucial role in forming the function space of observable nonrigid internal motions in the cases when it is not enough to employ only the Hamiltonian symmetry group (see Sections 6 and 7).

If the class of nonrigid molecules is considered, the researcher can see that in addition to the electron, vibrational, and rotational motions there are observed numerous transitions between the different minima of the effective nuclear interaction potential (what are known as nonrigid transitions). Therefore, at least at this juncture, it is unclear what must be done to establish a general procedure for applying symmetry methods to describe their internal dynamics. As a result, one is forced to extend the range of applicability of symmetry methods to separate classes of molecules with certain types of nonrigid motions. Although this process appears to be limitless, its importance is emphasized by the fact that there are a large number of formulated topical problems for fairly simple molecules for which no meaningful solution can be found due to the absence of adequate methods of analyzing the symmetry properties. Such is the problem of the internal dynamics in the PF₅ molecule with allowance made for Berry pseudorotation, a problem formulated nearly three decades ago [12].

The present review basically covers the applications to such specific classes of molecules for which adequate methods of symmetry analysis have been developed since the time the previous review [11] was written. One more factor should be kept in mind when estimating the practical importance of the methods currently being discussed. The stage in the analysis at which the symmetry properties of the basis functions for the space of stationary states of the molecular system and the symmetry properties of the physical quantity operators specified in this space (including the system Hamiltonian) are determined is called the stage of classifying the stationary states. After the analysis has been completed, we can attempt to write out the model equations of motion in terms of certain internal coordinates of the molecule and solve them. However, for nonrigid molecules this approach to describing the internal dynamics spectrum is most often too complicated.

At the same time, symmetry methods make it possible to realize a highly effective (I would say, extremely effective) alternative approach. The essence of this approach is as follows. Any internal motion is specified by a certain collection of symmetry transformations that determine the complete set of basis wave functions for this motion. All the transformations enter (often in a highly nontrivial manner due to the noncommutativity of the transformations specifying individual motions) the complete symmetry group of intramolecular dynamics, which makes it possible to construct, by purely algebraic methods, from the basis functions of individual motions the basis functions of the overall motion that transform according to the allowed types of symmetry of the complete group. Similarly, the complete set of self-adjoint operators specified in the subspaces of individual motions is used to construct, in the form of perturbation-theory series, what are known as the effective operators of physical quantities (including the effective Hamiltonian), which are defined in the complete function space. Here, it is quite important to note that in calculating the matrix elements of self-adjoint operators characterizing individual types of motion we need not the explicit form of the basis wave functions for these types of motion but only their symmetry properties (see Section 5). As a result, only the phenomenological constants acting as the coefficients of the symmetry-allowed combinations of the self-adjoint operators from the obtained complete set of them remain undefined in the effective operators. The numerical values of these functions are usually found by comparing the theoretical

results with the experimental data. In such an approach to describing intramolecular dynamics there is simply no space for a set of internal coordinates. Due to the profound conceptual and technical differences from other approaches, this approach is presently the only one that can be used to solve any complex problems of the dynamics of nonrigid molecules.

In discussing the current state of the closed qualitative approach to describing quantum intramolecular dynamics, the author will replace, where possible, all technical aspects with references to the original works. However, in comparison to such literature sources, the treatment in the present review is more consistent and rigorous. In Section 8, I discuss some of the typical qualitative mistakes related to the incorrect usage of the symmetry properties of intramolecular dynamics.

3. Geometrical symmetry groups of rigid molecules

As pointed out above, when we are dealing with rigid molecules, by a 'dynamical group' we always mean an invariant group. A well-known example of the realization of such a group is provided by the problem of motion of a charged particle in a spherically symmetric Coulomb attractive field. The explicit symmetry shows its worth in any spherically symmetric field, being specified by the group R_3 of rotational transformations which transfer a sphere into itself². This leads to conservation of the angular momentum vector. But for a Coulomb field there is also another vector that is conserved [4] (it is called the Runge–Lenz vector for historical reasons [7, 8]). This fact can be interpreted in such a way that the Hamiltonian has a broader implicit symmetry [13]. What is important is that the appropriate symmetry group not only pertains to a specific field but also depends on the system's energy. In the case at hand, for bound states this is the group of rotations in a certain four-dimensional space, while for the continuous spectrum this group coincides with the Lorentz group [7].

Thus, is there any reason to believe that the effect, determined by a point group, of some geometrical structuring of the internal dynamics in the bound states of a rigid molecule has no relation to the BO approximation? First we note that the concepts of an electronic state, an effective Hamiltonian pertinent to this state, and, respectively, an effective nuclear interaction potential are all retained even if we take nonadiabatic corrections into account (corrections to the BO approximation) [14]. This is all the more important because the formulation of the BO approximation is ambiguous and sometimes dissimilar variants of this approximation even lead to different symmetries of the molecular equilibrium configurations. For instance, according to Bersuker [15], for the ammonia (NH_3) molecule in a formulation corresponding to the simple adiabatic approximation, the equilibrium configuration happens to be a planar configuration with the point group D_{3h} . Only nonadiabatic (or vibronic) corrections make such a configuration unstable and transform it into the actually observed shape of a regular triangular pyramid with the point group C_{3v} . At the same time, in the formulation corresponding to the adiabatic approximation the equilibrium configuration of this molecule has the symmetry group C_{3v} from the outset. In other words, nonadiabatic correction may play an important role in determining the correct symmetry of the equilibrium configuration; therefore, this symmetry should not, generally speaking, be linked to the BO approximation.

Notice that there exists a consistent procedure for using a point group to describe the complete internal dynamics [4, 5, 9]. It is important here that comparison of the results obtained by this procedure with the experimental data does not indicate symmetry breaking with increasing displacement from the equilibrium position. The Jahn-Teller effect merits separate consideration. In 1934, L Landau hypothesized that the symmetric nuclear configuration of a nonlinear molecule in an orbitally degenerate (due to this symmetry) electronic state is unstable [4]. This idea formed the basis of a theorem proved by Jahn and Teller [16]. The scientific literature devoted to the corollaries of this theorem is vast, while two dramatically different interpretations of the theorem being known. In one of these interpretations, originating with the authors of the theorem, it is stated that the instability of the symmetric configuration breaks the symmetry of the system and, as a result, the degeneracy of the electronic state is completely removed. This, however, is true only of a static system, while if the dynamics of the system is taken into account, the physically meaningful interpretation is that of Bersuker and Polinger [3, 15] (see also Ref. [17]) who found that quite a few the energy-equivalent minima of the nuclear interaction potential form a symmetric pattern in relation to the instability point. Formally, the need to account for several minima means the dynamics is that of a nonrigid molecule. Since the minima are transferred into each other under the transformations of the point group corresponding to the instability point, the delocalization of the quantum system over these minima do not break the symmetry and the degeneracy is not removed, but the type of degeneracy becomes electron-vibrational or vibronic.

Thus, it would be logical to assume that in the case of rigid molecules a point group determines the geometrical structuring of the internal motion for all discrete levels in each electronic state. According to this viewpoint, the symmetry of the equilibrium configuration is only an elementary consequence of such structuring, but not vice versa. There are also other physical systems that act similarly. An interesting example is the motion of the nucleons in an atomic nucleus. Conclusive data suggest that this motion in heavy nuclei is structured [4, 7]. Such a structure behaves as an integral whole (has a rotational spectrum) and is characterized by a point group for which D_{∞} is usually chosen due to the large number of nucleons (~ 150). This all occurs in the absence of an analog of a small parameter for the nucleus, a parameter related to the large difference in nucleus and electron masses and used in molecular dynamics to substantiate the BO approximation. A crystal constitutes another example of a similar but already macroscopic system. A characteristic feature of all these systems is the execution of essentially collective motions, i.e. motions that cannot be interrupted within a finite energy range. In connection with the concept of essentially collective motion we would like to draw the reader's attention to the fact that for systems that are not structured (atoms and some nuclei) the description of the motion of each separate particle in the averaged field of all the other particles is a good zeroth approximation. When the collective motion is executed, such a zeroth approximation is entirely out of the question, which is quite understandable

since even a zeroth approximation must correctly reproduce all the qualitative features of the system's behavior.

Thus, there is every reason to believe that the point group of a rigid molecule characterizes the rigorous problem of internal coordinate motion. Because, as noted earlier, this group depends on the type of electron excitation, this group can be only the dynamical group of this problem. Unfortunately, we know of no method that could help us to derive this group from the rigorous equations of motion. And since without this group any description of the internal dynamics by perturbation methods is impossible, we are forced to add this group by empirical means³. Naturally, the solution of the group problem would yield much additional information, for example, restrictions on the possible shape of the effective potential of nuclear interaction in the molecule.

We can substantiate the assumed status of the point group of a molecule by approaching from a somewhat different angle. We begin by presenting the point of view on this group, which was expressed by Elliott and Dawber [7]. Its basis is formed by the idea that the total coordinate Hamiltonian possesses the symmetry group R_3 , since it depends only on the relative distances between the nuclei and the electrons. As for the point group that corresponds to the equilibrium arrangement of the nuclei and is a subgroup of R_3 , it can be used only to describe the electron-vibrational motion. This fact is interpreted as some spontaneous lowering (breaking) of the symmetry from R_3 to the point group due to exclusion of the system's rotation, i.e. molecular symmetry is restored if in addition to the motion of the electrons and the vibrations of nuclei we allow for rotation of the molecule.

Making an appropriate comment on the above reasoning it must be first noted that if the point group contains improper transformations (orthogonal transformations with a determinant equal to -1), it is not a subgroup of R_3 . However, in accordance with our desire we can, by additionally allowing for inversion, introduce on the same grounds a group that is broader than R_3 . What is more important, however, is that R_3 cannot be used in the above sense as the symmetry group of the total Hamiltonian. To be persuaded of this, let us consider the well-known solution of the problem on the symmetry group of the rotational motion of a solid. This problem is directly related to the internal dynamics of rigid molecules, since it is the physically meaningful initial approximation for describing the rotational spectra of such molecules. The sought group has a maximum of six independent infinitesimal operators corresponding to the rotations about three axes of the Cartesian laboratory (fixed) coordinate system (LCS) and three axes of the Cartesian moving coordinate system (MCS) attached to the solid. Since the infinitesimal operators for LCS and MCS commute among themselves, the maximum symmetry group comes out as $R_3 \times R_3$. The rotational group in LCS is sometimes called the extrinsic group, and that in MCS the intrinsic group.

The states of physical systems are realized by only those irreducible representations of the group $R_3 \times R_3$ for which

³ Actually, the trivial group C_1 may serve as such a group. But even in this case we must be sure that the dynamical group of the structured system has an elementary form that makes it possible to achieve a meaningful description by perturbation methods. It must also be noted that it is a mistake to attempt a transition to a description with a higher symmetry from the obtained description with a lower symmetry by imposing in the latter the additional constraints on the parameters of the system (see Section 8).

the indices of the irreducible representations of the extrinsic and intrinsic groups coincide (J-J representations). Since the presence of an extrinsic group is related to the spatial isotropy, its maximum variant R_3 is realized for every solid. The intrinsic group characterizes the symmetry of the solid proper and incorporates only rotations with respect to which the ellipsoid of inertia is invariant. Hence its maximum variant characterizes the symmetry of rotational motion executed by only solids of the symmetric-top type [8]. For rigid bodies of the symmetric-top and asymmetric-top types this symmetry is determined by the groups D_{∞} and D_2 , respectively, while the group R_3 acts as the dynamical noninvariant group. In this role R_3 is also important, because it determines the complete basis set of the rotational function space in MCS. Actually, the presence of an extrinsic group makes it possible to characterize the rotational states by the use of a quantum number J of the total angular momentum. However, the system-related symmetry and hence the specific form of the Hamiltonian are determined by the intrinsic group. Even in the limiting case of a rigid top model, this latter group may not coincide with R_3 .

Now let us discuss the passage from this limiting case to a model that incorporates all internal motions and has a Hamiltonian in which only the contributions caused by the nuclear and electron spins are ignored. Clearly, the extrinsic group does not change under this passage, but not all rotational elements of the intrinsic group remain the same. Indeed, by allowing for the nonadiabatic corrections (a feature that sets this model apart from the BO approximation) we retain the concepts of an electronic state and the effective Hamiltonian inherent in such a state. Hence, it may be declared that the mapping transformation of the potential onto itself is a necessary condition for the existence of a geometrical symmetry element of the effective Hamiltonian. Naturally, the equilibrium configuration is also transferred into itself, i.e. only the rotational elements belonging to a point group remain. If we now take into account the improper symmetry elements of the potential, we obtain the point group in its entirety. Then it is logical to assume that this group is the symmetry group not only of the interaction potential but also of the total effective Hamiltonian. This statement is in good agreement with the procedure of using a point group to describe the overall internal motion in a rigid molecule, where to each element of the point group a permutation of identical nuclei in a force field invariant with respect to these elements is assigned. As a result, in the general case a homomorphous mapping of the molecular point group onto a subgroup of its identical-nuclei permutation group emerges [9, 11].

The fundamental properties of symmetry imply that the Hamiltonian of coordinate motion belongs to the completely symmetric coordinate Young diagram of the permutation group. The unit representation for the Hamiltonian in the point group emerges as a corollary of this exact symmetry, i.e. the point group is a dynamical invariant group. However, one must bear in mind that the identical-nuclei permutation group itself contains no information about the structuring of the molecular dynamics, which is present in the case of bound states. This fact manifests itself most vividly in a linear molecule. Even when there are no identical nuclei, the point group of such a molecule has the highly nontrivial form of the continuous group $C_{\infty v}$.

The above explains such a fundamental property in the behavior of a microsystem as the presence or absence of a

rotational spectrum. Generally speaking, the very fact that a microsystem exhibits such a spectrum is remarkable, since in this case the system must rotate as a whole or, in other words, must have the properties of a solid. As a first step in understanding such a behavior we note that in all descriptions of the internal dynamics of the known microsystems with a rotational spectrum there must necessarily be an intrinsic geometrical symmetry group. Next, the characteristic feature of a physically meaningful rigid-body model presenting the initial approximation used to describe the rotational motion of the microsystem is that it has an intrinsic geometrical group determining the symmetry of the structure of this body. Thus, it is the presence of geometrical structuring in the internal dynamics of a microsystem that leads to the appearance of its rotational spectrum, which is caused by the rotation of the emerging dynamical structure as a whole. For a given electronic state, the MCS attached to the molecule is 'frozen' into the effective nuclear interaction potential inherent in this state, which for a rigid nonlinear molecule is equivalent to fixing the MCS with respect to the equilibrium nuclear configuration. Finally, what is interesting is that within this setting a molecule and an atom are qualitatively different systems.

4. Effect of numerical methods on the description of intramolecular dynamics

The modern numerical methods used in calculating the quantum intramolecular dynamics change nothing in the above picture, since they are also based on the BO approximation [18]. Hence, the same problems emerge when transferring the correct symmetry properties of rigorous dynamics to the approximate model employed, i.e. we must specify in advance the implicit geometrical symmetry group with respect to which the wave functions allowing for the types of molecular motion considered and the operators of physical quantities defined in the space of these functions have the correct symmetry. In other words, analysis of the symmetry properties with allowance made for the implicit group becomes basically important and should precede the calculation of approximate solutions.

It must also be emphasized that in quantum mechanics of bound states it is very important to choose the function space correctly, since in this case one is forced to separate the physically significant solutions against the background of a huge number of formal solutions. Indeed, the discrete spectrum corresponds to the states taken from the function space L_2 (the space of square-integrable functions, because only such functions can be normalized). An attempt to solve the Schrödinger equation without first separating such a space leads to a replacement of the discrete spectrum by a continuous spectrum, i.e. the superposition of the set of additional formal solutions with a power of the continuum on the denumerable (or finite) set of the physically significant solutions. When numerical methods are applied, the above factor seriously complicates the search for solutions even in the simplest problems. Since a numerical solution of the problem of intramolecular dynamics is based on perturbation methods, additional problems associated with obligatory consideration for symmetry emerge. Thus, the widely accepted idea that the description of such dynamics can be achieved by purely numerical methods (without the support of analytical methods) is erroneous.

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5. Chains of symmetry groups

When perturbation theory is used, the passage to the zeroth approximation is done by constructing a number of (increasingly rough) models embedded in one another until the exact solution of a given model problem becomes possible. Thus we have a chain of models and a chain of symmetry groups characterizing these models. For instance, if we ignore the contributions from the nuclear and electron spins to the Hamiltonian, the symmetry of the overall coordinate internal motion of a rigid molecule is specified by its point group, and in the zeroth approximation the symmetry of the rotational motion is related to the rigid-top type, etc. Naturally, there emerges the problem of determining 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 of physical quantities) when we go over from one model to its neighbor in the chain. No conventional solution of this problem exists. Within the symmetry-group chain concept, the problem is solved as follows. In quantitative calculations the passage from one model to its neighbor must be continuous, which means it is possible to describe the distinction between the two models by a power series in a small parameter⁴. However, the groups representing these models may be different, i.e. the symmetry changes abruptly. The reason is that an approximate model is based on a certain physical idea and may contain information about less exact types of symmetry of internal motion. But this means that at least some information about the symmetry of motion in the more rigorous model is lost. As a result, the symmetry groups of all the models play a strikingly independent role. Their join into a chain is determined by the sewing conditions. More precisely, in the groups of neighboring models one must identify equivalent elements in relation to which the wave functions and the operators of physical quantities transform in the same way. In other words, the passage from one model to a neighboring model is accompanied by the emergence of certain nontrivial restrictions imposed on the correspondence in symmetry types.

To illustrate, let us examine the use of sewing procedure in the conceptually interesting case of a linear molecule. To be more specific, we follow paper [19] and select a molecule that has no identical nuclei. As a result, the identical-nuclei permutation group degenerates into π_1 , and $C_{\infty v}$ is the point group. Naturally, in a given electronic state there are identical permutations of the nuclei (the nuclei are transferred into themselves) associated with all transformations of the point group, i.e. there emerges a homomorphous mapping of the $C_{\infty v}$ group onto π_1 (see Table 1). Then for the quantities characterizing the overall coordinate motion only those representations of the point group are realized that behave in the same way for elements homomorphically mapped onto one element of the permutation group. Such exclusions are called geometrical [9]. As a consequence, in the case at hand only the identical representation A_1 is allowed for the coordinate multiplets (for the representations of the complete coordinate wave function).

Table 1. Homomorphous mapping of the point group $C_{\infty v}$ of a linear molecule onto the identical-nuclei permutation group π_1 .

$C_{\infty v}$ classes	Ε	$2C_{\varphi}$	σ_v			
π_1 classes	{1}	{1}	{1}			
$C_{\infty v}$ irreducible representations		A_1	A_2	E_1	 E_n	
π_1 irreducible representations		[1]	_	_	 _	

The interactions of interest are also invariant with respect to spatial inversion i of all the particles comprising the molecule. Since this symmetry operation associated with the properties of space commutes with all the operations specified by the geometrical symmetry of the molecule, we can introduce the group $C_{\infty v} \times C_i$. The presence of a direct product in the latter group has profound physical meaning, since otherwise not all the stationary states of such an isolated system as a molecule would exhibit a definite behavior in respect to *i*, which would violate one of the basic principles of nonrelativistic quantum mechanics [4]. Thus, the multiplets are characterized by their behavior with regard to *i*, which will be specified by the superscripts '+' or '-'. Next we must indicate the relationship between the multiplets and the zeroapproximation solutions. In this approximation, electron motion is determined for a fixed (equilibrium) configuration of the nuclei, while nuclear motion is resolved into independent vibrational and rotational components, which are described using the harmonic oscillator and rigid top models. The symmetry groups of the electron and vibrational problems formally coincide with the point group, but their elements act on the electron and vibrational coordinates, respectively.

The situation with the symmetry group of the rotational problem is more complicated in the case of a linear molecule. The matter is that the zeroth approximation here corresponds to the movement of a point over a spherical surface, which is parametrized by only two polar angles. Hence, the symmetry group consists only of the extrinsic group R_3 , while the internal structure of the molecule is completely ignored. To correct this situation, we add the intrinsic group R_3 with allowance made for the rule of realization of only J-J representations for a physical system. This group simply determines the complete basis set of the rotational function space in the MCS attached to the molecule. The sewing together of the multiplets with the zero-approximation solutions shows up as

$$(\Gamma_{\text{mult}})_{C_{\infty v} \times C_{i}} = (\Gamma_{\text{el}})_{C_{\infty v}} \times (\Gamma_{\text{vib}})_{C_{\infty v}} \times (\Gamma_{\text{rot-inv}})_{C_{\infty v} \times C_{i}}.$$
 (1)

Here, Γ_{el} and Γ_{vib} are the irreducible representations of the group $C_{\infty v}$ for the zero-approximation wave functions of the electron and rotational motions, respectively, and $\Gamma_{rot-inv}$ are the irreducible rotational–inversion representations of the group $C_{\infty v} \times C_i$. The possible types of these latter representations for a given rotational representation of the intrinsic group R_3 are obtained using the correlation between the groups R_3 and $C_{\infty v} \times C_i$ (see Table 2) through their common subgroup D_{∞} . The arrow in expression (1) indicates that the behavior in respect to operation *i* characterizes only a multiplet and has no physical meaning for the wave functions

⁴ Here we do not dwell on the extremely complicated problem of substantiating the procedure of using such series. We only note that the presence of a small parameter provides neither necessary nor sufficient test for the convergence of the series.

Table 2. Correlation between the groups R_3 and $C_{\infty v} \times C_i$ for a linear molecule with the point group $C_{\infty v}$.

R_3	D_{∞}	$C_{\infty v} imes C_i$
J = 0	A_1	$A_1^{(+)}, A_2^{(-)}$
1	$A_2 + E_1$	$A_1^{(-)}, A_2^{(+)} + E_1^{(\pm)}$
2	$A_1 + E_1 + E_2$	$A_1^{(+)}, A_2^{(-)} + E_1^{(\pm)} + E_2^{(\pm)}$
3	$A_2 + E_1 + E_2 + E_3$	$A_1^{(-)}, A_2^{(+)} + E_1^{(\pm)} + E_2^{(\pm)} + E_3^{(\pm)}$

of separate types of motion [9]. Indeed, since otherwise a purely formal agreement about the action of this operation on the MCS attached to the molecule is needed, and there can be an infinite number of variants of such an agreement. For instance, Hougen [20] proposed a variant in which *i* does not act on the MCS and, respectively⁵, one finds

$$i\Phi_{\rm rot} = \Phi_{\rm rot} \,. \tag{2}$$

A frequently used idea comes to that of complete or partial compensation for the changes in the equilibrium positions of the nuclei in the MCS that occur as a result of the inversion operation i via rotation of this coordinate system [6]. Complete compensation is possible only for the molecules whose configurations are either linear or planar. For linear molecules in this case we have the well-known relationship [4]

$$i\Phi_{\rm rot} = (-1)^J \Phi_{\rm rot} \,, \tag{3}$$

where J is the quantum number of the square of the total coordinate angular momentum.

Thus, referring to equation (1) with consideration for the restrictions on the allowed multiplets furnishes a clue to the classification of the rotational levels with a given value of J in an arbitrary vibronic state. Figure 1 illustrates this finding for $\Gamma_{\rm el} = A_1$, $\Gamma_{\rm vib} = E$, and $\Gamma_{\rm el} = \Gamma_{\rm vib} = E_1$. The exclusion of some of the levels with small values of J from the classification is due to the well-known fact [4] that the projection of angular momentum onto the symmetry axis of a linear molecule depends only on electron-vibrational motion. Naturally, the angular momentum vector cannot be shorter than its projection which is finite in degenerate electron-vibrational states and is taken into account by the symmetry types in $\Gamma_{\rm el} \times \Gamma_{\rm vib}$. It should also be noted that in the spectra of linear and planar molecules there is no place for what is known as inversion level doubling, since in the case at hand the inversion transformation of the nuclear configuration is equivalent to its rotation as a whole. In building the classification scheme this is taken into account automatically by the homomorphous mapping (which comes into being for such molecules) of the point group onto the identical-nuclei permutation group. Moreover, in rigid molecules of other types the existing inversion doublets are not split. Hence, in describing the real splitting of energy levels for any rigid molecules, instead of the group $\Gamma_{\text{point}} \times C_i$ we must use its rotational subgroup, or the D_{∞} subgroup in our case.

A linear molecule presents a striking example of the conceptual difficulties associated with using the CNPI group to analyze even the rigid molecules. Indeed, in the case under





Figure 1. Energy level classification of a linear molecule with the point group $C_{\infty v}$ in the vibronic states $\Gamma_{\text{el}} = A_1$, $\Gamma_{\text{vib}} = E_1$, and $\Gamma_{\text{el}} = \Gamma_{\text{vib}} = E_1$. The chain $(\Gamma_{\text{rot}})_{R_3} \rightarrow (\Gamma_{\text{rot-inv}})_{C_{\infty v} \times C_i} \rightarrow (\Gamma_{\text{mult}})_{C_{\infty v} \times C_i} \rightarrow (\Gamma)_{D_{\infty}}$ is shown for every multiplet.

consideration this group comes to $\pi_1 \times C_i$, which by definition must incorporate all the symmetry operations needful to analyze the problem of the bound states in the molecule. However, it does not allow us to describe even formally the rich geometrical symmetry of a linear molecule. To overcome this difficulty, Bunker and Papousek [21] introduced an extremely artificial extension of the CNPI group, $\pi_1^{\epsilon} \times C_i$, continuous in the parameter ϵ . The zero-approximation wave functions of the linear molecule are then written explicitly and the action of the elements of this group on these functions is specified. Generally speaking, the concepts of symmetry in the CNPI approach are 'secondary', since their application is based on the knowledge of the approximate solutions and basically serves as a means for simplifying calculations.

The concept under discussion incorporates quite naturally the important notion of the coordinate spin of a molecule [11], on the basis of which a complete set of self-adjoint operators for finite-dimensional function spaces is readily formed. Such spaces correspond to essentially quantum types of motion and appear, for example, in the description of configuration degeneracy in nonrigid molecules and of vibrational and orbital electron degeneracies already present in rigid molecules. Similar spaces emerge in the description of quasidegeneracies. Notice that in the description of coordinate motions the standard finite-dimensional spaces correspond to integral values of the quantum number of the spin squared and have an odd dimension [4]. The components of the coordinate spin operator \mathbf{e} in the LCS form what is known as a three-dimensional Lie algebra of the kind

$$[e_{\alpha}, e_{\beta}] = i\varepsilon_{\alpha\beta\gamma}e_{\gamma}, \qquad (4)$$

where $\varepsilon_{\alpha\beta\gamma}$ is the absolutely antisymmetric third-rank tensor. Since spin is a coordinate physical quantity, for the commutation relations between the components of the total coordinate angular momentum **J** and the components of **e** we obtain in the LCS the following result [4]

$$[J_{\alpha}, e_{\beta}] = i\varepsilon_{\alpha\beta\gamma}e_{\gamma} \,. \tag{5}$$

For the MCS unit vectors λ_i we have, respectively, the relations

$$[J_{\alpha}, \lambda_{i\beta}] = i\varepsilon_{\alpha\beta\gamma}\lambda_{i\gamma}, \qquad [e_{\alpha}, \lambda_{i\beta}] = 0.$$
(6)

The second relationship in Eqn (6) implies that the introduced coordinate spin operators do not rotate the MCS. Then equations (4)-(6) lead to the following relationships for the components in the MCS:

$$[e_i, e_j] = i\varepsilon_{ijk}e_k, \quad [J_i, e_j] = 0, \qquad (7)$$

i.e. the commutation relations for the components of \mathbf{e} are invariant with respect to passage from LCS to MCS. In this regard the coordinate spin of a molecule behaves like the ordinary nuclear and electron spin. At the same time, for the components of \mathbf{J} there is no such invariance [4]:

$$[J_{\alpha}, J_{\beta}] = i\varepsilon_{\alpha\beta\gamma}J_{\gamma}, \qquad [J_i, J_j] = -i\varepsilon_{ijk}J_k.$$
(8)

The change in sign in the commutation relations for the **J** components in the MCS plays an important role and is related to the fact that these components rotate the MCS. In analyzing intramolecular motions it is also important to bear in mind that equations (7) hold true for two types of behavior of the spin components under time reversion: either all three components are *t*-odd or any two components are *t*-even while the third component is *t*-odd. It should be emphasized that in nonrelativistic quantum mechanics the time-reversal operator is antiunitary and antilinear, and that the consideration of the behavior with respect to this operation has physical meaning only for operators and not for wave functions [7].

To illustrate this approach, we again turn to a molecule with the point group $C_{\infty v}$ and consider the energy levels with $\Gamma_{\rm el} = \Gamma_{\rm vib} = E_1$. For the basis vectors of the electronic E_1 representation we can take the unit vectors $|\pm 1_e\rangle$ belonging to such a pair of the complex-conjugate representations of $C_{\infty v}$ that $C_{\varphi} |\pm 1_e\rangle = \exp(\pm i\varphi) |\pm 1_e\rangle$. The group $C_{\infty v}$ can be written in the form $C_{\infty} \wedge C_S$, where the symbol \wedge stands for a semidirect product [7], which emerges due to the noncommutativity of the operations of the invariant subgroup C_{∞} of the group $C_{\infty v}$ and the operations of the factor group $C_S = (E, \sigma^{(xz)})$.⁶ Owing to the properties of a semidirect product, the elements of the group C_S also act in the basis of the group C_{∞} :

$$\sigma^{(xz)}|1_e\rangle = |-1_e\rangle, \qquad (9)$$

i.e. the unit vectors $|\pm 1_e\rangle$ realize the two-dimensional representation E_1 of the group $C_{\infty v}$.

The unit vectors $|\pm 1_v\rangle$ of the vibrational E_1 representation are introduced in a similar manner. The group D_∞ specifying the pattern of rotational-vibronic (or rovibronic) splittings can be written in the form $C_\infty \wedge U_2$. We select the nontrivial element of the group U_2 in the form $U_2^{(y)} = \sigma^{(xz)}i$. Then the symmetry properties of the vibronic quantities in D_∞ coincide with those in $C_{\infty v}$ to within the substitution of $\sigma^{(xz)}i$ for $\sigma^{(xz)}$. Allowing for the well-known symmetry properties of rotational functions in the intrinsic group R_3 [4], we arrive at the following complete set of rovibronic basis vectors of the A_1 type in the group D_∞ :

$$|s_{0}\rangle = |J,0\rangle \left(|-1_{e}\rangle|1_{v}\rangle + \omega|1_{e}\rangle|-1_{v}\rangle\right) \frac{1}{\sqrt{2}},$$

$$|s_{2}\rangle = \left(|J,2\rangle|1_{e}\rangle|1_{v}\rangle + \omega|J,-2\rangle|-1_{e}\rangle|-1_{v}\rangle\right) \frac{1}{\sqrt{2}},$$
(10)

where $\omega = (-1)^J$. The complete set of basis vectors $|a_0\rangle$ and $|a_2\rangle$ of the A_2 type follows from formulas (10) if $-\omega$ is substituted for ω . It is important here that the basis vectors contain only products $|J, k\rangle |A_e\rangle |l_v\rangle$, in which $k = A_e + l_v$, i.e. the construction pattern allows for the fact that the projection of angular momentum onto the *z*-axis is due to vibronic motion (all four basis vectors for a given value of *J* are present only if $J \ge 2$).

The electron parts of the operators of physical quantities are built up around the coordinate spin operator Λ with the quantum number of the spin squared equal to unity. Here, the unit vectors $|\pm 1_e\rangle$ are related to the eigenvectors of the operator Λ_3 with eigenvalues ± 1 . Inasmuch as the eigenvector with a zero eigenvalue is excluded from our picture, of all the spin operators admissible in the three-dimensional space only the following four are independent:

$$I_e, \Lambda_3, \Lambda_+^2, \Lambda_-^2,$$
(11)

where I_e is the unit operator, and $\Lambda_{\pm} = \Lambda_1 \pm i\Lambda_2$ are the raising (+) and lowering (-) operators, respectively. Knowing the properties of the eigenvectors under transformations intrinsic in the group $C_{\infty v}$ and under time reversion T, viz.

$$T|0_e\rangle = |0_e\rangle, \quad T|1_e\rangle = |-1_e\rangle,$$
(12)

we can easily obtain the symmetry properties for the spin operators (11). The coordinate spin operator I for building up the vibrational parts of the operators of physical quantities is introduced in a similar manner. For the effective electronic– vibrational–rotational or rovibronic Hamiltonian only the $A_1^{(+)}$ representation of the group $C_{\infty v} \times C_i$ is possible, and, as a result, the representation A_1 of D_{∞} . Employing the same procedure as in building up the wave functions and allowing for the fact that the Hamiltonian is *t*-even, we arrive at the following general expression for this Hamiltonian in the state with $\Gamma_{el} = \Gamma_{vib} = E_1$ [19]:

$$H = h_1 + (\Lambda_3 + l_3)^2 h_2 + (\Lambda_+^2 l_-^2 + l_+^2 \Lambda_-^2) h_3 + (l_+^2 J_+^2 + J_-^2 l_-^2) h_4 + (\Lambda_+^2 J_+^2 + J_-^2 \Lambda_-^2) h_5 + (\Lambda_+^2 l_+^2 J_+^4 + J_-^4 l_-^2 \Lambda_-^2) h_6,$$
(13)

where $h_i = \sum_{p=0}^{\infty} a_p^{(i)} J^{2p}$, $J_{\pm} = J_x \mp i J_y$ are the raising and lowering rotational operators, whose definition is opposite to that of similar spin operators due to the difference in the signs in the commutation relations in the MCS, and $a_p^{(i)}$ are real-

⁶ The elements of the point group are specified in the MCS, with the *z*-axis coinciding with the symmetry axis of an infinite order. Note that the *x*- and *y*-axes are fixed in the vibronic problem.

valued phenomenological constants, usually called spectroscopic constants. Clearly, the action of the Hamiltonian on the basis vectors does not violate the condition $k = \Lambda_e + l_v$. When $J \ge 2$, due to the mixing of the basis vectors with |k| = 0, 2, there emerges a nonpolynomial dependence of the energy on J(J+1), and k^2 ceases to be a good quantum number. Naturally, such a description also allows for the Renner effect [2], which the BO approximation does not cover.

As noted in Section 2, we do not need to know the explicit form of the wave functions (10) when calculating the matrix elements of the Hamiltonian (13) — it is enough to know the symmetry properties of these functions. As a simple illustration of this important statement, we shall calculate the matrix elements of the projections J_{α} of angular momentum onto the LCS axes in the basis of the eigenfunctions $|J, M\rangle$ of the square of angular momentum and its projection onto the z-axis:

$$J^{2}|J,M\rangle = J(J+1) |J,M\rangle,$$

$$J_{z}|J,M\rangle = M |J,M\rangle.$$
(14)

The solution of these equations [4] implies that the spherical functions Y_{JM} are the eigenfunctions $|J, M\rangle$. Furthermore, the well-known result of action of the operators $J_{\pm} = J_x \pm i J_y$ on these functions can easily be obtained:

$$J_{+}|J,M\rangle = \sqrt{(J+M+1)(J-M)} |J,M+1\rangle,$$

$$J_{-}|J,M\rangle = \sqrt{(J+M)(J-M+1)} |J,M-1\rangle.$$
(15)

Expressions (14) and (15) make it possible to calculate the matrix elements of any products of the components J_{α} . It occurs, however, that these expressions can be derived in a purely algebraic manner [4], solely from the commutation relations for the components J_{α} in the LCS. The commutation relations are in turn determined by the properties of the three-dimensional rotation group R_3 in the LCS, while the quantum numbers J and M emerge as the symmetry indices [5].

Another important property of the derived effective Hamiltonian relates to the fact that its operative range depends on the range of applicability of the geometrical group $C_{\infty v}$. In other words, this Hamiltonian describes rigorous coordinate dynamics. Introduction of the BO approximation is required only when we wish to interpret the phenomenological constants, an objective that is beyond the means of symmetry methods. Thus, the effective Hamiltonian concept makes it possible to separate the construction of a model for describing the excitation spectrum from interpreting the phenomenological constants in this model. Generally speaking, each such constant contains contributions determined by the BO approximation and contributions related to different types of nonadiabatic corrections. It is quite another matter that the effective Hamiltonian can be written as a Taylor series in the components of angular momentum in the MCS and in doing so it represents a perturbation series in powers of an ordinarily small rotational distortion. Reasoning in a similar manner, we can build up the effective operator of any other physical quantity that characterizes the molecule, for example, the effective operator of the electric dipole moment, which must transform according to the representation A_2 of the group D_{∞} .

Finally, note that the methods of the group chain concept make it possible to easily carry out such analysis for any rigid molecule in an arbitrarily chosen vibronic state. More than that, it is easy to give a description within a unified model and a whole set of vibronic states. The latter is important in the case where the interaction of vibronic states is fairly strong (allowing for what is known as random resonances).

6. Geometrical symmetry groups of nonrigid molecules with energy-equivalent configurations

When analyzing the dynamics of nonrigid molecules in a given electronic state, we must (in addition to the case of rigid molecules) allow for the transitions between the various minima of the nuclear interaction potential. We begin with a situation where all the equilibrium configurations belong to a single point group G_0 , i.e. the energy minima are equivalent. Here, the geometrical symmetry of the internal motion is characterized by what is known [9, 11] as an extended point group G that additionally incorporates (in comparison to G_0) elements determining the nonrigid transitions. Such elements belong to the exchange and nonexchange types. When elements of the exchange type act, the nuclear interaction potential is transferred to itself. Hence, the spatial arrangement of the equilibrium configuration does not change, and nuclear motion is associated with permutation of identical nuclei. In this respect the situation is fully similar to the case of a rigid molecule. If all the elements that extend the group G_0 to G belong to the exchange type, then G is the dynamical invariant symmetry group of the rigorous model of coordinate motion in a nonrigid molecule. The torsion motions of CH₃ tops in the molecules of methanol (CH₃OH) and ethane (C_2H_6) are the typical examples of nonrigid motions of this type

The main characteristic feature of elements of the nonexchange type is that they are not symmetry transformations of the field of nuclear forces. Hence, the spatial arrangement of the equilibrium configuration changes, and nuclear motion cannot be associated with the permutation of identical nuclei. The latter means that the symmetry properties of the Hamiltonian of the overall coordinate motion for the permutation of identical nuclei lead to the requirement that the Hamiltonian be invariant only with respect to the exchange-type elements belonging to the group G, with such elements comprising a subgroup G_H of this group. Naturally, G_H includes G_0 as a subgroup. As a result, G becomes a dynamical noninvariant group. The inversion motion in ammonia (NH₃) molecule is a simple example of nonrigid motion of the nonexchange type.

For the internal dynamics of a nonrigid molecule, the extended point group plays the same role as the point group does for a rigid molecule. Both of them characterize the geometrical structuring of the overall coordinate motion for bound states. However, in practical importance they cannot even be compared, since in most cases involving nonrigid motions we do not know a priori the solution of the problem on the symmetry properties of the basis vectors of the function space and the effective operators of physical quantities, defined in this space (the effective Hamiltonian included). Knowing this solution is basically important in order to provide a description, via perturbation methods, of the internal dynamics of a system with collective motions. Naturally, the geometrical symmetry group of a nonrigid molecule is not determined by the symmetry groups of the molecular equilibrium configurations, which may even be different. Hence, building up such a group can be a highly

nontrivial problem. The solution is based usually on information about the symmetry groups of the equilibrium configurations and about the geometry of the nonrigid transitions between these configurations. Generally, the geometry of such a transition is defined in terms of the symmetry of an intermediate configuration [11]. It is much easier to select such a configuration if one knows the heights of the barriers for nonrigid motions calculated by methods of quantum chemistry. One must also bear in mind that, in contrast to the symmetry groups of equilibrium configurations, the geometrical groups of nonrigid molecules most often have not been tabulated. Another very difficult physical problem is that of resolving the various types of motion within the constructed geometrical group. To achieve such a resolution, we must know how to build up the function subspaces needed for the description of separate types of motion on the basis of the irreducible representations of this group.

6.1 Molecules with nonrigid exchange-type transitions

To illustrate the various aspects in describing molecules with nonrigid transitions of exchange type, we shall examine the interesting case (from the conceptual and technical angles) of allowing for Berry pseudorotation in XPF4 and PF5 molecules. The equilibrium configuration of the phosphorous pentafluoride (PF₅) molecule is depicted in Fig. 2 and it corresponds to the point group D_{3h} . In this configuration, the nuclei F occupy two nonequivalent positions — in the plane of a triangle (equatorial), and in the straight line perpendicular to this plane (axial). It has been established without doubt (e.g., see Ref. [22]) that the nonrigid motion called Berry pseudorotation transfers the F nucleus from an equatorial position to an axial one, and vice versa. In the example presented in Fig. 2, the equatorial nucleus F_1 retains its position, while the remaining four F nuclei pass through an intermediate configuration (whose symmetry point group is C_{4v} with simultaneous rotation through an angle of $\pi/2$ about the pseudorotation axis C_4 (F₁P-axis). All this does not change the spatial arrangement of the equilibrium configuration, while the permutation of identical nuclei is related to the nuclear motion. The fact that the PF₅ molecule has three pseudorotation axes passing through three vertices of the equatorial triangle results in a very complicated internal motion with transitions between 20 independent equilibrium configurations. Until recently all corresponding qualitative analysis was based on Dalton's classical research [12] done nearly three decades ago. However, Dalton's treatment of the problem was, to a large extent, empirical. Indeed, the level



Figure 2. Initial (a) and final (b) equilibrium configurations of the molecule PF₅, related through Berry pseudorotation about the F₁P-axis (the arrows in the left figure indicate the motion of the F nuclei through an intermediate configuration with the C_{4v} symmetry without regard for the rotation of the molecule through an angle of $\pi/2$ about the F₁P-axis).

splitting due to pseudorotation was described as a result of mixing the wave functions of independent rigid molecules, with the mixing matrices built up intuitively as one- and two-dimensional matrices alone⁷. Here, the mixing of only 4 such molecules is taken into consideration (one reference molecule and the three 'nearest' to it in the number of pseudorotation steps) instead of 20 on hand.

Following Ref. [23], we turn to a molecule with much simpler internal dynamics, XPF_4 , where X [CH₃ or (CH₃)₂N among other molecules] replaces one of the equatorial atoms. As is well known (e.g., see Ref. [24]), in this case Berry pseudorotation plays the leading role in the transfer of F nuclei between the equatorial and axial positions. But now only one pseudorotation axis mixes the equivalent configurations and it is enough to allow for only two such configurations.

The group π_4 is the permutation group for the identical F nuclei in the XPF₄ molecule. Since the spin of the F nucleus is 1/2, the total wave function (if we ignore the hyperfine interactions related to nuclear spins) is the convolution of the spin and coordinate parts that transform according to mutually dual Young diagrams [5] (here only spin Young diagrams with a number of rows no greater than two are admissible). Specifying their attendant coordinate Young diagrams and sewing together the group π_4 with the point group $^{8} C_{2v} = (E, C_2^{(z)}, \sigma^{(xz)}, \sigma^{(yz)})$, we obtain the following allowed coordinate multiplets for the rigid molecule XPF₄:

$$1A_1, (5+3+1)A_2, 3B_1, 3B_2.$$
(16)

The number in front of the symbol designating the multiplet represents the statistical weight of the nucleus, which is specified by the spin Young diagram corresponding to the multiplet [5]. The sewing together of the multiplets with the zero-approximation solutions can be written in the form of relation (1) to within the substitution of C_{2v} for $C_{\infty v}$. The correlation between the rotational – inversion representations of the group D_2 of a rigid asymmetric top in terms of the (z, y, x) coordinates follows from the association of the given groups through their common subgroup D_2 . As a result, we have a classification scheme for the levels in an arbitrary vibronic state, which for $\Gamma_{el} \times \Gamma_{vib} = A_1$ as an example is shown in the first two columns in Fig. 3. All the levels are unsplit inversion doublets.

When Berry pseudorotation is taken into account, the molecule becomes delocalized over two independent equilibrium configurations symmetrically arranged near the unstable intermediate configuration. Hence, the geometrical group of the unstable configuration, C_{4v} , is the extended point group. The presence of pseudorotation is due entirely to the distortion of the equilibrium configuration as compared to the intermediate configuration. Here the nonequivalence in the positions of the identical nuclei participating in the motion in the intermediate configuration is eliminated,

⁷ The dimension of the mixing matrices is selected by analogy with the dimensions of the matrices of the irreducible representations of the point group D_{3h} of a rigid molecule, although when Berry pseudorotation is taken into account the geometrical symmetry group of the internal motion is isomorphic to π_5 and has no two-dimensional irreducible representations whatsoever.

⁸ The MCS is selected in such a way that the *z*-axis coincides with the XP-axis, and the yz reflection plane with the plane of the equatorial triangle.



Figure 3. Energy level classification of the molecule XPF₄ in a vibronic state of the A_1 type in the group C_{2v} .

which is characteristic of the exchange type motion [11]. As a result, with the operations C_4^1 and C_4^3 , which determine the pseudorotation in the group C_{4v} , we can associate the permutation of identical nuclei in the group π_4 . This statement agrees with the results of Dalton [12] who simply used the permutations of identical F nuclei to describe Berry pseudorotation. Matching π_4 with C_{4v} yields the following allowed coordinate multiplets for the nonrigid molecule:

$$1A_1, \ 3A_2, \ (5+1)B_2, \ 3E.$$
 (17)

Next, sewing together the group C_{4v} with the group C_{2v} yields a detailed classification of levels with allowance made for nonrigid motion (Fig. 3 depicts this case for $\Gamma_{el} \times \Gamma_{vib} = A_1$). Inasmuch as Berry pseudorotation is specified in the group C_{4v} by the rotational elements C_4^1 and C_4^3 , then to describe the real splitting of levels in a given vibronic state we take (instead of the group $C_{4v} \times C_i$) its rotational subgroup D_4 , with the result that the inversion doublets in the spectrum of a nonrigid molecule remain unsplit (one sublevel of such a doublet is sometimes absent due to the fact that the multiplet B_1 of the group C_{4v} is forbidden).

In setting up a description it is convenient to write the group D_4 in the form $C_4 \wedge U_2$, where the factor group can be written as $U_2 = (E, U_2^{(y)})$. What is important is that the group C_4 contains not only the pseudorotation elements C_4^1 and C_4^3 but also the element C_4^2 whose action is equivalent to ordinary rotation of the molecule. Hence, the complete set of basis vectors in the pseudorotation subspace consists only of two unit vectors $|a\rangle$ and $|b\rangle$ belonging in the C_4 group to the completely symmetric representation *a* and the representation *b* antisymmetric in the elements C_4^1 and C_4^3 . Only such unit vectors are invariant with respect to the purely rotational element C_4^2 . The dimensionality of this subspace determines the number of mixed independent equilibrium configurations in the given problem. The action of the elements of the factor group U_2 in the basis of the invariant subgroup C_4 for these vectors is trivial:

$$U_2^{(y)}|a\rangle = |a\rangle, \qquad U_2^{(y)}|b\rangle = |b\rangle, \qquad (18)$$

i.e. in the D_4 group the vectors $|a\rangle$ and $|b\rangle$ belong to the irreducible representations A_1 and B_2 , respectively. Bearing in mind the well-known behavior of the rotational functions

Table 3. Partition of the basis vectors of the function space for the configuration – rotational motion of the XPF₄ molecule in the vibronic state of the A_1 type in the group C_{2v} into irreducible representations of the group D_4 .

D_4	Basis vectors
A_1	$A_1 a angle,B_2 b angle$
A_2	$A_2 a angle,B_1 b angle$
B_1	$B_1 a angle,~A_2 b angle$
B_2	$B_2 a angle, A_1 b angle$
F	$E_1 a\rangle$ $E_1 b\rangle$
L	$E_2 a\rangle^{'}E_2 b angle$

under transformations belonging to D_4 , we arrive at the partition of the configuration – rotational basis vectors into the irreducible representations of this group for the case $\Gamma_{\rm el} \times \Gamma_{\rm vib} = A_1$ (see Table 3). The rotational parts of the basis vectors have been written in terms of the irreducible representations of D_4 , with E_1 and E_2 being the components of the *E* representation that are specified by the conditions $U_2^{(y)}E_1 = E_1$ and $U_2^{(y)}E_2 = -E_2$.

With allowance made for pseudorotation, the effective operators of physical quantities describing the rotational motion of the XPF₄ molecule belong to the coordinate Young diagram [4] of the group π_4 . Matching π_4 with C_{4v} yields one allowed representation A_1 for such operators in the group C_{4v} . Next, sewing together $C_{4v} \times C_i$ with D_4 leads in the D_4 group to the A_1 and A_2 representations associated with the physical quantities that are, respectively, invariant with respect to inversion *i* or change their sign. The representation for the operators of the coordinate spin **e** acting in a nonstandard two-dimensional coordinate space with basis vectors $|a\rangle$ and $|b\rangle$ can be written in terms of the well-known Pauli matrices [4]:

$$e_{3} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad e_{2} = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad e_{1} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.$$
 (19)

The complete set of self-adjoint operators in the twodimensional space consists of the three components e_i and the totally symmetric unit operator *I*. Bearing in mind the behavior of the basis vectors under transformations belonging to D_4 and under time reversion:

$$T|a\rangle = |a\rangle, \quad T|b\rangle = |b\rangle,$$
 (20)

we find that the operator e_3 is *t*-even and belongs to the representation A_1 of the D_4 group, while the operators e_1 and e_2 are, respectively, *t*-even and *t*-odd and both belong to the representation B_2 .

The Hamiltonian and the operator of the electric dipole moment are the most interesting effective configuration– rotational operators. The Hamiltonian belongs to the representation A_1 of D_4 and is realized through the following two spin–rotational schemes:

$$(A_1)_{\rm sp} \times (A_1)_{\rm rot}, \quad (B_2)_{\rm sp} \times (B_2)_{\rm rot}.$$
 (21)

As a result, its complete expression can be written in the following symbolic form

$$H_{\rm eff} = (I, e_3) \times A_1 + (e_1, e_2) \times B_2 \,. \tag{22}$$

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This expression implies that each term of the Hamiltonian is a combination of products of angular momentum components J_i in the MCS of symmetry A_1 or B_2 in the group D_4 , while the parameters in front of this combination are linear functions of the spin operators of the same symmetry that correlate with the combination. Since the Hamiltonian is *t*-even, when we write down the last expression explicitly we get

$$H_{\rm eff} = \sum_{n=0}^{\infty} \left[H_{2n}^{(A_1)} + H_{2n+2}^{(B_2)} + H_{2n+3}^{(B_2)} \right].$$
(23)

The superscripts on the terms in the right-hand side of this expression indicate the type of irreducible representation of D_4 , to which the combinations of angular momentum components refer, while the subscripts stand for the total power over these components. The coefficients of these combinations in the first, second, and third terms in Eqn (23) depend on the spin operators \hat{c} , \hat{d} , and \hat{f} , respectively:

$$\hat{c} = c^{(1)}I + c^{(2)}e_3, \quad \hat{d} = de_1, \quad \hat{f} = fe_2,$$
(24)

where c, d, and f are the real-valued spectroscopic constants. The electric dipole moment belongs to the representation A_2 of the D_4 group, and the complete expression for it reads as

$$\mu_{\rm eff} = (I, e_3) \times A_2 + (e_1, e_2) \times B_1 \,. \tag{25}$$

The one thing we must bear in mind when writing down this expression explicitly is that the rotational part of the operator of the μ_{α} component along the α -axis of the LCS contains, in addition to the components J_i in the MCS, the direction cosines of the MCS with respect to the LCS (see Section 7.2).

Interestingly, the passage to the limit of an impermeable barrier can be formulated in terms of spin operators. Indeed, for such a barrier the description procedure is independent of the type of symmetry of the nonrigid transition. Hence, in such a description the mere spin operators are retained that are invariant with respect to permutation of indices in the spin subspace, viz. I and e_3 . What is important is that their space is closed with respect to the operation of multiplication in the Lie algebra, i.e. the operation of calculating commutators, since otherwise the condition of conservation of the description procedure under admissible unitary transformations would be violated. As a result, only the rotational contributions with

$$\hat{c} = c^{(1)}I, \quad \hat{d} = de_1$$
 (26)

remain in the effective operators. In the basis set from Table 3 we go over to spin vectors of the form

$$|1\rangle = \frac{|a\rangle + |b\rangle}{\sqrt{2}}, \quad |2\rangle = \frac{|a\rangle - |b\rangle}{\sqrt{2}}.$$
 (27)

It is of importance that when the parameters \hat{c} and \hat{d} are chosen in form (26), the unit vectors are not mixed with spin vectors $|1\rangle$ and $|2\rangle$ by the terms of the effective operator of any physical quantity, i.e. the basis set can be partitioned into the direct sum of two independent sets. Since in each set the spin vector is the sole one, it can be discarded, with the result that the spin parts in the effective operators can be discarded, too. Thus, we arrive at effective operators (the effective Hamiltonian included) corresponding to a rigid molecule with the point group C_{2v} . In other words, the vectors $|1\rangle$ and $|2\rangle$ describe the localization of the molecule in two equivalent





minima of the interaction potential with equilibrium configurations of symmetry C_{2v} .

The above analysis shows that when describing nonrigid motions it is important to isolate the rotational transformations of the molecule as a whole that correspond to the motion without a barrier. In this respect, molecules with a linear core and two equivalent torsion tops may be of interest. Here, sequential torsion motion of the tops through the same angle is equivalent to rotation of the molecule as a whole. This leads to conceptual difficulties when the CNPI group [6] is involved, namely, one is forced to deal with two-valued wave functions (which describe individual purely coordinate motions) that change sign upon a rotation through 2π , which physically is quite meaningless. Consequently, what are known as dual groups are brought into the picture, groups that were introduced for the systems with a half-integer spin [4]. No such difficulties arise in the approach we are currently discussing. The classical example here is the ethane (C_2H_6) molecule. The equilibrium configuration of this molecule (see Fig. 4) corresponds to the point group $D_{3d} = C_{3v} \times C_I$ [25] which contains the inversion element I. When analysis is limited to one minimum, the group used is $C_{3v} \times C_I \times C_i$, which involves two inversion operations of an equal status, despite the fact that they have different physical meanings. However, allowance made for torsion motion leads to a geometrical symmetry specified by an extended point group of the form [26]

$$G_{72} = (c_{3v} \times c_{3v}) \wedge C_I, \qquad (28)$$

where the operation *i* still commutes with all the elements of the geometrical group of the molecule. Table 4, which lists the characters of the group G_{72} , has been borrowed from Ref. [27]. When there are two inversion operations, in the relation between the rotational representations of a rigid symmetric top and the rotational – inversion representation of a sewing together of type (1), two analogs in group $D_{3d} \times C_i$ correspond to each element of the group D_{∞} . For the analogs to coincide, we choose the natural requirement that the element *iI* in this relation be equivalent to the identity rotational transformation. As a result we have the following correlation:

$$g \leftrightarrow +, \quad u \leftrightarrow -,$$
 (29)

where g and u refer to the rotational-inversion representation of the group $D_{3d} \times C_i$, and the '+' and '-' signs refer to the multiplet. Figure 5 shows the classification scheme of the torsion-rotational levels for $\Gamma_{el} \times \Gamma_{vib} = A_{1g}$. The actually

Table 4. Characters of the extended point group G_{72} allowing for torsion motions in the ethane (C₂H₆) molecule (the classes of the group G_{72} are denoted in a way similar to that used in denoting the classes of the group π_6 , while the figures in the row under the classes stand for the number of elements in each the class).

G ₇₂	${1^6}$ 1	${1^33}$ 4	${3^2}$ 4	${1^42}$ 6	${1^2 2^2}$ 9	{123} 12	${2^3}{6}$	{6} 12	{24} 18
A_1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	1	-1	-1	-1
A_3	1	1	1	-1	1	-1	1	1	-1
A_4	1	1	1	-1	1	-1	-1	-1	1
Ε	2	2	2	0	$^{-2}$	0	0	0	0
T_1	4	1	$^{-2}$	-2	0	1	0	0	0
T_2	4	1	$^{-2}$	2	0	-1	0	0	0
T_3	4	$^{-2}$	1	0	0	0	$^{-2}$	1	0
T_4	4	-2	1	0	0	0	2	-1	0



Figure 5. Classification of the torsion–rotational levels of the ethane (C_2H_6) molecule in a vibronic state of the A_{1g} type in the group D_{3d} .

observed level splittings of a rigid top, caused by k-doubling and torsion motion, are described by the rotational subgroup $H_6 \times D_3$ of the group $G_{72} \times C_i$, where D_3 is the rotational subgroup of the group D_{3d} . The group H_6 isomorphic to D_3 has the form $H_3 \wedge H_2$, with the invariant subgroup $H_3 = (E \times E, c_3 \times c_3^2, c_3^2 \times c_3)$ and the factor group $H_2 = (E, Ii)$. Specifying torsion motion by the elements $c_3 \times c_3^2$ and $c_3^2 \times c_3$, we arrive at an independent description of torsion and rotational motions via the groups H_6 and D_3 . The variant with an independent description is only possible if stringent restrictions are imposed on the symmetry of the problem. A less symmetric case occurs in molecules with planar torsion tops, such as ethylene (C_2H_4 , point group D_{2h}) and allene (C₃H₄, point group D_{2d}). Here, the top axis is only a binary axis, so that there is no way in which the group of torsion-rotational motion can be represented as the direct product of the groups describing different types of motion. The matter is that the top identity requires that the torsion operations $c_2 \times E$ and $E \times c_2$ be used symmetrically, and their product $c_2 \times c_2$ is equivalent to ordinary rotation of the molecule as a whole. But to resolve the motions, it is enough to match the requirement that the operation $c_2 \times c_2$ is only specified in the rotational subspace. In many respects the situation is similar to the case where the operation C_4^2 is applied to describing Berry pseudorotation in the XPF₄ molecule.

The problem of resolving the internal motions in the PF_5 molecule is much more complicated [28]. As is known [12], the symmetry group of the coordinate motion is isomorphic to π_5 with allowance made for three pseudorotation axes passing through the vertices of the equatorial triangle. Since the operations of the rotational subgroup D_3 of the point group D_{3h} do not mix independent equilibrium configurations, the number of such configurations is 5!/6 = 20. Notice that when analyzing the XPF4 molecules we extensively used the following two properties of the geometrical symmetry group C_{4v} for the pseudorotation intermediate configuration. First, this group incorporates as a subgroup the point group C_{2v} of both the equilibrium configurations and, hence, characterizes the equilibrium configurations as well as the transitions between them. Second, the group in question is a transformation group of a single geometric figure, which makes it possible to easily resolve the rotation of the molecule as a whole.

The situation with the PF₅ molecule is altogether different. And the matter is that it is not because the number of independent equilibrium configurations mixed by the Berry pseudorotation increases dramatically. It is important that the mixing proceeds through three intermediate configurations that do not exist simultaneously and they are arranged differently in space with differing sets of four identical F nuclei, and that the symmetry group C_{4v} of an intermediate configuration does not incorporate the point group D_{3h} as a subgroup. In other words, the transformations belong to different geometric figures, and their rotational interpretation cannot be extended to the system as a whole. Therefore, separation of the rotational transformations is a complicated problem, and its solution requires a detailed analysis of the geometrical structure of the symmetry group of internal motion. Only recently (see Ref. [28]) was it found that the geometrical symmetry group isomorphic to π_5 can be represented in the form

$$G_{120} = Y \wedge C_S \,, \tag{30}$$

where the invariant subgroup Y is isomorphic to the group of 60 rotations about the axes of an icosahedron (or pentagonal dodecahedron) [29], and the only nontrivial element of the factor group $C_S = (E, \sigma)$ is the reflection in the plane of the equatorial triangle. What is interesting is that the group G_{120} can be built up [28] solely on the grounds of the rotational elements of D_3 and the pseudorotation element which also has a rotational interpretation in the group C_{4v} . But in the group G_{120} the only rotational elements are those that belong to the subgroup Y, which does not contradict the group-building

procedure precisely because pseudorotation proceeds through three intermediate configurations that do not exist simultaneously and are arranged differently in space. What has been said is readily illustrated by the fact that the group G_{120} incorporates as a subgroup the point group D_{3h} containing among other things improper transformations.

In this section we demonstrated the possibilities of applying qualitative methods to the solution of problems of varying complexity that describe the internal motions in molecules with nonrigid transitions of exchange type. The effectiveness of these methods is most vividly illustrated by the fact that we were able to rigorously solve the extremely complicated classical problem of the internal motion in molecules of ML_5 type (PF₅, SbCl₅, NbCl₅, TaBr₅, etc.) with allowance made for polytope regrouping of the type of Berry pseudorotation between twenty independent equilibrium configurations of such molecules. This makes it possible to look with optimism on the outlook for the development of the qualitative quantum dynamics of molecules.

The effectiveness of these methods largely stems from the fact that in describing nonrigid motion one does not need to determine the trajectory of such a motion in terms of a set of internal coordinates - one should only indicate an intermediate nuclear configuration [11] whose transformations specify the symmetry of this motion. If the identical nuclei participating in the nonrigid motion are arranged in an equilibrium configuration in a geometrically equivalent way, the intermediate configuration simply coincides with the equilibrium configuration. In doing so, the extended point group differs from the point group in that it incorporates not only transformations of this configuration as a whole. A typical example is the ethane (C_2H_6) molecule. The molecular extended point group G_{72} specified in Eqn (28) additionally allows for (in comparison to the point group D_{3d}) the rotation of the methyl tops with respect to each other. However, if the identical nuclei participating in the nonrigid motion are arranged in an equilibrium configuration in a geometrically nonequivalent way, the intermediate configuration differs from the equilibrium configuration. What makes the intermediate configuration so special is that the identical nuclei are arranged in it equivalently with respect to geometrical operations that force the nuclei to change places. It should be emphasized that in the case of nonrigid motion the intermediate configuration is not obliged to correspond to the top of the barrier. Such correspondence occurs only when the barrier originates entirely due to a distortion of the equilibrium configuration as compared to the intermediate configuration. This is precisely the situation when the molecules with a Berry pseudorotation are involved.

6.2 Molecules with nonrigid nonexchange-type transitions

Of all the examples of intramolecular motions of the nonexchange type considered up to this time, the most interesting is that involving the hydrazine (N_2H_4) molecule [30]. An important consequence of these motions is the mixing of what are known as stereoisomers [4], although the geometrical symmetry group of a nonrigid molecule contains no improper transformations of the molecule as a whole (similarly to the case of the point group of the molecular equilibrium configuration).

A characteristic feature of the N₂H₄ molecule is the proximity of its equilibrium configuration belonging to the point group $C_2 = (E, C_2^{(y)})$ [31] to the intermediate molecular configuration (the left part of Fig. 6). In this intermediate



Figure 6. Intermediate configurations for the stereoisomers of the N_2H_4 molecule (the *z*-axis coincides with the straight line connecting the centers of mass of the equivalent NH_2 structures).

state the two equivalent NH2 structures are isosceles triangles, with the dihedral angle between them being equal to $\pi/2$. Therefore, each NH₂ structure can be climbed over a fairly low potential barrier [32, 33] into an energy-equivalent position either through reflection σ_2 in the plane passing through the z-axis parallel to the HH segment (inversion motion) or through rotation by the angle π about the z-axis (internal rotation). These four motions (which belong to the nonexchange type) delocalize the molecule through an intermediate configuration among eight independent equilibrium positions. The availability of a molecular stereoisomerism means [4] that there is not a single rotation as a whole that can make the inverted equilibrium configuration of the molecule coincide with the initial one. The latter is possible if the point group contains no improper transformations. The probability of mixing the stereoisomers of rigid molecules is exceptionally low, and we can speak of their 'right' and 'left' modifications whose energy levels coincide. It is easily comprehended that mere nonrigid motions of the nonexchange type can mix stereoisomers, since only they alter the spatial position of the initial configuration. But this is a necessary condition, while the full answer to the question of the availability of such a mixing depends on the specific geometry of motions of nonexchange type.

The noninvariant dynamical group of the N_2H_4 molecule is expressed in terms of the geometry of the unstable intermediate configuration as follows:

$$D_{32} = (c_{2v} \times c_{2v}) \wedge C_2, \qquad (31)$$

where the direct product of the groups $c_{2v} = (E, c_2^{(z)}, \sigma_1, \sigma_2)$ describes the symmetry of the motions of the two NH₂ structures, while the group C_2 accounts for the fact that these structures are identical. The configuration obtained from the intermediate one through spatial inversion *i* is depicted on the right of Fig. 6. Its geometry is used to express the symmetry of the internal motion of a stereoisomer. Comparing the two configurations, we easily establish that

$$i = (\sigma_2 \times \sigma_1) U_2^{(1)} = (\sigma_1 \times \sigma_2) U_2^{(2)},$$
 (32)

where the $U_2^{(k)}$ indicate the rotations of the molecule through the angle π about the axes k = 1, 2 that run along the bisectors of the angles between the x- and y-axes, i.e. the group D_{32} takes into account the possibility of stereoisomer mixing. The element $\sigma_1 = c_2^{(z)} \sigma_2$ belonging to the exchange type describes



Figure 7. Energy level classification of the N₂H₄ molecule in a vibronic state of the *A* type in the group $C_2(e_{1,n} \text{ and } e_{2,n} \text{ are the two components of the representation } E_n$ of the group D_{32} with n = 3, 4 into which, as shown in Table 5, these representations split under reduction of the group D_{32} into its Hamiltonian symmetry subgroup G_8).

a consecutive realization of two motions of nonexchange type inherent in the NH₂ structure. Hence mixing takes place over a fairly low potential barrier. To completely define the operations $U_2^{(k)}$, we must know their permutation relations with the elements of the group D_{32} . According to the condition of commutation between *i* operation and the elements of the group D_{32} , the operations $U_2^{(k)}$ commute with the elements of the group $c_{2v} \times c_{2v}$, while their permutation relations with $C_2^{(y)}C_2^{(y)}$ are ordinary rotational relations: $C_2^{(y)}U_2^{(1)} = U_2^{(2)}C_2^{(y)}$. In the group D_{32} , the symmetry subgroup of the

In the group D_{32} , the symmetry subgroup of the Hamiltonian of the overall internal coordinate motion can be written in the form

$$G_8 = (c_S \times c_S) \wedge C_2 \,, \tag{33}$$

where $c_S = (E, \sigma_1)$. The group D_{32} has eight one-dimensional representations A_k and six two-dimensional representations E_k , while the group G_8 has four one-dimensional representations a_k and one two-dimensional representation e [34]. Notice that the group G_8 is much broader than the point group of the molecule, although all the nonrigid motions belong to the nonexchange type. It is important to emphasize the fact that in such systems the symmetry group of the Hamiltonian determines the degeneracy of the levels (observed in the energy spectrum) and their nuclear statistical weights [7]. In the case at hand we have

$$6a_1, 3a_2, 45a_3, 36a_4, 27e.$$
 (34)

The classification of the energy levels made in Ref. [30] is shown in Fig. 7 for a vibronic state of the A type in the group C_2 . The following remarks are in order.

(1) When operations of nonexchange type are taken into account, the symmetry of the rotational motion becomes broader and is defined by the group D_4 which incorporates rotational transformations of the molecule as a whole that belong to the group $D_{32} \times C_i$. The extension is associated with the fact that in the formation of such transformations of the group $D_{32} \times C_i$ not only the element *i* is used but so are other elements of nonexchange type as well. The behavior with respect to all such elements must refer to a multiplet, which leads to modification of the structure in stage (1) (in Section 7.2 this modification is made for a case that technically is simpler).

(2) Levels of the E_3 and E_4 types split into doublets, since on reducing the group D_{32} into the group G_8 determining the degeneracy of the levels and their nuclear statistical weights these two-dimensional representations are decomposed into one-dimensional (see Table 5).

(3) The group $H_2 \times H_8$, where $H_2 = (E, (E \times c_2)U_2^{(2)})$ and $H_8 = (c_2 \times c_2) \wedge C_2$, is the rotational subgroup of the

Table 5. Correlation between the irreducible representations of the noninvariant group D_{32} , which allows for motions of nonexchange type in the hydrazine (N₂H₄) molecule, and the irreducible representations of the symmetry group G_8 of the Hamiltonian bearing the responsibility for its intramolecular motion.

G_8	D ₃₂
a_1	$A_1, A_5, e_{2,3}$
a_2	$A_2, A_6, e_{1,3}$
<i>a</i> ₃	$A_3, A_7, e_{2,4}$
a_4	$A_4, A_8, e_{1,4}$
е	E_1, E_2, E_5, E_6

group $D_{32} \times C_i$ and it plays only an auxiliary role, since it is unable to account for all the splittings (improper transformations correspond to half the nonrigid motions).

(4) The energy level diagram for $\Gamma_{\rm el} \times \Gamma_{\rm vib} = B$ can be obtained from Fig. 7 by the formal replacements $A_1 \leftrightarrow B_2$ and $A_2 \leftrightarrow B_1$ of the representations of the group D_4 .

The method of building up the function space and the operators of the coordinate physical quantities, defined in this space, can be found in Ref. [30]. Here it should only be noted that for such operators (the Hamiltonian included) only one completely symmetric representation a_1 of the group G_8 and a full three types of transformations belonging to the group D_{32} are allowed:

$$A_1, A_5, e_{2,3},$$
 (35)

where only one component $e_{2,3}$ of the representation E_3 is admissible (see Table 5). The latter circumstance does not lead to contradictions, since the components $e_{1,3}$ and $e_{2,3}$ of the representation E_3 are mixed only by operations of nonexchange type, which change some of the elements of the Hamiltonian symmetry group simultaneously (the symmetry axis of the point group changes its position from y to x, or vice versa). It is the noninvariant terms in the Hamiltonian that split the levels of the E_3 and E_4 types into doublets (see Fig. 7). Note that such terms also play a significant role in the passage to the limit of impermeable barriers for nonrigid intramolecular motions.

The emergence of dynamical noninvariant groups in the description of molecules with nonrigid motions of the nonexchange type can be explained by the fact that the geometrical symmetry group of the Hamiltonian in such systems does not simultaneously 'look after' all the necessary independent equilibrium configurations, since they are related by noninvariant transformations. As for the expression 'symmetry group' in relation to a dynamical noninvariant group, the term 'symmetry' should be understood here in a broader sense than 'invariance'. Finally, the effectiveness of the methods being discussed is well illustrated by the example of the hydrazine molecule, which was used to provide the first description of the effect of stereoisomer mixing by nonrigid motions. Since the given effect is possible only if motions of nonexchange type are present in the system, there is no way in which we can describe it without using noninvariant groups.

7. Geometrical symmetry groups of nonrigid molecules with energy-nonequivalent configurations

For a very large class of molecules the description of the observed nonrigid motion stems from the necessity to take into account the mixing of energy-nonequivalent configurations. All such problems can be divided into two groups. The first group concerns the molecules with transitions between nonequivalent configurations in a single electronic state. A typical example is the partially deuterated isotopic form CH_2DOH of the methanol molecule, where the torsion motion of the distorted methyl group still mixes the three equilibrium configurations. Two of these are energy-equivalent stereoisomers with the point group C_1 and correspond to the case where the D nucleus occupies a position to the left and right of the COH structure plane, while the third equilibrium configuration with the point group C_S has its D nucleus in the COH plane.

The second group deals with problems of describing the electronic states of a molecule with different isomeric forms within a unified model. Changes in the isomeric forms of the molecule caused by alterations in the electronic state are often encountered, and the classical example here is the formaldehyde (H₂CO) molecule. It is commonly known (see Ref. [31]) that the equilibrium configuration of this molecule in the ground electronic state is planar and belongs to the point group C_{2v} (the left part of Fig. 8). But in some excited electronic states the C-O bond does not lie in the plane of the H₂C structure [35], and the point group C_S is realized (the right part of Fig. 8). Owing to the fairly small displacement from the plane, inversion motion between the two energyequivalent configurations can be observed, with the configurations transferring into one another under the molecular reflection in the yz-plane. A qualitative analysis within the framework of a unified model of electronic states with different isomeric forms is necessary, above all, for a description of the electromagnetic transitions between these states.



Figure 8. Equilibrium configurations of two isomers of the formaldehyde (H_2CO) molecule (in the nonplanar configuration, the *z*-axis passes through the center of mass of the CH₂ structure and the O nucleus).

7.1 Molecules with transitions between nonequivalent configurations in a single electronic state

The main idea behind analyzing such systems is that they are interpreted as distorted systems with energy-equivalent configurations. For the isotopic form CH_2DOH , the CH_3OH molecule represents the undistorted system, whose dynamical invariant group (allowing for molecular internal rotation) coincides with the dynamical noninvariant group for the form CH_2DOH [36].

Following paper [37], we will show the reasonableness of such an approach by the example of describing the rotational spectrum of the isotopic form PH₂D of the rigid phosphine molecule. The isotopically symmetric form PH₃ is characterized by the point group C_{3v} [31]. Figure 9 illustrates the classification scheme of the rotational levels of this form for $\Gamma_{\rm el} \times \Gamma_{\rm vib} = A_1$. The rotational subgroup D_3 of the group $C_{3v} \times C_i$ is used to describe the observed level splitting. The



Figure 9. Classification of the rotational levels of the isotopically symmetric form PH_3 of the phosphine molecule in a completely symmetric vibronic state.

partition of the rotational function space into the irreducible representations of D_3 and building up of the properly defined effective operators of physical quantities in this space are trivial. In particular, only combinations of the components of angular momentum in the MCS that transform according to the representation A_1 of the D_3 group enter into the effective Hamiltonian.

When we go over to the isotopically asymmetric form PH₂D, let us assume that changes in the qualitative analysis are independent of the H-to-D mass ratio but are fully determined now by the presence of two identical nuclei instead of three. The group C_{3v} is retained as the dynamical noninvariant group, while C_S is its Hamiltonian symmetry subgroup. The latter incorporates reflection in the plane, which interchanges the position of H nuclei. Then for the allowed coordinate multiplets of C_{3v} we find

$$3A_1, 9A_2, 3E_1, 9E_2.$$
 (36)

The components E_1 and E_2 of the *E* multiplet in expression (36) correspond to various levels with different statistical weights, since on reducing the group C_{3v} into C_S (its Hamiltonian symmetry subgroup) this two-dimensional representation is decomposed into two one-dimensional representations (we encountered a similar situation when having used noninvariant groups to study the N₂H₄ molecule). The rotational group D_3 also becomes the noninvariant group, and its representation *E* determines two levels with differing energies, with the levels corresponding to the components E_1 and E_2 which are transferred into the representations A and B under the reduction of D_3 to C_2 (its Hamiltonian symmetry subgroup). Figure 10 demonstrates the modified classification of the rotational levels of the PH₃ molecule (see Fig. 9) for its isotopic form PH₂D.

The admissible transformations in the group D_3 for the effective rotational Hamiltonian are A_1 and E_1 . It is the presence of a transformation of the noninvariant type that distorts the picture of the description corresponding to a symmetric top with the point group C_{3v} . A specific building up shows that the distorted picture is fully equivalent to the description of a molecule of asymmetric-top type with the



Figure 10. Modification of the rotational level classification caused by the passage to the isotopically asymmetric form PH_2D of the phosphine molecule.

point group C_S . Including the degenerate vibronic states of the group C_{3v} in the picture signifies allowing for resonance interactions within the quasi-degenerate set of these states, which emerges in the reduction of C_{3v} into C_S . Notice that for rigid molecules the advantages of a description with the inclusion of distortion are not really significant. What is important in such circumstances is that all the description schemes implicitly use the three-dimensional rotational group R_3 in the MCS (which specifies the complete set of basis vectors $|J,k\rangle$ in the rotational space) as the dynamical noninvariant group.

Systems similar to the CH₂DOH molecule have also been studied. Among these are the HF-DF dimer [37] and the isotopic form CH₂D-CH₂D of the ethane molecule [38]. In the planar equilibrium configuration of the dimer (HF)₂, the monomers are arranged in an energy-nonequivalent manner [31]. As a result, the dimer is delocalized onto two independent equivalent configurations that differ in monomer permutation and are symmetrically positioned in the neighborhood of an unstable intermediate configuration with an energy-equivalent arrangement of the monomers. The symmetry of the intermediate configuration corresponds to the symmetry of internal motion, provided that the nonrigid transition through this configuration is taken into account.

The most probable are the *trans*- and *cis*-transitions [39] whose intermediate configurations have the symmetry groups C_{2h} and C_{2v} , i.e. two equivalent minima are related through two transitions belonging to the exchange type. The fact that there are two different transitions for a single set of minima does not make it more difficult to analyze the system [11]. When one H nucleus is replaced by a D nucleus, the equilibrium configurations become nonequivalent and the internal dynamics present for the symmetric form (HF)₂ grow distorted. As a consequence, the groups C_{2h} and C_{2v} become noninvariant.

More interesting, however, is the case of the CH_2D – CH_2D isotopic form of the ethane molecule. In describing the torsion motion of this isotope-substituted molecule one must take into consideration the fact that the distorted methyl tops are identical. Here, the extended point group G_{72} [defined by expression (26)] of the C_2H_6 molecule is used as the dynamical noninvariant group incorporating the torsion motion operations. To set apart the Hamiltonian symmetry subgroup G_H from this group, we allow for the fact that in the noninvariant group C_{3v} of the methyl top only the reflection in the plane that interchanges the positions of the H nuclei has an analog in the identical-nuclei permutation group $\pi_2^H \times \pi_1^D$. Although torsion motion delocalizes this plane, the function space and the operators of physical quantities specified in this space can be written out for any of its reference positions. The most appropriate position of this plane is the one in which the D nuclei of both methyl tops in Fig. 4 are in the *yz*-plane. Then we can write down G_H in the form

$$G_H = (c_S \times c_S) \wedge C_I, \tag{37}$$

where $c_S = (E, \sigma^{(yz)})$. The group G_H determining the degeneracy of the levels and their nuclear statistical weights has four one-dimensional representations a_k and one two-dimensional representation e:

$$6a_1, 3a_2, 45a_3, 36a_4, 27e$$
. (38)

Eventually we arrive at a modification of the torsion– rotational level classification of the ethane (C₂H₆) molecule (see Fig. 5) for its isotopic form CH₂D–CH₂D (Fig. 11). The following remarks are in order: (1) the components $T_{i,k}$ of the four-dimensional irreducible representation T_i (two onedimensional components with the subscripts k = 1, 2, and one two-dimensional with the subscript k = 3) are determined by the splitting conditions for these representations in the



Figure 11. Modification of the torsion–rotational level classification caused by the passage to the isotopically asymmetric form CH_2D – CH_2D of the ethane molecule.

Table 6. Correlation between the irreducible representations of the noninvariant group G_{72} which allows for torsion motions of nonexchange type in the CH₂D – CH₂D isotopic form of the ethane molecule and the irreducible representations of the symmetry group G_H of the Hamiltonian of its intramolecular motion.

G_H	<i>G</i> ₇₂
a_1	$A_1, T_{2,1}, T_{4,1}$
a_2	$A_2, T_{2,2}, T_{3,1}$
<i>a</i> ₃	$A_3, T_{1,1}, T_{4,2}$
a_4	$A_4, T_{1,2}, T_{3,2}$
е	$E, T_{1,3}, T_{2,3}, T_{3,3}, T_{4,3}$

reduction of the group G_{72} to G_H (Table 6), i.e. each level of the T_i type can, in principle, split into three sublevels; (2) the real level splittings are described by the noninvariant group $H_6 \times D_3$ with the Hamiltonian symmetry subgroup $H_2 \times C_2$, where $C_2 = (E, C_2^{(x)})$; (3) no statistical weights for the representations of the noninvariant group D_{3d} exist, because in this approximation there is more than one set of such representations due to the realizations of different point groups for isolated equilibrium configurations of the CH₂D-CH₂D molecule. A total of three independent configurations are possible here: the reference configuration and the two configurations obtained from it through the transformations $c_3 \times c_3^2$ and $c_3^2 \times c_3$. The reference configuration has the point group C_{2h} , while the other two are stereoisomers with only one symmetry element $C_2^{(p)}$, where p stands for the binary axis of the DCCD structure; (4) in the group $H_6 \times D_3$, the degeneracy of the levels is completely removed, and the sublevels due to splitting are denoted by the components E_1 and E_2 of the representation E of the H_6 and D_3 groups. These components are determined by the conditions needed for a passage to the symmetric and antisymmetric representations of the H_2 and C_2 groups, and (5) the Hamiltonian symmetry lowered considerably, but the nuclear statistical weights of the torsion-rotational levels assume two values, 78 and 66 (they are obtained by summing the statistical weights for the multiplets of the group G_{72} , which are transferred into a single torsion-rotational level of the group $H_6 \times D_3$). Naturally, in the limit of an impermeable torsion barrier the nuclear statistical weights of the stationary states are transformed into well-known expressions. The validity of this limiting process is verified by the fact that the energy levels of the stereoisomers are coincident.

The complete set of the torsion basis vectors, $|0\rangle$ and $|\pm 1\rangle$, is determined by three irreducible representations of the subgroup H_3 of the group H_6 . In the latter these basis vectors realize the following symmetry types:

$$|0\rangle \to A_1, \qquad |s\rangle = \frac{|1\rangle + |-1\rangle}{\sqrt{2}} \to E_1,$$

$$|a\rangle = \frac{|1\rangle - |-1\rangle}{\sqrt{2}i} \to E_2.$$
 (39)

In the upshot we have Table 7 which clearly demonstrates the division of torsion – rotational basis vectors according to the types of transformations belonging to the group $H_6 \times D_3$. The torsion part of the operators of physical quantities specified in this space is built around the coordinate spin operator **e**. In its standard definition in the space with the basis vectors $|0\rangle$ and $|\pm 1\rangle$, the operator e_3 is a diagonal operator with eigenvalues 0 and ± 1 , while the operators $e_{\pm} = e_1 \pm ie_2$ are the raising and lowering operators. Using the symmetry properties of the torsion basis vectors in the

Table 7. Division of torsion-rotational basis vectors for the CH₂D-CH₂D isotopic form of the methane molecule according to the symmetry types of the group $H_6 \times D_3$ (the rotational parts are denoted by the symmetry types of the group D_3).

$H_6 \times D_3$	Basis vectors	$H_6 \times D_3$	Basis vectors	$H_6 \times D_3$	Basis vectors
$A_1 \times A_1$ $A_1 \times E_1$ $E_1 \times A_1$ $E_1 \times E_1$	$\begin{array}{l} 0\rangle \times A_1 \\ 0\rangle \times E_1 \\ s\rangle \times A_1 \\ s\rangle \times E_1 \end{array}$	$A_1 \times A_2$ $A_1 \times E_2$ $E_1 \times A_2$ $E_1 \times E_2$	$\begin{array}{l} 0\rangle \times A_2 \\ 0\rangle \times E_2 \\ s\rangle \times A_2 \\ s\rangle \times E_2 \end{array}$	$E_2 \times A_1$ $E_2 \times E_1$ $E_2 \times A_2$ $E_2 \times E_2$	$\begin{array}{l} a\rangle \times A_1 \\ a\rangle \times E_1 \\ a\rangle \times A_2 \\ a\rangle \times E_2 \end{array}$

group H_6 and in relation to the time inversion T, viz.

$$T|0\rangle = |0\rangle, \quad T|1\rangle = |-1\rangle,$$
(40)

we find that e_3 is a *t*-odd operator belonging to the representation A_2 of the group H_6 , and the operators e_1 and e_2 are *t*-even operators that realize the representation *E*. Inasmuch as for three-dimensional space the highest total order of the product of spin components cannot be larger than two, altogether there are nine independent self-adjoint spin operators which are listed in Table 8.

Table 8. Symmetry properties of the complete set of independent spin operators used in describing torsion motion in the isotopic form CH_2D – CH_2D of the ethane molecule ([,]₊ stands for an anticommutator).

H_6	<i>t</i> -even	<i>t</i> -odd
A_1	I, e_3^2	-
A_2	-	<i>e</i> ₃
Ε	$E_1 = e_+ + e$	
	$\mathbf{i}E_2 = e_+ - e$	$iE_1 = [e_3, e_+ - e]_+$
	$E_1 = e_+^2 + e^2$	$E_2 = -[e_3, e_+ + e]_+$
	$iE_2 = -e_+^2 + e^2$	

All the torsion-rotational operators of physical quantities belong to the identity representation of G_H . The sewing together of $G_H \times C_i$ with $H_6 \times D_3$ yields, within the latter group, the transformation kinds as follows

$$A_1 \times A_1, \ A_1 \times E_1, \ E_1 \times A_1, \ E_1 \times E_1 \tag{41}$$

for the operators of physical quantities invariant with respect to inversion *i*, and

$$A_2 \times A_1, \ A_2 \times E_1, \ E_2 \times A_1, \ E_2 \times E_1 \tag{42}$$

for the operators of the quantities that change their signs when acted upon by *i*. In particular, according to Eqn (41), the complete expression for the effective torsion–rotational Hamiltonian can be written in the following symbolic form

$$H = (I, e_3^2, e_+ + e_-, e_+^2 + e_-^2, i[e_3, e_+ - e_-]_+) \times (A_1, E_1).$$
(43)

In other words, each term in the Hamiltonian is a combination of the components J_i of angular momentum in the MCS of symmetry A_1 or E_1 in the group D_3 , while the coefficients of the combination depend on the spin operators correlating with this combination. When we wish to write out the expression (43) explicitly, we must bear in mind that the Hamiltonian is a *t*-even operator. No difficulties also arise in building up the operators of other physical quantities [38].

Above we have examined the conceptual aspects of applying symmetry methods to such molecules with nonrigid internal motions between energy-nonequivalent equilibrium configurations for which these motions in a certain highsymmetry form of the molecule become those of the exchange type and already correspond to transfers between energyequivalent configurations, i.e. the description of a real system is patterned as a distortion of the description of the highsymmetry system. To this end, the invariant geometrical group of the high-symmetry problem, the group that allows for nonrigid motions, is used as a noninvariant group in describing the distorted system. In particular, the nuclear statistical weights of the stationary states of the distorted system can easily be found. The given problem is classical as regards the usage of symmetry methods, but for systems of this sort it has been solved for the first time. Its nontrivial nature is indicated by the simple fact that the nuclear statistical weights of the stationary states of rigid molecules, corresponding to nonequivalent equilibrium configurations, are distinct, generally speaking. Finally, note that the role of a high-symmetry system is also apparently prominent when the equations of motion are solved analytically. This is corroborated by Rebane's calculations [40] of the binding energies for different forms of four-particle mesomolecules.

7.2 Joint description of the electronic states of a molecule with different isomeric forms

The situation where a change in the electronic state of a molecule is accompanied by an alteration in the molecular isomeric form is rather common. Developing a unified model that describes such states is very useful. The point is that even if the electronic states with distinct isomeric forms remain practically unmixed due to the large difference in energies, their analysis within a unified model is needed, for instance, in order to describe the electromagnetic transitions between them. Following paper [41], we shall examine the joint description of two electronic states with distinct isomeric forms for the formaldehyde (H₂CO) molecule. As noted earlier, the equilibrium configuration of the molecule in the ground electronic state is planar and belongs to the point group $C_{2v} = (E, C_2^{(z)}, \sigma^{(xz)}, \sigma^{(yz)})$ (the left part of Fig. 8), while in some of its excited electronic state the C-O bond does not lie in the plane of the H₂C structure, so that the point group $C_S = (E, \sigma^{(xz)})$ is realized (the right part of Fig. 8). Due to the relatively small deviation from planarity, the inversion motion is executed between two energy-equivalent configurations, with the configurations transferred into one another under the reflection of the molecule in the yz-plane.

The analysis of isolated isomers is trivial, and here we briefly give the results needed in our future exposition. For a rigid nonplanar isomer, the coordinate multiplets 1A' and 3A'' are admissible multiplets, and all the rotational levels in an arbitrary vibronic state are unsplit inversion doublets. To allow for inversion motion, let us introduce the extended point group $G_4 = C_S \times C'_S$, where $C'_S = (E, \sigma^{(yz)})$. Inversion motion belongs to the nonexchange type, with the result that G_4 is a noninvariant group. The allowed coordinate multiplets of this group are given in the form

$$1A'_{s}, 1A'_{a}, 3A''_{s}, 3A''_{a},$$
(44)

where the subscripts s and a indicate the symmetric and antisymmetric representations of C'_S , respectively.

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When an inversion transfer is taken into account, the symmetry of the rotational motion broadens and is specified by the group $D_2 = (E, C_2^{(z)}, C_2^{(y)}, C_2^{(x)})$ which incorporates the rotational transformations of the molecule as a whole from the group $G_4 \times C_i$. The extension is needed because in the formation of such transformations of the group $G_4 \times C_i$ not only the element *i* is used but also the element $\sigma^{(yz)}$ of nonexchange type. The behavior with respect to these elements must refer to the multiplet, thus leading to a natural modification of the structure in stage (1):

$$(\Gamma_{\text{mult}})_{C_{S} \times C'_{S} \times C_{i}} = (\Gamma_{\text{el}})_{C_{S}} \times (\Gamma_{\text{vib}})_{C_{S}} \times (\Gamma_{\text{rot-inv}})_{C_{S} \times C'_{S} \times C_{i}},$$

$$(45)$$

where the rotational-inversion representations of the group $C_S \times C'_S \times C_i$ follow from the rotational representations of the group D_2 via the relationship of the given groups through their common subgroup D_2 . According to the classification, the inversion doublets are now split.

The point group of a planar isomer can be represented in the form $C_S \times C'_S$, and the allowed coordinate multiplets are $1A'_s$ and $3A''_s$. Representations of the 'a' type are not realized as multiplets due to the planarity of the isomer. For this reason there can be no inversion level doubling. This is a particular case of the general statement formulated in Section 5.

To describe two electronic states with distinct isomeric forms in a combined manner, we shall introduce the dynamical noninvariant group $G_{12} \times C_S$, where $G_{12} =$ $c_{3v} \times c_S$. The c_{3v} group specifies the transformations of the CH_2 structure, with the c_3 -axis passing through the center of mass of this structure parallel to the y-axis, while one of the symmetry planes coincides with the *yz*-plane. Here, the fact that the angle between the CH₂ planes in the planar and nonplanar isomeric forms differs substantially from $2\pi/3$ is unimportant, since such a distinction can be interpreted, for instance, as a distortion of the nonplanar form. Naturally, this distortion is also determined by the difference in bond lengths in the planar and nonplanar isomers. The only thing that is important here is that qualitatively the group c_{3v} correctly conveys the picture of transfers between the three configurations considered (two of which are energy-equivalent) and, as a consequence, determines the complete set of basis vectors of the function space used in the description of these transfers. The $c_S = (E, \sigma^{(yz)})$ group, which specifies the transformations of the O structure, makes it possible for the group G_{12} to describe the reflection of the molecule as a whole in the yz-plane with the aid of the element $\sigma^{(yz)} \times \sigma^{(yz)}$. Only the identity representation of the group c_S has physical meaning, and this trivial behavior will be discarded when we write out the symmetry types of the group G_{12} . The group c_{3v} can be represented as $c_3 \wedge c'_S$, where $c'_S = (E, \sigma^{(yz)})$, which is convenient when the planarity of the CH₂ structure is taken into account. Indeed, let us assume that the molecule is localized in the yz-plane. Then the planarity of the CH_2 structure leads to a situation in which only one out of two representations of the group c'_S is physically realized. The delocalization of the initial configuration is described by the representations of the cyclic group c_3 , and the prohibition of the asymmetric representation of the group c'_S makes the representation A_2 of the c_{3v} group in the multiplets of the group G_{12} to be forbidden, too. As a result, the allowed multiplets of the noninvariant $G_{12} \times C_S$ group have the form

$$1(A_1 \times A'), \ 3(A_1 \times A''), \ 1(E \times A'), \ 3(E \times A'').$$
 (46)



Figure 12. Energy level classification of the formaldehyde (H_2CO) molecule with a joint description of two electronic states with different isomeric forms.

It should be emphasized that despite equal nuclear statistical weights, the components of the degenerate multiplets in Eqn (46) determine different levels.

If we allow for nonrigid motions between the three equilibrium configurations, the rotational symmetry is specified by the subgroup D_2 of rotations of the molecule as a whole in the group $G_{12} \times C_S \times C_i$. The pattern of the configuration splittings of the rotational levels of the group D_2 is shown in Fig. 12. In addition, we depict in this figure the behavior of the levels when an isolated description of the isomers is introduced (the passage from the group $G_{12} \times C_S \times C_i$ to the group $C_S \times C'_S \times C_i$). Notice that the correspondence between the representations of the $C_S \times C'_S \times C_i$ group and the rotational representations of D_2 depends on the type of their vibronic states in the point group (C_S or C_{2v}).

In building up the function space of configurationrotational motion, we shall use the basis functions of the group D_2 , which describe the rotation of a nonrigid molecule as a whole, and the basis configuration functions of the group c_{3v} , which describe nonrigid transitions. The latter functions, in view of the planarity of the CH₂ structure, are built only around the unit vectors $|0\rangle$ and $|\pm 1\rangle$, which are defined by the three irreducible representations of the group c_3 . As a result, the symmetry properties of the configuration basis vectors in the group c_{3v} and with respect to time reversion are given by the expressions (39) and (40). Here, there is no basis vector of the A_2 type, in full agreement with the classification. Next, from the correlation of the representations of the D_2 and $G_{12} \times C_S \times C_i$ groups follows Table 9 which exhibits the division of the configuration-rotational basis vectors according to the irreducible representations of the $G_{12} \times C_S \times C_i$ group.

The effective operators of physical quantities that describe the configuration – rotational motion of the H₂CO molecule belong to the coordinate Young diagram [2] of the group π_2^H .

Table 9. Division of configuration – rotational basis vectors according to the symmetry types of the group $G_{12} \times C_S \times C_i$ for the formaldehyde molecule with a joint description of two electronic states with distinct isomeric forms (the rotational parts are denoted by the symmetry types of the group D_2).

$G_{12} \times C_S \times C_i$	Basis vectors	$G_{12} \times C_S \times C_i$	Basis vectors
$(A_1 \times A^{\prime})^{(+)}$	0 angle imes A	$(A_1 \times A')^{(-)}$	$ 0 angle imes B_1$
$(E_1 imes A^{\prime})^{(+)}$	$ s\rangle \times A$	$(E_1 imes A')^{(-)}$	$ s angle imes B_1$
$(E_2 \times A^{\prime\prime})^{(-)}$	$ a\rangle \times A$	$(E_2 \times A'')^{(+)}$	$ a\rangle imes B_1$
$(A_1 \times A^{\prime\prime})^{(-)}$	$ 0 angle imes B_2$	$(A_1 \times A^{\prime\prime})^{(+)}$	$ 0 angle imes B_3$
$(E_1 \times A'')^{(-)}$	$ s angle imes B_2$	$(E_1 \times A'')^{(+)}$	$ s angle imes B_3$
$(E_2 \times A')^{(+)}$	$ a angle imes B_2$	$(E_2 \times A')^{(-)}$	$ a\rangle \times B_3$

As a consequence, the following transformation kinds belonging to the group $G_{12} \times C_S$ are allowed for these operators:

$$(\Gamma \times A'), \quad \Gamma = A_1, A_2, E_1, E_2.$$
 (47)

The configuration part is formed on the basis of the coordinate spin operator **e**. The symmetry properties of the complete set of independent spin operators are similar to those listed in Table 7 to within the replacement of the H_6 group with the c_{3v} group isomorphic to it. It is interesting that there is a spin operator of the A_2 type, although it is impossible to build up the similar spin function. This, however, does not lead to a contradiction, since $e_3|A_1\rangle = 0$.

The most interesting effective operator is that of the electric dipole moment. If, in addition to Eqn (47), we shall allow for the fact that this operator changes sign when acted upon by the inversion operation i, the complete expression for the operator can be written in the symbolic form

$$\mu_{\rm eff} = (A_1, E_1) \times B_1 + (A_2, E_2) \times B_3.$$
(48)

In other words, each term of the electric dipole moment is a combination of the rotational symmetry operators B_1 (or B_3) in the group D_2 , while the parameters in front of this combination are linear functions of the spin symmetry operators A_1 , E_1 (or A_2 , E_2) in the group c_{3v} (the spin operators must correlate with this combination). Next we allow for the fact that the component μ_{α} of the electric dipole moment along the α -axis of the LCS can be written as follows

$$\mu_{\alpha} = \lambda_{\alpha i} (\hat{d}^{(i)} + \hat{d}_{k}^{(i)} J_{k} + \hat{d}_{k l}^{(i)} J_{k} J_{l} + \ldots), \qquad (49)$$

where $\lambda_{\alpha i}$ are the direction cosines of the MCS with respect to the LCS, i.e. the rotational part of expression (48) contains, in addition to the components J_i in the MCS, similar components of the λ_{α} vectors. We can easily rewrite equation (48) with the explicitly specified direction cosines:

$$\mu_{\alpha} = \lambda_{\alpha z} \left[(A_1, E_1) \times A + (A_2, E_2) \times B_2 \right] + \lambda_{\alpha y} \left[(A_1, E_1) \times B_3 + (A_2, E_2) \times B_1 \right] + \lambda_{\alpha x} \left[(A_1, E_1) \times B_2 + (A_2, E_2) \times A \right].$$
(50)

Here, the rotational parts in the form of irreducible representations of the group D_2 contain only combinations of the components of angular momentum. Below we shall write out the specific expression for terms not related with the sufficiently weak rotational distortion of the molecule:

$$\mu_{\alpha} = \lambda_{\alpha z} \left[d^{(1)} I + d^{(2)} e_3^2 + d^{(3)} (e_+ + e_-) + d^{(4)} (e_+^2 + e_-^2) \right] + \lambda_{\alpha x} i \left[d^{(5)} (e_+ - e_-) + d^{(6)} (e_+^2 - e_-^2) \right],$$
(51)

where the $d^{(k)}$ are the real-valued spectroscopic constants. Since the electric dipole moment is invariant with respect to the *T* operation, equation (51) contains no *t*-odd spin operators.

In the above analysis we considered only one vibronic state for each individual isomeric form. However, our treatment can easily be extended to, say, a set of such states formed, for instance, by a certain set of vibrational excitations in each electronic state. To do this, there is a need to introduce (in addition to the group c_{3v}) the group $c_{\infty v}$, for which the number of irreducible representations (the number of excitations) taken into account is related to the number of vibronic states considered. Besides the formaldehyde molecule, such a description of the effect of modifying the isomeric form under changes of the electronic state has been given for the ethylene molecule [42, 43]. As is well known (see the monograph [25]), the equilibrium configuration of the ethylene molecule in the ground electronic state is planar and belongs to the point group D_{2h} . However, in some excited electronic states the planes of two CH2 structures are orthogonal, and the point group D_{2d} is realized [6]. What is important here is that, notwithstanding the strong hindering [44], we must also allow for torsion motions inside the isomers, because the geometry of the problem makes it impossible to resolve these motions from the nonrigid motions between the isomers, which, incidentally, are also related to the torsion type. This leads to the emergence of a four-dimensional torsion space which is constructed as a segment of a standard five-dimensional space.

In closing it must be stressed that the mathematical apparatus of the theory of dynamical noninvariant groups, used within the concept of a symmetry-group chain, is extremely flexible. For instance, in the formaldehyde molecule, the transfer between two isomeric forms cannot be described at all by symmetry transformations in the traditional sense of the word. Here, the difficulties also stem from the fact that inside a nonplanar form we must take into consideration the inversion motion, whereas inside a planar form such a motion is impossible in principle.

8. Some typical mistakes in using symmetry properties

Let us discuss some of the widespread qualitative mistakes made in describing intramolecular dynamics and related to the incorrect interpretation of its symmetry properties. We begin with the often ignored fact that coordinate degeneracies caused by the intrinsic geometrical symmetry group of the Hamiltonian do not lead to observable degeneracy of the energy levels. In particular, any level of a rigid molecule (an electron-vibrational-rotational level), relating to a degenerate irreducible representation of the point group associated with the molecule, corresponds to only one physically observable state. This very strange (at first glance) statement has a purely quantum justification. The matter is that to each invariant transformation of the geometrical group an identical-nuclei permutation is assigned (see Sections 3 and 6) and, as a result, the spin-coordinate wave function must satisfy the fundamental symmetry requirements for the permutation of such nuclei (i.e. be invariant or change sign under permutations depending on whether the nuclei are bosons or fermions). Here it occurs that all distinct coordinate wave functions belonging to a single irreducible representation of the Hamiltonian geometrical symmetry group are incorporated into a single regular spin-coordinate function $[5]^9$.

This leads us to a very important corollary. But before we shall formulate this corollary, let us examine a purely model problem concerning the changes in the rigid molecule spectrum on distortions of the molecular internal dynamics, distortions accompanied by symmetry breaking (for example, the point group is reduced from T_d to C_{3v}). Here we assume that the distortion is so weak that it has almost no effect on the position of the levels revealing themselves in the spectrum. However, even a weak distortion partially removes the coordinate degeneracies, so that instead, say, of a three-fold degenerate level belonging to the group T_d there emerge two levels with almost equal energies: a single two-fold degenerate level and a single nondegenerate level, both belonging to the group C_{3v} , i.e. the number of different physically observable states changes abruptly¹⁰, with the result that a number of characteristics governing the internal dynamics of the molecules also change abruptly (including such an integral characteristic as the partition function [5]).

Therefore, generally speaking, it is a mistake to go over from a description with a lower symmetry to one with a higher symmetry by imposing additional constraints on the parameters of the system in the former case. A passage of this type can be made only for the slowly varying characteristics of the description, such as the position of the molecular energy levels (with the exception of cases where singularities emerge in passing from one description to another; a similar case is examined below), but not the intensities of transitions between the levels, which change abruptly already.

We will now show how important it is to correctly take into account the alterations in the geometrical symmetry group, caused by changes in the system's excitation energy. A simple and yet topical example is the description of the water (H₂O) molecule. The equilibrium configuration of this molecule is an isosceles triangle (the oxygen nucleus is at the vertex singled out) and corresponds to the point group C_{2v} . As long as we consider this molecule rigid, no qualitative problems emerge. However, the motion with a large amplitude is executed in such a molecule, the motion that links two energy-equivalent equilibrium configurations and proceeds through a potential barrier whose top corresponds to an intermediate linear configuration. Although the barrier is fairly high (30 kcal mol⁻¹ [45]), passings over it must be taken into account [14] in describing the modern precision data on the spectrum of the water molecule. However, when we attempt to write out in the BO approximation the model C_{2v} -symmetry equations which explicitly allow for nonrigid motion, and then to solve these equations either analytically or numerically, we are confronted with the problem of a singularity emerging in the centrifugal energy of the rotation of the molecule as a whole [46]. Technically, the reason for this is a vanishing of the moment of inertia with respect to the molecular axis in the intermediate configuration. Naturally, the energy of such a system cannot become infinite. The rather serious mistake is made when all changes in the geometrical symmetry group, caused by allowance for the nonrigid transition, have been ignored. If for a given excitation energy this transition is essential for an adequate description of the internal molecular dynamics (this depends on the accuracy of the experimental data as well), then the correct geometrical symmetry group is the intermediate-configuration point group $D_{\infty h}$ incorporating the group C_{2v} as a subgroup, i.e. in this problem there are no gradual changes even in the positions of the energy levels, when we pass to a description with a higher symmetry.

Finally, the correct choice of the symmetry properties of motion between independent equilibrium configurations is also highly important. The point is that actually, for a given choice of such configurations, this motion can be executed in different ways. To clarify the problem we turn to the classical example of the methanol (CH₃OH) molecule which clearly exhibits torsion motion of the methyl group CH₃ between three energy-equivalent configurations across a potential barrier that is about 1.1-kcal mol⁻¹ high [44]. The presence of such a motion is entirely due to the fact that in its equilibrium configuration the COH structure is nonlinear, rather than occupying the maximum symmetric linear position along the triad axis of the methyl group CH₃. Hence, the point group decreases from the maximum possible group C_{3v} to the actually observed group C_S [31]. To allow for torsion motion, the extended point group $G_{12} = c_{3v} \times c_S$ is introduced [11], where the groups c_{3v} and c_S are determined by the geometries of the CH₃ and COH structures. The operation of rotation about the triad axis of the group c_{3v} , which specifies the rotation of the CH₃ structure with respect to the COH structure, does not present the rotation of the molecule as a whole and is only defined in the torsion space. As a result, this leads to a relatively small number of possible torsion contributions to the effective operators of physical quantities (the effective Hamiltonian included).

This operation is also often defined in the rotational space of the molecule [47, 48]. Here, the problem of torsion tunnelling between three equivalent configurations remains, but the number of possible torsion contributions grows, which may improve the quantitative description of precise experimental data. However, an analysis of the symmetry of the motions has shown (see Refs [11, 49]) that it is correct to believe that the given operation can be defined in the rotational subspace if the torsion motion is executed through the intermediate configuration with the maximum possible point group C_{3v} . Since the potential barrier for such a torsion motion is fairly high (as noted earlier, a chemically similar barrier for the linearization of the water-molecule configuration is about 30-kcal mol^{-1} high), at least for the lowest torsion states this procedure of extending the number of torsion contributions to the effective operators of physical quantities is strictly formal and all the additional contributions have no physical meaning. It is useful to note here that this procedure is based on the use of the CNPI group. But this group is too 'poor' to geometrically distinguish between the various types of nonrigid motions for a single set of equilibrium configurations. For instance, in the methanol molecule two possible geometries of a torsion motion merge in this group, since in both geometries the symmetry transformations correspond to the same permutations of identical nuclei¹¹. This could be the reason for the appear-

⁹ What stands apart here are the linear molecules, for which the point groups $(C_{\infty v} \text{ or } D_{\infty h})$ have no degenerate representations for the complete coordinate electron-vibrational-rotational wave function due to the existing homomorphism of the point group onto the identical-nuclei permutation group (see Section 5).

¹⁰ It can be said that the effectiveness of using coordinate wave functions to form physically observable states grows as the symmetry lowers.

¹¹ This situation is quite typical. For instance, it also emerges in the description of torsion motions of *trans*- and *cis*-type in the $(HF)_2$ dimer [11].

ance of the description with an extended number of torsion contributions.

9. Conclusions

Thus, a molecule comprises a multiparticle system with collective, geometrically structured internal coordinate motions. As a result, in a given bound electronic state, its internal dynamics is characterized by a geometrical group that is the dynamical group of the problem on the discrete levels of the molecule, where only contributions related to nuclear and electron spins are ignored in the Hamiltonian. Unfortunately, there is still no algorithm for obtaining this group from the rigorous equations of coordinate motion. An indication of such a behavior of the quantum microsystem is the presence of a rotational spectrum that is related to the rotation of the emerging dynamical system as a whole. In this respect a molecule differs dramatically from an atom. Since both the analytical and numerical methods of describing the internal coordinate motion in a molecule are based on perturbation theory, it is imperative to ensure that the qualitative properties of rigorous dynamics are 'implanted' in the approximate models.

Hence there emerges the problem of finding the geometrical group by empirical means. For rigid molecules in nondegenerate electronic states, this group is the point group of their single equilibrium configuration. Here, the symmetry of this configuration is an elementary consequence of the symmetry of the internal dynamics (but not the other way around), and only in the above simple case do these two symmetries coincide. It should be emphasized that, actually, to describe intramolecular motion by perturbation methods, one must know not only the geometrical symmetry group but also to solve the problem of the symmetry properties in the given group for the basis vectors of the function space of the types of motion considered and the operators of physical quantities specified in this space (the Hamiltonian included). And again, for rigid molecules the answer is well known. Therefore we can even pay no serious attention to the physical meaning of the concept of applying symmetry methods.

The situation changes radically when we turn to nonrigid molecules. First, the geometrical symmetry of the nonrigid molecule dynamics is not determined by the point groups of the molecular independent equilibrium configuration, which may even be nonequivalent, and can only incorporate them as subgroups. Hence, in the general case there arises a markedly nontrivial problem of finding such a symmetry, and rather often the groups specifying this symmetry have not even been tabulated. Another very complicated (from the standpoint of physics) problem is that of resolving different types of motion within the context of a newly built up geometrical group. For this purpose we must point to the procedure of forming the function subspaces needed for describing separate types of motion on the basis of the irreducible representations of this group. These factors stress the antecedence of symmetry methods in analyzing the internal coordinate motions of nonrigid molecules.

Estimating the results of applying symmetry methods to the description of nonrigid motions in specific molecules, I would like to note the following. Although the review considers a fairly broad range of applications of symmetry methods, the discussed types of nonrigid motions are only a small segment of the enormous variety of such motions. It is in view of the existence of this variety that we cannot even imagine a general approach to employing symmetry methods for nonrigid molecules. I believe that further development in this field of research will be in the direction of expanding the range of applicability of these methods to separate classes of molecules with definite types of nonrigid motions. More than that, I have almost entirely ignored the very interesting and rich segment of phenomena that deals with coordinate degeneracy of electronic states. What I mean are the corollaries of the Jahn-Teller effect, whose description constitutes a serious problem even in the simplest case of rigid molecules [15]. Nevertheless, the significance of the newly obtained results allows us to optimistically look at the outcome in the development of the qualitative quantum dynamics of molecules. We must also bear in mind that the present research is a necessary stage in building an adequate theory of intramolecular motions.

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