METHODOLOGICAL NOTES

Qualitative intramolecular quantum dynamics

A V Burenin

Contents

Abstract. **The state-of-the-art symmetry methods for the consistent quantum-mechanical treatment of intramolecular motions are reviewed. It is shown that for a broad class of topical problems, these methods are not only self-sufficient but, at present, the only possible ones. In particular, they greatly simplify the analysis of nonrigid molecules, for which conventional, analytical equation-of-motion methods run into serious mathematical difficulties even at low excitation energies.**

1. Introduction

The development of symmetry methods for the construction of a consistent quantum description of intramolecular motions is a very topical problem nowadays. The point is that for a wide range of important current problems these methods present a highly efficient alternative to the traditional analytical methods based on the solution of the equations of motion, which encounter serious mathematical difficulties. Quite a natural requirement on the qualitative methods is their selfsufficiency. In other words, the description should proceed entirely from the symmetry principles without any appeal to the equations of motion. Unfortunately, the most widespread qualitative approach, which leans upon the conception of the so-called complete nuclear permutation-inversion (CNPI) group [1], does not satisfy this requirement. At the present time, the only approach which is complete in this sense is that proposed by the present author and based on the conception of a chain of symmetry groups [2, 3]. This approach is a nontrivial generalization of the solution of this problem adopted in the Russian scientific school [4]. The generalization concerns, in particular, the

A V Burenin Institute of Applied Physics, Russian Academy of Sciences
ul. Ul'yanova 46, 603600 Nizhniĭ Novgorod, Russian Federation
Fax (7-8-312) 36 37 92
E-mail: buran@appl.sci-nnov.ru

extension of the analysis to nonrigid molecules. It is of interest that one of the main reasons for the introduction of the CNPI group conception in the pioneering work [5] was associated with the impossibility of such an extension. The ideological difference between the two approaches is rather significant, which may even imply the existence of fundamental errors in monograph [4] (see, for example, Ref. [6]). In view of the present state of the conception of a symmetry group chain, which is drastically different from the one presented in reviews [2, 3], we shall emphasize the following.

(1) The basic operative approximation in the description of intramolecular motions is the Born–Oppenheimer (BO) approximation [7]. The concept of the nuclear field of force and, consequently, the notion of a set of equilibrium configurations corresponding to the field minima separated by barriers are specially introduced for this particular approximation. From the qualitative point of view, a molecule or, in the more general case, a molecular system (for instance, a dimer) is assumed to be nonrigid if the transitions between these configurations are to be taken into account. The most topical analysis now is that of systems with transitions between energetically equivalent configurations. In the conception of symmetry group chains, the geometry of the internal motion of such a system is characterized by an extended point group which includes additional (compared to the point group) elements that determine the nonrigid transitions. It is of importance here that for a certain type of transitions the extended group becomes a so-called noninvariant dynamic group [8], i.e. wider than follows from the Hamiltonian symmetry. It is, in fact, the disregard of this circumstance that led the authors of Ref. [5] to the conclusion that the existing methods cannot be extended to nonrigid molecules. The creation of a very formal and therefore sometimes physically erroneous CNPI conception is, among other things, an attempt to restrict the analysis in the BO approximation to the Hamiltonian symmetry group.

(2) In the CNPI conception, the analysis begins with writing down the explicit form of at least approximate solutions for stationary states relevant to the types of intramolecular motions of interest for us, which becomes quite a nontrivial problem for nonrigid molecules. The notion

of symmetry is 'secondary' because its application rests upon the knowledge of approximate solutions and serves mostly to simplify the computations. In the conception of a group chain, the notion of symmetry is 'primary' because the description proceeds entirely from the symmetry properties. Within such an approach, it is precisely the latter properties that totally determine the Hamiltonian of the motions of interest, which is contrary to the usual statement of the problem.

(3) An adequate description of the internal molecular dynamics in the presence of nonrigid transitions pertains to the most topical and complicated contemporary problems in the theory of high-resolution molecular spectra. For example, in a hydrazine molecule N_2H_4 (containing only six atoms!) it is necessary to allow for four such transitions delocalizing this molecule over eight equivalent configurations, and in one of the simplest dimers $(HF)_2$ two transitions are possible, which link two equivalent configurations. The analytical solution to the problem of the spectrum of such involved quantum systems is practically impossible without the application of symmetry methods. However, the formality and internal incompleteness of the CNPI group methods lead to an exceedingly cumbersome procedure for the description, which in addition is only possible in the assumption that the nonrigid motions are independent (the examples mentioned above can be found in Refs [9, 10]). At the same time, the methods discussed here are used in such cases without particular difficulties.

It can be said that we are speaking about the development of a closed formulation of the qualitative intramolecular quantum dynamics, which provides substantial progress in the solution of a wide class of topical problems in the theory of high-resolution molecular spectra.

2. Chains of symmetry groups

The main operative method in the traditional analytical solution to the problem of stationary states of a molecule proceeds from perturbation theory. The passage to the zeroth approximation is realized by constructing a number of (increasingly rough) models embedded in one another until the exact solution of a given model problem becomes possible.

The symmetry properties of any model in this chain are specified by its symmetry group. For example, in the BO approximation the symmetry of the internal motion of a rigid molecule is characterized by the point group of a single equilibrium configuration, while in the zeroth approximation the rotational symmetry is specified by the rigid top symmetry, etc. While working within the framework of only one model we do not encounter any special difficulties in qualitative analysis. However, the situation becomes much more complicated when we attempt to consider the evolution of the symmetry properties of intramolecular motion (i.e. the evolution of the symmetry properties of the wave functions and operators of physical quantities) in passing over to a neighboring model. There exists no conventional solution of this problem now. Within the conception presented here it is solved as follows. In the quantitative calculation, the passage between neighboring models should be continuous, i.e. the distinctions between them must be describable as a series in a small parameter of the theory. In spite of this requirement, symmetry groups of these models may be different, i.e. the symmetry changes abruptly because an approximate model

is based on a certain physical idea and as a consequence may have additional qualitative information about the internal motion. The latter information is contained in the symmetry group of a given model, which therefore plays a clearly pronounced independent role compared to groups of more rigorous models. All the groups are united in a chain by the sewing together conditions, namely, equivalent elements are indicated in the groups of neighboring models, with respect to which the wave functions and the operators of the physical quantities must be transformed in a similar way. In other words, passages between neighboring models are accompanied by some nontrivial restrictions upon correspondence in the types of symmetry. Concrete formulations of sewings together for a chain of basic molecular models are presented in Ref. [2].

An important notion of the coordinate spin of a molecule [1], on whose basis a complete set of self-adjoint operators is readily formed for functional finite-dimensional spaces, is quite naturally introduced [3] into our conception. Such spaces correspond to essentially quantum types of motion and arise, for example, in the description of (a) configuration degeneracy in nonrigid molecules, and (b) vibrational and orbital electron degeneracies and quasi-degeneracies which already exist in rigid molecules. Components of the coordinate spin operator **e** in the Cartesian laboratory reference frame (LRF) form the well-known three-dimensional Lie algebra of the type

$$[e_\alpha, e_\beta] = i\varepsilon_{\alpha\beta\gamma}e_\gamma, \tag{1}$$

where $\varepsilon_{\alpha\beta\gamma}$ is an absolutely antisymmetric tensor of rank three. 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 LRF [4]

$$[J_\alpha, e_\beta] = i\varepsilon_{\alpha\beta\gamma}e_\gamma. \tag{2}$$

For the unit vectors λ_i of the Cartesian molecular reference frame (MRF) we have

$$[J_\alpha, \lambda_{i\beta}] = i\varepsilon_{\alpha\beta\gamma}\lambda_{i\gamma}, \quad [e_\alpha, \lambda_{i\beta}] = 0. \tag{3}$$

The last of relations (3) implies that the coordinate spin operators do not rotate the MRF. Then from (1)–(3) it follows that

$$[e_i, e_j] = i\varepsilon_{ijk}e_k, \quad [J_i, e_j] = 0. \tag{4}$$

Thus, the commutation relations for the **e** components are invariant under passing over from LRF to MRF. Note that for the **J** components such an invariance does not occur [4]. It is also important that relations (4) hold for two types of behavior of spin components under time inversion [2]: either all the three components are *t*-odd or any two components are *t*-even, while the third component is *t*-odd. In the analysis of intramolecular motions both these types are realized.

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[1] Spin is a coordinate quantity in the sense that it helps in the description of usual coordinate degrees of freedom.

[2] In nonrelativistic quantum mechanics, the time inversion operator is antiunitary and antilinear. As a result, the behavior under this operation has a physical meaning for operators rather than wave functions [8].

3. Dynamic noninvariant symmetry groups

As a first step in the understanding of the cause of the appearance of dynamic noninvariant groups in the description of intramolecular motions, we shall consider a system with two equivalent equilibrium positions separated by a finite potential barrier. Suppose that the description of tunnelling can be reduced to a one-dimensional problem for an unrestricted variable x. There exist two versions for the realization of such a situation. In the first one, the potential of the system depicted at the top of Fig. 1 shows two equivalent minima. For the transformation group [3] which specifies the tunnelling event we have $C_S = (E, \sigma)$, where σ is a reflection para to the point $x = 0$. As a consequence, the complete set of the basis functions in the functional space of a given problem consists of the unit vectors $|s\rangle$ and $|a\rangle$ belonging to the symmetric and antisymmetric representations of the group C_S. Now, in the functional space it is necessary to construct a complete set of self-adjoint operators. A two-dimensional representation of the Lie algebra for the coordinate spin operators in the space of the functions $|s\rangle$, $|a\rangle$ is written in terms of the well-known Pauli matrices [4]:

$$e_3 = \frac{1}{2}\begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}, \quad e_2 = \frac{1}{2}\begin{vmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{vmatrix}, \quad e_1 = \frac{1}{2}\begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}. \quad (5)$$

It is readily seen that the operator e_3 pertains to the representation s of the group C_S, while the operators e_2 and e_1 pertain to the representation a. In view of the fact that these representations are nondegenerate and real, we also obtain that the operators e_3 and e_1 are t-even, while the operator e_2 is t-odd. In a two-dimensional space, a complete set of self-adjoint operators consists of three components e_i and a completely symmetric unit operator I. The tunnelling Hamiltonian must clearly be t-even and in this case invariant with respect to the transformations of the group C_S. As a result, we arrive at the following expression for this Hamiltonian:

$$H = c_0 I + c_3 e_3, \quad (6)$$

where c_0 and c_3 are real phenomenological constants. Hamiltonian (6) describes the splitting (due to the tunnelling) of the system levels into two sublevels of s and a symmetry.

In the second version, the system potential presented on the bottom of Fig. 1 shows a single minimum, but there may occur tunnelling with a rearrangement of the spatial position of the potential symmetrically about the point $x = 0$. The group defining the transformation under this motion is C_S as before. However, the condition of Hamiltonian invariance under this transformation is now lifted (the potential does not go over to itself), and C_S becomes a dynamic noninvariant group. As a result, instead of (6) we have

$$H = c_0 I + c_3 e_3 + c_1 e_1. \quad (7)$$

Hamiltonian (7) also describes the splitting of the system levels into two sublevels, but the presence of the last term does not allow assignment of s and a types of symmetry to them. Nevertheless, in this simple case the nonzero matrix elements of the Hamiltonian are invariant under C_S and, as a consequence, so are its eigenvalues. The latter fact is quite obvious from simple geometrical considerations.

We shall now proceed to intramolecular motions. In line with Ref. [2], the energetically equivalent equilibrium configurations of a nonrigid molecule, separated by a potential barrier, will be called independent, and the transitions between them will be divided into exchange and nonexchange types. The geometrical symmetry of the internal motion in the BO approximation with allowance for transitions between the independent configurations is specified by the extended point symmetry group G which includes additional (compared to the point group G_0 of the molecule) elements defining nonrigid transitions. Under exchange type transitions, the spatial position of the nuclear field of force (i.e. the spatial position of the electron configuration) and, accordingly, the spatial position of the equilibrium configuration remain unchanged and the nuclear motion in this field of force reduces to exchanging places of identical nuclei. Hence, all the transformations of the group G have analogs in the permutation group π of identical nuclei. The fundamental symmetry properties require that the Hamiltonian of a purely coordinate motion be transformed according to the completely symmetric coordinate Young scheme of the group π. From sewing together the groups π and G it follows that only a unit representation of the group G is possible for the Hamiltonian. As a result, the extended point group coincides with the symmetry group of the Hamiltonian in the BO approximation. An obvious example of nonrigid exchange type motions are torsion motions of CH_3 tops.

Nonexchange type transitions are primarily characterized by a change in the position of the nuclear field of force. As a consequence, the spatial position of the equilibrium molecular configuration changes. The electron – nuclear transformations of the group G, which specify such transitions, do not naturally have any analogs in the group π. Therefore, the fundamental symmetry properties for permutations of identical nuclei lead to the requirement that in the BO approximation the Hamiltonian should be invariant only under exchange type operations of the group G, which form its
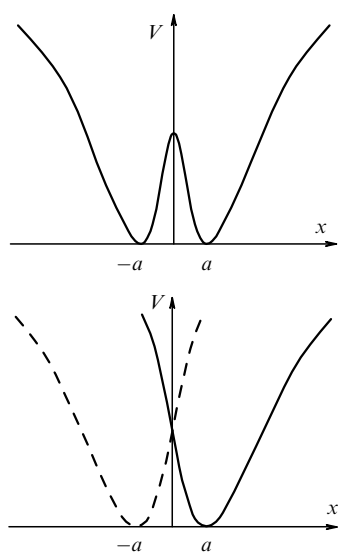
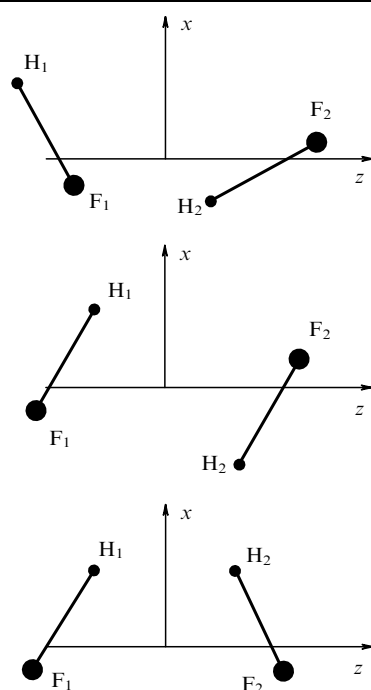**Figure 1.** Two versions of tunnelling in a one-dimensional system with two equilibrium positions.

[3] The standard notation for symmetry corresponds to that introduced in Refs [4, 11].

subgroup G_H. Notice that G_H includes G_0 as a subgroup. As a result, the group G becomes a dynamic noninvariant group. A simple example of a nonrigid nonexchange type motion is the inversion motion in an ammonia molecule NH_3.

4. The extended point group and unstable configurations

In the BO approximation, the symmetry of the internal motion of a rigid molecule is specified by the point group of a unique equilibrium configuration, which is stable by definition. However, for a certain class of nonrigid molecular systems the symmetry of the internal motion can be specified by the geometry of an unstable configuration. As an example, we shall consider one of the simplest dimers $(HF)_2$ whose equilibrium configuration [12] is shown in the upper part of Fig. 2. The characteristic feature of this equilibrium configuration is the paucity of its point group C_S, which is due to the energetically nonequivalent position of identical monomers HF. Such equilibrium configurations will be called distorted[4]. In this case, the dimer is delocalized over two independent distorted configurations differing by permutation of monomers and positioned symmetrically in the neighborhood of the unstable intermediate configuration with an equivalent position of monomers. Because of this, it is the symmetry of the intermediate configuration that determines the symmetry of motion with allowance for the nonrigid transition made through it.

The analysis shows [10] that most probable are *trans*- and *cis*-transitions whose intermediate configurations have symmetry groups C_{2h} and C_{2v} (see Fig. 2). The major transition is here the *trans*-tran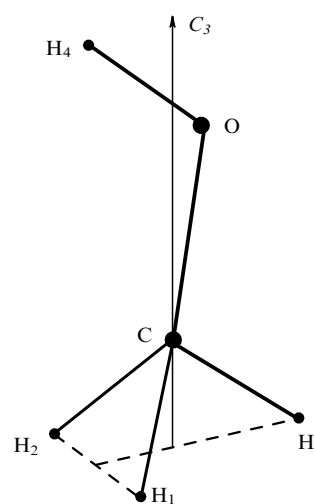sition because it takes place through a lower barrier. A simultaneous account of both transitions naturally requires the solution to the problem of combination (in a unified description) of two geometric symmetry groups of the problem in the BO approximation. We shall also note that the analysis of systems with distorted equilibrium configurations suggests the possibility of *a priori* attributing the nonrigid motion to the exchange or nonexchange type. In the case of the dimer $(HF)_2$, whose spectrum observed unambiguously points to the exchange type of transitions, the higher symmetry of the intermediate configuration is due to elimination of the distortion in the position of identical nuclei. This is apparently a sufficient indication of a nonrigid exchange type motion.

The interest in complexes has arisen rather recently. A classical example of a system of the class in question is the methanol molecule CH_3OH, in which there exists a clearly pronounced torsion motion of the methyl group CH_3 between three energetically equivalent minima. Such a motion is entirely due to distortion of the equilibrium configuration of the molecule depicted in Fig. 3 [12]. The distortion causes a lowering of the point group from the maximum possible C_{3v} to the actually observed $C_S = (E, \sigma^{(yz)})$. Accordingly, the three nuclei H of the methyl group do not occupy energetically equivalent positions. More precisely, the positions of the nucleus H in the yz-plane is not equivalent to the positions of the nuclei H outside this plane, which is indicative of a slight distortion of the regular pyramidal structure of the CH_3 group. Hence, the symmetry of the internal motion is characterized by an unstable configuration, in whose neighborhood three independent configurations are symmetrically located.

For energetically most advantageous transitions (with a barrier of 1.07 kcal mol^{-1} [13]), the symmetry is specified by a configuration close to an equilibrium one but having an undistorted structure of the methyl group[5]. The extended

Figure 2. Equilibrium and intermediate configurations for *trans*- and *cis*-transitions (downward) in the dimer $(HF)_2$ (in all the configurations the nuclei lie in the xz-plane, and the z-axis is coincident with the straight line joining the centers of mass of the monomers).

Figure 3. Equilibrium configuration of the CH_3OH molecule (the H_3, C, O, and H_4 nuclei and the C_3-axis of the methyl group for the intermediate configuration of the low-energy channel of torsion motion lie in the symmetry plane of the C_S group).

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[4] The conventional point of view on the mechanisms of such a distortion as manifestations of the Jahn-Teller pseudoeffect is presented in Ref. [7].

[5] We emphasize that an intermediate configuration is introduced for the description of the symmetry of internal motion and is not obliged to correspond to the barrier top. Such a correspondence holds if by analogy with the case of the dimer $(HF)_2$ the barrier is entirely due to a distortion of the equilibrium configuration as compared to the intermediate one.

point group has the form $G_{12} = c_{3v} \times c_S$, where the groups c_{3v} and c_S are specified by the geometry of the structures CH_3 and COH. The analytical solution of the Schrödinger equation in a given electron-vibrational state is much easier here owing to the possibility of a simple one-dimensional parametrization for a nonrigid motion. Nevertheless, the necessity of constructing a perturbation series with allowance for this motion already in the zeroth approximation causes considerable difficulties, and the problem of the description is now under discussion [14]. However, there exists another intermediate configuration corresponding to the maximum possible point group C_{3v} which now plays the role of an extended point group. This channel of exchange with a barrier which is only due to distortion of the equilibrium configuration will lead to qualitatively new contributions in the description of the internal motion. The quantitative estimation of these contributions requires the use of quantum-chemical methods. It can be noted, however, that a chemically similar barrier for a configuration with the maximum possible symmetry group $C_{\infty v}$ of the water molecule H_2O (30 kcal mol^{-1} [15]) should be taken into account in the analysis of microwave data [6]. It is of importance for us here that the analytical solution of the Schrödinger equation for a nonrigid methanol molecule in the case of two exchange channels seems to be rather problematic.

In what follows, concrete examples are given to consider the main regularities of the use of the presented qualitative methods for describing the internal motion in molecular systems. Purely technical aspects will whenever possible be replaced by references to original papers. However, compared with these papers our presentation may appear to be more consistent and rigorous.

5. The description of torsion exchange type motions in molecules

Exchange type torsion motions seem to be the most widespread nonrigid motions in molecules and their complexes. For the first step in the presentation it is convenient to choose the methanol molecule CH_3OH. It is sufficient to write out its permutation group of identical nuclei H in the form $\pi_3 \times \pi_1$, where π_3 determines the permutation symmetry of the methyl group. Neglecting hyperfine interactions due to nuclear spins, one can represent the total molecular wave function as a convolution of the coordinate and spin parts [11] transforming by mutually dual Young schemes. Specifying the admissible Young schemes and sewing together the group $\pi_3 \times \pi_1$ with the point group C_S (for the technical details see Ref. [17] and the references therein), we obtain in the BO approximation for a rigid molecule the following allowed multiplets:

$$4A', \quad (8+4)A''. \tag{8}$$

The figures before the multiplet mark its nuclear statistical weight. The interactions of interest are also invariant under the operation of spatial inversion i of all the particles of a molecule. Since this operation is associated with the properties of the space, it must commute with the operations specified by the molecular geometry, which makes it possible

to write out the symmetry group $C_S \times C_i$ in the BO approximation. This means that the multiplets are also characterized by their behavior under i, which will be given by the postsuper ($\pm$) in their notation. It is then necessary to find the relation between the multiplets and the solutions of the zeroth approximation. In the zeroth approximation, the motion of the nuclei is divided into independent vibrational and rotational motions which are described using the harmonic oscillator and rigid rotator models. The relation is specified by the sewing together of the symmetry group in the BO approximation and the symmetry groups of the zeroth approximation:

$$(\Gamma_{\text{mult}})_{C_S \times C_i} = (\Gamma_{\text{el}})_{C_S} \times (\Gamma_{\text{vib}})_{C_S} \times (\Gamma_{\text{rot-inv}})_{C_S \times C_i}. \tag{9}$$

Here Γ_{el} and Γ_{vib} are irreducible representations of the C_S group for the wave functions of the zeroth approximation for the electronic and vibrational motions, $\Gamma_{\text{rot-inv}}$ are irreducible rotation-inversion representations of the group $C_S \times C_i$. The correlation of the latter with the rotational representations of the group D_2 of a rigid asymmetric top follows from the relation between these groups by their common subgroup $C_2 = (E, C_2^{(x)})$. The arrow in (9) implies that the behavior under the operation i has a physical meaning for a multiplet only. As a result we observe the evolution of rotational levels in an arbitrary electron-vibrational state when we pass over from the zeroth to the BO approximation. The first two columns in Fig. 4 illustrate this evolution for $\Gamma_{\text{el}} \times \Gamma_{\text{vib}} = A'$.

To take into account the low-energy channel of the torsion motion it is necessary that the extended point group $G_{12} = c_{3v} \times c_S$ be introduced into the chain between the groups $\pi_3 \times \pi_1$ and C_S. Sewing together the groups $\pi_3 \times \pi_1$ and G_{12} we obtain the following allowed multiplets for a
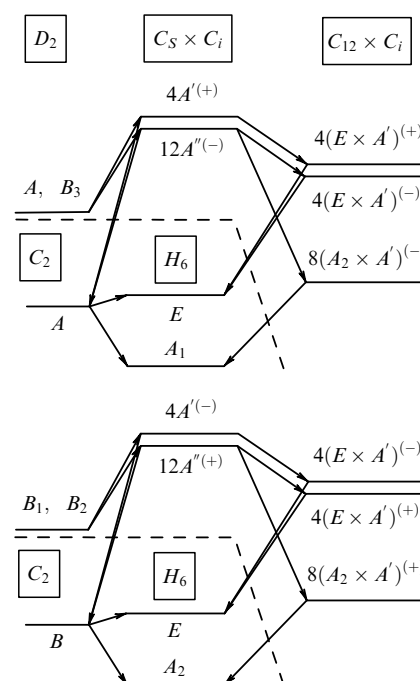
Figure 4. Classification of the stationary states of the CH_3OH molecule with allowance for the low-energy channel of torsion motion (the notation of the H_6-group irreducible representations corresponds to the notation of the group D_3 isomorphic to the group H_6).

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[6] A nonrigid motion in a water molecule does not of course make qualitatively new contributions to the description, and we speak of the corrections in the interpretation of spectroscopic constants [16].

nonrigid molecule:

$$8(A_2 \times A'), \quad 4(E \times A'). \tag{10}$$

Notice that the multiplet $A_1 \times A'$ has zeroth nuclear statistical weight and the representations $\Gamma \times A''$ are not realized in the form of multiplets because the COH structure is planar. The operation i commutes as before with all the geometric elements of the molecular symmetry, and each of the multiplets in (10) is characterized by the signs $(\pm)$. Sewing together now the groups G_{12} and C_S, we arrive at a detailed classification of stationary states of a nonrigid molecule, which is shown in Fig. 4 for $\Gamma_{\rm el} \times \Gamma_{\rm vib} = A'$. The levels of rigid and nonrigid molecules constitute nonsplit inversion doublets, but for one-dimensional states of a nonrigid molecule one of the sublevels of such a doublet is absent because the multiplet $A_1 \times A'$ is forbidden. As follows from the classification, for constructing the description of torsion-rotational levels in a given electron-vibrational state, instead of the group $G_{12} \times C_i$ it suffices to take its rotation subgroup $H_6 = H_3 \wedge C_2$. The symbol $\wedge$ means a semidirect product [8] which arises because the operations of the torsion motion group $H_3 = (E \times E, C_3 \times E, C_3^2 \times E)$ do not commute with the operations of the rotation group C_2 of the molecule as a whole. The complete basis set of torsion unit vectors $|0\rangle$ and $|\pm 1\rangle$ is determined by three irreducible representations of the group H_3 isomorphic to C_3. Because of the properties of the semidirect product, the action of the elements of the quotient group C_2 is also defined in the basis of the invariant subgroup H_3. In view of the classification, for the completely symmetric electron-vibrational state one can write

$$C_2^{(x)}|0\rangle = |0\rangle, \quad C_2^{(x)}|1\rangle = |-1\rangle. \tag{11}$$

Allowing also for the behavior of the rotational functions under transformations of the group C_2 [4], we can readily arrive at a partition of the complete basis set of the torsion-rotational unit vectors around the irreducible representations of the group H_6.

Next consider the physical quantities that determine the torsion-rotational motion of a molecule. Their effective operators must be transformed according to the Young coordinate scheme [3] $\times$ [1] of the group $\pi_3 \times \pi_1$. Sewing together the latter group with G_{12} we have a single allowed representation $A_1 \times A'$ for such operators in the BO approximation. Next, the sewing together of the groups $G_{12} \times C_i$ and H_6 gives the representations A_1 and A_2, respectively, for the physical quantities invariant under the inversion i and those reversing sign under it.

The effective operators of the physical quantities are constructed from the elementary operators which include, in particular, components (in MRF) of the total angular momentum $\mathbf{J}$ and coordinate spin $\mathbf{e}$. The $\mathbf{e}$ components realize the three-dimensional representation of the Lie algebra (4) in the basis of the functions $|0\rangle$, $|\pm 1\rangle$. In the standard definition, e_3 is a diagonal operator with eigenvalues $0, \pm 1$, and $e_\pm = e_1 \pm ie_2$ are the raising and the lowering operators. From the transformation properties of the torsion basis it follows that the operator e_3 is t-odd and realizes the representation A_2 of the group H_6, while the operators e_1 and e_2 are t-even and realize the representation E. For a three-dimensional space, products of spin components of summary power not higher than two are admissible. As concerns the combinations of the $\mathbf{J}$ components, in the group H_6 they only

realize the representations A_1 and A_2 to which there respectively refer combinations of the types A, B_3 and B_1, B_2 of the group D_2. Therefore, the torsion-rotational operators of physical quantities may include only the following three independent spin operators:

$$I, \quad e_3^2 \rightarrow A_1, \quad e_3 \rightarrow A_2. \tag{12}$$

For example, the effective Hamiltonian is invariant under the operation i and is therefore transformed by the representation A_1 of the group H_6, which can be realized by two torsion-rotational (or spin-rotational) structures:

$$(A_1)_{\rm sp} \times (A_1)_{\rm rot}, \quad (A_2)_{\rm sp} \times (A_2)_{\rm rot}. \tag{13}$$

Bearing in mind the t-parity of the Hamiltonian, it is easy to write a complete expression for it in the form of a Taylor series in components of the angular momentum with coefficients dependent on the spin operators (12). Such a representation of a Hamiltonian does not explicitly contain operators with respect to the angle of internal rotation of the methyl group, which radically simplifies its structure. The simplification is essentially based on the fact that as distinct from the usual elementary torsion operators the elementary coordinate spin operators are introduced with allowance for the required number of independent equilibrium configurations. That is, the elementary spin operators are integral in the sense that they immediately involve a large-amplitude motion over its entire range.

The distinctions in the analysis of the high-energy channel of the torsion motion are connected with the replacement of the extended point group G_{12} by C_{3v}. For the multiplets of a nonrigid molecule, the representation $\Gamma \times A'$ of the group $c_{3v} \times c_S$ is changed by the representation Γ of the group C_{3v}. The minimum symmetry group which takes adequate account of all the types of torsion-rotational levels is now the group $D_3 = C_3 \wedge C_2$, and the basis set of torsion unit vectors $|0_\tau\rangle$ and $|\pm 1_\tau\rangle$ is specified by three irreducible representations of the group C_3. The action of the quotient group C_2 in this basis is analogous to Eqn (11). But the operations C_3 also comprise the rotations of a molecule as a whole. This naturally has an effect on the partition of the complete basis set of the torsion-rotational unit vectors around the irreducible representations of the group D_3.

For a given channel of torsion motion we shall introduce the coordinate spin operator τ. The properties of the τ_i components are similar to those of e_i up to the replacement of the group H_6 by D_3. But since the combinations of the J_i components realize all the three irreducible representations of the group D_3, it follows that all the nine independent spin operators participate in the construction of the torsion-rotational operators. The effective Hamiltonian is transformed by the representation A_1 of the group D_3 and the contributions to it are already made by three spin-rotational structures. In addition to (13) there arises the structure $E_{\rm sp} \times E_{\rm rot}$ with the most numerous contributions.

So, we have two pictures of the internal molecular motion, differing in the geometrical symmetry in the BO approximation, and they should be combined under a unified description. Then the basis unit vectors should be represented as products of two spin functions for two types of nonrigid motion by the rotational function and they must simultaneously belong to certain representations of the groups H_6 and D_3. The following two points are of importance here: (i)

the indicated groups intersect in the group C_2, and (ii) only states for which the representations of the groups H_6 and D_3 coincide are realized. The latter circumstance is due to the fact that similar elements of the group π_3, appearing in the symmetry group of a rigorous problem, correspond to both the nonrigid motions or, in other words, these motions are connected to one and the same set of three independent configurations. It is also readily seen that the elements of H_3 act on the functions $|0\rangle, |\pm 1\rangle$, the elements of C_3 — on the functions $|0_\tau\rangle, |\pm 1_\tau\rangle, |J, k\rangle$, and the elements of C_2 act on all these functions. As a result we obtain the partition of the complete basis set of torsion-rotational unit vectors around the irreducible representations of the groups H_6 and D_3. The effective torsion-rotational operators of physical quantities, which now contain products of three types of operators, are constructed in an analogous way. Since the effective Hamiltonian transforms by the representation A_1 of the groups H_6 and D_3 and is t-even, one can write out a complete expression for it. In particular, for the main contribution from the torsion motion we have

$$H_{\text{tor}} = (c^{(1)}I + c^{(2)}e_3^2)I_\tau + (c^{(3)}I + c^{(4)}e_3^2)\tau_3^2 + c^{(5)}e_3\tau_3, \quad (14)$$

where $c^{(k)}$ are real spectroscopic constants. The advantages of such a description due to the absence of an explicit dependence on the coordinates of the torsion motions are of much greater importance here than in the one-channel version. Furthermore, the solution of such a problem by other analytical methods now seems to be rather problematic.

The next thing to do is to analyze the torsion exchange type motion in molecules with a center of inversion. Such a situation is of great interest because if it is realized then (i) there are no less than two identical torsion tops, and the symmetry operations are important in the analysis, which define both the internal rotation and the identity of the tops, with these two types of operations being not commuted, and (ii) there are two inversion operations characterizing respectively the symmetry of the space and the symmetry of equilibrium configurations, which require a clear physical interpretation of their use.

The classical example is the ethane molecule C_2H_6 (for the aspects of the analysis not included here see paper [18] and the references therein). In its equilibrium configuration, the groups CH_3 have a common three-order axis aligned with the chemical bond $C-C$, and they are turned with respect to each other through $\pi/6$ [12]. In this case all identical nuclei occupy equivalent positions. The corresponding point group D_{3d} possesses the element of inversion I. Allowing for invariance of the considered interactions under the spatial inversion i, we can write out the symmetry group $D_{3d} \times C_i = C_{3v} \times C_I \times C_i$ in the BO approximation for a rigid ethane molecule. In spite of their different physical meanings, the two inversion operations enter here symmetrically. The situation however changes radically for a nonrigid ethane molecule. The experimentally examined internal rotation of two identical tops CH_3 relative to the chemical bond $C-C$ proceeds through a low potential barrier [13] and belongs to the exchange type. The extended point symmetry group is written in the form

$$G_{72} = (c_{3v} \times c_{3v}) \wedge C_I. \quad (15)$$

The direct product of two groups c_{3v} describes the geometrical symmetry of the two tops, and the group C_I allows for their identity. In this case the element I does not commute with the elements of the group $c_{3v} \times c_{3v}$ being an invariant subgroup of the group G_{72}. But the element of the inversion i characterized by space symmetry commutes as before with all the symmetry elements determined by the geometry of the molecule, and one can write out the symmetry group $G_{72} \times C_i$. Here the presence of the direct product has a deep physical meaning since otherwise not all the stationary states of such an isolated system as a molecule will show a definite behavior under the operation i, which violates one of the main principles of nonrelativistic quantum mechanics [4].

In a nondegenerate electron-vibrational state, the rotational levels classified according to the group D_∞ of a rigid symmetric top split owing to the effects of k-doubling and torsion motion. To construct a complete description of such splittings, it suffices to employ the rotation subgroup entering the group $G_{72} \times C_i$. This subgroup is represented in the form

$$H_{36} = H_6 \times D_3. \quad (16)$$

Here D_3 is the rotation subgroup of the group D_{3d}, involving only rotation of the molecule as a whole, and the group H_6 isomorphic to the group D_3 is $H_3 \wedge H_2$, where $H_3 = (E \times E, C_3 \times C_3^2, C_3^2 \times C_3)$ is a subgroup of the group $c_{3v} \times c_{3v}$ and $H_2 = (E, Ii)$. In the ethane molecule, as generally in molecules with a linear skeleton and two identical tops, there arises a problem of the resolution of intramolecular motions into torsion and rotational motions. The difficulty is that when using torsion motions alone one can realize the rotation of a molecule as a whole about the linear skeleton. Expression (16) allows the realization of a very simple version of resolution in which the groups H_6 and D_3 describe respectively the torsion motion and the rotation of a molecule as a whole. The motion is assumed here to be purely torsion if it is defined by the elements of the group H_3, and the other motions are unambiguously resolved into the given torsion and rotational motions. The complete basis set of torsion unit vectors $|0\rangle, |\pm 1\rangle$ is determined by three irreducible representations of the group H_3 isomorphic to C_3. Making use of the properties of the semidirect product and the results of the classification, we obtain that in a completely symmetric electron-vibrational state the unit vectors $|0\rangle$ and $|\pm 1\rangle$ belong respectively to the representations A_1 and E of the group H_6. As a result we arrive at a partition of the complete basis set of torsion-rotational unit vectors around the representations of the group H_{36} [7]. Furthermore, in the torsion space a complete set of coordinate spin operators is introduced and their symmetry properties under the group H_6 transformations are determined. Also taking into consideration the well-known behavior of the operators of components of the angular momentum under the group D_3 transformations, one can construct an effective

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[7] It is noteworthy that H_{36} is isomorphic to the so-called MS group of a nonrigid ethane molecule, which by definition bears all the necessary information for an analysis within the CNPI group conception (the writing out of the MS group as a direct product of two groups has not been considered). But the formality of the construction and the use of the MS group leads, for molecules with a linear skeleton and two identical tops, to the appearance (in the description of some purely coordinate internal motions) of two-valued wave functions reversing sign upon rotation through 2π, which is physically quite incorrect. As a consequence, the MS group is replaced by its dual group. The latter were introduced for the description of physical systems with a half-integer spin [4].

torsion-rotational operator for any physical quantity of interest.

The indicated version of resolution into torsion and rotational motions in molecules with a linear skeleton and two identical tops implies, in fact, the possibility of an independent analysis of these motions, which is only realized under strict requirements on the symmetry of the problem. The fairly serious specificity of such a resolution, occurring in a more general case, can be conveniently considered for the example of the ethylene molecule C_2H_4 whose equilibrium configuration in the ground electronic state is planar and corresponds to the point group $D_{2h} = C_{2v} \times C_I$ [12]. The MRF will be so chosen that for the group C_{2v} the two-order axis will coincide with the z-axis, and the plane $\sigma^{(yz)}$ with the plane of the molecule. The internal rotation of two identical tops CH_2 about the double chemical bond $C-C$, which belongs to nonrigid exchange type motions, is strongly decelerated [13], but its analysis is of great methodological interest. The extended point group in this case is [19]

$$G_{32} = (c_{2v} \times c_{2v}) \wedge C_I. \tag{17}$$

To construct a complete description of the torsion splittings of the rotational levels classified by the group D_2 of a rigid asymmetric top, we shall single out the rotation subgroup from the group $G_{72} \times C_i$:

$$H_{16} = U_2 \times H_8. \tag{18}$$

Here $U_2 = (E, \sigma^{(yz)}i)$ and $H_8 = (c_2 \times c_2) \wedge C_2$, where $c_2 \times c_2$ and $C_2 = (E, C_2^{(x)})$ are subgroups of the groups $c_{2v} \times c_{2v}$ and D_{2h}, respectively. The structure of H_8 is such that it cannot be represented as a direct product of two groups whose elements act only in the rotation and torsion spaces. Hence, we have to choose $c_2 \times c_2$ as the group defining the torsion motion. In this case (i) the complete set of basis unit vectors is formed from the torsion unit vectors $|p_1\rangle$, $|q_1\rangle$ and $|p_2\rangle$, $|q_2\rangle$, corresponding to the symmetric and antisymmetric representations of the groups $c_2 \times E$ and $E \times c_2$, and the rotation unit vectors transformed by the representations of the group D_2 which includes the rotation of a molecule as a whole from the group H_{16}; (ii) the operations of the group U_2 are defined in the rotation space only, the element $\sigma^{(yz)}i$ specifying the same rotation as the element $C_2^{(x)}$. As a consequence, their action on the rotation unit vectors must coincide (the element Ii in the rotation space is equivalent to the identical element); (iii) the group of torsion motions contains the element $C_2^{(z)}$ of rotation of a molecule as a whole, and therefore a part of the combinations of the torsion unit vectors will make a contribution to this rotation, and (iv) four torsion unit vectors are intended for the description of only two independent configurations of the ethylene molecule, but the symmetry requirement does not admit redundant torsion-rotational unit vectors.

The torsion-rotational unit vectors obtained in Ref. [19] do not contain rotational B_2 and B_3 parts of the group D_2, which correspond to the projection of the angular momentum onto the z-axis with an odd quantum number. This means that such a projection of the total angular momentum is formed thanks to the torsion component, the contribution to the molecular rotation being made by the spin parts $|p_1\rangle|q_2\rangle$ and $|q_1\rangle|p_2\rangle$ with an asymmetric excitation of the tops. However, the angular momentum $\mathbf{J}$, which in the zeroth approximation refers to the rigid top rotation, evolves in the

BO approximation into the total angular momentum. Therefore, in the torsion-rotational unit vectors it is necessary that the torsion contribution to the rotation be transported onto the rotational parts [8]. To this end we make the following substitution of the rotational parts in asymmetrically excited spin states:

$$A \to B_2, \quad B_1 \to B_3. \tag{19}$$

With allowance for (19), all the four rotational types enter into the torsion-rotational unit vectors. A complete set of coordinate spin operators is introduced thereafter and the effective torsion-rotational operators of any physical quantities of interest are constructed. In particular, for the main contribution of the torsion motion into the Hamiltonian we have

$$H_{\text{tor}} = c^{(1)}I_1I_2 + c^{(2)}e_{3,1}e_{3,2} + c^{(3)}(I_1e_{3,2} + e_{3,1}I_2), \tag{20}$$

where the spin operators are analogous to (5). The subscripts 1 and 2 indicate the ordinal number of the spin subspace (or the ordinal number of a top).

It should be emphasized that the completeness of the geometrical symmetry groups considered in the BO approximation is of vital importance. For example, an attempt to simplify the extended point group by eliminating operations which do not directly refer to the torsion motion (the symmetry planes of the tops) leads to a notable distortion of the results of the sewings together. This is absolutely clear because the information on the symmetry of the internal molecular motion is distorted. Such errors can of course be rectified when the correct result is known in advance. But in that case the main advantage of the proposed conception of qualitative analysis, i.e. its completeness, proves to be lost.

6. The description of torsion exchange type motions in complexes

We shall now proceed to the consideration of the peculiarities in the analysis of torsion exchange type motions in molecular complexes, which has lately been a fairly topical case. To begin with, we shall note that a typical feature of the complexes is a distortion of the equilibrium configuration. This is apparently associated with a shallow potential well, which also leads to a rapid increase in the number of possible nonrigid motions as the structure of the complex is complicated. As a result, even for such simple complexes as the dimer $(HF)_2$, the nonrigid motions were described by the CNPI group methods only on the assumption of their independence and using a fairly formal and cumbersome procedure [10].

As has already been mentioned, in the dimer $(HF)_2$ *trans*- and *cis*-transitions are possible, whose intermediate configurations correspond to the symmetry groups C_{2h} and C_{2v}. Figure 5 gives the classification of the stationary states of $(HF)_2$ in the ground electron-vibrational state with allowance for *trans*-transition predominance due to a smaller barrier height. Note that because of the planar equilibrium config-

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[8] Within a more consistent construction of torsion-rotational quantities it is immediately taken into account that the real motion corresponding to the element $c_2^{(z)} \times c_2^{(z)}$ is a normal rotation of a molecule as a whole. This element must therefore be defined in the rotation subspace only. This automatically leads to a complete resolution of the torsion motion and the rotation of the molecule as a whole.
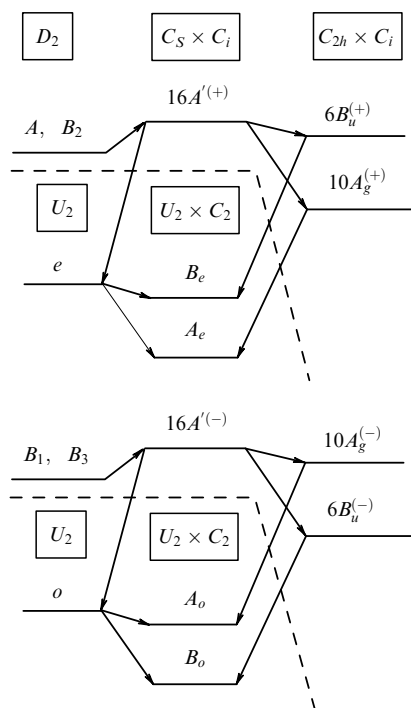
Figure 5. Classification of the stationary states of the dimer $(HF)_2$ with allowance for the *trans*-transition (e, o are symmetric and antisymmetric representations of the group U_2).

uration the spectrum does not contain inversion doublets. In the group C_{2h}, the mixture of two independent configurations is specified by the subgroup $C_2 = (E, C_2^{(y)})$ and the barrier is only due to the distortion of the equilibrium configuration as compared to the intermediate one.

The rotational type of mixing operation allows the *trans*-transition to be called a torsion motion. To describe the related splittings of the rotational levels, classified by the group D_2 of the rigid asymmetric top, it suffices to single out the rotation subgroup $U_2 \times C_2$ from the group $C_{2h} \times C_i$, where $U_2 = (E, \sigma^{(xz)}i)$. The complete basis set of torsion unit vectors $|A\rangle$, $|B\rangle$ is defined by the irreducible representations of the group C_2. But the operations of the latter group constitute also rotations of the dimer as a whole, which act on the rotation unit vectors. The operations of the group U_2 act on the rotation unit vectors only. From the point of view of the rotation of a dimer as a whole, the elements $\sigma^{(xz)}i$ and $C_2^{(y)}$ specify one and the same turn, and therefore their actions on the rotation unit vectors coincide. As a result, we have a partition of the complete basis set of the torsion-rotational unit vectors around the irreducible representations of the group $U_2 \times C_2$, the rotational part of the unit vectors allowing for the torsion contribution to the rotation of the dimer as a whole.

Next, in the torsion space the coordinate spin operator $\mathbf{e}$ with components of the type (5) is introduced, whose symmetry properties under the group $U_2 \times C_2$ are defined in a trivial manner:

$$e_3 \rightarrow A_e, \quad (e_2, e_1) \rightarrow B_e, \tag{21}$$

the components e_3, e_1 being *t*-even, and the component e_2 — *t*-odd. As concerns the combinations of the components of the angular momentum, they belong to the representations A_e

and B_o. The torsion-rotational operators of physical quantities belong to the coordinate Young scheme $[2] \times [2]$ of the group $\pi_2^F \times \pi_2^H$. The sewing together of the latter with C_{2h} in the BO approximation gives them a unique representation A_g. When passing over to the group $U_2 \times C_2$, we have the representations A_e and A_o for the physical quantities respectively invariant and reversing sign under the inversion i. For example, the effective Hamiltonian is transformed by the representation A_e realized with the help of the unique spin-rotational structure $(A_e)_{\mathrm{sp}} \times (A_e)_{\mathrm{rot}}$.

The distinctions in the analysis of the *cis*-transition are due to the replacement of C_{2h} by C_{2v} and, consequently, C_2 by $C_2' = (E, C_2^{(x)})$. The classification of the stationary states follows from that for the *trans*-transition when one uses the following correlations between the representations of the replaced groups:

$$A_g \leftrightarrow A_1, \quad B_u \leftrightarrow B_1, \quad A \leftrightarrow a, \quad B \leftrightarrow b, \tag{22}$$

where a and b are symmetric and antisymmetric representations of the group C_2', which specify the set of torsion unit vectors $|a\rangle$, $|b\rangle$ for the *cis*-transition. Taking into consideration the action of the group C_2' on the rotational functions too, we obtain the partition of the torsion-rotational unit vectors around the representations of the group $U_2 \times C_2'$. Next, in the space $|a\rangle$, $|b\rangle$ the coordinate spin $\boldsymbol{\sigma}$ is introduced, which has components of the type (5) whose symmetry properties are analogous to those of e_i up to replacement of the representations A, B according to (22). Since the combinations of the components of the angular momentum realize all the four irreducible representations of the group $U_2 \times C_2'$, then for the effective torsion-rotational Hamiltonian belonging to the representation a_e of the group $U_2 \times C_2'$, two spin-rotational structures, $(a_e)_{\mathrm{sp}} \times (a_e)_{\mathrm{rot}}$ and $(b_e)_{\mathrm{sp}} \times (b_e)_{\mathrm{rot}}$, are possible.

It is also easy to unite the *trans*- and *cis*-pictures of the internal motion in a unified description. In this case, the torsion-rotational unit vectors are written out as a product of two spin unit vectors for the two variants of the nonrigid motion by the rotation unit vector and they simultaneously belong to definite representations of the groups $U_2 \times C_2$ and $U_2 \times C_2'$. It is necessary to take into account here that (i) the indicated groups are intersected by the subgroup U_2, and (ii) the dimension of the functional space should not increase since the same elements of the group $\pi_2^F \times \pi_2^H$ correspond to both the transitions in the symmetry group of a rigorous problem. That is, these transitions mix up one and the same independent configurations, which for admissible torsion-rotational unit vectors leads to the correlation (22) between the representations of the groups C_2 and C_2'. The torsion-rotational operators of physical quantities are constructed in a similar way. For example, for the effective Hamiltonian undergoing transformation by the representation (A_e, a_e), the following complete expression holds [20]:

$$H = \sum_{n=0}^{\infty} \left(H_{2n}^{(A)} + H_{2n+2}^{(B_2)} + H_{2n+1}^{(B_2)} \right), \tag{23}$$

where the superscript specifies the type of the irreducible representation of the rotation group $D_2 = C_2 \times C_2'$, by which admissible combinations of components of the angular momentum are transformed, and the subscript stands for the summary degree of these components. The coefficients of the rotational combinations in the first, second and third

contributions to Eqn (23) depend respectively on the spin operators $\hat{c}$, $\hat{d}$, and $\hat{g}$:

$$\hat{c} = (c^{(1)}I + c^{(2)}e_3)I_\sigma + (c^{(3)}I + c^{(4)}e_3)\sigma_3 \,,$$

$$\hat{d} = (d^{(1)}I + d^{(2)}e_3)\sigma_1 \,,$$

$$\hat{g} = (g^{(1)}I + g^{(2)}e_3)\sigma_2 \,, \tag{24}$$

where $c^{(k)}$, $d^{(k)}$, and $g^{(k)}$ are real spectroscopic constants. The characteristic feature of the unified description is the presence in Eqns (24) of nontrivial cross terms related to the two types of nonrigid motion.

However, in the analysis of the complexes there arise problems associated not only with the necessity of allowance for a comparatively large number of nonrigid motions. As an illustration we shall consider the water dimer $(H_2O)_2$. Beginning with the pioneering paper [21], intensive studies by high-resolution spectroscopy have accumulated rich experimental material which shows the delocalization of this dimer over all its eight independent configurations. The main contribution to this delocalization is made by nonrigid motions through the intermediate *trans*-configuration. Among these motions there are three torsion exchange type motions.

An analytical solution of such a difficult problem is impossible without the application of the symmetry approach. The most developed method of solution using the CNPI group conception is the generalized method of internal axes [22, 23]. But as has already been mentioned, the CNPI group conception requires knowledge of a complete set of basis wave functions, which is a very serious problem for a water dimer. As a consequence, with the help of a rather cumbersome and formal procedure [9] only the main contribution to the solution was obtained on the assumption that due to tunnelling transitions the potential barriers between independent configurations are much larger than the observed level splittings, and the contributions from the nonrigid motions can simply be summed up. Such an assumption looks rather unrealistic, which is confirmed by experiment [24].

The complete description of torsion exchange type motions in terms of the intermediate *trans*-configuration, which was based on the conception of the symmetry group chain, can be found in Ref. [25]. Here we shall only emphasize a novel aspect of this description. Figure 6 displays the equilibrium configuration of the dimer $(H_2O)_2$ [26] with the point group $C_S = (E, \sigma^{(xz)})$ and the intermediate *trans*-configuration. When the analysis is restricted to exchange type transitions, the extended point group has a form similar to (17), where the direct product of the groups c_{2v} describes the symmetry of two monomers. In sewing together the groups C_S and G_{32}, the operation $\sigma^{(xz)}$ passes over to $\sigma_1 \times \sigma_2$, where σ_1 is the element of the left monomer reflection under which the H nuclei exchange places (the *xz*-plane), and σ_2 is the element of the right monomer reflection which leaves the H nuclei in their places (the monomer plane). This peculiarity is due to the fact that the operation $\sigma_1 \times \sigma_2$ is already not a transformation of the dimer as a whole. This circumstance, which has not occurred before, leads to some rather serious consequences.
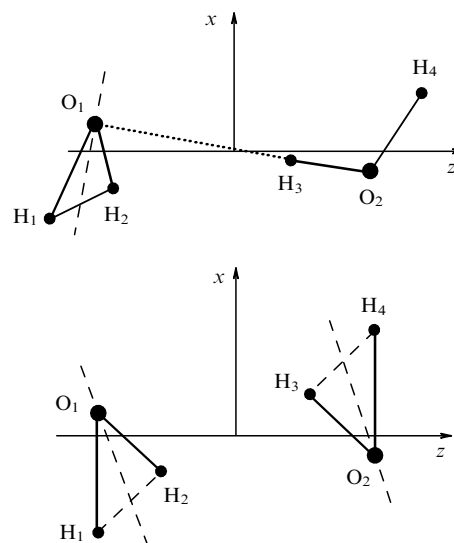
Figure 6. Equilibrium (upper) and intermediate (lower) configurations for the water dimer $(H_2O)_2$ (the *z*-axis coincides with the straight line joining the centers of mass of the monomers. In the equilibrium configuration, the plane of the monomer $H_1H_2O_1$ is orthogonal to the *xz*-plane and the plane of the monomer $H_3H_4O_2$ coincides with this plane. The dotted line shows the hydrogen bond between the monomers. In the intermediate configuration, the planes of both the monomers are orthogonal to the *xz*-plane).

7. The description of nonrigid nonexchange type motions

Nonrigid nonexchange type motions are very frequently encountered in molecular systems. A simple example is the so-called inversion motion in the ammonia molecule NH_3 [4]. In this case $G_H = G_0 \equiv C_{3v}$, and the point group more extended than G_H has the form $G_{12} = C_{3v} \times C_S$, where the nontrivial element of the group C_S, which determines the inversion motion, specifies reflection in the plane passing through the center of mass of the molecule and orthogonal to the three-order axis of the point group. The operator of any coordinate physical quantity (including the Hamiltonian) must belong to the coordinate Young scheme [3] of the permutation group π_3 of three H nuclei. Sewing together the groups π_3 and G_{12} implies that for such an operator in the BO approximation the representations

$$A_{1s}, \quad A_{1a} \tag{25}$$

are possible. Here s and a are symmetric and antisymmetric representations of the group C_S, which specify the complete set of unit vectors $|s\rangle$, $|a\rangle$ for the inversion motion. Let us consider the inversion-rotational motion in the ground electronic vibrational state. The relation $C_{3v} \times C_S \times C_i = D_6 \times C_S$ facilitates the partition of the inversion-rotational unit vectors around the irreducible representations of the group $G_{12} \times C_i$. Introducing the coordinate spin operator **e** with components of type (5) in the inversion space, one can readily construct the effective inversion-rotational operator for a physical quantity of interest. The results of such a construction for an effective Hamiltonian are equivalent to those of Ref. [2]. Because the Hamiltonian contains noninvariant terms, the subscripts s and a are not symmetry indices for stationary wave functions. Nevertheless, the consequences associated with the dynamic noninvariant group G_{12} are here sufficiently trivial, which is

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[9] In particular, as for the ethane molecule, in the description of separate purely coordinate motions the two-valued wave functions are used and, as a consequence, the *MS* group of the water dimer is replaced by its dual group.

due to the simple structure of this group. Namely, its subgroup G_H coincides with G_0 and the elements of the latter are invariant under nonexchange type transformations. As a result, nonzero matrix elements of the Hamiltonian are invariant under the dynamical group and, therefore, so are the eigenvalues of this Hamiltonian.
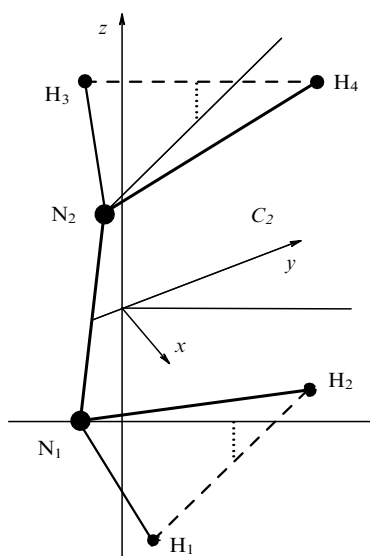
The description, considered in Ref. [27], of nonrigid nonexchange type motions in the hydrazine molecule N_2H_4 is much more interesting. A very important feature of this molecule is the closeness of its equilibrium configuration [12] with the symmetry group $G_0 \equiv C_2 = (E, C_2^{(y)})$ and the intermediate configuration shown in Fig. 7. In the latter configuration, two equivalent NH_2 structures are isosceles triangles and the dihedral angle between them is equal to $\pi/2$. As a result, each NH_2 structure may escape a shallow potential barrier [28, 29] and find itself at an energetically equivalent position both via the reflection σ_2 in the plane passing through the z-axis parallel to the segment $H-H$ (inversion motion) and by rotation through an angle π about the z-axis (internal rotation). These four nonexchange type transitions delocalize the molecule over eight independent equilibrium positions lying in the neighborhood of the unstable intermediate configuration whose geometry defines the symmetry of the intramolecular motion in the BO approximation. The dynamical group has a fairly involved structure

$$D_{32} = (c_{2v} \times c_{2v}) \wedge C_2 , \qquad (26)$$

where the direct product of the two groups $c_{2v} = (E, c_2^{(z)}, \sigma_1, \sigma_2)$ describes the symmetry of nonrigid motions of two NH_2 structures. Accordingly, the symmetry group of the Hamiltonian, G_H, has the form

$$G_H = (c_S \times c_S) \wedge C_2 , \qquad (27)$$

where $c_S = (E, \sigma_1)$. The element σ_1 which is of the exchange type describes the result of a successive realization of two nonexchange type motions typical of the NH_2 structure. For this reason, the group G_H is appreciably more extended than the group G_0. Moreover, part of the elements of G_H are

noninvariant under nonexchange type transformations because the latter change the position of the symmetry axis of the point group from y to x and vice versa. As a result, the presence of a noninvariant dynamic symmetry group in the BO approximation suggests serious conclusions. We shall stress the following of them. The group D_{32} has 14 irreducible representations: eight one-dimensional A_i, and six two-dimensional E_i [10]. The rotational symmetry in view of nonrigid motions is given by the subgroup $D_2 = C_2 \times O_2$ of rotations of a molecule as a whole in the group $D_{32} \times C_i$. The presence of $O_2 = (E, C_2^{(z)})$ is due to the possibility of molecular rotation about the z-axis with the help of the element $c_2^{(z)} \times c_2^{(z)}$. The complete picture of the rotational level splittings due to nonrigid motions for the ground completely symmetric electron-vibrational state is presented in Fig. 8. Since the group D_{32} does not contain improper transformations of a molecule as a whole, stereoisometry takes place [4], and all the levels are nonsplit doublets $\Gamma^{(\pm)}$. For the effective operators of purely coordinate physical quantities, including the Hamiltonian, the representations

$$A_1, \quad A_5, \quad E_3 \qquad (28)$$

are allowed. In this case due to stereoisometry the behavior of the operator of a physical quantity under the operation i does

Figure 8. Picture of splitting of the rotational levels of the N_2H_4 molecule with allowance for nonrigid motions ($E_{n,1}$ and $E_{n,2}$ are two components of the E_n representations with $n = 3, 4$).
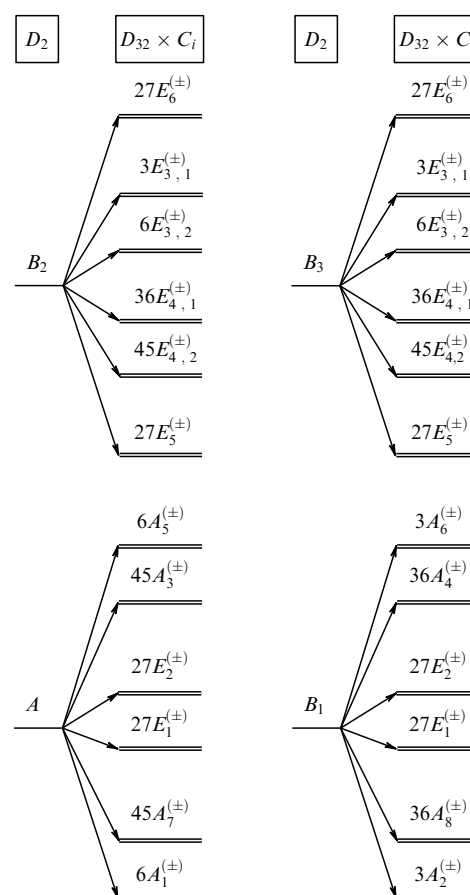

Figure 7. Intermediate configuration of the N_2H_4 molecule (the z-axis coincides with the straight line joining the centers of mass of the NH_2 structures).

[10] The numbering over the index i begins with 1. In the one-dimensional case, $i = 1$ corresponds to a unit representation.

not affect its construction. In the group G_H which has five irreducible representations (four one-dimensional a_i and one two-dimensional e), the Hamiltonian belongs to the representation a_1. Upon a reduction of G to G_H, the representations E_3 and E_4 fall respectively into the representations a_1, a_2 and a_3, a_4, while the representations E_1, E_2, E_5, E_6 pass over to e. This means that for the Hamiltonian only a single component E_3 is admissible. Nevertheless, there is no contradiction here because under nonexchange type operations which transform the components E_3 into each other, part of the elements of the group G_H change their positions. It is very important that the presence of noninvariant terms in the Hamiltonian leads to a splitting of E_3 and E_4 type states into doublets. This effect is a particular case of the general rule [8] saying that the degeneracies observed in the energy spectrum and nuclear statistical weights of states are determined by the symmetry group of the Hamiltonian. Notice also that under the transformations of the group D_{32} the eigenvalues of the Hamiltonian are noninvariant here as well. Such an invariance is incompatible, for example, with splitting of the states E_3 and E_4.

The application of noninvariant dynamic groups is essential for the description of intramolecular dynamics in the presence of nonrigid nonexchange type motions because the geometrical Hamiltonian symmetry group does not in this case simultaneously 'see' all the necessary independent equilibrium configurations of a nonrigid molecular system. To justify the use of the expression 'symmetry group' as applied to a noninvariant group, we note that the latter determines precisely the symmetry of molecular motion in the BO approximation. But the term 'symmetry' should be understood here in a wider sense than 'invariance'.

8. Conclusions

The proposed methods of qualitative intramolecular quantum dynamics are also fairly promising in a whole number of other fields of application, which we have not touched upon here. We would like to single out the following of them:

(i) there exists a wide class of molecular systems for which the analysis of observed nonrigid motions requires allowance for energetically nonequivalent equilibrium configurations. The description of such motions is not typically carried out by qualitative methods. The reason is simple — the symmetry elements cannot relate nonequivalent configurations. As a result, the symmetry group in the BO approximation does not 'see' them simultaneously.

The idea of the analysis of such systems consists in the introduction into the chain of a so-called virtual symmetry group in the BO approximation, which assumes all necessary equilibrium configurations to be equivalent and, consequently, has information on the transitions between them. Although the virtual symmetry later lowers to become real, the information is not lost. The first steps in this direction were made in Refs [30, 31];

(ii) in the above examples the analysis is restricted to physical quantities characterizing the internal motion of a molecular system. However, the operators describing transitions in this system under the action of the electromagnetic field are easily constructed. The construction of an electric dipole moment operator [32, 33] including the terms responsible for the so-called forbidden transitions is of great interest in this respect [34];

(iii) interesting and diversified are the range of phenomena in rigid molecules, which are associated with coordinate degeneration or quasi-degeneration of electronic states. In particular, for nonlinear molecules these are consequences of the Jahn–Teller effect, whose description encounters serious difficulties [7]. Naturally, the qualitative methods presented may appear to be very useful there. For the present they have only been used for a relatively simple case of the linear molecule [35]. It is however quite obvious that the role of these methods becomes especially significant when the description is extended to nonrigid molecules.

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