Physics – Uspekhi **49** (8) 821 – 829 (2006)

METHODOLOGICAL NOTES

PACS numbers: 31.15.Hz, 33.15.Bh

On the physical meaning of the molecular point group

A V Burenin

DOI: 10.1070/PU2006v049n08ABEH005963

Contents

Abstract. **It is argued that the most important result of applying the Born – Oppenheimer approximation to intramolecular dynamics is not the separation of electron and nuclear motions but the transition to the problem formulation in which the symmetry properties of the point group transformations characterizing a molecule in a chosen electron state can be correctly taken into account. It is shown that this group should be used as a rigorous symmetry group of total (electron – vibration – rotational) motion in this state.**

1. Introduction

An isolated molecule is a complex multiparticle system whose internal dynamics are described, with good accuracy, by a Hamiltonian that ignores the contributions associated with the spins of the electrons and the nuclei. The symmetry properties of this purely spatial Hamiltonian are fixed by the properties of space and time (the external symmetry) and by the requirements imposed on the permutations of identical particles (the internal symmetry). However, when we try to solve the time-independent Schrödinger equation with such a Hamiltonian by employing perturbation-theory techniques (which are at present the only realistic approach for analytic and numerical solutions), we suddenly find that a certain internal geometric symmetry group must be introduced if we want to describe the molecule. This step is important because otherwise it is impossible to write an approximate Hamiltonian, and the Born – Oppenheimer (BO) approximation is the leading one [1, 2]. It is in this approximation that the concept of an effective potential describing the interaction between nuclei in a given electron state and, hence, the concept of a set of equilibrium configurations corresponding to the minimum of this potential are introduced.

Qualitatively, molecules can be divided into two groups, the rigid and the nonrigid. For rigid molecules in nondegenerate electron states, the idea of an effective potential with one minimum is meaningful, while for nonrigid molecules, we must allow for several minima, because internal motion includes transitions between them. It has been known for a fairly long time that for rigid molecules, the additional geometric group should be selected in the form of the point group of their unique equilibrium configuration, by definition including all the geometric transformations of the given structure as a whole that map this structure onto itself. According to [3, 4], this group is characterized by the total (electron – vibrational – rotational) inner motion when deviations from the equilibrium position are small. Although the concept of a small deviation is not clarified, the meaning of this restriction is based on the assumption that the symmetry of the internal dynamics in the vicinity of the equilibrium configuration is determined by the symmetry of this configuration. This assumption is not very convincing because even the smallest asymmetric deviation of the nuclei from the equilibrium position abruptly reduces the geometric symmetry of their configuration. On the other hand, it was assumed in [5 – 7] that the point group characterizes only the electron vibrational motion and cannot be applied to the rotational (and, hence, complete spatial) motion. Such contradictions in the status of the empirically introduced point group are caused by the absence of a general standpoint regarding its nature. Therefore, significant progress in resolving these contradictions is related to the assumption [8, 9] that this group is an implicit (or dynamic) [10] internal symmetry group of the rigorous problem of spatial motion in a given electron state. This assertion has been logically justified by analyzing the observable properties of molecular systems.

The implicit geometric group differs significantly in its behavior from the permutation group, although both characterize the internal symmetry. First, the implicit group may change under electron excitation, because different isomeric forms of a molecule may be realized in different electron

---

A V Burenin Institute of Applied Physics, Russian Academy of Sciences,
ul. Ul'yanova 46, 603950 Nizhnii Novgorod, Russian Federation
Tel. (7-8312) 16 49 53. Fax (7-8312) 36 37 92
E-mail: buran@appl.sci-nnov.ru

Received 9 November 2005
Uspekhi Fizicheskikh Nauk **176** (8) 847 – 856 (2006)
Translated by E Yankovsky; edited by A M Semikhatov

states. Clearly, the permutation group is independent of the excitation. Second, an implicit symmetry characterizes the rigorous spatial Hamiltonian as a whole but not its kinetic and potential parts taken separately. On the other hand, the two parts are invariant under permutation transformations. Thus, these groups characterize different aspects of internal dynamics, with the geometric group being responsible for the dynamical structure that appears in each electron state and leads to rigid collectivization of internal motions. An indication of such behavior by a quantum microsystem is the presence of a rotational spectrum related to the rotation of the given structure as a whole. We note that an atom does not belong to such microsystems and therefore has no rotational spectrum.

The first part of the present paper (Sections 2 and 3) is devoted to analyzing the role that the BO approximation plays in studying the symmetry properties with respect to point-group transformations. The result of this analysis is formulated as follows. The most important consequence of the BO approximation is not the separation of electron and nuclear motions but the transition from a physical system with an implicit internal geometric symmetry to a model of such a system with an explicit internal geometric symmetry within a certain limited range of excitations. Such an approach ensures the solution to the Schrödinger equation for the steady states of molecules via analytic as well as numerical methods, irrespective of whether the electron and nuclear motions are separated (the case of nondegenerate electron states) or not (the case of degenerate electron states).

The second part (Sections 4 – 6) analyzes the effect of the transformations of the molecule point group characterizing the given electron state in an arbitrary (primarily, nonequilibrium) nuclear configuration of the molecule. It is found that the effect is equivalent to a permutation of identical nuclei in an invariant (under transformations of this group) effective potential describing the interaction between the nuclei. In view of this, the point group in a given state must be used as the geometric group of the rigorous symmetry of the total (electron – vibrational – rotational) motion. The exposition relies in part on the results in Refs [11, 12].

2. Nondegenerate electron states

For an isolated molecule, the spatial Hamiltonian in the laboratory Cartesian fixed coordinate system (FCS) can be written as

$$H = T_{\mathrm{el}} + T_{\mathrm{nucl}} + V_{\mathrm{el-el}} + V_{\mathrm{nucl-nucl}} + V_{\mathrm{el-nucl}} \,, \tag{1}$$

where T_{el} and T_{nucl} are the kinetic energies of electrons and nuclei, and $V_{\mathrm{el-el}}$, $V_{\mathrm{nucl-nucl}}$, and $V_{\mathrm{el-nucl}}$ are the respective energies of the Coulomb interaction between electrons and electrons, nuclei and nuclei, and electrons and nuclei. When the perturbation theory is used to solve the problem of bound steady states, the most important approximation is the Born – Oppenheimer one, which is based on the large difference in the electron and nuclear masses:

$$m_{\mathrm{el}} \ll M_{\mathrm{nucl}} \,. \tag{2}$$

Condition (2) allows considering the nuclei a slow subsystem and the electrons a fast subsystem. This means that the state of the electron subsystem adiabatically follows the state of the nuclear subsystem. Therefore, we first solve the problem of electron motion in the field of fixed nuclei with a given configuration,

$$(T_{\mathrm{el}} + V_{\mathrm{el-el}} + V_{\mathrm{nucl-nucl}} + V_{\mathrm{el-nucl}})\Psi_{\mathrm{el}}^{(n)} = E_{\mathrm{el}}^{(n)}\Psi_{\mathrm{el}}^{(n)} \,, \tag{3}$$

where the superscript n stands for the set of electron quantum numbers. Then, for each electron state, we solve the problem of nuclear motion with the effective potential of their interaction in the form $E_{\mathrm{el}}^{(n)}(X_{\mathrm{nucl}})$, which by definition depends on the instantaneous nuclear configuration

$$\left[T_{\mathrm{nucl}} + E_{\mathrm{el}}^{(n)}(X_{\mathrm{nucl}})\right]\Phi_{\mathrm{nucl}}^{(n,v)} = E_{\mathrm{nucl}}^{(n,v)}\Phi_{\mathrm{nucl}}^{(n,v)} \,, \tag{4}$$

where the superscript v stands for the set of nuclear quantum numbers. The simplicity of implementing such an approach is misleading, because so far we have not taken the dynamic structure of the molecule into account. Some important remarks should be made in this connection.

(1) So far, we have not specified the equation of nuclear motion. The presence of a dynamic structure results in the molecule having a rotational spectrum. Hence, the effective nuclear Hamiltonian in model (4) must involve a Cartesian coordinate system linked to the moving molecule (a moving coordinate system, or MCS), which makes it possible to define the very concept of the rotational motion of a molecule as a whole. This is a nontrivial procedure [2] requiring a transition to collective variables. A physically meaningful definition of rotational motion requires that in a given electron state, the MCS be 'quenched' into the effective nuclear potential in this state, which for a rigid nonlinear molecule is equivalent to fixing the MCS in relation to its equilibrium configuration.[1] We note that the criterion for the absence of rotation of the molecule as a whole does not coincide with the requirement that the angular momentum of the molecule be zero [3].

(2) The kinetic and potential parts of the nuclear Hamiltonian written in terms of collective variables must be invariant under transformations belonging to the geometric group that are defined in the MCS. This amounts to passing to a model with a manifest geometric symmetry. However, the price for this is a narrower applicability range, since, generally speaking, the geometric group depends on the electron excitation.[2] In nondegenerate electron states of rigid molecules, the effective potential has one minimum, with the result that the symmetry of the equilibrium configuration necessarily coincides with that of the effective potential. In other words, the symmetry of the equilibrium configuration is an

---

[1] This assertion immediately follows from the requirement that the rotational motion of an isolated molecule be free. Indeed, this requires that rotational displacements not alter the positions of the nuclei in the effective potential describing their interaction (all other internal motions are related to changes in the arrangement of the nuclei in the effective potential, i.e., are 'slowed down' by this potential). Hence, the only physically meaningful definition of rotational motion is the one that leads to a rotation of the effective nuclear potential as a whole with the arrangement of the nuclei in it remaining unaltered. In other words, the MCS must be 'frozen' into the effective nuclear potential. Any other choice of the MCS violates the requirement that the rotational motion be free in an isotropic space.

[2] It must be noted at this point that Hamiltonian (1) also describes the continuous spectrum. However, the geometric group necessarily changes in passing to the continuous spectrum, because the degeneracy multiplicities of energy levels become infinite as a result of such a transition.

elementary consequence of the symmetry of internal dynamics, and not vice versa, as is often claimed.

(3) A meaningful spatial wave function of a steady state in the BO approximation must belong to one of the irreducible representations of the geometric group. Only for a nondegenerate electron state does this condition hold when such a function is selected in the form of the simple product

$$\Psi_{\mathrm{el}}^{(n)}\,\Phi_{\mathrm{nucl}}^{(n,v)}\,, \tag{5}$$

which means the separation of the electron and nuclear motions. This result means that the BO approximation corresponds to geometrically structured independent electron and nuclear subsystems. Because the geometric symmetry is a characteristic of a rigorous spatial Hamiltonian, it is retained even when nonadiabatic corrections to this approximation are taken into account, in which case the electron and nuclear motions cannot be separated. Or, to put it more accurately, there is no way in which the electron and nuclear structures can be examined independently in this case.

Hence, the BO approximation plays an important role in obtaining solutions with meaningful symmetry properties, because only with its help can we build equations of motion in which the geometric group is explicitly taken into account.

3. Degenerate electron states

We first note that the time-independent Schrödinger equation in the case of degenerate electron states is also solved in two stages that use Eqns (3) and (4) written under the assumption that the electron subsystem adiabatically follows the nuclear subsystem. The result of such a solution is that the electron and nuclear subsystems do not separate. When the solution for the spatial wave function is written in form (5), there is no way in which it can belong to one of the irreducible representations of the geometric group. The correct solution is constructed in the form of a linear combination of products of electron and nuclear functions whose coefficients are fully determined by the requirements of geometric symmetry and in no way are related to condition (2). This means that there forms a unique electron – nuclear structure (there is no small parameter that would allow separating the electron and nuclear structures, even approximately).[3] Such steady states are called vibronic and their manifestations determine the essence of the Jahn – Teller effect [13, 14] in nonlinear molecules and the Renner effect [2] in linear molecules.

We examine the nontrivial problem concerning the geometric group of a rigid molecule in a nondegenerate electron state. According to the Jahn – Teller theorem [15], a symmetric equilibrium nuclear configuration of a nonlinear molecule is always unstable in an electron state, which is orbitally degenerate due to this symmetry. In other words, there are nuclear displacements for which the effective potential has a nonzero derivative in this configuration. A degenerate electron state, together with vibrational modes that destabilize the symmetric configuration, form a Jahn – Teller system. For instance, the geometric group C_{3v} corresponds to the ammonia molecule NH_3 in the nondegenerate ground electron state. In a doubly degenerate electron state of type E, the equilibrium configuration with the C_{3v} symmetry becomes unstable under vibrational displacements of the same type (a Jahn – Teller $E-E$ system). This leads to an effective potential with three equivalent minima and an equilibrium configuration with the C_S symmetry in each of them. For several decades, it was assumed that reduction of the symmetry of an equilibrium configuration leads to lifting the degeneracy. However, numerous experimental attempts to corroborate this assumption have failed (a brief historical note can be found in Ref. [13]). The presence of several minima in the effective potential means that the molecule has become nonrigid and that the geometric symmetry of the internal dynamics ceases to coincide with the symmetry of an equilibrium configuration. In this case, one should build an extended point group [8, 9] that characterizes not only local notions within each minima but also transitions between the minima. The transformations belonging to this extended group, which determine transitions in the Jahn – Teller problem, are of the exchange type,[4] with the result that they are symmetry transformations of the spatial Hamiltonian. As a consequence of all this, the geometric symmetry of the Hamiltonian coincides with the symmetry of the unstable configuration, and therefore the degeneracy is not lifted. But the type of degeneracy becomes collective electron – vibrational or vibronic. For the ammonia molecule, the extended point group is given by

$$C_3 \wedge C_S = C_{3v}\,, \tag{6}$$

where the invariant subgroup C_3 takes the symmetry of motion between the three minima into account, and the quotient group C_S accounts for the symmetry of motion in a single minimum. The symbol $\wedge$ stands for the semidirect product [6, 9], which occurs because of the noncommutativity of the elements of the C_3 and C_S groups.

The electron states in linear molecules can only be doubly degenerate, with the effective potential in the degenerate state having a zero derivative in all nuclear displacements in the linear configuration. However, in the case of a strong Renner effect, the maximum of the effective potential may occur in the linear configuration, while the minimum may correspond to a bent configuration. Nevertheless, the axial symmetry of the internal dynamics is restored because of over-barrier transitions corresponding to the linear configuration. Naturally, these transitions connect dependent configurations in this case, because the final configuration can be obtained as a result of the ordinary rotation of the initial configuration about the linearization axis.

Geometric symmetry is a characteristic of the rigorous spatial Hamiltonian and is therefore preserved even when the corrections to the description of vibronic states based on the approximation in Eqns (3) and (4) are taken into account. Clearly, calculation of the corrections here differs signifi-

---

[3] It is customary to assume that in degenerate electron states, the electron and nuclear motions strongly interact, with the result that the BO approximation breaks down. Actually, symmetry requirements lead here to a rigid (nonforce) coupling between these two types of motion. The force interaction (nonadiabatic corrections) is weak and can be taken into account as a perturbation, just as in the case of a nondegenerate electron state. Such a situation is similar to the coupling between the spatial and spin types of motion due to symmetry restrictions imposed on permutations of identical particles. In other words, the symmetry alone makes it impossible to reduce the condition of the nuclear subsystem being followed adiabatically by the electron subsystem to the condition of separation of the electron and nuclear motions.

[4] A transformation of this type is associated with a permutation of identical nuclei in a nuclear-interaction effective potential that is invariant under such a transformation.

cantly from the case of a nondegenerate electron state, but the initial approximation still plays a leading role in obtaining solutions with meaningful symmetry properties.

Finally, we note that the problem of describing the entire set of quasidegenerate electron states is a fairly regular one. A separate or isolated study of each of these states on the basis of Eqns (3) and (4) leads to solutions in which the corrections usually contain no small parameter. In other words, such solutions are far from being realistic [it is said that there remain 'strong interactions' between the states described by Eqns (3) and (4)]. Hence, we are confronted with the serious problem of summing the corrections. To avoid this problem, all the quasidegenerate states are examined together. For nonlinear molecules, such a situation means that the Jahn – Teller pseudoeffect must be taken into account. From the symmetry standpoint, such effects can be interpreted as the presence of a certain leading contribution to the rigorous spatial Hamiltonian of an extended geometric group.

4. Transformations of the point group of the H_2O molecule

As an example, we study the rigid molecule of water, H_2O. We select a coordinate system in which it is most convenient to examine the point group transformations. The common (and simplest) approach is to introduce such transformations as the transformation of the object with the coordinate system remaining fixed. Because the MCS does not satisfy this requirement (the orientation of its axes changes under transformations corresponding to the rotation of the molecule as a whole), we use a system of coordinates whose x, y, and z axes are fixed in relation to the elements of the point group.

The white circles in Fig. 1 correspond to the equilibrium configuration of the H_2O molecule in the ground electron state, a configuration that belongs to the point group

$$C_{2v} = \left(E, C_2^{(z)}, \sigma_v^{(xz)}, \bar{\sigma}_v^{(yz)}\right) \tag{7}$$

and forms an isosceles triangle [16]. All irreducible representations of this group are one-dimensional, and therefore the possible bound electron states are nondegenerate. In this case, the symmetry of the equilibrium configuration, which is a consequence of the symmetry of the internal dynamics, simply coincides with the latter. In other words, the effective nuclear Hamiltonian is the sum of the kinetic and potential parts, which are invariant under transformations belonging to the C_{2v} group and describe the vibrational – rotational motion of the nuclei.[5] The H_2O molecule has three vibrational modes, two of the A_1 symmetry and one of the B_1 symmetry. The most interesting case is that of asymmetric nuclear displacements. Hence, we examine the action of a transformation belonging to the C_{2v} group on the nuclear configuration marked in the upper part of Fig. 1 by black circles, whose configuration corresponds to the B_1 mode. We begin with the transformation $C_2^{(z)}$. Since the effective nuclear potential is invariant under transformations belonging to the point group, we only need to determine how $C_2^{(z)}$ acts in the vibrational – rotational configuration space. The transformation of the vibrational coordinates (the result is shown in the middle part of Fig. 1) leads to a fairly simple change in the displacements of the nuclei with the arrangement of the equilibrium configuration remaining unchanged, because the MCS does not rotate. The question of rotational transformations is more complicated. Rotational motion is specified by the rotation of the MCS, and, in the action on the rotational coordinates and hence on the rotational wave function, infinitely small rotations of the MCS are equivalent to infinitely small inverse rotations of the FCS [3]. Hence, in the coordinate system with the x, y, and z axes, the rotations corresponding to rotational transformations must be the inverse of rotations corresponding to the vibrational transformations. This is an extremely important fact, although it is of no significance for the rigid molecule of H_2O because the geometric symmetry elements here coincide with the inverse elements. The total result of the action of $C_2^{(z)}$ on the vibrational and rotational coordinates is shown in the lower part of Fig. 1. Clearly, the result is equivalent to a permutation of the identical hydrogen nuclei. The following facts should be mentioned in this connection.

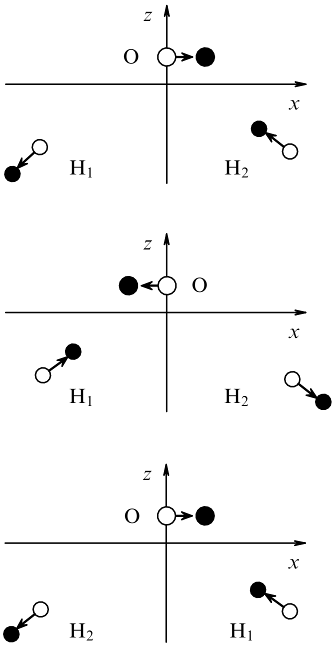

Figure 1. The action of the $C_2^{(z)}$ transformation in the nuclear configuration of the H_2O molecules corresponding to the type-B_1 vibrational mode.

(1) Under transformations belonging to $C_2^{(z)}$, vibrational and rotational changes are balanced such that the spatial arrangement of an arbitrary nuclear configuration is preserved and only identical nuclei exchange their positions. According to Refs [8, 9], this is a transformation of the exchange type. The invariance of the Hamiltonian of the total internal spatial motion in a given electron state under such transformations immediately follows from the fundamental asymmetry properties for permutations of identical nuclei.

(2) The action of $C_2^{(z)}$ on the instantaneous configuration in the case of asymmetric nuclear displacements does not coincide with its ordinary geometric action. Naturally, the latter is not equivalent to a permutation of identical nuclei. However, in Ref. [7] this fact is erroneously assumed to be an argument in favor of not using the point group to describe the strict symmetry of the problem of intramolecular motion.

---

[5] Although the concept of an effective nuclear Hamiltonian emerges because of the approximation specified by Eqns (3) and (4), it remains meaningful even when corrections are taken into account [17].

(3) A permutation of identical nuclei that is equivalent to a transformation belonging to $C_2^{(z)}$ can easily be obtained by basing our reasoning on the equilibrium configuration of the molecule, because the action of $C_2^{(z)}$ then coincides with its ordinary geometric action.

We now turn to $\bar{\sigma}_v^{(yz)}$. Here we must additionally allow for the fact that the motions corresponding to improper transformations belonging to the point group are not realized in a rigid molecule. In other words, $\bar{\sigma}_v^{(yz)}$ is not defined in the vibrational–rotational configuration space. The real structure of the energy spectrum of a rigid molecule is described by the rotational subgroup of $G_{\text{point}} \times C_i$, where C_i is the spatial inversion group [8, 9]. The action on the spatial Cartesian coordinates of all the particles of the molecules related to the properties of the space of the external symmetry operation of the nonexchange type i is an ordinary geometric action. For a given electron state in the system of coordinates x, y, and z, this operation inverts the effective interaction potential of the nuclei and their coordinates. For the group $C_{2v} \times C_i$, the rotational subgroup is

$$D_2 = \left(E, C_2^{(z)}, C_2^{(y)} = i\sigma_v^{(xz)}, C_2^{(x)} = i\,\bar{\sigma}_v^{(yz)}\right). \qquad (8)$$

It suffices to determine the action of $i\,\bar{\sigma}_v^{(yz)}$ on the positions of the nuclei, because the spatial position of the effective potential follows immediately from the position of the equilibrium configuration. The given transformations allow only one representation in the vibrational–rotational configuration space,

$$\left(i\,\bar{\sigma}_v^{(yz)}\right)_{\text{nucl}} = \left(C_2^{(x)}\right)_{\text{rot}} \times \left(\bar{\sigma}_v^{(yz)}\right)_{\text{vib}}, \qquad (9)$$

with the vibrational transformation preserving the position of the equilibrium configuration, as it should. Equation (9) yields

$$\left(\bar{\sigma}_v^{(yz)}\right)_{\text{nucl}} = \left(C_2^{(x)}\right)_{\text{rot}} \times \left(\bar{\sigma}_v^{(yz)}\right)_{\text{vib}} \times i_{\text{nucl}}. \qquad (10)$$

All three stages in the action of the transformations in the right-hand side of Eqn (10) on the initial nuclear configuration shown in the upper part of Fig. 1 are depicted (from top down) in Fig. 2. Clearly, the action of $\bar{\sigma}_v^{(yz)}$ is equivalent to a permutation of identical hydrogen nuclei in an invariant (under such a transformation) effective nuclear potential. This action by $\bar{\sigma}_v^{(yz)}$ does not, understandably, coincide with its ordinary geometric action.

Using that $\sigma_v^{(xz)} = C_2^{(z)}\bar{\sigma}_v^{(yz)}$, we can see that the action by $\sigma_v^{(xz)}$ is equivalent to the identical nuclear permutation in an invariant (under such a transformation) effective nuclear potential. For the water molecule, this result is quite obvious, because all three nuclei of this molecule lie in the xz plane. We note that the above analysis of the actions of the operations belonging to the point group on the instantaneous nuclear configuration of the molecule is based largely on the use of a physically meaningful procedure of introducing the concepts of vibrational and rotational motions. Precisely, for a fixed center of mass, the motion is said to be rotational when it is responsible for changes in the spatial arrangement of the equilibrium configuration and vibrational when it is responsible for changes in the displacements of the nuclei from the equilibrium position [2].

The above implies that there is no need for a special analysis of the case of symmetric nuclear displacements. Thus, the action of transformations belonging to the point group C_{2v} is equivalent to permutations of identical particles in an effective nuclear potential invariant under such transformations. Hence, the group C_{2v} is combined with the group π_2 of permutations of the identical hydrogen nuclei as is illustrated in Table 1 (this ensures a relation between the elements and, as a result, between the irreducible representations). From the fundamental symmetry properties, we easily find (see Ref. [9]) that the operators of the physical quantities characterizing the total internal spatial motion are transformed according to the completely symmetric coordinate Young tableau of the group of permutations of identical nuclei. From the combination in Table 1, we see that all such operators, including the Hamiltonian, belong to the unit representation of the point group. In other words, the point group is the geometric group of the strict symmetry of the total (electron–vibrational–rotational) motion in the electron state it characterizes, and this fact carries no limitations on the size of displacements of the nuclei from the equilibrium position.

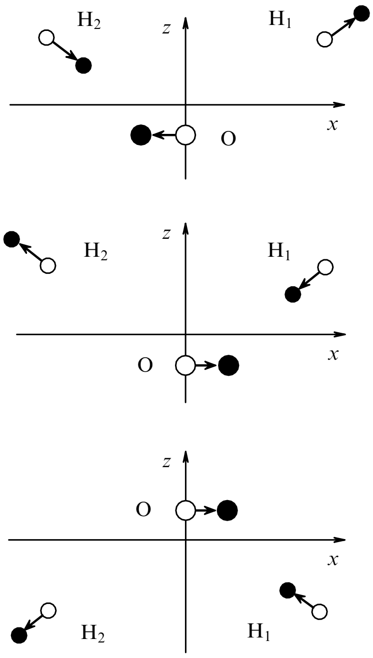

Figure 2. The action by the $\bar{\sigma}_v^{(yz)}$ transformation on the nuclear configuration of the H_2O molecules corresponding to a type-B_1 vibrational mode.

Table 1. Combination of the point group C_{2v} with the permutation group π_2 (for the permutation group the coordinate Young tableaux are given).

Classes of C_{2v}	E	$C_2^{(z)}$	$\sigma_v^{(xz)}$	$\bar{\sigma}_v^{(yz)}$
Classes of π_2	$\{1^2\}$	$\{2\}$	$\{1^2\}$	$\{2\}$

Irreducible representations of C_{2v}	A_1	A_2	B_1	B_2
Irreducible representations of π_2	[2]	—	$[1^2]$	—

The admissible irreducible representations of the point group for the complete spatial wave function are known as the coordinate multiplets of the molecule. The data in Table 1 suggest that the only possible multiplets are

$$A, B_1. \qquad (11)$$

The multiplets B_2 and B_3 are excluded because of the presence of a homomorphic map of the group C_{2v} onto the group π_2 (to each element of π_2, there correspond two elements of C_{2v}), which occurs because the nuclear configuration of the molecule happens to be a planar configuration (actually, it is sufficient that the equilibrium configuration be planar). In Refs [8, 9], such exclusions are called geometrical. They lead to a rigorous correlation between the types of symmetry of the electron, vibrational, and rotational parts when a multiplet is formed.

5. Transformations of the point group of an arbitrary molecule

We now extend the results in the previous section to the case of an arbitrary rigid molecule. Generally, the point group transformations of a molecule may be rotations, reflections, and mirror rotations. The effective nuclear potential is invariant under all transformations of the point group. We need only study their action in the vibrational – rotational configuration space. We start with rotation. Its action in the vibrational and rotational subspaces is opposite in direction, and the action in the vibrational subspace does not change the position of the equilibrium configuration. As a result, the vibrational and rotational changes balance each other such that the spatial arrangement of an arbitrary nonequilibrium nuclear configuration is preserved up to an exchange of places of identical nuclei. It is easy to obtain the corresponding permutation of identical nuclei from the action of a rotation on the equilibrium configuration of the molecule. We note that the point group of a molecule with a linear equilibrium configuration incorporates a continuous set of rotations about an infinite-order axis, for which the vibrational and rotational changes perfectly balance each other. Hence, all such rotations are equivalent to the identical permutation of the nuclei.

Motions corresponding to improper transformations that belong to the point group are not realized in a rigid molecule and, accordingly, the operations of reflection and mirror rotation are not defined in the vibrational – rotational space. Instead of containing improper elements, the rotational subgroup of $G_{\text{point}} \times C_i$, which describes the real structure of the energy spectrum, contains products of these elements with the element i of spatial inversion. Similarly to the results in the previous section, we have the following representation of the transformation $i\sigma$ in the vibrational – rotational configuration space:

$$(i\sigma)_{\text{nucl}} = (C_2)_{\text{rot}} \times (\sigma)_{\text{vib}} \,, \tag{12}$$

where C_2 is the rotation by the angle π about the axis of the orthogonal plane σ. For any molecule, the nuclei are divided, in relation to the reflection operation, into singular and pair, which in the equilibrium configuration are arranged, respectively, in the plane σ and symmetrically with respect to this plane. Obviously, pair nuclei must be identical. In both cases, we examine the transformation σ using the example of the H_2O molecule.

According to the definition in Refs [3, 4], a mirror rotation S_n by the angle $2\pi/n$ is written in the form

$$S_n = C_n \sigma_h \,, \tag{13}$$

where σ_h is the reflection plane orthogonal to the rotation axis of C_n. In other words, a mirror rotation is a combination of the transformation types discussed earlier. Accordingly, for the transformation iS_n in the vibrational – rotational configuration space, we obtain the representation

$$(iS_n)_{\text{nucl}} = (C_{n+2})_{\text{rot}} \times (S_n)_{\text{vib}} \,, \tag{14}$$

where C_{n+2} is the rotation by the angle $(2\pi/n) + \pi$.

Thus, all the transformations belonging to the point group of an arbitrary molecule are equivalent to the permutations of the molecule's nuclei; these permutations are easy to find by studying the results of the action of these transformations on the equilibrium configuration. When the equivalent elements of the permutation group and the point group are combined, there generally occurs a homomorphic map of the point group of the molecule onto a subgroup of the permutation group of identical nuclei [8, 9], with the unit representation of the point group corresponding to the completely symmetric coordinate Young tableau of the permutation group. Hence, the point group characterizing the molecule in the given electron state must be used as the rigorous symmetry group of the complete electron – vibrational – rotational motion in this state. It is important that this fact carries no limitations on the size of displacements of the nuclei from the equilibrium position.

The homomorphism in the combination leads to geometrical exclusions for coordinate multiplets and occurs only for molecules with planar and linear equilibrium configurations. In the latter case, this fact plays an important role. For instance, for multiplets of a molecule with the point group $C_{\infty v}$, only the unit representation may occur from an infinite (although countable) number of irreducible representations (Table 2).[6] As a result, only steady states in which the projection of the total spatial angular momentum on the C_∞ axis originates from vibronic motion are allowed [8, 9].

Table 2. Combination of the point group $C_{\infty v}$ with the permutation group π_1.

Classes of $C_{\infty v}$	E	$2C_\varphi$	σ_v
Classes of π_1	{1}	{1}	{1}

Irreducible representations of $C_{\infty v}$	A_1	A_2	E_1	...	E_n	...
Irreducible representations of π_1	[1]	—	—	...	—	...

In many molecules in a given electron state, even subjected to excitations much lower than the dissociation energy, the transitions between the different minima of the effective nuclear potential must be taken into account. The key question here is how the substitution of a nonrigid molecule for a rigid molecule changes the symmetry transformations. As noted in Section 3, for a nonrigid molecule, we must construct an extended point group that characterizes local motions in each minimum and the transitions between the minima. Obviously, the extended point group must contain the point groups corresponding to the minima of the potentials as subgroups. The elements that specify the transitions can belong to the exchange type or to the

---

[6] Such molecules have no identical nuclei or the nuclei are located asymmetrically in relation to the center of mass. In both cases, to all transformations that belong to the point group, there corresponds the identical permutation of the nuclei.

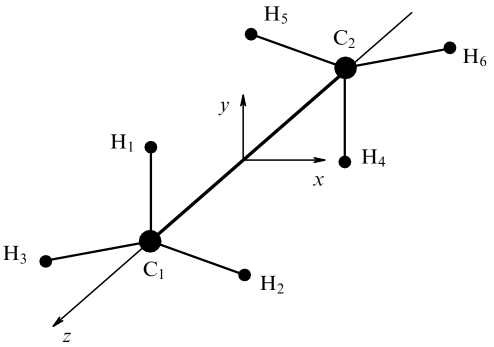

Figure 3. The equilibrium configuration of the ethane molecule C_2H_6 for the ground electron state.

nonexchange type. The latter are not symmetry elements of the Hamiltonian of the total spatial motion, and therefore do not interest us here.

Transitions of the exchange type can connect only energy-equivalent minima of the effective potential with the same point group. Under the action of the elements that specify such transitions, the effective nuclear interaction potential is mapped into itself and the spatial arrangement of the equilibrium configuration remains unchanged. We take the ethane molecule C_2H_6, whose equilibrium configuration in the ground electron state belongs to the point group $D_{3d} = C_{3v} \times C_I$ [18], as shown in Fig. 3. It is well known that internal rotation of two identical CH_3 tops about the chemical bond of the carbon atoms occurs in this molecule and that the motion is slowed down by a low potential barrier [19]. The rotation of each internal top from the point of minimum potential through angles $2\pi/3$ and $4\pi/3$ leads to an equivalent minimum point, with the spatial arrangement of the equilibrium configuration being preserved. The extended point group is [9, 20]

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

where the two groups c_{3v} are determined by the symmetry of the two CH_3 tops. The operations of G_{72} that are not included in its subgroup D_{3d} act on the equilibrium positions of the nuclei and mix the rigid molecules that belong to different minima of the effective nuclear potential. Clearly, in this case, the arrangement of an arbitrary nuclear configuration in space is preserved up to a change in labeling the identical nuclei. In other words, the group G_{72} is the symmetry group of the total internal spatial motion of the nonrigid ethane molecule. The operations of the point group D_{3d} can be formed from the operations of G_{72} that are not included in the point group. For instance,

$$C_3^1 = (c_3^1 \times E) \times (E \times c_3^1) \,.$$

We note that it is important that the actions of the left- and right-hand sides in such equations on an arbitrary nuclear configuration coincide. It can be easily verified that this is indeed the case.

Qualitatively, the configuration space of nuclear mixing of nonrigid molecules in the given electron state is divided into regions corresponding to separate rigid molecules. Naturally, the displacements of the nuclei in each rigid molecule are limited by the respective region. It must also be noted that the improper operations that belong to the point group not realized in the vibrational–rotational configuration space of a rigid molecule are operations of mixing with equivalent rigid molecules. Clearly, the action of such operations, which was discussed at the beginning of the present section, on an arbitrary nuclear configuration is similar to the permutation of equilibrium positions of identical nuclei.

6. Nuclear statistical weights

Presently, there are two very different approaches to the study of the symmetry properties of intramolecular motion, approaches that are based on different ideas. In the first approach, already discussed in the first edition of the well-known book on the nonrelativistic theory of quantum mechanics by Landau and Lifshitz [21] for the case of rigid molecules, the symmetry of the total (electron–vibrational–rotational) motion in a given electron state is determined by the point group that characterizes this state. The use of the geometric group within the concept of a chain of symmetry groups has been substantiated and generalized in Refs [8, 9], where generalization largely accounts for introducing nonrigid molecules. In the second approach, suggested in the pioneering work [5] (with the modern situation with this approach described in [7]), it is assumed that the geometric group cannot be used to determine the symmetry of the total spatial motion and that the point group can be used only as an auxiliary tool in describing electron–vibrational motion. The total motion is characterized by the molecular symmetry (MS) group, which incorporates permutations of identical nuclei and the products of these permutations with the spatial inversion operation that correspond to the realized configurations.[7] In the case of a rigid nonlinear molecule, the MS group is much closer to the rotational subgroup of $G_{\text{point}} \times C_i$ and is obtained from this group by replacing the elements of G_{point} with equivalent permutations of identical nuclei. In particular, the MS group of the H_2O molecule is

$$C_{2v}(M) = (E, P_{12}, i, iP_{12}) \,, \tag{16}$$

where P_{12} is the permutation of the two hydrogen nuclei. It is important that in contrast to the point group, the MS group contains elements that are not equivalent to the permutation of identical nuclei. Naturally, these groups are used differently in the approaches based on them.

The substantial differences between the ideas on which the two approaches are based may lead to difficulties in using the results of one approach in the other. The misunderstanding associated with the calculation of nuclear statistic weights is most characteristic. We recall that the degeneracy of coordinate multiplets related to the point group do not lead to the actually observable degeneracy of the energy levels; the transformations belonging to this group are equivalent to a perturbation of identical nuclei, with the result that the spin–coordinate wave function must satisfy the fundamental symmetry requirements for such permutations. It turns out that all spatial functions of the multiplet form only one meaningful spin–coordinate function [4, 9]. Generally, several coordinate Young tableaux may correspond to one coordinate multiplet of a given symmetry, with each diagram

---

[7] The realized transformations connect the configurations between which the transition is achieved by the types of motion considered.

forming a contraction with a similar or dual spin Young tableau depending on whether the identical nuclei are bosons or fermions. Accordingly, to each spin Young tableau, there corresponds one or several values of the total spin of identical nuclei. If we ignore the hyperfine interactions associated with nuclear spin, the energy of a molecular state depends neither on the value of the total spin nor on its orientation in space. The multiplicity of a given degeneracy is called the nuclear statistical weight. For the H_2O molecule, the spatial Young tableaux of the π_2 group are

$$[\lambda_{\text{coord}}]: [2], [1^2]. \tag{17}$$

Because the hydrogen nuclei are fermions ($s_{\text{H}} = 1/2$), the spatial tableaux form contractions with the dual spin tableaux:

$$[\tilde{\lambda}_{\text{sp}}]: [1^2], [2]. \tag{18}$$

The first tableau in (18) corresponds to the total spin $S = 0$ and the second to the total spin $S = 1$. Using the combination in Table 1, we obtain

$$1A, 3B_1, \tag{19}$$

where the numerical factor in front of the respective multiplet is the nuclear statistical weight, not including the spin of the oxygen nucleus. The total nuclear statistical weight is given by

$$\rho_{\text{nucl}} = \rho^{(\lambda)}_{\text{nucl}}(\text{H}) \times (2s_{\text{O}} + 1). \tag{20}$$

For the main isotope of the oxygen nucleus, ^{16}O, the spin is zero and the second factor in (20) is equal to unity. In Ref. [3], a method was developed that considerably simplifies the procedure for finding the nuclear statistical weights of the coordinate multiplets of any rigid molecule. In this method, one has to first calculate the characters for the operations G of the point group:

$$\chi(G) = \prod (2s_a + 1)(-1)^{2s_a(n_a - 1)}, \tag{21}$$

where n_a is the number of nuclei in each group of identical nuclei that exchange their positions under G, and s_a is the spin of the nuclei in this group. The product is over all groups of nuclei. Next, decomposing representation (21) into irreducible representations, we obtain all the possible types of coordinate multiplets together with their nuclear statistical weights. Naturally, for the $H_2{}^{16}O$ molecule, this procedure yields the result coinciding with (19) and (20). However, it was claimed in [22] that a basic mistake was made in [3] in deriving formula (21), since the behavior of the multiplet under spatial inversion was not taken into account when the action of operators G was considered. Hence, formula (21) should hold only for positive (or even) states, while a correction is needed for negative (or odd) states. This conclusion is wrong because formula (21) was used in [22] for the MS group, which incorporates permutations of identical nuclei and their products with the spatial inversion operation, which leads to mistakes in the case of negative levels. Hence, the results in [22] can be interpreted only as an adaptation of the method developed in Ref. [3] for operating with the MS group.[8] Unfortunately, the version advocated in [22] proved to be fairly widespread (e.g., see Ref. [7]).

7. Conclusion

Thus, a molecule is a quantum microsystem with a rigid collectivization of internal motions that leads to the emergence of a dynamical structure. An indication of such a microsystem is the presence of a rotational spectrum related to the rotation of the system as a whole. The point group characterizing the dynamical structure in a given electron state of a rigid molecule determines the geometric symmetry of the complete spatial motion in this state. The fact that such symmetry must be taken into account leads to serious changes in the interpretation of the BO approximation. We note another important aspect in using internal geometric symmetry.

The use of Eqns (3) and (4) in describing the internal dynamics of polyatomic molecules constitutes an extremely complicated problem, especially in the presence of nonrigid motions. First, calculations by quantum chemistry methods of the effective nuclear potential with an accuracy required by high-resolution spectroscopy even in the simplest case of a nondegenerate electron state require enormous amounts of computer time. Even supercomputers make such calculations possible only for triatomic molecules (e.g., see Refs [24–26]). Hence, the effective potential of a polyatomic molecule is usually represented in the form of various expansions that involve empirical constants. Second, one is forced to write the adiabatic Hamiltonian of nuclear motion in terms of collective variables (taking the remarks made in Section 2 into account) and then to try and solve the resulting equation by analytical or numerical methods. Implementing such an approach is extremely difficult for nondegenerate electron states even for the simplest nonrigid molecules. The values of the corrections to the description specified by Eqns (3) and (4), whose calculation is even more complicated, may often exceed the accuracy of the experimental data. Common symmetry methods for analyzing nonrigid molecules based on the concept of the MS group change the picture very little. The reason is that to apply such methods we must write the nuclear Hamiltonian in terms of collective variables and obtain solutions for the steady states, at least approximately. After that, we must specify the action of the symmetry elements on the collective variables. The obtained symmetry properties of the approximate solutions can be used only to somewhat simplify the procedure of refining them.

At the same time, recently developed methods that use the concept of group chains, methods by which the description of the internal dynamics of any molecule is built only around symmetry principles, allow implementing an effective (one could say, very effective) alternative approach. The essence of this approach is as follows. Each internal motion is specified by a certain set of symmetry transformations that determine, via symmetry indices, a complete set of basis wave functions for this motion. All these transformations are incorporated (often in a quite nontrivial way, because of the noncommutativity of the transformations specifying the separate motions) into the complete symmetry group of the internal dynamics, which allows building the basis functions of the total motion by using the basis function of individual motions. Then complete sets of self-adjoint operators are formed in the subspaces of individual types of motion and are

---

[8] We note that an earlier version of such an adaptation was developed in [23].

used to construct the effective operators of physical quantities (including the effective Hamiltonian). It turns out that to calculate the matrix elements of the self-adjoint operators characterizing the individual types of motion, we need not the explicit form of the basis wave functions of these types of motion but only their symmetry properties. Here, the matrix elements are simple elementary functions of the symmetry indices (the quantum numbers of the problem). We can say that symmetry selects the most suitable basis. The only thing that remains undefined in the effective operators are the spectroscopic constants, which are factors of the combinations of self-adjoint operators allowed by the symmetry of the problem. The values of these constants are usually found by comparing theory and experiment. The resulting model rigorously describes all possible (within the given symmetry) interactions of the different types of internal spatial motion and leads to a simple, purely algebraic calculation scheme for the positions of the levels in the energy spectrum and the intensities of transitions between them [27 – 29].

In the given approach to the description of intramolecular dynamics, the configuration space of the collective variables is not introduced explicitly and, as result, the wave functions of these variables are not examined explicitly. But thanks to its profound ideological and technical aspects, this is presently the only possible approach to solving nontrivial problems in the internal dynamics of nonrigid molecules. It is important that the validity of the obtained molecular models is limited only by the proper choice of the symmetry of the internal dynamics. It is also worth noting that this approach occupies an intermediate position between the description of the molecular spectra on the basis of solving the nonempirical Schrödinger equation (the *ab initio* methods) and the description based on an empirical formation of energy matrices. According to [30], such intermediate models are the optimal ones.

The author is grateful to N A Poklonskii and A T Vlasov for their useful remarks made in the course of reading the manuscript.

References

1. Davydov A S *Kvantovaya Mekhanika* (Quantum Mechanics) (Moscow: Nauka, 1973) [Translated into English (Oxford: Pergamon Press, 1976)]
2. Braun P A, Kiselev A A *Vvedenie v Teoriyu Molekulyarnykh Spektrov* (Introduction to the Theory of Molecular Spectra) (Leningrad: Izd. LGU, 1983)
3. Landau L D, Lifshitz E M *Kvantovaya Mekhanika. Nerelyativistskaya Teoriya* (Quantum Mechanics: Non-relativistic Theory) (Moscow: Nauka, 1974) [Translated into English (Oxford: Pergamon Press, 1977)]
4. Kaplan I G *Simmetriya Mnogoelektronnykh Sistem* (Symmetry of Many-Electron Systems) (Moscow: Nauka, 1969) [Translated into English (New York: Academic Press, 1975)]
5. Longuet-Higgins H C *Mol. Phys.* **6** 445 (1963)
6. Elliott J P, Dawber P G *Symmetry in Physics* (London: Macmillan, 1981) [Translated into Russian: Vol. 2 (Moscow: Mir, 1983)]
7. Bunker P R, Jensen P *Molecular Symmetry and Spectroscopy* (Ottawa: NRC Research Press, 1998) [Translated into Russian (Moscow: Mir, 2004)]
8. Burenin A V *Usp. Fiz. Nauk* **172** 813 (2002) [*Phys. Usp.* **45** 753 (2002)]
9. Burenin A V *Simmetriya Kvantovoi Vnutrimolekulyarnoi Dinamiki* (Symmetry of Quantum Intramolecular Dynamics) (Nizhnii Novgorod: Izd. IPF RAN, 2003)
10. Barut A O, Rączka R *Theory of Group Representations and Applications* (Warszawa: Polish Sci. Publ., 1977) [Translated into Russian: Vol. 2 (Moscow: Mir, 1980)]
11. Burenin A V, in *XXIII S''ezd po Spektroskopii, Zvenigorod, Moskovskaya obl., 17 – 21 Oktyabrya, 2005 g.* (23th Spectroscopy Congress, Moscow region, October 17 – 21, 2005) (Moscow, 2005) p. 191
12. Burenin A V *Opt. Spektrosk.* **100** 737 (2006) [*Opt. Spectrosc.* **100** 675 (2006)]
13. Bersuker I B, Polinger V Z *Vibronnye Vzaimodeistviya v Molekulakh i Kristallakh* (Vibronic Interactions in Molecules and Crystals) (Moscow: Nauka, 1983) [Translated into English (Berlin: Springer, 1989)]
14. Bersuker I B *Effekt Yana – Tellera i Vibronnye Vzaimodeistviya v Sovremennoi Khimii* (The Jahn – Teller Effect and Vibronic Interactions in Modern Chemistry) (Moscow: Nauka, 1987) [Translated into English (New York: Plenum Press, 1984)]
15. Jahn H A, Teller E *Proc. R. Soc. London Ser. A* **161** 220 (1937)
16. Harmony M D et al. *J. Phys. Chem. Ref. Data* **8** 619 (1979)
17. Makushkin Yu S, Tyuterev V G *Metody Vozmushchenii i Effektivnye Gamil'toniany v Molekulyarnoi Spektroskopii* (Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy) (Novosibirsk: Nauka, 1984)
18. Sverdlov L M, Kovner M A, Krainov E P *Kolebatel'nye Spektry Mnogoatomnykh Molekul* (Vibration Spectra of Polyatomic Molecules) (Moscow: Nauka, 1970) [Translated into English (New York: Wiley, 1973)]
19. Orville-Thomas W J (Ed.) *Internal Rotation in Molecules* (London: Wiley, 1974) [Translated into Russian (Moscow: Mir, 1977)]
20. Burenin A V *Opt. Spektrosk.* **84** 222 (1998) [*Opt. Spectrosc.* **84** 183 (1998)]
21. Landau L D, Lifshitz E M *Kvantovaya Mekhanika. Nerelyativistskaya Teoriya* (Quantum Mechanics: Non-relativistic Theory) (Moscow: Gostekhteorizdat, 1948) [Translated into English (London: Pergamon Press, 1958)]
22. Jonas D M *J. Chem. Phys.* **90** 5563 (1989)
23. Zhilinskii B I, Perevalov V I, Tyuterev V G *Metod Neprivodimykh Tenzornykh Operatorov v Teorii Spektrov Molekul* (The Method of Irreducible Tensor Operators in Molecular Spectra Theory) (Novosibirsk: Nauka, 1987)
24. Partridge H, Schwenke D W *J. Chem. Phys.* **106** 4618 (1997)
25. Tyuterev Vl G et al. *Chem. Phys. Lett.* **316** 271 (2000)
26. Tyuterev Vl G et al. *CR*: *Phys.* (France) **5** 189 (2004)
27. Burenin A V *Opt. Spektrosk.* **97** 917 (2004) [*Opt. Spectrosc.* **97** 860 (2004)]
28. Burenin A V *Opt. Spektrosk.* **97** 924 (2004) [*Opt. Spectrosc.* **97** 867 (2004)]
29. Burenin A V *Opt. Spektrosk.* **98** 236 (2005) [*Opt. Spectrosc.* **98** 202 (2005)]
30. Gribov L A *Zh. Fiz. Khim.* **79** 688 (2005) [*Russ. J. Phys. Chem.* **79** 587 (2005)]