

8. A. A. Galeev and R. Z. Sagdeev, "Nonlinear theory of a plasma," in: Problems in Plasma Theory [in Russian], No. 7, Atomizdat, Moscow (1973).
9. V. A. Gudkova, V. A. Liperovskii, and V. P. Shalimov, Kosm. Issled., 13, 687 (1975).
10. V. A. Liperovskii and S. A. Mart'yanov, Geomagn. Aeron., 13, 311 (1973).
11. V. A. Liperovskii and M. Khakimova, Izv. Vyssh. Uchebn. Zaved., Radiofiz., 18, 335 (1975).
12. S. A. Grib, Geomagn. Aeron., 13, 788 (1973).

# QUALITATIVE CONSTRUCTION OF ROTATIONAL OPERATORS OF PHYSICAL QUANTITIES IN THE THEORY OF MOLECULAR SPECTRA

A. V. Burenin, V. L. Vaks,  
and V. N. Markov

UDC 539.194

A new method for the qualitative construction of purely rotational operators in the theory of molecular spectra is proposed. The contributions to the rotational Hamiltonian operator related to the presence of interactions in the molecule that are not invariant to spatial inversion are considered for the first time.

A molecule is a multiparticle system for which an accurate solution of the quantum-mechanical problem cannot be obtained. As a result, it is necessary to use the methods of perturbation theory. The zeroth approximation can be obtained by constructing a series of models imbedded in one another (increasingly coarsely) until an accurate solution of the model problem becomes possible. From the point of view of a quantitative calculation, there should obviously be continuity on transferring between neighboring models, which is expressed by the possibility of describing the difference between them in the form of a series in a small parameter. Despite this requirement, the symmetry groups of the models employed are different, i.e., the symmetry changes abruptly. Here it is important to note that a change to any approximate model is based on a certain physical idea. Hence, the approximate model always contains additional qualitative information on the molecule considered, and this information is contained in the symmetry group of the approximate model. As a result this group plays a clear independent role with respect to the symmetry groups of the more rigorous models. Consequently, for the complete qualitative characteristic of any solution it is necessary to specify the conditions of its evolution on transferring between neighboring models. In other words, it is necessary to specify the conditions under which the symmetry properties of the solution are matched, i.e., to indicate in the symmetry groups of neighboring models the equivalent elements with respect to which the solution must be converted in the same way. It is very important that in this case the model ideas are not used outside the framework of the model. This approach has been used successively to classify vibrational-rotational molecular energy levels [1].

In the present paper this idea is used to give a qualitative description of purely rotational molecular operators. To be specific we will apply this construction to the methane molecule ( $\text{CH}_4$ ), which has been studied qualitatively in the theory of molecular spectra in a large number of papers (see the review given in [2]).\*

\*The traditional scheme for classifying molecular states is in fact constructed only using the symmetry group of the rigorous problem of the stationary states of the molecule. To do this the action of all the operations on the coordinates which occur in the model of the zeroth approximation and, consequently, on the wave functions constructed in the zeroth approximation is specified formally. In particular, the action of the operation of spatial inversion on purely rotational coordinates is specified. This approach, from our point of view, does not have such a clear physical meaning and depends very much on the type of molecule. In addition, it is nonunique and leads to many classification schemes for the same molecule.

---

Institute of Applied Physics, Academy of Sciences of the USSR. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Radiofizika*, Vol. 23, No. 12, pp. 1406-1415, December, 1980. Original article submitted December 11, 1979.

## Classification of the Energy States of the Methane Molecule

The permutation group of identical nuclei for the  $\text{CH}_4$  molecule is  $\pi_4$ . The hydrogen nuclei are fermions, and the total wave function when hyperfine interactions connected with nuclear spin are neglected can be represented in the form of the convolution of the coordinate and spin parts, which are converted in accordance with the mutually dual Young schemes [3]. Since the spin of the hydrogen nucleus is one half, the dimensionality of the spin space is 2 and only three (of five) Young spin schemes  $[\lambda_{\text{spin}}]$  are allowed: [4], [31], [2<sup>2</sup>]. The corresponding values of the total spin of the hydrogen nucleus are 2, 1, 0, and the corresponding Young coordinate schemes  $[\lambda_{\text{coord}}]$  are [1<sup>4</sup>], [21<sup>2</sup>], [2<sup>2</sup>].

In the Born–Oppenheimer approximation the idea of a point group of the molecule arises. For the methane molecule this group is  $T_d$ . According to [1], in the most general case of the matching of the elements of symmetry of the permutation group of identical nuclei of the molecule and its point group, the point group can be homomorphously represented by a subgroup of the group of permutations. This is done by comparing the action of the transformations of these groups on the equilibrium configuration of the nuclei. In this case only those multiplets will be allowed which behave in the same way with respect to the elements of the point group, represented homomorphously in one element of the permutation group.\* In the case of the methane molecule we have isomorphism of the groups  $\pi_4$  and  $T_d$  and correspondingly the following one-to-one correspondence between their irreducible representations:

Irreducible representations	$\pi_4$	[4]	[1 <sup>4</sup> ]	[2 <sup>2</sup> ]	[21 <sup>2</sup> ]	[31]
Irreducible representations	$T_d$	$A_1$	$A_2$	$E$	$F_1$	$F_2$

(1)

Consequently, the following multiplets are allowed:  $5A_2^{(\pm)}$ ,  $3F_1^{(\pm)}$ ,  $1E^{(\pm)}$ . The number in front of the letter of the multiplet gives the nuclear statistical weight, while the plus and minus signs correspond to the behavior of the coordinate wave function due to the action of the transformation of spatial-coordinate inversion of all the particles of the molecule with respect to its center of mass. Henceforth, it will be necessary to know from which electron, vibrational, and rotational functions obtained in the zeroth approximation one can construct the allowed multiplets. According to [1] the solution of this problem for the methane molecule on the basis of the electron state can be represented in the form

$$(\Gamma_{\text{multiplet}})_{T_d \times C_1} = (A_{\text{el}})_{T_d} \times (\Gamma_{\text{vib}})_{T_d} \times (\Gamma_{\text{rot.in}})_{T_d \times C_1}. \quad (2)$$

Here  $A_{\text{el}}$  and  $\Gamma_{\text{col}}$  are the irreducible representations of the  $T_d$  group, according to which the wave functions of the electron and vibrational motion are transformed, and  $\Gamma_{\text{rot.in}}$  is the irreducible rotational-inversion representation. The correlation between the rotational representations of the symmetry group of a spherical top  $R_3$  and the rotational-inversion representations of the  $T_d \times C_1$  group, which is given in Table 1, is obtained by the coupling of these groups with respect to their general nuclear rotational subgroup  $O$ . In this representation  $T_d$  relates to the rotational function while the representation  $C_1$  relates to the multiplet, as shown by the arrow in expression (2). It is clear that only those combinations on the right side of (2) are possible which lead to allowable multiplets. As an example, Fig. 1 shows a classification of the rotational states of the methane molecule in the main vibrational-electron state. This classification can be changed to the one traditionally employed for the methane molecule [2] by making the following formal substitution:  $A_2^{(+)} \rightarrow A_2$ ,  $A_2^{(-)} \rightarrow A_1$ ,  $F_1^{(+)} \rightarrow F_1$ ,  $F_1^{(-)} \rightarrow F_2$ ,  $E^{(\pm)} \rightarrow E$ . By considering this result alone it can be seen that the traditional classification scheme has the following drawbacks: firstly, there is no clear form for the behavior of the multiplet with respect to the operation of spatial inversion, while for the multiplet  $E$  this information is generally not available; secondly, to denote the symmetry of the coordinate function the forbidden multiplets  $A_1$  and  $F_2$  are employed.

Using the symmetry-group matchings considered, we will change to the qualitative construction of the molecular rotational operators, represented in the form of a series in terms of the components of the angular momentum. We will confine ourselves to the Hamiltonian and dipole-moment operators. Since the corresponding physical quantities have classical analogs, we can work with their classical expressions. The change to the operator form can be made without difficulty, using the symmetry and Hermitian properties, corresponding to the classical analog and the commutation rule.

\*Homomorphism arises and plays the main role for linear and plane molecules [1].

TABLE 1. Table of the Correlations for the CH<sub>4</sub> Molecule between the Rotational Representations of the R<sub>3</sub> Group and the Rotational-Inversion Representations of the T<sub>d</sub> × C<sub>i</sub> Group

$R_3$	0	$T_d \times C_i$
$J=0$	$A_1$	$A_1^{(+)}, A_2^{(-)}$
1	$F_1$	$F_1^{(+)}, F_2^{(-)}$
2	$E + F_2$	$E^{(\pm)} + F_2^{(+)}, F_1^{(-)}$
3	$A_2 + F_1 + F_2$	$A_2^{(+)}, A_1^{(-)} + F_1^{(+)}, F_2^{(-)} + F_2^{(+)}, F_1^{(-)}$
4	$A_1 + E + F_1 + F_2$	$A_1^{(+)}, A_2^{(-)} + E^{(\pm)} + F_1^{(+)}, F_2^{(-)} + F_2^{(+)}, F_1^{(-)}$
5	$E + 2F_1 + F_2$	$E^{(\pm)} + 2(F_1^{(+)}, F_2^{(-)}) + F_2^{(+)}, F_1^{(-)}$
6	$A_1 + A_2 + E + F_1 + 2F_2$	$A_1^{(+)}, A_2^{(-)} + A_2^{(+)}, A_1^{(-)} + E^{(\pm)} + F_1^{(+)}, F_2^{(-)} + 2(F_2^{(+)}, F_1^{(-)})$
7	$A_2 + E + 2F_1 + 2F_2$	$A_2^{(+)}, A_1^{(-)} + E^{(\pm)} + 2(F_1^{(+)}, F_2^{(-)}) + 2(F_2^{(+)}, F_1^{(-)})$
8	$A_1 + 2E + 2F_1 + 2F_2$	$A_1^{(+)}, A_2^{(-)} + 2E^{(\pm)} + 2(F_1^{(+)}, F_2^{(-)}) + 2(F_2^{(+)}, F_1^{(-)})$
9	$A_1 + A_2 + E + 3F_1 + 2F_2$	$A_1^{(+)}, A_2^{(-)} + A_2^{(+)}, A_1^{(-)} + E^{(\pm)} + 3(F_1^{(+)}, F_2^{(-)}) + 2(F_2^{(+)}, F_1^{(-)})$
10	$A_1 + A_2 + 2E + 2F_1 + 3F_2$	$A_1^{(+)}, A_2^{(-)} + A_2^{(+)}, A_1^{(-)} + 2E^{(\pm)} + 2(F_1^{(+)}, F_2^{(-)}) + 3(F_2^{(+)}, F_1^{(-)})$
11	$A_2 + 2E + 3F_1 + 3F_2$	$A_2^{(+)}, A_1^{(-)} + 2E^{(\pm)} + 3(F_1^{(+)}, F_2^{(-)}) + 3(F_2^{(+)}, F_1^{(-)})$
12	$2A_1 + A_2 + 2E + 3F_1 + 3F_2$	$2(A_1^{(+)}, A_2^{(-)}) + A_2^{(+)}, A_1^{(-)} + 2E^{(\pm)} + 3(F_1^{(+)}, F_2^{(-)}) + 3(F_2^{(+)}, F_1^{(-)})$

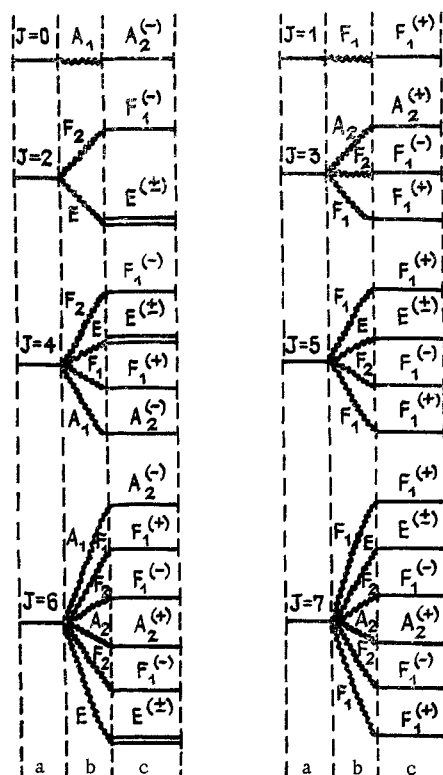


Fig. 1. Classification of the rotational states of the CH<sub>4</sub> molecule in the ground vibrational and electron states: a) irreducible representations of the R<sub>3</sub> group, according to which the rotational functions are converted in the rigid-top approximation; b) irreducible representations of the nuclear rotational subgroup O; c) irreducible representations of the T<sub>d</sub> × C<sub>i</sub> group, according to which the multiplets are transformed.

# Construction of the Rotational Hamiltonian Operator for the CH<sub>4</sub> Molecule

The general expression for the rotational Hamiltonian of the molecule can be written in the form

$$H = h_{ik}^{(2)} P_i P_k + h_{iklm}^{(4)} P_i P_k P_l P_m + h_{iklmnr}^{(6)} P_i P_k P_l P_m P_n P_r + \dots \quad (3)$$

Here  $P_i$  ( $i = x, y, z$ ) is the component of the angular momentum along the "i" axis of the system of coordinates connected with the molecule,  $h^{(n)}$  are phenomenological coefficients, where "n" is an even number as a consequence of the requirement that the Hamiltonian should be invariant with respect to the operation of time reversal. In the rigid-top approximation only quadratic combinations with respect to the angular momentum components that are invariant with respect to transformations of the rotational group of the molecule are retained in this series. For the methane molecule, the rotational group of which is  $R_3$ , there is only one such combination. As a result  $H_{(2)} \sim P^2$ .

The change to the Born–Oppenheimer approximation leads to the following consequences: firstly, in the rotational Hamiltonian there may be terms that are not quadratic with respect to the components of the angular momentum, which is due to narrowing of the configuration space of the molecule for describing its complete internal motion down to the rotational subspace; secondly, invariance of the Hamiltonian is only preserved with respect to transformations of the symmetry group  $T_d \times C_1$ .

Hence, in series (3) we must obtain those rotational combinations which, on transferring to the Born–Oppenheimer approximation, evolve into a solution with symmetry  $A_1^{(+)}$ . Using the table of the correlation between the  $R_3$  and  $T_d \times C_1$  groups (Table 1), which intersect with respect to the nuclear rotational point subgroup O, it is easy to obtain the required rotational combinations, which must be transformed using representation  $A_1$  of subgroup O. It is easy to separate these combinations individually for each term with a specified "n" in series (3). The quadratic combinations of the angular momentum can be converted using the tensor representation  $U_3 \times U_3$ , where  $U_3$  is the three-dimensional representation of the group of unitary transformations of three-dimensional space. This tensor representation can be split into irreducible representations  $U_3^{[\lambda]}$ , each of which corresponds to a certain Young scheme  $[\lambda]$  of the permutation group  $\pi_2$ . When considering the classical Hamiltonian only the combinations which are transformed in accordance with the symmetrized representation  $U_3^{[2]}$  differ from zero.\* When reducing the group of unitary transformations to a group of  $R_3$  rotations, we have  $[3] U_3^{[2]} \doteq D^{(2)} + D^{(0)}$ . It is easily seen from Table 1 that from the existing irreducible representations  $R_3$  in this case only  $D^{(0)}$  contains representation  $A_1$  of subgroup O. Hence, there is one quadratic combination that is invariant to the group  $T_d \times C_1$ . It is clearly identical with  $P^2$ . Hence, new quadratic terms do not manifest themselves in the Born–Oppenheimer approximation although, of course, nonrigidity may make a contribution to the phenomenological constant. For the quarternary combinations we correspondingly obtain  $U_3^{[4]} \doteq D^{(4)} + D^{(2)} + D^{(0)}$ , where the representation  $A_1$  of subgroup O is only contained in  $D^{(4)}$  and  $D^{(0)}$ . Consequently, there are two independent allowed combinations. We can choose as these†

$$\begin{aligned} H_{(4),1} &\sim P_x^4 + P_y^4 + P_z^4, \\ H_{(4),2} &\sim P^4. \end{aligned} \quad (4)$$

The expression for  $H_{(4),1}$  is the first allowed combination which leads to tetrahedral splitting of the rotational levels of the methane molecule with a specified quantum number J of the total angular momentum (see Fig. 1). Carrying out this procedure for all the terms with  $n \leq 12$ , we have

\*When considering the construction from the beginning in the operator formulation combinations which are transformed according to representation  $U_3^{[\lambda]}$  corresponding to the Young schemes  $[\lambda]$  with a number of rows greater than one will also differ from zero. However, when taking the commutation rules into account for the components of the angular momentum these additional terms lead only to overspecification of the phenomenological coefficients compared with the Hamiltonian operator obtained from the constructed classical Hamiltonian.

†Note that the choice of allowed combinations is nonunique. However, this nonuniqueness only leads to overdetermination of the phenomenological constants in the rotational Hamiltonian.

$$H_{(6), 1} \sim P_x^6 + P_y^6 + P_z^6, \quad (5)$$

$$H_{(6), i+1} \sim P^2 H_{(4), i} \quad (i = 1, 2);$$

$$H_{(8), 1} \sim P_x^8 + P_y^8 + P_z^8,$$

$$H_{(8), i+1} \sim P^2 H_{(6), i} \quad (i = 1, 2, 3); \quad (6)$$

$$H_{(10), 1} \sim P_x^{10} + P_y^{10} + P_z^{10},$$

$$H_{(10), i+1} \sim P^2 H_{(8), i} \quad (i = 1, 2, 3, 4); \quad (7)$$

$$H_{(12), 1} \sim P_x^{12} + P_y^{12} + P_z^{12},$$

$$H_{(12), 2} \sim (P_x^6 + P_y^6 + P_z^6)^2, \quad (8)$$

$$H_{(12), i+2} \sim P^2 H_{(10), i} \quad (i = 1, 2, 3, 4, 5).$$

The rotational contributions (4)–(8) to the Hamiltonian operator of the methane molecule obtained by this method, which describe its nonrigidity in the Born–Oppenheimer approximation, are equivalent to those previously considered elsewhere:  $n=4$  [4],  $n=6$  [5],  $n=8$  [6, 7], and  $n=10, 12$  [7].

When the Born–Oppenheimer approximation is violated, the invariance of the Hamiltonian must be considered with respect to the group  $\pi_4 \times C_1$ . Correspondingly, we must distinguish those rotational combinations in series (3) which evolve into representations  $[4]^{(+)}$  of this group. From the correspondence (1) between the irreducible representations of the groups  $\pi_4$  and  $T_d$  it can be seen that there is a one-to-one relationship  $[4] \leftrightarrow A_1$ . Consequently, we can easily obtain by purely qualitative methods using the example of the methane molecule the well known result [8] that for completeness of the symmetrical electron state of the molecule there are no new terms in the rotational Hamiltonian compared with the Born–Oppenheimer approximation, and we can only deal with the additional contributions to the existing phenomenological constants.

To conclude this section we will consider the construction of rotational combinations which occur in the Hamiltonian that are not invariant to the operation of inversion of the spatial coordinates of the nuclei and electrons which form the molecule. As is well known [9] there can be intermolecular interactions that are not invariant to this operation. In this connection the interesting problem arises of whether these qualitative effects should not be introduced into the rotational spectrum of the molecule. To answer this it is necessary to separate in series (3) the rotational combinations which evolve in the solution with symmetry  $A_1^{(-)}$  in the Born–Oppenheimer approximation. It can easily be obtained from Table 1 that these combinations should be converted in accordance with representation  $A_2$  of the point rotational subgroup  $O$ . Carrying out this procedure, as previously, we obtain for  $n \leq 12$

$$H_{(6)}^- \sim (P_x^2 - P_y^2)^3 + (P_y^2 - P_z^2)^3 + (P_z^2 - P_x^2)^3; \quad (9)$$

$$H_{(10), 1}^- \sim (P_x^5 - P_y^5)^3 + (P_y^5 - P_z^5)^3 + (P_z^5 - P_x^5)^3,$$

$$H_{(10), 2}^- \sim P^4 H_{(6)}^-; \quad (10)$$

$$H_{(12), 1}^- \sim (P_x^4 - P_y^4)^3 + (P_y^4 - P_z^4)^3 + (P_z^4 - P_x^4)^3,$$

$$H_{(12), i+1}^- \sim P^2 H_{(10), i}^- \quad (i = 1, 2). \quad (11)$$

Hence, the rotational dependence of the contributions to the Hamiltonian of the molecule, connected with the weak noninvariance of the molecular interactions with respect to spatial inversion, has been obtained for the first time. Note that the sign of the constant in front of the rotational combinations (9)–(11) changes on inversion.

### Reduced Rotational Operator of the Hamiltonian of the CH<sub>4</sub> Molecule

The rotational spectra of molecules are the main object of study by microwave spectroscopy. It is important that the accuracy of microwave measurements of the frequencies of the spectral lines should be 6–7 orders of magnitude higher than the accuracy with which their intensities are measured. Hence, it is advisable to consider the reduced rotational Hamiltonian operator [10] in which the parameters necessary to describe only the absorption frequencies of the spectral lines are retained. The basis of the reduction is the

fact that the position of the energy levels and, consequently, the frequencies of the spectral lines are described using the Hamiltonian operator, defined apart from an arbitrary unitary transformation. Unlike the ideas developed in [10], we will carry out the analysis within the framework of classical mechanics, i.e., we will assume that the classical Hamiltonian is defined apart from an arbitrary canonical transformation. The main contribution to the transformed Hamiltonian can be described in the form  $\{H, S\}$ , where  $\{ \}$  are Poisson brackets, while  $S$  is the transformation generator, which can be represented as

$$S = s_i^{(1)} P_i + s_{ikl}^{(3)} P_i P_k P_l + s_{iklmn}^{(5)} P_i P_k P_l P_m P_n + \dots \quad (12)$$

Here  $s^{(k)}$  are certain phenomenological coefficients. The transformation generator satisfies the same properties of symmetry as the Hamiltonian, with the exception of the operation of time reversal, with respect to which  $S$  is antisymmetrical.\* It follows from the latter requirement that "k" is an odd number. Using the previously employed constructional technique, we obtain that the first rotational operator which evolves in the Born-Oppenheimer approximation into the expression with symmetry  $A_1^{(\pm)}$  appears for  $k=9$ . It is easy to show that

$$\{D^{(9)}, D^{(4)}\} = D^{(12)} + D^{(10)} + D^{(8)} + D^{(6)},$$

$$\{A_1, A_1\} \in A_1 \quad (\text{for subgroup O}).$$

It follows from an analysis of these expressions that by choosing the constant in the generator  $S_{(9)}$  appropriately, we can eliminate one of the terms of the twelfth degree with respect to the components of the angular momentum in the rotational Hamiltonian. This is equivalent to the result obtained in [7] by direct calculation of the commutators, which occur when carrying the corresponding unitary transformation. The remaining possible generators of the canonical transformations of the type  $A_1^{(\pm)}$  lead to reduction of terms in the rotational Hamiltonian with  $n > 12$ , and we will not consider them here. When intermolecular interactions, invariant to the operation of spatial inversion, are taken into account, the class of unitary transformations will include transformations of the type  $A_2$ . Reduction of the terms of the Hamiltonian with  $n \leq 12$  will also be carried out using generators of the third, seventh, and ninth degrees with respect to the components of the angular momentum. These canonical transformations enable one to eliminate all terms of the type  $A_2$  in the Hamiltonian with  $n \leq 12$ . It is easy to show that the latter statement holds for arbitrary  $n$ .

#### Rotational Generator of the Dipole Moment of the $\text{CH}_4$ Molecule

For the most intense electric dipole transitions (which occur without a change in the symmetry of the spin state) the dipole moment is transformed in accordance with the completely symmetrical Young coordinate scheme of the permutation of identical nuclei, i.e., in this case in accordance with representation [4] of the group  $\pi_4$ . Taking relation (1) into account we obtain that for the dipole moment in the Born-Oppenheimer approximation the representation  $A_1^{(\pm)}$  is allowed, where the minus sign corresponds to the electric dipole moment, and the plus sign corresponds to the magnetic dipole moment. Hence, in particular, we have the selection rule  $\Gamma_{\text{multiplet}} \leftrightarrow \Gamma_{\text{multiplet}}$  ( $\Gamma = A_2, E, E_1$ ), where "+"  $\leftrightarrow$  "-" for electric dipole transitions and " $\pm$ "  $\leftrightarrow$  " $\pm$ " for magnetic dipole transitions. Any dipole transitions including "forbidden" transitions (forbidden in the zeroth approximation) are subject to the selection rules.

The general expression for the component of the rotational electrical dipole moment in a fixed system of coordinates can be written in the form

$$\mu_\alpha = \lambda_{\alpha i} (\mu_i^{(1)} + \mu_{ikl}^{(3)} P_k P_l + \mu_{iklmn}^{(5)} P_k P_l P_m P_n + \dots). \quad (13)$$

Here  $\lambda_{\alpha i}$  are the direction cosines for the system of coordinates connected with the molecule, and  $\mu^{(n)}$  are phenomenological coefficients, where "n" is an odd number due to the requirement that the electric dipole moment should be invariant with respect to the operation of time reversal. It is necessary to distinguish in series (13) those combinations which, on changing to the Born-Oppenheimer approximation, evolve into solutions with symmetry  $A_1^{(-)}$ . It was previously shown that these combinations should be converted in accordance with representation  $A_2$  of the point rotational subgroup O.

The first term in series (13) is converted in accordance with the irreducible representation  $U_3^{[1]}$  of the group of unitary transformations of three-dimensional space. The reduction to the group  $R_3$  gives  $U_3^{[1]} \doteq D^{(1)}$ . Representation  $D^{(1)}$  does not contain the representation  $A_2$  of subgroup O. Hence, the term with  $n=1$  makes no

\*A generator that does not satisfy these properties will lead to the appearance in the transformed Hamiltonian of new phenomenological parameters in front of the terms with symmetry differing from the symmetry of the initial Hamiltonian.

contribution to the electric dipole moment. This corresponds to the simple fact that the methane molecule has no constant electric dipole moment and all of its purely rotational electric dipole transitions belong to the "forbidden" class [11].

The term with  $n=3$  is converted in accordance with the representation  $U_3^{[1]} \times U_3^{[2]} \doteq U_3^{[3]} + U_3^{[21]}$ . By reducing it to the  $R_3$  group we obtain  $U_3^{[3]} \doteq D^{(3)} + D^{(1)}$ ,  $U_3^{[21]} \doteq D^{(2)} + D^{(1)}$ . From the irreducible representations of the subgroup  $R_3$  which exist here only  $D^{(3)}$  contains the representation  $A_2$  of subgroup  $O$ . The corresponding allowed combination has the form

$$\mu_\alpha^{(3)} \sim \lambda_{ax} P_y P_z + \lambda_{ay} P_x P_z + \lambda_{az} P_x P_y, \quad (14)$$

which is equivalent to the expression used to calculate the intensities of the "forbidden" transitions of the methane molecule [11]. The construction is also easily carried out for terms with arbitrary "n."

In conclusion, we will consider the rotational magnetic dipole moment. We have for its components in a fixed system of coordinates

$$m_\alpha \sim \lambda_{\alpha i} (m_{ik}^{(2)} P_k + m_{iklm}^{(4)} P_k P_l P_m + \dots), \quad (15)$$

where  $m^{(n)}$  are phenomenological coefficients, and "n" is an even number due to the requirement that the sign of the magnetic dipole moment should change when the time-reversal operation is carried out. It is necessary to obtain combinations in the series (15) which transform according to representation  $A_1$  of the point rotational subgroup  $O$ . The first of these combinations appears for  $n=2$ . In fact  $U_3^{[1]} \times U_3^{[1]} \doteq D^{(1)} \times D^{(1)} \doteq D^{(2)} + D^{(1)} + D^{(0)}$ . From the representations of the group  $R_3$  which exist here only  $D^{(0)}$  contains the representation  $A_1$  of subgroup  $O$ . The corresponding combination has the form

$$m_\alpha^{(2)} \sim \lambda_{\alpha i} P_i. \quad (16)$$

It is easy to show that for  $n=4$  there are two allowed combinations, namely

$$m_{\alpha,1}^{(4)} \sim \lambda_{ax} P_x^3 + \lambda_{ay} P_y^3 + \lambda_{az} P_z^3, \quad m_{\alpha,2}^{(4)} \sim P^2 m_\alpha^{(2)}. \quad (17)$$

Hence, we have constructed operators describing the main contribution to the effect [8] of the occurrence of a coordinate magnetic dipole moment due to distortion of the molecule when it rotates. In particular this moment leads to "forbidden" magnetic dipole transitions.

In conclusion, we will briefly summarize the problem of purely rotational corrections to the Hamiltonian operator of the molecule due to the presence of weak intermolecular interactions that are not invariant with respect to the operation of spatial inversion. We have constructed corrections of this type in this paper for the methane molecule and we have shown that they do not make any contribution to the qualitative effects connected with the position of the rotational energy levels, i.e., to the splitting of the levels and to the change in their dependence on the quantum numbers. This conclusion holds for all molecules not possessing stereoisomers.\* Hence, the observed qualitative effects of the manifestation of weak interactions in the rotational spectrum of such molecules are due solely to nonconservation of the parity of the wave functions of the energy states. This leads in particular to rotation of the plane of polarization of electromagnetic radiation [13]. This effect has been studied in detail for optical atomic transitions [14]. The consideration of these effects in the rotational molecular spectrum has the advantage that the use of expressions of the form (9)–(11) enables one to predict their dependence on the quantum numbers of the rotational state.

#### LITERATURE CITED

1. A. V. Burenin and V. N. Markov, Sixth Colloquium on High-Resolution Molecular Spectroscopy, Tours (1979); A. V. Burenin and V. N. Markov, *Izv. Vyssh. Uchebn. Zaved., Radiofiz.*, **23**, No. 3, 287 (1980).
2. J. T. Hougen, *MTP Int. Rev. Sci. Phys. Chem. Ser. 2 Spectroscopy*, D. A. Ramsay (ed.) (1976).
3. I. G. Kaplan, *Symmetry of Multielectron Systems* [in Russian], Nauka, Moscow (1969).
4. A. J. Dorney and J. K. G. Watson, *J. Mol. Spectrosc.*, **42**, 135 (1972).
5. S. M. Kirschner and J. K. G. Watson, *J. Mol. Spectrosc.*, **47**, 347 (1973).
6. I. Ozier, *J. Mol. Spectrosc.*, **53**, 336 (1974).

\*For stereoisomeric molecules a similar construction leads to rotational contributions to the Hamiltonian operator, splitting the rotational levels with a different behavior with respect to the operation of spatial inversion. The dependence of this splitting on the rotational state is determined by the difference between the usual spectroscopic constants for the systems of "+" and "-" levels. Experimental work to observe such splitting in the vibrational-rotational spectrum of molecules has been carried out [12].

7. J. K. G. Watson, *J. Mol. Spectrosc.*, 55, 498 (1975).
8. C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, Dover (1975).
9. S. Weinberg, *Phys. Rev.*, D5, 1412 (1972).
10. J. K. G. Watson, *J. Chem. Phys.*, 46, 1935 (1967).
11. M. R. Aliev, *Usp. Fiz. Nauk*, 119, 557 (1976); T. Oka, in: *Molecular Spectroscopy: Modern Research*, Vol. II, K. N. Rao (ed.), Academic Press (1976).
12. O. N. Kompanets et al., *Opt. Commun.*, 19, 414 (1976); E. Arimondo, P. Glorieux, and T. Oka, *Opt. Commun.*, 23, 369 (1977).
13. Ya. B. Zel'dovich, *Zh. Eksp. Teor. Fiz.*, 36, 964 (1959).
14. V. A. Alekseev, B. Ya. Zel'dovich, and I. I. Sobel'man, *Usp. Fiz. Nauk*, 118, 385 (1976); A. N. Moskalev, R. M. Ryndin, and I. B. Khriplovich, *Usp. Fiz. Nauk*, 118, 409 (1976).