

Ordering (grouping) schemes for rotational-vibrational perturbations in quasi-rigid molecules

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The principles of the theory of linked ordering schemes of rotational-vibrational interactions have been developed for quasi-rigid molecules. Within the confines of the developed theory, the problem of indeterminacy of effective Hamiltonians is formulated and solved for the first time. The dependence of reduction contact transformation generators on ordering schemes in the problem of accidental resonance interactions has been proved. Physical interpretation is given to limiting ordering schemes of rotational-vibrational interactions. The “unravel technique” of exponential operators is applied to evaluation of the relationships between vibrational contact transformation generators in the Watson–Mikhailov limiting ordering schemes and in the Amat–Nielsen scheme with an integer λ -order. For dipole moments of rotational transitions in the ground and excited vibrational states, nonpolynomial models in the Pade form have been developed for the first time within the framework of the theory of linked rotational-vibrational interactions.

Introduction

Intense recent studies of molecular spectra in many spectroscopic centers all over the world have made much progress in understanding of the structure of molecules and radicals, in general, and physical and chemical processes proceeding in the Earth's atmosphere, in particular. Physical and chemical molecular processes under actual atmospheric conditions proceed, as a rule, through highly excited rovibronic states of molecules and radicals that form one of the principal atmospheric components. The study of these processes by theoretical and experimental spectroscopic methods is an urgent problem of atmospheric physics and optics.

This paper is devoted to the development of principal aspects of the theory of linked schemes of ordering (grouping) rotational-vibrational (RV) interactions in quasi-rigid molecules. The urgency of this problem is caused, first of all, by the need in global description of molecular spectra formed by transitions to and from high-excited, quasi-degenerate RV states or, in other words, vibrational or rotational-vibrational polyads.

From the viewpoint of the inverse spectroscopic problem, strong accidental resonances are one of the most problematic points in description of molecular spectra, rotational-vibrational analysis of energy regions in which gives the worst statistical results as compared to regions with weak resonances or those free of resonances. Another important problem in the analysis of the energy spectrum of molecules is a prediction of the behavior of RV energy levels at high rotational energies. From the viewpoint of the direct spectroscopic problem, theoretical study of the

rotational dependence of anharmonic vibrational and rotational-vibrational resonances is of considerable interest in analysis of the dynamics of molecular vibration and rotation. This is due to the necessity to derive equations for effective parameters in the model Hamiltonian with molecular constants and to propose new spectroscopic models for resonance energy regions.

The operators, such as q^2J^m , q^3J^m , q^4J^m , etc., of vibrational q and rotational J variables in the effective rotational Hamiltonian (ERH) have been studied more or less thoroughly for various molecular systems. However, they have not been discussed in the literature from some general viewpoint of ordering intramolecular perturbations for quasi-degenerate vibrational states. Coriolis, Fermi, and Darling–Dennison resonance parameters obtained by different authors for different groups of RV interactions differ. As was found in this paper, these differences are consequences of the fundamental problem of indeterminacy of the effective Hamiltonian (EH) due to difference in a choice of the initial molecular Hamiltonian. In this paper, we prove the statement that there exists an infinite, but countable set of different schemes of ordering rotational-vibrational interactions in quasi-rigid molecules.

Many other problems formulated in molecular spectroscopy, such as rotational-vibrational dependence of the energy of quadrupole bond, Stark shift, spectral line halfwidths and shifts, etc. have not been systematically studied from the viewpoint of the theory of ordering rotational-vibrational interactions in molecules. Individual attempts look rather as trials to study the relation between spectroscopic and molecular parameters depending on the ordering of noncommuting operators of intramolecular interactions.

It is important to note that the physical literature, especially, on quantum electrodynamics, for a long time uses the language of T -products, i.e., functions of ordered operators. Thus, Feynman in Ref. 1 noted that if the criterion of action is introduced for noncommuting operators, then $(A + B) = \sum_k C_n^k B^k A^{n-k}$, where A and B are self-conjugate operators in the Gilbert space, and, as a consequence,

$$e^A e^B = \sum \frac{(A + B)^n}{n!} \stackrel{\text{def}}{=} e^{(A + B)}.$$

Feynman believed that once the designations determining, which of operators acts the first, which one acts the second, etc., are introduced, they can be treated as the commuting operators. Maslov in the Preface of Ref. 2 supposed that such an approach and its results are connected with the spectral resolution of functions of ordered operators. The corresponding theory³ allows overcoming some difficulties of the method of perturbation theory and formulating identities not so obvious as the above one.

The approach presented in this paper is based on the concept of ordering rotational-vibrational interactions in a quasi-rigid molecule depending on the order of magnitude of matrix elements of vibrational and rotational operators. In the operator formulation, exact analytical equations can be found for operator terms in the EH and the effective operator of observation (these operators are constructed in different ordering (grouping) schemes).

According to the basic ideas of the theory of RV interactions, there exists a possibility to separate vibrational and rotational variables in the molecular Hamiltonian in the ground and nondegenerate electronic states of semi-rigid molecules,⁴ at which both the initial Hamiltonian and the EH are infinite sums of the series in rotational variables for each elementary vibrational excitation (exciton) or vibrational variables for each elementary rotational excitation (exciton). As it will be shown in this paper, this approach can be extended to the effective moments of transitions, including electric and magnetic dipole moments, quadrupole moment, and moments of higher orders, as well as the polarizability tensor in the Plachek theory. The main condition of applicability of the developed approach is based on the generally known ideas, earlier applied⁵ to solution of problems of rotational-vibrational spectroscopy. It consists in the possibility to expand the operator of observation into a series in terms of small displacements of nuclei with respect to the reference (equilibrium) configuration.

Mathematical models of expansion of the EH (or the effective operator of observation) in terms of rotational or vibrational "solitons" have the following physical interpretations: (i) ultrafast rotator: rotational energy of a molecule reaches (approaches) a value comparable with the electronic energy (for rotation in the ground vibronic state this value is about the energy

of the first excited electronic term); (ii) overexcited vibrator: vibrational excitation of a molecule (on average) approaches the electronic energy.

These models were proposed in 1985 by Watson⁶ and Mikhailov.⁷ They form the basis for construction of the EH and the effective dipole moment (EDM) in nonpolynomial forms. In this paper, the definition of observation as a theoretical uncertainty of ordering (grouping) for a parameter will be substantiated. Based on this definition, accidental resonances will be classified as strong, medium, and weak, and the algorithm for construction of the EDM will be proposed based on the inverse sequence of unitary transformations. This result seems important when calculating moments of transitions in high-order approximation, because it allows the direct use of the available spectroscopic information on the moments of transitions in lower orders. For dipole moments of rotational transitions in the ground and excited vibrational states, nonpolynomial models in the form of Pade approximant are developed for the first time within the framework of the theory of bound RV interactions.

The initial point of application of a quasi-rigid molecule to consideration of problems of rotational-vibrational spectroscopy is an expansion of the initial molecular Hamiltonian, which is considered in this paper from the new viewpoint of ordering RV interactions along with related problems.

1. Expansion of the rotational-vibrational Hamiltonian of a quasi-rigid molecule

Rotational-vibrational dependences of energy levels of isolated states, natural and accidental resonance interactions, electric dipole moments of states and transitions, spectral line broadening parameters, etc. are among the main areas of molecular spectroscopy. Solution of such problems is closely connected with the problem of eigenvalues and eigenfunctions of the complete rotational-vibrational Hamiltonian of a quasi-rigid multiatomic molecule. The simplest form of the molecular Hamiltonian, in cm^{-1} , has been proposed by Watson⁴:

$$H_{\text{VR}} = \frac{1}{2} \sum \omega_n p_n^2 + V(q) + \frac{\hbar}{2hc} \sum_{\alpha\beta} \mu_{\alpha\beta} (J_\alpha - \pi_\alpha)(J_\beta - \pi_\beta) - \frac{1}{8} \frac{\hbar^2}{hc} \sum_{\alpha} \mu_{\alpha\alpha}, \quad (1)$$

where ω_n are vibrational frequencies, p_n are dimensionless momenta, $p_n = -i\partial/\partial q_n$, $V(q)$ is the potential energy, $\mu_{\alpha\beta}$ is the effective inverse inertia tensor, J_α are components of the total angular momentum (dimensionless), π_α are components of the vibrational angular momentum (dimensionless), $\hbar = h/2\pi$ is the Planck's constant, and c is the speed of light.

Once the matrix I_e of the equilibrium inertia tensor with the elements $I_{\alpha\beta}\delta_{\alpha\beta}$ and the matrix a_n with the elements $a_n^{\alpha\beta} = (\partial I_{\alpha\beta} / \partial Q_n)_e$, being derivatives of the inertia tensor I over normal coordinates, have been introduced as well as the matrix $a = \sum_n a_n \left(\frac{\hbar^2}{hc\omega_n} \right)^{1/2} q_n$, the tensor μ can be expressed in a simple form⁴

$$\mu = I_e^{-1} \left(E + \frac{1}{2} a I_e^{-1} \right)^{-2}, \quad (2)$$

where E is a unit matrix. Expansion of $(E + \frac{1}{2} a I_e^{-1})^{-2}$ can be easily performed, because the matrices E and $(a I_e^{-1})^{-1}$ commute, and the ordinary binomial expansion can be used:

$$\mu = I_e^{-1} \left\{ E + \sum_{S=0}^{\infty} (S+1) \left(-\frac{1}{2} \right)^S (a I_e^{-1})^S \right\}. \quad (3)$$

The potential energy $V(q)$ can be presented as the well-known Taylor expansion in terms of normal coordinates^{4,5,8,9}

$$V(q) = \frac{1}{2} \sum_n \omega_n q_n^2 + \frac{1}{6} \sum_{lmn} \Phi_{lmn} q_l q_m q_n + \dots \quad (4)$$

The Schrödinger equation with the rotational-vibrational Hamiltonian H_{VR} of a molecule cannot be solved exactly,^{4,5} and the perturbation theory is used to find eigenvalues and eigenfunctions.⁸ In this connection, IR and MW spectra are analyzed not directly through the force field and structural constants, but through an intermediate stage – so-called spectroscopic models. Only in such an approach, experimental energy levels are described in many cases within the experimental errors. The selection and interpretation of spectroscopic models is based on the method of effective Hamiltonian and the method of effective dipole moments. The application of the method of effective Hamiltonian to the rotational-vibrational Schrödinger equation of a multiatomic molecule reduces to construction and reduction of the effective rotational Hamiltonian (ERH) in an isolated or interacting vibrational states.

The ERH can be constructed empirically and then fitted to a measured spectrum. However, to determine the force field and constants of the equilibrium configuration of the molecule, it is necessary to find theoretically the relation between spectroscopic constants and molecular parameters. The ERH can be constructed using different methods of the perturbation theory, but the method of contact transformations (CT) is used most widely.

The description of this method and the review of spectroscopic results, obtained earlier with its help, can be found in Refs. 6–8. It should be noted that the presented results were obtained in different schemes of ordering the intramolecular interactions, and in the literature there are no relations between these results. This paper gives a solution to this problem. The essence

of application of the CT method to construction of the effective operator of observation is that the operator of observation is subjected to the same series of unitary transformations, as the initial, in this case, RV Hamiltonian. In the formal perturbation theory, the Hamiltonian is presented as $H = H_0 + \lambda H_1 + \lambda^2 H_2 + \dots$ (or $H = H_0 + \lambda V$). Expansion of the RV Hamiltonian (inverse inertia tensor and potential function) in series in terms of nuclei displacements in the Watson's system of designations has the form

$$H_{VR} = \sum_{mn} H_{mn} = H_{vib} + H_{cor} + H_{rot}, \quad (5)$$

where H_{mn} is the group of terms with the vibrational operators (q_l or p_l) in the power m and the rotational operators (J_α) in the power n

$$H_{vib} = H_{20} + H_{30} + H_{40} + \dots$$

$$H_{cor} = H_{21} + H_{31} + H_{41} + \dots$$

$$H_{rot} = H_{02} + H_{12} + H_{22} + \dots \quad (6)$$

The coefficients in H_{mn} have the order of magnitude of

$$\chi^{m-2-2n} \omega_{vib}; \quad (7)$$

χ is the Born–Oppenheimer parameter $\approx \left(\frac{m_e}{m_n} \right)^{1/4} \approx \frac{1}{10}$.

In (mn) designation, the Eckart rotational conditions⁵ are equivalent to $H_{11} = 0$.

For low quantum numbers, the Hamiltonian of a set of harmonic oscillators H_{20} gives the dominant contribution to the matrix of rotational-vibrational energy. The EH is constructed by consequent contact transformations by the following scheme:

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots, \quad (8)$$

where $H^{(0)} = H_{20}$, $H^{(1)}$, $H^{(2)}$, ... are higher order terms grouped in a certain way. The transformed Hamiltonian has the form

$$\begin{aligned} \tilde{H} &= \dots e^{-i\lambda^4 S^{(4)}} e^{-i\lambda^3 S^{(3)}} e^{-i\lambda^2 S^{(2)}} e^{-i\lambda S^{(1)}} \times \\ &\times H e^{i\lambda S^{(1)}} e^{i\lambda^2 S^{(2)}} e^{i\lambda^2 S^{(3)}} e^{i\lambda^2 S^{(4)}} \dots = \\ &= H^{(0)} + \lambda \tilde{H}^{(1)} + \lambda^2 \tilde{H}^{(2)} + \dots, \end{aligned} \quad (9)$$

where $S^{(1)}$, $S^{(2)}$, $S^{(3)}$, ... are the Hermitian operators selected so that $\tilde{H}^{(1)}$, $\tilde{H}^{(2)}$, $\tilde{H}^{(3)}$, ... have no off-diagonal matrix elements between wave functions corresponding to energy levels in the zero order, i.e., generators $S^{(n)}$ in the CT method satisfy the condition $\langle S^{(n)} = 0 \rangle$; $\langle \dots \rangle$ is the operator of separation of the diagonal part in $H^{(0)}$. It should be noted that the commutator expressions for the operators of the transformed Hamiltonian $H^{(N)}$ and the transformed operator of observation $O^{(N)}$, written in the nonrecurrent form, have formally the same form.^{6–9} However, there is a principal difference between them. It consists in the fact that the rule $(2N+1)$ of the

perturbation theory is fulfilled when constructing the EH, whereas this rule is not fulfilled when constructing the effective operator of observation.⁶⁻¹²

2. Problem of ordering the rotational-vibrational interactions in molecules

Before applying the consequent contact transformations (9) to the RV Hamiltonian (5), it is necessary to answer the following questions^{7,13}: (1) what order of smallness in λ the operator term H_{mn} in $H^{(2)}$ corresponds to or, in other words, how the expansion $H = H^{(0)} + \sum_n \lambda^n H^{(n)}$ and the expansion in the form $H = H_{20} + \sum_{mn} H_{mn}$ relate to each other; (2) to what order in λ relate the vibrational and rotational commutators arising from the common commutator (the question arises, because $S^{(n)}$ operators depend on vibrational and rotational operators)

$$[S, h] = [S_V S_R, h_V h_R] = [S_V, h_V] \left(\frac{1}{2}\right) [S_R, h_R]_+ + [S_R, h_R] \left(\frac{1}{2}\right) [S_V, h_V]_+, \quad (10)$$

where $S_V(h_V)$ and $S_R(h_R)$ are vibrational and rotational factors in $S(h)$, $[A, B]_+ = AB + BA$.

Thus, we necessarily come to the problem of ordering the perturbations H_{mn} in H_{VR} (5) (Refs. 7, 12-15). So, in the theory of rotational-vibrational spectra of quasi-rigid molecules we have to solve the problem of correspondence

$$H^{(N)} \longrightarrow H_{mn}$$

between the formal expansion of the Hamiltonian in the perturbation theory (PT) and the actual expansion of the RVH. This problem was first formulated by the author in 1985 in Ref. 7. It is a fundamental problem of the theory of molecular spectra, and unambiguous solution of the direct and inverse spectroscopic problems depends on its correct formulation and solution. Since the order of contribution to the energy depends strongly on quantum numbers, this can be taken into account formally by assigning the orders in λ to the vibrational and rotational operators in H_{mn} (and \tilde{H}_{mn}). Oka¹⁶ used the scheme of ordering perturbations, which was based on classification of H_{mn} according to the orders of magnitude of their coefficients. Bess also used this grouping for calculating the operator of the form $r^2 J^2$ (Ref. 17). Other ordering schemes (Amat-Nielsen,⁸ Aliev-Watson¹⁸), excluding the limiting ordering schemes,^{6,7} were analyzed in detail in Ref. 13.

The perturbation operator H_{mn} in the H_{VR} expansion (5) can be estimated as having the order of magnitude $\lambda^{f(m) + \varphi(n)}$, where $f(m)$ and $\varphi(n)$ are linear functions of powers of vibrational (m) and rotational (n) operators, respectively.^{7,12,13} The form of the functions $f(m)$ and $\varphi(n)$ is determined by the scheme of ordering rotational-vibrational perturbations. The

perturbation operator $H^{(N)}$ (of the order $\lambda^N \omega_e$) includes only that group of operators H_{mn} , for which

$$f(m) + \varphi(n) = N, \quad (11)$$

that is,

$$H^{(N)} = \sum_{[m, n]} H_{mn}^{(N)}, \quad (12)$$

where $[m, n]$ under the summation symbol means that the condition (11) is imposed on the summation over m and n . Application of the CT method to the Hamiltonian (5), in which all terms are grouped by Eq. (11)

$$H = \sum_N \sum_{[m, n]} H_{mn}^{(N)}, \quad (13)$$

allows S -operators to be found in any approximation and their operator structure to be determined. Let us determine the parameter of smallness of S -operators with respect to unity.^{6,7} It can be shown that the operator structures of S -operators of the order N ($\sim \lambda^N$) and the N th term of the Hamiltonian transformed k times ($\varepsilon^N \omega_e$) are determined from the same equation (11) as the N th term in the expansion (12),

$$S(N) = \sum_{[m, n]} S_{mn}^{(N)}, \quad (S_{mn}^{(N)} \sim \lambda^{f(m) + \varphi(n)}); \quad (14)$$

$${}_{(k)}H^{(N)} = \sum_{[m, n]} {}_{(k)}H_{mn}^{(N)}. \quad (15)$$

Let the quantity $[f(m) + \varphi(n)]$ be named the “ λ -order”

of the operator term \tilde{H}_{mn} (or S_{mn}). The RV Hamiltonian (1) transformed by the vibrational variables can be written as

$$\tilde{H} = \sum_N \sum_{[m, n]} {}_{(N)}H_{mn}^{(N)} = \sum_{[m, n]} \tilde{H}_{mn} = {}_{\infty}H, \quad (16)$$

where tilde denotes the completely transformed perturbation operator in H_{VR} .

3. Infinite, but countable set of ordering schemes

The order of magnitude of the operators \tilde{H}_{mn} and S_{mn} , in accordance with the above-said, is determined by the equations

$$\begin{aligned} \tilde{H}_{mn} &\sim \chi^{m-2+2n} r^m J^n \omega_{\text{vib}} \sim \chi^{m+2n} r^m J^n \omega_e, \\ S_{mn} &\sim \chi^{m-2+2n} r^m J^n, \quad (\text{or } \chi^{m+2n} r^m J^n), \end{aligned} \quad (17)$$

where ω_{vib} is the mean frequency of harmonic vibrations, ω_e is the mean value of the electronic energy of the ground vibronic state of a quasi-rigid molecule $\omega_e \sim \chi^2 \omega_{\text{vib}}$.

If “ λ -order” of $H_{mn}^{(N)}$ is determined as a value $\leq \alpha m + \beta n$, providing α and β are integer, then,

starting from some number $N \geq \alpha m + \beta n$, the operators H_{mn} and S_{mn} with different operator structure correspond to the same order. Such schemes will be called the ordering schemes with integer “ λ -order.” In these schemes, calculation by the CT method has a disadvantage that cross commutator terms like $[S_{12}, [S_{30}, [...]] + [S_{30}, [S_{12}, [...]]$ arise.⁹

Niroomand and Parker¹⁹ considered different sequences of S_{mn} operators from the viewpoint of inclusion of one operator $S_{mn} S^{(N)}$ of the general scheme of contact transformations. They showed that results for some lower operators in the transformed Hamiltonian are equivalent at different sequences of S_{mn} , but only in the approximation of an isolated vibrational state (see the below discussion).

Watson^{6,20,21} proposed to perform contact transformations sequentially by the increasing powers of rotational operators for every power of vibrational operators.

In Ref. 7, the sequence of contact transformations being an antipode of the sequence of Watson’s transformations, was proposed, in which transformations are performed by the increasing powers of vibrational operators for every power of rotational operators. The schemes of ordering rotational-vibrational perturbations, which form the basis of Watson’s (Ref. 6) and Mikhailov’s (Ref. 7) vibrational contact transformations, are, in fact, the consequence of two possible limiting estimates of vibrational and rotational molecular energy.

In the Watson’s model, it is assumed that the rotational energy described by the Hamiltonian H_{02} has the same order of magnitude as the electronic energy of the ground state, i.e., according to Eq. (17):

$$H_{02} \sim \lambda^0 \omega_e \sim \chi^4 \chi^{-4+\epsilon'} \omega_e, \quad \epsilon' \rightarrow 0, \quad (18)$$

$$H_{02} \sim \chi^2 \omega_e.$$

Herefrom we can estimate the orders of magnitude of vibrational and rotational operators

$$r \sim 1, \quad J \sim \chi^{-2+\epsilon} (\epsilon' = 2\epsilon), \quad \epsilon \rightarrow 0. \quad (19)$$

This model can be designated as an “ultrafast rotator.” The second Mikhailov’s (M) model can be identified as an “overexcited oscillator.” In this model, it is assumed that the vibrational energy described by the Hamiltonian H_{20} is comparable with the electronic energy ω_e , i.e., according to Eq. (17)

$$H_{20} \sim \lambda^0 \omega_e \sim \chi^2 \chi^{-2+\epsilon'} \omega_e, \quad \epsilon' \rightarrow 0,$$

$$H_{02} \sim \chi^2 \omega_{\text{vib}} \sim \chi^4 \omega_e. \quad (20)$$

Herefrom we have estimates of the orders of magnitude of vibrational and rotational operators

$$r \sim \chi^{-1+\epsilon}, \quad J \sim 1, \quad \epsilon \rightarrow 0. \quad (21)$$

In this scheme, anharmonic vibrational operators are automatically separated from rotational-vibrational interaction in the expansion of the molecular Hamiltonian:

$$H_{\text{VR}}^{(M)} = H_V + H'_{\text{VR}} = \sum_{m,n} \{H_{m0} + \sum_n H_{mn}^{(M)}\}. \quad (22)$$

Amat and Nielsen⁸ suggested to consider the vibrational quantum numbers ~ 1 and rotational quantum numbers ~ 10 as most usable. For the operators r and J this can be determined by imposition of the conditions:

$$r \sim \chi^0, \quad J \sim \chi^{-1}. \quad (23)$$

Equations (19), (21), and (23) that were found from model considerations can be extended to estimate the orders of magnitude of rotational-vibrational perturbations H_{mn} and S -operators S_{mn} , as well as vibrational and rotational commutators. The ordering schemes based on Eqs. (18) and (20) can be called the limiting schemes of ordering rotational-vibrational perturbations.⁷ In the ordering schemes applied in the theory of molecular spectra, λ -orders of H_{mn} (Refs. 5, 8, 6, and 7) are determined in the following way:

$$\lambda\text{-orders of } H_{mn}(S_{mn}) = \begin{cases} m + \epsilon n & \text{Watson (W)} \\ m + n & \text{Amat - Nielsen (A - N)} \\ m + 2n & \text{Born - Oppenheimer - Oka (B - O - O)} \\ \epsilon m + 2n & \text{Mikhailov (M)}. \end{cases} \quad (24)$$

If, as earlier, λ -order is determined as $\alpha m + \beta n$, but range of α and β is extended to include rational numbers, then λ -orders of the considered schemes can be plotted as rays in the Cartesian coordinate system (α, β) (Fig. 1).^{7,22}

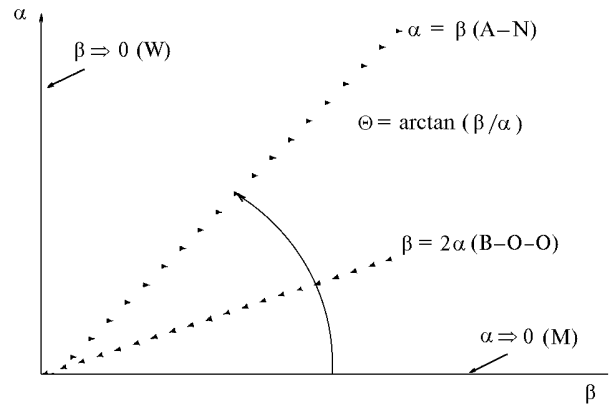


Fig. 1.

The conditions imposed on the orders of magnitude of vibrational and rotational operators and commutators⁶⁻⁸ follow from Eqs. (19), (21), and (23). They are tabulated below for the ordering schemes used in theoretical molecular spectroscopy:

	(W)	(B-O-O)	(A-N)	(M)
r	1	1	1	$\chi^{-1+\epsilon}$
J	$\chi^{-2+\epsilon}$	1	χ^{-1}	1
$[p, q]_V$	$-i$	$-i$	$-i$	$-i\chi^{-2+2\epsilon}$
$[J_\alpha, J_\beta]_R$	$-i\chi^{-2+\epsilon} J_\gamma$	$-iJ_\gamma$	$-i\chi J_\gamma$	$-iJ_\gamma$

(25)

4. Vibrational contact transformations in the limiting ordering schemes

The unitary operators of vibrational transformations in the limiting ordering schemes have the form:

$$U_W^{-1} = e^{-iS_{12}} e^{-iS_{13}^{(W)}} \dots e^{-iS_{21}} e^{-iS_{22}^{(W)}} \dots e^{-iS_{30}} e^{-iS_{31}} \dots, \\ U_M^{-1} = e^{-iS_{30}} e^{-iS_{40}} \dots e^{-iS_{21}} e^{-iS_{31}^{(M)}} \dots e^{-iS_{12}} e^{-iS_{22}^{(M)}} \dots. \quad (26)$$

The sequence order of unitary operators in U_M^{-1} and U_W^{-1} can be written in the form of the following ordered tables for generators of transformations²² for the overexcited oscillator (M)

$$\begin{array}{cccc} & & \rightarrow r & \\ S_{30} & S_{40} & S_{50} & \dots \\ S_{21} & S_{31}^{(M)} & S_{41}^{(M)} & \dots \\ S_{12} & S_{22}^{(M)} & S_{32}^{(M)} & \dots \downarrow \\ \dots & \dots & \dots & \dots J, \end{array} \quad (27)$$

and ultrafast rotator (W)

$$\begin{array}{cccc} & & \rightarrow J & \\ S_{12} & S_{13}^{(W)} & S_{14}^{(W)} & \dots \\ S_{21} & S_{22}^{(W)} & S_{23}^{(W)} & \dots \\ S_{30} & S_{31}^{(W)} & S_{32}^{(W)} & \dots \downarrow \\ \dots & \dots & \dots & \dots r. \end{array} \quad (28)$$

The limiting ordering schemes differ from the schemes with integer λ -order (A–N, B–O–O) by the fact that in these schemes the S -operator in every transformation order consists of one operator S_{mn} , and thus cross commutators do not arise at transformations. It should be noted that in the second approximation of the perturbation theory ($m+n \leq 4$) the scheme (M) coincides with the scheme (B–O–O), and the scheme (W) coincides with the scheme proposed in Ref. 18, which can be formulated as the conditions⁷:

$$r \sim 1, J \sim \chi^{4/3}; [p, q] = -i; \\ [J_\alpha, J_\beta] = -i\lambda^4 \sum_\gamma e_{\alpha\beta\gamma} J_\gamma; \lambda \sim \chi^{1/3}.$$

Analysis of calculation of \tilde{H}_{mn} \tilde{M}_{mn} of high orders^{6,7,15} shows that from the viewpoint of the number of commutators the scheme (W) allows one to calculate, in the shortest way, \tilde{H}_{mn} (\tilde{M}_{mn}) with high powers of n , and the scheme (M) allows calculation with low powers of n , but high powers of m . In any case, calculation in the limiting ordering schemes is free of cross commutators, which arise in the schemes with the integer λ -order and, especially, in the Amat–Nielsen scheme, being intermediate between the limiting ordering schemes (W) and (M). It should be noted that in Refs. 23 and 24 the rotational-vibrational Hamiltonian was presented in the form $H_{VR} = H_V + H'_{VR}$, and the operator terms in Ref. 24 were grouped by the Amat–Nielsen scheme. In the

ordering scheme (M), the anharmonic operators, H_{m0} , are automatically separated in the expansion of H_{VR} , and H_{VR} has the structure similar to those from Refs. 23 and 24 ($H'_{VR} = \sum_{mn} H_{mn}(1 - \delta_{m0})$). However, ordering of H_{mn} is performed, certainly, not by the Amat–Nielsen scheme. Therefore, it is more logical to consider the separation $H_{VR} = H_V + H'_{VR}$ as a certain ordering scheme that does not differ fundamentally from the Amat–Nielsen scheme, rather than some redefinition of the zero approximation.

Let us consider vibrational and rotational series in the EH: $H_{\text{vib}} = \sum H_{m0}$ and $H_{\text{rot}} = \sum_n H_{0n}$. Taking into account that in the limiting ordering schemes the operator term \tilde{H}_{mn} in the EH is comparable with the electronic energy ω_e , we can estimate the limiting terms of the considered series as:

$$\lim_{m \rightarrow \infty} \tilde{H}_{m0} \approx \lim_{m \rightarrow \infty} \chi^{1/m} \omega_e, \quad (29)$$

$$\lim_{n \rightarrow \infty} \tilde{H}_{n0} \approx \lim_{n \rightarrow \infty} \chi^{-1/n} \omega_e. \quad (30)$$

Thus, the expansion parameter (smallness parameter) for ordered operator terms in H^{eff} is determined by the equations

$$\lim_{p \rightarrow \infty} \lambda^p = \lim_{p \rightarrow \infty} \left\{ \begin{array}{l} \frac{1}{\sqrt[p]{\chi}} \rightarrow 1.00 \dots 1 \\ \frac{1}{\sqrt[p]{\chi}} \rightarrow 0.999 \dots \end{array} \right\} \rightarrow 1. \quad (31)$$

It is important to note that only calculations in the limiting ordering schemes lead to representation of the vibrational or rotational dependences of observation in terms of infinite series. These dependences can be presented as some series in terms of vibrational or rotational operators (or corresponding quantum numbers) similar to the Dunham series for diatomic molecules. Based on such presentation of the operators of observation, it becomes possible to apply the methods improving convergence of the series, for example, the method of Pade approximants, and the methods based on nonlinear transformations of series.²⁵

5. Problems of indeterminacy and ambiguity of effective Hamiltonians and approximation of an isolated vibrational state

The ERH, constructed in any of the considered ordering schemes and meeting the condition $[H_R^{(\text{eff})}, H_{20}] = 0$, where H_{20} is the Hamiltonian of a set of harmonic oscillators, is independent of the ordering scheme (due to the fact that the Hamiltonian eigenvalues are independent of the unitary transformation). At the same time, vibrational unitary transformation operators depend on the ordering

scheme, and the operators in different schemes are related to each other by unitary transformations, in particular, $U_W^{-1} = T^{-1}U_M^{-1}T$.

Note that the effective Hamiltonian in the Amat–Nielsen scheme can be represented in the form of a square ordered table $H^{\text{eff}}(\text{A-N}) = \sum_{N, mn} H_{mn}^{(N)}(\text{A-N})$, $m = n$. In any grouping with a finite λ -order, i.e., with $\lambda \sim \chi^{a/b}$ (a and b are integer), the EH degenerates into either column or row.²⁶ The process of finding rotational-vibrational energy levels and molecular characteristics from experimental data through the stage of spectroscopic models and spectroscopic constants is based on solution of two fundamental problems of molecular rotational and vibrational dynamics:

1) indeterminacy in expansion of the molecular Hamiltonian on ordering (grouping) of intramolecular interactions, when constructing the EH;

2) ambiguity of the EH, when constructing the reduced EH.

The two-stage character of calculation of the RV energy levels is illustrated in Fig. 2.

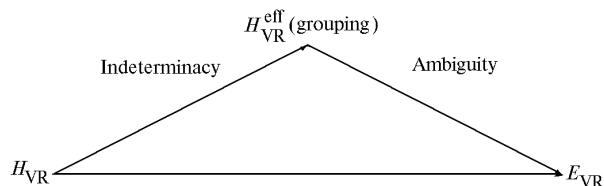


Fig. 2.

The parameters in the reduced Hamiltonian are connected with the parameters in the effective Hamiltonian as

$$\tilde{h} = {}_{(g)}h^{\text{eff}} + \Delta h({}_{(g)}S). \quad (32)$$

The dependence of the reduction generators on groups of rotational-vibrational interactions is discussed below.

Besides, the operator of the effective dipole moment constructed in accordance with the principle of transformation completeness^{7,13} also does not depend on the applied ordering scheme (in the absence of accidental resonances), i.e., the relation between the spectroscopic and molecular parameters is unique. This conclusion follows from the fact that the scalar product is invariant with respect to unitary transformation, i.e., conserves the length of a vector. In the case under consideration, such a vector is the matrix element of the dipole moment, modulo square is proportional to the partial probability of a transition (or line strength), which is just observable.

The formulated statements on independence of the ERH and the operator of effective dipole moment on the ordering schemes take place in the approximation of isolated vibrational states and are described by the following equations:

$$H^{(\text{eff})} = U^{-1}H_{\text{VR}}U;$$

$$U^{-1} = e^{-iS^{(1)}} e^{-iS^{(2)}} e^{-iS^{(3)}} \dots; \quad (33)$$

$$[H^{(\text{eff})}, H_{20}] = 0;$$

$${}_{(g)}H^{(\text{eff})} = {}_{(g')}H^{(\text{eff})}.$$

From the definition

$$H^{(\text{eff})} = \sum_{mn} \langle H_{2m}, n \rangle = \sum_{mn} \tilde{H}_{2m, n} \quad (34)$$

and Eq. (33) it follows

$${}_{(g)}\tilde{H}_{2m, n} = {}_{(g')}\tilde{H}_{2m, n}; \quad (35)$$

$$M^{(\text{eff})} = \dots e^{-iS^{(1)}} M e^{iS^{(1)}} \dots,$$

$${}_{(g)}M^{(\text{eff})} = {}_{(g')}M^{(\text{eff})}. \quad (36)$$

And from the definition

$$M^{(\text{eff})} = \sum_{mn} \tilde{M}_{mn} \quad (37)$$

and Eq. (36) it follows

$${}_{(g)}\tilde{M}_{mn} = {}_{(g')}\tilde{M}_{mn}. \quad (38)$$

Relations (35) and (38) do not keep true in the presence of Fermi or Coriolis accidental resonances (in the energy spectrum of a molecule). In other words, they do not hold in the presence of accidental degeneration for harmonic vibrational frequencies (fundamental or combination) or zero-order rotational-vibrational levels related by anharmonic or rotational-vibrational interactions of the order of detuning between vibrational or rotational-vibrational energetic levels. Classification of natural and accidental resonances in rotational-vibrational molecular spectra has been proposed by Nielsen and Amat.²⁷

6. Determination of theoretical uncertainties of ordering for EH and EDM

Relations (35) and (38) indicate independence of \tilde{H}_{mn} (\tilde{M}_{mn}) from (g) in the absence of accidental resonances. They can be formulated in other form, i.e., with the separated contribution from transformation of transition from one ordering scheme (g) to another (g') . Individual terms in $H^{(\text{eff})}$ and $M^{(\text{eff})}$ can be presented as

$$\begin{aligned} \tilde{H}_{mn}^{(g)} &= \tilde{H}_{mn}^{(g')} + \tilde{h}_{mn}^{(g \rightarrow g')}, \\ \tilde{M}_{mn}^{(g)} &= \tilde{M}_{mn}^{(g')} + \tilde{M}_{mn}^{(g \rightarrow g')}. \end{aligned} \quad (39)$$

Vibrational S -generators also can be presented as

$$S_{mn}^{(g)} = S_{mn}^{(g')} + S_{mn}^{(g \rightarrow g')}. \quad (40)$$

The parameters $h_{mn}^{(g \rightarrow g')}$, $M_{mn}^{(g \rightarrow g')}$, and $S_{mn}^{(g \rightarrow g')}$ can be determined as uncertainties of grouping or uncertainties of ordering the operator terms in the EH and DM, as well as vibrational generators of the CT method. The conditions imposed on $\tilde{h}_{mn}^{(g \rightarrow g')}$, $\tilde{M}_{mn}^{(g \rightarrow g')}$, and $S_{mn}^{(g \rightarrow g')}$ are equivalent to Eqs. (35), (38), and $\langle S^{(N)} \rangle = 0$:

$$\begin{aligned} \langle \tilde{h}_{2m,n}^{(g \rightarrow g')} \rangle &= \tilde{h}_{2m,n}^{(g \rightarrow g')} = 0, \quad \tilde{M}_{mn}^{(g \rightarrow g')} = 0; \\ \langle S_{m,n}^{(g \rightarrow g')} \rangle &= 0. \end{aligned} \quad (41)$$

As was noted above, Eqs. (35), (38), and, consequently, (41) are inapplicable to analysis of local perturbations in the energy spectrum due to accidental resonances.

7. Equation for vibrational generators of the CT method in different ordering schemes

The equations for vibrational S -operators (9) of the method of contact transformations in different ordering schemes can be derived either from definition of vibrational unitary transformations (26) applying the “unravel technique” to exponential operators²⁸ or from the definition of \tilde{H}_{mn} in the commutator form. That is, $S_{m,n}^{(g \rightarrow g')}$ and $h_{m,n}^{(g \rightarrow g')}$ can be found in such a way. In the third approximation ($m + n \leq 5$), the equations for S_{mn} in the limiting ordering schemes can be found from the simple equation:

$$e^a e^b = e^b e^a e^{K_1} e^{K_2}, \quad (42)$$

where

$$K_1 = [a, b], \quad K_2 = \frac{1}{2} ([a[a, b]] + [b[a, b]]).$$

Derivation of this equation is similar to derivation of the general Murray equation or Zassenhause equation.²⁸ Taking into account Eqs. (26)–(28) and (42), we can obtain $S_{m,n}^{(g \rightarrow g')}$ for the limiting ordering schemes:

$$m + n = 4:$$

$$\begin{aligned} S_{13}^{(M \rightarrow W)} &= i [S_{21}, S_{12}], \\ S_{22}^{(M \rightarrow W)} &= i [S_{30}, S_{12}], \end{aligned} \quad (43)$$

$$S_{31}^{(M \rightarrow W)} = i [S_{30}, S_{21}],$$

$$m + n = 5:$$

$$S_{14}^{(M \rightarrow W)} = i [S_{21}, S_{13}^{(W)}] - \frac{1}{2} [S_{21}, [S_{21}, S_{12}]],$$

$$S_{41}^{(M \rightarrow W)} = i [S_{40}, S_{21}] - \frac{1}{2} [S_{30}, [S_{30}, S_{21}]],$$

$$\begin{aligned} S_{23}^{(M \rightarrow W)} &= i [S_{30}, S_{13}^{(W)}] + \frac{1}{2} [[S_{21}, S_{12}], S_{30}] + \\ &+ i [S_{31}^{(W)}, S_{12}] + [[S_{21}, S_{30}], S_{12}], \end{aligned}$$

$$\begin{aligned} S_{32}^{(M \rightarrow W)} &= i [S_{30}, S_{22}^{(W)}] + i [S_{40}, S_{12}] + i [S_{21}, S_{12}]_R + \\ &+ \frac{1}{2} [S_{21}, [S_{30}, S_{21}]] + [[S_{30}, S_{12}], S_{30}], \end{aligned}$$

$$S_{05}^{(M \rightarrow W)} = \frac{1}{2} [S_{12}, [S_{21}, S_{12}]]. \quad (44)$$

In Ref. 18 the operator of sextic distortion was calculated both in the grouping (A–N) and in the grouping that coincides in the second approximation of the perturbation theory with the grouping (W). It can be shown⁷ that $S_{05}^{(A-N)} = S_{05}^{(W)} + \frac{1}{6} [S_{12}, [S_{21}, S_{12}]]$.

With this equation it can be readily found that $\tilde{H}_{06}^{(A-N)} = H_{06}^{(A-N)} + \frac{1}{6} [[S_{12}, [S_{21}, S_{12}]], H_{02}]$. However, since S_{mn} meets the condition (41), $\langle S_{05} \rangle^{(g \rightarrow g')} = 0$. It follows herefrom that $\langle \tilde{H}_{06}^{(W)} \rangle = \langle \tilde{H}_{06}^{(A-N)} \rangle$. The equality $\langle S_{05}^{(g \rightarrow g')} \rangle = 0$ can be easily proved by direct calculation of the commutators.

The Amat–Nielsen scheme was widely used in calculating the spectroscopic parameters in the ERH through molecular constants.⁸ Therefore, it is reasonable to present the equations for S -operators in the limiting schemes and the Amat–Nielsen scheme. In the second approximation of the perturbation theory, these equations can be obtained by generalizing the well-known Baker–Campbell–Housedorf equation²⁸ for the case of three operators¹⁵

$$\begin{aligned} e^a e^b e^c &= \\ = \exp \{ a + b + c + \frac{1}{2} ([a, b] + [a, c] + [b, c] + \dots) \}. \end{aligned} \quad (45)$$

The equations for S_{mn} ($m + n = 4$) in the Amat–Nielsen grouping and in the limiting groupings have the form:

$$\begin{aligned} S_{13}^{A-N} &= S_{13}^{(W)} + \frac{i}{2} [S_{21}, S_{12}] = S_{13}^{(M)} + \frac{i}{2} [S_{12}, S_{21}], \\ S_{22}^{A-N} &= S_{22}^{(W)} + \frac{i}{2} [S_{12}, S_{30}] = S_{22}^{(M)} + \frac{i}{2} [S_{30}, S_{12}], \\ S_{31}^{A-N} &= S_{31}^{(W)} + \frac{i}{2} [S_{30}, S_{21}] = S_{31}^{(M)} + \frac{i}{2} [S_{21}, S_{30}], \\ S_{40}^{A-N} &= S_{40}^{(W)} = S_{40}^{(M)}. \end{aligned} \quad (46)$$

Or, in the other form:

$$\begin{aligned} S_{mn}^{(A-N \rightarrow W)} &= -S_{mn}^{(A-N \rightarrow M)}, \\ S_{mn}^{(A-N \rightarrow g)} &= C_{mn}^{(A-N \rightarrow g)} K_{mn}, \quad g = (W), (M), \end{aligned} \quad (47)$$

where the coefficients $C_{mn}^{(A-N \rightarrow g)}$ and commutators K_{mn} are

$$C_{mn}^{(A-N \rightarrow g)} = \begin{cases} 1/2, & (A-N) \rightarrow (M) \\ -1/2, & (A-N) \rightarrow (W) \end{cases}, \quad (48)$$

$$K_{13} = i [S_{12}, S_{21}], \quad K_{22} = i [S_{12}, S_{30}], \quad K_{31} = i [S_{21}, S_{30}]. \quad (49)$$

In addition, for the operators S_{mn} ($m + n = 4$) in the groupings (A–N), (W), and (M) there exists the generalizing equation:

$$S_{mn}^{(A-N)} = \frac{1}{2} (S_{mn}^{(W)} + S_{mn}^{(M)}). \quad (50)$$

This equation was already found in Ref. 13 based on the commutator definitions of \tilde{H}_{mn} in the three groupings: (A-N), (B-O-O), and the grouping from Ref. 18. As was mentioned above, the last two groupings in the second approximation of the perturbation theory give the results coinciding with the results in the limiting groupings (M) and (W), respectively.

Thus, the above equations (43)–(50) were derived only from the definitions of the unitary operators of vibrational transformations (26) following from different ordering of the expansion of the Hamiltonian H_{VR} , by applying the unravel technique to exponential operators.

8. Determination of accidental resonances in spectrum

When applying the equations for transformation generators (S -functions) obtained in Section 7 to analysis of random resonances in a molecule, the total operators S_{mn} should be replaced by $S_{mn}^{(*)}$. Asterisk (*) means that resonance denominators are excluded from the considered operators S_{mn} in the process of their calculation.⁸ Let us determine the accidental resonances in the molecular energy spectrum using the function of harmonic frequencies

$$\Phi(\omega) = \sum_{i=1}^P m_i \sigma_i \omega_i, \quad (51)$$

where ω_i are harmonic frequencies of vibrations, m_i are natural numbers, $\sigma_i = \pm 1$ are signed variables, P is a polyad of vibrational states.

An accidental resonance in the molecular energy spectrum is determined by the condition imposed on the function

$$\Phi(\omega) \approx 0 \quad \text{or} \quad \Theta(\omega). \quad (52)$$

The equivalent form of this condition, used in the spectroscopic literature, is the following:

$$\sum_{j=1}^r m_j \omega_j \approx \sum_{k=r+1}^P m_{r+j} \omega_{r+j}. \quad (53)$$

It should be noted that the resonance condition can be rewritten in other form

$$\Phi(\Omega) = \sum_{i=1}^P m_i \sigma_i \Omega_i \approx 0 \quad \text{or} \quad \Theta(\Omega), \quad (54)$$

if the vibrational Hamiltonian of the form

$$H^{(0)} = H_{20} + \langle \tilde{H}_{40} \rangle + \langle \tilde{H}_{60} \rangle + \dots \quad (55)$$

with eigenvalues

$$\tilde{E}_i^{(0)} = \Omega_i (V_i + \frac{g_i}{2}), \quad \Omega_i = \omega_i + \chi_{ii} + \chi_{iiii} \dots \quad (56)$$

is taken as the initial approximation.

It is important to emphasize that the numbers m_i denote the degree of the vibrational ladder operator $a_j^{\sigma_j}$ ($a_j^{\sigma_j} = q_j - i \sigma_j p_j$), i.e. operators $(a_j^{\sigma_j})^{m_j}$ in the operator of resonance interaction, and the signed variables σ_j entering into $\Phi(\omega)$ meet the condition

$$\sigma_j (j = 1, \dots, r) = -\sigma_{r+k} (k = r + i, \dots, p). \quad (57)$$

It follows from Eqs. (53) and (57) that the dominant contribution to the operator of resonance interaction is determined by the operator of the form

$$\sim \prod_{j=1}^r (a_j^{\sigma_j})^{m_j} \cdot \prod_{k=r+1}^P (a_{k+r}^{-\sigma_{j+r}})^{m_{(k+r)}}. \quad (58)$$

The technique of projection operators allows separating the operator of resonance interaction from the general-form operator in the ERH

$$V = \sum_{q=\sum_{i=1}^P m_i} C_{n_1 n_2 \dots n_q}^{\sigma_{n_1} \sigma_{n_2} \dots \sigma_{n_q}} a_{n_1}^{\sigma_{n_1}} a_{n_2}^{\sigma_{n_2}} a_{n_q}^{\sigma_{n_q}}, \quad (59)$$

with summation over polyads.

The projection operator can be represented as a function of δ -symbols for character variables σ_i

$$\Delta(\text{Poliad}) = \prod_{a=1}^{m_1} \delta_{\sigma_1 \sigma_{na}} \dots \prod_{a=1}^{m_p} \delta_{\sigma_p, \sigma(a + \sum_{i=1}^{p-i} n_i)} \prod_{j=1}^r \delta_{\sigma_1 \sigma_j} \prod_{k=r+1}^P \delta_{-\sigma_1, \sigma_{k+r}}. \quad (60)$$

Then nonresonance part of the operator V equal to $V^{(*)}$ can be derived from Eq. (59) by introducing $(1 - \Delta)$ symbol, i.e.,

$$V^{(*)} = V - V(\text{Res}) = V(1 - \Delta). \quad (61)$$

For two interesting particular cases of double ($\omega_a \sim \omega_b$) and triple ($\omega_a \sim \omega_b + \omega_c$ or $\omega_a \sim 2\omega_b$) accidental resonances, the symbol $\Delta^{(P)}$ is determined as:

$$\Delta^{(2)} = \delta_{\sigma_a \sigma_{n_1}} \delta_{\sigma_a \sigma_{n_2}} \delta_{\sigma_a, -\sigma_b}, \quad (62)$$

$$\Delta^{(3)} = \delta_{\sigma_a \sigma_{n_1}} \delta_{\sigma_a \sigma_{n_2}} \delta_{\sigma_a \sigma_{n_3}} \delta_{\sigma_a, -\sigma_b}, \quad (63)$$

where n_1 , n_2 , and n_3 are summation indices in the interaction operator V .

As was found in Section 7, the determined operators in the EH can be presented as

$$\tilde{H}_{mn}^{(g)} = \tilde{H}_{mn}^{(g')} + h_{mn}^{(g \rightarrow g')}, \quad (64)$$

where $h_{mn}^{(g \rightarrow g')}$ are, in essence, theoretical indeterminacy of ordering of the operator elements in the EH. They vanish in the approximation of an isolated vibrational state, $\langle h_{mn}^{(g \rightarrow g')} \rangle = 0$, and depend explicitly on the function $\tilde{\Phi}(\omega)$ (51). Based on determination of the coefficients in

$$\begin{aligned}\tilde{\Phi}(\omega) &= [h_{mn}^{(M \rightarrow W)}]_{n_1 \dots n_m}^{\sigma_1 \dots \sigma_m} = \\ &= h_{n_1 \dots n_m}^{\sigma_1 \dots \sigma_m; \alpha_1 \dots \alpha_n} \cdot \prod_{i=1}^m a_{m_i}^{\sigma_i} \prod_{j=1}^n J_{\sigma_j},\end{aligned}\quad (65)$$

where $\sigma_i = \pm 1$, $\alpha_i = x, y, z$ (or $0, \pm 1$);

$$\tilde{\Phi}(\omega) = {}_{(M \rightarrow W)}h_{n_1 \dots n_m}^{\sigma_1 \dots \sigma_m; \alpha_1 \dots \alpha_n},\quad (66)$$

we can classify accidental resonance interactions as follows:

1) strong interaction (S): $\tilde{\Phi}(\omega) \approx 0$, an example of this type of accidental resonance is the dyad (v_1, v_3) in methane-type molecules,

2) medium interaction (M): $\tilde{\Phi}(\omega) \approx \Theta(\omega)$, an example is the dyad (v_2, v_4) in methane-type molecules,

3) weak interaction (W): $\tilde{\Phi}(\omega) \approx \omega$, an example is the triad of resonance states ($v_1 + v_2, v_3$) in asymmetric triatomic linear molecules XYZ.

The last type of the resonance interaction can occur at low values of quantum numbers. In calculations, it can be treated by the ordinary method of perturbations. In other words, the situation in the energy spectrum can be treated as a very weak (VW) intermode resonance interaction. However, in the energy region formed by combined modes, i.e., at high quantum numbers, the classification of accidental resonances should be corrected. Let us consider some examples of double and triple resonances in molecular models. The resonance parameter in $h_{22}^{(M \rightarrow W)}$ can be expressed through molecular constants as:

$$\tilde{\Phi}_{\text{dyad}}(\omega) = {}_{(M \rightarrow W)}h_{ab}^{\sigma_a \dots \sigma_b} = \sum_m \Phi_{ab,m} \frac{R_m(\omega_a - \omega_b)^2}{[(\omega_a - \omega_b)^2 - \omega_m]}.\quad (67)$$

It follows from Eq. (67) that at strict equality $\omega_a = \omega_b$ (approximation of an isolated vibrational state) $\tilde{\Phi}_{\text{dyad}}(\omega) = {}_{(M \rightarrow W)}h_{ab}^{\sigma_a \dots \sigma_b} = 0$. This confirms the results on independence of transformed operator terms in the EH from the ordering schemes in the absence of accidental resonances in the energy spectrum.

Let us consider the triple intermode resonance using the resonance $\omega_1 + \omega_2 = \omega_3$ for the operator \tilde{H}_{31} in XYZ linear molecules as an example:

$$\begin{aligned}\tilde{\Phi}(\omega)_{\text{triad}} &= {}_{(M \rightarrow W)}h_{123}^{\sigma_1 \sigma_2 \sigma_3} = \\ &= \sum_{m, \sigma_m} \frac{\Phi_{12m}(-R_m^3 + \gamma R_m^3)(\omega_1 + \omega_2 - \omega_3)\sigma_m}{(-\omega_3 + \gamma\omega_m)(\omega_1 + \omega_3 - \gamma\omega_m)}.\end{aligned}\quad (68)$$

The result following from Eq. (68) is analogous to the result for double resonances exactly at the strict equality $\omega_1 + \omega_2 = \omega_3$

$$\tilde{\Phi}(\omega)_{\text{triad}} = {}_{(M \rightarrow W)}h_{123}^{\sigma_1 \sigma_2 \sigma_3} = 0.\quad (69)$$

9. Problem of reduction and ordering the series of rotational-vibrational interactions

Let us now consider the problem of determining the operator forms of S -generators of reduction. When constructing the EH for an energy region of accidental resonance interactions, according to the existing concepts,^{7,8} the vibrational generators of the method of contact transformations (vibrational S -functions⁸) are replaced by the generators S^* , $S_{mn} \rightarrow S_{mn}^{(*)}$. Thus, in analysis of accidental resonances, the total S -function is presented as a sum $S_{mn} = S_{mn}^{(*)} + S_{mn}(\text{Res})$, in which $S_{mn}^{(*)}$ does not depend on resonance denominators and $S_{mn}(\text{Res})$ does. In the chosen ordering scheme, the EH for the energy region of the accidental resonance perturbation under study can be written in the form

$$\tilde{H} = \tilde{H}^{(*)} + \tilde{H}(\text{Res}).\quad (70)$$

The same is true for individual terms of the EH

$${}_{(g)}\tilde{H}_{mn} = {}_{(g)}\tilde{H}_{mn}^{(*)} + {}_{(g)}\tilde{H}_{mn}(\text{Res}),\quad (71)$$

where the subscript g in ${}_{(g)}\tilde{H}_{mn}$ denotes the ordering scheme, in which the operator contribution in the EH is calculated.

In accordance with the developed statements of the theory of related ordering schemes, both total vibrational generators (S -functions) S_{mn} and their nonresonance $S_{mn}^{(*)}$ and resonance $S_{mn}(\text{Res})$ parts also depend on the applied ordering scheme. The following important circumstance should be noted. Since the resonance S -functions, $S_{mn}(\text{Res})$, meet the same general requirements as the reduction generators, namely, invariance with respect to the Hermitian operator and alternation of sign at the time reversal operation, it becomes possible to determine the operator structure of S -generators of reduction at the stage of construction of the EH. This procedure of determining the structure of reduction generators can be performed by replacing the coefficients in ${}_{(g)}S_{mn}(\text{Res})$ and ${}_{(\text{grouping})}C_{\dots}(\sum \sigma_i \omega_i n_i \approx \{\frac{O}{O}(\omega)\})$ with some parameters in $S_{mn}(\text{reduction})$ and ${}_{(g)}S_{\dots}$, which are determined, when processing spectra. These arguments can be illustrated by the following scheme:

$$\begin{array}{ccc}{}_{(\text{grouping})}S_{mn}(\text{Res})(S_{mn}\Delta^{(n)}) & \longrightarrow & {}_{(\text{grouping})}S_{mn}(\text{reduction}), \\ \downarrow & & \downarrow \\ {}_{(\text{grouping})}C_{\dots}(\sum \sigma_i \omega_i n_i \approx \{\frac{O}{O}(\omega)\}) & \longrightarrow & {}_{(g)}C_{\dots}(\text{reduction}).\end{array}\quad (72)$$

It should be emphasized that the conclusion on dependence of the reduction parameters on the ordering

schemes applies only to off-diagonal elements of the operator reduction matrix

$${}_{(\text{grouping})}S(\text{reduction}) = \begin{bmatrix} S_{aa} & {}_{(g)}S_{ab} & \dots \\ \dots & S_{bb} & \dots \\ \dots & \dots & \dots \end{bmatrix}. \quad (73)$$

The problem of indeterminacy of the EH will be analyzed in greater detail when considering specific types of accidental resonances and molecular systems.

10. Effective dipole moments of rotational-vibrational transitions in molecules

In accordance with the concept of related ordering schemes, it is possible to construct asymptotic subsequences $\sum_n \tilde{M}_{m,n}$ (different in the order of magnitude) in the operator of effective IR or Raman moment M^{eff} of a rotational-vibrational transition. The unitary relation between these subsequences is determined exactly (in the method of construction of M^{eff} by consequent contact transformations, this relation is determined by applying the unravel technique to exponential operators). In the limiting schemes, M^{eff} is set as a series of unitary (vibrational) operators written in a symbolic form of a matrix table. It can be readily seen that at such a method of setting the series of transformation generators, each of the transformed operators in M^{eff} is expressed through transformed effective operators of a moment of lower powers. In addition, $\tilde{M}_{mn}^{(g)}$ can be presented in the form $\tilde{M}_{mn}^{(g)} = \tilde{M}_{mn}^{(g')} + \tilde{M}_{mn}^{(g \rightarrow g')}$. This form of presentation of the operators in M^{eff} is useful when estimating the theoretical indeterminacy of ordering $\tilde{M}_{mn}^{(g \rightarrow g')}$ of the effective operator \tilde{M}_{mn} . In this paper, we propose the following algorithm for constructing the operator \tilde{M}_{mn} :

I. The first transformation is performed with the generator S_{mn} (i.e., the operator form of S_{mn} is identical to the form of M_{mn}) assuming that all previous transformations of lower order and, correspondingly, lower powers of $r^m J^m$ have already been made. It is clear that we have the rotational commutator with the first term of expansion of the initial moment M ;

II. The second and following transformations are performed in accordance with the chosen limiting ordering scheme on the assumption that all previous unitary transformations have been already made. Thus, we propose the algorithm of constructing M^{eff} based on the inverse sequence of unitary transformations.

What is the profit? Some technical difficulty of the proposed inverse method of transformation is compensated by the following more important result: the transformed operator of structure $r^m J^n$ ($\tilde{M}_{mn}^{(g)}$) is directly written in the form of a function of the

operators of structure $r^i J^i$ of lower powers ($m+n \geq i+j$). This result seems important when applying M^{eff} , calculated in high approximations, to both construction of spectroscopic models of moments and use of available spectroscopic information on moments obtained from analysis of either spectra of other type or rotational-vibrational dependence of moments of the spectra under study.

Example: Moments of first overtones and combination tones.

The rotational and vibrational subsequences \tilde{M} ($\Delta V = 2$) are set in (W) and (M), respectively, by the series $\sum \tilde{M}_{2,n}^{(W)}$ and $\sum \tilde{M}_{2+m,0}^{(M)}$. In the considered example, most interesting for us is the relation of the operators $\tilde{M}_{mn}^{(g)}$ with the initial molecular data:

$$\tilde{M}_{21} = M_{21} + i[S_{21}, M_{01}] + i[S_{30}, M_{11}], \quad (74)$$

$$\tilde{M}_{22}^{(W)} = i[S_{22}^{(W)}, M_{11}] + i[S_{31}^{(W)}, M_{11}] - i[S_{12}, M_{11}] + i[S_{30}, \tilde{M}_{12}] + i[S_{21}, M_{21}] - \frac{1}{2} [S_{21}, [S_{21}, M_{01}]], \quad (75)$$

where

$$\begin{aligned} \tilde{M}_{12} &= i[S_{12}, M_{01}] + i[S_{21}, M_{11}], \\ \tilde{M}_{22}^{(M)} &= i[S_{22}^{(M)}, M_{01}] + i[S_{31}^{(M)}, M_{11}] + i[S_{12}, M_{11}] + \\ &+ i[S_{21}, \tilde{M}_{21}] + \frac{1}{2} [S_{21}, [S_{21}, M_{01}]]. \end{aligned} \quad (76)$$

It is seen from these equations that the effective operator $\tilde{M}_{22}^{(g)}$ is a function of either \tilde{M}_{21} or \tilde{M}_{12} . Thus, in analysis of F -factors in intensities of the first overtones and combination tones we can use both the data obtained from the results of measurement of integral intensities (\tilde{M}_{21}) of these tones and the data on F -factors of fundamental bands.

In this section, we present the concept of Pade approximants in the theory of intensity as a part of the theory of linked schemes of ordering intramolecular and intermolecular interactions in multiatomic systems. As an example, we use the effective dipole moments for rotational transitions in the ground and excited isolated vibrational states. The operator of effective moment of rotational transitions in isolated vibrational state, in accordance with the results obtained in Sections 6 and 7, satisfies the equations

$$\begin{aligned} M(R) &= \langle \tilde{M} \rangle, \\ [M(R), H_{20}] &= 0 \end{aligned} \quad (77)$$

and can be expanded into a series

$$M(R) = M_{01} + \sum \tilde{M}_{0n} + \sum \tilde{M}_{2m,n}(R). \quad (78)$$

In the ordering scheme of ultrafast rotator (W), $\tilde{M}(R)$ is represented as the following ordered table:

$$\begin{array}{cccc}
 M_{01} & \tilde{M}_{03} & \tilde{M}_{05} & \dots \\
 \tilde{M}_{21}(R) & \tilde{M}_{22}(R) & \tilde{M}_{23}(R) & \dots \\
 \tilde{M}_{41}(R) & \tilde{M}_{42}(R) & \tilde{M}_{43}(R) & \dots \\
 \dots & \dots & \dots & \dots
 \end{array} \quad (79)$$

In the ordering scheme of overexcited oscillator (M), $\tilde{M}(R)$ is represented as the following ordered table:

$$\begin{array}{cccc}
 M_{01} & \tilde{M}_{21}(R) & \tilde{M}_{41}(R) & \dots \\
 \tilde{M}_{22}(R) & \tilde{M}_{42}(R) & \tilde{M}_{62}(R) & \dots \\
 \tilde{M}_{03} & \tilde{M}_{23}(R) & \tilde{M}_{43}(R) & \dots \\
 \dots & \dots & \dots & \dots
 \end{array} \quad (80)$$

There exists an infinite, but countable set of perturbation series for the effective operator of dipole moment. These series are connected with different schemes of ordering RV interactions in molecules. In this set, the cases (79) and (80) corresponding to the two limiting ordering schemes can be separated for the effective dipole moment of rotational transitions. The effective operator $\tilde{M}(R)$ in the limiting ordering schemes is determined by the following series:

$$\begin{aligned}
 \tilde{M}^{(W)}(R) &= \sum_n \{ \tilde{M}_{0n} + \tilde{M}_{2n}(R) + \tilde{M}_{4n}(R) + \dots \} = \\
 &= M_{01} + \tilde{M}_{03} + \dots \tilde{M}_{21} + \dots, \quad (81)
 \end{aligned}$$

$$\begin{aligned}
 \tilde{M}^{(M)}(R) &= \sum_{m=0}^{\infty} \{ \tilde{M}_{m1} + \tilde{M}_{m2}(R) + \tilde{M}_{m3}(R) + \dots \} = \\
 &= M_{01} + \tilde{M}_{21} + \dots \tilde{M}_{03} + \dots. \quad (82)
 \end{aligned}$$

For analysis of the series (81) and (82) of interest from the viewpoint of application of Pade approximants, it is convenient to introduce the generating series of the form

$$g = C_0 + C_1x + C_2x^2 + C_3x^3 + C_4x^4 + \dots \quad (83)$$

Pade approximants for this series are well-known and can be applied to the problem under study after some adaptation. The model (W) is characterized by the correspondence $M_{03} = C_2$, $\tilde{M}_{21}(R) = C_3$, ... , and the model (M) is characterized by the correspondence $\tilde{M}_{21}(R) = C_2$, $\tilde{M}_{03}(R) = C_3$, ... for the model operator of the effective dipole moment $\tilde{M}(R)$ consisting of three terms M_{01} , $\tilde{M}_{21}(R)$, and $\tilde{M}_{03}(R)$ in accordance with Eqs. (79) and (80).

As in the case of the effective operator of quadrupole bond for $\tilde{M}(R)$ in the ground and excited vibrational states,²² we have the following equations for the first diagonal Pade approximants in the limiting groupings. In the grouping (W) [model (I)], the diagonal Pade approximant for $\tilde{M}(R)$ has the form

$$M_{01} + \frac{(\tilde{M}_{03})^2}{\tilde{M}_{03} - \tilde{M}_{21}(R)}. \quad (84)$$

In the grouping (M) [model (II)], this approximant has the form

$$M_{01} + \frac{(\tilde{M}_{21}(R))^2}{\tilde{M}_{21}(R) - \tilde{M}_{03}}. \quad (85)$$

The equations for the operators $\tilde{M}_{21}(R)$ and $\tilde{M}_{03}(R)$ entering into Eqs. (84) and (85) of the Pade approximant through molecular constants have the form

$$\begin{aligned}
 \tilde{M}_{21}(R) &= \\
 &= \sum_{\gamma i} \left\{ \left(\frac{\partial^2 \mu_{\gamma}}{\partial q_i^2} \right)_e - \frac{1}{2} \sum_m \Phi_{ijm} \left(\frac{\partial \mu_{\gamma}}{\partial q_m} \right)_e \Delta_{ij} \right\} \lambda_{f\gamma}, \quad (86)
 \end{aligned}$$

$$\begin{aligned}
 \tilde{M}_{03}(R) &= \\
 &= \sum_{\alpha\beta\gamma} \sum_i \left\{ \left(\frac{\partial \mu_{\gamma}}{\partial q_i} \right)_e \frac{B_i^{\alpha\beta}}{\omega_i} - \sum_{\delta\epsilon} S_{\alpha\beta\delta}(\mu_e)_{\delta\epsilon} e_{\delta\epsilon\gamma} \right\} J_{\alpha J \beta} \lambda_{f\gamma}, \quad (87)
 \end{aligned}$$

where $\left(\frac{\partial \mu_{\gamma}}{\partial q_i} \right)_e$ and $\left(\frac{\partial^2 \mu_{\gamma}}{\partial q_i^2} \right)_e$ are the first and the second derivatives of the dipole moment over dimensionless normal coordinates, Φ_{ijm} are cubic anharmonic constants, ω_m are harmonic frequencies of vibrations, $(\mu_e)_{\gamma}$ are components of the equilibrium dipole moment, $B_m^{\alpha\beta}$ are rotational constants, $e_{\alpha\beta\gamma}$ is a unit antisymmetric tensor, $S_{\alpha\beta\gamma}$ are parameters of the reduction generator S_{03} , $\lambda_{f\gamma}$ are the directional cosines.

It should be noted that the Pade approximants (84) and (85) have meaning only for the selection rules, to which the operators $M_{21}(R)$ and $M_{03}(R)$ satisfy simultaneously. In particular, for symmetric-top molecules such selection rules for the projection of the total angular momentum onto the symmetry axis are the well-known selection rules $\Delta k = 0$ for allowed transitions.

The Pade approximants (84) and (85) are constructed of different rows (or columns) of the ordered tables (79) and (80). Let us analyze the models I and II based on the general estimates of the orders of magnitude of various parameters in the effective dipole moment operator

$$\tilde{M} = \tilde{\mu}\Lambda, \quad (88)$$

where Λ is the matrix of directional cosines;

$$\tilde{M} = \sum_{mn} \tilde{M}_{mn}; \quad (89)$$

and

$$\tilde{\mu} = \sum_{mn} \tilde{\mu}^{mn}. \quad (90)$$

The orders of magnitude of the effective dipole operators \tilde{M} and $\tilde{\mu}^{mn}$ are determined by the equations^{9,13}

$$\tilde{M}_{mn} \approx \chi^{m-2+2n} q^m J^{n-1} \Lambda(ea_0) \quad (91)$$

and

$$\tilde{\mu}^{mn} \approx \chi^{m+2n} q^m J^n \Lambda(ea_0). \quad (92)$$

From estimates (91) and (92) it follows that the model I in the version (84) has a singularity in units of J in the region $J_{cr} \approx \chi^2$ and does not represent the behavior of $\tilde{M}(R)$ in this region and the behavior of $M(R)$ at small J up to J_{cr} because of a singularity in denominator. The model II in the version (85) also is of no interest for low J up to J_{cr} as follows from the estimates (91) and (92), and it is some variant of the polynomial model $M_{01} + M_{21}(R)$ in this region.

It is important to note the following circumstance concerning the application of the method of Pade approximants to the effective dipole moment operator.

For $M^{eff} = \tilde{M}$, $\tilde{M}(R)$, in particular, is presented in the limiting groupings as an infinite series in terms of rotational or vibrational variables for any elementary excitation. These series, like the series (81) and (82) for $M(R)$, constructed by the perturbation method, must satisfy the conditions of applicability of the method of Pade approximants. Thus, this method can be applied to the sequences of rows in the models (W) (79) and (M) (80).

Application of the method of Pade approximants to effective centrifugal dipole moments of the highest orders for the methane molecule is considered in Ref. 26. Let us present the first diagonal Pade approximants describing the rotational and vibrational dependences of the equilibrium dipole moment:

$$(W) \quad M_{01} + \frac{(\tilde{M}_{03})^2}{M_{03} - M_{05}}, \quad (93)$$

$$(M) \quad M_{01} + \frac{(\tilde{M}_{21}(R))^2}{\tilde{M}_{21}(R) - \tilde{M}_{41}(R)}. \quad (94)$$

For Eqs. (93) and (94), as well as for the similar equations (84) and (85), the requirement of simultaneous correspondence of all effective dipole operators entering into Pade approximants to the same selection rules is valid.

Conclusion

This paper is devoted to physical principles and application of the theory of linked schemes of ordering rotational-vibrational perturbations in quasi-rigid

molecules. Only this theory allows the effective Hamiltonians and effective operators of observation to be presented as infinite series in terms of components of the rotational angular momentum for an elementary vibrational perturbation and vice versa. Expansion into infinite series is used everywhere in mathematical analysis of scientific problems. However, no attempts have been undertaken by now to apply methods improving convergence of convergent series and summation of divergent or weakly convergent series to solution of the problems of rotational-vibrational spectroscopy of multiatomic quasi-rigid molecules. This theory will be applied to solution of the direct and inverse spectroscopic problems for specific molecular systems.

Application of nonlinear transformations to the series, obtained by the perturbation method within the framework of the developed concept of linked schemes of ordering the rotational-vibrational interactions, significantly extends the list of spectroscopic models for analysis of IR and Raman molecular spectra, as well as vibrational and rotational dependences of physical parameters. Thus, this approach is beyond the scope of traditional polynomial models.

The experience accumulated in application of nonpolynomial models²⁹⁻³⁴ confirms the need in development of physical and mathematical principles of the theory of ordering series of intramolecular interactions.

The following problems have been solved in this work:

1. It is justified that the range of values of vibrational and rotational quantum numbers in the problem of selection of spectroscopic models, different from the Amat–Nielsen model, can be extended.

2. The problem of correspondence between the expansion of the formal and initial rotational-vibrational Hamiltonians of a quasi-rigid molecule is solved.

3. The limiting schemes of ordering of intramolecular interactions are introduced.

4. It is proved that the effective Hamiltonians for polyads of vibrational states depend on the ordering schemes.

5. The rules for determining the operator structure of reduction generators are obtained.

6. The effective Hamiltonians and the effective operators of observation are presented in the form including the separated contribution due to perturbation ordering; it is proved that this contribution vanishes in the approximation of the isolated vibrational state.

7. The unravel technique is applied to exponential operators when deriving equations for vibrational transformation generators (S -functions) in various ordering schemes.

8. The algorithm is developed for constructing effective dipole moments in the limiting schemes of ordering RV interactions.

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