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Current questions concerning the theory of highly excited vibrational states

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ABSTRACT. Certain current questions concerning the theory of highly excited vibrational states have been examined. The change in the form and the objectives of the theory as a function of increased energy of the system has been analysed. Much attention has focused on the role of classical concepts in regard to both the definition of the objectives and the formation of concepts and models used to interpret experimental data in the field of high-energy states. The concept of localised quantum states has been introduced. This concept plays a key role in the interpretation of many processes in which highly excited vibrational states are involved. The experimental consequences of the formation of localised quantum states in different physical situations are discussed. Examples examined include rearrangements of vibrational polyads, the appearance of periodic orbits in wave functions and in low resolution spectra, and bound states in continua.

The bibliography contains 208 references.

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There has been much interest in the properties of polyatomic molecules in highly excited vibrational states as a result of the progress made in fields such as high-resolution spectroscopy, multiquantum processes, intramolecular dynamics, and laser chemistry. The appearance of new experimental data has provided a great impetus for the development of new strategies and methods associated with the highly excited vibrational states theory, and the appearance of new theoretical concepts and ideas.

The vibrational spectra of polyatomic molecules rapidly become complex with increase in energy. This leads to a change in the method used to interpret the experimental material. Certain traditional questions lose their significance and are replaced by new questions which are of a qualitatively different type. In the present review some of these new questions will be examined, and most attention will be paid to the role of classical ideas and concepts of the local quantum states.

I. Characteristics of the theory of highly excited vibrational states in different regions of the spectrum

1. The low energy range. The vibrational spectra in this energy range consist of separate clearly resolved lines. They are individual for each molecule and are used often to identify molecules or functional groups. The objectives of the theory for this energy range are traditional and involve a study of the individual states and the transitions between them. The construction of appropriate dynamic models is the main strategy for their resolution. There is currently a large selection of such models. Models of normal[1] and local[2,3] vibrations are most popular for the description of vibrational states at lower energy. In addition to the traditional models there are so-called algebraic models in which a Hamiltonian is constructed directly from generators of a dynamic group of the symmetry postulated for the system studied. In recent years such models have been widely used in the study of vibrational spectra and intramolecular dynamics of small polyatomic molecules (see Refs. 4–14, and the references cited in these reports).

Using several different models an equally satisfactory quantitative description of a limited section of the spectrum may be obtained. The simultaneous use of these models is of profound physical significance, since each model generates its own specific language, its set of quantum numbers by means of which lines in the experimental spectra may be assigned and the selection rules for different transitions may be determined, etc. In this case the states which do not have good quantum numbers in one particular model may have them in another model. Thus by using different models a more profound understanding of the quantum states may be acquired.

2. The transitional range. With increase in energy the system enters the transitional range, which separates the low-energy state range from the quasicontinuum. In this range models designed to describe low-lying states begin to lose their efficiency which is reflected as a sharp increase in computing difficulties when they are used and by the appearance of states which do not have good quantum numbers in any of the integrated models. The latter problem is of fundamental importance and is associated with the characteristics of the vibrational dynamics of polyatomic molecules in the classical limit.[15–17]

A description of the vibrational spectra of polyatomic molecules is based on the model of coupled anharmonic oscillators. At low

energies the classical dynamics of such a system is for the most part regular. This implies that under virtually all initial conditions the phase trajectories of the system lie on the surfaces of the N-dimensional tori and in the $2N$-dimensional phase space. During motion along such trajectories the meaning of the N integrals of the motion calculated along specially selected close curves on the torus are preserved. Such regular trajectories may be quantised by one of the variants of the quasiclassical method. In this case states with particular quantum numbers N will correspond to them.

Apart from regular trajectories the system contains chaotic trajectories, which fill a certain $2N$-dimensional region of the phase space. With increase in the energy in the system the relative volume of the phase space filled by chaotic trajectories usually increases. There is currently no sequential method available to quantise such trajectories, while the states corresponding to the trajectories do not have motion integrals distinct from the energy.

The rapid increase in the density of the vibrational states with increase in energy is another difficulty encountered with the theory in the transitional energy range. However in this case the characteristic groups of levels such as the vibrational and rotational polyads are preserved. This leads to the possibility of defining new objectives associated with the investigation of the properties of the separate groups of levels and the change in these properties with change in the different motion integrals.

Initially such objectives were defined in the theory of rotational spectra of highly symmetrical molecules.[18–27] In the theory of vibrational spectra the definition of analogous objectives began with the discovery of local modes, special vibrational states which arise with increase in energy within molecules containing equivalent A–H(D) bonds, where A is a heavy atom (usually O, C or N) characterised by an extremely asymmetrical distribution of vibrational energy between the bonds (see Ref. 2 and 3 and the literature cited in these papers). A distinctive feature of the vibrational spectra of such molecules is the existence of vibrational polyads, independent characteristic groups of levels corresponding to the excitation of the A–H bonds. In this case the states with $\sum n_k = N$ enter the Nth vibrational polyad, where n_K is the number of vibrational quanta in the k-th mode, whereas the number of the vibrational polyad N is expressed as the total number of vibrational quanta and is an approximated motion integral.

The appearance of local modes from normal vibrations on excitation of the molecules is a typical phenomenon caused by the significant linearity of the molecular vibrations.[28–36] It is reflected as a qualitative change in the structure (rearrangement) of vibrational polyads with increase in N and is an example of a broad class of vibrational localisation processes with increase in energy.

The rearrangements of the vibrational polyads do not exhaust all qualitative changes in the relative position of the levels with increase in energy. More complex phenomena are also known in vibrational-rotational spectra such as the redistribution of levels between different groups of states (see Refs. 37, 38 and 39, and the references cited in these papers).

3. The quasicontinuum. A further increase in energy in the system leads to a transition to the quasicontinuum, a region with a discrete spectrum with a very large density of states in which, in contrast to the transitional range, certain isolated groups of states are absent. It has also been relatively recently suggested that quasicontinua are structureless and homogeneous and that the density of the states in the quasicontinua grows systematically with increase in energy, whereas the wavefunctions of the states in the quasicontinuum are delocalised throughout the entire configuration space of the molecule. In such a study the quasicontinua of different molecules are found to be essentially constructed in an identical manner and their only important characteristic is the density of the states and the rate at which this density increases with increase in energy, i.e. in the quasicontinuum range the states of the molecules lose their individuality to a significant extent. Such a concept of the quasicontinuum is consistent with the postulates of the statistical theory of chemical kinetics of the Rice–Ramsperger–Kassel–Marcus theory.[40]

The above model was found to be too simple for many objectives. Thus, it does not explain the presence of regular periodic structures in the low resolution spectra and does not take into consideration the existence of a large number of vibrational states with localised wavefunctions.

Experimental investigations into the quasicontinuum range may be conveniently divided into two major groups, i.e. experiments with high and low spectral resolution. The first group of experiments is characterised by very high resolution and provides information on the individual states. They may be carried out only for relatively simple systems. The spectra obtained in this case have an extremely complex and irregular profile. There is a very large amount of information in these spectra, and a significant change in the method used to interprete the spectra is required. With such a large amount of information it is difficult to study the properties of all states and from a certain standpoint the study would be meaningless. The most important task was to describe and study the properties of the entire combination of states in a complete selected range of energies.

The natural approach to resolve this objective is to study the statistical properties of the selected combination of energy levels and to construct models the statistical properties of which coincide with those of the group of levels studied. A change in the properties of the combination of states with increase in energy usually has regular and irregular components. Thus for example with increase in energy the density of the states in the spectrum increases which leads to a systematic decrease in the distances $\delta_i(E) = E_i - E_{i-1}$ between adjacent levels (the regular component). We are not interested in the $\delta_i(E)$ values themselves but their fluctuations relative to the curve describing the average behaviour of these values with increase in energy (irregular component). A study of the statistical properties of these types of fluctuation in the relative position of the energy levels and in the matrix elements of certain operators (for example transition probabilities) represents the content of the statistical theory of spectra initially developed to describe the spectra of complex nuclei and recently used to analyse spectra of atoms and molecules (see Refs. 41–45 and the literature cited in these reports).

However, when this theory is used, the question arises, with which physical properties of the system are given statistical characteristics of its spectrum associated? The answer to this question proved to be quite unexpected. A profound and nontrivial relationship was found to exist between the statistical properties of the spectrum and the nature of its dynamics in the classical limit. It was thus possible to introduce the concept of regular and chaotic spectra, which differ markedly with respect to their statistical properties, and then with increase in energy a smooth transition for the first to the second is observed. In this case the statistical properties of the chaotic spectrum are described by a Gaussian orthogonal ensemble model consisting of an ensemble of symmetrical actual matrices, the elements of the latter being Gaussian random values.

A lucid and exhaustive account of the statistical theory of spectra and its application to specific physical systems may be found in

review articles.[43,45–50] The review concerning the molecular application should be noted in particular.[45]

The rapid increase in the density of the states with increase in energy of the system leads to the appearance of a new item for study, low resolution spectra obtained either directly as a result of experiments with an insufficiently high resolution or by a corresponding coarsening of high resolution spectra. By studying such spectra it was found that they often possess a structure which cannot be explained by the statistical theory. Clear examples of such a structure are the systematic oscillations of the density of the states and the regular oscillations of intensity associated with them found in the corresponding broadening in the spectra of systems such as the H atom in a magnetic field,[51–54] the molecular ion H_3^+,[55] acetylene molecules,[56] Na_3,[57] O_3,[58] and HCN.[59]

The properties of the separate states are also of interest in studies of the quasicontinuum range. However in this case the theory focuses on the search for and study of a relatively small number of special states which in certain ways are differentiated from the homogeneous background which surrounds them. The most useful and general criterion for the separation of the states from the quasicontinuum is the extent of the localisation of their wavefunctions which could be explained in different ways. It was found that the possible existence of vibrational states with localised wavefunctions and their properties is to a significant extent determined by the structure of the phase space of the system under investigation. This interrelationship is most lucidly expressed by the existence of "scars" of periodic orbits, the localisation of wavefunctions of highly excited states in the vicinity of unstable periodic orbits in configurational or phase spaces.

One more new feature of the theory in the quasicontinuum range is the interest shown towards dynamic objectives arising here quite naturally. In fact as a consequence of the high density of the states in the quasicontinuum, a coherent excitation of a large number of states occurs simultaneously on excitation of the molecule, which leads to the formation of a nonstationary wavepacket. Such wavepackets are usually spread very rapidly. In this case initially the vibrational energy, which is localised in one or in a small number of modes, is redistributed rapidly between all accessible modes. However this situation may alter abruptly, if states with localised wavefunctions which partially stabilise the wavepacket form part of the wavepacket. Thus the localised vibrational states may serve as a basis for special, relatively stable dynamic modes during the intramolecular redistribution of energy.

4. The continuous spectrum. The continuous spectrum range is situated at an even higher energy. In this range the theory ultimately focuses on the study of the dynamics and special states, the resonances of which are typical representatives of localised quantum states. As an example we shall examine below the effect of excitation capture in the continuous spectrum during the decay of a coherently excited group of (quasi)degenerate states.

II. Localised vibrational states

In the high-energy range of the system the special states which in some way can be differentiated from the homogeneous background surrounding them are of greatest interest. In order to understand the nature of such states it is necessary first of all to understand which properties of the vibrational states are typical at high energies. With this objective it was useful to analyse the dynamics of the system studied in the classical limit. In systems of coupled anharmonic oscillators, which are normally used to model the dynamics of nuclei in molecules, a transition from regular to chaotic dynamics with increase in energy is typical. In this regard Percival proposed that such a position is preserved also in the quantum limit in a quasiclassical approximation,[60] i.e. regular and chaotic quantum states with markedly different properties should exist. In this case the chaotic states will be typical by virtue of the principle of congruence.

Three different strategies are currently used to determine the randomness of separate quantum states. These strategies are based on the study of the nature of wavefunction localisation in the phase space, in the configurational space, and in the basis function space. A detailed discussion of these three kinds of localisation in relation to their use to distinguish chaotic and regular quantum states has been published.[49,50,61–65]

1. Localisation in the phase space. The dynamics of an arbitrary quantum system may be described not only in the Hilbert space of quantum mechanics but also in the normal phase space. Let $\mathbf{q}$ and $\mathbf{p}$ be a combination of generalised coordinates and momenta of the system studied respectively. Then the arbitrary wavefunction $\psi(\mathbf{q})$ determined in configuration space can be compared with a certain function $\rho(\mathbf{q}, \mathbf{p})$ determined in phase space and termed the quantum function of the distribution. This may be achieved by different methods.[66–68] The most well known of these methods was proposed by Wigner and leads to the quantum function of the distribution in the form:

$$\rho_W(\mathbf{q}, \mathbf{p}) = h^{-N} \int \ldots \int dx_1 \ldots dx_N \, \Psi^*(\mathbf{q}+\mathbf{x}/2)\, \Psi(\mathbf{q}-\mathbf{x}/2)\, e^{-i\mathbf{p}\mathbf{x}/\hbar}. \quad (1)$$

The description of the quantum states using the Wigner distribution function (1) facilitates significantly a comparison of the properties and dynamics of classical and quantum systems. However, in this case one should bear in mind that the equation of motion for the Wigner function transforms into the equation of motion for the classical distribution function (the Liouville equation) only in the limit $\hbar \to 0$. This permits the isolation of purely quantum effects in the dynamic behaviour of the system.[69]

Moreover the Wigner function does not have definite values at all points of the phase space, i.e. it possesses none of the most important properties of the classical distribution function. This property was found to be quite common for the quantum distribution functions and is associated with the need to satisfy the quantum-mechanical Heisenberg uncertainty principle according to which it is not possible to define simultaneously accurate values of the coordinates and the momenta of particles. Therefore in quantum mechanics the concept of a point in the phase space has no special physical significance and in addition the requirement for a definite value of the distribution function at each point also becomes physically meaningless. The requirement for a definite value of the coarse-grained distribution function obtained on coarsening of the distribution function with respect to the small region of the phase space is more acceptable from the point of view of the physical meaning.

One of the best known examples of such an approximated coarse-grained distribution function is the Husimi distribution function $\rho_H(\mathbf{q}, \mathbf{p})$, [70] which may be calculated as the square of the modulus of the overlap integral of function $\psi(\mathbf{q})$ with the wavefunction of the

specific state $|\alpha(\mathbf{q}, \mathbf{p})>$ parametrised by the coordinates of the phase space. Gaussian functions centred at point $(\mathbf{q}, \mathbf{p})$ are normally used as functions $|\alpha(\mathbf{q}, \mathbf{p})>$. The distribution functions thus formed are apparently positive and finite in the entire phase space.

What is the appearance of the distribution functions of chaotic and regular quantum states? In order to answer this question it would be useful to study the properties of the quantum distribution functions in the classical limit. The classical limit for the Wigner distribution function has been best studied (see discussion and literature cited in Ref. 50). When $\hbar \to 0$ the Wigner coarse-grained function is localised in the regions which fill its corresponding trajectories when $t \to \infty$. This implies that, when $\hbar \to 0$ the Wigner coarse-grained function of the regular state is localised on the surface of the N-dimension torus, whereas the chaotic state tends towards a microcanonical distribution. A similar result is also valid for the Husimi distribution function.[71,72] It would be logical to suggest that such a position is also preserved at small but finite values of $\hbar$.

Thus one might expect that at high energies the typical wavefunctions will be those, which correspond to strongly delocalised and isotropic coarse-grained higher functions more or less constant over the entire accessible volume of the phase space. In this case special states will be characterised by nonisotropic coarse-grained Wigner functions localised in only a small part of the isoenergetic hypersurface, i.e. they will be localised quantum states.

2. Localisation in the configurational space. A second possible approach to the study of the localisation of quantum states would be an investigation into their wavefunctions in the configuration space. The first attempts to use this approach were based on a study of the main surfaces of the wavefunctions. However it was found that in the transition from inseparable integrated systems to nonintegrated systems the topology of the unit surfaces does not undergo a qualitative change and therefore cannot be used to differentiate reliably these two types of states (see discussion in Refs, 49 and 50).

The methods used to isolate the regular quantum states based on the analysis of different statistical properties of their wavefunctions were found to be more valuable. The concept of the wavefunctions of chaotic states and of the random functions of coordinates in which there is no correlation between the values at adjacent points forms the basis of all of these strategies. In this case adjacent points not too close to each other should be selected with the objective of levelling the effects caused by the continuity and normalisation of the wavefunctions.

One should note the following methods, which have been used most widely to study the statistical properties of wavefunctions.[49,50,73–76]

1. Calculation of the normal autocorrelation function

$$F_\delta(\Psi) = \int \ldots \int \Psi^*(\mathbf{q}) \Psi(\mathbf{q}+\delta) \mathrm{d}q_1 \ldots \mathrm{d}q_N, \qquad (2)$$

or its discrete variant

$$F_m(\Psi) = (1/M) \sum_{i=1}^{M} \Psi^*(\mathbf{q}_i) \Psi(\mathbf{q}_{i+m}), \quad m \leqslant M. \qquad (3)$$

In formula (3) the points $\mathbf{q}_i$ are taken as lying on the closed curve in the configuration space and satisfying the condition $\mathbf{q}_{i+M} = \mathbf{q}_i$. In this case the chaotic wavefunctions differ from the regular functions with values close to zero $F_\delta(\psi)$ and $F_m(\psi)$ for all $m \leqslant M$.

2. Calculation of the moments $I_m = \int \ldots \int |\psi(\mathbf{q})|^{2m} \mathrm{d}q_1 \ldots \mathrm{d}q_N$. In the quasiclassical limit $I_m \to \infty$ for regular states and they remain finite for chaotic states.

3. Calculation of informational entropy

$$S = -\int \ldots \int |\Psi(\mathbf{q})|^2 \ln(|\Psi(\mathbf{q})|^2/\rho_{\mathrm{ref}}) \mathrm{d}q_1 \ldots \mathrm{d}q_N, \qquad (4)$$

where ρ_{ref} is the reference density of the probability corresponding completely to an ergodic situation. In this case the value of S for delocalised wavefunctions should be markedly greater than that for the localised wavefunctions.

4. Calculation of the distribution function of the wavefunction values at randomly selected points. In this case the chaotic states should be characterised by a Gaussian distribution.

5. Calculation of the fractal dimensionality D of the density of the probability $|\psi(\mathbf{q})|^2$ determined by the relationship

$$\int \ldots \int |\Psi(\mathbf{q})|^2 |\Psi(\mathbf{q}+\mathbf{q}')|^2 \theta(Y) \mathrm{d}q_1 \ldots \mathrm{d}q_N \sim L^D, \qquad (5)$$

where $Y = L - |\mathbf{q} - \mathbf{q}'|$, and $\theta(Y)$ is the Heavyside function equal to unity when $Y < 0$ or to zero when $Y > 0$.

6. A method based on the study of the surfaces of the level of density probability $[\psi(\mathbf{q})]^2$ has been widely used recently to study wavefunctions in systems with two degrees of freedom. With this method it is possible to determine directly the nature of wavefunction localisation in the configuration space. However one should note that this method becomes significantly less representative in studies of systems where the number of degrees of freedom is greater than two.

When all above analytical methods are used, the concept of random and typical states at high energies is associated with the delocalised state, and with the irregularity and isotropicity of their wavefunctions in the configuration space. It can also be seen that in such an approach the states with localised wavefunctions are separate.

3. Spatial localisation of base functions. The idea of the extent of delocalisation of wavefunctions in space of the decomposition coefficients with respect to eigenfunctions of the integrated models as a criterion of the randomness of quantum states was proposed for the first time by Nordholm and Rice.[77] The main idea of the strategy of these authors is easy to understand, if one remembers that the chaotic trajectory in general has no good integrals of motion apart from energy. One might naturally suggest that this assertion remains true also for chaotic quantum states. However this implies that the wavefunctions of such states cannot have compact decompositions with respect to the eigenfunctions of any integrated model. Let H_0 be the Hamiltonian of one such model. Then it would be natural to associate the degree of randomness of the quantum state with the width of distribution of the decomposition coefficients $\{a_k\}$ of its wavefunction with respect to the eigenfunctions of the operator H_0. In this case the greater the number of coefficients $\{a_k\}$ which are markedly different from zero the more chaotic is the state examined.

The selection of parameters for the quantitative evaluation of the degree of randomness of the quantum state with respect to the set of coefficients $\{a_k\}$ by certain authors remained an open question.[77] It has been suggested that the ratio of the share $p = \sum p_n^2$ or entropy $S = -\sum p_n \ln p_n$, where $p_n = [a_n]^2$ should be used for such an evaluation.[49] In this regard one should note that the values p and S

have been used for a long time to determine the degree of randomness of intramolecular dynamics (see Refs. 78–82 and the references cited in these reports).

A simpler criterion has been studied according to which the quantum state is regular, if an integrated model exists which is such that among the decomposition coefficients of its wavefunction with respect to the basis functions of this model there is a coefficient greater than 0.5.[83–85] By satisfying this criterion it is possible to characterise unambiguously the studied state by a complete set of good quantum numbers and provides convergence of the Brillouin–Wigner theory of perturbations for its wavefunction and energy.[83–85]

The absence of a systematic method for the reassembly of all possible integrated models is a major limitation of the approach examined for the determination of chaotic quantum states. In this regard the earlier suggestion to use a basis of natural orbits for this purpose is of interest.[86] With this approach it should be possible to systemise the search for regular states using a fixed selection of variables. However this possibility has not been exploited on account of the variation in the variables themselves.

In this approach the states localised in the space of the basis functions of a certain integrated model are specific. Although such a determination of localised quantum states is also somewhat arbitrary, since it is dependent on the selection of the basis model, it is found to be very useful when the basis functions have clear physical meaning.

III. Localisation in the vicinity of stable equilibrium positions: a qualitative theory of vibrational polyads and their rearrangements

We shall examine the molecule having M (quasi)degenerate vibrations, the frequencies of which differ markedly from the frequencies of the remaining vibrations. The local vibrations of CH bonds in organic compounds, symmetrical and antisymmetrical normal vibrations in type ABA nonlinear molecules with a heavy central atom, and many others are typical examples. The existence of vibrational polyads is a characteristic feature of the vibrational spectra of such molecules. For simplification we shall discuss the main ideas as an example the vibrational polyads formed by two vibrations. The three types of currently known polyads are illustrated in Fig. 1.

The type *a* so-called normal vibrational polyads correspond to the model of uncoupled harmonic oscillators with slightly different frequencies. The type *c* so-called local vibrational polyads are very satisfactorily described by the model of two identical uncoupled anharmonic oscillators. The type *b* vibrational polyads are mixed, their upper and lower parts corresponding to the model of normal and local vibrations respectively. In certain cases with increase in energy there is a rearrangement of the vibrational polyad-transition from polyad type *a* to polyads types *b* and *c*.

There are at present several approaches for explaining this qualitative phenomenon. One should note the strategies based on the analysis of classical trajectories,[28,29] and also later and accurate methods based on the construction and study of effective algebraic Hamiltonians for separate vibrational polyads.[30–36] We shall use as a basis a strategy developed in previous studies.[30–36] This approach not only provides a simple graphic relationship between the rearrangements of the vibrational polyads and the characteristics of the dynamics of the system under investigation in the classical limit but also permits the description of all possible simplest types of polyad and their rearrangements.

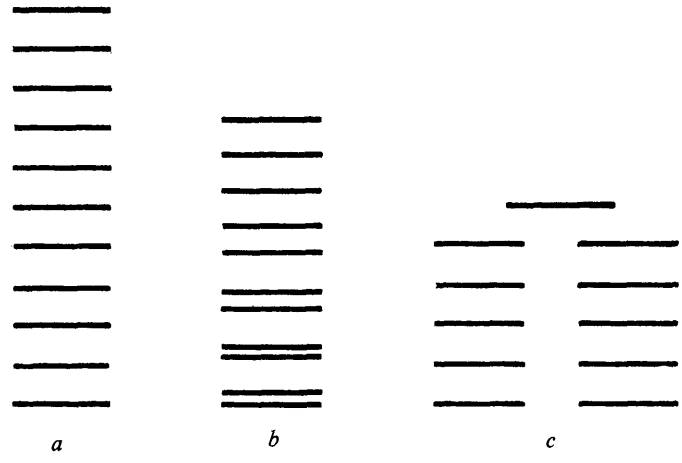


Figure 1. Types of vibrational polyads formed by two vibrations: *a*, normal; *b*, mixed; *c*, local.

We shall assume that the different vibrational polyads interact weakly with each other (N is an approximate integral of motion) and that the structure of the vibrational polyads is not perturbed by the resonance interaction with other molecular vibrations. With these assumptions the relative position of the energy levels in the N-th vibrational polyad may be described by an effective vibrational Hamiltonian $H_{\text{eff}}(N)$ parametrically dependent on N. Further analysis rests on the close relationship between the properties of the quantum system and its behaviour in the classical limit. We shall use this relationship to find a classical analogue of the quantum phenomenon studied here. This may be obtained schematically as a result of the following sequence of steps:

1) construction of the algebraic effective vibrational Hamiltonian $H_{\text{eff}}(N)$ describing the relative position of the energy levels in the N-th vibrational polyad,

2) transition to the classical limit; construction of the corresponding phase space and the Hamiltonian function H_{kl},

3) a study of the system of stationary points of the H_{kl} function and its rearrangements with increase in N.

As a simple example we shall examine the spectrum of stretching vibrations of the ABA molecule which in the formalism of the local vibrations is described approximately by the Hamiltonian

$$H/\hbar\omega = 0.5(P_1^2+Q_1^2+P_2^2+Q_2^2)+AP_1P_2+BQ_1Q_2+C(Q_1^3+Q_2^3)+ +DQ_1Q_2(Q_1+Q_2)+E(Q_1^4+Q_2^4)+FQ_1Q_2(Q_1^2+Q_2^2)+CQ_1^2Q_2^2, \quad (6)$$

where Q_k and P_k are normal dimensionless coordinates and momenta and the constants $A-G$ are dimensionless parameters of the model. If all constants $A-G$ are much less than unity, the energy levels of operator H_{eff} will be grouped into polyads. We shall now apply the above described analytical scheme to the Hamiltonian (6).

1. Construction of an effective vibrational Hamiltonian. We shall rewrite the vibrational Hamiltonian (6) using the creation-destruction vibrational operators a_k and a_k^+, where $a_k = (Q_k + iP_k)/2^{1/2}$, ($k$ = 1, 2) and we shall use the standard technique of canonical transformations for reducing it to an even form.[87]

Being limited for simplicity only by the first non-disappearing contributions from all terms introduced into the Hamiltonian (6) we obtain:[32,33]

$$H_{\text{eff}}/\hbar\omega = H_0 + [\alpha_1 + \alpha_2(J+0.5)]J_x + \gamma J_x^2 + \delta J_z^2, \quad (7)$$

where J_x and J_z are the pseudomomentum operators determined using the creation-destruction vibrational operators as

$$J_x = (a_1^+a_2 + a_2^+a_1)/2, \quad J_z = (a_1^+a_1 - a_2^+a_2)/2, \quad (8)$$

while parameters α_1, α_2, γ and δ are expressed by the known method through the constants $A-G$. All terms which are constant within the vibrational polyad are introduced into H_0. The operator J = 0.5 $(a_1^+a_1 + a_2^+a_2)$ is associated with the number of the vibrational polyad with a ratio of $N = 2J$ and is the motion integral.

The method described for constructing an effective vibrational Hamiltonian is far from being the only method. Moreover it is often more expedient to regard the Hamiltonian (7) as purely phenomenological and to determine the parameters contained in it from the experiment as in the case of algebraic models.

2. The classical limit. The construction of the classical limit for the quantum system is generally quite a complex operation resting on the theory of generalised coherent states.[88,89] In our case this operation is markedly simplified and amounts to a trivial replacement of the pseudomomentum operators by their quasi-classical expressions

$$J_x = L\cos\varphi\sin\vartheta, \quad J_z = L\cos\vartheta, \quad L = J + 1/2, \quad (9)$$

where L is the length of the pseudomomentum vector. Since the value l is conserved during motion, the phase space is a normal two-dimensional sphere. By omitting the term H_0 which is insignificant in our case we finally obtain the following expression for the function H_{kl}:

$$H_{kl} = (\alpha_1 + \alpha_2 L)L\cos\varphi\sin\vartheta + \gamma L^2\cos^2\varphi\sin^2\vartheta + \delta L^2\cos^2\vartheta. \quad (10)$$

3. Qualitative analysis. We shall study the behaviour of stationary points of function H_{kl} on change in N. They are important because closed closely localised trajectories are associated with the stationary points of the minimum or maximum type. Under certain conditions regular sequences of localised quantum states correspond to these trajectories. Thus from a study of the stationary points of the function H_{kl} it is possible to study the possible types of localised quantum states and their change on excitation.

We shall restrict ourselves to an examination of only Hamiltonians of a common form, when no additional limitations apart from those caused by the symmetry of the system were applied to the parameters. The stationary points of the Hamiltonian function (10) and their corresponding total energy values are presented in Table 1, and their behaviour with increase in L is schematically illustrated in Fig. 2. It is apparent from Table 1 and Fig. 2 that at low L values corresponding to the real excitation of the system the function H_{kl} has only two nondegenerate stationary points a and b, one of which is the maximum, the other being the minimum. With increase in energy such a position is preserved whilst L does not exceed a certain critical value $L\P$. When $L > L\P$, the dynamics of the model studied undergo a qualitative change, which is reflected as a change in the number and nature of the stationary points of function H_{kl}. The values of parameter L at which this occurs are called bifurcational, and the process itself is a bifurcation. The diagrams similar to that shown in Fig. 2 in which changes in the system of stationary points of the function are depicted on change in its parameters are called bifurcational diagrams and provide a convenient method for describing systems in which certain qualitative changes may arise when the parameters are continuously changing.

Table 1. Coordinates, energies and conditions for the existence of stationary points (SP) of the function H_{kl}.[33]

SP	φ	ϑ	Energy	Conditions for the existence
a	0	$\pi/2$	$E_a = \alpha L + \gamma L^2$	at all L
b	π	$\pi/2$	$E_b = -\alpha L + \gamma L^2$	at all L
$c_{1,2}$	$\pi[1 - \text{sgn}(r_1)]/2$	$\pm\arcsin\lvert r_1\rvert$	$E_{c_1} = E_{c_2} = \delta L^2 + \alpha^2/4(\delta - \gamma)$	$\lvert r_1\rvert < 1$
$d_{1,2}$	$\pm\arccos\lvert r_2\rvert$	$\pi/2$	$E_{d_1} = E_{d_2} = -\alpha^2/4\gamma$	$\lvert r_2\rvert < 1$

Notations: $\alpha = \alpha_1 + \alpha_2 L$, $r_1 = (\alpha_1 + \alpha_2 L)/2L(\delta - \gamma)$, $r_2 = -(\alpha_1 + \alpha_2 L)/2L\gamma$.

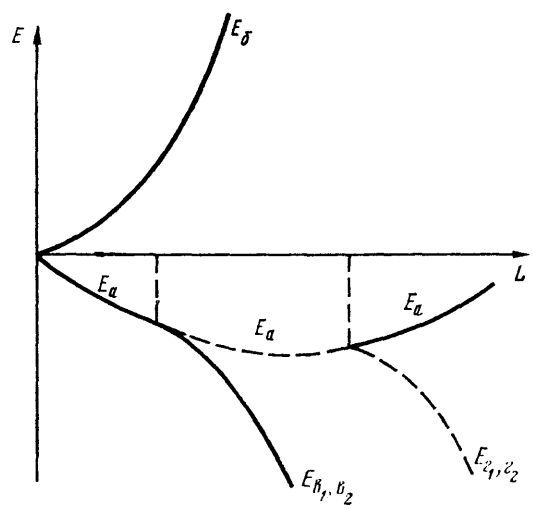


Figure 2. Bifurcational diagram describing the changes with increase in energy of the system of stationary points of the Hamiltonian function (10) for the case of the H_2O molecule.[30]

The system of two harmonic oscillators associated with quadratic potential and kinetic interactions is the simplest system described by the Hamiltonian (6). This system is described by a Hamilton function (10) with $\gamma = \delta = 0$ and is equivalent to two non-interacting harmonic oscillators with slightly different wavenumbers.

Its spectrum is a polyad structure with polyads of a purely normal type, and their structure does not alter with increase in energy. It is apparent from Table 1 that in the case examined with function H_{kl} there are only two non-degenerate stationary points *a* and *b* for all values of *L*. This implies that in the above model the upper and lower parts of the vibrational polyads are constructed from regular sequences of the non-degenerate energy levels which is in total agreement with the results of accurate quantum-mechanics calculations.

We shall now consider the anharmonicity of oscillators which corresponds to the selection of a nontrivial value of coefficient δ. Analysis of the stationary points shows that when $L = L\P = [\alpha_1/2\delta]$ bifurcation occurs in the system. When $L < L\P$ the function H_{kl} has two non-degenerate stationary points *a* and *b*. As in the previous example the vibrational polyads are of the normal type. When $L > L\P$ one of the stationary points is split into two degenerate stationary points of the same type as the point of their origin, and one saddle point. The appearance of two degenerate stable stationary points leads to the formation of a regular sequence of double degenerate energy levels in the vibrational polyads. In this case that end of the vibrational polyads at which the double degenerate energy levels appeared will be better described by a local vibration model, whereas the other end of the polyad will continue to correspond to the normal vibration model.

We shall examine the question of what is the physical nature of the double degenerate localised quantum states arising as a result of the bifurcation. With increase in energy let the distances between the adjacent energy levels of the initial oscillators decrease systematically, which is a typical situation in molecular problems. In this case the double degenerate localised quantum states are formed in the lower part of the vibrational polyads, and the states themselves correspond to vibrations with an extremely asymmetrical energy distribution between the oscillators, i.e. they are well studied local modes.[2,3]

Thus the qualitative analysis of the function H_{kl} gives a simple and clear picture of the formation of local modes from normal vibrations on excitation. It shows that the formation of local modes with increase in energy is a typical phenomenon and is not dependent on the specific values of the Hamiltonian parameters. However one should note that the experimental observation of rearrangements associated with this process in the specific molecules may be made difficult by too great or small values of $L\P$.

Within the framework of the approach examined there are no significant differences between normal and local vibrations. Both are examples of localised quantum states with wavefunctions localised close to the stable stationary points of function H_{kl}. Thus the states described above are a natural generalisation of local and normal vibrations.

Two new effects appear when all coefficients of the effective vibrational Hamiltonian differ from zero: 1) a new type of localised quantum states corresponding to stationary points *d* may arise, and 2) localised quantum states existing only in a limited energy range may appear.

The results obtained from the use of a qualitative approach to the analysis of experimental spectra of stretching vibrations in H_2O, SO_2, and O_3 molecules and vibrations of the CH and CD bonds in C_2H_2 and C_2D_2 molecules taken from literature data are presented in Table 2.[33]

The small values of $L\P$ for C_2H_2 and H_2O molecules are in good agreement with the fact that the vibrational polyads in these molecules have a clearly expressed local nature beginning from the lowest part itself. The vibrational polyads in the C_2D_2 and SO_2 molecules belong to the normal type, which is also in good agreement with the $L\P$ values for these molecules. The ozone molecule spectrum is of greatest interest. Using this as an example it is possible to follow the transition from vibrational polyads of a normal type at low *N* values to the mixed type of vibrational polyads when $N \geqslant 3$. It should be emphasised that the accuracy of the results obtained from the qualitative analysis increases with increase in *N*. At low *N* values one can expect that they agree only qualitatively with the experimental data. In this case the vibrational polyad rearrangements predictable by the theory are more sharply manifested the greater is the value of *N*. Taking into account the comments made the results obtained from analysis of the experimental spectrum presented in Table 2 should be recognised as being unexpectedly good.

Table 2. Analysis of the bifurcations of effective vibrational Hamiltonians of certain molecules.[33]

Molecule	Region of existence of stationary points	
	c	d
H_2O	$L>0.4$	$5.9<L<36.5$
SO_2	$L>6.5$	$L>13.7$
O_3	$L>0.6$	$L>10.8$
C_2H_2	$L>0.4$	Absent
C_2D_2	$L>3.2$	$L>22.8$

The transition from the normal to the mixed polyads in the model spectrum of molecule C_2D_2 may serve as a classical example of the rearrangement of vibrational polyads. A sufficiently large value of $L\P$ corresponding to $N = 6$ leads to a clearly pronounced sharp transition.

Thus we have achieved the objective set at the beginning of this chapter and have found a classical analogue of the quantum rearrangement. We have shown that bifurcations of the Hamilton function, expressed as a change in the number and nature of its extremal points, correspond to rearrangements of the vibrational polyads.

Qualitative changes in the Hamilton function with increase in energy lead to qualitative changes in the phase picture of the system studied and hence to a change in possible forms of its dynamic behaviour. Of great interest in this regard are earlier studies in which a strategy is developed which in the case of two vibrations allows phase pictures of vibrational polyads to be constructed from experimental spectra.[90–94]

In concluding the discussion of the qualitative theory of vibrational polyads and their rearrangements one should note the work in which all kinds of typical elementary rearrangements of vibrational polyads are found in a system of two associated anharmonic oscillators,[33] and a study in which a generalisation of the theory to the case of an arbitrary number of vibrations is presented.[95]

IV. Localisation in the vicinity of isolated periodic orbits: "Scars" of the periodic orbits in the wavefunctions and low resolution spectra

In the systems of interest to us a transition from regular to chaotic dynamics is typical with increase in energy. In this case the volume of the phase space filled by regular trajectories approaches zero. However even in the region of totally chaotic dynamics in the phase space a large number of isolated and unstable periodic orbits is preserved. Since the extent of the volume of the phase space occupied by them is equal to zero, it would appear that they should not appear as quantum properties. In fact the unstable periodic orbits are not only markedly reflected in the quantum properties but also determine them to a significant extent especially at high energies.

The first theory associating the properties of isolated periodic orbits with the quantum characteristics of the system was developed mainly in the work by Gutzwiller, Balian, and Bloch. A good review of this theory and a comparatively comprehensive list of early studies may be found in the literature.[96] The central result of this theory is the formula:

$$n(E)=\bar{n}(E)+\sum_r\sum_j a_{rj}(E)\cos\{j[S_r(E)-\mu_r]\}, \qquad (11)$$

linking the quasiclassical density of states $n(E)$ with the characteristics of isolated periodic orbits. Here $\bar{n}(E)$ is the average density of the Thomas–Fermi states which can be determined by the volume of the phase space enclosed within the isoenergetic surface with energy E, the index r denotes different primitive periodic orbits, the sum with respect to j takes into account the contribution from a multiple inversion at the primitive periodic orbits, while S_r and μ_r represent the action and the index of Maslov for the r-th primitive periodic orbit. It is important to understand that formula (11) establishes the conformity not between individual periodic orbits and quantum states but between the entire spectrum of the system and the combination of all of its periodic orbits in the classical limit.

In recent years attempts have been made to use the formula (11) to calculate quasiclassical spectra of a number of simple model systems both in the regular and chaotic regions. Of the more successful applications one should note that it has been used to resolve the problem described by Kepler[97] regarding the quantisation of free particle motion on a pseudosphere,[98] and in different billiards,[99,100] and the calculation of the H atom spectrum in a magnetic field.[101–105] The generalisation of this formula by introducing into it the contributions from classically forbidden complex periodic orbits, which enable the tunnel distributions to be calculated,[106–109] is of significant interest.

A more general application of the formula (11) for calculating the spectra encounters certain difficulties. The most serious of these problems is the absence of sufficiently general and effective methods to search for all periodic orbits in a chosen energy region, the exponential growth in the number of isolated periodic orbits with increase in their period and the very slow convergence of the series (11). Nevertheless the method based on its use is at present the only sequential approach to the quasiclassical calculation of the spectrum in the field of chaotic dynamics.

In formula (11) contributions remain only from the periodic orbits with periods less than the somewhat fixed time T, although it gives a value $n(E)$ obtained in experiments with a fixed resolution $\Delta E = h/T$ with respect to energy. An interesting consequence of such a rough approximation assuming experimental verification is the confirmation that the quasiclassical density of the states is a multiperiodic energy function and that its oscillation periods are determined by periods of motion with respect to the periodic orbits. Such oscillations of the state densities were in fact observed in spectra of a number of simple systems.[51–59] One should note that the existence of the narrow resolution of different structures in the spectrum indicates that at high energies in the system studied regions of quasiregular motion occur against a background of largely chaotic dynamics.

Low resolution spectra: the dynamic theory. If unstable isolated periodic orbits play such an important role in the formation of chaotic spectra, the question arises as to whether it is possible to obtain information on dynamically existing periodic orbits directly from the spectra, and if so, how? The natural answer to this question is provided by the dynamic theory of spectra,[110,111] which we shall illustrate by the example of the electronic emission spectra.

The process of electron excitation of molecules is often regarded as an instantaneous Franck-Condon transfer of the wave function Φ of the principal vibrational level of the original electronic state into a certain ultimate electronic state in which Φ is already a wave packet describing a nonstationary state. The emission spectrum from this nonstationary state contains information on the dynamics of energy redistribution between different degrees of freedom of the molecule.

The principal idea of the dynamic theory of the spectra resides in the transfer of information within the spectrum from the energy language to the temporal language by calculation of the correlation function $C(t) = <\Phi|\Phi(t)>$. In our case the link between $C(t)$ and the spectrum of infinitely high resolution has the form:

$$S(E)=(1/2\pi)\lim_{T\to\infty}\int_{-T}^{T} C(t)\exp(iEt/\hbar)\,dt, \qquad (12)$$

from where it follows that the information provided by the spectrum of infinitely high resolution is equivalent to that provided by the dynamics of the system studied over an infinitely long period. At high energies it is usually impossible to obtain spectra in which all lines have been totally resolved. Instead spectra with broad spectral contours with a more or less clearly pronounced vibrational structure are obtained. From the dynamic standpoint this implies that such spectra contain information on the dynamics of the system only over a certain final time interval, T. The corresponding spectral contour $S_T(E)$ is given by the formula:

$$S_T(E)=(1/2\pi)\int_{-T}^{T} C(t)\exp(iEt/\hbar)\,dt. \qquad (13)$$

We shall examine the excitation process in which the centre of the Gaussian wave packet, which corresponds to the wave function of the principal vibrational level of the lower electronic state, encounters one of the periodic orbits. The dynamics of the Gaussian wave packets in smooth potentials have been studied in considerable detail.[112] In our case the centre of the packet will move along the periodic orbit, while the packet itself will gradually spread more rapidly the more stable is the periodic orbit. In this case the function $|C(t)|$ will have the characteristics of damped vibrations. Its maxima are associated with the reversions of the wave packet to the starting point, whereas the systematic decrease in their height was caused by the spreading of the packet. Thus each dynamically significant periodic orbit generates in the correlation function a series

of equidistant maxima, their separations being equal to the transformation period along this periodic orbit.

The analysis shows that, in contrast to the high resolution spectra, the low resolution spectra in the chaotic region contain information not on individual states of the quantum system but on the dynamically significant isolated periodic orbits. Therefore it is possible to use the low resolution spectra to study the intramolecular redistribution of vibrational energy in the quasicontinuum.

Another approach to explain the appearance of isolated unstable periodic orbits in the low resolution spectra which is close in principle to the Feshbaich theory of resonances has been developed by other authors.[113–115]

The above-mentioned analytical scheme for the low resolution spectra based on the extraction of information on periodic orbits which they contain has been successfully used to interpret the spectra of the H atom in a magnetic field,[52–54,101–105,113–118] the molecular ion H_3^+,[115–121] Na_3,[116,122,123] O_3,[124,125] CO_2,[126] and HCN[127–129] molecules.

Another interesting manifestation of unstable periodic orbits in the properties of quantum systems was found by Heller in a study of wavefunctions of highly excited states of the quantum billiard "Stadium" consisting of two hemispheres connected by segments of straight lines.[130–132] The classical limit "Stadium" is an example of a totally chaotic system at all levels. Therefore one would expect that in accordance with the quasiclassical analysis and the principle of concordance its wavefunctions will be strongly delocalised. The real position was found to be much more interesting. Analysis of the surfaces of the level of the function $[\Psi_k]^2$ showed that the wavefunctions of many excited states clearly have a tendency to be localised close to the periodic orbits. Heller named this effect as the scars of the periodic orbits in the wavefunctions. Such scars were subsequently found also in other systems including those with smooth potentials.[133] The theoretical basis of this effect from different standpoints may be found in earlier reports.[131,134–137] However the scars of the periodic orbits in the configurational space have not been widely studied. Study of the scars in the phase space with the aid of the quantum cross sections by Poincare for the distribution functions of Wigner[138] or Husimi[139] was found to be markedly more fruitful. Both of these approaches have been compared,[137,140] and it was concluded that the use of the Husimi distribution function was preferable.

Thus the unstable periodic orbitals separate certain special states in the chaotic region which are typical representatives of localised quantum states with the wavefunctions localised in the vicinities of these orbits. From the extent of the localisation of wavefunctions of such states it is possible to develop effective methods for their calculation. As an example one should note the variation method as the basis of Gaussian wavefunctions with the adjacent centres and in the corresponding periodic orbit[113–115,119,141,142] analogous to the stabilisation method used in the calculation of the positions of the resonances and which allows information to be obtained on the class of localised quantum states of interest to us without calculating all lower-lying states.

Another effective approach to the study of localised quantum states under discussion is the use of the adiabatic approximation for separating slow motion along a periodic orbital and rapid vibrations perpendicular to the orbit.[117,133] Such a separation operates more efficiently the less unstable is the corresponding periodic orbit, i.e. the longer the trajectory which will stay in the vicinity of its origin. It was found that only adiabatically stable, attracting periodic orbitals, which possess the same property, lead to scars, and that any trajectory having started in the vicinity of such an orbit, before vacating it will certainly intersect the projection of the periodic orbit on to the configurational space.[133,143] One should note that adiabatically stable periodic orbits may be totally unstable in the Lyapunov sense.

One should also note the method of calculation based on the quasiclassical quantisation of unstable periodic orbits[144,145] which is successfully used to explain the low resolution spectra of the H_3^+ ion.[121]

Nonlinear normal vibrations at which all generalised coordinates at any time period are proportional to one of them and which in the small energy limit is reduced to the usual normal vibrations[146–149] are the most simple periodic motions in nonlinear mechanical systems permitting systematic study. The number of nonlinear normal vibrations is dependent not only on the number of degrees of freedom in the system studied but also on its symmetry. Thus with the CH_4 molecule the number of linear and nonlinear normal vibrations is equal to 9 and 63 respectively.[147]

From a sequential study of the evolution and bifurcation of the system of nonlinear normal vibrations with increase in energy, it is possible to find all periodic orbits of the system originating from the normal linear vibrations. Such periodic orbits and the quantum states localised near them are termed regular orbits.[150] In addition to them irregular periodic orbits may exist in the system which are genetically unassociated with any of the linear normal vibrations. Irregular periodic orbits are of significant interest, since the localised quantum states, the properties of which cardinally differ from those of the localised quantum states associated with the regular periodic orbits, correspond to them.

In recent years it has become more evident that "scars" of periodic orbits in the wavefunctions are only the most simple example of a broad class of effects, which could have been determined as the manifestation of different elements of the phase picture of the system (the structure of the phase space) in its quantum properties. Apart from the above-mentioned, scars from such elements of the phase picture as families of unstable periodic orbits,[115–121,151–153] resistant and nonresistant invariant varieties of periodic orbits,[152,153,160] invariant tori, the dimensionality of which is less than the number of corresponding degrees of freedom,[122–123] homo- and heterocyclic structures,[154,155] and separatrix varieties (see Refs. 152, 155–157, 140 and literature cited in these articles) and cantori (see Refs. 158, 159, 140 and the literature cited in these articles) have so far been observed in the wavefunctions. In particular one should note the manifestations of the cantori, the noteable "bottlenecks" playing an important role in the intramolecular redistribution of energy.

V. Spatial localisation of the basis functions: bound states in a continuous spectrum

As a clear example illustrating the effectiveness of studying the localisation of quantum states in the space of the basis functions we shall discuss the effect of excitation capture in the continuous spectrum caused by the existence of quasibound states in a continuum. In its mathematical form this effect is analogous to such widely known quantum-optical effects as superradiant radiation in a system of identical double-level systems (the Dikke model)[161] and the coherent capture of the occupancies in the N-level systems containing metastable states or interacting with a certain continuum in the presence of intense multimodal laser radiation (see Refs. 162–187

and the literature cited in these articles). In contrast to quantum optics the effect of excitation capture in the theory of nonradiative intramolecular transitions has been studied in considerably less detail,[201,202] although the basic principle that bound states exist in a continuum was substantiated quite a long time ago.[188–191] Such a position is associated with the fact that in the objectives of intramolecular dynamics there are no natural controlling parameters analogous to the intensity of irradiation and to the frequency difference of the resonance in quantum optics, which could have been changed as desired and continuously in order to satisfy the conditions essential for the expression of the effect under discussion.

(Quasi)stationary states in the continuous spectrum may also arise during the decay of quantum systems in stable outer fields.[192–196] In this case the outer field strength plays the role of the continuous controlling parameter. A good example of such an effect is the narrowing of the autoionisation widths of the Rydberg states in the regions of their quasi-intersections which arises as a result of the destructive interference between different decay channels (see Refs. 194–196 and the references cited in these papers).

In a recent series of studies the possibility that (quasi)bound states of a purely intramolecular nature could exist in a continuum was demonstrated. Such states naturally arise during the decay of a coherently excited group of discrete (quasi)degenerate levels interacting with one or several continua. An analogous effect may also arise during the interaction of several continua.[203,204] In a discussion of the theory of this effect we will not give a concrete definition of the physical nature of the discrete states and the continuum; this enables us to obtain results applicable to a very broad range of processes.

We shall examine N degenerate discrete states interacting with a single continuum by means of potential V. We shall assume that the wavefunctions of the discrete states $\{\varphi_k,\ k = 1, \ldots, N\}$ and the continuum φ_E were selected as actual, whereas the interaction V has matrix elements differing from zero only between the states of the discrete and continuous spectra ($V_{kn} = V_{EE'} = 0$, $V_{ke} = 0$) and the matrix elements are not dependent on E. Such assumptions are normal in the theory of nonradiative transitions.[205]

In a description of the decays it is convenient from the start to exclude from examination the states of the continuous spectrum. One of the simplest ways of achieving this is to construct an effective Hamiltonian acting in the subspace of discrete states and implicitly taking into account their interaction with the states of the continuum. Such an effective Hamiltonian may usually be reduced to the form:

$$H=H_0-i\alpha W, \tag{14}$$

where H_0 is the unperturbed Hamiltonian describing the discrete states in the absence of a continuum, W is the effective potential describing their interaction with each other by means of the continuum, while $\alpha > 0$ is a certain parameter characterising the intensity of this interaction. In our case the operators H_0 and W are actual symmetrical matrices with a dimensionality of $N \times N$, and the matrix W was positively determined.

We shall examine the decay of the N-fold degenerate level within the generalised Weisskopf–Wigner formalism.[206,207] Let only the discrete states be coherently excited at the initial moment of time,

$$\Phi(0)=\sum a_k(0)\varphi_k, \tag{15}$$

which corresponds to the situation realised in different physical experiments. The variation in the amplitude vector $\mathbf{a}(t)$ as a function of time is determined by the equation

$$i\dot{\mathbf{a}}(t)=\mathrm{H}\mathbf{a}(t), \tag{16}$$

where the matrix elements of the effective Hamiltonian have the form

$$H_{kn}=-i\alpha\gamma_{kn},\quad \gamma_{kn}=(\gamma_k\gamma_n)^{1/2},\quad \gamma_k=\pi V_{kE}V_{Ek}>0. \tag{17}$$

Here we have used the atomic system of units ($\hbar = 1$) and have set the energy of the degenerate level = 2 and introduced the designation γk for the initial halfwidth characterising the decay rate of the k-th state in the absence of other states. The dynamics of our system is most simply described on the basis of the wavefunctions of the effective states, which are eigenfunctions of operator H. The eigenvalues $\lambda_n = E_n - iG_n$ correspond to them, where E_n determines the position, and G_n determines the halfwidth of the n-th effective state. In our case the spectrum of the matrix h has a very simple form:

$$\lambda_1=\mathrm{Tr}(H)=-i\alpha\sum\gamma_k,\qquad \lambda_2=\ldots=\lambda_N=0. \tag{18}$$

A number of important physical corollaries result from formula (18).

1. The interaction between the degenerate states via the continuum does not reduce their degeneracy.

2. As a result of such an interaction the $N-1$ bound state and only one unbound state with halfwidth G_1 and wavefunction Ψ_1 which were predetermined by the expressions are formed:

$$\Gamma_1=|\mathrm{Tr}(H)|=\alpha\sum\gamma_k,\qquad \Psi_1=\sum(\alpha\gamma_k/\Gamma_1)^{1/2}\varphi_k. \tag{19}$$

Thus we arrive at a very surprising result, i.e. interference between different decay pathways of a coherently excited system of degenerate states each of which in the absence of the other states would have decayed at its own particular rate determined by the halfwidth leads to a situation in which only one rapid channel of decay remains. All remaining decay routes are found to be closed. the effect under discussion is universal and is not dependent either on the number of states in the group or on the magnitude of the halfwidth γk.

3. The probability that the system examined will remain coupled up to the time moment t is given by the equation

$$P(t)=A\exp(-2\Gamma_1 t)+B, \tag{20}$$

where

$$A=\left[\sum(\alpha\gamma_k/\Gamma_1)^{1/2}a_k(0)\right]^2,\qquad B=1-A. \tag{21}$$

From (20) and (21) it follows that relaxation in the process of excitation of the effective states Ψ_k with $k = 1$ leads to the capture of excitation in the continuous spectrum. Thus initial relaxation is significantly dependent on the nature of the physical process (polarised irradiation, short and ultrashort laser pulses, nonradiative transitions, etc.) used for its creation, and the effect under discussion may be used to control both the rate and the direction of the chemical process by localisation of the excitation in a given group of states. It could have been used in particular for the local heating of individual fragments of molecules such as various functional groups and ligands.[208]

4. We shall discuss how the effect examined alters in the case of the disorganisation of the group of quasidegenerate levels. It has already been shown that the interaction between the group of

quasidegenerate states and the continuum leads to two interesting effects which can be seen in Fig. 3 and Fig. 4,[198] in which the dependence of the effective states of two model systems with an initial equidistant arrangement of the energy levels (normal vibrational polyads) and with equal zero halfwidths ($\gamma_1 = \ldots = \gamma_N = \gamma$) on the α axis and the halfwidths are schematically represented. It can be seen that interaction with the continuum leads to the contraction of the group of interacting states and to the redistribution of the widths in favour of a single effective state. In this case instead of the bound states in the continuous spectrum long-lived resonance states are formed with lifetimes which contrary to expectations increase with increase in the intensity of the interaction between the original states φ_k and the continuum.

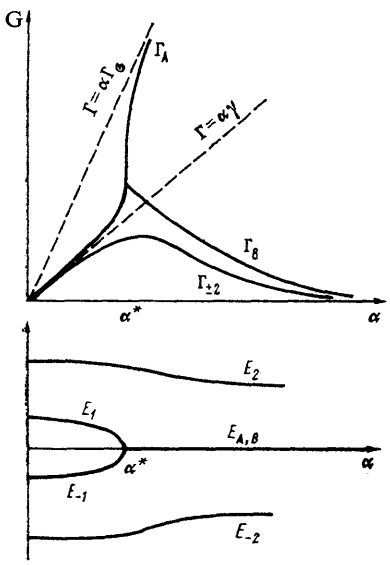


Figure 3. Changes in the positions $\{E_k\}$ and halfwidths $\{G_k\}$ of resonance states in the equidistant N-level system with increase in parameter α, characterising the intensity of the interaction of the coupled states with the continuum. All levels have identical zero halfwidths equal to $\alpha\gamma$, $G_\sigma = N\gamma$. Case $N = 4$.[198]

In general the interaction of N discrete states with the continuum leads to the formation of two different types of resonance state. Firstly the A-resonances the widths of which increase with increase in the interaction between discrete states and the continuum, which lead to their diffusion in the continuous spectrum in the limit $\alpha\to\infty$, and secondly the B-resonances, which in the same limit are transformed into exceptionally long-lived quasistationary states. It is possible to show that the number of A-resonances coincides with the rank of matrix W, which in turn is determined by the number of different decay channels of the system.[198–200] In the Weisskopf–Wigner model the rank of matrix W is equal to unity, which explains the formation of only one A-resonance during the decay. The results obtained have been generalised for the case of the decay of the system in certain of the interacting continua.[199]

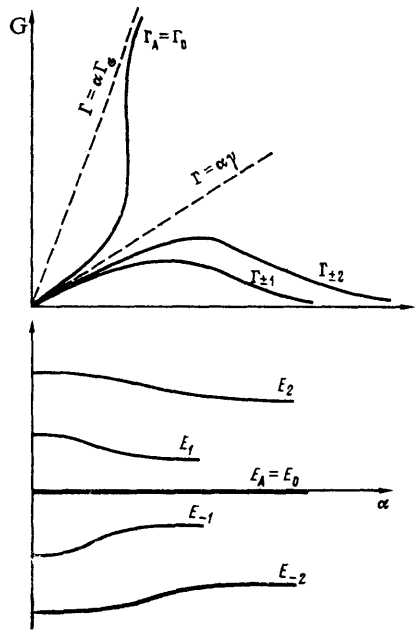


Figure 4. As for Fig. 3, but for case $N = 5$.[198]

VI. Conclusion

The examples considered in this review show that classical concepts play an extremely important role in the theory of highly excited quantum states.

Firstly they serve as the basis for the construction of effective numerical methods of calculation, the most well-known examples being the numerous variants of the quasiclassical method. Moreover information on the characteristics of classical dynamics may be successfully used to increase the efficiency of the standard quantum-mechanical methods of calculation such as the variation method (the selection of the optimum basis) and the adiabatic approximation (the selection of optimum variables).

Secondly the classical concepts serve as a source of both ideas for the design of particular experimental studies and concepts used to interpret the experimental data in the high energy range of the system.

Another important conclusion from the above analysis is the perception of that role played by the concept of localised quantum states by means of which it is possible to examine a set of the most diverse phenomena from common positions.

Thus many rearrangements of vibrational polyads with increase in energy in the transitional range of the spectrum are associated with a change in the nature of the localisation of vibrations on excitation. By studying localised quantum states in the quasicontinuum range it is possible to find and study systematically special relatively stable dynamic regimes and also to observe how they change with increase in energy. Localisation in the continuous spectrum leads to the formation of long-lived resonances and bound states.

A study of the localised vibrational states is of significant interest also because it provides a means of exploring a route to perform selective chemical reactions. From general considerations it is clear that the possibility of controlling a chemical reaction should apparently be closely associated with the possibility of preparing a

molecule in certain special states which have different probabilities for the various reaction pathways. Currently the localised vibrational states are the most practicable candidates for this role.

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