A transition with a large number of quanta presupposes overcoming the first several vibrational levels as a result of the "anharmonicity overlap" due to rotational, field-induced, etc. broadening. For small anharmonic shifts, on the order of several reciprocal centimeters, this condition is easily realized in a large number of molecules. The highly excited vibrational states are in turn well described by the solution of the classical problem (see (8)). For the parameters written out above and at $V_{12}\sim 0.1|V_{11}-V_{22}|$, $p\sim 1D$, $M\sim 10^{-25}$ g, $\gamma\sim 10^{11}$ sec^{-1}, and $n=50$ it is easy to verify with the aid of formulas (4) and (7) that the threshold value of the field intensity, at which complete excitation of the gas takes place, is $F\sim 10^5$ V/cm.

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1) We note that the definition of $\mu_{1,2}$ includes a phase φ_0, which can be found by the method of the adjoint equation.[13] We shall consider below, however, the case $\nu\gg 1$, as $\varphi_0\to 0$.

2) See the remark in the paper by Bychkov and Dykhne[15] concerning the applicability of the theory to the case of strong fields.

3) In the case of the nonlinear time regime, it is possible to obtain from (2) an equation for the probability $W_2(t)$ of the population of the excited level, analogous to formula (6) of Kraĭnov's paper,[16] in which we must put $R^2\equiv b^2$.

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Nonlinear resonance in quantum systems

É. V. Shuryak

Nuclear Physics Institute, Siberian Division, USSR Academy of Sciences

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Both perturbation theory and a quasiclassical method for calculating the quasienergy spectrum have been developed for the problem of a nonlinear quantum oscillator with a resonant force. The results are applied to a description of intermode resonances in autonomous systems. It is shown that quantum effects lead to strong restrictions on the existence of stochastic layers and Arnol'd diffusion and examples of magnetic traps, accelerators, and the solar system are considered. The problem of the decay of an excited mode in molecules and nonlinear chains is discussed. An estimate is made of the limits of transition to a stochastic regime of motion in molecules. A number of the results of the theory is applied to a description of collisionless dissociation of molecules in the field of an intense resonance wave.

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1. INTRODUCTION

In recent years significant progress has been achieved in understanding the overall picture of the motion of an n-dimensional classical system of a general form. It is due to the work of mathematicians, in particular that of Kolmogorov and Arnol'd,[1–3] to the development of the theory and practice of such systems as accelerators of elementary particles, plasma oscillations etc., and particularly to "mathematical experiments" using electronic computers with different model systems.[4–7] This theory is based on a consistent taking into account of the terms of the Hamiltonian that vary least rapidly with time (or resonance terms) in a restricted region of phase space which leads to the concept of isolated resonance. The next step is to take into account interaction between resonances. If they are separated by distances exceeding their nonlinear widths, then this interaction is exponentially small and the motion is basically stable.[1-3] In the opposite case (the so-called Chirikov[7] criterion) the motion is unstable, quasirandom and statistical methods are applicable.

The present work has two aims. The first consists of transferring the ideas and methods of this theory to the case of quantum systems. The second consists in its application to the motion of atoms in an isolated molecule, and also to a molecule in the field of an intense electromagnetic wave which is resonant with respect to one of its modes.

The theory of nonlinear resonance in the quantum case is presented in Sec. 2 using the simplest example of one-dimensional motion (nonlinear oscillator) under the action of a perturbation periodic in time. Depending on the ratio of the width of the resonance to the Planck constant two regimes are possible, in one of which perturbation theory is applicable, and in the other the quasiclassical method. In the latter case it is convenient to carry out the quantization in terms of the action-angle variables. A number of examples of applying this method is given, in particular a simple derivation is presented of the spectrum of quasienergies[8,9] for linear parametric and linear external resonances which are already known from an exact solution.[10,9] An investigation is made of the "standard"[11,7] nonlinear resonance, and also of nonlinear resonance near a ground state which occurs when molecules are excited by a resonance field.

Section 3 is devoted to a discussion of the role of resonances in multidimensional autonomous systems, and in particular to their effect on the spectrum. The quasiclassical results of this section generalize in a certain sense the results of[12,13].

Interaction between sufficiently separated resonances is discussed in Sec. 4. Its principal effect consists of the formation of a stochastic layer near the separators of the resonances which forms the base for a universal slow instability—the Arnol'd difussion.[3,7] In the quantum case the stochastic layer is not always present. Moreover, the conditions for its existence turn out to be so rigid that they might not be satisfied for what would appear to be perfectly classical systems: magnetic traps, colliding beams, the solar system. In order to avoid misunderstandings it should be said that quantum effects have entered the problem as a result of investigation of subtle effects accumulated over a long period of time.

In Sec. 5 the problem is considered of a lengthy evolution of an initial excitation of molecules or of nonlinear chains of a nature similar to them. The simplest case is when a single linear mode is excited in the beginning. It is shown that its decay is determined by intermode resonances which are investigated both in the classical and in the quantum formulation. The rate of decay has a number of thresholds as a function of the nonlinearity or of the amplitude of the perturbation. The results are applied to the problem of a polyatomic molecule in the field of a resonance wave. In particular, we succeed in giving rough upper estimates on the threshold values of the intensity of the wave and in explaining why in the experiments[14] with $I_w \lesssim 10^9$ W/cm^2 dissociation of BCl_3, OsO_4, SF_6 was observed, while dissociation of OCS, CCl_4 was not observed.

The sixth and last section is devoted to a description of the transition from the dynamic motion of atoms in a polyatomic molecule to stochastic motion. An estimate is given of the excitation energy at which this transition takes place. On its basis it is possible, in particular, to understand why monomolecular decay of molecules with a number of atoms $N_a \geqslant 4$ takes place in better agreement with the statistical theory of Kassel'[15] than with the theory of Slatter,[16] cf.,[17,18]. At the same time nonstatistical anomalies exist in the case of triatomic molecules.[17] Transition to a stochastic regime leads to an unrestricted accumulation of energy by a molecule situated in the field of the wave, and this leads to its dissociation. The accumulation of energy takes place by an irregular, "diffusion" route. An estimate of the diffusion coefficient enables one to estimate the average energy accumulated by the molecules during a laser pulse, and the results agree with the data of[14].

2. ISOLATED RESONANCE OF A QUANTUM NONLINEAR OSCILLATOR

We begin the study of quantum nonlinear resonance with the simplest case of a one-dimensional system subjected to the action of a periodic perturbation. This system possesses a set of states $\Psi_n(t)$ having the following property[8,9]:

$$\Psi_n(t+T)=\exp\left(-\frac{i}{\hbar}\varepsilon_n T\right)\Psi_n(t), \tag{1}$$

where T is the period of the external force, ε_n is the so-called quasienergy. Being eigenfunctions of the operator representing evolution over a period, the states Ψ_n constitute a complete orthogonal set, so that an expansion in terms of them describes the evolution of any arbitrary state.

To provide a complete picture we begin with the case of a sufficiently small perturbation. It is clear that in this case Ψ_n are close to the unperturbed stationary states, while ε_n are close to the unperturbed energies E_n so that one can use perturbation theory. It differs somewhat from the standard theory presented in textbooks since instead of a definite initial condition we must satisfy condition (1). For lack of space we shall not present it here but only state the *expression for* ε_n to second order:

$$\begin{gathered}\varepsilon_n=E_n+V_{nn}^{(0)}+\frac{1}{\hbar}\sum_{m,L}\frac{|V_{mn}^{(L)}|^2}{L\Omega-\omega_{mn}}+\dots,\\ \hbar\omega_{mn}=E_m-E_n,\quad V_{mn}^{(L)}=\oint dt\exp(iL\Omega t)\langle m|V(t)|n\rangle,\end{gathered} \tag{2}$$

which is of sufficiently usual form. As can be seen from (2), at resonance $|L\Omega-\omega_{mn}|\ll|V_{mn}^{(L)}|/\hbar$ perturbation theory is no longer applicable. If only a single pair of levels are in resonance then the problem is easily solved exactly. Under the above condition the quasienergies are simply $\varepsilon_{1(2)}=E^{+}_{1(2)(-)}|V_{12}|$. The fact that the correction became linear in V is a consequence of autophasing which will be discussed below.

If the number of levels involved in transitions is not small, then it is natural to utilize the quasiclassical method. The conditions for the applicability of the following discussion can be represented in the form of restrictions on the magnitude of the perturbation

$$\hbar D^2\Big/\frac{d\omega}{dn}\gg V\gg\hbar\frac{d\omega}{dn}. \tag{3}$$

Here

$$\frac{d\omega}{dn}=\frac{d^2E_n}{dn^2}(n_0)$$

is the nonlinearity near the resonance

$$\Omega=\omega(n_0)=\frac{dE_n}{dn}(n_0),$$

D is the distance between the harmonics of the perturbation. For a periodic perturbation $D=\Omega$, but when (3) is satisfied one can consider also more general perturbations which contain a discrete set of incommensurable harmonics. Violation of the first inequality leads to the overlapping of resonances, i.e., to stochasticity (cf., below), while violation of the second inequality brings us back to the domain of applicability of perturbation theory.

A quasiclassical investigation of the neighborhood of the resonance turns out to be particularly convenient also because in this approximation it is possible to make a transition to the action-angle variables, in terms of which an investigation of resonance phenomena is particularly convenient. We note that the question of canonical transformations in quantum mechanics remains open, specifically the difficulties in making the transition to action-angle variables are discussed in the review.[19] These difficulties do not occur in the quasiclassical approximation.

In the absence of perturbation the quasiclassical quantization in terms of the action-angle variables is trivial since in terms of them the Hamiltonian depends only on the action $H_0(I)$. Making the replacement $\hat{I}\to i\hbar\partial/\partial\theta$, we have the Schrödinger equation

$$H_0(I)\Psi_E(\theta)=E\Psi_E(\theta), \tag{4}$$

the solution of which is

$$\Psi_E(\theta)=\frac{1}{\sqrt{2\pi}}\exp\left[-\frac{i}{\hbar}I(E)\theta\right], \tag{5}$$

where $I(E)$ is a function inverse to $H_0(I)$. The condition of periodicity with respect to θ leads to quantization of action and of energy: $I_n=n\hbar$, $E_n=H_0(n\hbar)$.

In the presence of perturbation the Hamiltonian has the form

$$H(I,\theta,t)=H_0(I)+V(I,\theta,t). \tag{6}$$

In virtue of the periodicity of the Hamiltonian with respect to angle and time it can be represented in the form of a double Fourier series

$$V(I,\theta,t)=\sum_{m,n}V_{mn}(I)\exp(im\theta-in\Omega t). \tag{7}$$

Resonances appear at values of the action such that for integer and k and l we have

$$k\omega(I_0)=l\Omega,\quad \omega(I)\equiv dH_0/dI. \tag{8}$$

It is essential that near resonances the perturbation terms with m, n such that $mk=nl$ play a special role, since their dependence on the time is the slowest. In other words, in a certain approximation it is possible to restrict oneself only to a part of the perturbation $u(I,\alpha)$ which depends on the angle and the time only in the combination $\alpha\equiv k\theta-l\Omega t$, which is called the resonance phase. Going over to the variable I_α, conjugate to α, where we shall in future omit the index α, we obtain the time-independent resonance Hamiltonian ($k=l=1$ for the sake of simplicity):

$$\tilde{H}(I,\alpha)=H_0(I)-\Omega I+u(I,\alpha). \tag{9}$$

The role of the neglected terms will be discussed later.

Before going on to quantize this Hamiltonian we shall show that its eigenfunctions possess definite quasienergies coinciding with its own eigenvalues. For this it is sufficient to write them in terms of the initial variables θ, t

$$\Psi_n(\theta,t)=\tilde{\varphi}_n(\theta-\Omega t)\exp\left(-\frac{i}{\hbar}\tilde{E}_n t\right), \tag{10}$$

where $\tilde{\varphi}_n(\alpha)$ is an eigenfunction of $\tilde{H}(I,\alpha)$. In virtue of the periodicity with respect to angle of the functions $\tilde{\varphi}_n(\alpha)$, Ψ_n evidently possess the property (1). We recall that the definition (1) fixes the quasienergy up to an additive term $N\hbar\Omega$, just as in the case of the quasimomentum.

Quantization of the Hamiltonian (9) in the quasiclassical approximation, for example in the α-representation, is carried out in the following manner. The wave function is a superposition of solutions of the form

$$\varphi(\alpha)=\exp\left(-\frac{i}{\hbar}\int^{\alpha}I_e(\tilde{E},\alpha')d\alpha'\right), \tag{11}$$

where $I_e(\tilde{E},\alpha)$ is a solution of the equation $\tilde{E}=\tilde{H}(I_e,\alpha)$ with coefficients guaranteeing periodicity with respect to α. We shall demonstrate this procedure with a number of examples.

The first of these is the standard nonlinear resonance,[11,7] corresponding to the smallness of the width of the resonance compared to the resonance value of the action I_0. This enables us to expand the quantities appearing in (9) near I_0 and to bring it to the form

$$\tilde{H}(I,\alpha)=\frac{d\omega}{dI}(I_0)\frac{(I-I_0)^2}{2}+u(I_0,\alpha)+\text{const}, \tag{12}$$

which has the usual form of the sum of potential and kinetic energy. The regions of finite and infinite motion are separated by a special trajectory, the separator, which will be important for the discussion of Sec. 4. The existence of restricted oscillations in phase is known as autophasing of nonlinear oscillations.[21] The width of this region, or simply the resonance width, is

$$\Delta I_r=\left(\frac{2\Delta u}{d\omega/dI}\right)^{1/2}, \quad \Delta\omega_r\equiv\Omega_p=\left(\Delta u\frac{d\omega}{dI}\right)^{1/2}, \quad \Delta u=\max u-\min u, \tag{13}$$

and therefore the condition of applicability of this approximation can be represented in the lucid form

$$\frac{u}{\tilde{E}(I_0)}\ll\frac{d\omega}{dI}(I_0)\frac{I_0}{\omega(I_0)} \tag{14}$$

describing the smallness of the dimensioness perturbation compared with the dimensioness nonlinearity. The quantization of such a Hamiltonian is standard and we shall not dwell on it.

The next example is linear parametric resonance, i.e., the periodic modulation of the frequency of a linear oscillator. In this case the resonance Hamiltonian has the form

$$\tilde{H}(I,\alpha)=\varepsilon I+V(\alpha)I, \tag{15}$$

where $\varepsilon=2\omega-\Omega$ is the deturning of the frequency, $\alpha=2\theta-\Omega t$. Following the prescription formulated above we easily obtain the quasienergy spectrum

$$\tilde{E}_n=n\hbar\lambda, \quad \lambda^{-1}=\frac{1}{2\pi}\int_0^{2\pi}\frac{d\alpha}{\varepsilon+V(\alpha)}, \tag{16}$$

in agreement with the result of the exact solution.[10] The condition for the finiteness of λ^{-1}: $|\varepsilon|>|V(\alpha)|$ is the well-known condition for the stability of parametric resonance. This conclusion is of a general nature: in the domain of instability the spectrum of quasienergies $\tilde{E}_n$ is continuous. In this region it is convenient to introduce a small nonlinearity which stabilizes the resonance and makes the spectrum discrete, in analogy to the standard device of placing the system with a continuous spectrum into a fictitious box.

The resonance of a linear oscillator with an external force is described by a perturbation of the type $xf\cos\Omega t$ and this leads to

$$\tilde{H}(I,\alpha)=\varepsilon I+fI^{1/2}\cos\alpha, \tag{17}$$

so that the spectrum of quasienergies is $\tilde{E}_n=\varepsilon n+f^2/4\varepsilon$, again in agreement with[10].

The last example is less trivial, it refers to nonlinear resonance near the ground state, when (14) does not hold. Just such is the situation in the excitation by an intense laser pulse of molecules which were initially in the ground state. This problem was considered in[22] for a diatomic molecule, but in classical formulation. It was shown in particular, that rotation does not play any serious role in a typical situation and essentially only changes the nonlinearity somewhat. The resonance Hamiltonian for this problem can be written in the form

$$\tilde{H}(I,\alpha)=\varepsilon I+{}^1/_2\omega' I^2+fI^{1/2}\cos\alpha, \quad \omega'=d\omega(0)/dI, \tag{18}$$

where $\varepsilon=\omega(0)-\Omega$ is the deturning of the frequency, ω' is the nonlinearity, $f=e\bar{x}E/\hbar^{1/2}$, where E is the field of the wave, $e\bar{x}$ is the dipole moment for the first transition $V=0\to V=1$. The dynamics determined by this Hamiltonian can be understood most simply with the aid of the socalled phase portrait, i.e., of a system of equipotentials on the phase plane (Fig. 2). Of particular interest is the case a in which there exist two regions with the same value of $\tilde{E}$: $(I_1 I_2)$, (I_3, I_4). In the classical case one can arrive in such a region under different methods of excitation, for example, in the case of an adiabatic variation of frequency from the case c to a we find ourselves on the upper branch. In the quantum case there exists a probability of a tunneling transition, which can be conveniently written in the I-representation:

$$W=\exp\left[-\frac{2}{\hbar}\int_{I_2}^{I_3}\operatorname{Im}\alpha_e(\tilde{E},I')\,dI'\right], \tag{19}$$

$$\alpha_e(\tilde{E},I)=\arccos\left(\frac{\tilde{E}-\varepsilon I-\omega' I^2/2}{fI^{1/2}}\right). \tag{20}$$

Quantization is determined by the condition that the area between the equipotentials $\tilde{E}_n$ and $\tilde{E}_n+1$ is equal to $2\pi\hbar$. The corresponding formulas are quite cumbersome, and it is simpler to calculate the quasienergy spectrum numerically in a specific situation. We note only that the molecule situated in the field absorbs and emits frequencies $\tilde{\omega}_{mn}=(\tilde{E}_m-\tilde{E}_n)/\hbar$, where $\tilde{E}_{m(n)}$ are certain values of quasienergy (with an accuracy up to an integral multiple of Ω[8]). These frequencies are of the order of magnitude

$$\tilde{\omega}\sim\left(\frac{\omega'}{\hbar}\right)^{1/3}(e\bar{x}E)^{2/3}. \tag{21}$$

Their dependence on the field may find practical applications. So far they have not yet been observed experimentally.

Now a few words on the dissociation of diatomic molecules in a field. In a classical formulation[22] it is possible only in a field of intensity $I_w\approx 10^{14}$ W/cm^2. Quantum tunneling makes this possible at any arbitrary intensity, but with a very low probability. The "tunneling length" diminishes in the case of negative detuning of ε (Fig. 2b). Estimates show that an optimum choice of ε can diminish the threshold I_w by approximately an order of magnitude. So far no experiments have been conducted with such intensities.

Having concluded the discussion of the quantization of a nonlinear resonance we note the most important features. The perturbation gives rise to an essential reconstruction of the wave functions in the region of resonance. In contrast to unperturbed states which do not have an average value of the phase, the exact solutions

(11) do have such a value, and it rotates with the resonance frequency Ω. Outside the region of resonance the reconstruction of states sharply decreases, and this can be more definitely verified by calculating the probability of overlapping of the states (11) and the unperturbed functions (5):

$$a_{mn}=\int_0^{2\pi}\frac{d\alpha}{2\pi}\exp\left[in\alpha-\frac{i}{\hbar}\int^{\alpha}I_{э}(\tilde{E}_{m'}\alpha')\,d\alpha'\right]. \tag{22}$$

Near resonance this integral has a real saddle point and outside resonance it has a complex saddle point, so that a_{mn} falls off exponentially with departure from resonance.

3. RESONANCES IN AUTONOMOUS MULTIDIMENSIONAL SYSTEMS

Resonances between degrees of freedom essentially complicate the motion of a multidimensional system, since they lead to subtle effects cumulative with time. Formally this manifests itself in the form of divergence of the perturbation theory series due to "small denominators," c.f., for example[2]. Naturally they also complicate the problem in its quantum formulation. A well-known example of such type in molecular physics is the Fermi resonance in CO_2. Resonances of special form—periodic motions—have been studied in the theory of resonators,[12] in nuclear theory[23] and in quantum field theory[24] in the quasiclassical approximation.

In quantum-mechanical language resonances denote degeneracy, or more accurately—anomalous condensation, of definite values of the total energy. Indeed, the validity of the relation $\sum k_i\omega_i\approx 0$ (k_i are integers, ω_i are frequencies of individual modes) means that as the occupation numbers vary by k_i the total energy will undergo only a small change. Thus, for example, for a two-dimensional system consisting of two uncoupled nonlinear oscillators this change is equal to

$$E(n_1+Nk_1,n_2+Nk_2)-E(n_1,n_2)\approx{}^1/_2N^2(\omega_1'k_1^2+\omega_2'k_2^2), \tag{23}$$

where $\omega_{1,2}'$ are the nonlinearities of the oscillators, i.e., it is small when $\omega_{1,2}'$ are small. If we now switch on a perturbation which introduces a coupling between modes and which has matrix elements of the order of V, then for $V\gg\hbar^2\omega'$ it leads to an essential reconstruction $\Delta N_r\sim(V/\hbar^2\omega')^{1/2}\gg 1$ of states in the region of condensation of levels. Therefore, in spite of the absolute smallness of V, it cannot be taken into account using perturbation theory. In the opposite case $V\ll\hbar^2\omega'$ it is naturally applicable.

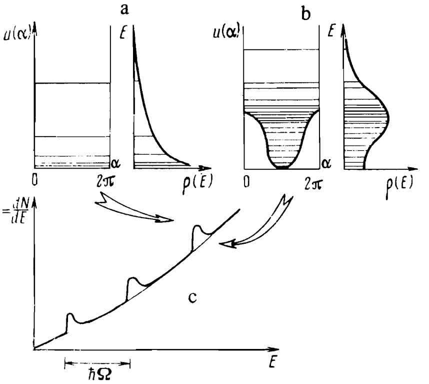

FIG. 1. Phase potential $u(\alpha)$ and the structure associated with it of the condensation of levels due to resonance in a two-dimensional system: a—in the absence of mode coupling, b—in presence of coupling; c—distribution of condensations in the spectrum. Near the threshold $\rho\sim(E-E_{\text{th}})^{-1/2}$ in case a and $\rho=1/\hbar\Omega_p$ in case b, which corresponds to the approximation of small phase oscillations (26). A further increase in ρ is associated with condensation near a separator (cf., Sec. 4).

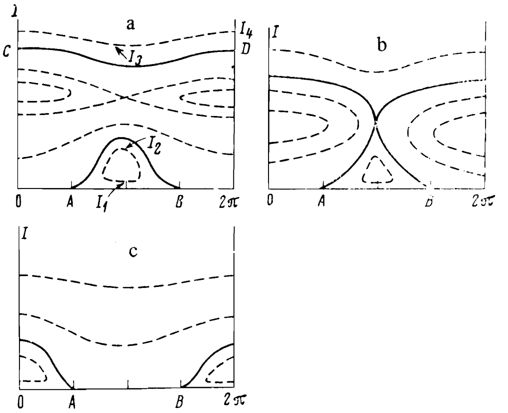

FIG. 2. Phase portraits of the Hamiltonian (18) in three cases: a) $\varepsilon>\varepsilon_k=-3(\omega'f^2/2)^{1/3}/2$, b) $\varepsilon=\varepsilon_k$, c) $\varepsilon<0$, $\omega'<0$. The solid curve corresponds to the trajectory with $E=0$; in case a there are two such trajectories: AB and CD. The broken curves correspond to other trajectories. The values of I_1, I_2, I_3, I_4 shown in diagram a correspond to the limits of phase oscillations at a certain energy.

The quasiclassical method developed in the preceding section can be applied to the description of this reconstruction of states near resonance due to coupling between modes, the physical meaning of which consists of their mutual phasing. We shall demonstrate this with a two-dimensional autonomous system as an example.

Going over from the action-angle variables for individual modes $I_1, I_2, \theta_1, \theta_2$ to the variables

$$\begin{gathered}\alpha=k_1\theta_1+k_2\theta_2,\quad \theta={}^1/_2(k_1\theta_1-k_2\theta_2),\\ I_\alpha=I_1/2k_1+I_2/2k_2,\quad I_\theta=I_1/k_1-I_2/k_2,\end{gathered} \tag{24}$$

and picking out only the α-dependent part of the perturbation $u(\alpha, I_\alpha, I_\theta)$, we obtain the resonance Hamiltonian according to which I_θ is conserved and the problem becomes in essence one-dimensional. For the "standard" case when (14) holds it assumes the form ($\varkappa=\omega_1'k_1^2+\omega_2'k_2^2$)

$$H(\alpha,I_\alpha,I_\theta)=\Omega(I_\theta-I_\theta^{(0)})+{}^1/_2\varkappa(I_\alpha-I_\alpha^{(0)})^2+u(\alpha,I_\alpha^{(0)},I_\theta^{(0)}), \tag{25}$$

where $\Omega=\Omega(I_\alpha^{(0)}, I_\theta^{(0)})$ is the frequency at resonance. From this it can be seen that in the energy spectrum there are condensations separated from each other by the quantity $\hbar\Omega$—while the structure of the condensations themselves is determined by the quasiclassical quantization of the phase oscillations in the potential $u(\alpha)$. Schematically the structure of inhomogeneities of the spectrum brought about by resonance is shown in Fig. 1.

If the amplitude of phase oscillations is small, i.e., if it is in the lower part of the condensation, then their spectrum is naturally of an oscillator form. Just such a result was obtained in[13] as a result of a fairly awkward evaluation of integrals along the trajectories by the saddle point method

$$E_{m,n}=E^{(cl)}_{m,n}+\sum_{i=1}^{N-1}(n_i+{}^1/_2)\hbar\beta_i \tag{26}$$

where $E^{(cl)}_{m,n}$ corresponds to the Bohr–Sommerfield quantization along the orbit, while $\beta_i=d\nu_i/dT$, where ν_i are the so-called stability indices. Our method, in which we first make a transition to convenient variables and only then introduce quantization, does not require the phase oscillations to be small, but only that they should be quasiclassical.

If the number of degrees of freedom is greater than two, then our method effectively reduces the number of variables near resonance, but in the case of several oscillating phases additional assumptions are required for the solution of the problem in explicit form. Generally, as will become clear from subsequent discussion, in multidimensional systems the number of resonances is so large that finding stationary states and expanding in terms of them becomes complicated and in many cases inadequate for the desired aims.

4. INTERACTION OF RESONANCES AND STABILITY OF MOTION

In the preceding sections we restricted ourselves to taking into account only the resonance part of the perturbation near resonance. We now go on to a discussion of the nonresonance terms which when taken into account yield the phase Hamiltonian

$$H(I,\alpha,t)=\tilde{H}(I,\alpha)+V(I,\alpha,t), \tag{27}$$

where $\tilde{H}(I,\alpha)$ corresponds to (9), while V contains the dependence on the time with frequencies equal to the difference in the frequencies of the initial perturbation Ω^* and the resonance frequency Ω. If these differences significantly exceed the frequency of phase oscillations (which is equivalent to the first inequality (3)), $|\Omega^*-\Omega|\gg\Omega_p$, then, as has been shown by Kolmogorov and Arnol'd,[1-3] the effect of nonresonance terms is small. The point is that in this case $V(t)$ oscillates rapidly and its matrix elements contain the "adiabatic smallness"[7]

$$\langle V\rangle\propto\exp\left[-\text{const}\frac{|\Omega^*-\Omega|}{\Omega_p}\right]. \tag{28}$$

If we introduce the parameter of the smallness of the perturbation ε, then since in accordance with (12) $\Omega_p\sim\varepsilon^{1/2}$ and $\langle V\rangle\propto\exp(-\text{const}/\varepsilon^{1/2})$. The nonanalytic nature of this dependence shows that although this effect is of the same order of smallness as ε, it cannot be obtained by perturbation theory.

The nonresonance terms (28) can become significant only owing to resonances of the second order[7,25] of the type $|\Omega^*-\Omega|=n\Omega_p$, which condense near the separator, where $\Omega_p\to0$, and create a stochastic layer.[7] Although such layers are exponentially thin (28), they in a multidimensional case form an intersecting net which serves as the basis of the universal weak instability—the Arnol'd diffusion.[3]

We consider the following question: what are the conditions for the existence of stochastic layers in quantum systems? In virtue of the discrete nature of quantum levels the frequency of phase oscillations near the separator does not reach zero value, and its minimum value is of the order of

$$\Omega_p^{(min)}\sim\Omega_p/\ln\left(\frac{\Delta I_r}{\hbar}\right), \tag{29}$$

where $\Omega_p=(\omega'\Delta u)^{1/2}$, while $\Delta I_r=2(\Delta u/\omega')^{1/2}$ (13). This means that near the separator a condensation of levels by a factor of $\ln(\Delta I_r/\hbar)$ occurs, i.e., in order for quasiclassic resonances of the second order to exist we must have $\ln(\Delta I_r/\hbar)\gg1$, which is much stronger than the usual condition for a quasiclassic situation to exist $\Delta I_r\gg\hbar$.

Further, the magnitude of the perturbation must exceed the distances between the levels, otherwise its role will be small and it would be possible to take it into account by means of perturbation theory. Taking (28) into account this can be written in the form of a condition on the perturbation parameter

$$\varepsilon\gtrsim\left[\frac{\text{const}}{\ln(I_0/\hbar)}\right]^2, \tag{30}$$

where I_0 is a certain characteristic value of the action which need not be known more accurately since it only appears as the argument of a logarithm. We consider a number of examples which will show how rigid is this condition. We start with the case of an adiabatic magnetic trap[26] which confines particles in the transverse direction by a magnetic field and in the longitudinal direction by magnetic barriers. Resonances between the longitudinal motion (of frequency $\Omega_\parallel$) and the Larmor frequency $\omega_H=eH/mc$ in the case $\omega_H\gg\Omega_\parallel$ correspond to a perturbation parameter which itself contains the adiabatic smallness parameter:

$$\varepsilon\sim\exp\left(-\text{const}\frac{\omega_H}{\Omega_\parallel}\right), \tag{31}$$

so that the condition (30) for the existence of stochastic layers along which it is possible to escape from the trap acquires the form

$$\frac{\Omega_\parallel}{\omega_H}>\frac{\text{const}}{2\ln\ln(I_0/\hbar)}. \tag{32}$$

An estimate under experimental conditions[27] leads to a value of the right-hand side of approximately 0.1, while the left-hand side has a value of 0.3–0.1. This means that the experiments were carried out very close to the quantum domain, and that in connection with this further investigations would be of interest.

The second example refers to the stability of particles in storage rings which has also been discussed in detail by Chirikov.[7] Resonances are possible between transverse (betatron) oscillations, which are excited by the colliding beam, by the inhomogeneities of ionization along the orbit, and by other perturbations. In this case the nonlinearity itself is $\sim \varepsilon$, so that $\Omega_p \sim \varepsilon$ and not $\varepsilon^{1/2}$. For this reason (30) contains in its right hand side the first and not the second power. The author is grateful to B. V. Chirikov for this remark.

An estimate gives for ε a limiting value of approximately 1/30. At the same time Arnol'd diffusion has been found experimentally[28] for $\varepsilon \gtrsim 1/20$. In[29] it is proposed to explain by the same mechanism the slow beam blow-up of colliding proton beams of CERN but according to our estimate ε in this case is not greater than 10^{-2}. Thus, the question remains open.

Finally, the last example which has no application significance, but is quite interesting, refers to the solar system. Could one of the planets be expelled from it to infinity? A negative answer has been "proved" repeatedly in the sense that ever weaker instabilities have been eliminated. In accordance with[3] the Kolmogorov instability can be destroyed by effects of the Arnol'd diffusion type. This means that the times for the development of instabilities for all the large planets are much greater than the time of existence of the Universe, while for certain asteroids this is not so, and this enables one to explain the so-called Kirkwood gaps in the case of resonances with Jupiter.[7]

The quantum condition for the existence of stochastic layers (30) restricts the smallness parameter of the perturbation to a value of the order of 10^{-5}, while its actual value roughly speaking is

$$\varepsilon \sim e^q M/M_\odot, \quad q = |n_1 - n_2|, \tag{33}$$

where n_1, n_2 are obtained from the resonance condition $\omega_1 n_1 = \omega_2 n_2$, $M, M_\odot$ are the masses of the planet and of the sun, e is the eccentricity of the orbit. Even in the case of Jupiter $M/M_\odot = 10^{-13}$, while e is of the order of a percent. As a result of this condition (30) is in general not satisfied for all the planets, i.e., Arnol'd diffusion does not exist even in the academic formulation of the problem for infinitely long times. For resonance asteroids, (33) exceeds 10^{-5} at $q \lesssim 4$.

5. INTERACTION OF MODES IN POLYATOMIC MOLECULES AND NONLINEAR CHAINS

In this section we study the lengthy evolution of an initial excitation of the system. Because of its simplicity, and also of its practical importance, we shall basically study the case in which the initial excitation is an excitation of only one of the linear modes. Closely associated with this case is the case of continuous resonance excitation of one of the modes which occurs in the case of a molecule situated in the field of a resonance wave. The questions of interest to us are as follows: How and at what rate is the energy transferred from the excited mode which we shall denote by the subscript 1 to other modes. The characteristic feature of this problem consists of the fact that the excited modes are near the ground state and their nonlinearity is less than the interaction with the exciting mode 1. This makes inapplicable the "standard" resonance (Sec. 2) and the Kolmogorov theorem associated with it concerning the stability of motion.[1] As a result of this the initial state of the type under consideration necessarily decays in the presence of any arbitrarily small nonlinearity, although of course the rate of decay can be very small. This conclusion agrees with numerical experiments conducted in recent times with nonlinear chains[7,30] (of course, with the exception of the special case of exactly integrable chains).

In the approximation of small oscillations the Hamiltonian can be represented in the form

$$H = \sum_i H_i^{(l)} + E \sum_i c_i x_i + \sum_i H_i^{(nl)} + H^{(int)} + H^{(e\,nl)}, \tag{34}$$

where $H_i^{(l)} = (\dot{x}_i^2 + \omega_i^2 x_i^2)/2$ is the energy of the individual modes in the linear approximation, x_i are the normalized displacements of atoms from the equilibrium position, the second term is the linear dipole interaction with the field, $H_i^{(nl)} = a x_i^3 + b x_i^4 + \cdots$ gives the nonlinearity of the modes, and the interaction between them $H^{(int)}$ is given by

$$H^{(int)} = \sum_i A_{i_1 i_2 i_3}^{(3)} x_{i_1} x_{i_2} x_{i_3} + \ldots \tag{35}$$

and, finally, the nonlinear corrections to the interaction with the field are

$$H^{(e\,nl)} = E \left(\sum_i a_{i_1 i_2}^{(2)} x_{i_1} x_{i_2} + \ldots \right). \tag{36}$$

The smallness of the amplitude of the oscillations leads to the smallness of the last three terms in (34), but because of resonances perturbation theory in terms of them is still inapplicable for the description of a sufficiently lengthy evolution. In particular, in Sec. 3 we discussed their role in the case of stationary states.

In this section we consider the stage in the decay of the initial state at which it is possible to limit oneself to a single leading resonance. This means that we are considering times much longer than a period of oscillation, at which resonance effects already become separated from nonresonance oscillations, but, on the other hand, much smaller than those at which other resonances become significant. Such a description has a meaning which is curious from the formal point of view: we are investigating an approximate Hamiltonian whose eigenstates are not stationary and not even close to them, and yet are conserved during a restricted time period.

We begin with the case of three-frequency resonance, i.e., we assume that the frequency of the excited mode ω_1 is close to $\omega_2 + \omega_3$. The resonance term in (35) corresponding to this case is $A_{123}^{(3)} x_1 x_2 x_3$ which is the only one that we retain. It can be easily seen that if $x_2 = x_3 = \dot{x}_2 = \dot{x}_3 = 0$ for $t = 0$, then this will also hold for all t in this approximation. However under certain conditions this solution is unstable, i.e., the initial values $x_2(0)$, $x_3(0), \ldots$ later grow. Assuming x_2, x_3 to be small we neglect their nonlinearity, and also their effect on x_1, i.e., we consider $x_1(t)$ to be a given function of the time.

Following the prescription of Sec. 2 we go over from

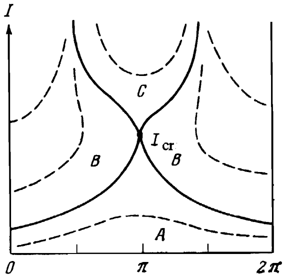

FIG. 3. Schematic representation of the phase portrait of the intermode resonance (41). The solid curve shows the stability boundary, the broken curves represent certain trajectories in the stable A and unstable B, C regions. The critical value of the action shown in the diagram is equal to $I_{cr} = [2\varepsilon/(m-1)V]^{2/(m-3)}$.

the variables I_2, I_3, θ_2, θ_3 to the resonance variables $\alpha = \theta_2 + \theta_3 - \theta_1(t)$, $\theta = \theta_2 - \theta_3$, $I_\alpha = (I_2 + I_3)/2$, $I_\theta = (I_2 - I_3)/2$ and introduce for the frequency detuning the notation $\varepsilon = \omega_2 + \omega_3 - \omega_1$. Further, we pick out from the perturbation the resonance part, i.e., the part depending on α. As a result of this we obtain the resonance Hamiltonian of the following form:

$$\bar{H} = (\omega_2 - \omega_3) I_\theta + \varepsilon I_\alpha + u(I_\alpha^2 - I_\theta^2)^{1/2} \cos\alpha, \quad u = A_{123}^{(3)} \bar{x}_1 \bar{x}_2 \bar{x}_3 I_1^{1/2} \hbar^{-3/2}. \tag{37}$$

Since in this approximation I_θ is conserved, then it is equal to its initial value, i.e., to zero. As a result of this (37) turns out to be identical to the Hamiltonian for parametric resonance (15). The classical equations of motion can be easily solved, the behavior of the solutions depends on the ratio of ε and u. If $|\varepsilon| > |u|$, then the motion has the nature of bounded beats, while in the opposite case exponential growth occurs

$$I_\alpha(t) = I_\alpha(0) \exp[(u^2 - \varepsilon^2)^{1/2} t]. \tag{38}$$

Of course, this growth is stopped by a nonlinearity or simply by the storage of energy in the case of mode 1.

A quantum investigation of the Hamiltonian can be carried out using quasiclassical methods, as in Sec. 2, or with the aid of the exact results of[10,9] for parametric resonance. As usual, in problems associated with the linear oscillator the difference between quantum results and classical results is not great. In particular, the condition for stability and the law for the growth of instability (38) are not altered. There is one important difference: the instability can be developed also starting from the ground state. We present the probability of transition into the state $n_2 = n_3 = n$ for this case:

$$W_n = \frac{(2n)!}{2^{2n} n!} \rho^n (1-\rho)^{1/2}, \quad \rho = \frac{\varepsilon^2 \sin^2[(\varepsilon^2 - u^2)^{1/2} t]}{\varepsilon^2 - u^2 + \varepsilon^2 \sin^2[(\varepsilon^2 - u^2)^{1/2} t]}, \tag{39}$$

and this yields for large values of the time and of n

$$W_n = \left(\frac{2\hbar}{\pi n I(t)}\right)^{1/2} \exp\left(-\frac{\hbar n}{I(t)}\right), \quad I(t) = \frac{\hbar \varepsilon^2}{4(u^2 - \varepsilon^2)} \exp[(u^2 - \varepsilon^2)^{1/2} t]. \tag{40}$$

Comparison of (40) with (38) enables us to state that the growth of instability arises from zero-point oscillations.

If the leading resonance includes a large number of frequencies, $\omega_1 = \omega_2 + \cdots + \omega_m$, the discussion is conducted in an analogous manner. Going over to resonance variables, and retaining only the part of the Hamiltonian depending on $\alpha = \theta_2 + \cdots \theta_m - \theta_1$ and I_α, we have

$$\bar{H} = \varepsilon I_\alpha + V I_\alpha^{(m-1)/2} \cos\alpha, \quad V = A_{1\ldots m}^{(m)} \bar{x}_1 \ldots \bar{x}_m I_1^{1/2} h^{-m/2}. \tag{41}$$

The regions of instability and other characteristics of the motion described by the Hamiltonian (41) can be understood with the aid of the phase portrait shown in Fig. 3. For $m > 3$ the solution for large values of the time has an "explosive" behavior in the region of instability

$$\begin{gathered} I_\alpha(t) = I_\alpha(0)\left[1 - \frac{t}{t_0}\right]^{-2/(m-3)}, \\ t_0^{-1} = V \frac{m-1}{2} (I_\alpha(0))^{2/(m-3)}. \end{gathered} \tag{42}$$

Of course, the applicability of the approximations made above ceases at $t < t_0$ and nothing actually becomes infinite. We do not dwell on the quasiclassical quantization of (41), since it is completely analogous to the examples of Sec. 2. For our purposes it is sufficient to recognize the fact that the characteristic time for the building up of the resonance is of the order of $t_0 \sim \hbar/(A^{(m)} \bar{x}^m)$, and it grows rapidly with increasing order of resonance m. Therefore usually the decay of a given mode is determined by a single resonance which lies sufficiently closely in frequency and at the same time is not too weak. Since the net of resonances is everywhere dense, the decay will occur by one means or another. As the nonlinearity, i.e., the coefficients $A^{(m)}$ in (35), is changed the rate of the decay of the mode undergoes sharp jumps, as soon as the detuning of the frequency becomes comparable with the width of the region of instability. Such phenomena have been observed in numerous experiments.[7,30]

These conclusions can be easily generalized to the case of a molecule situated in a field of frequency which is in resonance with mode 1. As was shown in Sec. 2, in this case oscillations in phase θ_1 arise and in the classical formulation near the frequency ω_1 there appear in the sectrum also modulation frequencies $\omega_1 \pm \Omega_p$, $\pm 2\Omega_p, \ldots$, where Ω_p is the frequency of the phase oscillations (21). In the quantum formulation of the problem they correspond to the frequencies $\tilde{\omega}_{m,n} = (\bar{E}_m - \bar{E}_n)/\hbar$, where $\bar{E}_{m(n)}$ are the values of the quasienergies. It is clear that the decay of mode 1 becomes possible if at least one of these frequencies from its spectrum falls in the region of instability of some intermode resonance. Since these frequencies of phase oscillations (21) grow with increasing magnitude of the field of the wave, there exist definite values of the magnitude of the field at which they attain values of deturning up to the boundary of the region of instability of sufficiently close resonances. For these threshold values of the field the rate of transfer of energy from mode 1 to other modes increases sharply, in analogy to the threshold phenomena as a function of nonlinearity which were referred to earlier.

We shall demonstrate this line of argument by concrete examples. We first of all estimate the characteristic times for the build-up of molecular resonances in

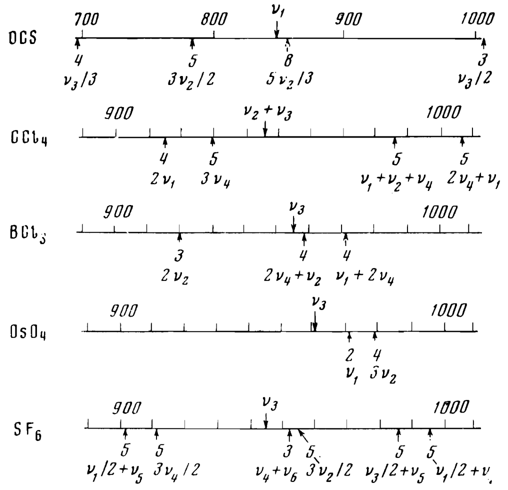

FIG. 4. Schematic representation of the positions of intermode resonances in COS, BCl_3, CCl_4, OsO_4 and SF_6 molecules, the values of the frequencies were taken from[31]. The quantity m is the index of the resonance, i.e., the number of frequencies contained in it. Frequencies are given in cm^{-1}.

order to be able to determine whether it has time to occur during the time of action of the field under experimental conditions. One can make a rough estimate of the amplitude of the terms of the Hamiltonian (35) in the following manner: $A^{(m)}\bar{x}^m \sim \hbar\omega_0 A^{m-2}$, where ω_0 is the characteristic value of the frequency, the constant $A = 0.03$–0.1. The time for the build-up of the m-frequency resonance is of order of A^{2-m} periods, while the duration of the laser pulse in experiments[14] is of order of 10^{-7} sec or 10^6 periods. Thus, resonances with $m \gtrsim m_0 = 6$–7 are unimportant, while those with $m < m_0$ lead to a significant transfer of energy.

The arrangement of the resonances between frequencies for some molecules, and in particular for COS, BCl_3, CCl_4, OsO_4, and SF_6, which have been studied experimentally,[14] is shown in Fig. 4. The values of the frequencies are taken from the handbook[31]. It can be easily seen that as the number of atoms increases the net of resonances become more dense. This effect would have been even stronger if these molecules were not symmetric, resulting in degeneracy of a number of frequencies.

A preliminary estimate of the order of magnitude of the threshold intensity of the resonance field at which an effective transfer of energy to other modes can take place may be obtained by equating the frequency of phase oscillations (21) to the distance to the nearest resonance with $m < m_0$. In such a case we have (in W/cm^2): $I_w \sim 10^{12}$ for COS, 10^8 for BCl_3, 10^{10} for CCl_4, 10^9 for OsO_4, 3×10^8 for SF_6. Thus, already this estimate enables us to explain why in experiments[14] with $I_w \lesssim 10^9$ W/cm^2 dissociation of BCl_3, OsO_4, SF_6 occurred, and did not occur in the case of COS, CCl_4. It is clear that for collisionless dissociation the possibility of transfer of energy to other modes is essential (cf., also Sec. 6).

However, the accuracy of this estimate is not great. Firstly, it is determined simply by the accuracy of the values of the frequencies from[31]. Moreover, in the case of degeneracy of the frequency being excited the role of the width of its band of frequencies can be assumed not by field broadening, but simply by the distance between its branches. In the special case of SF_6 it was noted[14] that the anharmonism can be compensated by a transition to the other branch, i.e., "triple resonance" is possible. Finally, the mechanism considered by us is "classically allowed." Owing to quantum "tunnel" effects, there exists a definite probability of the process also below threshold. All these effects can diminish the threshold intensities, so that the estimates given above should be regarded as overestimates. And, indeed, the experimental value of the threshold[14e] in the case of SF_6 is smaller by an order of magnitude than according to the above estimate. In order to obtain more accurate estimates one must have spectrometric information which is at present unknown, at least to this author.

6. THE STOCHASTIC NATURE OF THE MOTION OF ATOMS IN MOLECULES

In the preceding section we have studied the initial state of decay of modes in which it was possible to restrict oneself to an investigation of a single leading resonance, and also to neglect the reaction on the exciting mode 1. What happens further?

In principle the nonlinearity may stop the transfer of energy via an intermode resonance, and the motion will have possibly a more complicated but still a periodic character. This type of motion of nonlinear chains was observed already in the first numerical experiment.[4] However, for a sufficiently long period of time, as in the problem concerning molecules which is of interest for us, necessarily other resonances will become included which excite other modes, etc. We note, that the net of resonances becomes more dense also because resonances $\omega_1 = \sum n_i\omega_i$ with negative values of n_i become effective. As a result of this the motion becomes considerably more complicated and it becomes difficult to hope for a detailed description of it. Nevertheless under certain conditions this process carries on so far that statistical methods become applicable to its description. This question was studied on model systems in[6,7].

We begin a discussion of this question with the following remark. In the preceding discussion the frequencies of the modes were regarded as given quite definite quantities. However interaction of modes leads to their being smeared out, in a manner completely equivalent to broadening by an external force (Sec. 2) by an amount of the order of

$$\Delta\omega_1 \sim (\omega_1'/\hbar)^{1/3}(A^{(3)}_{123}\bar{x}_1\bar{x}_2\bar{x}_3\bar{n})^{2/3}, \tag{43}$$

where $\bar{n}$ is the average number of quanta in modes 2, 3 (we have in mind the resonance $\omega_1 = \omega_2 + \omega_3$). As the degree of excitation of the molecule grows, i.e., as $\bar{n}$ grows, the nonlinear broadening (43) increases and at a certain value of $\bar{n}$ becomes equal to the distance in frequency to another resonance of the same order, for example, $\omega_1 \approx \omega_3 + \omega_4$. We denote this distance by Δ_0, an obvious estimate of its magnitude is $\Delta_0 \sim \omega_0/N_f^2$, where

ω_0 is the characteristic value of the frequency, while N_f is the number of frequencies of the system.

When resonances overlap, i.e., in the case $\Delta\omega \gg \Delta_0$, the motion of each mode is determined simultaneously by many resonance terms of the Hamiltonian. In this case the motion acquires a quasirandom or stochastic character and statistical methods are applicable. This assertion, known as Chirikov's stochasticity criterion, has been repeatedly verified on different model systems (cf., [7]). We note that according to Chirikov[7] this condition is the same for resonances of any arbitrary order.

Thus, the stochasticity criterion for molecules can be written in the form

$$\bar{n} \geqslant \left(\frac{\omega_0}{\hbar\omega'}\right)^{1/2} \frac{\hbar\omega_0}{|A^{(3)}\bar{x}^3|} \frac{1}{N_f^3} \sim \frac{10^2}{N_f^3}, \tag{44}$$

where we have substituted typical values of the nonlinearity $\hbar\omega'/\omega_0 \sim 10^{-2}$, $A^{(3)}\bar{x}^3/\hbar\omega_0 \sim 10^{-1}$; the quasiclassical nature of (14) requires $\bar{n} \gtrsim 1$. Stochasticity in an essentially quantum region will be discussed in a separate paper.

Even this estimate enables us to draw a number of important conclusions. Thus, for example, it enables us to explain the following observations concerning monomolecular dissociation of excited molecules. At one time the theory of these reactions was developing along the following two directions. In one of them, the Slatter theory, [16] the intermode transfer of energy was neglected, while in the statistical theory of Kassel' *et al*[15] a sufficiently rapid relaxation within the molecule was assumed. Numerical[17] and certain "real" experiments[18] have shown that for molecules with the number of atoms $N_a \geqslant 4$ Kassel's theory works better, while in triatomic molecules there are anomalies, for example, the nonexponential distribution with respect to lifetime. But there was no clear understanding of these facts. In accordance with the estimate (44) at an energy of several electron volts (dissociation energy) molecules with $N_a \geqslant 4$ already fall within the domain of stochasticity and thereby explain the validity of Kassel's theory. If the nonlinearity of the molecules were smaller the result would be different.

Another important phenomenon associated with transition to stochasticity occurs in the problem of a molecule in the field of a wave. It is known as stochastic instability[7] and consists of an unlimited accumulation of energy by a molecule prior to dissociation. Its qualitative content can be explained as follows. The action upon mode 1 on the part of the other modes irregularly jolts its phase θ_1. As a result the difference between θ_1 and the phase of the field Ωt becomes random, i.e., the problem essentially becomes the same as in the case of a random external force, when an unlimited accumulation of energy is obvious.

A quantitative description of this phenomenon can be given in the following manner. We write the Hamiltonian for the effect on mode 1 on the part of other modes in the form of a sum of resonance contributions lying within the nonlinear width (43) in the form

$$H_1^{(int)} = I_1^{1/2} \sum_n F_n \cos(\theta_1 - \theta_n). \tag{45}$$

This interaction alters the quasienergy (9) of mode 1 in the following manner:

$$\frac{d\tilde{E}_1}{dt} = I_1^{1/2}(\Omega - \omega(I_1)) \sum_n F_n \sin(\theta_1 - \theta_n) - \frac{e\bar{x}_1 E}{2\hbar^{1/2}} \sum_n F_n \sin\theta_n. \tag{46}$$

The first term describes the intermode relaxation, while the second term describes the interaction with the field which is of interest to us. Considering the phase θ_n to be random we see that $\langle \Delta\tilde{E}_1 \rangle = 0$, while

$$\langle (\Delta\tilde{E})^2 \rangle = D(\tilde{E})t. \tag{47}$$

This means that the accumulation of energy is irregular, of the type of diffusion with the coefficient $D(\tilde{E})$. The calculation of $D(\tilde{E})$ is carried out similarly[7] to the result

$$D(\tilde{E}) = \frac{\pi}{4\hbar}(e\bar{x}_1 E)^2 J(\Omega), \quad J(\Omega) = \frac{|F(\Omega)|^2}{\Delta_0}. \tag{48}$$

The quantity $J(\Omega)$ has the simple meaning of spectral intensity of the perturbation (45) at the frequency of the wave of the field. A knowledge of $D(\tilde{E})$ enables us to describe the process by means of a Fokker–Planck equation

$$\frac{\partial P(\tilde{E},t)}{\partial t} = \frac{\partial}{\partial \tilde{E}} D(\tilde{E}) \frac{\partial P(\tilde{E},t)}{\partial \tilde{E}}. \tag{49}$$

We note that this equation, well known in molecular physics, is here utilized in an essentially new situation: there are no collisions (heat reservoir), and the force is not random but completely determined. The statistical element in the problem is brought about exclusively by the complex character of intramolecular motion.

In conclusion we note that in[32,33] a hypothesis was also advanced concerning the possibility of an unlimited accumulation of energy in the quasicontinuum of states lying above a certain excitation energy. However the conditions for the existence of this phenomenon were assumed to be the following: the spectrum of states is dense and the lines of the spectrum overlap by the finite width of rotational bands. The insufficiency of this condition can be already seen from the fact that the nonlinearity of the molecule plays no role in it. And yet it is clear that in the absence of coupling between modes the density of the spectrum of the states is useless, since the matrix elements for transitions into them are equal to zero. A large number of rotational states also does not help since angular momentum is conserved and states with different values of angular momentum do not mix. In this sense rotation is analogous to translational motion, which makes the spectrum continuous, but does not help in the absorption of quanta. In our discussion the mixing of states is brought about by nonlinear intermode resonances.

Formula (47) can be applied to estimate the rate of accumulation of energy by a molecule in the regime of stochasticity. The magnitudes of F_n and Δ_0 (the amplitude of the three-particle resonance and the distance between them) are estimated as has been done previously. As a result we obtain

$$\langle\tilde{E}\rangle(\mathrm{eV}) \sim 10^{-1}\, e\bar{x}(\mathrm{D})\,[I_w(\mathrm{MW/cm^2})\, t(\mathrm{nsec})]^{1/2}\,. \tag{50}$$

For $t = 10^{-7}$ sec the amount of energy accumulated during a laser pulse agrees in order of magnitude with experimental data[14h] and at the same time the basic dependence on the intensity of the wave is also well satisfied. Moreover, as has been noted in the literature,[14d] the rate of dissociation for compound transitions is proportional not to the square of the dipole moment of the transition, as for a usual absorption line, but to its first power. This characteristic feature is also satisfied in accordance with (50).

Further study of the questions touched upon above presents a wide open field for experimenters. Thus it is of interest to discover the frequencies of phase oscillations of the mode being excited to check the dependence of the average energy accumulated during a pulse (50) on its duration in order to verify its diffusion character etc. Of interest are experiments with two synchronized lasers of different frequencies.[14f] If the first one brings the molecule into the regime of stochasticity, then the frequency of the second one is no longer of importance and accumulation of energy takes place anyway. We note that in addition to interesting applications, for example, separation of isotopes[14] and other selective reactions, the behavior of a polyatomic molecule in the field of a wave is of interest also from a theoretical point of view as an example of a transition from dynamic motion to statistical motion in a finite quantum system.

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