Statistics of energy levels when the integrals of motion are violated

G. M. Zaslavskiĭ

Physics Institute Siberian Division, USSR Academy of Sciences
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The energy spectrum of excited molecules is considered. At an excitation energy higher than critical (E_c) the integrals of motion that supplement the total energy are violated, and the trajectories become stochastic. In this case, the general picture of the behavior of the trajectories in phase space is the same as for the motion of particles that are scattered by arbitrary surfaces of negative curvature ("Sinaĭ billiard table"). Starting from the analogy between the motion of atoms and the motion of particles in Sinaĭ billiard table, quantization rules that determine the statistical distribution of the levels in the region $E > E_c$ are obtained. Universal law is derived for the probability of the distance ΔE between the nearest levels (as $\Delta E \to 0$), namely $|\Delta E| \nu$, where ν^{-1} is of the order of the growth rate of the instability of the trajectories on the Sinaĭ billiard table. The appearance of a low-frequency "tail" in the vibrational spectra of nonradiative transitions of the dissociating molecule is predicted and its shape is determined.

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1. INTRODUCTION

At sufficiently high excitation energy of heavy nuclei, the shell structure of the energy levels is distorted so strongly and irregularly that a statistical description of the energy spectrum becomes more suitable for the real situation. The authors of this idea, Wigner[1] and Landau and Smorodinskiĭ[2] have pointed out also one fundamental singularity connected with the unusual interpretation of energy as a random variable: for levels of one symmetry the probability $P(\Delta E)$ of observing two neighboring levels at a distance ΔE from each other should tend to zero as $\Delta E \to 0$ (the level "repulsion" principle). A statistical theory of level distribution was constructed by Dyson[3] on the basis of the hypothesis of the equivalence of the distribution of the levels and eigenvalues of an ensemble of random matrices of definite symmetry.

The present paper is devoted to further development of these ideas for the purpose of determining the energy spectrum of strongly excited molecules. In contrast to nuclei, we succeed here in deriving, from rather general considerations, a certain universal level–distribution law characterized by a probability $P(\Delta E)$. There is no need to introduce any hypothesis, and the form of $P(\Delta E)$ is uniquely determined by the properties of the Hamiltonian of the molecule.

If the molecule has M degrees of freedom, then in the fully-integrable case there are exactly M integrals of motion, to which M quantum numbers correspond. At an energy exceeding a certain critical value E_c, some of the integrals of motion may be violated because of the nonlinearlity of the Hamiltonian. The classical trajectories of the system become stochastic, whereas at $E < E_c$ these trajectories were conditionally periodic. The stochastic mechanism of violation of the integrals of motion has by now been quite well studied (see[4,5]). It operates already in a two-particle system, as was numerically demonstrated by a number of workers[6–8] for different types of interaction potentials.

The question arises of the quantization of the Hamilto-

nian that describes the stochastic motion of the system at $E > E_c$. It should be noted that the first to formulate the problem of quantization of a system with violated integrals of motion was Einstein,[9] in connection with Poincaré's result that the three-body problem is nonintegrable. In a particular case, the problem of the spectrum of electrons "glancing" along a non-ideal metal surface in a magnetic field was solved for $E > E_c$ in[10]. A discussion of certain properties of the energy spectrum at $E > E_c$ was presented by Percival,[11] and an extensive numerical analysis of the levels of diatomic and triatomic molecules in the region where the integrals of motion are violated was carried out by Rice and co-workers.[12]

It is seen from the foregoing that it has become necessary to examine from a different standpoint the structure of the energy spectrum of complex systems, particularly molecules. This is important not only from general physical considerations, but also in connection with different applications (for example, to the theory of dissociation of molecules and to the theory of the velocities of monomolecular reactions[12]). Subject to limitations of quite general character, quantization rules are derived in the region of stochastic violation of the integrals of motion, and the law of distribution of the distances between nearest levels is determined.

2. QUANTIZATION RULES

At sufficiently high molecule-excitation energies, we can confine ourselves to the quasi-classical asymptotic approach. It is necessary in this connection to determine the general picture of the behavior of classical trajectories of the system in phase space in the case of stochastic violation of the integrals of motion. It can be stated[4] that the motion of such systems is analogous in their main to the motion of particles in the "Sinaĭ billiards table" in which a particle is elastically scattered by convex surfaces. Examples of such billiards are shown in Figs. 1 and 2. Their study in connection with the problem of the formulation of statistical mechanics
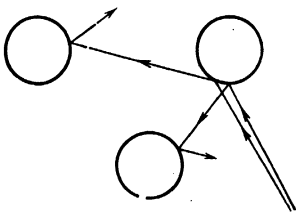
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FIG. 1.

FIG. 3.

was initiated by Krylov[13] and carried out in the most general form by Sinaĭ.[14] Under the condition[13]

$$K \equiv R/a > 1, \qquad (2.1)$$

where a is the radius of the scattering region in Fig. 1 and R is the characteristic distance between these regions, the trajectories of the particles are a random process of the Markov type.[15] In the molecule, the quantity a determines the characteristic radius of the scattering potential of the atom, and R is a function of the molecule energy: $R = R(E)$.

Thus, the equation

$$R(E_c) \approx a \qquad (2.2)$$

makes it possible to determine the critical molecule excitation energy above which the classical trajectories become randomized. The foregoing arguments can be easily understood by recognizing that R usually increases with increasing E. Then at $R/a \lesssim 1$ the potential wells become closely packed and the motion of each atom[1) takes place in a certain self-consistent field (in analogy with the model of independent particles in the nucleus). The system of energy levels has in this case a regular form. To the contrary, under the condition (2.1) the molecule becomes friable and, as will be seen below, it is precisely in this region that the level distribution has a random character.

To determine the energy eigenvalues E_k we use the expression for the response function

$$g(E) = \int dq\, G(q,q,E) = \sum_k \frac{1}{E - E_k}, \qquad (2.3)$$

where $G(q'', q', E)$ is the Green's function and q is the aggregate of the coordinates. In the quasiclassical approximation G takes the form

$$G(q'', q', E) = A \exp i[S(q'', q', E)/\hbar + \psi], \qquad (2.4)$$

where the action is

$$S(q'', q', E) = \sum_{i=1}^{M} \int_{q'}^{q''} dq_i p_i(q, E), \qquad (2.5)$$

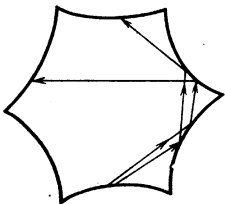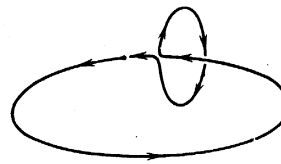and A and ψ are the pre-exponential factor and the phase,

FIG. 2.

which can be determined. Since A and ψ necessitate small corrections to the quantization rules, they will henceforth be disregarded, and we confine ourselves to the result that is valid as $\hbar \to 0$.

We examine first the quantization rules that are obtained in the presence of a complete set of integrals of motion, i.e., at $E < E_c$. We make use next of Gutzwiller's idea[16] and represent g in the form of a sum over all the periodic paths of the classical particle. The expressions for $g(E)$ is determined by the extremum of the function G, meaning that

$$\frac{\partial S(q,q,E)}{\partial q_i} = \left[\frac{\partial S(q'', q', E)}{\partial q_i''} + \frac{\partial S(q'', q', E)}{\partial q_i'} \right] = p_i'' - p_i' = 0 \qquad (2.6)$$

at $q_i'' = q_i' = q_i$, $(i = 1, 2, \ldots, M)$, where p_i' and p_i'' are respective momenta at the initial and final points of the trajectory. The condition (2.6) means that at the saddle point the action $S(q, q, E)$ which determines in accord with (2.3) and (2.4) the function $G(q, q, E)$, is taken along a closed trajectory. In the stable case $(E < E_c)$ such trajectories consist of periodic trajectories and $S(q, q, E) = S(E)$, i.e., is independent of q.

It is next necessary to use the fact that the expression

$$\sum_{i=1}^{M} p_i dq_i$$

is not only an invariant, but at $E < E_c$ also a total differential. Therefore expression (2.5) for S does not depend on the form of the integration contour. Taking into account the foregoing and taking $G(q, q, E)$ in (2.3) outside the integral sign at the extremum point, we obtain

$$g(E) \approx \text{const} \sum_{\Pi} \exp\left[\frac{i}{\hbar} S_\Pi(E) \right], \qquad (2.7)$$

where $S_\Pi(E)$ is the action (2.5) taken along an arbitrary contour Π that is closed in phase space, and the constant is a function that depends weakly on E.

At $E < E_c$ the system moves along an M-dimensional torus and there exist M different closed trajectories C_k $(k = 1, \ldots, M)$ that cannot be contracted into a single point (in the sense in which they were defined by Einstein[9]). Therefore expression (2.7) can be written in the form

$$g(E) = \text{const} \sum_{m_1=0}^{\infty} \cdots \sum_{m_M=0}^{\infty} \exp\left\{ \frac{i}{\hbar} \sum_{k=1}^{M} m_k S_k(E) \right\},$$

$$S_k(E) = \oint_{C_k} \sum_{i=1}^{M} p_i dq_i. \qquad (2.8)$$

For example, at $M = 2$ the term in (2.8), for which $m_1 = m_2 = 1$, corresponds to the phase-space trajectory shown in Fig. 3.
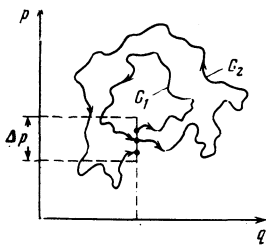
FIG. 4.

The arbitrary term at $M = 2$ correspond to m_1 large loops and m_2 small loops in any sequence. Expression (2.8) is identically transformed into

$$g(E) = \text{const } g_1(E) g_2(E) \ldots g_M(E),$$

$$g_k(E) = \sum_{m=0}^{\infty} \exp\left[\frac{im}{\hbar} S_k(E)\right], \qquad (2.9)$$

i.e., the poles $g(E)$, which determine the eigenvalues of E, consist of the poles $g_k(E)$. From (2.9) follows the equation

$$g_k(E) = 1 + \exp[iS_k(E)/\hbar] g_k(E),$$

whence

$$g_k(E) = \{1 - \exp[iS_k(E)/\hbar]\}^{-1}. \qquad (2.10)$$

The eigenvalues are thus obtained from the equations

$$S_k(E) = 2\pi n_k \hbar, \quad (k = 1, 2, \ldots, M), \qquad (2.11)$$

where $n_k > 0$ are arbitrary integers. The quantization rules (2.11) coincide exactly with those proposed by Einstein.[9]

The approach described above will now be extended to the case $E > E_c$, when the trajectories are stochastic. It is meaningless in this case to speak of closed trajectories, since their measure is very small. We note that the condition (2.6) is approximate. It is possible to introduce in its stead a small momentum region Δp and consider trajectories that go out of the point (q, p') and return to the point (q, p'') with $|p'' - p'| < \Delta p$. We can then write in lieu of (2.7)

$$\bar{g}(E) = 1 + \frac{1}{\mu \Delta p} \sum_{C_1(\Delta p)} \frac{1}{\mu \Delta p} \sum_{C_2(\Delta p)} \cdots \frac{1}{\mu \Delta p} \sum_{C_\infty(\Delta p)}$$

$$\times \left\{ \exp\left[\frac{i}{\hbar} S^{(1)}(E)\right] + \exp\left[\frac{i}{\hbar} S^{(1)}(E) + \frac{i}{\hbar} S^{(2)}(E)\right] + \ldots \right.$$

$$\left. + \exp\left[\frac{i}{\hbar} S^{(1)}(E) + \frac{i}{\hbar} S^{(2)}(E) + \ldots + \frac{i}{\hbar} S^{(\infty)}(E)\right] \right\}, \qquad (2.12)$$

where $\bar{g}$ differs from g by the constant factor of (2.7), $C_m(\Delta p)$ denotes a trajectory in phase space between its $(m-1)$st and m-th return to the region Δp (see Fig. 4), and $S^{(m)}(E)$ is the action on this trajectory

$$S^{(m)}(E) = \int_{C_m(\Delta p)} \sum_{i=1}^{M} p_i dq_i. \qquad (2.13)$$

In addition, we have introduced in (2.12) the normalization factor $\mu \Delta p$, which is equal to the product of the smearing region Δp by the trajectory density μ in p space.

At energies $E > E_c$ but near the limit E_c, the periodic trajectories change into random ones. Therefore the form of the trajectories in this transition region is quite complicated.[17] With increasing difference $E - E_c$ (i.e., with increasing K in accordance with (2.1)), however, the degree of mixing of the trajectories in phase space becomes ever stronger, and the system distribution functions becomes ever more homogeneous. In this case the contours $C_m(\Delta p)$ are equivalent in a statistical sense, independently of m, i.e., regardless of the number of the return of the system to the region Δp. By virtue of the foregoing, the properties of the set of values of $S^{(m)}(E)$ coincide for all m (as well as in the statistical sense). It follows directly therefore that (2.12) can be rewritten in the form

$$\bar{g}(E) = 1 + \left\{ \frac{1}{\mu \Delta p} \sum_{C(\Delta p)} \exp\left[\frac{i}{\hbar} S^{(1)}(E)\right] \right\} \bar{g}(E), \qquad (2.14)$$

where $S^{(1)}(E)$ is the action exerted on the trajectory $C(\Delta p)$ by the first return to the region Δp. From (2.14) we get

$$\bar{g}(E) = \left\{ 1 - \frac{1}{\mu \Delta p} \sum_{C(\Delta p)} \exp\left[\frac{i}{\hbar} S^{(1)}(E)\right] \right\}^{-1}$$

and the poles $\bar{g}(E)$ are obtained from the equation

$$\frac{1}{\mu \Delta p} \sum_{C(\Delta p)} \exp\left[\frac{i}{\hbar} S^{(1)}(E)\right] = 1. \qquad (2.15)$$

Expression (2.15) represents the new quantization rules in the case of stochastic violation of the integrals of motion. The left-hand side is a sum of random quantities, and therefore the roots E_j of Eq. (2.15) are random. We determine below the character of their distribution.

3. DISTRIBUTION OF THE LEVEL SPACINGS

We confine ourselves to a qualitative investigation of the behavior of the roots of (2.15), in analogy with the procedure of[10]. We need for this purpose a more detailed picture of the behavior of the trajectories in systems of the type of scattering billiard balls. A sufficiently strong excitation of the molecule means a parameter $K \gg 1$. In this case the colliding atoms are scattered mainly through small angles. The relaxation to the equilibrium state has two strongly differing time scales[4]: fast mixing in terms of some variable ϑ such as a phase (or coordinate), and slow diffusion in the action S. If $\Delta \vartheta_0$ is the initial small phase-space region from which the trajectories emerge, then after N collisions of the atoms these trajectories will cover in phase space a region with

$$\Delta \vartheta_N \sim K^N \Delta \vartheta_0. \qquad (3.1)$$

The time N_0 within which $\Delta \vartheta_{N_0}$ reaches a value on the order of unity and the initial volume $\Delta \vartheta_0$ spreads out completely can be obtained from (3.1):

$$N_0 = \frac{\ln(1/\Delta \vartheta_0)}{\ln K}, \qquad (3.2)$$

where $\ln K$, according to (3.1) is the growth rate of the

instability that leads to an exponential speedup of the trajectories in phase space.

We shall assume the dimensions of the system to be large enough so that many scatterings take place during the average time of one return of the trajectory. In this case the distribution of the action $S^{(1)}(E)$ in (2.15) has a sharp maximum corresponding to some value $\bar{S}(E)$. The random deviations of the positions of the levels from those determined from (2.15) with the aid of $\bar{S}(E)$ yield the ensemble of energy levels. Let E_0 be a certain energy level, i.e., a solution of (2.15). We can then indicate a trajectory for which the action is

$$S_0(E_0) \approx 2\pi\hbar n_0, \tag{3.3}$$

i.e., at $E = E_0$ the distribution of the actions has a sharp maximum at $S^{(1)} = W_0$. If $E_0 + \Delta E$ is the level closest to E_0, we have analogously

$$S_0'(E_0 + \Delta E) \approx 2\pi\hbar n_0', \tag{3.4}$$

where $|n_0' - n_0| \sim 1$ at sufficiently small ΔE. In other words, the action on the extremal trajectories corresponding to two neighboring eigenvalues of the energy differ by a finite amount $\sim 2\pi\hbar$. Let us explain how to perturb, as $\Delta E \to 0$, the trajectory $S_0(E_0)$ such as to change its action by an amount independent of ΔE.

Perturbation of a trajectory with energy E_0 by an amount ΔE alters the initial value of the variable ϑ by an amount

$$\Delta\vartheta_0 \sim \left(\frac{dK}{dE}\right)_{E=E_0} \Delta E, \tag{3.5}$$

with (3.5) independent of the nature of ϑ and determined from (3.1) with $N = 1$. The characteristic time (number of collisions) N_0 after which the perturbation of E_0 by an amount ΔE leads to a mixing of the phases ϑ is, according to (3.2) and (3.5),

$$N_0 = \frac{\ln(1/|\Delta E|) + \ln(1/(dK/dE))}{\ln K} \xrightarrow[\Delta E \to 0]{} \frac{\ln(1/|\Delta E|)}{\ln K}. \tag{3.6}$$

Thus, after N_0 scatterings, the phases ϑ, which determine also the change of S due to scattering, become random and diffusion with respect to action sets in. This means that after $N > N_0$ collision the action can take on any value, including (3.4). In the opposite case, when less than N_0 collisions are realized on the trajectory, stability obtains with respect to a small perturbation ΔE and the deviation ΔS is also small ($\Delta S \propto \Delta E$).

The probability $P(\Delta E)$ of the appearance of a level at a distance ΔE from E_0 can be defined as the probability that more than N_0 scatterings occur on the trajectory and instability sets in. On the other hand, at the value of S_0 in (3.3) the distribution of the number of collisions on the trajectory has a sharp maximum near a certain value N_S that depends only on E_0. As $\Delta E \to 0$ we get, according to (3.6), $N_0 \to \infty$ as well as the inequality

$$N_0 \gg N_s. \tag{3.7}$$

The condition (3.7) means that a probability of more than N_0 collisions during the time of one return is the probability of a very rare fluctuations. It is known that the **order** of magnitude of such a probability is

$$P(\Delta E) \sim \exp(-\text{const}\, N_0), \tag{3.8}$$

where the constant is of the order of unity. Substitution of (3.6) in (3.8) yields

$$P(\Delta E) \sim |\Delta E|^{\text{const}/\ln K}. \tag{3.9}$$

Formula (3.9) shows that as $\Delta E \to 0$ the probability of the appearance of a neighboring level at a distance ΔE in the region of the energy E tends to zero (repulsion) in power-law fashion. The critical exponent is of the order of $1/\ln K$, which according to (3.1) is the time of development of instability of the trajectories in phase space. The expression for the constant in (3.9) as well as the pre-exponential factor were obtained for glancing electrons in[10]. A similar method is suitable also for other problems. We, however, will not stop to calculate these quantities, but will emphasize in turn some general character of formula (3.9).

As already mentioned in Sec. 2, an increase of the molecule energy E causes an increase of the characteristic parameter R, and hence of the value of K. This leads to a decrease of the critical exponent in (3.9), and the dependence of P on ΔE becomes weaker. This means that the distribution of the levels at large E becomes more uniform.

4. CONCLUSION

The main result obtained above is that at sufficiently strong molecule excitations the energy spectrum becomes restructured and stochastic and as $\Delta E \to 0$ the probability $P(\Delta E)$ tends to zero in power-law fashion. In contrast to Dyson's theory, the exponent is determined directly from the properties of the Hamiltonian of the system and is due to the stochastic instability of the trajectories.

It is of interest to compare the distribution of the distances between the levels for two cases: a disordered system and a system with violated integrals of motion of the considered type.

The value of $P(\Delta E)$ for a one-dimensional disordered system was calculated by Pokrovskiĭ.[18] It follows from his results that $P(\Delta E)$ does not follow a power law in this case and the level repulsion has an exponential character. This result remains in force apparently also in the non-one-dimensional case, since the trajectory instability develops more slowly in disordered systems than in the case of stochastic violation of the integrals of motion.

The universal character of the obtained expression (3.9) allows us to apply it to a large class of physical systems. In particular, the law (3.9) should hold for the oscillation frequencies of plates and resonators with boundary shapes such as shown in Fig. 2.

We ascertain now how a strongly excited molecule should radiate in the course of dissociation. If the dis-

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sociation proceeds stepwise, i.e., the molecule executes in succession transitions to the nearest levels, then its emission spectrum has the following character: Owing to the random distribution of the level, a broad band of low frequencies that correspond to small ΔE appears. Assuming $\hbar\omega = \Delta E$, we can obtain from (3.9) the intensity $I(\omega)$ for the low-frequency "tail" of the spectrum:

$$I(\omega) \sim P(\Delta E = \hbar\omega) \sim \omega^{\mathrm{const}/\ln K}. \qquad (4.1)$$

It should be noted that since no publication contained a clear-cut picture of the behavior of the levels of excited molecules, there was no idea of what information should be sought concerning the spectrum. The results (2.15), (3.9), and (4.1) can serve as a first step towards filling this gap. One cannot exclude the possibility that the very broad low-frequency band observed in the fluorescence spectrum of pentacene ($C_{22}H_{14}$) molecules[19] is due to randomization of the molecule levels.

The author has recently learned of a new study by Gutzwiller,[20] where a correspondence is established between the anisotropic Kepler problem (which arises when the motion of an electron in the field of an impurity ion is considered) and the motion on a billiard table with walls of negative curvature. This result means that in the case of sufficiently strong anisotropy in the Kepler problem the distribution of the energy levels of the bound states should be random and possess the properties described above.

1)We recall that collision of spheres of equal radius can be replaced by the equivalent problem of the scattering of a point by a sphere of double the radius.

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