INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

APPROACH TO BOND SELECTIVE DISASSOCIATION OF MOLECULES

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Chem. Bond

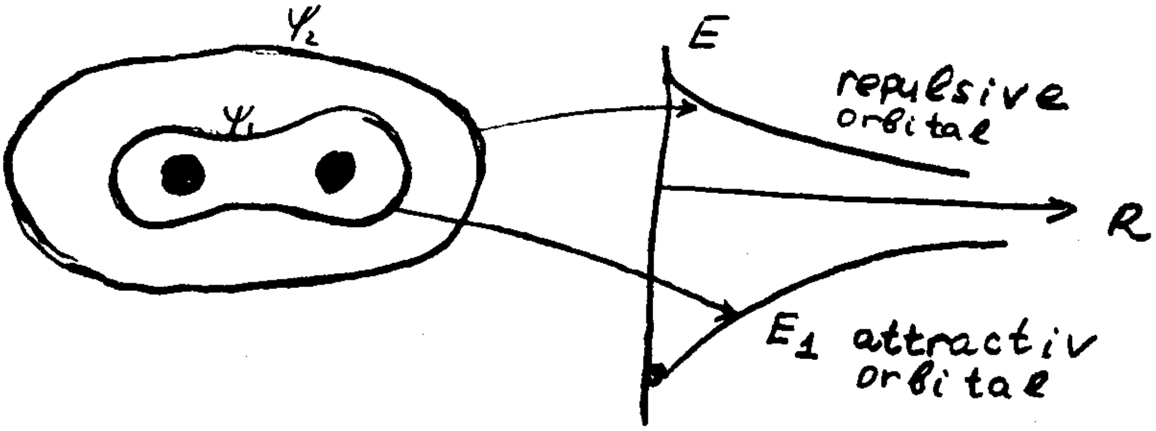
Hartree-Fock theory

$$i\hbar\dot{\psi} = -\frac{\hbar^2}{2m}\nabla^2\psi + U\psi$$

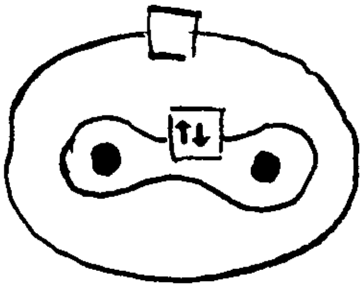
$$U = U_n - \int e^2 \frac{\sum_n \psi_n(r')\psi_n^*(r')c_n}{|r-r'|}\, d^3r'$$

$$\psi_n(r) = \psi_n(r,\{R_j\}) \qquad E_n = E_n(\{R_j\})$$

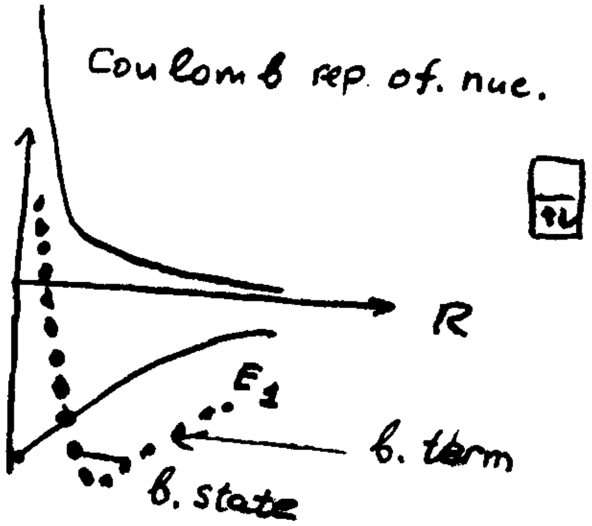
diatomic



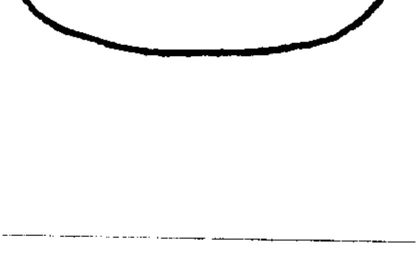
g.e.s.



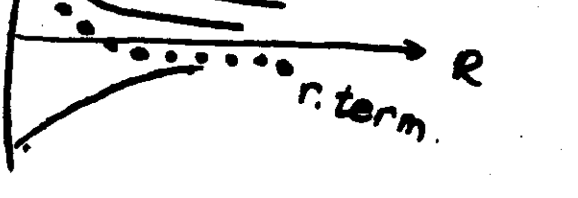
$$U = U_n + 2E_1$$

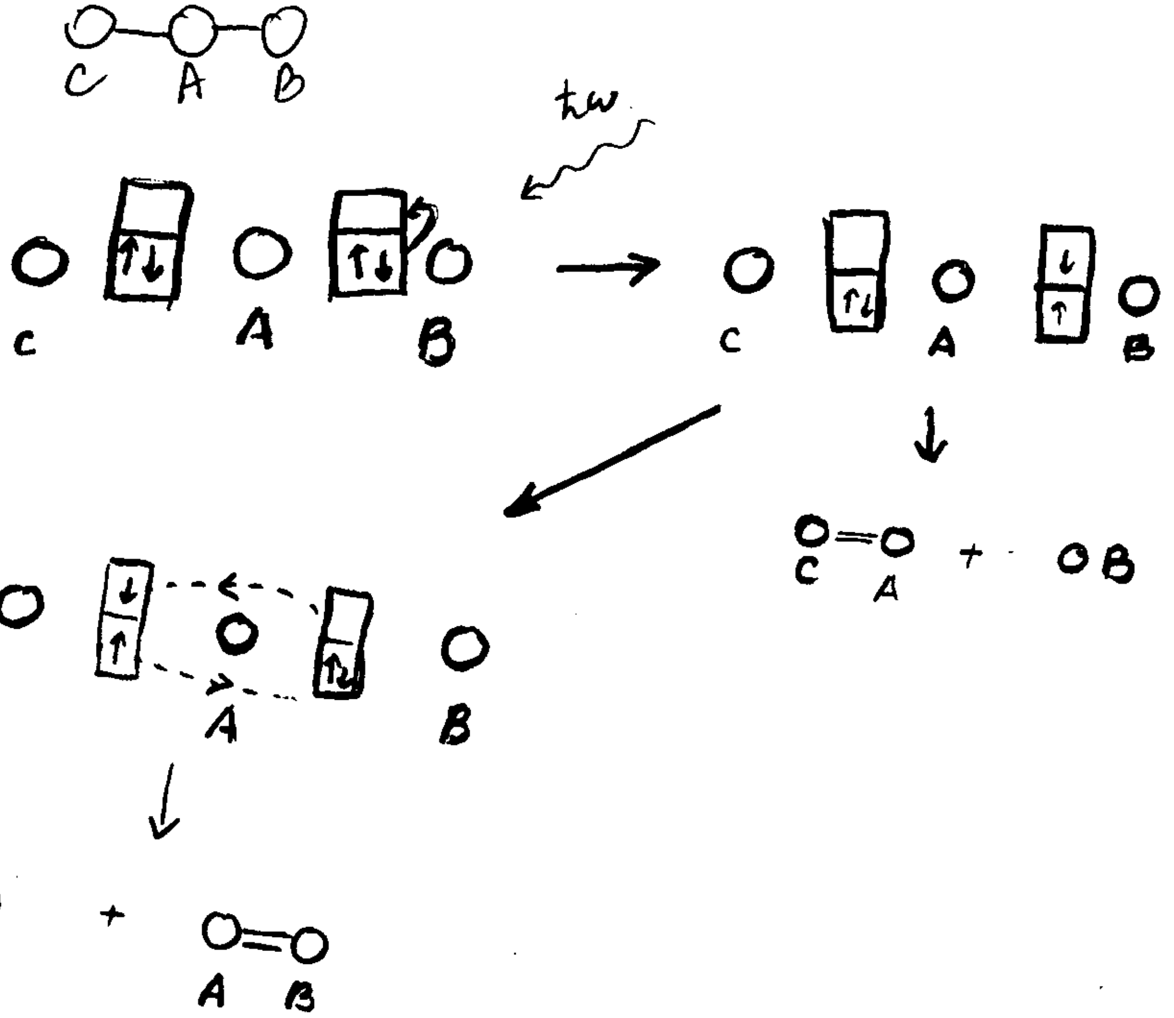


e. ex. s.

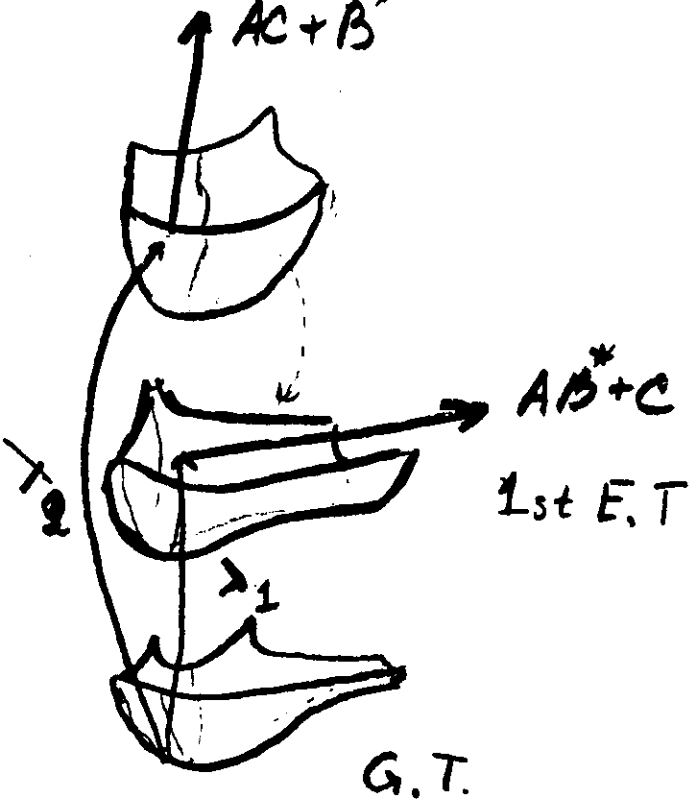


$$U = U_n + E_1 + E_2$$





correct discription



$$ABC + \underset{\lambda_1}{\hbar\omega} \longrightarrow AB^* + C$$

$$ABC + \underset{\lambda_2}{\hbar\omega} \longrightarrow AC + B^*$$

$$\dashrightarrow AB^* + C + \underset{\lambda_3}{\hbar\omega}$$

Commentary

Figure 1

According to Hartree-Fock theory chemical bond is formed as a result of distributing of electrons among different electron states, obtaned by solving one-electron Schrodinger equation in self-consistent electrical field. One-electron states, increasing their energy with lenghening of intranuclear distance, are named bounding orbitals, while those decreasing are called repulsive. Potential energy of molecule - molecular term - results from summation of coulomb's nuclear potential and electron configuration energy. Usually attractive orbitals energies are lower then those of repulsive ones. Transferring one electron from attractive orbital to repulsive one (this can be done via absorption by electron cloude of the photon of certain frequency) sometimes results in change of the form of term's potential curve. In other words, obtained electron term may become repulsive. In this case the bond breaks.

Figure 2

Polyatomic molecules have a number of bonds. Attempting to break one of them by transferring one of the electrons from attractive orbital to repulsive one, may fail because of electron cloud energy redistribution: electron vacancy, created on attractive orbital will be filled by electron from another bond, while electron from repulsive orbital will go into another bond. These factors are taken into account when considering exact molecular term (ground and excited). Electron cloud transition to certain excited state may result in potential curve

New York · Chichester · Brisbane · Toronto

Photochemistry of small molecules

Hideo Okabe

National Bureau
of Standards

$OCS \xrightarrow{h\nu} CS + O(^3P) \quad \lambda < 1820$ Å
$OCS \xrightarrow{h\nu} CO + S(^1S) \quad \lambda < 2110$ Å
$OCS \xrightarrow{h\nu} CS + O(^1D) \quad \lambda < 1410$ Å

$H_2S \xrightarrow{h\nu} H + H + S \quad \lambda < 1650$ Å
$H_2S \xrightarrow{h\nu} H + SH \quad \lambda < 3170$ Å
$H_2S \xrightarrow{h\nu} H_2 + S \quad \lambda < 4060$ Å

$ClC_2H \xrightarrow{h\nu} ClC_2H^*$
$ClC_2H^* \longrightarrow ClC_2H + h\nu'$
$ClC_2H^* \longrightarrow ClC_2H^{**}$
$ClC_2H^{**} \longrightarrow Cl + C_2H$

$CH_3I \xrightarrow{h\nu} CH_3 + I(^2P_{1/2})$

$CH_3I \xrightarrow{h\nu} CH_3 + I(^2P_{3/2})$

$HNCS \rightarrow HNC + S(^3P)$
$HNCS \rightarrow NCS + H$

$NH_3 \xrightarrow{h\nu} NH_2(\tilde{X}\,^2B_1) + H \quad < 2800$ Å
$NH_3 \xrightarrow{h\nu} NH(a^1\Delta) + H_2 \quad < 2240$ Å
$NH_3 \xrightarrow{h\nu} NH(X^3\Sigma) + H + H \quad < 1470$ Å

$HFCO \xrightarrow{h\nu} HF + CO$

$HFCO \xrightarrow{h\nu} F + HCO$

$N_2O \xrightarrow{h\nu} N_2 + O(^3P)$
$N_2O \xrightarrow{h\nu} NO + N(^4S)$

$HNCO \xrightarrow{h\nu} H + NCO\ (A^2\Sigma)$

$HNCO \xrightarrow{h\nu} NH(c\,^1\Pi) + CO$

$HCHO \xrightarrow{h\nu} H_2 + CO \quad \varphi_{55}$

$HCHO \xrightarrow{h\nu} H + H + CO \quad \varphi_{56} \quad \lambda < 2830$ Å

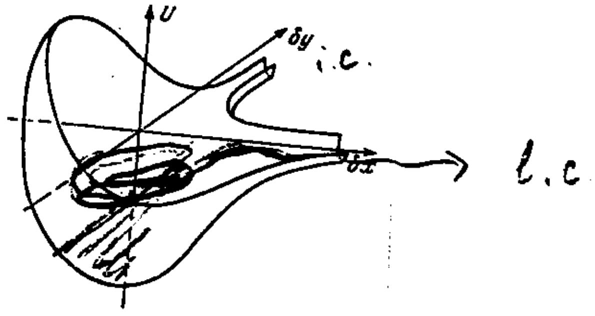
$C_2H_2 \xrightarrow{h\nu} C_2H_2^* \rightarrow C_2 + H_2$
$C_2H_2 \xrightarrow{h\nu} C_2H_2^* \rightarrow C_2H + H$

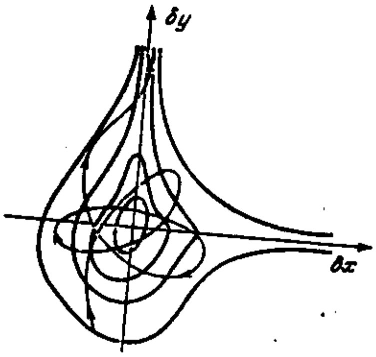
$PH_3 \xrightarrow{h\nu} PH(X^3\Sigma) + H_2$
$PH_3 \xrightarrow{h\nu} PH_2(\tilde{X}\,^2B_1) + H$

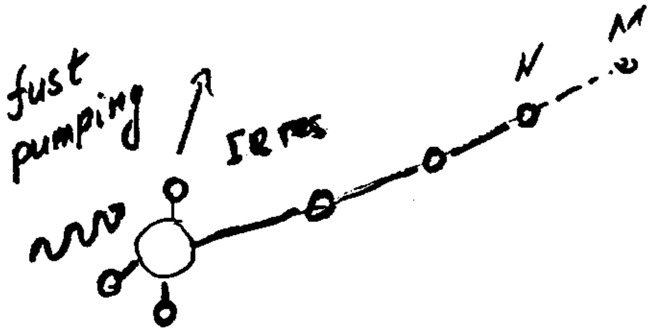
secondary processes take plase in
uncontrolable way.

Ground term processes

Usualy vibrational stochasticity prevents to brake a band which is not ~~the~~ weakest one







N-M vibraticns

either don't excite at all

or do it too slowly

photon absorbtion rate - $I\sigma \gg \varkappa \nabla T$ -

- Energy transmition velocity

formation corresponding to breaking of chosen bond. How to break a certain bond? - Just finde excited term repulsive in needed direction and produce aqppropriate transition by one- or multiquantum photoeffect. However electron state of fragments created may be highly excited, and number of secondary processes may take place.

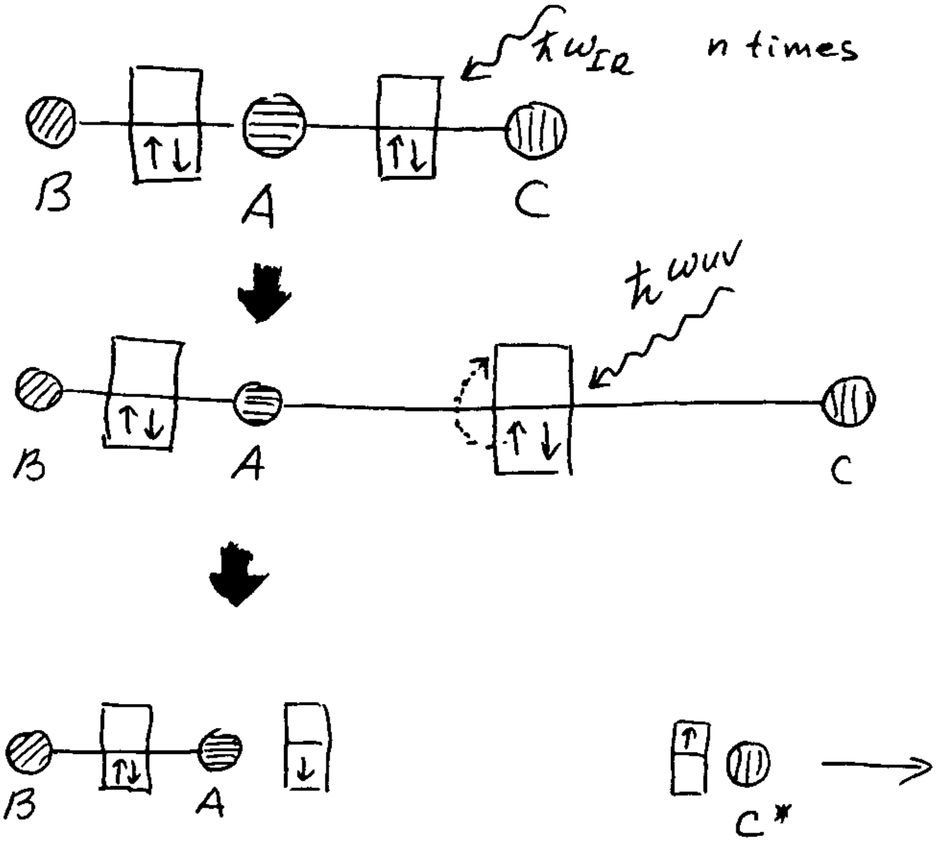
Figure 3

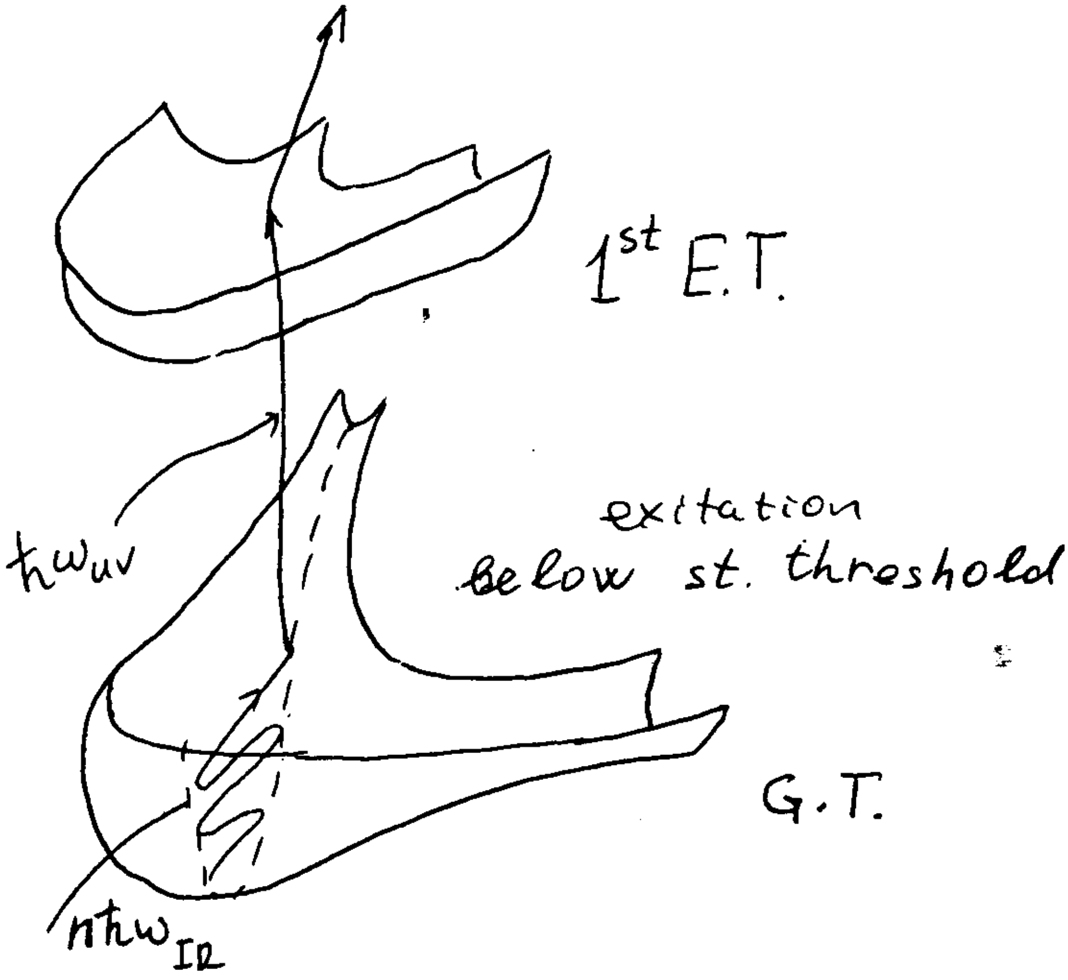
Here is number of exsamples of different photochimical processes. One can see that usually by making radiation wavelength shorter it is possible to switch on some new chanales of decay without switching off previous ones. It take place due to secondary processes, when absorbed energy lead either to heating or to luminescence.

Figure 4

If appearence of highyly electronicaly excited fragments is undesireble, an attempt should be made to break chosen bond by resonant vibrational excitation within the frame of ground electron term. However usually it is not easy to achive due to nonliniar interaction of different vibrational degrees of freadom - vibrational energy of one bond is quickly transferred to the other ones; thus the bond broken is not the swung one, but the weakest. In order to succeed it is necessary either to find an excitation method free from vibrational thermalisation, or to pump energy to intended bond fast enough to

IR-UV-action UV(Vis)





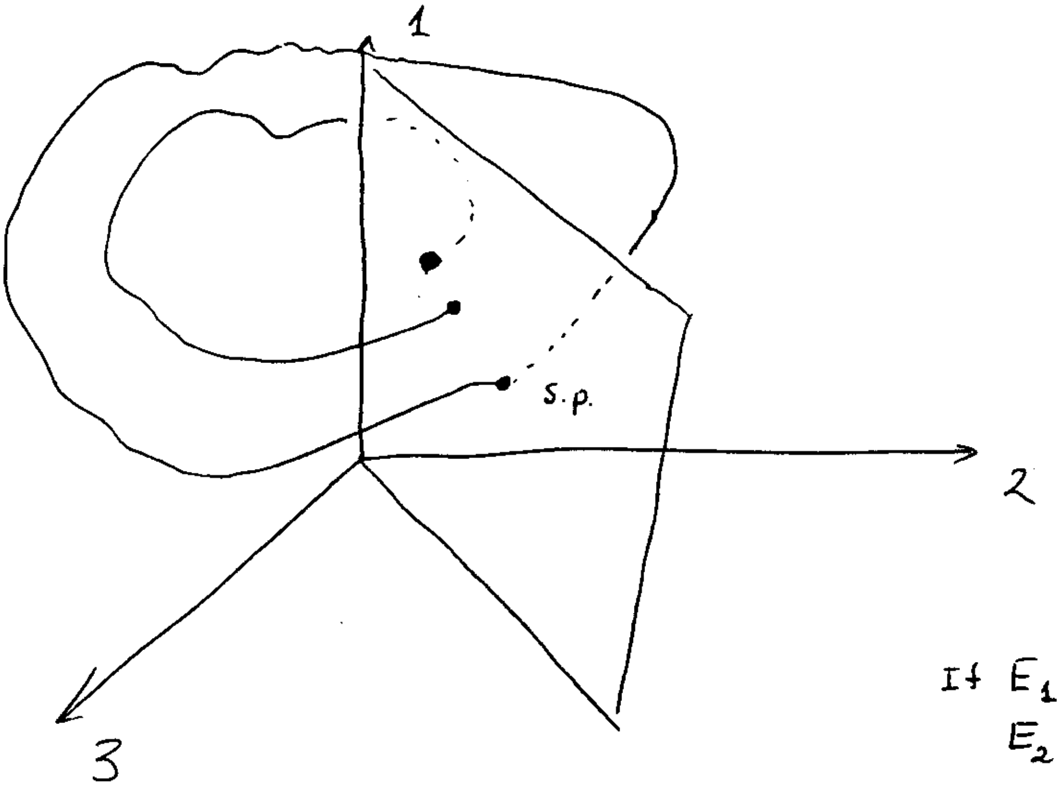
STOCHASTICITY
WHAT IS IT?

Poincaré section

2 - dim. case

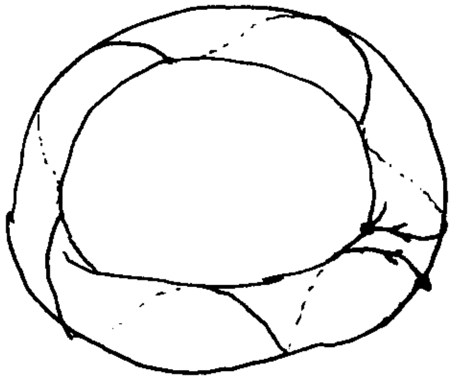
4 - dim. ph. sp. $x_1 \otimes x_2 \otimes p_1 \otimes p_2$

3 - dim En. surf $E = \mathrm{const}.$



If $E_1 = \mathrm{const}$
$E_2 = \mathrm{const}$

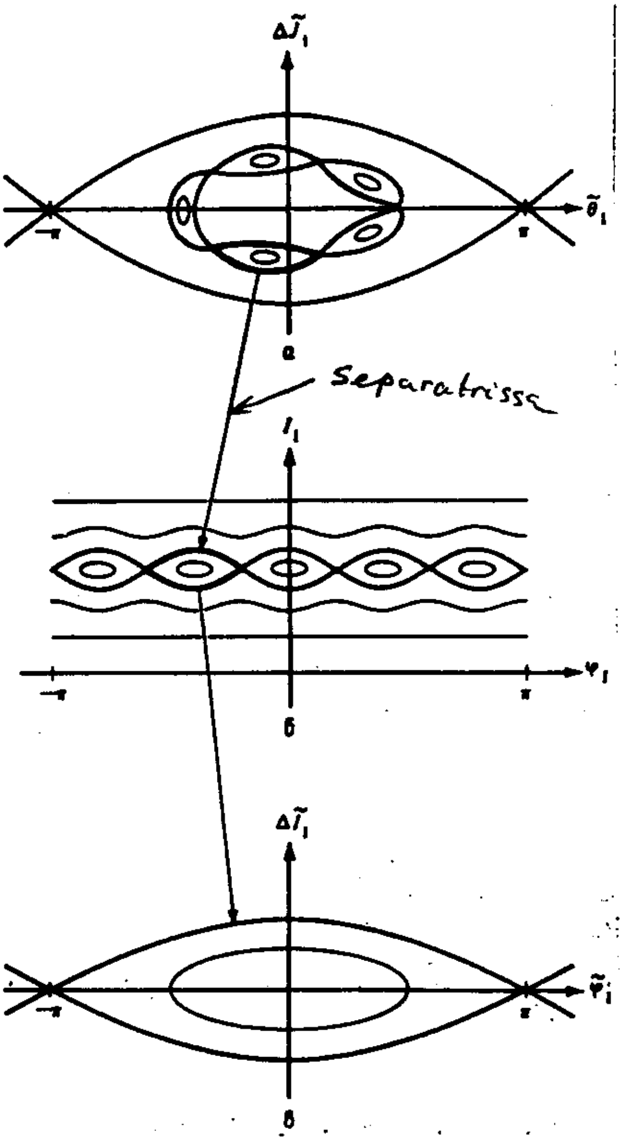
Invariant
Tor.

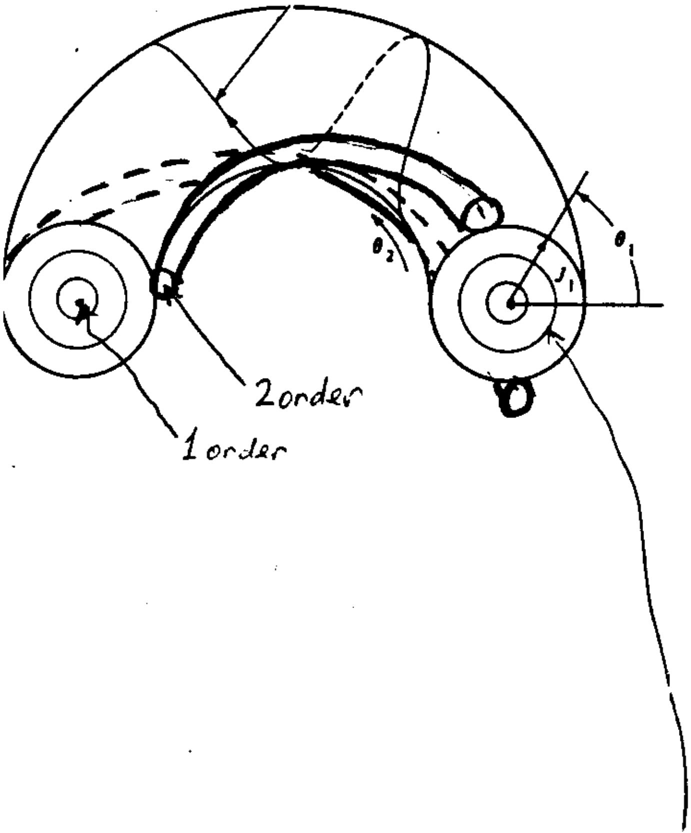


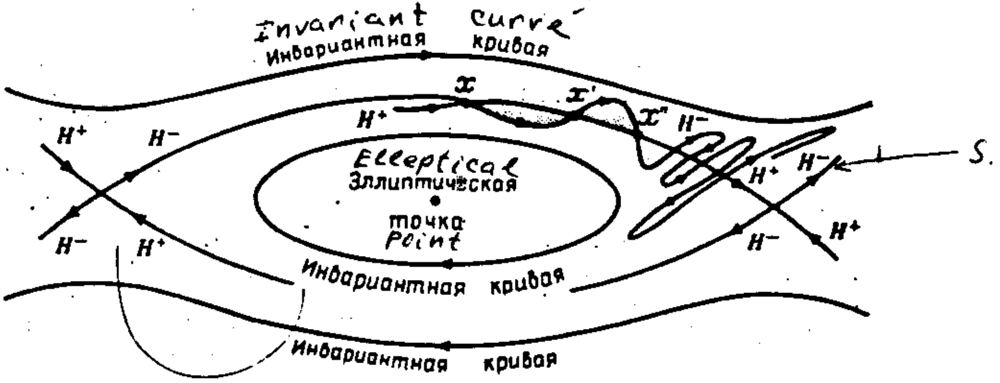
If there are full number of invariants trajectoly must wind itself on the surface of tor. Otherwise it may be everywhere.

M. A. Lieberman   STOCHASTIC MOTION

SPRINGER-VERLAG
NEW YORK   HEIDELBERG BERLIN

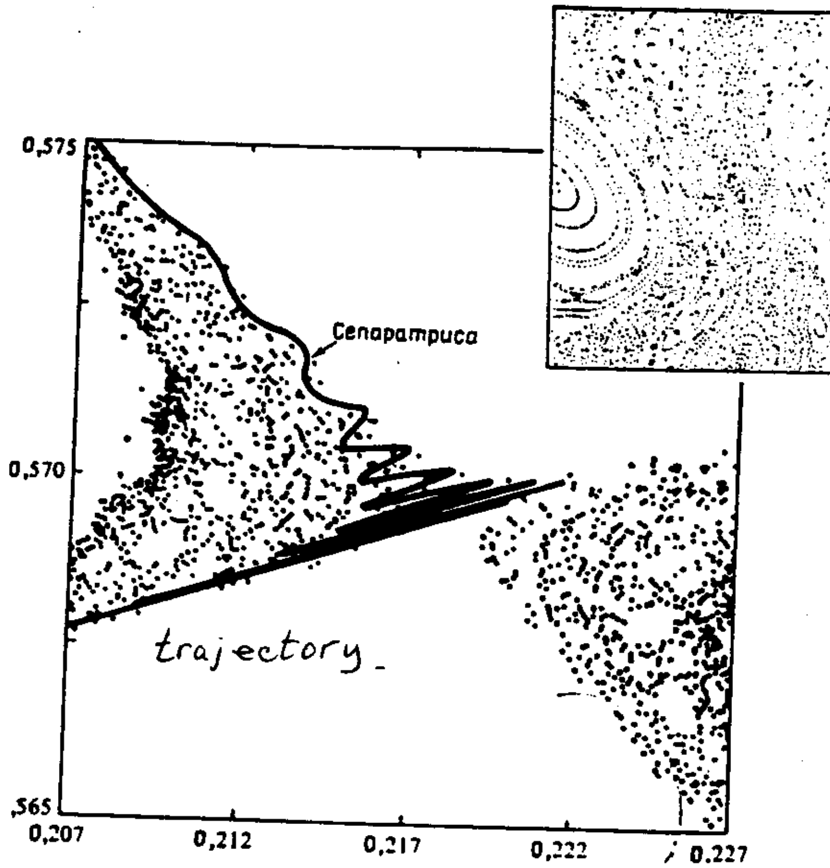




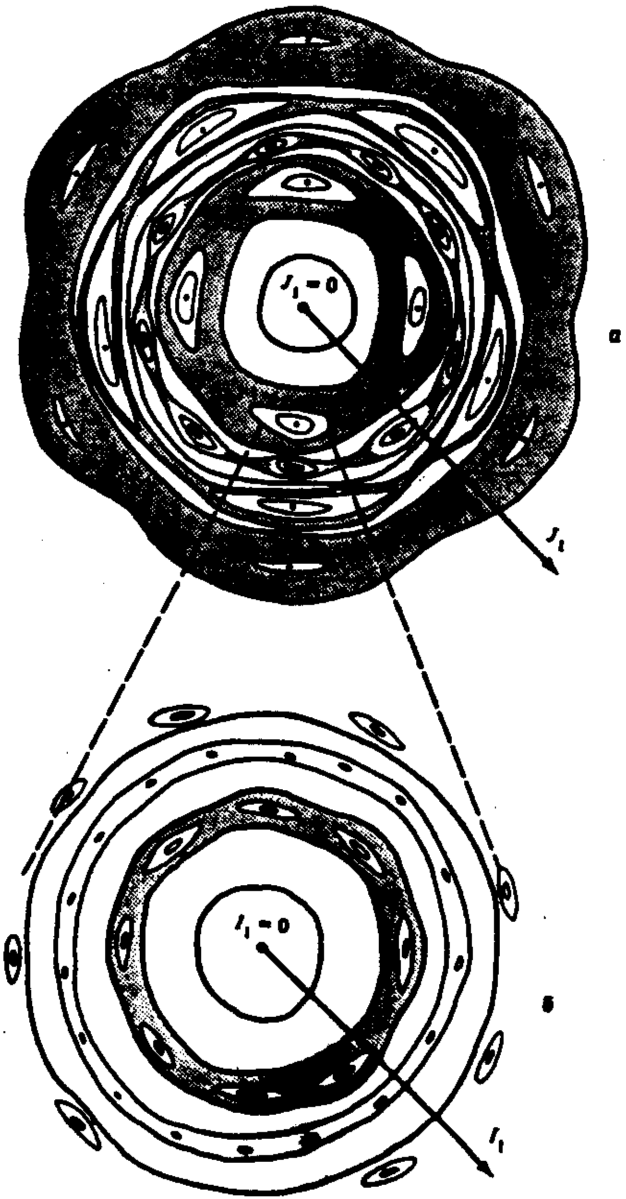


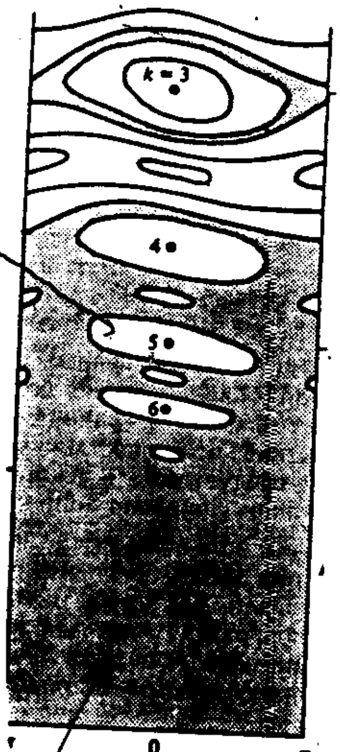
There are trajectories which came at the same point at P.s after one turn, other ones returns after several periods. Between them there is a curve deviding different kind at motion - separatrissa It has complex structure, repeating in more and more detailed scales. Small perturbations of general type destroy the motion near sepant

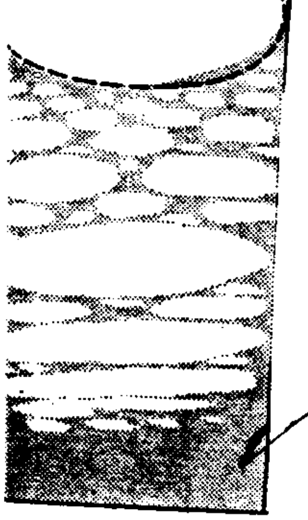
NUMERICAL
SOLUTION



trajectory

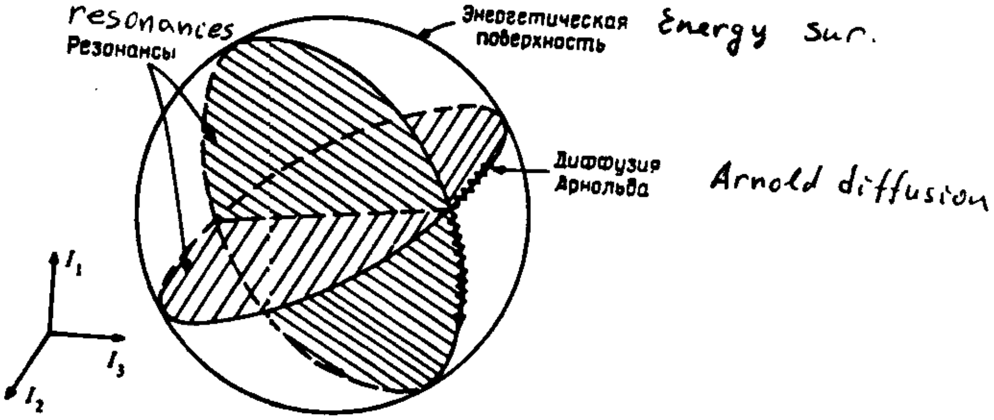




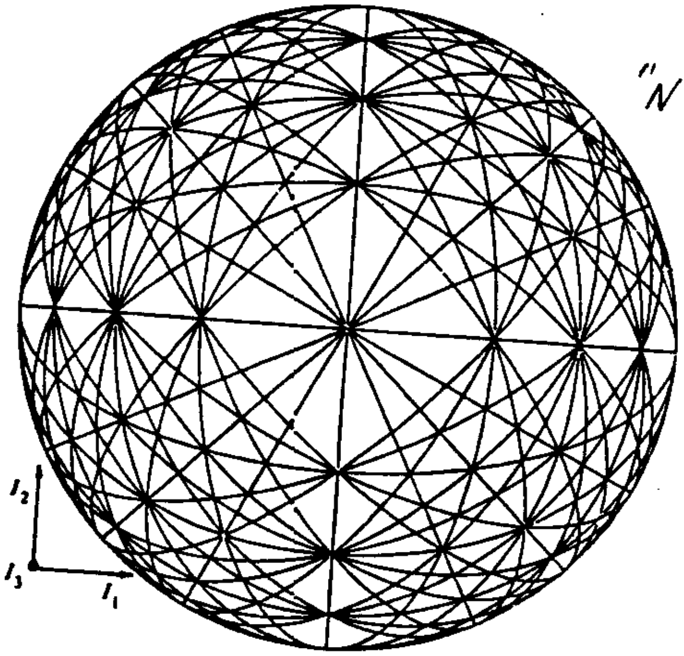


stab. "islend"

chaos ("sea")



a



In the multy-dimentional case there is dense "net" of resonaces. Topology of space permits to come from one region of stochasticity to another, so the stochasticity take place in each point of energy surface.

prevent its transmition to the weakest bond. It can be done only in case when the bond destined for breaking is located far enough from the weakest one. The approach presupposes the necessity to find the way of description of stochastical vibrations excitation.

Figure 5

There's one more intermidiate possibility. If the first excited term is not repulsive for bond of interest, but vibrational energy needed for its break is relatively low, it is possible to excite molecule vibrationally within the frame of ground electron term along the needed bond below the level of stochastization before electron transition. This approach allows to expect the appearance of fragments at relativly low level of electron excitation. However, description of such a vibrational-electronic process is much more labour-consuming.

Figures 6-9

Approach to stchastization problem is well developped in classical mechanics. What is needed for stochasticity? First, at least bidimentionality of motion. In this case phase spase is 4-dimensional, iswoenergetic surface is 3-dimensional and its Poincare' section is bidimensional. An exsample of such a section is shown in figure 7. Regions of stable motion are separated by regions of stochasticity. When non-linearity is small regions of stochasticity are small too and corresponds to those points in space, where overlap at least two resonances, i.e. $\Sigma(\partial H/\partial I_k)\ N_k = 0$ for two different sets of $\{Nk\}$. For

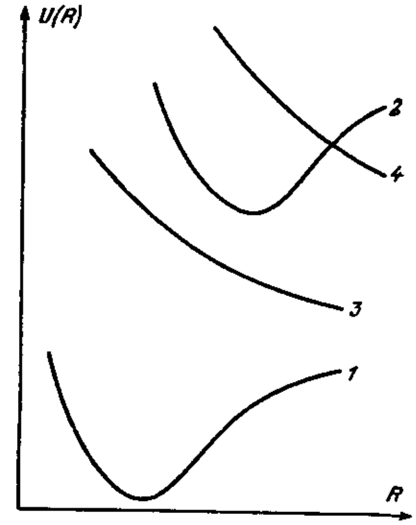
$$\left.\begin{aligned}&\mathcal{E}_v \approx MV^2 \sim a^2\partial^2U/\partial R^2 \sim a^2U/R^2,\\ &\mathcal{E}_r \approx MR^2\Omega^2.\\ &mvR \approx \hbar,\quad MVa \approx \hbar,\quad MR^2\Omega \approx \hbar.\end{aligned}\right\} \Rightarrow$$

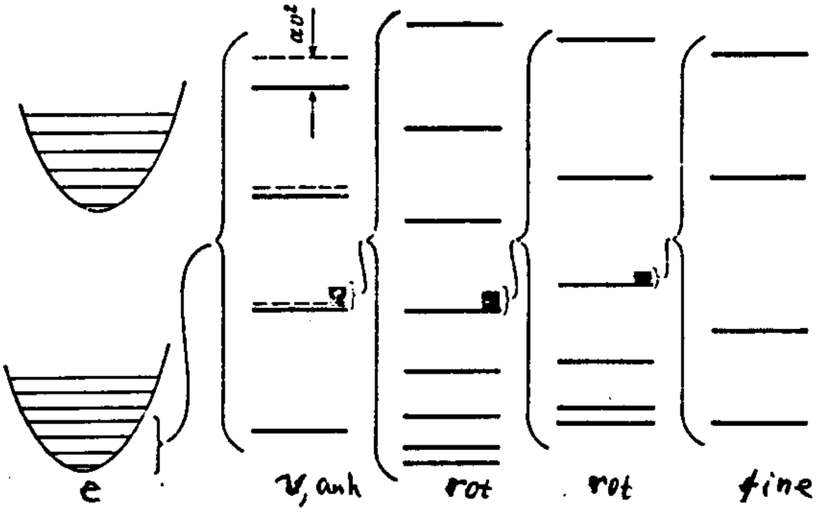
$$\approx (M/m)^{1/2} = 1/\Lambda^2$$

$$a/R \approx (m/M)^{1/4} = \Lambda,$$

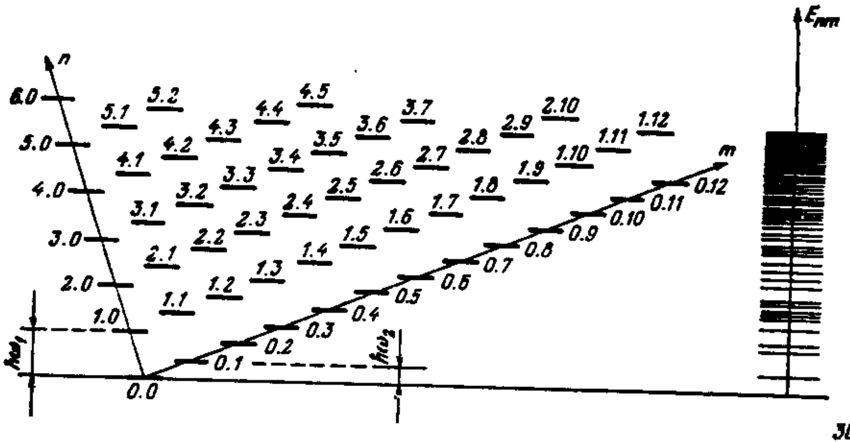
$$v/V \approx (M/m)^{3/4} = 1/\Lambda^3.$$

$$\Lambda = (m/M)^{1/4},$$

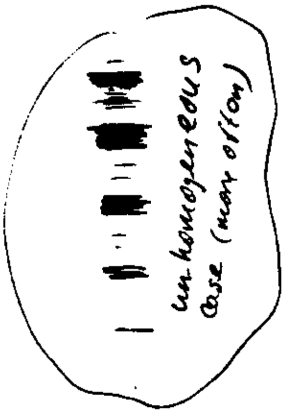




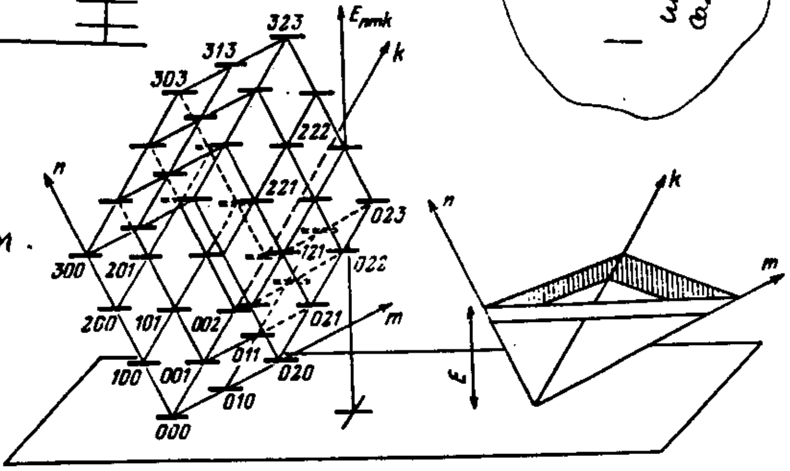
Hyerarchya of spectra

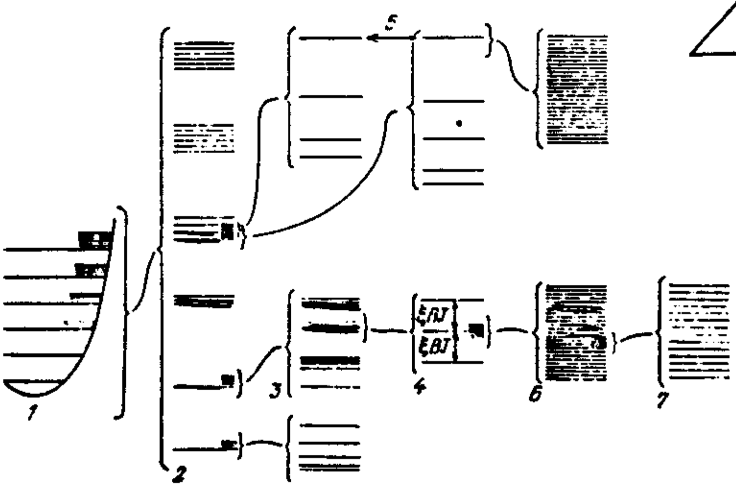


two dimentions



three dim.





degenerate mode

coincid. resonances

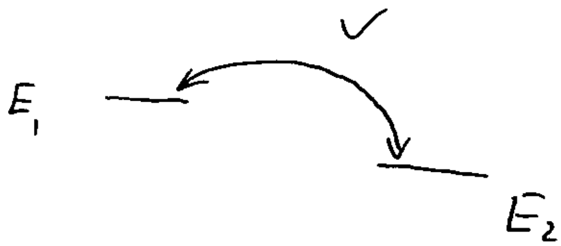
(cl. st.)

Fermi resonance

of two states

$$\hat{H} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

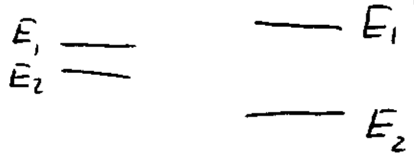
e.f $\psi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $\psi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$



$$\hat{H} = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix}$$

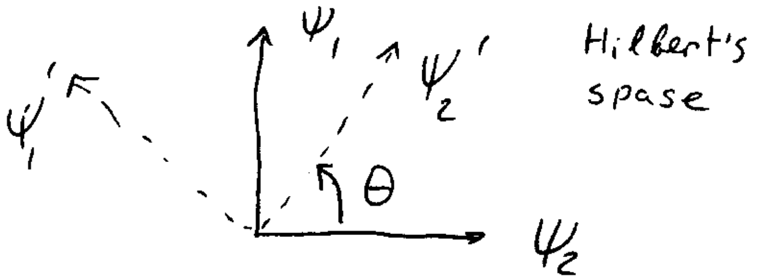
$\Downarrow$

e.f. : $\psi_1' = \begin{pmatrix} \sin\theta \\ \cos\theta \end{pmatrix}$; $\psi_2' = \begin{pmatrix} \cos\theta \\ -\sin\theta \end{pmatrix}$

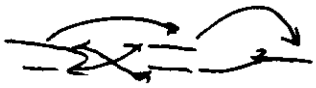


$$E_{1,2}' = \frac{E_1+E_2}{2} \pm \sqrt{\left(\frac{E_1-E_2}{2}\right)^2+V^2}$$

$$\mathrm{tg}\,\theta = \frac{2V}{E_1-E_2}$$



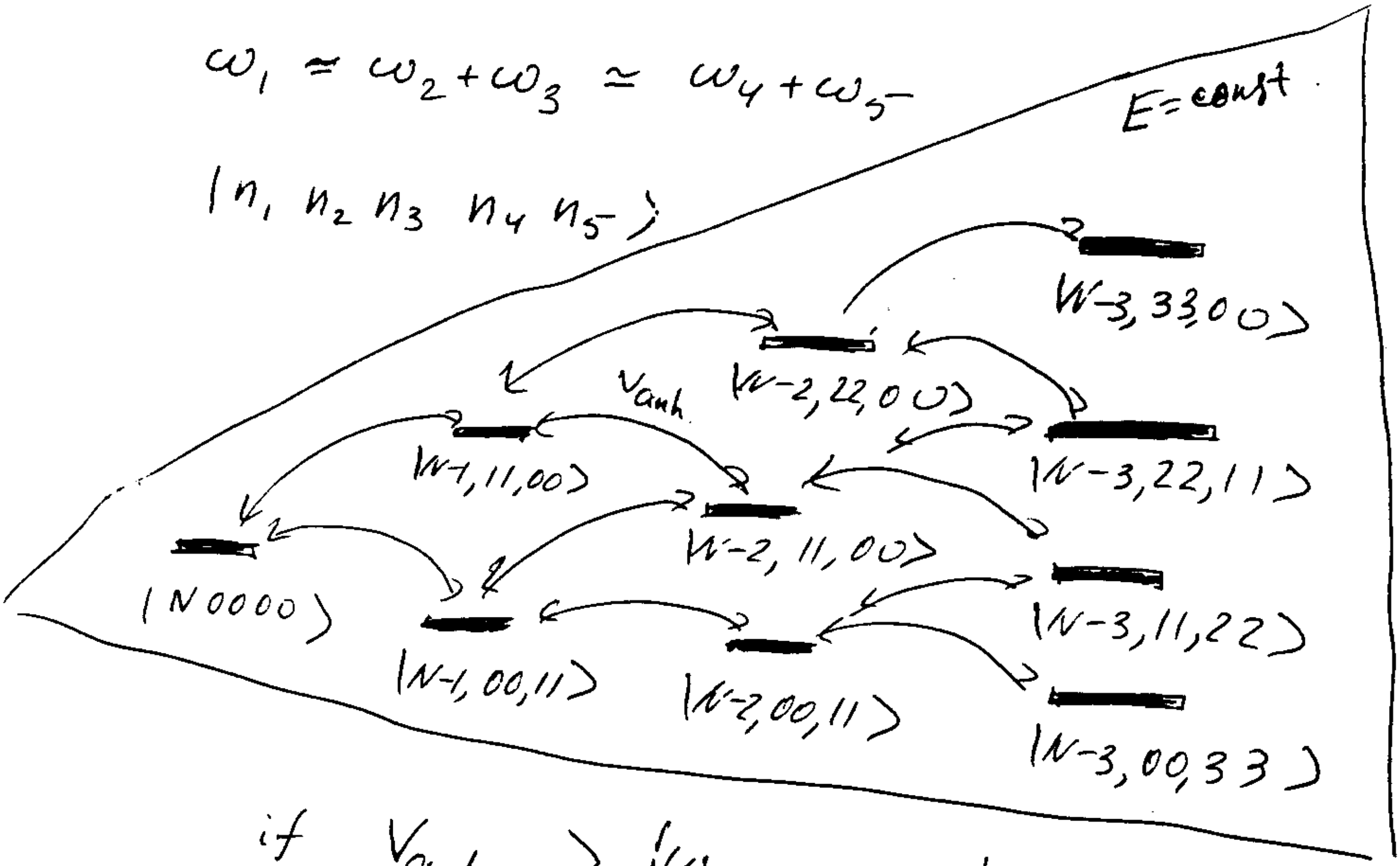
many dimentions



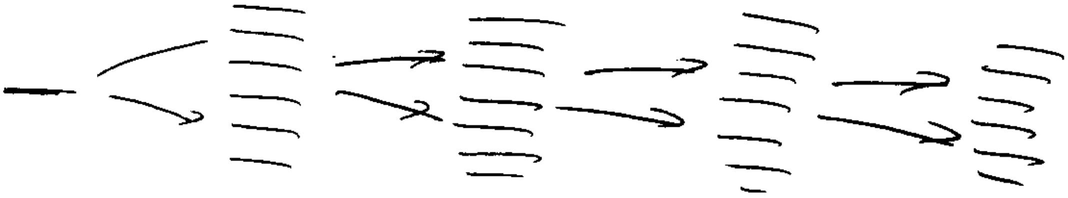
Fermi resonances of vibrations

$$\omega_1 \simeq \omega_2+\omega_3 \simeq \omega_4+\omega_5$$

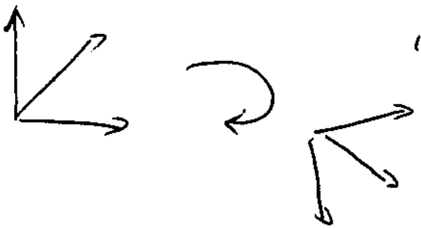
$|n_1\, n_2\, n_3\, n_4\, n_5\rangle$



if $V_{anh} > |\omega_1-\omega_2-\omega_3|; |\omega_1-\omega_4-\omega_5|$ then F.R.C. is fulfiled for number of levels



New e-v. b



is strongly "turned" whith respect to old one in Hilbert spac

smal variation of parametr gives big additional "turning."

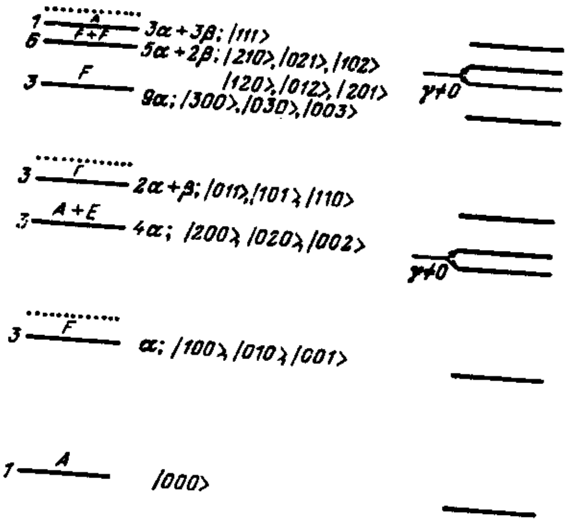
V_3 degenerate mode ⟹ under tensor anharmonical perturbation.

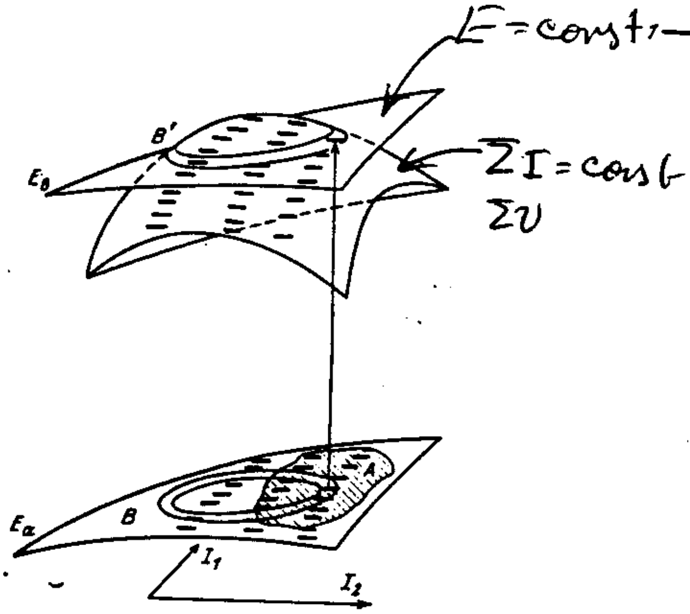
⇓

$H_{anh} =$

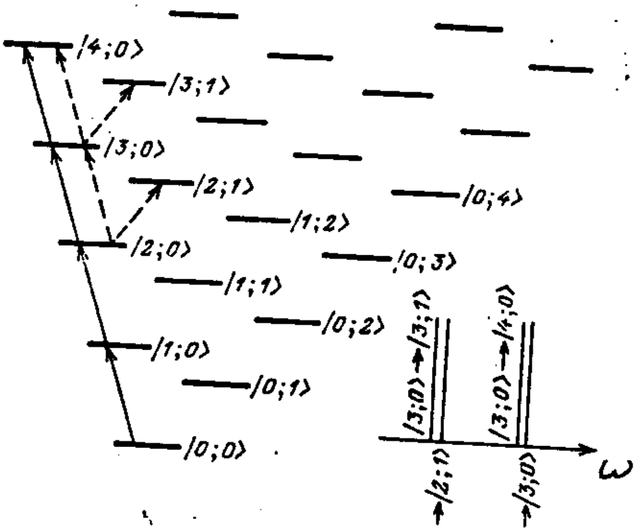
$$= \alpha(v_1^2 + v_2^2 + v_3^2) + \beta(v_1 v_2 + v_1 v_3 + v_2 v_3).$$

$$+ \beta(a_1^+ a_1 a_2^+ a_2 + a_1^+ a_1 a_3^+ a_3 + a_2^+ a_2 a_3^+ a_3) +$$
$$+ \gamma(a_1^+ a_1^+ a_2 a_2 + a_1^+ a_1^+ a_3 a_3 + a_2^+ a_2^+ a_3 a_3 +$$
$$+ a_1 a_1 a_2^+ a_2^+ + a_1 a_1 a_3^+ a_3^+ + a_2 a_2 a_3^+ a_3^+),$$



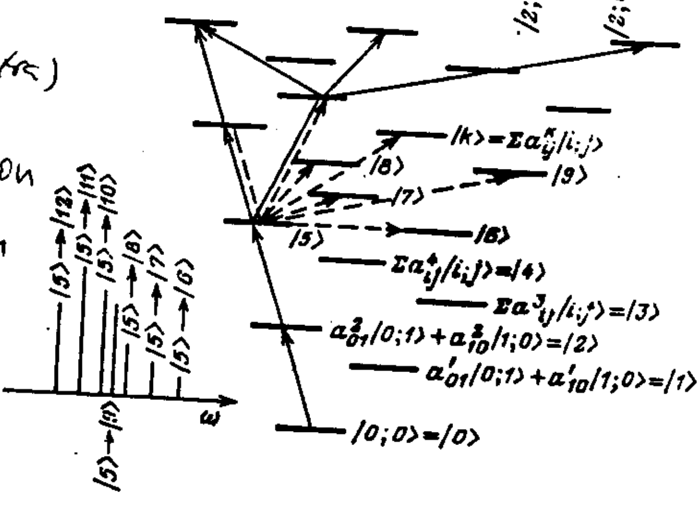


$$\hat{H}_{anh} = \begin{pmatrix} 4\alpha & 2\gamma & 2\gamma & 0 & 0 & 0 \\ 2\gamma & 4\alpha & 2\gamma & 0 & 0 & 0 \\ 2\gamma & 2\gamma & 4\alpha & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\alpha+\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\alpha+\beta & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\alpha+\beta \end{pmatrix}.$$



consequences:

1. no degeneration
2. no prohibition rules (many line in transition spectra)
3. sensitivity to perturbation
4. destruction of quantum numbers



multidimentional problem, even for small nonliniarity there is a dense net of resonances, so that stochasticity region can cover vast domaine of phase space. In the vicinity of "islends of stability" motion is a superposition of independent vibrations of two degrees of freadom (they do not necessarily corresponds to initial coordinats, being rather a complex non-linear combination of them). Energy is not transmitted from one degree of freadom to another. But how to obtain such vibrations? And what happens in quantum case? In order to answer these questions, one must resort to the theory of molecular spectra and theory of spectrally complex systems.

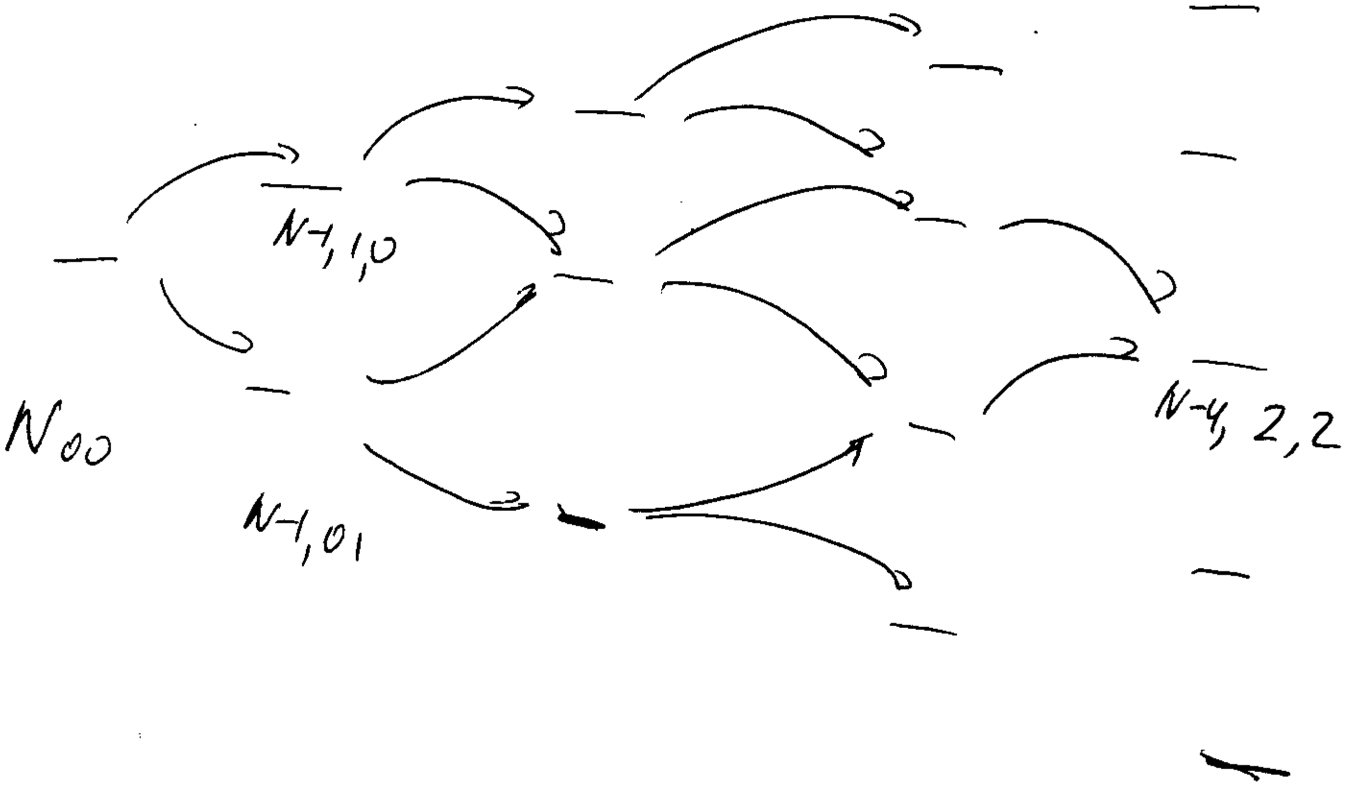
Figure 10

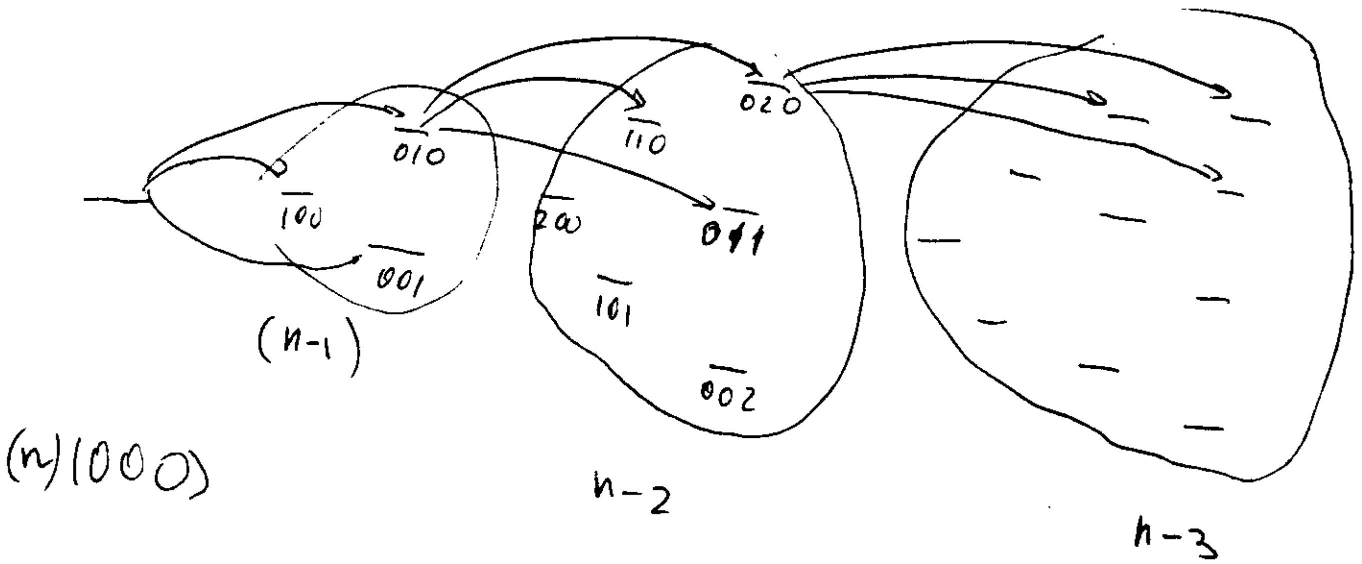
As one of many-body problems, the description of polyatomic multielectron molecule is possible only due to small parameter existence (Born-Oppenheimer parametr $(m_e/M)^{1/4}$). Due to this parameter existence the molecular hyerarchya of spectra appears. Electron motion is of zero order of magnitude, vibrational quanta of second order, cubical anharmonicity - of third one, rotational energies and 4th order anharmonicity are of forth order. In one-dimensional case - for 2-atom molecule - this nearly always allows to separate completely electron vibrational and rotational degrees of freadom.

Figure 10-13

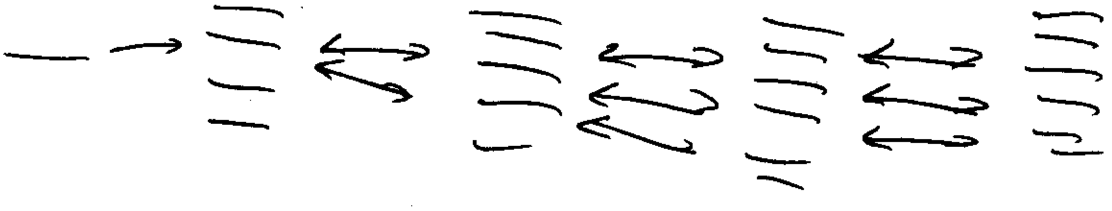
In multidementional case (polyatomic molecule) situation is much more complicated. In harmonic approximation levels are characterized by

Quantum numbers destruction and excitation problems as an analog processes in multylevel sistems





aggregate of bands problem



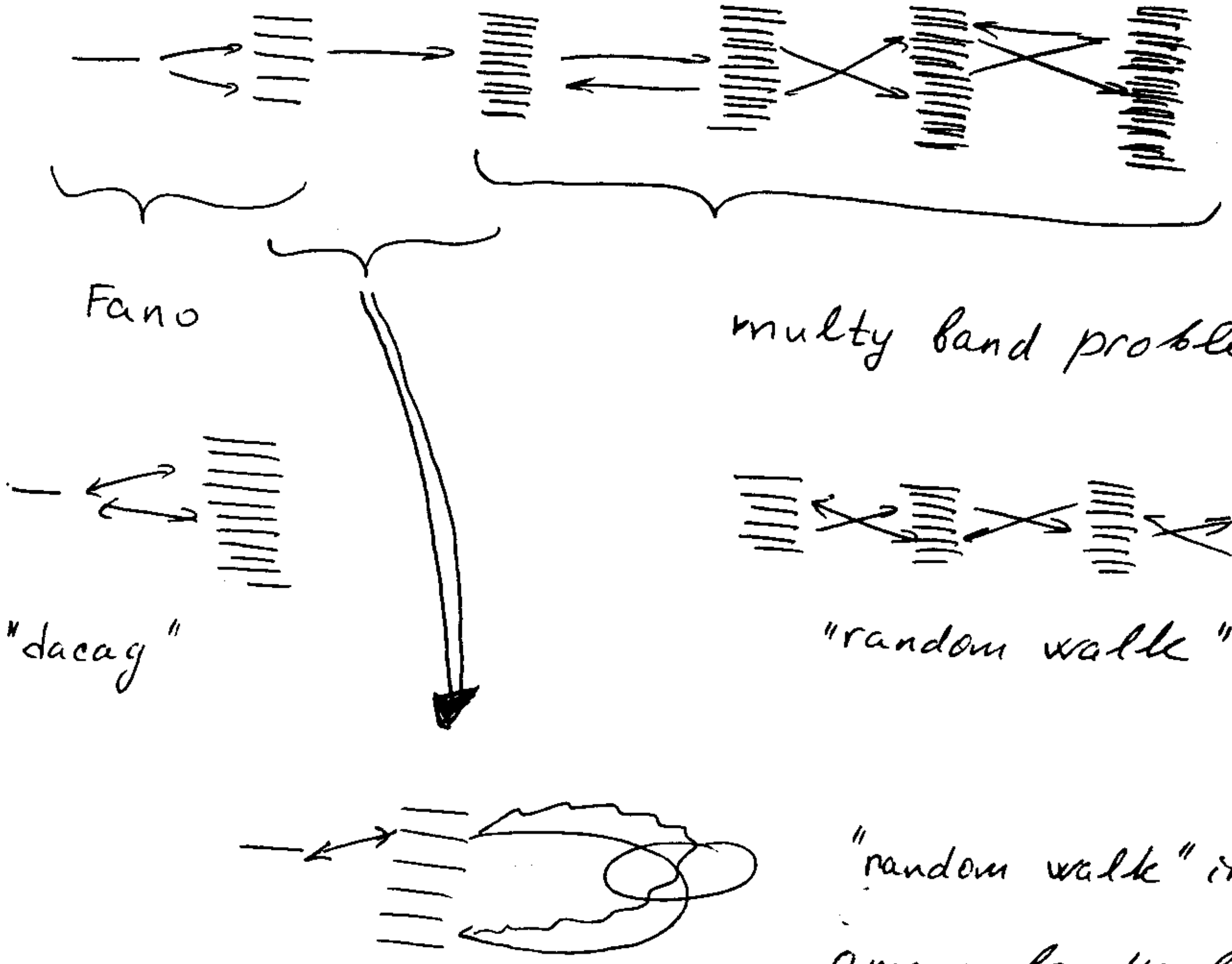
sets of quantum numbers (different modes occupation numbers), density of states increases quickly with the growth of energy $g \sim \mathcal{E}^{d-1}$, d - number of vibrational degrees cf freadom. Many levels are close to each other. Anharmonic interaction brings them to Fermi resonances. States $|a\rangle$ and $|b\rangle$, whose energies difference $|E_a - E_b| < V$ - is smaller than their interaction value, are considerably restructured to form new eigenfunction basis. If resonance of frequencies occurs, for example $\nu_i - \nu_j - \nu_k < V_{anh}^{i,j,k} / \hbar$, anharmonic interaction is capable of making total change in vibrational spectrum. Condition of Fermi resonance is an additional (quantum) demand with respect to the classical case. Under these conditions the destruction of quantum numbers may occur.

Figure 14

For polyatomic molecule placed into external monochromatic field quasienergetic representation can be employed. Sometimes external field can be treated as an additional mode. The situation is completely analogous to the case of molecule with vibrational space dimensionality larger by 1. Matrix structure of the equation sistem for both problems is practically identical. Whether quantum states having definite energies in modes decay in these conditions (Fermi resonances) and to what extent depends upon spectra and interaction operator structures. What characteristics describe this process adequately and what is criterion of tdtal stochasticity in this (quantum) case? Answer to these questions lies in solution of model many-level problems.

aggregate of bands problems

$$i\hbar\dot{\Psi}_{nm} = \Delta_{nm}\Psi_{n,m} + \sum_{m'} V_{n,m}^{n-1,m'}\Psi_{n-1,m'} + \sum_{m'} V_{n,m}^{n+1,m'}\Psi_{n+1,m'}$$



"random walk" interection among band's levels

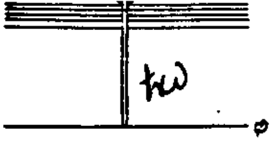
"anderson localization" in the long time limit.

3 parts of aggregate of band problem.

1) levil - band
2) random walk in multyband sistem.
3) conjugation problem

ТЕНСИВНЫЕ
ЗОНАНСНЫЕ
АИМОДЕЙСТВИЯ
КВАНТОВОЙ
ЕКТРОНИКЕ

А «НАУКА»
АЯ РЕДАКЦИЯ
О-МАТЕМАТИЧЕСКОЙ ЛИТЕРАТУРЫ

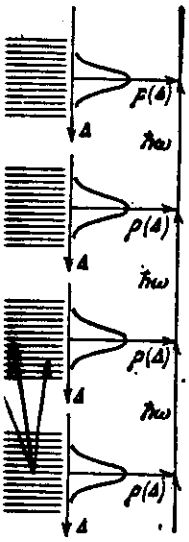


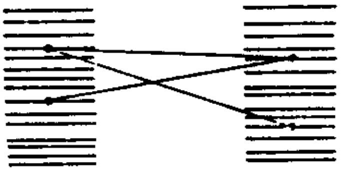
$$|n, n_y, \ldots, n_z, n_{z'}, n_{z''}, \ldots\rangle \Rightarrow$$

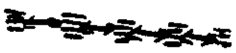
$$\Rightarrow \begin{cases} \rightarrow |\ldots\ldots\ldots\ldots\rangle \\ \rightarrow |n, n_y - 1, \ldots\ldots\ldots\rangle \\ \rightarrow |n, n_y - 1, \ldots n_z + 1, n_{z'}, n_{z''}, \ldots\rangle \\ \rightarrow |n, n_y - 1, \ldots n_z, n_{z'} + 1, n_{z''}, \ldots\rangle, \\ \rightarrow |n, n_y - 1, \ldots n_z, n_{z'}, n_{z''} + 1, \ldots\rangle \\ \rightarrow |n, n_y - 1, \ldots n_z, n_{z'}, n_{z''}, \ldots\rangle \\ \rightarrow |\ldots\ldots\ldots\ldots\rangle \end{cases}$$

$$j\hbar\dot{\psi} = \sum_k \frac{\mu_k E_0}{2}\psi_k, \quad j\hbar\psi_k = \hbar\Delta_k\psi_k + \frac{\mu_k E_0}{2}\psi, \quad \psi(t=0)=1, \quad \psi_k(t=0)=0.$$

Fano







THE MODEL

1) the level groups are localized in the vicinities of the energy values $n\hbar\omega$;

2) in each vicinity there is a large number $N_n \gg 1$ of levels, which are numbered by the index m;

3) the dipole moment differs from zero only for $\Delta n = \pm 1$ transitions between neighboring bands.

The Schrödinger equation for such a system is written in the form

$$i\dot{\psi}_{n,m} = \Delta_{n,m}\psi_{n,m} + \sum_{m'} V_{n,m}^{n\pm1,m'}\psi_{n\pm1,m'}$$

where $\mu_{n,m}^{n',m'}$ are the matrix elements of the transitions with random dipole moments.

assumptions

1. The energy position Δ_k of each of the levels k is statistically independent of the positions of all the other levels of this set, $\{k\}$ (we assume that it is equally probable over the interval from $-\Gamma$ to Γ; we will later take the limit $\Gamma \to \infty$) and also statistically independent of the value of the matrix element V_{0k}.

2. The state density of the band, $\{\alpha\}$, is so high that the band can be regarded as infinitely dense.

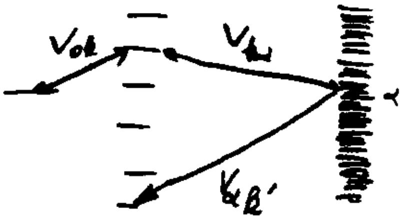
3. The matrix elements $V_{k\alpha}$ are random quantities, such that the only nonzero ensemble averages of sums are of the type $\Sigma_\alpha V_{k\alpha}V_{\alpha k}X(\alpha)$, where $X(\alpha)$ is an arbitrary smooth function of the level energy, while averages of the type $\Sigma_\alpha V_{k\alpha}V^*_{k'\alpha}X(\alpha)$ vanish.

4. The ensemble average of the quantity

$$\sum_{\alpha\alpha'} V_{k\alpha}V_{\alpha k'}V^*_{k\alpha'}V^*_{\alpha' k'}(\varepsilon-\Delta_\alpha)^{-1}(\xi-\Delta_{\alpha'})^{-1},$$

which is proportional to the population flux from one level (k) to another (k'), does not depend on the particular levels k and k' which it couples. It is equal to some function $f(\varepsilon,\xi)$ which is identical for all pairs.

5. The ensemble average of the decay rate of the band levels $\{k\}$ into the band (α), given by $\Sigma_\alpha V_{k\alpha}V_{\alpha k}(\varepsilon - \Delta_\alpha)^{-1}$, does not depend on the index k. We denote this value by $\gamma(\varepsilon)$.



S. eq.

$$i\dot{\psi}_0 = \sum_k V_{0k}\psi_k,$$

$$i\dot{\psi}_k = \Delta_k\psi_k + V_{k0}\psi_0 + \sum_\alpha V_{k\alpha}\psi_\alpha,$$

$$i\dot{\psi}_\alpha = \Delta_\alpha\psi_\alpha + \sum_k V_{\alpha k}\psi_k,$$

$$\psi_0(t=0)=1, \quad \hbar=1, \quad \int \psi_k(t)e^{-i\varepsilon t}\,dt = \psi_k(\varepsilon),$$

$$\int \psi_k^*(t)e^{-i\xi t}\,dt = \psi_k(\xi),$$

why random?

Figure 15

The problem of many-level resonance may be divided to three problems: decay of one level to a band, multiband problem and a problem of the combination of two first.

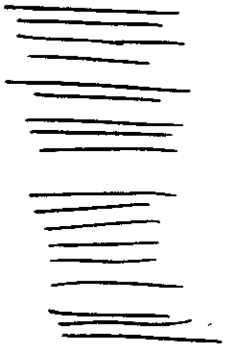
Figure 16

There are some types of many-level problems (general enough) that allow detailed analitical solutions. The best known one, Fano problem, can be solved in quadratures. Exact solution in a long enough interval of time can be also found for the problem of aggregate of zones population dynamics, when initially only one levil of one of the zones was populated, while all states of neiboring zones are coupled by perturbation with matrix elements changing irregulary. Exact solution may be obtained for the problem of decay of single level into the zone with all its states interchanging populations by means of so called "random walk" process with preset correlative properties. In order to obtain analitical solution of these problem (especially for two last ones), it is necessary to use Wigner's idea of ensemble averaging. Ensemble avareging naturally arises in problems where stochasticity exists. Fano's problem provides us with answer to the question about chosen harmonic state's decay, becouse of its interaction (due to anharmonism) with other states which are suppousd not interacting. Second,aggregate of zones,problem simulates anharmonic interaction of these states with other, similar, ones. The third one shows the complex zone states interaction influence on level's decay into such a zone. It

The stochastisity manifests itself in quantum case as randomness of matrix elements of operators in the eginenergy representation. and randomness of energy levels positions.

$$\begin{pmatrix} \ddots & & 0 \\ & H_{nn} & \\ 0 & & \ddots \end{pmatrix} \qquad \begin{pmatrix} V_{ij} & \cdot & V_{kl} \\ & V_{pp} & \cdot \\ \cdot & & \end{pmatrix}$$

random spectrum of $\hat{H}_0$



H_0

nonconserv. operator $\frac{1}{N}\sum_{i=1}^{N} V_{ij} \to 0$ $\frac{1}{N}\sum_{i=1}^{N} V_{il} V_{A} - \delta_{kp} V^2$

$H_0 + \delta H_0$

quantum

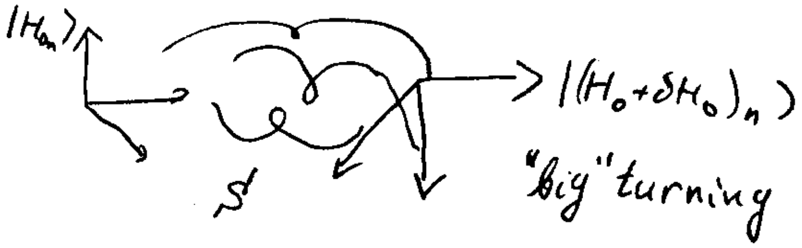
classical

$|H_{0_n}\rangle \longrightarrow |(H_0+\delta H_0)_n\rangle$

eginenergy functions are changing dramaticaly. ⟺ exponen. diverg. of trajector.

$|H_{0_k}\rangle = S_k^n \, |(H_0+\delta H_0)_k\rangle$

↑ complex (random) matrix



$$\begin{pmatrix} S_{ik} & \cdot & \\ \cdot & \cdot & S_{pq} \\ \cdot & \cdot & \cdot \end{pmatrix}$$

operator V in new basis dramaticaly differ from V in old one

$\hat{S}^{+} \hat{V}_{old} \hat{S} = \hat{V}_{new}$

$V_{ik} \in$ (Wigner ansamble) $w(V_{ik}) \sim \exp(-V_{ik}^2/V^2)$

Ensamble averaging = averaging by small perturbation, δH_0

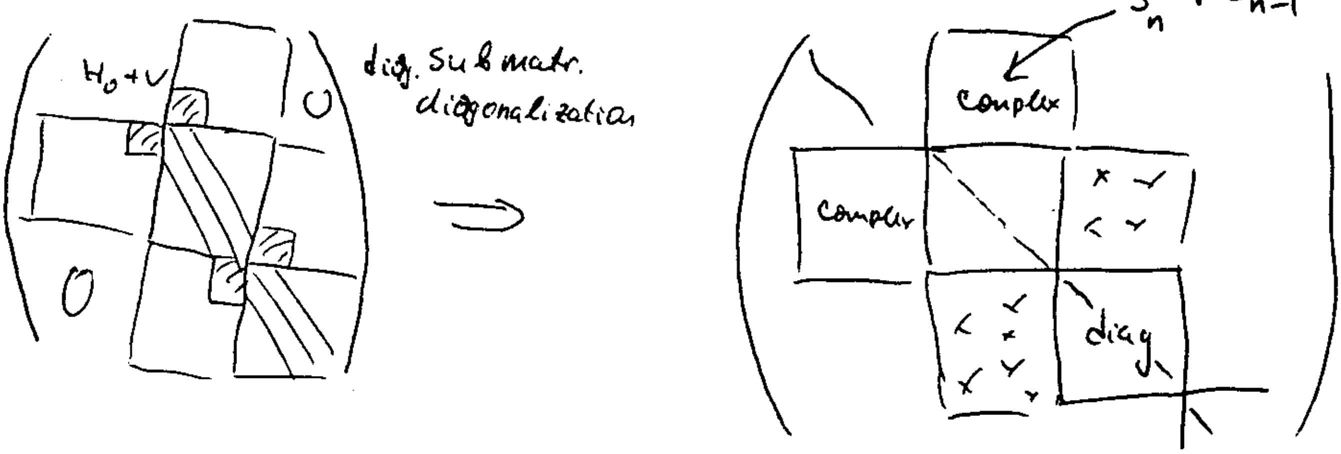
If unperturbated sistem is nonstochastical

$$\underset{H_0}{\begin{pmatrix} \ddots & & \\ & H_{0n} & \\ & & \ddots \end{pmatrix}} + \underset{V}{\begin{pmatrix} \ddots & 0 \quad V_{n,n+1} & 0 \\ V_{n+1,n} & 0 & \ddots \\ 0 & \ddots & \ddots \end{pmatrix}}$$

Simple structure

But H_0+V sistem became stochastical. (as usual it do)
then

Scaling procedure



gives us the same situation.

sort of conjurgation of two previous problems.

Figure 17

Classical motion stochasticity manifests itself in exponential instability of trajectory with respect to small change of hamiltonian or of initial conditions. Quantum system motion stochasticity is revealed in the complisity of matrices corresponding to operators of unconservable values. They change dramaticaly as a result of transformation of energy basis due to small perturbation of hamiltonian. Averaging by small perturbations of hamiltonian is equivalent to averaging by ensamble of interaction matrices. Statistics of distances between neighbouring levels (e.v. of $\hat{H}_o'$) for totaly stochastisated motion is described one of Dyson's distributions. If stochasticity is not total, this distribution is of Poisson's type. Matrix elements of interaction operator should obey to Wigner's statistics.

Figure 18

Even if initial hamiltonian $\hat{H}_o$ corresponds to nonstochasti motion, and interaction operators $\hat{V}$ structure is simple enough, the procedure of ensamble averaging can still be used. This happends if interaction $\hat{V}$ itself causes stochastization. In this case $\hat{H}_o$ and $\hat{V}$ wouldn't generate some simple algebra - their different commutators wouldn't commutate between themselves. Then by dividing matrix $\hat{H}_o+\hat{V}$ in coarse enough blocks (larger "stochastization lenghth" or "free path"

$$\rho_{00} = \langle 0| \frac{1}{\varepsilon - \hat{H} - \hat{V}} |0\rangle \langle 0| \frac{1}{\xi - \hat{H} - \hat{V}} |0\rangle$$

$$\frac{1}{\varepsilon - \hat{H} - \hat{V}} = \frac{1}{\varepsilon - \hat{H}} + \frac{1}{\varepsilon - \hat{H}} \hat{V} \frac{1}{\varepsilon - \hat{H}} + \frac{1}{\varepsilon - \hat{H}} \hat{V} \frac{1}{\varepsilon - \hat{H}} \hat{V} \frac{1}{\varepsilon - \hat{H}} + \dots$$

=

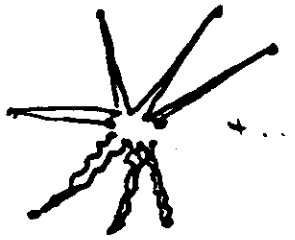
$$\frac{1}{\xi - \hat{H} - \hat{V}} = \frac{1}{\xi - \hat{H}} + \frac{1}{\xi - \hat{H}} \hat{V} \frac{1}{\xi - \hat{H}} + \frac{1}{\xi - \hat{H}} \hat{V} \frac{1}{\xi - \hat{H}} \hat{V} \frac{1}{\xi - \hat{H}} + \dots$$

=

Ɛn. Av.

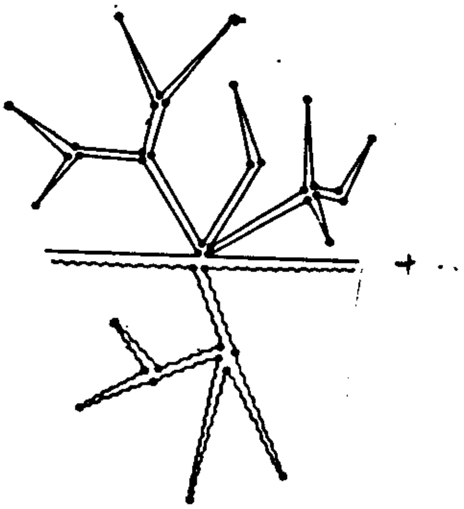
direct product ⊗

Fano



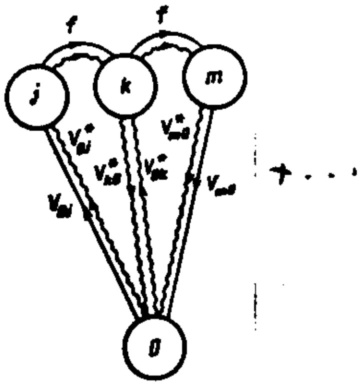
bush

bands (zones)



tree

level into random walk.



self intersections

"loops"

length) and by diagonalizing diagonal blocks, we'll obtain a matrix with randomness in of-diagonal blocks. This procedure resembles scaling.

Figure 19

General approach to many-level problems consists in the following. Population evolution operator is written down in the form of direct product of Green's functions for <...| - "bra" and - |...> - "ket"; each of them is represented as a perturbation power series of interaction operator. In the graphs unperturbated Green's functions $(\varepsilon-H_0)^{-1}$ are represented by points, and operator's $\hat{V}$ matrix elements - $V_{i,k}$ - by lines, straight for "ket" and undurlatory for "bra". Series, thus obtained, is averaged over $\langle\hat{V}\rangle$ ensamble. As a result only "stuck" graphs survive, where each transition is passed even number of times. Topological structure of graphs thus obtained differs for different problems. In Fano problem they are "bush"-like,and "dress" ground state. In many-zones problem, at time scale when graphs' selfintersections are neglectable, they are "tree"-like, and permit renormalization of eginenergies ("dressed" states), acquiring as a result imaginary additions. Third problem graphs' topology is complex, they contains numerous returns and selfintersections. The same graph may be passed through in different ways, i.e. many different trajectories give the same contribution to sum. Interference of returns occures (like in optical resonator). In order to estimate correctly this circumstance, it is necessary to take into account the expression

Fano

$$j\hbar\dot{\psi} = \sum_k \frac{\mu_k E_0}{2}\psi_k,$$
$$j\hbar\psi_k = \hbar\Delta_k\psi_k + \frac{\mu_k E_0}{2}\psi.$$

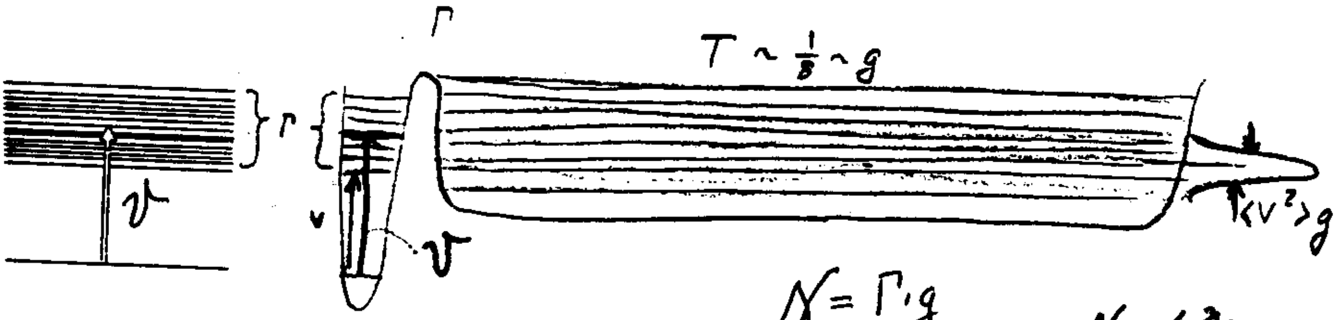
$$\xrightarrow{\text{F. t.}}$$

$$\varepsilon\hbar\psi = \sum_k \frac{\mu_k E_0}{2}\psi_k - j\hbar/2\pi$$
$$\varepsilon\hbar\psi_k = \hbar\Delta_k\psi_k + \frac{\mu_k E_0}{2}\psi.$$

$$\psi = \frac{-j}{2\pi}\left[\varepsilon - \sum_k \frac{\mu_k^2 E_0^2}{4\hbar^2(\varepsilon-\Delta_k)}\right]^{-1}.$$

$t < g$

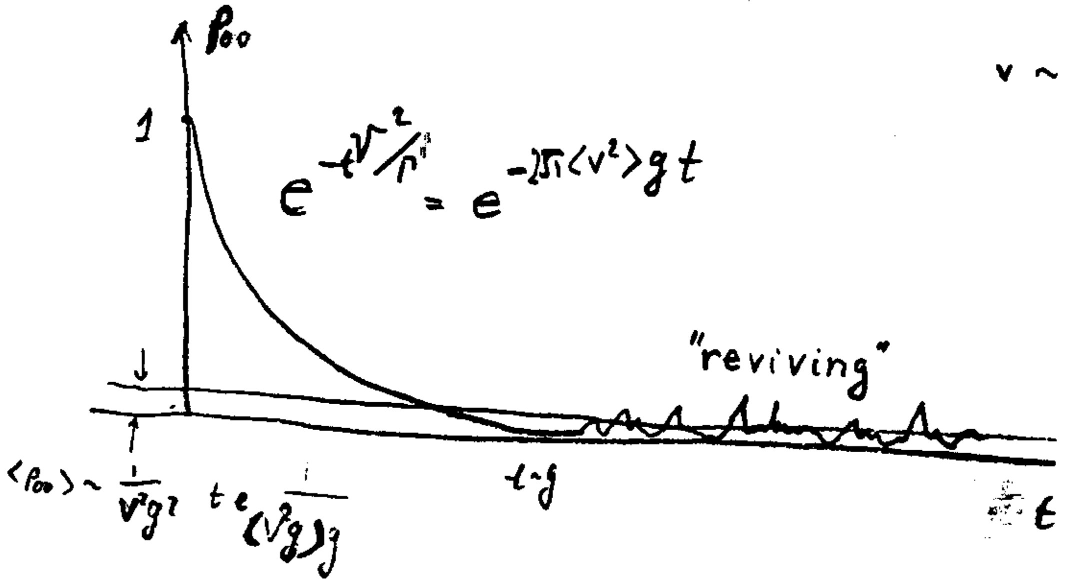
$$\psi = \frac{-j}{2\pi}\left[\varepsilon - \int \frac{\mu^2(\Delta)E_0^2}{4\hbar^2(\varepsilon-\Delta)}g(\Delta)\,d\Delta\right]^{-1}$$



$\mathcal{N} = \Gamma \cdot g$
lev in zone

$\mathcal{N} = \langle v^2\rangle g \cdot g.$
lev. in res.

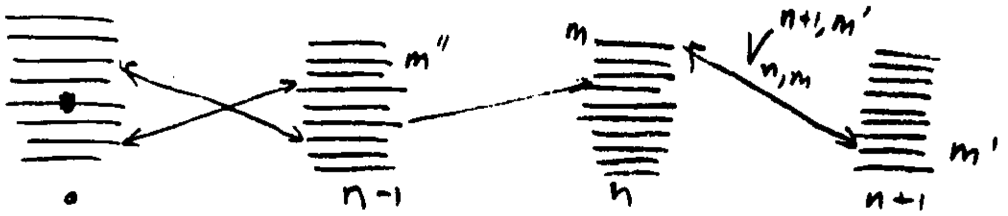
$v \sim \frac{\nu}{\sqrt{\mathcal{N}}}$



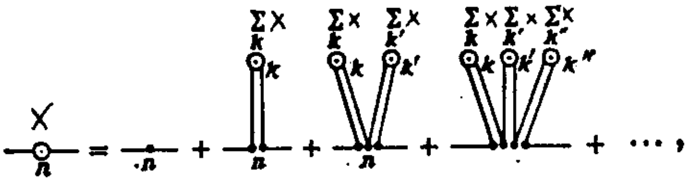
for number of Eiler's roundwalks of orgraphs. Next figures dwell on these problems in details.

Figure 20

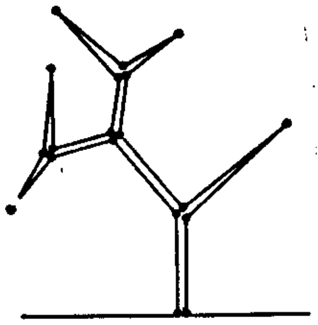
Schrodinger's equation for Fano problem gives, after Fourier transformation over times, the well-known expression for ground state population probability amplitude. Behaviour of the sistem differs qualitativly on small times (lower than zone states density-g) and large times scales. On small time scale, due to uncertainty principle levels of zone are not spectrally resolved and summing may be replased integrating by $gd\Delta$. Exponential decay take place as a result. Fano problem solution is conveniently illustrated by the example of resonant transition between two states; the upper one due to under-barrier transition may with probability Γ decay into long and shallow potential pit. Particle's time-of-flight between walles is T, levels density $g \sim T$. Zone of vidth Γ containing Γg levels replaces upper state as a result of tunnel interaction. Interaction $\mathcal{V}$ will distribute its cross-section among these levels, which will give for partial amplitudes values $V \sim \mathcal{V}/(\Gamma g)^{1/2}$. On times $t<g$ upper level's dacay is irreversible and population of lower level is decreasing exponentially $\rho \sim \exp(-\mathcal{V}^2/\Gamma t) \sim \exp(-V^2 \pi g t)$. When $t>g$ reverse streams of population from the large pit to the level (Javanainen) are significant and population ρ_o stabilizes its average value at $\rho_o \sim (Vg)^2$. In order to obtain considerable extent of population decay it's necessary to have $V^2g^2 \gg 1$. Zone population is localized at V^2g vicinity of the resonance



$$i\dot{\Psi}_{n,m} = \Delta_{n,m}\Psi_{n,m} + \sum_{m'} V_{n,m}^{n+1,m'}\Psi_{n+1,m'} + \sum_{m'} V_{n,m}^{n-1,m'}\Psi_{n-1,m'}$$



$\Leftarrow$



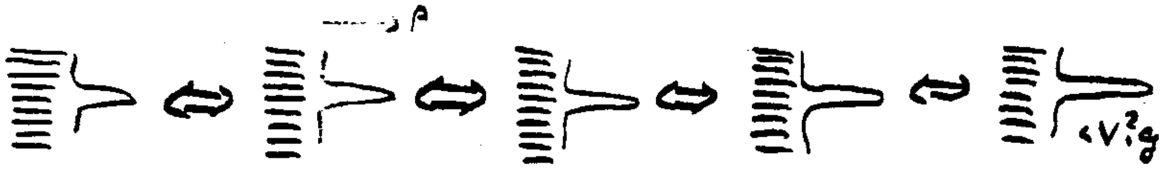
tree $t < v^2 g^3$

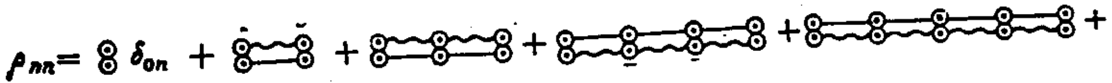
$$(\varepsilon) = \frac{1}{\varepsilon-\Delta_n} + \frac{1}{\varepsilon-\Delta_n}\left(\frac{\mu E_0}{\hbar}\right)^2 \sum_k x_k(\varepsilon)\frac{1}{\varepsilon-\Delta_n} +$$

$$+ \frac{1}{\varepsilon-\Delta_n}\left(\frac{\mu E_0}{\hbar}\right)^2 \sum_k x_k(\varepsilon)\frac{1}{\varepsilon-\Delta_n}\left(\frac{\mu E_0}{\hbar}\right)^2 \sum_{k'} x_{k'}(\varepsilon)\frac{1}{\varepsilon-\Delta_n} +$$

$$+ \frac{1}{\varepsilon-\Delta_n}\left(\frac{\mu E_0}{\hbar}\right)^2 \sum_k x_k(\varepsilon)\frac{1}{\varepsilon-\Delta_n}\left(\frac{\mu E_0}{\hbar}\right)^2 \sum_{k'} x_{k'}(\varepsilon)\frac{1}{\varepsilon-\Delta_n} \times$$

$$\times \left(\frac{\mu E_0}{\hbar}\right)^2 \sum_{k''} x_{k''}(\varepsilon)\frac{1}{\varepsilon-\Delta_n} + \dots \Rightarrow \quad x_k(\varepsilon) = \left[\varepsilon - \Delta_k - \left(\frac{\mu E_0}{\hbar}\right)^2 \sum_n x_n(\varepsilon)\right]^{-1};$$





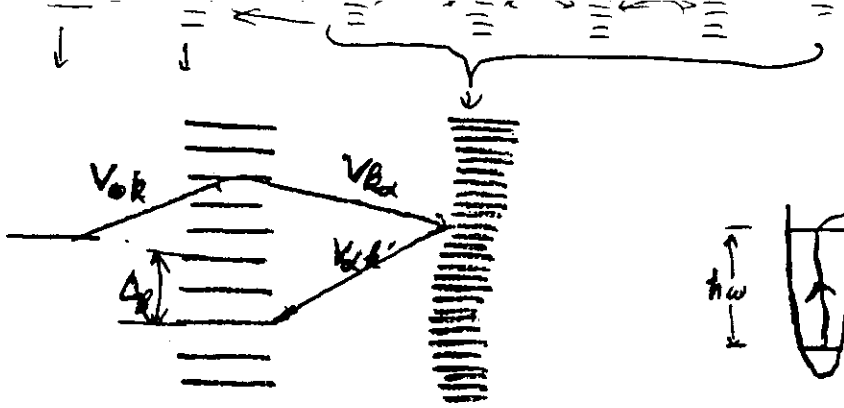
$$\hat{V} = \hat{\mu} E$$

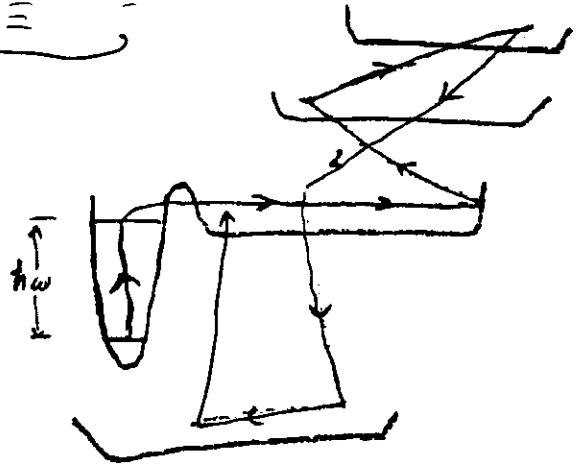
$$\dot{\rho}_n = -\pi g_{n+1}\frac{\mu_{n+1,n}^2 E_0^2}{\hbar^2}\rho_n - \pi g_{n-1}\frac{\mu_{n-1,n}^2 E_0^2}{\hbar^2}\rho_n + \pi g_n \frac{\mu_{n,n+1}^2 E_0^2}{\hbar^2}\rho_{n+1} + \pi g_n \frac{\mu_{n,n-1}^2 E_0^3}{\hbar^2}\rho_{n-1},$$

$t > v^2 g^3$

$\rho_n \sim \exp(-n/v^2 g^2)$ (Shepeliansky)

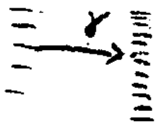
(Anderson's localization)





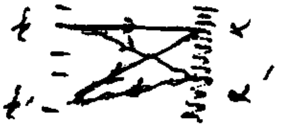
ans. av.
$\langle \quad \rangle$

$$\gamma = \left\langle V_{k\alpha} \frac{1}{\varepsilon - \Delta_\alpha} V_{\alpha k} \right\rangle$$

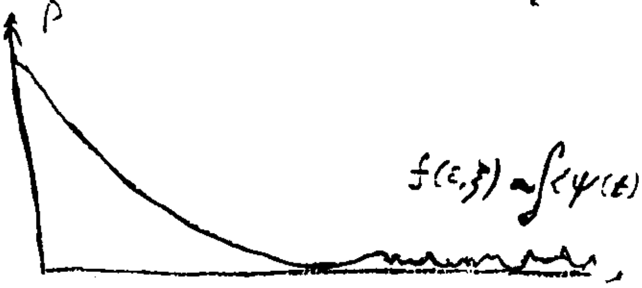


γ-decay rate

$$f(\varepsilon,\xi) = \left\langle V_{k\alpha} \frac{1}{\varepsilon - \Delta_\alpha} V_{\alpha k'} V_{k\alpha'} \frac{1}{\xi - \Delta_{\alpha'}} V_{\alpha' k'} \right\rangle$$

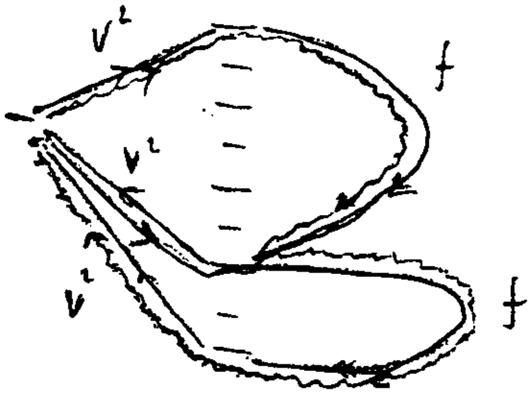


returns



$$f(\varepsilon,\xi) \sim \int \langle \psi(t)\, \psi^*(\tau) \rangle\, e^{-i\varepsilon t + i\xi\tau}\, d\tau\, dt$$

f – reviving characteristic



$$M = \varepsilon^{-2}\xi^{-2}(\varepsilon-\Delta_j-i\gamma)^{-1}(\varepsilon-\Delta_k-i\gamma)^{-1}(\varepsilon-\Delta_m-i\gamma)^{-1}(\xi-\Delta_j+i\gamma)^{-1}\cdot$$
$$(\xi-\Delta_k+i\gamma)^{-2}(\xi-\Delta_m+i\gamma)^{-1}V_{0j}V_{0j}^{*}V_{m0}V_{m0}^{*}V_{0k}^{*}V_{k0}^{*}[f(\varepsilon,\xi)]^2.$$

interferation –

- same value for different trajectoris

"statistical weights,"

and

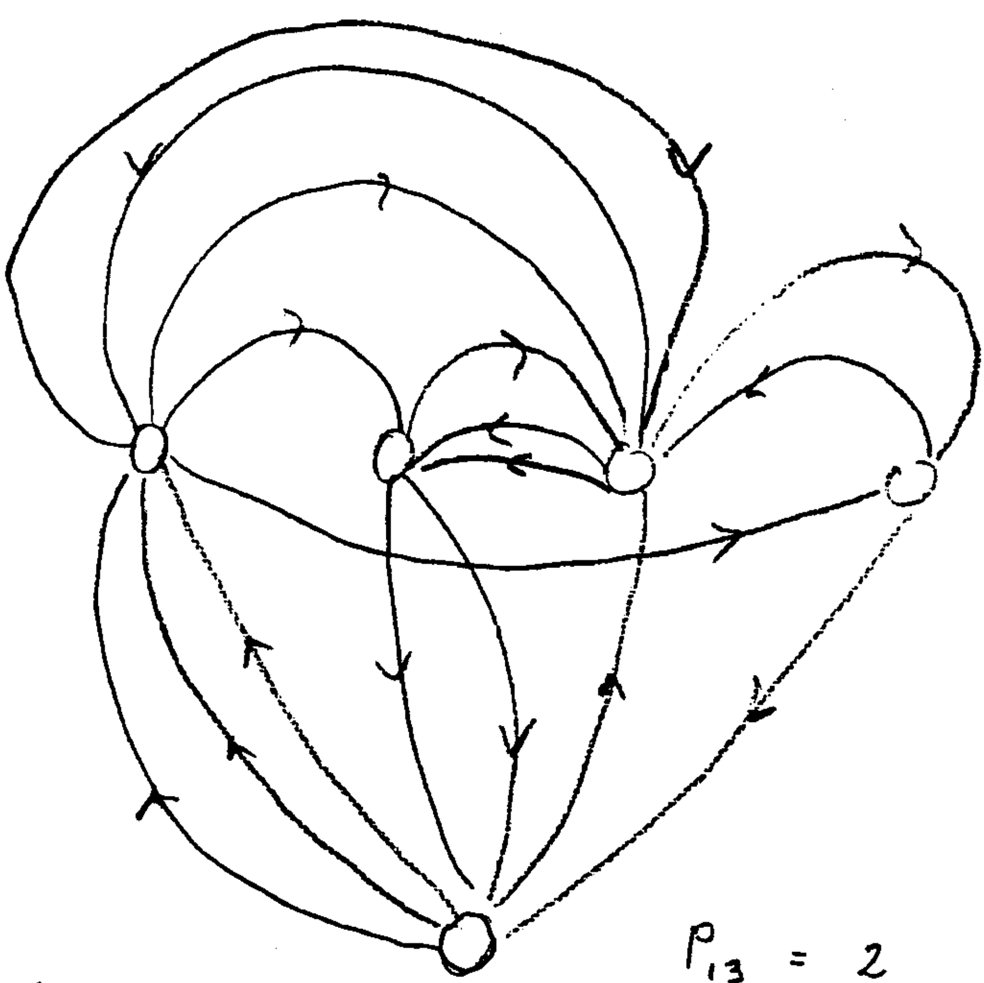
and has lorentzial form over energies. This is Ferme's golden rule correction by higher orcers of perturbation theory. Value $V^2g^2=g(V^2g)$ is a number of levels, participating in resonance.

Figure 21

Many-zone system is described by Schrodinger's doble-index equation. Procedure of developing to perturbation series and subsequent ensamble averaging permit at $t<g^3V^2$ (when graps, selfintersections are not actual) to "dress up" levels and to renormolize its energies. Correspondent equation for new Green's functions X results from geometrical seria. Series for total populations of zones are redused to geometrical series as well. Only nearest ($\sim V^2g$) vicinities of resonances become populated. Zones total populations dynamics is described by balance equation. "Random walk" process takes place among vicinities of resonances. Analysis of problem on large time scale (Shepelyansky) shows that at $t\gg g^2V^3$ quantum limitation of diffusion occurs (Anderson's localization phenomenon). Sometimes it seems that population in stochactic quantum systems wouldn't "like' moving far away from initial states.

Figure 22

Solution of problem of level's decay into the region of "random walk" is aimed at answering the question about extent of population localization on the level under conditions when it can decay into the zone where interstates transitions may be fulfilled inderectly due to



number of "Eulerian paths."

$P_{13} = 2$ $\quad d_1 = 4$

$P_{31} = 1$ $\quad d_3 = 5$

$P_{32} = 2$

$$g = \left\{\prod_j (d_j - 1)!\right\} \det\|p_{ij}\|,$$

$$\rho = \sum_i M_i \times \mathcal{E}_{left} \times \mathcal{E}_{right}$$

after summarizing we obtain

$$\rho = \frac{1}{2\pi^2\zeta}\int d\sigma'\,dz\,d\eta\,d\tau\,dx\,dy\,[(1-A_L)(1-A_R)(1-A_3)^{-1} - A_{RL}(1-A_3)^{-1} - |A_2|^2(1-A_3)^{-2}]\exp(J - \sigma' - iz\eta - x^2 - y^2).$$

where

$$J = \frac{1}{2}\pi^{1/2} g \int_{-\infty}^{\infty} (-V_0^4(\sigma'^2\zeta^{-2} + z^2) + [V_0^2(\sigma'^2\zeta^{-2} - z^2)^{1/2} - 2i(f\tau)^{1/2}x]^2 - 4f\tau y^2 + V_0^2\sigma'\zeta^{-1}[\zeta/2 - i\eta + (f\tau)^{1/2}Y])\{[V_0^2(\sigma'^2\zeta^{-2} - z^2)^{1/2} - 2i(f\tau)^{1/2}x]^2 - [\zeta - 2i\eta + V_0^2\sigma'\zeta^{-1} + 2(f\tau)^{1/2}Y]^2\}^{-1/2}\exp(-Y^2)\,dY,$$

$$A_3 = -\frac{gf\tau}{2i\pi^{1/2}}\int_{-\infty}^{\infty}(Z^2 - r^2)^{-1/2}\exp(-Y^2)\,dY,$$

$$A_2 = -e^{i\varphi}\frac{gf\tau}{2i\pi^{1/2}}\int_{-\infty}^{\infty}[Zr^{-1}(Z^2 - r^2)^{-1/2} - r^{-1}]\exp(-Y^2)\,dY,$$

$$A_{R,L} = i\pi^{1/2} gf\tau \int_{-\infty}^{\infty}\left[\frac{V_0^2}{2}\left(\frac{\sigma'}{\zeta} \pm z\right)Z(Z^2 - r^2)^{-3/2} - r^2(Z^2 - r^2)^{-3/2}\right]\exp(-Y^2)\,dY,$$

$$A_{RL} = \frac{\pi^{1/2} g f^2\tau^2}{2i}\int_{-\infty}^{\infty}[2 + 3r^2(Z^2 - r^2)^{-1}](Z^2 - r^2)^{-3/2}\exp(-Y^2)\,dY$$

$\zeta = \varepsilon - \xi$

$\eta = \varepsilon + \xi$

returns lead to localization.

interaction through the other states. This interaction is characterized by ensamble average of two-time evolutionary operator for density matrix - f(t,τ) or it's Fourier image f(ε,ξ). Similar situation may arise if in Fano problem model particle from long pit is capable of jumping back and forth into other similar pits. Main problem consists in correct estimation of graph's selfintersections, i.e. correct calculation of interference of amplitudes of probabilities of returns into the zone. Many different trajectories possess same graphs. The simplest case, that of orgraph, permiting two possible round walks (two different trajectories with the same contribution), is taken as an example.

Figure 23

Step-by-step solution of the problems requires determination of numbers of roundabout ways for every graph (Eiler's ways). Result is determined by character of f-function. If "random walk" is returnable, and characterized by finite correlation time τ_c then on the time scale when number of returns of "random walk" will exceed g/τ^2, population will reach its assymptotic value, exponentially small over parametr V^2g^2. In other words weak localization is present - localized componen measure is exponentially small over parametr V^2g^2.If "random walk" is unreturnable, decay is total.

Figure 24

Now one can say what is needed for stability islends existence in

result

decay (stokhastization, q. num. distruction):

1. is <u>total</u> if

a) random walk is irreturnable (3-dim. random wak = 3 overlaped resonances $\delta\omega < v$. = 4 inter. modes)

б) random walk is δ-correlated $\langle \psi(t)\, \psi^*(t+\tau) \rangle = \delta(\tau)$

2. is <u>non total</u> if

<u>weak localization</u>

a) random walk is returnable

(2 dim. random walk 3 inter. modes)

localized (non stoch.) states measure

$\sim \exp(-v^2 g^2)$

<u>strong localization</u>

б) random walk is one dimentional

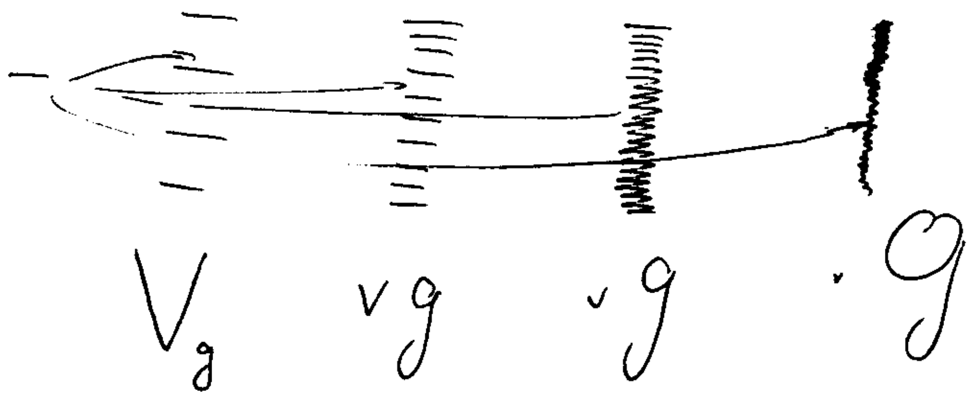
(2 inter. modes or 3 inter. modos and 1 add. invariant)

localized population at least $\frac{1}{v^2 g^2}$

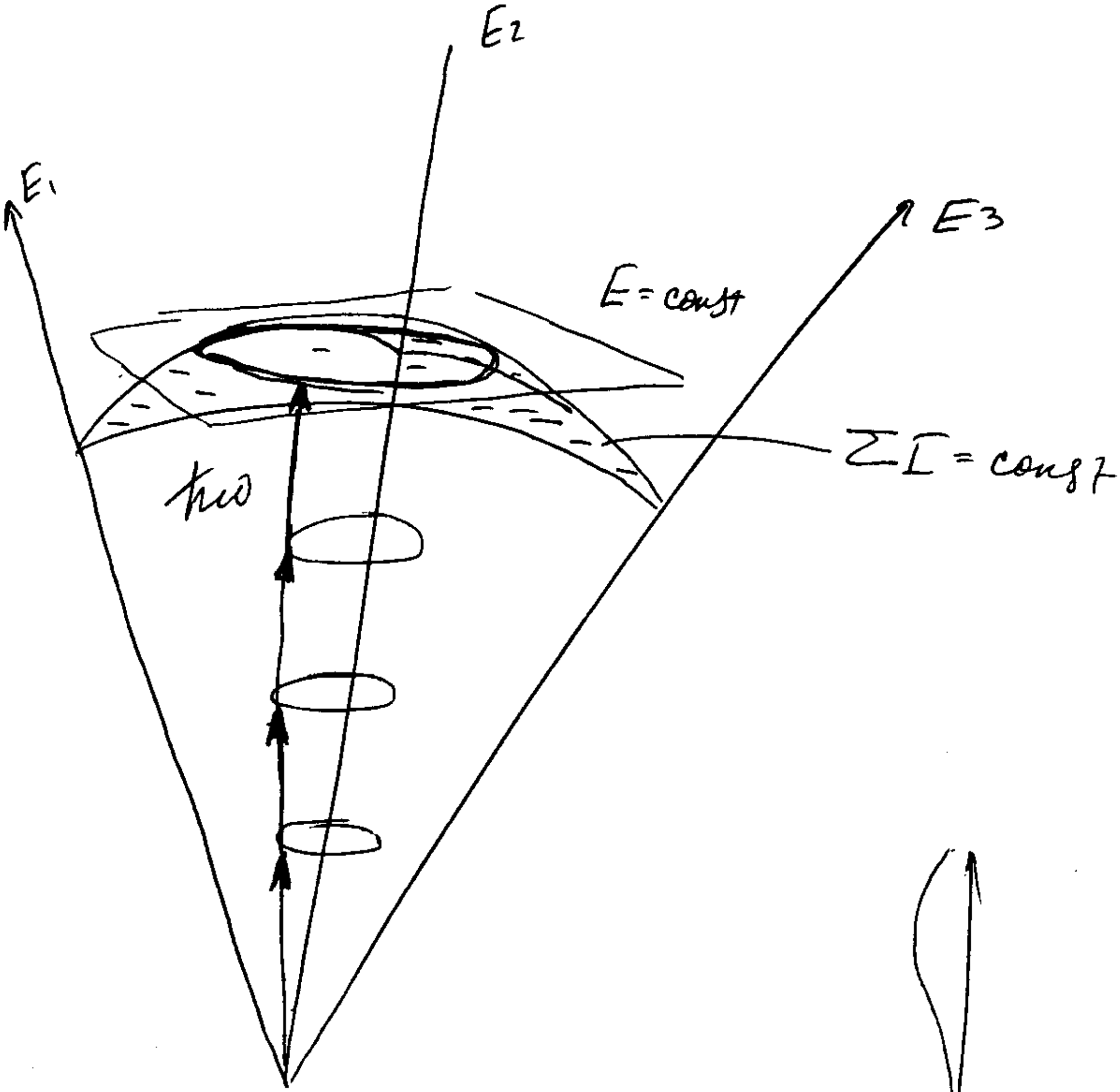
correct determination of $v^2 g^2$

$(\sum_s g_s v_s)^2$

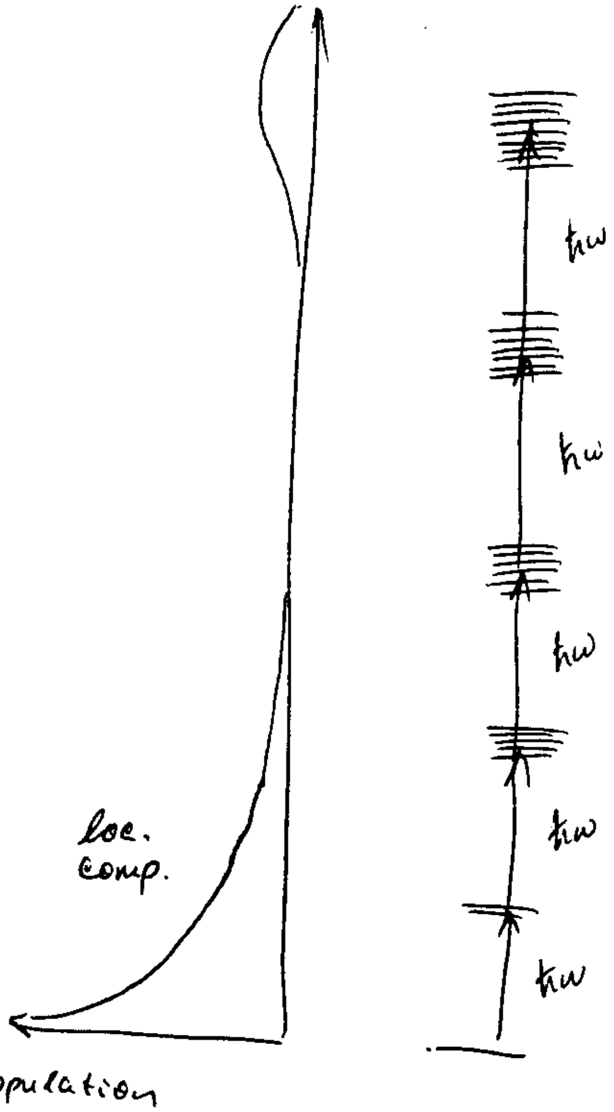
s - scale



V_3 mode in



two dimentional st.s.
returnable random walk.
$\exists$ "localization"



quantum case. If mode comes into Fermi-resonance with three different hybrid vibrations, then total stochastization occurs. In case of two resonant hybrid vibrations, small over phase volume archipelago of islends of stability exists even when interaction V exceeds spectral density of resonanses. Single- or double hybrid resonance, if the last with additional invariant of motion, leads to strong localization. Dynamic component measure in this case is big. Sometimes anharmonic interaction of mhigher orders must be taken into account. Higher the order of anharmonism, higher, usually, the density of ultimate states. Correct estimation of value g^2V^2 presupposes summing up over all orders (over all scales).

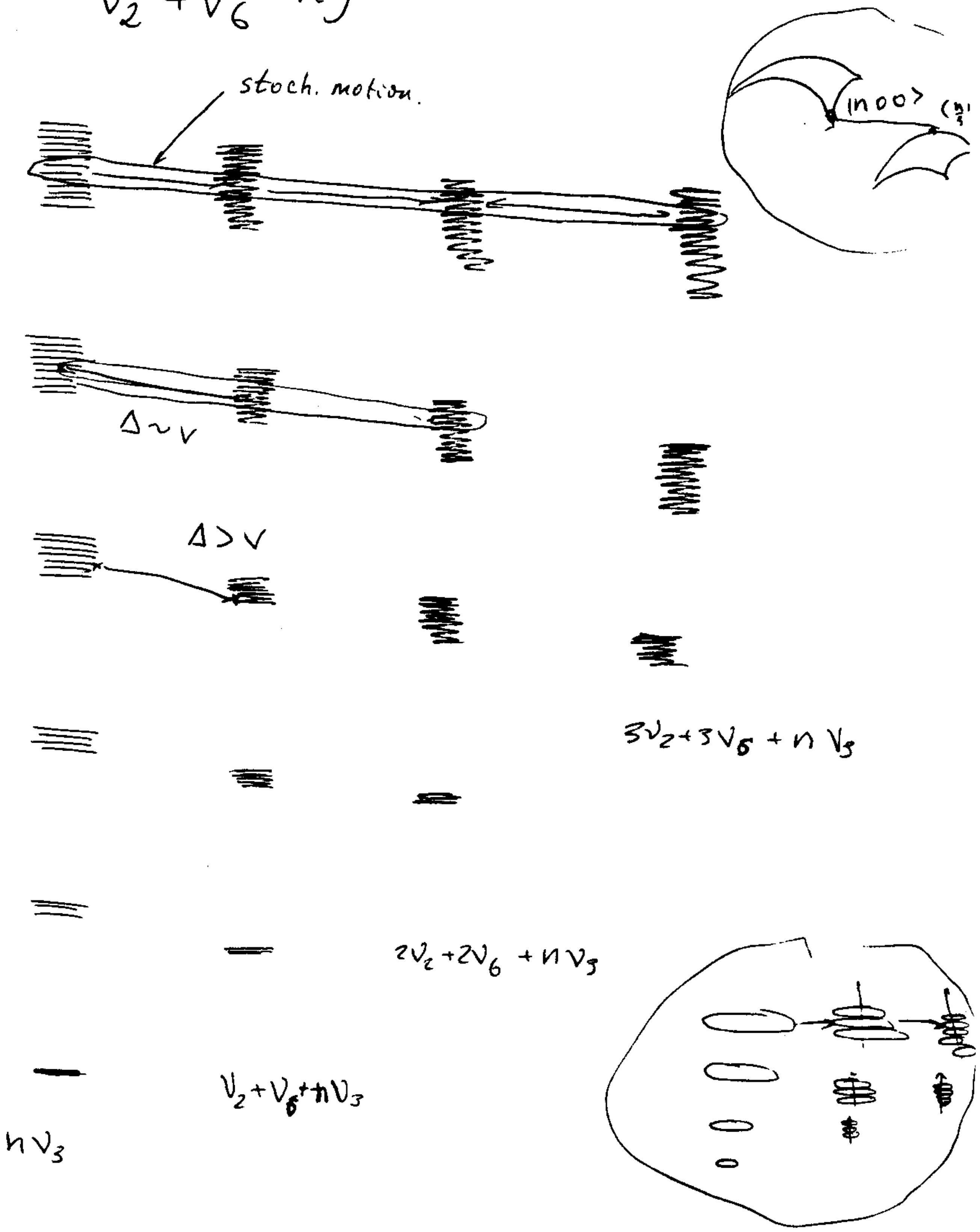
Figure 25

In SF_6 molecule Three times degenerated mode may be tuned at resonance with IR-radiation from CO_2-laser. Intramodal tensor anharmonism leads to splitting of initianaly many times degenerated excited levels and formation of zones. Howevrr conservation of sum of quantum numbers $n_1+n_2+n_2$ corresponding to three degrees of freadom appears as an additional invariant. As a result, resonance (isoenergetic) space is one-dimentional. Strong localization is present. In the external resonant field it becomes bidementional (in this case it is isoquasienergetic surface) and weak localization of population on lower levels is possible.

Figure 26

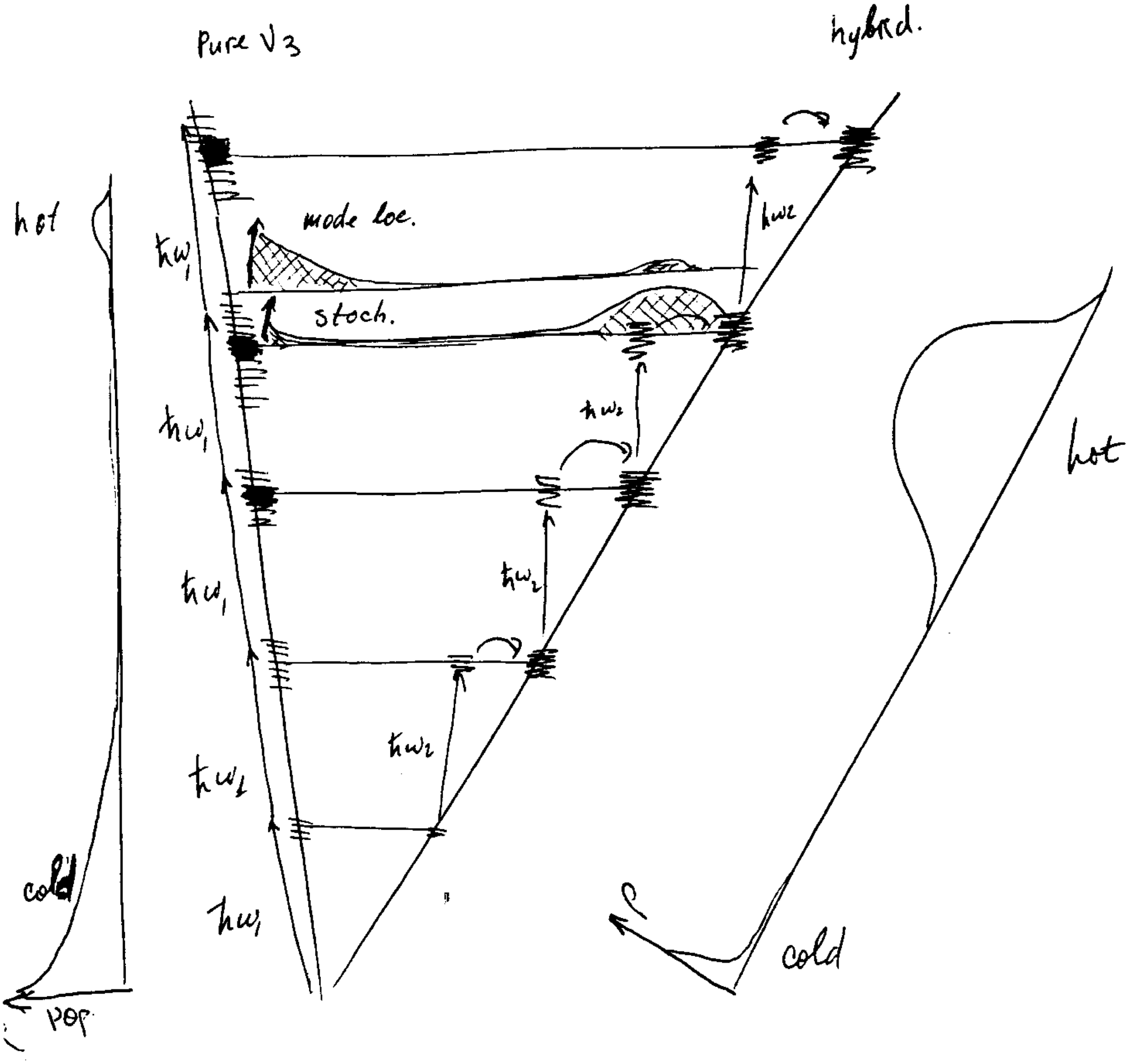
ν_3 mode in resonance with

$\nu_2 + \nu_6$ hybrid vibration



central parts of high $n\nu_3$ zones are in resonance ($V > \Delta$) with central parts of hybrids $m\nu_3 + (n-m)(\nu_2 + \nu_6)$

For smal polyatomics intermodal resonance is not an universal property ($V < \Delta\omega$ if $d \lesssim 2\sqrt[4]{\frac{M}{m_e}}$) i.e. $\sum_s V_s g_s \ll 1$. only near resonances ($\sum V_s g_s \gtrsim 1$), and stochasticity take place



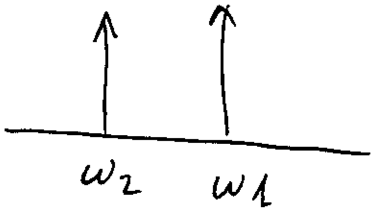


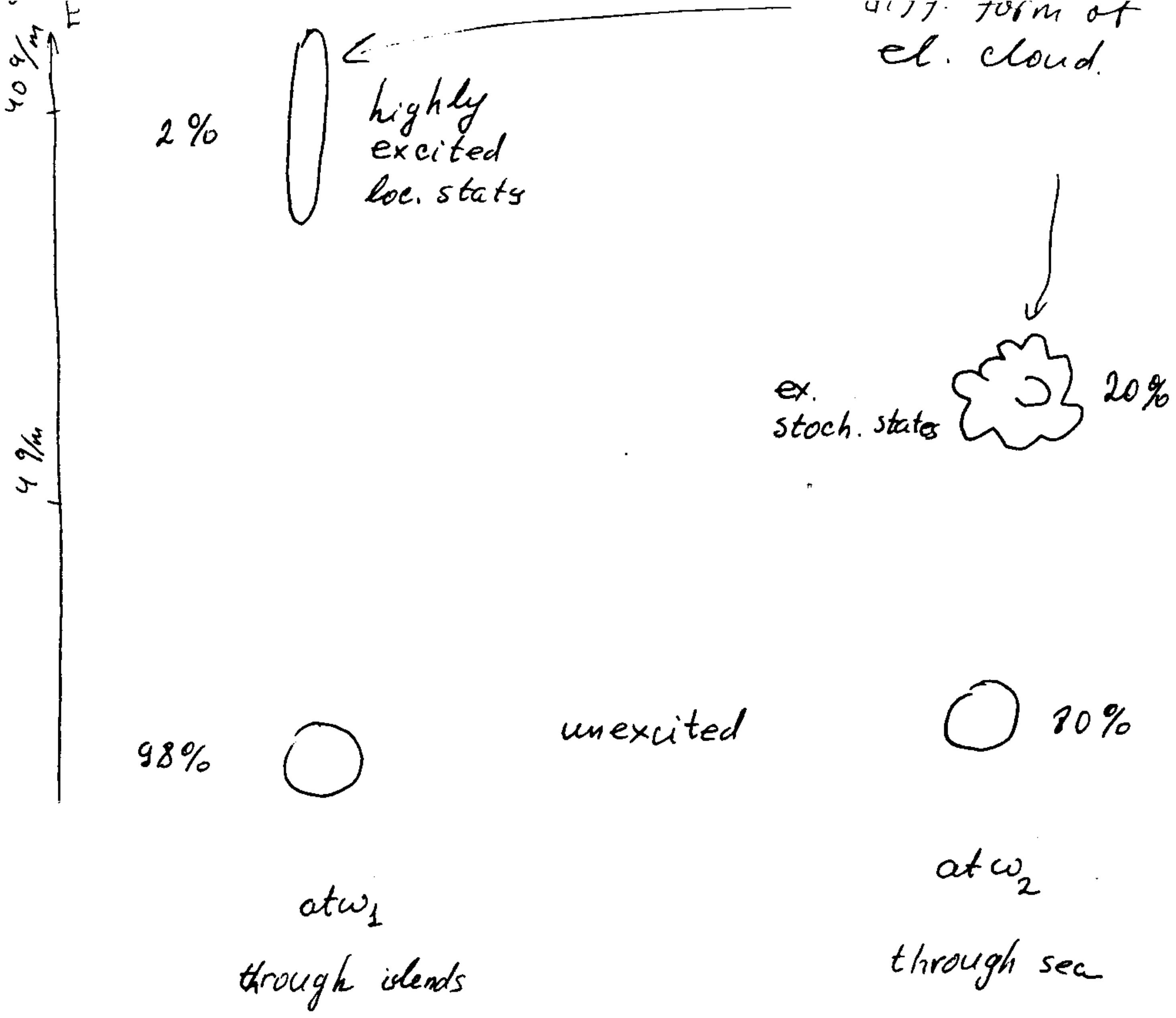
Figure 26

Hybrid vibration frequency $\nu_2+\nu_6$ is close to ν_3 frequency, and when excitation extent is relativly high, they hit the Fermi-resonance. The first ones to enter the resonance are levels of ν_3 zone centre. As vibration ν_2 is two-time and ν_6-three-time degenerated, their switching in must consequently destroy stability islends of ν_3 mode and lead to total stochastization, involving other modes too. This can exert certain influence on localized in ground state population component as well.

Figure 27

In molecules, possessing relatively low number of degrees of freadom - d, which, multiplied by Born-Oppenheimer parameter, gives value less than 1, value $\Sigma V_s g_s$ in averege over the phase volume is less then 1. Evaluetion shows that it take place for less then 10-12 atomic molecules. In other words, dynamic behaviour is typical for them. However, in the vicinity of Fermi-resonance $(\Sigma V_s g_s)^2 \gg 1$, (because g is large there) and stochastization of motion is possible.

Let's consider model system. Mode ν_3 is excited by radiation. Central parts of zones come into Fermi-resonance with vibrations $\nu_2+\nu_6$ and are included into stochasticity region. If the frequency of the radiation is such that we get into unstochastizated parts of the zone, bidementional process is taking place. Considerable part of population remains in ground state because of localization, while the other part goes up through stability islends to high enough energy levels. In this



Same energy absorbed but
different consequences

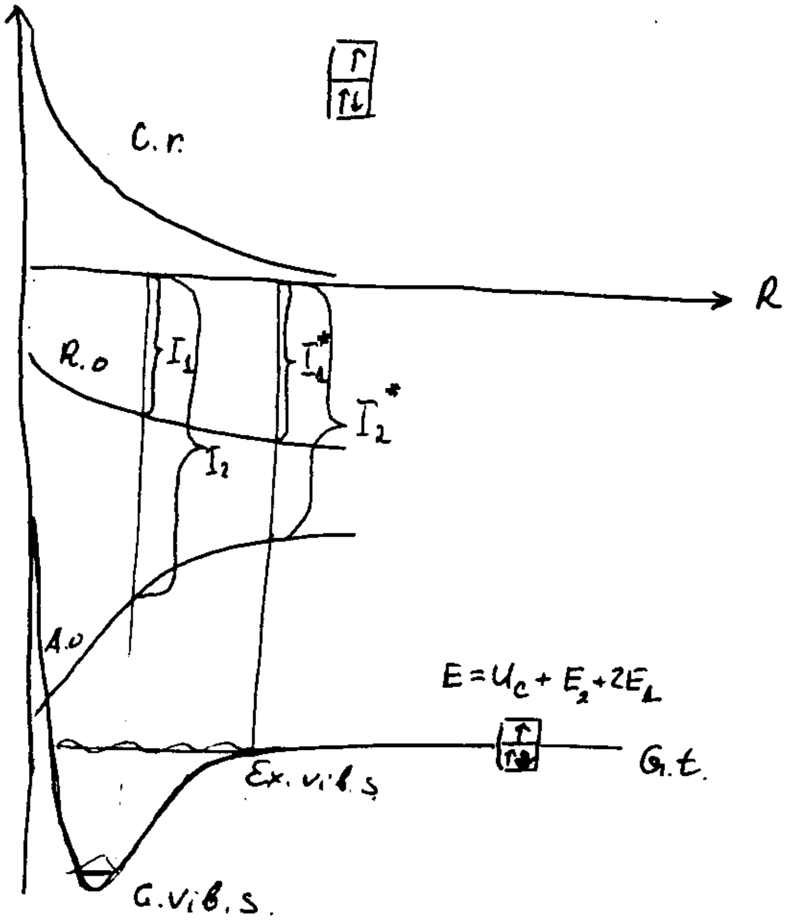
We have to find the way to measure the
energy of excited part of molecules

case population of totaly stochastic states caused by quantum tunnel decay from stability islends is small. Excitation at frequencies, corresponding to centres of zones leads to total stochastization of motion. Ground state in this case must keep considerably smaller part of population. Dissociation is more likely from stochastical states. It must be mentioned that in real situation stability islends may correspond not only to the levels of mode ν_3. Interaction with other degrees of fredom not leading to stochastization (resonances of not large enough dimensionality) can cause their vibrations, linked by phase to vibration of mode ν_3. The last circustomstance impedes the use of such a method of finding stability regions as, for example, Raman's scattering.

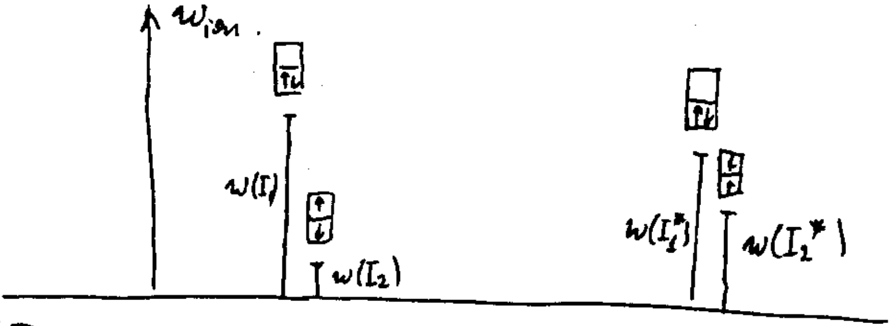
Figure 28

Phenomena of quantum localization is responsible for appearance of vibrationally cold and vibrationally hot ensembles in laser field and for localization of vibrational excitation in small number of degrees of freedom. Affecting at different frequencies it is possible to obtain a situation when same average absorbed energy is distributed in different ways among molecule states. When excitation trough stability islands is prodused, relativly small portion (because of returnability and low dimensionality) of molecules can be highly excited into states corresponding to preferentional energy contribution into certain degrees of freadom. In this case excited molecules becomes "stretched"). When stochastizated states are being excited,

TOF masspectr. diagnostics



$E = U_c + E_2 + 2E_L$

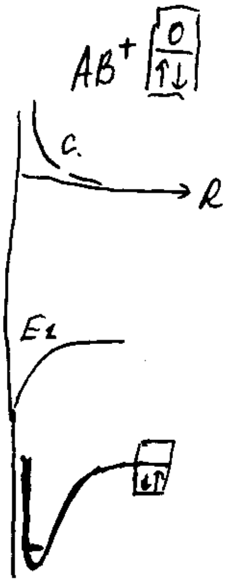


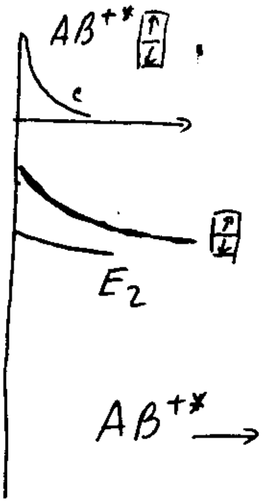
$AB + e \nearrow AB^+ + 2e$ $w(I_1)$

$\searrow A^* + B^+ + 2e$ $w(I_2)$

$AB_2^* + e \nearrow AB^+ + 2e$ $w(I_1^*)$

$\searrow A^* + B^+ + 2e$ $w(I_2^*)$





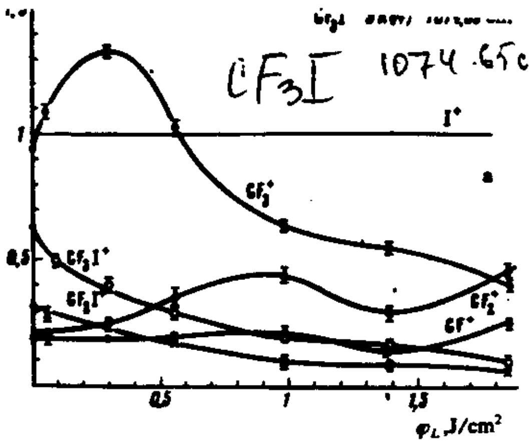
$AB^{+*} \longrightarrow A^* + B^+$

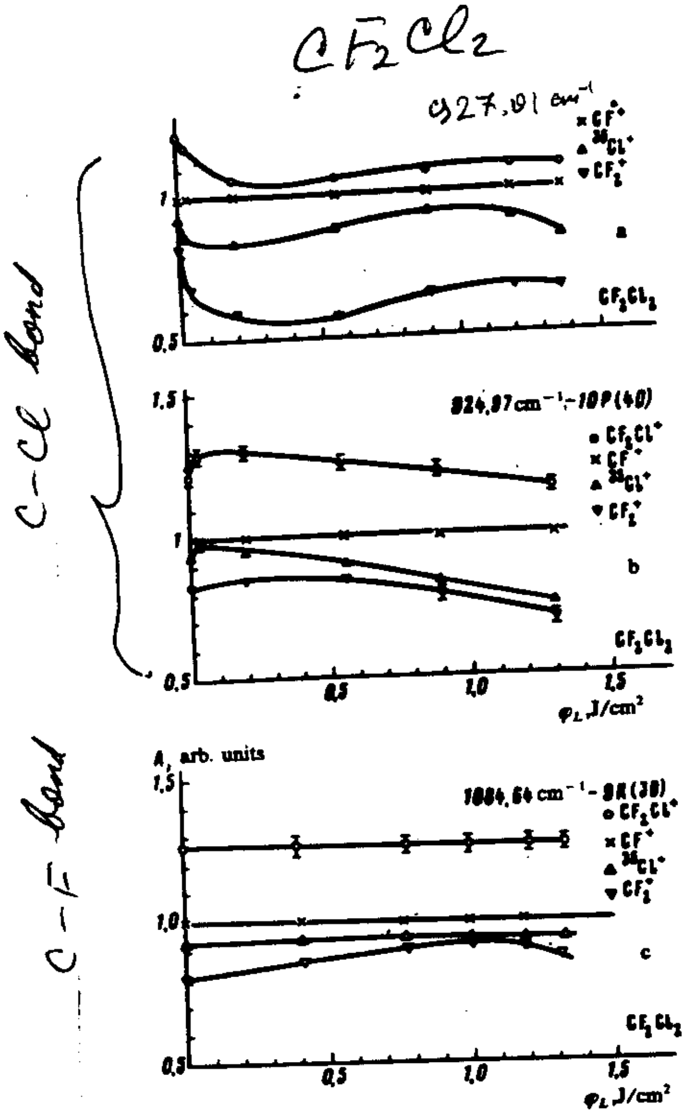
1 chanal 2 chanal

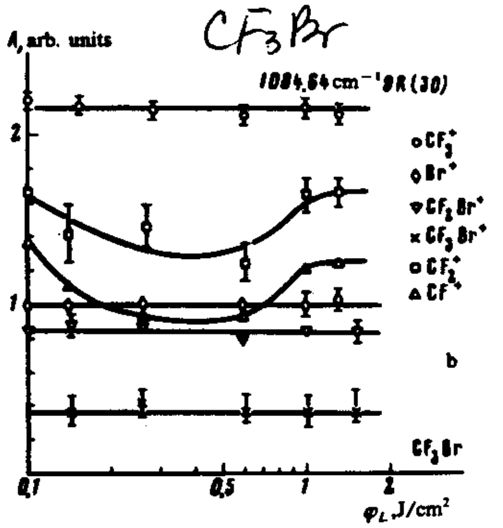
considerably larger number of molecules will get excited up to smaller energies. Then equal distribution of energy among degrees of freadom will take place. If equal distribution of energy among degrees of freadom will take place. If experimental proof of this is found, a hope for bond-selective IR-UV processes appears.

Figure 29

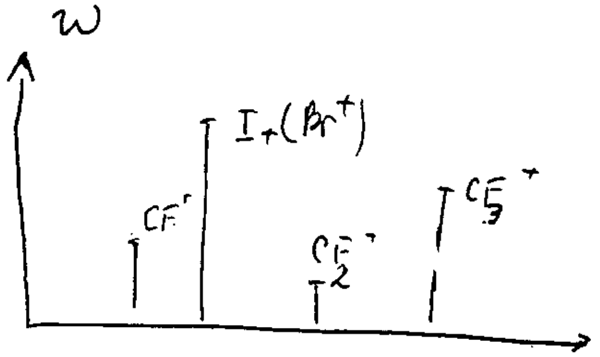
TOF-masspectrometry is one of the methods for stability islands of vibrational motion searching. What is the phisics of this method? Electron cloud shape of molecule in ground state differs from that of a molecule in a "stretched", vibrationally excited, state. That's why energies of electrons, occupying corresponding orbitals differ as well. Whenever bond is stretching, energy of electrons at repulsive orbitals decreases, while energy of electrons at attractive ones increases. Hence probability of ionization by electron impact with dislodging of repulsive electrons and as a consequencs formation of stble molecular ion decreases, while probabilityof dislodging of attractive electrons leading to formation of unstable dissociativ molecular ion increases. Corresponding changes of fragmentation pattern - ratios of probabilities of formation of different ion-molecular fragments, created by electron impact - observed by masspectrometr. Electron cloud of the same shape must lead to observing same fragmentation patterns. By comparing fragmentation patterns,it is possible to compare shapes of electron clouds, shapes of molecules.

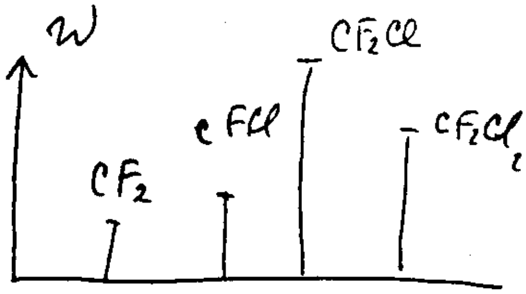






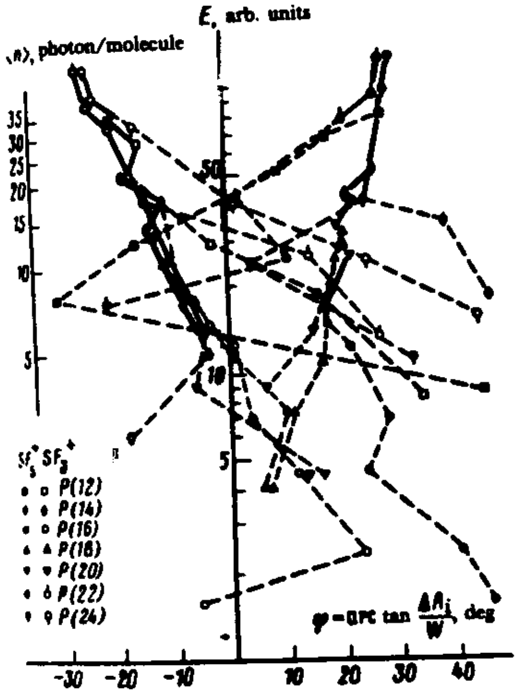
These facts show that the nature of the fragmentation of the molecule caused by electron impact depends strongly on the vibrational state of the molecule.

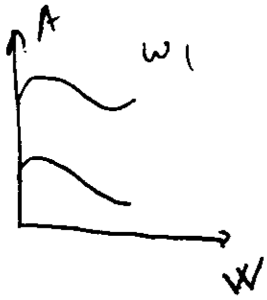


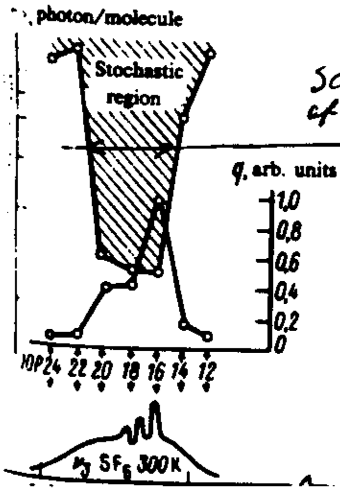


TOF-mas contains information about el. cloud

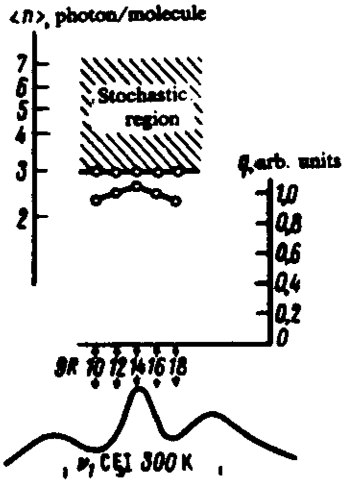
To avoid any effect of a change in the fraction of excited molecules with varyin frequency and intensity of the laser beam, we used the following procedure to analyz he experimental results. The electron impact causes a fragmentation of both excited nd unexcited molecules. The signal (A_i) representing the ion current of fragment i onsists of the signals coming from excited and unexcited molecules. The increment in he current upon excitation is proportional to the fraction of excited molecules, q, and o the change in the cross section for the production of charged fragments with inreasing energy of the molecule, E: $\Delta A_i \sim q\{\sigma_i(E) - \sigma_i(0)\}$. This value of q also deternines the relationship between the average absorbed energy W, measured by the coustooptic method, and the energy of the excited molecules, E: $W = qE$. The ratios $\Delta A_i/W) \sim [\sigma_i(E) - \sigma_i(0)]/E$ do not depend on q and are determined exclusively by the nergies of the excited molecules and the nature of their fragmentation. These ratios an accordingly be selected as parameters that describe the state of the molecules. If he vibrational motion has become stochastic, then the values of these parameters, at a xed energy E, are the same for all frequencies of the exciting IR field. Although we o not know E, its logarithm differs from that of the measured quantity, W, by an dditive increment of $\ln q$. If, by choosing this additive increment appropriately, we anage to bring all the curves of $\ln W$ versus the parameter $\Delta A_i/W$ for the various xcitation frequencies into coincidence at large E, we can thereby determine not onl e randomization boundary but also the fraction of excited molecules.







Same form of electron cloud



CF_2Cl_2.

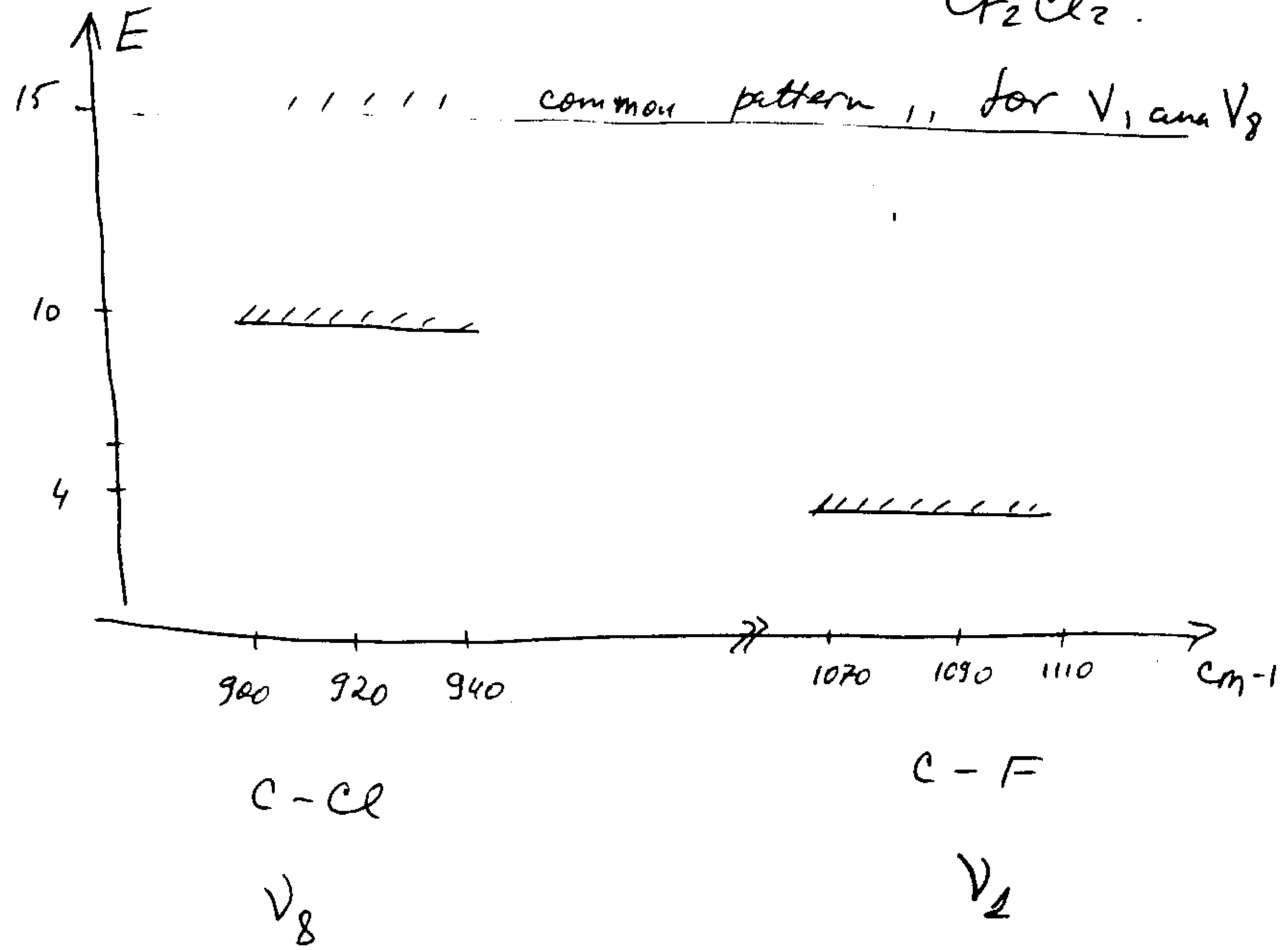


Figure 30

One can see how probability of molecular ion fragments formation depends upon vibrational excitation of molecule. Fragmentation pattern is sensitive not only to the type of molecule and absorbed energy but also to type of vibration and friquency of excitation. Small polyatomics excited in a different way have different form of electron cloud.

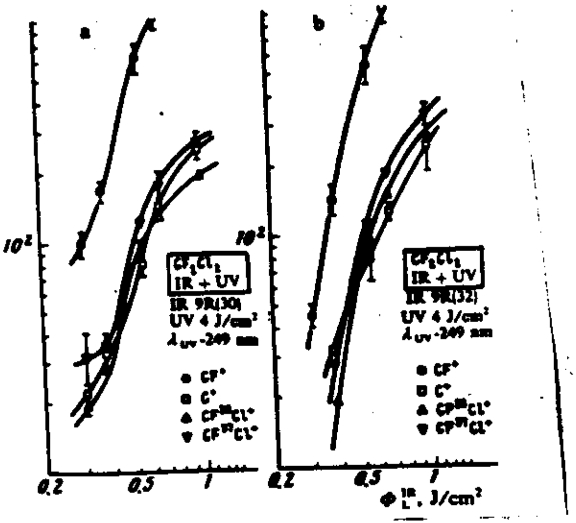
Figure 31

To avoid the effect of localization and to finde the stochasticity borders position some kinde of fitting procedure may by used.

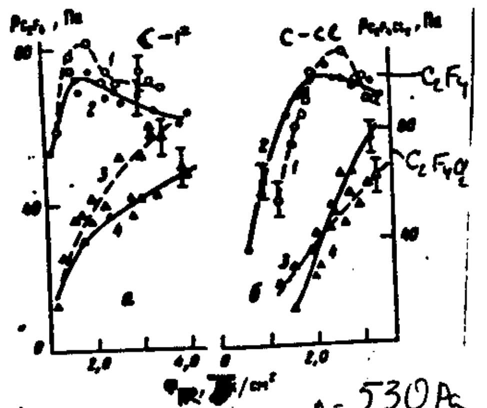
Figure 32

Here is experimental dependence of character of fragmentation of SF_6 molecules on energy E absorbed by "hot"ensemble ("cold" ensemble excluded), and on frequency of excitation. Within the limits of shaded area (s.r.) fragmentation pattern with E fixed doesn't depend on frequency. In other words,that is stochasticity region. Stochasticity region is limited. Beyond its limits shape of electron cloud differs from one within. It is important to mention that even near dissociation border total stochasticity wouldn't exist. This gives some hope. Ratio of excited molecules - q - decreases when the border of stochasticity region rises over energy. This corresponds to the ideas about localization length behavior. Similar pattern was obtained for CF_2Cl_2 molecule as well. When bond C-Cl is being vibrationally excited, 35

Orajevskii



KrF



p = 530 Pa

ArF 193nm

$$CF_2Cl_2 \nearrow Cl + CF_2Cl,\ \Delta H_{298} = 326{,}8 \text{ кДж/моль}$$

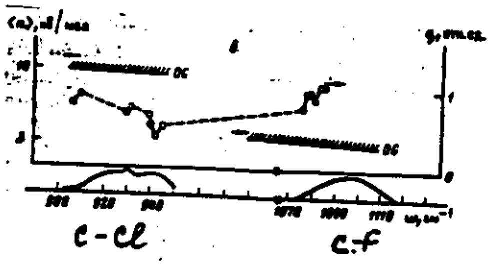
$$CF_2Cl_2 \searrow Cl_2 + CF_2,\ \Delta H_{298} = 310{,}1 \text{ кДж/моль}$$

Figure shows the heights of the peaks representing the current of ion fragments of the CF_2Cl_2 molecule versus the energy absorbed by the ν_1 mode, which correspond to valence vibrations involving C–F bonds. During excitation of the mode ν_6, wich corresponds to a vibration involving a C–Cl bond, we do not observe a decay of the molecule into charged fragments

effect of nonstochasticity

e-beam testing

chemical testing



dependence of fragmentation pattern on frequency dissappears already after absorbtion of 4 quanta, and for bonds C-F after 10 quanta. However fragmentation patterns for excitation of C-F and C-Cl bonds are different and coincid only at the level of 15 absorbed quanta. In other words, vibrations manifest local, not total, stochasticity up to 15ħω energy. F atoms vibrational energy is not transmitted to Cl atoms. Thus it is not surprizing, that switching of channals of UV photochemical reactions of these molecules using vibrational excitation is achieved (Orajevsky).

Figure 35

Nonstochasticity of CF_2Cl_2 vibrations permits to carry out bond selectiv chemistry in ArF^* laser radiation field.

P.S.

Crucial experiments on selective IR-UV bond destruction, what would they look like? It seems, they must be performed on isotopic molecules of HDCO or CH_2D_2 type (Frequency of C-D bond vibrations are close to CO_2-laser generation bond); IR-excitation of deterium vibrations, followed by subsequent transitioon of molecule into electronicaly excited term must lead to preferable decay with deiterium tearing off.

It seems very likely, that molecule excited into locolized state must have completely different spectrum of electron transitions (in visible or UV-regions) with respect to molecule in stochastizated state.

There are several possibilities to provide bond selectiv dissosiation of molecule. The first universal one is one- or multiphoton electron transition. In the frame of this approach requested bond dissosiation is accompanied by high extent of electronical excitation of fragments obtained. This is a way of traditional photochemistry. Second rather exclusive one - is to reach dissosiation of requested bond using its multiphoton infrared resonant vibrational excitation. This way is far from universal one and may be sucsesful if either the bond is separated spationally far enough from weakest one end energy pumping is sufficiently fust or vibrational spectrum of molecule permits the existence of bond locked highly excited vibrations up to dissosiation intended. The third, most promising approach, is a combination of the previous two. By exciting of intended bond beyong stochastization level,through stability "islends" in stochastic "sea", and providing subsequent electronical excitation sometimes one could obtain bond selective dissosiation while electronical excitation of fragments isn't very high.

Decay of an isolated level into a continuum corresponding to an infinite random walk

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The decay of a level into a continuum corresponding to an infinite random motion of a quantum-mechanical particle is analyzed. All the interference effects which result from returns of the particle to its initial state in the course of the random walk are taken into account exactly by an ensemble-average method, without any appeal to renormalization-group considerations or requirements of spatial uniformity "on the average." The level decay laws are found for long times for the cases of random walks which do and do not involve a return. The conditions for an "incomplete" decay of the level are determined. In other words, the conditions for the existence of a localized component of the population, consisting of the requirement that the random walk return and the requirement that the correlation time be finite, are determined. The time required for the population of the level to reach its asymptotic value is estimated. A possible mechanism for the formation of a "cold" ensemble during the excitation of polyatomic molecules by a resonant electromagnetic method is discussed. The process by which the motion becomes stochastic (by which the quantum numbers are destroyed) in quantum-mechanical systems of large dimensionality is also discussed.

1. STATEMENT OF THE PROBLEM AND BASIC RESULTS

The problem of the decay of an isolated level into a continuum is encountered in many fields of physics.[1-7] Although this problem does have a formal solution in quadratures, it is generally not possible to draw any really meaningful conclusions about the nature of the decay. Even the answer to the qualitative question of whether the level decays completely depends substantially on the details of the spectral density and the matrix elements which couple it with the continuum.

In this paper we wish to examine the problem—not of universal applicability but a fairly general particular case—of the decay of a level into a continuum, in which it is possible to reach some substantial conclusions. This analysis applies to systems in which an isolated level interacts directly with a relatively small fraction of the quantum-mechanical states of the continuum (a large finite or countable subset), which, not being eigenenergy states, interact in turn with all the other states and thereby indirectly with each other.

We will analyze the asymptotic behavior after a long time—longer than any of the temporal parameters in the problem. The asymptotic behavior of such a system is related to the well-known problem of localization[1,8-10] which arises in a study of one-electron states in solids with randomly distributed impurities. The approach taken in the present paper is significantly different from the approaches which are customarily taken in solid state physics to solve problems of this sort. We wish to formulate several rather general assertions regarding the nature of the motion in the system. Thereafter we will make no assumptions of the nature of the existence of a renormalization group. Our approach is thus valid for studying systems of arbitrary spatial dimensionality, and there is no requirement that the systems be spatially uniform "on the average."

The physical processes which can be described by the level-continuum model (or the model of a level and a dense band) are extremely diverse. They include processes which correspond to the complete decay of states which are initially filled [spontaneous emission,[2] many-photon ionization of atoms,[3,4] and the formation of an absorption line during the interaction of electronic configurations in atoms[5] (autoionization)] and processes in which the decay of the states is incomplete (the excitation of low-lying levels of polyatomic molecules by a resonant field,[6] the formation of localized states in Anderson insulators,[1] etc.). Problems involving the destruction of quantum numbers and the appearance of quantum chaos, which are usually studied numerically for simple systems,[7,11,12] can also be reduced to level-continuum systems and studied analytically. This comment also applies to complex systems, if physically reasonable assumptions are made regarding the random walk in the stochastic layer.

The nature of the decay of a level into a dense band (continuum) of course depends on the statistics of the energy levels of the band and the size of the matrix elements of the operator representing the interaction of the level with the band. The statistics are in turn determined by the particular features of the dynamic process which resulted in the formation of the band. We believe that the most convenient way to incorporate the statistics is to use the method of ensemble averaging,[13,14] which can be used successfully in problems involving randomly inhomogeneous systems.[15] The analytic expressions can be made insensitive to the microstructure of the spectrum by appropriately choosing the ensemble of systems having identical average values of the characteristics important to the process under consideration, and then averaging the perturbation series for the level population over this ensemble. The procedure of ensemble-averaging is closed by a test to see whether the variances of these expressions are small.

In this paper we will apply the procedure of ensemble-averaging only to that fraction of the continuum states

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which are directly coupled to the level. We assume that the distribution function of the values of the interaction matrix elements is given, and we assume that the energy position of each of the states selected is statistically independent of the positions of all of the other states selected. The interaction of the states with each other, mediated by all the other states of the dense band, is assumed to be complex and to have the characteristics of a random walk. The probability for the transfer of population from one state to another over a fixed time t is determined exclusively by the relative energy positions of the levels.

In other words, we are dealing with the dynamics of the filling of state 0 (which we will sometimes refer to below as the "ground state") in a system described by the Schrödinger equation

$$\begin{gathered} i\dot{\psi}_0=\sum_k V_{0k}\psi_k, \\ i\dot{\psi}_k=\Delta_k\psi_k+V_{k0}\psi_0+\sum_\alpha V_{k\alpha}\psi_\alpha, \\ i\dot{\psi}_\alpha=\Delta_\alpha\psi_\alpha+\sum_k V_{\alpha k}\psi_k, \\ \psi_0(t=0)=1, \quad \hbar=1, \quad \int\psi_k(t)e^{-i\varepsilon t}\,dt=\psi_k(\varepsilon), \\ \int\psi_k^*(t)e^{-i\xi t}\,dt=\psi_k(\xi), \end{gathered} \tag{1}$$

with respect to which we adopt the following assumptions.

1. The energy position Δ_k of each of the levels k is statistically independent of the positions of all the other levels of this set, $\{k\}$ (we assume that it is equally probable over the interval from $-\Gamma$ to Γ; we will later take the limit $\Gamma\to\infty$) and also statistically independent of the value of the matrix element V_{0k}.

2. The state density of the band, $\{\alpha\}$, is so high that the band can be regarded as infinitely dense.

3. The matrix elements $V_{k\alpha}$ are random quantities, such that the only nonzero ensemble averages of sums are of the type $\Sigma_\alpha V_{k\alpha}V_{\alpha k}X(\alpha)$, where $X(\alpha)$ is an arbitrary smooth function of the level energy, while averages of the type $\Sigma_\alpha V_{k\alpha}V^*_{k'\alpha}X(\alpha)$ vanish.

4. The ensemble average of the quantity

$$\sum_{\alpha\alpha'}V_{k\alpha}V_{\alpha k'}V^*_{k\alpha'}V^*_{\alpha'k'}(\varepsilon-\Delta_\alpha)^{-1}(\xi-\Delta_{\alpha'})^{-1},$$

which is proportional to the population flux from one level (k) to another (k'), does not depend on the particular levels k and k' which it couples. It is equal to some function $f(\varepsilon,\xi)$ which is identical for all pairs.

5. The ensemble average of the decay rate of the band levels $\{k\}$ into the band (α), given by $\Sigma_\alpha V_{k\alpha}V_{\alpha k}(\varepsilon-\Delta_\alpha)^{-1}$, does not depend on the index k. We denote this value by $\gamma(\varepsilon)$.

In other words, we have singled out from the entire dense band those states $\{k\}$ which interact directly with level 0, and we diagonalize the Hamiltonian in terms of all the other states of the band. As a result of the latter procedure, we form a set of levels $\{\alpha\}$, which is related to the levels $\{k\}$ by the random matrix elements $V_{\alpha k}$. The rate at which population flows from one level k to another level from the same set in the course of a process similar to a random walk is determined by—only the function $f(\varepsilon,\xi)$, which is identical for all pairs. In other words, all the levels of band $\{k\}$ are equivalent from the standpoint of the redistribution of population among states of the continuum.

To avoid any misunderstanding, we wish to stress that the interaction of levels $\{k\}$ with continuum states $\{\alpha\}$ generally does not have to lead to a complete and irreversible (exponential) decay of these levels. In other words, the interaction of some level with a dense set of other states can be described in by no means all situations by introducing a decay—a corresponding imaginary increment in the energy of this level. Under conditions such that this interaction is complicated, irregular, and even a discontinuous function of the energy of the state in the continuum, the dynamics of the decay of a noneigen state will generally not be exponential. In a problem of this sort, the particular function $f(\varepsilon,\xi)$ is responsible for this irregularity, as it is for the nature of the decay process.

A distinction is drawn between two types of motions, depending on the nature of the behavior of the function $f(\varepsilon,\xi)$ in the limit $\varepsilon\to\xi$. The motion is a "returning" motion if we have $f\to\infty$ as $\varepsilon\to\xi$, or it is a "nonreturning" motion if we have $f\to 0$ as $\varepsilon\to\xi$. For a nonreturning motion, a quantum-mechanical particle which is in one of the band levels $\{k\}$ at the time $t=0$ will leave this level, and in the limit of large t it will not return to any of the other levels of this band. In this case, the decay of level of the band $\{k\}$ to states of the band $\{\alpha\}$ is irreversible. In the case of a returning random walk, we are dealing with a different situation. This type of motion corresponds to a repeated return of the quantum-mechanical particle to levels of band $\{k\}$; i.e., the integral of the total population of all these levels over time diverges at the upper limit. If the probability for the particle to be in the states $\{k\}$ is calculated by a path-sum method, the implication is that in the limit of interest here (long times) the situation is dominated by paths which undergo repeated self-intersections at the levels of the band $\{k\}$. We are actually talking about incorporating an interference among the wave functions which arise as a result of the repeated returns of the particles to the given group of states.

Incorporating the effect of path self-intersections is the basic problem in carrying out a summation. Although the topology of the Feynman diagrams which arise in the course of the calculations is considerably more complex than usual (trees, ladders, etc.), it nevertheless turns out that these diagrams can be summed. The procedure required here, which is based on certain methods of graph theory, is extremely laborious; we will present it in the following section of this paper. At this point we think it is worthwhile to preview the results which are found as a result of this summation and to list the characteristics of the system which are responsible for the decay of the ground state.

The most important results are two in number. First, a nonreturning random walk leads to a complete decay. Long times correspond to a decay law of the type $\rho_0\propto\exp(-\mathrm{const}\ t^{1/2})$ (slower than exponential) for the population of state 0. The reason for this decay law is the existence in the selected ensemble of some improbable realizations of bands which do not have levels k which are sufficiently close to state 0. In this case, self-intersections of paths are inconsequential.

The second important result refers to the case of a return random walk. If a particle repeatedly returns to the levels of band $\{k\}$, all the paths will intersect repeatedly, thereby leading to a substantial change in the pattern as a result of interference effects. In such a situation, a return random walk leads to an incomplete decay of the level. In the limit of long times, an exponentially small fraction $\exp\{-V_0^2g^2 \text{ const}\}$ of the population remains at this level; here g is the state density of band $\{k\}$, and V_0^2 is the mean square value of the interaction matrix element $|V_{0k}|^2$.

An important role is played here by the characteristic correlation time of the random walk, τ_c: the time over which the wave functions of the states of band $\{k\}$ are changed by the nondiagonal matrix elements $V_{k\alpha}$ of the Hamiltonian. Although this time does not appear explicitly in the result, it determines just when the asymptotic distribution of populations is established. This event occurs when the number of returns in the random walk exceeds the number of levels in band $\{k\}$ which fall within a τ_c^{-1} neighborhood of the energy of level 0. If the correlation time is exceedingly small, $\tau_c \to 0$, on the other hand, and the asymptotic value ρ is not reached over the time intervals of interest, then the random walk may be regarded as noncorrelated. Correspondingly, we would have $f(\varepsilon,\xi) \propto f(\varepsilon-\xi)$. As a result we have the intermediate asymptotic behavior $\rho_0 \propto \exp(-\text{const } t^{2/3})$. This functional dependence, as in the case of a nonreturning random walk, results from the influence of improbable realizations of the system. Consequently, the asymptotic time dependence of the population of level 0 is determined by two characteristics: the correlation time and whether the random walk is of a return nature.

2. CALCULATION OF THE DECAY PROBABILITY

It is convenient to seek a solution of Eq. (1) in the form of an infinite power series in the interaction V. In this case the probability amplitude for the filling of the ground state can be written as a sum over all possible closed paths which begin and end at level 0. Each path corresponds to a particular term in the series. A path is represented as a sequence of transitions between levels $\{0, \{k\}, \{\alpha\}\}$; each of the levels met along the path corresponds to a factor ε^{-1}, $(\varepsilon-\Delta_k)^{-1}$, or $(\varepsilon-\Delta_\alpha)^{-1}$, and each of the transitions corresponds to a factor V_{0k} or $V_{k\alpha}$, which is the probability amplitude for the given transition.

Over the long time intervals in which we are interested here, the system has time to undergo many transitions. The corresponding paths are thus long, with many self-intersections. If we represent each path by an oriented graph (orgraph), the graph will have a large number of parallel edges, since a given transition occurs repeatedly, or pairs of levels from the band $\{k\}$ are connected by different nonintersecting paths. Since only the numbers of levels and transitions encountered along the path—not the particular order in which they occur—contribute to the series in a perturbation theory in V, many paths will have identical orgraphs and will thus contribute identically to the sum of the series. A summation over paths can then be replaced by a summation over different orgraphs with appropriate "statistical weights," i.e., with the numbers of various possible circuits of the orgraph or "Eulerian paths." An explicit expression is available[16] for a number of this sort:

$$\mathscr{E} = \left\{\prod_j (d_j-1)!\right\}\det\|p_{ij}\|, \tag{2}$$

where d_j is the multiplicity of node j, i.e., the number of edges which leave it (the number of times level j is encountered on the path), and $\det\|p_{ij}\|$ is any of the minors of the connectedness matrix $\|p_{ij}\|$, which consists of the matrix elements p_{ij}, which (with $i \neq j$) give the numbers of parallel edges connecting nodes i and j or (with $i = j$) are assumed to be equal to the total number of edges which leave the node $p_{ii} = \Sigma_j p_{ij}$. For definiteness below, we will always deal with the minor which corresponds to the deletion of the row and the column which correspond to the ground state.

We are interested in the population, not the wave function, of state 0. To find the population we need to go through a completely analogous procedure—taking Fourier transforms, carrying out a series expansion in a perturbation theory in the interaction, and writing the series as a sum over orgraphs—for the complex-conjugate wave function, which we denote by $\psi(\xi)$, using a different variable ξ, which is conjugate of the time. We then need to multiply the resulting series term by term. Most of the terms in the series for the populations which is formed in this way vanish after we carry out the ensemble-averaging, by virtue of assumption 3. The only terms that are left are those for which the parts of the orgraphs which differ in topological structure from trees and which correspond to the levels of band $\{k\}$ and $\{\alpha\}$ and to transitions between them, $V_{k\alpha}$, are completely identical for the right-hand and left-hand brackets. If we also allow for the fact that the parts of the orgraphs which do have the topology of trees can be summed separately, with the result that we find a renormalization of the node factors [the level energies Δ_k acquire imaginary increments $\gamma(\varepsilon)$ and $\gamma(\xi)$ which are positive for ξ and negative for ε], then we can assert that the only terms of the series for the populations which are nonvanishing are those for which the orgraphs of the transitions between states of the $\{k\}$ and $\{\alpha\}$ bands are identical. By virtue of assumption 2, we can ignore self-intersection of the diagrams at the levels of band $\{\alpha\}$. By virtue of assumption 4, we can associate identical factors $f(\varepsilon,\xi)$ with all coincident edges of the orgraphs for the right-hand and left-hand brackets connecting different levels of band $\{k\}$ and passing through levels of $\{\alpha\}$.

It thus becomes possible to further simplify the structure of the perturbation series for calculating a population. Specifically, we can now eliminate the energy levels of band $\{\alpha\}$ from consideration. The nodes of the orgraphs will then refer exclusively to the $\{k\}$ band. Each edge connecting these nodes can be associated with a factor $f(\varepsilon,\xi)$. The matrix elements of the connectedness matrix p_{ij} now refer only to the number of parallel edges between nodes of band $\{k\}$, and a combinatorial factor compensates for the indistinguishability of the nodes of band $\{\alpha\}$ which results from this procedure.

$$\Bigl(\sum_{i,j\neq i} p_{ij}\Bigr)! \Big/ \prod_{i,j\neq i} (p_{ij}!)$$

The difference between the number of Eulerian circuits for the right-hand and left-hand brackets now results exclusively from the difference between the orgraphs at the levels of band $\{k\}$ and level 0. If we denote by m_{0k} the number of

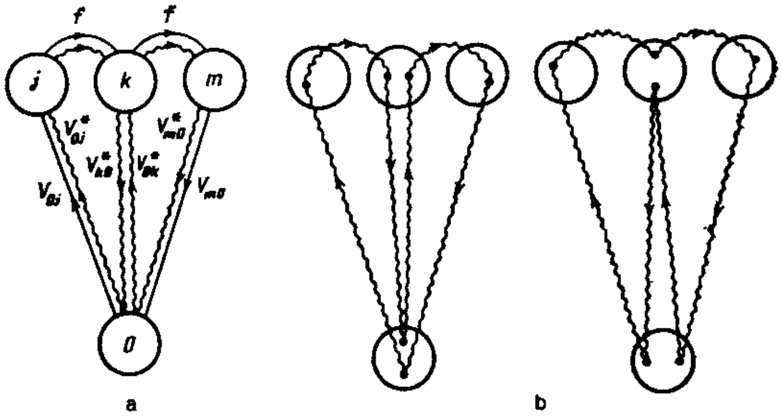

FIG. 1.

transitions V_{0k} which are encountered for the left-hand bracket, and by n_{0k} the corresponding number for the right-hand bracket, we can write the following expression for the population of the ground state:

$$\rho(\varepsilon,\xi)=\frac{1}{4\pi^2\varepsilon\xi}\sum_{\{p_{kj}\}}\sum_{\{n_{0k}\}}\sum_{\{m_{0k}\}}\Big(\sum_k m_{0k}\Big)!$$
$$\cdot\Big(\sum_k n_{0k}\Big)!\Big(\sum_{k,\,j\neq k}p_{kj}\Big)!\det\Big\|p_{kj}$$
$$-\delta_{kj}\Big(\sum_{k'}p_{k'j}-m_{0j}\Big)\Big\|\det\Big\|p_{kj}$$
$$-\delta_{kj}\Big(\sum_{k'}p_{k'j}-n_{0j}\Big)\Big\|\prod_{k,\,j\neq k}\left\{\frac{f(\varepsilon,\xi)^{p_{kj}}}{p_{kj}!}\right\}$$
$$\cdot\prod_k\left\{\frac{(V_{0k})^{n_{0k}}(V_{k0})^{n_{0k}-\Sigma_j(p_{kj}-p_{jk})}}{\varepsilon^{n_{0k}}[\varepsilon-\Delta_k-i\gamma(\varepsilon)]^{n_{0k}+\Sigma_j p_{kj}}}\right.$$
$$\left.\cdot\frac{(V_{k0})^{m_{0k}}(V_{0k})^{m_{0k}-\Sigma_j(p_{kj}-p_{jk})}}{\xi^{n_{0k}}[\xi-\Delta_k-i\gamma(\xi)]^{m_{0k}+\Sigma_j p_{kj}}}\right\},\qquad(3)$$

$[n_{0k}-\sum_j(p_{kj}-p_{jk})]!$

$[m_{0k}-\sum_j(p_{kj}-p_{jk})]!$

where a summation over $\{p_{ij}\}$ means a summation over all of the p_{ij}, each of which takes on values from 0 to ∞. Similar comments apply to n and m.

As an example, Fig. 1(a) shows a graph representation of one of the terms of the series for the population (straight lines correspond to the right-hand bracket, and wavy lines to the left-hand bracket). Corresponding to the orgraph is a term of the following form in the series for the population:

$$\varepsilon^{-2}\xi^{-2}(\varepsilon-\Delta_j-i\gamma)^{-1}(\varepsilon-\Delta_k-i\gamma)^{-1}(\varepsilon-\Delta_m-i\gamma)^{-1}(\xi-\Delta_j+i\gamma)^{-1},$$
$$(\xi-\Delta_k+i\gamma)^{-2}(\xi-\Delta_m+i\gamma)^{-1}V_{0j}V_{0j}^*V_{m0}V_{m0}^*V_{0k}^*V_{k0}^*[f(\varepsilon,\xi)]^2.\qquad(4)$$

Here $p_{jk}=1$; $p_{km}=1$; the number of Eulerian paths for the right-hand bracket is equal to 1; and that for the left-hand bracket is equal 2. Figure 1(b) shows Eulerian paths for the left-hand bracket.

For convenience in the calculations, we will make one more change in the order of the summation. The reason is that there are many different levels in band $\{k\}$, and a path of finite length is incapable of reaching all of them. This assertion means that among the factors in expression (3) there are many 1s (zeroth powers). We eliminate them from consideration. To do this, we choose exclusively those levels through which the paths of the given orgraph pass, and we call the set the "carrier of the orgraph." We carry out a summation over all orgraphs with a given carrier, and we then carry out a summation over all carriers. With the summation in this order, the value of $n_{0k}+m_{0k}+\Sigma_j p_{kj}$ is a natural number for any node k. Expression (3) can then be put in the form

$$\rho(\varepsilon,\xi)-\sum_{\{X\}}\frac{1}{4\pi^2\varepsilon\xi}\sum_{\{p_{kj}\}}\sum_{\{n_{0k}\}}\sum_{\{m_{0k}\}}(\ldots),\qquad(5)$$

where the sum over $\{X\}$ means a summation over all possible carriers.

We now make use of assumption 1: In our ensemble, each level k is distributed at random in the band, and it can take on values Δ_k from $-\infty$ to ∞ with equal probabilities. We average the terms of series (3), noting that we have

$$\int_{-\infty}^{\infty}\frac{1}{(a-\Delta)^m}\frac{1}{(b-\Delta)^n}g\,d\Delta=\frac{2\pi ig}{(a-b)^{m+n-1}}\frac{(n+m-2)!}{(n-1)!(m-1)!}\qquad(6)$$

for $n, m>0$. In the cases $n=0$, $m=1$, and $n=1$, $m=0$ the integral is equal to $\pm ig\pi$ (depending on the sign of the imaginary part of a and b). Using the integral representation of the factorials

$$\Big(\sum_j X_j\Big)!=\int_0^\infty\prod_j\{\sigma^{X_j}\}e^{-\sigma}\,d\sigma.\qquad(7)$$

we find the following expression for the population of the ground state:

$$\rho=\frac{1}{4\pi^2\varepsilon\xi}\sum_{\{X\}}\sum_{\{n_{0k}\}}\sum_{\{m_{0k}\}}\sum_{\{p_{kj}\}}\int_0^\infty d\lambda\int_0^\infty d\sigma\int_0^\infty d\tau$$
$$\times\exp(-\lambda-\sigma-\tau)\prod_{k,\,j\neq k}\left\{\left[\frac{-f(\varepsilon,\xi)\tau}{(\varepsilon-\xi-2i\gamma)^2}\right]^{p_{kj}}\frac{1}{p_{kj}}\right\}\det\Big\|p_{kj}$$
$$-\delta_{kj}\Big(\sum_l p_{kl}-m_{0k}\Big)\Big\|\det\Big\|p_{kj}-\delta_{kj}\Big(\sum_l p_{kl}-n_{0k}\Big)\Big\|\prod_k$$
$$\times\left\{-\int_0^\infty d\tau_k\frac{\exp(-\tau_k)}{\tau_k^2}2\pi ig_k(\varepsilon-\xi-2\gamma)\right.$$
$$\times\left(\frac{-|V_{0k}|^2\lambda\tau_k}{\varepsilon(\varepsilon-\xi-2i\gamma)}\right)^{n_{k0}}\left(\frac{|V_{0k}|^2\sigma\tau_k}{\xi(\varepsilon-\xi-2i\gamma)}\right)^{m_{k0}}$$

$$\times |V_{0k}|^{2\sum_j (p_{kj}-p_{jk})} \tau_k^{2\sum_j p_{kj}} \Big[n_{k0}!\, m_{k0}! \Big[n_{k0} + \sum_j (p_{kj}-p_{jk})\Big]!\, \Big[m_{k0} + \sum_j (p_{kj}-p_{jk})\Big]! \Big]^{-1} \Big\}, \qquad (8)$$

where $2\gamma = \gamma(\varepsilon) + \gamma(\xi)$.

The idea of the following transformations is to put the population of the ground state in the form of a product of factors each of which depends on only the parameters corresponding to one level. An averaging is then carried out over these parameters. In this approach, the primary difficulty stems from the presence of determinants which depend on the indices of many levels in expression (8). The levels can be split, however, by using generating functions. The actual procedure, in the form in which we have managed to carry it out, is extremely involved, and we do not have space here to reproduce it in detail. It is summarized in the Appendix, where the appropriate notation is also introduced. The final expression is

$$\rho = -[4\pi^2(\varepsilon - i\pi g\langle V^2\rangle)(\xi + i\pi g\langle V^2\rangle)]^{-1}$$
$$\cdot \int_0^\infty\int_0^\infty\int_0^\infty d\lambda\, d\sigma\, d\tau \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\, dy \int_\Phi du$$
$$\cdot \int dv\, (4\pi uv)^{-1} \exp(-\lambda - \sigma - \tau - x^2 - y^2)$$
$$\cdot [(1-u^{-1})(1-v^{-1})(1-A_2)^{-1}$$
$$\cdot \exp(A_1 - A_2) + |A_3|^2 (1-A_2)^{-2} \exp(A_1 - A_2)], \qquad (9)$$

where we are using the notation

$$A_1(k) = \int \frac{g(V)dV}{2\pi i} \int_{C(\mu)} d\nu\, \nu^{-2} \int_{-\pi}^{\pi}\int_{-\pi}^{\pi} \Big[f\tau\nu^2(1+u) - \frac{\partial}{\partial s} - \frac{\partial}{\partial R}\Big]\Big[f\tau\nu^2(1+v) - \frac{\partial}{\partial s} - \frac{\partial}{\partial L}\Big] e^{\Lambda(k)}\, d\theta\, d\vartheta \Big|_{s,R,L=0},$$

$$A_2(k) = -\int \frac{g(V)dV}{2\pi i} \int_{C(\mu)} d\nu \int_{-\pi}^{\pi}\int_{-\pi}^{\pi} f\tau e^{\Lambda(k)}\, d\theta\, d\vartheta \Big|_{s,R,L=0},$$

$$A_3(k) = -\int \frac{g(V)dV}{2\pi i} \int_{C(\mu)} d\nu \int_{-\pi}^{\pi}\int_{-\pi}^{\pi} d\theta\, d\vartheta\, f\tau \cdot \exp[\Lambda(k) + i(\theta+\vartheta)] \Big|_{s,R,L=0},$$

$$\Lambda(k) = -(\varepsilon - \xi - 2i\gamma)\nu e^{-s/2} + 2(|V|^2\nu)^{1/2} \cdot \Big[\Big(\frac{-\lambda \exp(4 - s/2)}{\xi + i\pi g\langle V^2\rangle} \Big)^{1/2} \cdot \cos\Big(\theta - i\frac{L}{2} + i\frac{s}{4}\Big) + \Big(\frac{\sigma \exp(R - s/2)}{\varepsilon - i\pi g\langle V^2\rangle}\Big)^{1/2} \cdot \cos\Big(\vartheta - i\frac{R}{2} + i\frac{s}{4}\Big)\Big]$$
$$+ 2i(f\tau)^{1/2}\nu[x\cos(\theta+\vartheta) + y\sin(\theta+\vartheta)] + f\tau\nu^2. \qquad (10)$$

Here Φ is a contour around the origin, and $C(\mu)$ is a contour consisting of a ray which starts from the origin and goes off to infinity at an angle μ from the real axis. The phase μ is chosen in such a way that all the integrals converge. The quantity $g(V)$ is the spectral density of those levels for which the matrix element of the interaction with the ground state lies in a dV interval around V.

Expression (9), along with expressions (10), describes the behavior of the population of a state associated with a band of levels between which the transitions described by the transfer function $f(\varepsilon,\xi)$ occur as a result of a mediated interaction through a dense band. Although this point cannot be seen directly from the expressions written here, the population of the ground state remains equal to unity at all times in the case $V \equiv 0$. To verify this physically obvious fact, it is necessary to carry out several transformations which consist basically of using the relations found for the Bessel functions after integrating over $d\theta$ and $d\vartheta$, introducing the new variable $J = A_1 - A_2$, and integrating by parts.

For the transformations below, we make use of the specific functional form of $g(V)$, which makes it possible to substantially simplify the expressions derived above:

$$g(V) = (2gV/V_0^2)\exp(-V^2/V_0^2), \qquad (11)$$

where $V_0 \equiv \langle V^2\rangle^{1/2}$ is the mean square matrix element of the transition operator, and g is the spectral density of all levels. Noting that V and $\theta - \vartheta$ can be treated as polar coordinates under integration, carrying out the corresponding integrations in terms of the equivalent Cartesian coordinates $V\cos(\theta - \vartheta)$ and $V\sin(\theta - \vartheta)$, changing the order of the integration over $d(\theta + \vartheta)$ and the differentiation, introducing the change of variables $\nu \to \nu \exp(s/2)$ and then differentiating with respect to ds, dL, and dR, we find an expression for the population. After the terms in the relation for the quantity $J = A_1 - A_2$ which are proportional to ν^{-1} are eliminated through the use of recurrence relations for the Bessel functions; after we use the identity

$$\exp(f\tau\nu^2) = \pi^{-1/2} \int_{-\infty}^{\infty} \exp[(f\tau)^{1/2}\nu Y - Y^2]\, dY; \qquad (12)$$

and after we introduce the variables

$$Z = (\varepsilon - \xi - 2i\gamma) + V_0^2[\sigma(\varepsilon - i\pi g V_0^2)^{-1} - \lambda(\xi + i\pi g V_0^2)^{-1}] + 2(f\tau)^{1/2} Y,$$
$$r^2 = 4\{V_0^2[-\lambda\sigma(\varepsilon - i\pi g V_0^2)^{-1}(\xi + i\pi g V_0^2)^{-1}]^{1/2} + i(f\tau)^{1/2}x\}^2 - 4f\tau y^2, \quad \varphi = \mathrm{arctg}(y/x) \qquad (13)$$

and

$$\sigma' = \zeta[\zeta(\varepsilon - i\pi g V_0^2)^{-1} - \lambda(\xi + i\pi g V_0^2)^{-1}, \quad \zeta = \varepsilon - \xi, \quad \eta = \varepsilon + \xi,$$
$$s = \sigma(\varepsilon - i\pi g V_0^2)^{-1} + \lambda(\xi + i\pi g V_0^2)^{-1}; \qquad (14)$$

this expression for the population takes the form

$$\rho = \frac{1}{2\pi^3\zeta} \int d\sigma'\, dz\, d\eta\, d\tau\, dx\, dy [(1-A_L)(1-A_R)(1-A_2)^{-1} - A_{RL}(1-A_2)^{-1} - |A_3|^2(1-A_2)^{-2}] \exp(J - \sigma' - is\eta - x^2 - y^2), \qquad (15)$$

where

$$J=\frac{1}{2}\pi^{1/2}g\int_{-\infty}^{\infty}\{-V_0^4(\sigma'^2\zeta^{-2}+z^2)+[V_0^2(\sigma'^2\zeta^{-2}-z^2)^{1/2}$$
$$-2i(f\tau)^{1/2}x]^2-4f\tau Y^2$$
$$+V_0^2\sigma'\zeta^{-1}[\zeta/2-i\gamma+(f\tau)^{1/2}Y]\}\{[V_0^2(\sigma'^2\zeta^{-2}-z^2)^{1/2}$$
$$-2i(f\tau)^{1/2}x]^2$$
$$-[\zeta-2i\gamma+V_0^2\sigma'\zeta^{-1}+2(f\tau)^{1/2}Y]^2\}^{-1/2}$$
$$\exp(-Y^2)\,dY,$$

$$A_3=-\frac{gf\tau}{2i\pi^{1/2}}\int_{-\infty}^{\infty}(Z^2-r^2)^{-1/2}\exp(-Y^2)\,dY,$$

$$A_2=-e^{i\varphi}\frac{gf\tau}{2i\pi^{1/2}}\int_{-\infty}^{\infty}[Zr^{-1}(Z^2-r^2)^{-1/2}-r^{-1}]\exp(-Y^2)\,dY,$$

$$A_{R,L}=i\pi^{1/2}gf\tau\int_{-\infty}^{\infty}\left[\frac{V_0^2}{2}\left(\frac{\sigma'}{\zeta}\pm z\right)Z(Z^2-r^2)^{-1/2}-r^2(Z^2-r^2)^{-3/2}\right]$$
$$\times\exp(-Y^2)\,dY,$$

$$A_{RL}=\frac{\pi^{1/2}gf^2\tau^2}{2i}\int_{-\infty}^{\infty}[2+3r^2(Z^2-r^2)^{-1}](Z^2-r^2)^{-3/2}$$
$$\times\exp(-Y^2)\,dY. \qquad (16)$$

We consider the following cases in more detail.

a) We assume $f\equiv0$ and $\gamma\equiv0$. In other words, we assume that there is no interaction between band $\{k\}$ and band $\{\alpha\}$. We then have $A_2=A_3=A_{R,L}=A_{RL}=0$, and the expression for the population of the ground state becomes the same as that found in Ref. 6 for a level-band system. Under the condition $V_0g\ll1$, there is essentially no decay of the level, while at $V_0^2g^2\gg1$ a steady-state population $\rho_0\sim(V_0g)^{-2}$ is reached after a long time.

b) The case of a nonreturning random walk ($\gamma\neq0$, and $f\to0$ in the limit $\zeta\to0$) corresponds to

$$A_R=A_L=A_{RL}=A_2=A_3=0,\ J=-{}^1/_2\pi g(V_0^2\sigma' i\gamma/\zeta)^{1/2}, \qquad (17)$$

from which we find

$$\rho_0=\frac{1}{\pi\zeta}\int d\sigma'\exp\left\{-\sigma'-\frac{\pi g}{2}\left(\frac{V_0\sigma' i\gamma}{\zeta}\right)^{1/2}\right\}, \qquad (18)$$

and, at long times,

$$\rho_0\sim(t\gamma g^2V_0^2)^{1/4}\exp\{-{}^1/_2(t\gamma g^2V_0^2)^{1/2}\}. \qquad (19)$$

c) The case of an uncorrelated return random walk, i.e., the case $\gamma\neq0, f(\xi,\eta)\to2\pi i f(\zeta)$, corresponds to

$$A_{R,L}={}^1/_2 i\pi g[V_0^2\sigma'\zeta^{-1}(f\tau)^{1/2}]^{1/2}c_{R,L}(x),$$
$$A_{RL}={}^1/_2 i\pi g[V_0^2\sigma'\zeta^{-1}(f\tau)^{1/2}]^{-1/2}c_{RL}(x),$$
$$A_2=e^{-i\varphi}A_3={}^1/_2 igf\tau[V_0^2\sigma'\zeta^{-1}(f\tau)^{1/2}]^{-1/2}c_2(x),$$
$$J={}^1/_2\pi g[V_0^2\sigma'\zeta^{-1}(f\tau)^{1/2}]^{1/2}c_J(x), \qquad (20)$$

where $c_R(x)$, $c_L(x)$, $c_{RL}(x)$, $c_R(x)$, $c_j(x)$ are functions of the integration variable x, which are of order unity. Using the expressions given above; carrying out the integration $d\sigma'$ (the $1-A_2$ pole) and over $d\tau$ by the method of steepest descent, in which we make use of the small values of the quantities $V_0^{-2}g^{-2}$, f^{-1}, and ζ; taking a Gaussian integral over dy and a steepest-descent integral over dx, we find the following expression for the principal component of the population after a long time:

$$\rho_0(t)=\frac{(gV_0^2t)^{1/4}}{g^2f(g^{-1/2}V^{-1}t^{-1/2})}\exp[-\mathrm{const}(gV_0^2t)^{1/2}]. \qquad (21)$$

d) The case of a returning random walk with a finite correlation time τ_c leads to the following expressions for f and γ in the asymptotic expressions for large values of η, i.e., at $\eta\gg\tau_c^{-1}$:

$$f(\zeta,\eta)\sim f(\zeta)/\tau_c\eta^2,$$
$$\gamma(\varepsilon)+\gamma(\xi)=\gamma(\zeta,\eta)=\gamma(\zeta,0)/\tau_c^2\eta^2. \qquad (22)$$

Specifically large values of η are responsible for the incomplete decay of state 0. After a long time, we should retain in expression (13) for the quantity Z only terms of order $V_0^2\sigma'$ and of order $V_0^2\sigma'\zeta^{-1}(f\tau)^{1/2}$. Since in the limit $\xi\to0$ we assume $f(\zeta)\zeta\to0$, we have $A_2\to A_3\to A_{RL}\to0$, and the integral over $d\sigma'$ is evaluated by the method of steepest descent. The saddle-point value σ' is such that in the limit $\zeta\to0$ both A_R and A_L tend toward zero. After the change of variables

$$\eta=(f(\zeta)\tau/\tau_c\zeta^2)^{1/2}\eta',\quad z=(\zeta^2\tau_c/f(\zeta)\tau)^{1/2}z' \qquad (23)$$

and an integration over $d\tau$, we find

$$\rho_0\sim\int\frac{V_0g}{\zeta}U(\eta';x)$$
$$\times\exp\{-i\eta'z'-V_0^2g^2\Psi(\eta';x)\}\,d\eta'\,dz'\,dx,$$

where $\Psi(\eta';x)$ and $U(\eta';x)$ are functions which are of order unity for arguments of order unity. Evaluating the integral over dz' and the integrals over $d\eta'$ and dx by the method of steepest descent ($V_0^2g^2\gg1$), we find

$$\rho_0\sim\zeta^{-1}g^{-1}V_0^{-1}\exp(-V_0^2g^2\,\mathrm{const}), \qquad (24)$$

which yields, in the limit $t\to\infty$,

$$\rho_0\sim g^{-1}V_0^{-1}\exp(-V_0^2g^2\,\mathrm{const}). \qquad (25)$$

The correlation time τ_c does not appear in the result for the population. It determines not the steady-state value ρ_0 but the time which is required to reach a steady state. Specifically, since the saddle-point value is $\eta'\sim1$, we have $\eta\sim[f(\zeta)\tau_0^{-1}\zeta^{-2}]^{1/2}$, so satisfaction of the condition $\eta\gg\tau_c^{-1}$ requires

$$\zeta^{-2}f(\zeta)\gg\tau_c^{-1}. \qquad (26)$$

Using $\zeta\approx t^{-1}$, we find from this expression an estimate of the time required for the population to reach its asymptotic value.

3. DISCUSSION OF RESULTS

Limiting cases **b** and **c**, which correspond to a nonreturning random walk and an uncorrelated returning random walk, can be given a graphic interpretation on the basis of the idea that the spectra for Poisson and Dyson ensembles differ in "hardness." For this purpose we need to examine the probability for returns of a random walk to the levels of band $\{k\}$ as an effective interaction between them. A returning random walk in the asymptotic behavior at large t then corresponds to a strong interaction, while a nonreturning random walk corresponds to asymptotically noninteracting states.

The temporal behavior of the population of the ground state, ρ_0, as $t\to\infty$ determines those realizations of the band which correspond to the slowest decay, i.e., bands which do not have levels which lie close to state 0 along the energy scale. The probability that there will be no levels of band $\{k\}$ in a Δ neighborhood of this state under the condition $g\Delta\gg 1$ is of order $\exp(-g\Delta)$ for a Poisson (noninteracting) ensemble and of order $\exp(-g^2\Delta^2)$ (to within the coefficient of the exponential function) for Dyson ensembles. The rate of the decay of the population of level 0 to states of band $\{\alpha\}$ through a level of band $\{k\}$, tuned an amount Δ away from resonance, is determined by the composite matrix element W, which can be estimated to be

$$W(\Delta)\sim V_0^2\gamma/\Delta^2. \tag{27}$$

The rate of the decay through this and all other levels of band $\{k\}$, detuned by a greater amount, is

$$W=\int\limits_{|h|>\Delta} W(h)g\,dh\sim V_0^2\gamma g|\Delta|^{-1}. \tag{28}$$

This is the decay rate of level 0 in the case in which the nearest of the states in the realization of the band $\{k\}$ lies a distance Δ away along the energy scale. We can thus write

$$\rho_0 \quad \exp(-V_0^2\gamma g t/|\Delta|). \tag{29}$$

Taking an average of this quantity over the probability distribution for the formation of an energy gap of size Δ in a Poisson ensemble $\exp(-g\Delta)$, we find

$$\rho_0=\int\exp\left(-\frac{V_0^2\gamma g^2 t}{|\Delta|g}-g|\Delta|\right)g\,d\Delta$$

$$\sim(V_0^2\gamma g^2 t)^{1/4}\exp[-2(V_0^2\gamma g^2 t)^{1/2}], \tag{30}$$

which agrees with expression (19). Taking an average of expression (29) over a Dyson ensemble, $(g\Delta)^\alpha\exp(-g^2\Delta^2)$, we find

$$\rho_0\sim t^{\alpha/3}\exp[-\mathrm{const}(\gamma V_0^2 g^2 t)^{2/3}], \tag{31}$$

which agrees to within the coefficient of the exponential function with expression (21). If the function f in the asymptotic region of small ζ is represented in the form $\zeta^{-\beta}$, then there is complete agreement between expressions (21) and (31) under the conditions $\alpha=7-\beta$, and $\gamma g\sim 1$. Since we have $1>\beta>0$ for a returning random walk, we find that the quantity α lies in the interval $7>\alpha>6$. In other words, the interaction of states as the result of an uncorrelated returning random walk leads to the formation of ensembles which are harder than ordinary Dyson ensembles. Here, however, we are talking about that hardness which determines the coefficient of the exponential function in the asymptotic expression for the case of large separations between levels. Furthermore, since we are dealing with a repulsion of decaying levels in this example, it is totally meaningless to talk about their relative positions at distances smaller than the decay rate.

We should emphasize that the results found for cases **b** and **c** indicate that after long times the ground-state population is not self-averaging. It is dominated by systems which lead to a slow decay of the level and which are encountered only rarely in the ensemble. Consequently, the results found here cannot be used to describe any single system, and validity of the model requires the physical existence of an ensemble of different systems.

The situation is quite different in limiting case **d**, in which the wave functions have a finite correlation time, and the level decay is incomplete. The reason is that the asymptotic expression for its population should obviously be a continuous function of the microscopic parameters of the system (the extent to which the levels are "detuned," the matrix elements of the transition operator, etc.). Consequently, if the mean value of the population of state 0 is finite in the limit $t\to\infty$, then it must also be finite for the overwhelming majority of possible specific realizations of the system. The exceptional case comprise a set of measure zero. In other words, a finite value of the correlation time leads to the existence of a localized component of the population.

The role played by the requirement that the correlation time be finite can be understood by noting that only when this requirement is met does there exist a nonvanishing population flux from a state of band $\{k\}$ to level 0. Specifically, if the quantity $\Sigma_k V_{0k}\psi_k(t)$ (the flux of probability amplitude) varies irregularly with a typical correlation time τ_c, its time integral can be estimated from

$$\sum_k\int_0^{t\gg\tau_c}V_{0k}\psi_k(t)\,dt\sim\left(\frac{t}{\tau_c}\right)^{1/2}\int_0^{\tau_c}\sum_k V_{0k}\psi_k(t)\,dt$$

$$\sim\sum_k\langle V_{0k}|\psi_k|\rangle(\tau_c t)^{1/2}, \tag{32}$$

which corresponds to diffusion population fluxes $\sim V_0^2\tau_c\Sigma_k\rho_k$.

We would also like to call attention to the circumstance that the correlation time τ_c does not appear in the expression for the asymptotic value of the population. This time determines not the steady-state value ρ_0 but the time which is required to reach the steady state. Condition (26), which is a necessary condition here, means that the quantity $gf(\zeta)\zeta^{-2}$ exceeds the number $(g\tau_c^{-1})$ of levels which fall in a τ_c^{-1} neighborhood of the resonance. We note that the variable ζ is related to the time by $\zeta\sim t^{-1}$. We also note that the function $f(\zeta)$ signifies the Fourier transform of the probability for observing a particle at time t in some level k of band $\{k\}$ under the condition that at $t=0$ the particle was at a level $k'\neq k$ of this band and first returned to it at the time t. We then see that the quantity $\zeta^{-2}f(\zeta)g$ is an order-of-magnitude estimate of the time integral of the total flux of the population which returns to band $\{k\}$ by the time $t\sim\zeta^{-1}$. When the value of this quantity per state of band $\{k\}$ participating in the process (there are $g\tau_c^{-1}$ such states) becomes of order unity, the decay of the ground state is terminated. The return fluxes of population from the band to the level stabilize its average population.

This statement means that a necessary condition for the termination of the decay is that the quantum-mechanical particle described by the Schrödinger equation (1) must be in each state of band $\{k\}$ which satisfies the resonance condition with a probability close to unity. It can also be asserted that the steady-state value of the level population is reached after the quantum-mechanical particle which was originally localized in a phase volume $\mathscr{V} \sim (2\pi\hbar)^5$ of one state of the band goes, in the course of the random walk, into a phase volume corresponding to another state of the band. The time required for this event is essentially the Poincaré recurrence time for the minimum (consistent with quantum mechanics) phase volumes.

There is yet another interesting circumstance here. In a quantum-mechanical system consisting of an isolated level and a discrete band,[17–19] the band may be thought of as a continuum with smoothly varying parameters—the square amplitude of the transition probability and the state density—at times $t < g$, when the typical distance between levels, $\delta \sim g^{-1}$, is smaller than the uncertainty in the their energy position, $\sim t^{-1}$. For such a system, the wave function of the ground state is

$$\psi_0(t) = \exp(-V^2 gt \,\text{const}). \tag{33}$$

By a time $t \sim g$, i.e., by the limiting time for which the analysis is valid, the population of the level is

$$\rho_0 \propto \exp(-V_0^2 g^2 \,\text{const}), \tag{34}$$

which agrees to within the coefficient of the exponential function with (25). At times $t > g$, "revivals"—return probability fluxes from the band to the level—begin to play an important role. These revivals subsequently lead to an increase in the population of the level, to a value $g^{-2}V_0^{-2}$, corresponding to the principle of detailed balance. Specifically, if $t \gg g$, and if the phase shift between neighboring states satisfies $|\Delta_k - \Delta_{k-1}| t \gg 1$, these population fluxes may be regarded as random, rapidly oscillating fluxes, equal on the average to g^{-1}. Equating the forward and return fluxes, $\rho_0 V_0^2 g = g^{-1}$, we find $\rho_0 \sim V_0^{-2} g^{-2}$. In other words, the population of the level is on the order of N^{-1}, where $N = g(V^2 g)$ is the number of states of the band which have reached resonance.

The presence of an interaction between the levels of band $\{k\}$, mediated through the states of band $\{\alpha\}$ in the course of the random walk, apparently has the consequence that the phases of the wave functions of levels k are interacting—locked together or correlated. The phase shift between neighboring levels, on the other hand, is not a random quantity. Accordingly, that linear combination $\Sigma V_{\alpha k} \psi_k(t)$ of the wave functions of band $\{k\}$ which determines the probability amplitude flux to the ground state can no longer be estimated from of the wave functions of band $\{k\}$ which determines the probability amplitude flux to the ground state can no longer be estimated from $V_{\psi\Sigma} N^{1/2} V_0/N^{1/2} \sim V_0$, as in the summation of N randomly oriented vectors each of length $V_0/N^{1/2}$. The uniform arrangement of the phases of the ψ functions on a circle leads to the estimate $V_{\psi\Sigma} \sim V_0 \exp(-N)$, which agrees to within the coefficient of the exponential function with expression (34) and which leads to expression (25). The phase capture suppresses the "revival" process.

In conclusion we would like to discuss two physical problems which can be solved through the use of the model system which we have been discussing here. The first of these problems concerns the dynamics of the filling of the low-lying levels of polyatomic molecules in an electromagnetic field which is resonant with one of the vibrational modes. We are interested in the mechanism for the formation of a so-called cold ensemble, i.e., a significant fraction of the molecules which, despite the existence of an external field, either are not excited or are excited only slightly. This analysis can be carried out on the basis of the model of a multilevel band-type system.[20] The role of the factor which forms the ensemble of systems is played by the rotational motion of the molecule as a whole, which, by virtue of the thermal distribution of the molecules among rotational states and by virtue of the vibrational-rotational interaction, can lead to irregularities in the vibrational spectrum and in the matrix of the dipole-moment operator. At times shorter than the Poincaré time, such a system can be described by balance equations, and the average populations of the levels which have reached resonance decay in accorance with a random-walk law. Limiting d makes it possible to describe the behavior of a system at times longer than the Poincaré recurrence time. State 0 is understood in this case as the only level which is occupied at $t = 0$ (and which corresponds to the vibrational ground state); the states $\{k\}$ are understood as levels which are dipole-accessible from this state; and the function f is understood as representing those transitions which, under the influence of the radiation, couple levels k through higher-lying states. If the spectral width of the absorption band is finite, so that its inverse—the correlation time of the random walk—is also finite, the decay by a random-walk law will come to a halt, the population distribution will reach a steady state, and a level which initially had a population $\rho = 1$ will be populated only slightly: $\rho \propto \exp(-V_0^2 g^2 \text{const})$. A situation of this sort corresponds to quantum-mechanical steady states localized within a region $l \propto \exp(V_0^2 g^2 \text{const})$ in terms of band indices.

The existence of localized states can explain the formation of a cold ensemble during the infrared excitation of a system of small polyatomic molecules.[21] Specifically, if the density of quantum states in the region of the low-lying vibrational levels and the spectral widths of the bands are small, the time required for dissociation of the molecule, t_D, may be much longer than the Poincaré recurrence time for the low-lying levels, t_p. There will thus exist a time interval $t_D \gg t \gg t_p$ within there are localized states in the low-lying levels. Because of the rapid growth of the number density of quantum levels with increasing energy, the population distributions corresponding to these localized states decay rapidly with increasing index of the excited level.

The second problem concerns the disruption of integrals of motion (quantum numbers) in nonlinear physical systems when they are subjected to a perturbation. In classical mechanics, a resonance between the periodic motions corresponding to these integrals can be achieved by appropriately choosing various values of the integrals of motion which are conserved with any prescribed accuracy in the unperturbed system. In systems with three or more dimensions, this situation can be arranged at essentially any point in the space of the action variables; i.e., the grid of resonances is dense everywhere (Ref. 22, for example). For this reason, if a perturbing interaction is not degenerate because of some symmetry, it will lead to the complete destruction of all the integrals in motion other than the energy, and it will lead to the appearance of a stochastic motion over the entire constant-energy surface.

In the quantum-mechanical case, the situation is more complicated. On the one hand, because of the discrete nature of the spectrum it is not always possible to satisfy the resonance conditions. On the other hand, even in the absence of an intermediate resonance there may be an effective tunneling interaction. To what extent the integrals of motion are violated in the process can be determined by solving the problem discussed above. For this purpose, we can take state 0 to be any state of the unperturbed Hamiltonian which corresponds to a completely integrable motion and which can therefore be described by a set of quantum numbers $\{n_i\}$. A perturbation V of a sufficiently simple structure gives rise to probability amplitudes for transitions from this state to other eigenenergy states of the unperturbed Hamiltonian with quantum numbers $\{n_i'\}$ which differ from $\{n_i\}$ by a relatively small change in the values of n_i in a relatively small number of positions. The set of these states, along with those which are reached in higher-order perturbations in V as a result of tunneling through greatly "detuned" levels, should be treated as a band of levels $\{k\}$.

If, on the other hand, we also know that this interaction is capable of leading to the formation of a stochastic layer (states for which the nondiagonal terms in V are greater than the energy differences) for at least a relatively small fraction of the eigenenergy states, and if the random walk corresponding to this layer is a returning walk, then we can choose as band $\{\alpha\}$ the set of eigenenergy states which are formed in the layer when V is taken into account. If the correlation time of the random walks (the reciprocal of the width of the stochastic layer in energy space) is finite, the state does not decay completely—only to a magnitude $\exp(-g^2V^2)$. A nonreturning walk and an infinitely short correlation time may lead to the complete violation of the integrals of motion (quantum numbers). It can also be assumed that approximately $\exp(-g^2V^2)\cdot 100\%$ of the total number of quantum states are states which have not decayed and which are described by the previous quantum numbers. A fraction of undecayed states of this magnitude corresponds to realizations of the $\{\alpha\}$ band which have no levels in a V neighborhood of the resonance. The quantity $\exp(-g^2V^2)$ under the condition $gV \gg 1$ describes the probability for such a realization in Dyson ensembles.

We wish to thank N. V. Karlov for a discussion of these results.

APPENDIX

Let us go through the procedure for deriving (9) from expression (8). Using standard relations of the type $x=(\partial/\partial y)_{y=0}\exp(xy)$ we introduce variables L_k, R_k, α_{kj}, and s_k, which are the adjoints of n_{k0}, m_{k0}, p_{kj} and $\Sigma_j p_{kj}$, respectively, in the determinants. In this case the determinants become differential operators of the type

$$\det\left\|\frac{\partial}{\partial\alpha_{kj}}+\delta_{kj}\left(\frac{\partial}{\partial s_k}+\frac{\partial}{\partial R_k}\right)\right\|,$$

and they act on the expression as a whole. We then carry out a summation[1] over n_{k0} and m_{k0}. As a result, Bessel functions arise. These functions can be expressed by means of the variables θ_k and ϑ_k in terms of the corresponding standard Sommerfeld integral representations. We then carry out a summation over p_{jk}, and as a result we find an exponential function of argument $f\tau$:

$$\sum_{j,k\neq j}\nu_k\nu_j\exp(i\theta_k+i\vartheta_k-i\theta_j-i\vartheta_j+\alpha_{jk}),$$

where $\nu_k=\tau_k(\varepsilon-\xi-2\gamma)^{-1}\exp(s_k/2)$.

After the order of the summation and the integration is changed, this exponential function is acted upon by two differential determinant operators. As a result, the first determinant acquires, in place of the arguments $\partial/\partial\alpha_{kj}$, arguments $(\ldots)\exp\alpha_{kj}$ and itself becomes the object acted upon by the second determinant. The action of the second determinant on the exponential function leads to the appearance of the same arguments as in the first case, along with which we should retain the operator part $\partial/\partial\alpha_{kj}$. After this procedure is carried out, the variables α_{kj} in the argument of this exponential function, "carried through" the differentiation operators $\partial/\partial\alpha_{kj}$, are assumed to be zero, and they become a bilinear form of variables corresponding to different levels: $\Sigma_{j,k\neq j}a_k a_j^*$. For the exponential function of this bilinear form there exists a two-dimensional integral representation $[\int dx dy\exp(-x^2-y^2)(\ldots)]$ of the quantity $\exp(xA+yB+C)$, which is multiplicative in terms of the variables with different indices, where

$$A\sim\sum_k \operatorname{Re}a_k,\quad B\sim\sum_k\operatorname{Im}a_k,\quad C\sim\sum_k|a_k|^2.$$

In this step, the only quantity which is not multiplicative in terms of the variables corresponding to different levels is the product of the determinants. Since the order of the derivatives with respect to each of the α_{kj} is no higher than the first, it can be written in the form

$$\det\Big\|-f\tau\nu_k\nu_j+\exp[i(\theta_k+\vartheta_k-\theta_j-\vartheta_j)]\frac{\partial}{\partial\alpha_{kj}}$$

$$+\delta_{kj}\left(\frac{\partial}{\partial s_k}+\frac{\partial}{\partial R_k}\right)\Big\|\det\left\|-f\tau\nu_j\nu_k(1-\alpha_{jk})+\delta_{jk}\left(\frac{\partial}{\partial s_k}+\frac{\partial}{\partial L_k}\right)\right\|.$$

Expanding the determinant of the sum of the two matrices in minors, we have

$$\sum_{\substack{\{C\}\subset\{X\}\\ \{C'\}\subset\{X\}}}\det\left\|-f\tau\nu_j\nu_k-\delta_{kj}\left(\frac{\partial}{\partial s_k}+\frac{\partial}{\partial R_k}\right)\right\|\det\left\|-f\tau\nu_k\nu_j+\delta_{kj}\left(\frac{\partial}{\partial s_k}+\frac{\partial}{\partial L_k}\right)\right\|\Bigg|_{k\subset\{C\},j\in\{C'\}}\det\left\|\frac{\partial}{\partial\alpha_{kj}}\right\|\det\|\alpha_{kj}\|\Bigg|_{k\in\{X\}/\{C\},j\in\{X\}/\{C'\}}$$

where {C} is the set of rows, and {C} is the set of columns (which have identical numbers of elements). The first two determinants, however, are nonzero only if {C} and {C′} differ by no more than a single element. The product of the last two determinants is a numerical factor, equal to the number of nonzero terms in the determinant with a zero mean diagonal or a zero diagonal nearest the mean diagonal. The nonzero determinants can be written in multiplicative form:

$$\det\|-f\tau v_k v_j-\delta_{kj}\hat{c}_k\|\,|_{k,j\in\{C\}}$$

$$=\frac{1}{2\pi i}\oint_{\Phi}(-u^{-2}+u^{-1})\prod_{k\in\{C\}}[f\tau v_k^2(1+u)-\hat{c}_k]\,du,$$

$$\det\|-f\tau v_k v_j-\delta_{kj}\hat{c}_k\|\,|_{k\in\{C\}\cup m,\,j\in\{C\}\cup n}=-f\tau v_m v_n\prod_{k\in\{C\}}(f\tau v_k^2-\hat{c}_k),$$

where contour Φ circumvents point 0 in the positive direction.

Since a summation is carried out over all possible carriers, a summation over minors can also be incorporated in it. The reason is that the minors differ from diagonal minors by no more than a single element. The transformation from a summation over carriers to an integration over the parameters of the levels and a summation over repeated levels with identical parameters is then made. In other words, we carry out a chain of transformations of the type

$$\sum_{\{X\}}\prod_{k\in\{X\}}a(V_k,g_k)$$

$$\to\prod_{\substack{V_k\in\{V\}\\ g_k\in\{g\}}}\sum_{n(V_k,g_k)=0}^{\infty}\frac{[N(V_k,g_k)\,a(V_k,g_k)]^{n(V_k g_k)}}{n(V_k g_k)!}$$

$$\to\exp\int N(V,g)\,a(V,g)\,dV\,dg,$$

where $N(V_k, g_k)$ is the fraction of levels with parameters V_k and g_k, and $n(V_k, g_k)$ is the number of their repetitions.

[1)] When the effect of the parts of the diagrams which have a tree topology is taken into account (this effect reduces to a renormalization,[18] and it generates imaginary increments in ε and ξ).

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Dynamics of excitation of multilevel systems of the band type in a laser field

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With the population of high-lying vibrational state of polyatomic molecules as an example, we consider the problem of the kinetics of population of multilevel systems of the band type. Physical arguments are advanced to show that for sufficiently complex molecules the dipole-moment matrix elements can be regarded as random and satisfying the Wigner "microcanonical" distribution. Within the framework of this hypothesis we consider the limiting cases of strong and weak interactions of the system with a laser field. For strong interactions we obtain and analyze an expression for the population distribution over the bands. For the case of weak interaction we derive a balance equation that describes the kinetics of the population of a multilevel system. It is shown that multilevel systems of the band type exhibit simultaneously both coherent and stochastic properties.

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The action of laser radiation on vibrational degrees of freedom of molecules was first considered in[1]. The model of the anharmonic oscillator[2,3] is extensively used at present. This model describes the excitation of diatomic molecules and the buildup of the nondegenerate modes of polyatomic molecules. At the same time, much attention is being paid to a process recently observed in experiment, collisionless dissociation of polyatomic molecules under the influence of a high-power electromagnetic field that is at resonance with the degenerate modes of polyatomic molecules.[4–6] The anharmonic-oscillator model turned out to be inadequate for the explanation of this effect and it was found necessary to take into account a peculiarity of polyatomic molecules that manifest themselves in a high density of the vibrational states.[7–9]

A direct approach to this problem would be to calculate the spectrum of the vibrational states of the polyatomic molecule and the matrix elements of the dipole moments, followed by a solution of the Schrödinger equation. However, owing to the large number of different vibrational states that actually take part in this process, none of the stages of such an analysis can be realized in practice. To describe the effect of collisionless dissociation one uses therefore various model approaches. A distinction can be made between two groups of model approaches. In the first[7,9] are considered almost-resonant single levels and a coherent energy acquisition. In the other one uses a stochastization hypothesis[10] and thermodynamic considerations.[11] These models have a limited applicability. Thus, in coherent models no account is taken of the large number of closely-lying levels (which are also resonant), and one neglects effects of interference of a large number of excitation channels that proceed via different levels with comparable amplitudes. Allowance for this circumstance can cause the energy acquisition by the molecule to have in a number of cases a random-walk character. Statistical methods, in turn, ignore completely the coherent effects that can cause, for example, only narrow vicinities of the resonances to be substantially populated. Yet in the problem of excitation of a multilevel system with a complex spectrum an important role may be assumed (and is in fact assumed) simultaneously by coherent and stochastic process. As a first step we wish to propose solvable models that do not ignore either of these aspects of the phenomenon.

The purpose of solving this type of model problems is to find those characteristics of the spectrum and of the Hamiltonian of the interaction of the system with the field, to which the results are most sensitive (e.g., the efficiency of energy acquisition). There are physical grounds for assuming that the number of these characteristics is small. In this case the behavior of an entire ensemble of multilevel systems with different spectra and interaction operators turn out to be the same. It is therefore natural to use the method of averaging over the ensemble. This part of the problem is general in character, does not depend on the actual structure of the molecules, and can be used to describe any system with a complex spectrum and with a "stepwise" character of the interaction. In this paper we restrict ourselves only to this part.

The subsequent program could consist of a direct calculation of the aforementioned characteristics for concrete molecules. In this approach there is hope of getting rid of the influence of a large number of degrees of freedom, so that the problem might be solved by a direct method.

1. THE MODEL

We have chosen the following model of the spectrum:

1) the level groups are localized in the vicinities of the energy values $n\hbar\omega$;

2) in each vicinity there is a large number $N_n \gg 1$ of levels, which are numbered by the index m;

3) the dipole moment differs from zero only for $\Delta n = \pm 1$ transitions between neighboring bands.

The Schrödinger equation for such a system is written in the form

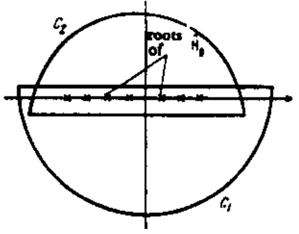


FIG. 1.

$$i\dot{\psi}_{n,m}=\varepsilon_{n,m}\psi_{n,m}+\sum_{n',m'}E\mu_{n,m}^{n',m'}\psi_{n',m'}\cos\omega t,\quad \hbar=1, \qquad (1)$$

where $\mu_{n,m}^{n',m'}$ are the matrix elements of the transitions.

Carrying out the transformation $\bar{\psi}_{n,m}=\psi_{n,m}\exp(-in\omega t)$ and neglecting the oscillating terms, we reduce Eq. (1) to the form

$$i\dot{\psi}_{n,m}=\Delta_{n,m}\psi_{n,m}+\sum_{n',m'}E\mu_{n,m}^{n',m'}\psi_{n',m'}, \qquad (2)$$

where $\Delta_{n,m}=\varepsilon_{n,m}-n\omega$. We write down the solution of (2):

$$\psi_{n,m}(t)=\sum_{n',m'}\{\exp-i\hat{H}t\}_{n,m}^{n',m'}\psi_{n',m'}(0), \qquad (3)$$

where

$$\hat{H}=\hat{H}_0+\hat{V}=\delta_n^{n'}\delta_m^{m'}\Delta_{n,m}+E\mu_{n,m}^{n',m'}.$$

From (3) follows an expression for the diagonal elements of the density matrix

$$\rho_{n,m}^{n,m}=\langle n,m|e^{-i\hat{H}t}\hat{\rho}(0)e^{i\hat{H}t}|n,m\rangle \qquad (4)$$

or, using the formula for the function of the operator,

$$\rho_{n,m}^{n,m}=\frac{1}{4\pi^2}\int_{C_1}d\varepsilon\int_{C_2}d\xi\, e^{-i(\varepsilon-\xi)t}\langle n,m|\frac{1}{\varepsilon-\hat{H}}\hat{\rho}(0)\frac{1}{\xi-\hat{H}}|n,m\rangle, \qquad (5)$$

where the integration contours C_1 and C_2 are shown in Fig. 1. If we use the expansion

$$(x-\hat{H}_0-\hat{V})^{-1}=(x-\hat{H}_0)^{-1}+(x-\hat{H}_0)^{-1}\hat{V}(x-\hat{H}_0)^{-1}+\ldots,$$

then the integrand in (5) can be represented as a sum over the trajectories

$$\sum_{\{l\}\{k\}}(\varepsilon-\Delta_{n,m})^{-1}V_{l,k}^{n,m}\ldots V_{n_0,m_0}^{l',k'}(\varepsilon-\Delta_{n_0,m_0})^{-1}\rho_{n_0,m_0}^{n_0,m_0}\cdot$$
$$\cdot(\xi-\Delta_{n_0,m_0})^{-1}V_{l'',k''}^{n_0,m_0}\ldots V_{n,m}^{l''',k'''}(\xi-\Delta_{n,m})^{-1}. \qquad (6)$$

If each term of the series is represented in graphic form, then we obtain diagrams of the type shown in Fig. 2. The wavy lines in this figure correspond to the right-hand operator bracket and the straight lines to the left-hand bracket. Each straight or wavy line joining the point (a,b) with the point (c,d) corresponds to the matrix element $V_{c,d}^{a,b}=E\mu_{c,d}^{a,b}$ of the interaction operator. To each point (a,b) on a wavy line corresponds to a factor

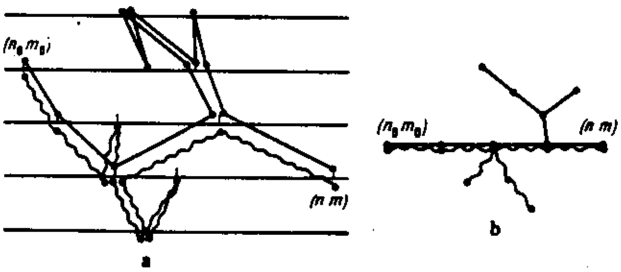
The wave and straight lines start out from points corresponding to levels populated at the instant time $t=0$, and terminates at the point (n,m) of interest to us. If only a certain level (n_0,m_0) is populated at the instant of time $t=0$, then the population of the (level (n,m) is expressed as the sum of all the possible trajectories that begin at the point (n_0,m_0) and end at the point (n,m).

The subsequent analysis of the problem depends essentially on the statistics of the dipole moments. We confine ourselves in this paper to an analysis of a system with random dipole moments. The physical arguments favoring such a model are the following: The presence of anharmonicity of the vibrations of polyatomic molecules causes the levels of various degenerate and multiple modes to experience Fermi resonances, as a result of which the dipole moment of the oscillatory transition becomes smeared out between them. This smearing has a complicated and irregular character. The only requirement that the matrix elements of the transition dipole moments must satisfy is the sum rule (the sum of the squares must be constant). A natural model that describes this situation is the total ignorance model, which leads to the "microcanonical" Wigner distribution function[1)]

$$g(\{\mu_{n,m'}^{n+1,m}\})=\delta\left[\sum_{m,m'}(\mu_{n,m'}^{n+1,m})^2-(\mu_n^{n+1})^2\right]\prod_{m,m'}d\mu_{n,m'}^{n+1,m}. \qquad (7)$$

According to the distribution (7), the matrix elements of the dipole moments do not correlate with one another.

As a result of the distribution (7) the essential contribution to the sum (6) is made only by those trajectories in which each pair of points is joined by two lines (see (8), where diagram b is the schematic representation of diagram a).



(8)

In addition, the condition $N_n\gg 1$ over times shorter than the Poincare return point allows us to sum only the

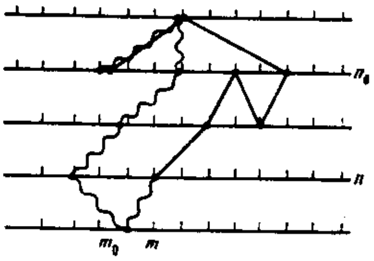
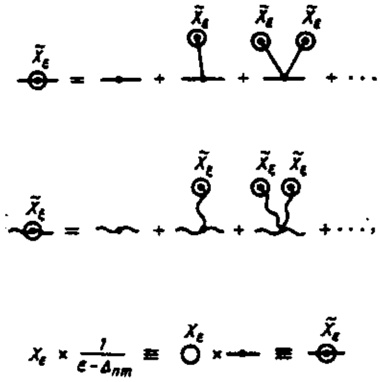


FIG. 2.

principal sequence of the series (6) and neglect the self-intersection of the trajectories. This form of the diagrams allows us to renormalize the operators corresponding to points on the straight and wavy lines. The operators are obtained from the recurrence relations (9):



(9)

The concrete form of these operators depends on the relation between the interaction Hamiltonian and the dimension of the band of levels γ_n. If $V \gg \gamma_n$, the interaction is "strong" and we can neglect the size of the band and regard it as degenerate. In the opposite limiting case we can let the band dimension tend to infinity, after fixing the average level density.

The quantity $\rho_{n_0 m}^{n\, m}$ is self-averaging. In fact the small contribution $O(1/N)$ of the self-intersecting trajectories means that the variance is small:

$$\langle\rho_{n,m}^{n,m}\rangle^2-\langle(\rho_{n,m}^{n,m})^2\rangle=O(1/N).$$

This means that for the overwhelming majority of systems with noncorrelating matrix elements of the dipole-moment operator the distribution of the populations over the bands is the same. This justifies the use of the technique of averaging over the ensemble for the description of a concrete system with random dipole moments.

2. TWO DEGENERATE LEVEL BANDS

We consider the problem of two degenerate levels such that dipole transitions are allowed between all the sublevel. In this case each line corresponds to a factor $V=E\mu_m^{m'}$, and each point on a wavy (straight) line corresponds to a factor $\xi^{-1}(\varepsilon^{-1})$. For this case, relation (9) takes the form

$$X_\varepsilon=\sum_{n=0}^{\infty}\left(\frac{u}{\varepsilon^2}X_\xi\right)^n=\frac{\varepsilon^2}{\varepsilon^2-uX_\xi},\quad X_\xi=\frac{\xi^2}{2u}-\left[\left(\frac{\xi^2}{2u}\right)^2-\left(\frac{\xi^2}{u}\right)\right]^{1/2}\qquad(10)$$

where $u=N\langle(E\mu_m^{m'})^2\rangle$, and $\langle\cdots\rangle$ means averaging over the Wigner ensemble. The summary population of the upper level is given by

$$\rho_2^2=-\frac{1}{4\pi^2}\int_{C_1}d\varepsilon\int_{C_2}d\xi\,\frac{X_\varepsilon X_\xi}{\varepsilon\xi}\,\frac{\varepsilon\xi uX_\varepsilon X_\xi}{(\varepsilon\xi)^2-(uX_\varepsilon X_\xi)^2}\,e^{-i(\varepsilon-\xi)t},\qquad(11)$$

and the population of the lower level is

$$\rho_1^1=-\frac{1}{4\pi^2}\int_{C_1}d\varepsilon\int_{C_2}d\xi\,\frac{X_\varepsilon X_\xi}{\varepsilon\xi}\,\frac{(\varepsilon\xi)^2}{(\varepsilon\xi)^2-(uX_\varepsilon X_\xi)^2}\,e^{-i(\varepsilon-\xi)t}.\qquad(12)$$

We define the quantities $I_1=\rho_2^2+\rho_1^1$ and $I_2=\rho_1^1-\rho_2^2$. Taking (10) into account and making the change of variables $\xi=(2u)^{1/2}\cosh\varphi$, $\varepsilon=(2u)^{1/2}\cosh\psi$, $\tau=(2u)^{1/2}t$, we get

$$I_{1,2}=\int_{C_1'}\int_{C_2'}(e^{\varphi+\psi}\mp1)^{-1}\operatorname{sh}\psi\operatorname{sh}\varphi\exp[i\tau(\operatorname{ch}\psi-\operatorname{ch}\varphi)]\,d\varphi\,d\psi,\qquad(13)$$

where the integration contour C_1' is the segment $\operatorname{Re}\varphi>0$, $\operatorname{Im}\varphi\in(-\pi/2;3\pi/2)$ and the contour C_2' is the segment $\operatorname{Re}\psi>0$, $\operatorname{Im}\psi\in(3\pi/2;-\pi/2)$. The integrals (13) can be evaluated:

$$I_1=1,\quad I_2=J_0(\tau)+J_2(\tau)=\frac{2}{\tau}J_1(\tau).\qquad(14)$$

We ultimately get

$$\rho_1^1=\frac{1}{2}\left[1+\frac{2}{E(N\langle(\mu_m^{m'})^2\rangle)^{1/2}t}J_1(E(N\langle(\mu_m^{m'})^2\rangle)^{1/2}t)\right],\qquad(15)$$
$$\rho_2^2=\frac{1}{2}\left[1-\frac{2}{E(N\langle(\mu_m^{m'})^2\rangle)^{1/2}t}J_1(E(N\langle(\mu_m^{m'})^2\rangle)^{1/2}t)\right].$$

As $t\to\infty$ the populations become equalized at a rate

$$\langle|\rho_{11}-\rho_{22}|\rangle_t\sim t^{-3/2}.\qquad(16)$$

It must be noted that this result can be obtained also in another manner. For a two-band degenerate submatrix the dipole moment submatrices can be diagonalized. As a result, the band-population problem reduces to a determination of the average level population of an aggregate of two-level systems whose transition dipole-moment matrix elements are described by the known "semicircular" density distribution[2)] [13]: $g(\mu)=(2\pi u)^{-1}\times(4\pi u-\mu^2)^{1/2}$. The population of the upper levels is given in this case by the expression

$$\rho_2^2(t)=\int(4\pi u-\mu^2)^{1/2}\sin^2(E\mu t)\,d\mu.$$

We emphasize that the expression for the eigenvalue density of a random matrix was obtained in[13] for a "canonical" Wigner distribution. In our problem we used a "microcanonical" Wigner distribution, which led to the same result. This result is natural, inasmuch as over times much shorter than the Poincaré return time only a small fraction of the dipole moments (subsystem) has become involved, and the microcanonical distribution reduces to a canonical one.

3. INFINITE SYSTEM OF DEGENERATE LEVELS

Such a system simulates the acquisition of energy by a polyatomic molecule in the case of a strong interaction with a laser field ($\gamma_n\ll E(N_n\langle(\mu_{n-1,m}^{n,m'})^2\rangle)^{1/2}$). In this problem, the operators X_ε and X_ξ retain the same form as in Sec. 2. To determine the population of the n-th level it is necessary to find the number of trajectories that go from the point n_0 into the point n and consist of wavy and straight line jointly. For an infinite system of levels the number of trajectories of length M, joining n and n_0, is determined by the number of combinations the n-th level at the instant of time t is given by

$$\rho_n^n = \sum_M \int_{C_1} d\varepsilon \int_{C_2} d\xi \frac{X_\varepsilon X_\xi}{\varepsilon\xi} C_M^{\frac{1}{2}(M-n+n_0)} \left(\frac{2\pi X_\varepsilon X_\xi}{\varepsilon\xi}\right)^M e^{-i(\varepsilon-\xi)t}. \tag{17}$$

If we use the relation

$$\sum_{k=0}^{\infty} x^{k+1} C_k^{\frac{1}{2}(k-s)} = \left(\frac{1}{4x^2}-1\right)^{-1/2} \cos\left(s \arccos\frac{1}{2x}\right), \tag{18}$$

which is obtained with the aid of the integral representation for C_b^a, then we obtain from (17) and (18) for the case $\rho_n^n(0) = \delta_n^{n_0}$:

$$\rho_n^n = \int_{C_1} d\varepsilon \int_{C_2} d\xi\, e^{-i(\varepsilon-\xi)t} \left[\left(\frac{\varepsilon\xi}{X_\varepsilon X_\xi \pi}\right)^2 - 1\right]^{-1/2} T_{n-n_0}\left(\frac{\varepsilon\xi}{X_\varepsilon X_\xi \pi}\right). \tag{19}$$

At large n this is a saddle-point integral. It can be represented in the form

$$\rho_n^n \sim t^{-1/2} G(n^2/t), \tag{20}$$

where $G(n^2/t)$ is a certain universal function that attenuates exponentially at infinity and contains oscillations in the vicinity of $n^2 \lesssim Et(N\langle\mu^2\rangle)^{1/2}$. The oscillations of the function G are the traces of the coherence, and the dependence on the argument n^2/t is a consequence of the stochastic behavior. In the essential regions $n^2 \sim Et(N\langle\mu^2\rangle)^{1/2}$, where $G \sim 1$, the contributions of the coherence effects and stochasticity are of the same order. We shall not present the explicit form of the function G, which can be expressed in terms of parabolic-cylinder functions. We note only that (20) enables us to show that the acquisition of energy by the molecule in the case of a strong interaction is given by

$$\mathcal{E} \sim [Et(N\langle\mu^2\rangle)^{1/2}]^{1/2}. \tag{21}$$

4. CASE OF WEAK INTERACTION

We consider the case of a relatively weak interaction, such that

$$\gamma_n/N_n \ll E[\langle(\mu_{n-1,m}^{n,m'})^2\rangle]^{1/2} = V \ll \gamma_n. \tag{22}$$

This model describes most probably the acquisition of energy by a polyatomic molecule. For simplicity we consider the case of an equidistant spectrum[3)] $\Delta_{n,m} = \alpha m$ and set α equal to π. This means that the energy-dependent quantities are measured in units of α/π and the time in π/α.

Equation (9) leads in this case to the relation

$$\frac{X_\varepsilon(n,m)}{\varepsilon-\Delta_{n,m}} = \left[\varepsilon-\Delta_{n,m}-V^2\sum_{n',m'} X_\varepsilon(n',m')(\varepsilon-\Delta_{n',m'})^{-1}\right]^{-1}. \tag{23}$$

If we put

$$Q_\varepsilon = \sum_{n',m'} X_\varepsilon(n',m')(\varepsilon-\Delta_{n',m'})^{-1},$$

$$\frac{X_\varepsilon(n,m)}{\varepsilon-\Delta_{n,m}} = \frac{1}{\varepsilon-\Delta_{n,m}-V^2 Q_\varepsilon} \tag{24}$$

and for Q_ε we have the equation

$$Q_\varepsilon = \sum_m \frac{1}{\varepsilon-V^2Q_\varepsilon-m\pi} = \mathrm{ctg}(\varepsilon-V^2Q). \tag{25}$$

At $V^2 \gg 1$ there exist roots of (25) that do not depend on the microstructure of the spectrum: $Q_{\varepsilon,\xi} = \pm i$. In this case the following recurrence relation holds for the total populations of the bands:

$$\rho_n^n = \frac{1}{2}(\rho_{n+1}^{n+1}+\rho_{n-1}^{n-1}) \sum_m \frac{V}{\varepsilon-iV^2-m\pi}\frac{V}{\xi+iV^2-m\pi}. \tag{26}$$

After summing (at $V^2 \gg 1$) and taking the inverse Fourier transform we arrive at the equation

$$\dot\rho_n^n = V^2(\rho_{n+1}^{n+1}+\rho_{n-1}^{n-1}-2\rho_n^n). \tag{27}$$

This is the usual kinetic equation. From its solution we find that at V independent of n the total acquired energy is

$$\mathcal{E}(t) = \sum_n \omega n \rho_n^n \sim (V^2 t)^{1/2} = \left(\frac{\pi E^2\langle\mu^2\rangle}{\alpha} t\right)^{1/2}. \tag{28}$$

If we sum all the terms of the type (7) of the series (6), taking into account the distribution of the populations over the levels in the band, i.e., without summation over the initial and final points, then we can show that the levels that are substantially populated are those deviating by not more than $2V^2$, i.e., by $2\pi E^2\langle\mu^2\rangle/\alpha$, for the harmonic position of the energy. The population distribution over an individual band takes the form of a Lorentz curve:

$$\rho_{n,m}^{n,m} = \rho_n^n \frac{2V^2}{\Delta_{n,m}^2+4V^4}. \tag{29}$$

It is easy to modify the problem of Sec. 4 to accommodate the case of two bands. Then

$$\rho_{1,m}^{1,m} = \int_{C_1} d\varepsilon \int_{C_2} d\xi \frac{V}{\varepsilon-iV^2}\frac{V}{\xi+iV^2}\frac{1}{1-q^2}\frac{V}{\varepsilon-\Delta_{1,m}-iV^2}\frac{V}{\xi-\Delta_{1,m}+iV^2}, \tag{30}$$

$$\rho_{2,m}^{2,m} = \int_{C_1} d\varepsilon \int_{C_2} d\xi \frac{V}{\varepsilon-iV^2}\frac{V}{\xi+iV^2}\frac{q}{1-q^2}\frac{V}{\varepsilon-\Delta_{2,m}-iV^2}\frac{V}{\xi-\Delta_{2,m}+iV^2},$$

where

$$q = \sum_m V^2(\varepsilon-iV^2-\pi m)^{-1}(\xi+iV^2-\pi m)^{-1} = (1-i(\varepsilon-\xi)(2V^2)^{-1})^{-1}.$$

The integrals (30) yield directly an exponential equalization of the populations, with a characteristic time $(2V^2)^{-1}$, with the stationary populations localized in the $2V^2$ vicinity: $\Delta_{1,m} \sim \Delta_{2,m} \sim 0$.

The obtained kinetic equation shows that in a multilevel system of the band type, under conditions of weak interaction, the phase shifts of the off-diagonal elements of the density become effectively randomized. At first glance this condition contradicts the localization of the populations in small vicinities of levels with $\Delta = 0$. Actually, however, these conditions do not contradict one another. The population of a band is given according to (29) by a Lorentz curve and behaves like Δ^{-2} as $\Delta \to \infty$, while the probability amplitude tends to zero like Δ^{-1}. While the integral of Δ^{-2} converges at infinity, the integral of Δ^{-1} diverges at infinity. Thus, the phase randomization, which is determined by the interference of the probability amplitudes, receives contributions from states far from resonance, while the population receives contributions only from states close to resonances.

We emphasize that the foregoing analysis was based essentially on the hypothesis that the dipole-moment matrix elements are random and have a zero mean value. If the dipole moments correlate, then the results can change significantly. Thus, in the case of complete correlation it turns out that the acquired energy relaxes exponentially to its stationary value. This question will be considered in detail separately.

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1) Dyson[12] advances arguments that the Wigner distribution is incorrect for Hamiltonians and has therefore no physical realization. In our problem the submatrix of the dipole moments is not a Hamiltonian and because of the sum rule it satisfies the Wigner distribution.

2) We derive this distribution in a manner simpler than in[13]: $g(\mu) = \mathrm{Im}\,\mathrm{Sp}(\varepsilon - V - i\delta)^{-1}|_{\varepsilon=\mu} = \mathrm{Im}\, X_\varepsilon \varepsilon^{-1}|_{\varepsilon=\mu} = (2\pi\varkappa)^{-1}(4\pi\varkappa - \mu^2)^{1/2}$ at $|\mu| < (4\pi\varkappa)^{1/2}$. This is in fact the Rabi frequency distribution.

3) If the inequality (22) is satisfied, the answer does not depend on the concrete structure of the spectrum of an individual band.

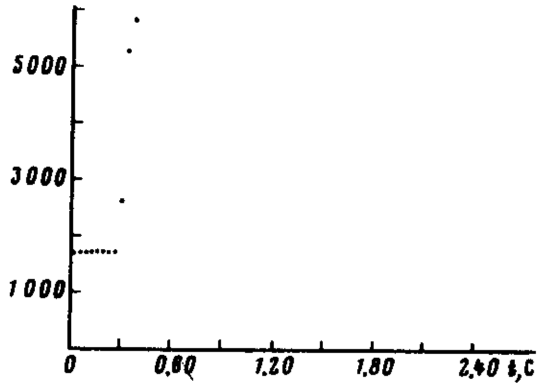

FIG. 1. Thermogram of the heating of a graphite sample in helium at a pressure of 5×10^7 Pa.

At pressures above 1.5×10^7 Pa, we found traces of molten carbon at the bottom of the crater resulting from the evaporation. These traces consisted either of droplets up to 1 mm in diameter, with a metallic luster, or flow regions on the crater walls. The large droplets at the bottom of the craters had a flat surface. Sections cut through the samples in a plane passing through the axis of a crater revealed a melting zone with an isotropic fine-grain structure with a crystallite size $\gtrsim 10$ μm; this structure differed sharply from the original layered structure of the pyrolytic graphite.

The resulting heating thermograms (Fig. 1) have a characteristic plateau, i.e., a region of a steady-state temperature, which corresponds to an intense evaporation of liquid carbon at the given external pressure. The temperature of this plateau depends on only the external pressure and ranges from ≈ 5000 K at a pressure of 10^7 Pa to ≈ 7000 K at 10^8 Pa.

Estimates show that the evaporation of the carbon which occurs under these experimental conditions is not far from equilibrium; i.e., there are no significant hydrodynamic effects at the liquid-vapor interface. The saturation vapor pressure of the evaporated carbon should be approximately equal to the pressure of the surrounding inert gas under these conditions. The results found in measurements of the plateau temperature as a function of the external pressure thus trace out the equilibrium line of the liquid and vapor phases of the carbon (the saturation line). The experimental data obtained here can be described by

$$\ln p,\ \mathrm{Pa} = (24.7 \pm 0.4) - (4.3 \pm 0.3)\,10^4\,\frac{1}{T,\mathrm{K}} \qquad (T = 5000-7000\,\mathrm{K}).$$

We used this expression to determine the latent heat of vaporization of liquid carbon: $\Delta H_{\mathrm{vap}} = 360$ kJ/mole. According to Ref. 4, the average number of atoms in a molecule of carbon vapor is about four in the temperature interval 5000–7000 K. For this value we find $\Delta H_{\mathrm{vap}} = 90$ kJ/(g-at C), in good agreement with the estimate[4] $\Delta H_{\mathrm{vap}} = 84$ kJ/(g-at C).

other possible applications in the synthesis of refractory compounds in research on the phase diagrams of these compounds, in the laser processing of materials, etc.

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Controlling the electron-impact fragmentation of molecules through IR-laser excitation of vibrational modes

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The monomolecular fragmentation of the vibrationally excited molecules CF_3I, CF_3Br, and CF_2Cl_2 by electron impact has been studied. It has been found possible to effectively control the composition of fragmentation products. A mechanism for this control effect is proposed.

Study of the effect of intense IR laser beams on the vibrational degrees of freedom of molecules has demonstrated that the molecules can be selectively excited and selectively dissociated by mechanisms involving an equilibrium thermal decomposition.[1,2] Although there has been no study of the possibility of a nonthermal decomposition of molecules by IR laser beams, it would seem that this process could be implemented in a small number of molecules which have a particular valence-bond structure.

In general, electronic degrees of freedom must be involved in a change in the nature of the fragmentation of a molecule, i.e., in a change in the composition of the primary products of the decomposition of the molecule. These degrees of freedom can be influenced by electron impact, which causes a breakup of a molecule by a variety of mechanisms, including mechanisms involving the formation of charged fragments. It thus becomes possible to use the methods of conventional mass spectrometry to visualize the products of the elementary collision events between the vibrationally excited molecule and the electron.[3] We would like to study that range of energies of the incident electron which would cause an electronic transition in the molecule in accordance with the Franck-Condon principle. The high sensitivity of mass spectrometry

For the present study of the fragmentation of a vibrationally excited molecule by electron impact we used an apparatus consisting of an MSKh-4 time-of-flight mass spectrometer modified to allow injection of the laser beam and equipped with a microchannel-plate device for detecting ions (46 mm in diameter, $K_{\text{ampl}} = 10^8$) and with a pulsed electron gun (pulse length of 1 μs, electron energy on the order of 80 eV). The molecules in the working volume of the mass spectrometer were vibrationally excited by the beam from a pulsed TEA CO_2 laser which was discretely tunable over the CO_2 emission lines by means of a diffraction grating with 100 lines/mm. The laser pulse length, which was monitored by a photon-drag detector, was 100 ms at the 0.1-maximum level. The pulse energy was measured with a pyroelectric calorimeter and was varied over the course of the experiments with a calibrated CaF_2 attenuator. The laser beam was coupled into the working volume of the mass spectrometer through a BaF_2 window by a cylindrical NaCl lens with a focal length of 20 cm. This lens formed a caustic with a cross section of 15×2.5 mm^2. The change in the cross section over a distance equal to the diameter of the aperture in the ejecting electrodes did not exceed 10%. The plane beam from the pulsed electron gun was transported in the plane of the laser beam in the bombardment region. An effusion beam of the test gas at a temperature of 300 K entered the working volume of the mass spectrometer along the axis normal to the plane of the laser beam. The pressure in the working chamber was 7×10^{-6} torr. The heights of the peaks in the mass spectra were measured with an S8-2 oscilloscope. The average height of each peak and the relative measurement error were determined by measuring the mass spectra ten times at each of the fixed laser energy densities.

We selected the gases CF_3I, CF_3Br, and CF_2Cl_2 to study the dependence of the nature of the fragmentation of the molecules on the degree of their vibrational excitation. The experimental results are shown in Figs. 1 and 2.

The CF_3I and CF_3Br molecules have identical spatial structures; they have a C_{3v} symmetry and approximately equal normal-vibrational frequencies. When these molecules are excited at frequencies corresponding to the Q branches of the fundamental bands of the ν_1 mode (1074 cm^{-1} and 1084 cm^{-1}, respectively), the degrees of vibrational excitation of these molecules by identical laser pulses are equal in order of magnitude. It can be seen from Fig. 1a that the vibrational excitation substantially changes the nature of the fragmentation of the molecules. Furthermore, the particular way in which the nature of the fragmentation changes with the energy density of the laser pulse is qualitatively different in the cases of CF_3I and CF_3Br. The differences can be seen most clearly by comparing the probabilities for the production of CF_3^+ and I^+ ions from the CF_3I molecule with the probabilities for the production of CF_3^+ and Br^+ ions from the CF_3Br molecule. It should be noted that the effect observed here reaches a maximum at laser-beam energy densities considerably lower than the threshold for dissociation in single-frequency bombardment. Consequently, during excitation of the ν_1 mode of the CF_3I and CF_3Br molecules (this mode corresponds to valence vibrations of C-F bonds), despite the identical symmetry and approximately equal spatial structures and spectral structures of the vibrational bands, the effect of the excitation on the nature of the fragmentation during electron impact is different for these two molecules.

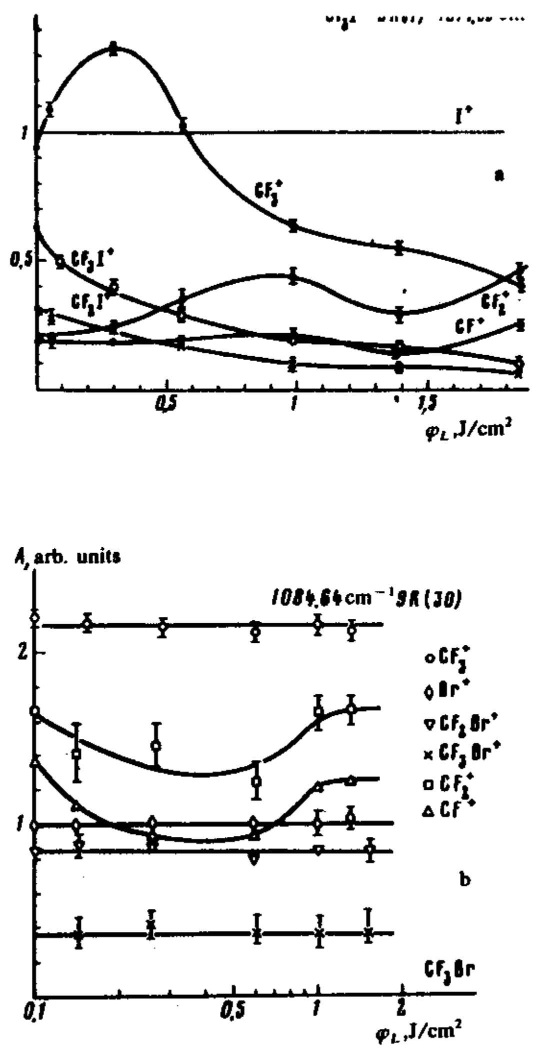

FIG. 1.

To study the effect of the distribution of vibrational energy among modes on the nature of the fragmentation, we used the CF_2Cl_2 molecule. Figures 2a and 2c show the yields of the various ion fragments during excitation of this molecule at the frequencies ν_1 and ν_8, respectively, which correspond to pumping of vibrations of the C-F and C-Cl bonds. Comparison of these figures shows that the curves corresponding to the excitation of the molecules in different vibrational bands are qualitatively different. In other words, the nature of the fragmentation of the molecule is sensitive to the mode composition of the vibrational excitation. Comparison of Figs. 2a and 2b show that

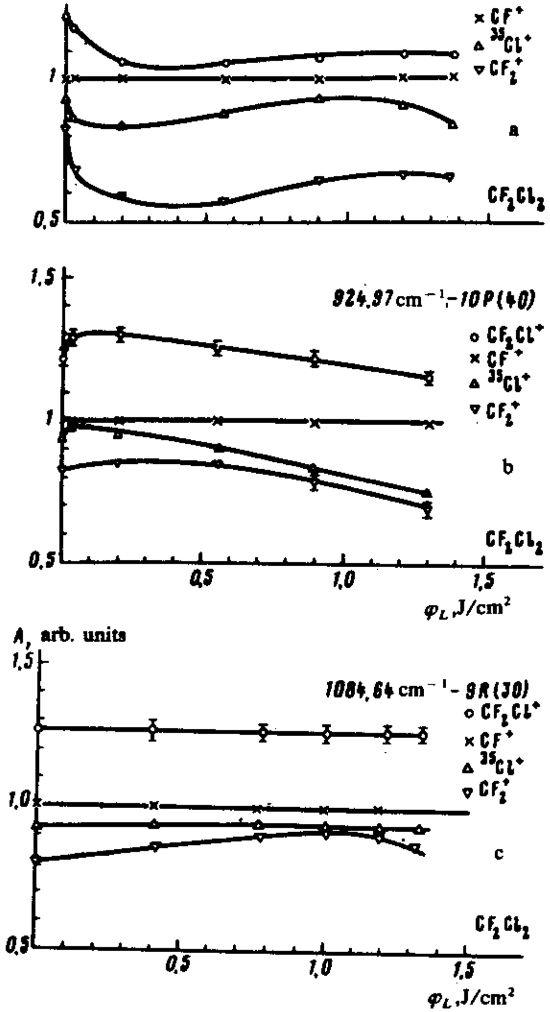

FIG. 2.

there are also some more subtle trends, which reflect changes in the nature of the fragmentation upon changes in the frequency structure of the radiation within a single vibrational band.

These facts show that the nature of the fragmentation of the molecule caused by electron impact depends strongly on the vibrational state of the molecule. We believe that these experimental results can be explained in the following way. It can be shown that, according to the Franck-Condon principle, the probability for transitions between molecular terms by electron impact is dominated by those points of the trajectory at which the coordinate, momentum, and force parameters of the vibrational motion are equal. When the vibrational state of the molecule is changed by the laser

of the vibrational wave function at these points through laser bombardment one can control the magnitudes and directions of the momenta of the nuclei, and again the consequence will be a change in the nature of the fragmentation of the molecules.[4]

Two conclusions of practical importance can be drawn from these results. First, the combined effects of IR light and electron impact on a molecule open up the possibility of controlling the process—producing certain ions and radicals as desired—and optimizing this process. There is the further possibility of controlling the composition of ion beams. Second, refinement of this method will make it possible to determine the isotopic selectivity of the elementary photodissociation even under clearly collisionless conditions. Third, the results of this study raise the hope that the method proposed here may prove a reliable method for determining the nature of the vibrational motion of polyatomic molecules and the extent to which this motion is stochastic.

We wish to thank E. K. Karlova for assistance in this study.

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Motion of Brownian particles in a tilted periodic potential

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The Langevin equation for a Brownian particle in a tilted periodic potential (TPP) with weak friction is reduced to two integral equations in energy variables. The dependence of the average velocity of the particle on the slope of the potential is found and a relationship is established between the expression obtained and the current-voltage characteristic (IVC) of a concentrated Josephson junction.

The motion of a Brownian particle in a TPP is the exact mechanical analog of fluctuations of the phase of the order parameter in a concentrated Josephson junction, which determines the IVC of the junction in a fixed range of currents and voltages. The most difficult, in terms of finding a solution, situation is the situation correspond-parameter at the film edges decreased the critical current I_c responsible for the development of the vortex instability by an order of magnitude (Fig. 3). This made it possible to identify the discrete nature of the transition of the films to the resistive state for a wide range of temperatures $0.2 < T/T_c < 0.95$. For high bias voltages, $eV \gg \Delta$, the *I–V* characteristic of the samples consists of fragments with constant and multiple differential resistance $R_N = NR_0$ (Fig. 3) and a linear dependence of the current I on the voltage $V = (I - I_s^N)R_N$. Here I_s^N is the value of the current obtained by extrpolating the slope of the *I-V* characteristic of the N-th fragment to $V = 0$ (the "excess" current). At low temperatures the "excess" current I_s^N increases with the number N and approaches a limit I_s^0 (Fig. 3); as $T \rightarrow T_c$, we have $I_s^0 \sim \Delta^2(T)$. The shape of the initial sections of the *I-V* characteristic of Al and Sn films differs markedly from the voltage jumps characteristic for the vortex instability[1,2] and from the shape of the *I-V* curves caused by the phase-slip centers in long superconducting channels.[4] First of all, the *I-V* curve (Fig. 1) is characterized by a wide, smooth plateau with a high differential resistance dV/dI and a sharp increase in current at $eV = 2\Delta$. As the temperature is raised, the jump in the current becomes more pronounced and the resistance of the plateau, dV/dI, increases. If the second feature does not follow immediately after the first one on the *I-V* curve, then the differential resistance of the curve asymptotically approaches the resistance $R_N = NR_0$ of the fragment in the normal state.

4. We see from the shape of the *I-V* curve (Fig. 3) that the observed localized bjects have a differential resistance R_0 and can stabilize the average transmitted upercurrent, i.e., the excess current I_s^N, even if the value of I_s^N, is much lower than the imiting value I_s^0, for a given sample. This property of the objects, called below the hase-slip line, shows that the total current flowing through the region of the PSL here the electric field is nonvanishing, can increase due to the normal component of he current. For this reason, the features of the *I-V* curve can be caused by various rocesses that increase the density of nonequilibrium quasiparticles, such as the reshold absorption by the film of the experimentally observed electromagnetic field at is self-generated by the PSL. The experiment involved a mixing of the signal from n external heterodyne at a frequency $f = 9.8$ GHz with the free-generation signal om the PSL and separation of the intermediate frequency $\Delta f = 100$ MHz in the gion of the plateau on the *I-V* curve. From the relation $\hbar\omega_J = 2eV$, which holds for y resistive system,[4] it follows that the features on the *I-V* curve (peaks in the conductivity) occurring at $eV = \Delta(T)/n$ (where n is the number of the harmonic of the alternating field of the PSL, and ω_J is the oscillation frequency) must correspond to the reshold mechanism for the production of nonequilibrium quasiparticles. The same atures arise as a result of the decay of Cooper pairs into quasiparticles as they pass an celerating potential V, when $2eV + n\hbar\omega = 2\Delta(T)$. The fact that such channels for rmation of nonequilibrium quasiparticles can occur is confirmed by the observed bharmonic structure of the *I-V* characteristics studied by us: peaks in the conductivity of films at eV, which are multiples of $\Delta(T)/n$ (Fig. 2). But why are the observed tures identical to the equilibrium values of the energy-gap parameter $\Delta(T)$, in spite the obviously nonequilibrium nature of the object being studied here (in the region $\sim\Delta$, $\hbar\omega_J$ and $\omega_J\tau_\epsilon \gg 1$, where τ_ϵ is the energy-relaxation time of the quasiparticles stabilize the "hot" core of the PSL are localized is much smaller than the resistive region which is determined by the penetration depth of the electric field, $\delta_E = R_0W/2R_\square \sim 10^{-3}$–$10^{-4}$ cm; and $\delta_E \gg \xi$. At $eV < \Delta$ at low temperatures $T \ll \Delta$, the exponentially small quasiparticle density in this case is approximately equal to the equilibrium density almost in the entire resistive region. The threshold production of nonequilibrium quasiparticles in the region where the electric field penetrates into superconductors could therefore be responsible for the sharp increase in the quasiparticle current on the phase-slip line at $eV = \Delta(T)$.

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Determination of the boundary for randomization of vibrational motion by a method of IR laser excitation and electron impact

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Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 10, 432–434 (25 November 1984)

The boundaries of the regions of randomization of the vibrations of CF_3I and SF_6 molecules have been detected. The dependence of these boundaries on the excitation frequency has been determined. The fractions of molecules that go into the randomization region have been determined for various excitation frequencies.

The nature of the fragmentation of molecules caused by electron impact depends on their vibrational state.[1] If the vibrational motion is stochastic, the fragmentation should not depend on the particular method by which the vibrations are excited. Consequently, a study of the fragmentation of vibrationally excited molecules as a function of the excitation frequency and the absorbed energy may yield information about the position of the randomization boundary.

In this letter we report the first observation of the randomization boundary for the vibrational motion of molecules. We have also determined the spectral dependence of this boundary. The experiments were carried out for CF_3I and SF_6 molecules, which differ in symmetry, in the apparatus described in Ref. 1. The laser excitation of these molecules was carried out in the absorption bands of the vibrational modes ν_1 and ν_3, respectively. An acoustooptic method was used to determine the absorbed energy.

To avoid any effect of a change in the fraction of excited molecules with varying frequency and intensity of the laser beam, we used the following procedure to analyze the experimental results. The electron impact causes a fragmentation of both excited and unexcited molecules. The signal (A_i) representing the ion current of fragment i consists of the signals coming from excited and unexcited molecules. The increment in the current upon excitation is proportional to the fraction of excited molecules, q, and to the change in the cross section for the production of charged fragments with increasing energy of the molecule, E: $\Delta A_i \sim q\{\sigma_i(E) - \sigma_i(0)\}$. This value of q also determines the relationship between the average absorbed energy W, measured by the acoustooptic method, and the energy of the excited molecules, E: $W = qE$. The ratios $(\Delta A_i/W) \sim [\sigma_i(E) - \sigma_i(0)]/E$ do not depend on q and are determined exclusively by the energies of the excited molecules and the nature of their fragmentation. These ratios can accordingly be selected as parameters that describe the state of the molecules. If the vibrational motion has become stochastic, then the values of these parameters, at a fixed energy E, are the same for all frequencies of the exciting IR field. Although we do not know E, its logarithm differs from that of the measured quantity, W, by an additive increment of $\ln q$. If, by choosing this additive increment appropriately, we manage to bring all the curves of $\ln W$ versus the parameter $\Delta A_i/W$ for the various excitation frequencies into coincidence at large E, we can thereby determine not only the randomization boundary but also the fraction of excited molecules.

We used this procedure for CF_3I molecules (using the fragments CF_3I^+, CF_2I^+, I^+, CF_2^+, CF_3^+, and CF^+) and for SF_6 molecules (SF_5^+ and $SF_3^+S^+$). The ion currents of the remaining fragments were measured with a low relative accuracy, so that the corresponding parameters for these fragments agreed in all cases. Figure 1 shows $\ln E$ versus $\tan^{-1}(A^{(i)} - A_0^{(i)})/W$ for the case of SF_6 for the fragments SF_5^+ and SF_3^+. The coincidence was found for the output lines from $P12$ to $P24$ from a CO_2 laser. The coincidence was reached by displacing the curves along the ordinate. Figure 2 shows the boundaries (found in this manner) of the region in which the vibrations become stochastic, along with the spectra of the fraction of excited molecules, q. For an absolute calibration of the ordinate in units of photons per molecule, we used the data of Ref. 2 found for the $P20$ line. We assume that the results of Ref. 2 refer to the excitation of a molecule in a collisional regime with a q factor of approximately unity. Shown for comparison are the line absorption spectra of gaseous SF_6 and CF_3I at 300 K. The curves in Fig. 2 are evidence that the vibrational motion in molecules with a cubic anharmonicity (CF_3I) becomes stochastic in a manner different from the corresponding process in molecules with a fourth-order anharmonicity (SF_6). In the latter case the intermode coupling is weaker, as can be seen in particular in the stronger spectral dependence of the randomization boundary.

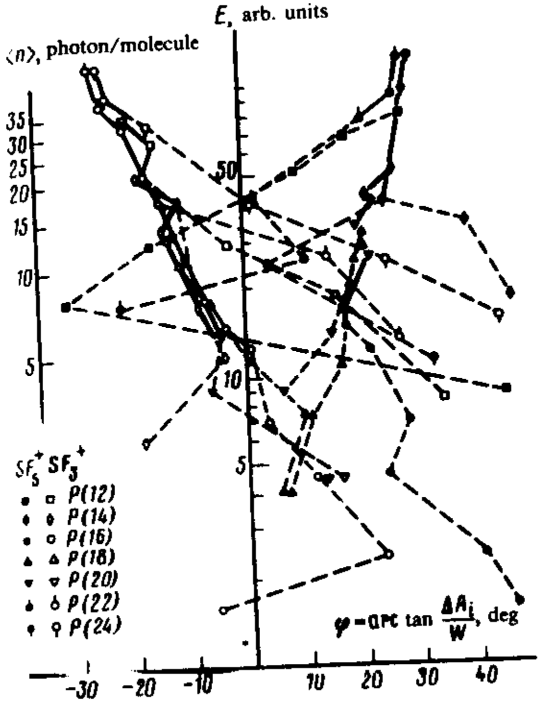

FIG. 1.

The spectral dependence of the randomization boundary of the SF_6 mo corresponds qualitatively to the theoretical boundary in terms of position, shape, and value at the minimum.[3] It is , however, more difficult to make a qu tive comparison because of our imprecise knowledge of the constants of the intra and intermodal anharmonicity and the crudeness of the model of two ensembl

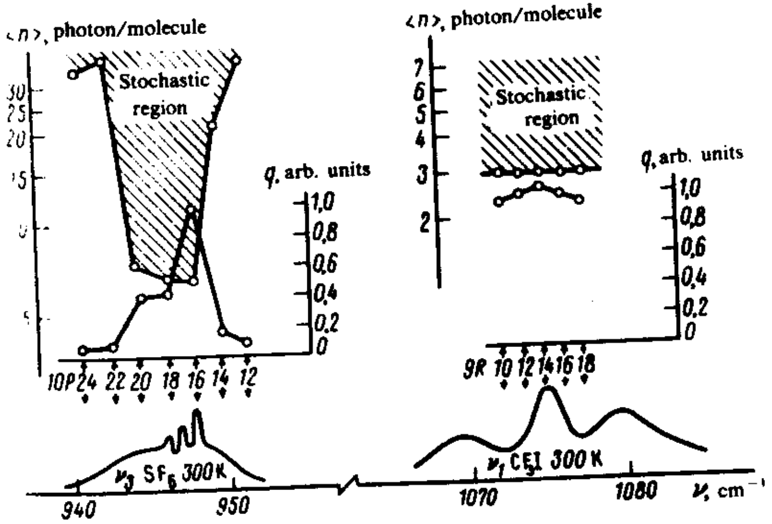

FIG.

unexcited and highly excited molecules. We might note that the use of a CO_2 laser with a continuously tunable frequency would make it possible to determine the boundary of the stochastic region more accurately.

These results refer to the randomization that occurs upon the excitation of one of the IR-active modes. It would be interesting to study the randomization of the vibrational motion during excitation in various modes, with multifrequency excitation (IR-IR, IR-UV, etc.). Such studies would be completely feasible by the new method reported here.

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Detection of quasi-surface excitons in the reflection spectra of layered BiI_3 single crystals

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Quasi-surface excitons are observed for the first time in the reflection spectra of layered BiI_3 semiconductors.

Surface excitons were predicted by Selivanenko[1] and Pekar[2] and their dynamics was developed by Sugakov.[3] The possibility for the existence of quasisurface excitons in molecular lattices was pointed out by Tovstenko.[4] The energy levels of surface excitons are situated outside the exciton band, whereas the levels of quasi-surface excitons are located inside it. The former have been reliably detected in the spectra of molecular crystals,[5–7] whereas the latter thus far have not been observed.

Our purpose in this study was to detect quasi-surface excitons in semiconductors. At $T = 4.2$ K in E⊥C polarization we studied the reflection spectra of layered BiI_3 single crystals in the region of excitonic transitions with allowance for the controllable states of the surface.

The samples were obtained by Bridgman's method. The state of the surface was altered by mechanical grinding and polishing, treatment with ethyl alcohol, and cleavage with a chisel along the cleavage surface in air and with a knife in liquid helium. In the latter case, special attention was given to the possibility of avoiding deformations. Although the surface of the

mirror-smooth, small inclusions in the form of islands, formed by residues of the u layers, appeared nevertheless at some sites due to cleavage in liquid helium.

The reflection spectra were recorded using the apparatus described in Ref. 8 a spectral resolution better than 1 Å.

As is well known, the surface of real crystals contains an abundance of diff types of structural defects: cracks, dislocations, vacancies or groups of vacancies, eign atoms that come to the surface, adsorbed atoms and molecules, etc. As a re the spectra of the surface excitonic states are very sensitive to the state of the sur

As expected, the reflectivity of BiI_3 single crystals which were treated with alcohol and mechanically ground and polished turned out to be lower than that o cleaved single crystals. The excitonic reflection spectra of the former single cry reproduced those described previously.[9] We have therefore focused our atte mainly on the study of the spectra of the cleaved samples. Typical curves are show Fig. 1. Curve 1 shows the reflection spectra of crystals cleaved in air; curve 2 sl the same spectra for crystals cleaved in liquid helium. In the first case we see the dispersion curve $R(\lambda)$ with a structural feature in the form of a small dip at $\lambda =$ nm in the long-wavelength wing of the fundamental oscillation. This dip, which cides in frequency with the peak of the absorption and photoluminescence banc associated with the surface defects of the crystal lattice.[10] The stronger and we oscillations, whose reflection peaks are situated at $\lambda = 598.0$ and $\lambda = 568.2$ nm, c spond to the ground state $n = 1$ and the excited state $n = 2$ of the allowed "di exciton, respectively.[9] The inflection point of the first oscillation is locate $\lambda - 591.2$ nm and its half-width amounts to 39.6 meV

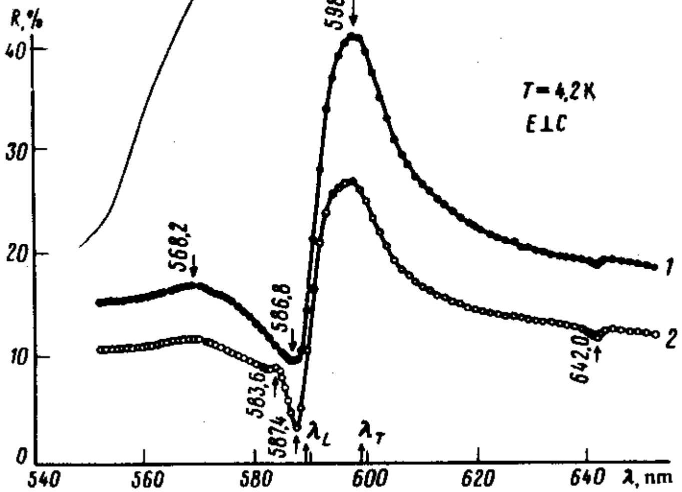

FIG. 1. Excitonic reflection spectra of layered BiI_3 single crystals cleaved in air (1) and in liquid heliu $T = 4.2$ K; E⊥C. (λ_L and λ_T are the wavelengths of optical transitions for longitudinal and tran

UV many-photon ionization of vibrationally excited polyatomic molecules

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Experiments reveal that vibrational excitation of polyatomic molecules influences their UV many-photon conversion accompanied by the formation of molecular ions and charged fragments. When various conversion pathways come into play, and when switches occur between these pathways, there are some observable consequences. Changes are also observed in the number of photons involved in the corresponding processes upon a change in the vibrational state of the molecule.

Vibrational excitation of molecules changes the positions of their electronic absorption bands[1] and thereby significantly increases the capabilities of classical UV photochemistry. There are known cases[2] of a switching of a UV photochemical reaction by the IR field which excites vibrations of a definite mode composition of a CF_2Cl_2 molecule. The mechanism for this effect has not been studied at the level of the elementary event.

In this letter we report observation of the elementary event of many-photon ionization of CF_3I and CF_2Cl_2 molecules by the light from a KrF laser. We have studied the effect of IR vibrational excitation on this process. The experiments are carried out in a time-of-flight mass spectrometer. The IR beam from a pulsed TEA CO_2 laser[3] enters the working chamber of the ion source of the spectrometer, which contains molecules of the gas under study at a pressure $\sim 5\times 10^{-6}$ Torr. The ionization is performed by the focused beam from a KrF excimer laser (wavelength of 248 nm), in a pulse 30 ns long with an energy density of 4 J/cm^2.

Figure 1 shows the heights of the peaks representing the current of ion fragments of the CF_2Cl_2 molecule versus the energy absorbed by the ν_1 mode, which corresponds to valence vibrations involving C–F bonds. During excitation of the mode ν_8, which corresponds to a vibration involving a C–Cl bond, we do not observe a decay of the molecule into charged fragments (at the sensitivity level of the ion detector, which is 10^{-7} of the number of bombarded molecules). This result is evidence that a stochastic situation does not occur at the excitation levels reached. Further evidence for this conclusion comes from experiments on electron-impact fragmentation of the molecule, carried out by the method described by us in Ref. 4. It is interesting to note that the heights of the ion peaks remain in the same proportions as the absorbed energy is varied and also as the excitation frequency is varied within the ν_1 band. This result is apparently a consequence of the excitation of only one of the terms of the molecular ion, which corresponds to dissociation with fixed proportions of the decay products.

A qualitatively different behavior of the heights of the ion peaks of the charged fragments is seen in the case of the CF_3I molecule (Fig. 2). Since the vibrational motion

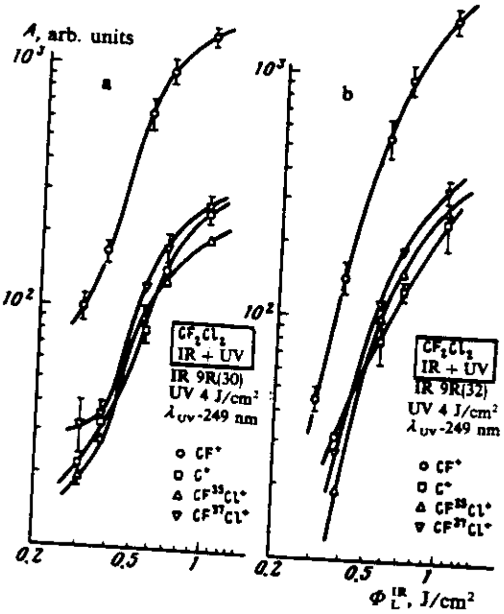

FIG. 1.

of this molecule becomes stochastic starting at only the third or fourth level of the ν_1 mode,[4] we do not observe a frequency dependence of the fragmentation in the UV field in this case. For this molecule, on the other hand, there are changes in the relative heights of the ion peaks for the CF^+ fragment, on the one hand, and the height of the ion peak of the CF_3I^+ fragment, on the other. The latter ion appears during the laser bombardment only after a preliminary vibrational excitation of the molecule. The change in the fragmentation proportions is evidence that the UV light performs its ionization through a transfer over several (at least two) terms of the molecular ion

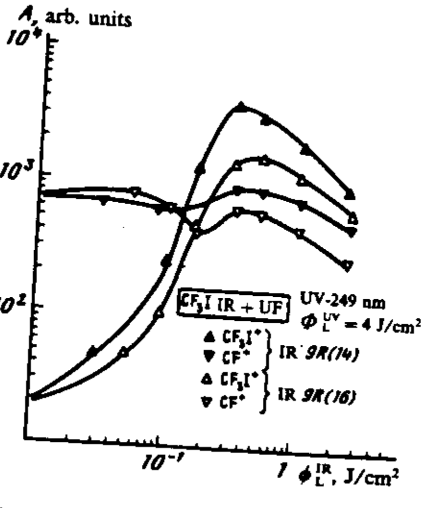

FIG. 2.

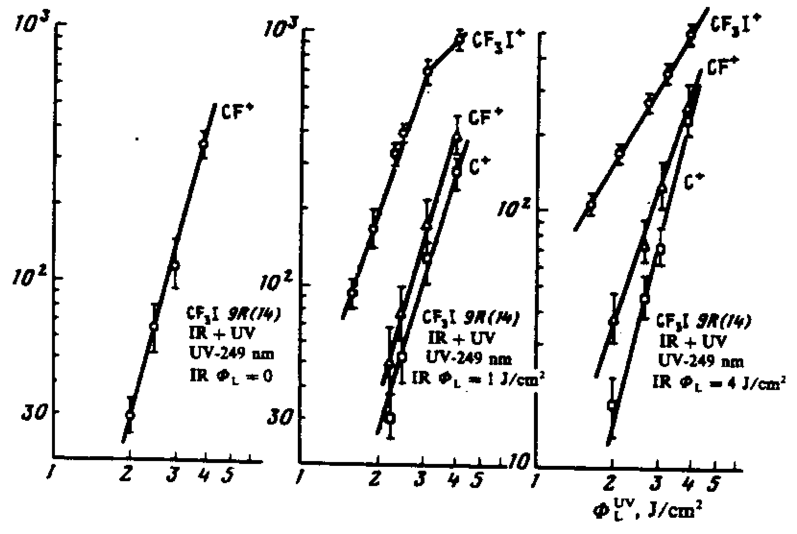

FIG. 3.

CF_3I^+, one of which corresponds to a bound state, and the other to an unstable state. The same conclusion is implied by the observation of a dependence of the fragment formation probability on the UV intensity (Fig. 3). The number of photons involved in the process involving the formation of the CF^+ ion is four and is independent of the vibrational excitation level; only the cross section for this process changes. The number of photons involved in the transition accompanied by the formation of the CF_3I^+ ion changes both with an increase in the reserve of vibrational energy and with an increase in the UV intensity.

We believe that the results found on the UV many-photon photoionization of vibrationally excited molecules can be explained qualitatively in the following way. The ionization of the molecule by the UV light occurs through intermediate states corresponding to vibrational levels of excited electronic terms. Upon a change in the vibrational state of the electronic ground term, which is the starting point for the UV process, due to the IR excitation, there are changes in the frequencies of Franck–Condon transitions to intermediate terms, so that there is a change in the structure of the intermediate resonances which changes the cross section for the many-photon transition. The same explanation can be offered for the behavior observed for the CF_2Cl_2 molecule. To explain the effects that occur in the CF_3I molecule, we should take into account the possible existence of different pathways for the UV excitation, corresponding to processes involving different numbers of photons. A change in the starting level causes different small changes in the intermediate levels for the various pathways, thereby changing the relative probabilities for the formation of various ion fragments. In polyatomic molecules, whose vibrational motion is inherently multidimensional, the number of intermediate states involved in a Franck–Condon transition is large, and their density is high. For this reason, the many-photon transitions do not go through isolated intermediate levels but through zones of levels formed by the vibrational substructure of the electronic terms. Consequently, in intense fields, in which the condition for the existence of a quasicontinuum is satisfied (the Stark broadening of the levels is greater than the characteristic distance between the adjacent states), we should expect changes in the power-law dependence of the ion formation probability on the UV intensity. We are apparently observing such a change in the formation of the CF_3I^+ ion during vibrational excitation of the CF_3I molecule to the level $3\nu_1 \approx 3000$ cm^{-1}.

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Stimulated-Raman conversion of multisoliton pulses in quartz optical fibers

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A mechanism of stimulated-Raman amplification from an incident wave self-induced by a phase self-modulation is proposed. When a fiber is pumped with light with $\tau = 30$ ps at $\lambda = 1.5$–1.65 μm, single pulses with $\tau = 200$ fs and $P = 56$ kW are produced at the Stokes frequency.

Single-mode glass optical fibers, used as a nonlinear medium, can perform a phase self-modulation of light pulses in a uniform manner over the beam cross section. This self-modulation leads to a significant expansion of the spectra of these pulses. When frequency-modulated pulses of this sort propagate through a medium with a negative group-velocity dispersion ($dV_g/d\lambda < 0$), they will undergo a self-compression.[1] Quartz optical fibers have[2] $dV_g/d\lambda < 0$ at $\lambda > 1.3$ μm, and this property has been exploited[3–5] to achieve both soliton propagation regimes and a self-compression of picosecond pulses. The possibility of a nonlinear conversion of a three-soliton pulse into a single-soliton pulse involving 90% of the energy during a stimulated-Raman amplification