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Quantum–Classical Mechanics: Statistical Approach to Molecular Collisions †

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Abstract: The chaotic dynamics of the transient state in molecular and physicochemical transitions in quantum–classical mechanics (Egorov, V.V. Heliyon Physics 2019, 5, e02579; Egorov, V.V. Mathematics 2022, 10, 1443) is considered in relation to the problem of redistribution of the vibrational-rotational energy of polyatomic molecules M and M_1 in their pairwise collisions based on the microcanonical distribution. The statistical (canonical) distribution of the probability of energy change due to collisions in the case of a small impurity M in an equilibrium medium of M_1 is obtained, as well as all the moments *n* of this distribution, which, under the conditions of applicability of the semiclassical approximation for the density of vibrational-rotational states, are some polynomials of the *n*-th order . The theory is compared with experimental data on monomolecular reactions at low pressures for NO_2Cl, C_2H_5NC, and C_5H_{10} molecules in various gas-phase media.

Keywords: quantum-classical mechanics; molecular collisions; polyatomic molecules; microcanonical distribution for collisions; canonical distribution for collisions; moments of the canonical distribution for collisions; gas phase reactions; monomolecular reactions at low pressures

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1. Introduction

As is known, the theory of quantum transitions in quantum mechanics is based on the convergence of a series of time-dependent perturbation theory. This series converges in atomic and nuclear physics. In molecular physics, the series of time-dependent perturbation theory converges only if the Born-Oppenheimer adiabatic approximation and the Franck-Condon principle are strictly observed. Obviously, in real molecular systems there are always at least small deviations from the adiabatic approximation. Within the framework of quantum mechanics, these deviations lead to singular dynamics of molecular quantum transitions. The only way to eliminate this singularity is to introduce chaos into the electron-nuclear dynamics of the transient state. As a result of the introduction of chaos, we no longer have quantum mechanics, but quantum–classical mechanics, in which the initial and final states are quantum in the adiabatic approximation, and the transient chaotic electron-nuclear(-vibrational) state is classical due to chaos, and the transitions themselves are no longer quantum, but quantum–classical [1,2]. This procedure for introducing chaos into the transient state was done in the simplest case of quantum–classical mechanics, namely, in the case of quantum–classical mechanics of elementary electron transfers in condensed media. Chaos is introduced by replacing the infinitely small imaginary additive in the energy denominator of the total Green's function of the "electron + nuclear environment" system with a finite value [1,2]. This chaos is called dozy chaos, and quantum–classical mechanics is also called dozy-chaos mechanics. The analytical results obtained in this new fundamental physical theory make it possible to explain a large number of experimental data, for example, on the shape of the optical bands of polymethine dyes and their aggregates [2]. Relative simplicity of the case of quantum–classical mechanics of elementary electron transfers in condensed media and the possibility of obtaining the corresponding analytical result are connected, in particular, with the possibility of neglecting local oscillations of nuclei and taking into account only non-local oscillations in the theory. There is another "simple" problem in the quantum–classical mechanics [1,2] of complex physical systems, where a similar success in the application of analytical methods can be achieved. This problem is the problem of molecular collisions in gases, which has applications to monomolecular reactions at low pressures. If in the problem of elementary electron transfers in condensed media the electronic state changes significantly, then during such molecular collisions in gases, the electronic states of the molecules do not change, and it is only necessary to take into account the redistribution of vibrational energy between local vibrations in colliding polyatomic molecules. In this case, the transient chaotic state of the motion of nuclei that occurs during molecular collisions can be described by statistical methods based on the use of the microcanonical distribution for molecular collisions [3]. Whereas in the problem of elementary electron transfers in condensed media the singular dynamics of the transient state is damped by dozy chaos, in this statistical approach to molecular collisions in gases, the dynamics of energy redistribution between local vibrations in colliding polyatomic molecules is taken into account by separating all modes into active and passive. Active modes include low-frequency vibrational modes and rotational modes that rapidly exchange energy at the moment of collision. Passive modes include high-frequency vibrational modes, which are effectively included in the process of energy redistribution after the elementary act of molecular collision has already been completed. Analytical results are obtained for the distribution function of the probability of energy transfer in collisions of molecules, as well as for all moments of the *n*-th order of the distribution function, which have the form of certain polynomials of the *n*-th order.

2. Main Text

Consider collisions of polyatomic molecules M and M_1:

$$\mathrm{M}(x)+\mathrm{M}_1(v_1)\rightarrow \mathrm{M}(x')+\mathrm{M}(v_1').$$

Here x and v_1 are the vibrational-rotational energies before the collision; the stroke marks the states after the collision.

It is known that the process of collision of molecules is characterized by the function $w(\Gamma_i', \Gamma_i)$ or the effective cross section of collisions $d\sigma$, which is related to this function as follows [3]

$$d\sigma = w(\Gamma_i', \Gamma_i)\prod_i d\Gamma_i' / \left|\vec{V}' - \vec{V}_1'\right|.$$

Here Γ_i is the phase volume (some part of the phase volume, see below) of the vibrational-rotational motion of either the M molecule or the M_1 molecule, or the phase volume of their relative motion. The function w depends on all the enumerated *i*-th phase volumes (parts of the phase volumes); $\left|\vec{V}' - \vec{V}_1'\right|$ is the modulus of relative velocity.

The distribution function for collisions $w(\Gamma_i', \Gamma_i)$ must obey two fundamental relations,

$$w(\Gamma_i', \Gamma_i) = w\left(\Gamma_i^{\mathrm{T}}, \Gamma_i'^{\mathrm{T}}\right) \tag{1}$$

and

$$\int w(\Gamma_i', \Gamma_i)\prod_i d\Gamma_i' = \int w(\Gamma_i, \Gamma_i')\prod_i d\Gamma_i' = 1 \tag{2}$$

[3], which follow from the symmetry of the laws of mechanics with respect to the time sign reversal operation T and from the possibility of writing the probability normalization condition for collisions in two equivalent forms.

Bearing in mind the relatively large number of degrees of freedom of the system M + M1 and its quasi-closure at the moment of collision, we can assume that the function

$$\rho \equiv d\sigma / \prod_i d\Gamma_i' = w(\Gamma_i', \Gamma_i) / \left|\vec{V}' - \vec{V}_1\right|$$

is the following microcanonical distribution for collisions:

$$\begin{aligned} &\rho\big[\Gamma_a'(x_a'), \Gamma_p'(x_p'), \Gamma_{1a}'(v_{1a}'), \Gamma_{1p}'(v_{1p}'), \Gamma_t'(v_t'); \\ &\Gamma_a(x_a), \Gamma_p(x_p), \Gamma_{1a}(v_{1a}), \Gamma_{1p}(v_{1p}), \Gamma_t(v_t);\big] \\ &= \text{const}\, \delta\left(x_a' + x_p' + v_{1a}' + v_{1p}' + v_t' - x_a - x_p - v_{1a} - v_{1p} - v_t\right) \\ &\times \delta\left(x_p' - x_p\right)\delta\left(v_{1p}' - v_{1p}\right). \end{aligned} \tag{3}$$

Here the index *t* denotes the energy of the relative motion of M and M1. The first δ-function in Equation (3) expresses the law of conservation of energy in collisions. The other two δ-functions imply the presence of two additional integrals of motion in collisions corresponding to the molecules M and M1. They express the fact that only parts of the phase volumes $\Gamma(x)$ and $\Gamma_1(v_1)$ of the molecules M and M1 change during the collision. Such parts of the phase volumes and the corresponding degrees of freedom and energy will be called active. They are marked with index *a*. Accordingly, the remaining parts of the phase volumes, degrees of freedom and energies will be called passive (index *p*). Thus, the last two δ-functions in Equation (3) represent the conservation of the passive energies of the molecules M and M1 during collisions.

It is easy to see that the microcanonical distribution (3) satisfies the fundamental relations (1) and (2).

The constant in Equation (3) is found from the normalization condition (2). As a result, for the function *w* we have the following expression:

$$\begin{aligned} w = &\left|\vec{V}' - \vec{V}_1\right| \delta\left(x_a' + x_p' + v_{1a}' + v_{1p}' + v_t' - x_a - x_p - v_{1a} - v_{1p} - v_t\right) \\ &\times \delta\left(x_p' - x_p\right)\delta\left(v_{1p}' - v_{1p}\right)\left[\Omega^p\left(x_p\right)\Omega_1^p\left(v_{1p}\right)\int_{x-x_a}^{x+v_a}\Omega^a\left(x' - x + x_a\right)\Im_a\left(x + v_a - x'\right)dx'\right]^{-1}, \end{aligned} \tag{4}$$

where

$$x = x_a + x_p,$$

$$v_a = v_{1a} + v_t,$$

and

$$\Im_a(y) = \int (y - z)\Omega_1^a(z)dz, \qquad y = x + v_a - x'.$$

Here $\Omega(\varepsilon) \equiv d\Gamma/d\varepsilon$ is the density of states.

Further operations with the microcanonical distribution (4) are determined by the subsequent formulation of the problem.

Let us assume that molecules M constitute a small impurity in the equilibrium medium of molecules M$_1$. Then the collisions of M with each other are relatively rare, and we can assume that the molecules M collide only with the molecules M$_1$. Let us find under these conditions the probability of transition $P(x',x)$ in the collision of the molecule M from one state with energy x to a unit energy interval at the point x'. By integrating over all variables corresponding to the final states of the molecules M and M$_1$, except for the variable x', and averaging over the initial states of M and M$_1$ and their relative motion, we obtain

$$P(x',x) = \Omega^{-1}(x)\Re^{-1}\int_0^\infty dv \exp(-v)\int_0^v \Im_a(v_a)D(x',x;v_a)\Omega_1^p(v - v_a)dv_a, \tag{5}$$

$$D(x',x;v_a) = \int_0^x \Omega^a(x_a)D(x',x;x_a,v_a)\Omega^p(x - x_a)dx_a, \tag{6}$$

$$D(x',x;x_a,v_a) = \Omega^a(x' - x + x_a)\Im_a(x + v_a - x')\theta(x' - x + x_a)\theta(x + v_a - x')$$
$$\times\left[\int_{x-x_a}^{x+v_a} \Omega^a(x' - x + x_a)\Im_a(x + v_a - x')dx'\right]^{-1}, \tag{7}$$

$$\Re = \int_0^\infty dv \exp(-v)\int_0^v \Im_a(v_a)\Omega_1^p(v - v_a)dv_a. \tag{8}$$

Here the energy is measured in units of $k_\mathrm{B}T$. In Equation (7), the quantity θ is a θ-function. It is natural to call the distribution $P(x',x)$ the canonical distribution for collisions of polyatomic molecules. It satisfies the normalization condition

$$\int_0^\infty P(x',x)dx' = 1$$

and the detailed balance principle

$$P(x',x)\Omega(x)\exp(-x) = P(x,x')\Omega(x')\exp(-x').$$

The moments of the energy transferred during collisions

$$\left\langle(\Delta x)^n\right\rangle = \int_0^\infty (x' - x)^n P(x',x)dx'; \qquad n = 1, 2, 3, \ldots$$

under the conditions of applicability of the semiclassical approximation for the density of states $\Omega(\varepsilon)$ are the following polynomials with respect to the energy x:

$$\left\langle (\Delta x)^n \right\rangle = \sum_{m=0}^{n} (-1)^m C_n^m x^m \prod_{\alpha,\beta,\gamma=1}^{n,n-m,m} \frac{\left(N^a+\beta-1\right)\left(N_1^a+\beta+1\right)\left(N^a+\gamma-1\right)\left(N_1^a+\gamma+1\right)}{\left(N^a+N_1^a+\alpha+1\right)\left(N+\gamma-1\right)} \equiv \mathrm{CMP}_n(x), \tag{9}$$

where N is the sum of the number of vibrational and half the number of rotational degrees of freedom, and C_n^m is the number of combinations of *n* by *m*. It is natural to call these moments (polynomials) the canonical moments (polynomials) $\mathrm{CMP}_n(x)$ for collisions of polyatomic molecules. For example, according to Equation (9) $\mathrm{CMP}_{n=1}(x)$ and $\mathrm{CMP}_{n=2}(x)$ have the following expressions:

$$\left\langle \Delta x \right\rangle \equiv \mathrm{CMP}_{n=1}(x) = \frac{N^a\left(N_1^a+2\right)}{N^a+N_1^a+2}\left(1-\frac{x}{N}\right), \tag{10}$$

$$\left\langle (\Delta x)^2 \right\rangle \equiv \mathrm{CMP}_{n=2}(x) = \frac{N^a\left(N^a+1\right)\left(N_1^a+2\right)\left(N_1^a+3\right)}{\left(N^a+N_1^a+2\right)\left(N^a+N_1^a+3\right)}\left[\frac{x^2}{N(N+1)} - \frac{2N^a\left(N_1^a+2\right)x}{N\left(N^a+1\right)\left(N_1^a+3\right)} + 1\right]. \tag{11}$$

Determining the numbers of active degrees of freedom N^a and N_1^a in the M + M1 system is the task of applying the theory to specific conditions for the occurrence of chemical reactions during collisional, laser, chemical, etc. activation. It follows from physical considerations that active degrees of freedom can be formed from rotational (taking into account internal rotations) and low-frequency vibrational degrees of freedom, as well as from those degrees of freedom of the M + M1 system for which there are low-order resonances for the transfer of vibrational-rotational energy. Estimates of N^a values using experimental $\left\langle \Delta x \right\rangle$ data for NO_2Cl, C_2H_5NC and C_5H_{10} molecules in various gas phase media are given in Table 1.

Table 1

Molecule M	**Molecule M1**	$-\left\langle \Delta x \right\rangle$	N^a
NO_2Cl (T = 476.5 $^{\mathrm{O}}$K; x = 32; see [4])	Ar	0.6	0.2
	Xe	1.2	0.4
	N_2	1.1	0.4
NO_2Cl (T = 476.5 $^{\mathrm{O}}$K; x = 32; see [4])	CO_2	1.6	0.5
	SiF_4	2.5	0.9
	CCl_2F_2	5.5	2.0
C_2H_5NC (T = 504 $^{\mathrm{O}}$K; x = 39; see [4])	He	0.6	1.4
	Ne	0.7	1.8
C_2H_5NC (T = 504 $^{\mathrm{O}}$K; x = 39; see [4])	Ar	1.2	9.0
C_5H_{10} (T = 298 $^{\mathrm{O}}$K; x = 192.5; see [5,6])	CO	6.8	3.3
	C_4H_8	19.3	6.1

The value of $\left\langle \Delta x \right\rangle$, according to Equation (10), weakly depends on N_1^a, therefore, when calculating N^a, it was assumed that $N_1^a = N_1$. The found values of N^a are much less than the total number of degrees of freedom N, and they are the lower limit of the possible numbers N^a in the molecular systems under consideration, for example, due to the possible variation of the number $N_1^a \le N_1$. The inequality $N^a < 1$ (NO_2Cl in Ar, Xe, N_2 and CO_2) indicates that energy transfer is hindered due to adiabatic collisions. The number N^a in this case can be considered as some characteristic of the degree of statistical nature of the activation mechanism.

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