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*Campus Schenefeld, main building (XHQ) room E1.172*

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## **Where and why quantum mechanics ceases to work in molecular and chemical physics**

Let's turn to the basics of quantum mechanics. In atoms, the nucleus is essentially only a source of a potential electric field in which electrons move. Quantum mechanics works here: we write a Hamiltonian for electrons in this field and solve the corresponding Schrödinger equation. In molecules in a stationary state, where the adiabatic approximation works, on the contrary, electrons are considered as a source of a potential electric field in which the nuclei vibrate. Here quantum mechanics also works, but the price of this is the adiabatic approximation. Note that both in the former and in the latter cases, in essence one of the subsystems is "switched off" dynamically: in the case of atoms the nucleus is "turned off", and in the case of molecules the electrons are "turned off". Quantum mechanics works in molecules only until the electrons are dynamically "off". As soon as we begin to consider molecular quantum transitions, we are forced to treat electrons dynamically, that is, for transitions we already have two essential dynamical systems: nuclei that oscillate, and electrons whose charge distribution changes during the transition. And both systems strongly (through the Coulomb field) interact with each other. The whole "trouble" is that the mass of the electron is a colossal number of times smaller than the mass of the nuclei. In molecules, in their essential dynamics, when there is a structural reorganization of the nuclear subsystem in molecular quantum transitions, this fact leads to a singularity in the probabilities (per unit time) of quantum transitions. This singularity means that the joint motion of electrons and nuclei, when both subsystems are dynamically full-fledged, can not be regular. Therefore, this singularity must be damped by introducing chaos (dozy chaos) into dynamics of molecular quantum transitions or elementary chemical reactions, which is done by the author. But after the damping procedure is introduced, the whole theory ceased to be quantum mechanics: because of chaos in the intermediate dynamic state, we have a continuous spectrum of energy in this state, which is a sign of classical mechanics[1]. Shortly speaking, the physical nature of molecular quantum transitions is associated with a certain, recently discovered, unique property of an electron that binds atoms to molecules. This property consists in provoking by a light electron of chaos in the vibrational motion of very heavy nuclei "for the purpose" to control their motion in the processes of molecular quantum transitions. Thus, an electron being a quantum micro-particle in an atom, which performs quantum jumps, in a molecule in the processes of molecular quantum transitions, it acquires the features of a classical motion[2]

In the formal language, the situation is as follows. As is known, the theory of quantum transitions in quantum mechanics is based on the convergence of a series of time-dependent perturbation theory. In atomic and nuclear physics, the quantum-mechanical series of time-dependent perturbation theory converges because in the corresponding matrix elements of the transitions due to quantum jumps the dynamics of quantum transitions is absent by definition. On the contrary, this series diverges in molecular and chemical physics, since in these matrix elements the dynamics of "quantum" transitions, which is determined by the joint motion of a light electron (or electrons) and very heavy nuclei, is already present by definition. Strictly speaking, only two methods can eliminate the singularity in the quantum-mechanical series of time-dependent perturbation theory. The first method was proposed almost 100 years ago and consisted essentially in refusing to consider the dynamics of molecular "quantum" transitions by introducing an additional postulate in the form of the Franck-Condon principle into molecular quantum mechanics, in which the adiabatic approximation is used. The second method was proposed by the author [3, 4] and consists in replacing the infinitely small imaginary additive in the energy denominator of the total Green's function of the molecular system by its finite value. It follows from a comparison of the new theory with experiment that the modulus of this imaginary additive is much larger than the quantum of vibrations of the nuclei. This means that in the process of quantum transitions there is an exchange of motion and energy between the electron and the nuclei, and this exchange is so intense that chaos arises in the transient state. This chaos is called dozy chaos, since it is not present either in the initial or final states, and it arises only during molecular quantum transitions. The effectiveness of the damping procedure for the above singularity is demonstrated by the example of a new (dozy-chaos) theory of elementary electron-charge transfers in condensed media and its applications to the optical band shapes in polymethine dyes and their aggregates [1, 5].

[1] Egorov V V, 2017, Royal Society Open Science 4: 160550.

[2] Egorov V V, 2018, RG Preprint. DOI: 10.13140/RG.2.2.14105.52323

[3] Egorov V V, 2001, Chem. Phys. Lett. 336 (3-4): 284.

[4] Egorov V V, 2001, Chem. Phys. 269 (1-3): 251.

[5] Egorov V V, 2017, 2nd International Conference on Atomic and Nuclear Physics, Nov 08- 09, 2017, Las Vegas, Nevada, USA.