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**Review Article**

# Quantum-Classical Electron as an Organizing Principle in Nature

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**Abstract:** We are introducing briefly to the new theory of “quantum” transitions in molecular and chemical physics — quantum-classical mechanics, in which an electron behaves dynamically in two ways: both as a quantum and as a classical elementary particle. Namely, in the initial and final adiabatic states of molecular “quantum” transitions, the light electron exhibits its quantum properties. On the contrary, in the transient molecular state, the electron, provoking the so-called dozy chaos in the vibrational motion of very heavy nuclei “in order” to shift the equilibrium positions of their vibrations to new positions corresponding to the new distribution of the electron charge, because of the continuous energy spectrum in the transient state, manifests itself as a classical elementary particle. The article discusses mainly studied and some promising applications of the organizing role of an electron in nature. Among the well-studied applications, the quantum-classical organization of optical absorption band shapes in polymethine dyes and their J-aggregates is discussed. For example, the well-known narrow and intense J-band of J-aggregates is one of the striking examples of the implementation of the so-called Egorov resonance, in which the motion of the reorganization of the nuclei of the environmental medium significantly contributes to the electron transition in the optical pi-electron chromophore of J-aggregates. This effect can also be interpreted as the transfer of dozy chaos from the peak of the J-band into its wing by a chaotic motion of the quantum-classical pi-electron state of the J-chromophore. The dynamic role of the quantum-classical electron in the joint organization of the absorption and luminescence spectra, and an extension of quantum-classical mechanics to nonlinear optical processes are discussed. The probable leading role of quantum-classical electrons in the evolution of molecular matter and possibility of applications of quantum-classical mechanics to the study of cancer and viruses are discussed as a future research perspective.

**Keywords:** Molecular Quantum Transitions, Dozy Chaos, Quantum-Classical Mechanics, Optical Spectra, Polymethine Dyes, Bioimaging, Cancer, Virus

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## 1. Introduction

In Ref. 1, a critical revision of modern physical concepts about the dynamics of molecular quantum transitions based on quantum mechanics is carried out, and a fundamentally new physical theory having universal nature — quantum-classical mechanics — is proposed. It is shown that the existing and widespread physical ideas about the dynamics of molecular quantum transitions, based on the Born-Oppenheimer adiabatic approximation [2] and the Franck-Condon principle [3–6] (see also Refs. 1, 7), become untenable due to the appearance of a significant singularity in

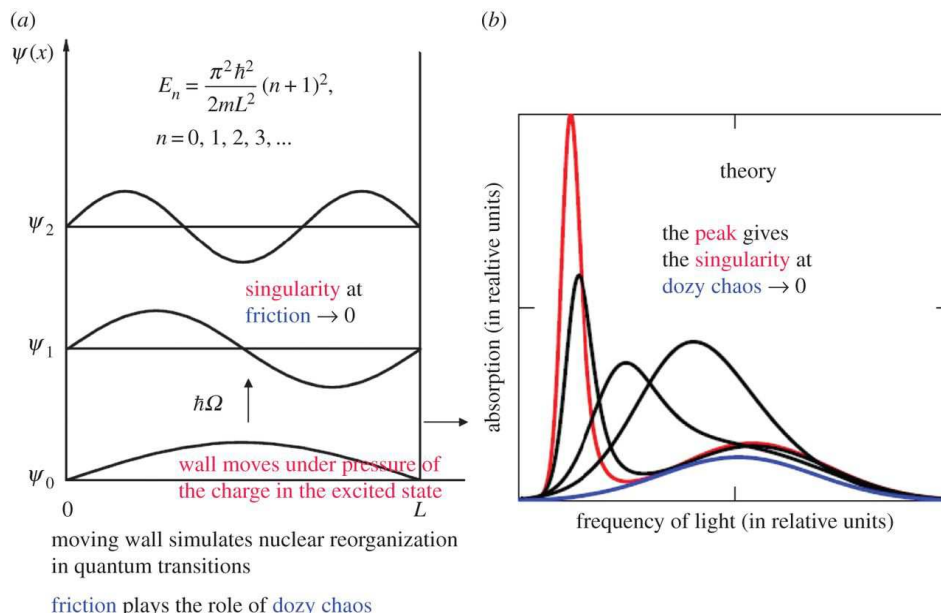
the rates of molecular transitions as a result of going beyond the adiabatic approximation.

## 2. Franck-Condon Principle as a Primitive Damper and Dozy Chaos as a Full-Fledged Damper

In the framework of the adiabatic approximation, the electronic subsystem of the molecule is not dynamically full-fledged, since it forms only the electric potential in which the nuclei vibrate. When going beyond the adiabatic approximation, the electronic subsystem of the molecule

becomes dynamically full-fledged along with its nuclear subsystem, and therefore, due to the enormous difference in the masses of light electrons and heavy nuclei, the aforementioned singularity in the transition rates arises. This singularity can be easily demonstrated by the example of a one-dimensional potential box with a movable wall (see

Figure 1) moving without friction, in which such a wall simulates a nuclear reorganization [1, 8, 9]. This example can serve as the simplest model of a molecule [1]. The simplest model of an atom in this example is a potential box with a rigid, fixed wall.



**Figure 1.** Singularity in the rate of molecular quantum transitions: a potential box with a movable wall (a) and the optical absorption band shape dependent on the dozy chaos available to a given quantum transition (b); the band shape with the strongly pronounced peak (J-band) corresponds to the least dozy chaos [1, 8, 9]. The wall is fastened to the abscissa axis by a freely movable hinge and can move with a certain friction or without friction against the axis. Such a wall simulates the environmental nuclear reorganization in the molecular “quantum” transitions, where dozy chaos plays the role of friction. In the theory [1, 10, 11], this results in the dozy-chaos dependent optical absorption band being displaced to the red spectral region and narrowed (b). (Original citation)—Reproduced by permission of The Royal Society of Chemistry.

There are only two ways to eliminate the aforementioned singularity. The first method was proposed about 100 years ago and is associated with the Franck-Condon principle, which suggests taking the initial and final electron-nuclear states in the matrix elements of molecular quantum transitions in the adiabatic approximation, that is, when the full-fledged dynamics of the transient state is not considered at all. Here, then, the singularity in electron-nuclear dynamics is eliminated by completely ignoring this dynamics itself. Such a primitive picture, which underlies modern molecular spectroscopy, often agrees well with experimental data. This agreement is due to the fact that for small molecules, which molecular spectroscopy usually deals with, the rates of “quantum” transitions depend mainly only on the structure of the initial and final electron-nuclear states and are very weakly dependent on the dynamics of the transient molecular state itself. For large molecules, the dynamics of the transient molecular state becomes so significant that the Franck-Condon principle loses its physical meaning as a primitive means for damping the dynamic singularity that occurs in the transient state. Thus, in a physical theory that takes into account the full-fledged electron-nuclear dynamics of a transient molecular state, a need also arises for a full-fledged method of damping this singularity.

Such a full-fledged method of damping the singular

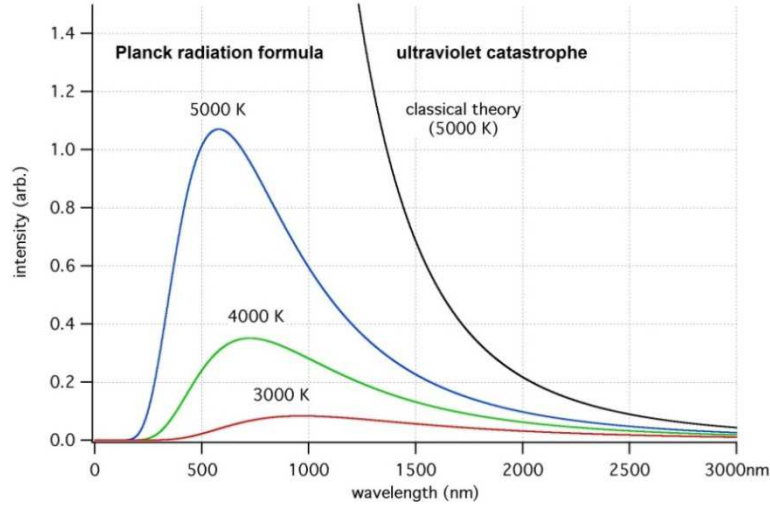
electron-nuclear dynamics of a transient molecular state was proposed by the author (V.V.E.) and demonstrated on the simplest example of molecular quantum transitions — elementary electron transfers in condensed matter [1, 10, 11]. This method consists in replacing the infinitesimal imaginary additive  $i\gamma$  ( $\gamma > 0$ ) included in the energy denominator of the spectral representation of the total Green function of the electron-nuclear system

$$G \equiv G(\mathbf{r}, \mathbf{r}'; q, q'; H) = \sum_s \frac{\Psi_s(\mathbf{r}, q) \Psi_s^*(\mathbf{r}', q')}{E_H - E_s - i\gamma} \quad (1)$$

by a finite value ( $\Psi_s(\mathbf{r}, q)$  are the eigenfunctions of the total Hamiltonian  $H$  of the system,  $(\mathbf{r}, q)$  is the set of all electronic and nuclear coordinates,  $E_s$  are the eigenvalues of  $H$ , and  $E_H$  is the exact value of the total energy of the system; the energy denominator vanishes when  $\gamma=0$ ) [10, 11]. Such a replacement of the  $\gamma$  value by its finite one takes physical theory beyond the scope of quantum mechanics, similar to how the introduction of the finite value of the elementary action, the Planck constant  $\hbar$ , which eliminates the singularity in the spectrum of an absolutely black body [12]

$$f(\Omega, T) = \frac{\hbar \Omega^3}{4\pi^2 c^2} \frac{1}{\exp(\hbar \Omega / k_B T) - 1}, \quad (\hbar \rightarrow 0, \quad f(\Omega, T) = \frac{k_B T}{4\pi^2 c^2} \Omega^2), \quad \phi(\lambda, T) = \frac{2\pi c}{\lambda^2} f\left(\frac{2\pi c}{\lambda}, T\right), \quad (2)$$

took the physical theory beyond the scope of classical mechanics and gave us subsequently quantum mechanics itself ( $\Omega$  is the circular frequency of the radiation, and  $T$  is the absolute temperature; see Figure 2) [1].



**Figure 2.** Distribution function of black light  $\phi(\lambda, T)$  (Eq. (2)) and singularity in this function in the framework of classical mechanics (on the right).

Successful comparison of the new theory with a large number of experimental data, for example, on the optical spectra of polymethine dyes and their aggregates shows that the  $\gamma$  value far exceeds the magnitude of the quantum of nuclear vibrations  $\hbar\omega$ :  $\gamma \gg \hbar\omega$ . The energy  $\gamma$  could be interpreted as the width of the electron-vibrational energy levels in the transient molecular state, which provides the exchange of energy and motion between the electron and the nuclei in the transient state. However, due to the anomalously large  $\gamma$  indicated above, this exchange occurs so intensely that it leads to chaos in the motion of both the vibrating nuclei and the electron itself. This chaos is called dozy chaos [13, 14], since it exists only in a transient molecular state and is absent in the initial and final adiabatic states. The energy  $\gamma$  is called dozy-chaos energy [13, 14].

Dozy chaos is a mix of chaotic motions of the electronic charge, nuclear reorganization, and the electromagnetic field (dozy-chaos radiation) via which the electrons and nuclei interact in the transient state [15, 16]. Since the electron is a light and mobile elementary particle in comparison with heavy nuclei, it is precisely the electron that provokes chaos in the vibrational motion of nuclei in the transient state “in order” to coordinate their spatial configuration with the new distribution of the electron charge in the final state. Thus, from a physical point of view, we are talking about the discovery in theory of a new property of an electron [1]. In atoms, an electron makes quantum jumps from one discrete energy level to another, while in molecules, to transfer from one adiabatic state to another, the electron is “forced” to provoke chaos in the vibrational motion of nuclei “in order” to control their motion in the transient state. In other words, a light electron, provoking dozy chaos, “causes” the very

heavy nuclei to “shift themselves” to new equilibrium positions of their vibrational motions. Due to chaos (dozy chaos) in the transient state, its energy spectrum is continuous; this indicates the classical nature of the motion of an electron and nuclei in a transient state, which no longer obey the laws of quantum mechanics. At the same time, the initial and final adiabatic states differ sharply in their electron-nuclear structure and obey the laws of quantum mechanics. Therefore, the new theory is called quantum-classical mechanics [1].

It can be assumed that the main mechanism of the occurrence of dozy chaos is determined by the interaction of the electron charge and spin with the bound (induction) electromagnetic field of optical phonons. A more definite answer to this question can be obtained in the framework of the future quantum-classical electrodynamics, which will be a generalization of quantum-classical mechanics, just as standard quantum electrodynamics [17–19] is a generalization of quantum mechanics [20, 21] (see the continuation of the discussion on quantum-classical electrodynamics below).

We note that the Franck-Condon principle [3–6], (see also Refs. 1, 7) which involves the classical motion of nuclei “towards” a quantum electronic transition at their turning point (see, e.g., Figure 3 in Ref. 7), essentially serves as a prerequisite for creating quantum-classical mechanics [1]. However, an attempt to formalize the Franck-Condon principle in the framework of quantum mechanics leads to a singularity in the rates of “quantum” transitions, which is eliminated in a regular way only in quantum-classical mechanics [1].

### 3. Quantum-Classical Organization of Optical Absorption Band Shapes in Polymethine Dyes

The simplest example of quantum-classical mechanics is the aforementioned quantum-classical mechanics of elementary electron transfers in condensed matter [1]. The simplest illustration of the organizing principle of the electron is the dependence of the shape of the optical absorption band on the value of dozy-chaos energy (see Figure 1). The position, the intensity and the width of the optical absorption band are determined by the ratio between the dozy-chaos energy  $\gamma$  and the nuclear reorganization energy  $E$  [8, 9]. The smaller the value of  $\gamma$  is, the higher the degree of organization of the molecular “quantum” transition, and the more the intensity and less the width of the optical band. The position of the wing maximum is determined by the energy  $E$ , whereas the position of the peak is determined by the energy  $\gamma$ . In more detail, if the energy  $\gamma$  decreases, a peak (the so-called living peak or L-peak) [11, 22, 23] gradually forms, which shifts to the red region of the optical spectrum and narrows, and the Gaussian-like wing (the so-called dead band or D-band) [11, 22, 23] practically stands still, but broadens. This can be interpreted so that *chaos (dozy-chaos) is pumped by a quantum-classical electron* from the resulting red L-peak into the blue D-band, that is, an organized dynamics in the red region of the spectrum arises from the disorganization of the dynamics in the blue region of the spectrum. This example is the simplest illustration of competition, which already arises at the elementary level of physics in complex physical systems, in this case, competition between “red” and “blue” electron-phonon transitions.

In Figure 1, the results for the shape of the optical absorption bands correspond to an important special case in the dynamics of elementary electron transfers, namely, the so-called transferon resonance [11, 13, 14, 24, 25] (see also Ref. 1) or, according to Ref. 23, the Egorov resonance

$$(2\tau_e)^{-1} = \tau^{-1}, \quad (3)$$

where  $\tau_e$  is the characteristic time of motion of the electron in the donor-acceptor system, and  $\tau$  is the characteristic time of motion of the reorganization of nuclei in the environment. These times are given by the following equations

$$\tau_e = \frac{L}{\sqrt{2J_1/m}}, \quad (4)$$

where  $L$  is the distance between the donor and the acceptor of an electron ( $L$  is equal to the length of the polymethine chain — the main optical chromophore of polymethine dyes) [8–11, 13, 14, 24, 26],  $J_1$  is the binding energy of the electron on the donor (electronic energy of the ground state of the dye) [8–11, 13, 14, 24, 26],  $m$  is the effective mass of the electron, and

$$\tau = \frac{\hbar}{E}, \quad (5)$$

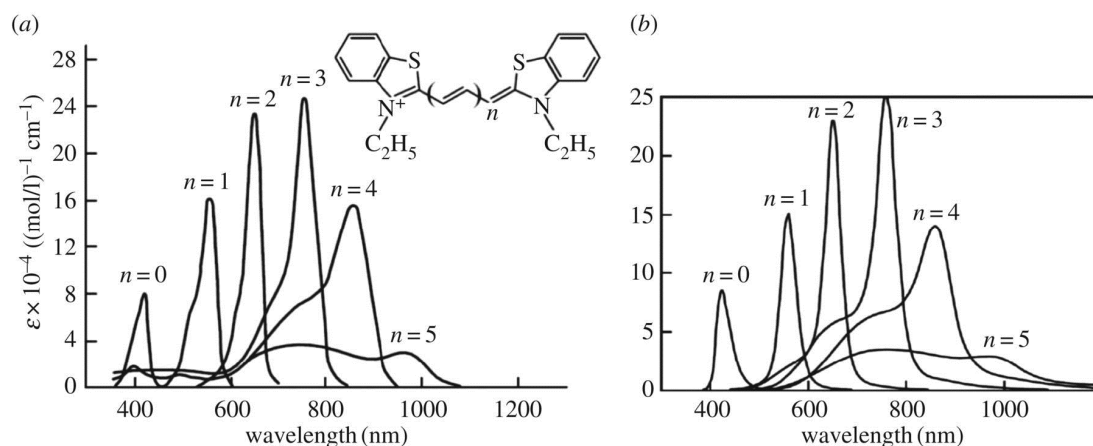
where, as mentioned above,  $E$  is the energy of reorganization of the nuclei of the medium. In theory [1, 11, 24], a dimensionless parameter arises

$$\theta = \frac{\tau_e}{\tau} = \frac{E \cdot L}{\hbar \sqrt{2J_1/m}}. \quad (6)$$

In the case of the Egorov resonance (Eq. (3)), it is obvious that

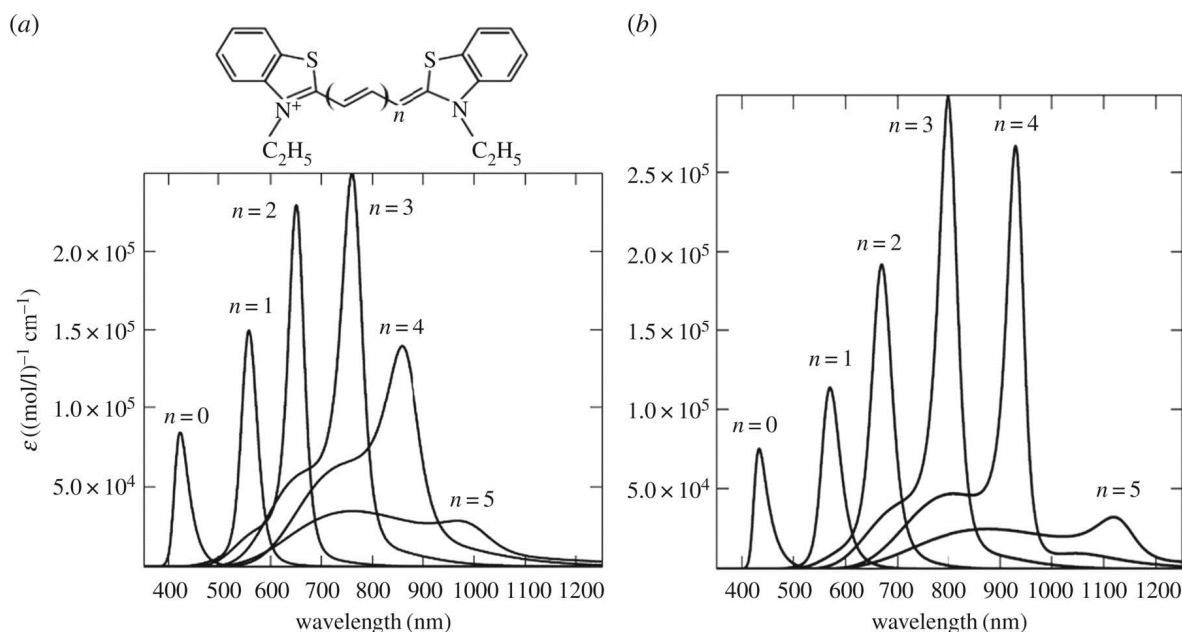
$$\theta = \frac{1}{2}. \quad (7)$$

Experimentally, Egorov resonance manifests itself, for example, in polymethine dyes [8–11, 13, 14, 24, 26], namely, in the resonance nature of the dependence of the shape of the optical absorption band on the length of the polymethine chain  $L$  (see Figure 3).



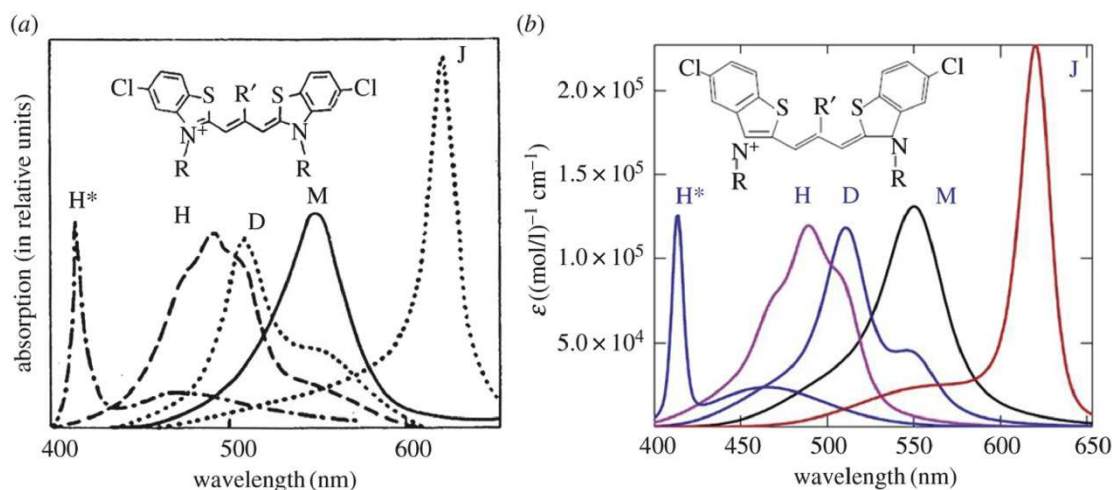
**Figure 3.** Experimental [27, 28] (a) and theoretical [24] (b) monomer's optical absorption spectra dependent on the length of the polymethine chain (thiapolymethinecyanine in methanol at room temperature;  $\epsilon$  is the extinction coefficient) [8, 9, 29]. (Original citation) — Reproduced by permission of The Royal Society of Chemistry.

The weakening of the interaction of the electron with the medium during the transition from a more polar solvent to a less polar solvent, that is, when moving to lower  $E$ , leads, according to Eqs. (3)–(5), to a shift of the Egorov resonance to the region of larger lengths of the polymethine chain  $L$  [9, 22] (see Figure 4), which is consistent with experimental data in Ref. 30.



**Figure 4.** The shift of the Egorov resonance to the region of larger lengths of the polymethine chain during the transition from a more polar solvent (see Figure 3) to a less polar solvent [9, 29].

Another striking example of the manifestation of Egorov resonance in an experiment is the shape of the optical absorption band of the J-aggregates of polymethine dyes, in other words, the so-called J-band [1, 9–11, 13, 14, 24, 26, 31–34]. The J-band of J-aggregates is shifted relative to the monomer band (M-band) to the red region of the spectrum and is much narrower and more intense than the M-band (see Figure 5).



**Figure 5.** Theoretical optical absorption spectra [9, 29, 35, 36] (b) in thiapolymethinecyanines adjusted to the fundamental experimental data [28] (a) on polymethine dye monomers (M), dimers (D), H-, H\*-, and J-aggregates.

The J-band effect in J-aggregates is a significant enhancement of the Egorov resonance that we have in a series of polymethine dye monomers (see Figure 3, where the resonance band with  $n=3$  is the J-band for the monomer) [1, 9, 13, 14, 24]. Such an increase is caused by an increase in the interaction of the quantum-classical electron transition [1, 26] with the motion of environmental nuclei due to

J-aggregation [10, 11, 13, 14, 24]. As a result, under resonance conditions (see Eq. (3)), the motion of the reorganization of the nuclei of the medium significantly contributes to the electronic transition in the optical pi-electron chromophore of J-aggregates. Similarly to the case of Figure 1 (right), this effect can also be interpreted as the transfer of chaos (dozy chaos) [1, 9, 13–16] from the

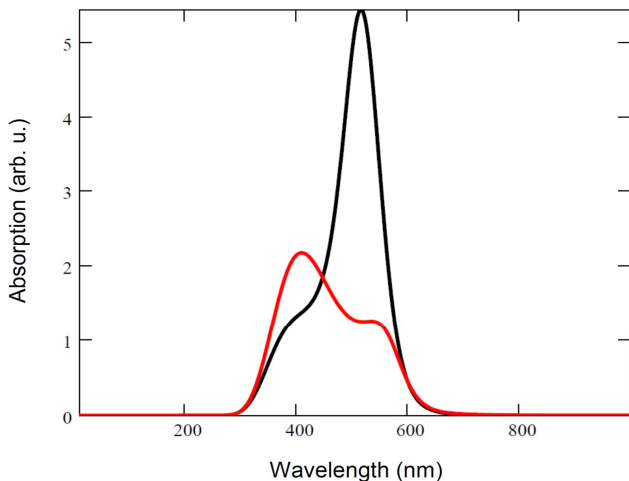


peak of the J-band into its wing by a chaotic motion of the quantum-classical pi-electronic state of the optical J-chromophore [1, 26].

Among polymethine dyes, in addition to the example of “extreme” pumping dozy chaos by an electron from the “red” peak of the J-band to its “blue” wing, there is another example of this kind of pumping, which is associated not with the electron but with the exciton mechanism. We are talking about pumping dozy chaos by the Frenkel exciton [37–39] from the “blue” peak of the H\*-band to its “red” wing (see Figure 5), which is observed for H\*-aggregates whose optical chromophore is the H\*-dimer [9, 40]. Other cases of the interaction of electron dynamics with exciton dynamics when taking into account dozy chaos, which are realized for dimers (D) and H-aggregates (Figure 5), are considered in Refs. 8, 9.

#### 4. Organization of One- and Two-Photon Absorption

The J-band (see Figure 1; Figure 3,  $n=3$ ; Figure 5) is a striking example of the pumping of dozy chaos by a quantum-classical electron from the “red” peak (L-band or L-peak) [11, 22, 23] of the optical band into its “blue” wing (D-band or D-wing) [11, 22, 23] in the case of linear processes, in this case, single-photon absorption. An example of the reverse, “parasitic” pumping of dozy chaos from the D-wing of the J-band of monomers of a polymethine dye into its L-peak during the transition from single-photon absorption to non-linear, two-photon absorption was recently demonstrated in Ref. 23 (see Figure 6). At elementary physical level, we show below that is similar to going far beyond the Egorov resonance in the framework of the single-photon absorption theory (see Ref. 11 and Figure 4 therein).



**Figure 6.** Transformation of the theoretical spectra of a model polymethine dye with different deviations from the resonance condition  $\theta = 0.5$ . The black curve describes an optical band corresponding  $\theta = 0.44$  (near the resonance band corresponding to  $\theta = 0.5$ ), the red curve describes an optical band corresponding  $\theta = 0.88$ , that is far beyond the resonance band (shown on different scales). See details in the Egorov, Vladimir (2020), Mendeley Data, V1, doi: 10.17632/c4h9rm5xk6.1.

So, this “parasitic” effect is easy to understand if, together with the Egorov resonance (see Eqs. (3)–(5)), we consider the law of energy conservation for the case of single-photon absorption [1, 9, 11, 13, 14, 24, 26, 41]

$$\hbar\Omega = J_1 - J_2 + \Delta \quad (8)$$

and for the case of two-photon absorption

$$2\hbar\Omega = J_1 - J_2 + \Delta, \quad (9)$$

where  $J_1 - J_2$  is the energy gap of electronic excitation, and  $\Delta$  is the heat release. These conservation laws correspond to the entire shape of the optical band as a whole: by varying the heat release  $\Delta$ , we vary the frequency of light  $\Omega$  and determine one or another part of the absorption band [1, 9, 11, 13, 14, 24, 26, 41]. Let's rewrite equation (8) for the case of a single act of photon absorption, substituting the reorganization energy of the nuclear subsystem  $E$  instead of the heat release  $\Delta$ :

$$\hbar\Omega = J_1 - J_2 + E. \quad (10)$$

The obvious physical meaning of this equality is that the energy of a photon  $\hbar\Omega$  is spent on the energy of electronic excitation  $J_1 - J_2$  and on the reorganization energy of nuclei  $E$ . Then for two-photon absorption from Eq. (9) we have similarly

$$2\hbar\Omega = J_1 - J_2 + E', \quad (11)$$

where

$$E' = E + \Delta E > E. \quad (12)$$

To estimate the two-photon energy of a nuclear reorganization  $E'$ , we can put

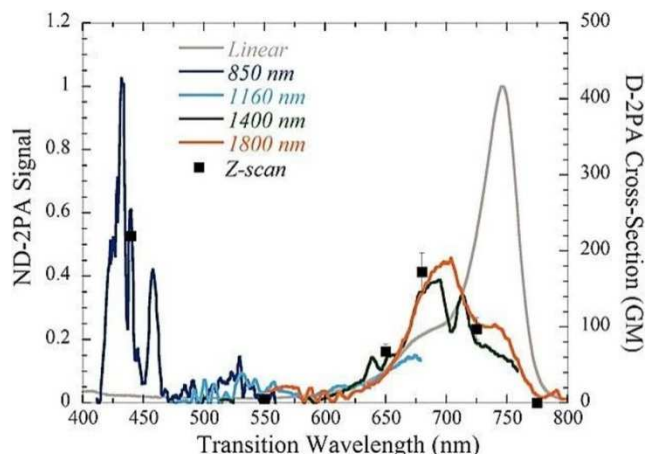
$$\Delta E \equiv E, \quad (13)$$

that is

$$E' = 2E. \quad (14)$$

Thus, replacing the energy of the nuclear reorganization of  $E$  with  $2E$  in the Egorov resonance (Eqs. (3)–(5)), that is, replacing the parameter  $\theta = \frac{1}{2}$  (Eq. (7)) with the parameter  $\theta = 1$  (see Eq. (6)), when passing from single-photon to two-photon absorption, shifts the physical system far beyond the limits of the resonance, which can be interpreted as the “parasitic” pumping of dozy chaos by a quantum-classical electron [1, 26] from the wing of the J-band to its peak (see Figure 6,  $\theta = 0.44 \approx 0.5$  and  $\theta = 0.88 \approx 1$ ). This explains important experimental data [42] on two-photon absorption (see Figure 7). In order to bring the system with parameter  $\theta = 1$  back to the resonance desired in applications, Eq. (7) ( $\theta = \frac{1}{2}$ ), but already under the new conditions of two-photon absorption, it is necessary to reduce the product  $E \cdot L$  by 2 times (see Eq. (6) and Figure 6 with  $\theta \approx 1$  and  $\theta \approx 0.5$ ). In other

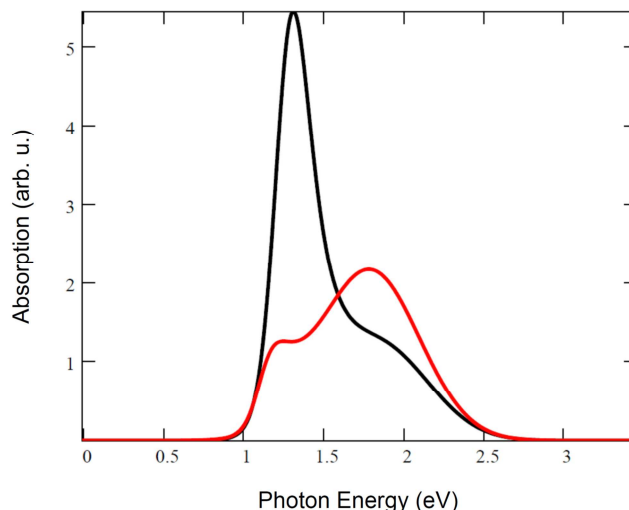
words, in the simplest case, it is necessary to reduce the polarity of the medium ( $E$ ) or to halve the length of the polymethine chain ( $L$ ) — the main optical chromophore. For example, instead of chloroform used as a solvent in Ref. 42, one can take a solvent with a less polarity. Unfortunately, it is impossible to give a more definite prediction in the former case, since there are currently no quantum-chemical calculations that relate the energy of nuclear reorganization in the solvent  $E$  to the polymethine chain parameters and solvent polarity.



**Figure 7.** Nondegenerate 2PA spectra for a solution of selenopyrylium-terminated polymethine dye Se-3C dissolved in chloroform [42]. Different pump wavelengths were used to observe the full ND-2PA spectra. Solid circles are degenerate 2PA (D-2PA) cross sections derived from femtosecond-pulsed Z-scan measurements. 1 GM is defined as  $1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ . Experimental uncertainties in the values were estimated to be  $\pm 10\%$ . The linear absorption spectra are shown as reference. Reproduced from Ref. 23 – Open Access with CC-BY license.

(The origin of the 200 nm difference between the experimental absorption J-peak of Se-3C in Figure 7 and the computational J-peak in Figure 6 is different from the  $J_1 - J_2$  values in Se-3C and the model thiocyanine dye used to compute the spectra in Figure 6 [23].) We note that in Ref. 23 another possible, but much more complicated theoretical interpretation of this simple experimental fact is given, which, unfortunately, does not take into account the law of energy conservation for two-photon absorption (Eq. (9)). In formulating the two-photon absorption problem in Ref. 23 (Supplementary Material), unfortunately, the need of the transition to the new (two-photon) energy conservation law (Eq. (9)) is also not indicated. A comprehensive theoretical interpretation of the experimental data on two-photon absorption [42] (Figure 7) can be obtained by regularly generalizing [23] quantum-classical mechanics [1, 11, 24] to the case of two-photon absorption, which should also take into account the new form of the energy conservation law.

It is easy to see that the problem of a two-photon resonance band shape in polymethine dyes can be finally clarified on a qualitative level if we reproduce the results for the band shapes in Figure 6 as dependent not on the photon wavelength but on the photon energy (see Figure 8).



**Figure 8.** The same as in Figure 6, but for photon energies on the abscissa axis. Here, for simplicity, the energy gap  $J_1 - J_2 \equiv 0$ . See details in the Egorov, Vladimir (2020), Mendeley Data, V1, doi: 10.17632/c4h9rm5xk6.1.

Under resonance conditions with single-photon absorption, it can be said that single acts of absorption of photon energy occur most likely in the region of the band peak and with less probability in the region of its wing (see Figure 8). In the transition from resonant single-photon absorption to two-photon absorption, according to Eqs. (10)–(14), a substantial shift of the main photon absorption region, namely, from the low-energy peak of the band to its high-energy wing, occurs. In other words, the physical system “polymethine dye + environment”, which was resonant under single-photon absorption conditions, goes far beyond this resonance under two-photon absorption conditions, which finds expression in the non-resonant shape of the band, with an evident attenuation of the absorption band at low energies of photons (the former peak of the band) and its intensification at high photon energies (the former wing of the band). To return the physical system “polymethine dye + environment” to the Egorov resonance, but already under conditions of two-photon absorption, it is necessary to change the physical parameters of this system as described above.

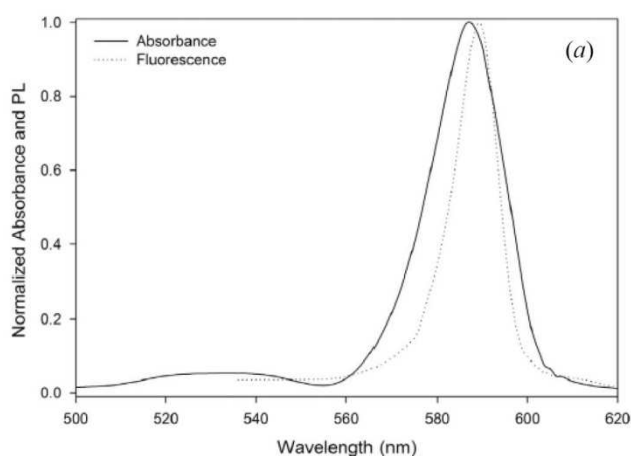
Note that from the results for the shape of the optical absorption bands in Figure 8, modeling the experimental data in Ref. 42, one can estimate the reorganization energies  $E$ ,  $E'$  and  $\Delta E$ , which are included in Eqs. (10)–(12):  $E \approx 1.3$  eV,  $E' \approx 1.8$  eV, and, accordingly,  $\Delta E \approx 0.5$  eV. Thus, in reality, we may not have equality  $\Delta E \approx E$  (see Eq. (13)), but nearly a strong inequality  $\Delta E \ll E$ . This means that in order to restore the resonance conditions for two-photon absorption in the experiment of Ref. 42, it is quite possible that, without changing the parameters of the dye itself, it is enough to just select another solvent with a slightly lower polarity. In another extreme case, if the solvent is unchanged, you will have to choose another dye with a slightly shorter polymethine chain.

## 5. Organization of Absorption and Luminescence Spectra

To date, on the basis of quantum-classical mechanics [1, 11, 24], it has been possible to systematically explain a large amount of experimental data on the optical absorption spectra of polymethine dyes and their various aggregates [1, 9], as well as a number of other fundamental experimental data (see Ref. 1). In the analytical result for the shape of the optical bands in polymethine dye monomers and their J-aggregates [1, 9, 11, 24, 26], the transition from absorption spectra to luminescence spectra is carried out by changing the sign before the heat energy  $\Delta$  [26, 41], *i.e.* in Eq. (8)

$$\Delta \rightarrow -\Delta \quad (15)$$

and then

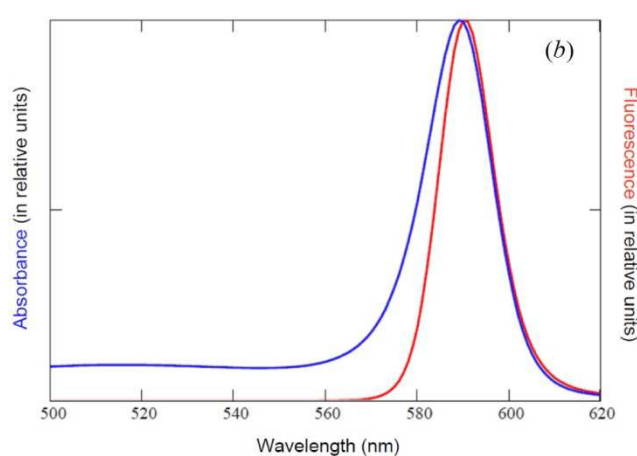


$$\hbar\Omega = J_1 - J_2 - \Delta, \quad (16)$$

and before the length of the optical chromophore (electron-transfer distance)  $L$  [26], *i.e.* in Eqs. (4),(6)

$$L \rightarrow -L. \quad (17)$$

Theoretical absorption and fluorescence spectra [26], fitted to the experimental data [43] on the J-aggregates, are shown in Figure 9. The asymmetry of the shape of the fluorescence band with respect to the shape of the absorption band and its smaller width are explained by better self-organization of the dynamics of elementary acts of photon emission by pi-electrons of J-aggregates compared with the self-organization of the dynamics of elementary events of their photon absorption [26].



**Figure 9.** Experimental [43] (a) and theoretical [26] (b) absorption and fluorescence spectra of J-aggregates.

The very small experimental value of the Stokes shift (1 nm in the J-band) is explained by two factors, both of which are associated with a high degree of self-organization of molecular “quantum” transitions in J-aggregates [26]. The first of these is related to the stimulation of the electronic transition in the J-chromophore by the chaotic dynamics (weak dozy chaos) of the environmental nuclear reorganization, which leads to the well-known narrow, and shifted to the red region of the absorption spectrum, J-band (see above). The second factor is associated with the spontaneous loosening of the excited electronic state immediately before the act of production of a photon by an electron during spontaneous emission [26]. For polymethine dyes and J-aggregates, the universal effect of spontaneous dynamic loosening is abnormally strong due to the very long pi-electron systems in which the quantum-classical transitions under consideration occur. For a detailed theoretical study of the spontaneous loosening of the excited electronic state in the future, along with the development of quantum-classical mechanics [1, 11, 24], taking into account the dynamics of the joint motion of an electron and nuclei, it will also be necessary to create quantum-classical

electrodynamics (see also the aforementioned discussion), which will also take into account the dynamics of photon radiation [26]. In quantum-classical electrodynamics, which generalizes quantum-classical mechanics, the relativistic properties of microparticles should be taken into account, similarly to what is done in standard quantum electrodynamics [17–19], which generalizes quantum mechanics [20, 21].

A quantitative explanation is also given for the position and shape of the optical bands in J-aggregates for luminescence and optical absorption in the case of an admixture of polymethine dye monomers in an aqueous solution [26]. The experimental fact of the absence of the optical band of the monomers on the shortwave wing of the J-band of luminescence with its apparent presence on the shortwave wing of the J-band of optical absorption (see Figure 10) is explained by a significant increase in the dynamic self-organization of quantum-classical transitions in J-aggregates as compared to just a small increase in the dynamic self-organization of these transitions in the monomers upon the change from optical absorption to luminescence [26].



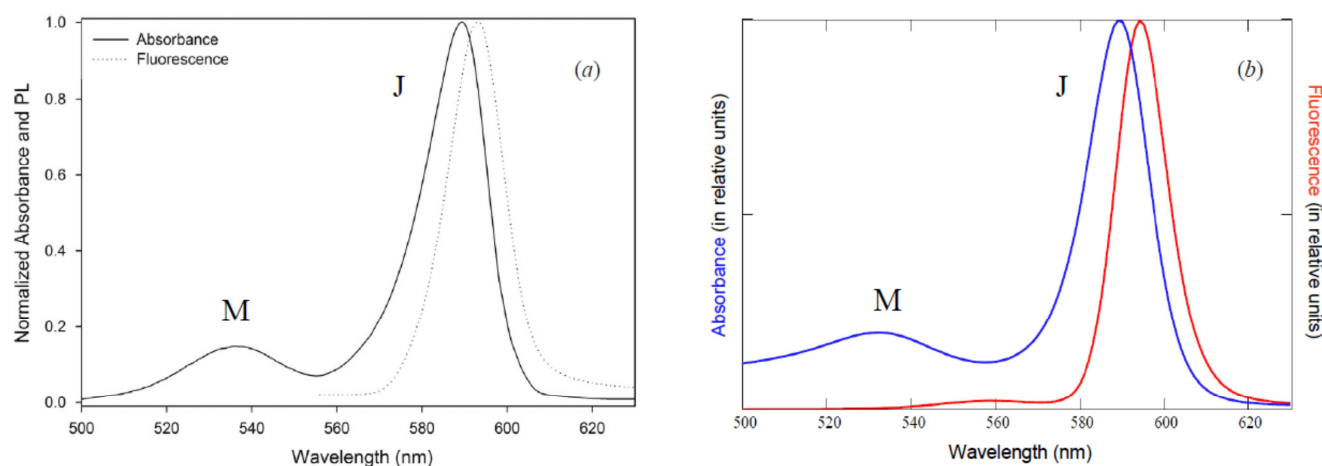


Figure 10. Experimental [43] (a) and theoretical [26] (b) absorption and fluorescence spectra of a C18S4 aqueous solution [43].

## 6. Conclusions and Challenges

As it follows from the above, future research should focus on generalizing quantum-classical mechanics to nonlinear optical processes, in particular, two-photon absorption spectra of polymethine dyes and J-aggregates, which will make it possible to rationalize, for example, a series of experimental studies in the field of bioimaging [44–47] and photodynamic therapy [48, 49].

On the other hand, from the point of view of theoretical physics, it is of interest to formulate quantum-classical mechanics in which the initial Hamiltonian is Hermitian [1], as in the well-known theory of multiphonon transitions [41], in the language of non-Hermitian Hamiltonians (see, for example, Refs. 50–57). In other words, it is of interest to solve the inverse problem: by the form of the complete Green function of the system (see Eq. (1)), in which the infinitesimal imaginary additive  $i\gamma$  in the energy denominator of its spectral representation is replaced by a finite value, to find the form of the original non-Hermitian Hamiltonian that corresponds to such a modified Green function. In quantum-classical mechanics, in contrast to the initial Hermitian Hamiltonian with a linear electron-phonon interaction, in the non-Hermitian Hamiltonian obtained from the solution of the inverse problem, this interaction can turn out to be nonlinear.

As follows from Section 2, the presence of dozy chaos is a prerequisite for the implementation of molecular “quantum” transitions, elementary electron transfers in condensed matter, and their more general form — elementary chemical reactions. Therefore, the discovery of dozy chaos and quantum-classical mechanics shows us the physical source of the complication and self-organization of molecular matter, up to the emergence of living matter and man himself [1], which are the results of the “targeted” dynamic activity of an astronomically large number of light electrons in nature, subordinating to their “will” an equally astronomically large number of very heavy nuclei. The “ultimate goal” of such electron activity is to create the human brain and the associated human consciousness in the evolution, and the

living brain is that part of the body in which dozy chaos is concentrated to the greatest extent [1]. Since the onset of cancer is usually associated with damage to the genes in cells, for example, by radiation, then the bound (induction) radiation of dozy chaos (see above) of the living brain in its pathological functioning, for example under stress, is one of the main physical causes of the natural onset and development of cancer [1]. This implies the exceptional importance of the further development of quantum-classical mechanics, for example, for the purposes of its application in biomedicine.

Just as quantum-classical mechanics has already found its application to simple organic systems, such as polymethine dyes, the main optical chromophore of which is the polymethine chain, one of the most important upcoming applications of quantum-classical mechanics to living systems will be its applications to such simple living systems as, for example, viruses whose structure is based not on DNA but on RNA [58]. The COVID-19 pandemic, that has arisen in our days, requires our immediate response also, and especially in this direction [59].

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## Data Statement

The data on which this article is based are available as an online resource with digital object identifiers (DOI) 10.5061/dryad.t0r3p [29], and 10.17632/h4g2yctmvg.2, 10.17632/ym798wy75g.3 [26], <https://doi.org/10.17632/c4h9rm5xk6.1>.

## Conflict of Interest Statement

The authors declare that they have no competing interests.

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