Polymethine dyes and J-aggregates: quantum–classical theory of the shape of optical bands

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Highlights:

- Theory of elementary electron transfers in condensed matter.

- Joint chaotic and regular dynamics of the transient state.

- Nature of the optical J-band of J-aggregates.

- Egorov nano-resonance.

- Chaotic component of electron–phonon interaction.

Abstract: A new theoretical approach is proposed to explain the nature of the well-known narrow and intense optical J-band of J-aggregates of polymethine dyes. The old approach proposed by Franck and Teller in 1938 and based on the Frenkel exciton theory does not take into account the specific properties of the main optical chromophore of polymethine dye monomers—the polymethine chain. In the new approach proposed by Egorov and based on a new fundamental physical theory—quantum–classical mechanics, which takes into account the chaotic and regular dynamics of the transient state, the optical properties of the polymethine chain and monomers as a whole are considered as a key factor determining the unique optical properties of J-aggregates. The J-band is explained by the so-called Egorov resonance, the presence of which follows from quantum–classical mechanics. Many other experimental facts have also been explained on the basis of quantum–classical mechanics. These include: asymmetry of the shape of the luminescence bands of J-aggregates relative to their optical absorption, an anomalously small Stokes shift of the J-band; the shape of the optical bands of dimers, H- and H*-aggregates; strong detuning of the Egorov resonance during the transition from one-photon to two-photon absorption. The conditions for the restoration of the Egorov resonance during two-photon absorption are predicted.

1. Introduction

In the theory of quantum transitions (see, for example, [1]), the convergence of a series of time-dependent perturbation theory takes place in atomic and nuclear physics, as well as in molecular and chemical physics under the conditions of application of the Born–Oppenheimer adiabatic approximation [2–6] and the Franck–Condon principle [7–10]. It is obvious that in real molecular systems there are always at least small deviations from the conditions for the observance of the adiabatic approximation. This means that, in essence, in molecular and chemical physics, the series of time-dependent perturbation theory always diverges [11], and the physical picture based on the Franck–Condon principle of fast vertical electronic transitions and the subsequent slow adjustment of a very heavy nuclear subsystem to a new electronic charge distribution is erroneous. Nevertheless, the results of the theory existing in molecular spectroscopy and based on this physical picture are often in good agreement with experimental data [12–14]. With some reservations related to the use of various modeling methods in the theory, a similar conclusion also applies to chemical physics [11]. Thus, in molecular and chemical physics, an erroneous theory and an erroneous physical picture often agrees with experimental data. Moreover, it is impossible to clarify the theory and the corresponding physical picture, since the main "approximation" in the theory and the picture are erroneous. At the same time, the agreement of the existing theory with a large number of experimental data indicates only that the theory itself and the corresponding physical picture are not regular, but some kind of interpolation. Note that we are dealing with a similar interpolation while on the surface of the Earth: the erroneous geocentric picture of the world, in which the Sun moves across the sky, is in good agreement with our everyday experience.

In the case of molecular and chemical physics, the divergence of the series of time-dependent perturbation theory in quantum mechanics can be eliminated, first of all, by including the electron–nuclear dynamics of the transient state in the theory of "quantum" transitions. Due to the huge difference in the masses of electrons and nuclei, this dynamics is singular in the framework of quantum mechanics [11]. The only physical way to eliminate this singularity is to introduce chaos into the joint motion of electrons and nuclei [11]. Within the framework of the mathematical apparatus of quantum mechanics, this chaos is most easily introduced by replacing the infinitely small imaginary additive $i\gamma$ in the energy denominator of the total Green's function of the electron–nuclear system by a finite value, which significantly exceeds the value of the nuclear oscillation quantum $\hbar\omega$: $\gamma >> \hbar\omega$. Such a replacement obviously leads to the exit of the entire physical theory beyond the framework of quantum mechanics. As a result of this replacement procedure, we obtain a new physical theory, namely, quantum–classical mechanics, in which the initial and final states for "quantum" transitions are quantum in the adiabatic approximation, and the transient state, being chaotic, is classical [11]. This chaos in the electron–nuclear(–vibrational) transient state is called dozy chaos [11,15] and the transitions themselves are called quantum–classical [11]. If the dozy-chaos energy γ is comparable to the nuclear reorganization energy E ($\gamma \cong E$) or becomes greater than E, then quantum–classical mechanics leads to the same result for transition rates as standard quantum mechanics [1–10] does, which erroneously but often successfully is applied in molecular and chemical physics. This is explained by the independence of the transition rates from the highly chaotic dynamics of the transient state.

In the case of weak dozy chaos, $\gamma << E$, the rates of quantum–classical transitions already depend on the specific dynamics of the transient state, that is, against the background of chaos,

elements of dynamic self-organization arise in the joint motion of electrons and nuclei. This dynamic self-organization and the transition rates corresponding to it can no longer be successfully described within the framework of quantum mechanics, but can only be described within the framework of a new theory, namely, quantum–classical mechanics [11]. The same chaos, which for small molecules with a size much smaller than a nanometer ($L \ll 1\,\mathrm{nm}$) can turn out to be strong, for large molecules, whose size L is on the order of or more than a nanometer (nano-molecule), $L \geq 1\,\mathrm{nm}$, is already weak. In other words, if quantum mechanics, with the above reservations, can still be used to describe optical transitions and spectra of small molecules, then for nano-molecules, only quantum–classical mechanics should be used for these purposes. Thus, we can say that quantum–classical mechanics is one of the main theoretical foundations of nanophotonics.

One of the most striking results of the new theory is the so-called Egorov resonance [16,17], where the electron–nuclear interaction in the transient state under conditions of weak dozy chaos ($\gamma \ll E$) turns out to be so strong that the reorganization motion of very heavy nuclei is no longer a potential barrier for electronic transitions in the optical chromophore, instead, it promotes these transitions. At present, the nature of the well-known narrow and intense J-band of J-aggregates [15,16,18–27], which was discovered by Jelley [28,29] and independently by Scheibe [30,31] in 1936, is explained by the Egorov resonance. The Egorov resonance was discovered in the simplest case of quantum–classical mechanics—the quantum–classical mechanics of elementary electron transfers in condensed matter [11]. The relative simplicity of this case in theory is due to the possibility of using the propagator as the Green's function of the electron, as well as taking into account only non-local phonons, neglecting local phonons [11].

2. Motivation and history of the J-band research

The shape of the optical bands of polymethine dyes and their J-aggregates has been intensively studied for more than half a century. Great interest in this problem is associated with the unique spectral characteristics of these organic systems, which determine their wide practical application associated with the conversion of light energy. Detailed information about the applications can be found, for example, in recent reviews (see [25,27] and references therein). The chromophores of these polymethine systems have a relatively simple structure (see below, Sections 4 and 5). Therefore, these systems can find wide application in the design and development of targeted molecular systems. Relatively narrow and intense bands are observed in their absorption and fluorescence spectra. To date, there is no unified viewpoint in the wider scientific community on the nature of the narrow and intense J-band of J-aggregates. Therefore, the theoretical explanation of the experimental data on the shape of the optical bands of polymethine dyes and their J-aggregates has been an urgent challenge for theorists since 1936 [28–31] to the present day. In addition, an important motivation for studying polymethine dyes and their J-aggregates, and in particular their optical properties, is the fact that they serve as the simplest example of structural–dynamic self-organization of molecular matter, which may be relevant to the possible discovery of the physical cause of life.

The optical absorption J-band arises as a result of the formation of J-aggregates with an increase in the concentration of polymethine dyes in their aqueous solutions [19,20]. Compared to dye monomers, this band is narrow and high intensity, and redshifted. The narrowness and high intensity of the J-band are used in many applications (see [25,27] and references therein). In 1938, Franck and Teller [32],

assuming the formation of molecular aggregates (J-aggregates after Jelley [28,29]) in aqueous solutions of polymethine dyes, gave a theoretical explanation of the redshift of the J-band and its high intensity based on the Frenkel exciton model [33–35]. In 1984, based on the same exciton model, Knapp explained the shape of the J-band and its anomalously small width [36]. Knapp's work [36] provoked a large flow of theoretical work on the development and application of exciton theory to J-aggregates [37–42], in which the author of the present article also took part [15]. A detailed criticism of the explanation of the nature of the J-band based on exciton theory can be found in the review [15]. Unfortunately, the existing exciton theory does not take into account the specific optical properties of the monomers of polymethine dyes that are part of the J-aggregates. This drawback is fundamental, since the experiment shows the J-effect only for polymethine dye molecules and no others [15]. An alternative explanation for the J-effect is given by Egorov as a certain resonance (see Section 1) [11,16] arising in a new fundamental physical theory—quantum–classical mechanics [11], which takes into account the chaotic and regular dynamics of the transient state in quantum theory. This Egorov resonance is a resonance between the electron motion in an extended optical J-chromophore and the motion of reorganization of environmental nuclei under conditions of weak chaos (dozy chaos [15]) in the transient state. On the basis of quantum–classical mechanics, not only the shape of the optical bands of J-aggregates, but also the shape of the optical bands of the monomers of polymethine dyes included in their composition is successfully explained. At present, a number of experimenters (see, for example, [23,25–27]) and theoreticians (see, for example, [40,41]) continue to adhere to the traditional (exciton) point of view on the nature of the J band. The recent idea of Guerrini *et al.* to theoretically explain the nature of the J-band on the basis of plasmon resonance led them to a negative result [42].

We emphasize that the difference in the physics of explaining the nature of the J-band based on the Frenkel exciton model and on the basis of quantum–classical mechanics is that in the former theoretical approach it is assumed that in the J-aggregate the properties of the monomers forming it are leveled, whereas in the latter approach, on the contrary, these properties develop [15]. In other words, the Egorov resonance already exists in monomers with certain lengths of the polymethine chain (the main optical chromophore) in certain solvents, but it is less significant than in J-aggregates.

As mentioned above, the exciton approach erroneously assumes that the J-band can arise for any type of molecule, whereas the experiment shows that the J-band arises only for polymethine dyes. As an example of the erroneous interpretation of the J-band, I will present here the results of our work on its computer modeling using the highly efficient calculation method proposed by us [15], widely known in the literature as smoothing techniques [37,39].

The capabilities of the smoothing techniques are demonstrated particularly in the case when the aggregate consists of molecules of two types that differ only in the average transition energy (bi-Gaussian disorder) [15]:

$$P(\varepsilon_1,...,\varepsilon_N) = \frac{1}{\sigma^N (2\pi)^{N/2}} \prod_{n=1}^{N} \left[b\exp\left(-\frac{(\varepsilon_n - \hbar\Omega_0 + a/2)^2}{2\sigma^2} \right) \right.$$
$$\left. + (1-b)\exp\left(-\frac{(\varepsilon_n - \hbar\Omega_0 - a/2)^2}{2\sigma^2} \right) \right], \ a > 0, \ 0 < b < 1. \tag{1}$$

Figure 1 shows the results of calculations of the shapes of absorption bands for linear aggregates of $N = 100$ molecules [15]. For a symmetric spectrum of a monomer ($b = 1/2$, Figure 1(a)), the inclusion

of intermolecular interaction leads to a noticeable asymmetry of the aggregate band already with interaction $v/a = -0.1$. The asymmetry of the band increases with increasing interaction. Ultimately, as in the case of Gaussian disorder, the aggregate band becomes a narrow band with Gaussian long-wavelength and Lorentzian short-wavelength wings. For the asymmetric spectrum of the monomer ($b = 3/4$, Figure 1(b)), a similar picture of changes in the band shape with increasing intermolecular interaction is obtained.
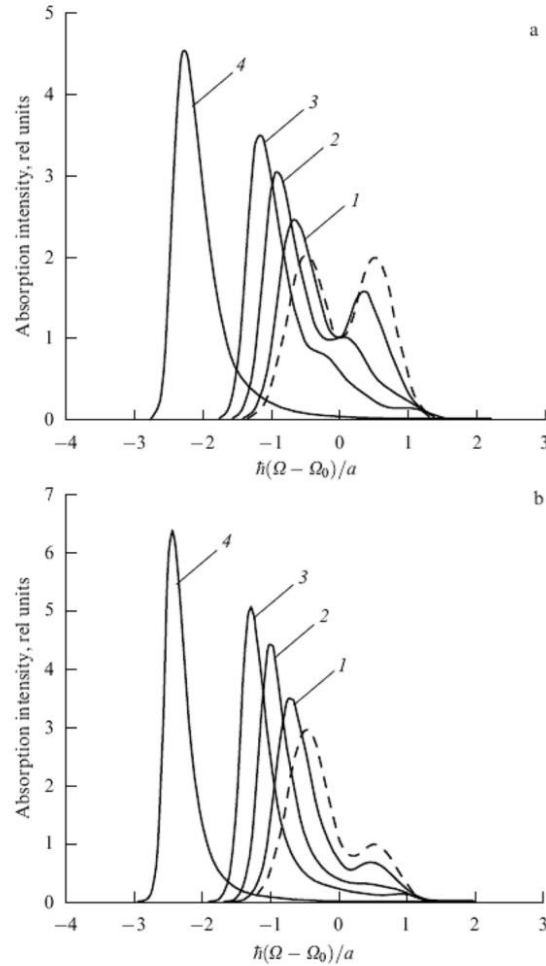

Figure 1. Absorption bands of one-dimensional aggregates with bi-Gaussian diagonal disorder (Equation (1)). Source: Phys. Procedia © 2009 CC BY-NC-ND 3.0 [15]. (Available: https://www.sciencedirect.com/science/article/pii/S1875389209000492)

3. Quantum–classical shape of the optical absorption band and Egorov resonance

Quantum–classical mechanics in the framework of the Einstein model $\omega_\kappa = \text{constant} \equiv \omega$ of nuclear oscillations gives the following result for the optical absorption $K = K(\Omega)$ (Ω is frequency of light) [11]:

$$K = K_0 \exp W , \tag{2}$$

$$W = \frac{1}{2} \ln\left(\frac{\omega\tau \sinh \beta_T}{4\pi \cosh t} \right) - \frac{2}{\omega\tau}\left(\coth \beta_T - \frac{\cosh t}{\sinh \beta_T} \right)$$

$$+ \left(\beta_T - t\right)\frac{1}{\omega\tau\,\Theta} - \frac{\sinh \beta_T}{4\omega\tau\,\Theta^2 \cosh t} , \tag{3}$$

$$1 << \frac{1}{\omega\tau\,\Theta} \leq \frac{2\cosh t}{\omega\tau\sinh\beta_T} \quad , \tag{4}$$

where $\beta_T \equiv \dfrac{\hbar\omega}{2k_B T}$, T is the absolute temperature,

$$t = \frac{\omega\tau_e}{\theta}\left[\frac{AC+BD}{A^2+B^2} + \frac{2\Theta(\Theta-1)}{(\Theta-1)^2+(\Theta/\theta_0)^2} + \frac{\theta_0^{\,2}}{\theta_0^{\,2}+1}\right] \quad , \tag{5}$$

$$|\theta_0| >> \frac{E}{2J_1} \quad , \tag{6}$$

$$\theta \equiv \frac{\tau_e}{\tau} = \frac{L\,E}{\hbar\sqrt{2J_1/m}} \quad , \quad \Theta \equiv \frac{\tau'}{\tau} = \frac{E}{\Delta} \quad , \quad \theta_0 \equiv \frac{\tau_0}{\tau} = \frac{E}{\gamma} \quad , \tag{7}$$

$$\tau_e = \frac{L}{\sqrt{2J_1/m}} \quad , \quad \tau = \frac{\hbar}{E} \quad , \quad \tau' = \frac{\hbar}{\Delta} \quad , \quad \tau_0 = \frac{\hbar}{\gamma} \quad . \tag{8}$$

Here, we use the notation

$$A = \cos\left(\frac{\theta}{\theta_0}\right) + \Lambda + \left(\frac{1}{\theta_0}\right)^2 N \quad , \tag{9}$$

$$B = \sin\left(\frac{\theta}{\theta_0}\right) + \frac{1}{\theta_0}M \quad , \tag{10}$$

$$C = \theta\left[\cos\left(\frac{\theta}{\theta_0}\right) - \frac{1-\xi^2}{2\theta_0}\sin\left(\frac{\theta}{\theta_0}\right)\right] + M \quad , \tag{11}$$

$$D = \theta\left[\sin\left(\frac{\theta}{\theta_0}\right) + \frac{1-\xi^2}{2\theta_0}\cos\left(\frac{\theta}{\theta_0}\right)\right] - \frac{2}{\theta_0}N \quad , \tag{12}$$

and

$$\xi \equiv \left(1 - \frac{E}{J_1}\right)^{1/2} \quad (J_1 > E \text{ by definition}) \quad , \tag{13}$$

and where we finally have

$$\Lambda = -(\Theta-1)^2 E + \left[\frac{(\Theta-1)\theta}{\rho} + \Theta(\Theta-2)\right]E^{\frac{1-\rho}{1-\xi}} \quad , \tag{14}$$

$$M = 2\Theta(\Theta-1)E - \left[\frac{(2\Theta-1)\theta}{\rho} + 2\Theta(\Theta-1)\right]E^{\frac{1-\rho}{1-\xi}} \quad , \tag{15}$$

$$N = \Theta\left[\Theta E - \left(\frac{\theta}{\rho} + \Theta\right)E^{\frac{1-\rho}{1-\xi}}\right] \quad , \tag{16}$$

$$E \equiv \exp\left(\frac{2\theta}{1+\xi}\right) \quad , \quad \rho \equiv \sqrt{\xi^2 + \frac{1-\xi^2}{\Theta}} \quad . \tag{17}$$

The factor K_0 becomes

$$K_0 = K_0^e K_0^p \quad , \tag{18}$$

where

$$K_0^e = \frac{2\tau^3 J_1}{m} \frac{\left(A^2 + B^2\right)\rho^3\Theta^4\xi}{\theta^2\left[\left(\Theta - 1\right)^2 + \left(\dfrac{\Theta}{\theta_0}\right)^2\right]^2\left[1 + \left(\dfrac{1}{\theta_0}\right)^2\right]} \cdot \eta,$$
(19)

and

$$\eta \equiv \exp\left(-\frac{4\theta}{1 - \xi^2}\right),$$
(20)

and

$$K_0^p = \frac{1}{\omega\tau}\left[1 + \frac{\sinh\left(\beta_T - 2t\right)}{\sinh\beta_T}\right]^2 + \frac{\cosh\left(\beta_T - 2t\right)}{\sinh\beta_T}.$$
(21)

The result for K is obtained taking into account the conservation of energy

$$\hbar\Omega = J_1 - J_2 + \Delta,$$
(22)

where J_1 and J_2 are the electron energy levels at the donor and acceptor (1 and 2), and Δ is the heat generation (see Equations (7) and (8)). The remaining designations in Equations (7) and (8) are as follows: L is the distance between the donor and acceptor, which models the length of the main optical chromophore of polymethine dyes—the polymethine chain (see details below, Section 4) [11,15,43–46]; m is the effective mass of an electron; E is the energy of reorganization of the nuclear environment; γ is the energy characterizing the measure of chaos in the dynamics of the transient state (the so-called dozy-chaos energy) [15]. The physical meaning of the times in Equation (8) is discussed in [11,15,43].

Equating the characteristic inverse time of electron motion between the donor and acceptor $\left(2\tau_e\right)^{-1}$, where

$$\tau_e = \frac{L}{\sqrt{2J_1/m}}$$
(23)

(see Equation (8)), and the characteristic inverse time of the motion of the reorganization of nuclei τ^{-1}, where

$$\tau = \frac{\hbar}{E}$$
(24)

(see Equation (8)), we obtain the Egorov resonance

$$\left(2\tau_e\right)^{-1} = \tau^{-1}.$$
(25)

The formula

$$\mathcal{E} = \frac{4\pi^2 q^2 N_A \Omega}{3\hbar c n_{refr}} K$$
(26)

establishes a relationship between the optical absorption K and an experimentally measured quantity—the extinction coefficient $\mathcal{E}$ [3]. Here q is the total electron charge that is transferred along the polymethine chain; N_A is Avogadro's number; c is the speed of light in vacuum, and n_{refr} is the refractive index.

4. Optical transitions in polymethine chain

The main optical chromophore of polymethine dyes is the polymethine chain (Figure 2) [47,48]. Upon optical excitation of the polymethine chain, charge transfer along the chain occurs due to alternation of charges on adjacent carbon atoms and alternative charge redistribution upon excitation [48]. Complete charge transfer along a long chain consists of a sequence of charge transfers over short distances between adjacent carbon atoms in the chain [43,44]. Therefore, in Equation (19), the tunneling factor η (Equation (20)) can often be

neglected, taking it equal to or close to unity [15,43–46]. Another simplification is associated with the sufficiently large length of the polymethine chain and the resulting possibility of neglecting the interaction of the electron charge transfer with local phonons and taking into account its interaction only with nonlocal phonons [15,43–46]. Under this assumption, Equations (2)–(22) are obtained. The dominant role of charge transfer interaction with nonlocal phonons is consistent with the experimental fact that the Egorov resonance is observed not only for J-aggregates (see below, Section 5) but also for polymethine dye monomers (see below); see the discussion above, Section 2.
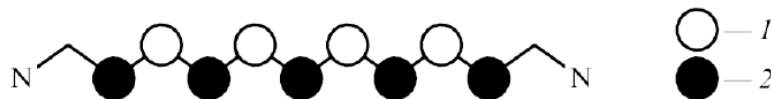

Figure 2. Quasilinear polymethine chain [45,47,48]. Source: RSC Adv. © 2013 The Royal Society of Chemistry [45]. (Available: https://pubs.rsc.org/en/content/articlelanding/2013/ra/c3ra22148b/u nauth)

Figure 3 shows that in the dye series with varying polymethine chain length L [49], the Egorov resonance is in close proximity to the most intense band for $n = 3$ or chain length $L = 1.4$ nm. Therefore, this resonance is called nano-resonance.

Near the Egorov nano-resonance, the M-band (see Figure 3, $n = 2$, 3 and 4) has a certain peak in the red region of the optical spectrum (L-band (living band) or L-peak) and a wing in the blue region of the spectrum (D-band (dead band)) [18,50]. The width and intensity of the L-band, as well as its red position on the wavelength axis, are very sensitive to changes in dozy-chaos energy γ, while the D-band weakly depends on γ [50]. The appearance of the L-peak against the background of the D-band is explained by the strengthening of the dynamic organization of the electronic transition (transfer) in the polymethine chain (the main chromophore in the dye monomer) with a decrease in the dozy-chaos energy γ due to the strengthening of the component of the movement of the reorganization of nuclei of the environment, which is coherent to the transition (transfer).
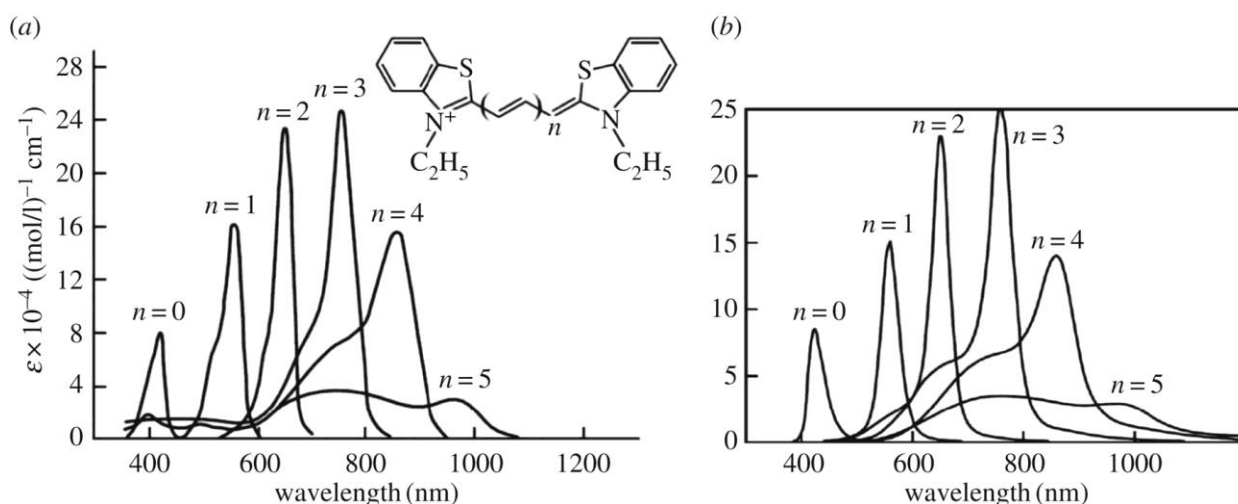

Figure 3. Change in the shape of the optical absorption band of a dye with change in the length L of the polymethine chain [43,45]. (*a*) Experimental data of Brooker *et al.* [49] (see also [19]). (*b*) Theoretical band shapes from Equations (2)–(22), (26) [11,43,45]. The band for $n = 3$ and $L = 1.4$ nm is the Egorov (nano-)resonance. Source: RSC Adv. © 2013 The Royal Society of Chemistry [45]. (Available: https://pubs.rsc.org/en/content/articlelanding/2013/ra/c3ra22148b/unauth)

5. Shape of the J-band—Egorov nano-resonance

A brilliant experimental demonstration of the appearance of the J-band of J-aggregates was made by Herz [19,20] using the example of increasing the concentration of benzimidazolocarbocyanin in water, see Figure 4 (**left**).

Following Hans Kuhn (see [51] and references therein) and the law of mass action, Herz showed that the optical J-chromophore forms a brickwork-like structure of four molecules (see Figure 5), which form a J-aggregate in the form of a long thin rod [15,43,44,46,50].

The results of my fitting theoretical Equations (2)–(22), (26) to the discussed Herz's data are shown in Figure 4 (**right**).
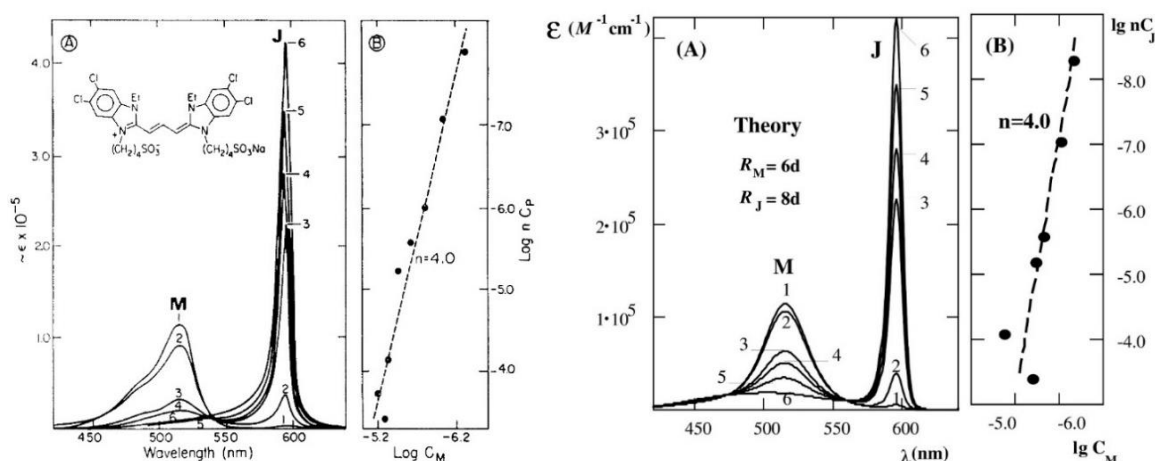

Figure 4. At the (**left**): Concentration equilibrium of monomers (M) and J-aggregates (J) in an aqueous solution and their optical absorption bands [19,20]. At the (**right**): Theoretical absorption bands from Equations (2)–(22), (26) [46,50]. Source: Chem. Phys. Lett. © 2001 Elsevier B.V. [46]. (Available: https://www.sciencedirect.com/science/article/abs/pii/S0009261401001002)
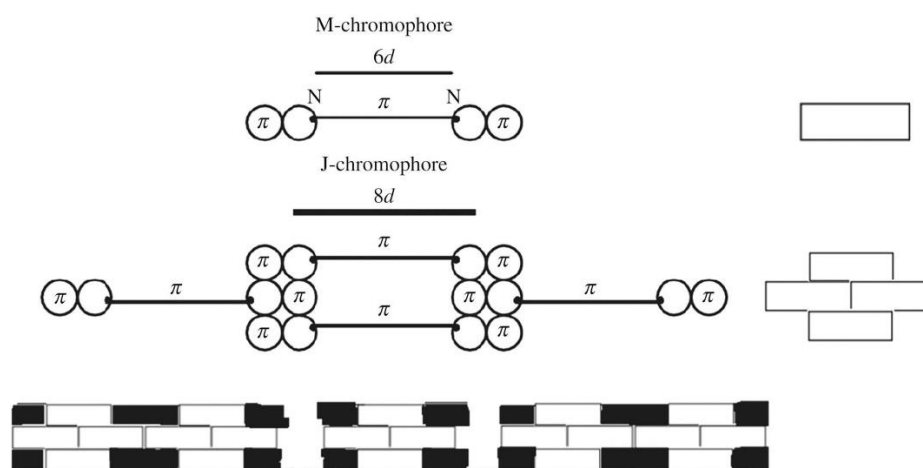

Figure 5. A brickwork-like structure of J-chromophore of four molecules and J-aggregate (**bottom**) [15,19,20,43,44,46,50,51]. Source: R. Soc. Open Sci. © 2017 CC BY 4.0 [43]. (Available: https://royalsocietypublishing.org/doi/full/10.1098/rsos.160550)

The physical mechanism leading to the enhancement of the electronic transition in the Egorov nano-resonance is the stimulation of the electronic transition by the movement of nuclear reorganization

of the medium under conditions of weak dozy chaos [15,43,46,50]. Compared to nano-resonance in monomers M (see Figure 3), a significant increase in nano-resonance in J-aggregates (Figure 4) is associated with the transition from the one-dimensional geometry of the optical M-chromophore to the two-dimensional geometry of the J-chromophore due to the stacking of the π-electronic structure of the quasi-one-dimensional polymethine chain of one molecule with π-electronic structures of flat benzene rings of two neighboring molecules (Figure 5), which leads to a significant increase in the interaction of the electronic transition with the surrounding nuclei and an increase in nano-resonance [15,43,44,46,50].

Figure 6 shows how the J-band of J-aggregates as the Egorov nano-resonance (Enr) looks in relation to the optical bands of various other aggregates of polymethine dyes, which cannot be explained within the framework of quantum mechanics, but can be explained within the framework of quantum–classical mechanics.
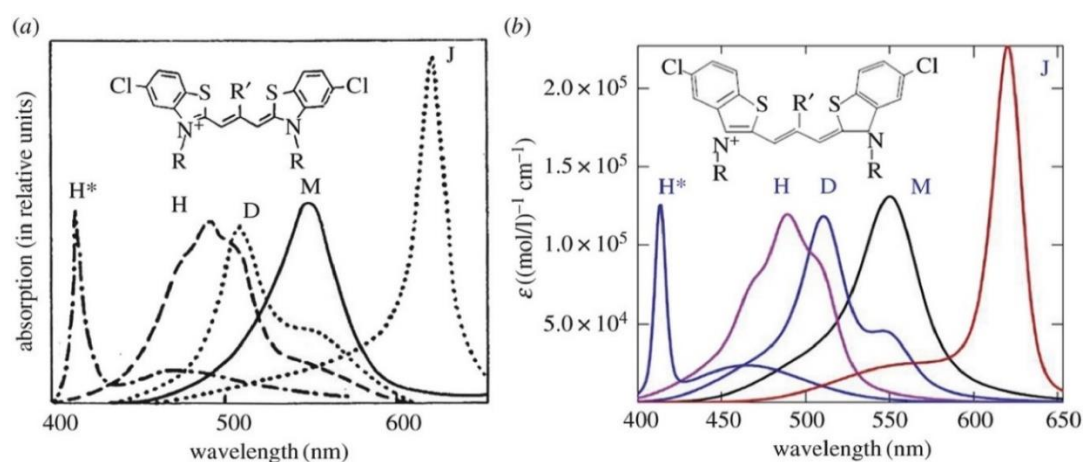

Figure 6. The shapes of optical absorption bands in monomers (M), dimers (D), H-, H*- and J-aggregates of a polymethine dye. (*a*) Experiment [19]. (*b*) Theory [43,45]. Source: R. Soc. Open Sci. © 2017 CC BY 4.0 [43]. (Available: https://royalsocietypublishing.org/doi/full/10.1098/rsos.160550)

A remarkable result is the fact that the nature of the band shape of polymethine dye monomers (M) and their J-aggregates (Figure 6) is determined only by charge transfer, whereas the nature of the band shape of their dimers, H- and H*-aggregates (Figure 6) is determined by both charge transfer and the Frenkel exciton effect [43,45].

The explanation of the shape of the M-band in Figure 6 is similar to the explanation of the shape of the optical bands of the dye monomers in Figure 3 near the Egorov resonance (see Section 4).

6. Explanation for the shape of optical bands in dimers, H- and H*-aggregates

In dimers of polymethine dyes, the shape of the optical bands is determined both by the chaotic dynamics of the transition in their constituent monomers and by the dynamics of the Frenkel exciton (dozy-chaos–exciton coupling) [33–35,43,45]. In dimers, there are the shift in the electronic excitation energy level of the monomer (exciton shift) and its splitting (exciton splitting) due to intermolecular interaction [43,45]. The exciton shift and exciton splitting can be calculated by knowing the transition dipole moments of the constituent molecules, their mutual orientation and intermolecular distance. The angle between the dipole moments of the transition determines the strengths of the oscillators of radiative transitions to the low

energy and high energy states, which have mutually perpendicular polarizations. This pattern is called Davydov splitting [35] of the optical absorption band of the monomer (see Figure 6, D-band).

Broad optical H-bands are explained by dozy-chaos–exciton coupling in H-aggregates resulting from inelastic binary collisions of polymethine species in solutions [43]. Results of theoretical fitting to the experimental band shape indicate both the looseness of the structure of the H-chromophore (tetramer) and the looseness of the structure of the entire H-aggregate formed from H-chromophores connected in some way to each other. This picture differs significantly both from the picture of the ordered compact structure of J-aggregates (Figure 5) and from the picture of the structure of H-aggregates in the form of an ordered compact deck of cards reported in the literature [43] (see also [15,19] and references therein).

The narrow optical band in H*-aggregates is explained by strong dozy-chaos–exciton coupling effect which follows from structural features of polymethine dyes that form H*-aggregates[43]. Namely, H*-monomers are cyclic bis-thiacarbocyanines, in which the polymethine chains of two identical uniplanar monomers are cross-linked at their ends by hydrocarbon radicals [20]. During the formation of H*-aggregates, this structure leads to a significant strengthening of the excitonic coupling within them.

7. Asymmetry of the shape of the luminescence bands of J-aggregates relative to their optical absorption. Anomalously small Stokes shift of the J-band

According to standard quantum theory, which does not take into account the dynamics of the transient state, the transition from absorption spectra to luminescence spectra is carried out by changing the sign of the heat generation

$$\Delta \rightarrow -\Delta , \qquad (27)$$

i.e., in Equations (7) and (8), as well as in the law of conservation of energy, Equation (22) [3,44]. Applying Equation (27) to the optical bands in the Aviv–Tischler experiment for J-aggregates in Langmuir films (see Figure 7*a* and Figure 8) [24], we theoretically obtain mirror-symmetrical luminescence and absorption bands (see Figure 7*b*), while the experiment shows their asymmetry (Figure 7*a*).
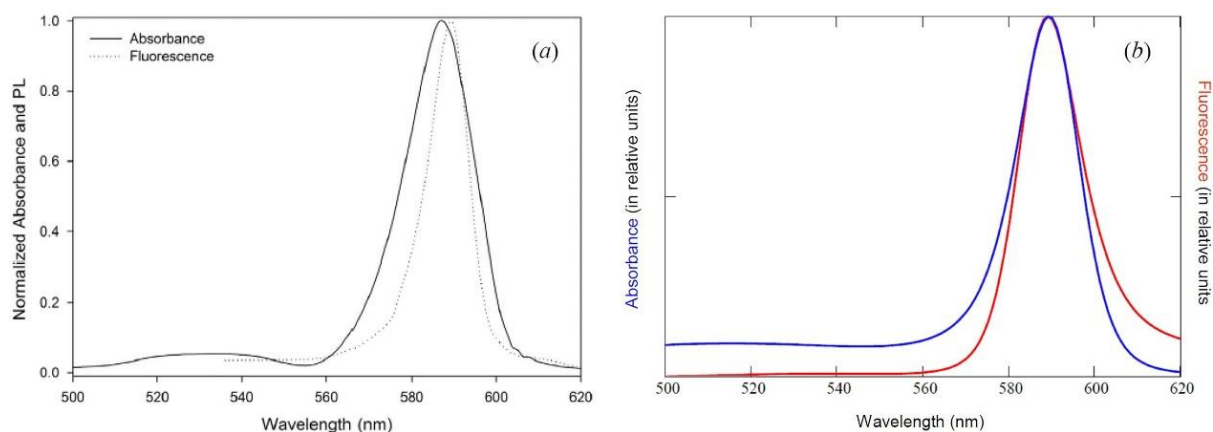

Figure 7. The absorption and fluorescence J-bands of J-aggregates in Langmuir films. (*a*) Experiment [24]; the fluorescence and absorption J-bands are asymmetric. (*b*) Theory [44]; the fluorescence J-band is obtained from the absorption J-band by changing the sign in the heat generation Δ (Equation (27)); the fluorescence and absorption J-bands are symmetric. Source: Results Phys. © 2019 CC BY-NC-ND 4.0 [44]. (Available: https://www.sciencedirect.com/science/article/pii/S2211379718335186)

The asymmetry of the absorption and luminescence spectra (Figure 7*a*) in the Aviv–Tischler experiment [24] is well reproduced [44] (Figure 9) if we follow the rules not of standard quantum theory [3] but the rules of quantum–classical mechanics, according to which to obtain luminescence spectra from the absorption spectra, not only the sign of the heat generation Δ (Equation (27)), but also the sign of the distance L in Equations (7),(8) and (20) should be changed [44]:
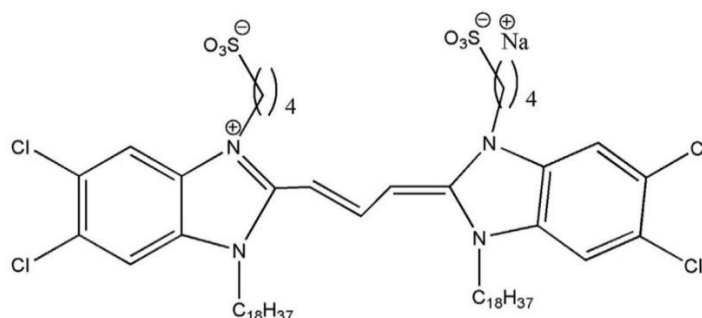
$$L \to -L. \tag{28}$$

Figure 8. Chemical structure of the dye studied in [24]. Source: J. Lumin. © 2015 Elsevier B.V. [24]. (Available: https://www.sciencedirect.com/science/article/abs/pii/S0022231314005900)
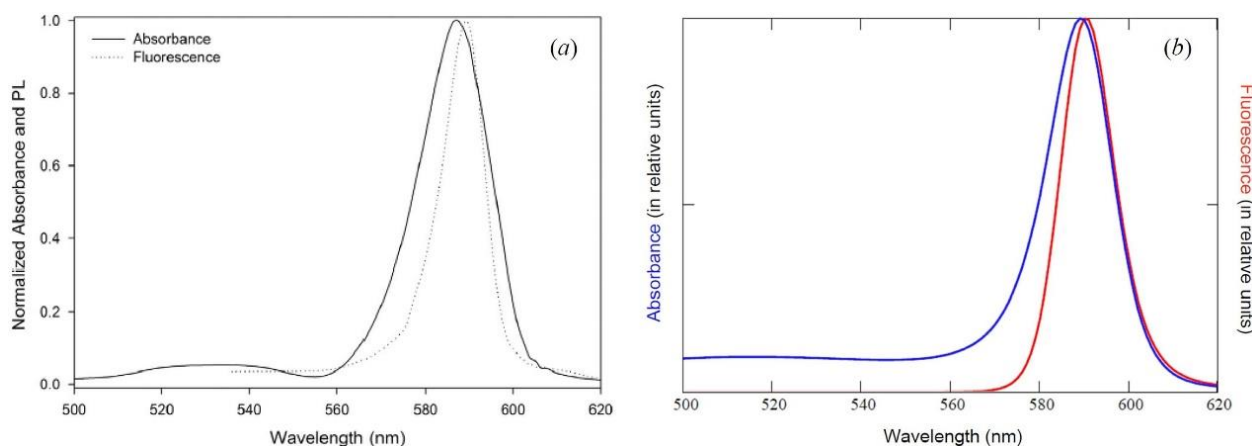

Figure 9. The absorption and fluorescence J-bands of J-aggregates in Langmuir films. (*a*) Experiment [24]; the fluorescence and absorption J-bands are asymmetric. (*b*) Theory [44]; the fluorescence J-band is obtained from the absorption J-band by changing the sign both in the heat generation Δ (Equation (27)) and in the J-chromophore length L (Equation (28)); the fluorescence and absorption J-bands are asymmetrical as in the experiment. Source: Results Phys. © 2019 CC BY-NC-ND 4.0 [44]. (Available: https://www.sciencedirect.com/science/article/pii/S221137971 8335186)

The more significant narrowness of the luminescence J-band compared to the absorption J-band and its asymmetry with respect to it can be explained by a higher degree of organization of the dynamics of the electron–phonon transient state during luminescence compared to the dynamics during absorption [44]. Namely, the π-electronic system, as it were, learns, remembering, through interaction with the environment, its route of movement when the system is optically excited, therefore, in the process of removing this excitation, knowing this route, it behaves in a more organized manner.

The very small value of the Stokes shift (Figure 9) is explained by two effects [44]. The first effect is associated with the convergence of Egorov nano-resonances associated with absorption and luminescence, as a result of an anomalously high degree of regularization of mixed, chaotic and regular, transient states [44]. Formally, a high degree of regularization corresponds to the very small dozy-chaos energy γ (see Figure 1 in [44]). The second effect is associated with an anomalously strong loosening of the excited π-electronic state due to its large extent. This leads to an anomalously high energy of the excited state and, as a consequence, to the emission of a J-aggregate with an anomalously high frequency of light [44].

8. Strong detuning of nano-resonance upon transition from one-photon to two-photon absorption. Conditions for recovery of nano-resonance at two-photon absorption

In [52], the shape of the optical absorption band (Figure 10) of a selenopyrylium-terminated polymethine dye (Figure 11) in chloroform was investigated for one-photon and two-photon absorption. For one-photon absorption, the band is narrow and intense. In the case of two-photon absorption, the shape of the band is greatly deteriorated. This effect is explained by the strong detuning of the Egorov nano-resonance (one-photon band) upon transition to two-photon absorption [16,17].
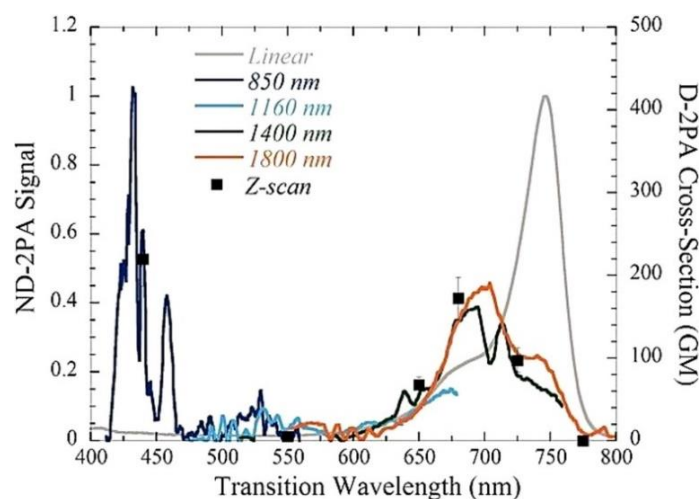

Figure 10. Experimental two-photon absorption band (brown curve) [52]. Source: Science © 2010 American Association for the Advancement of Science (AAAS) [52]. (Available: https://www.science.org/doi/abs/10.1126/science.1185117)

When going from resonant one-photon absorption to two-photon absorption, a significant shift occurs in the main region of photon absorption, namely from the low-energy peak (long-wavelength peak) of the band to its high-energy wing (short-wavelength wing) [17] (see Figure 12, black and red curves). This shift, as follows from the law of conservation of energy (see Equation (22)), corresponds to an increase in the reorganization energy E, included in the dynamic parameter

$$\theta \equiv \frac{\tau_e}{\tau} = \frac{E\,L}{\hbar\sqrt{2J_1/m}} \tag{29}$$

(see Equations (7), (23) and (24)), approximately twofold, which corresponds to the replacement of the parameter $\theta = 1/2$ (Egorov nano-resonance) with the parameter $\theta = 1$ during the transition from one-photon to two-photon absorption [17]. This can be interpreted as a "parasitic" pumping of dozy

chaos by a quantum–classical electron [11,17,44] from the wing of the J-band to its peak (see Figure 12, $\theta = 0.44 \cong 0.5$ and $\theta = 0.88 \cong 1$). Thus, important experimental data [52] on two-photon absorption (see Figure 10) find their explanation.
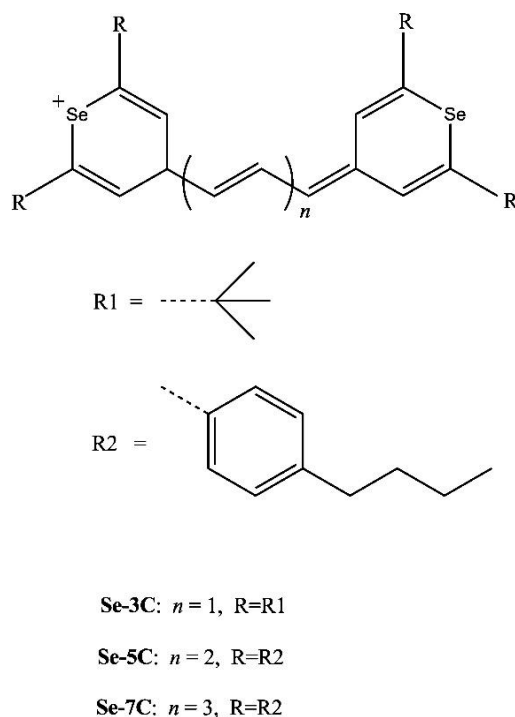
Se-3C: $n = 1$, R=R1

Se-5C: $n = 2$, R=R2

Se-7C: $n = 3$, R=R2

Figure 11. Chemical structure of the dye studied in [52]. Source: Science © 2010 American Association for the Advancement of Science (AAAS) [52]. (Available: https://www.science.org/doi/abs/10.1 126/science.1185117)
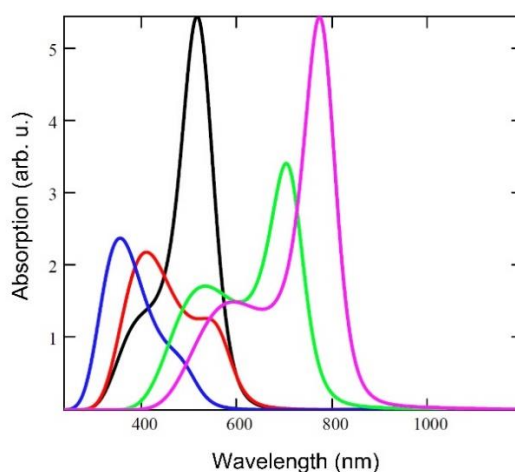
Figure 12. Detuning of the Egorov nano-resonance during the transition from one-photon (black curve) to two-photon (red curve) absorption and the predicted reconstructed Egorov nano-resonance during two-photon absorption (magic curve) due to a decrease in the reorganization energy of the environment (in the experiment, due to a decrease in the polarity of the solvent) [17]. Source: Nano-Struct. Nano-Objects © 2021 Elsevier B.V. [17]. (Available: https://www.sciencedirect.co m/science/article/abs/pii/S2352507X20301232)

To return a system with parameter $\theta = 1$ to the resonance $\theta = 1/2$ desired in applications, but under new conditions of two-photon absorption, it is necessary to reduce the product $E \cdot L$ by a factor of 2 [17] (see Equation (29), and Figure 12 with $\theta \cong 1$ and $\theta \cong 0.5$). In other words, under experimental conditions it is necessary to reduce the polarity of the medium corresponding to the reorganization energy E and/or the length L of the polymethine chain, which is the main optical chromophore.

According to the result in Figure 12, to restore the Egorov nano-resonance for the two-photon absorption, the reorganization energy $E = 1 \, \text{eV}$ (red) must be reduced to $E = 0.6 \, \text{eV}$ (magic), that is, in the experiment it is necessary to use a less polar solvent [17]. In this case, nano-resonance shifts to the long-wave region of the optical spectrum.

9. Discussions

9.1. Chaotic nature of the transient molecular state

Quantum mechanics in molecular and chemical physics becomes a singular theory due to the incommensurability of the masses of electrons and atomic nuclei [11]. This singularity is eliminated by introducing chaos into the transient state of "quantum" transitions [11]. The question may arise as to why introducing chaos is the only physical way to eliminate the singularity. To answer this question, let us turn for a moment from quantum mechanics and turn to a similar and well-known singularity in classical physics, namely, the singularity in the spectrum of black body radiation at high frequencies, which has been called the ultraviolet catastrophe. As is well known, quantum theory began with the elimination of this singularity by Planck by introducing the quantum hypothesis into classical physics [53]. Planck assumed that the emission and absorption of electromagnetic radiation does not occur continuously, as all physicists had been confident of before him, but in leaps and bounds—in quanta. As we know, this simple but revolutionary physical concept radically changed not only all of physics, but also the entire face of human civilization. Quantum mechanics, which was subsequently created by a large number of theoretical physicists, gave a brilliant and exhaustive explanation for all experimentally known atomic spectra. The overwhelming majority of theoretical physicists are convinced that physical processes during a quantum leap, if they exist, lead to very weak experimental effects. One of such weak effects is, for example, the well-known Lamb shift in atomic spectra (see [11]).

The first important step in extending the ideas of quantum mechanics from atoms to molecules was the well-known work of Born and Oppenheimer [2], who proposed the adiabatic approximation to create a theory of molecules. Physically, the adiabatic approximation allows one to separate the very fast motion of a very light electron from the slow motion of heavy nuclei. As a result, electrons in a molecule create an electric potential in which the nuclei oscillate. In the adiabatic approximation, the total wave function of the electron and nuclei can be represented in a simplified manner as the product of a wave function that depends only on the electron coordinates and a wave function that depends only on the nuclear coordinates. Therefore, Franck and Condon proposed calculating molecular spectra similarly to atomic spectra [7–9]. This hypothesis was subsequently called the Franck–Condon principle [10]. Using the Franck–Condon principle, it was possible to successfully explain the optical spectra of many molecules, which laid the theoretical foundations for modern molecular spectroscopy. However, in comparison with atomic spectroscopy, in molecular spectroscopy a fundamentally important question arises related to the structural restructuring of the nuclear subsystem, which is a consequence of adjusting

the charge of atomic nuclei in the molecule to the new distribution of the electron charge resulting from its quantum transition in the molecule. This new effect, in comparison with atoms, is called the reorganization of the vibrational motion of nuclei, in which their equilibrium positions are shifted, or, in short, the effect of reorganization of nuclei. Due to the incommensurability of the masses of the electron and nuclei, this effect cannot be explained within the framework of quantum mechanics [11]. The series of the time-dependent perturbation theory, on which the theory of quantum transitions in quantum mechanics is based [1], converges only in the adiabatic approximation. Beyond the adiabatic approximation, this series diverges, and thus the theory of quantum transitions, and along with it the entire quantum mechanics in molecular and chemical physics, becomes a singular theory, or, simply put, stops working [11].

It is clear that in a real physical experiment, there are always, at least small, deviations of the electron–nuclear dynamics in the studied molecular system from the adiabatic approximation. This means that quantum mechanics, becoming a singular theory here, is not applicable to the description of real molecular transitions. The question arises of how one can restore the functionality here, if not of quantum mechanics, then at least of physical theory as a whole.

It is quite clear that in these new conditions, compared to the theory of atoms, it is necessary to consider in much greater detail the interaction of the electron and nuclei in the transient state of these, supposedly still quantum, transitions in molecules and molecular systems. It is clear that some radical step must be made in the theory, which, unlike the adiabatic approximation, would not separate the motion of the electron and nuclei, but, on the contrary, would connect them. Such a single step is to write the Schrödinger equation in an integral representation, that is, in the form of the Lippmann–Schwinger integral equation, and then search for a solution no longer of the Schrödinger equation, but of the Lippmann–Schwinger equation, the kernel of which is the full Green's function of the electron–nuclear molecular system [11].

In practice, such a procedure and the subsequent construction of a new theory are most easily implemented for the problem of elementary electron transfers in condensed media, which is the subject of study in chemical physics. The relative simplicity of this problem is associated, as indicated above (Section 1), with the possibility of representing the electron part of the Green's function in the form of a propagator and with the possibility of neglecting local phonons in the theory and taking into account only nonlocal phonons. The above singularity in quantum mechanics is eliminated by replacing the well-known infinitesimal imaginary addition $i\gamma$ in the energy denominator of the Green's function with a finite value. A successful explanation of known experimental data by the results of a new theory shows that the value of $\gamma \gg \hbar\omega$, where ω is the phonon frequency. In the case of the inverse strong inequality $\gamma \ll \hbar\omega$, the value of γ could be interpreted physically as the width of the electron–vibrational levels in the transient state. In our case, which we have from a comparison of theory with experiment, the strong inequality $\gamma \gg \hbar\omega$ means that all transient electron–vibrational states are not separated, but entangled, *i.e.* participate in a joint chaotic motion. The corresponding chaos is called dozy chaos. Dozy chaos is very specific in relation to the chaos that arises from nonlinear interactions in physical systems. In our case, *i.e.* in the case of the problem of elementary electron transfers in condensed media, in the original Hamiltonian, the term responsible for the electron–phonon interaction is linear [11].

Because of chaos, the energy spectrum in the transient state is continuous, which is a sign of the classical nature of the motion of a physical system. Therefore, the corresponding new quantum mechanics, in which the Green function is modified in the above manner, is called quantum–classical mechanics.

Let us sum up. In the transition from classical mechanics to the new theory, Planck was forced to introduce quantum leaps into physical theory, thereby creating the basis for the creation of quantum mechanics. In the transition from quantum mechanics to the new theory, Egorov was forced to introduce dozy chaos, which transformed quantum leaps into "quantum" transitions with a continuous energy spectrum. As a result, the foundations of quantum–classical mechanics were created in the form of the theory of elementary electron transfers in condensed media. The transition from classical mechanics to quantum mechanics is carried out in only one way, namely, by introducing into the theory of quanta and Planck's constant $\hbar$ (universal constant) [53]. It was stated above that the only constructive step for eliminating the singularity of quantum mechanics in molecular and chemical physics is the transition from the Schrödinger equation to the Lippmann–Schwinger equation. Therefore, the transition from quantum mechanics to quantum–classical mechanics is also carried out in only one way, namely, by introducing into the theory of chaotic dynamics of transitions and the constant γ [11,46,50]. The energy γ is determined by the properties of a specific physical system and in practice is a value in the region between the order of magnitude of the reorganization energy E and $E/(6 \div 7)$ (see [15], the caption to Figure 16 therein).

9.2. Egorov resonance and nonlocal/local phonons

Natural vibrations (local phonons) in the monomer of polymethine dyes and/or their J-aggregates, as well as in molecules in general, are a barrier to the electronic transition, which only leads to the broadening of the optical bands [3,4]. On the other hand, nonlocal phonons [3] of the environment interacting with polymethine dyes and/or their J-aggregates are not only a barrier to the electronic transition in them. Under the conditions of the Egorov resonance (see Equations (23)–(25)), nonlocal phonons, on the contrary, largely contribute to the electronic transition (transfer) in the quasi-one-dimensional optical chromophores of the monomers of polymethine dyes and/or their J-aggregates (see Figures 2 and 5). For the quasi-one-dimensional geometry of these optical chromophores, the number of nonlocal phonons of the environment that effectively interact with them significantly exceeds the number of local phonons present in the chromophores themselves (see Sections 4 and 5). Therefore, only nonlocal phonons are taken into account in the reorganization energy E included in the formula for the Egorov resonance (Equations (23)–(25)).

9.3. J-band is a signature of polymethine dyes

One may ask why the Egorov resonance and the corresponding narrow and intense J-band of J-aggregates appear only in polymethine dyes. The answer is that the reorganization motion of the surrounding medium (methanol in the case of monomers or water in the case of J-aggregates) effectively promotes an electronic transition (see Sections 4, 5 and 9.2) only when this electronic transition is a charge transfer along some straight line, in the case of a monomer—along the quasi-linear polymethine chain (see Section 4). J-aggregation simply enhances the interaction of charge transfer with the reorganization motion of the surrounding medium (water) due to the combination of the quasi-one-

dimensional π-electron system of the polymethine chain with the quasi-two-dimensional π-electron system of the benzene rings of neighboring molecules (Section 5, Figure 5, π-stacking). The two-dimensional geometry of benzene rings provides enhanced interaction of the π-system with the environment, promoting electronic transition (transfer) at or near the Egorov resonance.

The author is not aware of any other types of dyes other than polymethine dyes that show the J-effect.

The question of why polymethine dyes form J-aggregates only in water and do not form them in other solvents currently remains open. Note that the solution to this question lies not in the realm of quantum–classical mechanics considered here, but in the realm of quantum chemistry.

10. Conclusions

A new physical theory, quantum–classical mechanics, which takes into account the presence of a transient state in molecular transitions and the chaotic and regular dynamics of electron–nuclear motion in it, substantiates the possibility of using the Born–Oppenheimer adiabatic approximation [2] and the Franck–Condon principle [7–10], as well as quantum mechanics as a whole, in the case of strong transient (dozy) chaos that occurs in sufficiently small molecules in standard optical spectroscopy [11]. In photochemistry and nanophotonics of large molecules, in the dynamics of a transient state against the background of dozy chaos, regular motion arises, which in principle is not described by the mathematical apparatus of quantum mechanics, but is described mathematically by quantum–classical mechanics [11].

One of the most striking results of quantum–classical mechanics is the resonance between electron motion and nuclear reorganization motion in the transient state, called Egorov nano-resonance [15–18]. Egorov's nano-resonance currently explains the nature of the well-known narrow and intense J-band of J-aggregates of polymethine dyes [15–18], which occurs in aqueous solutions of their monomers (Figures 4 and 5), as well as a resonance-like change in the shape of the optical band of a dye monomer with change in the length of its polymethine chain (Figure 3).

Unlike previous theories of the shape of optical bands of molecular aggregates, based on quantum mechanics and Frenkel's exciton theory, our theory, based on quantum–classical mechanics and Egorov's nano-resonance, makes it possible to explain not only the nature and shape of the J-band of J-aggregates, but also the nature and shape of the polymethine dye monomer bands from which these J-aggregates are formed. This fact made it possible for the first time to theoretically explain all the existing experimental shapes of optical bands of monomers and J-aggregates in well-known concentration equilibria in aqueous solutions of polymethine dyes, as well as to determine the number of molecules that make up the optical J-chromophore, which is four (see Figures 4 and 5).

Based on quantum–classical mechanics [11], the asymmetry of the shape of the luminescence bands of J-aggregates relative to their optical absorption (Figure 9) is also explained, which is associated with a higher degree of organization of the elementary luminescence process compared to the absorption process. The well-known anomalously small Stokes shift of the J-band (Figure 9) is explained by the anomalously large regular component in the chaotic dynamics of the quantum–classical J-transition and the anomalously high degree of loosening of the excited π-electron state of J-aggregates. The shape of the optical bands of dimers, H- and H*-aggregates (Figure 6) is explained by both the presence of charge transfer dynamics and the Frenkel exciton effect (for details, see Section 6). The detuning of the nano-resonance upon the transition from one-photon to two-photon absorption (Figures 10 and 12) is explained by a shift of the main absorption region to the high-frequency region of optical absorption.

The conditions for restoring nano-resonance in two-photon absorption are predicted, which consist of replacing the solvent with a less polar one and/or choosing a dye with a shorter polymethine chain length.

Acknowledgment

Conflicts of interests

The author declares no conflict of interest.

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