computer sciences and mathematics forum

Proceeding Paper

Quantum–Classical Mechanics and Franck-Condon Principle †

Vladimir V. Egorov

Russian Academy of Sciences, FSRC "Crystallography and Photonics", Photochemistry Center, 7a Novatorov Street, 119421 Moscow, Russia; egorovphotonics@gmail.com

† Presented at the 1st International Online Conference on Mathematics and Applications; Available online: https://iocma2023.sciforum.net/.

Abstract: Quantum–classical mechanics and the Franck-Condon principle related to quantum mechanics are discussed as two alternative theoretical approaches to molecular optical spectroscopy. The statement of the problem is connected with the divergence (singularity) of the series of time-dependent perturbation theory in molecular and chemical physics, on which the theory of quantum transitions in quantum mechanics is based. On the example of elementary electron transfers in condensed media, it is shown that this singularity is eliminated by introducing chaos into the electron-nuclear(-vibrational) transient state. This chaos is called dozy chaos, and quantum mechanics itself, supplemented by dozy chaos, is called quantum–classical mechanics. It is shown that the results of quantum–classical mechanics for the case of strong dozy chaos correspond to the physical picture based on quantum mechanics and the Franck-Condon principle. The same chaos can be strong for small molecules in standard molecular spectroscopy and weak at the same time in photochemistry and nanophotonics of large molecules, where quantum mechanics no longer works, but quantum–classical mechanics works, taking into account the chaotic dynamics of transitions. Thus, the erroneous Franck-Condon physical picture of molecular "quantum" transitions is workable from a practical point of view as long as we are dealing with sufficiently small molecules, just as the erroneous geocentric picture of the world is workable until we went out into outer space.

Keywords: transient state dynamics; dozy chaos; quantum–classical mechanics; Franck-Condon principle; charge transfer; condensed matter; optical band shapes; polymethine dyes; J-aggregates; Egorov nano-resonance

Citation: Egorov, V.V. Quantum–Classical Mechanics and Franck-Condon Principle. *Comput. Sci. Math. Forum* **2023**, *6*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s):

Published: 28 April 2023

1. Introduction

As is known, quantum mechanics is inextricably linked with classical mechanics. Its justification is connected with the need to consider the interaction of a microparticle with a macroscopic classical measuring device [1]. The basic dynamical equation, the Schrödinger equation, was postulated by Schrödinger but actually derived from the Hamilton-Jacobi equation for action in classical mechanics by introducing the wave function in some form, which is now called the semiclassical approximation. The width of the levels, "inside which" the energy spectrum is continuous, is a sign of the partially classical nature of the dynamics in quantum systems. Quantum–classical mechanics is not a "mixture" of quantum mechanics and classical mechanics, but is a substantially modified quantum mechanics, in which the initial and final states are quantum in the Born-Oppenheimer adiabatic approximation [2–6], and the chaotic transient state due to chaos is classical. The Franck-Condon principle [7–10] in molecular physics avoids the consideration of transient state dynamics, which is unreasonably assumed to be unimportant. Classicality, which is immanently inherent in quantum mechanics itself, in molecular physics, is supplemented by classicism, which is associated with the Franck-Condon principle. It is assumed that the quantum transition (fast vertical jump) of an electron from the ground to the excited electronic state of the molecule occurs between the turning points of classically moving nuclei, where the nuclei are at rest. In fact, the classical nature of motion in molecular physics is not associated with the Franck-Condon principle, but with the chaotic dynamics of the motion of an electron and nuclei in a transient state.

As is known, the theory of quantum transitions in quantum mechanics is based on the convergence of a series of time-dependent perturbation theory [11]. This series converges in atomic and nuclear physics, as well as in molecular physics, provided that the Born-Oppenheimer adiabatic approximation and the Franck-Condon principle are strictly observed. If this condition is not met, the series of time-dependent perturbation theory diverges. Obviously, in real molecules, the adiabatic approximation is not strictly observed, which makes the application of Franck-Condon principle unfounded in theory, and with it the whole physical picture of molecular transitions based on it. The only physical way to eliminate the singularity of the series of time-dependent perturbation theory in molecular physics is the postulate of the presence of dynamics in the transient electron-nuclear(-vibrational) state, which the Franck-Condon principle ignores, and that this dynamics is chaotic. In this case, in the case of strong chaos, as in the case of the Franck-Condon picture of molecular transitions, the transition rates do not depend on the specific dynamics of the transient state, but depend only on the initial and final states, taken in the adiabatic approximation. In the case of weak chaos, against the background of chaos, the regular nature of the dynamics of the transient state manifests itself. Chaos, which is weak in the case of large molecules, may be strong in the case of small molecules. Therefore, the Franck-Condon picture of transitions often gives good agreement with experimental data on optical spectra in conventional molecular spectroscopy [12–14] of small molecules. In photochemistry and nanophotonics, where, as a rule, we deal with large molecules, where chaos is not strong, but weak, elements of dynamic self-organization often appear in the chaotic dynamics of the transient state. A striking example of this is the well-known narrow and intense J-band of J-aggregates of polymethine dyes [15–24], which can no longer be explained on the basis of quantum mechanics, but finds its explanation in quantum–classical mechanics as a Egorov nano-resonance [25–34]. Thus, in the case of small molecules, the Franck-Condon principle gives the correct result, although an erroneous theory and an erroneous physical picture are used. In the case of large molecules, this erroneous theory and the erroneous physical picture no longer lead to the correct result. The analogue of this situation is well known.

This analogue is the collision between two pictures of the world, namely, geocentric and heliocentric. As is well known, the correct picture is the heliocentric picture of the world, in which the Earth rotates both around the Sun and around its own axis. However, being on the surface of the Earth, the rotation of the Earth around its own axis is perceived by the observer as the movement of the Sun across the sky, which is well simulated by an erroneous geocentric picture. It is even customary to talk about the time of sunrise and the time of its sunset at a given particular point on the surface of the Earth. However, the exit from the surface of the Earth to a sufficiently large distance into space directly shows the fallacy of the geocentric picture of the world.

At present, quantum–classical mechanics and the physical picture of molecular "quantum" transitions corresponding to it are based on their simplest example, namely, on the example of quantum–classical mechanics of elementary electron transfers in condensed media [31,35]. Here, chaos is introduced into the transient state by replacing the infinitely small imaginary additive in the energy denominator of the total Green's function of the system by a finite value [27,31,35]. This chaos is called dozy chaos [28,29].

It is shown below that the result of quantum–classical mechanics of elementary electron transfers for the case of strong dozy chaos corresponds to the result based on quantum mechanics and the Franck-Condon principle. Also, using the example of the transformation of the shape of the optical absorption band in quantum–classical mechanics, it is shown how, with a decrease in the extent of the quantum–classical transition, the result of quantum–classical mechanics, where dozy chaos is rather weak, passes into the result of quantum mechanics, where the same dozy chaos is already strong enough.

2. Quantum–Classical Mechanics of Elementary Electron Transfers in Condensed Media

In a sense, quantum–classical mechanics of elementary electron transfers in condensed media [31,35] is a generalization of the theory of many-phonon transitions [3] based on quantum mechanics, the Born-Oppenheimer adiabatic approximation and the Franck-Condon principle, where the simplest problem solved was the problem on the shape of optical bands arising as a result of many-phonon transitions in F-centers [36–39]. It was in the case of this problem of elementary electron transfers that the Egorov nanoresonance (see Sections 1 and 3) was discovered [30–32]: the region of space of the molecular system, in which such a resonant transition is localized, is determined by the distance between the donor and acceptor, when it is on the order of a nanometer. Compared to the simplest Hamiltonian, which was used in the F-center problem, our Hamiltonian is complicated only by an additional electron potential well [3,28–32,35]:

$$H = -\frac{\hbar^2}{2m}\Delta_{\mathbf{r}} + V_1(\mathbf{r}) + V_2(\mathbf{r}-\mathbf{L}) + \sum_{\kappa} V_{\kappa}(\mathbf{r})\, q_{\kappa} + \frac{1}{2}\sum_{\kappa}\hbar\omega_{\kappa}\left(q_{\kappa}^2 - \frac{\partial^2}{\partial q_{\kappa}^2}\right), \quad (1)$$

where the first term corresponds to the kinetic energy of the electron with an effective mass m, the last term corresponds to the kinetic and potential energy of vibrations of the nuclei of the medium in the harmonic approximation, q_{κ} are the real normal phonon coordinates, ω_{κ} are the phonon frequencies, $V_1(\mathbf{r})$ and $V_2(\mathbf{r}-\mathbf{L})$ are the potential wells of the electron donor 1 and acceptor 2 separated by distance $L \equiv |\mathbf{L}|$, the term $\sum_{\kappa} V_{\kappa}(\mathbf{r})\, q_{\kappa}$ corresponds to the electron-phonon interaction, κ is the phonon index.

The considered below energy (Sections 3–5)

$$E = \frac{1}{2}\sum_{\kappa}\hbar\omega_{\kappa}\tilde{q}_{\kappa}^2\,, \quad (2)$$

is the energy of reorganization of the medium nuclei associated with the localization of an electron on the donor or acceptor. The quantities $\tilde{q}_{\kappa}$ are the shifts of the normal phonon coordinates q_{κ} associated with this presence of an electron in the medium.

As shown in my pioneering works [30–32], an attempt to take into account the transient state dynamics by the Green’s function method in quantum mechanics with Hamiltonian (1) leads to a significant singularity in the rates of “quantum” transitions.

This singularity is eliminated by replacing the infinitesimally small γ with a finite quantity [28–35,40] in the Green’s function

$$G_H(\mathbf{r},\mathbf{r}';q,q';E_H) = \sum_{s}\frac{\Psi_s(\mathbf{r},q)\,\Psi_s{}^{*}(\mathbf{r}',q')}{E_H - E_s - i\gamma}, \quad (3)$$

where $\Psi_s(\mathbf{r},q)$ are the eigenfunctions of the Hamiltonian (1); $(\mathbf{r},q)$ are all electronic and nuclear coordinates; E_s are the eigenvalues of H, and E_H is the total energy of the system. The aforementioned replacement of γ with a finite quantity in Equation (3), or in similar Green’s functions of more complex molecular and/or condensed matter systems, lies at the foundation of a new theory—dozy-chaos or quantum–classical mechanics [35] (cf. Section 1).

Comparison of theory with experiment shows that $\gamma >> \hbar\omega$ ($\omega_{\kappa} = \text{constant} \equiv \omega$, see below, Section 3) [25,26,28–34,40]. Therefore, the energy γ is a measure of dynamic or dozy chaos in the transient state and can be called dozy-chaos energy [28,29] (see Figure 1). Dozy chaos is a “sum” of chaotic motions of the electronic charge and nuclear reorganization and “plus” fluctuating electromagnetic field (dozy-chaos radiation) that provides interaction between electrons and nuclei [41,42].

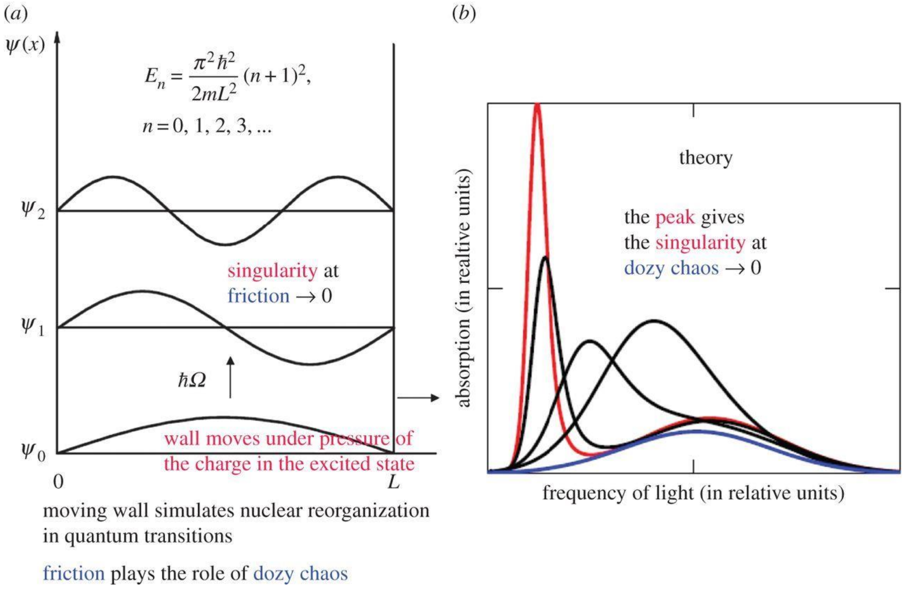

Figure 1. The simplest demonstration of singularity in the rate of molecular "quantum" transitions [33–35,40]. (***a***) The physical picture of quantum transitions in a potential box with a moving wall simulates the presence of a singularity in molecular "quantum" transitions when the wall moves without friction [33–35,40]. The case of a wall moving with friction corresponds to quantum–classical (dozy-chaos) mechanics [30–32,35], in which dozy chaos plays the role of friction. (***b***) Shapes of optical absorption bands obtained from dozy-chaos mechanics, as a function of dozy-chaos intensity [33–35,40]. The band with the most pronounced peak (J-band, red) corresponds to the weakest dozy chaos. The Gaussian-like band (blue) corresponds to the strongest dozy chaos. (Original citation)—Reproduced by permission of The Royal Society of Chemistry.

The main source of dozy chaos is a light and mobile electron, the motion of which, together with the entire molecular system associated with it, is subject to a new, dozy-chaos mechanics [35] (cf. Section 1).

The emergence of dozy-chaos mechanics can be considered as some generalization of the well-known theory of many-phonon transitions [3], which is a quantum mechanics of condensed matter [43].

Due to chaos, the energy spectrum of the entire system in a transient state is continuous. Therefore, dozy-chaos mechanics can also be called quantum–classical mechanics [35] (cf. Section 1).

Apparently, the root cause of the emergence of dozy chaos lies in the interaction of the actual electron with the induction field of optical phonons [43]. However, the clarification of this issue can be obtained only after creating quantum–classical electrodynamics, which will be created in future similarly to how quantum electrodynamics [44–46] was created in due time after the creation of quantum mechanics [1,11].

There is an obvious analogy in the history of the discovery of the elementary quantum of action, Planck's constant $\hbar$ [47], and the discovery of the dozy-chaos energy γ [28–32,35,41,43]. However, $\hbar$ is a universal physical constant, while γ is not a universal physical constant and its value depends on a specific physical systems. As a comparison of theory with experiment shows, the numerical value of the energy γ is not completely indefinite, but approximately ranges from $\gamma \cong E$ (strong dozy chaos) to $\hbar\omega << \gamma << E$ (weak dozy chaos).

If we keep in mind the inseparable connection between quantum mechanics and classical mechanics, which was noted above (see Section 1), then we can say that Planck's constant $\hbar$ is a hidden parameter in classical mechanics, and dozy-chaos energy γ is a hidden parameter in quantum mechanics.

3. Shape of the Optical Absorption Band and Egorov Nano-Resonance (Enr)

In this section, we present the analytical result for absorption band shapes $K = K(\Omega)$ (Equations (4)–(24), Ω is frequency of light) [28–35,40] shown below (see Figures 1 and 2Figure 1; Figure 2). In the framework of the Einstein model of nuclear vibrations ($\omega_\kappa = \text{constant} \equiv \omega$) this result is as follows [31,32,35]:

$$K = K_0 \exp W, \tag{4}$$

$$\begin{aligned} W = \frac{1}{2}\ln\left(\frac{\omega\tau\sinh\beta_T}{4\pi\cosh t}\right) - \frac{2}{\omega\tau}\left(\coth\beta_T - \frac{\cosh t}{\sinh\beta_T}\right) \\ + (\beta_T - t)\frac{1}{\omega\tau\Theta} - \frac{\sinh\beta_T}{4\omega\tau\Theta^2\cosh t}, \end{aligned} \tag{5}$$

$$1 << \frac{1}{\omega\tau\Theta} \le \frac{2\cosh t}{\omega\tau\sinh\beta_T}, \tag{6}$$

where $\beta_T \equiv \hbar\omega/2k_\mathrm{B}T$, T is the absolute temperature,

$$t = \frac{\omega\tau_\mathrm{e}}{\theta}\left[\frac{AC+BD}{A^2+B^2} + \frac{2\Theta(\Theta-1)}{(\Theta-1)^2 + (\Theta/\theta_0)^2} + \frac{\theta_0^{\,2}}{\theta_0^{\,2}+1}\right], \tag{7}$$

$$|\theta_0| >> \frac{E}{2J_1}, \tag{8}$$

$$\theta \equiv \frac{\tau_\mathrm{e}}{\tau} = \frac{L\,E}{\hbar\sqrt{2J_1/m}}, \quad \Theta \equiv \frac{\tau'}{\tau} = \frac{E}{\Delta}, \quad \theta_0 \equiv \frac{\tau_0}{\tau} = \frac{E}{\gamma}, \tag{9}$$

$$\tau_\mathrm{e} = \frac{L}{\sqrt{2J_1/m}}, \quad \tau = \frac{\hbar}{E}, \quad \tau' = \frac{\hbar}{\Delta}, \quad \tau_0 = \frac{\hbar}{\gamma}. \tag{10}$$

Here, we use the notation

$$A = \cos\left(\frac{\theta}{\theta_0}\right) + \Lambda + \left(\frac{1}{\theta_0}\right)^2 \mathrm{N}, \tag{11}$$

$$B = \sin\left(\frac{\theta}{\theta_0}\right) + \frac{1}{\theta_0}\mathrm{M}, \tag{12}$$

$$C = \theta\left[\cos\left(\frac{\theta}{\theta_0}\right) - \frac{1-\xi^2}{2\theta_0}\sin\left(\frac{\theta}{\theta_0}\right)\right] + \mathrm{M}, \tag{13}$$

$$D = \theta\left[\sin\left(\frac{\theta}{\theta_0}\right) + \frac{1-\xi^2}{2\theta_0}\cos\left(\frac{\theta}{\theta_0}\right)\right] - \frac{2}{\theta_0}\mathrm{N}, \tag{14}$$

and

$$\xi \equiv \left(1 - \frac{E}{J_1}\right)^{1/2} \qquad (J_1 > E \text{ by definition}), \tag{15}$$

and where we finally have

$$\Lambda = -(\Theta-1)^2 \mathrm{E} + \left[\frac{(\Theta-1)\theta}{\rho} + \Theta(\Theta-2) \right] \mathrm{E}^{\frac{1-\rho}{1-\xi}}, \tag{16}$$

$$\mathrm{M} = 2\Theta(\Theta-1)\mathrm{E} - \left[\frac{(2\Theta-1)\theta}{\rho} + 2\Theta(\Theta-1) \right] \mathrm{E}^{\frac{1-\rho}{1-\xi}}, \tag{17}$$

$$\mathrm{N} = \Theta\left[\Theta\mathrm{E} - \left(\frac{\theta}{\rho} + \Theta \right) \mathrm{E}^{\frac{1-\rho}{1-\xi}} \right], \tag{18}$$

$$\mathrm{E} \equiv \exp\left(\frac{2\theta}{1+\xi} \right), \qquad \rho \equiv \sqrt{\xi^2 + \frac{1-\xi^2}{\Theta}}. \tag{19}$$

The factor K_0 becomes

$$K_0 = K_0^e K_0^p, \tag{20}$$

where

$$K_0^e = \frac{2\tau^3 J_1}{m} \frac{\left(A^2 + B^2\right)\rho^3 \Theta^4 \xi}{\theta^2 \left[(\Theta-1)^2 + \left(\frac{\Theta}{\theta_0} \right)^2 \right]^2 \left[1 + \left(\frac{1}{\theta_0} \right)^2 \right]} \cdot \eta, \tag{21}$$

and

$$\eta \equiv \exp\left(-\frac{4\theta}{1-\xi^2} \right), \tag{22}$$

and

$$K_0^p = \frac{1}{\omega\tau} \left[1 + \frac{\sinh(\beta_T - 2t)}{\sinh \beta_T} \right]^2 + \frac{\cosh(\beta_T - 2t)}{\sinh \beta_T}. \tag{23}$$

In Equations (9) and (10), $\Delta > 0$ is the heat energy associated with the energy $\hbar\Omega$ of the absorbed photon by the law of energy conservation:

$$\hbar\Omega = J_1 - J_2 + \Delta, \tag{24}$$

where J_1 and J_2 are the electron binding energy at the donor 1 and acceptor 2.

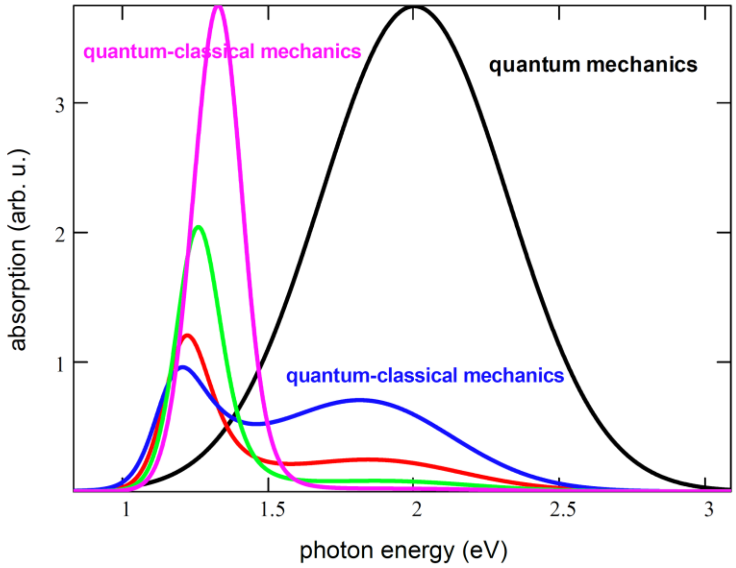

Figure 2. Quantum–classical mechanics: transformation of the theoretical absorption spectra of a model polymethine dye with different extents of quantum–classical transitions (different lengths of polymethine chains) L. Optical bands are calculated from Equations (4)–(24) (η = 1 [28–34,40] in Equations (21) and (22)). The following numerical values of the parameters are used: $m = m_e$, where m_e is the electron mass; n_{refr} = 1.33; $\omega = 5 \times 10^{13}$ s^{-1}; J_1 = 5 eV; $J_1 - J_2$ = 0.5 eV; E = 1 eV; γ = 0.34 eV; and T = 298 K [26,27]. In this figure, for simplicity, the energy gap $J_1 - J_2 \equiv 0$. Extent of the quantum–classical transition $L = 1.4\, L_0$ (blue), L_0 (red), 0.7 L_0 (green), 0.45 L_0 (magic), где $L_0 \equiv L$(Enr) = 0.384 nm [26,27]. **Quantum mechanics:** Gaussian absorption spectrum (black) given by Equation (28), where E = 1 eV and T = 298 K.

The time scales given by Equation (10) control the chaotic dynamics of the transient state of elementary electron transfers in condensed media. They are discussed in [28,29,32,33,35,48–50]. The donor–acceptor distance L is also equal to the length of the polymethine chain—the main optical chromophore of polymethine dyes, where the electronic charge on carbon atoms alternates along the chain and alternatively redistributes upon optical excitation; therefore, in Equations (21) and (22), we can often take $\eta \approx 1$ [28–34,40].

Given by Equation (10) the time scales

$$\tau_e = \frac{L}{\sqrt{2J_1/m}} \tag{25}$$

(the characteristic time of motion of the electron in the donor–acceptor system) and

$$\tau = \frac{\hbar}{E} \tag{26}$$

(the characteristic time of motion of the reorganization of nuclear vibrations in the environment) are included in the Egorov nano-resonance (see Section 1) [25–34] as follows

$$(2\tau_e)^{-1} = \tau^{-1}. \tag{27}$$

4. Passage to the Standard Theory Based on Quantum Mechanics, Born-Oppenheimer Adiabatic Approximation and Franck-Condon Principle

Just as there is no strict limit transition from quantum mechanics to classical mechanics, so there is no strict limit transition from quantum–classical mechanics to quantum mechanics. The standard result in the theory of many-phonon transitions [3] is effected from Equations (4)–(24) by $\gamma \to \infty$ ($\theta_0 \to 0$ according to Equation (9)) in Equation (7) for t (see Figure 3 in [35]) and by $\gamma \to 0$ ($\theta_0 \to \infty$) in Equation (21) for K_0^e (see Equation (162) in [35]) [31,35]:

$$K = \frac{a^2\hbar}{\sqrt{4\pi\lambda_\mathrm{r} k_\mathrm{B} T}} \exp\left(-\frac{2L}{a}\right) \exp\left[-\frac{(\Delta - \lambda_\mathrm{r})^2}{4\lambda_\mathrm{r} k_\mathrm{B} T}\right], \tag{28}$$

where $a \equiv \hbar / \sqrt{2mJ_1}$ and $\lambda_\mathrm{r} \equiv 2E$. The Gaussian formula (Marcus formula, see below)

$$K = K(\Delta) \propto \exp\left[-\frac{(\Delta - \lambda_\mathrm{r})^2}{4\lambda_\mathrm{r} k_\mathrm{B} T}\right]$$

is the well-known simplest result in the theory of many-phonon transitions for $k_\mathrm{B} T > \hbar\omega/2$ (see [3,4]) and is associated with the works of Marcus on his electron-transfer model [51–56], and with the previous works by Huang and Rhys [57], Pekar [36–38], Lax [58], Krivoglaz and Pekar [39], and Krivoglaz [59]. Usually, the aforementioned Gaussian formula is called the Marcus formula, and the energy λ_r is called the Marcus reorganization energy. In contrast to Equations (4)–(24), where the dynamics of the transient state is properly taken into account, in Equation (28) and the Marcus formula the dynamics of the transient state is completely neglected.

So, the result (4)–(24) of quantum–classical mechanics, in none of the limiting cases of γ, zero or infinity, does not pass into any result of quantum mechanics. With $\gamma \to 0$, we get infinity for the transition rate, and with $\gamma \to \infty$, we get zero for it. This situation is easy to understand from a qualitative examination of quantum–classical transitions in a potential box with a movable wall, the movement of which simulates the reorganization of the positions of the nuclei in space during electronic transitions, see Figure 1*a*; the graphs in Figure 1*b* (Equations (4)–(24)) explain this situation as well.

In Figure 1*b*, the shift of the optical band peak to the red region and its narrowing with decreasing γ is explained by the decrease in friction at the base of the moving wall (see Figure 1*a*): higher wall mobility leads to a greater decrease in the effective gap between the ground and excited electronic energy levels and to a higher the degree of organization of the quantum–classical transition.

The fact that there is no rigorous transition from quantum–classical mechanics to quantum mechanics indicates the fundamental novelty of quantum–classical mechanics, which is fundamentally not reduced to quantum mechanics [27].

5. Extent of Quantum–Classical Transitions as a Measure of Dozy Chaos

From general considerations, one can expect that weak chaos of any physical nature in large systems can turn out to be strong chaos for small systems. Therefore, one would expect dozy chaos to be no exception in this respect. In other words, the weak dozy chaos in long-extended quantum–classical transitions can look like a strong dozy chaos for short-extended quantum–classical transitions. Figure 2 demonstrates this. The Gaussian shape of the optical band (Figure 2, black graph), obtained as a result of the "limit transition" from quantum–classical mechanics to quantum mechanics, i.e., as a result of the limiting transition of dozy-chaos energy γ to infinity in the exponent (see details in Section 4), corresponds to an extremely strong dozy chaos. This means that if, for example, with a decrease in a sufficiently large length of the polymethine chain *L* (a decrease in the extent of the quantum–classical transition) and the constancy of all other parameters of the system, including a sufficiently small value of γ, corresponding to weak dozy chaos ($\gamma << E$, see Section 2), as a result, we obtain a Gaussian-like band, then this band corresponds to effectively strong dozy chaos at small *L*. Figure 2 (colored graphs) demonstrates the transformation of the shape of the optical band as a result of a decrease in the extent of the quantum–classical transition, which leads to just such a transient state with an effectively strong dozy chaos (magic graph).

The shift of the Gaussian-like band (magic) to the red region and its narrowing with respect to the Gaussian band (black) from quantum mechanics is explained by the presence of a chaotic transient state in quantum–classical mechanics, which is absent in quantum mechanics by definition. The presence of a chaotic transient state leads to some effective reorganization energy of lesser energy *E*: a part of the reorganization energy *E* is represented in quantum–classical mechanics as a chaotic, dynamic transient state reorganization energy, which is formally expressed in dozy-chaos energy γ. Another way of interpreting the discussed effects follows from the consideration of a potential box with a movable wall (Figure 1*a*). We can say that the moving wall, which simulates nuclear reorganization in quantum–classical mechanics, has a much smaller "mass" compared to the "mass" of a fixed wall in quantum mechanics. If we correlate the "mass" of the wall with the value of the reorganization energy, similarly to how we correlated the friction value at the wall base with the value of dozy-chaos energy above, then here the discussed effects find their analogous explanation at the qualitative level [26,27]. Another qualitative explanation of the ''redshift'' and narrowing with decreasing nuclear reorganization energy is based on the use of standard theory and can be found in [40] (see Figures 3 and 4 therein).

Thus, using the example of the transformation of the shape of the optical absorption band, it is shown that with a decrease in the extent of the quantum–classical transition, the result of quantum–classical mechanics, where the dozy chaos is sufficiently weak, essentially passes into the result of quantum mechanics, where the same dozy chaos is already sufficiently strong. Therefore, as a measure of dozy chaos, one can consider not only the dozy-chaos energy γ, but also the extent of quantum–classical transitions *L*.

6. Conclusions

It is shown that in quantum–classical mechanics, in the case of strong dozy chaos, which is almost always realized for sufficiently small molecules, the rates of quantum–classical transitions do not depend on the specific dynamics of the transient state, but depend only on the initial and final states. As is known, we have the same result in the standard Franck-Condon picture obtained in the framework of quantum mechanics (see, e.g., [11]). Thus, we get an explanation why the erroneous standard Franck-Condon picture [7–10] (see Section 1), in the case of sufficiently small molecules, is able to interpolate experimental data [12–14] well in standard molecular spectroscopy. We note that a sophisticated researcher, especially a theoretical physicist, should not be confused by the conclusion that an erroneous theory and an erroneous physical picture can often agree with experimental data. For example, the erroneous Aristotelian geocentric picture of the world has existed in human civilization for hundreds of years and quite suited it from a practical point of view. If we ignore the genius of Galileo and other innovators like him, then the need for the appearance of a correct, namely heliocentric, picture of the world arose in practice only with the release of mankind into space. A similar need arises in our time in the quantum physics of molecular physico-chemical systems and in the quantum physics of condensed matter. Namely, this need is expressed in the creation and development of quantum–classical mechanics in their exhaustive completeness to account for the chaotic dynamics of the transient state in extended systems.

Funding: This work was performed within the State assignment of Federal Scientific Research Center "Crystallography and Photonics" of Russian Academy of Sciences.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Landau, L.D.; Lifshitz, E.M. *Quantum Mechanics, Non-Relativistic Theory*, 3rd ed.; Elsevier: Amsterdam, The Netherlands, 1977.
2. Born, M.; Oppenheimer, J.R. Quantum theory of the molecules. *Ann. Phys.* **1927**, *84*, 457–484.
3. Perlin, Y.E. Modern methods in the theory of many-phonon processes. *Sov. Phys. Uspekhi* **1964**, *6*, 542–565.
4. Frank-Kamenetskii, M.D.; Lukashin, A.V. Electron-vibrational interactions in polyatomic molecules. *Sov. Phys. Uspekhi* **1975**, *18*, 391–409.
5. Bersuker, I.B.; Polinger, V.Z. *Vibronic Interactions in Molecules and Crystals*; Springer: New York, NY, USA, 1989.
6. Stanke, M. Adiabatic, Born-Oppenheimer, and non-adiabatic approaches. In *Handbook of Computational Chemistry*; Leszczynski, J., Kaczmarek-Kedziera, A., Puzyn, T., Papadopoulos, M.G., Reis, H., Shukla, M.K., Eds.; Springer: Cham, Switzerland, 2017; pp. 173–223.
7. Franck, J.; Dymond, E.G. Elementary processes of photochemical reactions. *Trans. Faraday Soc.* **1925**, *21*, 536–542.
8. Condon, E.U. A theory of intensity distribution in band systems. *Phys. Rev.* **1926**, *28*, 1182–1201.
9. Condon, E.U. Nuclear motions associated with electron transitions in diatomic molecules. *Phys. Rev.* **1928**, *32*, 858–872.
10. Condon, E.U. The Franck-Condon principle and related topics. *Am. J. Phys.* **1947**, *15*, 365–374.
11. Davydov, A.S. *Quantum Mechanics*; Pergamon Press: Oxford, UK, 1976.
12. Herzberg, G.; Spinks, J.W.T. *Molecular Spectra and Molecular Structure. 1. Spectra of Diatomic Molecules*; Prentice-Hall: New York, NY, USA, 1939.
13. Herzberg, G. *Molecular Spectra and Molecular Structure. 2. Infrared and Raman Spectra*; D. Van Nostrand: Princeton, NJ, USA, 1945.
14. Herzberg, G. *Molecular Spectra and Molecular Structure. 3. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, NY, USA; London, UK, 1966.
15. Jelley, E.E. Spectral absorption and fluorescence of dyes in the molecular state. *Nature* **1936**, *138*, 1009–1010.
16. Jelley, E.E. Molecular, nematic and crystal states of 1:1′-diethyl-ψ-cyanine chloride. *Nature* **1937**, *139*, 631–632.
17. Scheibe, G. Variability of the absorption spectra of some sensitizing dyes and its cause. *Angew. Chem.* **1936**, *49*, 563.
18. Scheibe, G. On the variability of the absorption spectra in solutions and the secondary bonds as its cause. *Angew. Chem.* **1937**, *50*, 212–219.
19. Herz, A.H. Aggregation of sensitizing dyes in solution and their adsorption onto silver halides. *Adv. Colloid Interface Sci.* **1977**, *8*, 237–298.
20. James, T.H. (Ed.) *The Theory of the Photographic Process*; Macmillan: New York, NY, USA, 1977.
21. Kobayashi, T. (Ed.) *J-Aggregates*; World Scientific: Singapore, 1996.
22. Würthner, F.; Kaiser, T.E.; Saha-Möller, C.R. J-aggregates: From serendipitous discovery to supra-molecular engineering of functional dye materials. *Angew. Chem. Int. Ed.* **2011**, *50*, 3376–3410.
23. Aviv, H.; Tischler, Y.R. Synthesis and characterization of a J-aggregating TDBC derivative in solution and in Langmuir-Blodgett films. *J. Lumin.* **2015**, *158*, 376–383.
24. Bricks, J.L.; Slominskii, Y.L.; Panas, I.D.; Demchenko, A.P. Fluorescent J-aggregates of cyanine dyes: Basic research and applications review. *Methods Appl. Fluoresc.* **2018**, *6*, 012001.
25. Petrenko, A.; Stein, M. Toward a molecular reorganization energy-based analysis of third-order nonlinear optical properties of polymethine dyes and J-aggregates. *J. Phys. Chem. A* **2019**, *123*, 9321–9327.
26. Egorov, V.V.; Thomas, S. Quantum-classical mechanics: On the problem of a two-photon resonance band shape in polymethine dyes. *Nano-Struct. Nano-Objects* **2021**, *25*, 100650.
27. Egorov, V.V. Quantum–classical mechanics: Nano-resonance in polymethine dyes. *Mathematics* **2022**, *10*, 1443.
28. Egorov, V.V.; Alfimov, M.V. Theory of the J-band: From the Frenkel exciton to charge transfer. *Phys. Uspekhi* **2007**, *50*, 985–1029.
29. Egorov, V.V. Theory of the J-band: From the Frenkel exciton to charge transfer. *Phys. Procedia* **2009**, *2*, 223–326.

30. Egorov, V.V. Electron-transfer approach to the nature of the optical lineshape for molecular J-aggregates. *Chem. Phys. Lett.* **2001**, *336*, 284–291.
31. Egorov, V.V. On electrodynamics of extended multiphonon transitions and nature of the J-band. *Chem. Phys.* **2001**, *269*, 251–283.
32. Egorov, V.V. Nature of the optical transition in polymethine dyes and J-aggregates. *J. Chem. Phys.* **2002**, *116*, 3090–3103.
33. Egorov, V.V. Nature of the optical band shapes in polymethine dyes and H-aggregates: Dozy chaos and excitons. Comparison with dimers, H*- and J-aggregates. *R. Soc. Open Sci.* **2017**, *4*, 160550.
34. Egorov, V.V. Quantum-classical mechanics: Luminescence spectra in polymethine dyes and J-aggregates. Nature of the small Stokes shift. *Results Phys.* **2019**, *13*, 102252.
35. Egorov, V.V. Quantum-classical mechanics as an alternative to quantum mechanics in molecular and chemical physics. *Heliyon Phys.* **2019**, *5*, e02579.
36. Pekar, S.I. Theory of F-centers. *Zh. Eksp. Teor. Fiz.* **1950**, *20*, 510–522. (In Russian)
37. Pekar, S.I. To the theory of luminescence and light absorption by impurities in dielectrics. *Zh. Eksp. Teor. Fiz.* **1952**, *22*, 641–657. (In Russian)
38. Pekar, S.I. On the effect of lattice deformations by electrons on optical and electrical properties of crystals. *Uspekhi Fiz. Nauk* **1953**, *50*, 197–252. (In Russian)
39. Krivoglaz, M.A.; Pekar, S.I. The shape of the spectra of the impurity light absorption and luminescence in dielectrics. *Tr. Inst. Fiz. Akad. Nauk UKR SSR* **1953**, *4*, 37–70. (In Russian)
40. Egorov, V.V. Optical lineshapes for dimers of polymethine dyes: Dozy-chaos theory of quantum transitions and Frenkel exciton effect. *RSC Adv.* **2013**, *3*, 4598–4609.
41. Egorov, V.V. Discovery of Dozy Chaos and Discovery of Quanta: Analogy Being in Science and Perhaps in Human Progress. In Chaos and Complex Systems, Proceedings of the 4th International Interdisciplinary Chaos Symposium, Antalya, Turkey, 29 April–2 May 2012; Stavrinides, S.G., Banerjee, S., Caglar, H., Ozer, M., Eds.; Springer: Berlin, Germany, 2013; pp. 41–46.
42. Egorov, V.V. Dozy Chaos in Chemistry: Simplicity in Complexity. In Chaos and Complex Systems, Proceedings of the 4th International Interdisciplinary Chaos Symposium, Antalya, Turkey, 29 April–2 May 2012; Stavrinides, S.G., Banerjee, S., Caglar, H., Ozer, M., Eds.; Springer: Berlin, Germany, 2013; pp. 219–224.
43. Egorov, V.V. Dozy-chaos mechanics for a broad audience. *Challenges* **2020**, *11*, 16.
44. Dirac, P.A.M. The quantum theory of the emission and absorption of radiation. *Proc. R. Soc. Lond. Ser. A Math. Phys. Sci.* **1927**, *114*, 243–265.
45. Fermi, E. Quantum theory of radiation. *Rev. Mod. Phys.* **1932**, *4*, 87–132.
46. Berestetskii, V.B.; Lifshitz, E.M.; Pitaevskii, L.P. *Quantum Electrodynamics*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1982.
47. Planck, M. On the law of distribution of energy in the normal spectrum. *Ann. Phys.* **1901**, *309*, 553–563.
48. Egorov, V.V. Dynamic symmetry in dozy-chaos mechanics. *Symmetry* **2020**, *12*, 1856.
49. Egorov, V.V. Dynamic symmetry in dozy-chaos mechanics. In *Symmetry in Chaotic Systems and Circuits*; Volos, C., Ed.; Multidisciplinary Digital Publishing Institute (MDPI): Basel, Switzerland, 2022; pp. 199–217.
50. Egorov, V.V. Dynamic pumping of elementary charge transfer by environmental dissipative reorganization. *Russ. J. Electrochem.* **2003**, *39*, 86–96.
51. Marcus, R.A. On the theory of oxidation-reduction reactions involving electron transfer. I. *J. Chem. Phys.* **1956**, *24*, 966–978.
52. Marcus, R.A. Electrostatic free energy and other properties of states having nonequilibrium polarization. *J. Chem. Phys.* **1956**, *24*, 979–989.
53. Marcus, R.A. On the theory of oxidation-reduction reactions involving electron transfer. II. Applications to data on the rates of isotopic exchange reactions. *J. Chem. Phys.* **1957**, *26*, 867–871.
54. Marcus, R.A. On the theory of oxidation-reduction reactions involving electron transfer. III. Applications to data on the rates of organic redox reactions. *J. Chem. Phys.* **1957**, *26*, 872–877.
55. Marcus, R.A.; Sutin, N. Electron transfers in chemistry and biology. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.
56. Marcus, R.A. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* **1993**, *65*, 599–610.
57. Huang, K.; Rhys, A. Theory of light absorption and non-radiative transitions in F-centres. *Proc. R. Soc. A* **1950**, *204*, 406–423.
58. Lax, M. The Franck-Condon principle and its application to crystals. *J. Chem. Phys.* **1952**, *20*, 1752–1760.
59. Krivoglaz, M.A. The theory of thermal transitions. *Zh. Eksp. Teor. Fiz.* **1953**, *25*, 191–207. (In Russian)