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The Excitonic Insulator Route through a Dynamical Phase Transition Induced by an Optical Pulse¹

S. Brazovskii^{a, b*} and N. Kirova^c

^a LPTMS, CNRS, Univ. Paris-sud, Université Paris-Saclay 91405, Orsay, France

^b Jozef Stefan Institute SI-1000, Ljubljana, Slovenia

^c LPS, CNRS, Univ. Paris-sud, Université Paris-Saclay 91405, Orsay, France

*e-mail: brazov@lptms.u-psud.fr

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Abstract—We consider a dynamical phase transition induced by a short optical pulse in a system prone to thermodynamical instability. We address the case of pumping to excitons whose density contributes directly to the order parameter. To describe both thermodynamic and dynamic effects on equal footing, we adopt a view of the excitonic insulator for the phase transition and suggest a formation of the Bose condensate for the pumped excitons. The work is motivated by experiments in donor–acceptor organic compounds with a neutral-ionic phase transition coupled to the spontaneous lattice dimerization and to charge transfer excitons. The double nature of the ensemble of excitons leads to an intricate time evolution, in particular, to macroscopic quantum oscillations from the interference between the Bose condensate of excitons and the ground state of the excitonic insulator. The coupling of excitons and the order parameter also leads to self-trapping of their wave function, akin to self-focusing in optics. The locally enhanced density of excitons can surpass a critical value to trigger the phase transformation, even if the mean density is below the required threshold. The system is stratified in domains that evolve through dynamical phase transitions and sequences of merging. The new circumstances in experiments and theory bring to life, once again, some remarkable inventions made by L.V. Keldysh.

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1. INTRODUCTION

1.1. Aftermaths of Optical Pulses: from Bose–Einstein Condensation of Excitons to the Excitonic Insulator

Phase transformations induced by short optical pulses are a new mainstream in studies of cooperative electronic states (see materials of recent meetings [1–3] and the collection [4]). In experiments on pump-induced phase transitions (PIPT) in electronic systems, the pumping usually proceeds via transitions among filled and empty electronic bands. A more special and rare technique is the pumping to bound excitations; the excitons whose concentration can reach a very high value of 10% per unit cell.

In its pure form, such an ensemble of excitons can already show a number of coherent effects, including their Bose–Einstein condensation (BEC), the idea of which was pioneered by Keldysh and co-authors [5]. In theory, this prediction was followed and elaborated through decades till nowadays (see, e.g., [6] and recent review [7]). About the same time, the word “exciton”

was introduced in another concept, that of an excitonic insulator [8], following a vague suggestion in [9] and its first elaboration in [10]. The excitonic insulator is a hypothetical phase of a semiconductor that appears if the total energy of an exciton $E_{\text{ex}} = E_g - E_b$ vanishes, $E_{\text{ex}} \rightarrow 0$. This possibility implies that the conduction gap E_g and the binding energy E_b can be manipulated (e.g., by pressure or composition) independently. Soon, it became clear that the excitonic insulator is a mirror part of the Keldysh–Kopaev state that had already been suggested in [11]. The “excitonic insulator” became the common nickname for a state formed by the appearance of the electron-hole condensate on top of a semiconducting or a semimetallic state. A large number of theoretical studies followed soon (e.g., [12–15] in the first wave). The notion of the excitonic insulator is revived nowadays as a convenient interpretation of phase transitions in various electronic materials [16–18]. We also recall the old suggestions and attempts to reach the excitonic insulator state by means of extreme conditions such as high

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magnetic fields (see [19, 20] for experiments and [21, 22] for peculiarities in a theory).

Already in static conditions, the microscopic theory of the thermodynamic excitonic insulator phase just below the transition and the theory of the BEC of optically pumped excitons are closely related, differing mostly by the respective monitoring parameters: the chemical potential μ_{ex} and the density n_{ex} of excitons. For the optical pumping, this duality was strongly emphasized later, around 1990, in a new wave of the theory of intense optical pumping in semiconductors. A more recent publication [23] offers a good literature review and a systematic refinement of these results. The studies were provoked by observations of the optical Stark effect for a nonresonant pumping (with the photon energy below E_{ex}) when the excitonic insulator appears virtually and lasts only in the course of pumping. For what was called a resonant pumping (i.e., above E_{ex} or even above the fundamental edge $E_g > E_{\text{ex}}$), the excitonic insulator appeared as a persistent phase [24], but the stationary state may not be achievable [25]. Rather, the system exposes long-lasting large-amplitude oscillations, which is in line with the modern knowledge in PIPT.

The arrival of the PIPT science gives a new momentum to studies of ensembles of excitons with opening to coherent effects. By now, experiments were limited to the so-called neutral-ionic transitions, but actually the range of realizations is unlimited since all non metallic systems prone to phase transitions have one type of exciton or another available for pumping. Recently, we presented [26, 27] a phenomenological modeling of spacio-temporal effects expected when optical excitons are coupled to the order parameter of a first-order phase transition, as it happens in the neutral-ionic case. The phenomenological approach allowed describing the thermodynamic transition jointly with the evolution of the optically pumped ensemble of excitons.

In our picture, a quasi-condensate of excitons appears as an inhomogeneous macroscopic quantum state, which then evolves while interacting with other degrees of freedom prone to instability. Via these interactions with soft modes, the excitons are subject to self-trapping (cf. [28] for polarons and [29] for fluctuations), akin to self-focusing in optics. This locally enhances their density, which can surpass a critical value to trigger the phase transformation, even if the mean density is below the required threshold for the global transition. We have recovered dynamical interplays of fields such as the collective wave function of excitons, the electronic charge transfer and polarization, and the lattice dimerization. We have found various transient effects: self-trapping, dynamic formation of domains separated by walls, subsequent merging of domains and collapse of walls, and emittance of propagating wave fronts.

That model and the results could be applicable to situations where the excitons and the order parameter are essentially different while interacting fields. This could be the case of pumping to high-energy intramolecular excitons in donor–acceptor systems with the neutral-ionic transition, as it has been realized experimentally in [30].

In this article, we consider the case where the transition order parameter and the intensity of pumping excitations are of the same origin as it happens for the low-energy charge-transfer excitons [31] in the neutral-ionic transition. The BEC of excitons is involved in both situations, but the last case also brings to light the excitonic insulator state coupled to the BEC.

To describe both thermodynamic and dynamic effects on the same root we adopt a view of the excitonic insulator for the phase transition. With only the main ingredient, the vanishing of the excitation energy, the concept is too broad, as just a generic view of quantum phase transitions in electronic systems. The focused concept of the excitonic insulator is distinguished when the number of excitons, both in the ground state and out-of-equilibrium, is approximately conserved. (If it is conserved precisely as had been stated in most theories before the clarifying work by Keldysh and co-authors [12], then the thermodynamics of the phase transition is not affected essentially but there would be no dynamical path to the excitonic insulator state, which is of particular importance in the context of PIPT; see precisions in the next section.)

The theory of PIPTs faces great challenges when started ab initio at the microscopic level (see, e.g., [32] for a review and [33]). But over longer time scales, the evolution should be governed by collective variables like the order parameter and lattice deformations. The effectiveness of such a phenomenological approach has been proved by a detailed modeling of coherent dynamics of a macroscopic electronic order through destruction and recovering of the charge density wave state. That allowed describing effects such as dynamic symmetry breaking, stratification in domains and subsequent collapses of their walls, all in detailed accordance with experiment (see, e.g., [34]). Another example was the modeling [35] of the recently discovered [36] switching to a truly stable hidden state of a polaronic Mott insulator in 1T-TaS₂. The phenomenological approach becomes inevitable when considering spatially inhomogeneous regimes that ultimately appear here. That is what we keep using in the presented study.

1.2. The Neutral-Ionic Transition as an Excitonic Insulator

Relevant neutral-ionic transitions occur in bimolecular donor–acceptor chains ($D^{\rho}-A^{\rho}$, in particular TTF-CA, see the references in [31, 37]) that show a variable charge transfer ρ between the lower ρ_N in the

quasi-neutral high-temperature phase and a higher ρ_I in the low-temperature ionic phase. The first-order transition in ρ alone would go without a symmetry breaking and could be described by a generic double-well curve for the free energy $W(\rho)$ with two minima at neutral and ionic states. In spite of the essential distance ($\rho_N = 0.32$ and $\rho_I = 0.52$ at the phase coexistence), the separating barrier is small, and hence we deal with a first-order phase transition that is close to a second-order one. That is confirmed by observations of a critical increase in the dielectric constant [37] as a precursor of ferroelectricity and of the Kohn anomaly (see [38] and the references therein) as a precursor for the lattice dimerization instability. More richness comes from another degree of freedom, the alternating molecular displacements h : the ionic phase is accompanied by lattice dimerization, and hence there is a symmetry breaking and the transition could have been of the second order, which is not the case nevertheless: the jump in h is concomitant with the jump in ρ .

Remarkably, TTF-CA and related materials possess two types of observable and treatable excitons: the intramolecular Frenkel-type excitons as a high-energy (2.33 eV) mode of the TTF molecule and the low-energy (0.6 eV) charge-transfer excitons. In the last case, an electron is activated from the predominantly donor-formed band to the acceptor-formed band, but the electron and the hole are kept bound as for Wannier–Mott excitons in semiconductors. The charge-transfer exciton increases the charge disproportion ρ above its initial value, coming from the simple hybridization of donor- and acceptor-originated bands. Thus, the neutral-ionic transition can be viewed as accumulation of virtual $e-h$ pairs in the ionic ground state. With the charge-transfer exciton as the bound state lying well below the unbound $e-h$ threshold $E_g \approx 1.5$ eV, the charge transfer can be seen as coming predominantly from excitons, whence the picture of the excitonic insulator. The cases of the intramolecular exciton and the charge-transfer exciton correspond to profound experimental studies by Koshihara [30] and Okamoto [31] with co-authors. Our earlier theoretical work [26, 27] can refer to the case of the intramolecular exciton.

We underline the quantum nature of the charge-transfer exciton in both its internal structure and motion. Internally, this is a symmetric superposition of states where dipole dimers are formed by the charge transfer from a donor site to the surrounding acceptor sites. Within the classical illustration, that is used sometimes, there would be either left- or right-directed dimer with corresponding opposite electric polarizations. But with the quantum superposition, the dipole moment vanishes, to be weakly restored after lattice dimerization, which breaks the inversion symmetry and mixes states of excitons of even and odd parities. With respect to the motion as a whole, the lowest-energy state of the exciton is ideally (up to

inhomogeneities as we see below) a plane wave delocalized over the sample in the state with the momentum $k = 0$, like in condensates of polaritons (see [39] for a review). This description is complementary to the popular classical picture of classical domain walls (the solitons) propagating as a falling domino array.

2. THE MODEL

2.1. Integration of the Bose Condensation of Excitons and of the Excitonic Insulator in Dynamics of Neutral-Ionic Transitions

In the case of pumping into the intramolecular exciton near the neutral-ionic transition, the excitons and the order parameter were essentially different while interacting fields, and it was therefore quite straightforward to formulate a phenomenological model [26, 27]. In case of the charge-transfer exciton, both the excitation and the long-range ordering are built from processes of electronic transfer between donor and acceptor molecules. Although the number of independent fields is reduced, conceptually this case is more intricate.

The dualism of the exciton density q and the thermodynamic order parameter $\rho - \rho_N$ already outlined in Section 1.2 do not seem to be quite compatible: the thermodynamic charge transfer is given by a redistribution of the charge density ρ , which is the single real field both in equilibrium and in evolution. The charge-transfer density from the pumped ensemble of excitons is given by the exciton number density $q \propto |\Psi|^2$, and hence the field is still real but its evolution is given by the complex wave function $\Psi = q^{1/2} \exp(i\varphi)$ of the BEC, and a hidden degree of freedom—the phase φ —comes to the sight. The evolution of this phase can be traced directly because its time derivative gives the observable instantaneous energy of the exciton $E_{\text{ex}}(t) = -\hbar\partial_t\varphi$ in the frame of their ensemble.

This dualism between the density of microscopic excitons and the thermodynamic charge ordering calls for refining another dualism: among explicit coherent oscillations of the order parameter and those of the wave function of excitons, which interfere but keep the different origins. In general, collective oscillations might be superimposed on the frequency $E_{\text{ex}}(t)/\hbar$, but now, with strong variations of E_{ex} , the two time dependences cannot be disentangled and must be considered on equal footing.

2.2. The Energy Functional and Evolution Equations

To build a unified approach to two faces of the charge transfer, we describe the phase transition as the one of the excitonic insulator state—a view that is becoming popular, nowadays, as one can see from the papers we have cited above. The notion of the excitonic insulator can be applied to a large category of quantum phase transitions where the instability comes

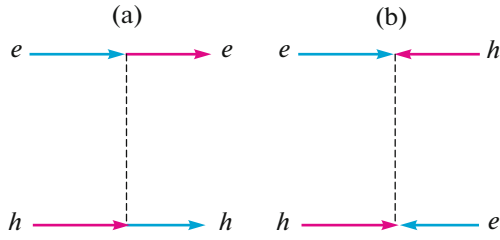


Fig. 1. (Color online) Coulomb interactions of the electron and the hole: (a) normal and (b) anomalous, with the annihilation of exciton pairs.

from the vanishing of the energy E_{ex} of an excitation which is here a bound state of the $e-h$ pair. The instability for negative $E_{\text{ex}} < 0$ is compensated by repulsion of excitons which determines the equilibrium concentration. A particular convenience is that the excitonic insulator and BEC theories are identical except that the first is monitored by the chemical potential while the second one by the mean density. The time evolution generalizes and unifies both views, which we shall exploit in what follows.

The increase in the average charge-transfer intensity does not break the symmetry, similarly to the liquid-vapor transition; a first-order phase transition is then expected in general. (In systems of our interest, there is also a discrete symmetry breaking thanks to appearing of the lattice deformations h , which can take the values $\pm h_0(\rho)$ in equilibrium at a given ρ ; but for the sake of transparency we disregard this variable for a while.) The energy functional $W(\rho)$ is minimal in equilibrium, which can occur at two values ρ_1 and ρ_2 , one of which is metastable except at the transition temperature T_c of the first-order transition, where $W(\rho_1) = W(\rho_2)$.

At short times of PIPTs and/or at low temperature, the system behaves dynamically as is described by a Hamiltonian containing the kinetic energy density proportional to $\dot{\rho}^2$. It leads to a second-order differential equation $\partial_t^2 \rho \propto -\delta W/\delta \rho$, which does not preserve ρ at all and does not result in a bottleneck for transformations among phases with different mean values of ρ . In conditions of PIPT, such a system performs large-amplitude pendulum oscillations (see a clear experimental example in [34]). With some dissipation taken into account, it is eventually driven towards one of equilibrium states ρ_1 or ρ_2 .

Actually, the optical pumping gives rise initially to a high density of excitons, which, in case of resonant pumping or after relaxation in general, can be described by the common wave function Ψ of the quasi-condensate with the density $q = |\Psi|^2$ contributing to $\rho = \rho_1 + q$. The system of excitons itself can be described as interacting bosons whose phenomenological treatment at low temperature can be based

upon the adapted Gross–Pitaevskii theory. And that would lead to a kind of nonlinear Schrödinger equation (NLSE), which commonly preserves the number of excitons, and would therefore prohibit any evolution of ρ .

The escape from these contradictions can be found following the work by Keldysh and co-authors [12]: there are processes of creation and annihilation of pairs of excitons from/to the vacuum coming from matrix elements of the Coulomb interaction, which transfer two electrons across the gap, between filled and empty bands (see Fig. 1). That gives rise to the amplitude S of simultaneous annihilation of two excitons. Finally, the excitonic insulator free energy acquires the phase-fixing terms

$$(S^* \Psi^2 + S \Psi^{*2})/2, \quad S = |S| e^{i\alpha}$$

and hence the generalized Ginzburg–Pitaevskii equation (see below) does not preserve the total number of particles. (Here and hereafter, we assume the given phase $\alpha = 0$ which can always be done by shifting the origin of the variable phase φ .) For the founding excitonic insulator scenario of condensation of Wannier–Mott-type excitons, these anomalous terms are small compared with the dominant Coulomb energy E_b as $|S|/E_b \propto (a/R)^d$, where a is the lattice spacing, $R \gg a$ is a large exciton radius, and d is the space dimension. For local excitons with $R \propto a$, there is no smallness; the phase can be strongly fixed and the system must show the behavior expected of the generic scalar order parameter.

By the definition of the excitonic insulator, the phase-fixing terms are small, $|S| \ll 1$, and hence the total complex order parameter Ψ still is to be exploited. For a typical neutral-ionic material, the bare value of S may not very be small: both because R is only of a few a and because of low $d = 1$. But the same fact that the system is nearly one-dimensional brings, as always in one dimension, strong phase fluctuations that reduce functions periodic in φ . Hence, the effective value

$$|S| \rightarrow |S| \langle \exp(2i\varphi) \rangle \approx |S| \exp(-2 \langle \varphi^2 \rangle)$$

can be small; it can even be renormalized to zero.

We work with a special form of the Ginzburg–Pitaevskii equation that is applicable when boson occupation numbers for all relevant states are much bigger than unity. For the system of excitons on a d -dimensional lattice, the condition is that their mean density per lattice site is $x \gg (T/D)^d$. With the exciton bandwidth $D \sim 10^3$ K, this inequality can always be satisfied for a typical experimental value $T \sim 10$ K. Even if the initial value of x is not sufficiently high, the kinetics of many-particle cooling feeds the low-energy states such that the Ginzburg–Pitaevskii theory becomes applicable sooner or later. This is an advantage of the fast PIPT technique, where the integral

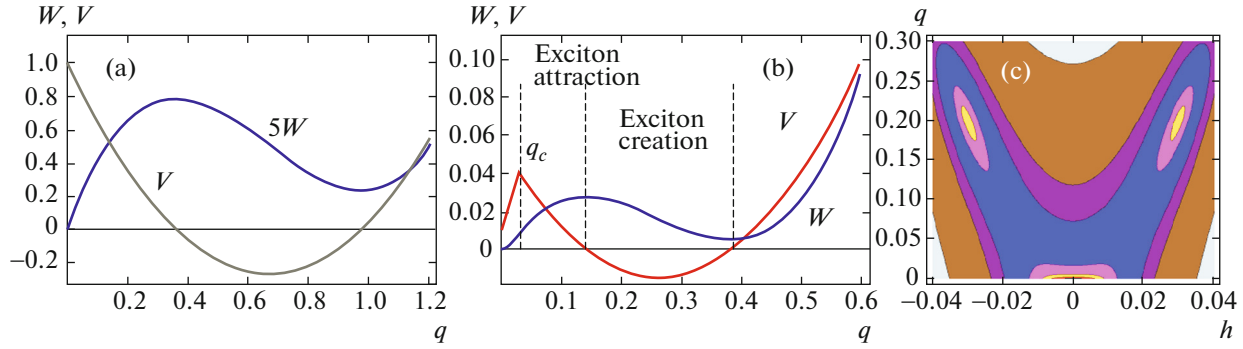


Fig. 2. (Color online) Plots of the ground-state energy $W(q)$ and the potential $V(q) = dW/dq$ above the first-order transition: (a) for a metastable generic excitonic insulator; (b) for the neutral-ionic system after minimization of $W(q, h)$ over the lattice displacement h . Vertical dashed lines separate four intervals of q (from left to right): repulsion, attraction, creation, and again repulsion of excitons. (c) density plot of $W(q, h)$ showing all three locally stable states.

time of observations is shorter than the recombination time of excitons.

Varying the energy functional W (to be specified in Eq. (6) below) over Ψ yields the generalized Ginzburg–Pitaevskii equation

$$i\hbar\partial_t\Psi + i\hbar\Gamma\Psi = \frac{\delta H}{\delta\Psi^*} = -\frac{\hbar^2}{2M}\partial_x^2\Psi + V(q)\Psi - S\Psi^*, \quad (1)$$

$$V(q) = dW/dq = E_{\text{ex}}.$$

The perturbations proportional to Γ (see below Eq. (2)) and S describe the respective relaxation of amplitude and locking of the phase. The relaxation rate Γ might have a complicated behavior, passing through different regimes. In the most dilute limit of isolated excitons, apparently $\Gamma = 1/\tau_{\text{ex}}$ is the inverse life time for the exciton recombination. Actually, our vanishing q still assumes a macroscopic concentration when the radiational recombination is dominated by stimulated emission; then, according to the Bose–Einstein statistics, Γ decreases as $\Gamma \propto q$. Approaching the high- q equilibrium phase at $q \approx q_0$, where the excitons constitute the ground state, $\Gamma \rightarrow 0$ should vanish since there is no channel of decay at the energy minimum. That is rigorously true below the neutral-ionic transition when the high q state has a minimal energy. If it is metastable, then we neglect its evaporation over the barrier towards the $q = 0$ region. If there were no phase dependence through the S term, then simply Γ should vanish together with V , and hence we can write a qualitative interpolation between the two limits as $\Gamma \Rightarrow G(q)qV(q)/\hbar$, where $G(q)$ is some structureless dimensionless function of q (which we take as a constant in the illustrative numerical modeling). This expression tells us that $\Gamma < 0$ (meaning amplification instead of the decay) in the region between the barrier and the high- q minimum where $V < 0$ (see Fig. 2). This is not unphysical since here the system is indeed unstable with respect to spontaneous creation of excitons whose energy becomes negative as in the excitonic insulator. Bringing the system to this range of q

by pumping the excitons is similar to instantaneous crossing the boundary of the excitonic insulator state by varying a thermodynamic monitoring parameter.

In view of the phase dependence, the equilibrium state is determined by both q and ϕ approaching the energy minimum $\phi = 0$ (modulo π), $q \approx q_0$ in some complicated way. Instead of guessing Γ as a function of two variables, it is more instructive and basic to realize that the energy relaxation terminates when $\partial_t\phi = 0$. Then

$$\Gamma \Rightarrow -\frac{G}{2i}(\Psi^*\partial_t\Psi - \Psi\partial_t\Psi^*) = -Gq\partial_t\phi$$

$$= \frac{Gq}{\hbar}E_{\text{ex}}(t, x), \quad G \approx \text{const.} \quad (2)$$

The equations for q and ϕ written below show that this expression is indeed a generalization of the relation $\Gamma \Rightarrow G(q)qV(q)$.

For the zero dimension $D = 0$ of a quantum dot or for a spatially homogeneous regime $\partial_x\Psi \equiv 0$, it is instructive to write the above equations in the variables q, ϕ ($\partial_t\phi = \dot{\phi}$, $\partial_tq = \dot{q}$):

$$\hbar\dot{\phi} = -V + |S|\cos(2\phi), \quad (3)$$

$$\dot{q} = -\Gamma q + 2|S|q\sin(2\phi) = Gq^2\dot{\phi} + |S|q\sin(2\phi)$$

$$= -(G/\hbar)q^2(V - |S|\cos(2\phi)) + |S|q\sin(2\phi). \quad (4)$$

The polar trajectory $q(\phi)$ is given by the solution of the equation

$$\frac{dq}{d\phi} = \frac{q^2(V - |S|\cos(2\phi))G/\hbar - |S|q\sin(2\phi)}{V - |S|\cos(2\phi)}. \quad (5)$$

Approaching the neutral phase with a residual but still macroscopic density of excitons, $q \rightarrow 0$, $V \rightarrow E_{\text{ex}}^0$, we obtain the vanishing concentration of isolated excitons with the shifted energy $E_S = \sqrt{(E_{\text{ex}}^0)^2 - |S|^2}$. The wave function oscillates as

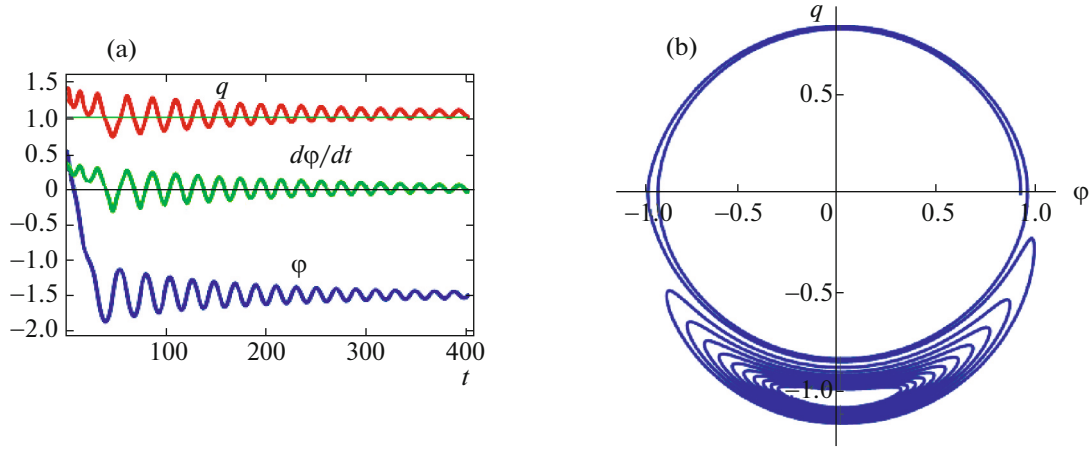


Fig. 3. (Color online) Plots for (a) t dependences of q , ϕ , and $d\phi/dt$ and (b) the polar trajectory $q(\phi)$ for the generic excitonic insulator after additional pumping.

$$\Psi \propto (\sqrt{E_{\text{ex}}^0 - |S|} \cos(\omega_S t) + i\sqrt{E_{\text{ex}}^0 + |S|} \sin(\omega_S t)),$$

where $\omega_S = E_S/\hbar$. For the high- q phase, unlike the $q = 0$ one, the energy has a smooth minimum at q_0 where $V(q_0) = 0$; then $\partial_t \Psi = 0$ implies that

$$\sin(2\phi) = 0, \quad -V + |S|\cos(2\phi) = 0,$$

i.e.,

$$\phi_0 = \pi n/2, \quad V(q_0) = |S|(-1)^n.$$

We note that the equilibrium value is displaced from q_0 by the effect of the S term.

2.3. Taking Account of Dimerizations

We now come to the realities of neutral-ionic transitions by recalling the symmetry breaking order parameter, the dimerization h . We work with the energy function

$$W(q, h) = E_{\text{ex}}^0 q + \frac{a}{2} q^2 + \frac{b}{3} q^3 + \frac{d}{2} (q_h - q) h^2 + \frac{f}{4} h^4, \quad (6)$$

$$V(q, h) = \frac{\partial W(q, h)}{\partial q} = E_{\text{ex}}^0 + aq + bq^2 - \frac{h^2 d}{2}.$$

The phenomenological model of the generic excitonic insulator would contain only the terms without the symmetry breaking field of displacements h ; then, to obtain the regime with the (meta) stable state at $q_0 > 0$ coexisting with the still stable state at $q = 0$, we might assume the negative $a < a_{\text{cr}} = -2\sqrt{bE_{\text{ex}}^0}$ (attraction of excitons), but positive $E_{\text{ex}}^0 > 0$. In applications to neutral-ionic transitions, we leave $a > a_{\text{cr}}$ (it can even be positive $a > 0$, corresponding to the repulsion of excitons, which guarantees local microscopic stability), because the energy minimum at $q > 0$ is built with the help of the induced instability, at all $q > q_h$, of the field h describing the dimerization. The effect of h cannot

depend on its sign, whence the coupling proportional to $-qh^2$; it can be viewed as a decrease in the exciton energy by dimerization, which can come from the mixing of even and odd excitonic states when the inversion symmetry is broken at $h \neq 0$. As a second-order perturbation in h , it should be negative as we have specified. We can also add a higher order coupling proportional to $-q^2 h^2$ which is the effect of dimerization on the interaction of excitons. In the presence of $h \neq 0$, the inversion symmetry is broken (the state is ferroelectric!), and the excitons acquire dipole moments along the chain, whence the attractive dipole-dipole contribution, which guarantees the negative sign of this interaction. Taking both effects into account, we can write the interaction term as $(q_h - q)(d_1 + d_2 q)h^2/2$, with $d_1, d_2 > 0$.

The equation for $h(t, x)$ follows from the variation over h of the energy functional augmented by the lattice kinetic energy and elasticity:

$$K(\partial_t^2 + \gamma \partial_t)h - Ks^2 \partial_x^2 h + d(q - q_h)h + fh^3 = 0. \quad (7)$$

Here, s is the sound velocity and $q_h d/K = \omega^2$, where ω is the h -mode frequency in the virgin state $q = 0$. Equations (6), (7), and (2) with $V(q)$ generalized to $V(q, h)$ from (6) constitute the full system used in our minimalistic modeling.

3. RESULTS OF NUMERICAL MODELING

3.1. Generic Excitonic Insulator

We first consider the generic model of the excitonic insulator schematically. Here, the transition is of the second order, governed by only one field Ψ , and the phenomenological energy has the simplest form

$$W(q) = E_{\text{ex}}^0 q + aq^2/2, \quad V(q) = E_{\text{ex}}^0 + aq.$$

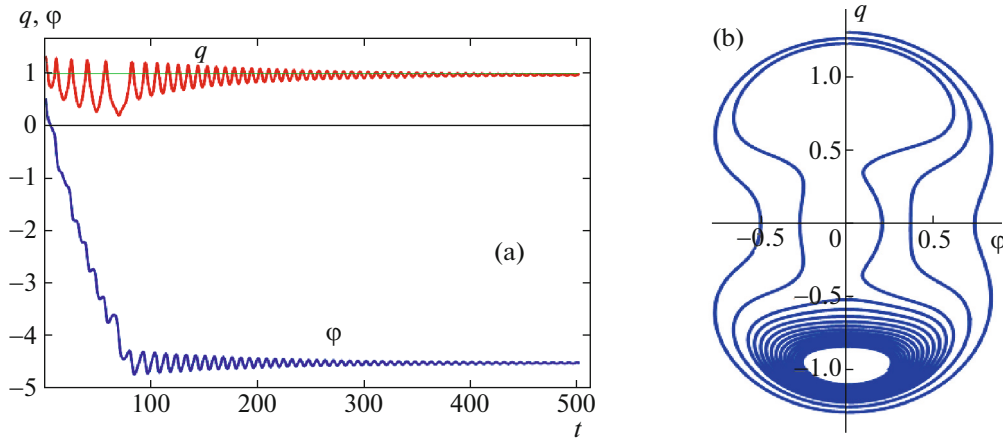


Fig. 4. (Color online) Plots for (a) t dependences of q and ϕ and (b) the polar trajectory $q(\phi)$ for the metastable excitonic insulator after a high pumping to $q_i = 1.3 > q_0$.

In the excitonic insulator phase, $E_{\text{ex}}^0 < 0$. We select the equilibrium position $q_0 = -E_{\text{ex}}^0/a = 1$ and hide the coefficient a in time rescaling. In the thus reduced equations, we choose $S = 0.1$ and fix the attenuation coefficient in (2) as $G = 0.01$. The pumping intensity determines the initial value q_i . The results are shown in Fig. 3 as linear plots for $q(t)$ and $\phi(t)$ and as parametric polar plots for $q(\phi)$.

There is a small critical deviation $q_i - q_0$ (to any side) beyond which the phase is unlocked (the S term is not effective), q oscillates with little attenuation around q_i , and the phase rotates almost linearly in t (superimposed by oscillations as well as $q(t)$). This regime corresponds to the collective mode of excitons with oscillations coming from a macroscopic quantum interference due to the particle production to/from the excitonic insulator ground state. But with time the attenuation proceeds towards the energy minimum, q crosses the critical deviation towards q_0 , and the phase locks via a dynamical transition. With attenuating oscillations, the phase approaches an equilibrium value from the sequence $\pi(n + 1/2)$, where n is the number of half-periods processed before the locking. Also with attenuated oscillations, $q(t)$ approaches the equilibrium value displaced from 1 by effect of the S term.

Figure 3 shows the time dependences for the phase and the amplitude, and the trajectory as a parametric polar plot for $q(\phi)$. The initial deviation (pumping from the equilibrium $q_{\text{eq}} = 1.05$ to some initial $q_i = 1.4$ at a given equilibrium phase $\phi = \pi/2$) provokes the unlocked regime, which lasts until $t \approx 40$ with nearly two (there can be many) rotations over the initial circular trajectory. Here, the amplitude is close to a constant (the number of excitons in the condensate is nearly conserved), while the phase decreases almost linearly in time, with a nearly constant exciton energy. With $q(t)$ slowly decreasing because of relaxation in the number of excitons, a locking transition takes

place after which the amplitude gradually returns to thermodynamic equilibrium while the phase is locked at a new allowed value $\pi(n + 1/2)$, here with $n = -3$.

3.2. Generic First-Order Phase Transition

We now turn to the case of a generic first-order phase transition which may be due to attraction of excitons, as is sometimes considered for semiconductors [5, 40, 41]. This example also builds a bridge to our primary goal of a multi-field system. We choose the ground state energy as

$$W(q) = \frac{q}{1.05} [(q-1)^2 + 0.05], \quad V(q) = \frac{dW}{dq},$$

which is plotted above in Fig. 2. $W(q)$ is normalized such that the bare exciton energy is $E_{\text{ex}}^0 = V(0) = 1$. With these parameters, we are below the thermodynamic phase transition to the excitonic insulator state, which nevertheless can exist as a metastable state (the minimum of $W(q)$ at $q_0 \approx 1$).

For a very high pumping exceeding the position of the metastable excitonic insulator, $q_i > q_0$, the behavior shown in Fig. 4 is qualitatively similar to the above case of the generic excitonic insulator with the second-order transition (Fig. 3).

At a lower pumping, but still above the position of the barrier in $W(q)$, $q_0 > q_i > q_b \approx 0.36$, there is a fast crossover to the regime of oscillating relaxation towards the excitonic insulator state, with no clear unlocked regime, as demonstrated in Fig. 5 for $q_i = 0.35935$ (just above the barrier). After some waiting time (which is pronounced here because of the chosen close proximity to the critical pumping), strong oscillations develop in both q and ϕ . After a long relaxation accompanied by attenuating oscillations, q finds a new equilibrium at the position of the metastable excitonic

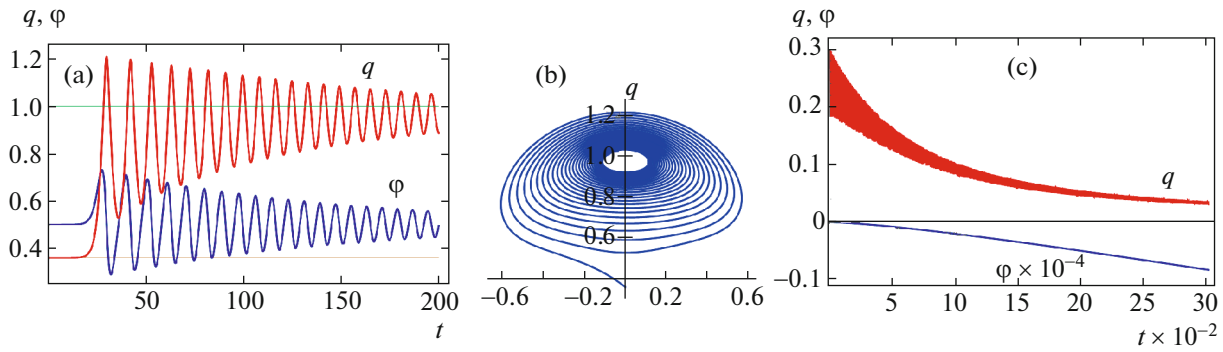


Fig. 5. (Color online) Plots for (a) t dependences of q and ϕ and (b) the polar trajectory $q(\phi)$ for the metastable excitonic insulator after a just-super-barrier pumping, $q_i = 0.35935$; and (c) t dependences of q and ϕ for the sub-barrier pumping, $q_i < q_b$.

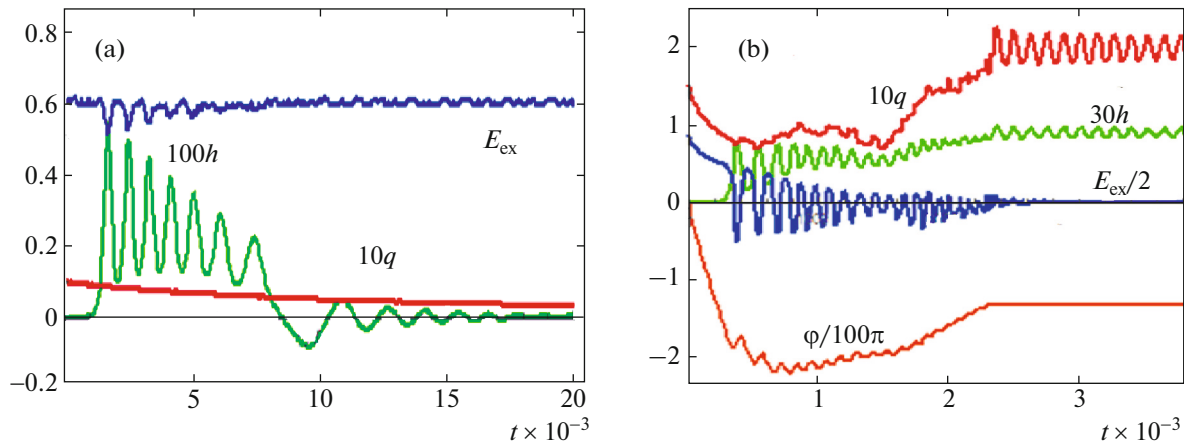


Fig. 6. (Color online) Plots for t dependences E_{ex} , q , and h at (a) the subcritical pumping and (b) the supercritical one.

insulator while the phase returns to the initial value $\pi/2$.

For an even lower sub-barrier pumping $q_i < q_b$, the system relaxes to the virgin no-exciton state, as is also shown in Fig. 5. The curves are superimposed by oscillations, which, at least at sufficiently long t , correspond to the energy E_{ex}^0 of the bare exciton.

3.3. Multi-Field Model for the Neutral-Ionic Transition

The modeling is based on Eqs. (1), (6), and (7) describing a coupled evolution of the complex order parameter Ψ and of the dimerization h . Numerically, we try to stay within the range of parameters known or estimated for a real material with a neutral-ionic transition. The plausible numbers are given in the Appendix.

3.3.1. Neutral-ionic system at space independent conditions. First, we generalize the generic models considered previously by looking for a space-independent solution. The time dependences are shown in the plots in Fig. 6; they have been calculated for the real-

istic parameters described in the Appendix. Figure 6a shows results for the subcritical regime when the system is pumped from the neutral state to $q_i = 0.01 < q_h = 0.03 \ll q_l$, keeping the unperturbed initial $h_i = 0$. (Recall, see Fig. 2b, that $q_l \approx 0.2$ and $|h_l| \approx 0.03$ in equilibrium of the ionic phase.) After some waiting time $t_h \approx 1000$, pronounced oscillations in $h(t)$ emerge and then decrease with a tendency to saturation at $h \approx 0.002$. But at $t^* \approx 9000$, the dynamical regime switches abruptly to weaker oscillations around $h = 0$. All the way, $q(t)$ decreases monotonically while E_{ex} stays nearly constant close to the unperturbed value $E_{\text{ex}}^0 = 0.6$. On both sides of the transition, oscillations in $E_{\text{ex}}(t)$ are small but change in character (as it could be seen by comparison with the modeling at $S = 0$, which is not shown). At $t < t^*$, $E_{\text{ex}}(t)$ oscillates together with $h(t)$ at the lattice frequency ω , while at $t > t^*$, the oscillations of $E_{\text{ex}}(t)$ are seen only if $S \neq 0$, and hence they are related to the macroscopic quantum interference: excitons pair creation from the vacuum admixes the basic state at E_{ex}^0 with states at $3E_{\text{ex}}^0$ and $-E_{\text{ex}}^0$.

Figure 6b shows the results for the supercritical regime after pumping to the level much higher than the threshold q_h but still below the new equilibrium: $q_i = 0.15 < q_I = 0.2$ (again starting with the unperturbed $h_i = 0$). At short times, we see a smooth decrease in $q(t)$ and $E_{\text{ex}}(t)$ until the initiation of $h(t)$ at $t^* \approx 300$. It is followed by formation of lattice oscillations, now around a finite value of h together with a finite value of the weaker oscillating $q(t)$. In this regime of an accidentally found intermediate equilibrium, the exciton energy strongly oscillates around zero such that the mean phase does not change much. After another crossover at $t \approx 1700$, the oscillations of $E_{\text{ex}}(t)$ make preferable excursions to negative values: we see this from the phase, which starts anomalously growing in average. In this regime, the excitons are preferably generated from the vacuum, and hence $q(t)$ starts to increase (with time it rises above the initial pumping level). Then, after the clearly seen lock-in transition at $t_{\text{lock}} \approx 2600$, the final equilibrium becomes apparent, but with the new rise of strong oscillations in $q(t)$ and $h(t)$ provoked by this final dynamical transition.

3.3.2. Spontaneous domain structure. For an extended system, spatially homogeneous solutions may not be stable because of the interaction between the excitons and the order parameter. For a low concentration and above the BEC transition, that would be effects of self-trapping of individual excitons [28]. For the macroscopic description of the BEC, the effect resembles self-focusing in nonlinear optics. In the last case, the optical “bright solitons” appear because of the negative nonlinearity—the term $a|\Psi|^2\Psi$ with $a < 0$ in the NLSE. When the NLSE for classical waves becomes the Ginzburg–Pitaevskii equation for an ensemble of quantum Bose particles like the excitons, the negative a means attraction of particles, which gives rise to the microscopic instability [41] of the Bose gas with respect to the collapse to a liquid state (for cold atoms) or with a probable dissociation to e – h droplets for excitons (this is one more opportunity to recognize another very well-known invention by Keldysh, see [40]). In our case, the excitons themselves are repulsive, $a > 0$; but if the order parameter is excluded (which is not possible explicitly), then the direct repulsion is overcome by effective attraction. Microscopically, this attraction is indirect and retarded, and hence it may not lead to an instability towards the dense phase. But at larger time and space scales, the effective attraction can win, leading to spatially modulated structures. The effect has been modeled in detail [26, 27] for a system where the excitons and the order parameter are essentially different entities, like intramolecular excitons with respect to charge transfer in materials with the neutral-ionic transition. The effect is also present here within the model of the excitonic insulator for the neutral-ionic transition with the pumping to charge-transfer excitons.

Below we present results of modeling the spatio-temporal behavior with the anomalous interaction neglected, $S = 0$. In all cases, the initial wave function is taken as the lowest state in the box of the width $2L = 200$ (in units of the intermolecular spacing):

$$\Psi(x, 0) = \Psi_i(x) = \sqrt{q_i} \cos(\pi x/2L).$$

The initial maximal intensity is chosen as $q_i \approx 0.15$ – 0.17 , which is well above the barrier but still below the equilibrium value $q_0 = 0.2$ of the ionic state, and a further $1/\sqrt{2}$ below the mean equilibrium value for the whole sample. The dimerization field $h(x, t)$ is seeded as a very small value $h(x, 0) = h_i(x) \sim 10^{-8}$.

Figure 7 shows the results for the homogeneous seeding $h_i(x) = \text{const}$. The density q first decreases maintaining the broad initial shape. Then the self-trapping progresses, culminating at $t \approx 10000$ by a sharp rise of the central peak; soon, a rectangular shape is formed separating the system into a narrow domain of the perfect ionic phase surrounded by the wings of the nearly perfect neutral phase. The dimerization $h(x, t)$ becomes pronounced by $t \approx 300$; by $t \approx 500$, the two strong side peaks are visible in the cross section. The three-dimensional plot shows that these are passing waves emitted by the fast nucleation of self-trapping. The later evolution resembles the one for $q(x, t)$. The difference is that oscillations of q are concentrated within the narrow nucleation region.

Because of the two-fold degeneracy with respect to the field h , the self-trapping direction of h depends on the sign of the initial seeding of h_i , irrespective of how small its magnitude is. With the constantly present initial inhomogeneities, the nucleation of different domains becomes inevitable. For a transparent illustration, we make the stepwise seeding $h_i(x)$ with opposite signs at two halves of the sample. The results are shown in Fig. 8. The antisymmetric shape of $h(x, t)$ is preserved at all t , and hence the domain wall (the kink-soliton) is always present around $x = 0$. The humps in $h(x)$ rise to the order of magnitude of the final scale $\pm h_0$ at $t \approx 300$. Soon, at $t \approx 600$, $h(x)$ spreads wider in the course of high-amplitude oscillations, which actually are of dynamical origin, from a sequence of waves emitted at the early time of fast growth at small x . At higher t , the shape becomes smooth again. The final profile shows the ideally flat plateaus at $|x| < 50$ of the pure ionic phase with exactly $h(x) \equiv \pm h_0 = \pm 0.03$. They are surrounded by crossover layers of decreasing $h(x)$, spreading over $50 < |x| < 80$, which makes a difference with respect to the previous case. Beyond the sharp boundary towards the outer regions at $80 < |x|$, the system stays at the prepumping neutral state with $h(x) \equiv 0$. The plots of $q(x, t)$ confirm the formation of the ionic phase at $|x| < 50$ but the plateau is fragmented by a sequence of narrow deep rims. In contrast to $h(x, t)$, there is no sharp second boundary towards the neutral phase: $q(x)$ keeps tails compa-

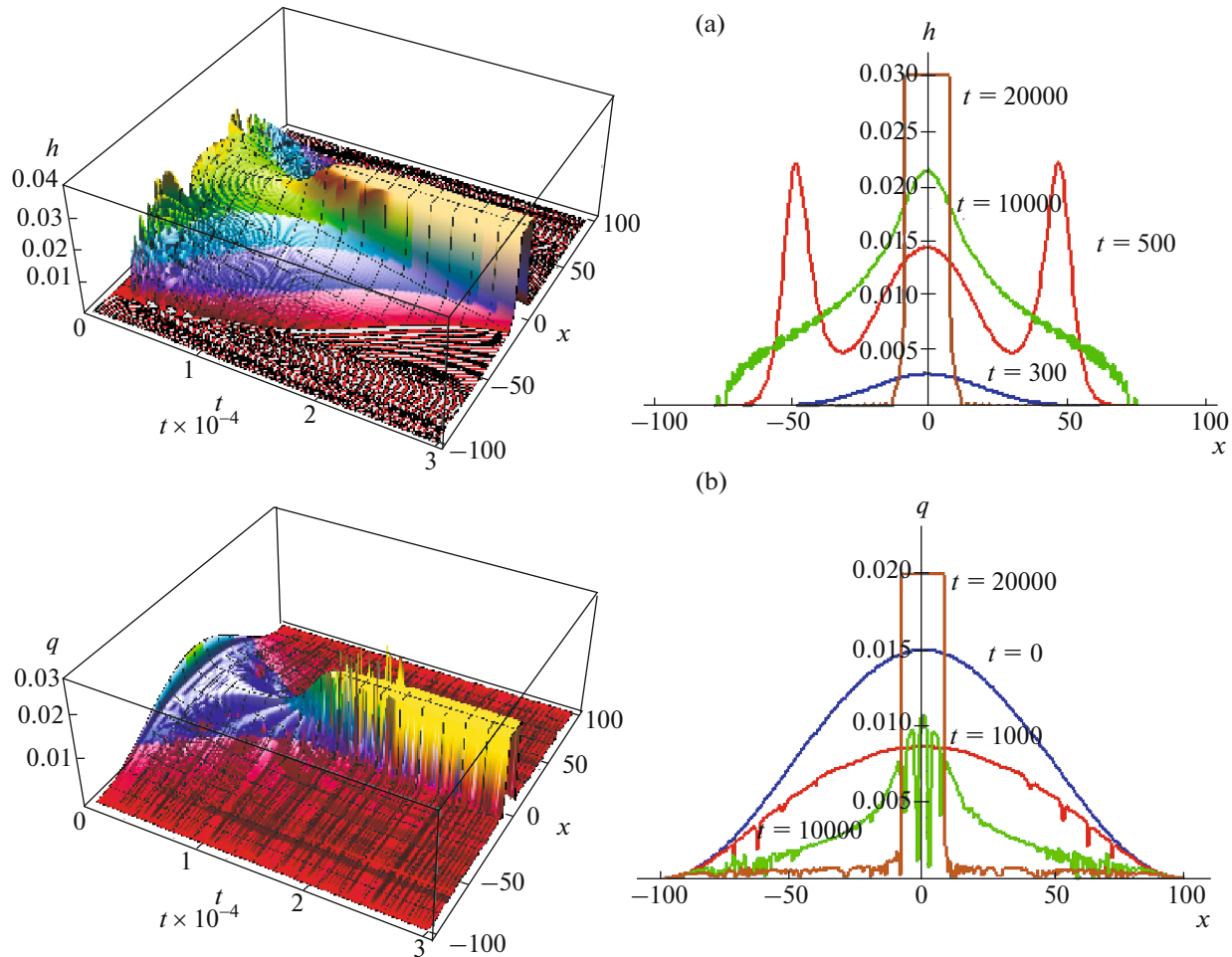


Fig. 7. (Color online) Plots for the post-pumping evolution of (a) $h(x, t)$ and (b) $q(x, t)$ for a homogeneous seeding of $h(x, 0)$.

erable with the initial distribution just after the pumping.

Formation of flat sharply bounded plateaus corresponding to an ideal phase separation was not expected from a common experience with NLSE and Ginzburg–Pitaevskii equations, where the self-focusing profiles show smooth bell-shaped humps. The difference seems to come from the threshold formation of h with increasing q , giving rise to the kink in the dependence $V(q)$ as shown above in Fig. 2.

There is an apparent correspondence between the shown pictures and the earlier schemes invoking solitons [42, 43]. Thus, the final domain wall between domains with opposite signs of h corresponds to the always allowed, presumably spin-carrying, solitons in [42]. The humps within the domains of a given sign of h , appearing here because of self-trapping, correspond to pairs of charged spinless solitons that are the walls framing the ionic string within the neutral domain [43]. Indeed, these solitons are always confined in pairs except exactly at the transition temperature.

Solitons in neutral-ionic systems in relation to the ferroelectricity will be reviewed in more detail in [44].

4. THE WORK TO BE DONE: A TWO-FLUID KINETICS

The excitons forming the excitonic insulator ground state are in the condensed form by definition. In the modeling presented above, we have additionally supposed that all the pumped excitons also form the BEC, and hence the whole ensemble can be described by a single wave function Ψ of the collective state. Certainly, there is also the normal component because the temperature is not very low and because of the initial incoherent background coming from excitons that were excited non-resonantly, with the phonon-assisted absorption of photons. Within this article, we do not discuss the very important questions of kinetics of non condensed particles, relying on experimental facts of fast initial equilibration. A future microscopical study can be advanced thanks to the progress in the theory of equilibration in a gas of excitons [45] and polaritons [46–48], and to the general understanding

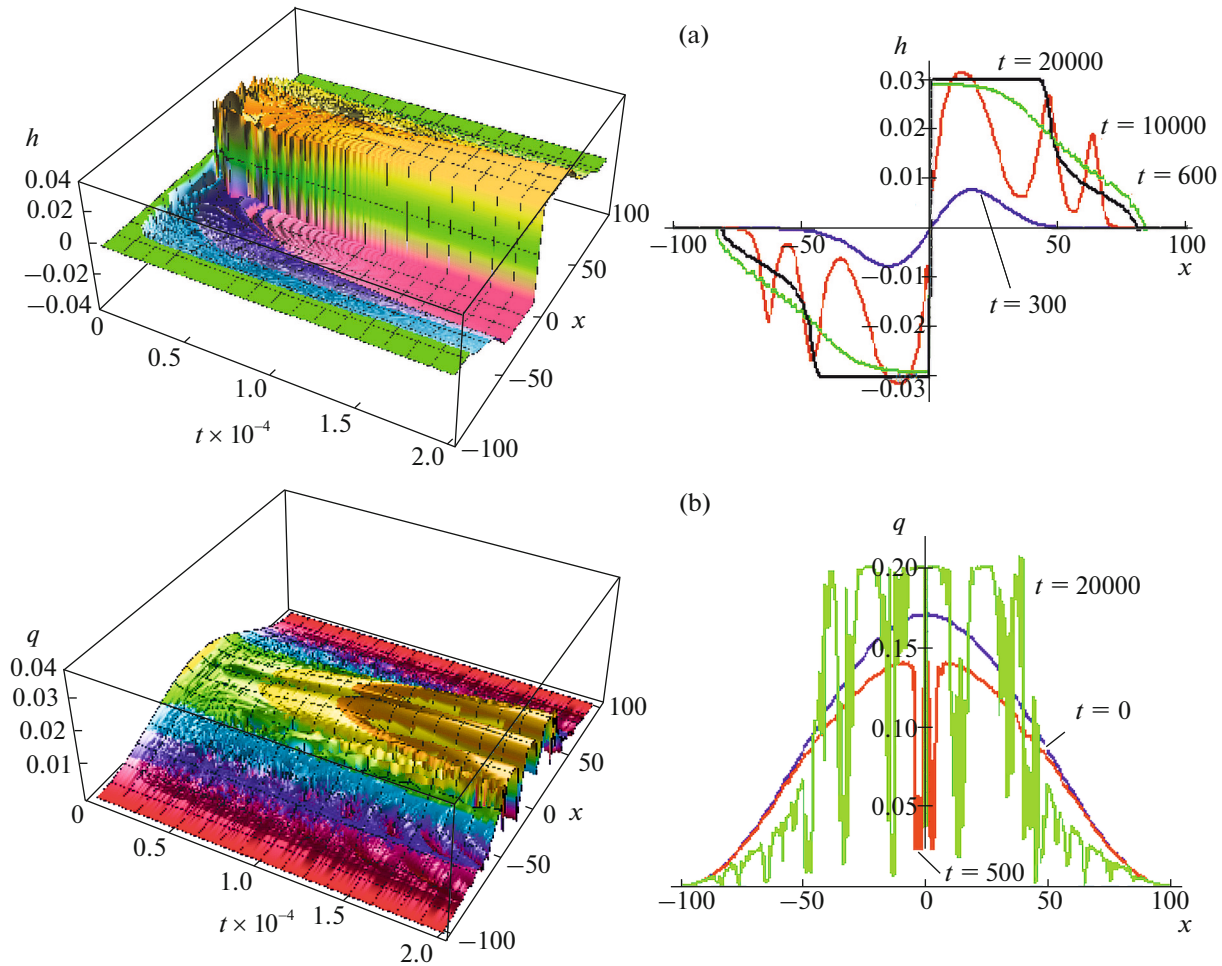


Fig. 8. (Color online) Plots for the post-pumping evolution of (a) $h(x, t)$ and (b) $q(x, t)$ for development of a two-domain configuration after the stepwise seeding of $h(x, 0)$.

of a non equilibrium Bose gas motivated by problems in cold atoms [49–51]. There are two levels of difficulties on this way. One, having been surpassed reasonably in the existing literature, is the kinetics of occupation numbers leading to the growing of the low-momentum peak while approaching the BEC. Another is the establishing of coherence, allowing the Ginzburg–Pitaevskii description to be introduced; this final step has not been passed yet, to our knowledge, to treatable implementations, except a heavy duty numerical work [52, 53]. For the ideal model of the weakly interacting Bose gas, there is a fair overlap between the regime of the microscopical kinetic and the collective NLSE-based descriptions. But the price is that turbulent mixing must be taken into account in the NLSE [52, 53] or equivalently the Ginzburg–Pitaevskii equation must be considered stochastically rather than deterministically [48]. For applications in solid state physics, the universality of the NLSE is not much helpful as regards the BEC of excitons and polaritons, because other channels of the relaxation become more important than collisions of bosons:

emission of phonons [45] or disorder [54]. New features appear such as the final threshold for pumping to reach the BEC of excitons even at $T = 0$ [45].

For the stationary BEC of polaritons, the theory is usually simplified by considering the normal component as a separate quasi-equilibrium reservoir, which can be characterized by the density n or the chemical potential μ_n (see [39, 46–48]). While this approach, mainly reduced to the cases of the stationary pumping, will doubtfully be extended to our systems, we briefly outline its possible application below as an absolutely minimalistic description.

A certain ground for the separation into two distinct, particle-exchanging reservoirs comes from suggesting a bottleneck—a minimum E_{\min} of the kinetic energy—where the pumped excitations accumulate after the initial rapid cooling. It is tempting to associate E_{\min} with the energy of the lowest lattice mode interacting with excitons. In our case, a good candidate is the soft mode in the dip of the Kohn anomaly, which should exist as a precursor for the lattice

dimerization instability (see [38] and the references therein). That can also be the Debye frequency of the acoustical spectrum; both candidates converge to $E_{\min} \sim 100$ K.

We can make a simplifying, and quite plausible, suggestion that all reservoirs of excitons contribute additively to the order parameter: the charge transfer becomes $\Delta\rho = q + n$, where still $q = |\Psi|^2$. Then the system energy and the particle potential are simply $W(q + n)$ and $V(q + n)$. Now Ginzburg–Pitaevskii equation (2) is further generalized to

$$i\hbar\partial_t\Psi = -\frac{\hbar^2}{2M}\partial_x^2\Psi + V(|\Psi|^2 + n)\Psi + \frac{i}{2}Rn\Psi - \frac{1}{2}S\Psi^*,$$

where R is a conversion rate. This has to be complemented by an equation for n , which we choose as a simple rate equation (cf. [46])

$$\partial_t n - \partial_x b \partial_x \mu_n n = P - Rn|\Psi|^2, \quad |\Psi|^2 = q,$$

where $\mu_n(n)$ and $b(n)$ are the chemical potential and the mobility (see [54]) of normal particles, $P(t)$ is the pump intensity profile; being short, it can be omitted in favor of the initial condition $n(0) = n_0 = \int P(t)dt$.

Since we are now considering relatively short times, we omit the decay terms proportional to G for the total number of excitons but instead introduce the conversion rate R regulating the exchange between the reservoirs. The function R must change sign as a function of the discrepancy $\delta\mu = \mu_n - \mu_c$ of chemical potentials in the normal and condensed subsystems. We shall adopt the simplest linear form valid at $|\delta\mu| \ll T$; otherwise, it can be generalized to $R \propto \sinh(\delta\mu/T)$ or to a more complicated nonsymmetric form. With a common definition for the chemical potential μ_c of the BEC, we have

$$\mu_c = -\hbar\partial_t\phi + \frac{\hbar^2}{2M}(\partial_x\phi)^2, \quad \mu_n = V(|\Psi|^2 + n) + E_{\min},$$

$$R = k(\mu_n - \mu_c)/\hbar.$$

The equation of state $\mu_n(n)$ can be estimated from the standard theory of a weakly interacting Bose gas. Now, the space-independent Eqs. (3) and (4) are generalized as

$$\hbar\dot{\phi} = -V(q + n) + S \cos(2\phi), \quad (8)$$

$$\dot{q} = qR + Sq \sin(2\phi) = kqn(\dot{\phi} + \mu_n/\hbar) + Sq \sin(2\phi) \quad (9)$$

$$= (k/\hbar)qn(E_{\min} + S \cos(2\phi)) + Sq \sin(2\phi),$$

$$\dot{n} = P - kqn(\dot{\phi} + \mu_n/\hbar) \quad (10)$$

$$= P - (k/\hbar)qn(E_{\min} + S \cos(2\phi)).$$

The equation for h is generalized as

$$K(\partial_t^2 + \gamma\partial_t)h - Ks^2\partial_x^2h + d(q_h - q - n)h + fh^3 = 0. \quad (11)$$

The numerical modeling of the resulting equations and, hopefully, of more complicated dynamical-kinetic system, will be discussed elsewhere.

5. DISCUSSION AND CONCLUSIONS

We have presented results of a phenomenological modeling for a system prone to a weakly first-order phase transition after it is exposed to the optical pumping to a high concentration of excitons. We focused on the cases where the excitation density and a thermodynamic variable present the same entity. The best-known example is the neutral-ionic transition in donor-acceptor compounds where the charge-transfer excitons play the role of optical excitations and give the inter-molecular electronic transfer as the phase transition order parameter. Both thermodynamical and dynamical effects can be described on the same root by viewing the ordered state as an excitonic insulator. Our main assumption was that a quasi-condensate of optically pumped excitons appears sufficiently early as a macroscopic quantum state. It evolves by interacting with other degrees of freedom prone to instability, leading to self-trapping of excitons akin to self-focusing in optics. A distinguished feature is the appearance of oscillations coming from the macroscopic quantum coherence.

Our studies are only most natural first steps in the complicated problem, and it is necessary to quote what has not or could not be done. We have been working within a phenomenological approach that can be characterized as the one that would be valid if it could be derived microscopically. Even within these reservations, it is desirable to also take the normal, non-condensed density of excitons and its (re)conversion (from) to the condensate into account. Indeed, temperatures in the experiments are comparable with the estimated degeneracy temperature of the BEC, and they are further enhanced in the early stage after the pumping pulse. The not-quite-resonance pumping also contributes to the initial incoherent density. With a progressive dilution of the exciton number, the BEC transition must be passed back even at low temperature.

Our primary emphasis was upon the quantum nature of the exciton motion, which forces their delocalization into plain waves. That would happen inevitably for an ideal resonance pumping when a single photon creates a single exciton with the momentum $k = 0$. In reality, a large part of photons is absorbed with an excess energy, which gives rise to the exciton in a complex with other modes whose total momentum is still zero, but the exciton acquires a momentum and the associated kinetic energy. The initial relaxation by collisions leaves the exciton as a wave packet rather than a pure state, which still cannot be viewed as localized at a single molecule or a dimer, as it is commonly pictured in the scenario of “falling dominos.” The loss of the kinetic energy from such a sharp localization will be more than 0.1 eV as estimated from the exciton bandwidth in optical absorption. Then, with cooling below 1000 K the exciton descends to the plane wave state at the bottom of its band. The smooth localiza-

tion, which we have modeled here and previously [35], then develops as self-trapping; its length is determined by the balance between gaining the potential energy and losing the quantum kinetic energy of the exciton. In either case, the kinetics of cooling must be taken into account and the incoherent component of the exciton ensemble should be added. Microscopic theories of the dynamical BEC offer an important experience to learn, being motivated by problems in polaritons (see, e.g., [46, 47] and more references in a review [39]) and cold atoms [48, 49, 51]. The theory is able to reproduce the growing of occupation numbers at lowest energies, as it was beautifully traced in experiments with cold atoms. But establishing phase coherence has not been clearly derived yet; the Ginzburg–Pitaevskii-type equations appear from the microscopic theory in a stochastic rather than deterministic form.

Contrary to a simple and treatable microscopic nature of excitons in semiconductors, polaritons, and cold atoms, we here face a very complicated origin of the exciton and of the affected instabilities: intramolecular electronic correlations as a source of charge transfer against the Coulomb and kinetic energies, cooperative correlations leading to the spin–Peierls instability of lattice dimerization.

Our more detailed study focused on the generic model will be presented elsewhere [55]. Among applications to neutral-ionic transitions in organic donor–acceptor materials, we face the fermionization of excitons as initially repulsive Bose particles, because of the rather one-dimensional structure of these materials. More specifically, there is an unresolved problem of the commonly accepted interpretation of the absorption peak at 0.6 eV as the charge-transfer exciton energy E_{ex} , because it keeps nearly the same position in the ionic phase as in the neutral one. This is not compatible with our, and probably any, phenomenological theory: the strongest effect of excitons on the equilibrium value of changes in ρ implies the reciprocal effect of ρ on E_{ex} . The extensive microscopic modeling in [32] also shows the expected strong dependence.

We believe that the suggested picture, the approach, and the illustrations will encourage a more solid theoretical work and will stimulate experimental studies of PIPT in systems possessing features of the excitonic insulator and/or allowing pumping to the excitation modes coupled to a parameter of a nearby phase transition.

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APPENDIX

Physical Parameters and Estimations

We must relate the constants in Eqs. (2), (6), and (7) with physical parameters and estimate their values.

q_I : the charge transfer goes from $\rho_N = 0.32$ to $\rho_I = 0.52$, whence $q_I = 0.2$.

E_{ex}^0 : the charge-transfer exciton energy $E_{\text{ex}}^0 = 0.6$ eV is known.

a : a is the parameter of excitons’ interaction, which is bounded from above by the energy of exciton dissociation, that is, $a \sim 10^{-1}$ eV.

c and q_h : at the transition temperature T_{NI} , $W_I = W_N$ and $dW_I/dq = 0$ which yields $q_h \approx 0.01$ and $c \approx 1.4$.

f : in units of $d = 7.4$ Å, the dimerization in the ionic phase is $h_I = 0.03$ [37]. Knowing q_I and h_I , we obtain $f/c = (q_I/q_h - 1)/h_I^2$.

b : the requirement for the correct boundary between neutral and ionic states gives $b \approx 50$. We note the much higher value of b compared with the estimation $b \propto a/q_I = 5a$ from considering the energy term bq^3 as an unharmonism with respect to aq^2 .

m : the experimental width of the exciton absorption line gives the estimate $\hbar^2/2md^2 = 0.2–0.3$ eV.

ω , γ : the period of coherent oscillations is $T_{\text{osc}} = 0.6$ ps, and the dimer mode frequency is then $\omega = 2\pi/T_{\text{osc}} \approx 10^{-2}$ fs $^{-1}$. Their relaxation time is $\tau_h = 3–7$ ps [31]; taking it as 5 ps, the damping parameter is $\gamma = 1/\omega\tau_h \approx 0.02$.

G : the inverse lifetime of residual ionic segments is $\tau_I = 20$ ps [31], and therefore the modeling should yield the dynamical phase transition at a time of the order of $10T_{\text{osc}}$. This requires $G \sim 10^{-3}$.

A : it is expressed via ω and the sound velocity s as $A/c = s^2/\omega^2 \approx 0.02$ from the estimate $s \propto d/T_{\text{osc}} \approx 10^5$ cm/s, which is on the scale of values measured for other charge-transfer compounds.

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