



Dynamical patterns of phase transformations from self-trapping of quantum excitons



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ABSTRACT

Phase transitions induced by short optical pulses is a new mainstream in studies of cooperative electronic states. Its special realization in systems with neutral-ionic transformations stands out in a way that the optical pumping goes to excitons rather than to electronic bands. We present a semi-phenomenological modeling of spacio-temporal effects applicable to any system where the optical excitons are coupled to a symmetry breaking order parameter. In our scenario, after a short initial pulse of photons, a quasi-condensate of excitons appears as a macroscopic quantum state which then evolves interacting with other degrees of freedom prone to instability. This coupling leads to self-trapping of excitons; that 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. The system is stratified in domains which evolve through dynamical phase transitions and may persist even after the initiating excitons have recombined. We recover dynamic interplays of fields such as the excitons' wave function, electronic charge transfer and polarization, lattice dimerization.

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1. Introduction

Nowadays, transformations among cooperative electronic states can be performed by short optical pulses [1–4]. By these pump induced phase transitions (PIPT), various symmetry broken ground states are being tested: crystallization of electrons (charge order with ferroelectricity) or of electron–hole (e–h) pairs (charge/spin density waves – CDW,SDW), the superconductivity, Peierls and Mott insulators.

The theory of PIPTs faces very high difficulties when started ab initio at the microscopic level ([5] for review, [6]). But over longer time scales the evolution is governed by collective variables like an order parameter and lattice deformations. Effectiveness of such a phenomenological approach has been proven by detailed modeling of coherent dynamics of a macroscopic electronic order through destruction and recovering of the CDW state. That allowed to recover such effects as dynamic symmetry breaking, stratification in domains and subsequent collapses of their walls, all in detailed accordance with the experiment [7]. Another

example was a modeling [8] of the recently discovered [9] switching to a truly stable hidden state of a polaronic Mott insulator in 1T-TaS₂.

In most experiments on PIPTs, the electrons are excited to a high energy with their subsequent very fast cooling down to a quasi-equilibrium e–h population which provokes events of a subsequent evolution. A new situation can take place if the photons are tuned in resonance with excitations, whatever is their origin – intra-molecular excitons (IME) or bound electron–hole pairs – charge transfer excitons (CTE). With so high concentration (up to 10% in PIPT experiments or 1% in our modeling below), the quasi-condensate of excitons should appear as a macroscopic quantum state which then evolves interacting with other degrees of freedom. Consequently a theory [10] can better bridge between the classical macroscopic and the quantum microscopic regimes.

The common case of pumping to unbound electrons and holes is not excluded from this scenario, provided the early cooling leads first to formation of excitons; this is what is known to take place in light emitting polymers [11] or in conventional semiconducting lasers operating at low temperature (*T*).

Particularly, we are interested in effects of excitons' self-trapping [12–14], akin to self-focusing in the nonlinear optics [15] or to formation of polarons from electrons. The locally enhanced density of excitons can surpass a critical value to trigger a phase

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transformation in another coupled degree of freedom, even if the mean density n is below the required threshold.

In this article we shall demonstrate this principle on an experimentally elaborated example of optically provoked transformation between neutral N and ionic I phases in organic crystals like TTF-CA (see Ref. [16] and references therein). We shall build a minimal phenomenological model for IMEs which interaction with the inter-molecular charge transfer ρ leads finally to symmetry breaking lattice dimerizations and hence to the ferroelectric polarization. The numerical modeling will be performed showing formation, evolution, abrupt transitions, and sometimes the decay of sharply localized domains of the embedded new phase. As an application, we can already target earlier experiments [17,18] with the pumping into the high energy mode of the TTF molecule. A more specialized model will be necessary in the future to describe pumping to the lower energy inter-molecular CTE [19–21] where the internal structure of the exciton starts to play an important role.

2. Phenomenological approach to the neutral-ionic first order phase transition

2.1. The model free energy

The neutral-ionic (NI) transition takes place in a bi-molecular donor–acceptor chain (e.g. TTF-CA, see references in Ref. [16]) which shows a variable charge transfer (TTF ^{ρ} -CA^{- ρ}) between the lower ρ_N in the quasi-neutral (N) high T phase and the higher ρ_I in the low T ionic (I) phase.

The 1st order transition in ρ alone would go without a symmetry breaking and could be described by a generic double-well curve of Fig. 1 for the free energy $W(\rho)$ with two minima at ρ_N and ρ_I . The critical increase of the dielectric constant [16] tells us that, in spite of the N and I minima being quite distant (e.g. $\rho_N=0.32$ and $\rho_I=0.52$ at the phase coexistence), the separating barrier is small.

In TTF-CA and the family, the situation is more interesting because another degree of freedom – alternating molecular displacements h are involved; the I phase is accompanied by the lattice dimerization, so there is a symmetry breaking and the transition could have been of the 2nd order which is not the case nevertheless – the jump in h is concomitant with the one in ρ . (This observation concerns the transition under temperature, while may change under pressure [22]). But after the pumping, as we shall show, a sharp dynamical transition should be observed.

There are several ways to phenomenologically guess the appropriate function for the ground state energy [23–25]. Ours is different in two respects. First, we minimize the suggestions to the level that the double shape appears only from interactions of ρ and h without enforcing it to be already a property of ρ alone. Most importantly, we introduce the field of the multi-exciton coherent state as an integral part of the energy functional. Still we

shall not take into account particular features of CTEs keeping the form as generic as possible for applications in other possible situations in other materials.

The system will be described by the free energy as a functional of $q(x,t)=\rho-\rho_n$, lattice deformations $h(x,t)$ and (when under pumping) the excitons' common wave function $\psi(x,t)$. The initial wave function $\psi(x,0)$ is normalized to the total number N (or the concentration per site n) of pumped excitons:

$$\int_{-L}^L dx |\psi(x,0)|^2 = N = nL \quad (1)$$

where $2L$ is the sample length. Henceforth, all lengths ($x, L, |\psi|^{-2}$) are measured in units of the TTF-CA dimer size d which is the lattice period in the N phase. The energy functional density is

$$W(q, h, q_c, \psi) = \frac{a}{2}q^2 + \frac{b}{3}q^3 + \frac{c}{q_c}(q_c - q)h^2 + \frac{f}{2}h^4 + \frac{A}{2d^2} \left(\frac{\partial h}{\partial x} \right)^2 - gq |\psi|^2 + \frac{k}{2} |\psi|^4 + \frac{\hbar^2}{2md^2} \left| \frac{\partial \psi}{\partial x} \right|^2 \quad (2)$$

here $q_c = \rho_c - \rho_n$ is the critical value of q for reaching the instability in h when the energy minimum (in h at given q) moves from $h=0$ at $q < q_c$ to $h = \pm h_{eq}$ at $q > q_c$; g is the coupling constant of excitons with the charge transfer q , and k is the repulsion energy of excitons. Terms with x derivatives describe inhomogeneous states and m is the exciton's kinetic mass.

2.2. Physical parameters and estimations

Now we must relate the constants in Eqs. (1) and (4)–(6) with physical parameters and estimate their values.

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

f : In units of $d=7.4 \text{ \AA}$, the dimerization in the I phase is $h_I=0.03$ [16]. Knowing q_I and h_I , we get from Eq. (3) $f/c=(q_I/q_c-1)/h_I^2$.

b : We can consider bq^3 as an unharmonism with respect to aq^2 , hence $b \sim a/q_I = 5a$.

g : The experimentally known [17–19] downshift $\delta E_{ex} = -gq$ of the exciton energy with increasing ρ fixes $g=0.4 \text{ eV}$.

k : Repulsion of excitons as dipoles oriented transversely to their distance is estimated as 0.3 eV .

m : The experimental width of the exciton absorption line gives the estimate $\hbar^2/2md^2=0.1 \text{ eV}$.

ω, γ : Period of coherent oscillations is $T=0.6 \text{ ps}$, then the dimer mode frequency is $\omega=2\pi/T \approx 10^{-2} \text{ fs}^{-1}$. Its relaxation time is [19] $\tau_h=3-7 \text{ ps}$; taking it as 5 ps , the damping parameter is $\gamma=1/\omega\tau_h=0.02$.

τ : For the exciton life time we shall use $\tau=10^{-11} \text{ s}$, cf. $\tau \sim 10^{-12} \text{ s}$ for singlet excitons in conducting polymers [11]. There are no direct experimental data for these IMEs.

A : It is expressed via ω and the sound velocity as $A/c=s^2/\omega^2 \sim 0.02$ from an estimate $s=10^5 \text{ cm/s}$.

a : An excursion is necessary to the CTE which energy 0.6 eV is

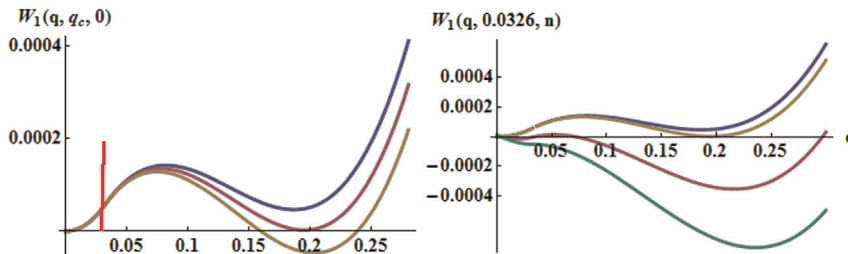


Fig. 1. Left: $W_1(q, q_c, 0)$ as functions of q for different q_c . From top to bottom: $q_c=0.0326$, $q_c=0.0322$, and $q_c=0.0318$. The vertical line indicates $q=q_c$. Right: $W_1(q, q_c, n)$ as functions of q for a fixed $q_c=0.0326$ at different n . From top to bottom: $n=0$, $n=n_{c1}=0.005$, $n=n_d=0.006$, and $n=n_{c2}=0.095$.

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